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Impact of coal mining on water quality of three artificial lakes in Morozini River Basin (Treviso, Santa Catarina State, Brazil)

Impacto da atividade de mineração na qualidade da água de três lagos artificiais da bacia do rio Morozini (Treviso, Estado de Santa Catarina, Brasil)

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Abstract: Aim: To assess water quality of three lakes located in an abandoned coal mining area, in the Morozini River basin (Treviso, Santa Catarina State, Brazil). **Methods**: The study sites were three lakes mining pits flooded after deactivation, near the drainage basin of the Morozini River (Treviso City, Santa Catarina State, Brazil). Samplings were carried out in profile in the limnetic region during two seasons (Summer in February and Winter in July). **Results**: In general, the three lakes showed high concentrations of SO_4^{-2}, Mg, Fe, Al, Ca, Ba, Si, Zn, Ni, Na, K, Sr, B, Cd, Cr, Pb and Cu. **Conclusions**: Coal mining activity and waste disposal practices adopted by the mining companies in the Morozini River basin have drastically affected the water quality of the examined lakes and made them inappropriate for diverse human uses, such as leisure, swimming and fishing.

Keywords: CONAMA, metals, water quality, acidification.

Resumo: Objetivo: Avaliar a qualidade da água de três lagos presentes em uma área abandonada de mineração de carvão. **Métodos**: Foram amostrados em perfil três lagos presentes na bacia de drenagem do rio Morozini (Treviso, Santa Catarina, Brasil), com coletas em duas épocas do ano (fevereiro – verão e julho – inverno). **Resultados**: De maneira geral, os três lagos estudados apresentaram elevadas concentrações de SO_4^{-2}, Mg, Fe, Al, Ca, Ba, Si, Zn, Ni, Na, K, Sr, B, Cd, Cr, Pb e Cu. **Conclusões**: Esta pesquisa sugere que a atividade de mineração e a prática de disposição de rejeitos adotada pelas companhias de mineração afetaram drasticamente a qualidade da água dos lagos estudados, tornando-os inapropriados a diversos usos humanos, tais como lazer, pesca e natação.

Palavras-chave: CONAMA, metais, qualidade da água, acidificação.

1. Introduction

The impact of coal mining activity on the environment is of great concern, especially due to acidification of surface water bodies. Hence, mining requires complex planning that takes into account the specificity of techniques and characteristics of the affected environment (Kopezinski, 2000).

Currently, thermal energy is responsible for 5% of energy matrix in Brazil. However, the government aims to increase this ratio to 15% by 2015. Rio Grande do Sul and Santa Catarina states account for 99% of known coal reserves, approximately 32 billion tons. Coal found in these states is of low quality: low calorific value and high ash (47 to 58%) and sulfur (1 to 4.7%) contents (JICA, 1995).

The main activities of coal mining (exploration, development, extraction, concentration, processing, refinement and deactivation) have a variety of impacts, which include soil damage, air pollution and water contamination (McAllister and Milioli, 2000). Areas that have been explored but not rehabilitated are a source of water pollution. This is mainly because of acid mine drainage (AMD), due to pyrite oxidation (FeS_2). When pyrite is in contact with oxygen and water, highly concentrated sulfuric acid is produced which solves metals (Rose and Cravotta, 1998; Asta et al., 2008).

The main objective of this work was to assess the water quality of three lakes situated in an abandoned coal mining area, submitted to anthropogenic impacts. It is expected that these lakes have strong use restriction, according to the Brazilian water quality regulation (CONAMA nº 357/2005).

2. Study Area

The study region, is located in the south region of Santa Catarina State (Brazil), and has an area of 9,049 km^2, 9.8% of the total area of the state (Figure 1); it has 39 towns and a population of more than 800,000 inhabitants. The studied lakes are located in the Morozini River micro basin, near the Treviso city. Morozini River micro basin is a tributary of the Mãe Luzia River and is located in a 4,200 m (large axis) by 3,400 m (small axis) valley, with a topographical gradient of about 320 m.

The Companhia Siderúrgica Nacional (CSN), established in the 1950s, is a company that explored and processed coal in the region. In the 1960s, coal mining was intensified closer to Treviso and became one of the most important economic activities. However, mining adversely affected other economic activities and also had social and environmental consequences causing a high level of pollution and reducing the water quality (Milioli, 1999).

Open-pit mining in this region began in 1982 and the resulting deposits have high sulfate concentration that reduces the pH in shallow lakes. The course of the Morozini River was modified many times due to surface coal mining, and, as final conformation, the river water flows through the mining pits that were dug by a Marion dragline. The pyrite waste was used to make gravel access roads to the mines. Many lakes near coalmines were used as dumps for the mining waste. Lakes have been formed in this region by the flow of underground and surface water into the mining pits (Waterloo, 2002). In the study area, at present, there is no more coal exploration and the lakes studied do not receive mining waste.

Climate type is wet subtropical with hot summer (Cfa - Köppen's classification). Mean annual temperature is 19 °C and total precipitation haste is 1600 mm, distributed along the whole year, without well defined dry season. Mean monthly temperature varies from 15 °C in the winter to 24 °C in summer, with possible incident of frost (Sônego et al., 2011). According to these authors, from March to September, there is predominance of hot air mass and moisture, causing strong heating during the days and formation of convective clouds. During the winter months, there is predominance of cold and dry polar air mass. For the series of 10 years (Figure 2), one can observe marked annual pattern of temperature, with lower values from

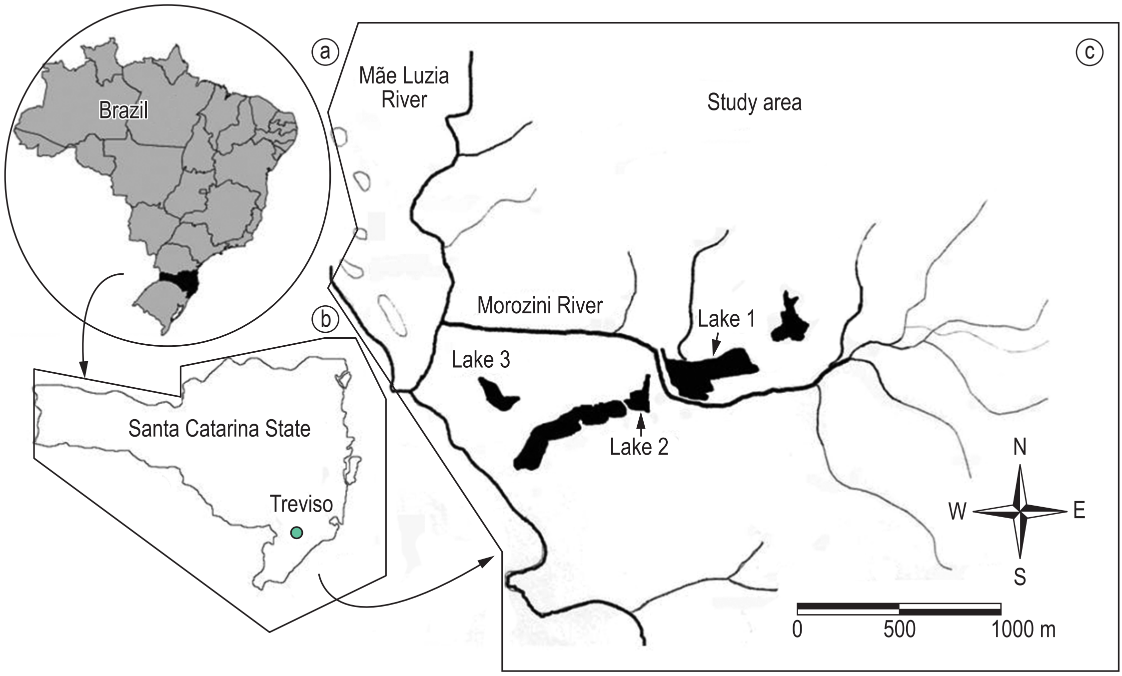


Figure 1. Study area (c) in Santa Catarina State (b), Brazil (a) and lakes studied (Lakes 1, 2 and 3).

May to October. In 2003, when this research was developed, the total precipitation was 1509.8 mm; annual mean minimum temperature was 15.4 °C and annual mean maximum temperature of 20.0 °C.

3. Material and Methods

The study sites consisted of 3 lakes, mining pits flooded after deactivation, near the drainage basin of the Morozini River (Treviso, Santa Catarina State, Brazil) (Figure 1). Samplings were carried out considering a profile through the limnetic region in two seasons (summer, the month of February, and winter, the month of July, 2003).

Physical and chemical variables of the water were analyzed (Table 1). To analyze the total and dissolved nutrients concentration, water samples were collected and filtered in situ through a Whatman GF/C 47 mm membrane. The filtered water was acidified with HNO_3 (1 mL) and maintained in polythene vials protected from light until analysis.

Principal components analysis (PCA) was carried out to identify possible relationships among lakes, depth and season. The analysis was based on a product-moment matrix obtained from a range-standardized matrix (Legendre and Legendre, 2003). The physical and chemical variables selected for the PCA were temperature (t), total solids (TS), calcium (Ca), aluminum (Al), silicon (Si), iron (Fe), zinc (Zn), nickel (Ni), pH, electric conductivity (EC) and dissolved oxygen (DO).

4. Results

Water from Lakes 1 and 2 were micro stratified during summer, and temperatures ranged from 27.2 to 31.1 °C. Water column of Lake 3 was relatively homogeneous in the summer, with temperature

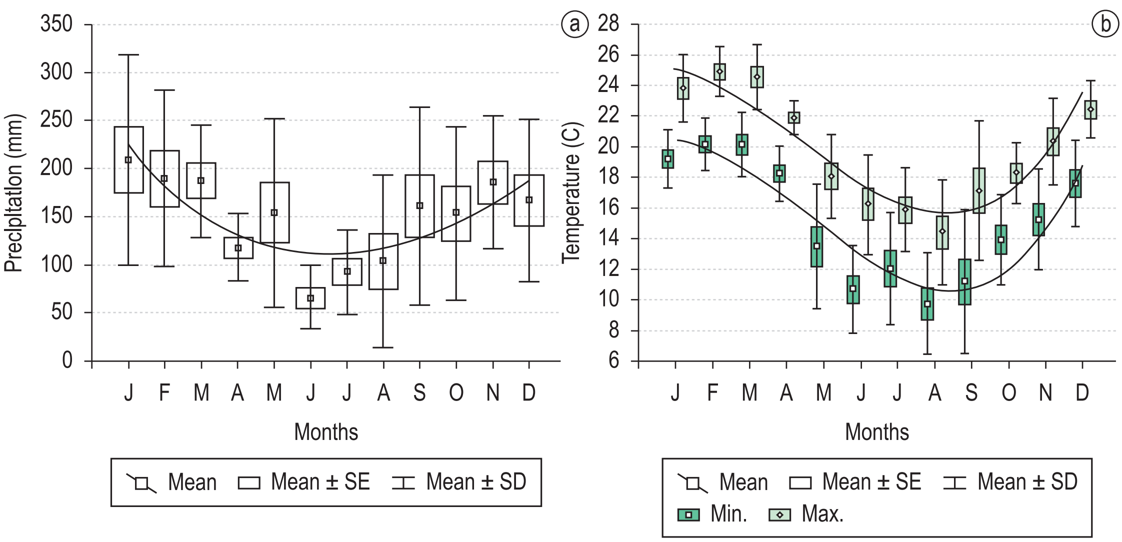


Figure 2. Precipitation (a) (mean total monthly) and temperature (b) (mean minimum and mean maximum for month), for 10 years (2001 to 2010), according Epagri/Ciram/Inmet (Urussanga Station, Santa Catarina State, Brazil, longitude: 49° 18' 53"; latitude: 27° 31' 55"). Tendency curve is a polynomial cubic function.

Table 1. Physical and chemical variables analyzed, units, methods and references.

Variable	Unit	Method	Reference
Water temperature	°C	Horiba U 10	
pH		Gehaka PG 1400	
Dissolved oxygen (DO)	$mg.L^{-1}$	Winkler	Golterman et al. (1978)
Electric conductivity (EC)	$\mu S.cm^{-1}$	Hanna HI 9033	
Euphotic zone	m	Secchi Dish	
Orthophosphate ($P\text{-}PO_4$)	$\mu g.L^{-1}$	Spectrophotometric / Shimadzu UV 1000 01	Strickland and Parsons (1960)
Silicate ($S\text{-}SIO_2$)	$mg.L^{-1}$	Spectrophotometric / Shimadzu UV 1000 01	Goltermam et al. (1978)
Total solids	$mg.L^{-1}$	Gravimetric	APHA (1985)
P, SO_4^{-2}, Mg, Fe, Al, Ca, Ba, Si, Zn, Ni, Na, K, Sr, B, Cd, Cr, Pb, Cu	$mg.L^{-1}$	Atomic emission spectrometry with induced coupled plasma (ICP-AES)	APHA (1985)

ranging from 24.5 and 31.1 °C. In the winter, none of the lakes was stratified, and temperatures were around 19 °C (Figure 3a).

In Lake 2, pH increased with depth and values were 5.1 at the surface and 6.2 at the bottom, while the highest pH value was found at the surface (6.9) and at the bottom was 6.4 in the winter. The pH value for Lake 3 was approximately 3 (Figure 3b). Lake 1 showed a pH ranging from 7.3 (epilimnion) to 5.7 (hypolimnion) in the summer and from 6.3 (surface) to 7.4 (bottom) in the winter.

EC values were high (700 to 900 μS.cm^{-1}) in Lakes 1 and 2 in both periods and tended to increase from epilimnion downwards to hypolimnion in the summer but were relatively homogeneous in winter (Figure 3c). Lower EC values (about 300 μS.cm^{-1}) were measured in Lake 3 in both periods.

In the summer, there was a decrease of DO from epilimnion (Lake 1, 7.23 mg.L^{-1} and Lake 2, 6.75 mg.L^{-1}) to hypolimnion (Lake 1, 1.01 mg.L^{-1} and Lake 2, 3.72 mg.L^{-1}). A different pattern was observed in winter, when an orthograde profile was found with DO values greater than 6 mg.L^{-1} (Figure 3d). Lakes 1 and 2 showed higher TS concentrations (982.5 to 1161.5 mg.L^{-1}) than Lake 3 (mean 230.6 mg.L^{-1}) (Figure 3e). Most part of TS was in the dissolved form (Table 2).

SO_4^{-2}, Ca, Mg and K concentrations were higher in Lakes 1 and 2 than in Lake 3. SO_4^{-2} concentration ranged from 505 to 676 mg.L^{-1} in Lakes 1 and 2, and from 93 to 111 mg.L^{-1} in Lake 3 (Figure 4a). Values for Ca concentration ranged from 177 to 213 mg.L^{-1} in Lakes 1 and 2, and from 5.9 to 8.7 mg.L^{-1} in Lake 3 (Figure 4b). Mg concentration ranged from 28 to 34 mg.L^{-1} in Lakes 1 and 2, and from 2.4 to 3.4 mg.L^{-1} in Lake 3 (Figure 4c). In Lakes 1 and 2, Na and K concentrations ranged from 5.6 to 6.1 mg.L^{-1} and 3.5 to 4.2 mg.L^{-1}, in

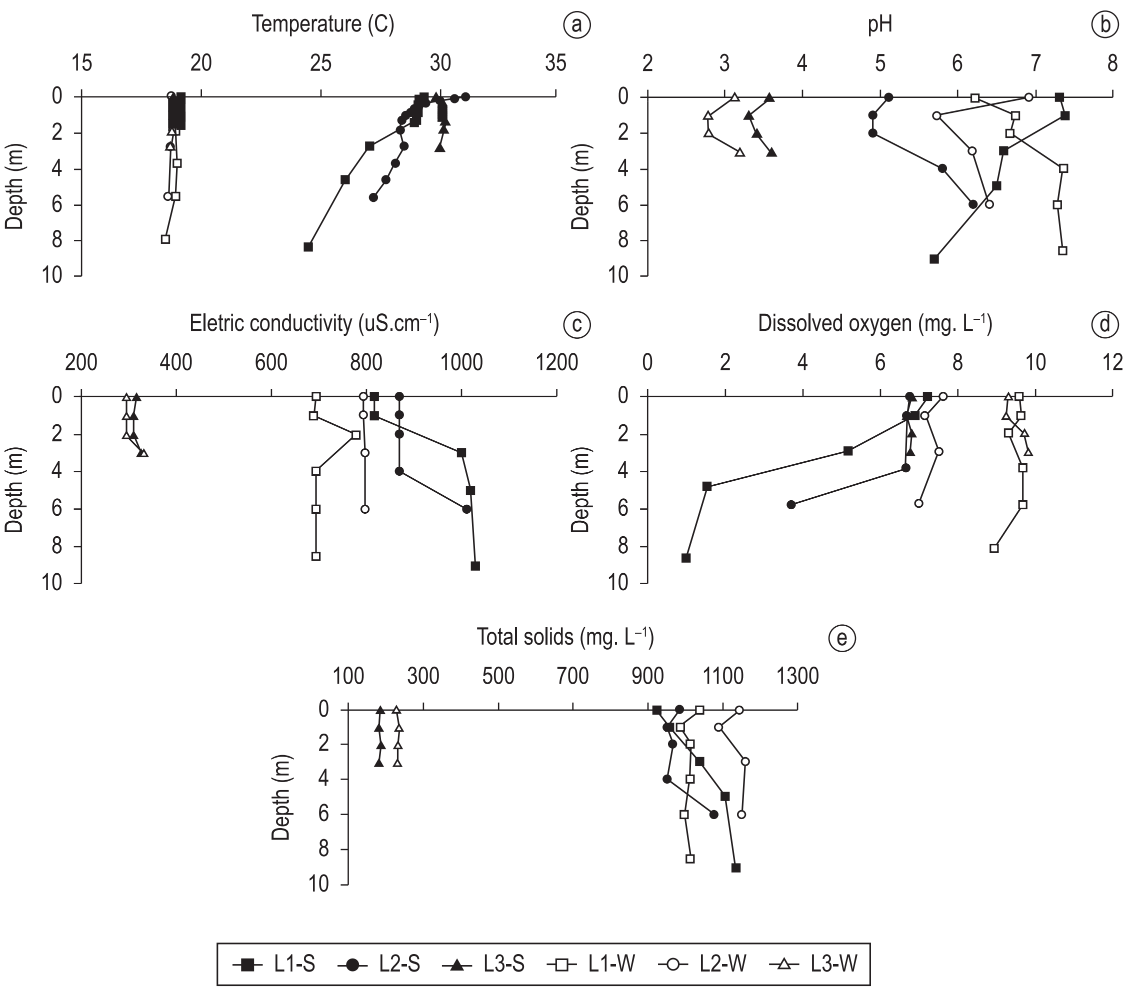


Figure 3. Depth profiles of temperature (a), pH (b), electric conductivity (c), dissolved oxygen (d) and total solids (e) in three lakes (Lake 1 - L1, Lake 2 - L2, Lake 3 - L3) at the Morozini River basin. Summer (S, full) and winter (W, lacked).

Table 2. Total solids (TS), particulate solids (PS) and dissolved solids (DS) determined in three lakes at the Morozini River basin, in the winter.

Lake	Depth (m)	TS ($mg.L^{-1}$)	PS ($mg.L^{-1}$)	DS ($mg.L^{-1}$)
1	0.0	1,038.0	1.71	1,036.3
	1.0	982.5	1.85	980.6
	2.0	1,011.5	1.71	1,009.8
	4.0	1,008.5	1.28	1,007.2
	6.0	996.5	1.14	995.4
	8.5	1,012.5	0.71	1,011.8
2	0.0	1,145.0	3.14	1,141.9
	1.0	1,091.5	2.71	1,088.8
	3.0	1,161.5	2.57	1,158.9
	6.0	1,151.0	2.57	1,148.4
3	0.0	227.0	0.71	226.3
	1.0	234.0	1.00	233.0
	2.0	231.0	1.00	231.0
	3.0	230.5	2.28	228.2

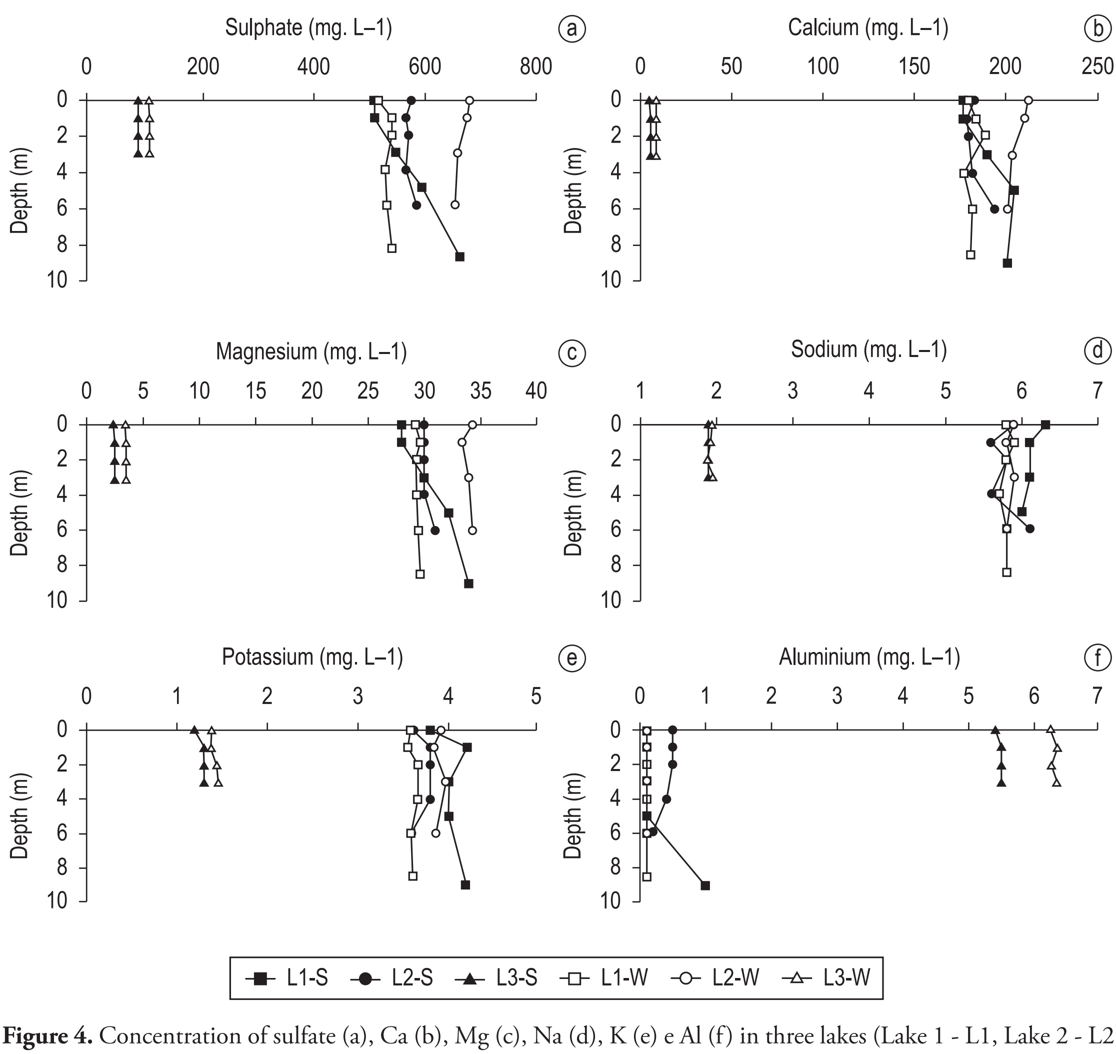


Figure 4. Concentration of sulfate (a), Ca (b), Mg (c), Na (d), K (e) e Al (f) in three lakes (Lake 1 - L1, Lake 2 - L2, Lake 3 - L3) at the Morozini River basin. Summer (S, full) and winter (W, lacked).

Lakes 1 and 2, respectively (Figure 4d-e). In Lake 3, the Na and K concentrations ranged from 1.2 to 1.9 mg.L^{-1}. Aluminium concentration for Lakes 1 and 2 ranged from 0.1 to 1.0 mg.L^{-1} while Lake 3 showed higher concentrations, ranging from 5.4 to 6.4 mg.L^{-1} (Figure 4f).

Silicon concentr ation ranged from 8.1 to 11.0 mg.L^{-1} in all lakes and study periods (Figure 5a). Low Fe concentrations were observed in Lake 1 during the winter (0.05 to 0.15 mg.L^{-1}). Generally the values ranged from 0.30 to 1.28 mg.L^{-1}, except in Lake 1, where during the summer values were 2.5, 6.0 and 11.0 mg.L^{-1} at depths of 3.0, 5.0 and 9.0 m, respectively (Figure 5b). Zn concentration varied from 0.045 mg.L^{-1} to 0.14 mg.L^{-1} (Figure 5e), and the Mn concentration ranged from 0.97 to 9.9 mg.L^{-1} (Figure 5d). Ni concentration ranged from <0.02 to 0.07 mg.L^{-1} in summer and <0.05 to 0.36 mg.L^{-1} in winter (Figure 5e). In both, winter and summer, Sr concentration was lower in Lake 3 (0.03 mg.L^{-1}) and higher in Lakes 1 and 2 (0.42-0.51 mg.L^{-1}, respectively) (Figure 5f).

B concentration ranged from 0.01 to 0.07 mg.L^{-1} in the three lakes and in both periods (Figure 6a), and Ba concentrations were below 0.04 mg.L^{-1} (Figure 6b).

The following elements were in concentrations below the detection limit of the method: Cd (<0.002 mg.L^{-1}), Cr (<0.004 mg.L^{-1}), Pb (<0.05 mg.L^{-1}), P (<0.2 mg.L^{-1}), and Cu (<0.02 mg.L^{-1}).

Orthophosphate concentrations were low, less than 10 µg.L^{-1}. The reactive silicate concentrations ranged from 1.1 to 9.7 mg.L^{-1} (Table 3).

The first two axes from the principal components analysis account for 74% of the original matrix total variance. The first and the second axis accounted for 44 and 30% respectively (Figure 7). The highest factor loadings on the first axis consisted of pH, Ca, TS and EC in opposition to Al concentration.

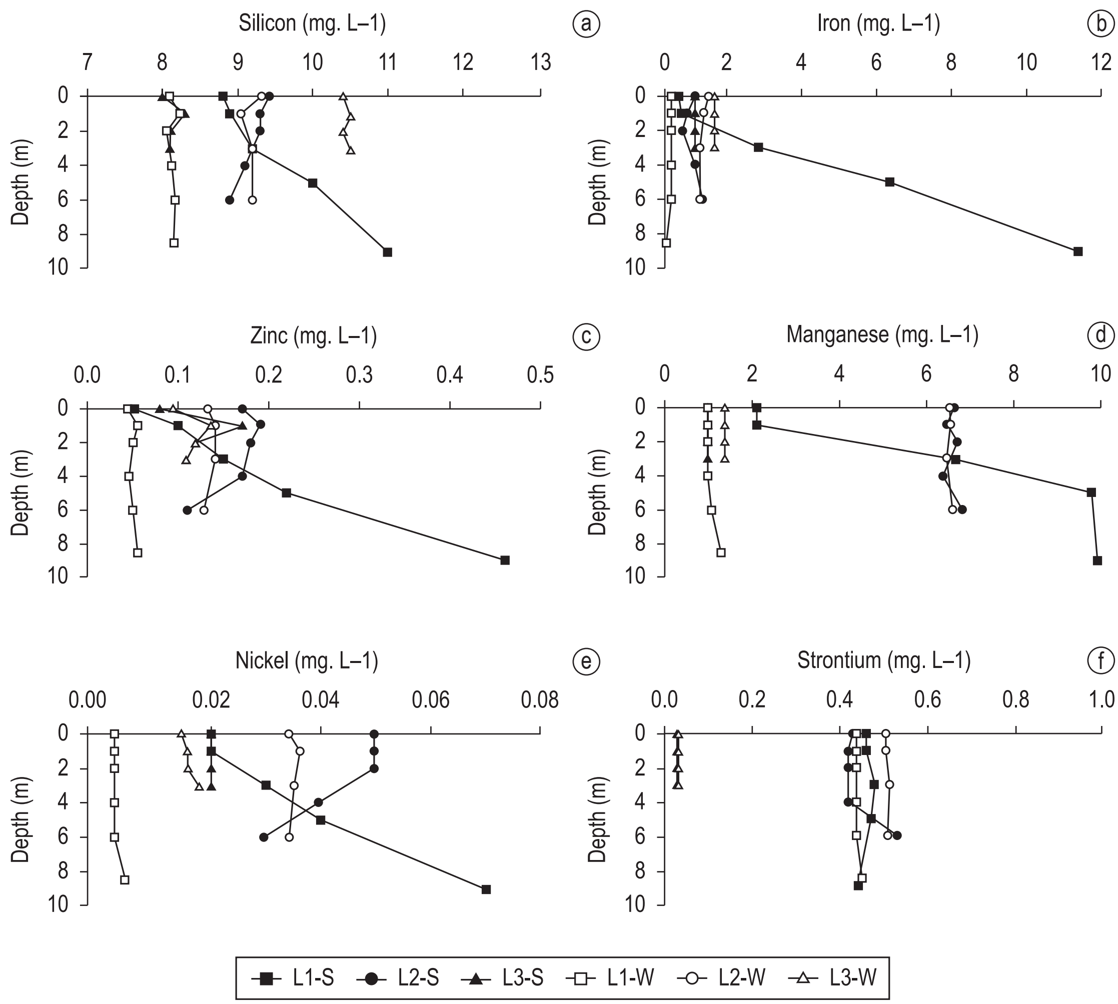


Figure 5. Concentration of Si (a), Fe (b), Zn (c), Mn (d), Ni (e) and Sc in three lakes (Lake 1 - L1, Lake 2 - L2, Lake 3 - L3) at the Morozini River basin. Summer (S, full) and winter (W, lacked).

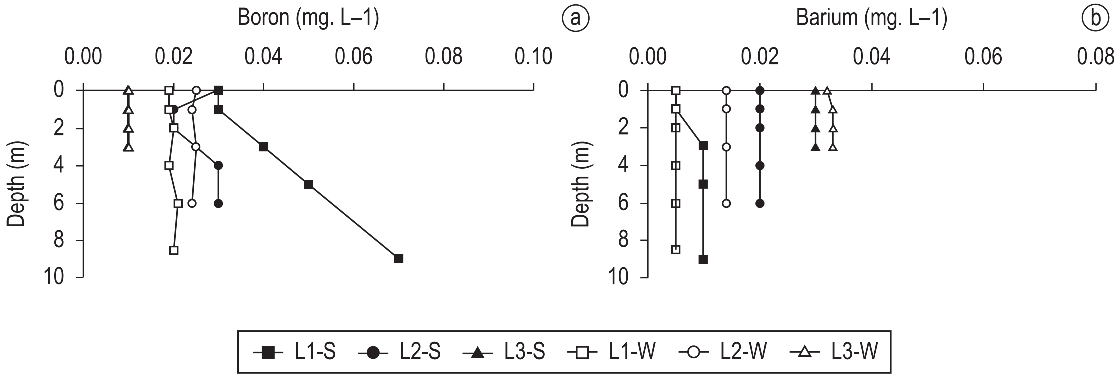


Figure 6. Concentration of B (a) e Ba (b) in three lakes (Lake 1 - L1, Lake 2 - L2, Lake 3 - L3) at the Morozini River basin. Summer (S, full) and winter (W, lacked).

Table 3. Depth profiles the P-PO_4^{3-} and S-SIO_2 in the Summer (S) and Winter (W) in three lakes at the Morozini River basin.

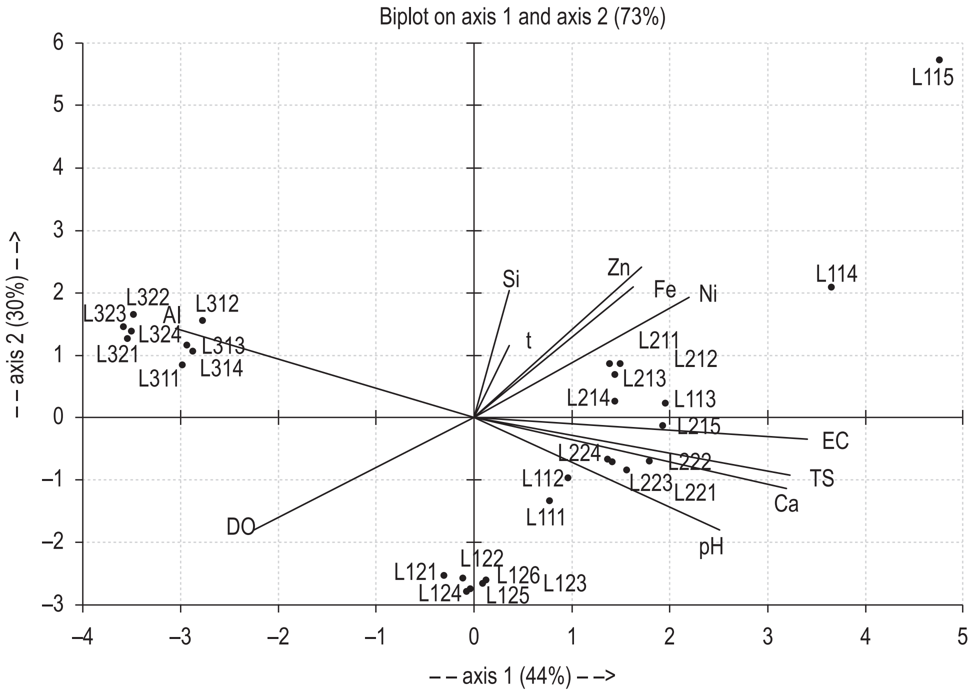
Lake	Depth (m)	P-PO_4^{-3} (µg.L^{-1})	S-SIO_2 (mg.L^{-1})	P-PO_4^{-3} (µg.L^{-1})	S-SIO_2 (mg.L^{-1})
		S	S	W	W
1	0.0	<10	8.15	<10	8.03
	1.0	<10	8.34	<10	7.95
	2.0				7.43
	3.0	<10	8.41	<10	
	4.0				7.80
	5.0	<10	1.96	<10	
	6.0				7.80
	9.0	<10	9.70	<10	7.72
2	0.0	<10	8.18	<10	8.16
	1.0	<10	8.22	<10	1.10
	2.0	<10	8.05		
	3.0			<10	8.21
	4.0	<10	8.24	<10	
	6.0	<10	7.95	<10	8.04
3	0.0	<10	7.37	<10	8.45
	1.0	<10	7.28	<10	8.55
	2.0	<10	7.51	<10	8.56
	3.0	<10	7.29	<10	9.29

Relevant factor loadings for the second axis were Zn, Fe and Si in opposition (negatively correlated) with pH and dissolved oxygen. A space effect was observed with Lake 3 apart from Lakes 1 and 2. Lake 3 presented higher Al concentration and lower Ca, pH and EC values in both studied periods. Despite lakes 1 and 2 presented small differences for the same season, the biggest differences observed for theses lakes were observed between the sampling periods (summer and winter).

5. Discussion

Water column was thermally homogeneous in all the lakes in winter. In summer, Lakes 1 and 2 showed micro stratifications, whereas Lake 3 was thermally homogeneous. This fact is probably due to depth differences between the lakes combined with the effect of the wind and also it can be related to the air temperature seasonal pattern observed in the region. Therefore, the differences observed between winter and summer for Lakes 1 and 2 could be explained by the marked pattern of temperature observed along the year in the study region (Figure 7). For Lake 3, the similarity among sampling periods, probably, is associated with the low depth, allowing wind action and constant water column mix.

The profiles of DO that were measured in the lakes also corroborated the hypothesis of chemical stratification in Lakes 1 and 2 and homogeneity in



Lxyz		
x _ _ Lake	_ y _ Station	_ _ z Depth
1	Summer: 1	1, 2, 3, 4, 5
1	Winter: 2	1, 2, 3, 4, 5, 6
2	Summer: 1	1, 2, 3, 4, 5
2	Winter: 2	1, 2, 3, 4
3	Summer: 1	1, 2, 3, 4
3	Winter: 2	1, 2, 3, 4

Figure 7. PCA of the three lakes studied in the Morozini River Basin. t: temperature; TS: total solids; Ca: Calcium; Al: Aluminium; Si: Silicon; Fe: Iron; Zn: Zinc; Ni: Nickel; pH; EC: electric conductivity; DO: dissolved oxygen. L111: it means, Lake 1, at summer (1) and to first depth (1), respectively for three lakes like shown in the following table:

Lake 3, in this case, like observed in two sampling periods. Low DO concentration in the deepest parts of Lake 1 in the summer is probably due to the consumption of oxygen in oxidation of pyrite, a process that results in dissolution of certain ions and metals such as SO_4^{-2}, Fe, Mn, Zn and Ni (Blunden et al., 2001).

Data obtained in the winter showed that most of the solid fraction in all three lakes is in dissolved form, SO_4^{-2} and Ca, mainly, and that the particulate matter accounts for only a small part of the TS.

The high EC values for Lakes 1 and 2 are probably due to the high ion concentration, especially SO_4^{-2} (above 500 $mg.L^{-1}$) and Ca (higher than 180 $mg.L^{-1}$) that also contribute to high TS values. In Lake 3, the lowest values of EC may be a consequence of the lower concentration of SO_4^{-2}, Ca, Mg, Na and K.

CSN Company is responsible for coal mining in this region and it is also in charge of the recovery of affected lakes. In the past $Ca(OH)_2$ was added to the Lakes 1 and 2 in order to increase their pH. However, SO_4^{-2}, Ca, Mg and Fe concentration remained high. In appropriate concentrations, these ions are important for the metabolism of various organisms, but they can cause toxic effects at higher concentrations. It is important to emphasize that water neutralization does not directly affect the causes of the acidity. Additionally, water neutralization can increase turbidity, which becomes then a new environmental problem.

The high concentration of SO_4^{-2} and Ca in Lakes 1 and 2 can be explained by the addition of

$Ca(OH)_2$, which increases the water solubility of these ions. A high SO_4^{-2} concentration was found by Silvano and Raya-Rodriguez (2003) in Lagoa Azul, a lake located close to the site of this study, in the coal-producing basin of Siderópolis city. These authors attributed this condition to the oxidation of pyrite from coal mining.

Data of pH, EC, TS, SO_4^{-2}, Ca Mg, Na, K, Al, and Sr, mainly in the Lake 3, indicate that coal mining has made a strong environmental impact. Lakes 1 and 2 discriminated from Lake 3, mainly because the last was strongly affected by the coal mining, due a CSN intervention with the addition of $Ca(OH)_2$. However, all three lakes remain exposed to high pyrite content and are, consequently, highly affected by the coal mining process.

Previous studies carried out in the basins of Rivers Conde, Ratos and Porteira (Rio Grande do Sul state, Brazil) registered mean pH values of about 6.0. Extreme values of 2.6 and 2.7 were found in some locations probably due to the impact of mining on the drainage basin. Low pH values in areas where coal mining takes place are often due to nearby pyrite deposits (Zanardi Junior and Porto, 1991).

The highest aluminium concentrations observed in Lake 3 are probably due to the lower pH values, which increase Al solubility. The concentration of Al in freshwater around the world varies according to pH values. Al concentrations are higher when pH is low (Siegfried et al., 1989). In the Pantano Lake, a pH of around 3.9 was associated with Al concentrations of 0.1 to 3.7 $mg.L^{-1}$ (Courtijn et al., 1987 apud Azevedo and Chasin, 2003). Lake Shield (Ontario and Quebec, Canada) showed pH values ranging from 4.4 to 7.1 and Al concentrations ranging from 0.05 to 0.37 $mg.L^{-1}$. Lake Ipê (Parana State, Brazil), an area relatively untouched by mankind, has low Al concentrations ranging from 8 to 21 $\mu g.L^{-1}$ (Barreto et al., 2005). In this study, Al concentrations are higher than those mentioned above.

Similar SO_4^{-2}, Fe, Al and Mg concentrations found in Morozini River lakes also were found in lakes of the Fiorita River basin (Siderópolis City, Santa Catarina State, Brazil) (Pompêo et al., 2004). These lakes in Fiorita River basin also are located in abandoned coal mining area, explored with the same procedures practiced in the Morozini River.

In a previous study in the lakes located in Morozini River basin, Waterloo (2002) stated that the lakes were used as dumps for coal mining waste, and the waste was considered responsible for the properties of surface and subterranean water in the Morozini mining field. The results of Waterloo (op cit.) are similar to those found in this study. However, our study found much lower pH values, which can be partly explained by the addition of $Ca(OH)_2$ in Lakes 1 and 2 after Waterloo's study.

The most extreme changes in water quality found by Waterloo (2002) were for the subterranean water (pH approximately 4.0; sulfate > 1000 $mg.L^{-1}$, Fe > 100 $mg.L^{-1}$). This author concludes that the higher pH values are due to the flow of oxidized SO_4^{-2} from the pyrite in the mining debris and also as a by-product of secondary reactions involving Fe in anaerobic conditions.

The Brazilian legislation, in accordance with CONAMA Resolution 357 (Brasil, 2005), classifies water quality in order to assess the environmental quality of lakes and ponds. The CONAMA Resolution also defines proper water use, according to the biological, chemical and physical characteristics of each class. Five freshwater classes have been defined for typical use and human consumption. The Special Class, represent the water crud used in the water supply after disinfection (more restrictive use), and the Class 1 to 4. Class 4 is to use less restrictive, such as navigation and harmonious landscape.

The lakes in our study had a range of chemical and physical characteristics, which show that the water quality was seriously affected. For some variables, these lakes failed to meet the necessary criteria for classification standards (Table 4). Based on the values found in the superficial water, the Lakes

Table 4. Water body conformity of the Lakes 1, 2 and 3 in relation to CONAMA Resolution 357 (Brasil, 2005).

Variable	Lake		
	1	2	3
Dissolved oxygen	4	4	1
pH	*	*	*
Total dissolved solids	4	4	3
Sulfate	4	4	3
Dissolved iron	3	3	3
Aluminium	4	4	4
Zinc	1	1	1
Manganese	4	4	4
Boron	1	1	1
Barium	1	1	1
Nickel	1	2	1
Recommendation	4	4	3

* Outside the limits for any of the established classes.

1 and 2 are in accordance to Class 4, and the Lake 3 in Class 3, according to CONAMA Resolution. According to our suggested classification, Lakes 1 and 2 should have their uses strictly limited to navigation and landscaping (Class 4) and Lake 3 should only supply water for human consumption after conventional or advanced treatment (Class 3).

6. Conclusions

Coal mining activity and waste disposal practices adopted by the mining companies in the Morozini River basin, has drastically affected the water quality of the examined water bodies and left them inappropriate for human use apart from landscaping. Immediate intervention is necessary because the local population uses the lakes for leisure, swimming and fishing.

Acknowledgements

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