Geochemistry of acid mine drainage from a coal mining area and processes controlling metal attenuation in stream waters, southern Brazil

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ABSTRACT

Acid drainage influence on the water and sediment quality was investigated in a coal mining area (southern Brazil). Mine drainage showed pH between 3.2 and 4.6 and elevated concentrations of sulfate, As and metals, of which, Fe, Mn and Zn exceeded the limits for the emission of effluents stated in the Brazilian legislation. Arsenic also exceeded the limit, but only slightly. Groundwater monitoring wells from active mines and tailings piles showed pH interval and chemical concentrations similar to those of mine drainage. However, the river and ground water samples of municipal public water supplies revealed a pH range from 7.2 to 7.5 and low chemical concentrations, although Cd concentration slightly exceeded the limit adopted by Brazilian legislation for groundwater. In general, surface waters showed large pH range (6 to 10.8), and changes caused by acid drainage in the chemical composition of these waters were not very significant. Locally, acid drainage seemed to have dissolved carbonate rocks present in the local stratigraphic sequence, attenuating the dispersion of metals and As. Stream sediments presented anomalies of these elements, which were strongly dependent on the proximity of tailings piles and abandoned mines. We found that precipitation processes in sediments and the dilution of dissolved phases were responsible for the attenuation of the concentrations of the metals and As in the acid drainage and river water mixing zone. In general, a larger influence of mining activities on the chemical composition of the surface waters and sediments was observed when enrichment factors in relation to regional background levels were used.

Key words: acid mine drainage, coal, metals, water quality.

INTRODUCTION

The presence of high concentrations of trace elements dissolved in surface and ground waters is one of the main problems associated with acid drainage generated in coal and sulfide mining areas. Acid mine drainage (AMD) results from the oxidation of sulfides, typically pyrite, and is characterized by low pH and high concentrations of SO_4^{2-}, Fe, metalloids, and many metals (Larsen and Mann 2005). Abandoned mines and tailings piles can be sources for AMD and represent risk to the equilibrium of different ecosystems (Moncur et al. 2005, Cravotta 2008), especially when efficient mitigating actions against acidity are not applied. These actions can include the neutralization of acid drainage by means of limestone, hydrated

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lime, ammonia, and fly ash (Akcil and Koldas 2006, Fungaro and Izidoro 2006). In some cases, however, the attenuation of acidity may take place naturally if carbonate rocks present in the local stratigraphic sequence interact with AMD (Wicks and Groves 1993, Webb and Sasowsky 1994, Campaner and Luiz-Silva 2009). In general, the attenuation results from the increase in pH and decrease in the solubility of metals and metalloids, and depends strongly on the nature and abundance of neutralizing materials (Cravotta et al. 1999).

In natural drainage systems affected by AMD, the concentrations of some trace elements (e.g., As, Cd, Cu, Ni, and Pb) can be minimized as a result of various mechanisms inherent to the water system. Physico-chemical conditions frequently favor chemical equilibrium and precipitation of these metals a few meters downstream from the acid discharge, removing chemical species in solution (Paulson and Balistrieri 1999, Chon and Hwang 2000, Butler et al. 2008). The adsorption and co-precipitation of elements in mineral phases are particularly important mechanisms (Rose et al. 1979, Lee and Chon 2006). Iron and Mn oxy-hydroxides, for example, are important compounds involved in metal retention in sediments from fluvial systems, due to their high specific surface, tendency to form colloids and cation exchange capacity (Horowitz 1991, Cravotta 2008). In the interface with water, the surface of these mineral phases can be deprotonated under high pH, or protonated under low pH conditions, making the surface more negative or more positive, respectively. At neutral to alkaline conditions, cationic trace metals tend to be adsorbed by surface negative charges, whereas oxyanions such as sulfate, arsenide and arsenate tend to be adsorbed by surface positive charges under low pH conditions (Stumm and Morgan 1996, Cravotta 2008). Additionally, the accumulation of metals in fluvial sediments affected by AMD can reach very high levels, with the possibility of desorption and risk of incorporation by living organisms (Stecko and Bendell-Young 2000).

Mineral coal in Brazil represents one of the major sources of non-renewable energy, and is especially used in thermoelectric power plants. The coal reserves of the country are 32 billions t, distributed in the states of Rio Grande do Sul (28 billions t), Santa Catarina (3.3 billions t), Paraná (103 millions t) and São Paulo (8.5 millions t) (Gomes et al. 2003). In response to the need to expand the electricity supply, proposals exist to increase the coal-fired power stations, which should promote an increase in coal consumption from ca. 6 millions t year^{-1} (2006) to 13.6 millions t year^{-1} in 2016, according to the Brazilian Ten-Year Energy Expansion Plan (2007-2016; Brazil 2007).

The Figueira region, state of Paraná, is one example of a Brazilian region affected by bituminous coal mining activities, with mines exploited since the mid 1990's. High levels of As (253 to 2176 mg kg^{-1}), Pb (118 to 340 mg kg^{-1}) and Zn (54.4 to 544 mg kg^{-1}) have been found in its coal (Campaner and Luiz-Silva 2009). However, studies on the environmental impact by coal mining are relatively recent in Brazil (Teixeira et al. 2000, Pampêo et al. 2004). Special attention has been given to acid drainage remediation (Fungaro and Izidoro 2006, Soares et al. 2006, Church et al. 2007), but few studies have focused on the regional characterization of water systems and AMD influence on their physico-chemical conditions. The main objective of this study was to evaluate the possible influence of the acid drainage coming from a mining area within the Figueira region on the quality of surface and ground waters particularly in relation to metals and As. Since fluvial sediments can act as a sink or a source of the elements of interest for the surface waters, possible geochemical anomalies of metals and As in sediments potentially affected by AMD were also evaluated.

STUDY AREA

The study area is located in the Figueira region, north of the state of Paraná, southern Brazil (Fig. 1), where coal deposits have been exploited since the 1940's.

This energy source has supplied a thermoelectric plant installed in the region by the end of the 1950's. The coal has been mined from open pits and galleries. Only a mine adit (named Mina 07, which will be replaced by a new mine adit in the next years) is in operation at present, producing ca. 97,000 t year^{-1} and generating ca. 620 t of tailings daily (V.P. Campaner and A. Spoladore, unpublished data). The pyrite-rich coal layers are up to 0.5 m thick and are found in the Rio Bonito Formation (of Eo-Permian age) of the Paraná Basin (Ordovician to Cretaceous; Ricardi-Branco et al. 2002, Jasper et al. 2011). The Rio Bonito Formation is divided into a basal unit, the Triunfo Member, where sandstones, shales and coal predominate; an intermediate unit, the Paraguaçu Member, constituted by siltstones and shales intercalated with thin sandstones and carbonate lenses; on top there is the Siderópolis Member, represented by very thin sandstones. The latter is poorly developed in the study area (Morrone and Daemon 1985). Data from drill holes in the Mina 07 area revealed a sedimentary sequence (ca. 38 m) overlying the coal layers formed by alternating meter-sized sandstone and siltstone layers, both occasionally calciferous at the base. In this sequence centimeter-sized impure limestone lenses occur (Campaner and Luiz-Silva 2009).

AMD remedial actions in this area are limited to acidity neutralization by applying a commercial product resulting from the calcination of calcareous rock (high CaO and MgO contents), and disposal of tailings between compacted soil layers, thus reducing its exposure to oxygen and rain water. Recently, Campaner and Luiz-Silva (2009) showed that the presence of limestone in the Mina 07 stratigraphy also contributes to the pH increase in acid flows discharged in the natural drainage, minimizing regional impact.
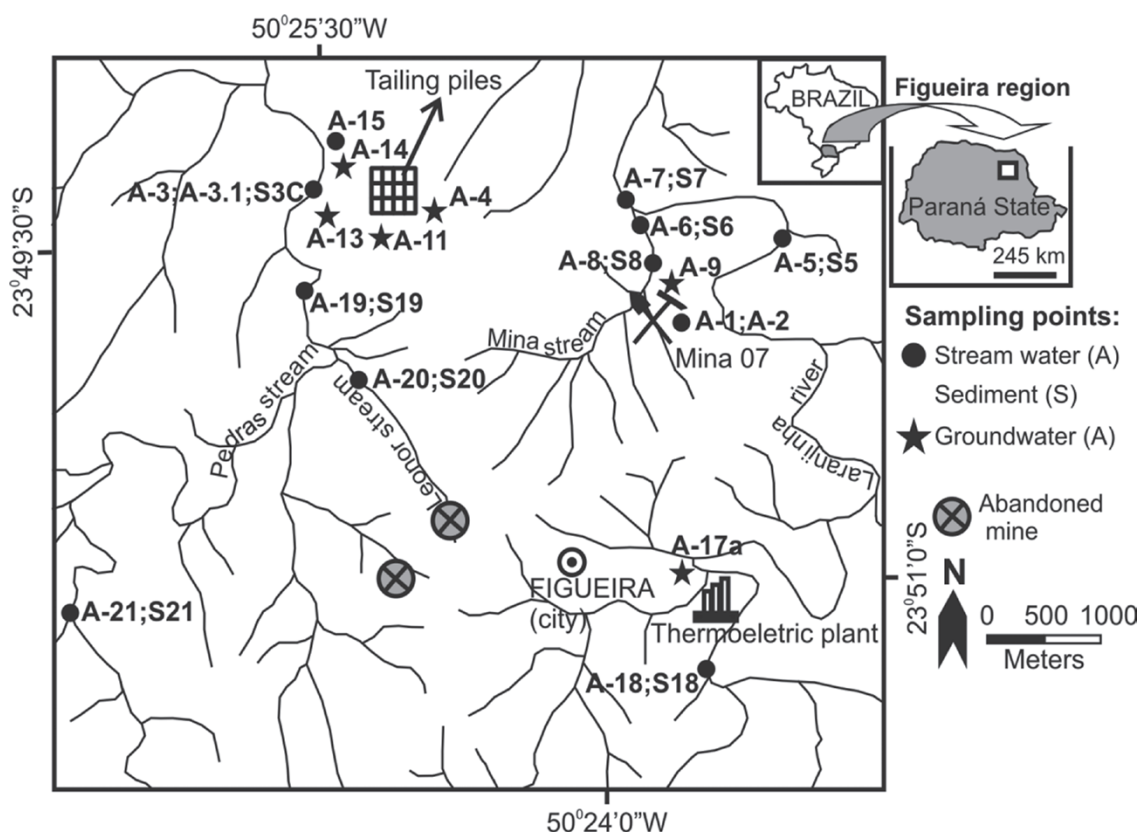

Figure 1 – Location of the sampling points in the study area.

MATERIALS AND METHODS

SAMPLING AND ANALYTICAL PROCEDURE

Samples of surface and ground waters (5 to 10 m depth) were collected in September 2006, during the dry season (Fig. 1). A fraction of each sample was used to measure physico-chemical parameters (temperature, pH and redox potential) with specific electrodes and previously calibrated equipment. Combined platinum electrodes and combined glass electrodes were used to measure redox potential and pH, respectively. In both, Ag:AgCl ($[KCl] = 3$ mol L^{-1}) was the reference electrode. The Eh measurements were recalculated to the standard hydrogen potential (Standard Hydrogen Electrode - SHE), using the following equation (in mV):

$$Eh_{SHE} = Eh_{measured} + 209 - 0.7\,(t - 25\,°C) \quad \text{(Equation 1)}$$

The value 209 represents the potential SHE (at 25 °C) and 0.7 is a correction factor, which is a function of the Eh acquisition temperature t (Nordstrom and Wilde 1998). Redox potential determination is not a simple task and no universally accepted procedures exist, especially for groundwater (Naudet et al. 2004). Regarding methodological limitations in determining precise and accurate redox potential values, the values presented in this study are taken as orders of magnitude equivalent to the real redox potential of each sample.

Alkalinity (considered for simplicity as HCO$_3^-$) was measured in stream water samples by tritation of 100 mL of the sample, using bromocresol blue as indicator and H$_2$SO$_4$ (0.16 N) as reagent (Radojevic and Bashkim 1999).

For the analysis of cations and anions, each sample was filtered soon after sampling with a Millipore® (0.22 μm-thick) membrane of cellulose acetate and divided in two aliquots. Only one of the aliquots (for the analysis of cations) was stabilized with suprapure HNO$_3$ Merck® (1% v/v)

(Concas et al. 2006) and all samples were kept in PET bottles (Jardim and Fadini 2000) at 4 °C.

In the same places where surface waters were collected, surface sediments (up to 3 cm depth) were sampled (3 kg) with a plastic shovel. In the laboratory, the sediment samples were homogenized and dried at 40 °C. After that, a 200 g aliquot was sieved using nylon mesh sieves to separate the fraction <63 μm for analysis. This fraction was adopted in order to minimize the chemical dilution caused by the sand fraction (Luiz-Silva et al. 2006). Additionally samples of the neutralizing AMD agent generated in Mina 07 were collected (sieving tests showed that this product was totally composed of particles <63 μm in size).

Chloride and SO$_4^{2-}$ analyses in water samples were carried out by ion chromatography, whereas other techniques were used in cation analysis. The concentrations of Al, Ca, Co, Cr, Fe, Mg, Mn, Ni, and Zn were determined by inductively coupled plasma optic emission spectrometry (ICPOES). Arsenic, Cu, K, and Na were determined by flame atomic absorption spectrometry (FAAS), and Cd and Pb were determined by graphite furnace atomic absorption spectrometry (GFAAS). These elements were also analyzed in samples of the AMD acidity neutralizing product (commercial calcinated calcareous rock) following the same procedures used for sediments. Aluminum, As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn contents in the silt-clay fraction of the sediments were determined after sample digestion in a 10 mL acid solution (2:2:1:1 H$_2$O-HF-HClO$_4$-HNO$_3$). The solutions were heated until fuming on a hot plate and taken to dryness. Then, 4 mL 50% HCl was added to the residue and heated in a microwave. After cooling the solutions were made to a 10 mL volume with 5% HCl. These solutions were analyzed by means of a Perkin Elmer ICPMS. To check the quality of the analysis, certified reference materials (SEM 1640/NIST – water and LKSD3/CANMET – sediment) were analyzed. The recovery values for all analyses of

reference materials ranged between 90 and 105% for all elements. Sample duplicates were also used, resulting in relative percentage differences lower than 15%. Blanks (deionized water filtered through a 0.22 μm membrane) were also prepared in order to take into account possible impurity of reagents and membranes. In this case, the concentrations of all analytes were close to or below the detection limits of the methods.

DATA TREATMENT

The chemical classification (Piper diagram) and the CO_3^{2-} concentrations in stream waters were obtained by means of the GwCHART program (Winston 2000). The geochemical anomalies in the surface sediments were evaluated using an enrichment factor (EF_s) based on the equation (modified after Gresens 1967):

$$EF_s = (C_i/C_{Al})_{sample} / (C_i/C_{Al})_{background} \quad \text{(Equation 2)}$$

We also used an enrichment factor for surface waters (EF_w) based on the equation:

$$EF_w = (C_i/C_{Cl})_{sample} / (C_i/C_{Cl})_{background} \quad \text{(Equation 3)}$$

The EF_s and EF_w quantified the concentration of the element of interest (C_i) in the sample, in relation to the (natural) geochemical background. In the sediments, the geogenic heterogeneities (effects caused by variations in grain size and mineral composition) were minimized using Al as the normalizing element (Cardoso et al. 2001, Luiz-Silva et al. 2006, 2008, Hortellani et al. 2008, Machado et al. 2008). The samples adopted as sediment and water background were those collected upstream the mining sites (S18 and S21; Fig. 1). With regards to EF_w, we adopted chlorine as the normalizing element because it is a conservative component in the geochemical processes (Faure 1998). Principal component analysis and Pearson correlation (< 0.05 significance level) were carried out to evaluate possible associations between variables (surface and ground water samples).

When the chemical concentration was below the detection limit we used half of this limit in the statistical procedures.

RESULTS AND DISCUSSION

GEOCHEMISTRY OF THE ACID MINE DRAINAGE

The physico-chemical parameters and the concentrations of the chemical constituents of the AMD from the tailings piles and Mina 07 are shown in Table I. In this table the compositional averages for the product used as AMD neutralizing agent in the study area are also shown. High SO_4^{2-} (between 2592 and 9100 mg L^{-1}) and Fe (between 294 and 2393 mg L^{-1}) concentrations and the low pH values (3.2 to 4.6) in the water samples indicate pyrite oxidation in both sampling environments. In fact, redox potentials ranged between 445 and 628 mV, implying oxidizing conditions. The presence of Al, As, Ca, Cd, Co, Cr, Cu, K, Mg, Mn, Na, Ni, Pb, and Zn in the acid solutions results from leaching of minerals (especially silicates, oxides and sulfides) associated with the coal layers and host rocks (sandstones, siltstones, shales, and limestones). In the study area, coal and host rocks contain arsenic-rich pyrite and in much lower quantities galena (PbS), sphalerite (ZnS) and other sulfides (V.P. Campaner, unpublished data). Acid drainage from coal disposal piles (samples A-3.1 and A-15) presented particularly higher concentrations of SO_4^{2-}, Al, As, Fe, K, Mg, Mn, Na, and Zn in relation to AMD from Mina 07 (samples A-1 and A-2). This can be a consequence of a larger exposure time of the fragmented material from the tailings to weathering, which has intensified pyrite oxidation (Cheng et al. 2009).

Sample A-2 represents the AMD that is treated with the calcinated calcareous rock (CaO). After the neutralizing agent is added, this acid effluent is discharged in a natural drainage. In this case, the neutralization process proved to be inefficient for some parameters. According to

TABLE I

Values of pH, Eh (mV) and chemical concentrations in acid drainage (in mg L^{-1}) and neutralizing AMD agent (CaO for commercial use made by calcareous sedimentary rock upon calcination; in mg kg^{-1}, except those indicated with %). Values shown with the "less than" symbol ("<") are detection limits, and CONAMA (Environmental National Council) values (in mg L^{-1}, except pH) are standards of effluent discharge (maximum permissible limits) of the Brazilian legislation (BRAZIL 2011).

	AMD – Mina 07		AMD – Tailings piles		AMD neutralizing agent	
	A-1	A-2	A-3.1	A-15	(n = 2)	CONAMA
pH	3.2	4.6	3.3	4.1	–	5–9
Eh	625	445	628	478	–	–
Cl$^-$	2.2	2.2	31	27.6	–	–
SO$_4^{2-}$	2969	2592	9100	8713	–	–
Al	95.5	21.3	458	301	0.08 ± 0.04	–
As	0.33	0.002	0.68	0.25	<0.2	0.5
Ca	393	554	418	449	27.1 ± 0.3%	
Cd	0.11	0.06	0.04	0.03	0.26 ± 0.04	0.2
Co	0.15	0.22	<0.05	<0.05	0.5 ± 0.1	–
Cr	0.07	<0.02	0.05	0.05	1.3 ± 1.1	0.5
Cu	0.08	0.03	0.03	0.04	0.82 ± 0.07	1
Fe	631	294	1937	2393	<0.02	15
K	3.59	4.04	20.5	40.1	0.06 ± 0.01%	–
Mg	151	151	397	294	14.96 ± 1.92%	–
Mn	12.8	9.55	40.4	31.7	67.5 ± 14.8	1
Na	74.4	77.3	502	462	0.015 ± 0.003%	–
Ni	1.13	0.86	1.22	1.04	2.4 ± 0.3	2
Pb	0.001	0.0003	0.001	0.001	1.09 ± 0.54	0.5
Zn	22.3	12.6	161	139	12.2 ± 1.8	5

Table I, in addition to the Ca and Mg, higher concentrations of trace elements (Cd, Co, Cr, Cu, Mn, Ni, and Pb) were found in the neutralizing agent, and ions of these elements can be added to water during the AMD treatment (sample A-2). However, an efficient removal of elements such as As, Al and Cr by precipitation was observed, as indicated by comparing samples A-1 and A-2 (Table I). The limiting values for the emission of effluents (Brazilian legislation) are listed in Table I. It may be noted that pH, Fe, Mn, and Zn (and to a lesser extent As) levels found in the AMD of the study area do not comply with the Brazilian legislation, whereas Cd, Cr, Cu, Ni, and Pb concentrations are lower than the limiting values.

GROUNDWATER

Table II shows the variation of the chemical constituents, pH and Eh for the groundwater samples collected in piezometric wells (5 to 10 m in depth) and the limiting values from the Brazilian legislation for groundwaters. In general, redox potential (Eh) in the wells varied from suboxic (241 mV) to very oxidizing (767 mV) conditions. Some very oxidizing conditions recorded (e.g., Eh >500 mV, uncommon in groundwaters) could possibly be due to contamination with atmospheric oxygen during sampling and/or measurement (Naudet et al. 2004). The wells sampled downstream of the tailings piles (samples A-11, A-13 and A-14) show a pH interval (between 3.1 and 3.9) similar to the acid drainage generated in these tailings (Tables I and II). Significant SO$_4^{2-}$, Al, As, Cd, Co,

Cr, Cu, Fe, Mn, Ni, Pb, and Zn concentrations in these wells could result from rainfall infiltration and subsequent leaching of mine wastes in the tailing deposits. Additionally, high Ca (107 to 448 mg L^{-1}) and Mg (59.5 to 2095 mg L^{-1}) concentrations were found in three wells sampled in the study area. Carbonate rocks present in the local stratigraphic sequence (Campaner and Luiz-Silva 2009) could be the mechanism controlling the high concentrations of these alkaline earth elements, although the low pH values and the presence of metals in solution suggest the occurrence of sulfide minerals oxidation, which makes neutralization difficult (Cravotta and Trahan 1999). The well located downstream of Mina 07 (sample A-9) showed concentrations lower than those for the acid drainage generated in the mine, despite the acid pH (4.1), oxidizing conditions (Eh = 580 mV) and significant SO_4^{2-} and metal (Al, Cd, Mn, and Zn; Table II) concentrations have been identified.

In general, sulfate, Al, Cd, Mn, Ni, and occasionally As, Fe, Na, and Zn contents, in groundwater wells studied exceeded the limits established by the Brazilian legislation (Table II). On the other hand, the AMD action at underground levels does not seem to have any influence in the groundwater extraction site for municipal public supply (upstream of coal mining sites; sample A-17a). It is revealed by the low metal levels and pH close to neutral, although Cd concentration slightly exceeded the limits adopted by the Brazilian legislation for groundwater (Table II).

TABLE II

Values of pH, Eh (mV) and chemical concentrations (in mg L^{-1}) of groundwater samples from piezometric wells. Values shown with the "less than" symbol ("<") are detection limits, and CONAMA (Environmental National Council) values (in mg L^{-1}) are maximum permissible limits established by the Brazilian legislation in groundwater used for human consumption (BRAZIL 2008).

	A-9	A-4	A-11	A-13	A-14	A-17a	CONAMA
pH	4.1	5.5	3.9	3.1	3.2	7.5	−
Eh	580	241	693	767	569	347	
Cl⁻	1.6	117	0.35	0.62	27.5	18.8	250
SO₄²⁻	229	9939	603	1584	12182	146	250
Al	5.21	28.4	5.6	55.2	358	0.14	0.2
As	<0.0006	0.48	<0.0006	<0.0006	0.89	<0.0006	0.01
Ca	56.5	445	107	267	448	12.3	
Cd	0.01	0.014	0.013	0.53	0.042	0.007	0.005
Co	<0.05	<0.05	0.14	0.52	<0.05	<0.05	−
Cr	<0.02	<0.02	<0.02	<0.02	0.05	<0.02	0.05
Cu	<0.01	0.03	<0.01	0.02	0.1	<0.01	2
Fe	<0.05	1434	<0.05	31.2	9484	<0.05	0.3
K	1.79	21.4	14.7	3.89	11.9	0.8	
Mg	9.56	2095	59.5	69.1	355	2.13	
Mn	0.45	42.7	14.8	34.2	59.8	<0.05	0.1
Na	10.6	1883	16.3	17.9	504	124	200
Ni	<0.08	2.1	0.1	0.55	1.6	<0.08	0.02
Pb	0.001	0.001	0.0008	0.003	0.01	<0.0003	0.01
Zn	0.47	16.9	0.49	10.1	164	<0.2	5

STREAM WATER

The physico-chemical parameters and chemical constituents of the surface water samples of the main river and streams that drain the coal mining area are shown in Table III together with the Brazilian legislation limiting values for stream waters. The surface waters presented a pH interval between 6 and 7.3, although, a higher value of 10.8 has been found in the Mina stream (see details below). Oxidizing conditions were observed with Eh varying between 394 and 425 mV, but in the Mina stream the redox potential was minor and ranged from 296 to 316 mV. In this last case, AMD treatment with CaO was used upstream and it could explain the lower Eh values found in the Mina stream. The CaO (lime) is considered to be a reducing agent due to the oxidation half-reaction:

$$CaO \Leftrightarrow Ca^{2+} + \frac{1}{2} O_2 \quad \text{(Reaction 1)}$$
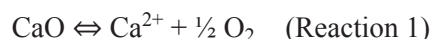
During the AMD treatment, the loss (reaction 1) and gain of electrons is thought to occur simultaneously and the oxidation-reduction reaction among calcium hydroxide (produced by treating lime with water), oxygen and pyrite to produce calcium sulfate and iron hydroxide could be an example (reaction 2):

$$8\ Ca(OH)_2 + 15\ O_2 + 4\ FeS_2 + 14\ H_2O \Leftrightarrow 8\ CaSO_4.2H_2O + 4\ Fe(OH)_3 \quad \text{(Reaction 2)}$$

Although oxidation and reduction half-reactions occur simultaneously (e.g., reaction 2), they may have different kinetics. For instance, we observed in the study area that the introduction of CaO during the AMD treatment caused an Eh decrease from 400 mV to values as low as −100 mV instantaneously. After some minutes the oxidizing process is started slowly and Eh reaches values between 30 and 90 mV in approximately six hours. This condition could affect the redox potential in the slow-flowing Mina stream (see below), after the AMD discharge treatment.

In general, changes caused by AMD in the chemical composition of water systems were not very significant, but two groups of affected samples can be recognized in Piper diagram (Fig. 2). Group I samples are located farther from AMD sources and reveal chemical compositions resulting from weathering processes affecting regional rocks. Group II, on the other hand, represents water samples directly affected by AMD and is characterized by the location of the sampling points close to the coal mining sources (Fig. 1) and high SO_4^{2-} concentrations (Table III).

In the mixing zone between the AMD discharge from the coal disposal piles (sample A-3.1 – Table I) and the natural drainage (sample A-3, downstream from a mixing zone – Table III), the concentrations of SO_4^{2-}, Al, As, Fe, Mn, Ni, and Zn were much lower than those found in the acid solution. In this case, precipitation and/or dilution of the chemical species are thought to occur naturally (Balistrieri et al. 2007). In Mina 07 mixing zone of acid drainage (sample A-2, Table I) with surface waters (sample A-8, downstream from a mixing zone), SO_4^{2-} and concentrations of metals decreased in accordance to the distance from the AMD discharge point. The extremely alkaline pH of sample A-6 (pH = 10.8) suggests that the carbonate rocks present in the local stratigraphic sequence can play an important role. Natural attenuation of the AMD impact has been observed in the water system, attributed to interaction with limestone (Campaner and Luiz-Silva 2009), as also documented in other studies (Webb and Sasowsky 1994). In the study case, we thought that carbonate-rich groundwater recharge had a greater influence on the extremely alkaline pH because the work was done during the dry season and the drainage flow was slow (ca. $0.1\ m^3\ s^{-1}$; V.P. Campaner, unpublished data).

Geochemical processes that are taking place in the study area could be explained by the

TABLE III

Values of pH, Eh (mV) and chemical concentrations (in mg L^{-1}) of surface water samples.
Values shown with the "less than"symbol ("<") are detection limits, and CONAMA
(Environmental National Council) values (in mg L^{-1}, except pH) are water quality
standards (class 2) of the Brazilian legislation (BRAZIL 2005). Contents of CO$_3^{2-}$ were
calculated by means of the GwCHART program (Winston 2000).

| | Mina stream | | Laranjinha river | | | Pedras stream | | | Leonor stream | |
	A-8	A-6	A-7	A-5	A-18	A-3	A-19	A-21	A-20	CONAMA
pH	6.4	10.8	7.3	6.2	7.2	6	7.1	6.6	6.8	6–9
Eh	316	296	394	412	417	420	427	425	411	–
Cl$^-$	1.8	1.1	1.7	2.2	1.4	2.8	2.5	2.4	18	250
CO$_3^{2-}$	0.0046	144.6	0.027	0.002	0.021	0.0018	0.029	0.0091	0.063	–
HCO$_3^-$	39	49	29	27	29	39	49	49	215	–
SO$_4^{2-}$	1587	773	12.6	14.4	2.3	75	62	6.8	994	250
Al	0.07	1.7	0.27	0.24	0.4	0.42	0.33	0.41	1.2	0.1
As	<0.0006	0.0007	0.0013	0.0007	<0.0006	0.0008	0.0008	<0.0006	0.0018	0.01
Ca	468	270	12.7	4.5	3.44	36.8	24.4	13.8	338	–
Cd	0.014	0.005	0.0008	0.004	0.004	0.005	0.004	0.003	0.0007	0.001
Co	0.06	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.05
Cr	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	0.05
Cu	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.009
Fe	20.3	12.4	<0.05	<0.05	<0.05	4.8	<0.05	0.11	4.87	0.3
K	3.45	2.25	3.56	3.86	3.16	5.38	4.89	4.29	9.92	–
Mg	45.2	2.3	2.4	1.52	1.45	7.8	4.64	3.07	63.8	–
Mn	2.3	0.05	0.07	<0.05	<0.05	0.87	0.59	0.05	31.8	0.1
Na	49.9	33	4.01	3.47	3.32	8.03	7.3	6.7	34.7	–
Ni	0.16	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	0.025
Pb	0.0013	<0.0003	<0.0003	<0.0003	<0.0003	0.0007	0.0004	<0.0003	0.0005	0.01
Zn	3.8	3.6	<0.2	0.3	<0.2	0.19	<0.2	<0.2	0.07	0.18
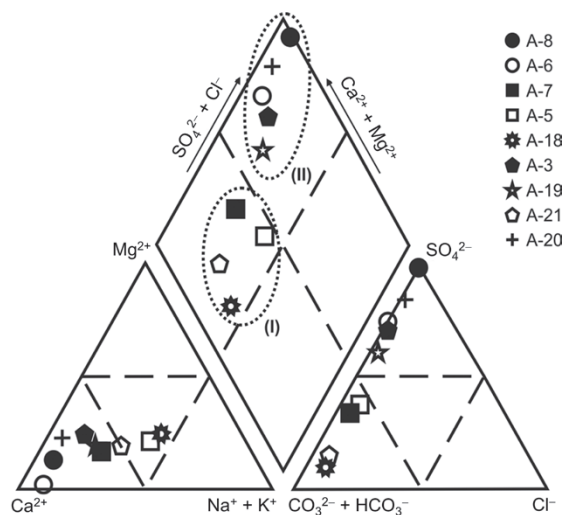
Figure 2 - Classification of stream waters of the study area, according to Piper diagram. Groups I and II refer to waters least and most affected by acid mine drainage, respectively.

carbonate system that is complex and involves the transference of carbon among the solid, liquid and gaseous phases. According to the Law of Mass Action, the predominant carbonate species in solution are H_2CO_3 in pH < 6.4, HCO_3^- in 6.4 < pH < 10.3 and CO_3^{2-} in pH > 10.3 (Krauskopf 1967). In the study area, the predominance of CO_3^{2-} over HCO_3^- at pH 10.8 (sample A-6; Table III) corroborates this fact. According to Garrels and Christ (1965), in areas where pyrite weathering occurs in the presence of carbonate rocks, the dissolution of calcite [$CaCO_3$] and dolomite [$CaMg(CO_3)_2$] occurs in the presence of strong acids. In general, the pH of the solution tends to values close to neutral due to the H$^+$ consumption followed by the H_2CO_3 dissociation and the ion

HCO_3^- stability in solution (Webb and Sasowsky 1994). Despite the fact that the relationship between carbonate species is controlled by pH, the alkalinity in water systems may be strongly controlled by the dissolution rate of carbonate rocks in the environment (Hornberger and Brady 1998). This can explain the high HCO_3^- (215 mg L^{-1}) levels in sample A-20, where the AMD influence is justified by the high SO_4^{2-} concentration (994 mg L^{-1}). In general, the sulfate represents an important guide to identify the influence of AMD because it is not significantly affected by conventional acid effluent neutralization processes (Akcil and Koldas 2006). Iron and Mn concentrations in sample A-20 seem to be AMD remains, where physico-chemical conditions for the removal of these constituents occurred after the discharge of these waters (pH = 6.8) in another natural drainage of pH 7.1 (sample A-19). At point A-19, the concentrations of all chemical constituents (except SO_4^{2-}, Ca and Mn) are comparable to those of the sample situated upstream of the coal mining sites (sample A-21).

Samples located upstream from the AMD sources (A-21, A-7, A-5, and A-18) had low concentrations of chemical elements. The Laranjinha river (samples A-7, A-5 and A-18) flow rate during the dry season is ca. 20 m^3 s^{-1} (V.P. Campaner, unpublished data) and it is the main source of public surface water supply in the study area. It yielded pH values and concentrations of chemical elements within the Brazilian standards, except for Al (Table III). Most surface water samples presented dissolved aluminum levels higher than Brazilian standards (0.1 mg L^{-1}), ranging between 0.27 and 0.41 mg L^{-1}, and occasionally 1.2 mg L^{-1} (Lenor stream) (Table III). This could be partly due to groundwater around the coal activity, with Al concentrations ranging from 5.21 to 358 mg L^{-1} (samples A-9, A-4, A-11, A-13, and A-14; Table II). In this case, aluminum solubility was strongly influenced by acid conditions in the groundwater because the metal

precipitation is generally expected to occur within a pH interval of approximately 4.5−9.0 (Faure 1998). However, aluminum occurred in the dissolved phase in the surface water from rivers and streams of the study area with pH ranging from 6 to 7.3, including this area situated upstream from the coal activities. It is thought that Al can be adsorbed onto colloids (0.001 to 1 μm particles). Although the water samples have been filtered using a 0.22 μm membrane (conventional definition for dissolved materials), colloids are traditionally included within the dissolved fraction. However, colloids are not considered to be truly dissolved, even though some of them pass through a 0.22 μm filter, and some operationally dissolved metals are considered to be "trapped" in colloidal aggregates (Bianchi 2007).

STREAM AND GROUND WATER INTEGRATED TRENDS

Principal component analysis (PCA) was performed to evaluate trace and major element trends in the whole datasets for surface and ground waters, as presented in Figure 3. The cumulative percentage of variation explained by the two main axes was 71.0%. Therefore, further discussions will be limited to the highly meaningful components 1 and 2, which explained 52 and 19%, respectively, of total data variance. Component 1 was especially marked by pH (more positive score) and sulfate (more negative score). Some elements presented negative correlation coefficients (r) with pH (Al, As, Ca, Cr, Cu, Fe, K, Mn, Ni, Pb, and Zn), with r ranging from −0.46 to −0.60 ($p < 0.05$), except Ca (r = −0.39), Fe (r = −0.41) and K (r = −0.14). These elements showed positive correlations with sulfate (r ranging between 0.62 and 0.92; $p < 0.05$). Therefore, component 1 substantially explained the acidification effect on water chemistry. On the other hand, component 2 was mainly determined by two other groups of variables, including Eh, Co and Cd (positively) and Cl^-, Mg and Na (negatively), being this second group composed of elements (r > 0.97; $p < 0.05$) of strong conservative behavior in water. The first

group showed significant positive correlation (p < 0.05) between Co-Cd (r = 0.92), Co-Eh and Cd-Eh (both with r = 0.60). While the effect of pH alone on

some metals such as cobalt is uncertain (ACMER 2005), this study showed that Co and Cd solubility was largely affected by redox conditions.
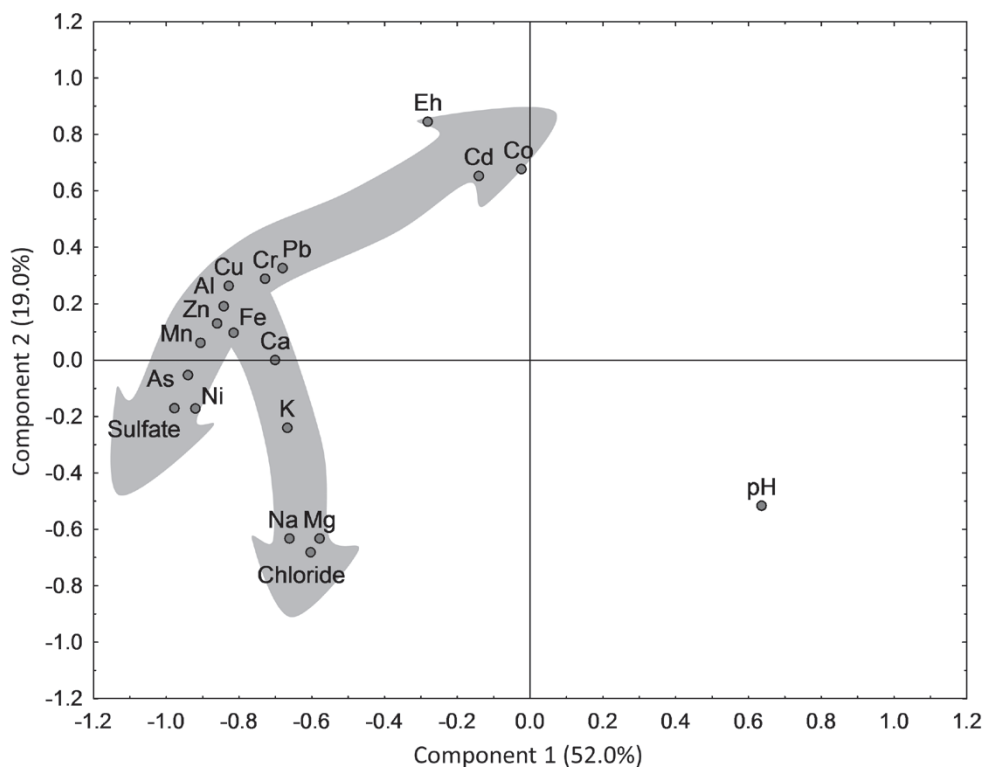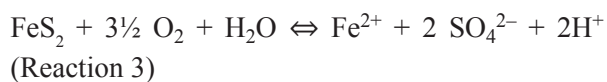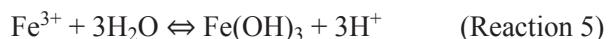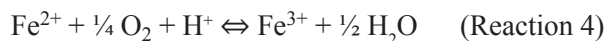

Figure 3 - PCA components 1 and 2 for surface and ground water data. Shaded arrows represent main association trends followed by major and trace elements (see text).

Two main distribution trends were observed in the PCA plot, represented by shaded arrows (Fig. 3). The major elements Ca, K, Na, and Mg presented a trend of increasing proximity to Cl⁻ (considered as the main indicator of a conservative behavior), However, Ca and K were predominantly affected by acidification processes (being significantly correlated with sulfate; r = 0.70 and 0.72, respectively; p < 0.05), probably due to dissolution of carbonate (and CaO acting as a neutralizing agent) and feldspar-bearing rocks from the regional stratigraphic sequence, respectively. On the other hand, most elements seemed to follow a distribution trend, from higher association with sulfate to higher association with Eh: sulfate-Ni-As-Mn-Fe-Zn-Al-Cu-Cr-Pb-Cd-Co-Eh. Besides, As, Ni and Mn also had significant positive correlations

with chloride (r ranging from 0.56 to 0.75). This analysis evidenced coupled effects of processes involving rock weathering, acid drainage, pH, and Eh. Furthermore, AMD effects on water chemistry can be attenuated by dilution processes resulting from a complex mixture of sources.

Although the correlation (r = 0.80) between Fe (soluble) and SO_4^{2-} was found to be high in the present study (AMD, stream and ground water samples), due to a common origin via iron sulfide (pyrite) oxidation, this relationship may not be linear. The following more detailed reactions show the key steps in pyrite oxidation forming SO_4^{2-}, Fe^{2+} and Fe^{3+}:

$$FeS_2 + 3\frac{1}{2}\ O_2 + H_2O \Leftrightarrow Fe^{2+} + 2\ SO_4^{2-} + 2H^+$$
(Reaction 3)

$$Fe^{2+} + \tfrac{1}{4} O_2 + H^+ \Leftrightarrow Fe^{3+} + \tfrac{1}{2} H_2O \quad \text{(Reaction 4)}$$

$$Fe^{3+} + 3H_2O \Leftrightarrow Fe(OH)_3 + 3H^+ \quad \text{(Reaction 5)}$$

Pyrite oxidation produces water-soluble components and acid (H^+; reaction 3). The relatively reduced ferrous iron ions (Fe^{2+}) are further oxidized to form ferric iron (Fe^{3+}) and water (H^+ is consumed; reaction 4). The kinetic of this reaction is pH dependent and proceeds slowly under acid conditions (pH 2-3; ACMER 2005). This reaction can be accelerated by Fe oxidation, but in many cases, the oxidation of Fe^{2+} to Fe^{3+} may only proceed after the mine water has travelled several kilometers off site (ACMER 2005). The ferric iron (Fe^{3+}) formation in water results in the hydrolysis of iron to form ferric hydroxide [$Fe(OH)_3$] and acid (H^+) (reaction 5). This reaction can promote accentuated removal of dissolved Fe, without SO_4^{2-} depletion, as possibly occurs in some sampling stations in the study area. A higher intensity of this process may explain the lower dissolved Fe in station A-9. Therefore, the relationship between dissolved Fe and SO_4^{2-} in water may be largely dependent on the kinetics of the reactions involved. As a result, a high sulfate concentration does not imply necessarily in high Fe concentration.

SEDIMENT GEOCHEMISTRY AND COMPARISON WITH WATER QUALITY

The concentrations of some metals and As in the fraction <63 μm of stream sediments are shown in Table IV. Among the elements analyzed, As (3.4 to 154 mg kg^{-1}), Cd (0.11 to 2.09 mg kg^{-1}), Co (6.6 to 88.8 mg kg^{-1}), Fe (2.05 to 8.84%), Mn (134 to 11876 mg kg^{-1}), Ni (8.5 to 90.1 mg kg^{-1}), and Zn (40.0 to 518 mg kg^{-1}) presented the largest variations (variation coefficients > 52%). At sites S18 and S21, which are characterized by non-contaminated sediments, the As content in sediment was 3.4 ± 0.3 mg kg^{-1}, whereas at site S3c (Pedras stream, next to the tailing piles from the coal mine) the As concentration in sediment

reached 154 mg kg^{-1}. Arsenic contents were also high in sediments at sites S20 (48.6 mg kg^{-1}, Leonor stream downstream of the abandoned mine) and S8 (34.3 mg kg^{-1}, Mina stream, downstream of coal mine in activity). In addition, higher Cd, Co, Fe, Mn, Ni, and Zn contents were recorded in sediments of the Pedras (S3c) and Leonor (S20) streams. So, along the study area, As, Cd, Co, Fe, Mn, Ni, and Zn contents in stream sediments are strongly dependent on the proximity of the inflow from contaminated areas, with the most significant concentrations in sediments close to the tailing deposits and abandoned mines. Inflow from contaminated areas promoted high EF of As, Cd, Co, Fe, Mn, Ni, and Zn in sediments (Table IV), with maximum values up to 12–28 (As, Cd and Mn), 6–8 (Co, Ni and Zn) and 2.5 (Fe). On the other hand, the variations in Al (3.48 to 6.43%), Cr (23 to 45 mg kg^{-1}), Cu (12.9 to 30.3 mg kg^{-1}), and Pb (14.7 to 38.0 mg kg^{-1}) concentrations in fluvial sediments along the study area were less significant (variation coefficient < 32%), with EF values < 1.6 for the last three chemical elements (Table IV). These results were consistent with very low contents of Cr, Cu and Pb in AMD (Table I).

For spatial comparisons of anthropogenic influences on trace elements from both surface waters (EF_w) and sediments (EF_s), enrichment factors (equations 2 and 3) in relation to average data from two reference sites taken as regional background levels (stations 18 and 21; Fig. 1) were used, as shown in Figure 4. Clear attenuation trends were observed for sediments from the Laranjinha river/Mina stream drainage systems in relation to As, Cd and Zn, considering that sediments from station S8 represents the main anthropogenic source to stations S6 and S7 downstream. Sediments from Laranjinha river station 5 (representative of a non-contaminated condition) appear to dilute these contaminations at station S7. In these drainage systems, Cd, Co, Pb, Ni, and Zn concentrations in water also decreased with increasing distance

TABLE IV
Total concentration of chemical constituents in stream sediments, background
values (in mg kg^{-1} unless otherwise indicated) and enrichment factors (EF).

	Mina stream		Laranjinha river		Pedras stream		Leonor stream	Background	EF
	S8	S6	S7	S5	S3c	S19	S20	S18 and S21	(interval)
Al (%)	4.44	5.67	5.43	6.43	5.72	4.04	5.99	3.48 ± 0.71	–
As	34.3	16.4	13.1	10.5	154	14.6	48.6	3.4 ± 0.3	1.7–27.6
Cd	1.35	0.77	0.65	0.22	2.09	0.33	1.2	0.11 ± 0.00	1.1–11.6
Co	6.6	11	15.6	12.5	33.7	13.2	88.8	8.6 ± 0.2	0.6–6.0
Cr	24	39	30	45	35	28	30	23 ± 6	0.8–1.1
Cu	12.9	25.6	16.1	30.3	23.8	16.3	15.9	16.3 ± 2.6	0.6–1.0
Fe (%)	3.71	4.35	2.85	3.22	6.18	2.79	8.84	2.05 ± 0.13	0.9–2.5
Mn	134	258	1295	776	2696	691	11876	466 ± 29	0.2–14.8
Ni	14.6	22.3	17.2	16.3	24.3	11.7	90.1	8.5 ± 2.6	1.0–6.2
Pb	22.7	22.4	32.2	21.1	38	19.8	32.5	14.7 ± 0.3	0.8–1.6
Zn	270	244	150	71.5	518	113	347	40.0 ± 0.4	1.0–7.9

downstream of the anthropogenic source. In contrast, a less clear trend was observed for As, with a lower EF_w at station A-8 than in stations A-5, A-6 and A-7, suggesting lower As solubility close to the contamination source. Sediment and water enrichment factors below or close to 1 were found for Cr and Cu within such drainage systems, as well as for Co, Ni and Pb EFs.

In the Pedras stream/Leonor stream drainage systems, while most elements remarkably showed water enrichment factor lower or close to 1 (just As presented an EF_w exceeding 2 at stations A-3 and A-19, and As at station A-19; Fig. 4), sediment enrichment factor values exceeding 2 were found for most elements (As, Cd, Co, Ni, and Zn). These elements always showed lower EF_s in the station S19, which receives the discharge from the uncontaminated section of the Pedras stream (Fig. 1). This contrast is expected because station S3c (with maximum EF_s for As, Cd and Zn) is closer to mining tailing piles, while station S20 (with maximum EF_s for Co and Ni) is closer to an abandoned mine upstream Leonor stream (Fig. 1). Contrarily to the Laranjinha river/ Mina stream drainage systems, the anthropogenic effect was stronger on the chemical composition of sediments than on the waters in the Pedras stream/

Leonor stream drainage systems, as indicated by enrichment factors. Possible explanations for this observation include probable differences in water flow rate (affecting dilution) and the fact that the mining activity within the Leonor stream drainage was abandoned.

When the scale of coal mining and related activities in the study area is taken into account, the environmental impact of mining and related activities on the stream sediments is relatively limited due to a high neutralizing capacity of the mining wastes which control the rapid precipitation of iron oxides and hydroxides as well as adsorption and/or co-precipitation of arsenic and trace metals. However, the observed high As and metals content in stream sediments close to the tailing deposits and abandoned mines may pose a potential environmental risk during accidental acid spikes, when significant fractions of As and metals in sediments can be re-mobilized.

CONCLUSIONS

The results of this study showed that acid drainage generated in the bituminous coal mining activities is a potential source of metals and As to water systems. The exposure of mining tailings to
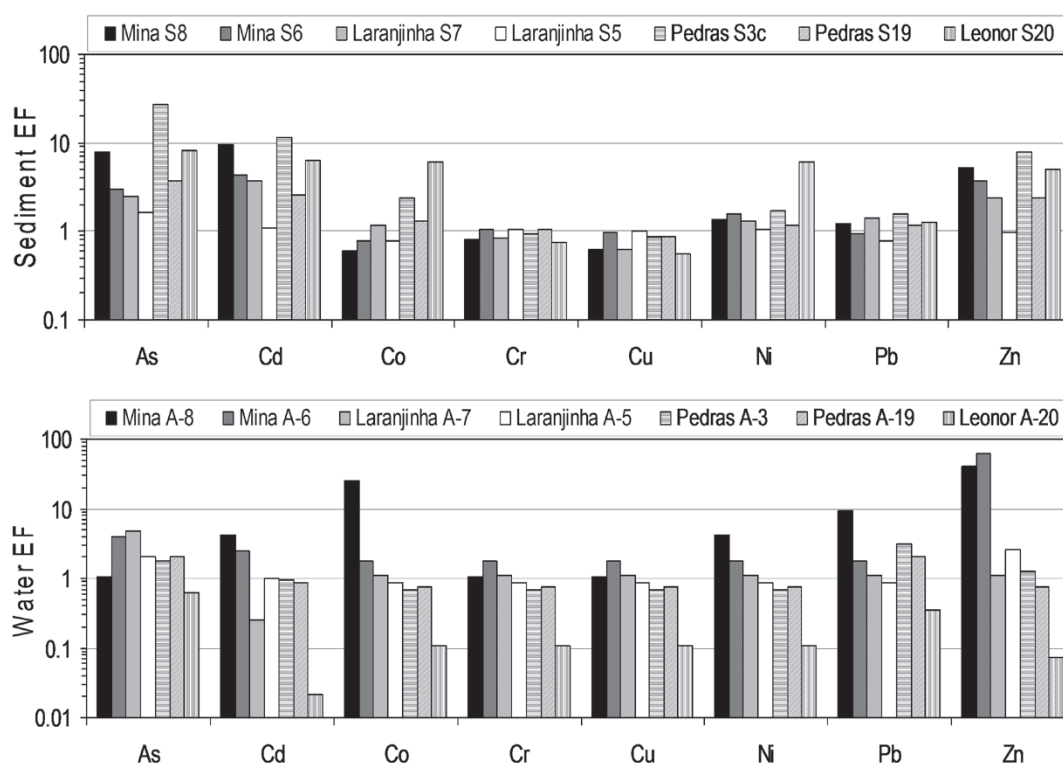
Figure 4 - Comparison of water enrichment factors (normalized to Cl⁻) and sediment enrichment factors (normalized to Al) obtained for the same sampling stations located at the Mina, Pedras and Leonor streams and the Laranjinha river.

weathering produced acid solutions with the highest metals and As contents, influencing the chemical composition of surrounding groundwater. In stream waters, precipitation and dilution mechanisms attenuated the concentrations of the AMD chemical constituents. In some situations, the presence of carbonate rocks in the local stratigraphic sequences seems to have played an important role in decreasing the AMD regional impact. As well as in stream waters, metals and As geochemical anomalies in fluvial sediments occurred near the AMD sources due to precipitation mechanisms.

ACKNOWLEDGMENTS

RESUMO

Influência de drenagem ácida sobre a qualidade de água e sedimento foi investigada em uma área de mineração de carvão (sul do Brasil). A drenagem ácida mostrou pH entre 3,2 e 4,6 e elevadas concentrações de sulfato, As e metais, dos quais, Fe, Mn e Zn excederam os limites para emissão de efluentes da legislação brasileira. Arsênio também excedeu levemente o limite. Poços de monitoramento de água subterrânea situados em áreas de mina ativa e pilhas de rejeitos revelaram intervalo de pH e concentrações químicas semelhantes aqueles da drenagem ácida. Entretanto, amostras de águas subterrânea e de rio utilizadas para o abastecimento público municipal revelaram pH entre 7,2 e 7,5 e baixas concentrações químicas, embora a concentração

de Cd tenha superado um pouco o limite adotado pela legislação brasileira para águas subterrâneas. Em geral, as águas de superfície mostraram grande intervalo de pH (6 a 10,8), e a influência da drenagem ácida em sua composição química não foi muito significativa. Localmente, drenagem ácida parece ter dissolvido rochas carbonáticas presentes na sequência estratigráfica local, atenuando a dispersão de metais e As. Anomalias destes elementos foram encontradas em sedimentos de corrente, e elas foram fortemente dependentes da proximidade de depósitos de rejeitos e minas abandonadas. Neste trabalho, processos de precipitação em sedimentos e diluição de fases dissolvidas foram considerados como os principais mecanismos responsáveis pela atenuação das concentrações de metais e As nas zonas de mistura entre drenagem ácida e água fluvial. Em geral, observou-se uma maior influência das atividades de mineração sobre a composição química de águas superficiais e sedimentos quando fatores de enriquecimento em relação aos níveis de background regionais foram utilizados.

Palavras-chave: drenagem ácida de mina, carvão, metais, qualidade de água.

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