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FOUR STORMS WITH SUB-EVENTS: SAMPLING AND ANALYSIS

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ABSTRACT

This study investigates the variation in the chemical composition and pH of four precipitation events that was sampled in İstanbul during a) January 21 - 23, 2004 b) November 9 - 11, 2003 c) February 12 - 13, 2004. d) October 27 - 28, 2003. These events lasted 53.3, 47.9, 27.5 and 13.2 hours and the number of collected samples for each event was 22, 14, 7 and 4, in order. Sub-event samplings were carried out for each precipitation event in the presence of online satellite images, 00 GMT surface maps and 500 hPa geopotential height maps. Precipitation events c and d include rain and snow together where precipitation started as rain and continued as snow after 16^{th} and 3^{th} sub-events. Average concentrations of SO_4^{2-}, Ca^{2+}, Na^+, Mg^{2+}, and K^+ for four precipitation events were found to be 3.90, 2.23, 2.16, 0.63, and 0.45 mg/L, and average pH value was obtained as 5.52. It is interesting to find that high values of pH and maximum concentrations of ions belong to the first samples of four cases. Then the concentration of ions and pH decreased until third and fourth samples. It was also detected that snow flakes were efficient scavenging agents, more efficient than the rain drops, and lead to an increase in the concentration of ions and pH in the samples just after the snowing starts.

Key Words: Acid precipitation, sub-event analysis, rain chemistry.

1. INTRODUCTION

The processes to control the composition of rain are complex and influenced by natural and anthropogenic sources. These processes that result in the incorporation of air pollutants into cloud droplets or the incorporation of the particles below the cloud in falling droplets are poorly understood and difficult to study experimentally. The relation of the chemical composition of precipitation to the associated meteorological conditions can improve our understanding of the causes of acid precipitation.

Wet deposition studies have been popular all over the world and many of them are carried out recently (; Akkoyunlu and Tayanç., 2003; Staelens et al., 2005). These studies investigated the variation of daily and monthly averages of wet deposition chemistry. Sakihama and Tokuyama (2005) studied the effect of typhoons on the behavior of chemical components. The work of Basak and Alagha (2004) was carried out near Büyükçekmece Lake, one of the important drinking water sources of İstanbul city, Turkey and concluded that the dominant anion was SO_4^{2-} and most of this ion came from non-sea salt. Topçu et al. (2002) studied the chemical composition of rainwater in Ankara and they also concluded that neutralization of the acidity plays an important role in that area. Akkoyunlu and Tayanç (2001) established the relationship between the chemical concentration of samples and the meteorological factors by using the trajectory analysis of cyclones.

The aim of this study is to analyze the variation of the chemical composition and pH in four precipitation sub-events that were sampled in İstanbul. In Section 2 the experimental techniques that were used to collect and analyze sub-event samples are explained. In results, the temporal variation of some ionic components and pH in sub-events during the passages of four cyclones are presented and comments on the results are given.

2. EXPERIMENTAL AND METHODOLOGY

This study presents the variation in the chemical composition and pH of four precipitation events that was sampled in İstanbul during a) January 21th - 23th 2004 b) November 9th - 11th 2003, c) February 12 – 13, 2004 and d) October 27 – 28, 2003. Sampling region was Maltepe, which is located on the European side of İstanbul, and has more domestic heating activities in comparison with industrial ones. Sub-event samplings were carried out by using a polyethylene funnel of 0.63 m^2 with circular area onto a polyethylene container. These events lasted 53.3, 47.9, 27.5 and 13.2 hours and the number of collected samples for each event was 22, 14, 7, 4, in order. At least 100 ml precipitation water must be collected in order to conduct all of the analyses. Thus, owing to the variability in the intensity of the precipitation and considering 100 ml precipitation water to be collected, it is impossible to keep the period constant for every sample collection. Sub-event samplings were carried out for each precipitation event in the presence of online satellite images, 00 GMT surface maps and 500 hPa geopotential height maps. Prior to installations the funnel and collectors used for sub-event sampling, rinsed with distilled water, soaked in a 5% nitric acid bath and then rinsed again with distilled water and dried. After precipitation, the sampled water was removed from the container and brought to the laboratory, and the sampling instrument was cleaned by distilled water and kept closed. Samples were filtered and stored in pre-cleaned polyethylene bottles in the refrigerator at 4^oC prior to chemical analysis.

Concentration of Mg^{2+} was determined by Unicam 919 Atomic Absorption Spectrometer. Concentrations of the SO_4^{2-} were determined by a high performance Dionex model 4001 ion chromatography (IC). Concentrations of Ca^{2+}, K^+ and Na^+ were determined by Jenway Flame Emission Spectrophotometer. A Metrohm-632 pH meter, equipped with a combination glass electrode, was used for pH measurements. The pH meter was calibrated before every measurement using standard pH 4.00 and 7.00 buffer solutions.

A ratio often used to distinguish aerosol sources is the enrichment factor (EF) (Vermette et al., 1988; Ahmed et al., 1990; Singer et al., 1993). This calculation is based on the elemental ratio found between ions collected in the atmosphere or in precipitation, compared with a similar ratio for a reference material, giving important information about the source of the elements. Non-sea salt (NSS) ion concentration is proportional to the enrichment factor. NSS ion concentration gives concentration of ions come from the anthropogenic sources or Earth crust. In this work, NSS ion concentration was calculated by using ratio of the ion, whose NSS concentration was calculated, to the reference ion in the reference material. Sodium was used as reference ion in this work.

3. RESULTS AND DISCUSSION

First Storm

İstanbul was under the effect of a strong cyclone on January 21 – 23, 2004 period deepening up to 994 mb over İstanbul. Significant warm and cold front passages were detected during the passage of the storm and snowing had been started at 25.5th hour after the initiation of precipitation and continued until the end of the storm. This storm was characterized by very low sea level pressure values, decreasing lower than 980 mb at its center located on the Aegean Sea and very low temperatures, -4°C in İstanbul.

Sub-event sampling was carried out during this period that precipitated 53.3 hours. 22 samples were collected during the storm of which the last 7 was snow. First container of the sub-event sampling was removed after 2.6 hour from the initiation of precipitation. Maximum pH level and ion concentrations were measured in this sub-event except SO_4^{2-} and Mg^{2+}. The maximum values of these ions that were measured in snow after 37.2 hours were found to be 6.9, 1.87 mg/L, respectively. Mean concentrations of ions ($SO_4^{2-} > Ca^{2+} > Na^{+} > K^{+} > Mg^{2+}$) can be ordered as 3.23, 1.95, 1.82, 0.58, 0.40 mg/l. Generally, $SO_4^{2-}$and Ca^{2+} were found to be the dominant ions. High sulfate concentration in samples was thought to be neutralized by the contribution of high concentrations of alkaline compounds. The average concentrations of ions and pH in samples taken between 7.00 and 22.2 hours after the start of rain were relatively lower than those of the initial sub-events and snow precipitation. All of ions have similar variability during the sampling period with a high correlation coefficient except Mg^{2+} and K^{+} correlation. The correlation coefficient between these ions was calculated as 0.45. Correlation coefficients of other ions found that ranges between 0.85 and 0.55.

Coarse particles in the atmosphere, that are the primary particles of wind blown dust, can contain high amounts of Ca^{2+}, Mg^{2+}, and K^{+} in them and these type of particles are more efficiently scavenged by precipitation than fine particles (Akkoyunlu and Tayanç, 2003). Fine particles of anthropogenic origin were formed by gas-to-particles processes and they can be considered as important sources of the precipitation acidity. With progressing time, concentration of large particles in the atmosphere was decreased by scavenging, thus leading to less and less concentration of suspended particles and in turn less amount of particles transferred into droplets, leading to the decrease in the levels of cations and more acidic wet deposition.

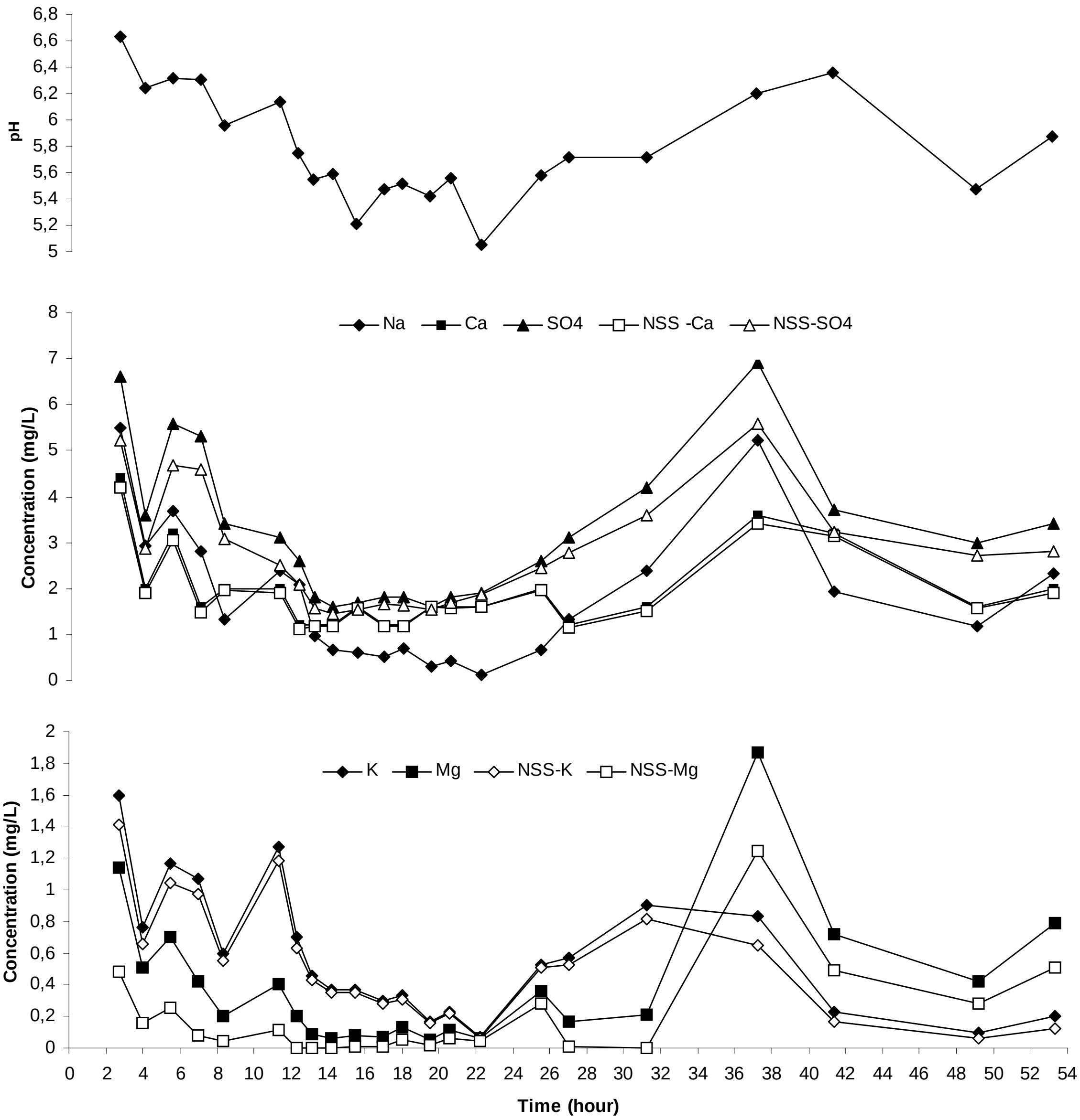

Figure 1. Variability of some ionic components and pH in sub-events as a function of time sampled on January 21 - 23 2004.

Precipitation of the first storm include rain and snow together, where precipitation started as rain and continued as snow after 22.2 hour (15th sub-event) from the initiation of rain. Average concentrations of SO_4^{2-}, Ca^{2+}, Na^{+}, K^{+}, and Mg^{2+} for snow precipitation events are found to be 3.84, 2.17, 2.14, 0.48, 0.65 mg/L, in order and average pH value is obtained as 5.85. It is interesting to find that maximum values of pH and maximum concentrations of ions belong to the first samples. It is also detected that snow flakes are efficient scavenging agents, more efficient than the rain drops, and lead to an increase in the concentration of ions and pH in the samples just after the snowing starts.

Second Storm

Other strong cyclone occurred in Istanbul on November 9 – 11, 2003. Precipitation lasted 47.9 hours with some small intervals in between without precipitation. 14 samples collected during the storm. Sub-event sampling was carried out during the period in the presence of online satellite images, 00 GMT surface maps and 500 hPa geopotential height maps. This storm was characterized by above normal sea level pressure values in İstanbul, decreasing to 1017 mb and normal temperatures with a minimum of 6°C.

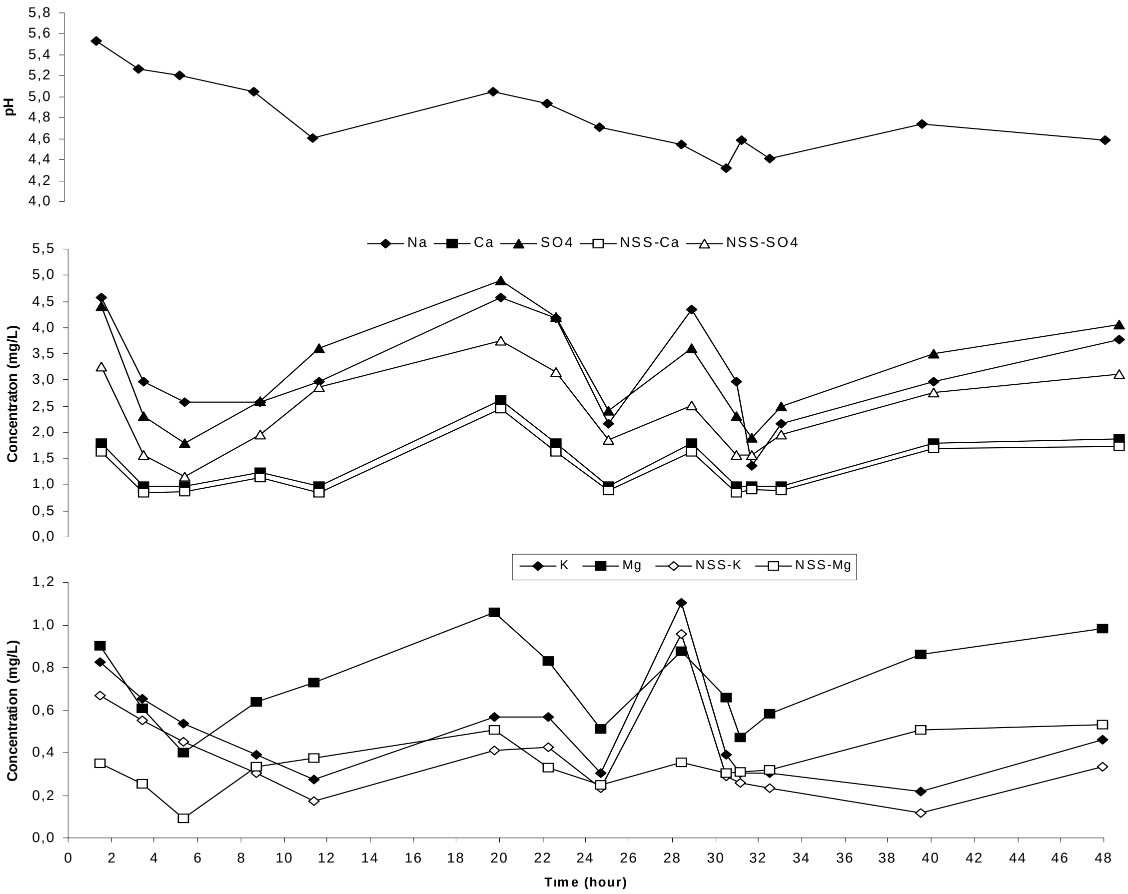

Figure 2. Variability of some ionic components and pH in sub-events as a function of time sampled on November 9 – 11 2003

Figure 2 presents the variation of some ion concentration, NSS concentration and pH in sub-events as a function of time during the passage of the cyclone. First container of the sub-event sampling was removed after 1.5 hour from the initiation of precipitation. High concentration and pH was found in this container, in addition, the sub-event sampled at 19.7^{th} hour after the start of precipitation produced the maximum concentrations of ions except K^+. While there was no significant front passages in this period of rain event, mixing of air was observed. From satellite picture animations and 500 hPa geopotential height animations the mixing was clearly be seen over western Black Sea region between 11.2 – 32.5 hour period. This situation may lead to the fluctuation of concentrations during this period of precipitation.

Besides that SO_4^{2-} and Ca^{2+} have maximum NSS concentrations, generally SO_4^{2-} and Na^+ were found to be the dominant ions in total concentrations (Table 1). There existed high correlation coefficients between all ions except K^+. The correlation coefficients between K^+ and others ranged between 0.35 and 040. Mg^{2+} has very high correlation with SO_4^{2-} and Ca^{2+} with coefficients as 0.94 and 0.90, in order.

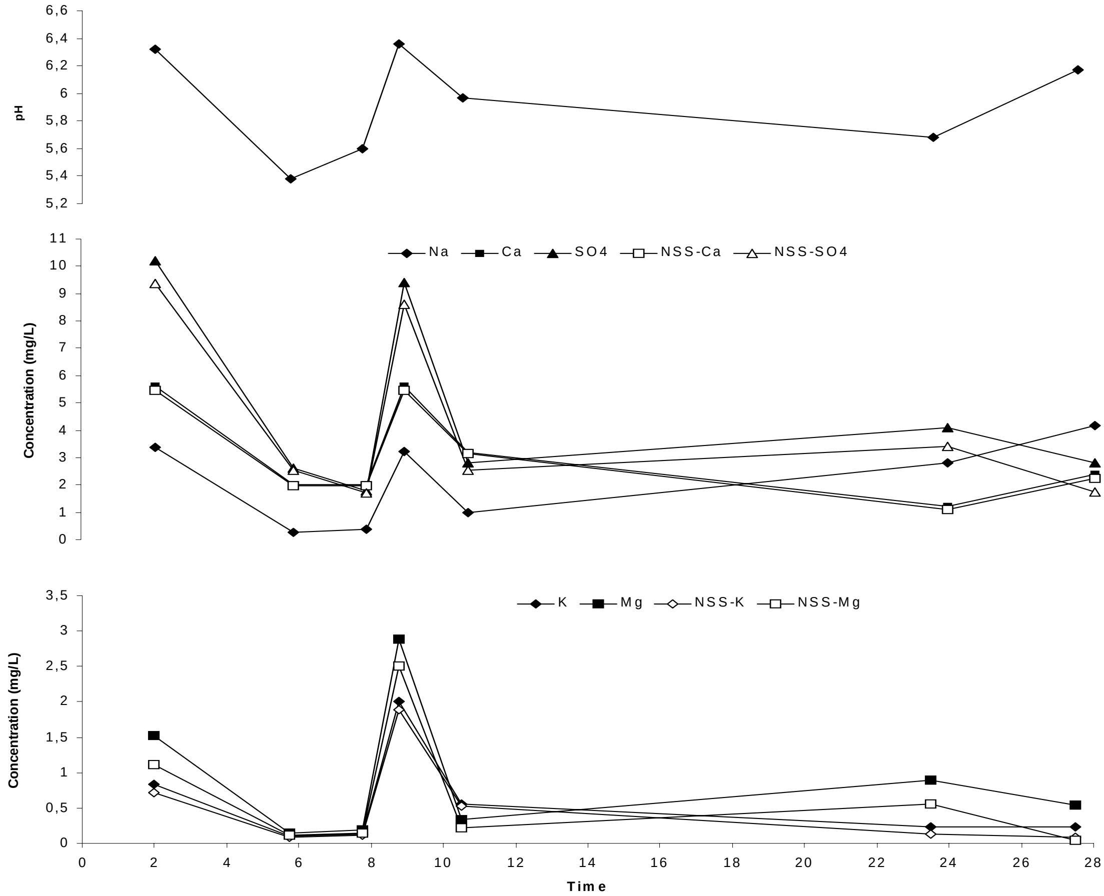

Figure 3. Variability of some ionic components and pH in sub-events as a function of time sampled on February 12 – 13, 2004.

Third Storm

On February 12 – 13, 2004, İstanbul was under the effect of a strong snow storm. It lasted 27.5 hours and 7 samples collected. Significant cold front passage was detected during the storm and snowing had been started after the two sub-event samplings and continued until the end of the storm. This storm was characterized by a slightly lower sea level pressure, 1009 mb, than the standart atmospheric value and very low temperatures, -7°C in İstanbul.

First and second sub-events that were sampled after 2 and 5.7 hours from the initiation of precipitation includes only rain (Figure 3). The first sampling resulted in a high value of pH and high concentration of ions. Especially very high SO_4^{2-} and NSS SO_4^{2-} concentrations were measured as 10.2 and 9.36 mg/L, respectively. Second and third sampling resulted in a lower concentration for these ions. Third sub-event has rain event together with snow. Precipitation lasted as snow after 4th sub-event. At this sub-event, 8.7 hour from the initiation precipitation, concentrations of ions increased dramatically. In third sample, which included only snow, concentrations of SO_4^{2-}, Ca^{2+}, Na^+, $Mg^{2+}$and K^+ were found as 9.4, 5.6, 3.21, 2.89 and 2.00 mg/l and NSS concentrations of SO_4^{2-}, Ca^{2+}, $Mg^{2+}$and K^+ ions were calculated as 8.60, 5.48, 2.5 and 1.89, respectively.

Fourth storm

The last storm studied in this work took place on October 27 – 28, 2003 and it precipitated only rain. Only 4 sub-events were collected through the storm that lasted in 13.2 hour. This storm was characterized by a minimum sea level pressure value of 1008 mb and a decrease of temperature from 13°C to 8°C.

pH and ions concentrations were found to be high in the first sub-events except SO_4^{2-} . The concentration of this ion increased continuously during the precipitation period (Figure 4). The concentration of cations decreased in the last sub-event. Owing to this decrease, acidity increased in this sample. Contrary to other storms, low correlation coefficients was found between SO_4^{2-} and other ions. It is believed that emissions of SO_4^{2-} from nearby areas due to domestic heating especially between 4.1 and 13.2 hours during the storm contributed into SO_4^{2-} concentrations. Other ions have variability similar to each other, with high correlation coefficients ranging between 0.99 and 0.75. Because anions do not have extra emissions during cooling periods, these anion concentrations in rain can decrease with time through the washout process and this may be the reason of finding a decrease in the acidity for the last sub-event sample. Anions and pH showed similar variability with a high correlation coefficient between them, ranging from 0.53 to 0.71.

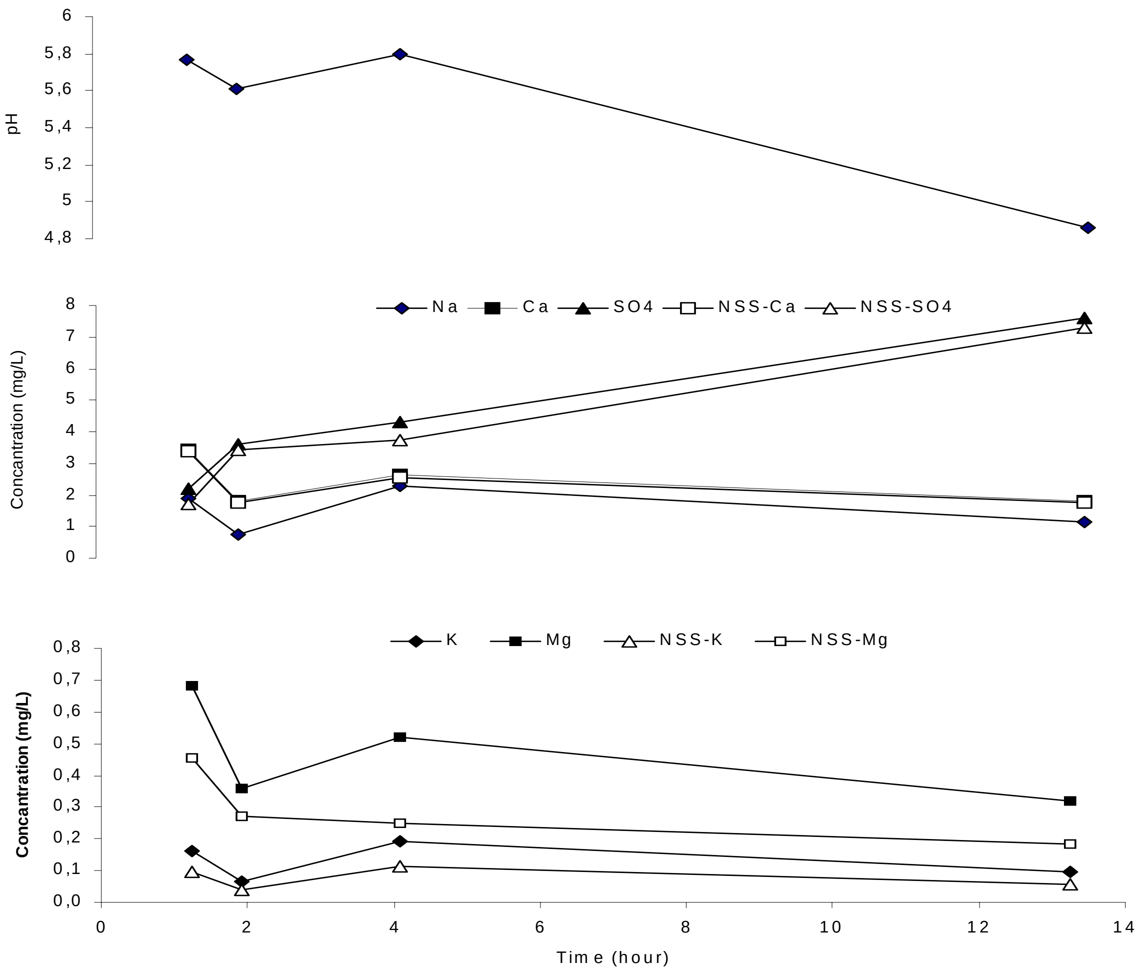

Figure 4. Variability of some ionic components and pH in sub-events as a function of time sampled on October 27 – 28, 2003.

Sources of the Ions

Mean concentrations and mean NSS concentrations of ions were depicted in Table 1. For the storms, mean NSS concentrations of SO_4^{2-}, Ca^{2+}, K^+, and Mg^{2+} were calculated as 3.37, 2.15, 0.37, 0.35 mg/L. Generally, SO_4^{2-} and Ca^{2+} were found to be the dominant ions. High sulfate concentration in samples was thought to be neutralized by the contribution of high concentrations of alkaline compounds. Results indicated that the ratio of the mean NSS concentration to the mean concentration of Ca^{2+} ranges between 0.91 and 0.98, suggesting that most of the calcium came from soil. Mg^{2+} seems to be diluted by sea and concentrated by soil. Average value of this ratio for Mg^{2+} was calculated as 0.55. This means that almost half amount of this ion came from non-sea sources. K^+ has a high ratio and main source of this ion can be expressed as soil. The ratio for SO_4^{2-} ranged between 0.75 and 0.92, leading to a possible conclusion that the industrial and domestic activities were the main source of this ion.

Table 1. Mean concentrations and mean NSS concentrations of ions (mg/L).

	Na^+	K^+	Ca^{2+}	SO_4^{2-}	Mg^{2+}	pH
January 21th - 23th, 2004	1.82	0.58-0.52	1.95-1.88	3.23-2.78	0.40-0.19	5.80
November 9th – 11th, 2003	3.15	0.49-0.39	1.41-1.29	3.15-2.36	0.72-0.34	4.83
February 12th – 13th, 2004	2.17	0.58-0.51	3.14-3.06	4.81-4.27	0.93-0.67	5.93
October 27th – 28th, 2004	1.51	0.16-0.06	2.41-2.36	4.43-4.08	0.45-0.18	5.51
Average	2.16	0.45-0.37	2.23-2.15	3.90-3.37	0.63-0.35	5.52

4. CONCLUSIONS

This study presents the variation in the chemical composition and pH in four precipitation events that was sampled in İstanbul. These events lasted 53.3, 47.9, 27.5 and 13.2 hours and the number of collected samples for each event was 22, 14, 7 and 4. Sub-event samplings were carried out for each precipitation event in the presence of online satellite images, 00 GMT surface maps and 500 hPa geopotential height maps.

All ions showed similar variability during all storms with high correlation coefficients, except for rain event sampled on October 27 – 28, 2003. SO_4^{2-} gave negative correlations with other ions during this storm. It is believed that emissions of SO_2 from nearby areas contributed into SO_4^{2-} concentrations.

Generally values of pH and concentrations of ions belonging to the first samples of all four cases were found higher than those of other sub-event samples taken in sequence. It is clearly observed that the concentration of ions and pH decreased until third and fourth samples. Coarse particles existing in the atmosphere, close to the surface, can contain high amounts of cations and these type of particles are more efficiently scavenged by precipitation than fine particles. On the other hand, fine particles are considered as important sources of the precipitation acidity. They can be found in low atmosphere as well as in high troposphere and can be removed from atmosphere by rainout and washout processes. With progressing time during a storm, concentration of large particles in the atmosphere was decreased by scavenging, thus leading to less and less concentration of suspended large particles in comparison with small acidic particles. Consequently, less amount of large particles transferred into droplets, leading to the decrease in the levels of cations and to the development of more acidic wet deposition.

The variation of concentration of ions depends on the meteorological conditions and precipitation types. Two precipitation events included rain and snow together where precipitation started as rain and continued as snow. In this study, it was shown that snow flakes are efficient scavenging agents, more efficient than the rain drops, and lead to an increase in the concentration of ions and pH in the samples just after the snowing starts.

For 4 storms, SO_4^{2-} and Ca^{2+} were found to be the dominant ions. There was high correlation between the total concentration and NSS concentration of ions. The main source of SO_4^{2-} was believed to be the industrial and domestic emissions. For all precipitation events, results indicated that most of the Ca^{2+} and K^{+} came from soil and half of the Mg^{2+} came from sea.

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