

Hydrogeochemistry of Sand Pit Lakes at Sepetiba Basin, Rio de Janeiro, Southeastern Brazil

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Abstract Four sand pit lakes, at the Rio de Janeiro Sand Mining District, were monitored from November 2003 to November 2005, in order to characterize their hydrogeochemistry aiming to provide information to their possible use as fishponds at the end of mining activities. The results show diluted waters (low electrical conductivity) with low pH (<4) and relatively high sulfate and aluminum concentrations. The major water components (in particular Fe, Mn, SiO₂, Al and SO₄) are related to water acidity, since it controls solubility of aluminum silicate minerals and Mn and Fe oxides. Fe, Mn and Al availability in these waters are probably associated to organic colloids formation. On the other hand, the SiO₂ content, as well as the decrease of sand mining in rainy season, may partially

control Al availability by the formation of hydroxi-aluminum silicates. These geochemical processes together with the interruption of sand mining in the rainy season and the dilution of sand pit lakes water by rainwater can support the use of these pit lakes as fishpond for aquaculture.

Keywords Hydrochemistry · Metal availability · Acidic water · Sand pit lakes

1 Introduction

Pit lakes, as defined in the ore mining industry, refer to artificial lakes originated by the mining activity, differing from natural lakes by the small diameter to depth ratio (Ramstedt et al. 2003). These lakes are usually associated with acidic waters since most metal ores are commonly in the form of sulphide minerals (Davis and Ashenburg 1989; Davis et al. 1996; Pellicori et al. 2005; Davis et al. 2006), therefore resulting in peculiar hydrochemical environments. These acidic waters could release trace metals to the water column, which are highly toxic to biota, depending on the geological setting of a given region. The most documented cases of water bodies contamination by pit lake acidic waters are from acid mine drainages (AMD), which are responsible for river and groundwater contamination by trace metals in many mining districts in the world (España et al. 2005; Lin et al. 2006; Saria et al. 2006).

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The present paper shows the hydrochemistry of sand pit lakes in Sepetiba basin, a Quaternary sedimentary basin with a great potential for sand mining. The geological history of this region resembles ancient environments of mangrove and brackish water swamps (Berbert 2003), which give conditions to the accumulation of organic matter and sulphide species formation, mainly pyrite (Lacerda 1998). Therefore, the pit lakes formation by sand mining in Sepetiba basin suggests similar features to those occurring in ore pit lakes characterized by acidic waters.

Since the end of the 1960s, the Seropédica-Itaguaí Sand Mining District, located in Sepetiba basin, became the main sand supplier (about 70%) for the civil construction in the Metropolitan Region of Rio de Janeiro. Nowadays, approximately 80 sand mining operations take place in that district. The sand extraction process consists in the removal of surface sedimentary layers (with a quartz-feldspatic composition), exposing the groundwater to surface (Piranema aquifer) and filling up the holes left behind. Opposite to ore mining processes, where the dewatering systems are used to remove water from surrounding aquifers to allow mining to proceed (Eary 1999), in the sand pits the water table rising facilitates hydraulic removal of the sediments.

Despite sand mining having an important economic role for civil construction in the metropolitan region of Rio de Janeiro, this activity generates negative impacts on the quality of the water supply to the peripheral areas of Seropédica and Itaguaí cities, where groundwater is the main water source to the population. Sand extraction culminates in the water table drawdown and exposing the groundwater surface to contamination by fuel oil from dredges and domestic and industrial effluents, resulting in groundwater quality degradation (Berbert 2003).

Sand pit lakes, as in ore mining, are left behind when this activity is finished. Studies are in progress to give a useful destination to these artificial lakes, such as fishpond for aquaculture. Fish aquaculture has been one of the activities most suitable for economical remediation of mining liabilities in many abandoned mining site in Brazil and other parts of the tropics, where extensive artisan farming practice is an important source of income to local populations (Waserman et al. 2007). Possible constraints to the utilization of mining lakes as fishponds are related to

poor water quality, which may select the better species to be farmed and the potential transfer of existing pollutants through fish consumption to humans. Therefore, the aim of this work is to characterize the water chemistry of the sand pit lakes, identifying the sources of the present components and describe the dominant hydrogeochemical processes occurring due to pit lakes opening, in order to access their potential usefulness as fishpond and the possibility of pollutant transfer through fish consumption.

2 Study Area

The Sepetiba Sedimentary Basin occupies an area of about 4% of the Rio de Janeiro State and its main tributary is the Guandu River, which is originated in Serra do Mar Mountains. The Guandu drainage basin occupies about 2,000 km², of which 90% is formed by alluvial plain deposits (SEMA 1996). The study area (Fig. 1) lies within this plain and is located at the horizontal UTM coordinates (North 7,470,000; 7,478,000) and vertical UTM coordinates (East 630,000; 638,000).

The Guandu River is the main potable water supply to the Rio de Janeiro Metropolitan Region. It receives waters from the Paraíba do Sul River by transposition and flows to the Guandu Water Treatment Station, the biggest water treatment plant in Latin America, supplying water to about 8.5 million people (Rios and Berger 2002; Molisani et al. 2006).

The surrounding topography of the study area exerts a strong influence on rainfall regime (Nimer 1977). Annual precipitation average is 800 mm and the annual temperature average is 20°C (SEMA 1996). There are two well-known precipitation periods based on the historical monthly averages between 1977 and 2005 (Santa Cruz Pluviometric Station, Fig. 2). Annual rainfall is higher from October to March and lower from April to September.

The geology of the region is composed by Quaternary sediments from alluvial environments (fluvial, fluvial-lacustrine and fluvial-marine) superimposed on a Pre-Cambrian basement known as the Piranema Formation (Góes 1994) and are represented by two units. The lower unit is characterized by Pleistocene sands of medium to coarse texture and gravel with essentially quartz-feldspatic mineralogy. The upper unit, also called alluvium cover, is composed by

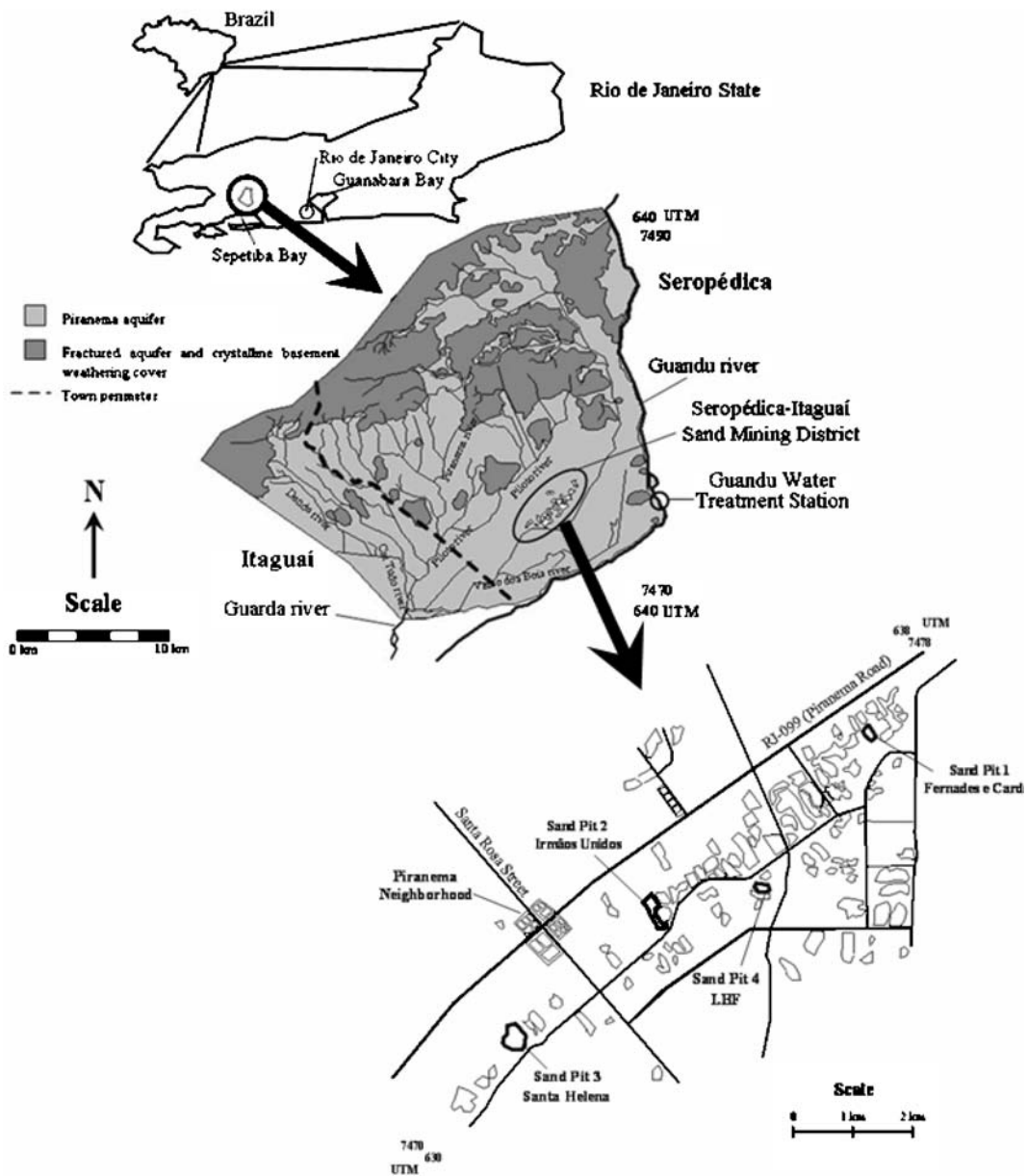


Fig. 1 The Piranema aquifer boundaries and localization of the studied area. The four studied sand pit lakes are highlighted by *thicker lines* on the lower figure

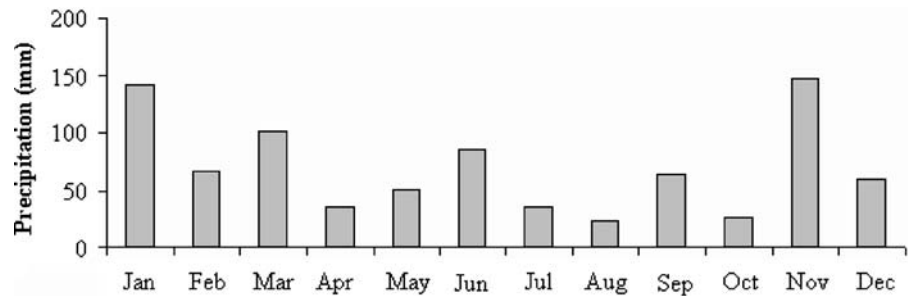
Holocene silts and clays. Sediment cores from the Piranema Formation showed thickness of 35 and 40 m, reaching depths as high as 70 m in some areas. The mineralogy of these sandy sediments was characterized by Berbert (2003), who reported 82% of quartz, 14% of feldspars (no indication of alkaline feldspars or plagioclase) and 2% of micas and rock fragments, classifying the sandy fraction as sub-arcosian.

The Piranema Sedimentary Aquifer System has an area of about 350 km² (70% of the area shown in Fig. 1)

and is located approximately 60 km western from Rio de Janeiro city. The free aquifer recharge system is distributed upon its occurrence area, trending to highest potentiometric level as high as the regional topography. So, the flux direction is controlled by topographic irregularity. The water table level ranges from 3 to 7.5 m, depending on season. Table 1 presents some data from aquifer hydrology.

The soil cover, originating from crystalline rocks, could generate an aquifer system with similar charac-

Fig. 2 Rainfall average from Sepetiba region (Santa Cruz pluviometric station) between 1977 and 2005 (source: GEORIO)



teristics of a sedimentary porous aquifer (coluvial deposits) and gradually, as depth increases, transforming into fractured systems. Together, the fractured aquifers and soil cover are responsible for 30% of the area (Fig. 1). The intercommunication among the sedimentary fractured and coluvial aquifers could increase the regional groundwater potential and determines the aquifer recharge and flow patterns (Eltrobt 2003). Table 1 shows some data from Piranema aquifer hydrology.

While the mean transposition flow is of about $166 \text{ m}^3 \text{ s}^{-1}$, the internal contribution of the Guandu River drainage basin is about $3.18 \text{ m}^3 \text{ s}^{-1}$ (Ottoni et al. 2002) and the Piranema Aquifer contributes with a flow of about $1.6 \text{ m}^3 \text{ s}^{-1}$. In spite of its limited potential, this aquifer has a strategic role for this region, as a source of potable water supply for short time periods.

3 Materials and Methods

Water samples ($n=14$) were collected (1 m below the surface) from November 2003 to November 2005 in four sand pit lakes, using a 2-l Van Dorn bottle and stored in clean polyethylene bottles. Electric conduc-

Table 1 Some hydrological data from Piranema aquifer (Terrabyte, 2000)

Hydrological data	Values
Total porosity	30%
Effective porosity	23%
Intrinsic permeability	0.1 darcy
Hydraulic conductivity	$10^{-4} \text{ cm.s}^{-1}$
0.8	0.3 m day^{-1}
0.26	0.1 m day^{-1}
0.24	0.09 m day^{-1}
Transmissivity (T)	$1.3 \text{ m}^2.\text{day}^{-1}$ for 15 m of a aquifer thick

tivity, temperature and pH were measured by WTW-LF electrodes (model 330) at the sampling sites.

In the laboratory, the samples were filtered through 0.45 and 0.22 μm filters (Millex[®]-GS Millipore filters). The filtered samples were divided in three equal aliquots of 50 ml. The first aliquot (0.45 μm) was used for silicates and phosphate analysis, the second one (0.22 μm) was acidified (pH 1) and used for metal analysis, and the third one (0.22 μm) was used to determine anions and silicate content.

Chloride, sulfate and nitrate determinations were carried out by ion chromatography (Shimadzu LC-10AD, conductivity detector CDD-6A). The determination of Ca^{2+} , Mg^{2+} , K^{+} and Na^{+} was performed by flame atomic absorption spectrometry (Varian SpectraA-300). Aluminum, iron and manganese determinations were carried out by Inductively Coupled Plasma Optical Emission Spectrometry (Jobin Yvon-Horiba, Ultima 2), which detection limits were 0.2, 0.2 and 0.05 $\mu\text{g.l}^{-1}$ respectively. Silica and phosphate were determined by specific spectrophotometric methods (Grasshoff et al. 1983) and analyzed with a Hitachi, U-1100 spectrophotometer.

Statistical analysis was performed using the Statistica 5.0 software, where the principal component analysis (PCA, Q-mode) was performed to simplify data interpretation. The PCA analysis was performed utilizing the orthogonal transformation method with Varimax rotation and retention of principal components whose eigenvalues were greater than unity. The correlation of each variable with each component was considered significant only for factor loadings >0.60 .

4 Results

The Piper–Hill diagram was used in order to characterize the hydrogeochemical facies of the sand pit waters. It was assumed the absence of bicarbonate

and carbonate ions in these waters due to the low pH values found. The resulting diagram (Fig. 3) indicated that those waters may be classified as Na–SO₄–Cl facies type, reflecting the main components in the water.

Table 2 shows the average ($n=14$), maximum and minimum values and standard deviation of dissolved Ca²⁺, Mg²⁺, Na⁺, K⁺, Fe (II and III), Mn²⁺, Al³⁺, SiO₂, Cl⁻, SO₄²⁻ and NO₃⁻ concentrations (mg.l⁻¹); pH and electric conductivity ($\mu\text{S.cm}^{-1}$) in the sand pit waters. Data are compared to those from Barbosa (2005), who studied groundwater chemistry in a nearby area. Major differences are found for Al³⁺, SO₄²⁻ and NO₃⁻ concentrations.

The groundwater from the studied region, which fills the mining pits, shows higher pH values (ranging from 4.6 to 5.7) compared to pit lake waters (Table 2). Sand Pit Lake 1 showed the lowest mean pH value (3.8), while sand pit lakes 3 and 4 showed the higher mean pH value (4.5). The electric conductivity values ranged from 111 (sand pit 3) to 388 $\mu\text{S.cm}^{-1}$ (sand pit lake 4), suggesting low mineralization of these waters (Marques et al. 2004). The average concentrations of Ca²⁺, Mg²⁺, Na⁺ and Mn²⁺ in sand pit lakes were comparable to those obtained by Barbosa (2005) in a study of groundwater collected through out wells in a nearby residential area, the Piranema District (Fig. 1). On the other hand, K⁺, dissolved Fe and Cl⁻ concentrations were slightly lower, while Al³⁺ and SO₄²⁻ were one order of magnitude higher than those found in groundwater (Barbosa 2005).

Nitrate concentrations in all studied sand pit lakes were below the detection limit of the analysis (<0.01

mg.l⁻¹). However, Barbosa (2005) found high NO₃⁻ concentrations (ranging from 1.3 to 68 mg.l⁻¹) in groundwater from Piranema District, which was attributed to untreated wastewater disposal from the surrounding urban area.

In general, among sand pit lakes, the highest mean values of the studied parameters were found at sand pit Lake 4 and the lowest at sand pit Lake 3, the most recently opened Pit Lake. This is particularly verified by the low SO₄²⁻ content of its waters. It is worth to notice that sand pit lake 1 showed the lowest pH values and the highest SO₄²⁻ concentration values, which may be related to the oxidation of iron sulphide from the peat horizon. However the higher pH values found at sand pit lake 4 is probably associated to the acidity buffering capacity of Ca²⁺, Mg²⁺, K⁺ and Al³⁺.

The maximum values found for Al³⁺ concentrations (14.7; 13.7; 12.3 and 14.4 mg l⁻¹ in sand pit lakes 1, 2, 3 and 4, respectively) are not common in natural waters (Hem 1985; Drever 1997; Faure 1998) and is probably associated to the acidification of sand pits water.

The average silica concentration exhibited a homogeneous distribution among the four sand pits (26.3, 26.6, 21.1 and 25.5 mg l⁻¹ in lakes 1, 2, 3 e 4, respectively). As for sodium and chloride, sand pit Lake 4 showed the highest average concentrations (33.3 and 36.3 mg.l⁻¹, respectively). The data from phosphate content in the pits lakes were below the detection limit (<0.001 mg.l⁻¹), probably due to precipitation as ferrous phosphate.

In general, the behavior of the dissolved species in the sand pit waters is controlled basically by pH and rainwater (Fig. 4). The highest concentrations of Al³⁺, dissolved Fe and SiO₂ are shown during dry season. On the other hand, the contents of SO₄²⁻ and Cl⁻ show an opposite behavior.

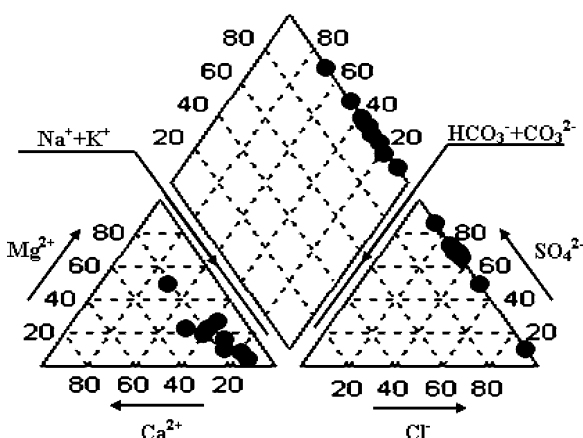


Fig. 3 Piper–Hill trilinear diagram showing the plotting from all the sand pits lakes samples

5 Discussion

Principal component analysis is extensively applied as a tool for elucidating the processes determining water chemical composition (Winter et al. 2000; Gangopadhyay et al. 2001; Ettazarini 2004; Cruz and França et al. 2006). Table 3 shows the result from PCA analysis. Four principal factors were obtained and explain 70% of the total data set variance. Factor 1 (30% of the total variance) shows positive and significant associ-

Table 2 Average, standard deviation and maximum and minimum values of the water components concentration ($\text{mg}\cdot\text{l}^{-1}$), pH and electrical conductivity from studied sand pits water and a groundwater study in the same region

	Ca^{2+}	Mg^{2+}	Na^+	K^+	Fe (II and III)	Mn^{2+}	Al^{3+}	SiO_2	SO_4^{2-}	Cl^-	NO_3^-	pH	EC
Sand Pit Lake 1													
Average	6.9	2.7	27.1	3.1	0.2	0.4	2.5	26.3	61.5	22.1	<0.01	3.8	295
SD	5.4	2	14	1	0.1	0.1	5.1	9.6	19	8	–	0.3	34.3
Maximum	21.0	5.6	66.1	5.2	0.46	0.6	14.7	34.4	96.0	33.3	–	4.9	329
Minimum	1.3	0.16	6.4	1.5	0.02	0.06	0.02	2.6	1.34	9.88	–	3.11	208
Sand Pit Lake 2													
Average	2.9	1.5	26.1	2.7	0.3	0.1	2.8	26.6	29.8	26.5	<0.01	4.4	194
SD	1.2	1	7.5	0.5	0.7	0.01	5	4.6	8.6	4.6	–	0.3	30.5
Maximum	4.6	3.12	63.3	4.7	2.05	0.22	13.7	32.8	41.1	33.1	–	5.2	223
Minimum	1.03	0.07	10	1.86	0.004	0.1	0.01	16.36	0.91	17.7	–	4.0	121
Sand Pit Lake 3													
Average	1.9	0.5	16.8	2	0.08	0.13	1.5	21.1	3.3	25.6	<0.01	4.5	127
SD	3.2	0.4	6.4	0.6	0.11	0.03	4.1	5.8	0.9	4.2	–	0.2	8.8
Maximum	10.9	2.0	64.1	3.1	0.3	0.18	12.3	29.9	4.8	30.5	–	5.1	143
Minimum	0.27	0.01	0.02	0.38	0.001	0.05	0.01	9.3	0.11	18.3	–	4.1	111
Sand Pit Lake 4													
Average	5.7	3.6	33.3	3.9	0.1	0.4	2.9	25.5	60.9	36.3	<0.01	4.5	301
SD	2.4	2.3	10.8	0.7	0.1	0.1	5.7	5.3	23.8	12	–	0.5	69.9
Maximum	9.8	6.5	71.3	5.8	0.66	0.65	14.4	33.8	97.6	58.4	–	5.2	388
Minimum	2.48	0.3	16.4	2.5	0.02	0.24	0.04	14	1.8	16.9	–	3.7	207
Groundwater data from Barbosa (2005)													
Average	3.6	3.6	31.1	4.8	0.8	0.2	<0.015	n.a.	6.5	43	29.8	5.0	203
SD	2.3	2.5	9.5	2.3	2.9	0.2	–	–	8.6	14.6	18.5	0.3	10.0
Maximum	10.0	12.0	56	11.5	14.3	0.8	–	–	39.3	76.4	67.9	5.7	230
Minimum	1.1	1.1	18.4	0.5	0.003	0.1	–	–	0.8	26.6	1.3	4.6	20

SD Standard deviation, EC electrical conductivity, n.a. non-analyzed component

ation with electric conductivity (EC), Cl^- , Mn^{2+} , Na^+ , K^+ and Mg^{2+} . The last three ionic species are derived from rock-forming minerals and at least in part also from atmospheric deposition (wet and dry) of sea salt. The primary source of Cl^- is believed to be atmospheric deposition of sea-salt. Factor 2 (16% of the total variance) shows significant and positive association with SO_4^{2-} and negative with pH, suggesting sulphide minerals oxidation from the sediments as the major processes controlling of sulfate abundance and pH values. Factor 3 (15% of the total variance) is negatively associated with rainfall and positively associated with aluminum. The negative association of this factor with rainfall may be due to interruption of the mining activities during the rainy season. Factor 4, (10% of total variance) shows significant association only with silica. The fact of SiO_2 is not associated with Factor 1 (representing minerals

weathering predominantly), suggests that some other processes, such as biological uptake, may control the silica behavior in pit waters (Miretzky et al. 2001; Gélabert et al. 2004).

5.1 Origin of the Acidic Water

The exposure of surface sedimentary layers, during sand mining, increases water acidity, accelerating weathering of this material which affects water chemical composition. This environment has the same acidification origin typical of pit lakes from ore mining, described by many authors (Sumer et al. 1995; Miller et al. 1996; Kleeberg 1998; Early 1999; Shevenell et al. 1999; Bachmann et al. 2001; Ramstedt et al. 2003). Nevertheless, the concentration of some components in ore mine waters, like SO_4^{2-} , Fe II and III, Mn^{2+} and Al^{3+} , are much higher in comparison to the studied

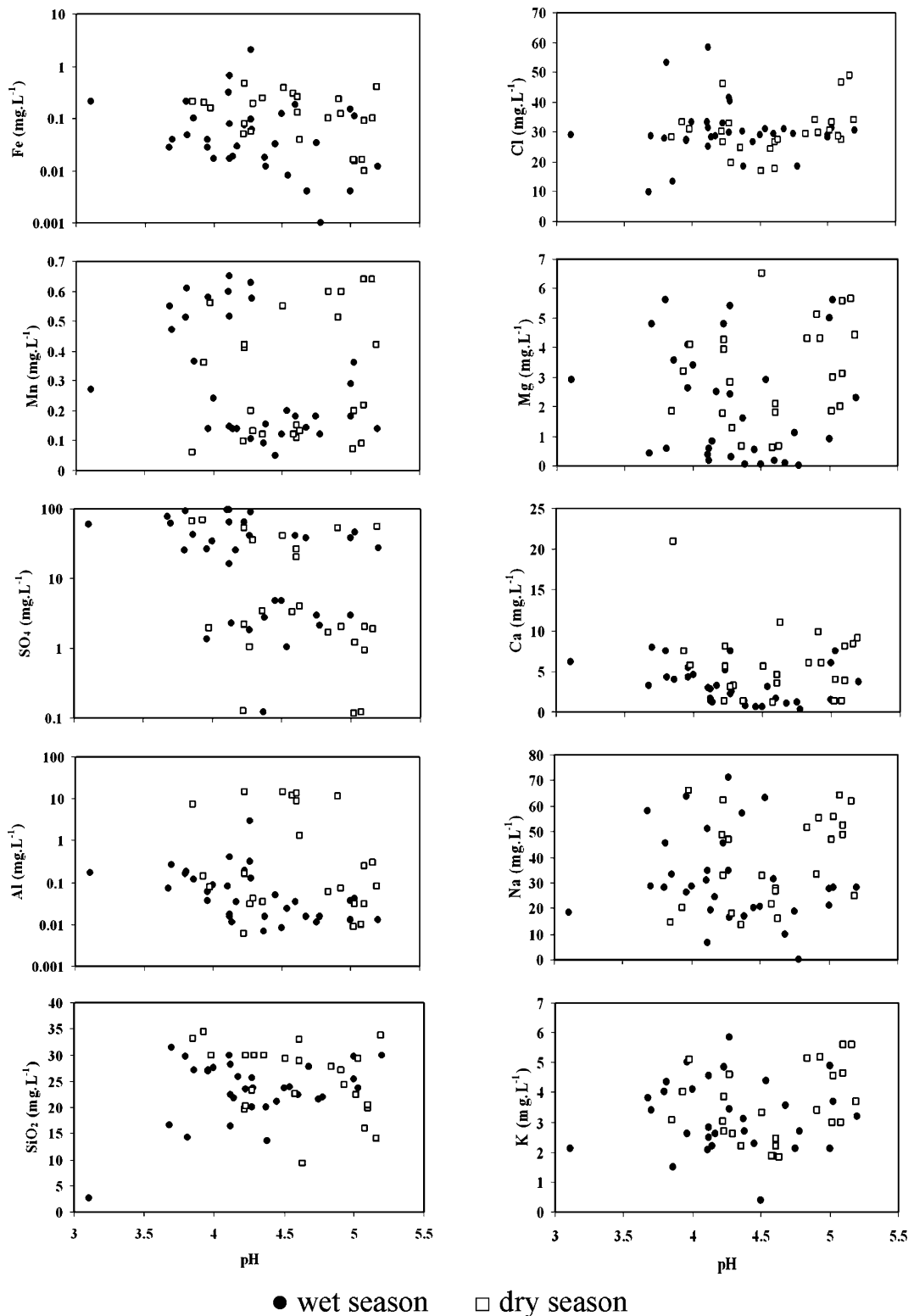


Fig. 4 Behavior of major species in the pH range along wet and dry season

Table 3 Segregate factors matrix (screening) by principal components analysis applied to the physical–chemical parameters from sand pits waters

Variable	Principal components analysis			
	Varimax rotation			
	Marked values ≥ 0.60			
Factor 1	Factor 2	Factor 3	Factor 4	
Ca ²⁺	0.45	0.11	0.39	0.42
Mg ²⁺	0.70	-0.21	0.07	0.52
Na ⁺	0.70	-0.34	-0.02	-0.23
K ⁺	0.83	-0.16	-0.24	0.16
Fe ²⁺	-0.02	0.30	0.44	0.09
Mn ²⁺	0.82	0.32	0.06	0.03
Al ³⁺	-0.14	0.00	0.75	0.38
SiO ₂	-0.03	0.09	0.07	0.80
SO ₄ ²⁻	0.14	0.87	0.21	0.06
Cl ⁻	0.63	0.13	0.03	-0.41
EC	0.81	0.52	0.03	0.03
pH	0.05	-0.74	0.19	0.02
PP	-0.06	0.24	-0.86	0.22
Eigenvalue	3.78	2.11	1.89	1.28
Variance %	30.00	16.00	14.53	9.85
Cumulative %	30.00	46.00	60.53	70.38

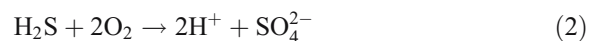
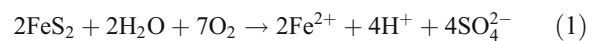
Highest scores for each factor are marked in bold.

EC Electrical conductivity, PP pluviometric precipitation

sand pit lakes, which is explained due the geological origin of the ores. As it can be seen in Table 4, Triantafyllidis and Skarpelis (2006), in a study of pit lake from Kirki in Greece, reported high SO₄²⁻ contents (over 1,000 mg.l⁻¹), as well as high dissolved Fe concentration (over 25 mg.l⁻¹) and Mn²⁺ (over 150 mg.l⁻¹) with low pH values (below 3.0). Ulrich et al. (2006) also found low pH values (2.85) and high dissolved Fe (276 mg.l⁻¹), Mn²⁺ (12.4 mg.l⁻¹), SO₄²⁻ (1,260 mg.l⁻¹) and Al³⁺ (39.2 mg.l⁻¹) in a uranium mine water from Königstein, Germany. In Berkeley pit lake, Montana, USA, a wide by known Cu–Zn–Pb–Ag–Mn ore mining are, Pellicori et al. (2005) presented values similar to those mentioned above, also highlighting the high contents of SO₄²⁻ (over 8,000 mg.l⁻¹), Al³⁺, dissolved Fe and Mn²⁺.

The studied sand pit lake waters have much lower contents of dissolved species, as well as species diversity, than sulphide ore mines and also coal mines pit lake waters (Denimal et al. 2005; Bloudau 2006). This may be partially due to the poor mineralogy of the Piranema aquifer and its relatively recent age

(Quaternary basin). However, the main reason for the acidification process to be more effective in ore mining pit lake waters is the sulphide mineralization, that is, higher sulphide content in their geological settings in comparison to the sand pit lakes (sedimentary origin). In the studied sand pit lakes, the acidification process is associated with oxidation of some reduced sediments, which have in their composition sulphide species, mainly pyrite (neo-formed) and hydrogen sulphide (Eqs. 1 and 2, respectively), pointing out an ancient sedimentary environment of mangrove and/or brackish water swamps (Lacerda 1998). Figure 5 shows a representative sediment core profile from the studied region. Sulphide species probably arise from grey sands (8–16 m depth) and green clay layers (3–5 and 16–19 m depths). The oxidation of sulphide species decreases water pH values and increases SO₄²⁻ content, according to the following equations (Stumm and Morgan 1996):



5.2 Na, Ca, K, Mg and Cl Behavior in Sand Pit Lakes

Potassium, Ca²⁺ and Mg²⁺ showed low concentrations in the studied waters. This fact may be related to

Table 4 Average concentration values (mg.l⁻¹) of Fe, Mn²⁺, Al³⁺, SO₄²⁻ and pH from sand pits lakes waters in comparison with other studies from literature in ore mining pit lakes

	Dissolved Fe	Mn ²⁺	Al ³⁺	SO ₄ ²⁻	pH
Sand Pit Lakes ¹	0.17	0.26	2.4	39	4.3
Königstein Uranium Mine ²	276	12.4	39.2	1,260	2.85
Kirki Pit Lake ³	27.1	112	–	1,700	2.9
Berkley Pit Lake ⁴	754	225	247.5	7,425	2.45

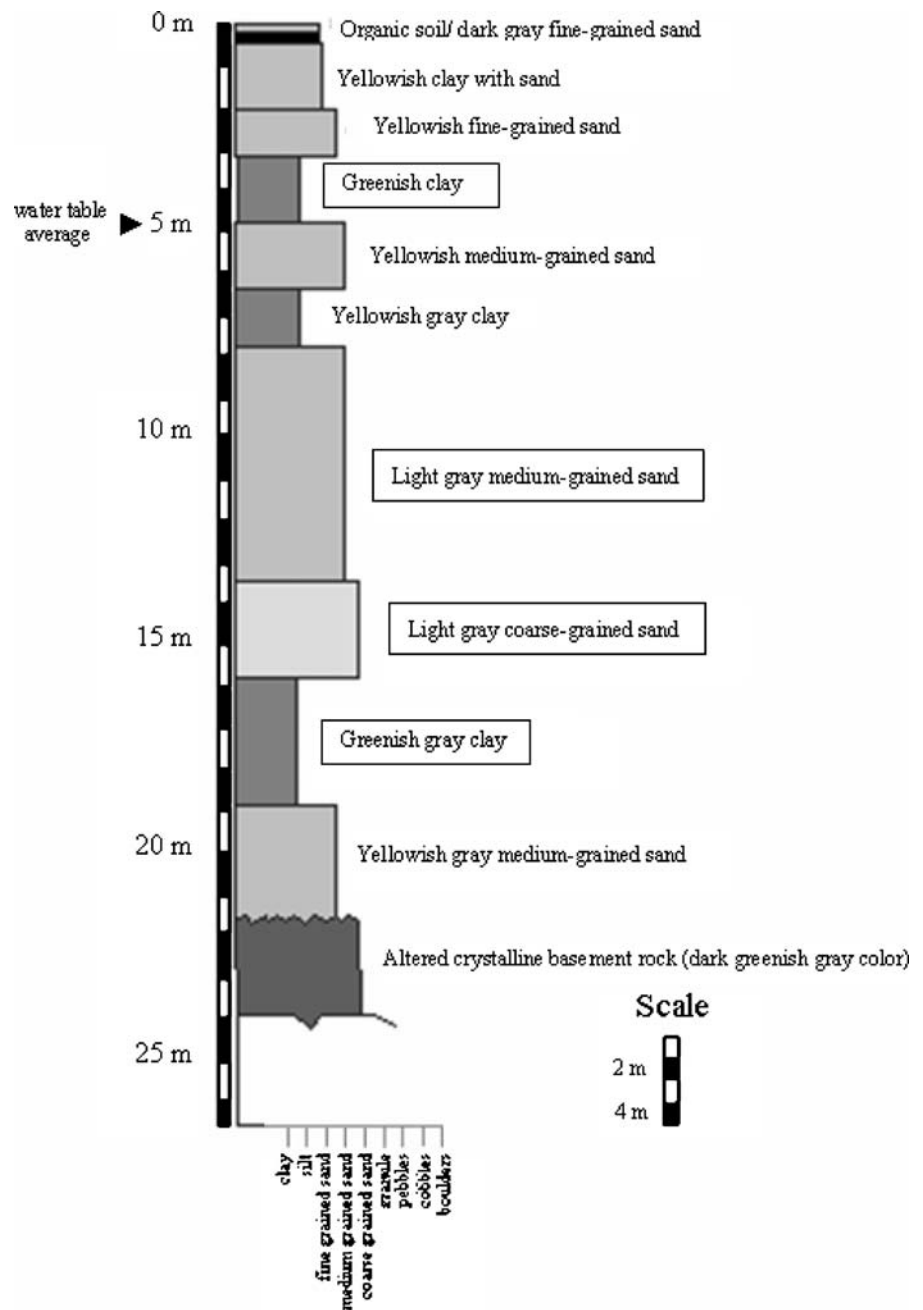
^a This study

^b Ulrich et al. (2006);

^c Triantafyllidis and Skarpelis (2006), data from September 2001;

^d Pellicori et al. 2005, average values from October 2003

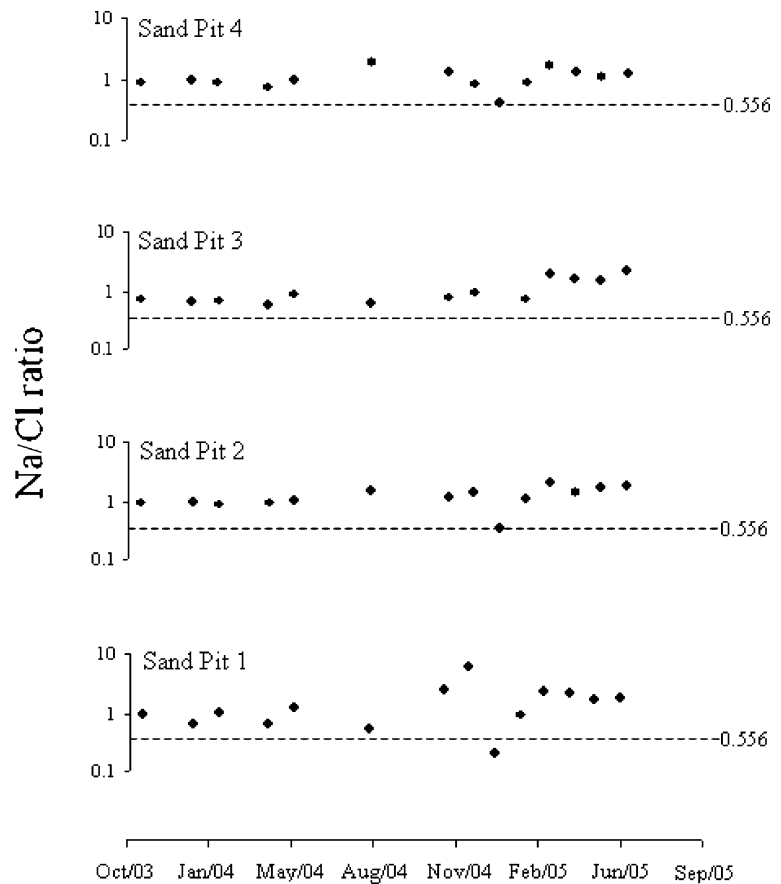
Fig. 5 Representative sedimentological profile from Piranema region. The lithologies highlighted in rectangles are probably sources of sulphides



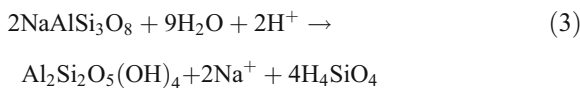
the lithology of this region, which shows minerals with low content of calcium and magnesium. On the other hand, the low potassium content could be also associated with its lower mobility and the higher weathering resistance of potassium feldspars. However, sodium showed higher concentration (above 50 mg l^{-1}), which indicates that besides weathering, this

ion could also come from atmospheric deposition of sea salt aerosols. Figure 6 shows Na^+/Cl^- ratio during the sampling period in comparison with seawater ratio ($\text{Na}^+/\text{Cl}^- = 0.556$ Drever 1997; Millero 2006). All samples are Na enriched, indicating that apart from atmospheric deposition of sea salt, mineral weathering is a significant source of Na^+ , represented by the

Fig. 6 Na^+/Cl^- ratio variations in the sand pit waters along the study period (the dashed line represents the seawater Na^+/Cl^- ratio)



incongruent reaction of Na-plagioclase weathering (Eq. 3), probably the most Na-containing mineral in the aquifer:

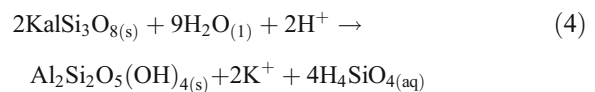


The Cl^- content in the sand pit waters probably results mostly from sea salt spray due its proximity to the coastal region (about 10 km southward of the study site). Besides this fact, the local groundwater flow lines converge into the sand pit lakes due to hydraulic head gradient between the aquifer (higher hydraulic head) and the pit lakes (lower hydraulic head), increasing chloride content, which has a conservative behavior in natural waters (Hem 1985; Drever 1997; Faure 1998). However, the lower chloride concentrations in the sand pit lake waters

compared to that of groundwater (Table 2) could be explained by dilution due to influence of direct rainwater deposition in the sand pits lakes waters and also runoff.

5.3 The Behavior of the pH-dependent Species in Sand Pit Lakes

The water acidification can also accelerate mineral weathering processes in the sand pit lakes, even to highly refractory minerals, like K-feldspar and quartz (Krauskopf and Bird 1995; Drever 1997; Faure 1998; Monterroso et. al. 1999), according to following Eq. 4:

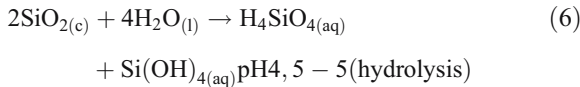
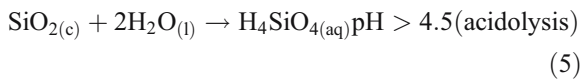


These minerals, besides the clay minerals, provide all the silica present in the sand pit lakes. Based on the measured pH values, silica could be present as

Table 5 Average content of silica after filtration in 0.45 and 0.22 μm filters in the studied sand pits waters

Sand Pit Lakes	Silica content (mg.l ⁻¹)	
	0.45 μm	0.22 μm
1	26.3	0.52
2	26.6	0.32
3	21.1	0.15
4	25.5	0.58

colloidal forms (Yariv and Cross 1979; Stumm and Morgan 1996; Faure 1998), more specifically as H₄SiO₄ and Si(OH)₄, depending on the water pH ranging.



This hypothesis is corroborated by the results shown in Table 5. It is possible to notice that water

filtered in 0.45 μm filters shows concentration values higher in all sand pit lakes compared to 0.22 μm filters, suggesting that colloids formation has an important role in silica and metals concentration in aquatic systems.

Manganese (associated to Factor 1) shows low water content and its source is also related to silicate minerals impurities, mainly in feldspars, as manganese oxide (Klein and Hurlbut 1997). The low iron concentrations in the water come from ferrous sulphide, present in the reduced sediment layers, and also from iron bearing minerals, which are in trace amounts minerals in sediments and more resistant to weathering (e.g., magnetite, ilmenite, and limonite) (Berbert 2003).

Considering Eh ranging from 0.4 to 0.6 V (unpublished data) and the pH values obtained in this study, it is possible to speculate that iron is probably around the equilibrium boundary between soluble Fe(II) and Fe(OH)₃ and manganese as Mn²⁺ (Fig. 7). Baumann et al. (2006) showed that even in oxidizing environments with high levels of dissolved organic carbon (DOC), iron and manganese are mainly present in aqueous solution and associated to small organic

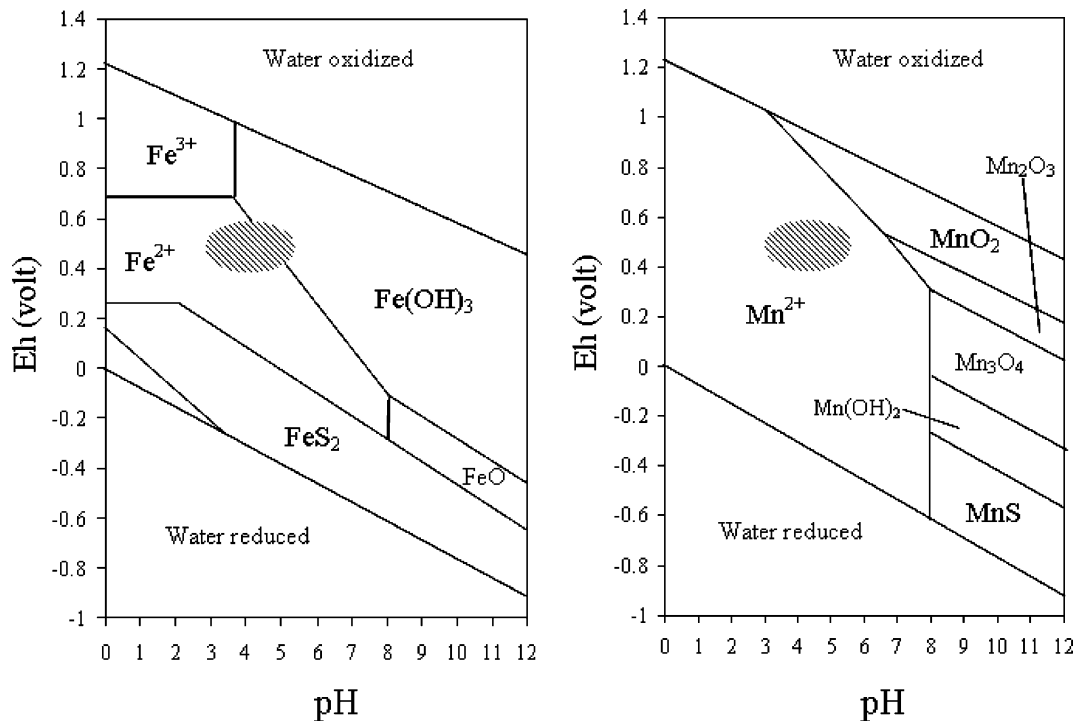


Fig. 7 Equilibrium diagrams of iron and manganese in function of Eh and pH at 25°C and 1 atm pressure. Activity of sulfur species 96 mg.L⁻¹ as , dissolved iron and manganese,

respectively, 0.56 and 0.55 mg.l⁻¹ (modified from Hem 1985). *Marked area in graphics* represents the major sand pits lakes samples

colloids ($>1 \mu\text{m}$). The slightly higher Mn levels compared to Fe may be due also to the formation of less stable complexes of organic matter with manganese (White and Driscoll 1986; LaZerte 1988; Bendell-Young et al. 1989; Bendell-Young and Harvey 1992). This hypothesis agrees with Brockamp (1976), in a study of manganese and iron lixiviation by aqueous solution in the presence of organic acids. This author showed that soluble manganese is more concentrated than iron in rock weathering solutions where iron is oxidized.

The aquifer mineral assemblage is also a source of aluminum present in waters. The pH values obtained in this study (from 3.1 to 5.2) suggest that the predominant aluminum species are Al^{3+} , $\text{Al}(\text{OH})_2^+$ and $\text{Al}(\text{OH})_2^+$. These monomeric species are more reactive (toxic) at cell membrane surface of aquatic organisms than polymeric forms and organically bound Al (Baird 1998; Gensemer and Playle 1999; Camilleri et al. 2003). High aluminum and sulfate

content probably provides the formation of AlSO_4^+ and $\text{Al}(\text{SO}_4)_2^-$ (Yariv and Cross 1979; Stumm and Morgan 1996; Munk et al. 2002), which may be responsible for the blue color as well as by the low suspended particulate material observed in the water.

Nevertheless, it is worth to point out that lower aluminum concentrations were obtained in waters with lower pH (Fig. 8). As mentioned previously this element shows negative association with rainfall (Factor 3, Table 3). The lowest aluminum concentrations were found during the rainy period (Fig. 9) and can be explained by the interruption of mining activities during this season, implying less sediment mobilization and, consequently, minor geochemical reaction rates, besides higher dilution due to higher rainfall.

According to Birchall et al. (1989) and Exley et al. (1991), the water silica content could control aluminum solubility due to the formation of hydroxi-aluminum silicates, such as imogolite a process that could also contribute to the low water pH values

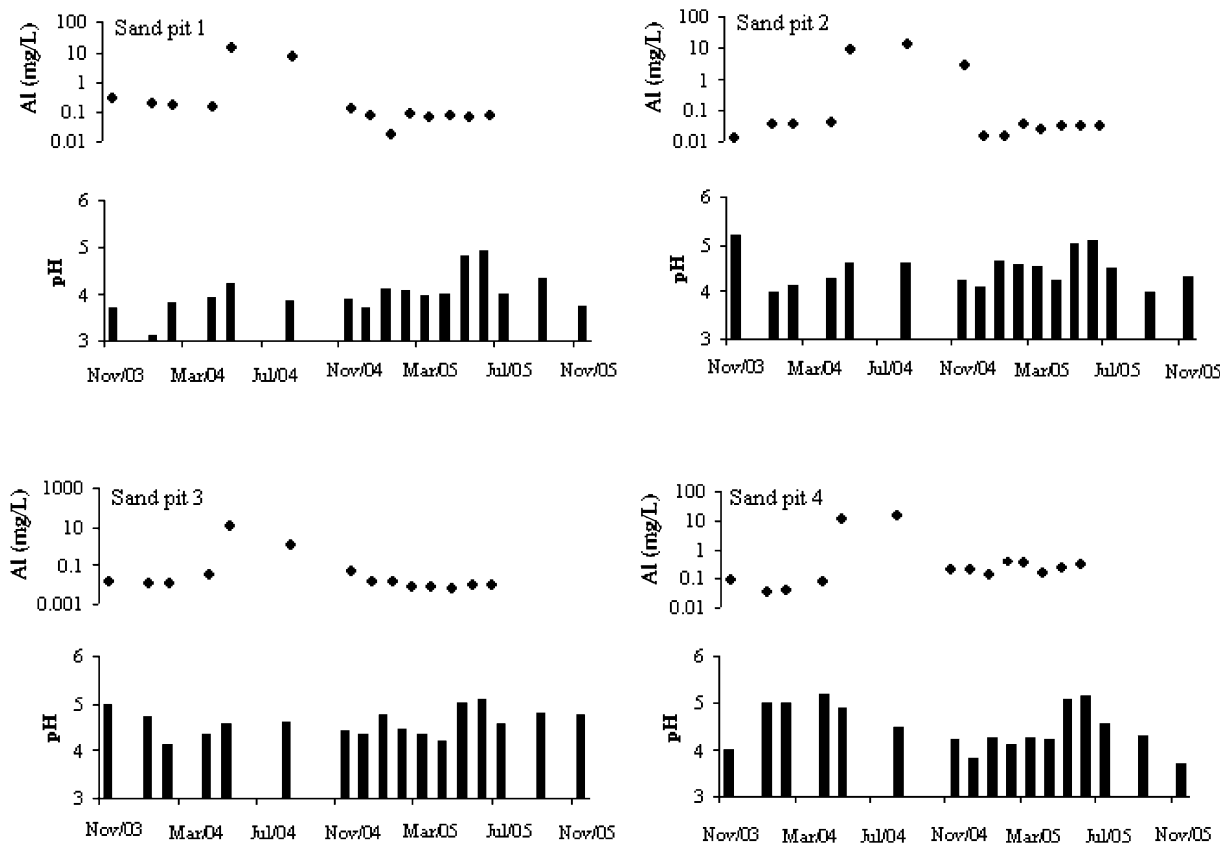
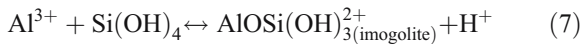


Fig. 8 Aluminum content and pH variations along sampled period

found (Duan and Gregory 1998; Camilleri et al. 2003), due to the following reaction.

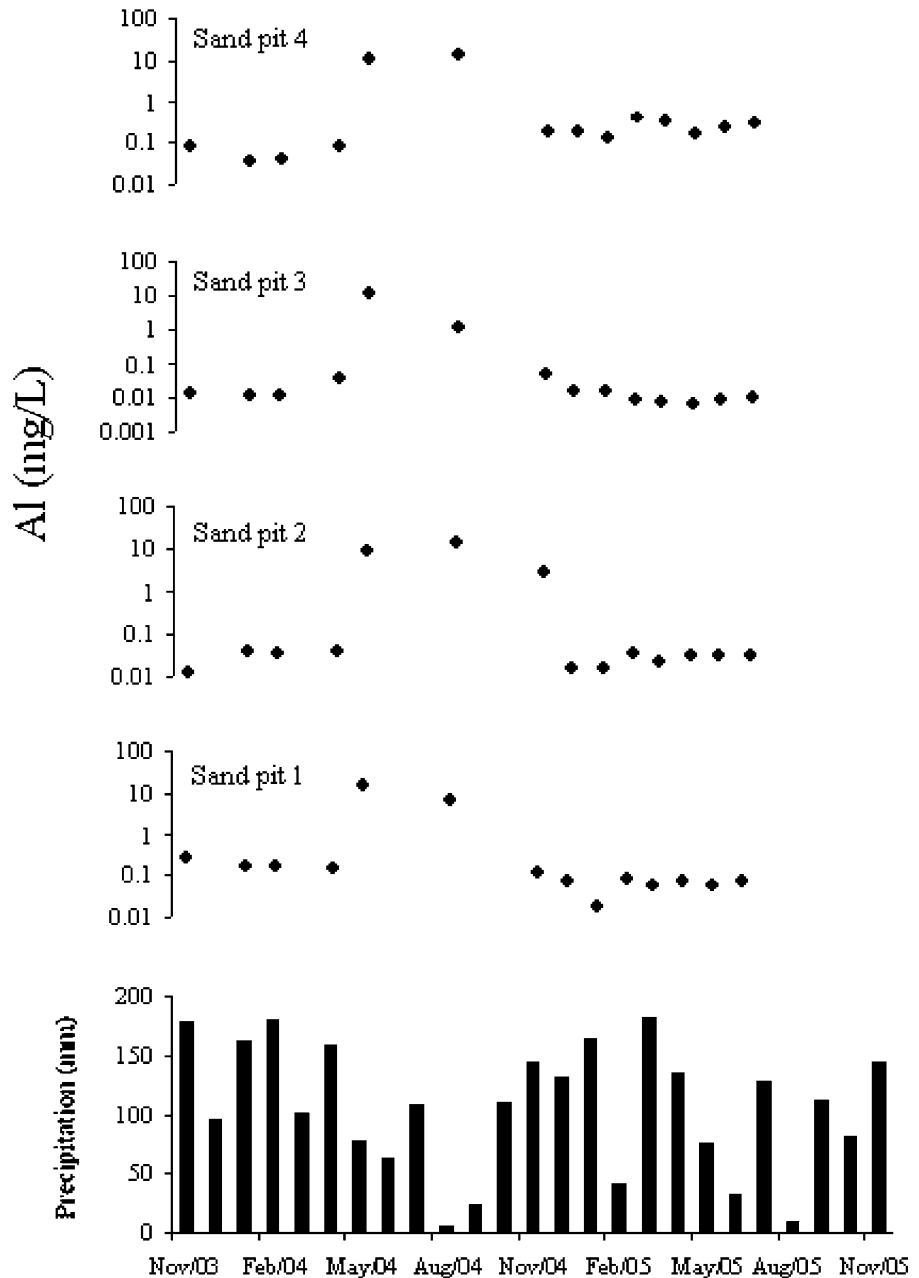


6 Use of the Pit Lakes for Fish Culture

Aquaculture can be an interesting socio-economic alternative for the remediation of mining impacts due

to pit lake formation. However, poor water conditions due to the presence of toxic substances may hamper pit lake use as fish ponds (Waserman et al. 2007). The pit lakes studied shows no significant concentrations of toxic substances posing neither any threats to fish, nor any pollutant which could be incorporated and eventually transferred to consumers. The relatively high acidity and aluminum contents and the low nutrient concentrations, on the other hand, suggest that these pit lakes waters should be treated prior to

Fig. 9 Aluminum content and rainfall variation along sampled period. Pluviosity data from Santa Cruz pluviometric station; source: GEORIO



use as fish ponds if sustainable economic revenues are expected. Typical tropical fish culture, *Colossoma* spp. (tambaqui) and *Piaractus* spp. (pacu) (Kubitza 2004), well developed in many areas in Brazil, may be limited by winter temperatures. However, Tilapia will be reared without problems, and has been used as a better alternative through the country (Conte et al. 2003). Notwithstanding, any fish growing in these lakes will require pH correction, which will simultaneously reduce aluminum availability. Fertilization, however, would be also required even for extensive farming practices, due to the oligotrophic nature of the waters, in particular the very low phosphorus and nitrogen contents.

7 Conclusion

A comparison between the groundwater and sand pit lake waters components indicates that the sand extraction process is responsible for the hydrochemistry changes of this system. Waters from the studied sand pit lakes show low content of dissolved elements and low pH values. However, Al^{3+} and SO_4^{2-} show unusual high levels compared to its content in natural waters. Despite the relative high content of components present in these waters compared to natural waters, the sand pit lakes present lower concentrations of most chemical species when compared to ore mining pit lakes, as a result of local geological features. This fact gives to the sand pit lakes the condition of a peculiar environment which requires more detailed studies.

The data screening based on PCA analysis revealed that water chemical composition of the sand pit lakes is determined basically by four processes: (1) the sediment weathering, (2) the oxidation of iron sulphide minerals present in the organic clays, (3) the intensification of sand mining activities during the dry season and (4) aluminum silicate formation.

Iron, Mn and Al availability in these waters are closely associated with the acidification process and are likely to form colloidal species in the presence of organic matter. On the other hand, the colloidal SiO_2 content, which can also control pH, may partially control Al availability by the formation of hydroxialuminum silicate.

Regarding the utilization of these pit lakes as fish ponds, rather than presenting toxicity to fish or

possible pollutant transfer through food chains, the water chemistry shows the environment at a limiting line for fish culture.

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