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Distribution and bioavailability of arsenic in natural waters of a mining area studied by ultrafiltration and diffusive gradients in thin films

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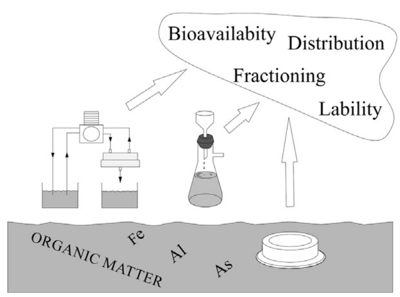
HIGHLIGHTS

- Fe and Al occurred mainly in the particulate fraction.
- Most of As was labile, bioavailable and in the free fraction.
- Dissolved Fe and Al mainly in colloidal phase was attributed to organic matter.
- Differences between results of ultra-filtration and DGT were pointed out.
- Probably influence of organic matter in the distribution of As.

GRAPHICAL ABSTRACT



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ABSTRACT

The distribution of metals and metalloids among particulate, dissolved, colloidal, free, and labile forms in natural waters is of great environmental concern since it determines their transportation behaviour and bioavailability. Organic matter can have an important role for this distribution process, since it is an important complexing agent and ubiquitous in the aquatic environment. We studied the distribution, mobility and bioavailability of Al, As and Fe in natural waters of a mining area (Quadrilátero Ferrífero, Brazil) and the influence of organic matter in these processes. Water samples were taken from 12 points during the dry and rainy seasons, filtrated at 0.45 µm and ultrafiltrated (<1 kDa) to separate the particulate, colloidal and free fractions. Diffusive gradients in thin films (DGT) were deployed at 5 sampling points to study the labile part of the elements. Total and dissolved organic carbon and the physico-chemical parameters were measured along with the sampling. The results of ultrafiltration (UF) and DGT were compared. The relationship among the variables was studied through multivariate analysis (Kohonen neural network), which showed that the seasonality did not impact most of the samples. Fe and Al occurred mainly in the particulate fraction whereas As appeared more in the free fraction. Most of the dissolved Fe and Al were inert (colloidal form) while As was more labile and bioavailable. The results

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showed that sampling points with a higher quantity of complexed Fe (colloidal fraction) showed less labile As, which may indicate formation of ternary complexes among organic matter, As and Fe.

1. Introduction

The aquatic environment is a complex system where metals and metalloids may exist in different chemical forms. They may be adsorbed in suspended particles, complexed or incorporated with macromolecular ligands, complexed with simple organic or inorganic compounds, adsorbed or assimilated by living organisms or they may occur as free (hydrated) ions (Buffle, 1991; Liu et al., 2013). In addition, these different forms have different behaviours in aquatic systems concerning their bioavailability, mobility and toxicity to living organisms (Forsberg et al., 2006; Tonello et al., 2007). Therefore, the study of such interactions is important in the management of water bodies since it helps to understand the fate of metals and metalloids in the environment, especially the toxic elements (Song et al., 2009).

A way to study the speciation of metals and metalloids in natural waters is the fractionation of their species in waters using different membranes. Based on the size, these fractions can be defined as particulate, colloidal, dissolved, and truly dissolved. The latter fraction can be also defined as a free fraction (FF) although the elements here may appear complexed with small organic or inorganic ligands or as hydrated ions (Forsberg et al., 2006; Tonello et al., 2007). Since toxic elements or metals show different geochemical behaviours in the different fractions, analysis of the total concentration of a metal does not provide information related to its mobility, bioavailability and toxicity. Even the dissolved fraction (DF) does not reveal its real level of contamination, since free ions are considered most toxic (Aung et al., 2008; Lenoble et al., 2015).

Tangential ultrafiltration (TUF) is an example of technique that may be used to characterise metal species of different sizes or molecular weights. The procedure is generally carried out with low pore size membranes (e.g. 1 kDa) to distinguish the free species from the colloidal ones. In this kind of system, the free species will be determined in the permeate (<1 kDa) and the colloidal species by the difference between dissolved and FF ones (0.45 μm–1 kDa, considering the operational definition used in this work) (Wen et al., 1997; Romão et al., 2003). However, the method has some disadvantages like very long time-consuming filtration step. Moreover, this fact limits the use of this method to study temporal variations of the water composition (Forsberg et al., 2006).

Another technique used in speciation studies is diffusive gradients in thin films (DGT). The DGT measures quantitatively labile species in aqueous solutions and can be used in complement to other techniques. It was developed by Zhang and Davison (1995) and has the advantage of pre-concentration of labile species *in situ* in aquatic systems. The labile fraction (LF) measured by this technique includes free metals and the species that can dissociate during the deployment time (Liu et al., 2013).

An important complexing agent in natural waters is the dissolved organic matter (DOM), especially the fraction of the humic substances (HS) (Tonello et al., 2007). HS make up 70–90% of the NOM in some waters and are known to influence the distribution and behaviour of metals (Sargentini et al., 2001; Lenoble et al., 2015). Other colloids in natural waters include clays, natural iron and manganese oxides, which also have an important role in the mobilisation and bioavailability of metals and metalloids (Allard et al., 2004; Domingos et al., 2015).

Arsenic is a metalloid of environmental concern due to its toxicity when present in surface and ground waters. The toxicity of this metalloid is linked to its chemical form and especially its mobility is controlled by adsorption on mineral surfaces (Sundman et al., 2014; de Oliveira et al., 2015). DOM, for example, influences As speciation because it prevents the binding of As onto solid-phase surfaces. It consequently increases As mobility in aquatic systems (Kumaresan and Riyazuddin, 2001). This process of mobilisation is explained through the formation of ternary complexes between DOM, some di and trivalent cations (e.g. Fe and Al) and As (Mikutta and Kretzschmar, 2011; Sharma et al., 2011).

The Quadrilátero Ferrífero (QF) is an area located in the State of Minas Gerais (Brazil) that covers the upper Rio Doce River Basin and the Rio São Francisco River Basin. Minerals containing As appear in this region along with gold deposits. As a result, the concentration of As is higher at some points and mining contributed to make this toxic metalloid more available in the environment (Deschamps et al., 2002; Borba et al., 2003; Varcjao et al., 2011). The problem with As is widely known and very high As levels were reported even in the urine of children (Matschullat et al., 2000). However, the role and dynamics of the colloidal DOM and its influence on the distribution of As and metals as Fe and Al (due to their role in As speciation) has never been considered before for this region. This work aimed to study the distribution of As and Fe and Al within the total, dissolved, colloidal, free, labile and inert fractions of some rivers in the QF and to identify probable associations (complexation) between DOM and As. Multivariate analysis through Kohonen neural network (KNN) was used to investigate these associations and possible relationships among other variables. In addition, results for the free fraction of TUF experiments were compared with the labile fraction measured by DGT.

2. Materials and methods

Samples were taken from 12 points in the upper Rio Doce River Basin, east of the QF. The points were selected considering the accessibility, probable presence of As (from previous studies: Matschullat et al., 2000; Deschamps et al., 2002) and HS (brown coloured waters). The points located around the Rio do Carmo River and the Rio Conceição River are important for As studies due to the proximity to main gold mine districts as mentioned by Borba et al. (2003). Fig. 1 shows a map of the studied area and all sampling points. A satellite image of the sampling area is also available in the supplementary section (Fig. A.1, Appendix A). The rainy season samples were taken in February 2014 and the dry season samples in October 2014.

Physicochemical parameters were analysed in order to characterise the waters because these parameters may affect speciation and phase distribution of metals and metalloids in natural waters (Liu et al., 2013). Conductivity (COND), dissolved oxygen (DO), pH, oxidation reduction potential (ORP), temperature (TEMP) and turbidity (TU) were measured *in situ* using an Ultrameter II (Myron L Company) and a Hanna HI9829 (for DO) probe. Total alkalinity (ALK), chloride (Cl^-) and sulphate (SO_4^{2-}) analyses were performed in the laboratory using potentiometric, argentometric and turbidimetric methods, respectively (Greenberg et al., 2005).