Ion Chromatographic Method for Determination of Heavy Metals in Water

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Snow (wet deposition) quality in Bucharest city of Romania was studied by investigating the metal ions composition using ion chromatography method. Ten sampling sites were selected and 100 snow samples were collected on in the monitored period. The snow samples were analyzed for the simultaneous determination of transition metals (lead, copper, cadmium, cobalt, zinc, and nickel) in wet depositions. The pH values varied from 5.06 to 7.26, indicating just a few acidic events. The dominance of Zn^{2+} *and* Cd^{2+} *ions was observed in this study. Cadmium presented the highest concentration of 671.15* μ*g/L, followed by lead with 84.34* μ*g/L, both exceeding the maximum allowed limit. However, it was found that the metal ions composition of snow samples does not present significant seasonal differences. The VWM of the heavy metals decreased in the* $Zn^{2+} > Cd^{2+} > Pb^{2+} > Cu^{2+}$ *order.*

Keywords: heavy metal, meteoric waters, IC, Bucharest

In recent years, environmental pollution with heavy metals became important due to their increasing spread, long lasting residuals and accumulation in soil, water, air, and human body, producing severe pathological alteration. High concentration of several metals can harm human health through consumption of drinking water and/or aquatic organisms, and may be cause harmful effects to aquatic life and plant ecosystems [1, 2]. Millions of tons of pollutants are released into the air, both from natural (volcanic eruptions, forest fires), and anthropogenic sources (industrial processes, industrial and residential combustion, terrestrial traffic). From air, heavy metals can be inhaled directly or contribute to pollution of soil by rainfall.

The precipitations studies [1-12] in the specialised literature were focused on the determination of anions and alkali and alkali-earth cations, the chemical interactions, the precipitation distribution, the sources of components in wet depositions (marine, terrestrial, and/or anthropogenic source), and meteorological variation. There are few reports on the quantification of heavy metals in meteoric waters, mostly using ICP coupled techniques [7] or atomic absorption [4-5]. Ion chromatography, the recommended method for routine analysis of anions and alkaline and alkaline-earth cations over the world, has been just briefly optimized for meteoric waters [6]. Lately it has been complemented by the determination of transition and lanthanide metal ions by chelation ion chromatography. Monitoring aqueous samples by IC offers a reliable method for determination of transition metals, Fe(II), Fe(III), Pb(II), Cd(II), Cu(II), Co(II), Ni(II) and Zn(II), being also suitable for the determination of analytes with multiple stable oxidation states [6].

Bucharest is one of the most polluted cities in Europe and, because of excessive pollution could fall into the health and environment high risk urban areas category. The main source of pollution in Bucharest is represented by urban traffic, and this is responsible for about 70% of the impurities in the air. Thermal power plants, industrial manufacturing sites, building sites, and even private domestic heating installations occupy, in order, the four places in the ranking. The maximum level of pollution with harmful substances and dust is frequently exceeded in Bucharest. On certain occasions the exceeded alert thresholds ask for rapid actions and a continuous monitoring of trace metals**.** As the ionic composition of wet depositions gives first hand information on the particles and pollutants present in the atmosphere at specific moments and sites, this paper presents an extended investigation on the heavy metals content of snow samples along 3 cold seasons in Bucharest urban area.

Experimental part

Sampling site description

Samples were collected in Bucharest (44°24’49” N latitude and 26°05’48” E longitude), a city located in the south-eastern part of Romania, at a 60 - 90 m altitude above sea level. The Bucharest metropolitan area, the most important in the country in terms of economic, political, commercial, cultural-scientific and touristic activity, consists of 238 km^2 with a population of 2,000,000 inhabitants.

The region climate is temperate–continental, cold in winter and hot in summer, with uniformly distributed precipitations throughout the year. The hot season lasts from May to September and the cold season lasts from November to March.

Ten sites in the city were selected for snow samples collection in this study (fig. 1). Seven of them are located in residential areas, while the remaining two sites are located in industrial zones. The industrial areas are

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Fig. 1. Map o sampling sites

represented by CET Grozavesti (CG) and Icechim (Ic). The residential areas are represented by Gara de Nord (GN), Crangasi (Cr), Pacii (Pc), Drumul Taberei (DT), Ghencea (Gh), Rahova (Rh), and Ferentari (Fr), being characterized by high population density and intense auto traffic. During the cold season, traffic and domestic heating represent the most important local emission sources.

Sample collection

The snow samples were collected manually during of each snow event, using sterile gloves and plastic bags. Once brought in the laboratory, samples were weighed and allowed to elt at room temperature. After approximately 24 h from collection, snow samples were transferred into a 250 mL polyethylene bottle. Each sample bottle was cleaned and rinsed with Milli-Q water (18.2 MΩ / cm) and dried before use.

Each melted sown sample was split in two aliquots, for *p*H measurements and composition analysis. All samples were stored in the dark, at 4°C until analysis was completed.

Analytical methods

The *p*H values were measured using a JENWAY – 3540 pH – meter, calibrated with *p*H 4.00 and 7 standard buffer solutions.

The metal ions concentrations were determined by ion chromatography using an ICS 3000 Dionex ion chromatographic system composed of an isocratic eluent delivery pump, derivatization reagent isocratic pump, CS5 separation column, WTV molecular absorption detector, and an AS40 autosampler. The IonPac CS5A column used for separation presents cation- and anion-exchange capacity, allowing metals to be separated as cationic or anionic species. The analytical column was accompanied by a CG5A guard column.

The eluent contained oxalic acid (0.008 M), tetramethyl ammonium hydroxide (0.010 M), and potassium hydroxide (0.005 M), thus ensuring a solution *p*H of 9.2. The metals of interest were detected by measuring the absorbance at 530 nm characteristic to the complexes they form with 4-(2-pyridylazo)resorcinol (PAR). The complexing reagent was introduced in the system after the separation column, with the aid of an isocratic pump. It was prepared by dissolving PAR in a mixture of 2-dimethyl amino ethanol (1.0 M), ammonia (0.50 M), and sodium acidic carbonate (0.30 M), and stored under nitrogen at all times to prevent decomposition.

All experiments were carried out in the isocratic mode, at 30°C, using as optimized operation conditions 1.2 mL/min eluent flow rate, 0.8 mL/min derivatization reagent flow rate, 1000 mL injection volume, and a 375-mL knitted reaction coil.

Ultrapure water, 18.2 ΩM/cm, free from all ions to be determined, vacuum degassed, and filtered through a 0.20 μm pore membrane, produced by a TDK system, was used for preparing standard solutions. Calibration standard solutions were prepared by diluting the certified concentration standard solutions for ion chromatography containing Pb(II), Cu(II), Co(II), Cd(II), Zn(II), and Ni(II) traceable to SRM NIST (Fluka, Germany).

The volumetric glassware used for standard solutions preparation was class A**.**

Results and discussion

A total of 100 snow samples were collected in three consecutive cold seasons, namely 30 samples in January – March 2011, 30 samples in January – March 2012, and 40 samples in December 2012 – March 2013.

The quantification method was subjected to 'in-house' validation, before shifting to routine exploitation. Linear calibration curves obtained in the 50-500μg/L concentration range were characterized by slopes between 0.03 and 0.30 with standard deviations, s_b, of 0.01 – 0.15, intercepts between 0.1 and 9.0 and intercepts standard deviations s_a, between 4.0 and 32, and correlation coefficients of 0.999 (table 1).

Detection (DL) and the quantification (DQ) limits were obtained from the calibration curves by multiplying the standard deviation of the lower standard concentration by 3 and 10, respectively. The DL values obtained were 1.85, 2.28, 4.26, 4.07, 2.54 and 1.17 μg/L for lead, copper, cadmium, cobalt, zinc, and nickel respectively, and the DQ were 6.17, 7.61, 14.20, 13.57, 8.48, and 3.92 μg/L.

The influence of site location on the metal content was tested by one-way ANOVA (table 2). The lead, copper, cadmium, and zinc contents prove to be influenced by the

Table 1
REGRESSION ANALYSIS RESULTS FOR THE CALIBRATION CURVES

Cation	Slope (b)	Slope standard deviation (s_b)	Intercept (a)	Intercept standard deviation (s_a)	Correlation coefficient (R^2)	Response standard deviation (s_y)
Pb^{2+}	0.03	0.01	0.098	3.93	0.999	6.22
Cu^{2+}	0.19	0.09	9.05	22.32	0.999	35.15
Cd^{2+}	0.11	0.06	3.22	13.52	0.999	21.30
Co^{2+}	0.28	0.02	5.81	31.28	0.999	49.27
Zn^{2+}	0.23	0.12	7.73	27.57	0.999	43.43
Ni^{2+}	0.27	0.13	3.77	32.00	0.999	50.40

Table 2
ONE-WAY ANOVA TEST

	Pb^{2+}	Cu^{2+}	Cd^{2+}	Zn^{2+}
F cal	125.68	43.88	3.15	15.44
F crit	3093	3.093	3.093	3.093
p-value	6.3E-17	3.5E-14	0.047	1.6E-06

collection site at a significance level of 0.05, for a critical Fisher value of 3.093.

Even if the seasonal variability of wet deposition heights is uniformly distributed throughout the year [8], the snow layer in the studied periods (fig. 2) according to the monthly precipitation averages reported by The Romanian National Administration of Meteorology (RNAM) has varied significantly. The amount of snow fallen in 2012 was above the climatologic average, while in 2011 and 2013 the snow falls were below the climatologic normal value. The snow events were rare and lasted from a few to 48 h (2 days) continuously. The largest snowfall, of 100 mm, was recorded in January 2012 and December 2012, followed by February and March 2012, with 51 mm. Monthly snow heights ranged between 15 mm in 2011 to approximately 30 mm in 2013.

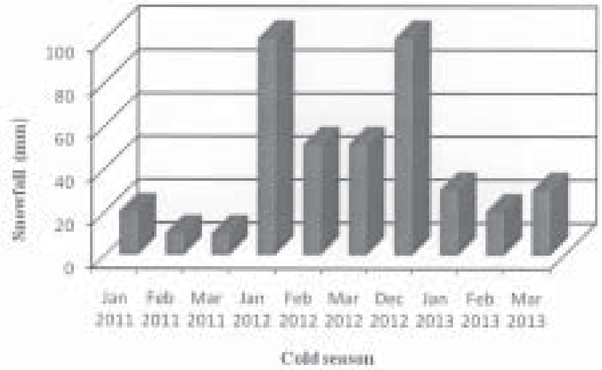

Fig. 2. Monthly variation of snowfall (RNAM)

pH distribution

Figure 3 shows the seasonal variation of *p*H values measured for all investigated periods. In the first sampling period, January – March 2011, *p*H varied in the 5.04 – 7.00 range, the lowest value, 5.035, being recorded in February 2011 on the Icechim sampling site. A neutral 7.26 value was recorded on March for CET Sud sampling site, located nearby the city outskirts, with fewer industrial establishments.

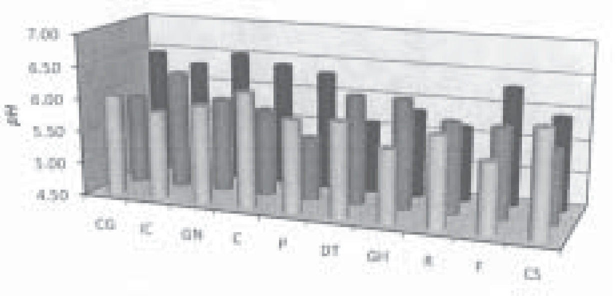

Fig. 3 Seasonal and site variability of *p*H for the collected snow samples

In January – March 2012 period, *p*H was found to vary in the 5.12 – 6.49 range, with the lowest value of 5.12 determined in January on the Pacii sampling site and the highest value of 6.49 measured in March on the Drumul Taberei sampling site.

*p*H in the December 2012 – March 2013 time interval varied from 5.10 to 6.74, the lowest value, 5.10, was recorded in February on the North Railway Station site, a residential area with extremely heavy traffic. The maximum *p*H value, 6.74, was characteristic for the Icechim site, an industrial area, in February.

The volume weighted mean (VWM) *p*H value determined in this study was 5.99, higher than the 5.6 value indicating the existence of equilibrium between atmospheric CO_2 and cold water [8-12]. Only 18% of the 100 snow samples displayed *p*H values below 5.6, being considered slightly acidic, while the rest shifted towards rather neutral values. The most acidic snow sample, with a *p*H of 5.04, fell in January 2011, while in March 2011 the highest value of 7.26 was registered. The average and the mean *p*H values for 2011 are 6.17± 0.47 and 5.96 respectively (table 3). Similar precipitation characteristics have been reported in Iasi, with a VWM *p*H value of 5.92 [8, 11].

Transition metal ions composition

The yearly average concentrations for the six transition metal ions in snow are collected in table 3. Lead, copper, cadmium and zinc were identified and quantified in all samples.

The lead ion content varied widely, in the 4.29 – 84.34 µg/L concentration range, with a mean of 18.24 µg/L. According to Law 311 published in 2004/06/28, which established an alert limiting value of 10 µg/L Pb^{2+} in environmental samples, 50 % of the measurements exceeded the imposed value. These samples were collected in January–March 2012 and varied in the 26.8 – 58.62 µg/L range. The largest lead level, 84.34 µg/L, was recorded in March 2012 on North Railway Station site located in a residential area, close to the largest railway station in Romania, characterized by a heavy railway and auto traffic. The rest of the samples collected in December 2012 – March 2013 were lower than the maximum allowed limit, in the 4.45 – 6.15 µg/L concentration range. The lowest Pb^{2+} level, 4.29 µg/L, was also recorded in this period.

The car market in Romania has suffered a significant blow in 2012, when the number of registered cars declined compared to 2011. In December 2013, the national car park in Bucharest counted 1,125,591 units, while in 2012 went down to 1,118,125 units, and in 2011 was as high as 1,131,807 units (according to statistics released by the Directorate for Driving Licenses and Vehicle Registration - DRPCIV).

According to official statistics, 1% of the total number of registered vehicles is represented by buses and 12% by vans, all using diesel as fuel. The remaining 87% are cars, out of which 60% used gasoline and 40% used diesel fuel. The new cars registered in Bucharest declined with 17% in 2012 compared to 2011, and registered a modest increase of 2.9% in 2013. It was also observed a significant increase of second-hand cars contribution, more than 55 % of the cars in traffic being at least 10-12 years old. In 2012 and 2013, there was a slight increase in the number of diesel cars at the expense of gasoline as follows: in December 2012 there were 329,997 registered cars on diesel and 561,802 on gasoline compared to the same period of 2011 with 325,303 units on diesel and 575,100 units on gasoline.

Table 3

SNOW METAL CONTENT (µg/L) AND *p*H FOR THE INVESTIGATED TIME INTERVAL

Component	Min	Max	Mean	SD	Median	Standard Error	VWM
*p*H	5.04	7.26	6.17	0.47	5.96		5.99
Pb^{2+}	4.29	84.34	18.24	18.85	5.58	2.28	18.22
Cu^{2+}	3.30	24.51	7.86	4.42	6.27	0.44	7.83
Cd^{2+}	1.30	671.15	31.88	78.91	12.32	7.89	31.68
Zn^{2+}	4.21	373.25	53.83	67.12	27.64	6.71	53.83

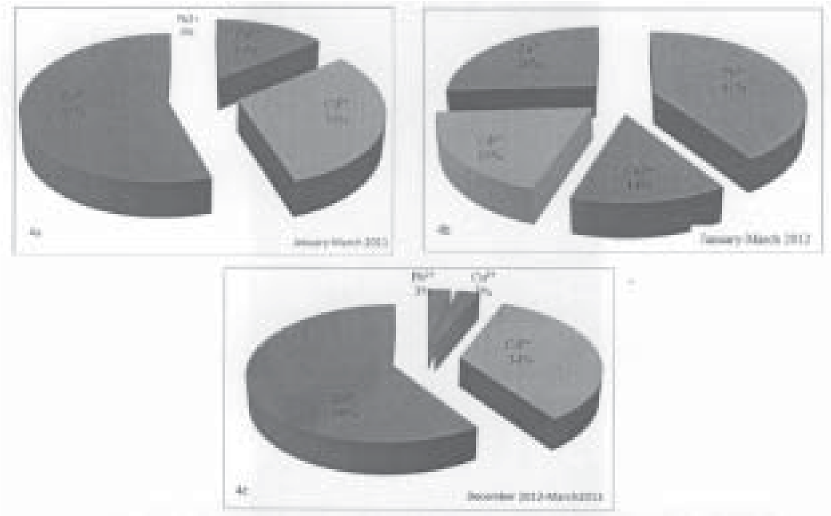

Fig. 4 Fractional contribution of transition metal ions in snow collected in Bucharest, 4a) January–March 2011 period, 4b) January–March 2012 period and 4c) December2012–March 2013 period

In 2013 there were 340,063 cars on diesel and 559,469 on gasoline. The low lead content and constant variation in December 2012-March 2013 interval compared to January 2012-March 2012 can be attributed to the fact that the total number of vehicles decreased, most of all gasoline cars, combined with the significant and repeated increase of the gasoline price.

The copper content varied in the 3.30 – 24.51 μg/L range, with a 7.86 μg/L mean. It is encouraging that no sample exceed the national maximum allowed limit in environmental samples of 100 μg/L Cu^{2+}. 85% of the samples, collected in January – March 2011 and December 2012 – March 2013 varied in the 4.22 – 9.69 μg/L and 4.27 – 6.35 μg /L range, respectively, differing by one order of magnitude from the threshold alert. The lowest copper concentration, 3.30 μg/L, was recorded in February 2011 for Pacii site, a dense residential area. The site presented the same copper level for the previous snowfall (March 2011). The December 2012 – March 2013 period was characterised by Cu^{2+} levels in the 8.82 – 22.2 μg/L range. The highest copper content, 24.51 μg/L, was recorded on March 2012 at North Railway Station, a value four times lower than the alert value. The site with the highest content and largest dispersion of concentrations was North Railway Station, demonstrating special pollution characteristics.

The cadmium levels varied from 1.3 to 671.15 μg/L, with 31.88 μg/L mean, for the three seasons monitored. The national alert value, 5 μg/L, was exceeded in most cases. Even more, 98% of the samples fell in the 2.86 – 42.48 μg/L range and were ten times higher than the allowed limit. There were 5 sites exceeding the allowed limit by at least two orders of magnitude in March 2013 (Pacii, North Railway Station, Icechim, Ferentari and Ghencea). In January – March 2011, January – March 2012 and December 2012 cadmium content varied in the 7.59 to 42.48 μg/L concentration range. If cadmium levels in January 2013 were around the 5 μg/L alert limit, in February they were two times higher, peaking in March with 178.5 μg/L for Icechim site, 226.07μg/L for Ferentari site, 344.88 μg/L for North Railway Station site, and 671.15 μg/L for Pacii site. The smallest cadmium value, 1.3 μg/L, was recorded in January 2013 on the Ghencea site. Since the five highest concentrations of cadmium were recorded during the same month for half of the sampling sites, it was highly possible that the cadmium pollution episode and pollution sources were accidental.

Zinc content varied in large limits, from 4.21 to 373.25 μg/L, with 58.83 μg/L mean. Zn concentrations are much lower compared to the maximum allowed limit of 5000 μg/L. Most values fall in the 7.06 – 48.41 μg/L, being at least two orders of magnitude smaller than the threshold alert. In the first two seasons there were no significant variations in the Zn content in time and space, while the last cold season came with a large dispersion of concentration values. Both the highest 373.25 μg/L value on CG site in January and the lowest 4.21 μg/L value for Ic in March were recorded in this season.

The fractional contribution of transition metal ions in figure 4 demonstrates that zinc was the major species, with no distinct pattern of variation. In the first sampling period Zn represented over 50% of the total metal ions contribution, dropping to 26 % in January – March 2012. In December 201 - March 2013 the zinc amount increased by 5% compared to the first period. Cadmium was the second significant contributor and varied uniformly. It accounted

Table 4
DESCRIPTIVE STATISTICS FOR THE SEASONAL SNOW COMPOSITION

	Mean	Standard Error	Median	SD	Sample Variance	Kurtosis	Skewness	Range	Min	Max
January-March 2011, n=30										
*p*H	5.90	0.10	5.84	0.55	0.30	0.18	0.67	2.22	5.04	7.26
Pb(II)	-	-	-	-	-	-	-		-	-
Cu(II)	7.12	0.65	6.56	3.56	12.68	1.55	1.39	14.02	3.30	17.32
Cd(II)	14.99	1.05	12.12	5.75	33.03	3.02	1.86	21.62	10.63	32.26
Zn(II)	26.96	5.91	15.68	32.37	1047.84	4.96	2.41	121.06	7.06	128.12
January-March 2012, n=30										
*p*H	5.90	0.06	5.94	0.35	0.12	-0.49	-0.38	1.37	5.12	6.49
Pb(II)	36.18	3.11	35.28	17.06	290.93	0.92	0.83	74.79	9.55	84.34
Cu(II)	12.35	0.83	10.62	4.53	20.15	1.83	1.71	16.49	8.02	24.51
Cd(II)	16.90	1.93	10.34	10.59	112.13	-0.51	0.88	34.89	7.59	42.48
Zn(II)	22.98	2.00	20.18	10.98	120.48	-0.34	0.69	39.53	8.88	48.41
December 2012-March 2013, n=40										
*p*H	6.12	0.07	6.13	0.46	0.21	-0.39	-0.33	1.86	5.05	6.91
Pb(II)	5.08	0.16	4.81	0.99	0.98	24.90	4.55	6.27	4.29	10.56
Cu(II)	5.05	0.15	4.80	0.92	0.86	-0.85	0.15	3.37	3.86	7.23
Cd(II)	55.78	19.18	15.85	121.33	14721.80	17.69	3.96	669.85	1.30	671.15
Zn(II)	97.12	13.56	79.10	85.78	7358.78	2.67	1.61	369.04	4.21	373.25

for more than a quarter of total contribution, with 31% and 34% in the first period and the last period. The contribution of lead to the total mass of metal ions varied significantly. If in the second period its contribution accounted for 41%, in the last period it went down to 3%. Lead was followed by copper, present in relatively low concentrations. In the first two periods the contribution was similar, 14%, but it dropped to 3 % in 2013. The fractional contribution of transition metal ions in the snow collected varied irregularly depending on the sampling period and the amount of fallen snow.

The descriptive statistics in table 4 signals normal distributions with low skewness and kurtosis values for all metals, but Pb and Cd in the last monitoring period, when high positive values indicate leptokurtosis distributions.

The VWM values are less than the arithmetic means, indicating that the high concentrations of metal ions are associated with low precipitations. The high relative standard deviations of average ion concentrations (4.42 – 78.91 μg/L) indicate a large variability of the metals level in each snow events [7]. It also signals a variable contribution from the fixed and mobile emission sources to the site pollution.

Conclusions

The VWM *p*H values of the snow collected in 10 sites from Bucharest downtown area was 5.99, which is slightly higher than the average rainwater *p*H of 5.6. Most *p*H values measured in January-March 2011, January- March 2012 and December 2012-March 2013 were in the 5.9 – 7.2 range, due probably to the cations transferred from soil dust.

Lead, copper, cadmium, cobalt, zinc, and nickel were simultaneously determined from wet depositions using an automated ion chromatograph ICS3000 Dionex system equipped with an isocratic eluent delivery pump, isocratic derivatization reagent pump, CS5 separation column, WTV molecular absorption detector, and an AS40 auto-sampler.

The major metals found varied in the $Zn^{2+} > Cd^{2+} > Pb^{2+} > Cu^{2+}$ order. The most abundant metal ion in snow samples was Zn^{2+}, all concentrations being much lower than the alert value. As for the cadmium and lead, they were generally present at much higher levels than the maximum allowed limit, raising a legitimate concern about the pollution level in certain downtown areas. The highest levels of lead, copper, and cadmium were recorded for the GN site, located next to the most important and largest railway station in Romania, and a busy intersection and lots of houses with individual coal- and wood-based heating systems. It should be further investigated if these emission sources can account for the extremely high found levels of toxic heavy metals.

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