Physics and Chemistry of the Earth 92 (2016) 44–51

Contents lists available at ScienceDirect

Physics and Chemistry of the Earth

journal homepage: www.elsevier.com/locate/pce

Geochemical modelling and speciation studies of metal pollutants present in selected water systems in South Africa

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ARTICLE INFO

Article history:
Received 26 March 2015
Received in revised form
3 July 2015
Accepted 5 August 2015
Available online 28 August 2015

Keywords:
Water
Metal pollutants
Modelling
Speciation
Bioavailability

ABSTRACT

Metal pollutants in water poses great threats to living beings and hence requires to be monitored regularly to avoid loss of lives. Various analytical methods are available to monitor these pollutants in water and can be improved with time. Modelling of metal pollutants in any water system helps chemists, engineers and environmentalists to greatly understand the various chemical processes in such systems. Water samples were collected from waste water treatment plant and river from highlands close to its source all the way to the ocean as it passing through areas with high anthropogenic activities. Pre-concentration of pollutants in the samples was done through acid digestion and metal pollutants were analysed using inductively coupled plasma-optical emission spectra (ICP-OES) to determine the concentration levels. Metal concentrations ranged between 0.1356–0.4658 mg/L for Al; 0.0031–0.0050 mg/L for Co, 0.0019–0.0956 mg/L for Cr; 0.0028–0.3484 mg/L for Cu; 0.0489–0.3474 mg/L for Fe; 0.0033–0.0285 mg/L for Mn; 0.0056–0.0222 mg/L for Ni; 0.0265–0.4753 mg/L for Pb and 0.0052–0.5594 mg/L for Zn. Modelling work was performed using PHREEQC couple with Geochemist's workbench (GWB) to determine speciation dynamics and bioavailability of these pollutants. Modelling thus adds value to analytical methods and hence a better complementary tool to laboratory-based experimental studies.

1. Introduction

Water is a public resource that is required by all living things on Earth. Safe drinking water is insufficient and the little available amount is polluted from various point and non-point sources (West, 2006). The usefulness of water depends upon its composition and the purpose of its use as biological and environmental systems produce substances that can alter the usefulness of water (OEA, 2014). Harmful chemical compounds in water systems pose great danger to life.

Therefore, metal pollutants must be monitored regularly in water systems to reduce adverse health effects. Different analytical methods and tools are available and new ones are continually being developed daily in order to improve the specificity and sensitivity of the available methods. Geochemical modelling of metal pollutants in water assists scientists to understand better the various chemical processes/dynamics in such systems and hence act as a decision making tool for policy makers.

Definition of water quality criteria for metals and routine monitoring programs have so far, only in few cases, included consideration of metal bioavailability and complex interactions among the components of aquatic systems and various organism species (Campbell, 1995). The reduced standards of water quality may result from anthropogenic activities such as mining, disposal of untreated and treated waste effluents containing toxic metals, as well as metal-chelate complexes from different industries. Different types of metal-chelate complexes may result from electrical industries, tannery, mechanical equipment industries, steel plants, and thermal power plants, which are potential sources of metal in water and sediment, therefore threatening human beings and sustainable aquatic biodiversity (Ammann, 2002; Hang et al., 2009). In Integrated water resource management (IWRM), water quality is the main goal. Hence speciation, saturation indices and complexation studies would go a long way in assisting to realize this goal. In addition, integration of analytical methods with computational modelling/studies on metal availability and speciation work is key in IWRM.

Metal speciation plays a key role on bioavailability, toxicity, transference metals into living organisms, risk assessment and

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http://dx.doi.org/10.1016/j.pce.2015.08.001
1474-7065/

remedial investigations (Campbell, 1995; Sigg and Behra, 2005; Van Leeuwen et al., 2005). Various interactions may affect speciation including; soluble species, complexes, precipitates of solid phases, adsorbed species to solid phases, and redox oxidation states (Templeton et al., 2000). Metals may be present in a variety of dissolved, colloidal, and particulate species in a large size range (from low molecular weight to macromolecular complexes, colloidal particulate, and larger particle species) as well as with hydrophilic or hydrophobic properties. The size range, thermodynamic stability, as well as kinetic dissociation properties of these species are important considerations for their bioavailability and mobility in the aquatic environment (Van Leeuwen et al., 2005). The environment in which these metal pollutants are available in any water system helps to understand the chemistry of the water as well as in choosing methods of eliminating/removing them from water systems. As a result, understanding the available species of a given pollutant is a critical decision making tool for determining its behaviour in aquatic systems.

The forms of chemical species of toxic metals in the water column, the organic and inorganic metal complexes and the free solvated metal ions, could be used as a predictor of bioavailability to a particular aquatic organism. This therefore implies that the extent to which a toxic metal is available for uptake is affected by the physico-chemical forms in the environment from which it is taken (Ritchie et al., 2001). According to (Brown and Markich, 2000), the free ion activity model states that there is a correlation between the toxicity of a metal to an organism and the thermodynamic activity of the free aquo-cation in solution. Although there are exceptions to the model (Campbell, 1995), several studies have broadly confirmed this correlation (Ritchie et al., 2001; Worms et al., 2006; Simpson et al., 2014; Hall et al., 1995; Traina and Laperche, 1999; Campbell et al., 2000).

Low concentrations of trace metals are usually observed in surface water, i.e. in the microgram or nanogram per litre range (Town and Montserrat, 2000). Therefore sensitive methods are necessary to reliably identify and quantify these concentrations. Standard spectrometric methods for trace metal analysis include inductively coupled plasma-optical emission spectrometry (ICP-OES) and inductively coupled plasma-mass spectrometry (ICP-MS) as well as atomic absorption spectrometry (AAS). In particular, ICP-MS allows the simultaneous quantitative measurements of a number of trace metals at the nanogram to microgram per litre level, and is thus very suitable for measurements of trace metals in natural water (Sigg, 2014).

The form or speciation of a metal in natural waters can change its kinetic and thermodynamic properties. For example, Cu(II) in the free ionic form is toxic to phytoplankton, while copper complexed to organic ligands is non-toxic. The form of a metal in solution can also change its solubility. Recent workers (Hirose, 1990, 2006; Town and Montserrat, 2000) have shown that many trace metals can form strong complexes with natural organic ligands. It is important to examine the methods used to study the formation of the complexes in natural waters between a metal (M) and organic ligand (L)

$$\mathrm{M} + \mathrm{L} \rightarrow \mathrm{ML} \tag{1}$$

Saturation index (SI) of any given material is governed by the solubility product and ion activation product (IAP) which both require equilibrium constant. Calculations of mineral solubility, solute concentrations and the speciation of these solutes are based on equilibrium thermodynamics, i.e. on the law of mass action. Thus, for a given mineral, A_aB_b, defined by the reaction formula:

$$A_aB_b = aA + bB, \tag{2}$$

With equilibrium constant K_S, the corresponding law of mass action is:

$$K_S = \{A\}a\{B\}b\{AaBb\} = \{A\}a\{B\}b \tag{3}$$

The curly brackets indicate activities (instead of concentrations). The right hand side of third equation follows from the fact that the activity of a pure phase is, by convention, equal to one: pure solid phase:

$$\{A_aB_b\} = 1. \tag{4}$$

When the solubility of the mineral is low only a small amount of ions will be dissolved (resulting in a water of low ionic strength). In this case, the activities of the ions can be replaced by the concentrations, and Eq. (3) reduces to the solubility product:

$$K_S = [A]^a[B]^b. \tag{5}$$

Therefore, each solid phase (mineral phase) is completely determined by the mass action equation, i.e.; by the reaction formula (stoichiometry) and by the equilibrium constant K_S (or $\log K_S$ value). Both are provided in the thermodynamic database (e.g. wateq4f) from which *aqion* program gets the data to solve second Eq. (2) above.

1.1. Ion Activation Product (IAP) and Saturation Index (SI)

The law of mass action in Eq. (2) determines the activities at *equilibrium*, $\{A\}_{eq}$ and $\{B\}_{eq}$: chemical equilibrium:

$$K_S = \{A\}^a_{eq}\{B\}^b_{eq} \tag{6}$$

However, a real solution may not be in equilibrium. The IAP has the same form as the equilibrium constant K_S, but involves the actual activities, $\{A\}_{\mathrm{actual}}$ and $\{B\}_{\mathrm{actual}}$: real solution: $\mathrm{IAP} = \{A\}^a{}_{\mathrm{actual}}\ \{B\}^b{}_{\mathrm{actual}}$. The ratio between IAP and $\mathrm{K_S}$ is used to define the saturation index: $\mathrm{SI} = \log(\mathrm{IAP}/\mathrm{K_S})$. The SI is a useful quantity to determine whether the water is saturated, unsaturated, or supersaturated with respect to the given mineral as follows:

$$\begin{array}{ll} \mathrm{SI} = 0 & \mathrm{IAP} = K_S \rightarrow \text{saturated (in equilibrium)} \\ \mathrm{SI} < 0 & \mathrm{IAP} < K_S \rightarrow \text{unsaturated} \\ \mathrm{SI} > 0 & \mathrm{IAP} > K_S \rightarrow \text{supersaturated} \end{array}$$

In this study speciation and bioavailability of metals present in selected surface water and treated water systems are reported. In addition, speciation modelling work was conducted in order to establish the most abundant species of a given metal. The analysis was conducted on ten different metals, including Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn using ICP-OES. These metals were chosen base on the anthropogenic activities taking place, which included agricultural activities and waste waters from townships, in the sampling regions and the source of the water collected for the case of treated water systems. These test results were then used to determine the abundance of species and their respective available forms in the respective water systems.

2. Materials and methods

2.1. Sampling and chemical analyses

Thirteen (13) sampling sites were chosen; seven (7) from a waste water treatment plants and six (6) from surface water (river) running from the Nagle dam (29.5836°S, 30.6169°E) in Cato Ridge, KwaZulu-Natal, South Africa all the way to the Indian Ocean, including a field blank (collected by rinsing a clean sampling