Scavenging by Precipitation of Major Chemical Constituents at Two Romanian Sampling Sites

GABRIELA IORGA[1,2]*, VICTORITA PAUN[3]

[1] Department of Physics and Applied Mathematics, Faculty of Chemistry, University of Bucharest, 4-12 Regina Elisabeta Blv., 030018, Bucharest, Romania

[2] Research Center for Ecological Services, Faculty of Biology, University of Bucharest, 90-92 Panduri Str., 76235, Bucharest, Romania

[3] S.C. VerCalTest SRL, 139B Calea Plevnei, 060011, Bucharest, Bucharest

Prediction of removal of atmospheric pollutants with mixed composition, as they are present in the atmosphere, is very difficult and many uncertainties affect the quantification of their effects on climate and ecosystems. Investigations of precipitation data are important for evaluation of forests and soil conditions and for comparison of precipitation chemistry time trends at local and regional scale. The aim of this study has been to contribute to the understanding of scavenging by precipitation of anthropogenic and naturally emitted aerosols and trace gases and might help to improve the understanding of scavenging process parameterizations, which are crucial in climate change simulations with numerical climate models. We analyzed extracted data from two published datasets of rainwater chemical composition as follows: one for Iasi urban area, Romania [1], and one dataset with acidic precipitation data [2] in Retezat Mountains, Romania. We added for comparison extracted data from Indian Ocean Experiment [3]. We constructed a synthetic dataset by considering SO_4^{2-}, Cl^-, NO_3^-, NH_4^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, *as constituents important in precipitation chemistry that may imply ecological effects after deposition. We established relationships between major ion total concentrations and for different ionic constituents and precipitation depth for both Romanian sites. The computed washout ratios represent the first ones derived for an urban and a mountain site in our country. We also show that an indicative concentration of atmospheric pollutant concentrations during rain can be derived. These results can be used in closure studies when a more extensive field campaign (atmospheric aerosols and rainwater collected simultaneously) can be performed, as well. Moreover, washout coefficients for the selected Romanian regions have not previously been reported.*

Keywords: rainfall chemical composition, precipitation depth, washout ratio, wet deposition

During the last 20 years, extensive researches have brought into attention many and complex effects of the pollutants on climate, air quality, human health, aquatic and terrestrial ecosystems etc. In the atmosphere, pollutants (aerosols and soluble trace gases) undergo the following cycle: emission-transport-transformation-deposition. Each compartment of this cycle needs to be thoroughly understood in order to deal with the multitude of the revealed/proven effects. By the deposition processes both harmful (acidifications) and beneficial (providing of nutrients) effects on ecosystems can be induced. Dry and wet depositions, fog droplet interception (especially in high altitude forests), dew, frost and rime icing count for the removal mechanisms that clean the atmosphere. In dry deposition, substances in the atmosphere reach the Earth' surface by Brownian diffusion (gases and particles), impact, interception, gravitational settling, etc. (particles). Wet deposition involves hydrological cycle, pollutants being first incorporated in hydrometeors and then are delivered to surface by precipitation. Similar mechanisms act during in-cloud scavenging and below-cloud scavenging. These mechanisms are: convective Brownian diffusion, interception, inertial impaction, thermophoresis, diffusiophoresis, airflow turbulence and electrostatic attraction (an extensive review on these processes is given in [4]).

Various factors can influence dry and wet deposition but mainly they are size-dependent: large particles usually deposit rapidly in nearby pollution sources, whereas small particles can be transported far from their sources to undergo further transformations, and eventually coagulate until they are large enough to reach the surface under their own weight or by inclusion in precipitation drops [5]. Wet deposition is faster than dry deposition but the wet process appears episodically while the dry one occurs all the time. Moreover, the wet removal by precipitation is by far the most efficient atmospheric aerosol sink.

Wet deposition investigation implies to get the chemical composition, acidity, measured as *p*H, conductivity and evaluation of emission sources. The simultaneous observations of the chemical composition of rainwater and size resolved atmospheric aerosols provide information about the aerosol scavenging processes and help the modeling community to test chemical tracer transport models.

In practice, the scavenging characteristics of a particular cloud or precipitation event are usually described by parameters which are accessible during field experiments, as scavenging coefficient, scavenging factor, scavenging or washout ratio [4].

The scavenging coefficient refers to the relative decrease of a pollutant concentration during the cloud and rain event:

$$\Lambda = -\frac{1}{C}\frac{\partial C}{\partial t} \tag{1}$$

The scavenging factor represents the ratio of the concentration of the scavenged pollutant in the rain or cloud

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* email :giorga@gw-chimie.math.unibuc.ro; Tel.: +4021 314 35 08 / 2163, 2212

water per unit volume of air to the concentration of the pollutant in the air:

$$F = \frac{C_{rain,cloud} \times LWC}{C_{air}} \qquad (2)$$

where LWC is the liquid water content, expressed in g water/m^3 air.

In this paper, we have estimated the washout coefficient W that represents the time-averaged concentration of a substance in precipitation (Cr) divided by the time-averaged concentration in the air entering in a cloud (Ca):

$$W = \frac{C_{rain}}{C_{air}} \qquad (3)$$

where C_{rain} is expressed in g L^{-1} and C_{air} in g m^{-3}, and W in kg m^{-3} (air)/ kg m^{-3} (water).

This allows the use of ground level measurements within the air mass from which the forming cloud is drawing its air, as the definition of W is based on the premise that the concentration of a substance in precipitation is directly related to its concentration in the feeding air of the cloud.

A large number of observations have been made on the chemical composition of bulk cloud and rainwater, and bulk water of melted snow [6, 2, 1, 7] and many theoretical and numerical studies were conducted to describe the removal of the substances from the atmosphere by precipitating clouds. These researches revealed important features of the mechanisms of transformation and scavenging of substances from the atmosphere. Being so many, we mention only few from the newest of these reports that appears to us as a meaningful sample of researches on this topic. In addition to above examples, it was found that scavenging ratios decreased linearly with higher rainfall intensity for some ions in both fine and coarse aerosol fractions [3]. The scavenging collision efficiency was found to vary with the size and the properties of aerosol particles [5]. The scavenging of NH_4^+, NH_3^-, and HNO_3 and estimated particle and gas scavenging contributions to wet deposition by nitrogen were investigated [8, 9]. Real-time wet scavenging of major chemical constituents of aerosols and the role of rain intensity in Indian region were investigated [10]. Relationships between rainfall intensity and scavenging coefficients were established [11], and between rainfall amount and scavenging ratios [12] for sulfate and nitrate. It was discussed the dependence of droplet size distributions on rain intensity and empirical relations between rain rate and different moments of the distribution such as radar reflectivity factor, liquid water content, and optical extinction were deduced from modeled size distributions [13, 14]. Scavenging coefficients have been directly measured recently in some field experiments [15,16]. The estimates of the below-cloud scavenging coefficients for reported aerosol size distributions measured during field experiments in various environments were reported [17]. The dependence of the in-cloud scavenging coefficient of nitric acid on the characteristics of droplet spectra was analyzed [18] and there were showed significant variations (the scavenging coefficient changes more than an order of magnitude (depending on the median diameter of the droplets) when it is calculated on lognormal basis versus a gamma basis) of the estimated scavenging coefficient due to different representations of droplet spectrum for the same liquid water content and number concentration. The results obtained for the scavenging coefficient of HNO_3 also apply to other strong acids (H_2SO_4, HCl, HBr, HI) that have a large solubility and are removed by precipitation. There were theoretically obtained scavenging coefficients for particles of different chemical species [19], and rainwater concentrations have been predicted on the basis of these results.

Nevertheless, mainly due to the complexity of cloud microphysics and dynamics, aqueous chemical transformation, the development of a simple and accurate model to describe and predict the pollutant removal process by wet precipitation is far to be achieved. Complete meteorological description is necessary to be correlated to above mentioned gas and aerosol physics and chemistry data in order to gain the full understanding of the wet removal phenomena. The understanding of wet removal processes still remains crucial in local and regional pollution studies [20-24], and the representation of aerosol removal processes in current aerosol transport models remains a source of uncertainty [25].

Despite of such intensive research all over the world, for Romanian region, data on scavenging pollutant are extremely scarce. We found only two studies, [1] dealing with rainwater chemistry and wet deposition fluxes for Iasi during 2003-2006 period, and anather [2], which is focused on the pollutants effects on forest damage at few inner alpine sampling sites in Retezat National Park. It was provided data of air concentration of O_3, NO_2, and SO_2 and average concentration of some more ions in bulk precipitation and throughfall samples for the summer season of 2000-2002 [2]. A very recent study reported the concentration of nitrate between 2.3 and 29.63mM in groundwater samples collected in the rural village of Letcani in Northeastern Romania but the study was focused on the photochemical generation of $\cdot OH$ and $\cdot NO_2$ radicals upon UV-A radiation irradiation [26].

Therefore, the specific question we wished to answer was: what are the washout ratios for the different ionic constituents, and to investigate the dependence of rainwater ionic concentration of precipitation depth for the Romanian sites.

Experimental part

Supporting databases and method

The experimental data we further investigated were extracted from the publications about mountain sites in Retezat National Park (RTZ) [2], and urban site [1]. We added for comparison extracted data from the Indian Ocean Experiment (INDOEX) performed in Indian Ocean and Arabian Sea, as this is one of the first programs that provided comprehensive rain chemistry measurements with a minimum of contamination from terrestrial sources or from the ship. Collection and chemical analysis (techniques (mainly ion chromatography), precision and detection limits for the various ions) of the samples are fully described in the above-mentioned studies.

We only point out here that the collection of the precipitation samples has been done in all cases in wet-only samplers consisting of a cylindrical part with a polypropylene funnel and a bottle following almost the same methodology. In addition, in INDOEX campaign, in order to avoid contamination of samples by pollution episodes, wet-only samplers have had a lid, of which opening was controlled by a pollution sensor. Samples were analyzed for major ions and weak acids and, for INDOEX campaign, some trace metals.

The precipitation samples in RTZ were collected at four inner alpine sites situated at altitudes between 800 and 1400 m asl between middle of July and middle of September in period of 2000-2002. The rainfall amount ranged between 220 and 328 mm. A number of 160 valid samples were collected at Iasi, far from pollution sources over a time span of 4 years, 2003-2006. Annual rainfall amount ranged between 350 mm in 2006 and 545 mm in 2005. The precipitation amount in the case of INDOEX experiment was significantly lower, ranging between 0.4 to 41 mm, and precipitation intensities ranged from 0.8 to 26.6 mm h^{-1}.

From all three datasets we extracted and constructed a synthetic dataset by considering SO_4^{2-}, Cl^-, NO_3^-, NH_4^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, as constituents important in precipitation chemistry that may imply ecological effects after deposition. The original ionic concentrations were converted into mg/L, and were related to the observed precipitation depth (table 1).

Results and discussions

The chemical composition of samples is quite different for urban samples from that of the remote mountain and oceanic samples.

Over the land, the total concentration is higher in the Iasi urban area than in mountain area by a factor of about 4, the most prominent ions being sulfate, calcium, chlorine and potassium in RTZ and sulfate, calcium and nitrate in IS. Over the ocean, the total concentration is higher than that at the mountain site by a factor of 1.5 and smaller than that over the urban area by a factor of about 3, the most two prominent ions being the sea salt components, chlorine and natrium. This indicates the exposure of the mountain area to local pollution sources and vegetation, and exposure to anthropogenic sources for urban area. Samples from ocean area were also impacted by some polluted air masses, as the sulfate appears to be the third prominent ion (sulfate in this case represents the non-sea salt component).

Rainwater concentration was found to follow a power-law dependence of rainfall depth:

$$C_{rain} = ah^{-b} \tag{4}$$

where C_{rain} is expressed in mg/L, and the rainfall depth h in mm (fig.1 and 2).

Ambient aerosol particles and gases incorporated in cloud raindrops contribute to the load of chemical species

Table 1
EXPERIMENTAL CONCENTRATIONS IN PRECIPITATION SAMPLES, EXTRACTED AND CONVERTED FROM DATASET OF BYTNEROWICZ ET AL., 2005 (SAMPLES M1-M4), OF ARSENE ET AL., 2007 (SAMPLES U1-U4, AVERAGE VALUES FOR PERIOD 2003-2006), AND OF GRANAT EL., 2002 (SAMPLES O1-O14)

Sample code	Precipitation depth (mm)	Rainfall concentrations (mg/l)								
		SO_4^{2-}	Cl^-	NO_3^-	NH_4^+	Na^+	K^+	Ca^{2+}	Mg^{2+}	Total concentration
M1	328	1.428	0.595	0.091	0.469	0.282	1.028	0.539	0.075	4.51
M2	256	1.813	0.55	na	0.532	0.528	0.558	0.617	0.078	4.68
M3	314	1.876	0.649	0.052	0.417	0.42	0.4	1.234	0.248	5.30
M4	220	1.76	0.828	0.339	0.826	0.466	0.536	1.103	0.122	5.98
U1	287	7.551	2.367	2.895	1.093	1.666	0.892	4.639	0.273	21.376
U2	500	8.233	2.049	3.528	1.090	1.456	0.919	5.709	0.215	23.199
U3	545	7.180	1.501	2.810	1.054	0.978	0.688	4.159	0.177	18.547
U4	350	7.656	1.432	5.266	1.455	0.965	0.843	5.709	0.302	23.628
O1	0.4	0.365	5.040	0.112	0.059	2.806	0.008	0.016	0.331	8.737
O2	1.2	0.077	3.360	0.056	0.034	2.162	0.000	0.008	0.209	5.906
O3	41.0	0.250	1.540	0.081	0.072	0.851	0.012	0.012	0.101	2.918
O4	1.6	0.662	5.110	0.453	0.113	2.898	0.043	0.152	0.334	9.765
O5	0.4	0.634	5.355	0.353	0.148	2.990	0.023	0.104	0.353	9.960
O6	1.0	0.806	4.760	0.608	0.241	2.668	0.031	0.060	0.314	9.489
O7	3.3	0.470	3.185	0.484	0.077	1.886	0.031	0.108	0.230	6.472
O8	4.2	0.173	3.010	0.025	0.031	1.679	0.008	0.008	0.199	5.132
O9	3.0	0.355	7.245	0.081	0.032	4.025	0.004	0.016	0.487	12.245
O10	8.6	0.662	0.700	0.099	0.198	0.414	0.027	0.016	0.048	2.165
O11	4.7	0.701	16.555	0.043	na	9.246	0.004	0.044	1.073	27.666
O12	2.2	0.115	2.205	na	0.009	1.173	0.000	0.004	0.139	3.645
O13	15.4	0.115	1.155	0.012	0.005	0.644	0.000	0.008	0.077	2.017
O14	9.0	0.173	0.560	0.186	0.025	0.276	0.000	0.008	0.034	1.262

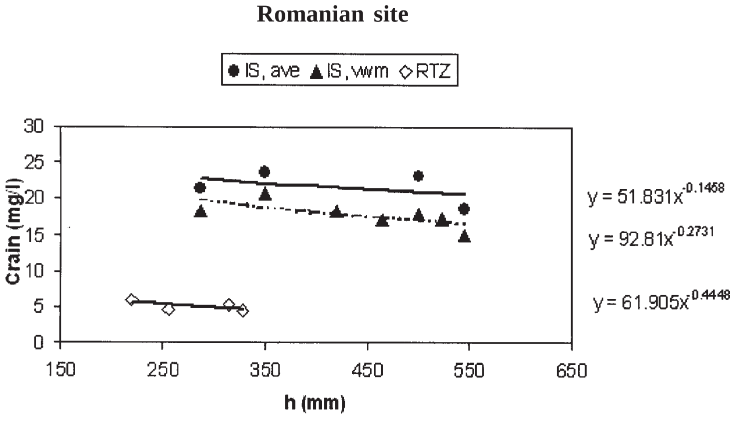

Fig. 1 Relationship between rainwater total concentration and precipitation depth for Romanian sites (RTZ-mountain site; IS, ave-urban samples, average values; IS, vwa-urban samples, volume-weighted averaged values)

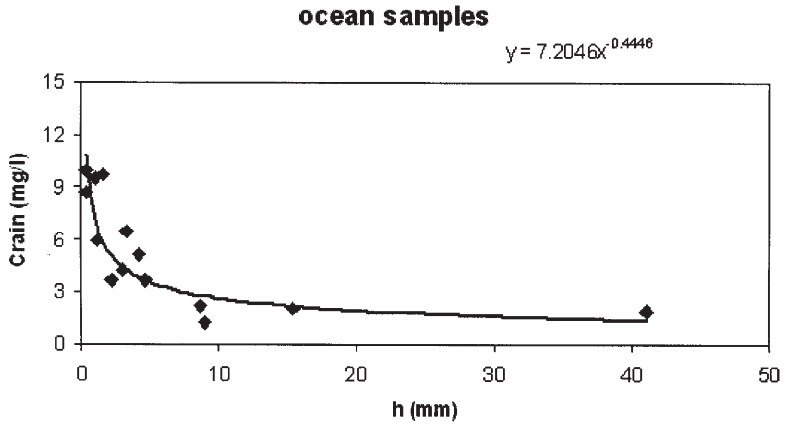

Fig 2 Relationship between rainwater total concentration and precipitation depth for ocean sampling sites

in cloud and precipitation water. Chemical composition in clouds is size-dependent [5], usually smaller aerosol particles are less effectively washed out and can remain distributed in the atmosphere even after a heavy rainfall. Larger raindrops are not densely concentrated due to their relatively small cross-sectional area to volume ratio; smaller raindrops will contribute more to the rainwater concentration. During their fall from cloud base to ground, the solute concentration in raindrops increases due to evaporation and below cloud scavenging of particle and gases.

The ion concentration clearly decayed with an increase of the precipitation amount (a dilution effect). At a beginning of a rain event, when precipitation depth is low, the concentration decreases sharply due to the depletion of the by rapid below-cloud scavenging. This is in agreement with the result of [19] who found that larger raindrops reach the ground within 2–3 min after leaving the cloud base. The further decrease of the rainwater concentration is slower because the amount of pollutant available for scavenging and drop evaporation decreases.

The functional relationship between specific ionic content is similar to the total concentration behavior. For single ionic species, the parameters of the equation (4) are summarized in the table 2. The correlation coefficient between total ionic content and precipitation depth, indicated in the parenthesis, increases as field campaign provided more samples. For Romanian samples, percentages of the variance in concentration that can be explained by the variation in the rainfall depth ranged from 64% (RTZ) to 43% for IS urban area, average values, while for ocean data a percentage of 83% has been obtained. This clearly shows the necessity to add some more data of this type to increase the accuracy of the analysis, and the necessity of more extensive campaigns in our country.

Because at present no other data are available for Romanian sites, the coefficients a and b of the functional dependence can be used when information is desired about the expected value of the rainwater concentration of a specific ion, in average meteorological conditions. For example, a precipitation event with an intensity of 20 mm h^{-1} (heavy rain) in a time of about 46 min will give a total major ion concentration of about 18 mg L^{-1} for RTZ and of about 44 mg L^{-1} for Iasi and only about 2 mg L^{-1} over the ocean. Two different aspects should be mentioned. In case of ISvwa data, for soil derived components Ca^{2+} and Mg^{2+}, an increase of calcium concentration with precipitation depth associated with an decrease of magnesium content was found despite the fact that the analysis [1] indicates a correlation coefficient between calcium and magnesium of 0.83. This behaviour we suppose to be due to re-suspended dust from traffic but sure the poor specific correlation coefficient for calcium (0.2) compared to that for magnesium (0.7) plays a role. The second issue is in the case of NO_3^- ion, for which the values of a = 0.196 and b = 0.304 for the coefficients of the functional dependence of rainfall depth were obtained but we discarded them as the correlation was too low due to large scatter of experimental concentration data points.

The washout ratio is also dependent on the precipitation depth, following a power-law relationship [12, 27]:

$$W = \alpha h^{-\beta} \tag{5}$$

and the coefficients α and β can be estimated for various sampling sites.

Combining this result with equations (3) and (4) the dependence of ionic concentration in air is:

$$C_a = \frac{a}{\alpha} h^{\beta - b} \tag{6}$$

Table 2

COEFFICIENTS OF THE DEPENDENCE OF RAINWATER CONCENTRATION OF RAINFALL DEPTH (RTZ-MOUNTAIN SAMPLES; IS, AVE-URBAN SAMPLES, AVERAGE VALUES, IS, VWA-URBAN SAMPLES, VOLUME-WEIGHTED AVERAGED VALUES, IND-OCEAN SAMPLES). THE CORRELATION COEFFICIENTS ARE INDICATED BETWEEN PARENTHESES

Site		SO_4^{2-}	Cl^-	NO_3^-	NH_4^+	Na^+	K^+	Ca^{2+}	Mg^{2+}
	a	8.76	14.92	na	2185.8	158.2	0.012	28.8	0.0123
RTZ (0.64)	b	0.291	0.558	na	1.477	1.058	0.692	0.633	0.397
	a	7.474	12.36	12.545	3.845	11.58	3.216	7.833	16.642
IS, ave (0.43)	b	0.004	0.321	0.212	0.2	0.373	0.225	0.075	0.708
	a	23.186	138.62	31.226	9.166	497.1	3.907	1.796	35.316
IS, vwa (0.62)	b	0.199	0.777	0.401	0.379	1.059	0.313	-0.14	0.863
	a	0.367	4.592	0.179	0.066	2.608	0.016	0.031	0.301
IND (0.83)	b	0.155	0.393	0.407	0.266	0.403	0.106	0.346	0.392

Table 3
SULFATE AND NITRATE WASHOUT RATIOS AND AIR CONCENTRATIONS FOR MOUNTAIN AND URBAN ROMANIAN SITES. C_{rain}-RAINFALL CONCENTRATION IN mg L^{-1}, h-PRECIPITATION DEPTH IN mm, W-WASHOUT RATIO, Ca-AIR CONCENTRATIONS IN μg m^{-3}

Site	C_{rain}	h	Wmin	Wave	Wmax	Ca,min	Ca,ave	Ca,max
RTZ, sulfate								
M1, Judele (1190m asl)	1.82	220	304	497	885	2.06	3.67	6.00
M2, Gura Zlata (800m asl)	1.74	256	288	475	854	2.04	3.68	6.06
M3, Baleia Sohodolu (1300m asl)	1.64	314	268	446	813	2.02	3.68	6.14
M4, Campusel (1400m asl)	1.62	328	263	441	804	2.02	3.68	6.16
IS, vwa, sulfate								
2003	18.17	287	276	459	830	830	9.05	16.4
2004	17.92	500	226	388	727	727	9.26	17.3
2005	14.95	545	219	378	712	712	9.29	17.5
2006	20.76	350	257	432	792	792	9.13	16.7
2004-2005	17.23	523	223	383	719	719	9.28	17.4
2004-2006	17.13	465	232	397	740	740	9.23	17.2
2003-2006	18.21	420	241	409	758	758	9.2	17
IS vwa, nitrate								
2003	7.52	287	392	712	829	9.07	10.56	19.16
2004	6.73	500	329	596	694	9.70	11.29	20.49
2005	6.62	545	320	580	675	9.80	11.41	20.71
2006	7.23	350	368	668	778	9.29	10.82	19.63
2004-2005	6.67	523	324	588	684	9.75	11.35	20.60
2004-2006	6.83	465	336	610	710	9.62	11.19	20.31
2003-2006	6.97	420	347	630	734	9.50	11.06	20.06

The values of sulfate washout ratio were computed for the precipitation depths measured at Romanian sites and they found to range between 441 (Campusel) and 497 (Judele) at RTZ sites with an average of 465 for all 4 sampling sites. For Iasi urban area, W for sulfate ranged between 378 (in 2005) and 459 (in 2003), with an average value of 407 for the entire sampling period. Table 3 also shows estimates of the extreme low (Wmin) and high (Wmax) end of the washout ratios and the correspondingly air concentrations for both sites. For RTZ site the nitrate washout ratio was not possible to be computed, as Crain could not be calculated from equation (4) as we explained. For Iasi, an average value of W= 626 was obtained for the nitrate. Washout ratio is slightly higher at the mountain site than at the urban site for sulfate. The sulfate rainwater concentration in urban area was 10 times higher than at the RTZ (about 18 mg L^{-1} compared to 1.7 mg L^{-1}) for an increase in the average precipitation of about 1.6 times. This implies that the pollutant scavenged mass remains associated with the main water mass. Therefore, the fraction of pollutant mass that reaches the ground is controlled by the precipitation efficiency of the cloud, namely the fraction of cloud water that is formed by condensation and reaches the ground as rain. This is determined by the autoconversion rate that describes how rapidly the cloud water converts into rainwater and it depends largely on the available liquid water content and droplet ion concentration [28].

A literature survey of earlier measured washout data shows W is typically between 10^2 and 10^6 [27, 29, 30] and [4]. Our data fits well within this range.

As mountain sampling sites were located at different altitudes, we found the air concentration during rain was found to follow the dependence Ca (μg m^{-3}) = -0.0085 x z (m) + 22.406, R^2 = 0.8, where z represents the altitude for the sites on the eastern slope of the mountains. This could help in further field campaigns, as in the area are not located any air pollution monitoring sites.

Conclusions

Chemistry observations at two Romanian sites have been used to illustrate how we can gain better insights of the man-made and natural substances are scavenged in our country. The method is applicable to the class of substances in which both gaseous and particulate precursors contribute to a pollutant concentration in precipitation.

The findings are summarized below

We established relationships between rainfall major ion total concentrations and for different ionic constituents and precipitation depth for both Romanian sites.

The computed washout ratios represents the first ones derived for an urban and a mountain site in our country.

We showed by this method that an indicative concentration of atmospheric pollutant concentrations during rain could be derived. These results can be used in closure studies when a more extensive field campaign (atmospheric aerosols and rainwater collected simultaneously) can be performed.

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