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# **SAMPLING AND ANALYSIS OF SNOW WATER: EXPERIMENTAL PROBLEMS AND INTERPRETATION OF RESULTS**

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Sampling and analyses of snow water at a mountainous site of northwestern Turkey were described. A snow sampler designed in our laboratory was used in the sampling. Ion chromatography, flame atomic absorption and emission spectrophotometry were very good techniques for the determinations of major ions in snow samples. The accuracy of results was tested by using different standard reference materials for both techniques. The results were in good agreement with the certified concentrations. The results of analyses were accepted if the error was less than 15%. The overall precision was in between 1–6%. The concentrations of snow samples were high compared with the literature values. The pH of them was found to be acidic with the average value of 4.3. Magnesium had the highest average scavenging ratio, and ammonium ion had the lowest average scavenging ratio. Sodium, K, Ca and Mg were mostly originated from the earth crust. Marine contribution to the sampling site was also effective.

*Keywords:* Snow water; major ions; IC; FAAS; FAES; standard reference materials; accuracy; precision; scavenging ratio

## **INTRODUCTION**

In atmospheric research, characterization of wet deposition has its unique importance, especially in mountainous areas where snow is the major form of the wet deposition. The determination of the chemical composition of snow is of increasing importance in acid deposition studies especially in forest areas as forest can be a temporary reservoir for pollutants. The subject of snow chemistry has become an important issue, for example, in Scandinavia where snow forms a large portion of the total annual precipitation<sup>1</sup>. The most commonly used

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analytical techniques for determining metals and ions in atmospheric precipitation are flame atomic absorption (FAAS) and emission spectrophotometry (FAES) and ion chromatography (IC). For example, determination of major anions and cations in snow and ice cores collected in Antarctica and Greenland by ion chromatography at trace level concentrations was presented by Buck et al.<sup>2</sup> and Legrand and Delmas<sup>3</sup>. Major cations and anions in snow of Scottish catchment<sup>4</sup>, in the central Washington Cascades<sup>5</sup> and a rural area in Champagne, France<sup>6</sup> were determined by AAS and IC respectively. Major anions and ammonium ion in snow collected in Alpine snow field of Switzerland<sup>7</sup> were measured by IC and major cations in snow collected in a rural upland site in Mid-Wales<sup>1</sup> were determined by flame AAS and AES. In addition, successful applications of IC and AAS were obtained to determine the chemical composition of precipitation in Albany<sup>8</sup>.

This work discusses the problems encountered on the sampling and analysis of snow water, applicability of the different analytical techniques used in the determination of major ions and the interpretation of the results.

## EXPERIMENTAL

### Sampling Site

Samples were collected at Uludağ Mountain of Bursa city. The altitude of the mountain was 1685 m and about 20 km away from the city. Bursa city has around three million population and is very polluted due to heavy industrialization, domestic coal burning and its geographical location. This site was chosen considering some important points like height of the sampling site, local meteorology, distance to local sources and to the forest. The sampling site (Sarialan region) is a 1 km<sup>2</sup> clearance within a pine forest. The nearest emission points and human activities are 1 km away. It was not possible to go very far away from the roadway and electricity because of severe winter conditions. The site is about 7 km north-west of a ski resort area. The Marmara Sea and Aegean Sea are located 40 km north and 200 km west of the sampling site respectively.

### Sample Collection and Handling

Sampling of snow is difficult especially in mountainous areas because of hard winter conditions. Therefore, we did weekly bulk sampling which means in between two snow events, dry deposition, little amount of rain and rime might also be collected. Since during the week it did not snow continuously. Sampling

was performed during the period of December 1993–April 1994. Average amount of the precipitation in long-term period (yearly) is 1483.6 mm and average amount of the precipitation in 1993 and in 1994 was 1285.3 mm and 2400.0 mm, respectively. Average snow heights at the sampling site in December 1993, and January, February, March, April 1994 were 60, 100, 138, 120 and 50 cm respectively.

The snow collector was designed in our laboratory and was placed in a platform which is 2–2.5 m above the ground. The collector is made up of a funnel which has a diameter of 23.5 cm and 25 cm height connected to a polyethylene barrel inside a 70 cm × 50 cm white-painted metal box attached to ground and the funnel was circulated with silk asbestos with a thermostat (15–30°C) on the outer walls of the funnel to melt the snowflakes. Snowing in Uludağ Mountain was so heavy that we could lose much of snow if it was not melted when it fell down to the funnel during one week period and the heating also avoided the contamination problems. Other purpose of the heating was to increase the collection efficiency because of the heavy snowing which accumulated a lot of snow during one week. If we did not use the heating system, the collected volume of snow would be 6–16 times less than the actual volume of snow. In order to obtain this rough information, the average volume of snow was calculated by multiplying the average snow heights in winter with the area of the funnel. This volume is divided by the volume of the funnel. Thus after collection, the barrel was removed from the sampler and closed immediately. Field blanks were also collected by carefully pouring 100 mL double distilled deionized water rinsing the sides of the funnel. Afterwards, they are exposed to all steps of sampling, sample handling and analysis.

Aerosol samples (particles having diameter of less than 10  $\mu\text{m}$ ) were collected daily on glass fiber filters by means of a MPSI 100 model (Environment S. A.) autoanalyzer equipped with PM-10 sample inlet with a flow rate of 25 L/min.

Substantial care was devoted during the whole work. Polyethylene gloves were used in all steps of the sampling and sample handling. As the air of the laboratory could be a source of contamination, all the sample handling before the analyses were done in a Class-100 clean room in Environmental Engineering Department of the University. The air flow to the room was through four HEPA (High Efficiency Particulate Filters) filters which remove particles greater than 0.1  $\mu\text{m}$  with 99.99% efficiency.

### **Reagents, Cleaning the Materials and Sample Preparation**

All chemicals used were of analytical grade. Since concentrations of cations in snow are very low, high purity reagents were used in all analyses. All solutions

were prepared with double distilled deionized water obtained from Nanopore, Ultrapure Water Purification System.

Standard stock solutions for ion chromatography were prepared from NaCl, NaNO<sub>3</sub> and K<sub>2</sub>SO<sub>4</sub>. The mobile phase for IC was 0.1 mM phthalic acid adjusted to pH of 4.93 to 4.95 by using saturated sodium borate (Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10 H<sub>2</sub>O) solution. Acetonitrile solution (30% (v/v)) was used for the column protection. After preparation, the solutions were degassed by ultrasonic shaker for 15 min in order not to damage the ion exchange column. Standard stock solutions of 1000 mg/L concentration for flame analysis were prepared from solid CaCO<sub>3</sub>, NaCl, KCl and Mg ribbon. In addition to these standard solutions, multielement standard solutions from Merck were also used for calibration. Additionally, field blanks, laboratory blanks which include all reagents used in all steps of analysis were prepared. Water blanks were prepared by taking double distilled deionized water samples from different water batches used during the preparation of the samples. For ammonium analysis a standard stock solution was prepared from (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> which was dried at 100°C for 1 hour. Polyethylene materials, glassware and polypropylene cups used for flame analyses were cleaned by soaking in 10% (v/v) nitric acid solution for at least 24 hours prior to their use, rinsed with double distilled deionized water and dried in the clean room. After pH measurements and filtration by using a clean all-plastic vacuum filtration unit through 0.2 µm pore size filters, a sample was divided into three fractions; the first one was poured into a water-washed polyethylene bottle to be analyzed for Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> by ion chromatography, the second one was poured into a water-washed bottle for the determination of NH<sub>4</sub><sup>+</sup> by colorimetry and the third aliquot was kept in the acid-washed polyethylene bottle for determinations of Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup>. Approximately 0.5 mL of suprapure nitric acid were added to the 100 mL sample bottles to desorb metals from the walls of the bottles. Solutions were kept frozen until the time of analysis.

### Analytical Techniques

Ion chromatography (IC) was used in this work for the determination of anions. The instrument was equipped with a Varian pumping system, a Vydac 302 ion exchange column and a Jasco 875 UV detector. Phthalic acid absorbs in UV range (254 nm). Therefore, a decrease in the background was observed during the elution of the individual anion. This method is called as indirect UV. The instrument was interfaced to a computer for peak fitting using a software Peak 2. During the analysis, the chromatogram was first observed on the screen of the computer, about ten minutes after the injection, three peaks of Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>,

$\text{SO}_4^{2-}$  were obtained. Concentrations of the anions according to the calibration were obtained after the peak identification. The sample was directly injected without pretreatment through a standard 100  $\mu\text{l}$  loop and eluted by a mobile phase following through the column at a rate of 3 mL/min.

Atomic absorption spectrophotometry (AAS) was used for the determination of Ca, Mg, K and Na. A Perkin-Elmer model 1100B atomic absorption spectrophotometer connected to a L-850 model Epson printer was used to analyze the samples and record the results. All samples were analyzed by using air/acetylene flame. Magnesium was determined by flame AAS; Na, K and Ca were determined by flame AES. Standard addition method was used to prepare calibration curves for all elements. Instrumental settings during FAAS and FAES analyses are summarized in Table I.

Ammonium ion was determined colorimetrically at 425 nm using a Unicam 8625 UV/VIS Spectrometer after having been complexed by Nessler's reagent to form yellow to brown color against a field blank after 20 minutes. The quartz cells used had an optical path length of 1 cm.

The pH of samples were measured with a Cole-Parmer 5985-80 model portable pH meter, equipped with a glass electrode. The pH meter was calibrated before measurements using standard buffer solutions of pH 4.00 and 7.00.

## RESULTS AND DISCUSSION

### Quality Control of the Analytical Techniques

The accuracy of flame analyses results were tested by the analysis of the standard reference materials (SRMs). Three different SRMs (GSP-1 U.S. Geological Survey, SRM-2704 Buffalo River Sediments from NIST and SRM-1646 Estuarine Sediment from NBS) were digested and analyzed with the samples. Laboratory blanks (acid and water blanks) were used in order to estimate the contribution of each reagent and the sample handling. Therefore, the reference materials with acid blanks and water blanks were analyzed every morning before starting the analyses and results were compared with the certified values. If

TABLE I Flame absorption and emission spectrophotometry conditions

	<i>Mg</i>	<i>Ca</i>	<i>Na</i>	<i>K</i>
Wavelength, nm	285.2	422.7	589	766.5
Slit width, nm	0.7	0.7	0.2	0.7
Technique	FAAS	FAES	FAES	FAES

the results were close to the certified values within an error limit of at most 15%, then the analysis was continued. Standard addition method was used in order to compensate the matrix effects. The results of analysis of the standards are given in Table II.

In IC analyses, the standard reference simulated rain water SRM 2694a-I and 2694a-II produced by NIST were used. For IC only water blanks were analyzed, since it was the only reagent used. The concentrations of field blanks and water blanks were below the detection limits. The results of SRMs analyses were compared with the certified values and presented in Table III. Measured concentrations were in good agreement with the certified concentrations.

Analytical precision of species measurements was determined by duplicate measurements and is given in Table IV. Typical precisions for  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  were 6%, 4%, 1% and 3%, respectively, in FAAS and FAES techniques. For IC measurements, typical precisions for  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$  were 3%, 1%, 2% respectively. In overall, the precision of measurements was very good for both techniques.

### Observed Concentrations, Temporal Variations and Scavenging Ratio

The concentrations of ions in snow are given in Table V. Snow samples were bulk samples including wet and dry depositions, therefore standard deviations were high. In addition to these when we compare our data with the literature values given in Table VI, it can be seen that our results are comparable with only the results of old snow samples collected in Plynlimon in Great Britain<sup>1</sup> which is located approximately 25 km from the west coast of Wales with an altitude range between 350 and 700 km above sea level.

Two types of samples were collected: fresh snow collected either during or within a few hours of snow fall and old snow collected from standing accumulations within 3 days or a week in depths of 50 and 200 mm below the surface by using wide-necked polypropylene jars and containing an accumulation of

TABLE II Concentrations of elements observed in standard reference materials compared with certified values

Element	Conc. unit	GSP-1		SRM-2704		SRM-1646	
		Certified conc.	This study average $\pm$ sd	Certified conc.	This study average $\pm$ sd	Certified conc.	This study average $\pm$ sd
Na	%	2.08	2.04 $\pm$ 0.17	0.76	0.68 $\pm$ 0.10	2.00	1.95 $\pm$ 0.13
K	%	4.57	4.54 $\pm$ 0.14	2.00	1.97 $\pm$ 0.10	1.63	1.79 $\pm$ 0.13
Ca	%	1.46	1.56 $\pm$ 0.18	2.60	2.40 $\pm$ 0.12	0.83	0.73 $\pm$ 0.16
Mg	%	0.59	0.61 $\pm$ 0.04	1.20	1.17 $\pm$ 0.15	1.09	1.05 $\pm$ 0.10

TABLE III Comparison of the IC results with the certified values (mg/L)

<i>Ions</i>	<i>2694a-I</i>		<i>2694a-II</i>	
	<i>Certified conc</i>	<i>This study average ± sd</i>	<i>Certified conc.</i>	<i>This study average ± sd</i>
Cl <sup>-</sup>	0.20	0.21 ± 0.04	1.00	1.05 ± 0.11
NO <sub>3</sub> <sup>-</sup>	0.50	0.70 ± 0.07	7.00	8.08 ± 0.71
SO <sub>4</sub> <sup>2-</sup>	2.00	2.04 ± 0.22	11.0	10.7 ± 1.20

black dust particles on the surface of snow. The composition of the two samples was very different from each other. It was suggested that a sequence of freeze-thaw cycles would probably tend to remove soluble impurities from the upper part of the snow cover and concentrate them in the lower part so old snow had become more concentrated in solutes and also old snow samples were found to be more acidic. The influence of marine aerosols was observed on the concentrations of Na, Mg and Cl. Other two literature values are comparable to each other but not to our study. The sampling for the first one was done in Washington Cascades at an elevation of 2054 m for one week period. Bulk samples were taken in the polyethylene buckets so they were open to the dry deposition. However, the chemical composition of snow in this site differs little from the composition of snow collected at remote stations in the world. Thus, this site was not influenced very much by the local sources. For the second work, fresh snow was sampled by removing 1–2 cm of surface snow and collecting sub-surface snow at elevations ranging from 1875 m to 2642 m. Since the samples were collected on event base, the chemical composition of snow was different from our site. The last two works were chosen because they represent our sampling site as being mountainous areas.

Temporal variations of SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> ions were similar. Also, Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup> showed similar temporal trend in all samples. An aerosol study<sup>10</sup> in the same sampling site done by our group indicated that these cations were mostly originated from the crust. However, chloride to sodium molar ratio

TABLE IV Typical precisions for ions

<i>Ions</i>	<i>Precision (%)</i>
Na <sup>+</sup>	6
K <sup>+</sup>	4
Ca <sup>2+</sup>	3
Mg <sup>2+</sup>	1
Cl <sup>-</sup>	3
NO <sub>3</sub> <sup>-</sup>	1
SO <sub>4</sub> <sup>2-</sup>	2



TABLE V Summary of major ion concentrations in snow ( $\mu\text{eq/L}$ )

<i>Ions</i>	<i>Mean</i>	<i>Standard Deviation</i>	<i>Min.</i>	<i>Max.</i>
H <sup>+</sup>	181	165	0.26	550
Ca <sup>2+</sup>	52.0	53.8	12.6	162
Na <sup>+</sup>	29.7	20.2	9.00	70.4
K <sup>+</sup>	2.35	1.20	0.64	3.89
Mg <sup>2+</sup>	19.8	15.6	5.84	55.2
NH <sub>4</sub> <sup>+</sup>	22.0	21.5	2.26	70.5
Cl <sup>-</sup>	29.0	15.0	11.8	50.9
NO <sub>3</sub> <sup>-</sup>	23.9	14.6	10.3	58.7
SO <sub>4</sub> <sup>2-</sup>	53.0	48.4	17.3	183

was 1.15 which is very close to the ratio in the bulk sea water of 1.18<sup>11</sup>. This result implies marine effect to the observed concentrations. Sodium was in excess because of the crustal contribution.

pH distribution in snow samples is shown in Figure 1. Average pH of samples is 4.3 indicating the acidic nature of snow. The acidity of samples were affected from organic acids coming from the trees<sup>10</sup> as well as from H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> which were scavenged from the atmosphere by snow. Samples 3, 4, 5, 6 and 7 were consecutive samples and pH of them increased as snow continued to fall. The 8th sample was collected two weeks after from the 7th one. The pH of this sample was decreased substantially as the pollutants were loaded in air during two weeks dry period.

TABLE VI Average levels of major ions in snow in the different parts of the world ( $\mu\text{eq/L}$ )

<i>Ions</i>	<i>This work</i>	<i>Plymimon (rural)</i>	<i>Great Britain<sup>1</sup></i>	<i>Washington<sup>5</sup> Cascades (mountain)</i>	<i>California<sup>9</sup> (mountain)</i>
		Fresh snow	Old snow		
pH	4.36	4.50	3.89	5.7	
H <sup>+</sup>	181	32	129	2.0	5.1
Ca <sup>2+</sup>	52	4	14	5.9	1.1
Mg <sup>2+</sup>	20	4	11	1.3	0.7
Na <sup>+</sup>	30	13	30	3.0	4.7
K <sup>+</sup>	2.4	1	5	1.1	0.5
NH <sub>4</sub> <sup>+</sup>	22			4.3	
Cl <sup>-</sup>	29	21	69	5.8	5.6
NO <sub>3</sub> <sup>-</sup>	24	11	64	11	5.3
SO <sub>4</sub> <sup>2-</sup>	53	16	78	7.6	3.4

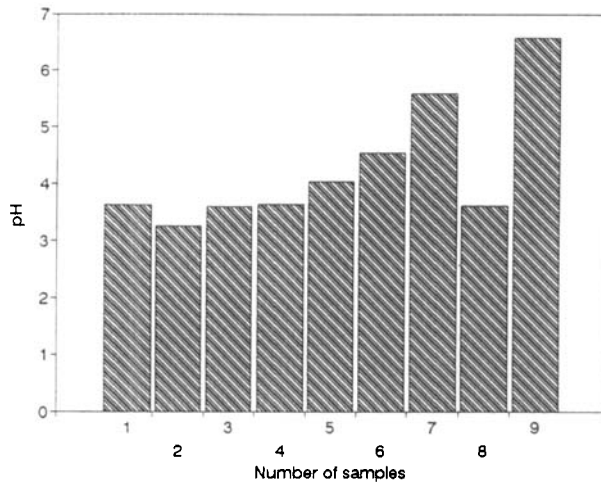


FIGURE 1 pH distribution in snow samples.

In order to relate airborne concentration to snow composition, scavenging ratios were calculated by taking the ratio of the concentration of ion in snow to the concentration of the same ion in air measured simultaneously and multiplied by the density of air to make the ratio a dimensionless quantity as it is given with the following relation

$$W = C_s/C_a \times d_a$$

where  $W$  = scavenging ratio,  $C_s$  = concentration of contaminant in snow ( $\mu\text{g/g}$ ),  $C_a$  = concentration of contaminant in air ( $\mu\text{g/m}^3$ ) and  $d_a$  = density of air ( $\text{g/m}^3$ ).

Aerosol samples were collected during the precipitation collection periods. The weekly concentrations of aerosol data represented as  $\mu\text{g/m}^3$ . In this calculation there are always some assumptions. Scavenging ratios have been calculated using ground-level measurements of concentrations measured over a time period longer than the precipitation event. Therefore, it is assumed that the atmospheric concentrations of the measured species are vertically and temporally constant during the measurement period. In addition, it is assumed that total deposition is due to only wet deposition and it neglects dry deposition. However, our samples include dry deposition. Also, in the calculation of scavenging ratios, density of air and snow were taken as  $1.2 \text{ g/m}^3$  and  $1 \text{ g/mL}$  at standard temperature and pressure, respectively. In spite of all these shortcomings, average scavenging ratios from various places of the world seem to be rather constant, although some values can change up to two orders of magnitude. This ratio gives a rough idea about the cleaning capacity of snow. A large

number of factors can also affect the scavenging ratios such as snow crystal type and size, aerosol particle size, precipitation depth, riming, vertical concentration gradients, cloud height, air temperature, relative humidity and electrical charge.<sup>7,12</sup>

Scavenging ratios of ions are tabulated together with the literature values in Table VII. As the snow scavenges the gaseous pollutants together with particulates, calculated sulfate and nitrate ratios included SO<sub>2</sub> and HNO<sub>3</sub> scavengings, respectively. Scavenging values of sulfate greater than 500 was probably caused by SO<sub>2</sub> scavenging during snow events<sup>12</sup>. Variation in ratios can also be attributed to differences in particle size of aerosols, with the smallest particles having the lowest ratio. It was expected to have high scavenging ratio for Ca<sup>2+</sup> as it is associated with large particles because of its dominant crustal source. But we observed moderately high calcium scavenging ratios. Ammonium ion had the lowest ratio as it was expected since it is usually associated with small particles. Magnesium had the highest ratio, as it has earth crust as a major source.

Binary correlations between measured ions were computed in order to obtain additional information on the sources and chemical forms of the ions. Correlation coefficients are shown in Table VIII. The highest correlation coefficients are for the ion pairs of Na<sup>+</sup> and Cl<sup>-</sup>, Ca<sup>2+</sup> and Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>, NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup> and SO<sub>4</sub><sup>2-</sup>, Ca<sup>2+</sup> and Na<sup>+</sup>. Most of these well correlated pairs have common sources or occur in snow as a result of a common source or compound like NaCl, CaCl<sub>2</sub>, NH<sub>4</sub>NO<sub>3</sub>, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and CaSO<sub>4</sub>. Calcium, K<sup>+</sup> and Na<sup>+</sup> ions are also correlated well. This suggests that they come from both soil and sea salt aerosols. The relatively high correlations of NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> and SO<sub>4</sub><sup>2-</sup> result from the reaction of nitric and sulfuric acids with gaseous ammonia. Likewise, the correlations of Ca<sup>2+</sup> with SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> may be the result of the reaction of these acids with alkaline compounds

TABLE VII Comparison of scavenging ratios

Ions	This work		Ref 12		Ref 7
	Scavenging Ratio	Range	Scavenging Ratio	Range	Scavenging Ratio
Cl <sup>-</sup>	950	88-1025			3200
NO <sub>3</sub> <sup>-</sup>	650	95-2780	1000		940
SO <sub>3</sub> <sup>2-</sup>	630	60-1630	570	60-2280	350
NH <sub>4</sub> <sup>+</sup>	180	10-340	410	40-2200	300
Mg <sup>2+</sup>	2000	240-7060			
Na <sup>+</sup>	675	17-2400			
K <sup>+</sup>	705	350-1060	1000		
Ca <sup>2+</sup>	310	25-960	2600	170-8190	

TABLE VIII Binary correlation coefficients between ions in snow

	$H^+$	$Cl^-$	$NO_3^-$	$SO_4^{2-}$	$Mg^{2+}$	$Na^+$	$K^+$	$Ca^{2+}$	$NH_4^+$
$H^+$	1.00								
$Cl^-$	-0.43	1.00							
$NO_3^-$	0.00	-0.43	1.00						
$SO_4^{2-}$	0.085	0.64	0.88	1.00					
$Mg^{2+}$	-0.48	0.23	0.25	0.27	1.00				
$Na^+$	-0.11	0.90	0.61	0.69	0.43	1.00			
$K^+$	-0.32	0.73	0.69	0.45	-0.035	0.64	1.00		
$Ca^{2+}$	-0.22	0.92	0.67	0.75	0.41	0.94	0.64	1.00	
$NH_4^+$	0.63	0.58	0.94	0.93	-0.05	0.66	0.56	0.66	1.00

containing  $Ca^{2+}$ . Good correlation between  $SO_4^{2-}$  and  $NO_3^-$  is probably due to the coemission of their direct precursors  $SO_2$  and  $NO_x$  from fossil fuel combustion. These results are supported further by anion versus cation combination. The correlation coefficient for  $(SO_4^{2-} + NO_3^-)$  versus  $(Ca^{2+} + Mg^{2+} + NH_4^+)$  is 0.83 and average of anion to cation equivalent ratio is 1.1. These results indicate that the major part of  $SO_4^{2-}$  and  $NO_3^-$  in snow samples is associated with  $NH_4^+$ ,  $Ca^{2+}$  and  $Mg^{2+}$  ions.

## CONCLUSION

Procedures for sampling and handling of snow water are described considering minimum contamination. The IC, FAAS and FAES techniques were very good techniques for the determinations of major ions in snow samples due to their speed, accuracy, sensitivity and precision. To test the quality of data, field blanks, laboratory blanks and the standard reference materials were analyzed with the samples. The measured concentrations generally showed a close agreement with the certified values for all ions in the standard reference materials within the precision of our results.

Concentrations in snow were high compared with other literature values. Sodium,  $K^+$ ,  $Mg^{2+}$ ,  $Ca^{2+}$  showed similar trends since they were mostly originated from the crust. However, marine contribution was also observed to the sampling site. The pH of the samples indicated the acidic nature of snow. However, the major part of  $SO_4^{2-}$  and  $NO_3^-$  ions were associated with  $NH_4^+$ ,  $Ca^{2+}$  and  $Mg^{2+}$  ions not with  $H^+$  ion.

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