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Comparison of Wet, Bulk and Dry Deposition Between Urban and Rural Regions of Kirklareli, Turkey

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Abstract. This study focuses on three types of atmospheric deposition; wet, bulk and dry that were collected in an urban and a rural area of Kirklareli city (Turkey) during the period of September 2010 – December 2010. The urban sampling station was located at the city center and the rural one located 3 km southwest from the center of Kirklareli. During the sampling period, 20 wet, 16 bulk and 12 dry samples were collected simultaneously in the city center and in the rural area. Concentrations of the main cations Na^+, Mg^{2+}, Ca^{2+}, K^+, NH_4^+ and the main anions Cl^-, NO^{3-}, SO_4^{2-} together with pH were measured. The mean wet deposition concentrations of all ions and the bulk deposition concentrations of all ions except K^+ sampled in the city center were found to be higher than those of the rural area. On the other hand, dry deposition concentrations of K+, NH_4^+, Cl^- and NO_3^- in the rural area were found higher than those of the city center. The samples of each type deposition collected in the rural area were found to be more acidic in comparison to the samples collected in the city center. The main reason of this can be the higher concentrations of Ca^{2+} measured in the urban station which is responsible for the neutralization of the acidity. In addition, sequential rain sampling in a rain event was carried out in Istanbul (Turkey) by using an automatic sequential rain sampler which was designed and produced in the project supported by TUBITAK (The Scientific and Technological Research Council of Turkey). Values of pH and concentrations of ions in the first sequential rain samplers collected in Istanbul were found higher than those of the other sequential samples taken in sequence owing to the strong initial washout of the atmosphere by raindrop.

Keywords: rain chemistry, sequential rain sampling, rural area.

1. Introduction

Dry and wet deposition are crucial removal processes of the particulate matter in the atmosphere to the Earth's crust. Acidic deposition is the combined total of wet and dry deposition, with wet acidic deposition being commonly referred to as acid rain. Basic compounds can also influence the pH. Calcium (Ca^{2+}), magnesium (Mg^{2+}) and ammonium (NH_4^+) ions are affective in the neutralization of the rain droplet and change the overall H^+ concentration. Dry deposition of gaseous SO_2, NO_2, and HNO_3 and acid aerosols occurs by coming in contact with or settling to the surfaces of water bodies, vegetation, soil, and other materials when it is not raining. The fall velocities of spherical particles as a function of size were given by Hanna et al. [1]. The course particles which have soil and sea sources in general have more fall velocity comparison to that of fine particles in the atmosphere originated from gas-to-particle conversion processes. Wet deposition is the scavenging of particles or gases that take place in clouds (rain out) by cloud droplets or

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below clouds (wash out) by precipitation. Many studies were carried out on the composition of wet only deposition such as Ahmed et al. [2], Okay et al. [3], Al-Momani et al. [4] and Gulsoy et al. [5]. Some studies investigated the wet deposition chemistry using the sequential rain sampling in the rain events in order to introduce interrelationships among the chemical species in the sequential samples and atmospheric variables [6], [7].

Bulk deposition includes both wet deposition and dry deposition that may fall into a collector that is kept open to the atmosphere continually. Bulk deposition chemistry is very susceptible to local contamination from wind-blow dust, birds and insects, so that the choice of the sampling site is crucial. If local contamination can be disregarded, bulk deposition, probably better approximates what actually falls on the soil surface than does wet deposition [8]. Some important studies were carried out in order to find the variations and sources of the chemical species in the bulk deposition [9], [10].

2. Experimental and Methodology

This study presents the chemical composition of wet, dry and bulk deposition sampled in Kirklareli (Turkey) during the period of September 2010 – December 2010 at two sampling stations and also sequential rain sampling in a rain event was carried out in Istanbul (Turkey) by using an automatic sequential rain sampler which was designed and produced in the project supported by TUBITAK (The Scientific and Technological Research Council of Turkey). The urban sampling station was located at the city center and the rural one located 3 km southwest from the center of Kirklareli (27°13′ E and 41°44′ N). Kirklareli is the medium-sized settlement in Turkey, with nearly 62.000 inhabitants in the city. During the sampling period 20 wet, 16 bulk and 12 dry samples were collected simultaneously in the city center and in the rural area. Precipitation samples were collected by using a polyethylene funnel of 20 cm fitted onto a polyethylene container. The collectors and funnels were mounted at a height of 180 cm above the ground. This height was necessary to avoid possible sources of contamination by the ground dust. After the collection of each bulk sample, a clean funnel and container was established that would be exposed until next precipitation event. Bulk collector exposed to the atmosphere continuously until the end of the rain included dry and wet deposition. Dry deposition container was established in such a way that it prevented the rain drops to enter into the funnel. Dry deposition sampler collected only particulate matter in the fifteen-day periods. Dry deposition funnel was washed with 1L distillate water at the end of the sampling periods. Wet only deposition collectors were washed by distilled water and dried every day. Prior to installations the funnel and collectors used for bulk and dry deposition were 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 precleaned polyethylene bottles in the refrigerator at 4 °C prior to chemical analysis.

Sequential sampling station was in Sisli, located on the European side of Istanbul, (28°59′ E and 41 °03′ N). Istanbul is the largest urban settlement in Turkey, with nearly 12 million inhabitants in the metropolitan area. Four sequential rain samples were collected in the rain event occurred on December 27th 2010. Just before the approach of a low pressure system the rain sampler device was established at a place where it would collect precipitation samples. Methods of the analyses were same for the wet, dry and bulk samples.

3. Results and Discussion

The comparison of the chemical species of wet, dry and bulk deposition between the urban and rural areas was done in this study (Figure 1). The mean concentration of anions for the wet deposition in the urban area can be ordered in a descending way as follows NO_3^-, Cl^-, SO_4^{2-}. The mean values of these anions were obtained as 11.59, 10.2, 2.92 mg/L, respectively. Mean concentrations of cations Ca^{2+}, Na^+, K^+, Mg^{2+}, NH_4^+ were found to be 17.84, 2.46, 1.34, 1.24, 1.15 mg/L, respectively. NO_3^- was found to be the dominant anion and Ca^{2+} was found to be the dominant cation. Mean concentrations of cations in the rural area (Ca^{2+}> NH_4^+ >Na^+> Mg^{2+}>K^+) were found to be 9.20, 1.48, 1.26, 1.12, 0.57 mg/L, respectively. NO_3^- was found to be the dominant anion and Ca^{2+} was found to be the dominant cation for both of the areas. Owing to the consumption of coal in small units used for domestic heating in Kirklareli during the sampling period, SO_4^{2-}

was generated by urban sources. It is clear in the dry deposition part of Figure 1 the concentrations of all ions except for SO_4^{2-} and Ca^{2+} in the rural area are higher than those of the urban area. However, the concentrations of all ions corresponding to the wet and bulk deposition in the rural area were found to be less than those of the urban area except for K^+ and NH_4^+. 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 [7].

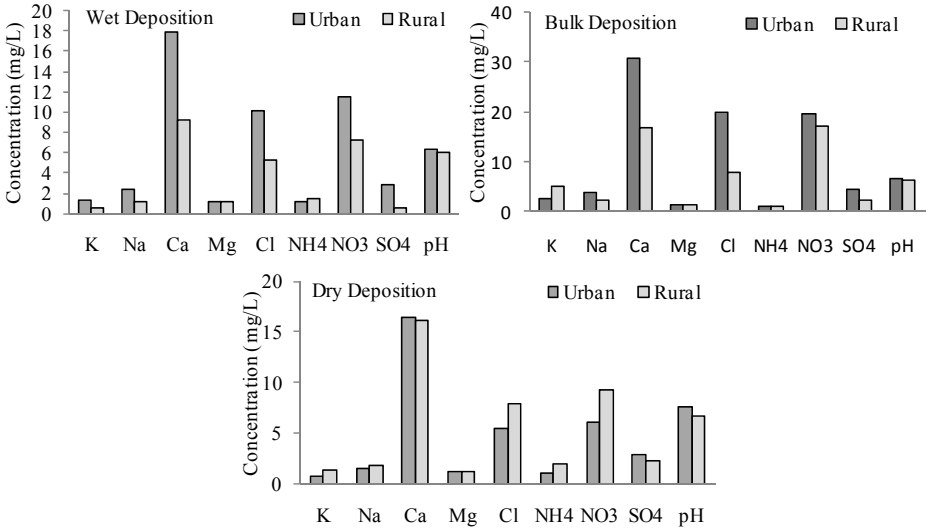

Fig. 1: Chemical species of wet, dry and bulk deposition in the urban and rural areas.

Intensive human activities like construction works and motor vehicles mobility in the city resulted in more mass of course dust particles in the urban area than that in the rural area in which there were less human activities. In the urban area wet and bulk deposition concentrations of ions were found to be higher than those in the rural area. The reason of this situation is believed to be the higher concentrations of coarse particles corresponding to higher scavenging rates in the urban area. Higher concentrations of SO_4^{2-} were found in the urban area in comparison to those in the rural area for all of the three deposition types. The main reason of high SO_4^{2-} concentrations in the city is the fact that the main source of SO_4^{2-} is the combustion processes of the domestic heating. In contrast to SO_4^{2-} , NH_4^+ concentration was found higher in the rural area than that in the urban area for the three deposition types due to the fact that the main source of this ion is the agricultural activities in the immediate surroundings of rural sampling location. It was found that the acidity of the samplings of the three deposition types in the rural sampling location were higher than those in the urban sampling station. The pH values of wet, bulk and dry deposition were found as 6.03, 6.40 and 6.65 in the rural and 6.33, 6.61 and 7.55 in the urban area, respectively. High sulphate concentration in the samples collected especially in the urban area was thought to be neutralized by the contribution of high concentrations of alkaline compounds (Ca^{2+}, Na^+ and K^+) in this area.

On December 27th 2010 an approaching weak cyclone was detected and sequential precipitation sampling carried out. The sampling lasted in 40 min, as with the precipitation, and altogether 4 samples were obtained (Figure 2). At least 100 mL precipitation water must be collected in order to conduct all of the analyses. Figure 2 presents the variation of SO_4^{2-}, NO_3^- and pH as a function of time during the rain event. The first sampling which resulted in a high value of pH, and high concentrations of SO_4^{2-} and NO_3^- were taken after 10 min from the initiation of the precipitation. Between second and third sampling times, 20–30 min, concentration of the ions increased slightly. After the initial high value of pH that was 7.51, a decrease with time was observed to a minimum value of 6.2. Coarse particles existing in the atmosphere, close to the surface, can contain high amounts of cations and these types 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 the atmosphere by rainout and washout processes. In the process time during a storm, the 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, a smaller amount of large particles is transferred into droplets, leading to the decrease in the levels of cations and to the development of more acidic wet deposition [7].

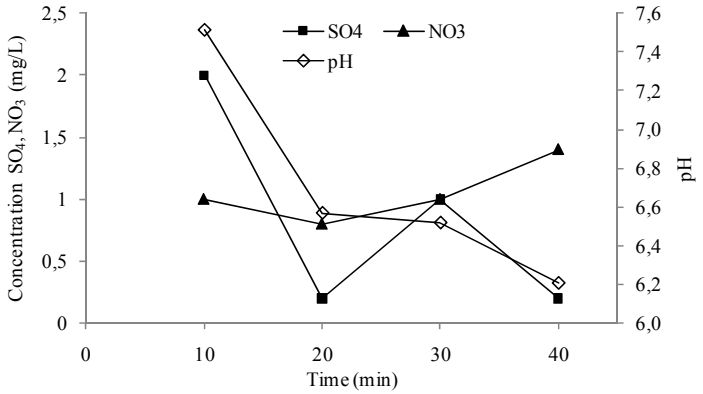

Fig. 2: Variation of SO_4^{2-}, NO_3^- concentrations during the rain event on December 27th 2010.

4. Summary and Conclusions

This study presents the results of three types of atmospheric deposition; wet, bulk and dry that were collected in an urban and a rural area of Kirklareli city (Turkey) during the period of September 2010 – December 2010. The concentrations of all ions in the dry deposition except for SO_4^{2-} and Ca^{2+} in the rural area were higher than those of the urban area. On the other hand, the concentrations of all ions corresponding to the wet and bulk deposition in the rural area were found to be less than those of the urban area except for K^+ and NH_4^+. Intensive human activities like construction works and motor vehicles mobility in the city can accumulate high amounts of coarse dust particles which can contain high amounts of Ca^{2+}, Mg^{2+}, and K^+ in them. These types of coarse particles are more efficiently scavenged by precipitation than fine particles. In the urban area wet and bulk deposition concentrations of ions were found to be higher than those in the rural area. The reason of this situation is believed to be the higher concentrations of coarse particles corresponding to higher scavenging rates in the urban area.

In contrast to SO_4^{2-} , NH_4^+ concentration was found higher in the rural area than that in the urban area for the three deposition types owing to the fact that the main source of this ion is the agricultural activities in the immediate surroundings of rural sampling location. It was found that the acidity of the collected samples belonging to the three deposition types in the rural sampling location were higher than those in the urban sampling station. High sulfate concentration in the samples collected especially in the urban area was thought to be neutralized by the contribution of high concentrations of alkaline compounds such as Ca^{2+}, Na^+ and K^+.

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