JOURNAL OF JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS, Vol. 11, No. 5, May 2009, p. 697 - 710

Qualitative assessment of heavy metals sources in pitcoal/biomass briquettes combustion using multivariate statistical analysis

T. FRENTIU[a], M. PONTA[a], A. MIHALTAN[b], E. CORDOS[b],
M. FRENTIU[b], G. LAZAROIU[c], L. TRAISTA[d], R. INDRIES[d]
[a]*Babes-Bolyai University, Department of Chemistry, Arany Janos 11, 400028 Cluj-Napoca, Romania*
[b]*National Institute for Research and Development of Optoelectronics Bucharest, Research Institute of Analytical Instrumentation, Donath 67, 400293 Cluj-Napoca, Romania*
[c]*University Politehnica of Bucharest Department of Electrical Engineering, Splaiul Independetei 313, 060042 Bucharest, Romania*
[d]*University of Petrosani, Universitatii Street 20, 332006 Petrosani, Romania*
[e]*National Institute of Wood, Fabrica de Glucoza 7, 020331 Bucharest, Romania*

The study based on multivariate statistical approach revealed new information about source of elements during the combustion of pitcoal/biomass(sawdust) briquettes. The Principal Components Analysis showed that the pattern of total element contents was defined by four latent factors explaining more than 92 % of the total variance of the system. According to their source these factors were associated to species coming from: *sedimentary minerals from pitcoal* (33.9%); *biomass (37.8%); silicates from pitcoal* (11.5%); *reducible species from pitcoal* (9.2 %). Four latent factors with variance over 85 % explained the sources of water available species: *free metal ions (32.5 %); adsorbed on secondary Al minerals (24.4 %); reducible species retained on oxides (14.5%); biomass (14.2 %).* The contribution of variance to element pattern was higher from pitcoal than biomass, since the latent factors attributed to pitcoal explained 54.6% of the variance for the total and 71.4% for the water leachable content, respectively. Results were confirmed by the cluster analysis that highlighted three groups of elements according to their affinities as well as samples clustering according to their nature. The Pearson's positive correlations among Fe and Al and most of trace elements attested their natural origin in both pitcoal and biomass, free from anthropogenic input.

(Received March 5, 2005; accepted May 25, 2009)

Keywords: Pitcoal/biomass briquettes, Principal components analysis, Cluster analysis, Pearson's correlation

1. Introduction

The final goal of a chemical analysis is the interpretation of experimental data resulted from laboratory measurements, which requests statistical processing. This stage is often difficult to achieve, especially in the case of complex systems, where several variables are measured for each specimen and a large volume of experimental data are collected.

When two or three variables are used to describe a system, the interpretation can be readily carried out using linear regression in order to identify possible correlations between variables [1-7]. A statistical non-complicated approach to assess agreement between two variables is the Bland and Altman test, which has the advantage to be applicable to variables of both normal and non-normal distribution. The method is also suitable for statistical analysis of variables unevenly spread over the concentration range under study and grouped at the extremes [6-10].

When more than four variables are measured for each sample, a valid interpretation asks for a multivariate analysis of data in finding patterns and relationship. Such approach is the Principal Component Analysis (PCA), which allows, among others, to identify the source of elements or chemical species as variables in the characterization of a system [1, 10]. Another approach of the multivariate analysis is the Cluster Analysis (CA), which divides a group of objects (elements, species, analytical parameters) into classes so that similar objects are in the same class [1].

PCA and CA have been widely used in environmental studies to identify pollution sources or find the natural or anthropogenic origin of various species [10-18]. These statistical approaches are also suitable for data analysis in chemical speciation of elements, in which, for the same element several species are determined [18-20]. PCA was used for detecting abnormal events and diagnosis of municipal solid waste incinerators in order to improve the safety and continuity of production [21]. PCA revealed that biomass burning is major pollutant source with metals coming from both domestic and industrial activities in Bangkok [5]. The Principal Components Analysis/Absolute Principal Components Scores (PCA/APCS) approach showed that the combustion sources (natural gas, wood, coal/coke, biomass) contributed 19-97% of various carcinogenic polycyclic aromatic hydrocarbons (PAHs) in India [22]. The same technique showed that the primary pollution sources in Central Taiwan include vehicle exhaust, coal/wood combustion, incense burning and incineration emissions. Open burnings of rice straw was estimated to contribute with 5.0-33.5% to atmospheric PAHs [23].

It is the aim of this paper to apply PCA and CA receptor modeling in order to obtain a pattern of heavy metals potential sources from pitcoal/biomass blend briquettes combustion. These approaches provide more reliable information and a better understanding of the role of blend parent materials during combustion in respect with total and water-leachable heavy metal concentrations. Additionally, the Pearson's correlation analysis was used to predict the natural or anthropogenic origin of heavy metals. In the statistical treatment of our data we used XLStat as a Microsoft Excel plug-in (Addinsoft).

2. Experimental

2.1 Sample analysis

Multivariate statistical analysis was applied on an input matrix of 19 samples x 20 variables. The analyzed samples were parent materials used in briquettes manufacturing (pitcoal and sawdust), briquettes containing 10-75% sawdust and the resulted bottom ashes. The variables were total element contents (As, Al, Ba, Cd, Cr, Co, Cu, Fe, Ga, K, Mn, Mo, Ni, P, Pb, Si, V, W, Zn, Zr) extracted in HNO_3-HF mixture by microwave digestion and water available species of elements at a solid/liquid ratio 1:2 (SR EN 12457/1:2003). Elements were determined in solutions by inductively coupled plasma optical emission spectrometry (ICP-OES) using the multichannel spectrometer Spectro Ciros^{CCD} (Spectro Analytical Instruments, Kleve, Germany). Details about instrumentation, analytical sample preparation and characterization of raw materials and bottom ashes are found in reference [24].

3. Theoretical

3.1. Principal Component Analysis [1,11]

PCA is a statistical technique, which can be applied to a large set of variables in order to reduce dimensionality. Therefore, the great number of intercorrelated variables is replaced with a smaller number of independent variables (i.e. five or six) called principal components (PCs) or latent factors. This substitution provides a new perspective in data structuring and interpretation. The selected PCs are not known and cannot be determined directly but they enclose the factor loadings obtained from the multiple regression for each studied component. Factor loadings are a quantitative expression of their role in a certain latent factor. In order to explain the variability of the system only the PCs with eigenvalues higher than 1 are taken into account. Eigenvalue gives the amount of variance in the data set, which is explained by PCA. Moreover, the percentage of the cumulative variance of the selected PCs should be above 70 % of the total variance. In the Varimax rotation mode the selected PCs are rotated in order to maximize the explained variance and increase the weight of the higher factor loadings, while reducing those of lower values. An examination of the rotated component loadings on the original elements allowed the identification of the PCs as sources affecting the data. Before carrying out the PCA raw data need to be transformed into a dimensionless standardized form by normalization with the standard deviation of each variable. This is essential for input matrix in which variables have different measurement units, different orders of magnitude and high differences among variables and large variances. The Varimax rotation approach on standardized data was used in this study in order to identify the sources of elements in the process of the pitcoal-biomass briquettes combustion.

3.2 Cluster Analysis [1]

The aim of the CA is to identify the similarities or dissimilarities within a large group of objects characterized by a certain number of variables. The homogenous objects are grouped on the basis of calculated distances between all objects. The similarity between objects results from the Euclidian distance or squared Euclidian distance. An appropriate linkage algorithm (single, average, centric linkage, Ward's method) is applied to link a cluster of objects with close distance and to separate those located at larger distances. The hierarchical dendrogram (Euclidian distance and Ward's method) was applied in this study in order to identify the similarities between elements using the total and water available content of elements. The same algorithm was used in the cluster analysis of the samples. Ward's method yields clearly structured and relatively stable cluster over a wide range of similarities.

4. Results and discussions

4.1. Pearson's correlation matrix

Correlation and regression analysis are mostly used to estimate natural and anthropogenic contribution of elements in sediments. Major constituents of sediments such as iron, aluminium and total organic carbon (TOC) are used as tracers in such studies. The reason to select Fe and Al tracer elements is that they have high and constant concentrations free of anthropogenic influences and retain heavy metals by adsorption and coprecipitation [4, 19, 25, 26]. A positive significant correlation between tracers and heavy metals suggests the natural origin of elements. In order to estimate the origin of heavy metals following combustion of pitcoal-sawdust briquettes, the correlation coefficients between Al and Fe content and heavy metals as possible pollutants were calculated (Table 1). The positive correlation among Al, Fe and As, Cd, Co, Cr, Cu, Ni, V, Mo, W proves their natural origin in parent materials. The inconsistent correlation coefficient for Pb suggests an anthropogenic origin.

The bold face intercorrelation coefficients stand for a common source of elements but this is difficult to identify.

Table 1. Pearson's Correlation matrix.

Variables	Al	K	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Cd	Ba	Pb	Si	P	V	As	Zr	Mo	W
Al	**1**	0.177	**0.516**	0.202	**0.925**	**0.900**	**0.744**	**0.378**	0.181	0.182	**0.406**	0.336	0.116	**0.469**	0.219	**0.926**	**0.673**	0.339	**0.635**	**0.844**
K		**1**	**0.711**	0.069	0.181	0.239	-0.129	-0.142	-0.032	0.035	0.195	**0.490**	**0.561**	-0.071	0.307	0.214	-0.245	0.020	0.258	0.029
Cr			**1**	0.279	**0.594**	**0.692**	**0.397**	**0.411**	0.144	0.246	**0.601**	**0.629**	**0.768**	0.033	**0.520**	**0.598**	0.149	0.196	**0.674**	**0.505**
Mn				**1**	0.116	0.216	0.022	0.127	**0.377**	**0.997**	**0.404**	0.261	0.360	0.189	**0.927**	-0.005	-0.105	-0.071	0.340	**0.427**
Fe					**1**	**0.984**	**0.788**	**0.569**	0.140	0.098	**0.529**	**0.418**	0.332	**0.417**	0.217	**0.964**	**0.667**	**0.389**	**0.713**	**0.899**
Co						**1**	**0.803**	**0.609**	0.184	0.195	**0.599**	**0.455**	**0.436**	**0.396**	0.336	**0.941**	**0.640**	**0.387**	**0.788**	**0.920**
Ni							**1**	**0.638**	0.212	0.005	0.304	0.009	0.035	0.267	0.048	**0.813**	**0.719**	0.322	**0.653**	**0.762**
Cu								**1**	-0.011	0.131	**0.604**	0.072	**0.397**	0.030	0.205	**0.506**	**0.418**	0.254	**0.541**	**0.587**
Zn									**1**	**0.379**	0.103	0.203	0.088	0.258	**0.384**	0.162	-0.014	0.068	0.155	0.340
Ga										**1**	**0.413**	0.262	0.350	0.182	**0.913**	-0.030	-0.121	-0.080	0.310	**0.414**
Cd											**1**	**0.583**	**0.695**	0.221	**0.516**	**0.428**	0.260	0.286	**0.585**	**0.604**
Ba												**1**	**0.643**	0.208	**0.381**	0.358	-0.087	0.252	0.199	0.369
Pb													**1**	0.005	**0.630**	0.211	-0.112	0.164	**0.564**	0.347
Si														**1**	0.179	0.354	**0.616**	**0.840**	**0.429**	**0.608**
P															**1**	0.103	-0.115	0.026	**0.519**	**0.478**
V																**1**	**0.662**	0.367	**0.649**	**0.820**
As																	**1**	**0.555**	**0.624**	**0.667**
Zr																		**1**	**0.442**	**0.493**
Mo																			**1**	**0.782**
W																				**1**
Values in bold are significantly different from 0 with a significance level alpha=0.05																				

4.2. Principal component analysis

The varimax rotated factor loading of four principal components of the total metals content in bottom ash, sawdust and pitcoal are presented in Table 2. The loadings in bold face correspond to elements with dominant influence on the selected latent factor.

Table 2. Varimax rotated factor loadings of the total metal concentrations in bottom ash, sawdust and pitcoal.

Variable	PC1	PC2	PC3	PC4
Al	**0.951**	0.238	0.178	-0.044
K	0.129	**0.901**	0.065	-0.381
Cr	**0.404**	**0.891**	-0.104	0.093
Mn	0.088	**0.953**	0.020	0.072
Fe	**0.973**	0.182	0.101	0.081
Co	**0.934**	0.309	0.096	0.140
Ni	**0.824**	-0.024	0.075	**0.481**
Cu	**0.479**	0.099	-0.059	**0.839**
Zn	0.254	**0.808**	-0.179	**0.444**
Ga	0.069	**0.966**	-0.003	0.100
Cd	**0.424**	**0.481**	-0.002	**0.357**
Ba	0.221	**0.873**	-0.023	-0.271
Pb	0.116	**0.948**	-0.137	0.195
Si	0.304	-0.106	**0.923**	-0.191
P	0.077	**0.953**	0.029	0.099
V	**0.970**	0.175	0.070	0.067
As	**0.680**	-0.299	**0.527**	0.201
Zr	0.185	-0.007	**0.905**	0.101
Mo	**0.547**	**0.548**	0.344	0.350
W	**0.902**	0.198	0.320	0.199
Variability / %	**33.9**	**37.8**	**11.5**	**9.2**

Four latent factors explain more then 92 % of the total variance of metal sources. The first latent factor responsible for 33.9 % of the total variance could be labeled as *sedimentary minerals from pitcoal* as it includes the metals found in high concentrations in pitcoal (Al, As, Cd, Co, Cr, Cu, Fe, Mo, Ni, Pb, V and W) [24]. This source corresponds to species bound on secondary Al and Fe minerals, which are dominant in pitcoal and are likely to retain element compounds by adsorption and coprecipitation. The existence of As in this factor is in agreement with its high concentration clays contained in coal mass [27]. The presence of Co in PC1 is supported by the fact that its content in rocks increases as silica decreases, which does not belong to this source [28]. Furthermore, Co occurs in secondary Fe minerals together with Ni and As. Chromium and V occur more in secondary argillaceous rocks. The presence of Cr and V in Fe containing minerals is explained by their similar ionic radius, which allows the substitution of Fe by the other two elements [27, 29]. Definite chemical affinities among elements such as that of As for Co and Pb, or Mo for W explain their enclosure in this PC. The second PC explaining 37.8 % of the variability was named *biomass factor* as it includes elements considered as macronutrient for plants (K and P). Besides, this latent factor comprises Ba, Cd, Ga, Mn, Pb and Zn present in carbonate rocks from where they are extracted by plants following dissolution in acetic acid secreted by roots under anaerobic conditions [30]. Elements belonging to PC2 showed high concentrations in ashes obtained by burning biomass and coal-biomass briquettes [24]. The third factor explaining 11.5% of the total variance encloses element species associated to *silicates from pitcoal.* It is noticeable the strong correlation between Si and Zr, in accordance with their affinity in zirconite ($ZrSiO_4$), the dominant mineral of Zr. The presence of As also in this PC is consistent with its tendency to be retained on silicate rocks [27]. With the last factor (explanation of 9.2% of the total variance) are associated mainly Cu and to a lesser extent Ni, Zn and Cd. This factor is conditionally named *reducible species from pitcoal* and could be attributed to sulfides as Cd, Cu, Ni and Zn show an affinity for S and other reducible species. Overall the contribution of variability to element pattern within the combustion of pitcoal-sawdust briquettes is 37.8% from biomass and 54.6% from pitcoal.

Table 3 presents the Varimax rotated factor loadings considering the water leachable metal concentrations in samples for a solid/liquid ratio of 1:2.

Table 3. Varimax rotated factor loadings of the water leachable metal concentrations from ash, sawdust and pitcoal for a solid/liquid ratio of 1:2.

Variable	PC1	PC2	PC3	PC4
Al	0.050	**0.826**	0.177	-0.133
K	-0.208	-0.026	-0.035	**0.930**
Cr	-0.105	**0.976**	-0.070	0.076
Mn	**0.966**	-0.105	-0.133	-0.029
Fe	-0.188	-0.099	**0.880**	-0.012
Co	**0.960**	-0.069	-0.110	-0.128
Ni	**0.813**	-0.093	-0.170	-0.142
Cu	-0.065	-0.026	**0.862**	-0.051
Zn	**0.952**	-0.089	-0.167	-0.125
Ga	**0.959**	-0.082	-0.133	-0.107
Cd	**0.850**	-0.069	0.369	-0.061
Ba	-0.227	0.021	0.372	**0.800**
Pb	-0.103	-0.114	**0.859**	0.057
Si	-0.038	-0.036	-0.173	**0.943**
P	-0.174	-0.137	0.177	**0.415**
V	-0.097	**0.985**	-0.077	-0.021
As	**0.942**	-0.015	0.012	-0.076
Mo	-0.103	**0.989**	-0.072	-0.028
W	-0.091	**0.979**	-0.081	-0.015
Variability / %	**32.5**	**24.4**	**14.5**	**14.2**

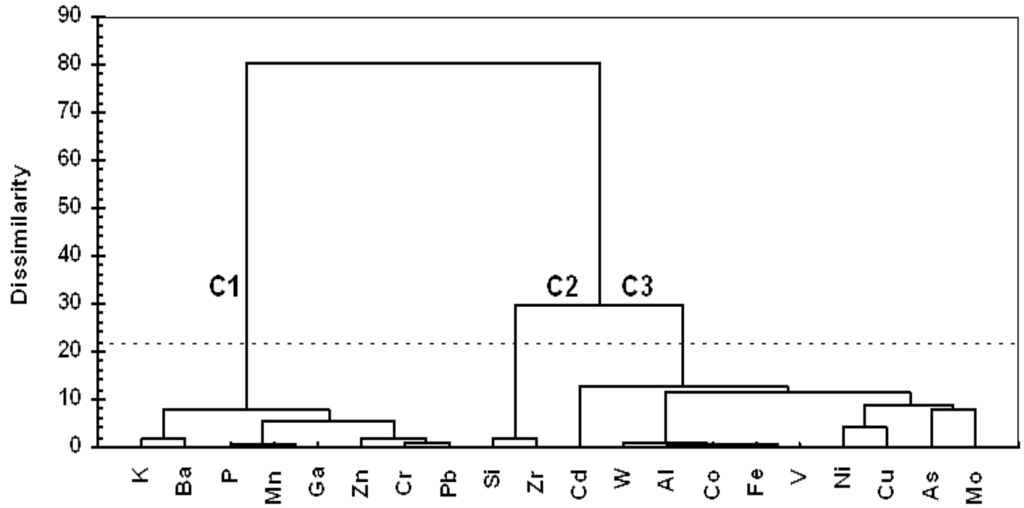

Fig. 1. Dendrogram of the cluster analysis on total element concentrations.

The four loading factors describe over 85% of the total variance. In this PCA Fe, Al and Mn are considered tracers in order to interpret the distribution of other elements on different fractions. The first PC explaining 32.5 % of the total variance is conditionally named the *free metal ions* and includes elements as easily water soluble species: As, Cd, Co, Ga, Mn, Ni, and Zn. This factor is attributed to the influence of pitcoal, since the water available fractions of these elements from pitcoal ash are higher than from sawdust ash [24]. The second latent factor with 24.4 % explanation of the total variance includes Cr, Mo and V, very likely adsorbed on secondary Al minerals, dominant in clay. This factor is attributed to pitcoal and can be defined as *adsorbed species on secondary minerals*. The third factor explaining 14.5% of the variance contains Cu, Cd and Pb, which are very probable adsorbed on the oxides of Fe, also present in this PC. Joining of Cu and Pb together with Fe is justified by the affinity of iron oxides to retain these elements [3, 4]. This factor corresponding to *species retained on oxides* is also attributed to pitcoal, since Fe content in this material is higher than in sawdust [24]. With the last factor are associated elements considered plant macronutrients (K, P) as well as Si. The reason of the presence of Si in this PC besides the two macronutrients is its extraction by plants from water soil containing silicic acid. As mentioned in ref. [24], the water available fraction of Si was higher in sawdust ash than that of pitcoal. This PC was attributed to *biomass* explaining 14.2% of the total variance. The PCA emphasized a contribution of 71.4% variability from pitcoal, which has a most important influence than biomass to mobility of element from ash.

4.3. Cluster analysis

The dendrogram presented in Fig. 1 is the result of the cluster analysis performed on total content of elements considered as objects.

As regards the total element contents two big clusters grouping the most of elements and one cluster containing only two elements were separated:

– cluster (C1) contains K, Cr, Mn, Zn, Ga, Ba, Pb and P coming from biomass

– cluster (C2) grouping Si and Zr coming from pitcoal

– cluster (C3) including Al, Fe, Co, Ni, Cu, Cd, V, As, Mo and W coming from pitcoal.

– The dendrogram in Fig. 2, which considers samples as objects and total element contents as variables allows the identification of three clusters corresponding to samples nature:

– cluster (C1) grouping sawdust (biomass) (10–14)

– cluster (C2) containing sawdust ash (5, 6)

– cluster (C3) including ash from pitcoal-sawdust briquettes (1–4), pitcoal ash (7–9) and pitcoal (15–18).

– Cluster (C3) can be additionally divided into sub-clusters according to sample nature.

– In the dendrogram considering the water leachable content of elements as objects (Fig. 3) three big cluster are outlined providing a similar grouping as PCA:

– cluster (C1) with two sub-clusters including Ni, Co, Zn and Cd, As, Mn, and Ga, respectively coming from pitcoal

– cluster (C2) grouping Al, Cr, V, Mo and W coming from pitcoal

– cluster (C3) including K, Fe, Cu, Ba, Pb, Si and P coming from biomass.

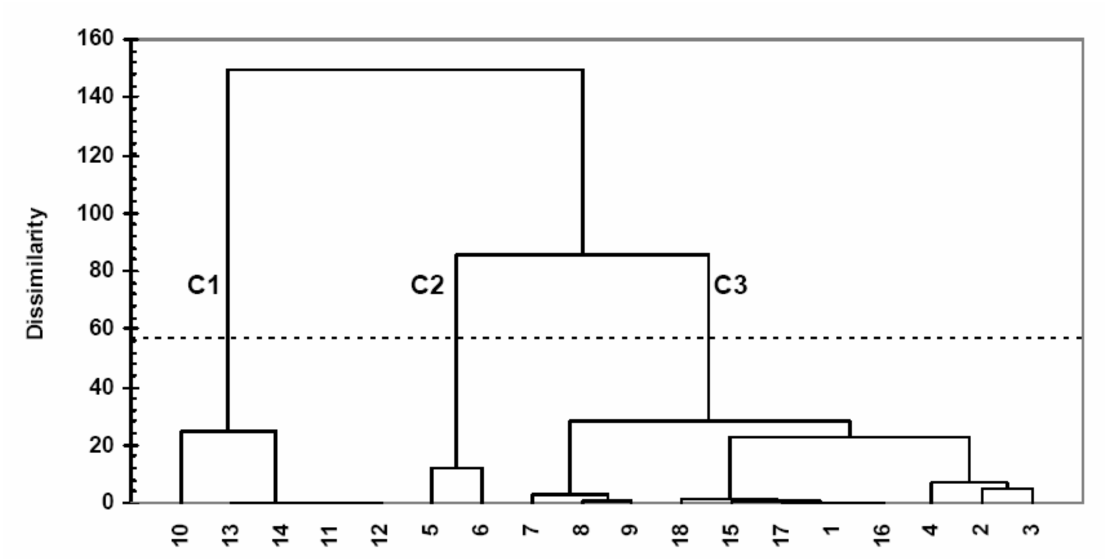

Fig. 2. Dendrogram of the cluster analysis on samples pattern as regards total element concentrations. 1–4 - pitcoal-sawdust briquettes ash; 5, 6 - sawdust ash; 7–9 - pitcoal ash; 10–14 - sawdust; 15–18 - pitcoal.

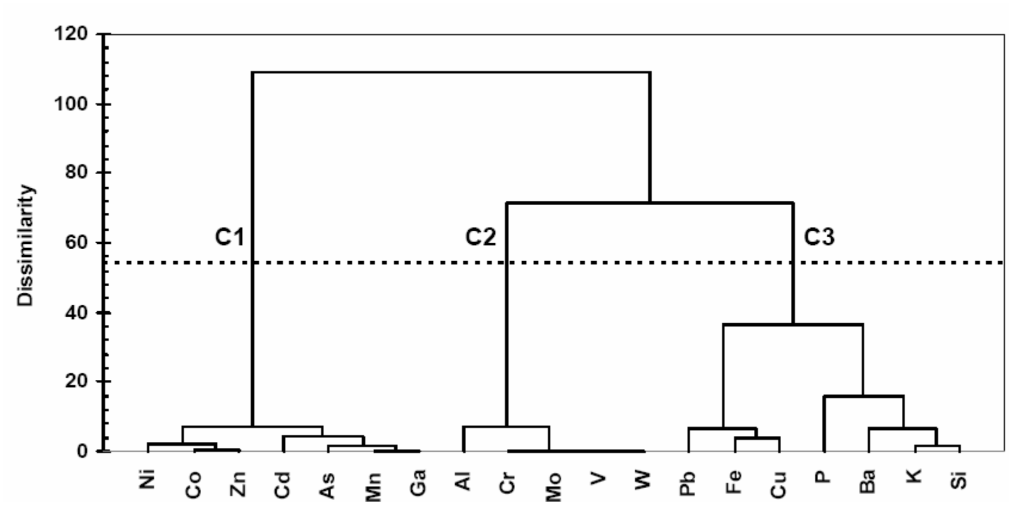

Fig. 3. Dendrogram of the cluster analysis on water leachable element concentrations.

Cluster analysis considering the sample nature as variable for the water leachable element concentrations is presented in Fig. 4.

This approach reveals five clusters:

– cluster (C1) grouping pitcoal ash (7–9)
– cluster (C2) containing sawdust ash (5)
– cluster (C3) including pitcoal-sawdust briquettes ash (1–4) and pitcoal (15–18)
– cluster (C4) containing a single sawdust ash sample (6)
– cluster (C5) grouping sawdust samples (10–14).

The CA on samples as objects and water leachable element concentrations as variables results in a higher number of clusters as compared to total element concentrations. This was predictable by PCA which explained over 92% of the total variance when considering the total concentrations compared to only 85% for available species. The difference is assigned to sources that could not be identified.

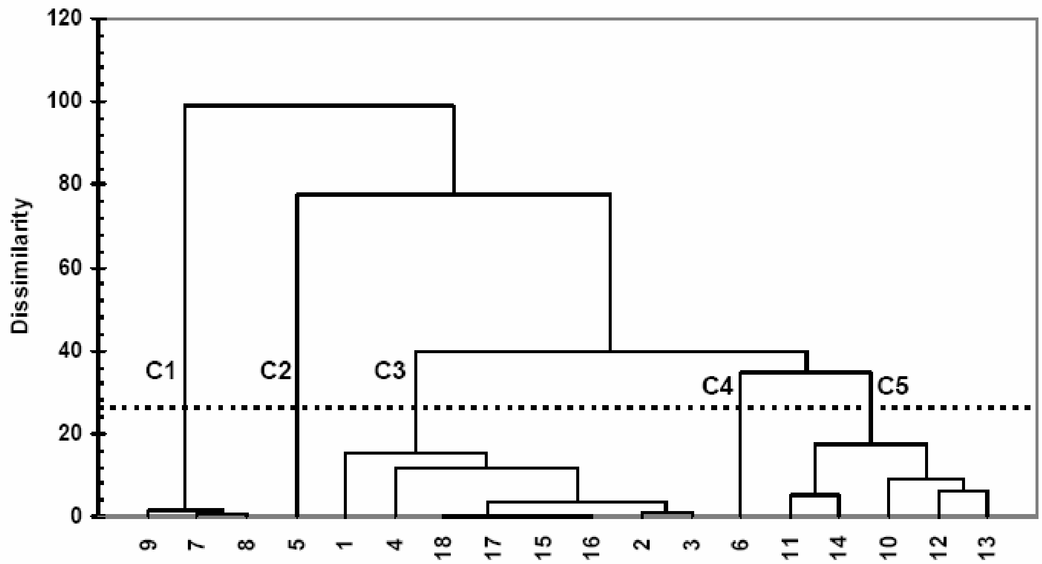

Fig. 4. Dendrogram of the cluster analysis on samples pattern as regards the water leachable element concentrations. 1–4 - pitcoal-sawdust briquettes ash; 5, 6 – sawdust ash; 7–9 - pitcoal ash; 10–14 - sawdust; 15–18 - pitcoal.

5. Conclusions

The multivariate statistical analysis applied to the study of pitcoal-sawdust briquettes combustion revealed a new level of information from conventional data and provides a better understanding of the process complexity in respect with the behavior of elements. This approach allowed the identification of the element sources and affinity between them as well as samples grouping according to their nature. The PCA analysis emphasized a higher influence of pitcoal than biomass on element sources in the blend combustion. Considering the total content of elements four sources were identified, of which three attributed to pitcoal. These sources correspond to the following element species: retained by adsorption and coprecipitation on Al and Fe sedimentary minerals; silicates species explaining the Si and Zr supply; reducible species as sulphides. The biomass factor is responsible for the macronutrients source (K, P) as well as elements present in soil as carbonates and extracted by plants. Analysis of water availability of heavy metals emphasized three latent factors corresponding to pitcoal and one to biomass. Sources attributed to pitcoal were: free metal ions including easily water available species; adsorbed species on secondary Al minerals; reducible species retained on oxides. The biomass factor explains largely the source of macronutrients. Latent factors attributed to pitcoal have a greater control on sources of available species than on the total. The variability of sources that could not be identified was higher in the case of leachable species. As a result of the affinity of elements three clusters were outlined for total and leacheate. Regarding their nature, samples were grouped in three and five clusters respectively, from the point of view of total and water available concentration of element species.

References

[1] J. N. Miller, J. C. Miller, Statistics and Chemometrics for Analytical Chemistry, Ellis Horwood Chichester 4th Ed. (2000).
[2] D. L. Massart, B. G. M. Vandeginste, L. M. C. Buydens, S. de Jong, P.J. Lewi, J. Smeyers-Verbeke, Handbook of Chemometrics and Qualimetrics: Part A, Elsevier, Amsterdam (1997).
[3] T. Frentiu, M. Ponta, E. Levei, E. Gheorghiu, M. Benea, E. Cordos, Chem. Spec. Bioavailab. **20**, 99 (2008).
[4] T. Frentiu, M. Ponta, E. Levei, E.A. Cordos, Chem. Pap. **63**, 239 (2009).
[5] T. Rungratanaubon, S. Wangwongwatana, N. Panich, Ann. NY Acad. Sci. **1140**, 297 (2008).
[6] T. Frentiu, M. Ponta, S. D. Anghel, A. Simon, I. Marginean, E. A. Cordos, Microchim. Acta **143**, 245 (2003).
[7] T. Frentiu, M. Ponta, E. Levei, E. Gheorghiu, I. Kasler, E. Cordos, Chem. Pap. **62**, 114 (2008).
[8] J. M. Bland, G. D. Altman, Stat. Methods Med. Res. **8**, 35 (1999).
[9] T. Frentiu, M. Ponta, E. Levei, M. Senila, M. Ursu, E. Cordos, J. Optoelectron. Adv. M., 9, 3505 (2007).
[10] D.L. Massart, L. Kaufman, The Interpretation of Analytical Chemical Data by the Use of Cluster Analysis, J. Wiley, New York (1983).
[11] G. D. Thurston, J. D. Spengler, Atmos. Environ. **19**, 9 (1985).

[12] I. Stanimirova, S. Tsakovski, V. Simeonov, Fresenius J. Anal. Chem. **365**, 489 (1999).
[13] H. F. Pop, J. W. Einax, C. Sarbu, Chemometr. Intell. Lab. In press. DOI: 10.1016/j.chemolab.2008.06.006 (2008)
[14] E. K. Yetimoğlu, Ö. Ercan, J.Brazil. Chem. Soc. **19**, 1399 (2008).
[15] T. Spanos, V. Simeonov, P. Simeonova, E. Apostolidou, J. Stratis, Environ. Monitor. Assess. **143**, 215 (2008).
[16] T. N. Wu, C. -S. Su, Proc. 5-th Intern. Conf. Fuzzy Systems and Knowledge Discovery, FSKD 2008, p. 236.
[17] P. Simeonova, C. Sarbu, T. Spanos, V. Simeonov, S. Tsakovski, Cent. Eur. J. Chem. **4**, 68 (2006).
[18] A. Astel, G. Glosinska, T. Sobczynski, L. Bosze, V. Simeonov, J. Siepak, Cent. Eur. J. Chem. **4**, 543 (2006).
[19] E. Levei, T. Frentiu, M. Ponta, M. Senila, M. Miclean, C. Roman, E. Cordos, Int. J. Environ. Anal. Chem. In press (2009).
[20] O. Abollino, A. Giacomino, M. Malandrino, E. Mentasti, M. Aceto, R. Barberis, Water Air Soil Poll. **137**, 315 (2006).
[21] J. Zhao, J. Huang, W. Sun, Waste Manage. **28**, 2406 (2008).
[22] K.P. Singh, A. Malik, R. Kumar, P. Saxena, S. Sinha, Environ. Monitor. Assess. 136, 183 (2008).
[23] K.S. Chen, H.K. Wang, Y.P. Peng, W.C. Wang, C.H. Chen, C.H. Lai, J. Air Waste Manage. **58**, 1318 (2008).
[24] G. Lazaroiu, T. Frentiu, L. Mihaiescu, A. Mihaltan, M. Ponta, M. Frentiu, E. Cordos, submitted for Publication in J. Optoelectron. Adv. Mater. **11**(5), 719(2009).
[25] K. Daskalakis, T.D. O’Connor, Environ. Sci. Technol. **13**, 470 (1979).
[26] P. Hanson, D. Evans, D. Colby, V. Zdanowicz, Mar. Environ. Res. **36**, 237 (1993).
[27] P.G. Jeffry, Chemical methods of rock analysis, 2nd ed. Pergamon Press (1975).
[28] V. A. Unksov, N. V. Lodochnikova, Geokhimiya **9**, 732 (1961).
[29] V. M. Goldschmidt, J. Chem. Soc. 655 (1937).
[30] S. Tokalioglu, S. Kartal, Int. J. Environ. Anal. Chem. **83**, 935 (2003).

*Corresponding author: ftibi@chem.ubbcluj.ro