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ESTIMATION OF MASS RELOCATION INTENSITY IN VICINITY OF THE FORMER CEMENT WORKS

OSZACOWANIE SKALI PRZEMIESZCZANIA SIĘ MATERII NA OBSZARZE BYŁEJ CEMENTOWNI

Abstract: Estimation of possible mass relocation in environment is crucial in assessment of threats resulting from industrial activity. In many regions the abandoned industrial estates can be found, which can be a source of harmful substances in environment. In such areas composition of soils can be changed as a result of industrial activity. Among others, the radioactive isotopes in significant concentrations could appear in processing of mineral materials as well as in branches of production where fossil fuels are combusted. Surface soil samples were collected in the area of the former cement plant "Piast", situated within Opole city borders. Concentrations of gamma radioactive isotopes were determined in the samples. A number of naturally occurring radioisotopes were found as well as artificial Cs-137. In results studies methods designed for compositional data analysis were utilized. It was found that the radioisotopes from the radium and thorium decay series were close to equilibrium state. Concentrations of U-235 and its daughter Th-231 are rather poorly related with each other. Concentration of K-40 is somewhat bound with concentrations of radionuclides from thorium decay chain. The Cs-137 concentrations were not related to concentrations of other radioisotopes. The results obtained suggest lack of an intense mass relocation in the area close to former cement works. Neither significant deposition or elution/leaching of matter in the investigated area can be supposed.

Keywords: industrial pollution, radioisotopes, relocation

Introduction

Knowledge about mechanisms and ways of matter transport may provide information about current and future state of environment. Among others, estimation of possible mass relocation in environment is crucial in assessment of threats resulting from industrial activity.

Radioactive isotopes of elements are common in environment. They can be found in living organisms and in mineral components. In low concentrations they are harmless for organisms. Because of their specific physical and chemical properties, the radioisotopes can be helpful in assessment of matter relocation in environment. Many radioisotopes can be arranged in decay series in which irreversible sequences from parent to daughter radioisotope is defined. Chemical properties of radioisotopes in decay chains are changed in each decay step. It is a consequence of change in the atomic number of the radionuclide, which determines chemical properties of an element.

Change in chemical properties of a radionuclide leads to change in chemical properties of parent compound. This change affects fate of the corresponding element in environment. It could be expected that investigation of common relationships between concentrations of radionuclides in the environment components will provide information about matter

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transport mechanisms, matter sources, matter distribution in space and/or in time, and assessment of potential future threats related to matter dispersion in an investigated region.

In this work the results of soil investigations which surface layers were collected in the area of former cement works are described.

Materials and methods

Soil samples were collected in the area of the former cement plant "Piast", situated in southeastern part of Opole (Poland). This plant was founded in 1906. Due to mineral deposits depletion and high harmfulness for the city, after over 70 years of cement production it was closed. From this area 11 samples of surface soil layers were collected.

Activity concentrations of radioisotopes were carried out by means of a gamma-spectrometer with a germanium detector HPGe (Canberra) of high resolution. Geometry of samples container was Marinelli, and measuring process and analysis of spectra were computer controlled with use of the software GENIE 2000. The radiation spectrum was recorded day and night.

Computations

Activity concentrations a of radionuclides were recalculated to their mass concentrations from the formula:

$$c = \frac{t_{1/2} M}{10^3 \ln 2 N_A} a \tag{1}$$

where: $t_{1/2}$ is the half life time of the radionuclide, M is its molar mass of radionuclide, N_A is Avogadro constant and c is mass fraction (concentration) of the radionuclide in sample.

The sample space of the calculated concentrations data can be regarded as a set of compositions with lower data limit equal to 0 and upper data limit equal to 1. This data type shows some specific features. The compositional data are not independent on each other. If content of one of components increases the others have to decrease. It is the main reason for which results of standard statistical analysis of the relationships between raw components or parts are spoiled by spurious effects [1, 2]. For this reason application of standard statistical techniques on such data in raw form lead to faulty statistical inferences. For example, a variance of concentration provides only poor (or not at all) information about variability in a component abundance. In the variance of a single component, variabilities of all other components are involved.

The main principles of compositional data analysis are:

1. Scale invariance - composition provides information only about relative values and not about the absolute ones.
2. Subcompositional coherence - the same results of statistical inference of common parts regardless of whether full composition or subcomposition was used in computations.

Utilization of variables ratios (or logratios) in computations supports both principles.

Compositional data occupy a restricted space where variables can vary only from 0 to a given constant. For the geometrical representation of sample space, the unit simplex was proposed. In such space a distance between points and basic operations are defined [3].

Linear relationship between variables is usually estimated on base of the Pearson correlation coefficient. This parameter cannot be used in comparison of compositional variables. As a result of constant sum of all concentrations in a system, phenomenon of "spurious correlation" appears in compositional data analysis [4]. Co-variability of two compositional variables *A* and *B* can be tested using variance of ratio *VR*:

$$VR = \mathrm{var}\left(\ln \frac{\boldsymbol{c}_A}{\boldsymbol{c}_B} \right) \tag{2}$$

where: $\boldsymbol{c}_A$ and $\boldsymbol{c}_B$ are vectors of, respectively, *A* and *B* concentration values. If *A* increase linearly with increase in *B* then $\boldsymbol{c}_A/\boldsymbol{c}_B$ ratio is constant and its variance is 0. If there is a weak or negative linear relationship between *A* and *B* then the *VR* value increases.

To study common relationships between concentrations a Principal Component Analysis (PCA) was utilized [5]. In this method an orthogonal basis is selected for data description so that the first coordinate (principal component, PC) represents the direction of maximum variability and then the consecutive PCs are sorted in order of decreasing variabilities.

Though PCA method cannot be directly applied to study compositional data, within some limitations it can be used in transformed data interpretation [6, 7]. Among possible compositional data transformations the centered logratio, clr, is one of the commonly used:

$$\mathrm{clr}(\boldsymbol{c}) = \ln\left(\frac{\boldsymbol{c}}{g(\boldsymbol{c})} \right) \tag{3}$$

where $g(\boldsymbol{c})$ is geometrical mean of $\boldsymbol{c}$.

Results and discussion

In soil samples the following radionuclides were determined: K-40, Cs-137, Pb-210, Bi-212, Pb-212, Bi-214, Pb-214, Ac-228, Th-231 and U-235. The isotopes Pb-210, Bi-214 and Pb-214 are members of radium decay series. The Bi-212, Pb-212 and Ac-228 isotopes belong to thorium series, and actinium decay chain contains Th-231 and U-235. The K-40 radionuclide is constituent in natural potassium, with constant abundance of 0.017%. This isotope is the main radioactivity source for organisms. The Cs-137 is an artificial radioisotope. It was introduced into environment with the global fallout, resulting from nuclear tests, particularly intensified in 1963-1964, as well as the nuclear power plants fallouts, for example Chernobyl 1986 [8] and Fukushima Daiichi 2011 [9]. Half-life times of these radioisotopes are shown in Table 1 [10].

Table 1

Half-life times of the radionuclides determined in soil samples. Membership in decay series is marked as follows: * - radium series, ** - thorium series, *** - actinium series

isotope	**K-40**	**Cs-137**	**Pb-210** *	**Bi-212** **	**Pb-212** **	**Bi-214** *	**Pb-214** *	**Ac-228** **	**Th-231** ***	**U-235** ***
$t_{1/2}$	$1.248 \cdot 10^9$ a	30.08 a	22.2 a	25 min	10.64 h	19.9 min	26.8 min	6.15 h	25.52 h	$7.04 \cdot 10^8$ a

In Table 2 the statistical parameters of the calculated radionuclides concentrations are shown. In table *min* and *max* are minimum and maximum values of concentrations, q_2 is median, q_1 and q_3 are, respectively, lower and upper quartile. Arithmetic mean of concentrations is *mean* and standard deviation is *SD*. Coefficient of variation (*CV*) is the ratio of *SD* (nominator) and *mean* (denominator).

Table 2

The statistical parameters of the calculated radionuclides concentrations

	K-40 $\cdot 10^7$	**Cs-137 $\cdot 10^{14}$**	**Pb-210 $\cdot 10^{14}$**	**Bi-212 $\cdot 10^{21}$**	**Pb-212 $\cdot 10^{19}$**	**Bi-214 $\cdot 10^{21}$**	**Pb-214 $\cdot 10^{21}$**	**Ac-228 $\cdot 10^{19}$**	**Th-231 $\cdot 10^{19}$**	**U-235 $\cdot 10^8$**
min	6.90	0.69	0.55	4.80	1.93	4.10	6.43	1.37	1.27	1.25
q_1	8.34	1.03	0.68	6.86	2.76	6.12	8.57	1.93	1.58	2.12
q_2	8.89	1.34	0.94	7.46	2.96	9.49	13.5	2.07	1.98	3.37
q_3	9.35	3.25	1.34	9.73	3.18	12.4	18.4	2.38	2.57	3.87
max	15.7	5.32	2.14	13.1	5.10	16.10	21.6	3.54	5.85	6.75
mean	9.28	2.09	1.08	8.31	3.03	9.53	13.8	2.16	2.34	3.29
SD	2.28	1.51	0.51	2.70	0.82	3.79	5.35	0.59	1.28	1.59
$CV \cdot 10^2$	2.46	7.23	4.73	3.24	2.71	3.98	3.87	2.72	5.50	4.82

The lowest determined concentrations were of 10^{-21} and the biggest were of 10^{-7} order of magnitude. Significant differences between mean and median q_2 indicate skewed distributions of Cs-137 concentrations. Also variability in Cs-137 concentrations was the highest among the radionuclides determined.

Relationship between pairs of radionuclides concentrations are illustrated by values of *VR* parameters shown in Table 3.

Table 3

The *VR* parameter values calculated for pairs of radionuclide concentrations

	K-40	**Cs-137**	**Pb-210**	**Bi-212**	**Pb-212**	**Bi-214**	**Pb-214**	**Ac-228**	**Th-231**
Cs-137	0.58								
Pb-210	0.27	0.27							
Bi-212	0.10	0.50	0.09						
Pb-212	0.04	0.45	0.14	0.03					
Bi-214	0.22	0.33	0.05	0.07	0.10				
Pb-214	0.17	0.36	0.06	0.05	0.07	0.01			
Ac-228	0.05	0.49	0.14	0.02	0.00	0.09	0.07		
Th-231	0.20	0.70	0.45	0.32	0.28	0.36	0.33	0.28	
U-235	0.27	0.40	0.18	0.20	0.22	0.10	0.11	0.20	0.21

The results presented in Table 3 suppose that the radioisotopes from the radium and thorium decay series were close to equilibrium state. Despite of significantly longer half-life time of Pb-210 in comparison with $t_{1/2}$ of Pb-214 and Bi-214, concentrations of these isotopes were proportional in soil samples. It supposes lack of Pb-210 deposition or leaching in the investigated area.

The thorium series is represented by short living radioisotopes. But in decay chain unstable Ac-228 is separated from short living Bi-212 and Pb-212 by moderately stable Th-228 ($t_{1/2}$ = 1.913 a). Concentration proportionality of the determined radioisotopes from

thorium series supposes absence of processes significantly influencing thorium content in soil.

In opposite to radium and thorium decay series, concentrations of U-235 and its daughter Th-231 from actinium series are rather poorly related with each other. The U-235 long-living radioisotope is the straight ancestor of rather unstable Th-231. Though concentrations proportionality of these radioisotopes could be expected, the data analysis reveals considerable values of measurement uncertainty, particularly for Th-231. For this reason proportionality of radium and thorium concentration could be masked.

Concentration of K-40 is somewhat bound with concentrations of radionuclides from thorium decay chain. It could be a result of K abundance in minerals containing Th-232, the prime, long-living ancestor in thorium series.

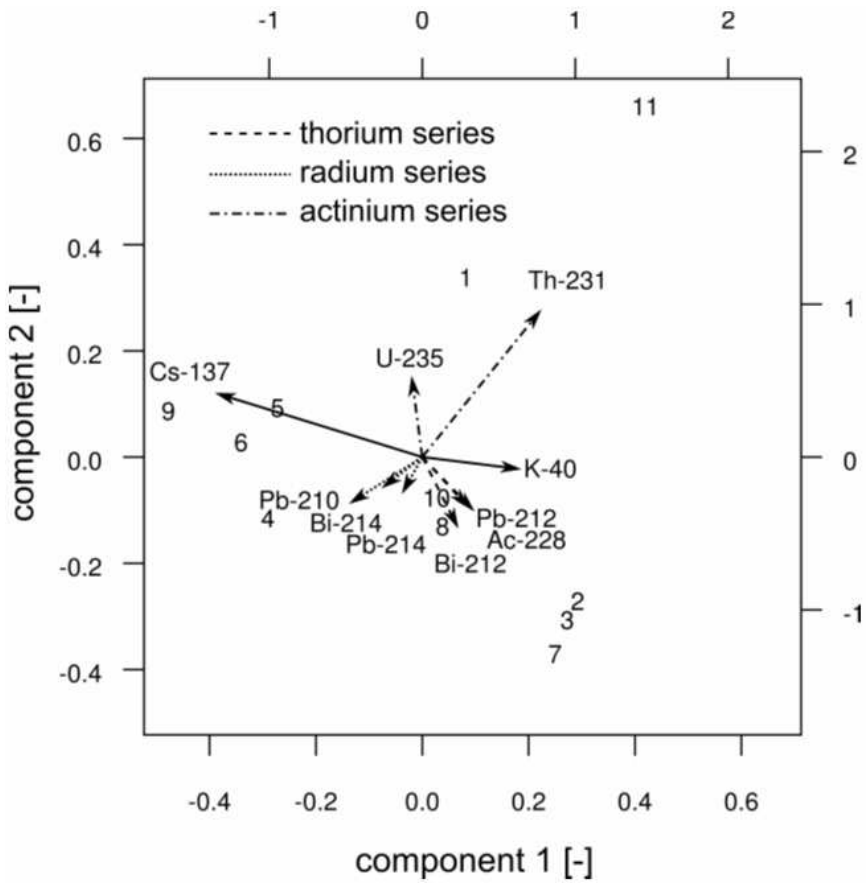

Fig. 1. Variables factor map of principal components calculated from clr transformed isotope concentrations

The Cs-137 concentrations were not related to concentrations of other radioisotopes. This radionuclide is still deposited from air on the soil surface. The dust containing Cs-137,

deposited on the soil surface, can be locally relocated by floating water from rains or by breaths of wind. This phenomenon occurs mainly on the ground surface, leaving practically unaffected somewhat deeper soil layers.

To investigate common relationship between radionuclide concentrations, the principal component analysis of clr transformed concentrations was carried out. The results obtained are illustrated in biplot (Fig. 1).

The results of PCA confirm conclusions drawn from the *VR* values. In the biplot small distances between arrowheads indicate positive co-variability between concentrations. Such relationship is observed for radionuclides of thorium series and for the radionuclides belonging to radium decay chain.

Conclusions

In the investigated area the radioisotope composition of soil surface layer remains nearly unchanged. It supposed absence of significant matter translocation in ground. It could be supposed that a possible soil contaminant, introduced in period of industrial activity, remains in soil. However due to contaminants specific chemical or physical properties (good solubility in water, high volatility) it could be moved outside borders of the polluted area. But such phenomenon would be finished soon after stopping contaminant delivery. Pollution bound with inorganic components of soil is well immobilized.

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OSZACOWANIE SKALI PRZEMIESZCZANIA SIĘ MATERII NA OBSZARZE BYŁEJ CEMENTOWNI

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Abstrakt: Oszacowanie skali wielkości przemieszczania się masy ma kluczowe znaczenie w ocenie zagrożeń wynikających z działalności przemysłowej. W wielu regionach znajdują się pozostałości po zakładach przemysłowych, które mogą być źródłem szkodliwych substancji w środowisku. Na tych obszarach można oczekiwać podwyższonego poziomu skażeń, których źródłem jest wcześniejsza działalność przemysłu. Na takich terenach mogą występować m.in. zwiększone ilości izotopów promieniotwórczych, powstających w wyniku przetwarzania surowców mineralnych lub spalania paliw kopalnych. Do badań pobrano próbki gleby zebrane na obszarze byłej cementowni „Piast", znajdującej się w granicach miasta Opole. W badanych próbkach oznaczono aktywności naturalnych izotopów gamma-promieniotwórczych. W próbkach gleby znajdował się także sztuczny izotop Cs-137. Podczas analizy danych wykorzystano metody analizy zmiennych złożonych. Stwierdzono, że izotopy z szeregu radowego i torowego znajdowały się w stanie zbliżonym do równowagowego. Aktywności U-235 i Th-231 były słabo ze sobą związane. Aktywność K-40 była w pewnym stopniu związana z aktywnościami radionuklidów pochodzących z szeregu torowego. Aktywność Cs-137 nie ma związku z aktywnościami pozostałych izotopów promieniotwórczych. Uzyskane wyniki sugerują ograniczone przemieszczanie się materii na obszarze byłej cementowni. Zarówno depozycja, jak i wymywanie/ługowanie materii na badanym obszarze jest ograniczone.

Słowa kluczowe: zanieczyszczenia przemysłowe, radioizotopy, translokacja