

# Study of water and sediment interactions in the Das Velhas River, Brazil – Major and trace elements

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## Abstract

Surface adsorption of metallic elements in aqueous solution by colloidal hydroxides affects the transport of elements in surface water systems. The study of the adsorption ability and the chemistry of hydroxides is important to the knowledge of the geological area, effluent and sewage treatments, and environmental management. In areas of ore exploitation, surface waters are subject to modifications of physicochemical properties: pH, dissolved oxygen, conductivity and alkalinity. A comparative study of the concentration of major and trace elements in water and sediment samples of the Das Velhas River, Brazil, was conducted using instrumental neutron activation analysis – INAA, and Inductively coupled plasma with mass spectrometry - ICP-MS. Water samples were collected and acidified *in situ* inducing a change in the natural pH, and consequently in the dispersion of metallic elements associated with Fe hydroxides (colloids) and with the particles in suspension. Results show the differentiated behaviour of the metal elements because of their chemical forms (cations or anions), solubility degree, Fe and rare earth elements (REEs) concentrations and pH variations.

## Introduction

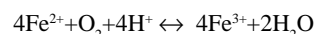
Surface adsorption of metallic elements in aqueous solution by colloidal hydroxides is a well-known phenomenon, and it is suspected to be an important process affecting the transport of trace elements in natural water systems (Benjamin and Leckie, 1981). The properties of colloid adsorption and the surface chemistry of hydroxides have been important for geology, analytical chemistry, water and wastewater treatment, and environmental management. Surface waters in mining area basins are very sensitive to disturbances such as acidification, which is directly linked to the phenomenon of oxidation (Toulhoat and Beaucaire, 1993). The distribution of elements in suspended matter and sediments along the course of a river, is generally controlled by natural processes: the relative importance of elemental transport phases, oxidation, precipitation and sedimentation of mineral species through the varying physicochemical conditions of the environment (Allen et al., 1993).

The physicochemical behaviour of many elements can be modified by changing water pH. Thus, the concentrations of all transition metal elements are considerably increased in acid waters.

The impurities commonly found in most natural waters in contact with mineral soils, and rocks in colloidal form are clay, silica (SiO<sub>2</sub>), ferric oxide (Fe<sub>2</sub>O<sub>3</sub>), aluminum oxide (Al<sub>2</sub>O<sub>3</sub>), and manganese dioxide (MnO<sub>2</sub>) (Tchbanoglous and Schroeder, 1987).

The Fe colloids, main product of pyrite (FeS<sub>2</sub>) oxidation, have good adsorption capacities for many transition metals. Consequently, the potential environmental impacts of these colloids have been carefully studied by Alauxnegrel et al. (1993). Other hydroxides, such as those of aluminium, manganese and silica, can also adsorb a great number of chemical species (Dzombak and Morel, 1990).

Oxidation-reduction reactions are important in natural systems, since these reactions may lead to other reactions with contaminants which may be present. The oxidation of iron (Fe<sup>2+</sup>) to (Fe<sup>3+</sup>) can be represented as follows:



Thus, depending on the oxidation-reduction potential, and on the solution pH, iron may exist either as Fe<sup>2+</sup> or as Fe<sup>3+</sup>. Oxidation of Fe<sup>2+</sup> is very slow below pH 6. At pH 3, half-times for the oxidation of Fe<sup>2+</sup> are around 1 000 d, while in the case of pyrite oxidation, by Fe<sup>3+</sup>, half-times of 20 to 1 000 min were observed by Stumm and Morgan (1981). The ability of iron to be oxidised or reduced in natural environments markedly affects its geochemical cycle and the cycles of other aqueous elements. Minear and Keith (1982) state two rules which govern the fixation and mobilisation of iron in solutions:

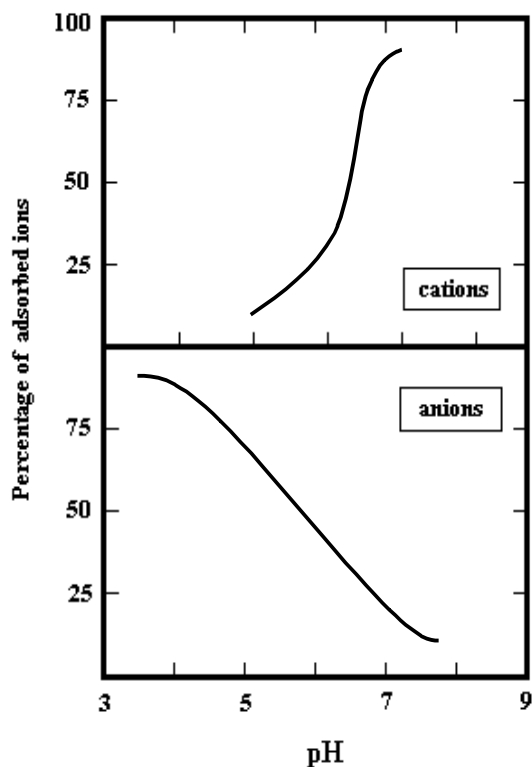
- Oxidising conditions promote the precipitation of iron, reducing conditions promote the solution
- Acid conditions generally promote the solution of iron, alkaline conditions promote the precipitation of iron.

Colloidal dispersions have electrical properties which are intimately associated with their ability to adsorb ions in solution, molecules of the medium, or both. There are many different forces that determine the stability of colloidal dispersions. The most important ones are Van der Waals dispersion forces, electrostatic forces and a diffuse electrical double layer around each colloidal particle (Ven, 1989, Tchobanoglous and Schroeder, 1987).

Cation and anion adsorption in hydroxides is highly dependent on pH. Cation adsorption increases strongly, from zero to 100% with increasing pH in the range of 5 to 7.5, while anion adsorption is more important at low pH since it decreases slowly with increasing pH (Dzombak and Morel, 1990, Allen et al., 1993). These phenomena are shown in Fig. 1.

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Received 7 January 1999; accepted in revised form 2 March 1999.



**Figure 1**

Adsorption vs. pH variations of cation and anion in hydroxides (Dzombak and Morel, 1990)

Examples of some elements in cation and anion forms present in aquatic environments at high concentrations of  $\text{Fe}_2\text{O}_3$  (Dzombak and Morel, 1990), are shown as follows:

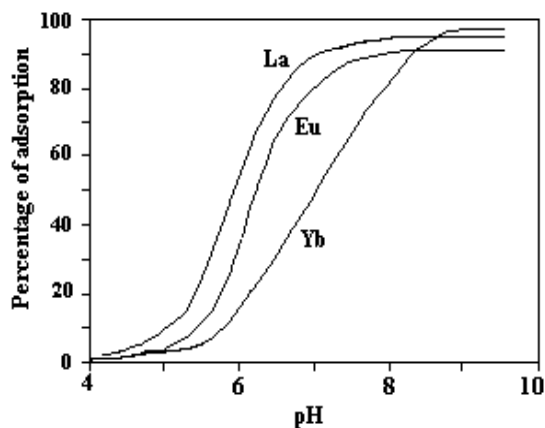
- Cations:  $\text{Ba}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Pb}^+$ ,  $\text{Hg}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{UO}_2^{2+}$ ,  $\text{Sn}^{2+}$
- Anions:  $\text{SO}_4^{2-}$ ,  $\text{SO}_3^{2-}$ ,  $\text{SeO}_4^{2-}$ ,  $\text{SeO}_3^{2-}$ ,  $\text{SiO}_3^{2-}$ ,  $\text{S}_2\text{O}_3^{2-}$ ,  $\text{CrO}_4^{2-}$ ,  $\text{WO}_4^{2-}$ ,  $\text{MoO}_4^{2-}$ ,  $\text{SbO}(\text{OH})^4$ ,  $\text{CNO}^-$ ,  $\text{CNS}^-$ ,  $\text{CN}^-$ ,  $\text{F}^-$ .

Metallic oxides can be associated to very fine particles - their colloids have a spherical shape, 1.5 to 3.5 nm in diameter in general. An ultracentrifugation, ultrafiltration, dialysis or gel filtration chromatography process is necessary for the separation of these colloids in natural water samples (Dzombak and Morel, 1990, Mora and Harrison, 1983).

A study on rare earth elements (REEs) demonstrated the processes of interaction of solid particles. REEs do not suffer significant changes in their chemical properties in relation to the increase of their atomic numbers (Dirk K., 1992). This author observed that in regions rich in Fe and Mn deposits, significant REE concentrations are found. An example of adsorption and pH variations of La, Eu and Yb in the hydroxides is shown in Fig. 2. These elements behave similarly to cations, i.e. the percentage of adsorption increases with increasing pH.

Instrumental neutron activation analysis (INAA) and inductively coupled plasma with mass spectrometry (ICP-MS) were used as analysis methods in this research. The comparison of these two analytical methods used in the control of Brazilian river water pollution is further detailed by Veado et al. (1997a,b), and Pinte et al. (1998).

The river waters in the particular region of Brazil known as the



**Figure 2**

Adsorption vs. pH variation of La, Eu and Yb in hydroxides (Dirk, 1992)

“Iron Quadrangle” are subject to perturbation of pH, induced by sulphide minerals, such as pyrite, pyrrhotite and arsenopyrite affected by mining wastes and gold mines (Figueiredo et al., 1999).

The objective of the present work was to study the water acidification phenomenon of the Das Velhas River and the water and sediment interactions of several elements analysed. Due to the adsorption phenomenon, the concentrations of Fe and REEs were associated with water and sediment samples collected in each sample site. The behaviour of major and trace elements in different cation and anion forms at low pH, was observed.

### Study area and sampling sites

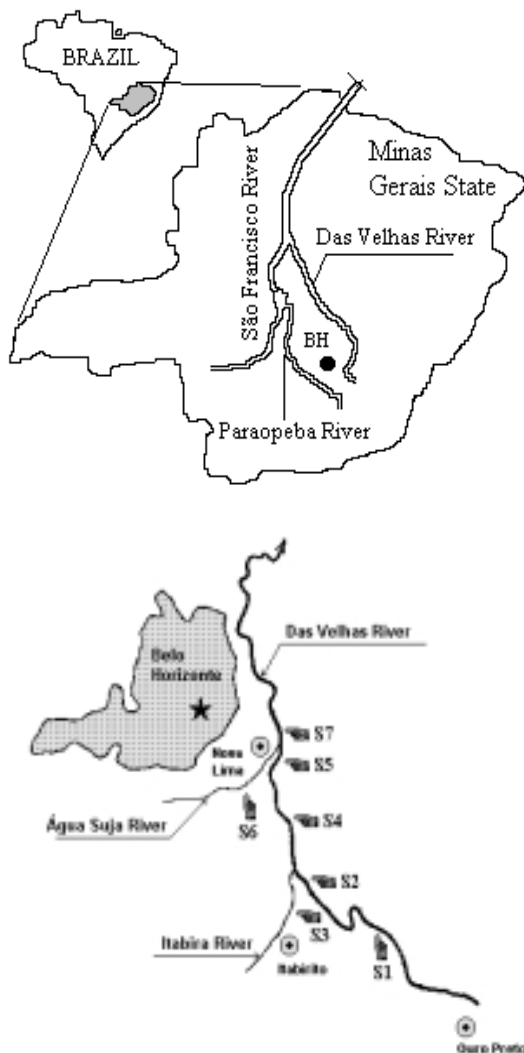
The Das Velhas River flows through the “Iron Quadrangle” region, an area approximately 7 000 km<sup>2</sup> in extent, and situated in the central part of Minas Gerais State, near the capital, Belo Horizonte, and other cities such as Ouro Preto, Itabirito and Nova Lima. It is distinct from other regional mining areas in its economic, geologic and social aspects. Its Fe ore reserves are about 20 bn. t (Quaresma, 1999, Nassif, 1999) and is served by the Das Velhas and Paraopeba basins. These basins are geologically rich in Fe, Au, Mn ores, dolomite, precious and semi-precious stones (COMIG, 1994).

Figure 3 shows the location of the Das Velhas River in Brazil and the sampling sites of this study. These sites have been numbered S1, S2, S4, S5 and S7 for those on the Das Velhas River, and S3 and S6 for two of its tributaries, the Itabira and the Água Suja Rivers. The Itabira River receives a large and direct volume of Fe mining wastes at S3, and the Água Suja River receives the wastes of an old Au mine and the contribution of an abandoned As deposit at S6.

### Materials and methods

The samples for this study were collected in January 1995. The water samples were collected near the river bank at a depth of 15 cm, and conditioned in 125 ml bottles (Nalgene). The sterile bottles were washed 3 times with river water before sampling (Batley and Gardner, 1977). The samples were acidified afterwards *in situ* with 5 drops of high purity nitric acid, (Norma-tom-60% (Prolabo), producing a pH change from 6.7 to 7.6, to about 2.

The sediment samples were collected together with water sampling on the surface layer of the river bank, and stored in 20 ml polystyrene flasks (Sterilin). After collection, all samples



**Figure 3**  
Location of study area and sample sites on the Das Velhas River and two tributaries

were stored at a temperature of 4°C for about 2 weeks before being analysed in France.

The elements Sc, Cr, Fe, Co, Zn, Zr, Sb, Cs, Hf, Ta, Au, La, Ce, Sm, Eu, Tb, Yb and Lu were analyzed by the INAA method and the elements Li, B, Mg, Al, Ca, Ti, V, Ni, Cu, As, Rb, Sr, Y, Nb, Mo, Ag, Cd, Sn, Ba, W, Tl, Pb, Th, U, Pr, Nd, Gd, Dy, Ho, Er, Tm were analysed by ICP-MS, because it had already been demonstrated to be the most reliable method for studies of these elements in this particularly Fe-ore-rich region (Veado, 1997b).

#### Instrumental neutron activation analysis (INAA)

The samples were irradiated for 17 h at a neutron flux of  $1.4 \times 10^{14}$  n-cm<sup>-2</sup>·s<sup>-1</sup> in an OSIRIS nuclear reactor, Laboratoire Pierre Süe – Commissariat à l’Energie Atomique, Saclay, France. The gamma rays subsequently emitted were counted for 8 h, after a decay time of 10 and 20 d, with a 100 cm<sup>3</sup> coaxial high-purity germanium (HPGe) detector coupled to a 4096 pulse height analyser (Revel, 1999). The computational K0 method was used to determine the concentration of the elements studied (Piccot et al., 1997, De Corte et al., 1986).

#### Inductively coupled plasma spectrometry (ICP-MS)

Measurements were carried out using the multi-element modes. An analytical program was established for both calibration and routine analysis. This program uses a series of automated operations to align the optics, select the analytical wavelength for the peaks and position the source at the entrance slit, in order to optimise the signal. The analytical wavelengths selected were the characteristic lines of the elements, which are free of spectral interference. This eliminates the need for corrections of the concentration level of interest. ICP-MS used in this study was a PQ 2-Plasma Quad with a Meinhard ultrasonic nebuliser. Data acquisition was controlled using PQ VISION software. Measurements were taken in duplicate, using the following operational conditions:

- ICP-MS power: 1.35 KW
- Coolant argon flow: 14 l/min
- Nebuliser argon flow: 0.8 l/min
- Auxiliary argon flow: 0.8 l/min
- Sample uptake rate: 0.6 to 1 ml/min.

The instrument was calibrated with standard solutions prepared from 10 ppb multi-elementary and 1 000 ppb Ca solutions. Blanks were also used in order to achieve an accuracy of 2 to 3% (Jarvis et al., 1992).

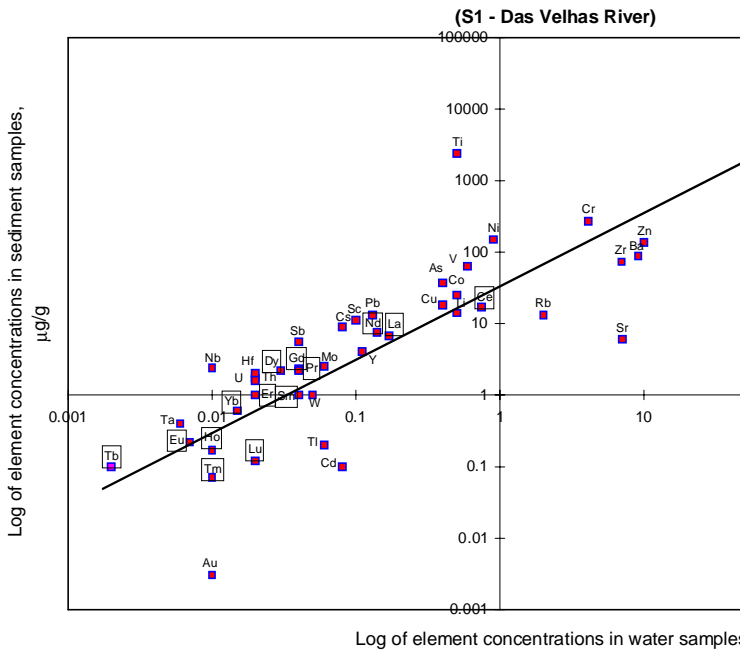
#### Results and discussion

Sulphide minerals, including pyrite, pyrrhotite and arsenopyrite occur in the mining area and alluvium downstream of the Das Velhas River. The elevated metal concentrations of this river water will probably be maintained for some time due to oxidation of pyrite and other sulphides. The rising river pH will probably cause precipitation of Fe hydroxide and thus has a positive effect on water quality, but this action may destabilize some of contaminant metal-bearing minerals, releasing metals to the aqueous system. This may occur during periods of high rainfall or flooding. Water samples were collected with acidification *in situ* inducing a change in the natural pH, and consequently the dispersion of the metallic elements associated with the Fe hydroxides (colloids) and with the particles in suspension.

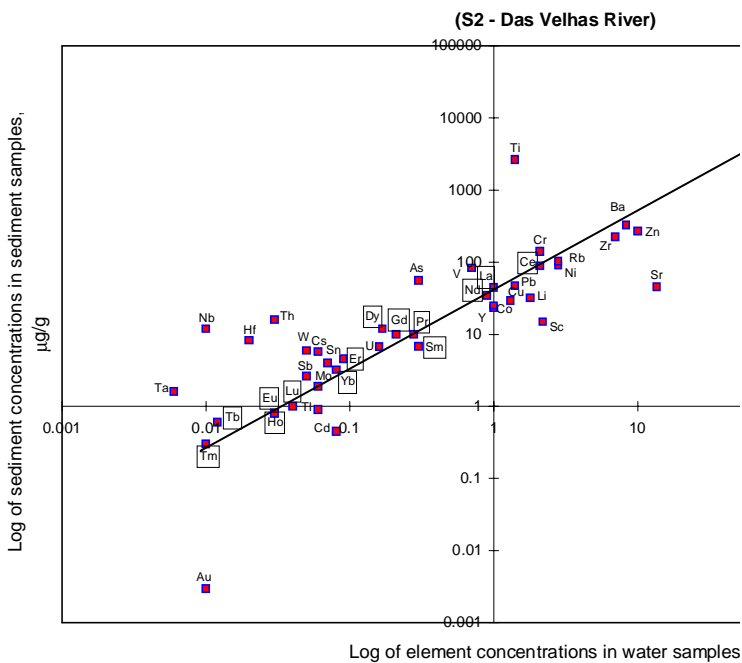
Figures 4 to 10 present the results in graph form on a logarithmic scale. The adsorption of colloids is associated with Fe and REEs, therefore the tendency curves shown in the graphs were calculated taking into consideration their corresponding concentrations.

The analysis of the tendency curves raised the following important considerations:

- The elements placed above the tendency curve are associated with sediment samples and conversely, the ones below are associated with water samples.
- The elements Al, REEs, transition metals and U are generally placed near the tendency curve. This can be associated with the liberation of these dissolved elements after the pH change from 7 to 2, in the acidification process.
- The more the tendency curve rises above the abscissa axis, the lower the concentration of metallic elements in the river waters, as shown by Fig. 4 (S1) and Fig. 5 (S2) for the Das Velhas River, and by Fig. 9 (S6) for the Água Suja River. On the other hand, the more the tendency curve goes down in relation to the abscissa axis, the higher the concentrations of metallic element cations in river water adsorbed by Fe hydrox-



**Figure 4**  
Tendency curve of water and sediment interactions to major and trace elements - S1 (Das Velhas River)



**Figure 5**  
Tendency curve of water and sediment interactions to major and trace elements - S2 (Das Velhas River)

ides, as shown by Fig. 6 (S3) for the Itabira River, and Fig. 7 (S4), Fig. 8 (S5) and Fig. 10 (S7) for the Das Velhas River.

- The elements Nb, Ta, Ti, Hf, Zr, and Th, very insoluble, are always located above the tendency curve. These elements are not associated with Fe hydroxides.
- The alkaline and alkaline earth elements, Rb, Mg, Ca, Sr and Ba, are always placed below the tendency curve, which explains their solubility properties.
- The elements W, Mo, As, Cr and Sb, normally present in anion forms, occur in smaller concentrations in water samples of the Das Velhas River. However, in Fig. 9 (S6), As and Sb are present in abnormally high concentrations in water samples of the Água Suja River, which explains why these elements are placed below the tendency curve. As and Sb are toxic elements in natural water, according to Förstner and Wittmann (1981).

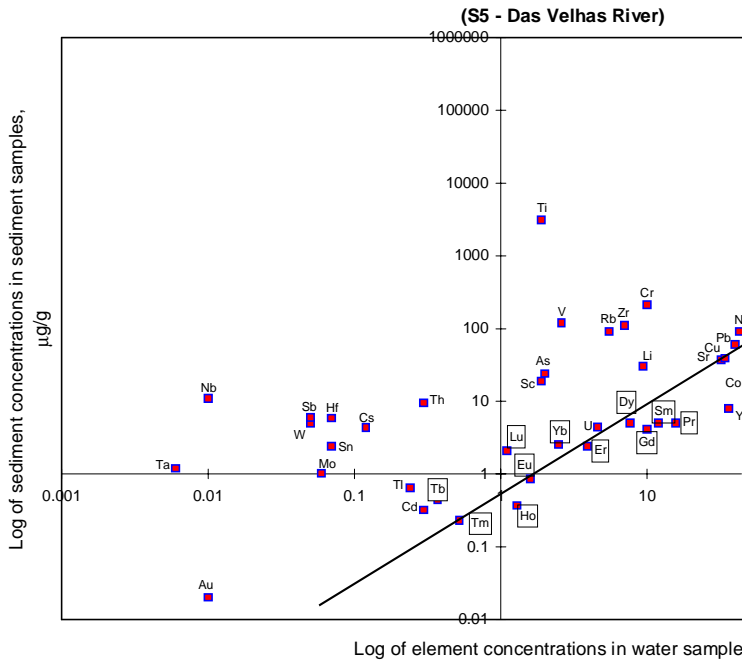
The high level of pollution here is clear and is probably due to an old As waste deposit situated a few kilometers upstream of S6.

- Au is always placed above the tendency curve in the Das Velhas River (S1, S2, S4, S5, S7) and Itabira River (S3) sampling sites, but in Agua Suja River (S6), Au is present in a very high concentration in water samples and it is placed below the tendency curve. This is due to the intensive exploitation of gold by the *Mina de Morro Velho* company.

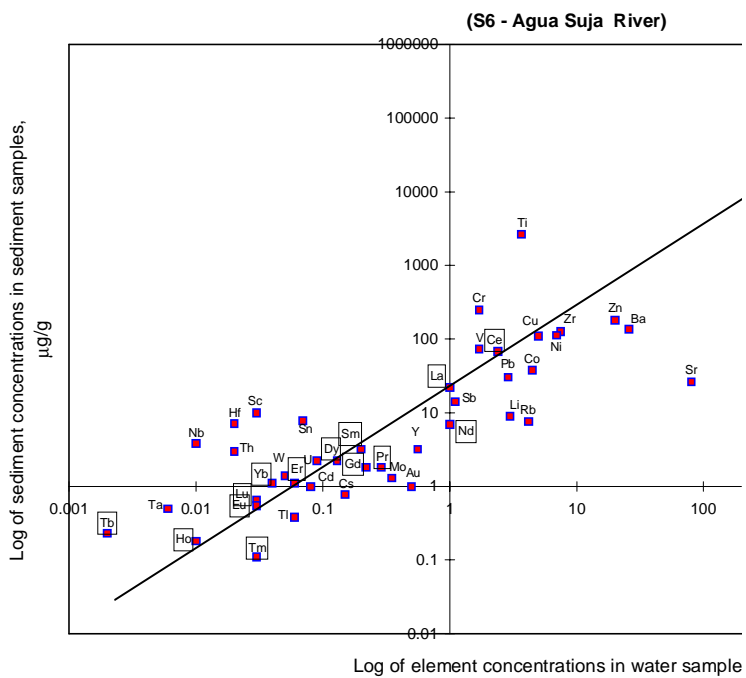
## Conclusion

The present study of multi-elementary analyses using the INAA and ICP-MS methods for water and sediment samples of the Das Velhas River, Brazil, clearly shows the differentiation of the





**Figure 8**  
Tendency curve  
of water and  
sediment  
interactions to  
major and trace  
elements - S5  
(Das Velhas  
River)

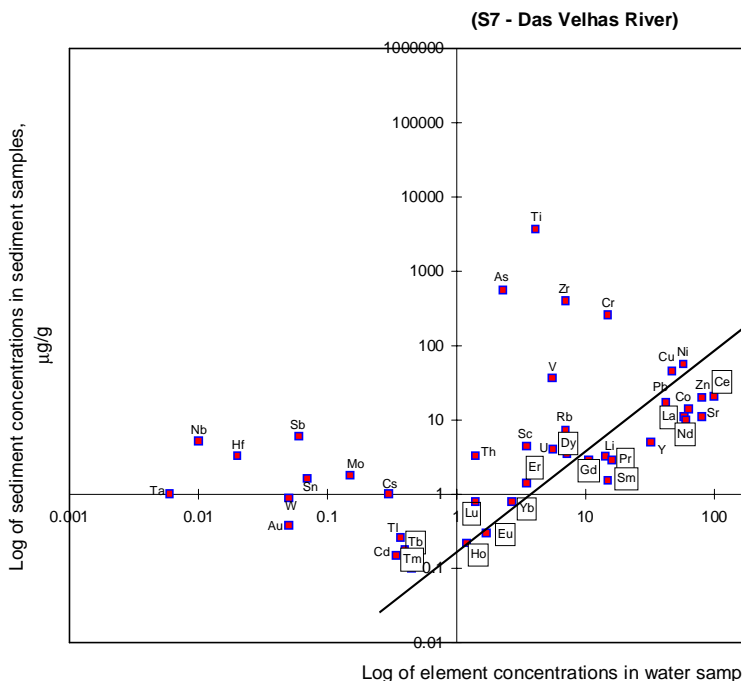


**Figure 9**  
Tendency curve  
of water and  
sediment  
interactions to  
major and trace  
elements - S6  
(Affluent, Água  
Suja River)

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**Figure 10**  
Tendency  
curve of water  
and sediment  
interactions to  
major and  
trace  
elements - S7  
(Das Velhas  
River)



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