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OPEN

DOI: 10.2478/ssa-2014-0010

SOIL SCIENCE ANNUAL
Vol. 65 No. 2/2014: 65–71

REVIEW PAPER

AGNIESZKA JESKE*

Institute of Environmental Protection-National Research Institute, Krucza 5/11, 00-548, Warsaw, Poland

Use of innovative and advanced computer simulations of chemical speciation of heavy metals in soils and other environmental samples

Abstract: The article presents several aspects of computer simulations and models of heavy metals speciation in environmental samples. The methods can be effectively used in environmental sciences, soil science, and assessment of mobility and bioavailability of heavy metals in contaminated areas. The article presents all of the methods based on examples, and with interpretation of results. The effect depends on the reliability of data used in models. The results are essential for predicting the fate and behaviour of elements in the environment, and can also be used to develop solubility curves.

Key words: chemical speciation, computer simulation, models, metals

INTRODUCTION

Modelling methods have been applied in the assessment of environmental risk (Risk Assessment-RA) related to heavy metals and a number of substances and chemical preparations or crop protection chemicals for years. Models are also used for the Life Cycle Assessment (LCA) of many products (Pizzol et al. 2012). Traditional methods of sequential analysis involve the consecutive extraction of the same sample with selectively working reagents. This permits the identification and quantitative determination of the fraction of a given element. The currently used methods of sequential analysis are subject to numerous modifications, or the approach of so-called hybrid sequential analysis is applied. It involves the separation and determination of the content of the analyte, or the entire group of analytes in an environmental sample with the application of techniques such as gas and liquid chromatography or capillary electrophoresis. Advanced software with varied applications in the analysis of environmental samples has been globally used in recent years.

The objective of the article was to present selected advanced speciation analysis computer software (among others MINEQL, SOILCHEM, MINTEQA2, PHREEQC-2, etc.) particularly used for speciation of heavy metals in environmental samples, as well as to present its practical application in scientific studies. The replacement of traditional analytical methods with digital methods has a significant economic and environmental aspect. The application of models also enriches the already existing studies with additional information necessary for environmental risk assessment.

METODS AND MODELS USED IN SOIL AND ENVIRONMENTAL SCIENCES

According to the definition by IUPAC, speciation studies involve the identification and/or measurement of the content of one or more chemical forms of a given metal in a sample. Speciation is defined as the determination of specific forms of occurrence of a given element (Rogan et al. 2008; Rastmanesh et al. 2010; Rutkowska et al. 2013). The determination of the current and potential bioavailability or mobility requires the distinguishing and determination of forms or fractions of heavy metals. This is particularly important in the case of contaminated soils. Predicting the behaviour of elements in the environment is based on the understanding of processes occurring in soils, and the knowledge of the existing relations. Therefore, in addition to the geochemical properties of a given element, the examination and analysis of fractions of selected elements should also consider the basic properties of soils (reaction, grain structure, content of organic carbon, content of carbonates, and structure and volume of the sorption complex), the type of soils, and binding of heavy metals with soil components

* agnieszka.jeske@ios.edu.pl

such as: organic matter, iron and manganese oxides, carbonates, phosphates, sulphates, and primary and secondary minerals.

The application of computer software in the speciation analysis of heavy metals in soil, water, or sediment samples aims at the development of models describing phenomena occurring in the environment by means of statistical, mathematical, or graphic methods. Such models are developed based on actual or simplified data which must be defined in detail, and described in controlled conditions. Models most commonly applied in soil sciences are the Langmuir and Freundlich models, used for the analysis of the phenomenon of sorption of contaminants in soils (Kowalkowski and Buszewski 1999; Lumsdon and Evans 2002; Vithanage et al. 2013). The majority of speciation methods are based on the assumption of thermodynamic balance between phases. The models additionally apply electrostatic forces affecting binding of metal ions in soils. The models can describe phenomena such as among others the intake of nutrients by plants, the accumulation of heavy metals and radionuclides in soils and sediments, transport of pollutants with the colloidal fraction of soils and sediments (e.g. surface runoff), or development of complex compounds with fulvic acids (Lumsdon and Evans 2000; Zachara et al. 1989; Davis and Kent 1990; Sposito et al. 1983, Sposito and Coves 1988; Goldberg et al. 2005). According to the division by Bonazountas (1986), models describing soil quality are composed of two parts:

- ***the deterministic part***, including the characteristic (module) of the studied medium, and involving the simulation of chemical reactions responsible for specific chemical composition of the analysed sample, considering e.g. hydrological cycles, cycle of elements in systems, e.g. soil-soil solution-water, plants;
- ***the stochastic part***, aimed at the prediction of routes of exposure (transport, mobility) of the studied compounds/metals/pollutants, soil transformations, or the degree of contamination and quality e.g. of soils occurring in the study area.

Research regarding computer speciation of elements in environmental samples commenced in the 1960's. One of the first programs proposed in the scope was COMICS (Perrin and Sayce 1967). In the following years, a number of new programs were developed, such as e.g. REDEQL (Morel and Morgan 1972), SIAS (Fardy and Sylva 1978), TITRATOR (Cabaniss 1987), SOILCHEM, and its modification – GEOCHEM (Mattigod and Sposito 1979; Sposito and Coves 1988). Since the development of the first computer software for heavy metal speciation analysis, a number of new models and programs appeared, permitting the description of phenomena occurring in the soil, such as mobility of heavy metals in soils, and their interactions with iron oxides or organic compounds. An example of such software is MINTEQA2, a geochemical equilibrium speciation model used for the calculation of the equilibrium composition of solutions in laboratory or field conditions. The program includes a complex database permitting defining appropriate data for the model. The model also applies data predefined by the program, such as: the content of Na^+ ions or $H_4SiO_4{}^0$ complexes (Allison et al. 1999). The model includes more than 1000 values of ion or particle forms which can develop heavy metals. Similarly as traditional methods applied in soil and environmental sciences, programs and models for speciation analysis are continuously modified. For example, MINTEQA2 version 4.0 has a Gauss model competitive towards the previous versions of the model, permitting the description of the phenomenon of complexation of heavy metals with organic matter (Allison et al. 1999). Speciation calculations can be performed under the condition of the determination of not only the analytical concentrations of heavy metals, but also pH, temperature, and redox potential.

pH and temperature values are used for the calculation of the ionic strength of a soil solution, ionic activity coefficients, and solution components (Winid 2013). Then, according to Winid (2013), molar activities and concentrations of complex compounds are calculated. This permits the determination of forms of elements and their percent contribution and activity in the studied medium (water, soil solution). The base values for calculations used in computer programs are obtained from data bases. Like in any model, the selection of the relevant data base has the decisive influence of the final results. It should be remembered that output data selected for the model must be credible and coherent. Data bases of the existing programs also differ from one another. This should be considered in the selection of the appropriate speciation analysis software. It should be emphasised that one computer program can apply a number of models (for example combined: diffusion layer model, triple layer model, etc.), simulating the complex conditions of the environmental conditions. Models included in a computer program develop the so-called "geochemical speciation code" (Kowalkowski and Buszewski 1999; Falc 1991). Modern models can be used for predicting the fate and behaviour of elements in soils, waters, or sediments based on the occurring forms and their binding with organic matter, iron and manganese oxides and hydroxides, and clay minerals (Goldberg et al. 2005). The table below presents selected programs and models with their application (Table).

TABLE. Selected computer programs and models used in the speciation analysis of environmental samples

Program Program	Przykładowe zastosowanie programów i modeli Example use of speciation programs and models	Źródło References
SOILCHEM	Speciation of heavy metals in soils, complexation reactions (among others heavy metals-fulvic acids), determination of the chemical equilibrium of soil solutions	Sposito and Coves 1988
GECOHEM	Speciation of heavy metals in soil solutions and other natural water systems	Sposito and Mattigod 1980
PHREEQE	Reactions of complexation with organic matter	Falc 1991 Crawford 1996
HYDRAQL	Determination of chemical equilibrium in water samples, complexation and adsorption of ions at phase boundaries	Papelis et al. 1988
MINTEQA2/ PRODEFA2	Speciation of heavy metals in soils, sediments (geochemical modelling)	Allison et al. 1999 EPA 1999
ECOSAT	Speciation of all elements in soils and waters (determination of among others gas, complex, mineral, and organic forms) Mobility of elements in the water-soil system	Keizer 1991
DDLM	Models of complexation of heavy metals with organic matter and hydrated iron hydroxides	Dzombak and Morel, 1990 Vithanage et al. 2013
TRANQL (MICROQL, ISOQUAD)	Simulation of transport of ions/forms, e.g. Cd in groundwaters, and surface complexation reactions	Cedeberg et al. 1985
UNSATCHEM	Simulation of transport of ions, assessment of the mobility of heavy metals in soils	Goldberg et al. 2005
ECCLES	Models of speciation of heavy metals in biological samples	Wesley et al. 2012
GEOSURF	Models of adsorption on mineral surfaces	Sahai and Sverjensky 1998

PRACTICAL USE OF COMPUTER PROGRAMS FOR SPECIATION OF ELEMENTS IN ENVIRONMENTAL SAMPLES

The application of computer programs and modelling in environmental sciences permits the assessment of the quality of the environment. Consequently, it also permits the assessment of the risk of exposure of people resulting from the toxic or cancerogenic properties of heavy metals. It can constitute an important element of the decision making process and adopting of strategies in the case of the existing threat to human health and life resulting from e.g. emission, or release of heavy metals to the environment. Five basic categories of application of models in environmental sciences are generally distinguished:

1. **Emission models** are used for the estimation of the release of pollutants to the environment (washing out of waste dumps, air pollution);
2. **Fate models** are used for the estimation of predicted concentrations/contents of pollutants in the studied medium (e.g. fate and behaviour of heavy metals in soils, groundwaters, or surface waters);
3. **Exposure models** are used for the analysis of routes of exposure, e.g. by inhalation, and the determination of predicted environmental concentrations;
4. **Risk models** are also known as models of determination of the dose-response relationships (e.g. in the assessment of environmental risk resulting from the application of crop protection chemicals), used in the human health risk assessment by the extrapolation of data from toxicity and ecotoxicity tests for animals;
5. **Cost/efficiency models** are used for health risk reduction by the application of corrective measures (e.g. phytoremediation and mycoremediation of soils) (Bonazountas 1986; Jóźwiak 2013).

The following diagram presents a simplified procedure of selection of computer programs and mathematical models for speciation analyses of heavy metals (Figure).

The following is a review of practical applications of speciation methods involving the use of models and computer programs in environmental samples. Goldberg et al. (2005) studied the mobility and adsorption of boron in soils with varying grain structure. The assessment of the mobility and binding

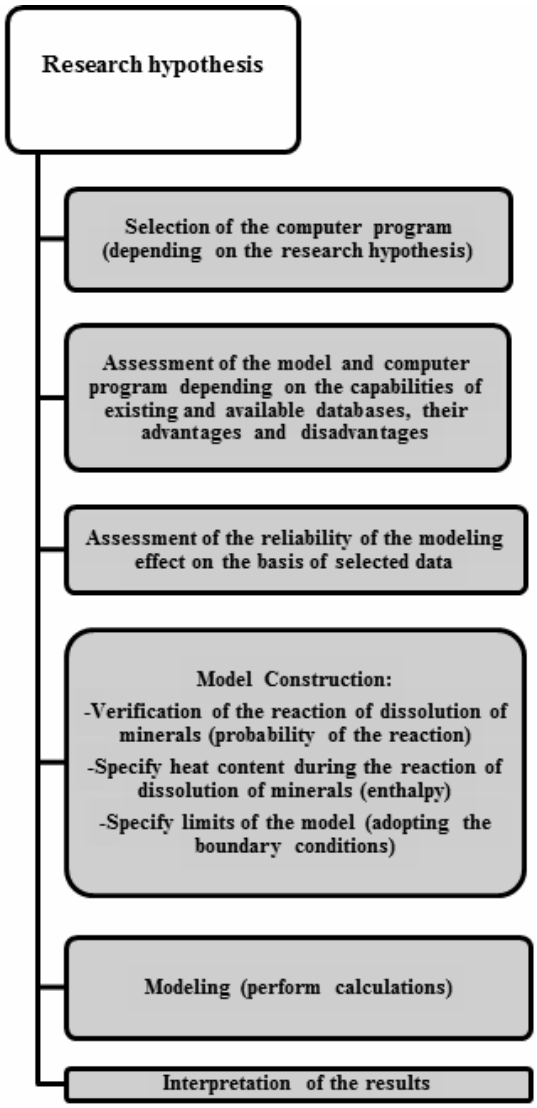

FIGURE. Procedure for the selection of computer software and models for speciation of heavy metals in environmental samples (after Jóźwiak 2013)

of the element in the studied soils was performed with the application of FITEQL version 3.2 and among others model UNSATCHEM. The application of the computer program allowed the authors to evidence that the adsorption of boron increased along with an increase in pH, reaching the maximum at pH=9. The analysis of the adsorption of the element was possible due to the determination of the constants of the surface complexation equilibrium. The phenomenon of copper adsorption on mineral surfaces was observed by Sahai and Sverjensky (1998) with the application of the GEOSURF software. The program was developed based on programs such as MINEQL, MICROQL, or HYDRAQL. According to the authors, the program permits effective analyses of samples with vary diverse chemical compositions, and in the case of redox reactions and surface complexation reactions, problematic in traditional methods.

Smal (1999) analysed among others the effect of acidification on the distribution of ionic forms in soil solutions of light soils with the application of the SOILCHEM software. The program permitted the presentation of the speciation of divalent and trivalent elements, whereas the main forms of particular elements were presented, e.g. iron-sulphate complexes ($Fe\text{-}SO_4$) with no consideration of other forms (e.g. $FeSO_{4+,}$ $Fe(SO_{4+})_2^-$). The application of the SOILCHEM software permitted the presentation of the detailed percent distribution in soil solutions in soil profiles of elements such as: lead(II), cadmium, copper(II), zinc, iron(III), aluminium, manganese(II), magnesium, and calcium (Smal 1999).

The speciation of cadmium and copper with the application of the Visual MINTEQ software was performed by Rathnayake et al. (2013). The authors analysed the effect of the content of Cu and Cd on the growth and development of bacteria in culture media. The application of the MINTEQ software permitted the determination of the chemical composition of the culture media, and the assessment of the toxic effect of heavy metals on bacteria. The effect of soil properties on the speciation of copper in a soil solution was also analysed (Rutkowska et al. 2013) with the application of the MINTEQA2 software. Based on the results, it was evidenced that copper mainly occurred in the soil solution in a form bound to humic acids. The obtained results were the most affected by the soils' reaction. In soils with acidic reaction, the content of free copper ions, complexes with organic matter, and forms bound with carbonates and sulphates, as well as forms of copper bound to hydroxyls decreased. The degree of contamination and grain structure of soils did not determine the percent contribution of particular copper forms in the soil solution. The authors also evidenced that soils with higher contents of organic carbon contained lower amounts of free copper ions with a simultaneous increase in the organic complexes of the element (Rutkowska et al. 2013).

Mohammed (2012) used the MINTEQ software for modelling zinc sorption in soils with varied pH. The model was determined to be appropriate for the prediction of the fate and behaviour of zinc in the soil environment, and particularly in samples in which the experimental analyses had not been possible before. The model can be applied for predicting the chemical composition of not only soils, but also wastes or run-offs from potentially hazardous waste dumps. Sorption of heavy metal ions in water solutions on sorbents modified with chelating agents can be described mathematically with the application of

the MINEQL (Visual MINTEQ) software. The program permits predicting the mechanisms of removal of metals e.g. from soils or waters by means of modified sorbents (Ołpiński et al. 2011).

Zhang et al. (2008) used the MINTEQ software for the assessment of washing out of heavy metals contained in ashes from a solid waste combustion plant. The model applied a simulation of mechanisms of dissolution and precipitation of Pb, Cd, Zn, and Ni. It was determined that washing out of all of the studied heavy metals depends on the pH value. Based on the modelling results, however, differences in the behaviour of the studied elements were observed. The mobility of Pb and Cd particularly depends on the release/precipitation reaction, and the mobility of Zn and Ni on the mechanisms of surface adsorption at a strictly defined range of pH values (Zhang et al. 2008).

Erten-Unal and Wixon (1999) used the MINTEQ software for the speciation of zinc and lead in water and mining sewage samples. It was evidenced that zinc mainly occurred in carbonate forms (70–80%), and lead in hydroxide forms. Binding of the elements with OH^-, HCO^-, and CO^- groups particularly depended on the pH. The application of the model also permitted the assessment of the bioavailability of the studied elements by stating e.g. that lead carbonate ($PbCO_3$) occurring in the analysed samples showed no tendency for dissociation to free Pb^{2+} forms. The obtained data also suggest that the complexation of ions particularly depended on the content of anionic forms in the samples, and on the pH values.

Bäckström et al. (2003) analysed the total content, content of particular fractions, and performed modelling (with the application of the PHREEQC-2 software) for elements such as Cd, Co, Cu, Pb, and Zn present in sewage from roads and streets. The obtained results permitted the assessment of the possibility of transport of the studied elements towards the nearby fields with surface runoff. The application of the model enabled the assessment of the effect of organic complexating compounds on the availability and binding of heavy metals in the analysed samples (Bäckström et al. 2003; Fest et al. 2008). Moreover, the calculations obtained due to the application of the PHREEQC-2 model permitted the interpretation of the results of speciation analysis conducted by the traditional method, only allowing for the determination of the fractions of a given elements, but not the identification of its forms.

Computer simulations constitute an important tool for speciation of radionuclides such as uranium, thorium, ruthenium, iodine, and technetium in environmental samples (Harvey and Leonard 2002). Computer programs are also effectively used in the analysis of biological samples. Harris et al. (2012) applied the ECCLES software for modelling the binding and movement of Fe^{3+}, Fe^{2+}, Cu^{2+}, Zn^{2+}, and Mn^{2+} in bast. According to the calculations, the analysed metals mainly occurred in bast in the forms of chelates, and the contribution of free ions was insignificant.

Results of research concerning speciation conducted with the application of various computer programs and by means of experimental methods usually show high conformity. This suggests the usefulness and justification of the application of digital methods for the determination of the mobility and bioavailability of metals in environmental samples (Fotovat and Naidu 1997; McGrath et al. 1986; Holm et al. 1995; Stephan et al. 2008). Due to the specificity of research methods based on calculations, however, like in the case of the speciation study, the obtained results are difficult to verify. In speciation analyses, the assessment of the credibility of the effect of modelling performed based on selected data is of high importance. Too low concentrations of heavy metals in solutions or lack of possibilities of the experimental determination of the speciation forms of a given metal may be problematic. Models and computer programs should be verified and improved based on the experimental data obtained from traditional speciation analyses. (Stephan et al. 2008). Models and software can also be used to verify traditional speciation methods.

CONCLUDING REMARKS

The total content and forms of occurrence of elements in soils depend on the changing conditions and physical and chemical parameters. Geochemical models applied in computer programs are a useful tool for predicting the effect of changes in the environment on the distribution, mobility, and bioavailability of heavy metals in soils and other components of the environment. They can be effectively applied for predicting the release of heavy metals e.g. from waste dumps. The condition of conducting speciation analyses in environmental laboratories by means of digital methods is the application of specialised computer software. According to many authors, a great challenge in the scope of speciation analysis is the development of high quality data bases based on which modelling reflecting the actual natural conditions can be performed. Obtaining more detailed and credible results in soil and agricultural sciences requires the implementation and application of computer programs, modelling, and simulation. Researchers as well as legislators in the scope of environmental protection

and soil sciences should be aware of the need of changes in national provisions regarding the content of heavy metals in soils (Mohammed 2012; Zhang et al. 2008; Bonazountas 1986), and consideration in such provisions of forms or fractions of heavy metals. This would permit the development of a data base which, supported by computer risk assessment methods, would provide the basis for the determination of heavy metals' mobility or potential toxicity.

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Received: March 19, 2014
Accepted: June 30,2014

Wykorzystanie zaawansowanych programów komputerowych do specjacji metali ciężkich w glebach i innych próbkach środowiskowych

Streszczenie: W pracy przedstawiono, wiele stosowanych z powodzeniem na całym świecie, komputerowych programów do specjacji metali ciężkich w próbkach środowiskowych. Programy te mogą być stosowane w ocenie mobilności, toksyczności, biodostępności metali ciężkich lub podatności zanieczyszczeń na biodegradację. W pracy podano przykłady, zastosowanie oraz interpretację wyników specjacji metali ciężkich w próbkach środowiskowych. Ideą zastosowania takich programów jest otrzymanie modelu specjacyjnego, który pozwala na określenie (teoretyczne) w jakich formach występuje dany pierwiastek w badanej próbce środowiskowej (gleba, woda, osad) co jest niezwykle istotne ze środowiskowego punktu widzenia. Efekt końcowy zależy od wyboru odpowiednich, rzeczywistych danych wejściowych i zastosowania ich w modelu. Wyniki służą do przewidywania losu i zachowania pierwiastków w środowisku, ale także mogą być wykorzystane w tworzeniu, np. krzywych rozpuszczalności.

Słowa kluczowe: specjacja, programy komputerowe, modelowanie, metale ciężkie