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Araştırma Makalesi / Research Article

Chemical Analysis of Wet Deposition Sequential Samples at Istanbul, Turkey

Ilker ORUC[1], Bulent Oktay AKKOYUNLU [2,*], Murat DOGRUEL[3], Mete TAYANC[4]

[1] Vocational College of Technical Sciences, Kirklareli University, Kirklareli, 39100, TURKEY
[2] Department of Physics, Marmara University, Goztepe, Istanbul, 34722, TURKEY
[3]Department of Electrical and Electronics Engineering, Marmara University, Goztepe, Istanbul, 34722, TURKEY
[4]Department of Environmental Engineering, Marmara University, Goztepe, 34722, Istanbul, TURKEY

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Abstract

In this study, the relations between wet deposition fluxes of major ions, concentrations and rain intensity in the precipitation events occurring on a) November 10th, 2007 and b) December 05th, 2007 are presented. The variations on the ion concentrations were investigated during the rain events. The concentrations of all ions drastically decreased to minimum levels in the first sub sequential events for each the rain events. Some ions had a significant decrease in concentrations in comparison with other ions, because they have higher concentration in the atmosphere as much as they exist in the large atmospheric particles which are being sourced from in the soil or sea. The strongest relation between the wet deposition flux and the rain intensity were found for Ca^{2+} and SO_4^{2-} among the all the ions sampled on November 10th, 2007. It was found that K^+ and NO_3^- concentrations sampled on December 05th, 2007 had a positive correlation with rain intensity; on the other hand, other ions had a negative correlation. Positive correlations were found between wet deposition flux and the rain intensity for all ions in each rain events.

Keywords

“Scavenging processes, wet deposition flux, rain intensity,”

bulentoktay@marmara.edu.tr

1. INTRODUCTION

Pollutants are abolished from the air by precipitation in two ways; namely, rainout and washout. As soon as the concentration of atmospheric particles is at peak, the result of washout during a precipitation process is predicted to be observed on the former samples gathered, and collision and coalescence process begins to abolish atmospheric particles (Akkoyunlu and Tayanç, 2008). Cerón et al. (2005) states that the pH of precipitation is formerly acidic due to the rainout occurrences of acidic material in the clouds; but then, during the downward passage of raindrops from the base of cloud, washout processes of alkaline materials in the atmosphere, bring about the swift neutralization of precipitation acidity. Since rainfall proceeds in time, washout of alkaline particles is completed; after that, precipitation acidity goes up again by cause of input because of rainout processes. Akkoyunlu et al. (2003) claim that in general, ions behaved in the same manner during the rainstorm; began with high concentrations, decreased abruptly, then showed a slight increase for a while and increased in an abrupt manner with the passage of the cold front. The chemical components in the rainout process due to the immense elimination of the washout can be explicated by the final phase of a precipitation process (Akkoyunlu and Tayanç, 2008). Sequential sampling permits the analysis of the variability of the chemical formation along precipitation events and the evaluation of contaminant elimination processes (Pelicho et al., 2006).

The aim of this study is to investigate the variation of the major ions and to analyze the wet deposition fluxes of these major ions in line with the rain intensity and concentrations in two rainfall events. This work was partially presented at 11th International Multidisciplinary Scientific GeoConference (SGEM2011) where it was delivered as an oral presentation (Akkoyunlu et al., 2011).

2. MATERIAL AND METHODS

This study aims to identify the relations between wet deposition fluxes of major ions, concentrations and rain intensity in the two rainfall. The samples were collected in Goztepe, situated on the Asian part of Istanbul (Figure 1). Istanbul is the most crowded metropolitan settlement in Turkey, with approximately 15 million dwellers in this mega city.

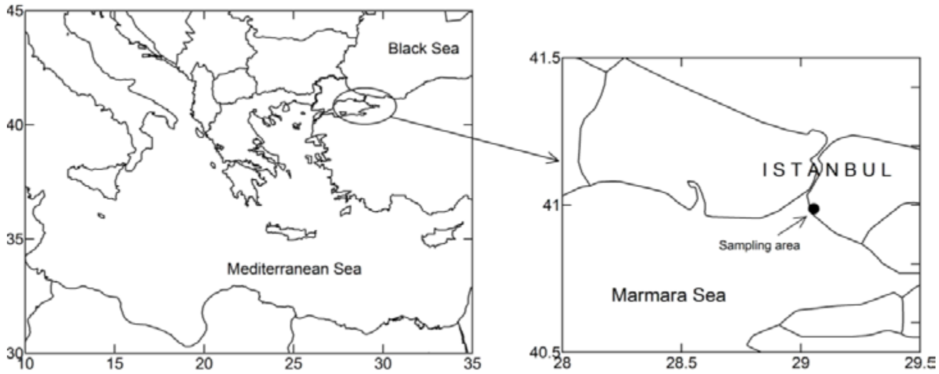

Fig. 1. Sampling Site: Goztepe

Wet deposition flux for major ions in a rainfall event was calculated as follows

$$W_i = C_i P \tag{1}$$

Where W_i is wet deposition flux for the ith major ions (mg m^{-2} h^{-1}), C_i is the concentration of the i^{th} major ions in rainwater (mg L^{-1}), and P is the matching rain intensity (mm h^{-1}).

An automatic sequential rain sampler, which was created and put under production as part of the project financed both by Marmara University Scientific Research Center and The Scientific and Technological Research Council of Turkey, was devised to collect the samples (Akkoyunlu et al., 2008; Akkoyunlu et al., 2011; Akkoyunlu et al., 2013). Sequential sampler device is of a polyethylene funnel of 0.28 m^2 with round area and 12 polyethylene cups of 200 cm^3 volume positioned on a sampler body. After the construction of the sampling device, it is tested; the funnel of the device was made to expose distilled water until all cups were filled up to approximately 20 ml, and it was seen the rain sampler instrument causes no pollution in the water. Then, for all ions, these blank samples were evaluated. In the presence of online satellite images, sequential samplings were executed for each precipitation event. The rain sampler instrument was installed at a place where it could gather precipitation samples shortly before the arrival of a low pressure system. The funnel and caps which were devised for sub-event sampling were rinsed with distilled water, then soaked in a bath (5% nitric acid), after that with distilled water rinsed once again, and dried before installations. Caps were separated from the sequential rain sampler body and transferred to the laboratory after precipitation sampling. Before chemical analysis, samples were filtered and kept in pre-cleaned polyethylene bottles in the fridge at 4 °C.

For the two rain events, thirty six sequential precipitation samples were gathered in the aggregate. Concentration of the main cations (K^+, Na^+, Ca^{2+}, and Mg^{2+}) were measured by atomic absorption spectrophotometer (Hitachi-180-80) and concentration of the main anions (Cl^-, NO_3^-, and SO_4^{2-}) were measured by ion chromatography (Dionex model 4001).

3. RESULTS AND DISCUSSION

3.1. ANALYSIS OF CHEMICAL SPECIES IN SEQUENTIAL SAMPLES

This study presents the relations between wet deposition fluxes of major ions, concentrations and rain intensity in the two rainfall events which occurred on a) November 10th, 2007 and b) December 05th, 2007. The NOAA HYSPLIT Trajectory Model was applied for air mass back trajectory analyses of two precipitation events (Draxler and Rolph, 2012). Air mass back-trajectories for every precipitation event at the heights of 1500 m, 2000 m and 3000 m were run. The back-trajectories were determined every 6 h intervals with a 24 h period. All precipitation events which have marine sources were connected to the air masses from the Middle Mediterranean Sea. They have similar low pressure system trajectories reaching Istanbul by passing through South Greece and Aegean Sea. The air parcels at the heights of 1500 m, 2000 m, and 3000 m in lower troposphere located around middle Mediterranean region came to the sampling side. The air parcel at the altitude of 3000 m came to the sampling side from the south of Italy without changing its height (Figure 2).

The first storm, which arrived to Istanbul on November 10th, 2007, was characterized by a warm frontal passage with significantly low sea level pressure value decreasing to 989 mb and temperature rising from 5˚C to 13˚C during the precipitation period. The second low pressure system reached to Istanbul on December 05th, 2007. The pressure just before the rain event was 1010 mb which rapidly decreased to 1004 mb accompanied by the start of the precipitation. The air temperature increased from 6˚C to 15˚C during the initial period of the storm. After the passage of the center of the cyclone, pressure slightly increased to 1006 mb at the end of the precipitation period and temperature showed a sudden and a strong decrease to 8˚C.

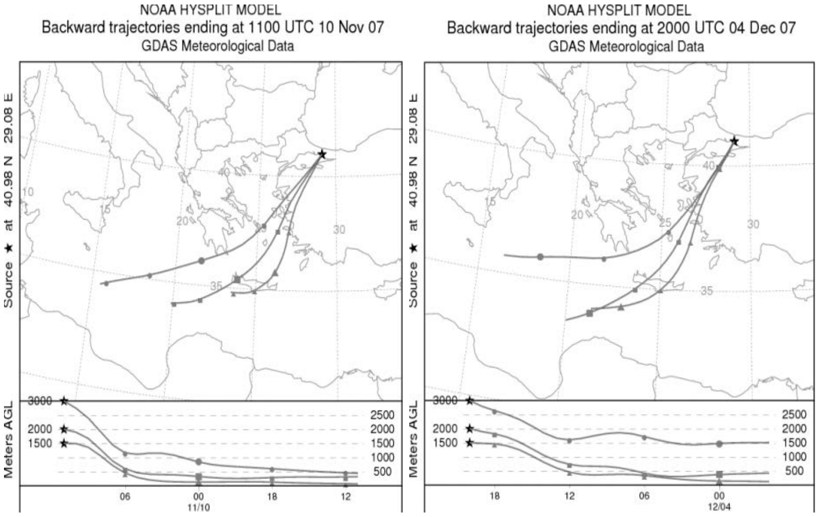

Figure 2. NOAA Hysplit Model Backward Trajectories.

Twenty one sequential samples were collected during the storm occurring on November 10th, 2007. Precipitation continued for 38.53 h with several dry intervals in between. Average rainfall intensity was determined as 0.35 mm h-1. In the first sample, high concentrations of ions were found (Figure 3). The concentrations values were calculated for the ions as follows Cl^- (72.95 mg L^{-1}), K^+ (56.20 mg L^{-1}), Ca^{2+} (15.82 mg L^{-1}), SO_4^{2-} (7.14 mg L^{-1}), Na^+ (3.99 mg L^{-1}), NO_3^- (2.37 mg L^{-1}), and Mg^{2+} (1.25 mg L^{-1}) in this period. For overall precipitation event, average values of these ions were 17.40, 3.50, 6.66, 6.86, 6.36, 1.67, and 1.08 mg L^{-1} and mean wet deposition flux of these ions were calculated as 2.84, 0.24, 2.22, 2.72, 1.49, 0.43, and 0.24 mg m^{-2} h^{-1}, respectively. Over the progressing time, during the storm concentrations of contaminants in the atmosphere were reduced by scavenging, hence giving way to less and less measured concentration of all chemical species in the rainwater. Until the end of the third sequential event, the decrease of concentration of all ions carried on.

An increase in the overall concentrations were found in the last sub sequential events. There could be three possible reasons for this situation. First, the increase of rain intensity in the last stage might have influenced the scavenging affect on the aerosols that relate to the cross sectional area of the rain drops, so for this reason the increase in the concentrations were absorbed in this stage. Secondly, the change in the synoptic systems at the upper atmosphere influenced the concentrations because of change of the global sources that are the sea and earth crust. The more the increase of Na^+ and Mg^{2+} as compared to other ions, which have sea as their main source, raises the possibility of it being the second reason. Third, a specific local source contaminate the rain-water during the last stage of the event, because concentrations of all the ions increased simultaneously, but the probability of the occurrence of this situation is low as compared to others.

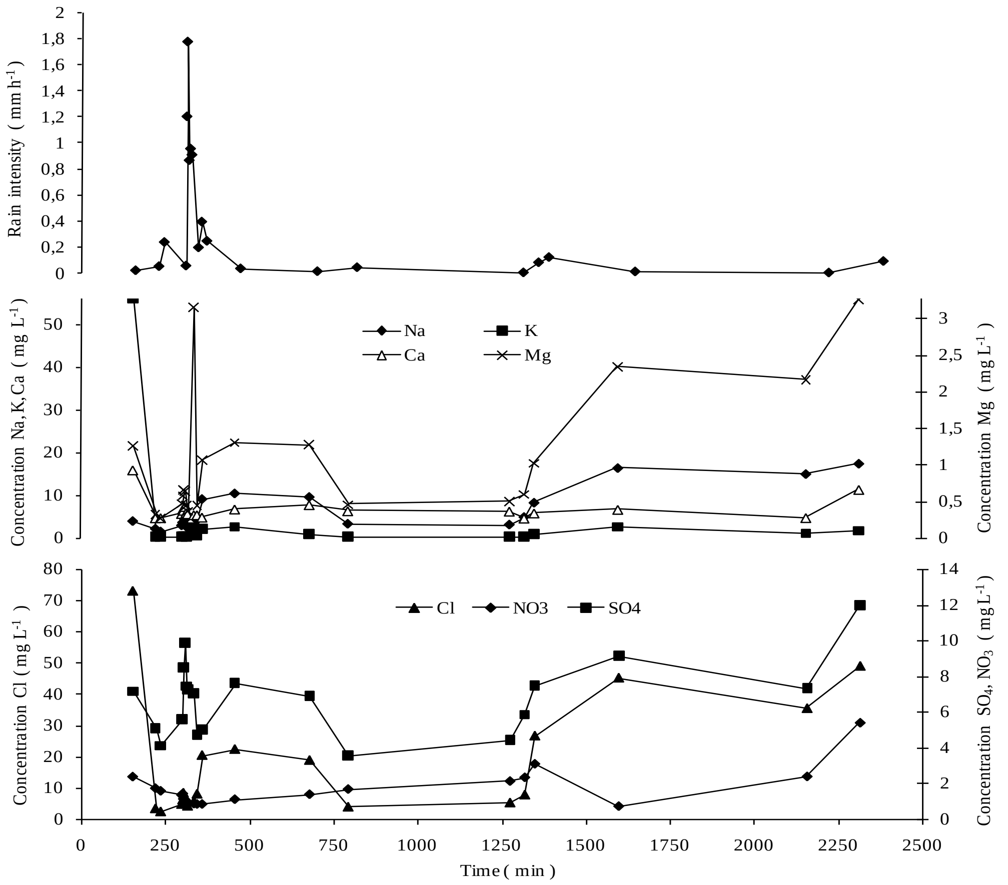

Figure 3. Variation of rain intensity and concentration of major ions with time during the rain event of November 10th, 2007.

A second cyclone occurred in Istanbul on December 05th, 2007. Precipitation lasted 7.5 hours and fifteen samples were gathered during the storm. Average rainfall intensity was calculated as 0.27 mm h^{-1}. Mean concentrations of SO_4^{2-}, Ca^{2+}, Cl^-, NO_3^-, Na^+, K^+, and Mg^{2+} were determined as 2.93, 2.57, 2.05, 1.45, 0.58, 0.36, and 0.25 mg L^{-1} and mean wet deposition flux of these ions were calculated as 0.75, 0.64, 0.53, 0.37, 0.14, 0.12, and 0.06 mg m^{-2} h^{-1}, respectively. The highest concentrations were found in the first sample for all ions. Swift decline of concentrations of all ions occurred during the first stage of rain event. The time period of this decrease is 122.5 min and 4.27 mm depth of rain took place (Figure 4). Mean concentration of these ions in this period were calculated as 8.67, 5.85, 7.26, 2.97, 2.96, 0.53, and 0.95 mg L^{-1}, respectively. Because of these results above, it can be claimed that the below-cloud scavenging effect was more dominant in the initial period of the rain event than rainout effect.

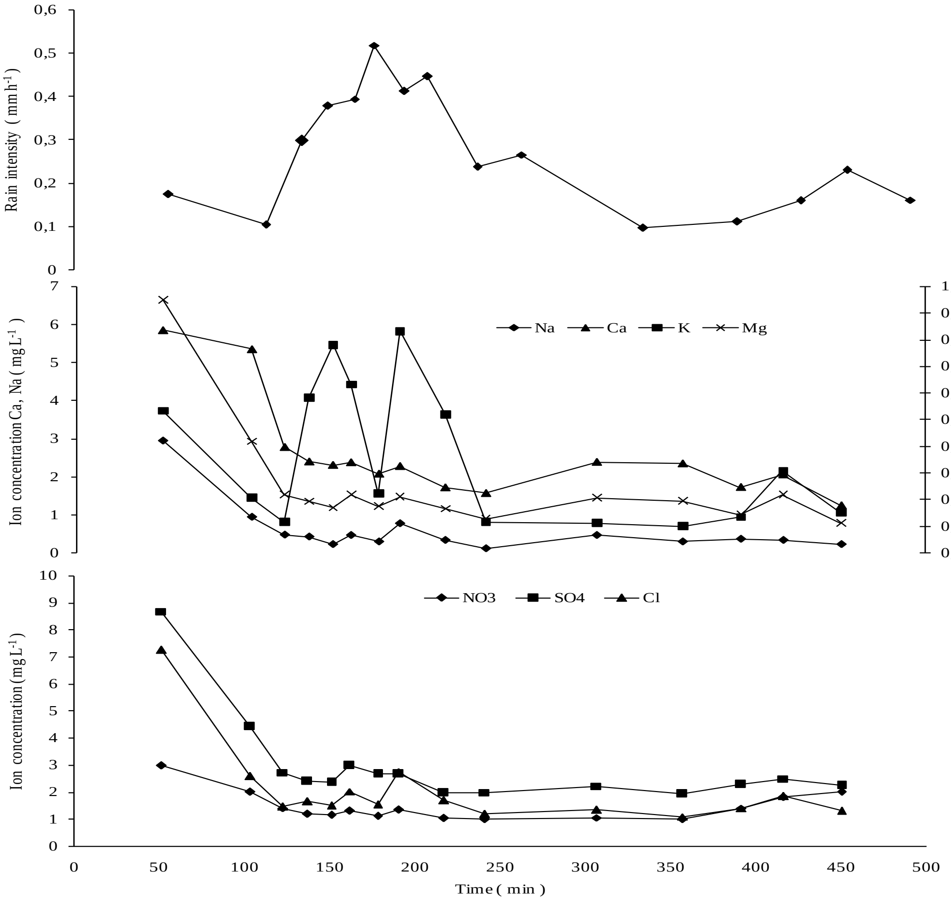

Figure 4. Variation of rain intensity and concentration of major ions with time during the rain event for December 05th, 2007.

3.2. DETERMINATION OF THE RELATIONSHIP BETWEEN THE ELEMENTS OF THE WET DEPOSITION

Ion concentration and rain intensity are two factors playing a crucial role in the determination of wet deposition flux. We investigated relationships between the concentration of the elements in the wet deposition with wet deposition flux and rain intensity via estimating Pearson correlation coefficients as illustrated in Table 1. Luo (2001) found rain intensities had strong correlations with wet-deposition fluxes. Nonetheless, the correlation of the wet-deposition fluxes with the concentrations for the elements in insoluble materials and soluble chemical species is weak. In this study, we found very strong relationship between the wet deposition flux and the rain intensity for all ions except K^+ sampled on November 10th, 2007. The negative or weak correlation between major ions concentration and rain intensity for all rain events except for K^+ and NO_3^- sampled on December 05th, 2007 was found (Table 1). The same results were emerged by (Ames et al., 1987; Durana et al., 1992; Gatz and Dingle, 1971).

Table 1. Correlation coefficients between the elements of the wet deposition.

	Correlation Variables	**Na^+**	**K^+**	**Ca^{2+}**	**Mg^{2+}**	**NO_3^-**	**SO_4^{2-}**	**Cl^-**
November 10th, 2007	Ion Concentration-Rain Intensity	).32	-0.04	0.05	0.32	-0.18	0.22	-0.36
	Wet Deposition Flux-Rain Intensity	0.94	0.36	0.99	0.89	0.96	0.99	0.91
	Wet Deposition Flux-Ion Concentration	).14	0.79	-0.05	0.04	-0.32	0.32	-0.36
December 05th, 2007	Ion Concentration-Rain Intensity	-0.18	0.68	-0.26	-0.23	0.60	-0.16	-0.08
	Wet Deposition Flux-Rain Intensity	0.33	0.84	0.80	0.50	0.84	0.74	0.65
	Wet Deposition Flux-Ion Concentration	0.84	0.94	0.35	0.72	0.24	0.54	0.68

4. SUMMARY AND CONCLUSIONS

Sequential rain samples were gathered in two rain events for the purpose of investigation wet deposition fluxes of the major ions, variation of ion concentrations and the rain intensity. A firm accord between rain intensity and wet deposition flux was observed for all ions except for K^+ in the sequential samples gathered on November 10th, 2007. In the rain event occurring on December 05th, 2007, the strongest correlation between wet deposition flux and ion concentration was found in K^+. Contrary to results observed in the rain event sampled on December 05th, 2007, negative correlations were found between the wet deposition flux and ion concentration for most of the ions which were sampled on November 10th, 2007.

Decrease rate of ions concentration in the first stage of the rain events depends on two main reasons aside from the change of the atmospheric conditions; first, the amount of particular matters in the atmosphere and second, scavenging coefficients which depends on the size of these particles. These two situations were observed in both rain events. K^+ and Cl^- concentrations were showed maximum decrease rate in the initial stage of the rain event occurred on November 10th, 2007. The main sources of these ions are sea and soil and these ions mostly exist on the large particles. However, SO_4^{2-} that exists in the small particles and has anthropogenic source has showed maximum degrease in the initial stage of the rain event occurred on December 05th, 2007.

The concentrations of all ions increased in the last sub sequential event in the rain event occurred on November 10th, 2007. Three reasons for this can be suggested which are; the increase of rain intensity in the last stages, the change of the synoptic systems in the upper atmosphere and specific local sources contaminate the rain-water during the last stage of the event.

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