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Analele Stiintifice ale Universitatii "Al. I. Cuza" din Iasi
Seria Geologie 62 (1–2) (2016) 47–64

AUI GEOLOGIE

The Distribution of Zr, Hf and Y in the soils of Iaşi Municipality: Case Study

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Abstract

Zr, Hf and Y contents were determined via 54 samples collected from the topsoils of the Botanical Garden in Iaşi. Statistical parameters suggest the presence of a relatively homogeneous population whose mean values (Zr = 265.733 $mg \cdot kg^{-1}$, Hf = 7.287 $mg \cdot kg^{-1}$, Y= 27.524 $mg \cdot kg^{-1}$) fall within the Zr, Hf and Y content variation range, determined in other urban soils in the world, but they are higher than the mean values calculated by various authors for the upper continental crust. Although positive, the correlation coefficients have significant values only for Zr–Hf (0.539) and Zr–Y (0.325). The values of the geochemical background determined via the upper 95% confidence limit of the 95th percentile, namely 267.174 $mg \cdot kg^{-1}$ (Zr), 7.297 $mg \cdot kg^{-1}$ (Hf) and 34.079 $mg \cdot kg^{-1}$ (Y), are higher than the mean calculated values for the upper continental crust. The distribution of values of the $Zr \cdot Hf^{-1}$, $Zr \cdot Y^{-1}$ and $Hf \cdot Y^{-1}$ ratios reflects, first of all, the geochemical characteristics of the predominant lithology, namely loesses in the northern area and clays in the southern area, potential anthropic inputs being limited to fertilizers specific to the flora in the Botanical Garden.

Keywords: soil, zirconium, hafnium, yttrium, geochemical background, Iaşi, Romania.

1. Introduction

The urbanization phenomenon, which certainly represents the future of human society, has currently gained momentum, and it will expand even more in the future. UN (2014) mentions that if in 1950, only 30 % of the world population lived in urban areas, in 2014, the percentage went up to 54 %, and it has been estimated that in 2050, 66 % of the world's population will be urban. If the advantages of urban centres, such as productive enterprises, public investments, social melting, cultural interchanges, social changes (Beall et al., 2010), opportunities to receive education and health care are incontestable, the urban

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population inevitably interacts with its environment (Boyle Torrey, 2004), thus generating an anthropic stress that has a direct impact on the quality of life. Thus, contaminators from water, air and soil, generated by anthropic activity, constitute the main challenge in the transition from the current urbanization phenomenon towards a healthier one, which would have much diminished effects on the environment. The interaction between human beings and one of the main components of the urban habitat, i.e. the soil, frequently affected by anthropic activities, is complex and difficult to quantify. The contact between humans and soil can be (a) directly and/or (b) indirectly achieved through the inhalation of soil-derived dust. Most studies on the impact of anthropic factors on urban soils focus on contaminators whose negative effect on the health of the urban population is certified by much medical research. Nevertheless, in the urban environment and, implicitly, in urban soils, there are also chemical elements considered potentially toxic, such as Zr, Hf, and Y whose effects on human health are still insufficiently studied (Filippelli et al., 2012).

A lithophile chemical element situated in the 4th group of the periodic system, Zr is present in soils especially as zircon (Sposito, 2008; Ramachandra, 2009; Abdu, 2010) and it reflects contents from parental rock (acidic > intermediate > basic > ultrabasic – Bowen et al., 1982). Thus, Zr contents determined by various authors in soils range between 5 and 1060 mg·kg^{-1} (Bowen et al., 1982; Salminen, 2005; Abdu, 2010; Birke et al., 2011; Bityukova and Birke, 2011; Šajn et al., 2011); higher content values can be due to the use of commercial fertilizers (Senesi et al., 1988; Kabata-Pendias, 2011). A biocompatible (Ikarashi et al., 2005) yet non-essential (Ayres and Hellier, 1997; Wiberg and Wiberg, 2001; Salminen, 2005) chemical element, Zr is found in the human body in quantities that vary between 4 and 420 mg·kg^{-1} (Whanger, 1982; Wiberg and Wiberg, 2001). Insufficient information concerning Zr toxicity makes this chemical element to be considered as representing a low risk for the environment (Salminen, 2005; Shahid et al., 2013) but inhalation of and/or exposure to Zr components can generate health issues (Shelley, 1973; Ayres and Hellier, 1997; Cheremisinoff, 1999; Smith and Huyck, 1999; Wiberg and Wiberg, 2001; Schaller, 2004; Merill et al., 2007; Haire et al., 2015).

Hafnium is a predominantly lithophile element situated in the 4th group of the periodic system and whose chemical properties, which are very similar to the ones of Zr, allow for substitutions in minerals (Mukherji, 1970; Taylor, 2002; Scerri, 2013; Pohl, 2011). In soils, Hf contents depend on the parent rock type (Kabata-Pendias, 2000) and/or the application of phosphate fertilizers (Kabata-Pendias, 2011), the values presented by various authors ranging between 0.2 and 34 mg·kg^{-1} (Bowen et al., 1982; Reimann and de Caritat, 1998; Salminen, 2005; Birke et al., 2011; Bityukova and Birke, 2011; Locutura and Bel-Ian, 2011; Batista et al., 2011). The chemical element considered biocompatible (Hon et al., 2004) yet non-essential for the human body and having unclearly defined biological functions (Haire et al., 2015), Hf and its components are considered non-toxic/weakly toxic for humans (Wiberg and Wiberg, 2001; Emsley, 2011), but also toxic (Shelley, 1973; Kabata-Pendias and Mukherjee, 2007; Pohanish, 2012; Haire et al., 2015).

Yttrium is a lithophile metallic element situated in the 3rd group of the periodic system and it is included in the pseudo-lanthanides group (Gschneidner, 1980; Möller, 1998; Pohl, 2011) on account of its chemical and physical properties and of its common uses, with rare earth elements. Although Y contents in soils are insufficiently studied (Kabata-Pendias, 2000), it has been admitted that they ultimately depend on pedogenetic processes (Kastori et al., 2010) and/or the application of certain phosphate fertilizers (Kabata-Pendias, 2011) ranging between 2 and 267 $mg \cdot kg^{-1}$ (Bowen et al., 1982; Salminen, 2005; Abdu, 2010; Birke et al., 2011; Bityukova and Birke, 2011; Šajn et al., 2011; Jeske and Gworek, 2013). Although present in the human body (Ayres and Hellier, 1997; Emsley, 2011) and considered non-essential for living organisms (Ayres and Hellier, 1997; Salminen, 2005) because its biological role is not yet well determined (Emsley, 2011), yttrium's effects on human health vary from not being toxic (Hathaway and Proctor, 2004; Hulla, 2014) to generating health problems (Smith and Huyck, 1999; Salminen, 2005; Kabata-Pendias and Mukherjee, 2007; Harbison and Johnson, 2015).

Occupational exposure correlates with Zr, Hf and Y fields of use (Krishnan and Asundi, 1981; Northwood, 1985; Krebs, 1998; Stwertka, 2002; Shikov et al., 2003; Toumanov, 2003; Salminen, 2005; Douglas et al., 2007; Manicone et al., 2007; Kabata-Pendias and Mukherjee, 2007; Schumann,2009; Lee et al., 2010; Kabata-Pendias , 2011; Moss et al., 2011; Pohl, 2011; Heyse et al., 2012; Rumbu, 2013; Pohanish, 2012; Kabata-Pendias, 2011; Pottier et al., 2014; Haire et al., 2015; Kabata-Pendias and Szteke, 2015).

2.Materials and methodologies

2.1 Research site

From a geological point of view, Iaşi municipality is situated on the Moldavian Platform, consisting of a crystalline basement and a sedimentary cover, whose formations belong to the Upper Vendian – Meotian interval, to which Quaternary formations are added (Ionesi, 1994). Research conducted in the area of the Iaşi municipality signals the presence of Sarmatian formations represented by clays, siltites, sands ± gravels, chalks and Quaternary formations made up of more or less transformed loessoide deposits (Butnaru, 1966; Martiniuc and Cosmulescu, 1968; Rotaru et al., 2005; Răileanu and Cazacu, 2009; Rotaru et al., 2011; Alupoie et al., 2013; Boti and Boti, 2015), with gravel infillings. Situated in the North-Western part of Iaşi municipality, on the Copou hill, in the basin of Podgoria Copou stream, on a field that initially was strongly degraded and which has been requiring multiple landscaping (Păstrăvanu, 2012; Search Corporation, 2015), the studied area coincides with the perimeter of the Botanical Garden (BG); the latter currently holds a surface of 83.18 hectares (Tănase and Oprea, 2013) on which there are more than 6,000 vegetal taxa originating in various biogeographical areas (Tănase and Oprea, 2013). Butnaru (1966) and Martiniuc and Cosmulescu (1968) notice that within the perimeter of the Botanical Garden, underneath Quaternary formations represented

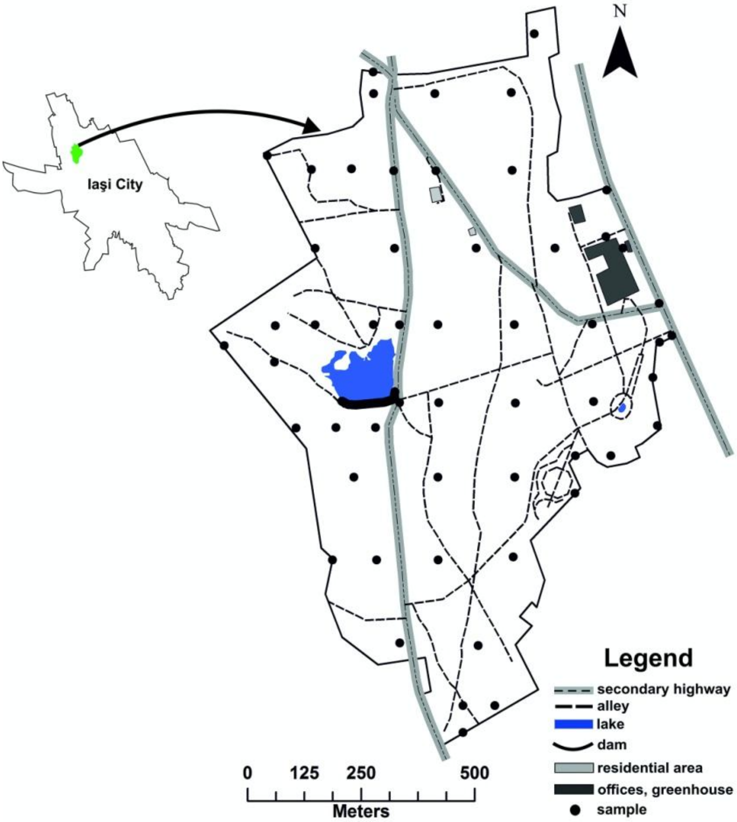


Fig. 1 Location map of study area.

by loess and/or loessoide deposits, sands and gravels, there are clays and Sarmatian marls. Secu (2008) ranks the Botanical Garden's soils (BGS) under the cambic chernozems category. So far, geochemical studies of the Zr, Hf and Y distribution in BGS have not been conducted.

2.2 Sampling and analysis

The samples were collected between the 1st of April and the 15th of June 2014 so as to avoid the impact of the urban microclimate upon the representativeness of the studied chemical elements in soils. A total of 54 topsoil samples (sensu Salminen, 2005) were collected (Fig. 1). The sampling interval was between 0.0 m and 0.3 m, while sample mass ranged between 1.5 and 2.0 kg. The samples were collected manually, using a stainless steel spade shovel, and they were then put in plastic bags. After extracting gravel and coarse organic matter or plant root residues, soil samples were oven dried at a temperature of 50 ºC for 72 hours and ground to pass through a 0.01 mm sieve. Sample reduction was performed through the coning and quartering method (Pitard, 1993), finally retaining 25 grams of sample. Zr, Hf and Y contents were determined through X-ray Fluorescence Spectrometry (EDXRF Epsilon 5), within the Department of Geology.

2.3 Descriptive statistics

A descriptive data analysis, including minimum and maximum values, mean, geometric mean (GM), mode, standard deviation (SD), skewness, kurtosis, and coefficient of variation (CV) was carried out. The value of the symmetry/asymmetry of the analysed contents has direct implications on the estimation of the type of distribution and implicitly, on the precision in determining the geochemical background. Singh et al. (1997) and Reimann and Filzmoser (2000) consider that in environmental studies, chemical element content distribution are frequently asymmetrical, usually featuring a long upper tail of larger values. Hence, for the most precise estimation of skewness, we have calculated both the skewness coefficient (SC) and octile skewness (OS) which is less susceptible to outliers (Brys et al., 2003):

$$SC = \sum(x_i - \mu)^3.(N\sigma^3)^{-1} \qquad (1)$$

$$OS = [(O_7 - O_4) - (O_4 - O_1)].[(O_7 - O_1)]^{-1} \qquad (2)$$

where: x_i is the i^{th} value of data set;
μ is the mean;
N is the number of data point;
σ is the standard deviation;O_x is the x^{th} octile of the data.

To identify Zr, Hf and Y outliers, we used the median absolute deviation test (Leys et al., 2013):

$$Me - k \cdot MAD < x_i < Me + k \cdot MAD \qquad (3)$$

$$MAD = b \cdot M_i\,(|x_i - M_j(x_j)|) \qquad (4)$$

where: Me is the median;
k = 2.0 (poorly conservative);
MAD is the median absolute deviation;
b = 1.4826.

To estimate the type of distribution, we have used Q-Q plots and the features of OS and SC coefficients. Q-Q plots compare the observed quantiles of the data with the quantiles that one would expect to see if the data were normally distributed. If OS is situated in the interval [-1;+1] (Brys et al., 2003) and SC in the interval [-0.2;+0.2] (Rawlins et al., 2005), then it is admitted that the data set can be treated as symmetrically distributed, and the presence of a Gaussian distribution is estimated.

The coefficient of variation (CV) was used to reflect the degree of discrete distribution of different metal element concentrations and to indicate indirectly the activeness of the selected element in the examined environment.

The Spearman correlation coefficients (SCC), very robust about outliers (Borradaile, 2003), were calculated to determine relationships among different chemical elements.

2.4 Geochemical background

The geochemical background (GBK), defined as the upper 95 % confidence limit of the 95th percentile (Cave et al., 2012; DBC, 2013; Ander et al., 2013), was determined according to the schema proposed by Johnson et al. (2012). Thus, the values of SC, OS coefficients and kurtosis indicate the form of Zr, Hf and Y content distribution. Depending on it, potential transformations (log, Box-Cox) necessary to produce Gaussian distribution

Tab. 1 Heavy metal concentrations of BGS (in mg/kg)

	Zr	Hf	Y
Mean	265.733	7.287	27.524
Median	266.175	7.280	27.245
SD	43.361	1.346	3.558
Kurtosis	-0.337	-0.567	-0.323
SC	0.041	0.022	0.198
OS	0.007	0.014	0.051
Minimum	175.160	4.580	20.850
Maximum	351.850	10.120	35.960
CV	0.163	0.184	0.129
UCC	237^1 193^2 190^3	5.8^1 5.3^2 5.8^3	21^1 21^2 22^3
Mean UCC^{-1}	1.121 1.376 1.398	1.256 1.374 1.256	1.311 1.311 1.251
Distribution	normal	normal	normal

1-Wedepohl (1995), in Rudnick and Gao (2003); 2-Rudnick and Gao (2003); 3-Taylor and McLennan (1985, 1995), in Rudnick and Gao (2003).

are performed. Depending on the type of distribution and the presence or absence of outliers, the 95th percentile (empirical, parametric, robust) and the lower and the upper 95 % are determined, thus establishing the value of GBK.

3. Results and discussions

3.1 Heavy metal concentrations

Descriptive statistics of Zr, Hf and Y concentrations in BGS are presented in Table 1 and Figures 2, 3 and 4. We can notice that the mean values of Zr, Hf and Y are inscribed in the field of contents determined in other soils in the world (Fig. 2) but they are higher than the mean values indicated by Wedepohl (1995), Taylor and McLennan (1985; 1995, in Rudnick and Gao, 2003) and Rudnick and Gao (2003) for the upper continental crust (UCC) (Tab. 1). The close values of mean and medians calculated for Zr, Hf and Y contents (Tab. 1) suggest the presence of homogeneous populations in BGS. However, the high value of SD in the case of Zr contents indicates a high level of spreading around the mean value, generated by the presence of potential outliers. CV belonging to the (0.0–0.4] interval (Tab. 1) would indicate the fact that in the case of Zr, Hf and Y, anthropic input is either null, or very low (Yongming et al., 2006). The values of kurtosis and especially those of SC and OS calculated for Zr, Hf and Y suggest the presence of symmetric distributions (Fig. 3), of a Gaussian type, a statement confirmed both by Q-Q plots (Fig. 4) and

Shapiro-Wilk test (Ghasemi and Zahedias, 2012). The values of the median absolute deviation test (Tab. 2) indicate the presence of outliers, an aspect which is not highlighted by box-whiskers plots (Fig. 5).

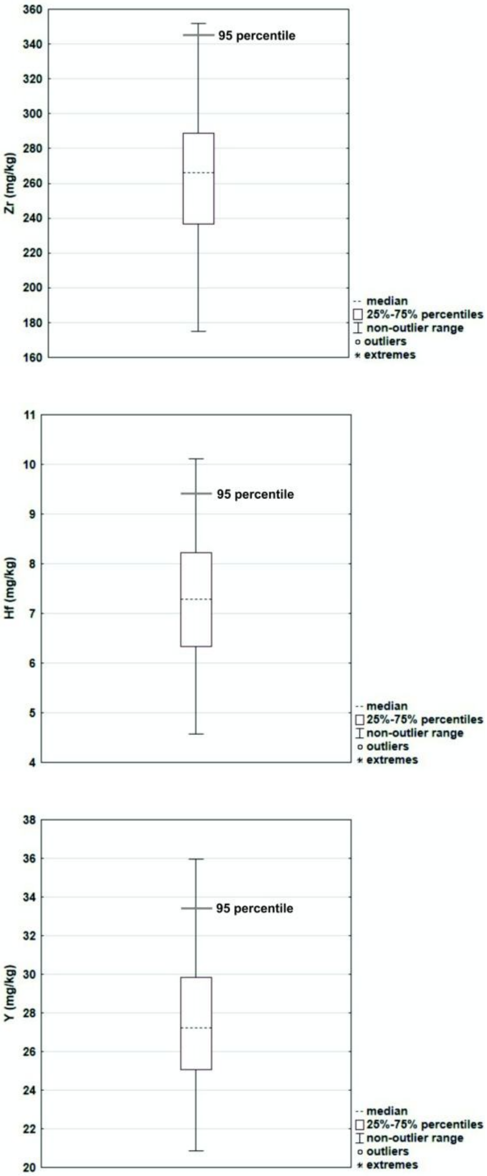


Fig. 2 Boxplot for the Zr, Hf and Y concentrations in the BGS.

3.2 Spearman correlation coefficient (SCC) analysis

The SCC values calculated for Zr, Hf and Y contents in BGS (Tab. 3) feature certain contradictory aspects, compared to data presented in specialised literature.

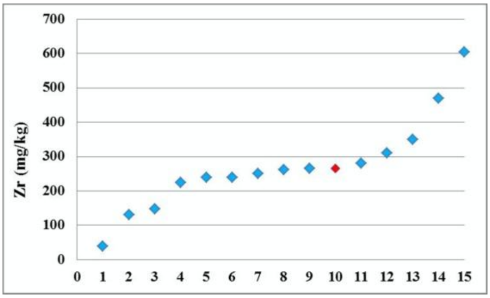
Thus, although positive (Ma et al., 2011), the value of SCC determined in the case of Zr and Hf contents in BGS (0.539) differ from the values of the correlation coefficients presented by Chandrajith et al. (2005), Salminen (2005), Scheib and Lee (2010), and Udousoro and Essien (2015), namely 0.985, 0.960, 0.920, and 0.955, respectively.

In the case of Zr and Y contents, the significant positive value of SCC (0.325) does not agree as order of size with the result obtained for soils in Europe by Salminen (2005), who mention that Zr in topsoil has a good correlation with Y (> 0.4).

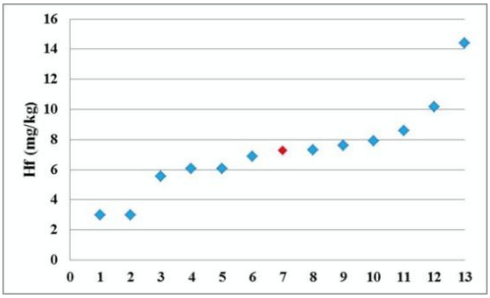
Although positive, the SCC value calculated for Hf and Y is in disagreement with the values of the Hf–Y correlations obtained by Salminen (2005) and Udousoro and Essien (2015), namely > 0.4, respectively 0.306.

3.3 Geochemical background

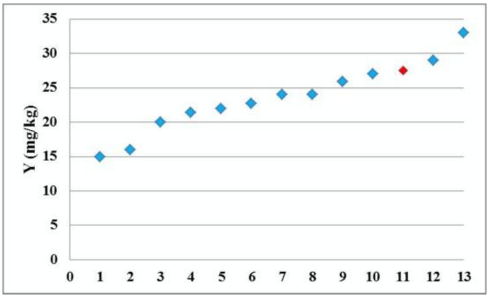
The presence of Gaussian distributions and of outliers in the right hand tail imposes the use of robust percentiles to determine GBK (DBC, 2013) (Tab. 4). It is worth noticing that, in comparison with Zr, Hf and Y contents established for UCC (Taylor and McLennan, 1985, 1995, in Rudnick and Gao, 2003; Wedepohl, 1995, in Rudnick and Gao, 2003; Rudnick and Gao, 2003) (Tab. 1) the mean values of $GBK_x \cdot UCC^{-1}$ ratios are supraunitary and they increase as follows: Y > Zr > Hf (Tab. 5). GBK excess probability maps for



a). 1-soils (Ljubljana, Slovenia; urban and suburban area) (Šajn et al., 2011); 2-soils (Tallinn, Estonia; urban region) (Bityukova and Birke, 2011); 3-soils (Tallinn region, Estonia) (Bityukova and Birke, 2011); 4-various soils (USA) (Kabata Pendias, 2011); 5-topsoils (Finland) (Bowen et al., 1982); 6-topsoils (USA) (Bowen et al., 1982); 7-topsoils (Europe) (Salminen, 2005); 8-topsoils (East Anglia, UK) (Scheib and Lee, 2010); 9-topsoils (Wales, UK) (Bowen et al., 1982); 10-this study; 11-soils (China) (Govindaraju, 1994); 12-soils (Stassfurt, Germany) (Birke et al., 2011); 13-soils (Australia) (Hutton, 1977); 14-deep loess deposit (European Russia) (Waganov and Nizharadze, 1981); 15-topsoils (Scotland, UK) (Bowen et al., 1982).



b). 1-soils (Tallinn, Estonia; urban region) (Bityukova and Birke, 2011); 2-soils (Tallinn region, Estonia) (Bityukova and Birke, 2011); 3-soils (Stassfurt, Germany) (Birke et al., 2011); 4-topsoils (Bulgaria) (Bowen et al., 1982); 5-topsoils (Europe) (Salminen, 2005); 6-topsoils (East Anglia, UK) (Scheib and Lee, 2010); 7-this study; 8-soils (China) (Govindaraju, 1994); 9-topsoils (Sweden) (Eriksson, 2001); 10-various soils (USA) (Kabata Pendias, 2011); 11-arable soils (Sweden) (Scheib et al., 2013); 12-soils (Madrid, Spain) (Locutura and Bel-Ian, 2011); 13-topsoils (Scotland, UK) (Bowen et al., 1982).



c). 1-soils (Alaska, USA) (Gough et al., 1988); 2-soils (Ljubljana, Slovenia; urban and suburban area) (Šajn et al., 2011); 3-soils (Tallinn, Estonia; urban region) (Bityukova and Birke, 2011); 4-soils (Stassfurt, Germany) (Birke et al., 2011); 5-soils (China) (Govindaraju, 1994); 6-topsoils (Europe) (Salminen, 2005); 7-soils (Tallinn, region Estonia) (Bityukova and Birke, 2011); 8-topsoils (Wales, UK) (Bowen et al., 1982); 9-soils (Madrid, Spain) (Locutura and Bel-Ian, 2011); 10-topsoils (Sweden) (Eriksson, 2001); 11-this study; 12-topsoils (USA) (Bowen et al., 1982); 13-topsoils (Scotland, UK) (Bowen et al., 1982).

Fig. 3 Mean values of the Zr (a), Hf (b) and Y (c) concentrations in different soils in the world and BGS.

the studied elements (Fig. 6) indicate, in the case of Zr, maximal values (≥ 75%) in BG's central-eastern and central-western areas which partially overlap those of Hf, while Y exceeds GBK only in BG's southern area.

3.4 $Zr \cdot Hf^{-1}$, $Zr \cdot Y^{-1}$ and $Hf \cdot Y^{-1}$ ratios in UCC versus BGS

The statistic parameters calculated for the $Zr \cdot Hf^{-1}$, $Zr \cdot Y^{-1}$ and $Hf \cdot Y^{-1}$ ratios of BGS indicate the presence of homogeneous populations (Tab. 6), whose mean values are inscribed in the fields of variation calculated for UCC, according to Zr, Hf and Y contents presented by Wedepohl (1995; in Rudnick and Gao, 2003) and Rudnick and Gao (2003) (Tabs. 1 and 6).

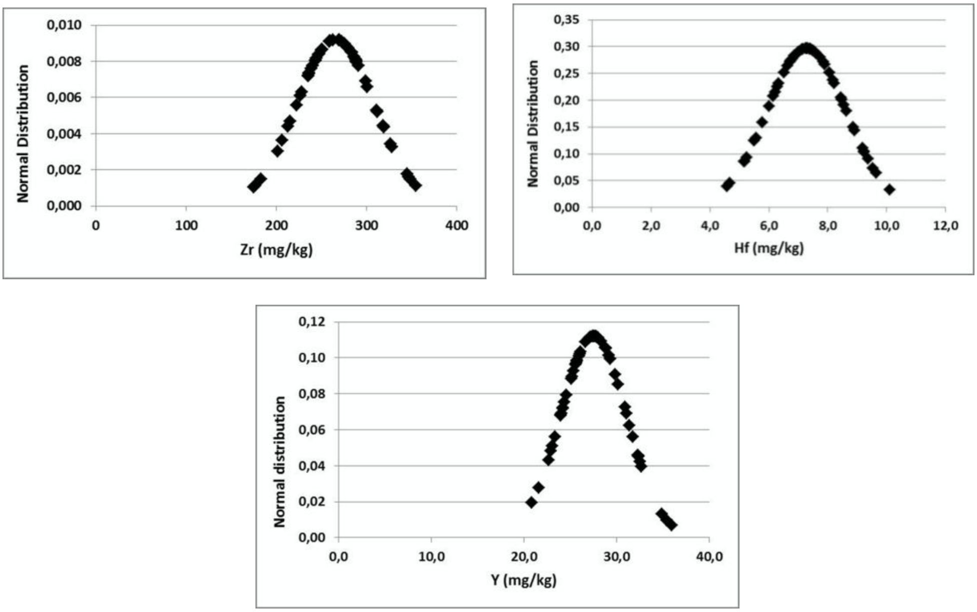


Fig. 4 Normal distribution plots of the Zr, Hf and Y concentrations in the BGS.

Tab. 2 The median absolute deviation

	Me - k·MAD Me + k·MAD (mg/kg)	X_i < Me - k·MAD (%)	X_i > Me+k·MAD (%)
Zr	187.731 344.619	5.5	3.7
Hf	4.478 10.082	0.0	1.9
Y	20.188 34.302	1.8	5.5

Yet, if we take as a landmark the values of Zr, Hf and Y contents from sedimentary and loess formation (Tabs. 1 and 6) presented by Taylor and McLennan (1985, 1995, in Rudnick and Gao, 2003), we can notice that BGS features mean values that are higher for Zr·Hf^{-1} and Zr·Y^{-1} ratios and a mean value that is approximately equal in the case of the Hf·Y^{-1}ratio. The distribution of Zr·Hf^{-1}, Zr·Y^{-1} and Hf·Y^{-1} ratios in BGS (Fig. 7) highlight the possibility of delineating two areas within the studied perimeter: the northern area in which the values of the Zr·Hf^{-1} and Zr·Y^{-1} ratios are high, and the southern area in which the Hf·Y^{-1} ratio is high. Starting from the premises that a) zirconium is the main Zr mineral present in sedimentary formations and especially in loess (Wang et al., 2008); b) Y features higher contents in clayish soils (Jeske and Gworek, 2013) and c) the Zr·Hf^{-1} ≠ $(Zr\cdot Hf^{1})_{UCC}$ ratios

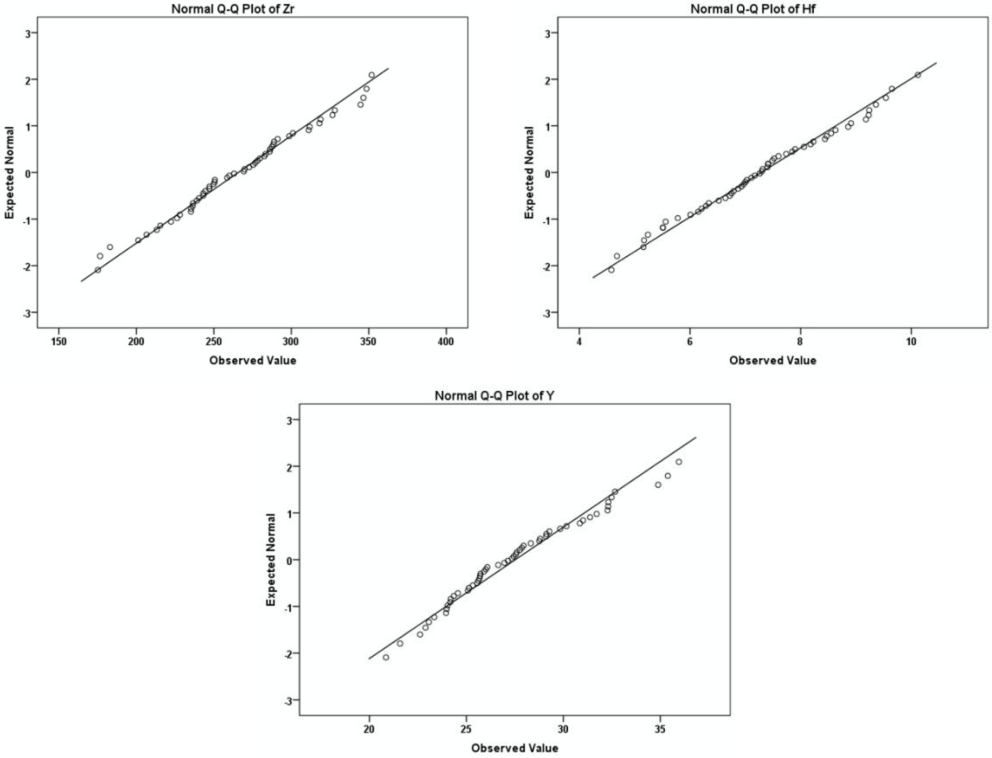


Fig. 5 Q-Q plots of the Zr, Hf and Y concentrations.

Tab. 3 SCC matrix for the Zr, Hf and Y concentrations

	Zr	Hf	Y
Zr	1		
Hf	0.539**	1	
Y	0.325*	0.215	1

* Correlation is significant at the 0.05 level (2-tailed);
** Correlation is significant at the 0.01 level (2-tailed).

(Taylor and McLennan, 1985, 1995) can reflect the presence of other Zr bearing minerals, in which the Zr·Hf^{-1} ratio is variable (Wang et al., 2008), we can admit that the BG's northern and southern areas reflect the geochemical characteristic of the predominant formations, respectively loesses (in north) and Sarmatian clays (in south). It is not excluded that the values of Zr·Hf^{-1}, Zr·Y^{-1} and Hf·Y^{-1} ratios determined in BGS could be influenced both by landslides and BG specific landscaping and maintenance works which, in certain cases, have

Tab. 4 The 95th percentile values and their confidence limits

	Empirical			Parametric			Robust		
	Value	LCL[1]	UCL[2]	Value	LCL[1]	UCL[2]	Value	LCL[1]	UCL[2]
Zr	345.291	318.840	351.850	345.291	333.726	356.856	267.057	266.939	267.174
Hf	9.423	9.1800	10.120	9.423	9.063	9.782	7.295	7.293	7.297
Y	33.447	32.310	35.960	33.447	32.497	34.396	34.005	33.930	34.079

[1] lower confidence limits; [2] upper confidence limit.

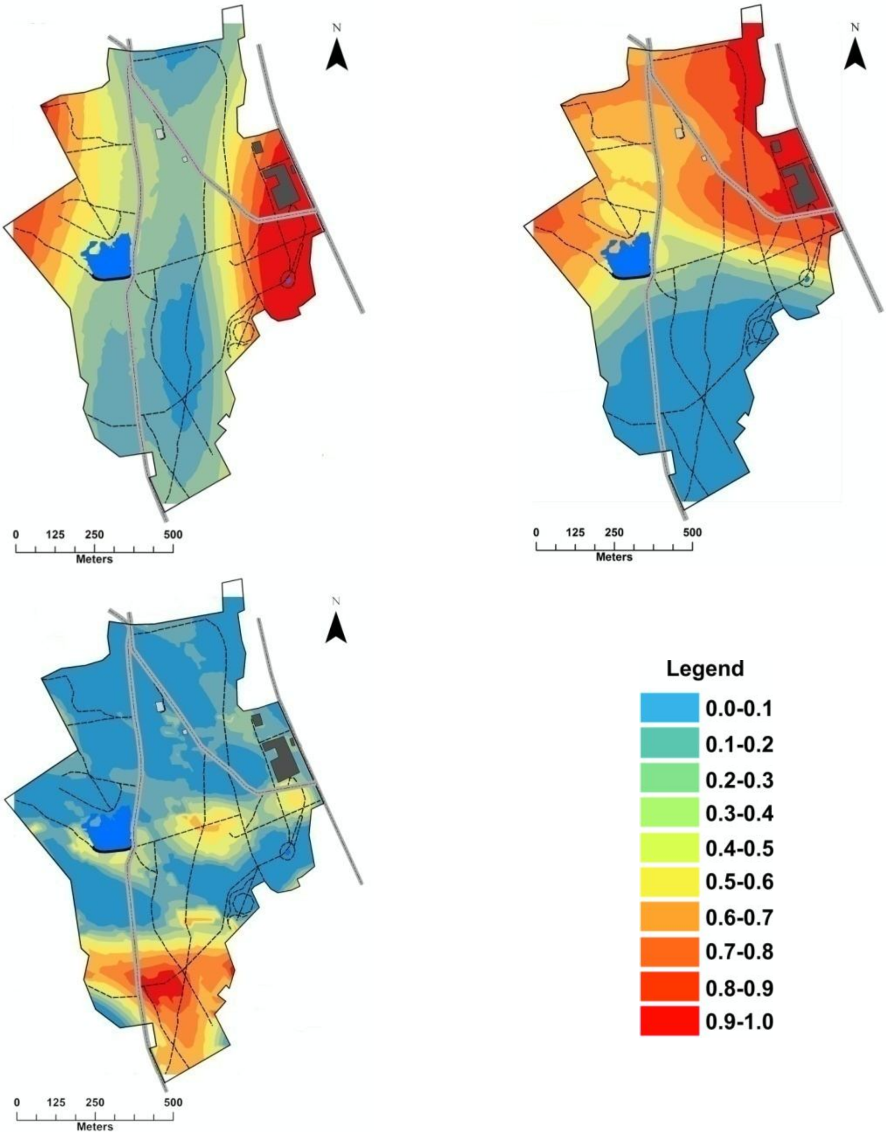


Fig.6 Probability chart of exceeding GBK in BGS.

Tab. 5 The ratio values $GBK \cdot UCC^{-1}$

Zr	$(GBK_{Zr} \cdot UCC^{-1})^{(a)}$	1.406
	$(GBK_{Zr} \cdot UCC^{-1})^{(b)}$	1.384
	$(GBK_{Zr} \cdot UCC^{-1})^{(c)}$	1.127
	Mean	1.305
Hf	$(GBK_{Hf} \cdot UCC^{-1})^{(a)}$	1.258
	$(GBK_{Hf} \cdot UCC^{-1})^{(b)}$	1,377
	$(GBK_{Hf} \cdot UCC^{-1})^{(c)}$	1,258
	Mean	1.297
Y	$(GBK_{Y} \cdot UCC^{-1})^{(a)}$	1.549
	$(GBK_{Y} \cdot UCC^{-1})^{(b)}$	1.623
	$(GBK_{Y} \cdot UCC^{-1})^{(c)}$	1.623
	Mean	1.598

[a] UCC (Taylor and McLennan (1985, 1995, in Rudnick and Gao, 2003); [b] UCC (Rudnick and Gao, 2003); [c] UCC (Wedepohl, 1995, in Rudnick and Gao, 2003).

Tab. 6 The ratio values $Zr \cdot Hf^{-1}$, $Zr \cdot Y^{-1}$ and $Hf \cdot Y^{-1}$

	a	b	c	BGS					
				Min.	Max.	Mean	St. Dev.	CV	GBK
$Zr \cdot Hf^{-1}$	36.415	40.862	32.758	22.351	61.878	37.477	8.282	0.221	36.614
$Zr \cdot Y^{-1}$	9.190	11.285	8.636	6.010	12.087	9.705	1.382	0.142	7.839
$Hf \cdot Y^{-1}$	0.252	0.276	0.264	0.157	0.395	0.267	0.055	0.206	0.214

a,b,c - ratio calculated according to the content values presented by: (a) Rudnick and Gao (2003); (b) Wedepohl (1995, in Rudnick and Gao, 2003); (c) Taylor and McLennan (1985, 1995, in Rudnick and Gao, 2003).

generated a lithological mix between loesses and Sarmatian clays, as well as by BG specific fertilizers.

4. Conclusions

Although the values of the averages, mean values, variation coefficients and distribution laws indicate the presence of an apparently homogeneous Zr, Hf and Y population, that can be correlated, from the point of view of the mean contents size order with other soils from urban areas, BG, seen as an anthropogenous ecosystem, is singled out by certain specific particularities. Thus, the potential Zr, Hf and Y anthropic inputs are, in our opinion, excluded if we consider: a) BG's geographic

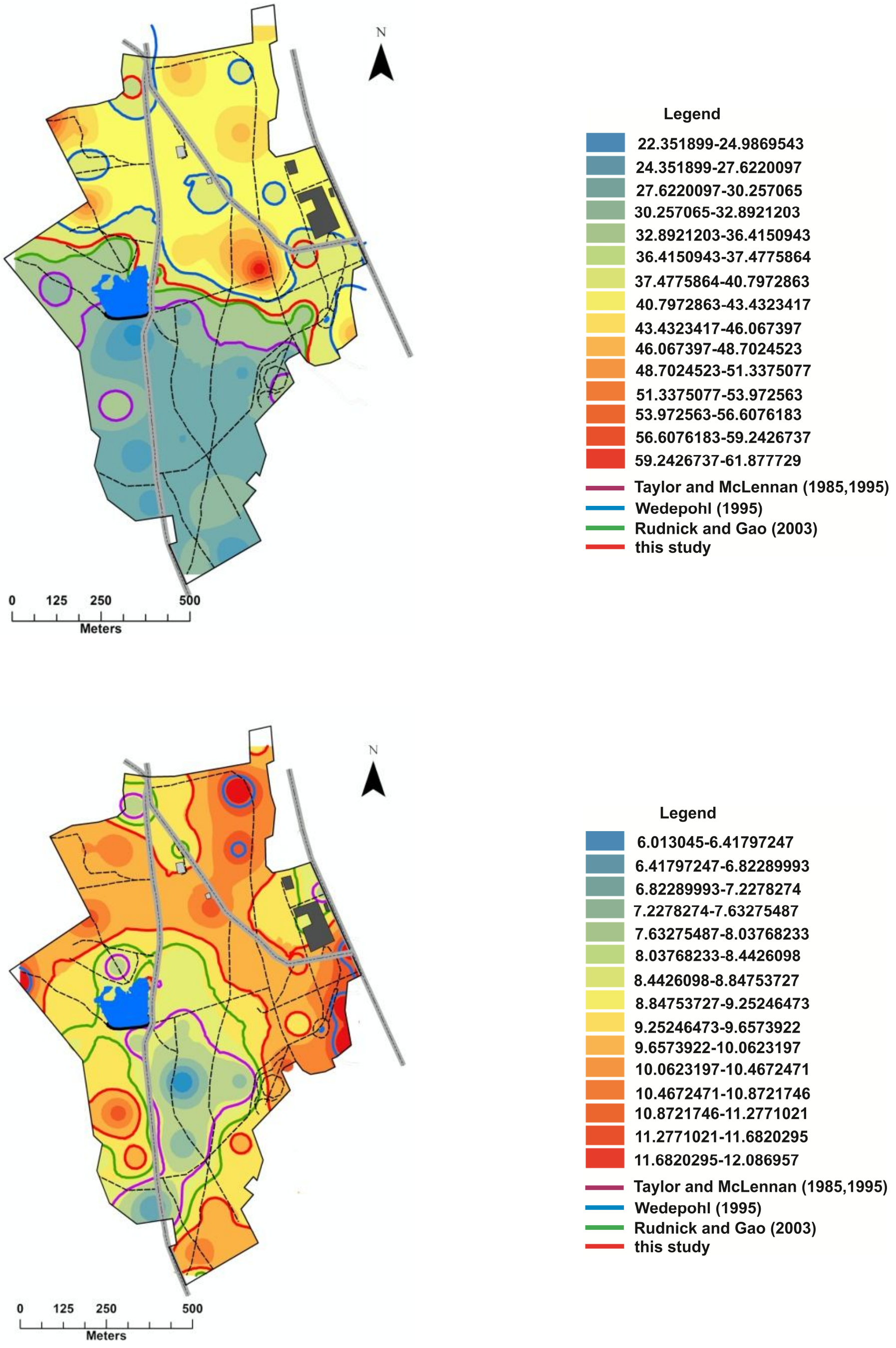


Fig. 7 Ratio values maps of $Zr \cdot Hf^{-1}$, $Zr \cdot Y^{-1}$ and $Hf \cdot Y^{-1}$ in the BGS.

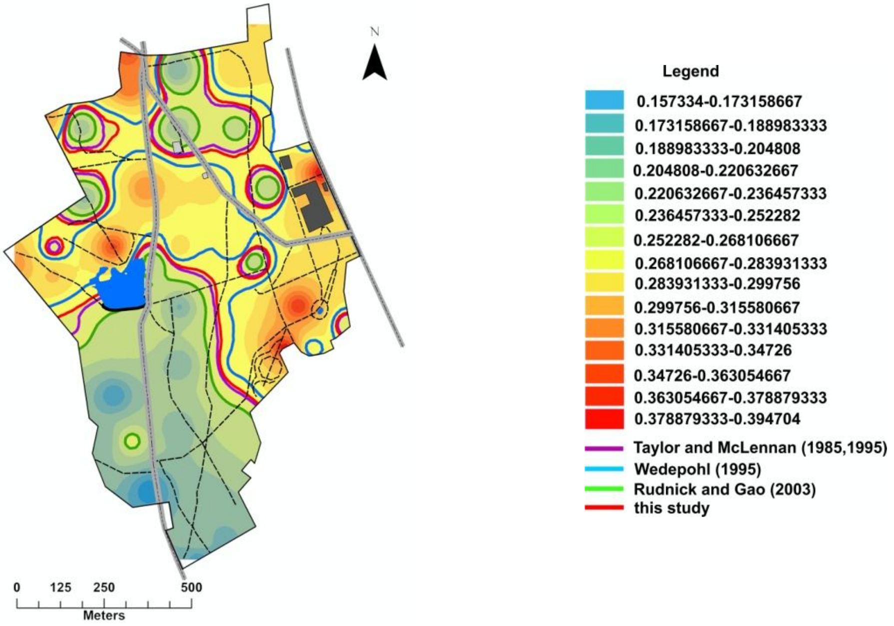


Fig. 7 Ratio values maps of $Zr{\cdot}Hf^{-1}$, $Zr{\cdot}Y^{-1}$ and $Hf{\cdot}Y^{-1}$ in the BGS. *(continuation)*

location in relation to potential sources that generate Zr, Hf, Y and b) specialised fields for the use of Zr, Hf and Y, which are not currently found in Iaşi municipality. At the same time, we do not exclude a very poor anthropic input generated by various fertilizers that have been used during the more than 60 years since the BG was opened, and whose effect is hard to quantify due to lack of information, but which is reflected, probably, in the presence of outliers. SCC values, partially non-concordant with other published data, the maximum probabilities to go beyond the GBK calculated for Zr, Hf and Y, as well as the distribution of the values of the $Zr{\cdot}Hf^{-1}$, $Zr{\cdot}Y^{-1}$ and $Hf{\cdot}Y^{-1}$ ratios, lead to the idea of certain lithological differences between the northern and the southern areas of the BG: thus, whereas in the northern area loesses predominate, in the southern area clays are preponderant. Although we admit that the Zr, Hf and Y distribution in BGS is influenced by geomorphological processes as well, expressed through landslides, and by landscaping and maintenance work which is specific to BG, their role is hard to estimate on the grounds of geochemical criteria only.

Acknowledgements

Our special thanks go to Professor dr. Cătălin Tănase (Faculty of Biology) for granting us permission to sample the soils of the Botanical Garden, to Professor dr. Nicolae Buzgar (Faculty of Geography and Geology), for the analyses of soil samples, and to Professor dr. Constantin Rusu (Faculty of Geography and Geology) for his suggestions on the lithology of the Northern area of Iasi municipality.

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