

ANALYTICAL CHARACTERIZATION OF PRECIPITATIONS[♦]

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Abstract: The properties of precipitation are mainly determined by solid, liquid and gaseous substances that exist in suspended or dissolved form. These substances come from many complex interactions between the atmosphere – hydrosphere – lithosphere – biota. The analytical characterization of precipitation has been based on the analysis of several chemical parameters: pH, conductivity, chloride, fluoride and ammonium ions, total hardness, alkalinity, H₂S and sulphides, COD (Mn), nitrites, phosphorous, metallic ions (total iron, copper and chromium). In this purpose were collected rainwater, ice and snow from different areas (cities Năvodari, Constanța, Buzău and Mihail Kogălniceanu) during November 2007 till February 2008. This study shows that chemical characteristics of the analyzed water samples vary from one region to another depending on the mineralogical composition of zones crossed, the contact time, temperature, weather conditions, the sampling period (day or night) and the nature of sample (rain, snow, ice).

Keywords: *analytical characterization, ice, rainwater, snow, traces metals*

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INTRODUCTION

The properties of precipitation are mainly determined by solid, liquid and gaseous substances that exist in suspended or dissolved form. These substances come from many complex interactions between the atmosphere - hydrosphere - lithosphere - biota.

Precipitation is the water released from clouds as rain, sleet, snow or hail. Precipitation is the major route by which atmospheric water returns to earth. Most of the precipitations are in the form of rain. Precipitation will vary both in time and geographically.

The chemical composition of wet precipitation has been studied in many countries during last decade [1 – 4]. The composition of rainwater actually reflects the composition of the atmosphere through which it falls.

Generally, rains wash pollutants from atmosphere and these pollutants are deposited on the ground. But also it washes the soil, helping to transport pollutants to the envoys. However, it should be noted that the rains favors the contamination of soil in depth. On the other hand rainwater can also have an important role as a source of phosphorus and other nutrients.

So, it can say that precipitation is an efficient removal mechanism for atmospheric organic matter, which is a mixture of organic compounds that can influence climate, air quality and ecosystem health [5, 6]. Also, the presence of trace metals in rain and snow is a major pollution factor which affects water, air and soil and may be toxic to living systems [7].

For Romania there are a few reports concerning the chemical composition of rainwater [8, 9] but none for snow and ice chemical composition, of our knowledge.

The present study reports on data of *pH*, conductivity, chloride, fluoride and ammonium ions, calcium hardness, total hardness, alkalinity, H_2S and sulphides, COD (Mn), nitrites, phosphorous, metallic ions (total iron, copper and chromium) in precipitation samples (rainwater, snow and ice). The samples were collected from November 2007 to February 2008.

MATERIALS AND METHODS

Sampling site

The city of Constanța is one of Romania's main industrial, commercial and tourist centers. The city is located on the Black Sea coast, having a beach length of 13 km. Constanța has a moderate continental climate with considerable maritime and some Mediterranean influences.

Năvodari is an important chemical and industrial town containing a car repairs factory and a factory specialized in petrochemical products and this town is located at 15 km from Constanța.

Near the town Mihail Kogălniceanu is an airport and a military air base. This town is located near the city of Constanța (25 km).

Buzău is a railway hub in south-eastern Romania and it lies between the south-eastern curvature of the Carpathian Mountains and the lowlands of Bărăgan Plain (located at 230 km from Constanța city).

Sampling

Samples were collected in autumn of the year 2007 (November), respective in winter of 2008 (February) and were analyzed for several chemical parameters. Rainwater samples were collected within 12 h of each rain event to minimize microbial degradation of dissolved organic matter and consumption of inorganic nutrients. Sample temperature and pH were measured immediately after collection.

Buckets used to collect precipitation samples for trace metal analysis, filtration flask and storage bottles for filtrated samples were washed and brushed, rinsed with distilled water, and soaked in 20% nitric acid (Merck) for 24 h, then rinsed several times with deionized water and sealed into double plastic bags. The buckets were installed on the roof of the buildings from the cities listed above, far from any possible local contamination sources.

The precipitation samples were filtered to remove particulate material, were stored in Teflon screw-capped tubes and kept refrigerated at 4 °C away from light prior to analysis.

Table 1. The basic information of samples

Sample no.	Sample type	Sampling area	Sampling date
1.	rainwater	M. Kogălniceanu	5.11.2007 - day
2.	rainwater	Buzău	6.11.2007 - day
3.	rainwater	Năvodari	6.11.2007 - day
4.	rainwater	Constanța	13.11.2007 - day
5.	rainwater	M. Kogălniceanu	13.11.2007 - night
6.	rainwater	Năvodari	10.11.2007 - day
7.	rainwater	Năvodari	13.11.2007 - day
8.	snow	M. Kogălniceanu	6.02.2008 - day
9.	rainwater	M. Kogălniceanu	27.02.2008 - night
10.	ice	M. Kogălniceanu	28.02.2008 - day

Chemical analysis

Measurement of pH was conducted using pH/ISE meter, Model Consort 530. The measurements of conductivity, chloride, fluoride and ammonium ions, total hardness, alkalinity, H₂S and sulphides, COD (Mn), nitrites, phosphorous, metallic ions (total iron, copper and chromium) were realized by the following techniques:

- titrimetric method with HCl for the determination of the alkalinity;
- titrimetric method with KMnO₄ for the determination of the COD (Mn);
- precipitation titration, with silver nitrate, in the presence of chromate ions for the determination of chloride ion;
- complexation titration with the disodium salt of EDTA at pH = 10, in presence of Eriochrome Black T for measuring the total hardness;
- redox titration with Na₂S₂O₃ for measuring H₂S and sulphides;

- potentiometric method with ion selective electrodes for determining the fluoride and ammonium ions;
- an LF 340A/SET conductivity instrument from WTW, Germany was used for conductivity measurements;
- molecular absorption spectrometry in visible for determining metals (copper, iron and chromium), nitrites and phosphorous [10].

In order to increase the sensitivity of the analytical determination of heavy metals the method of the standard addition was used [11]. The method is applied when the compounds to be determined are in low concentration and the chemical matrix is not constant in the samples to be analyzed. The precision of the determination of Fe, Cu, Cr, was evaluated under the optimum conditions; were studied the effects of *pH*, temperature, complexation time, reagent amounts [12]. For the measurement of studied heavy metals absorption spectra a DR-2000 spectrophotometer from Hach Company, USA, was used.

Phosphate ion (PO_4^{3-}) reacts with ammonium molybdates $(\text{NH}_4)_2\text{MoO}_4$ and forms the phosphomolybdate of ammonium $(\text{NH}_4)_3\text{H}_4[\text{P}(\text{Mo}_2\text{O}_7)]$, a yellow precipitate. The phosphomolybdate is reduced to a compound of unknown structure called molybdenum blue, which colors the solution in blue. For the reduction, SnCl_2 can be used [13].

Nitrite ion was measured by spectrometry of molecular absorption in visible with Griess reactive, the standard method SR ISO 1342/91.

For the measurement of fluoride and ammonium ions were used ion-selective electrodes. The fluoride ion-selective electrode (ISE) with LaF_3 membrane is the most widely applied ion-selective electrode for measurements of fluoride ion. The use of the ISE requires adjusting ionic strength and some cases *pH* of the solution. In the case of fluoride analysis, the ionic strength adjuster buffer (TISAB) is used. The fluoride – selective membrane electrode (Orion Research) model 94-09 was used for all measurements in combination with a reference electrode. Measurements of ammonium ions were performed with a DC 218 ISE ammonium combined electrode/Multiparameter analyser Consort C535, Belgium.

Calibration of potentiometer was detailed in a previous paper [14]. The calibration curve was linear for fluoride ion between 10^{-5} and $10^{-2} \text{ mol}\cdot\text{L}^{-1}$ and for ammonium ion between 10^{-6} and $10^{-2} \text{ mol}\cdot\text{L}^{-1}$.

RESULTS AND DISCUSSION

The highest value of *pH* has been observed to be 7.9, values of *pH* in all samples being higher than 6.2, which is a little higher than the *pH* of cloud water (5.6) at equilibrium with atmospheric CO_2 [3]. In contrast, in Iaşi (north-eastern Romania) much lower *pH* has been reported in 2006 (4.26) as a result of an air mass originating from NE Europe [8]. The alkalinity of rainwater is due to the high loading of carbonate and bicarbonate in the atmosphere. Slightly alkaline *pH* is preferable in waters, as heavy metals are removed by carbonate or bicarbonate precipitates [15].

This was correlated with the measurements of “m” alkalinity in the precipitation samples. The values of alkalinity varied from $0.2 \text{ meq}\cdot\text{L}^{-1}$ for snow samples to $4.78 \text{ meq}\cdot\text{L}^{-1}$ for rainwater (sample no. 5).

Observed concentration of the precipitations constituents were presented in Table 2. Values of chloride ion concentrations were very close, ranging in low limits between the samples. It may be noted from Table 2 that the highest concentration of chloride ion was at Constanța (coastal site) in the rainwater sample and the lowest in the snow sample at a site far from the sea, indicating the proportional relation of the distance from the sea with the concentration of chloride ion. In this case was demonstrated the marine contribution [16].

Table 2. Concentrations of chloride, fluoride, ammonium and phosphate ions in precipitation samples

Sample no.	Concentration			
	Cl ⁻ [mg·L ⁻¹]	F ⁻ [μg·L ⁻¹]	NH ₄ ⁺ [mg·L ⁻¹]	PO ₄ ³⁻ [mg·L ⁻¹]
1.	7	1.2	0.5	11.5
2.	13	0.96	1.0	8.5
3.	11	0.95	0.9	11.0
4.	20.23	12.5	1.6	14.0
5.	17	22.8	1.4	19.6
6.	16	12	1.5	19.6
7.	15	2.5	1.6	20.1
8.	5	1.7	1.0	21.2
9.	6	1.8	0.9	18.6
10.	16	3.0	1.5	21.25

Because of its chemical reactivity, fluorine is found in nature in a combined state, as fluoride ions. It has beneficial effects when ingested in small amounts, but has adverse effects when ingested in excessive amounts. The obtained fluoride concentrations in investigated samples have been found between 0.95 - 22.8 μg·L⁻¹. Analyzing variations of fluoride concentration was observed that the highest values occurred in November (samples 4, 5, 6).

It was noted that the highest quantity of NH₄⁺ was found for samples 4 and 7, collected from Constanța and Năvodari (1.6 mg·L⁻¹). These are rainwater samples collected on the same day, from two different sites, but both are industrial sites. In all the samples concentration values of NH₄⁺ were comparable with those reported by Iwachido *et al.* [17].

Phosphorous is one of the major nutrients contributing in the increased eutrophication of surface waters. The individual contribution tend to increase, because phosphorous is one of the main constituent of synthetic detergents. The phosphorous concentrations are large as it seen from Table 2 (8.5 – 21.25 mg·L⁻¹). Houston *et al.* reported a maximum concentration of PO₄³⁻ (15.86 mg·L⁻¹) lower than those found in this study and the researchers explain that the presence of PO₄³⁻ may be an indication of bird faeces contamination [18].

Nitrites are an important step in the metabolism of nitrogen compounds. They occur in the biogeochemical cycle of nitrogen as intermediate between ammonia and nitrate. Their presence is due to either bacterial oxidation of ammonia or nitrate reduction. The values of nitrite concentrations are presented in Table 3. Tetsuyuki and co-workers conducted a monitoring study for nitrate and nitrite in rainwater. Following determinations it was found that the concentrations obtained for rainwater fell at night

are higher [19]. Maybe this is an explanation for the nitrite concentrations in sample 5 ($0.500 \text{ mg}\cdot\text{L}^{-1}$) and sample 9 ($0.652 \text{ mg}\cdot\text{L}^{-1}$) which were collected at night.

Table 3. *Values of nitrite concentration from precipitation samples*

Sample no.	NO_2^- concentration [$\text{mg}\cdot\text{L}^{-1}$]
1.	0.064
2.	< LD*
3.	0.032
4.	0.073
5.	0.500
6.	< LD
7.	< LD
8.	< LD
9.	0.652
10.	< LD

* - LD – limit of detection

The concentrations of sulfides were between 0.001 and $0.0098 \text{ mg}\cdot\text{L}^{-1}$. These values are lower than the sulfides limits according to the ISO 13358 standard Romanian SR ($0.1 \text{ mg}\cdot\text{L}^{-1}$) [20].

The COD (Mn) (which is an overall indicator of water pollution) values obtained are higher than the limits imposed by ISO 13358 standard for all samples taken for analysis (0.5 to $4.0 \text{ mg O}_2\cdot\text{L}^{-1}$) [20]. The highest value was registered for ice ($10.69 \text{ mg O}_2\cdot\text{L}^{-1}$) and the lowest for the rainwater sample collected from Constanța site ($6.85 \text{ mg O}_2\cdot\text{L}^{-1}$).

Water hardness is a commonly reported aspect of water quality. It is a measure of the quantity of divalent ions such as calcium, magnesium and/or iron in water. There are many different divalent salts; however, calcium and magnesium are the most common sources of water hardness. From the obtained data it can be seen that the samples have hardness between 0.4 and $3.68 \text{ meq}\cdot\text{L}^{-1}$.

The values of trace metal concentrations are presented in Table 4. Iron concentrations in the samples of precipitation are less than those stipulated by legal regulations (0.01 – $5 \text{ mg}\cdot\text{L}^{-1}$) which means that in this respect water is not contaminated [21]. But these values are higher than those reported in other countries [1] and this can be explained by collecting samples from or near highly industrialized areas (like Constanța and Năvodari cities). The maximum limit for chromium is $0.01 \text{ mg}\cdot\text{L}^{-1}$ and for copper is $6.4 \text{ mg}\cdot\text{L}^{-1}$ [22, 23]. The concentration values obtained for these two metals in the precipitation samples were higher than the accepted limits (maximum value for chromium was recorded in the ice sample – $0.159 \text{ mg}\cdot\text{L}^{-1}$; maximum value for copper was recorded in rainwater collected from Constanța area – $38.9 \text{ mg}\cdot\text{L}^{-1}$).

The highest value of conductivity was observed for sample 7 ($181.2 \mu\text{S}\cdot\text{cm}^{-1}$), in autumn, when there were many precipitation events and winds. The values of conductivity for the other samples collected in autumn are similar with those found for sample 7. The variation of conductivity also demonstrates the influence of the sea environment.

Table 4. Concentrations of trace metals in precipitation samples

Sample no.	Concentration [mg·L ⁻¹]		
	Fe	Cr	Cu
1.	1.435	0.11	19
2.	1.351	0.05	30
3.	1.407	0.004	12.5
4.	1.571	0.16	38.9
5.	0.248	0.07	15
6.	1.199	0.09	8
7.	1.124	0.06	16
8.	0.114	0.02	3.26
9.	0.815	0.12	25
10.	0.469	0.16	12

CONCLUSIONS

Chloride ion appears to be significantly influenced by sea salt contribution. Also, the variation of conductivity demonstrates the influence of the sea environment.

Rainwater, snow and ice was collected from urban areas where air pollution is significant. So it must consider the impact of pollution on the water quality.

This study shows variations in precipitation composition which depend on the variability of meteorological conditions, the contact time, the sampling period (day or night), the geographic sampling area and the nature of sample (rain, snow, ice).

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