Mathematical and Chemometrical Models – Tools to Evaluate Heavy Metals Contamination

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Abstract

The aim of the this study is to present a combined view of bio – geo - chemistry, soil – plant interactions, mathematic models and statistic analysis, based on the correlation between the levels of soil contamination, and the remanence of polluting substances in soil and respectively in harvested fruits and vegetables. Most of the mathematical models which describe plant - soil interactions are integrated in plant growth models or climate change models. The models presented by this paper are Soil – Plant Interaction Models, Pollution Indices, The Indices for Evaluating the Adaptative Strategies of Plants and Chemo-metrical Methods, and they have the role to synthesize and evaluate the information regarding heavy metals contamination.

Keywords: Fingerprint, Freundlich-Like Equation, Pedotransfer Functions, Plant – Soil Interaction, TU Method

1. Introduction

The risks of heavy metal transfer from soil to plant and from there to the consumer are dependent on the mobility of the heavy metal species and their accessibility in the soil [1]. The risks connected to polluted soils are contamination of the food chain and they are directly associated to the bioavailability of toxic elements [2]. The bioavailability of heavy metals in soil [3] for a specific plant depends on soil properties, plant characteristics and capacity of accumulation and other influencing environmental factors. In time, many analytical methods were developed, to appreciate and estimate the heavy metals concentration in soil and plants [4]. The most important factors which need to be taken into consideration are: soil characteristics [5], floristic and development stage of plants [4] and the interrelationship soil - plants [6]. Diverse types of soil vary in microstructure, biotic influence and patterns of water movement through the soil profile [7]. The characteristics of the ions determine the strength of adsorption and conditions of desorption. The ions concentration in the soil solution is maintained by the buffering capacity of the soil which depends on cation exchange capacity and soil organic matter. Therefore, the amount of clay minerals and humus will decide the extent of buffering [8]. Plants heavy metals uptake is done by the roots and by the leaves. The dominant nutrition is considered as the one done by the roots and because of that the highest amount of heavy metals under the form of ions is absorbed by the roots. The absorption by roots is a process of ion exchange at the cell surface characterized by selectivity (certain ions are taken up preferentially), accumulation (in the plant cell the concentration of elements can

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become higher than in the external solution) and genotype (there are significant differences between plant species in ion uptake characteristics) [8]. To approximate the concentration of heavy metals in soil, pore water analysis and chemical extraction, a variety of chemical analytical methods have been developed [9]. Nevertheless, chemical analysis is slow and very costly. Heavy metals and soil/sediment parameters usually have complicated relationships among them [10]. To investigate the relationship between metals and the characteristics in soil/sediment, and soil – plant interactions different mathematical and/or chemometrical models were created to interpret the complexity of processes.

2. Materials and methods

For the development of the present study, well over hundreds of scientific researches were analyzed in the field of geochemistry, biology, agriculture, environmental sciences, mathematics and statistics in order to conduct a brief literature review on mathematical and chemo-metrical models to evaluate the study of heavy metals contamination. The images were created by using own experimental data in order to present the models. The chemometrical models were performed using PAST 3.06 and MVSP 3.22 software.

3. Results and discussion

The use of models depends on the easiness to control them and the structured information they offer. Some of the most important mathematical models used to describe soil – plant interaction and to help interpret heavy metals transfer from soil to plants are presented in Table 1. Chemometrical methods combine mathematical methods with chemical data and are used to solve both descriptive and predictive problems in investigational life sciences.

In soil science, using data from soil surveys **Pedotransfer Functions (PTF)** are predictive functions of certain soil properties. To create the PTF model are needed geospatial data (topography, management practices etc) associated with measured chemo-physical data and mathematical models. The pedotransfer concept (PTFs) can be applied to any soil attribute and due to this the development of PTFs for modeling biogeochemical processes becomes essential [11]. The most common method used for PTFs assessment is to utilize multiple linear regressions like equation (1). Because equations which show PTF relationships are unknown, a trend has emerged: e.g., artificial neural networks, combined mathematical models, support vector machines, clusters, decision trees, which are flexible enough to simulate highly nonlinear dependences hidden in analyzed data, but comes with a large number of coefficients that are difficult to estimate. Due to the fact that pedotransfer functions describe empirical regression type relationships, their precision outside their development region is unknown [12]. The elemental idea of PTFs may be widely extended to involve the derivation of any required soil aspect, which is not directly accessible, derived from available soils data [13].

The Freundlich-Like Equation known also as Freundlich adsorption isotherm or Freundlich adsorption equation describes the transfer of inorganic ions from soil solutions to plants and the uptake of contaminants by plants. The transfer of inorganic ions from soil solutions to plants might be interpreted as a biosorption process, where a Freundlich-like equation can be used to illustrate the uptake of contaminants by plants [14].

The Toxic Unit (TU) Method is used to evaluate the response addition model for the pollutant mixtures to estimate the combined effects of metals in plant systems- equation (3) called also TU model equation. The quotient ($\frac{c_i}{ECx_i}$) is generally termed as the TU of that component. The concentrations of individual metal tests may be transformed into Toxic Units using equation (4). EC_{50} refers to the molar concentration of an agonist (contaminant, drug etc), which produces 50% of the maximum response after a particular exposure time [15]. In the case of mixed heavy metals TU values were calculated using TU model equation where: n is the number of heavy metals; c_i is the concentration of an individual heavy metal in the mixture; ECx_i is the concentration of the ith mixture component that causes x% effect [16].

The Pollution Indices to better understand toxic concentrations of metals, calculated for soils, roots and aerial parts are presented in Table 1(B). The soil pollution index (*SPI*) and plant pollution index (*PPI*) calculated for different locations according to the equations (6 and 7) reported to the threshold values can be used to evaluate spatial distribution and their intrinsic properties using Single and multiple regression analyses and additional statistical methods [17].

The Indices for Evaluating the Adaptative Strategies of Plants (Table 1. C) are based on one of the three adaptive strategies: exclusion, indication, and accumulation [18] developed by plants growing in highly mineralized soils, based on the characteristic that they cannot restrict metal uptake but they can adapt and rather tolerate metal enriched zones. The mathematical relationships which are able to present the adaptative behaviors of plants growing in highly mineralized soils are: Bioconcentration Factor (BCF) which helps in identifying plants that sequester metals in roots, Translocation Factor (TF) which proves the indication strategy meaning equilibrium achievement between soil and shoot metal concentrations and Biological Accumulation Coefficient (BAC) which reveals the heavy metals accumulated in the aerial parts. Excluders maintain low shoot concentrations of metals over soil concentrations that range from unpolluted to polluted, indicators maintain the internal metal concentrations that are reflective of external conditions and accumulators concentrate metals in aerial parts in soils with either high or low metal concentrations. BCF shows the concentration of a metal contained in the roots of a plant divided by the concentration of that metal contained in the soils that the roots inhabit.

Chemometrics is considered to be the science of extracting information from chemical systems using multivariate analysis and applied mathematics to solve both descriptive and predictive problems in investigational life sciences. The chemo-metrical methods use linear algebra to formulate either quantitative or qualitative measurements of chemical data applied in exploratory analysis using investigative algorithms like: principal component analysis (PCA), principal component regression (PCR), partial least squares (PLS) and classification models like: cluster analysis, K-nearest neighbor (k-NN) [19] and or generalized linear models etc. In this context figure 1 presents the graphical representation of PCA, respectively pattern recognition (fingerprint) based on soils heavy metals concentration.

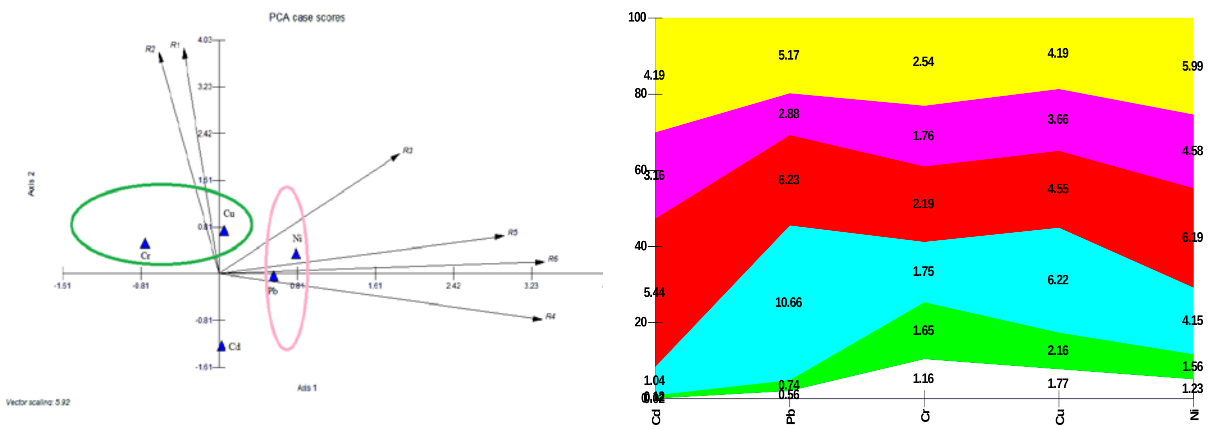
PCA and PCO are chemo-metric techniques used to find the patterns of heavy metals data in different environmental samples, based on heavy metals concentrations [20]. PCA algorithm finds the eigenvalues and eigenvectors of the variance-covariance matrix or the correlation matrix [21-23]. For example in figure 1 (A), by analyzing heavy metals soil concentrations using PCA we can easily identify two clusters: one is formed by R1 and R2, both location being characterized by higher concentrations of copper and chromium and cluster two, described by R3, R4, R5, R6 with higher concentration of nickel and lead. Cadmium concentration is similar to all investigated samples.

Chemical fingerprinting might be defined as a unique set of properties of the source material that can be used to distinguish it from other materials and whose traits are preserved in such a way that its main characteristics are still recognizable. Figure 1 (B) presents a fingerprint based on chemical data using MVSP software. Chemical pattern recognition, chemometric evaluation for evaluating figerprints and multivariate analysis as well as mathematical modeling all can be used as modern tools of quality control [22, 24]. Most applications of chemometric methods focus on establishing correlations between different pollutants and environmental parameters [25-27] determining geographical origin of investigated samples [28], quality of soil and water [29], quality of environment in general [30], modeling of heavy metals contaminants [24,31], or authentication of organic food [22].

PCA and CA correlation analysis allows highlighting mineralogical components specific to each plant species and country, separately, and permits the identification of the declared origins of used species and varieties [32]. Application of PCA for analyzing different environmental data can offer optimization of analytical procedures by selecting for analysis only the variables with maximum involvement in pollution assessment, and thus reduction of the analytical costs; differencing among polluted areas and types of contamination, based on soil analyses; selection of plant species which the highest or lowest accumulation of contaminants [22];

Table 1. Soil – Plant Interaction Mathematical Models

A. Soil – Plant Interaction Models		
The Pedotransfer Function Model [11, 12, 13]	**Freundlich-Like Equation Model [5,14]**	**The Toxic Unit Method [16, 33]**
$Y = aX_1 + bX_2 + cX_3 + \ldots$ (1)	$Q_p = k \cdot \frac{C_{s1}}{n}$ (2)	$\sum TU_i = \sum_{i=1}^{n} \frac{c_i}{ECx_i}$ (3) $TU = \frac{[Me]}{EC_{50}}$ (4)
where: Y - a depended variable; X_n - independent variable; a,b, c,…. - coefficients.	where: Q_p – Contaminant concentration in plants (mg·kg−1); C_{s1} – Concentration of soil contaminants (mg·kg−1); k - Sorption capacity (a superior K indicates a higher capacity), $1/n$ - indicator of the strength of sorption;	where: n – the number of mixture components; c_i – the concentration of an individual component in the mixture; ECx_i - is the conc. of the Ith mixture component that causes x% effect; $[Me]$ – metal concentration EC_{50} – half maximal effective conc.;
B. Calculation of Pollution Indices [17]		
Soil-Plant Transfer Coefficient	**Plant Pollution Index**	**Soil Pollution Index**
$TC = \frac{[Me]_{plant}}{[Me]_{soil}}$ (5)	$PPI = \frac{1}{n} \cdot \sum_{i=1}^{n} 100 \cdot \frac{VP_i}{LP}$ (6)	$SPI = \frac{1}{n} \cdot \sum_{i=1}^{n} 100 \cdot \frac{VS_i}{LS}$ (7)
where: $[Me]_{plant}$ – metal concentration in plant (mg·kg−1); $[Me]_{soil}$ - metal concentration in soil (mg·kg−1);	where: PPI - Plant pollution index n - Number of elements VP - Content of an element (heavy metals - HMe) in the plant, (mg·kg−1); LP - Limit values for an element (HMe) in the plant, (mg·kg−1);	where: SPI - Soil pollution index n - Number of elements (HMe) VS - Content of an element (HMe) in the soil, (mg·kg−1); LS - Limit values for an element (HMe) in the soil, (mg·kg−1);
C. Calculation of Plants Behavior Factors		
Bioconcentration Factor [18,33]	**Translocation Factor [33]**	**Biological Accumulation Coefficient [18]**
$BCF = \frac{[Me]_{roots}}{[Me]_{soil}}$ (8)	$TF = \frac{[Me]_{shoot}}{[Me]_{roots}}$ (9)	$BAC = \frac{[Me]_{shoots}}{[Me]_{soil}}$ (10)
where: $[Me]_{roots}$ – concentration of a metal contained in the roots of a plant; $[Me]_{soil}$ – concentration of that metal contained in the soils that the roots inhabit	where: $[Me]_{shoot}$ – concentration of a metal contained in a plant's shoots; $[Me]_{roots}$ – concentration of that metal contained in the plant's roots;	where: $[Me]_{shoots}$ – concentration of a metal contained in a plant's shoots; $[Me]_{soil}$ – concentration of that metal contained in the soil that the roots inhabit;
BCF values >1, illustrate that a plant can accumulate metals in its roots at higher concentrations than does the soil in which it resides [18, 33].	TF shows the ratio between soil and shoot metal concentrations [33]	BAC presents the level of heavy metals accumulated in the aerial parts [18, 33].



A. PCA representations of HMe concentrations B. Pattern identification based on HMe fingerprint

Figure 1. Graphical representation of chemometrical methods applied to soil HMe concentration data

Legend: R1, R2, R3, R4, R5, R6 = collection sites of soils

Generalized linear models (GLMs) are a large class of statistical models for relating responses to linear combinations of predictor variables [34].

4. Conclusions

Mathematical or chemo-metrical models are developed to reduce the complexity of soil – plant interactions and to simplify the interpretation of phenomena. The presented methods measure the possible response of plants to contaminants and to estimate the combined effects of metals in plant systems (TU method). The application of chemo-metrical methods permits an overall assessment of the interaction of the contaminants in the environment, as well as the health risk associated with their consumption. PCA may be used for reduction of the data set to only two variables (the two first components), for plotting purposes. Mineral composition based fingerprint can be used as vegetal products quality markers for the producers, as well as for the food processing industries.

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