



Ambient air particles: The use of ion chromatography and multivariate techniques in the analysis of water-soluble substances

ŽAKLINA N. TODOROVIĆ¹, JELENA M. RADULOVIĆ¹, IVANA D. SREDOVIĆ¹,
IGNJATOVIC², LJUBIŠA M. IGNJATOVIC^{3*}# and ANTONIJE E. ONJIA⁴

¹Anahem Laboratory, Mocartova 10, 11160 Belgrade, Serbia, ²University of Belgrade,
Faculty of Agriculture, Nemanjina 6, 11080 Belgrade, Serbia, ³University of Belgrade,
Faculty of Physical Chemistry, Studentski trg 12–16, 11000 Belgrade, Serbia and ⁴University
of Belgrade, Faculty of Technology and Metallurgy, Karnegieva 4, 11000 Belgrade, Serbia

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Abstract: Seventeen water-soluble substances (of sodium, ammonium, potassium, magnesium, calcium, formate, methanesulfonate, glyoxylate, chloride, nitrite, nitrate, glutarate, succinate, malate, malonate, sulfate and oxalate) in 94 samples of particle matter in the ambient air, collected over ten months, in a suburb of Belgrade (Serbia), were determined by ion chromatography. To apportion the sources of the air pollution, the log-transformed data were processed by applying multivariate techniques. Principal component and factor analysis identified three main factors controlling the data variability: stationary combustion processes with the highest loadings of oxalate, malonate and malate; landfill emission and secondary inorganic aerosol characterized by high levels of ammonium, nitrate and sulfate; a contribution of mineral dust composed of magnesium, calcium and chloride. The hierarchical cluster analysis pointed out a differentiation of the samples into five groups belonging to different variables inputs. For the classification of ambient air samples using nine selected ions, the recognition ability of linear discriminant analysis, *k*-nearest neighbors, and soft independent modeling of class analogy were 87.0, 94.6, and 97.8 %, respectively. Time-series analysis showed that the traffic emission is more pronounced in winter in contrast to the mineral dust influence, while the effect of waste combustion exhibits no trend.

Keywords: organic acids; pollution sources; PCA; emission factors; time-series.

INTRODUCTION

Over the last few decades, the analysis of ambient air particles by means of different analytical techniques and different receptor modeling methods has received increasing attention.^{1,2}

* Corresponding author. E-mail: lgnjatovic@ffh.bg.ac.rs

Serbian Chemical Society member.

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The complimentary use of inductively coupled plasma mass spectrometry (ICP-MS) for trace elements, and gas chromatography–mass spectrometry (GC–MS) for volatile and semi-volatile organics has been the traditional approach to the chemical analysis of ambient air samples.^{3,4} Of many other analytical techniques that are being used, high-performance liquid chromatography coupled to mass spectrometry (HPLC–MS) due to its good sensitivity and resolution power is receiving more and more popularity in trace organics quantification.⁵ On the other hand, ion chromatography (IC) gained an important role as a technique of choice for the analysis of water-soluble ions in atmospheric air particles.^{1,2,6–9}

Since water-soluble substances make up a third or more of the particulate mass of ambient air particles, these ions have been studied intensively in recent years.^{10–14} Those investigations provided essential information on the physico-chemical properties of ambient air particles, the mechanism of their formation and source of pollution. The surface acidity and hygroscopicity properties of ambient air particles govern their chemical and optical behaviors. These particles in ambient air mainly consist of inorganic ions.

Besides the mentioned inorganic matter, an organic component, *i.e.*, a considerable amount of low-molecular weight (LMW) organic acids, are present in the water-soluble part of a typical ambient air particle.^{15,16} Initially, this was proved by means of GC–MS, which is a suitable technique after a derivatization step that has to be performed in order to obtain these acids in their volatile form.¹⁷ The derivatization process is often troublesome, and it was shown that the application of IC for LMW organic acids analysis is more advantageous than GC–MS.¹⁸

An optimized IC method can readily be applied for the analysis of major cations (sodium, ammonium, potassium, magnesium, calcium) and inorganic anions (chlorides, nitrates, sulfates, oxalates, phosphates, bromides), even if they are present at a very low level in aqueous solution.^{19–21}

Here, an isocratic IC in the cation-exchange mode was applied for the analysis of five common cations, whereas twelve inorganic anions and LMW organic acids were simultaneously analyzed by anion-exchange gradient IC.

In order to obtain a better insight into ambient air particles at the studied site, the IC results were evaluated by different multivariate pattern recognition methods.

Multivariate analysis of water-soluble inorganic matter, measured together with PAHs, metals and reactive oxygen species, has been extensively studied.^{2,10,22} As mentioned above, this approach requires the use of several analytical techniques. Although there are many studies in which inorganic ions together and LMW organic acids were analyzed, there is a lack of literature on pattern recognition studies on such datasets.^{6,8–10} In addition, different conventional multivariate techniques produce different results, even when used together.²³ In this work, common non-supervised pattern recognition methods: principal

component analysis (PCA), factor analysis (FA), and hierarchical cluster analysis (HCA) were compared, while supervised pattern recognition methods, such as linear discriminant analysis (LDA), *k*-nearest neighbors (*k*-NN) and soft independent modeling of class analogy (SIMCA), were evaluated for their recognition ability. These methods assign the output values according to some specific machine learning algorithms. The method is supervised, provided that a training dataset is used. On the other hand, in an unsupervised method, it is possible to perform pattern recognition even if no dataset is present.²³

EXPERIMENTAL

The sampling procedure is presented in the Supplementary material to this paper.

Standard solutions. Individual stock standard solutions (1000 mg dm⁻³) were supplied by AccuStandard, Merck, or Fluka. For some ions, *i.e.*, most organic acid salts (glyoxylates, methanesulfonates, glutarates, succinates, malonates), there are no commercially available stock standard solution (1000 mg dm⁻³ or less). In this case, standards were made by dissolving an appropriate amount of an analyte in deionized water. The stock standards were stored at 4 °C, whereas composite working standards at lower analyte concentrations, in a select range similar to the expected analyte concentrations in the samples, were prepared before analysis. The concentrations were calculated from 5 points standard calibration curves using the external standard method. As a quality control measure, duplicates, blanks and spiked samples were also analyzed.

Anion IC system. A Dionex DX-500 ion chromatography system consisting of a gradient pump, ED40 electrochemical detector operating in the conductivity mode (detector current setting: 50 mA), injection valve fitted with 400 µL sample loop, ASRS-ultra self-regenerating suppressor (external water mode), an AS11 (250 mm×4 mm) analytical column, an AG11 (50 mm×4 mm) guard column, and a Peaknet 5.1 chromatography workstation. A mixture of HPLC grade methanol and hydroxide ions, at a flow rate of 2.0 ml min⁻¹, was used as the eluent. The following gradient program was applied: 1) time: 0.0 min, KOH: 0.175 mM, CH₃OH: 5.0 %, 2) time: 6.0 min, KOH: 0.575 mM, CH₃OH: 5.0 %, 3) time: 26.0 min, KOH: 8.575 mM, CH₃OH: 17.0 % and 4) time: 30.0 min, KOH: 10.175 mM, CH₃OH: 5.0 %.

Cation IC system. A Dionex DX-500 ion chromatograph with a conductometric detector, a CS12 (250 mm×4 mm) analytical column, a CG12 (50 mm×4 mm)×guard column, a CSRS-ultra self-regenerating suppressor operating in the recycling mode, and a Peaknet 5.1 chromatography workstation. The eluent was 20 mM methanesulfonic acid (isocratic). The injection sample loop was 100 µL. The system was operated at room temperature with a flow rate of 1.0 cm³ min⁻¹.

Data analysis. The statistical data analyses in this work was performed by means of Minitab, SPSS and PLS Toolbox for Matlab software packages. Details of PCA, FA, HCA, *k*-NN and SIMCA procedure are given elsewhere.²³

RESULTS AND DISCUSSION

Ion chromatography analysis

Typical IC chromatograms of ambient air particles extract are shown in Figs. 1 and 2. In the cation-exchange mode, five common cations (sodium, ammonium, potassium, magnesium and calcium) are easily separated in less than 10

min. In some samples, lithium-ion was detected at trace level, but it was not quantified in this study. Ordinarily, lithium is eluted as the first ion and fairly separated from sodium.

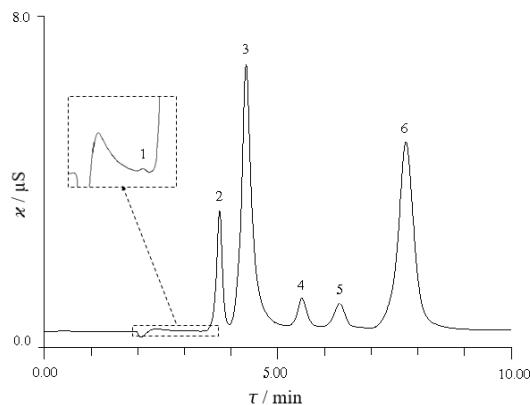


Fig. 1. Typical cation chromatogram of an ambient air particles sample extract. Column: Dionex CS12. Eluent: 20 mM methanesulfonic acid (isocratic). Peaks: 1) lithium, 2) sodium, 3) ammonium, 4) potassium, 5) magnesium, 6) calcium.

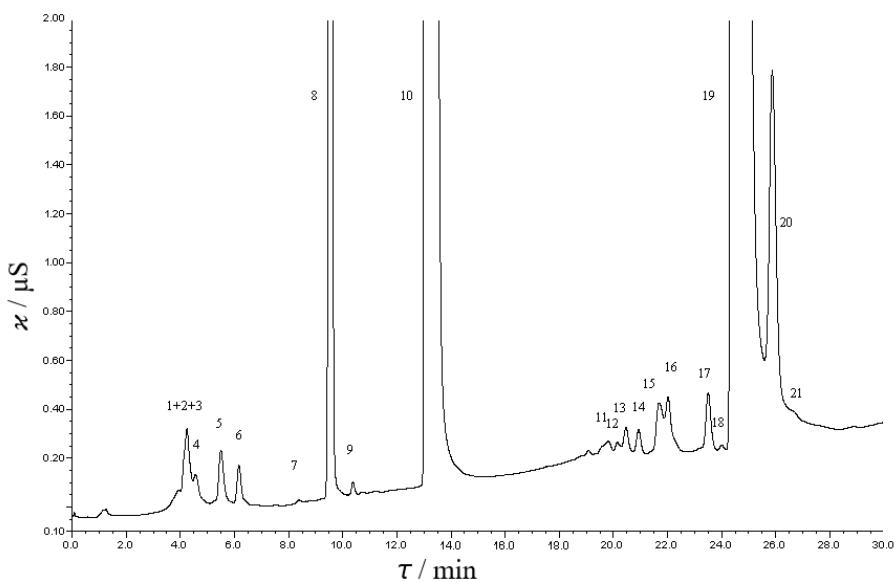


Fig. 2. Anion chromatogram of the same ambient air particles sample extract, as in Fig. 1. Column: Dionex AS11. Eluent: see the experimental part for details. Peaks: 1) fluoride, 2) lactate, 3) acetate, 4) glycolate, 5) formate, 6) methanesulfonate, 7) glyoxylate, 8) chloride, 9) nitrite, 10) nitrate, 11) glutarate, 12) pimelate, 13) succinate, 14) malate, 15) carbonate, 16) malonate, 17) sulfite, 18) fumarate, 19) sulfate, 20) oxalate, 21) azelate.

For any source apportioning method to be applied in an air pollution study, the number of measured chemical substances (variables) should be as high as possible. Preferably, there should be no missing values in the data set.

A few studies have made the apportionment of sources of air pollution even when using only major ions data.^{13,14,24} Although, it is known that not enough tracer information is carried by major ions only. Furthermore, LMW organic acids are shown to be important tracers for different particle emission sources.¹⁵

In this work, for the separation of anions, a multi-step gradient provided simultaneous separation of both inorganic ions (chloride, nitrite, nitrate, sulfate) and ionic form of LMW organic acids (formate, glyoxylate, methanesulfonate, glutarate, succinate, malate, malonate, oxalate). In addition to these anions, several other anions (bromide, phosphate, sulfite, benzoate, caproate, pimelate, fumarate, phthalate, acetate, lactate, glycolate, pyruvate, tartrate, azelate, etc. that were detected in some samples, are not included in this statistical evaluation. The reason was incomplete measurement results for these rarely detected anions in most samples so that some of these anions were often either below the quantification limit of the applied method (pyruvate, tartarate, bromide, phthalate, caproate, fumarate) or there were co-elution problems (fluoride/lactate/acetate, acetate/glycolate) or problem with their stability (sulfite, azelate). Thus, 17 ions were quantified in all samples.

Descriptive statistics

After the completion of IC measurements, the final data matrix 94×17 (observations x variables) was formed. In the first step of data examination, the Ryan–Joiner Test was used for testing the hypothesis of normal distribution.²³ In all statistical tests, the significance level was 0.05. As shown for oxalate in Fig. S-2a (Supplementary material), the plotted points do not approximate a straight line. The departures from linearity indicate that the actual data distribution deviates from a normal distribution. In contrast, the log-transformed data (Fig. S-2b) appear to be well fitted on the normal probability plot with R and p values well above 0.99 and 0.1, respectively. All other variables follow a similar distribution; however, for the sake of brevity, their graphs are not displayed. For further statistical evaluation, the transformed values were used. The data matrix was tested for outliers by applying the Rosner Test.²³ Two samples with high sulfate and ammonia concentrations were discarded as outliers. Therefore, explorative multivariate analysis was realized on the final 92×17 data matrix.

The arithmetic means, minimum values, maximum values, and standard deviations for the concentrations of all substances in the studied ambient air particles were calculated (Table I). It can be seen that the variables could be considered as major ions (nitrate, sulfate, ammonium, sodium, chloride, calcium), trace ions (formate, glyoxylate, methanesulfonate, nitrite, glutarate, succinate, malate, malonate), and those ones at medium to a high level (potassium, magnesium, oxalate). Skewness is a measure of the lack of symmetry varied between 0.5 and 2.5, which means that this data distribution is more or less right-skewed.

Since uniform distribution for different analytes is very rare, kurtosis values are used to estimate the size of tailings. This dataset has both low and high kurtosis, *i.e.*, ranged from –0.5 to 7.6.

TABLE I. Descriptive statistics of the data for the studied water-soluble substances in ambient air particles in Mirijevo outskirt of Belgrade in the period 09.09.2013–25.06.2014

No.	Variable	<i>c / ng m⁻³</i>						
		Mean	Median	Skewness	Kurtosis	St. deviation	Max.	Min.
1.	Sodium	617	581	1.1	1.1	254	1382	229
2.	Ammonium	2186	1707	1.0	0.4	1598	6700	304
3.	Potassium	167	154	1.1	1.3	67	408	69
4.	Magnesium	144	123	1.2	0.9	86	406	27
5.	Calcium	929	685	1.4	1.8	780	3781	94
6.	Formate	16.7	14.8	1.0	0.2	8.2	38.0	5.2
7.	Methanesulfonate	25.5	18.7	1.9	4.1	23.3	118	2.8
8.	Glyoxylate	9.5	7.9	1.0	0.2	5.7	25.8	1.2
9.	Chloride	1217	869	1.0	0.3	1030	4282	54.9
10.	Nitrite	20.9	18.3	0.5	–0.5	11.2	47.7	4.4
11.	Nitrate	3765	3405	0.8	0.2	2019	9837	634
12.	Glutarate	7.2	5.4	2.0	5.2	5.8	34.0	0.9
13.	Succinate	18.0	15.0	2.4	7.6	14.6	86.7	4.0
14.	Malate	15.8	8.9	2.5	6.4	19.0	94.2	1.6
15.	Malonate	19.5	9.2	1.8	2.5	25.7	108	0.1
16.	Sulfate	3230	2873	1.0	0.5	1736	8221	1105
17.	Oxalate	83.2	79.6	0.7	–0.2	42.7	193	17.1

Unsupervised pattern recognition

These data were subjected to several common multivariate pattern recognition methods, which are described in detail elsewhere.^{23,25,26}

Principal component analysis (PCA) is a method of removing the highly inter-correlated nature of variations in atmospheric concentrations. Thurston and Spengler suggest that the dataset must have many more samples than analytes if stable PCA results are to be derived.²⁷ Their requirements: $n \geq m + 50$ (where n is the number of samples; m is the number of analytes) is fulfilled in this work.

When PCA was applied to the autoscaled data matrix, three principal components (PCs) appeared to account for 84 % of the variance in the data. The eigenvalue and cumulative variance as a function of the number of PCs are shown in Fig. S-3 (Supplementary material). In this case, the descriptor space dimensionality is reduced to three since only the first three PCs were retained. These PCs meet the Kaiser criterion to have the eigenvalues higher than one.²³ All other PCs show eigenvalues lower than one, with an exponential trend in the decrease.

In order to highlight the relations between variables, the data set of concentration measurements was subjected to factor analysis (FA). This method was

applied with PCA extraction of the correlation matrix and varimax orthogonal rotation. The FA method identified three significant factors (Table II): the first (24.6 % of variance) comprises organic ions oxalate, malonate, malate with high loadings and glutarate, succinate, methanesulfonate, formate, nitrite, and sulfate with relatively lower loadings.

TABLE II. Varimax rotated factor loadings (values > 0.5 are in bold)

No.	Variable	Factor 1	Factor 2	Factor 3
1.	Sodium	0.257	0.223	0.192
2.	Ammonium	0.225	0.909	-0.210
3.	Potassium	0.140	0.146	0.288
4.	Magnesium	-0.255	-0.217	0.871
5.	Calcium	-0.396	-0.183	0.853
6.	Formate	0.449	0.214	-0.234
7.	Methanesulfonate	0.501	0.381	-0.199
8.	Glyoxylate	0.092	0.431	0.138
9.	Chloride	-0.453	0.195	0.687
10.	Nitrite	0.493	0.323	-0.359
11.	Nitrate	0.068	0.953	-0.029
12.	Glutarate	0.585	0.491	-0.299
13.	Succinate	0.596	0.650	-0.243
14.	Malate	0.837	0.165	-0.396
15.	Malonate	0.800	0.241	-0.302
16.	Sulfate	0.396	0.791	-0.017
17.	Oxalate	0.842	0.295	-0.295

All organic ions, except succinate and glyoxylate, have higher loadings in this factor than in the second one. Oxalate and malonate are markers for combustion processes.^{8,28} Hence, this factor identifies exposure to emissions from fuel combustion. Although, other biogenic sources could also contribute to the production of these two acids. Mainly composed of ammonium, nitrate, sulfate, and succinate, the second factor accounts for a further 22.7 % of the variance. The association between sulfate and nitrate suggests an anthropogenic origin. Waste landfill emissions that occur in the vicinity of the sampling site, as well as a secondary inorganic aerosol, might be responsible for this factor. The third factor with 16.8 % of the variance was composed of magnesium, sodium, chloride, and with a lower loading of potassium. This source profile strongly suggests that their concentrations are affected by mineral dust from both natural and anthropogenic sources. Except for potassium (loading = 0.536) and calcium (loading = 0.565), no significant loading value was obtained for any variable on Factors 4 and 5, which are responsible for 6.9 and 6.6 % of the total variance, respectively. It is relevant that some ions, such as methanesulfonate, nitrite, glutarate, sulfate, succinate, obtained rather high scores both on the first and second factor, indicating more than one possible significant emission source.

Hierarchical cluster analysis (HCA) was made on the variables that had previously been standardized.²⁹ An amalgamation rule employed the Ward method to link the objects, while for the measure the proximity between samples, the squared Euclidean distance was selected.³⁰ The dendrogram is shown in Fig. 3. As a result of applying HCA to the factor score matrix, the ambient air particles split into two main groups. Furthermore, each group could be subdivided into three or two sub-groups, respectively. There are, therefore, five clusters (C1, C2, C3, C4 and C5), the composition of which depends on the inputs of variables.

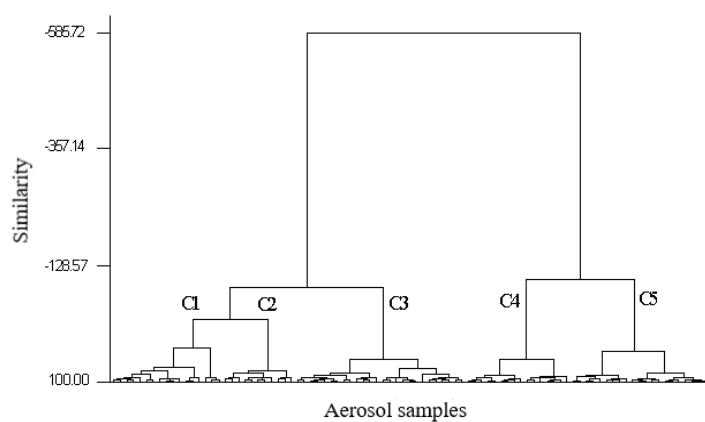


Fig. 3. Dendrogram of cluster analysis of ambient air particles.

Cluster C1 consists of the samples characterized by high score values for the combustion factor, whereas the second group of samples (C2) has high levels in the landfill emission and secondary inorganic aerosol factor. The samples with medium-low scores of both the combustion and waste emission/secondary inorganic aerosol factors (C1 and C2) are grouped in cluster C3. These three groups (C1, C2, and C3) form one of the two main groups that all samples can be split. The fourth cluster (C4) comprises samples with the highest levels of the variables (magnesium, calcium, chloride) for the mineral dust factor, while medium-high score values for the previous factor (C4) are characteristic for the samples in C5.

Supervised pattern recognition

In order to evaluate the possibility of classification of ambient air particles into these five groups, three common supervised pattern recognition techniques were employed, linear discriminant analysis (LDA), k-nearest neighbors (*k*-NN), and soft independent modeling of class analogy (SIMCA).^{31,32}

First, the samples were classified using all variables. Then, nine variables with the first three highest loadings in each Factor in Table II (malate, malonate, oxalate, ammonium, nitrate, sulfate, magnesium, calcium, chloride) were selected

as key features for classification. In all cases, the leave-one-out method of cross-validation was used.

Linear discriminant analysis (LDA) is a very simple supervised classification technique that reduces the dimensionality of the features in a similar way as PCA. LDA makes projection axes for separating the classes by minimizing the within-class variance and maximizing the between-class variance. In this case, LDA produced a classification success rate of 83.7 % for all samples and all variables. The separation of ambient air particles by two discriminant functions is shown in Fig. 4. When performing LDA with the reduced number of variables, 87.0 % of grouped samples were correctly classified.

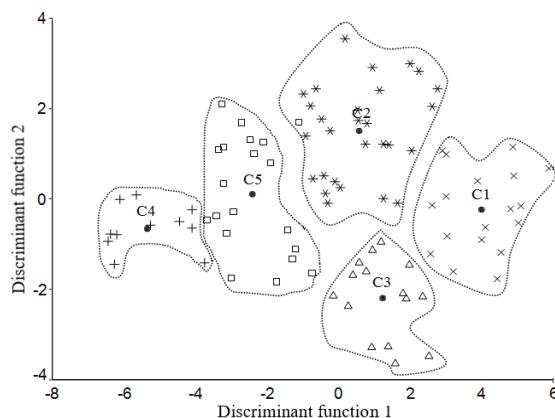


Fig. 4. Discriminant analysis of ambient air particles (solid symbols are the group centroids).

One of the simplest classifiers is the k -NN algorithm. It classifies an input feature vector by determining the k closest training vectors according to a distance metric. Then, this input vector is assigned to a class to which the majority of its k nearest neighbors belong. Here, the metric employed was the Euclidean distance.

As in the case of LDA, k -NN and SIMCA were performed using both all and selected variables. The obtained results are given in Table III. Using both methods, the recognition ability for the five classes was highly satisfactory; the percentages of classification obtained were 93.5–100 %.

TABLE III. Recognition and prediction ability (%) of LDA, k -NN and SIMCA to classify ambient air particles; (A) – all variables, (B) – nine selected variables

Ability for:	Method		
	LDA	k -NN	SIMCA
Recognition	(A)	83.7	93.5
	(B)	87.0	94.6
Prediction	(A)	52.8	94.6
	(B)	56.5	92.4

Another approach that can give a more realistic error rate is to split the data into two parts, one part to create the discriminant function or model, and the other part as a testing set. Randomly splitting an equal number of samples (46 samples) into these two sets, the *k*-NN method produces good prediction power (94.6 and 92.4 %), whereas LDA (52.8 and 56.5 %) and SIMCA (78.3 and 73.9 %) give a much lower percentage of the correctly classified samples than previously, for both all variables and nine variables, respectively.

Time-series analysis

To examine the trends of the concentration changes from each emission source, over a ten-month period (fall 2013 to summer 2014), the concentrations of indicator ions (with the highest loadings) for various emission sources were plotted by the moving averages for the samples in Fig. 5.

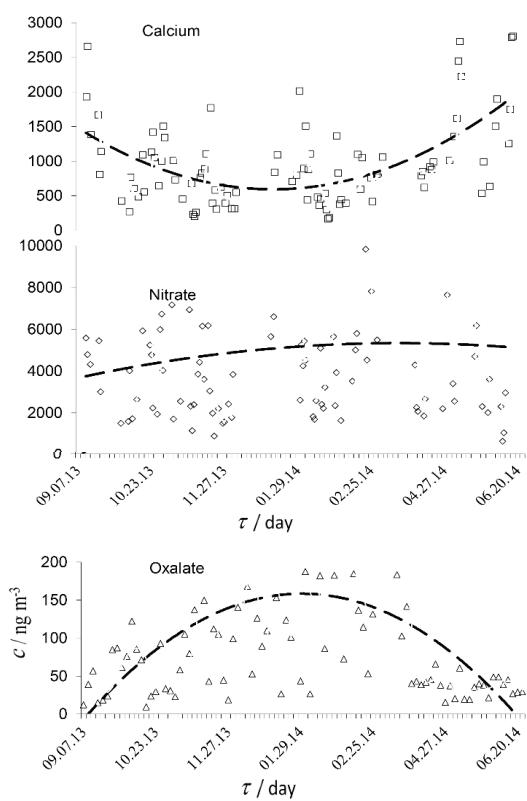


Fig. 5. Variation of ambient air particles concentrations of oxalate, nitrate, and calcium in the Mirijevo outskirt of Belgrade during the period 2013 to 2014. The dot lines indicate the quadratic fit.

The time-trends of these variables were also fitted by quadratic curves. Variables in Factor 1 show an affinity to change with time, increasing from low values in the fall to a maximum during the winter, followed by a slight decrease through the spring in 2014. This trend resembled that reported elsewhere.^{21,33}

The variables in Factor 3 showed the opposite trends over the same time period, whereas those in Factor 2 have no trend. Similar seasonal behavior for the ions comprising the latter two factors was obtained by other authors.^{22,24,33} A significant fluctuation is present with all analyzed variables. No monthly periodicity was revealed. The reason for seasonal variation could be found in the local climate and weather conditions. Hence, dust resuspension (Factor 1) is more intense in the summer, with many dry days with no snow coverage. On the other hand, the fuel combustion (Factor 3) is more intense in winter days. No seasonal changes in the municipally waste landfill activities was observed, causing no trend in Factor 2. Generally, these results could be explained by the occurrence of atmospheric transport on a local scale.

CONCLUSIONS

The combined use of ion chromatography and multivariate pattern recognition methods can provide valuable information for an ambient air particle research study. Some water-soluble substances, such as bromide and phosphate, which are traditionally measured in ambient air particle samples by NAA, XRF, PIXE, ICP-MS, and used as important source markers, can also be quantified by IC, but the applied IC separation in this work should to be additionally optimized. The obtained data chemical set showed the characteristic of log-normal distribution, while multivariate methods revealed a distinctive grouping of variables and observations. Of the three common supervised pattern recognition methods (LDA, *k*-NN and SIMCA), the classification prediction ability was only satisfactory when applying *k*-NN. Some variables do not contribute to the classification. The emissions from combustion processes, landfill emission together with secondary inorganic aerosol, and a contribution of mineral dust were identified as the three dominant factors that have an effect on pollutant levels at the studied site. The landfill emission/secondary inorganic aerosol undergoes no change in seasons, whereas the other two other factors show different behavior during winter and summer. In general, a considerable high level of sulfate, nitrate, ammonium, and LMW organic acids in the ambient air particles at the site pointed to a strong anthropogenic influence.

SUPPLEMENTARY MATERIAL

Additional data are available electronically at the pages of journal website: <https://www.shd-pub.org.rs/index.php/JSCS/index>, or from the corresponding author on request.

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ИЗВОД

ЧЕСТИЦЕ У АМБИЈЕНТАЛНОМ ВАЗДУХУ: ПРИМЕНА ЈОНСКЕ ХРОМАТОГРАФИЈЕ И МУЛТИВАРИЈАНТНИХ ТЕХНИКА АНАЛИЗЕ ВОДЕНО-РАСТВОРНИХ СУПСТАНЦИ

ЖАКЛИНА Н. ТОДОРОВИЋ¹, ЈЕЛЕНА М. РАДУЛОВИЋ¹, ИВАНА Д. СРЕДОВИЋ ИГЊАТОВИЋ²,
ЉУБИША М. ИГЊАТОВИЋ³ И АНТОНИЈЕ Е. ОЊИА⁴

¹Анахем Лабораторија, Моцаршова 10, 11160 Београд, ²Универзитет у Београду, Полојаривредни факултет, Немањина 6, 11080 Београд, ³Универзитет у Београду, Факултет за физичку хемију Студенчески ћар 12–16, 11 000 Београд и ⁴Универзитет у Београду, Технолошко-мештаварски факултет, Карнејијева 4, 11000 Београд

Методом јонске хроматографије одређен је садржај 17 супстанци растворљивих у води (које садрже натријум, амонијум, калијум, магнезијум, калцијум, формате, метан-сулфонате, глиоксилате, хлориде, нитрате, глутарате, сукцинате, малате, малонате, сулфате и оксалате) у укупно 94 узорка честица у амбијенталном ваздуху, који су узорковани током десет месеци у предграђу Београда. Да би се одредили извори загађења ваздуха, добијени резултати су најпре трансформисани у њихове логаритме, а потом анализирани применом мултиваријантних техника. Анализа главних компоненти и факторска анализа идентификовали су три главна фактора који контролишу варијабилност података: процес стационарног сагоревања са највећим оптерећењем оксалата, малоната и малата, емисија са депоније и секундарни неоргански аеросол које карактеришу високи нивои амонијум-јона, нитрата и сулфата и допринос минералне прашине која се састоји од материја магнезијума, калцијума и хлорида. Примена хијерархијске анализе кластера указала је на диференцијацију узорака у пет група које припадају различитим профилима аналита. За класификацију узорака амбијенталног ваздуха помоћу девет одабраних јона, способност препознавања методе линеарне дискриминантне анализе, методе *k*-најближих суседа и методе неког независног моделовања аналогне класе износили су 87,0, 94,6 и 97,8 %. Анализа временских серија показала је да је фактор емисије из саобраћаја у току зиме израженији, за разлику од фактора минералне прашине. Ефекат стационарног сагоревања не показује тренд.

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