Assessment of the impact of a phosphatic fertilizer plant on the adjacent environment using fuzzy logic

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Abstract: The impact of a phosphatic fertilizer plant on the adjacent environment was examined. Selected rare earth elements, heavy metals and metalloids were determined in substrates and products, waste by-product, and grass and soil samples. Concentration gradients of elements in grass and soil samples along the southerly and easterly directions were examined and compared with the content of interior soil and grass samples, substrates, and products. Results were compared with available data on soil permissible element concentration levels. Two fuzzy principal component analysis (FPCA) methods for robust estimation of principal components were applied and compared with classical PCA. The efficiency of the new algorithms is illustrated. The investigation explored the impact of the plant on the adjacent environment. The most reliable results, in good agreement with types of samples, were produced using the FPCA-O algorithm.

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1 Introduction

The products generated by fertilizer plants are necessary for increasing agricultural production. However, many of the plants are significant pollution sources for the environment because there are no efficient means for purifying waste water and residual gases. Thus, the main environmental compartments: water, air, and soil are seriously affected [1].

Soils are considered the most important environmental compartment functioning as a sink for trace elements released by human activities. Major developments in trace element research have been made in soil sciences. Elements can enter the soil by a number of pathways. The behavior and fate of elements in soils differ according to the source and species. Commercial fertilizers contain trace amounts of several elements as impurities originating from the parent rock materials or from the process and the chemicals used in production [2]. The release of dust and polluted waters from fertilizer production plants could be hazardous to the environment [3]. Once emitted, trace elements may travel long distances before deposition, can be dispersed over large areas from the point of emission, and are difficult to control and limit [2].

Micronutrient elements are essential for plant growth and/or human nutrition. Some micronutrient elements, for example chromium, molybdenum, nickel, selenium or zinc, may be toxic to both animals and humans at high concentrations. Other trace elements, such as arsenic, may inadvertently enter the food chain and pose health risks to humans and animals [4]. Trace elements are recognized as important cofactors or cofounders in the etiology of diseases such as cancer. Some evidence exists for the role of environmental and dietary trace elements in human health [2].

The trace element content of vegetation growing inside a plant and in the vicinity of a plant area is an important characteristic reflecting the level of environmental pollution [5]. To estimate the most probable sources of air pollution, samples of the primary materials, the final products and a by-product, phosphogypsum, were collected [6].

In this study, the range of the impact of the Gdansk Phosphatic Fertilizer Plant “Fosfory” J.S.C. (Joint Stock Company) on the adjacent environment up to 1 300 m distance from the pollution source was examined. The prevailing winds occurring in Gdańsk are of southerly and westerly directions; therefore, element enrichment, if present, should be identified in samples collected in northerly and easterly directions. To assess the range of impact of the fertilizer production plant on the adjacent environment, elemental concentration gradients were examined in grass and soil samples collected along the southerly (northerly was not possible) and easterly directions. The degree of elemental enrichment was determined by comparing the analytical results obtained for grass and soil samples, substrates and products, background levels, and samples collected on the premises of the plant.

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2 Classical PCA versus fuzzy robust PCA

2.1 Principal components analysis

Principal components analysis (PCA) is also known as eigenvector analysis, eigenvector decomposition or Karhunen-Loève expansion [7–11]. Many problems in chemistry and other technical fields can be described by PCA. The main purpose of PCA is to represent concisely the location of the data in a reduced coordinate system. Instead of \( m \)-axes (corresponding to \( m \) characteristics), only \( p \)-axes \( (p < m) \) are necessary to describe the data set while retaining the maximum possible information.

Principal components analysis transforms the original data matrix \( (X_{n \times m}) \) into a product of two matrices, one of which contains the information about the objects \( (S_{n \times m}) \) and the other about the variables \( (V_{m \times m}) \). The S matrix contains the scores of objects on \( m \) principal components (the scores are the projection of the objects on principal components). The V matrix is a square matrix and contains the loadings of the original variables on the principal components (the loadings are the weights of the original variables in each principal component).

Usually two or three principal components provide a good summary of the original variables. Loadings and score plots, respectively, are very useful as visual tools for examining the relationships between characteristics and between samples, and analyzing for trends, groupings, or outliers.

2.2 Fuzzy clustering

Fuzzy clustering is an important tool to identify structure in data [12]. In general, a fuzzy clustering algorithm with objective function is formulated as follows: let \( X = \{x^1, \ldots, x^n\} \subset \mathbb{R}^p \) define a finite set of feature (characteristics) vectors, where \( n \) is the number of objects (measurements) and \( p \) is the number of the original variables, \( x^j_k = [x^j_1, x^j_2, \ldots, x^j_p]^T \) and \( L = (L^1, L^2, \ldots, L^s) \) represent a \( s \)-tuple of prototypes (supports) each of which characterizes one of the \( s \) clusters composing the cluster substructure of the data set. A partition of \( X \) into \( s \) fuzzy clusters is performed by minimizing the following objective function

\[
J(P, L) = \sum_{i=1}^{s} \sum_{j=1}^{n} (A_i(x^j))^2 d^2(x^j, L^i) \tag{1}
\]

where \( P = A_1, \ldots, A_s \) is the fuzzy partition, \( A_i(x^j) \in [0, 1] \) represents the membership degree of feature point \( x^j \) to cluster \( A_i \), and \( d(x^j, L^i) \) is the distance from a feature point \( x^j \) to the prototype of cluster \( A_i \), defined by the Euclidean distance norm

\[
d(x^j, L^i) = \|x^j - L^i\| = \left[ \sum_{k=1}^{p} (x^j_k - L^i_k)^2 \right]^{1/2}. \tag{2}
\]

The optimal fuzzy set is determined by using an iterative method where \( J \) is successively minimized with respect to \( A \) and \( L \).
Depending on the choice of prototypes and the definition of the distance measure, different fuzzy clustering algorithms are obtained. If the prototype of a cluster is a point – the cluster center – spherical clusters are produced; if the prototype is a line, tubular clusters are produced, and so on. Also, elements with a high degree of membership in the \(i\)-th cluster (i.e. close to the cluster’s center) will contribute significantly to the weighted average, while elements with a low degree of membership (far from the center) contribute negligibly.

2.3 Fuzzy (first component) PCA

The Fuzzy (first component) PCA algorithm [13] was used to determine the fuzzy principal components and the corresponding scatter values. The particular membership degrees \(A(x)\) are determined such that the first principal component is best fitted along the items of the data set \(X\). The algorithm is a natural extension of the fuzzy 1-lines algorithm [14] and was used in (i) determining the optimal value of \(\alpha\) by calling “determine best alpha \(\alpha\)”;(ii) calling “determine fuzzy membership \(\alpha\)” with the value of \(\alpha\) computed above, and determining the optimal value of the fuzzy membership degrees; and, (iii) using the fuzzy membership degrees determined above, calculating the fuzzy covariance or correlation matrix \(C\) as in (3), and computing the eigenvalues and eigenvectors

\[
C_{kl} = \frac{\sum_{j=1}^{n} [A_i(x_j)]^m (x_{j,k} - \bar{x}_k)(x_{j,l} - \bar{x}_l)}{\sum_{j=1}^{n} [A_i(x_j)]^2} \tag{3}
\]

where \(\bar{x}_k\) is the arithmetic mean of the k-th variable and \(m > 1\) is the fuzziness index. The fuzzy set \(A\) is characterized by the linear prototype PC1 produced considering the fuzzy covariance matrix \(C\); \(\alpha\) is the membership degree corresponding to the farthest outlier of the data set.

2.4 Fuzzy PCA (orthogonal)

The primary issue concerning the fuzzy PCA algorithm described in the previous section was that the fuzzy eigenvectors were computed by the fuzzification of the first direction only. The algorithm discussed in this paragraph was designed to overcome this disadvantage. The algorithm produced the eigenvalues and eigenvectors denoted \(\lambda_1, \ldots, \lambda_p,\) and \(e_1, \ldots, e_p,\) respectively. The first fuzzy principal component was computed in the same manner as the fuzzy-PCA-first algorithm, e.g., by finding the optimal fuzzy membership degrees and the optimal linear prototype for the data set. The eigenvalues and eigenvectors produced in this way were denoted \(\lambda_1', \ldots, \lambda_p'\) and \(e_1', \ldots, e_p',\) respectively. Therefore,

\[
\lambda_1 = \lambda_1' \tag{4}
\]

and

\[
e_1 = e_1'. \tag{5}\]
The primary novelty of the algorithm was in the way the other fuzzy principal components were computed. The original data set was projected onto the hyperplane orthogonal to the first fuzzy principal component, i.e., determined by all the other principal components, as determined using the fuzzy first component PCA algorithm. The scores were computed and the first item was removed from the data vectors. Therefore,

$$x_j'^T = x_j^T \cdot (e'^1, \ldots, e'^p).$$

The first component of $x_j'$ was removed according to (7),

$$X' = \{(x_2', \ldots, x_p') \mid \exists j : x_j' = (x'^1, x'^2, \ldots, x'^p)\},$$

thus producing a subset $X'$ of $\mathbb{R}^{p-1}$ in Euclidean space of dimension $p-1$, where $p$ is the size of the original data set. The eigenvalues and eigenvectors produced were denoted $\lambda'^1, \ldots, \lambda''_{p-1}$ and $e'^1, \ldots, e'^{p-1}$, respectively. The first fuzzy principal component of the projected data set after being rewritten in terms of the original space, was orthogonal on the originally computed first fuzzy principal component. In order to account for the fuzziness in the fuzzy data sets, when the components were recalculated in terms of the original space, the eigenvalues computed in the $p-1$ sized space were multiplied by the fuzzy set fuzziness index $f_A$, given by

$$f_A = \frac{1}{n} \sum_{i=1}^{n} A(x_i)^m.$$  

Thus

$$\lambda_2 = \lambda''_1 \cdot f_A$$

and

$$e_2'^T = (0, e'^1)^T \cdot (e'^1, \ldots, e'^p)^T,$$  

where $(0; e'^1)$ denoted a vector equal to 0 for the first component and the vector $e'^1$ for the remaining components. In order to determine the third fuzzy principal component, the data set projected onto the hyperplane orthogonally to the first two fuzzy principal components. The twice-projected data set was in an Euclidean space of dimension $p-2$. After appropriate transformations were made at the superior level, the newly produced eigenvectors and eigenvalues (now in the $\mathbb{R}^{p-1}$ space) were denoted by $\lambda''_1, \ldots, \lambda''_{p-1}$ and $e'^1, \ldots, e'^{p-1}$, respectively replacing the previously computed values. A final transformation, computing the initial projection in reverse, reverted the eigenvectors and eigenvalues to the original space.

3 Experimental

3.1 Sampling

A sampling site scheme is presented in Figure 1 and sampling site identification is given in Table 1. Within this research various types of samples were collected including substrates:
various types of phosphorite raw materials originating from Tunis, Morocco, Northerly Sahara – Buckra and Togo; potassium salt used for production of phosphatic fertilizers (8 samples collected from storage at the fertilizer plant); fertilizer products: triple superphosphate and “Amofoska” (3 samples collected from storage at the fertilizer plant); the waste by-product, phosphogypsum (1 sample collected from the production line at the plant and 3 samples from the phosphogypsum dump located about 20 km from the plant); grass and soil samples (7 locations at the premises of the plant and 10 locations in the vicinity of the plant – grass and soil at the same sites along the southerly and easterly directions from 300 m to 1 300 m from the plant; soil and grass background samples collected in the woods of Ustka, Poland (2 samples).

Phosphate rocks, calcium salt, solid waste (phosphogypsum – sample No. 1), triple superphosphate and “Amofoska” (ready to use fertilizer) samples were collected randomly from waste piles. Additional phosphogypsum samples were collected from different areas within the dump that represented materials discarded in different years (samples No. 2-4).

In 2001, soil and grass samples were collected at ten sampling points in southerly and easterly directions. Five additional samples of both material types were collected inside the plant territory. In 2002, two soil samples were collected in two locations, near the phosphoric acid production shop and in the vicinity of the fertilizer packaging shop. These locations were free from grass cover, therefore only soil samples were available. Grass and soil samples were collected from the upper 0-20 cm.

The woods region in Ustka vicinities was chosen as a reference area. Control samples of soil and grass were collected. Ustka is characterized by a soil and vegetation profile similar to Gdansk. The area, situated about 130 km from Gdansk in the north westerly direction, is virtually free from industrial enterprises and specific sources of anthropogenic contaminants.

The analytical method chosen to process solid samples did not require specialized
pre-treatment. Samples were dried (50 °C), milled, packed, and transported for analysis. The elements Na, Mg, Al, K, Sc, Ca, Cr, Ti, V, Mn, Ni, Fe, Co, Zn, Se, As, Br, Sr, Rb, Mo, Ag, Sb, I, Ba, Cs, La, Ce, Eu, Sm, Tb, Dy, Yb, Hf, Ta, W, Th, and U were determined.

3.2 Materials and methods

The elemental content of raw materials, phosphogypsum, substrate (potassium salt), products (superphosphate and “Amofoska”), soil, and grass was determined using conventional and epithermal neutron activation analysis using the IBR-2 pulsed fast reactor at Frank Laboratory of Neutron Physics (FLNP), Joint Institute for Nuclear Research (JINR), Dubna, Russia. The analytical procedure was described elsewhere by Frontasyeva and Pavlov [15]. Quality control was based on the application of certified reference materials (CRMs): IAEA-336 (lichens), IAEA-SDM (lake sediment) and IAEA-SL1 (soil). The certified values and the results obtained by NAA were compared (Table 2). Concentrations of most elements were in good agreement with the CRMs except for Ti, Ni, Ce, Eu, Dy and Rb, which differed from the certified value as follows: Ti - 41.7 %, Ni - 26.5 %, Ce - 24.3 %, Eu - 32.9 % and Dy - 33.3 % in IAEA-SL1 (soil) and Rb - 20.6 % in IAEA-336 (lichens). For the 21 elements in agreement with the certified values the bias observed was below 20 %. For 11 elements (Al, V, Mn, As, Br, Sc, Cr, Sm, Na, Co and Sb), the bias ranged from 0.03 % to 5 %, for 5 elements (Fe, Zn, Ba, Th and Cs) the bias was greater than 5 % but lower than 10 %, and for 5 elements (La, Tb, Hf, Ta, and U) the bias was determined to be between 10 % and 20 %.

Samples of raw materials, phosphogypsum, substrate, products, soil (of about 0.1 g), and grass (0.3 g) were irradiated in cadmium-screened channels 1 and 2 of the pneumatic “Regata” system described elsewhere by Frontasyeva and Pavlov [15]. In order to determine elements associated with long-lived radionuclides, samples were irradiated for 100 hours. Spectra of induced gamma activity were recorded after 4 and 20-24 days of cooling. Short irradiations, 5 minutes for grass samples and 60 seconds for the remaining samples, allowed determination of Al, Ca, Cl, I, K, Na, Mg, Mn, Ti and V. Gamma-ray spectra were recorded after 5 and 12 minutes after irradiation. Data processing was performed using software developed at FLNP JINR [16, 17]. All gamma-spectrometers and counting electronics were made at JINR [16]. The software developed at FLNP JINR for peak searching, peak fitting, and nuclide identification routines were used for processing the amplitude spectra [16].

In the case of the lack of analytical data, there was a half of the detection limit inserted for each analyte [18]. Principal component analysis (classical PCA and fuzzy PCA) was performed as a tool for searching the possible correlations between environmental and industrial samples that could implicate the impact of phosphatic fertilizer production on the environment adjacent to the plant.
4 Results and discussion

The determination of analytes from various kinds of samples within this study (35 samples and 37 element concentrations) provided a large and diversified data set (Table 1 and 3) forming the basis for comparison with previous or future investigations. In many cases, the correlation coefficient exceeded 0.79. Several of the strongest correlations were observed between the following pairs: Ca/U (0.97), Ca/Eu (0.96), La/Sm (0.94), Ce/U (0.94), Ca/I (0.93), Sr/La (0.93), Sr/Sm (0.93), Ca/Ce (0.92), I/U (0.92), Sr/Tb (0.92), Ca/Br (0.91), Br/Eu (0.91), Br/U (0.90), Sr/Cr (0.90). The correlations are in good agreement with the composition of the fertilizer production substrates and products. Given such strong correlations among the data, principal components analysis was performed.

Data statistics including the mean, median, minimum, maximum, range, standard deviation, skewness, and kurtosis were calculated (Table 3). Skewness and kurtosis informed about the data distribution character. Skewness measured the deviation of the distribution from symmetry. If the skewness was clearly different from 0, the distribution was considered to be asymmetrical. Normal distributions were perfectly symmetrical [19]. Kurtosis measures the “peakedness” of a distribution. If the kurtosis was clearly different from 0, then the distribution was either flatter or more peaked than normal; the kurtosis of the normal distribution was 0 [19]. A characteristic property of the normal distribution was that 68 % of all observations fell within a range of ±1 standard deviation from the mean. A range of ±2 standard deviations included 95 % of the scores [19]. In most cases, the distribution of the data differed from normality as was observed for the elements K, Ca, Ti, V, Ni, Co, Zn, Se, As, Br, Ag, I, Ce, Eu, Tb, Dy, Hf, Ta and U. Environmental data are rarely normally distributed. The Gaussian data distribution was disturbed by the detection limit of the analytical technique and by the fact that most of the elements determined within this study occur in nature at low concentration levels. In most cases, the population of measurement results is greatest for the values closest to the determination limits.

Dendrograms classifying the elements analyzed by sample type were prepared (Figure 2). In both cases, 3 clusters were indicated according to the sharper criterion of Sneath’s index (33.3 % of d_{max}, where d_{max} is a maximum distance) used as the significance level of the clusters created. Cluster analysis (CA) was performed only to visualize the classes since this technique can be helpful to better understand the structure of the data. However, CA is not a very efficient tool for distinguishing among groups having important similarities. The results and correlations found during data analysis confirm that the variables (element concentrations) were related to each other and so their number could be reduced.

The eigenvalues of the correlation matrix were ordered from the largest to the smallest (Table 4) and the proportion for each component was identified. Comparing the proportion and cumulative proportion values presented illustrates that FPCA-O produced the best results.

Classical and fuzzy robust principal component analyses were performed to locate the
Fig. 2 Dendrograms presenting a division of analytes and samples into clusters according to the sharper version of Sneath’s index (33.3 % of $d_{\text{max}}$, where $d_{\text{max}}$ is a maximum distance) used as significance level of created clusters.

Trace element content ranges in fertilizers investigated previously were compared with common element content ranges found in soil and grass (Table 5). The comparison of raw materials used and products produced in the fertilizer plant with the literature data concerning world-wide average element concentration levels in such materials (Table 5) proved that the fertilizer plant used typical raw materials. Observation that the typical product composition did not differ much from reported world-wide averages indicated that the production process was probably operating efficiently. By analogy, comparison of phosphogypsum analyses with literature data (Table 5) demonstrated that most element
concentration levels were below world averages except for: Ti, Fe, Zn and Sr, for which concentration levels were exceeded.

The elements originating from fertilizer production were immobilized in grass and soil samples collected in the vicinity of the factory. Upon comparison to the background levels determined for the elements analyzed, it was determined that pollution of the environment of the studied site was indicated. The elemental concentration was elevated in comparison with background levels and in comparison with the characteristic distribution of elemental concentrations. Air-borne propagation of the elements was connected with the dusting effects resulting from processing raw materials and products. Both soil and
Fig. 4 Representation of scores for determined elements and analyzed cases in three-dimensional space (Classical PCA vs. FPCA-1 vs. FPCA-O).
grass samples demonstrated the same tendency. Most of the elements analyzed exhibited a characteristic distribution that decreased as the distance from the plant increased.

Data analysis clearly indicated that soil and grass in the vicinity of the plant were highly contaminated by heavy metals. From this study it was concluded that the Gdansk Phosphatic Fertilizer Plant “Fosfory” J.S.C. had significant impact on the adjacent environment and was considered to be a specific point source of pollution in the area investigated, evidenced by a unique elemental pollution profile. The presence and elevated levels of elements characteristic for phosphatic fertilizer production that were not naturally occurring in the environment under investigation supported the conclusion. The highest concentrations of Sm, As, and Br were observed near the fertilizer plant. Higher concentration levels for Sc, Ca, Cr, V, Ni, Co, Mo, Ba, Cs, La, Sm, Tb, Dy, Yb, Th, and U were determined in grass samples collected inside the plant in the vicinity of two major pollution sources, the H$_2$SO$_4$ shop and the fertilizer bagging shop, than were measured outside the plant. Principal component analysis showed that soil samples numbered 22, 23, 24, 25, 29 and 33, which were located at the positions sited 200 m P, 300 m S, 400 m S, 300 m E and 1300 m E (where P stands for plant area, S for southerly direction and E for easterly direction), respectively, were clustered with sample number 35, which represented the mean value calculated from all industrial samples. Therefore the samples in this group were considered highly polluted composed of elements originating from the fertilizer plant and, in the case of sample 33, probably also from the sulfur plant.

The impact of the Gdansk Phosphatic Fertilizer Plant “Fosfory” J.S.C. on the surrounding environment was determined to be of limited range, i.e. within 1 km. The highest elemental concentration levels were determined at the distance of 400 m from the emitter. In addition, an increase in the elemental concentrations for Mg, Al, Na, La, As, Sb, U, Sm, K, Br, Mo, Ta and V analyzed in samples collected about 1 km distant from the fertilizer plant in the Easterly direction indicated the presence of a second point source contribution to environmental pollution in the area, proposed to be the Gdansk Sulphur Plant “Siarkopol” J.S.C., located 800 m from the border of fertilizer plant.

The permissible elemental concentration levels in Polish soils**, according to regulations [20], are as follows: As – 60 mg·kg$^{-1}$ d.w. (dry weight), Ba – 1 mg·kg$^{-1}$ d.w., Cr – 500 mg·kg$^{-1}$ d.w., Zn – 1 mg·kg$^{-1}$ d.w., Co – 200 mg·kg$^{-1}$ d.w., Mo – 250 mg·kg$^{-1}$ d.w., and Ni - 300 mg·kg$^{-1}$ d.w. Zn and Ba concentration levels, inside and outside the fertilizer production plant territory, were determined to exceed the regulated concentration levels. Moreover, the maximum As concentration was determined in soil collected in the vicinity of the plant in the easterly direction, and exceeded the permissible concentration level for Polish soils.

4.1 Classical PCA

The first principal component explains only 48.23 % of the total variance while the second principal component explains 20.41 %; a two-component model, therefore, accounts

** In case of group C concerning industrial areas, mining areas and communication routes (0-2 m depth).
only for 68.64% of the total variance (Table 4). The first eigenvector indicated that the contribution to the first principal component was similar (Table 4). The greatest contribution was made by Th (-0.226), followed by Cr (-0.221), Sm (-0.220), Sr (-0.216), and La (-0.215). The contributions of Sc, Ce, Eu, Tb, Dy Yb and U to the first principal component were similar (~ -0.2). Similar contributions were also obtained for Na, Mg, Al, Mo, Sb, (-0.16) and Ca, Ni, Fe, I, Ba, Cs (-0.17). K (-0.015), Ag (-0.024), As (-0.082), Rb and Ti (-0.094) contributed the least to the first principal component.

The second principal component (PC2) described the variance remaining after the first principal component was considered. The greatest contribution to PC2 was obtained for K (0.316) followed by Br (0.272), Ca (0.236), I (0.227), and U (0.226). The least contribution to PC2 was observed for Th (0.017), Cr (-0.018), and V, and Mo (0.033). The primary contributions to the third principal component (PC3) were obtained for As (-0.403), Zn (-0.353), Mo (0.340), Ni (0.317), and Se (-0.296). These results were somewhat in agreement with the correlation data, while the positions of K and Ag were indicative of outliers. The observations were supported by two-dimensional (i.e., PC1 versus PC2) and a three-dimensional (i.e., PC1 versus PC2 versus PC3) representations of the loadings (Figure 3 and 4).

From the plot of the 37 elements on the plane described by PC1 and PC2 (Figure 3), the representative points of K, Ag and Br appeared clearly as outliers. Sc, Ti, V, Ni, Mo, W and Se formed a diffuse cluster well separated from the other elements. The lanthanides La, Ce, Sm, Eu, Tb, Dy, Yb, the actinides Th and U, and the elements Ca, Sr, I, and Cr formed a cluster. Two additional clusters composed of the elements Na, Cs, Mg, Ba, Al, Sb, and Fe and the elements Rb, Hf, Ta, Mn, Co, and As were also observed.

### 4.2 Fuzzy (first component) PCA

The results obtained using FPCA-1 were quite different than the results obtained when the same data set was analyzed using classical PCA. The first principal component explained 63.42% of the total variance in the data while the second principal component explained 8.91% of the variance in the data. The two-component FPCA-1 model accounted for 72.33% of the total variance as compared to 68.64% for classical PCA while the three-component FPCA-1 model accounted for 76.94% as compared to 75.34% for classical PCA (Table 4). Hence, the FPCA-1 model accounted for more of the variance than the classical PCA model. The greatest contributions to the first component was obtained for Al (-0.223), Sc (-0.220), V (-0.219), Cs (-0.218), Cr (-0.216), Ba (-0.210), La (-0.208), Na (-0.207), Mg (-0.205), Sr (-0.204), and Sm (-0.201). Lesser contributions were obtained for Ag (-0.021) Br (-0.024), Se (-0.061), and As (-0.080). With respect to the second principal component, the greatest contributions were obtained for Rb (-0.428), Mo (0.408), and Na (-0.300). The third component was associated primarily with loadings from W (-0.547), Rb (0.218) Se (-0.212), and Cs and Mn (0.127), respectively. Two-dimensional and three-dimensional representations of the loadings are depicted in Figure 3 and 4.
Visual examination of the results obtained by applying FPCA-1 (Figure 3) revealed the separation of the lanthanides cluster observed in the case of PCA into two subgroups: (1) Ce, Eu, U, Ca, I, Ti, and W and (2) La, Sm, Tb, Dy, Yb, Sr, Cr, V, and Ni, excluding Th. A third class composed of Na, Cs, Mg, Ba, Al, Sc, Ti, Ta, Mn, Sb, and Th and a closely associated pair formed by Zn and Co. Mo was added to the group of outliers including K, Br, and Ag, while Se, As, and Rb also appeared as outliers.

4.3 Fuzzy PCA (orthogonal)

When the fuzzy PCA orthogonal algorithm was applied, the eigenvalue corresponding to the first principal component was equal to that obtained by applying FPCA-1 (10.933), but the proportion of the variance accounted for was only 27.05%. The second principal component accounted for 36.67% and the third principal component for 2.46% of the total variance; therefore, the three-component fuzzy PCA orthogonal model accounted cumulatively for 66.18% of the total variance. As a consequence, the first eigenvector calculated using the fuzzy PCA orthogonal model was identical to the first eigenvector calculated using the FPCA-1 model. The greatest contributions to the second principal component were made by K (0.379), Br (0.357), Ca (0.276), Eu (0.269), U (0.255), Se (0.252), Ce (0.249), and I (0.237). The smallest contributions to PC2 resulted from Ag (-0.007), Mo (0.010), Ti (-0.024), and As (-0.056). For the third principal component the primary contributions were due to Mo (-0.497), Rb (0.473), and Na (0.454). Graphical representation of the loadings onto the plane described by PC1 and PC2 (Figure 3) illustrated four, well-delimited classes of ions.

In Figure 3, one group composed of Ce, Eu, U, Ca, and I and a second group composed of La, Sm, Dy, Yb, Sr, and Th were observed. Tb and Cr appeared as outliers. The ions contributing most to PC1, including Na, Rb, Cs, Mg, Ba, Al, Sc, V, Hf, Ta, Fe, Ni, and Sb form a compact and clearly defined cluster. Ti, Mo, W, Co, Zn, and As formed a small, more diffuse cluster. K, Br, Ag, and Se appeared to be outliers.

The principal components or eigenvectors calculated were orthogonal (first and third algorithms) and each was a linear combination of the original variables (properties). Thus, by reducing the number of features from 37 original concentrations (manifest variables) to two or three principal components (latent variables), the information was preserved enough to permit examination of the samples according to the mapping in a two-dimensional or a three-dimensional plot, respectively. By plotting the samples in the plane described by the first two eigenvectors and in the space defined by the first three principal components, relevant conclusions were derived.

In the plot of the 35 samples on the plane described by PC1 and PC2 (Figure 3), as well as in the space defined by the first three eigenvectors (Figure 4), sample 35 appeared clearly as an outlier. Samples 22-25, 29, and 33 formed a diffuse cluster well-separated from the other samples. Two additional classes were evident in Figure 3: (1) composed of the soil samples 17-21 and 28-32 and (2) composed of the soil samples 1-16 and 34.

The dendrograms (Figure 2) confirmed the observations derived from the PCA plots.
Sneath’s index (33.3 and 66.7 % of $d_{\text{max}}$, where $d_{\text{max}}$ is a maximum distance) was used to calculate a significance level of clusters created by each algorithm [21, 22].

5 Conclusions

The pollution profile developed in this research for a fertilizer production plant will be useful for comparison with other existing plants. The phosphogypsum dump still poses a problem in the region although the authorities of the Gdansk Phosphatic Fertilizer Plant “Fosfory” J.S.C. are making efforts towards land reclamation. The results of this study demonstrated that phosphogypsum discarded in exposed dumps at fertilizer facilities was a continuing source of pollution. The data presented a model study for the fertilizer industry in Poland and elsewhere.

Analysis of soil samples proved to be more useful than grass samples for investigation of pollution at the study site. Soil accumulated the elements through years of exposure, while grass assimilated elements during a one-year period only. Therefore, grass samples seemed to be inadequate as an indicator of pollution since the concentration levels observed were low.

PCA resulted in a different separation of the variables and samples onto the plane described by the first two principal components when compared with FPCA. In some cases, clearer differentiation of the variables and scores was obtained when FPCA was used. Classical PCA is sensitive to outliers and fuzzy PCA is not that sensitive, which is extremely important in case of analyzing diversified environmental data as in case of this study. A very important founding is that fuzziness does not change the natural relation of domestic (natural) data. This can be observed for instance on the basis of Co and Zn location in the case of all three kinds of principal components analysis. Moreover, Co and Zn which occur naturally in living organisms such as grass, were less distanced from one another in two- or three-dimensional space in the case of fuzzy robust principal analysis.

This study established the degree of pollution from elements in the environment extending for 1 km in two directions from the Gdansk Phosphatic Fertilizer Plant “Fosfory” J.S.C. For future research, an expanded investigation covering greater distances from the source of pollution, extending in multiple directions into the urban area in the vicinity of the plant, is planned.

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## Appendix

(Classical) – principal component analysis (based on classical logic rules),
PCA – cluster analysis, C1 – 1st cluster, C2 – 2nd cluster, C3 – 3rd cluster, C4 – 4th cluster,
CRM – certified reference material,
E – easterly direction,
FLNP – Frank Laboratory of Neutron Physics,
FPCA – fuzzy principal components analysis (based on fuzzy logic rules),
FPCA-1 – fuzzy (first component) principal analysis,
FPCA-O – fuzzy principal components analysis (orthogonal),
IAEA – International Atomic Energy Agency,
IAEA-336 – certified reference material – lichens,
IAEA-SDM – certified reference material – lake sediment,
IAEA-SL1 – certified reference material – soil,
JINR – Joint Institute for Nuclear Research,
NAA – neutron activation analysis,
P – plant area,
PC – principal component, PC1 – 1st PC, PC2 – 2nd PC, PC3 – 3rd PC,
S – southerly direction.

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### Table 1

| Sample Location | Sample Location | Sample Location | Sample Location |
|-----------------|-----------------|-----------------|-----------------|
| 1-15 – grass samples, 17-33 – soil samples, 17 - soil collected nearby H₂SO₄ shop, 18 - soil collected nearby bagging shop, 19 - m – meters, P – plant, S – Southerly direction, industrial mean – the mean value calculated for all industrial samples, blank values taken from analysis of grass and soil samples collected in Ustka region, Poland. | 1-15 – grass samples, 17-33 – soil samples, 17 - soil collected nearby H₂SO₄ shop, 18 - soil collected nearby bagging shop, 19 - m – meters, P – plant, S – Southerly direction, industrial mean – the mean value calculated for all industrial samples, blank values taken from analysis of grass and soil samples collected in Ustka region, Poland. | 1-15 – grass samples, 17-33 – soil samples, 17 - soil collected nearby H₂SO₄ shop, 18 - soil collected nearby bagging shop, 19 - m – meters, P – plant, S – Southerly direction, industrial mean – the mean value calculated for all industrial samples, blank values taken from analysis of grass and soil samples collected in Ustka region, Poland. | 1-15 – grass samples, 17-33 – soil samples, 17 - soil collected nearby H₂SO₄ shop, 18 - soil collected nearby bagging shop, 19 - m – meters, P – plant, S – Southerly direction, industrial mean – the mean value calculated for all industrial samples, blank values taken from analysis of grass and soil samples collected in Ustka region, Poland. |
| 1 | 200 m P | 8 | 500 m S |
| 2 | 200 m P | 9 | 800 m S |
| 3 | 200 m P | 10 | 1300 m S |
| 4 | 200 m P | 11 | 300 m S |
| 5 | 200 m P | 12 | 0 m P |
| 6 | 300 m S | 13 | 0 m P |
| 7 | 400 m S | 14 | 800 m E |
| 15 | 1300 m E | 16 | grass blank |
| 22 | 200 m P | 23 | grass blank |
| 24 | 200 m P | 25 | soil blank |
| 26 | 300 m S | 27 | soil blank |
| 28 | 1300 m S | 29 | soil blank |
| 30 | 400 m E | 31 | soil blank |
| 32 | 500 m S | 33 | soil blank |
| 34 | 800 m E | 35 | soil blank |
| 36 | 1300 m E | 37 | soil blank |
| 38 | 500 m E | 39 | soil blank |
| 40 | 800 m E | 41 | soil blank |
| 42 | 1300 m E | 43 | soil blank |
| Element | Experimental results (a) | Certified value (b) | Relative bias (%) | Experimental results (a) | Certified value (b) | ||b − a|/|b|| ⋅ 100 | Experimental results (a) | Certified value (b) | ||b − a|/|b|| ⋅ 100 |
|-------|-------------------------|---------------------|------------------|-------------------------|---------------------|---------------|-------------------------|---------------------|---------------|
| Na    | 676                     | 680                 | 0.65             | 1.28·10^4               | 1.35·10^4           | 4.96          | 8.1                     | 9.3                 |
| Al    | 2.4                     | 0.5                 | 0.65             |                         |                      |               |                         |                      |
| Sc    | 7.0                     | 6.4                 | 0.65             | 7.32·10^3               | 5.17·10^3           | 41.7          | 32                      | 7.2                 |
| Cr    | 99.4                    | 104                 | 4.39             |                         |                      |               |                         |                      |
| Si    | 12                      | 8.7                 |                  |                         |                      |               |                         |                      |
| Ti    |                         |                     |                  |                         |                      |               |                         |                      |
| Cr    | 99.4                    | 104                 | 4.39             |                         |                      |               |                         |                      |
| Co    | 8.0                     | 2.5                 | 0.03             | 14.0                    | 13.6                | 0.03          | 9.0                     | 4.0                 |

Table 2: Element concentrations in Reference Materials: IAEA-336 (lichens), IAEA-SL1 (soil) and IAEA-SDM (lake sediment) [mg·kg⁻¹].
| Element | Certified | Relative bias | Certified | Relative bias | Certified | Relative bias |
|---------|-----------|---------------|-----------|---------------|-----------|---------------|
| Zn      | 32.1      | 5.56          | 30.4      | 4.04          | 32.1      | 5.56          |
| As      | 0.658     | 2.93          | 0.639     | 10.71         | 0.658     | 2.93          |
| Br      | 13.1      | 5.50          | 12.9      | 25.50         | 13.1      | 5.50          |
| Rb      | 1.56      | 20.6          | 1.97      | 10.99         | 1.56      | 20.6          |
| Sb      | 1.09      | 14.51         | 0.99      | 6.7           | 1.09      | 14.51         |
| Ba      | 5.99      | 13.68         | 6.40      | 13.68         | 5.99      | 13.68         |
| Cs      | 7.45      | 13.11         | 7.00      | 2           | 7.45      | 13.11         |
| La      | 60.6      | 6.25          | 52.6      | 15.2          | 60.6      | 6.25          |
| Ce      | 145       | 14.81         | 117       | 4           | 145       | 14.81         |
| Yb      | 1.78      | 14.31         | 1.26      | 4.5          | 1.78      | 14.31         |
| Sm      | 0.69      | 30.4          | 0.45      | 30.4          | 0.69      | 30.4          |

Table 2 (continued): Element concentrations in Reference Materials: IAEA-336 (lignites), IAEA-SL1 (soil) and IAEA-SDM (lake sediment) [mg kg⁻¹].
| Element | IAEA-336 | IAEA-SL1 | IAEA-SDM |
|---------|----------|----------|----------|
|         | Experimental results (a) | Certified value (b) | Relative bias [%] | Experimental results (a) | Certified value (b) | Relative bias [%] | Experimental results (a) | Certified value (b) | Relative bias [%] |
| Eu      | 1.07     | 1.6      | 32.9     | 36.2     | 0.5      | 7.00     | 9.25      | 4.90     |
| Sm      | 9.70     | 9.25     | 4.90     | 5.7      | 5.5      | 5.00     | 7.5       | 33.3     |
| Tb      | 1.65     | 1.4      | 17.9     | 4.2      | 0.5      | 5.00     | 7.5       | 33.3     |
| Tb      | 1.65     | 1.4      | 17.9     | 4.2      | 0.5      | 5.00     | 7.5       | 33.3     |
| Dy      | 5.00     | 7.5      | 33.3     | 4.2      | 0.5      | 5.00     | 7.5       | 33.3     |
| Hf      | 4.97     | 4.2      | 18.4     | 15.5     | 13.9     | 102      | 28.4      | 18.4     |
| Ta      | 1.75     | 1.58     | 10.8     | 5.7      | 0.5      | 5.00     | 7.5       | 33.3     |
| Th      | 0.133    | 0.14     | 5.21     | 2.8      | 1.0      | 4.62     | 4.02      | 14.9     |
| U       | 4.62     | 4.02     | 14.9     | 8.3      | 1.0      | 8.3      | 1.0       | 8.3      |

Table 2 (continued) Element concentrations in Reference Materials: IAEA-336 (lichens), IAEA-SL1 (soil) and IAEA-SDM (lake sediment) [mg·kg⁻¹].
| Element | Valid N | Mean | Median | Minimum | Maximum | Range | Deviation | Skewness | Kurtosis |
|---------|---------|------|--------|---------|---------|-------|-----------|----------|----------|
| Na      | 35      | 354  | 99.7   | 9.00    | 9.39    | 2.09  | 0.914     | 0.310    |
| Mg      | 35      | 361  | 92.0   | 9.00    | 9.18    | 1.29  | 1.710     | 3.51     |
| Al      | 35      | 459  | 70.4   | 115.0   | 57.67   | 18.83 | 1.110     | 1.60     |
| K       | 35      | 910  | 100.0  | 90.00   | 100.0   | 10.0  | 3.420     | 15.80    |
| Sc      | 35      | 1   | 0.5    | 0.00    | 0.50    | 0.5   | 1.520     | 1.630    |
| Ca      | 35      | 466  | 100.0  | 20.00   | 200.0   | 190.0 | 4.200     | 20.70    |
| Cr      | 35      | 1    | 0.3    | 0.05    | 0.30    | 0.25  | 1.300     | 0.349    |
| Ti      | 35      | 297  | 100.0  | 1.50    | 14.39   | 12.89 | 2.290     | 5.920    |
| V       | 35      | 2    | 0.3    | 0.030   | 0.300   | 0.27  | 2.400     | 7.250    |
| Mn      | 35      | 222  | 100.0  | 26.68   | 843.9   | 817.2 | 1.520     | 2.710    |
| Ni      | 35      | 8.5  | 0.15   | 100.8   | 100.6   | 24.96 | 2.200     | 4.740    |
| Fe      | 35      | 9    | 6.02  | 102.66  | 102.0   | 12.40 | 1.700     | 2.450    |
| Co      | 35      | 1   | 0.003  | 68.5    | 68.5    | 14.60 | 3.230     | 10.700   |
| Zn      | 35      | 83   | 5.146  | 2170.0  | 2164.9  | 434.25| 2.640     | 8.310    |
| Se      | 35      | 1   | 0.003  | 16.5    | 16.5    | 3.43  | 3.060     | 10.000   |
| As      | 35      | 19   | 0.045  | 191.4   | 191.4   | 38.64 | 3.370     | 12.400   |
| Br      | 35      | 1   | 0.720  | 165.6   | 164.9   | 27.15 | 5.620     | 32.600   |
| Sr      | 35      | 1   | 0.400  | 896.5   | 896.1   | 233.34| 2.010     | 3.630    |
| Rb      | 35      | 28   | 4.090  | 83.20   | 79.10   | 20.45 | 0.749     | 0.260    |

**Table 3** Data statistics.
| Variable | Valid N | Mean [mg·kg⁻¹] | Median [mg·kg⁻¹] | Minimum [mg·kg⁻¹] | Maximum [mg·kg⁻¹] | Range [mg·kg⁻¹] | Deviation [mg·kg⁻¹] | Skewness | Kurtosis |
|----------|---------|----------------|------------------|------------------|------------------|----------------|---------------------|----------|----------|
| Mo       | 35      | 5.22           | 4.53             | 0.121            | 16.3             | 4.33           | 1.14                | 0.828    |
| Ag       | 35      | 1.12           | 0.19             | 0.002            | 25.1             | 25.1           | 4.22                | 5.70     | 33.1     |
| Sb       | 35      | 1.72           | 1.13             | 0.027            | 7.9              | 7.9            | 1.93                | 1.53     | 2.04     |
| I        | 35      | 4.83           | 2.02             | 0.050            | 41.8             | 41.8           | 8.15                | 3.28     | 12.7     |
| Ba       | 35      | 202.96         | 95.49            | 0.150            | 603.9            | 603.8          | 204.75              | 0.84     | -1.06    |
| Cs       | 35      | 0.81           | 0.56             | 0.022            | 3.7              | 3.7            | 0.88                | 1.82     | 3.38     |
| La       | 35      | 18.15          | 6.61             | 0.001            | 87.0             | 87.0           | 23.39               | 1.63     | 2.25     |
| Ce       | 35      | 24.97          | 4.47             | 0.010            | 233.4            | 233.4          | 43.03               | 3.60     | 16.3     |
| Eu       | 35      | 0.22           | 0.13             | 0.005            | 2.1              | 2.1            | 0.37                | 4.02     | 19.8     |
| Sm       | 35      | 2.82           | 1.07             | 0.011            | 15.5             | 15.4           | 3.60                | 1.76     | 3.19     |
| Tb       | 35      | 0.40           | 0.21             | 0.000            | 3.1              | 3.1            | 0.60                | 3.04     | 11.9     |
| Dy       | 35      | 3.11           | 0.88             | 0.010            | 20.4             | 20.4           | 4.49                | 2.09     | 5.27     |
| Yb       | 35      | 0.71           | 0.27             | 0.005            | 4.4              | 4.4            | 1.01                | 1.98     | 4.18     |
| Hf       | 35      | 1.64           | 1.01             | 0.001            | 10.6             | 10.6           | 2.13                | 2.38     | 8.20     |
| Ta       | 35      | 0.27           | 0.14             | 0.000            | 2.1              | 2.1            | 0.40                | 3.03     | 11.9     |
| W        | 35      | 0.77           | 0.27             | 0.018            | 3.8              | 3.8            | 1.07                | 1.63     | 1.71     |
| Th       | 35      | 2.21           | 1.43             | 0.006            | 11.0             | 11.0           | 2.66                | 1.52     | 2.18     |
| U        | 35      | 6.48           | 1.89             | 0.006            | 67.9             | 67.9           | 12.44               | 3.88     | 17.9     |

Table 3 (continued) Data statistics.
Table 4. Table of components.

| Principal Component | Eigenvalue | Proportion | Cumulative Eigenvalue | Proportion | Cumulative | Proportion | Cumulative | Proportion | Cumulative |
|---------------------|------------|------------|-----------------------|------------|------------|------------|------------|------------|------------|
| PCA-1               | 1.841      | 0.463      | 0.463                 | 0.322      | 0.785      | 0.685      | 0.971      | 0.096      | 0.867      |
| PCA-2               | 1.736      | 0.429      | 0.932                 | 1.603      | 0.812      | 1.485      | 2.757      | 0.091      | 0.959      |
| PCA-3               | 1.681      | 0.415      | 1.347                 | 1.584      | 0.797      | 2.231      | 4.338      | 0.090      | 0.949      |
| PCA-4               | 1.588      | 0.402      | 1.755                 | 1.754      | 0.800      | 3.034      | 6.382      | 0.091      | 0.938      |
| PCA-5               | 1.536      | 0.395      | 2.150                 | 1.955      | 0.802      | 4.839      | 7.227      | 0.088      | 0.926      |

Note: The table provides the eigenvalues and their cumulative proportions for principal components PCA-1 to PCA-5.
|                | Na      | Al  | K     | Sc     | Ca     | Cr     | Ti     | V     | Mn     | Ni     |
|----------------|---------|-----|-------|--------|--------|--------|--------|-------|--------|--------|
| Phosphate rock | 5.4·10^3\text{a} | -   | 580    | 8.7\text{a} | 32\%\text{a} | 291\text{a} | -      | -     | -      | -      |
|                | 1·10^4\text{b} | -   | 1.6·10^3\text{b} | 3.8\text{b} | 33\%\text{b} | 161\text{b} | -      | -     | -      | -      |
| Fertilizers \text{1,2} | 334-7·10^3 | 0.057-11\% | 0.41-8.7 | 0.29-3.7\% | 8.6-220 | -      | -     | -     | -      | -      |
|                | -       | -   | 0.50-0.72 | -       | 190    | 61-110 | 3.4-3.6 | 197   | 44     |        |
| Triple superphosphate \text{3} | -       | -   | 0.12-0.65 | -       | 32-111 | 16-197 | 45-347 | 67-248 | 27-36  |        |
| NP compounds \text{3} | -       | -   | 1.1-1.5 | -       | 22-34  | <0.20  | -      | 17-42 |        |        |
| Phosphogypsum \text{4,5} | -       | -   | -      | 0.08-5.00 \text{c} | 5.0-1·10^{3} | <1.0   | 3.0-230 | 200-3-10^3 | 1.0-200 | -      |
| Soil. Usual range \text{2,3,6} | - 0.45-10\% | -   | 20-500 | 0.18-6.5 \text{d} | 2.0-39 \text{c} | 80-2.4-10^{4} | 2.0-38 \text{c} | 200-3-10^{3} | 2.0-26 \text{c} | -      |
| Grass. Usual range \text{2} | - 10-1000 | -   | -      | 2.0-5.0 \text{c} | 5.0-1·10^{3} | -      | 50-100 | 37-1.1-10^{3}\text{c} | 5.0-500 | -      |

\text{\textsuperscript{a}}phosphorites from Morocco, \text{\textsuperscript{b}}phosphorites from Tunis, \text{\textsuperscript{c}}Sandy soils, \text{\textsuperscript{d}}Loamy soils

\text{\textsuperscript{1}[2]; \textsuperscript{2}[23]; \textsuperscript{3}[3]; \textsuperscript{4}[6]; \textsuperscript{5}[5]; \textsuperscript{6}[24]}

**Table 5** Range of trace element contents [mg·kg\(^{-1}\)] of previously investigated fertilizers and usual ranges found in soil and grass.
Table 5 (continued) Range of trace element contents \([\text{mg kg}^{-1}]\) of previously investigated fertilizers and usual ranges found in soil and grass.

| Trace Element | Soil, usual range | Grass, usual range |
|---------------|------------------|-------------------|
| Fe            | 2.0-4.0          | 2.0-21            |
| Cu            | 2.0-6.0          | 0.10-1.0          |
| Ni            | 0.01-1.0         | 0.001-0.5         |
| Pb            | 0.01-0.2         | 0.0005-0.05       |
| Zn            | 2.0-4.0          | 2.0-21            |
| Cr            | 0.10-1.0         | 0.10-1.0          |
| Cd            | 0.001-0.01       | 0.0001-0.01       |
| Mn            | 1.0-3.0          | 0.10-0.3          |
| Co            | 0.01-0.1         | 0.001-0.05        |
| As            | 0.10-1.0         | 0.10-1.0          |
| Se            | 0.01-0.1         | 0.001-0.01        |
| Re            | 0.001-0.01       | 0.0001-0.001      |
| Mo            | 0.01-0.1         | 0.001-0.05        |

*Prophorites from Morocco, phosphorites from Tunis, sandy soils, sandy soils with high contents of Fe, sandy soils with high contents of Zn, sandy soils with high contents of Cr, sandy soils with high contents of Cd, sandy soils with high contents of Cu, sandy soils with high contents of Mn, sandy soils with high contents of Co, sandy soils with high contents of As.
|                          | Ba  | Cs  | La  | Eu  | Sm  | Tb  | Yb  | W   | Th  | U   |
|--------------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| **Phosphate rock**       |     |     |     |     |     |     |     |     |     |     |
|                          |     | 109 | 3.9 | 13  | 2.3 | 14  |     | 3.4 | 127 |     |
|                          |     | 100 | 8.8 | 15  | 1.6 | 8.5 | 1.4 | 8.5 | 32  |     |
| **Fertilizers**          |     |     |     |     |     |     |     |     |     |     |
|                          |     |     |     |     |     |     |     |     |     |     |
|                          |     |     | 10-506 | 0.23-10 | 1.0-32 |     | 0.60-5.7 |     | 0.44-6.0 | 3.5-149 |
|                          |     |     |     |     |     |     |     |     |     |     |
| **Triple superphosphate**|     |     |     |     |     |     |     |     |     |     |
|                          |     |     |     |     |     |     |     |     |     |     |
|                          |     |     |     |     |     |     |     |     |     |     |
|                          |     |     |     |     |     |     |     |     |     |     |
| **NP compounds**         |     |     |     |     |     |     |     |     |     |     |
|                          |     |     |     |     |     |     |     |     |     |     |
|                          |     |     |     |     |     |     |     |     |     |     |
| **Phosphogypsum**        |     |     |     |     |     |     |     |     |     |     |
|                          |     |     |     |     |     |     |     |     |     |     |
|                          |     |     |     |     |     |     |     |     |     |     |
| **Soil. Usual range**    |     |     |     |     |     |     |     |     |     |     |
|                          |     |     |     |     |     |     |     |     |     |     |
|                          |     |     |     |     |     |     |     |     |     |     |
| **Grass. Usual range**   |     |     |     |     |     |     |     |     |     |     |
|                          |     |     |     |     |     |     |     |     |     |     |

Table 5 (continued) Range of trace element contents [mg·kg⁻¹] of previously investigated fertilizers and usual ranges found in soil and grass.

\(^a\) phosphorites from Morocco, \(^b\) phosphorites from Tunis, \(^c\) Sandy soils, \(^d\) Loamy soils

\(^1\)[2]; \(^2\)[23]; \(^3\)[3]; \(^4\)[6]; \(^5\)[5]; \(^6\)[24]