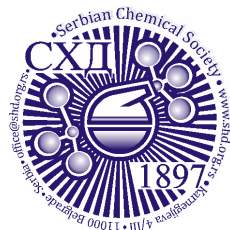


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The sources and seasonal variations of chemical components in the deposition samples in Kirklareli, Turkey

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Abstract: This study was carried out in the central district of Kirklareli province in Turkey. It presents the chemical composition of the three deposition types namely wet, bulk, and dry. In this study, 150 deposition samples (wet + bulk + dry) were collected for a year in the urban and suburban areas in the central district of Kirklareli. The concentrations of the main cations (Ca^{2+} , K^+ , Na^+ , Mg^{2+} , NH_4^+) and main anions (SO_4^{2-} , Cl^- , NO_3^-) were determined in the collected deposition samples. The seasonal variations of major ion concentrations in the three deposition types were studied. The wet and dry deposition fluxes of major ions were calculated. Among the major ions, the ion with the highest annual mean flux values in the wet deposition is Ca^{2+} ion in the urban area, while it is Cl^- ion in the suburban area. In the wet deposition, the annual mean flux values of Ca^{2+} ion in the urban area and Cl^- ion in the suburban area are 65.40 and 38.09 $\text{mg m}^{-2} \text{h}^{-1}$, respectively. The relationship between ion concentrations and acid deposition was also investigated and the sources of ions were determined. The arithmetic mean pH values of the samples in the urban and suburban areas were 6.39 and 6.14 in wet deposition, 6.75 and 6.41 in bulk deposition, and 7.36 and 6.56 in dry deposition, respectively. The backward trajectories arriving to the region during the study period were divided into two groups. In the first cyclone group, SO_4^{2-} ion was of anthropogenic in origin by 97 % both in the urban and suburban areas.

Keywords: ion concentration; deposition flux; trajectory analysis; enrichment factor.

INTRODUCTION

Air pollution has become a global problem due to the emissions of anthropogenic pollutants into the atmosphere.^{1,2} Air pollution is often thought of as a distinguishing characteristic of industrial and urban centers. There are certain processes that affect the life of the particles in the atmosphere. The residence time

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of the particles in the lower atmosphere can range from a few days to a week. The main mechanism for particle removal, which is very close to the ground, is effective and settled on the surfaces, although rainout and washout are superior removal mechanisms at altitudes above approximately one hundred meters.¹ Natural processes such as the scavenging of materials by cloud and fog drops, snow, rain, and transport to the earth are known as wet deposition (WD)³. Dry deposition (DD), which involves the direct collection of airborne particles and gases through the solid, liquid surfaces of the earth and vegetation, is a much slower and continuous process than wet deposition.⁴ Bulk deposition (BD) is the sum of wet deposition and dry deposition. Contamination of soil and water is the result of not only wet deposition but also dry deposition.⁵ In fact, bulk deposition studies may be more meaningful in determining the chemistry of natural deposition, as the natural process does not distinguish between wet and dry deposition.⁶ Variations between the concentrations of chemical components in wet, bulk, and dry deposition and their effects on acid deposition and changes according to atmospheric conditions are the subjects of many studies.

The wet, bulk, and dry deposition sampling were carried out between September 2010 and September 2011 in the urban and suburban areas in the central district of Kırklareli (Turkey). The enrichment factor (EF) and non-sea salt (NSS) estimations were performed to identify the ion sources in the three deposition types. The pH values of the three deposition types were compared and the factors affecting acidity were discussed. The difference between wet and dry deposition rates was calculated. For the three deposition types, the difference between the urban and suburban areas was revealed, and the effect of long-range cyclones on wet deposition was investigated. In the study carried out by Oruç⁷ in Kırklareli, it was stated that all of the dry deposition samples collected from two stations (Central District and Kaynarca Town) were alkaline. In both sampling stations, it was stated that the dominant cation was Ca^{2+} and the dominant anion was SO_4^{2-} . It was stated that the mean concentration values of Ca^{2+} ions in Central District and Kaynarca Town were 4.37 and 4.81 mg L^{-1} , respectively, and the mean concentration values of SO_4^{2-} ions were 6.33 and 6.12 mg L^{-1} , respectively.⁷ In the study conducted by Oruc *et al.*⁸ wet deposition sampling was carried out in the cross-border region between Bulgaria and Turkey. It was stated that the percentage distribution of the SO_4^{2-} , Cl^- , NO_3^- , Ca^{2+} , NH_4^+ , K^+ , Na^+ , Mg^{2+} ion concentrations in the wet deposition samples collected in the Turkish sites (Kırklareli and Kaynarca) were 45.68, 13.99, 3.21, 12.06, 11.00, 8.00, 4.64 and 1.07 %, respectively. In addition, it was stated that the percentage distributions of the concentrations of these ions in the wet deposition samples collected in the Bulgarian sites (Burgas and Ahtopol) were 19.46, 39.01, 14.14, 11.92, 1.39, 3.27, 2.64 and 8.17 %, respectively. As a whole, samples of the wet deposition in the study region and period have been reported to be characterized by high Cl^- and SO_4^{2-} , as

well as Ca^{2+} concentration and alkaline pH values.⁸ In another study conducted in Kırklareli, it was stated that the mean concentration values of Ca^{2+} , K^+ , Mg^{2+} , NH_4^+ , Na^+ , SO_4^{2-} , Cl^- , NO_3^- ions were found to be higher in bulk deposition samples than wet deposition samples. The relative contribution of dry deposition to bulk deposition for Ca^{2+} , K^+ , Mg^{2+} , NH_4^+ , Na^+ , SO_4^{2-} , Cl^- , NO_3^- ions were reported to be 23.27 %, 15.75 %, 14.90 %, 13.68 %, 10.52 %, 10.20 %, 6.69 %, 4.99 %, respectively.⁹ The novelty of this study, which was conducted in Kırklareli (Turkey), is that it covers the chemical evaluation of three atmospheric sampling types collected – wet, bulk, and dry deposition. The data obtained and the sampling period provide an opportunity to understand the air pollution dynamics.

EXPERIMENTAL

Sampling areas

Kırklareli is located in the Thrace part of the Marmara Region to the Northwest of Turkey. It is located between $41^\circ 13'$ and $42^\circ 05'$ north latitudes, $26^\circ 54'$ and $28^\circ 06'$ east longitudes. Kırklareli is surrounded by Bulgaria to the North, Black Sea to the East, Tekirdag to the South and Southeast, and Edirne to the West. Kırklareli has 180 kilometers of land border with Bulgaria and 60 kilometers of the seacoast to the Black Sea. Continental climate is dominant in the city center and the temperature difference is high between the summer and winter seasons. The population of Kırklareli city center is approximately 80,000 people.¹⁰ The urban area ($41^\circ 44' 03''$ N and $27^\circ 13' 15''$ E) and the suburban area (3 kilometers southwest of the city center) ($41^\circ 43' 13''$ N and $27^\circ 11' 36''$ E) were selected for wet, bulk, and dry deposition sampling (Fig. 1).

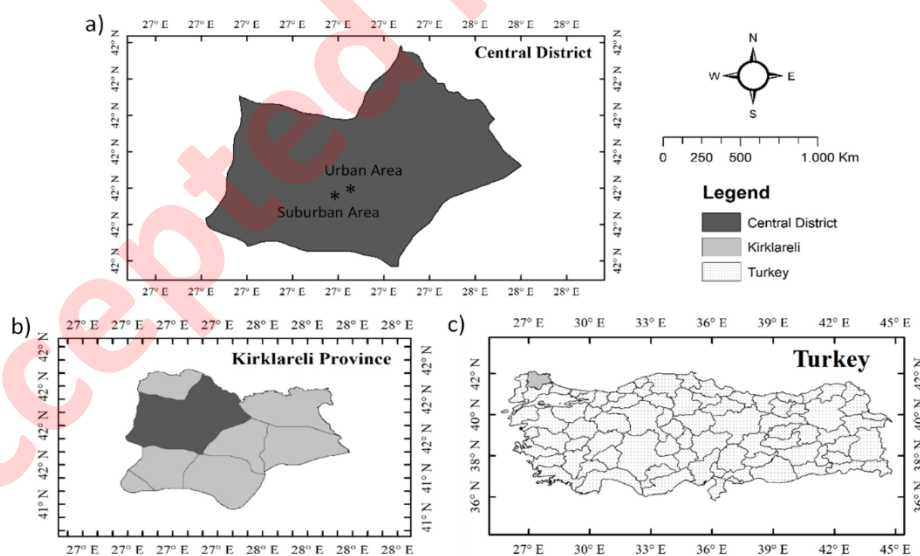


Fig. 1. The locations of a - Central District of Kırklareli, b - Kırklareli Province, c - Turkey

Deposition sampling and analysis

During the sampling period, a total of 150 deposition samples were collected including 54 wet depositions (27 urban and 27 suburban areas), 48 bulk depositions (24 urban and 24 suburban areas), and 48 dry depositions (24 urban and 24 suburban areas). The concentrations of major ions (Ca^{2+} , K^+ , Na^+ , Mg^{2+} , NH_4^+ , SO_4^{2-} , Cl^- , NO_3^-) and the pH values in the wet, bulk, and dry deposition samples were studied. Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPPLIT) Model was run to determine the backward trajectories of the air masses,¹¹⁻¹² and Sat24 satellite images were examined to observe the movements of air masses.¹³ For the temperature values, the data obtained from Kırklareli Atatürk Soil, Water and Agricultural Meteorology Research Institute Directorate were used. Only the wet and dry deposition sampling in the summer season were performed with Automatic Wet/Dry Deposition Device. During the sampling period, all other samplings were done manually. For this purpose, polyethylene funnels having 23 cm diameter and containers were used in the samples. Containers and funnels were mounted 180 cm above the ground. This height is necessary to avoid mixing dust on the ground. In wet deposition sampling, clean sampling containers were placed at sampling stations in the urban and suburban areas just before precipitation and the samples were transferred to bottles and stored for analysis at the end of precipitation. pH measurements of the samples were carried out immediately at the sampling sites. In the bulk deposition sampling, after precipitation, the clean funnel and container were kept open to the atmosphere until the next precipitation event. At the end of the precipitation, the samples were transferred to bottles. Dry deposition sampling was carried out in 15-day periods. The containers and funnels were placed in the arbor made of polyethylene with a high roof, without walls. In this way, contamination of the sampler is minimized. The sampling bowl was washed with 1 liter of deionized water at the end of 15 days. The wash-water was transferred to bottles for analysis. The same storage and analysis procedure applied in wet deposition was applied to bulk and dry deposition samples. Funnels and sampling containers were rinsed with deionized water before starting the sampling, then soaked with nitric acid (5 %) and then rinsed with deionized water and dried. The samples were stored in pre-cleaned polyethylene bottles in a refrigerator at 4 °C before the chemical analysis.^{6, 14-18} Orion Aplus Portable pH and ISE Meters device was used for pH measurement. The pH meter was calibrated using standard pH 4.00 and 7.00 buffer solutions before each measurement. Shimadzu UV-1601 spectrophotometer for NH_4^+ , SO_4^{2-} , and NO_3^- analysis and Jenway Flame Photometer (Clinical PFP7) device for Na^+ and K^+ analysis was used. Ca^{2+} , Mg^{2+} , and Cl^- analysis were carried out by titration.¹⁹

Ion sources

The enrichment factor (EF), one of the methods used to classify as the natural or anthropogenic sources of the pollutants was calculated using equation (1).^{8,18,20-23}

$$EF = \frac{(X/c)_{\text{precipitation}}}{(X/c)_{\text{reference material}}} \quad (1)$$

While calculating the enrichment factors of ions in the deposition samples according to the sea, Na^+ was chosen as the reference element and the concentration values of ions in seawater were used.²⁴ $(X/c)_{\text{precipitation}}$ is the ratio of the concentration of interested ion to Na^+ concentration in the deposition samples and $(X/c)_{\text{reference material}}$ is the ratio of the concentration of interested ion to Na^+ concentration in seawater. While enrichment factor values close to 1 indicate predominantly marine source, enrichment factor values higher than 1 indicate an enrichment compared to the seawater.²¹

Non-sea salt (NSS) ion concentrations were found using the equation (2).^{8,18}

$$c_{\text{NSS}} = \text{Total } X_p - c_p(X_n/c_r) \quad (2)$$

In the equation, X and c represent the concentration of the respective ion and the reference ion respectively, p and r represent ions in precipitation and ions in the reference material, respectively. The ratio of non-sea salt concentration to total concentration is the non-sea salt fraction (NSSF).^{8,18}

The wet deposition flux ($F_w / \text{mg m}^{-2} \text{ h}^{-1}$) of any chemical component in a rain event is expressed as in equation 3:²⁵

$$F_w = C_i P_i \quad (3)$$

where, c_i , is the concentration of the said chemical component in precipitation (mg L^{-1}), and P_i is the rain intensity (mm h^{-1}).

Dry deposition flux ($F_d / \text{mg m}^{-2} \text{ h}^{-1}$) is acquired by using the equation 4.²⁶

$$F_d = \frac{c \Delta V}{A \Delta \tau} \quad (4)$$

where, $c / \text{mg L}^{-1}$ is concentration (rinsing water included), $\Delta V / \text{L}$ is volume (rinsing water included), A / m^2 is the surface area, and $\Delta \tau / \text{day}$ is the sampling period.

RESULTS AND DISCUSSION

Seasonal variations of deposition samples

In the wet deposition, it was found that Ca^{2+} has the highest seasonal volume-weighted mean (VWM) concentration values among ions in autumn, both in the urban and suburban areas. The VWM concentrations of Ca^{2+} in autumn were 7.87 and 5.11 mg L^{-1} in the urban and suburban areas, respectively. Among all ions in wet deposition, it was observed that SO_4^{2-} had the highest seasonal VWM concentration (8.62 mg L^{-1}) in winter in the urban area. The VWM concentration of SO_4^{2-} in this season was 3.74 mg L^{-1} in the suburban area. The seasonal VWM concentration values of Na^+ in wet deposition in all four seasons were found to be higher in the urban area than in the suburban area. In the bulk deposition, the VWM concentration values of Cl^- in autumn in the urban and suburban areas were 7.57 and 5.12 mg L^{-1} , respectively. The seasonal VWM concentration values of Ca^{2+} and Mg^{2+} ions in the bulk deposition were higher in the urban area than in the suburban area in all four seasons. The VWM concentrations of K^+ ion were 1.23 and 1.19 mg L^{-1} in autumn in the urban and suburban areas, respectively. In the bulk deposition, anions other than Cl^- were found to have higher seasonal VWM concentration values in the urban area than in the suburban area in all four seasons. In the dry deposition, it was observed that Cl^- had the highest seasonal VWM concentration value among ions in summer both in the urban and suburban areas. It was observed that seasonal VWM concentration values of Ca^{2+} in the urban and suburban areas were higher than seasonal VWM concentration values in these areas of other cations in all four seasons (Fig. 2). It has been stated that calcium is

abundant in the soil in the form of CaCO_3 and can be mixed into the troposphere as a result of wind erosion.^{8,18,27} Okay *et al.*²⁷ stated that generally continental air masses and storms can increase the deposition rates of calcium, ammonium, and potassium cations in the autumn and winter seasons.

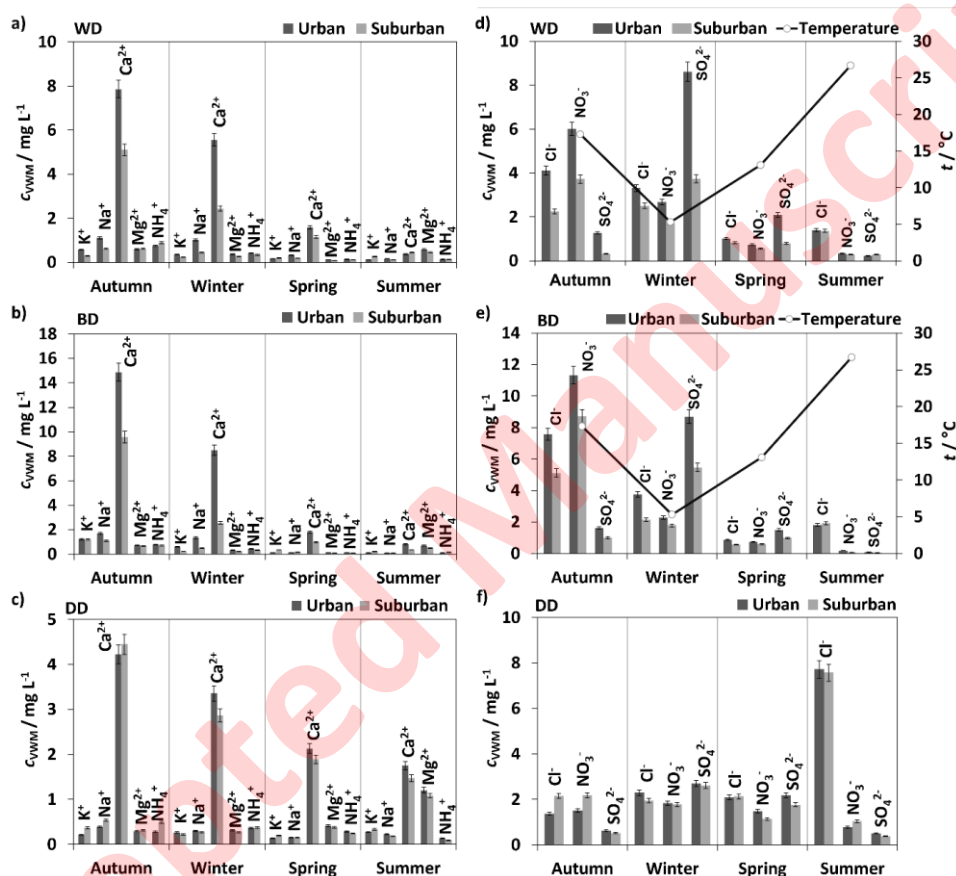


Fig. 2. Seasonal distribution of VWM concentrations of major cations in (a) wet, (b) bulk, and (c) dry deposition and major anions in (d) wet, (e) bulk, and (f) dry deposition.

Although no significant change was observed in the mean concentration of NO_3^- ion at air temperatures up to 20 °C, however, a decrease was observed in the mean concentration of this ion at 20 °C and higher air temperatures. Although the NO_3^- ion originated from the combustion of low-efficiency fossil fuels and biomass burning, another important source of this ion was motor land vehicles. It was clearly seen that as the air temperature increases, the mean concentration of SO_4^{2-} ions decreases (Fig. 3). The relationship of sulfate to temperature originates indirectly from emissions that were higher during the colder seasons. The ratio of the mean concentration of

SO_4^{2-} ion in precipitations that took place on days above 20°C of air temperature to the mean concentration of SO_4^{2-} ion in precipitations on days with air temperatures lower than 10°C is 5.89 and 19.65 %, respectively, in the urban and suburban areas. It was understood that the main reason for the high sulphate ratio on cold days was SO_2 emission resulting from the industry as well as domestic heating. No direct relation of other ions with air temperature was observed.

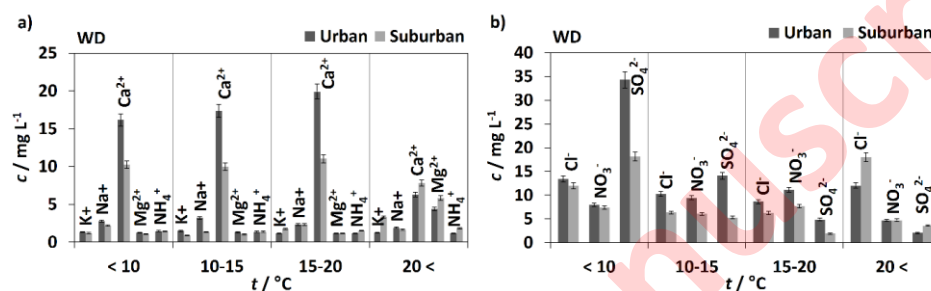


Fig. 3. Distribution of arithmetic mean concentrations of (a) major cations and (b) major anions in the wet deposition by temperature ranges.

It was observed that the mean concentration of SO_4^{2-} ions measured in the suburban area at air temperatures above 20°C is higher than that in the urban area. Assuming that there was no domestic origin of SO_4^{2-} in this temperature range, it can be concluded that the industrial sourced SO_2 emission is higher in the suburban area compared to the urban area. Anatolaki and Tsitouridou,²⁸ in their study showed that the gas and particle phase sulfur species have the highest concentration among all ions, and they found high SO_2 concentration in cold months.

Wet and dry deposition fluxes

In wet deposition, the annual mean flux values of K^+ , Na^+ , Ca^{2+} , Mg^{2+} , NH_4^+ , Cl^- , NO_3^- , SO_4^{2-} ions were calculated as 8.80, 15.87, 65.40, 20.29, 9.04, 60.86, 40.87 and $31.88 \text{ mg m}^{-2} \text{ h}^{-1}$ in the urban area, and as 12.05, 8.52, 35.57, 13.05, 8.44, 38.09, 26.30 and $18.33 \text{ mg m}^{-2} \text{ h}^{-1}$ in the suburban area, respectively. In dry deposition, the annual mean flux values of these ions were calculated 0.06 , 0.07 , 0.77 , 0.15 , 0.07 , 0.90 , 0.38 and $0.40 \text{ mg m}^{-2} \text{ h}^{-1}$ in the urban area, and as 0.07 , 0.08 , 0.71 , 0.14 , 0.08 , 0.92 , 0.41 and $0.35 \text{ mg m}^{-2} \text{ h}^{-1}$ in the suburban area, respectively (Fig. 4).

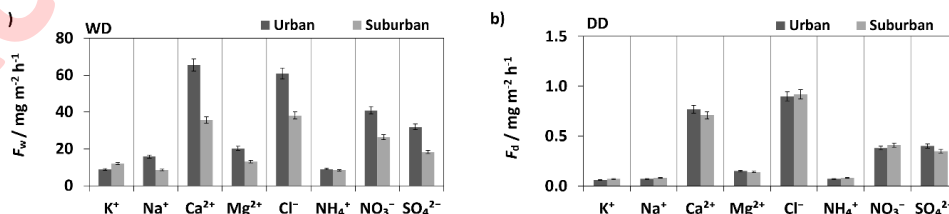


Fig. 4. Annual arithmetic means of the (a) wet and (b) dry deposition fluxes of major ions.

In general, the least difference between ion fluxes in the urban and suburban areas in wet and bulk deposition was observed for ions in the dry deposition. Especially for Ca^{2+} contained in coarse particles, the difference in wet deposition was higher than for other ions. Coarse particles containing large amounts of Ca^{2+} , K^+ , and Mg^{2+} have a higher dry deposition rate than fine particles.¹⁸ In the wet deposition, it was observed that all ions except K^+ ion had a higher deposition rate in the urban area than in the suburban area. However, it has been calculated that the difference in the rate of deposition decreases in the dry deposition in the urban and suburban areas and that K^+ , Na^+ , Cl^- , NH_4^+ , and NO_3^- ions have a higher deposition rate in the suburban area.

Acid deposition

The arithmetic mean pH values of the samples in wet, bulk, and dry deposition were 6.39, 6.75, and 7.36 in the urban area, and 6.14, 6.41, and 6.56 in the suburban area, respectively. Minimum and maximum pH values of the samples were 5.35 and 7.16 in wet deposition, 5.87 and 7.41 in bulk deposition, 5.60 and 8.56 in dry deposition, in the urban area; and 5.25 and 7.25 in wet deposition, 5.93 and 7.52 in bulk deposition, 5.73 and 7.88 in dry deposition, in the suburban area, respectively. The precipitations with the highest frequency value (37.03 %) in wet deposition in the urban area were alkaline and the pH values were between 6.5 and 7.0. The precipitations with the highest frequency value (55.56 %) in wet deposition in the suburban area were alkaline and the pH values varied between 6.0 and 6.5. (Fig. 5).

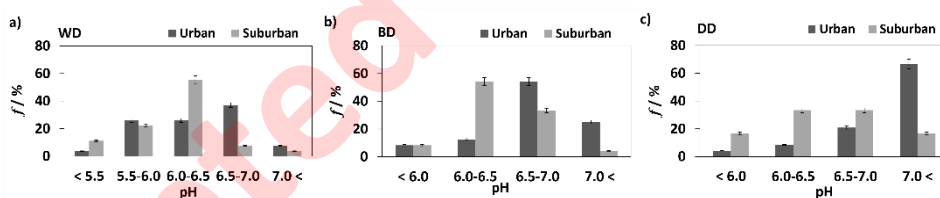


Fig. 5. Frequency distribution of pH values in the urban and suburban areas in (a) wet, (b) bulk, and (c) dry deposition

It can be said that as a result of the conversion of SO_2 originating from fossil fuels used for heating in cold months to SO_4^{2-} in the rain, relatively more acidic precipitation occurs in these months. Praveen *et al.* (2007) reported that the rainwater samples were acidic in the winter monsoon and alkaline in the summer monsoon.²⁹ Anatolaki and Tsitouridou³⁰ stated that 67 % of rain acidity was caused by sulfuric acid and 33 % by nitric acid. It was determined that the pH values of bulk deposition samples with the highest frequency value vary between 6.5 and 7.0 in the urban area and 6.0 and 6.5 in the suburban area. The pH values of dry deposition samples with the highest frequency value were higher than 7.0 in the urban area, while they had values varying between 6.0 and 6.5, and 6.5 and 7.0 in the suburban area. It can be said that the reason why the bulk and dry deposition samples are relatively alkaline

compared to the wet deposition samples is due to the more soil-borne particles collected in the sampler as a result of the bulk and dry deposition. These particles contain alkalinity-causing compounds such as Ca^{2+} , K^+ , and Mg^{2+} compared to sulfate-containing fine particles formed as a result of gas-to-particle transformation and settle faster as compared to acidic fine particles.¹⁸

Determination of ion sources

In the wet and bulk deposition, the annual NSS-VWM concentrations of K^+ , Ca^{2+} , Mg^{2+} , Cl^- , and SO_4^{2-} ions in the urban area were found to have higher values than the annual NSS-VWM concentrations of these ions in the suburban area. The annual NSS-VWM concentration values in the urban area of ions other than K^+ and Cl^- in the dry deposition were higher than the annual NSS-VWM concentration values in the suburban area. In the wet and bulk deposition, it has been observed that Ca^{2+} was the highest annual NSS-VWM concentration values in the urban and suburban areas. In the dry deposition, Cl^- was found to have the highest annual NSS-VWM concentrations in both the urban and suburban areas (Fig. 6).

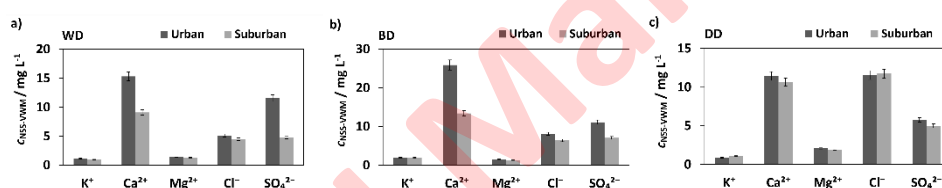


Fig. 6. Annual mean NSS concentrations of ions in (a) wet, (b) bulk, and (c) dry deposition.

It was observed that Ca^{2+} has the highest values in the seasonal mean EF values among ions in all four seasons in both the urban and suburban areas in the three deposition types (Fig. 7). In the three deposition types, SO_4^{2-} was found to have lower NSSF values in the suburban area compared to the urban area. The main source of Ca^{2+} was soil by 100 and 99 %, respectively in the bulk deposition both in the urban and suburban areas. The main source of K^+ , as in the wet deposition, was soil. It was determined that the lowest anthropogenic contribution to SO_4^{2-} concentration in bulk deposition occurred in the summer period. In the dry deposition in both areas, the K^+ was soil-borne as in wet and bulk deposition. Mg^{2+} originated from non-sea at the proportion of 93 and 92 % in the dry deposition in the urban and suburban areas, respectively. In dry deposition both the urban and suburban areas, 79 % and 80 % of Cl^- originated from non-sea, respectively. Wang and Han³¹ stated that SO_4^{2-} , NO_3^- , NH_4^+ , and Ca^{2+} are mostly of anthropogenic origin and K^+ , Mg^{2+} , and partially Ca^{2+} are mostly of mineral origin. Teixeira *et al.*³² explained that Cl^- , Na^+ , and Mg^{2+} ions in wet deposition are of marine origin, and SO_4^{2-} , NO_3^- , NH_4^+ , and F^- are anthropogenic origin. According to the results of EF analysis in the study by Feng *et al.*³³, half of Mg^{2+} was the crustal origin and half was ocean origin, most of Cl^- and

K^+ was ocean origin, and most of Ca^{2+} was the crustal origin. They explained that human activities contribute most of the SO_4^{2-} and NO_3^- .

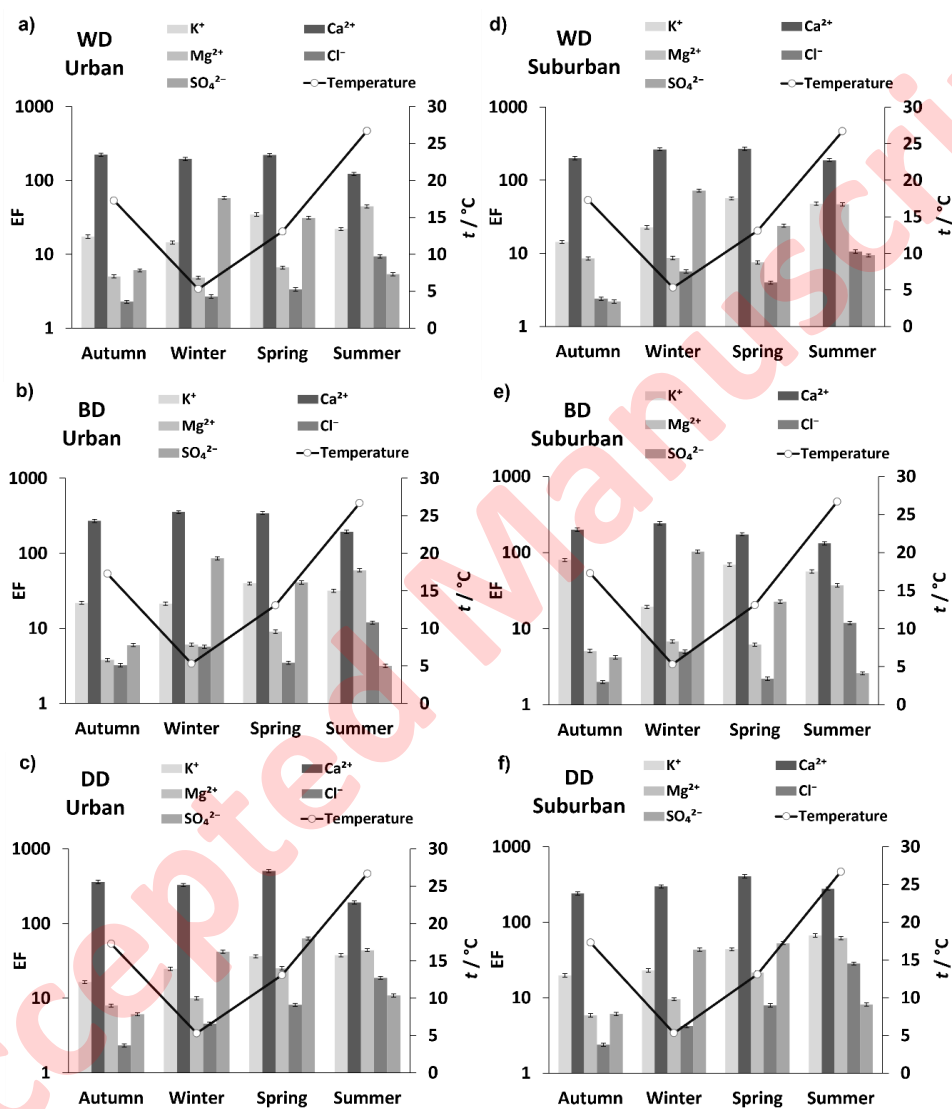


Fig. 7. Seasonal arithmetic means of enrichment factors of ions in the urban area in (a) wet, (b) bulk, and (c) dry deposition, and the suburban area in (d) wet, (e) bulk, and (f) dry deposition.

To evaluate the ion sources, Pearson's correlation coefficients between the analyzed species in the three deposition types in both the urban and suburban areas

were also examined. In wet deposition in the urban area, correlation coefficients were found between K^+ and Na^+ , Na^+ and Cl^- , Mg^{2+} and Cl^- as 0.459, 0.416, 0.510 respectively. The correlation coefficients between Na^+ and Cl^- , Mg^{2+} and Cl^- , and K^+ and Mg^{2+} in wet deposition in the suburban area were found to be 0.513, 0.698, and 0.517, respectively. The correlation coefficients between K^+ and Na^+ , Na^+ and Cl^- , K^+ and Ca^{2+} , Na^+ and Ca^{2+} , and Ca^{2+} and Cl^- in bulk deposition in the urban area were found to be 0.453, 0.447, 0.444, 0.569, and 0.575, respectively. The correlation coefficients between Na^+ and Cl^- , and Mg^{2+} and Cl^- were found to be 0.516 and 0.520, respectively, in the bulk deposition in the suburban area. The highest value of correlation coefficient in three deposition types was determined for 0.742 between Na^+ and Cl^- in the dry deposition in the urban area. In the dry deposition, the correlation coefficients between K^+ and Na^+ , Mg^{2+} and Cl^- , and Na^+ and Ca^{2+} were found to be 0.445, 0.677, and 0.460, respectively, in the urban area, and 0.420, 0.544, and 0.671, respectively, in the suburban area. In addition, the correlation coefficients between Na^+ and Cl^- , K^+ and Ca^{2+} , and K^+ and Cl^- in the dry deposition in the suburban area were found to be 0.693, 0.444, and 0.640, respectively. The low correlation coefficients were determined between other ions in the three deposition types in both the urban and suburban areas. Na^+ and Cl^- indicate the sea-salt source.^{18,27} The good correlation was observed between these two ions in all three deposition types in both the urban and suburban areas. Mg^{2+} is partly of marine origin^{18,27} and the highest correlation coefficient was observed between Mg^{2+} and Cl^- after the correlation coefficient between Na^+ and Cl^- in the three deposition types in both the areas. The main source of K^+ and Ca^{2+} is soil. Concentrations of these ions in sea salt are lower than Na^+ , Mg^{2+} , and Cl^- ions.^{18,27} Moderate correlation of K^+ and Ca^{2+} with ions indicates that the common source of these ions may be soil. The correlations of these ions with Cl^- and Na^+ ions indicate that these ions may also be partially of marine origin.

Comparison of precipitation in the urban and suburban areas by cyclone groups

The backward trajectories were determined using the HYSPLIT model,^{11,12} and Sat24 satellite images have been studied to observe the movements of air masses.¹³ In the HYSPLIT model, the backward trajectories were run by going back 72 hours. Sat24 satellite images were obtained in 6-hour periods by going back 24 hours. The backward trajectories were classified into two groups. The first group included trajectories arriving from the upper parts of the 42nd north latitude, while the second group includes the trajectories arriving from the lower parts of the 42nd north latitude. This grouping was carried out according to the results of some studies conducted to determine the dominant cyclone groups.³⁴ During the one-year sampling period, 48 % of the total precipitation originated from the first cyclone group and 52 % from the second cyclone group. Okay *et al.*²⁷ showed in their trajectory analysis that high sulphate and nitrate concentrations generally originate from northwest, central, and Eastern Europe. Ion concentrations in

precipitations were evaluated by comparing the outputs of the HYSPLIT model and Sat24 satellite images. In this evaluation, 27 HYSPLIT model outputs and 135 Sat24 satellite images were studied. In Fig. 8, two HYSPLIT Model outputs are given to represent the groupings carried out according to the cyclone groups of 09. 10. 2010 (originated from the first cyclone group) and 03. 01. 2011 (originated from the second cyclone group).

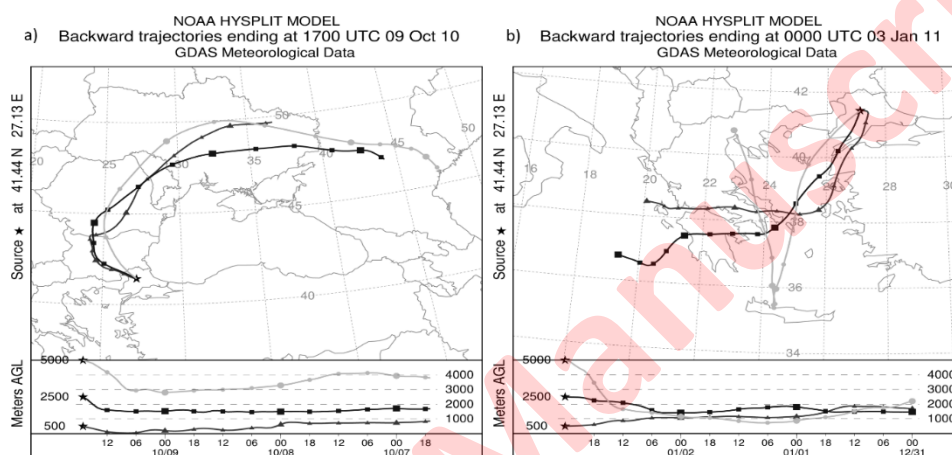


Fig. 8. HYSPLIT Model backward trajectories on (a) 09. 10. 2010 and (b) 03. 01. 2011

All the precipitation in summer was in the first cyclone group. The mean pH values of wet deposition in the first cyclone group in the urban and suburban areas were 6.25 and 6.16, respectively. In the second cyclone group, it was 6.51 and 6.12 in the urban and suburban areas, respectively. In the wet deposition, the ratio of mean ion concentration and NSS concentration of SO_4^{2-} in the first cyclone group to the mean ion concentration and NSS concentration of SO_4^{2-} in the second cyclone group was approximately 46 and 49 % higher, respectively, in the suburban area. In the wet deposition, the ratio of mean ion concentration and NSS concentration of Mg^{2+} in the first cyclone group to the mean ion concentration and NSS concentration of Mg^{2+} in the second cyclone group was approximately 53 % and 63 % higher, respectively, in the urban area. In the wet deposition, the ratio of mean ion concentration of Na^+ in the second cyclone group to the mean ion concentration of Na^+ in the first cyclone group was approximately 26 % higher in the urban area and approximately 24 % higher in the suburban area. In the wet deposition, the mean ion concentration and NSS concentration of K^+ in the first cyclone group in the urban area was approximately 13 % and approximately 15 % higher, respectively, than the mean ion concentration and NSS concentration of K^+ in the second cyclone group. In the wet deposition in the urban and suburban areas, the mean EF values of K^+ , Ca^{2+} , Mg^{2+} , Cl^- , and SO_4^{2-} ions in the first cyclone group were higher than the EF values of K^+ , Ca^{2+} , Mg^{2+} , Cl^- , and SO_4^{2-} ions in the second

cyclone group. Ca^{2+} originated from non-sea at the same proportion (100 %) in the first cyclone group and the same proportion (99 %) in the second cyclone group in both the urban and suburban areas. SO_4^{2-} was anthropogenic origin at the same ratio in both areas (97 %) in the first cyclone group, and 96 and 95 % in the urban and suburban areas in the second cyclone group, respectively.

CONCLUSION

In this study, it was determined that Ca^{2+} has the highest seasonal VWM concentration values among cations in all three deposition types. Among anions, it was found that SO_4^{2-} in wet deposition, NO_3^- in bulk deposition, and Cl^- in dry deposition had the highest seasonal VWM concentration values. In the wet deposition, 3.7 % of the total precipitation was acidic in the urban area, while 11.1 % in the suburban area was acidic. In the wet deposition, all the acidic precipitation in the urban and suburban areas occurred during colder months. In the wet deposition, it was determined that the highest anthropogenic contribution to SO_4^{2-} concentration occurred in winter in the urban and suburban areas. In this period, NSSF values of SO_4^{2-} ion in the urban and suburban areas was 98 and 99 %, respectively. In the urban and suburban areas, all the samples in bulk and dry deposition were alkaline. The annual VWM concentration values in the bulk deposition of all the ions except for SO_4^{2-} in the urban area and Mg^{2+} and NH_4^+ in the suburban area were higher than the annual VWM concentration values in wet deposition. The annual VWM concentration values of K^+ , Na^+ , Ca^{2+} , Mg^{2+} , Cl^- , NH_4^+ , NO_3^- ions in the bulk deposition in the urban area were found to be higher than wet deposition at values varying between 2-42 %. The annual VWM concentration values of K^+ , Na^+ , Ca^{2+} , Cl^- , NO_3^- , SO_4^{2-} ions in the bulk deposition in the suburban area were found to be higher at values varying between 26-49 % in wet deposition.

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ИЗВОД

ИЗВОРИ И СЕЗОНСКЕ ВАРИЈАЦИЈЕ ХЕМИЈСКИХ КОМПОНЕНТИ У УЗОРЦИМА ТАЛОЖЕЊА У ОКРУГУ КИРКЛАРЕЛИ, ТУРСКА

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Ова студија је спроведена у централном округу провинције Киркларели у Турској. Односи се на хемијски састав три типа таложења, мокро, укупно и суво. У овој студији, 150 узорака таложења (мокри + укупни + суви) прикупљено у периоду од годину дана у урбаним и приградским подручјима Киркларелија. У прикупљеним узорцима одређене су концентрације главних катјона (Ca^{2+} , K^+ , Na^+ , Mg^{2+} , NH_4^+) и главних анјона (SO_4^{2-} , Cl^- , NO_3^-). Проучаване су сезонске варијације концентрација јона у три типа таложења. Израчунати

су токови влажног и сувог таложења главних јона. Међу главним јонима, јон са највишим годишњим средњим вредностима флукса у влажном таложењу је јон Ca^{2+} у урбаном подручју, док је Cl^- јон у приградском подручју. Код влажног таложења, средње годишње вредности флукса Ca^{2+} јона у урбаном подручју и Cl^- јона у приградском подручју су 65,40 и 38,09 $\text{mg m}^{-2} \text{h}^{-1}$, респективно. Такође је испитан однос између концентрација јона и киселог таложења и утврђени су извори јона. Средње аритметичке рН вредности узорака у градским и приградским насељима биле су 6,39 и 6,14 у мокром таложењу, 6,75 и 6,41 у укупном таложењу и 7,36 и 6,56 у сувом таложењу, респективно. Повратне путање које су стизале у регион током периода истраживања подељене су у две групе. У првој групи циклona, јон SO_4^{2-} је био 97 % антропогеног порекла, како у градским тако и у приградским подручјима.

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