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Chemometric assessment of agricultural samples from the vicinity of a lead-zinc smelter

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In the present article the pervasion of toxic elements (As, Cd, Pb, Zn) in edible and forage parts of plants grown in the fields near a Pb-Zn smelter was studied in order to propose efficient measures to minimize adverse effects on human health and ecosystems in the region. Statistical treatment of results based on hierarchical cluster analysis (HCA) and non-hierarchical clustering algorithm (K-means) showed that soil and air contamination by toxic chemical elements is the major environmental problem especially near to a Zn-Pb smelter (Plovdiv, Bulgaria). Subject of the present paper are the amounts of 4 toxic elements in different parts (21) of plants collected in the above-mentioned area, which were introduced in the formed matrix for data classification and interpretation. The result of the chemometric examination accentuates on Cd pollution, especially the inadmissible Cd content in carrots planted on the fields about 5-7 km from the factory.

Keywords: Zn-Pb factory, toxic elements, uptake from agro products, chemometrics

INTRODUCTION

In the 60ies, a lead-zinc metallurgical complex and a plant for pesticides production near the smelter were built in the vicinity of Plovdiv city. The construction of these plants in the fertile fields of the Upper Thracian Plain, near the second-largest Bulgarian city, is an example of poor management decision causing constant eco-problems for the district. After the political changes in Eastern Europe at the end of the 80ies a series of studies have been carried out to assess the real level of anthropogenic pollution and to propose new measures for limitation of the waste emissions from both factories. Chemical pollution of the region, concomitant effect of Pb-Zn emissions and pesticides production is a subject of 2 important international projects [1, 2], as well as a subject of national monitoring (at the beginning of the 21th century automatic analytical stations have been installed to control emissions of pollutants). Most of the investigations performed in the region are devoted to the assessment of concentrations of toxic elements and their distributions in the environmental compartments – water, soil and air. The investigations confirmed that Pb, Cd, As and Zn are major toxicants and elevated contaminant concentrations are registered not only near the industrial facilities but pollution spreads and affects a larger region depending on the climatic conditions, geographical locations and local mineralogy.

The degree of biouptake of toxic elements in fruits and vegetables from the region has been the purpose of several comparative studies. The results of the analyses of some agricultural products obtained under the project WATMETAPOL [1] are slightly more favorable compared to the data from the previous international scientific project [2] in the Plovdiv area. Compared to other published data [3, 5, 6] for the vicinity of Pb-Zn factories the current results are almost identical.

Plants analysis would serve as an indirect approach to assess pollution of the region as far as the biouptake of contaminants in the plant species is from one side *via* roots or from the other side by direct atmospheric deposition onto the plant surfaces. In addition, biouptake depends on factors such as plant physiology, soil properties, climate and fertilization. It is worth mentioning that determination of toxic elements content in agro production would provide information to local administration concerning: (i) eco control on emitting factories; (ii) delineation of zones in risk for agriculture and recommendation for vegetables suitable to be grown in the region without adverse effect on animal and human health.

The major goal of the present study is the chemometric evaluation of similarities (or dissimilarities) of the quantities of toxic elements found in the samples (edible parts of vegetables and fodder grown in the region). This will allow clarification of the boundaries of the zones in risk, distribution and degree of pollution.

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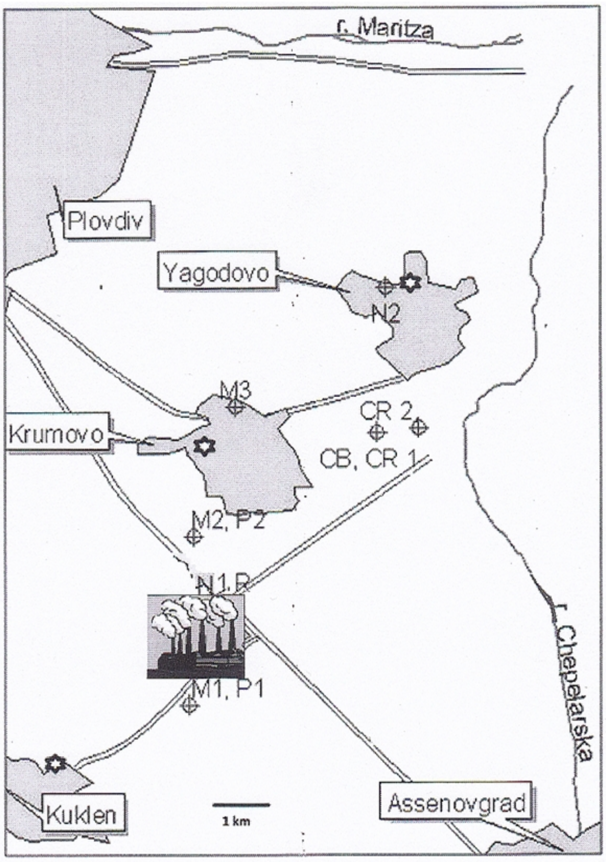
EXPERIMENTAL

Sampling and Analysis

Plants have been collected from different points in the risk zone, taking into account data for pollution spreading obtained in the frame of WATMETAPOL project and factors such as wind rose and soil composition. Plant samples were collected directly from the field, at the end of October, in this way ensuring longest possible aerosol exposure (Map 1).



Map 1. Test agricultural production from the region. The sampling points are marked as: M – maize (*Zea mays*); N – nuts (*Juglans regia*); P – peppers (*Capsicum spp.*); CR- carrots (*Daucus carota sativa*); CB – cabbage (*Brassica oleracea capitata*);

Collected plants were carefully washed and their edible and nonedible parts were separated. All parts were dried up at room temperature to constant weight (BDS EN 13804 [7]) and grinded. A total of 21 analytical samples were formed from leaves, stems, kernels and seeds [4].

About 0.5 g of dried sample, precisely weighed, was decomposed with nitric acid according to BDS EN 13805 [8]. Toxic elements were measured using ICP-OES and ETAAS under optimal instrumental parameters taking into account BDS EN 14082 [9] and our own experience [10]. The resulting toxic element concentrations are summarized in Table 1.

RESULTS

The inspection of the analytical results led to several conclusions:

1. Lead, zinc and cadmium oxides or carbonates from aerosol are retained on the surface of the leaves of the plants and further absorbed;
2. Difference in the concentrations between the leaves and veins (stalks) show that As biouptake is mostly from the soil;
3. Concentrations of toxic elements in corn leaves decrease 3-10 times between the outer and inner leaves;
4. Concentrations of Pb, Zn and As in walnut and maize grains are within acceptable limits, only cadmium slightly exceeding the permissible limits (Ordinance No 31 [11]).

Chemometrics

The statistical classification of the analytical results was undertaken with the idea to master the IBM's SPSS "Statistics" software package. The data set (matrix of 21 samples × 4 elements) was subjected to statistical cluster analysis (hierarchical and non-hierarchical mode). The raw data set was standardized by the use of a z-transform procedure in order to avoid differences in dimensions of the variables and to normalize the data. The hierarchical clustering was performed using squared Euclidean distances as similarity measure, Ward's method of linkage and Sneath's criterion for cluster significance. K-means method was used as non-hierarchical clustering approach. Both methods are well known and documented with detailed description [12].

The goal of the multivariate interpretation was to associate the variables (elements) or the cases (samples) in clusters according to the similarities on different steps of study. Further, it was of substantial interest to detect discriminating features for each of the identified clusters in order to better understand the reasons of clustering (classification). The first step of the intelligent data analysis was to detect specific relationships between the samples (patterns of similarity) which could be attributed to the content of the toxic elements and hierarchical cluster analysis was used for this procedure of grouping.

As can be seen from Fig. 1, the behavior of the pollutant As differs substantially from that of the other three metals studied. As it is evident that Pb and Zn content is due to industrial emitters, the biouptake of As probably depends on different sources (soil composition) or different biouptake mechanisms.

Table 1. Element contents [ppm] in the studied agricultural samples

No	Sample	Label	Pb	Cd	Zn	As
1	Walnuts, edible parts 1	N1	0.04	0.14	46.8	0.008
2	Walnut green husks	N1h	121.3	2.5	304.3	0.117
3	Walnuts, edible parts 2	N2	0.03	0.12	25.9	0.021
4	Cabbage leaves	Cb	11.7	<0.002	23.7	0.79
5	Carrots 1	C1	0.32	0.83	8.6	0.026
6	Carrot leaves 1	C1l	20.4	5.56	88.5	0.66
7	Carrots 2	C2	0.15	0.7	23.2	0.012
8	Carrots leaves 2	C2l	15.8	0.9	35.8	0.73
9	Peppers, edible parts 1	P1	11.6	1.53	35.4	0.148
10	Pepper leaves 1	P1l	128.1	5.05	500	2.43
11	Peppers, edible parts 2	P2	2.1	0.87	23.9	0.169
12	Pepper seeds 2	P2s	0.04	0.65	24.3	0.201
13	Pepper leaves 2	P2l	77.8	4.42	303	0.97
14	Veins from pepper leaves 2	P2v	59.3	3.12	232	0.03
15	Maize kernels 1	1M	0.02	0.17	31.2	0.015
16	Corn stalks 1	M1	0.16	0.44	25.5	0.286
17	Corn silks 1	M1s	0.48	0.39	93.7	1.77
18	Husk leaves – inside 2	M2i	14.2	0.46	28.9	0.6
19	Husk leaves – outside 2	M2o	56.9	2.8	314	0.51
20	Husk leaves – outside, washed 2	M2w	0.08	0.01	5.9	<0.002
21	Corn stalks 3	M3	19.3	1.14	87.9	0.85

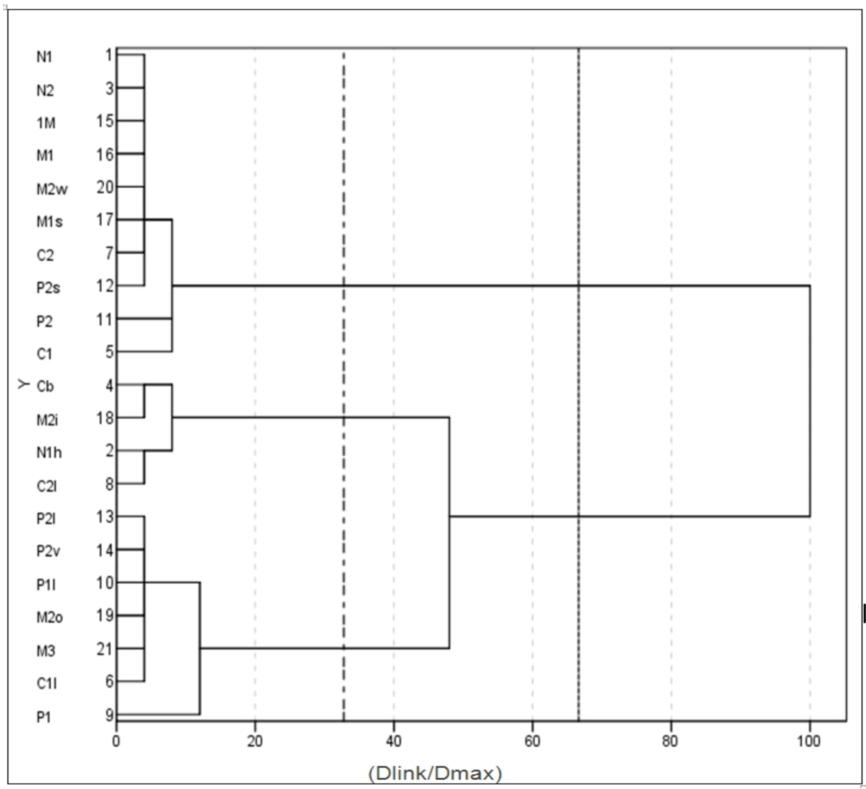


Figure 2. Hierarchical clustering of the 21 samples.

Table 2. Members of the 3 different clusters and distance from respective cluster center

Sample	No	Label	Distance
Members of Cluster No 1 (in21z) and distances from respective cluster center. Cluster contains 4 cases.			
Walnut green husks	2	N1h	.096
Cabbage leaves	4	Cb	.079
Carrots leaves 2	8	C2l	.039
Husk leaves – inside 2	18	M2i	.062
Members of Cluster No 2 (in21z) and distances from respective cluster center. Cluster contains 7 cases.			
Carrot leaves 1	6	C1l	.083
Peppers, edible parts 1	9	P1	.141
Pepper leaves 1	10	P1l	.034
Pepper leaves 2	13	P2l	.028
Veins from pepper leaves 2	14	P2v	.028
Husk leaves – outside 2	19	M2o	.109
Corn stalks 3	21	M3	.052
Members of Cluster No 3 (in21z) and distances from respective cluster center. Cluster contains 10 cases.			
Walnuts, edible parts 1	1	N1	.022
Walnuts, edible parts 2	3	N2	.021
Carrots 1	5	C1	.115
Carrots 2	7	C2	.025
Peppers, edible parts 2	11	P2	.110
Pepper seeds 2	12	P2s	.030
Maize kernels 1	15	1M	.020
Corn stalks 1	16	M1	.024
Corn silks 1	17	M1s	.049
Husk leaves – outside, washed 2	20	M2w	.029

Results for Cd undoubtedly showed that Cd pollution is due to natural presence of Cd together with main elements and confirming same industrial source of pollution.

The hierarchical clustering of the 21 different plant part samples is presented in Fig. 2. Three clusters are observed, after dividing by 33 and 66% statistical certainty. The smallest cluster includes 4 intermediately polluted samples. The second cluster contains 7 samples with the highest levels of pollutants. The biggest cluster 3 combines 10 samples – edible parts and inside leaves, relatively clean according to the analytical results.

Keeping in mind these results, non-hierarchical clustering was additionally performed. The K-means grouping of the into 3 clusters resembles almost the same clustering as already obtained by hierarchical clustering. In Table 2 the members of each supervised cluster and distances are indicated. The next figures 3 and 4 display the distribution of elements and samples according to the K-means clustering.

DISCUSSION

In general, the results of the hierarchical clustering confirm the obvious conclusions based on the results from chemical analysis. The observation on the separation of the variables (elements) (Figs. 1 and 3) marks the specific behavior of As and confirms previous findings that agricultural products absorb toxic metals from the air, but the source of the metalloid is contaminated soil. The positions of Cd (Figs. 1 and 3) do not clearly indicate how the pollutant accumulates in agricultural products. The concentrations of cadmium follow the Zn and Pb contents in the air and reflect their contents in the various industrial concentrates or ore sources supplied to the smelter. Discrimination of cases (samples) presented on Figs. 2 and 4 confirmed the conclusion that the leaves, owing to their large surface, additionally adsorb dust and atmospheric deposits, in this way accumulating higher levels of toxic elements. As seen, the inner parts of agricultural products such as corns and nuts are much more protected from pollution. It might be generally concluded that aerosol deposition of pollutants dominates over their biouptake from the soil.

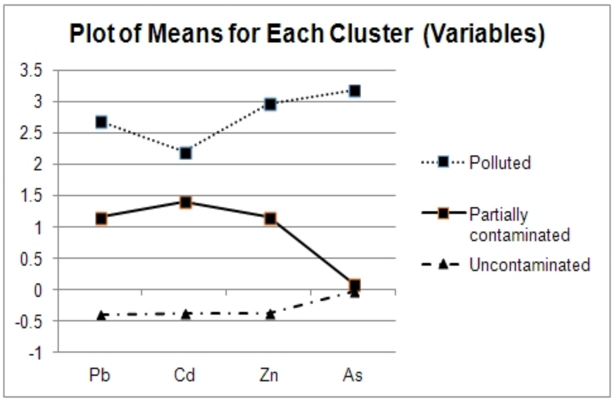


Figure 3. Averages for the 4 elements in each of the identified non-hierarchical clusters.

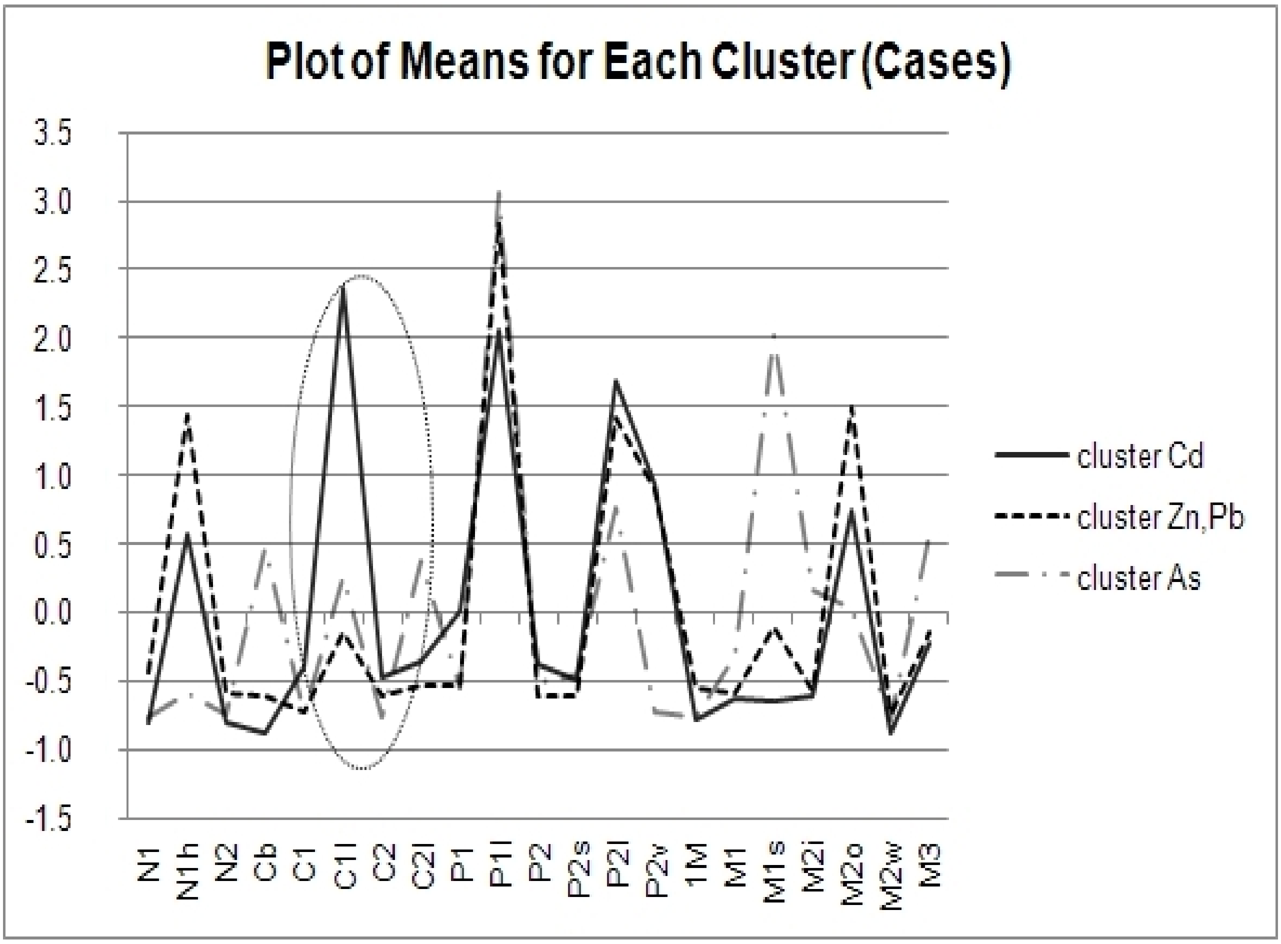


Figure 4. Averages for the 21 samples for each identified cluster.

The chemometric procedures mark new information to the peculiarities of Cd accumulation in agricultural products. The mean value for Cd in Fig. 3 marks a big Max for the moderately contaminated samples, insignificant Max for the relatively clean samples and a Min for the highly contaminated samples. This explains the neglect of Cd in a previous research with the participation of the present author [4] and its polluting impact. Carrot leaves C2l fall into the cluster of moderately contaminated samples (see Fig. 2) while C1l carrot leaves are among the most polluted, although the distance between the sampling points (map 1) is not large. This is even more clearly seen in Fig. 4 (the positions surrounded by an ellipse), with the C1l peak being the highest in the Cd series. Evidently, the high Cd content in the carrot leaves is not proportionally transferred to the edible parts of carrots.

Verma *et al.* [16] modeled the accumulation of cadmium in the vegetables (carrots, spinach, radishes and cabbage) and showed that the uptake rate was highest for the carrots, 1.5 times smaller for spinach and 2 times smaller for cabbage and radishes. Another conclusion from this modeling is that saturation with Cd in vegetables occurs for spinach and radishes after 40 days of planting, for cabbage after 65 days, and for carrots after 100 days. It follows that carrots are the most affected by cadmium contamination.

An overview of the analysis data in this study shows that such saturation occurs in the studied carrots, but at values exceeding about 8 times MPL [11] in edible parts of plants. The observed excess of 1.5 times in the edible parts of walnuts and corn might be estimated as an analytical error. (the presence of toxic elements in the edible parts of peppers is not representative because they were rimed).

The inadmissible Cd pollution in the carrots accentuated from the multivariate interpretation is described by several researchers from different countries [13-15]. Biological investigations consider this phenomenon as a critical problem, because it shows a direct transport of Cd from the carrots to the human through food chain [17, 18].

The latter sentence is an addition to a brochure, issued in 2013 by the Center for Risk Assessment – Bulgarian Agency for Food Safety [19] for Cd as a serious environmental pollutant. The current chemometric examination leads to the conclusion that cadmium is the most dangerous pollutant in the studied area and the practical recommendation to the agro producers could be: The carrot seedlings must be at least 10 km least distant from the Cd source.

CONCLUSION

In general, the chemometric analysis of the chemical results makes it possible to correctly assess the pollution risk with toxic elements, the mobility of the pollutants and the quality of life in an industrially impacted region. It is obvious that chemometric interpretation even for a small data set updates government documents and argues true instructions to local agro producers.

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