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ARSENIC SPECIATION IN GROUNDWATER USING THE SOFTWARES PHREEQC, GWB AND GEODELING

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ABSTRACT

Geochemical modelling speciation is used to understand the interactions that occur in the groundwater. Thermodynamic data, kinetic parameters, numerical methods are factors that affect any geochemical modelling system. The conceptual formulation of geochemical modeling calculates the distribution of chemically reactive species for an aqueous solution. The mathematical formulation of the model results in a system of nonlinear algebraic equations that are solved using numerical methods. Most programs allow the user to estimate the speciation model. Activities of aqueous species are usually calculated using the Davies equation, Debye-Hückel equation, or the extended Debye-Hückel equation. We perform a comparative study of geochemical speciation using three different software: PHREEQCTM, Geochemist's WorkbenchTM (GWB) and GEODELING. Details of each software take into account the distribution, mobility, and availability of chemical species in groundwater. We can observe very similar results in speciation when working with low-temperature systems (20 to 80°C). GWBTM, PHREEQCTM, and GEODELING employ an integrated system to define when to use Davies, Debye-Huckel or B-dot equation, according to the value of the solution ionic strength. The geochemical speciation aimed to compare the results of simulators able to predict the chemical species present in groundwater. The utilization of GEODELING allows comparing the results with software GWBTM and PHREEQCTM with a high degree of acceptance for low temperatures. The numerical methods used by GWBTM, PHREEQCTM, and GEODELING software are able to seek its own best set of numerical solutions to achieve the equilibrium. Users must be cautious when choosing geochemical modeling software, as an essential factor for choosing a simulator is to know the temperature range that will be used.

Keywords: *Hydrogeochemistry, Carcinogenic Metalloid, Arsenic Prediction Model, Geostatistical, Reactive Transport.*

1. INTRODUCTION

Arsenic (As) and its compounds are present in nature and exhibit both metallic and nonmetallic character in their properties. The trivalent (3+) and pentavalent (5+) forms are the most common oxidation states (Arsic *et al.*, 2018). From a toxicological point of view, the arsenic compounds can be classified into three groups: inorganic arsenic compounds; organic arsenic compounds; and arsine gas. Inorganic compounds with 3+ valency are arsenic trioxide, sodium arsenite, and arsenic trichloride. In turn,

compounds with valency 5+ are arsenic pentoxide, arsenic acid and arsenates (lead arsenate and calcium arsenate) (Bennett *et al.*, 2012). Common organic arsenic compounds are arsanilic acid, methylarsonic acid, dimethylarsinic acid (cacodylic acid) and arsenobetaine (Yu *et al.*, 2018).

Arsenic trioxide is only slightly soluble in water; in sodium hydroxide forms arsenite and with concentrated hydrochloric acid in the form of arsenic trichloride. Sodium arsenite and sodium arsenate are high soluble in water. Interchanges of valence state may occur in aqueous solutions, depending on the pH and on the presence of other substances which can be reduced or oxidized

(Correia *et al.*, 2010). Arsenic appears in nature mainly in the form of sulfides associated with silver ores, lead, copper, nickel, antimony, cobalt, and iron (Lock *et al.*, 2018).

Trace amounts of arsenic are found in soils and other geological environments. Arsenic is mainly transported into the environment by water. In aqueous environment arsenic usually occurs as arsenate (AsO_4^{3-}), but under reducing conditions, for example, in deep waters, the arsenite (AsO_3^{3-}) species predominates (Wang *et al.*, 2015).

In oxygenated soil, inorganic arsenic is present in the pentavalent form. Under reducing conditions, it is in the trivalent form (Lock *et al.*, 2016a). Arsenic is released to the atmosphere from both natural and anthropogenic sources. The principal natural source is volcanic activity, with minor contributions by exudates from vegetation and windblown dust. Man-made emissions to air arise from the smelting of metals, the combustion of fuels, especially of low-grade brown coal, and the use of pesticides (Lock *et al.*, 2016b).

2. HYDROGEOCHEMISTRY OF ARSENIC

The models that can describe and predict the transport of arsenic into groundwater are very relevant to determine the extent of arsenic contamination and to evaluate alternatives for groundwater remediation. Such models should incorporate the various factors that affect the transport of arsenic into groundwater. The most common mineral with associated arsenic is arsenopyrite (FeAsS) (O'Neill, 1995; Pokrovski *et al.*, 2002, Webster, 1999), common in several mineral deposits with sulfides (Savage *et al.*, 2000). The oxidation of pyrite due to mining can cause acid drainage (Evangelou and Zhang, 1995), potentially mobilizing associated arsenic. The distribution of arsenic in sediments and soils is often controlled by the characteristics of the underlying rocks (Wang *et al.*, 2015). Inorganic arsenic is mainly present as $\text{As}(5+)$, forming arsenic acid (H_2AsO_4^- and HAsO_4^{2-}) species, while in the reducing waters $\text{As}(3+)$ is thermodynamically stable, forming the arsenous acid (H_3AsO_3) (Arsic *et al.*, 2018).

The geochemical mobility of arsenic in groundwater can be significantly delayed or increased due to reactions that occur in the water-rock interaction (Sun *et al.*, 2016). The properties of mineral surfaces and their interactions with arsenic are essential in determining the fate and transport of arsenic in groundwater. In general, physico-chemical processes such as precipitation, dissolution, complexation and ion exchange may have the properties of the element affecting its

availability in the geological environment (Wu *et al.*, 2017). This work aims to compare the speciation models generated by the GWB^{TM} , $\text{PHREEQC}^{\text{TM}}$ and GEODELING software of four sampling points underground water in arsenic concentrations. This study also allows us to validate the results of the commercial software (GWB^{TM} and $\text{PHREEQC}^{\text{TM}}$) with its own code (GEODELING).

3. CONCEPTUAL MODEL

3.1. Process simulation

The fate of arsenic does not depend only on physical processes of transport, also depending on geochemical reactions. Arsenic is a trace element whose speciation in groundwater is controlled by pH (hydrogen ions activity) and pE (electron activity - redox potential) (Wang *et al.*, 2015).

3.2. Initial conditions of the water speciation

A numerical simulation study, predicting the geochemical speciation of arsenic in groundwater, was carried out with GWB^{TM} and $\text{PHREEQC}^{\text{TM}}$ software with the aim of comparing the results obtained with GEODELING code. The temperatures used for simulations are 20, 40, 60 and 80 °C Table 1. The experimental temperatures were set according to Klunk *et al.*, 2015.

Table 1: Chemical composition of the arsenic in groundwater ($\times 10^{-3}$ g/L).

Element	AS1	AS2	AS3	AS4
As	8.19	7.44	5.67	4.82
pH	4.71	5.15	5.80	5.92
pE	9.03	8.72	8.55	8.43

The initial conditions of simulation using the GEODELING have as its starting point the combination of the chemical species. The new concentrations are calculated and represented by the logarithm activity of ionic species. The activity concentration is used to eliminate the effect of the interaction between the ions in solution. The partial pressure of CO_2 solution was 2.0 MPa (at pH value of about 5.0). The pressures were set as the hydrostatic pressure at about the depths corresponding to the strata temperatures (slightly adjusted). Was carry out four sampling point (AS1, AS2, AS3, and AS4) in groundwater.

3.3. Softwares de modelagem Geoquímica

GEODELING was developed from the thermodynamic model based on the numerical method of DISSOL™ (Fritz, 1975, 1981). This thermodynamic code was expanded through the introduction of kinetic laws governing the geochemical speciation (Helgeson and James 1968) in order to make numerical simulations possible in time functions (Lasaga et al., 1994). Thus, in the thermodynamic and kinetic model of the code GEODELING, the mineral reaction rates are controlled by the molecular diffusion of the aqueous phase and a porous layer formed by the dissolution or precipitation of a mineral. The own speciation code has application in the physical, chemical aqueous and geochemical useful tool with the intuitive and interactive interface.

Geochemist's Workbench™ (GWB™) was developed by the Department of Geology at the University of Illinois at Urbana-Champaign in 1978 (Bethke 2008). GWB™ use modules SpecE8 and GSS in "React Mode" for speciation model. The user sets the initial condition (concentration of species) of the geochemical system in thermodynamic equilibrium. So, the GWB™ start the calculation and necessary interactions that lead to speciation model. When GWB™ finished the simulation, output data is generated.

PHREEQC™ is software written in programming languages C and C++ designed to perform a wide range of geochemical calculations (Parkhurst and Appelo, 1999). PHREEQC™ is capable to (1) calculate the saturation index and speciation, (2) calculate the reactions in "batch model" and transport one-dimensional (1D), (3) use the Pitzer model for high salinity water that is an outside range of application of the Debye-Huckel theory (Pitzer, 1991). The software uses a numerical method of integration allowing solution of ordinary differential equations, which can be generalized for the reconstruction of three-dimensional trajectories (Parkhurst and Plummer 1993).

4. RESULTS AND DISCUSSION

Events predicted by numeric simulation between 20 and 80°C using GWB™, PHREEQC™, and GEODELING, are summarized in Figure 1.

GEODELING code was built to predict the species present in groundwater. The various simulations in this study enabled a comparative study of GEODELING behavior with commercial software speciation (Fig. 1). The results showed

that the use of different codes produces little different results during modeling low temperature (20 to 80°C). Generally, the simulation results show the same behavior, because each software uses similar numerical methods to solve a different set of reactions.

Each simulator has its algorithms based on numeric methods that are dependent on kinetic and thermodynamic parameters, contained in the database. Users must be careful when choosing a geochemical speciation software because, depending on the temperature range, different systems can produce very discrepant behaviors. GWB™, PHREEQC™, and GEODELING using a similar numerical method in this temperature range, the plotted profiles appear practically the same.

5. CONCLUSIONS

The present study of geochemical speciation compare the application of GWB™, and PHREEQC™ codes with GEODELING for the simulation of groundwater resulting in the follow conclusions:

1) Reactions at low temperatures (20 to 80°C) with different simulators reproduce quite the same behaviors. In this temperature range, which involves low energy, the reaction kinetics, and the thermodynamic parameters behave according to the particularities of each code. The numerical methods used by GWB™, PHREEQC™ and GEODELING software can achieve only limited convergence of results, with the high precision expected for reactions at low-temperature geological environments.

2) The geochemical speciation aimed to compare the results of simulators able to predict the chemical species present in groundwater. The utilization of GEODELING allows comparing the results with software GWB™ and PHREEQC™ with a high degree of acceptance for low temperatures.

3) The numerical methods used by GWB™, PHREEQC™, and GEODELING software are able to seek its own best set of numerical solutions to achieve the equilibrium.

Users must be cautious when choosing geochemical modeling software, as an essential factor for choosing a simulator is to know the temperature range that will be used.

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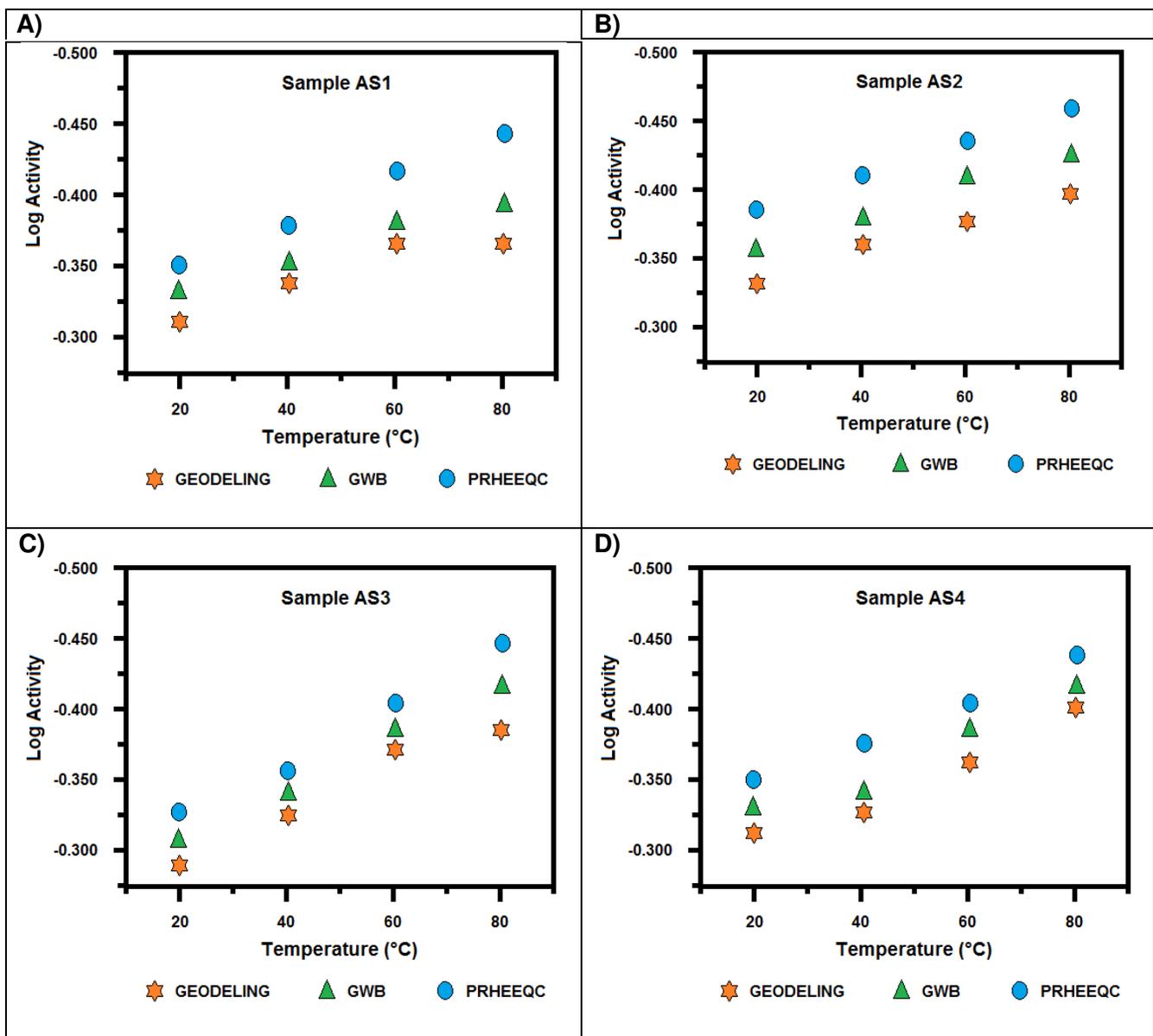


Figure 1. Speciation model using GEODELING, GWBTM and PHREEQCTM.

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