

An Overview of an Acidic Uranium Mine Pit Lake (Caldas, Brazil): Composition of the Zooplankton Community and Limnochemical Aspects

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Abstract Water samples were collected quarterly for 1 year from the newly created Osamu Utsumi uranium mine pit lake, Brazil, which is affected by acid mine drainage (AMD). The water presented mean pH values of 3.8, high mean electrical conductivity values (2391 $\mu\text{S}/\text{cm}$), manganese (74 mg/L), sulfate (1413 mg/L) and uranium (3 mg/L). The density of rotifera was significantly higher than that of cladoceran. Rotifera *Keratella americana*, *K. cochlearis* and the Cladocera *Bosminopsis deitersi*, *Bosmina* sp., are being reported for the first time in samples from a uranium pit lake with AMD. Of the species registered, the order Bdelloidea was the most important in terms of density (17,500–77,778 ind/m³), since it occurred throughout the whole sampling period. The combined effect of moderately acidic pH and other potential stress factors, such as high concentrations of stable and radioactive contaminants, probably influenced the zooplankton species composition in the pit lake.

Keywords Mine pit lake · Acid mine drainage · Bdelloidea

Introduction

The environmental problems caused by mining vary based on the material extracted, processing techniques used, local geography and geology and time scales involved. Although it is generally accepted that mining can negatively affect the local biota by altering the natural community structure and reducing biodiversity (Ciszewski et al. 2013; Durán et al. 2013; Holopainen et al. 2003; Lefcort et al. 2010), such areas may also support significant populations of rare or threatened fauna (Batty 2005; Moser and Weisse 2011). Pit lakes are a common legacy of modern, large-scale surface mining (Eary and Castendyk 2013) and result from the infilling of mine pits by rising groundwater and surface water from streams and rainfall after the cessation of open-cast mining (Nixdorf et al. 2005). Many pit lakes are young (only a few decades old) and the number of studies on physical, chemical, and biological processes in these artificial ecosystems is limited (Wendt-Potthoff 2013).

One environmental problem of pit lakes is acid mine drainage (AMD), which occurs when metal sulfides are exposed to atmospheric, hydrological, and biological weathering (oxygen, water, and chemoautotrophic bacteria). The reduced pH mobilizes some metallic elements (e.g. Al, Cu, Mn, Fe, Cd, Pb, Zn, U), depending on tailings and waste rock mineralogy (Campos et al. 2011; Luís et al. 2009; Lyew and Sheppard 1997, 2001; Sheoran and Sheoran 2006; Soucek et al. 2001). The high concentrations of dissolved metals and sulfate and the acidic pH adversely affect aquatic biota (Soucek et al. 2000, 2001).

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The first acidic pit lake formed as a result of uranium ore mining in Brazil is located in the elevated plateau region of the city of Poços de Caldas, Minas Gerais State, Brazil (Osamu Utsumi pit lake). This newly-created artificial lake was formed as a result of exploration of uranium deposits on the grounds of the Mineral Ore Treatment Unit of the Brazilian Nuclear Industries (UTM/INB). Complex mixtures containing uranium and other highly toxic metals can exist at a uranium ore deposit with AMD, and the effects of these on the environment have yet to be completely elucidated (Antunes et al. 2007). According to Riethmuller et al. (2001), uranium can be highly toxic to freshwater biota.

With respect to the zooplankton community in acidic pit lakes, most studies have been done in Germany, indicating the need to expand the knowledge concerning the organisms of these singular habitats outside Europe (Belyaeva and Deneke 2007, 2013; Deneke 2000; Lessmann et al. 1999; Nixdorf et al. 1998; Wollmann et al. 2000). Similarly, most studies about the differences in the sensitivity of zooplankton organisms to acidified water were carried out in Europe and North America. Therefore, the extrapolation of zooplankton sensitivity rankings to other regions, namely the tropics, is questionable (Saro et al. 2011). Moreover, little is known about zooplankton communities in newly created pit lakes (Wendt-Potthoff 2013). The present study was designed to assess the zooplankton community composition and physical and chemical characteristics of the water in an acidic uranium mining lake in a tropical region.

Materials and Methods

Description of the Studied Site

The Ore Treatment Unit of the Brazilian Nuclear Industries (Fig. 1) is located in the Poços de Caldas Plateau (Minas Gerais State, Brazil) at 1291 m above sea level. The area is in a tropical climatic zone, with two distinct seasons: the rainy season, between October and March, has an average temperature of 20 °C, while the dry season, between April and August, has an average temperature of 14 °C (Rodgher et al. 2013). The mine area was projected to treat 2500 t of ore/day, but mining was permanently suspended in October 1995. Currently, the environmental effects of the AMD represent an obligation and legal responsibility of UTM/INB with respect to the site's treatment, decommissioning, and recovery. The focus of this study was the Osamu Utsumi pit lake, located on the UTM/INB grounds. The uranium found in this mining area is associated with ferrous sulfide (FeS₂), which, in the presence of water and oxygen, provides adequate conditions for AMD. This

acidic effluent contains high concentrations of fluoride, sulfate, manganese, zinc, uranium, and other contaminants (Nascimento et al. 1988). Before being discharged into the environment, the AMD is treated with slaked lime and flocculating agents and then separated by decantation, with stable and radioactive metals having precipitated (Nóbrega et al. 2008). The precipitates, including the calcium diuranate formed as a result of this treatment, are returned to the pit lake, affecting the contaminant concentrations.

Experimental Design

Water samples were collected quarterly (two samplings in the rainy season and two in the dry season), for 1 year (2008–2009). The samples were collected close to the water surface of the pit lake (Fig. 1) using a vertical, 5 L Van Dorn flask, transferred to previously-washed plastic bottles, and stored at 4 °C until taken to the laboratory for analysis. The zooplankton community surface water was sampled using a plankton net.

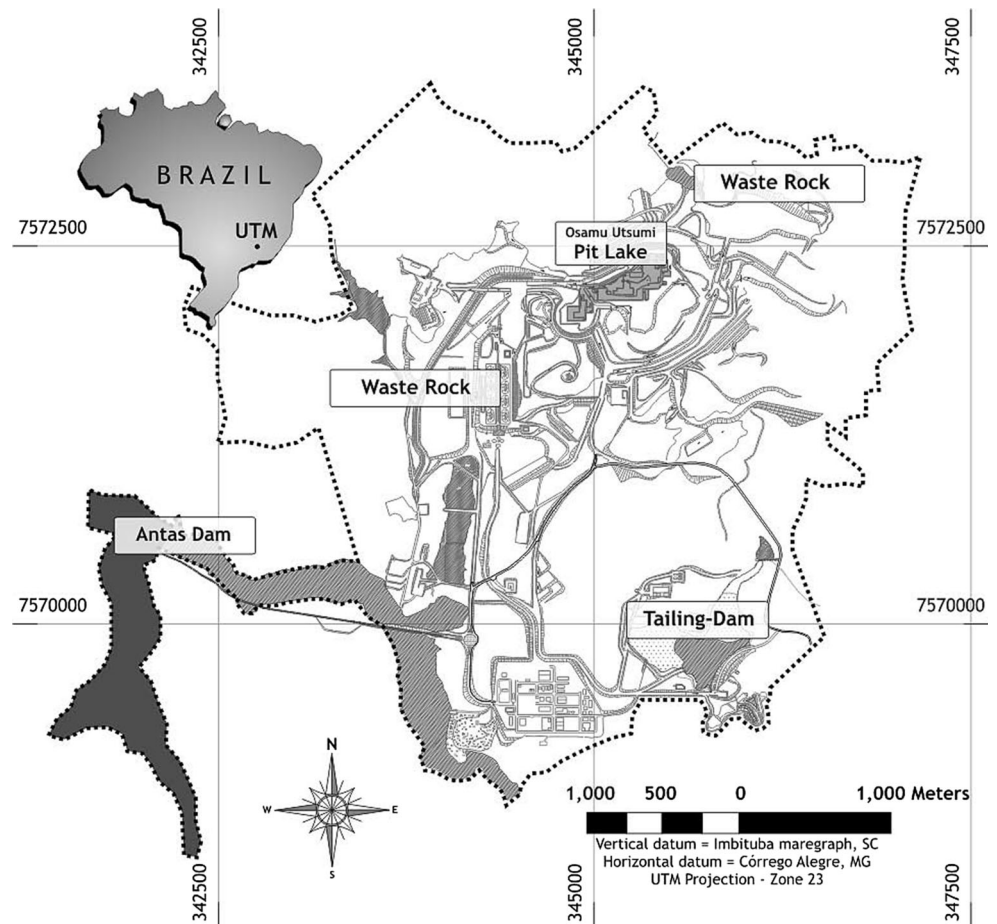
Physical Properties and Limnochemistry of the Water

A WTW model 597 pH meter (GmbH, Weilheim, Germany) was used to measure pH; the electrical conductivity (EC) was determined using a Digimed (São Paulo, Brazil) DM-31 conductivity meter. Fluoride concentrations were estimated using a potentiometric method with an ion-selective electrode (Nascimento et al. 1988), while sulfate was determined by UV–visible spectrophotometry using ASTM methodology (1980). To determine total Fe, Mn, Al, and Zn concentrations, samples were stored in polyethylene bottles and fixed with ultra-pure nitric acid to a final concentration of 0.2 M. The samples were digested as described in APHA (1995) and the concentrations were determined by inductively-coupled plasma atomic-absorption spectrometry with a Liberty RL sequential ICP-OES (Varian, USA). To analyze uranium, aliquots of the water samples were extracted with the solvent tributylphosphate, treated with a solution of the colorimetric reagent Arsenazo III, and the absorbance was measured at 650 nm in a UV–Vis spectrophotometer (Fukuma et al. 2001). Total nitrogen was determined based on the methodology described by Golterman et al. (1978), while total phosphorus was determined by the method described in APHA (1995).

Zooplankton Community

To analyze the zooplankton community, 100 L surface water samples were collected and subsequently filtered for Rotifera, using a net with 10 µm mesh. In acid mine lakes, one should consider the size of the organisms, since the

Fig. 1 Map of the sampling site in the Mineral Ore Treatment Unit of the Brazilian Nuclear Industries, showing the uranium mine pit lake



communities of these lakes are frequently dominated by small rotifers (Deneke 2000). Concomitantly, for Crustacea (Cladocera and Copepoda), 100 L of water were collected and filtered using a net of 60 μm mesh (Woelfl and Whitton 2000). The organisms were then fixed in 4 % formaldehyde (final concentration) and stored in glass flasks for subsequent identification of the main zooplankton groups (Cladocera, Copepoda, and Rotifera) under an optical microscope (Zeiss—Axioplan-2) with magnification up to 1000 \times . Cladocera and Copepoda counts were carried out using gridded acrylic plates under a stereoscopic microscope (Zeiss-Stemi SV11), with magnification up to 66 \times , counting sub-samples or even whole samples for rare organisms. For the Rotifera, 1 mL sub-samples were counted in a Sedgewick-Rafter chamber using the Zeiss optical microscope with magnification up to 1000 \times . Specialized literature was used to identify the zooplankton (De-Melo and Hebert 1994; Elmoor-Loureiro 1997; Koste 1978; Kotov et al. 2009; Shiel and Koste 1992, 1993). The zooplankton density results were analyzed using ANOVA and Tukey's test (post hoc test) using the BioEstat 4.0 program (Ayres et al. 2005) to detect significant differences between zooplankton groups.

Results

Physical Properties and Limnochemistry of the Water

The physical and chemical parameters of the Osamu Utsumi water samples are presented in Table 1. The water had a mean pH of 3.8. The EC values ranged from 1976 to 2760 $\mu\text{S}/\text{cm}$. Sulfate concentrations were elevated (366–1832 mg/L). The average concentrations of ions measured in the pit lake samples were: Al (81.9 mg/L), F^- (55.3 mg/L), Mn (74.5 mg/L), Th (0.15 mg/L), U (2.95 mg/L), and Zn (15.5 mg/L). The average concentrations of total Fe were 4.27 mg/L, with Fe^{3+} presenting higher concentrations (1.4–10.2 mg/L) than Fe^{2+} (<0.15–0.6 mg/L). The highest concentrations registered for total nitrogen and total phosphorus were 840 and 18 $\mu\text{g}/\text{L}$, respectively.

Zooplankton Community

Regarding the zooplankton community, low and high species densities were recorded throughout the whole study. The average density value for the Rotifer group

(66,390 ind/m³) was significantly higher ($P < 0.05$, Tukey's test) than that of the Cladoceran group (977 ind/m³). Four species belonging to the Rotifera phylum were identified (*Keratella americana*, *K. cochlearis*, *Cephalodella* sp., and Bdelloidea order), while only two species of the Cladocera group (*Bosmina* sp. and *Bosminopsis deitersi*) were registered (Table 2). For the Rotifer group, average density values of *Keratella americana* (143 ind/m³) and *K. cochlearis* (208 ind/m³) were significantly lower ($P < 0.05$, Tukey's test) than those for the *Cephalodella* sp. (25,350 ind/m³). Of the species registered in the pit lake samples, the Bdelloidea was the most important in terms of average density values (39,580 ind/m³), since it occurred throughout the whole sampling period, followed by *Cephalodella* sp. The Rotifera *Keratella americana* and *K. cochlearis* and the Cladocera *Bosminopsis deitersi* and *Bosmina* sp. were occasionally present. No members of the Copepod group (Crustaceans) were found.

Figure 2 presents photos of the zooplankton organisms registered in the uranium mine pit lake, with the respective body size measurements. The literature lacks information regarding the body size of organisms occurring in acidic pit lakes, and such information could be important, as well as other taxonomic features, such as dimensions, shape, and color of the zooplankton that colonized the pit lake. Figure 2e shows possible cell shrinkage in the post-abdomen region, observed in a specimen from the acidic pit lake.

Discussion

The water samples from the uranium mine pit lake presented moderately acidic pH throughout the study, according to the classification proposed by Nixdorf et al. (2005) for acidic pit lakes. With respect to EC, a high average value (2391 $\mu\text{S}/\text{cm}$) was recorded for the Osamu Utsumi samples when compared to values found in German mining lakes (Table 1). In pit lakes, EC values can exceed 5000 $\mu\text{S}/\text{cm}$, as observed by Lessmann et al. (1999) in a German pit lake, where EC values ranged from 3320 to 5840 $\mu\text{S}/\text{cm}$.

High values of Al, Mn, and Zn were present in the lake. According to Friese and Schultze (2013), Al, Fe, and Mn are typically the dominant dissolved metals in acidic pit lakes due to the increased solubility of the minerals containing these elements. The mean concentrations recorded for total nitrogen and total phosphorus were 752.5 and 11.8 $\mu\text{g}/\text{L}$, respectively. Mine lakes are very poor in phosphorus (Nixdorf et al. 2003), and total nitrogen content is much greater than total phosphorus, as observed in this study. The ranges of total nitrogen and total phosphorus observed are indicative of an oligo-mesotrophic environment (Carlson 1977).

One of the negative effects of AMD is reduced richness and diversity of aquatic species and replacement of intolerant by tolerant species (Lessmann et al. 1999; Luís et al. 2009; Nixdorf et al. 1998; Van Damme, et al. 2008; Wollmann et al. 2000). Acidic pit lakes are considered

Table 1 Minimum and maximum values found for the physical and chemical variables in acidic pit lakes with AMD: hydrogen potential (pH), electrical conductivity, fluoride, sulfate, aluminum, total

nitrogen, total phosphorus and total metals: total iron, manganese, zinc, uranium and thorium

	Lake Plessa 107 ^a	Lake ML 111 ²	Lake ML 117 ^b	Lake ML Felix ^b	Osamu Utsumi pit lake (n = 4) ^c
pH	2.1–2.5	2.6–2.9	2.8–3.0	3.4–3.8	3.6–4.1
EC ($\mu\text{S}/\text{cm}$)	3320–5840	2000–2800	1300	400–520	1976–2760
F ⁻ (mg/L)	–	–	–	–	33.4–75.1
SO ₄ ²⁻ (mg/L)	808–4440	1100–1800	400	150–500	366.6–1832
Al (mg/L)	22–60	35	1.9	1.8–3.8	68.3–106.5
Total Fe (mg/L)	390–670	130–200	20	0.4–5.0	1.76–10.8
Mn (mg/L)	1.3–43.5	–	–	–	71.5–143.0
Zn (mg/L)	1.69–2.91	–	–	–	10.8–19.9
U (mg/L)	–	–	–	–	0.1–4.2
Th (mg/L)	–	–	–	–	0.1–0.3
Total P ($\mu\text{g}/\text{L}$)	5–26	<5–7	5–7	<5–7	5.6–18
Total N ($\mu\text{g}/\text{L}$)	–	3.1–11.3	1.9–2.3	1–5	700–840

^a Lessmann et al. (1999)

^b Wollmann et al. (2000)

^c Four samples

Table 2 Species composition of zooplankton communities found in acidic pit lakes with AMD

	Lake Plessa 107 ^a	Lake ML 111 ^b	Lake ML 117 ^b	Lake ML Felix ^b	Osamu Utsumi pit lake (n = 4) ^c
Rotifera					
Order Bdelloidea					X
<i>Rotaria rotatoria</i> (Pallas, 1766)	X	X	X	X	
<i>Brachionus sericus</i> Rousselet, 1907			X	X	
<i>Cephalodella</i> sp.					X
<i>Cephalodella hoodii</i> (Gosse, 1886)	X	X	X	X	
<i>Cephalodella gibba</i> (Ehrenberg, 1830)			X	X	
<i>Elosa worrallii</i> Lord, 1891		X	X	X	
<i>Lecane lunaris</i> (Ehrenberg, 1832)				X	
<i>Lecane stichaea</i> Haring, 1913				X	
<i>Lepadella</i> sp.			X	X	
<i>Keratella americana</i> Carlin, 1943					X
<i>Keratella cochlearis</i> (Gosse, 1851)					X
<i>Trichocerca similis</i> (Wierzejski, 1893)				X	
Cladocera					
<i>Chydorus sphaericus</i> (Müller, 1785)			X	X	
<i>Bosminopsis deitersi</i> Richard, 1895					X
<i>Bosmina</i> sp.					X
Copepoda					
<i>Diacyclops</i> sp.				X	
Number of species	2	3	7	11	6

^a Lessmann et al. (1999)

^b Wollmann et al. (2000)

^c Four samples

harsh environments for zooplankton organisms (Nixdorf et al. 1998). In pit lakes with extremely low pH, the relative importance of rotifers within the zooplankton community increases since the small littoral or benthic rotifers dominate over zooplankton crustaceans (Belyaeva and Deneke 2013; Deneke 2000; Wollmann et al. 2000). This was also found in this study, since the Rotifera phylum was found in significantly higher densities (18,333–115,019 ind/m³) and number of species (4) compared to the zooplankton crustacean species, which were present at densities ranging from 258 to 3113 ind/m³, with only two species.

Studies in acidic pit lakes (pH ranging from 2.6 to 3.8) formed by coal mining in Germany (Deneke 2000; Lessmann et al. 1999; Nixdorf et al. 1998; Wollmann et al. 2000), lignite mining in Australia (Moser and Weisse 2011), and pyrite exploration in the Czech Republic (Hrdinka et al. 2013) also found that the zooplankton communities of these lakes were composed mainly of rotifers common to such environments, namely *Brachionus sericus*, *Cephalodella* sp., *C. gibba*, *C. hoodii*, *Elosa worrallii*, *Polyarthra* sp., and *Rotaria rotatoria* (Bdelloidea order), in addition to Cladocera *Chydorus sphaericus*. The latter were only found in lakes where the pH was slightly below three. In the present

study, out of the species cited above, only the rotifers of the Bdelloidea order and the *Cephalodella* genus were registered. On the other hand, the Rotifera *Keratella americana*, *K. cochlearis*, and the Cladocera *Bosminopsis deitersi* and *Bosmina* sp., are being reported for the first time in samples from a uranium mine pit lake with AMD, indicating the capacity of these zooplankton organisms to colonize extreme environments, despite ionizing radiation, low pH, and multiple chemical stressors.

In a study conducted on an oligo-mesotrophic dam (Bortolan) not impacted by AMD and at a 30 km distance from the uranium mine pit lake, Ferrari (2010) recorded a higher diversity of zooplanktonic species (43), than the number recorded in this study (6). Among the species registered at Bortolan dam, *Keratella americana*, *K. cochlearis*, order Bdelloidea, *Bosminopsis deitersi*, and *Bosmina* sp. were also found in our pit lake samples. On the other hand, that study did not detect the *Cephalodella* sp. that were found in this lake. Our findings corroborate the results obtained by Jersabek et al. (2011) in Austria and Germany and Deneke (2000) in Europe and North America, respectively, who found that *Cephalodella acidophila* sp., *C. gibba*, and *C. hoodii* were characteristic of acidic pit lakes.

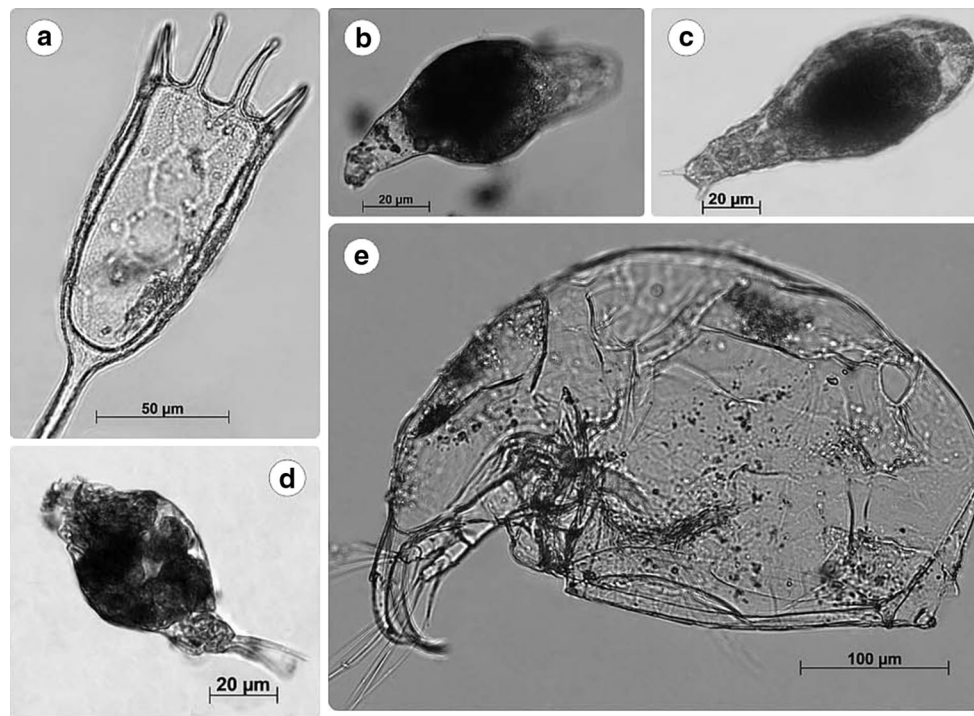


Fig. 2 Light microscope view ($\times 10$ – 40 magnification) of the identified Rotifera (**a** *Keratella americana*; **b**, **c**: order Bdelloidea—contracted body; **d** *Cephalodella* sp.) and Cladocera (**e** *Bosmina* sp.), in water samples from the uranium mine pit lake

Since the species registered in this study are not restricted to acid pH environments, they can be considered as more generalized. Moreover, they probably persisted due to their high physiological tolerance to severe acidic stress, in addition to the absence of more efficient prey—i.e. large-bodied zooplankton crustaceans (copepods, cladocerans) and planktivorous fish. According to Arnott and Vanni (1993) and Belyaeva and Deneke (2013), the water chemistry in acidic pit lakes notably influences the composition of the species in these habitats, since the pressure of the biotic factors (predators and competition) decreases at low pH. In acidic water, the organisms must maintain a circumneutral pH in the cytoplasm (Weithoff 2005). According to Havens (1993), the extinction of larger-bodied zooplankton might be due to the acid stress caused by the H^+ concentration and the toxic stress of metals that can impair the normal process of osmoregulation in acid-sensitive zooplankton.

In the Osamu Utsumi pit lake, an acidic and oligo-mesotrophic environment, both *Keratella americana* and *K. cochlearis* were registered. *K. cochlearis* is a very common cosmopolitan rotifer species, typically found in this kind of environment (Turner 1987; Xi et al. 2002) and acidic freshwater (Koste 1978). In a study carried out in an acid lake formed by uranium mining activities in the Harrison Peninsula, Canada, Kalin et al. (2001) registered the occasional occurrence of low densities (0.008 – 0.016 ind/ m^3)

of *Keratella* sp. In our samples, *K. americana* and *K. cochlearis* were registered with greater densities (575 and 833 ind/ m^3), respectively, than those registered by Kalin et al. (2001).

Cephalodella sp., with body sizes ranging from 86 to 98 μm , was registered in this study. Recently, a new species of *Cephalodella*, *C. acidophila* sp., was observed in two extremely acidic mine lakes ($pH < 3$) in Austria and Germany (Jersabek et al. 2011), while *C. hoodii* and *C. gibba* were described in studies in highly acidic mine lakes in Europe and North America (Deneke 2000). According to Viayev (2010), *Cephalodella* shows a wide range of environmental preference, which could explain the occurrence of *C. acidophila*, *C. gibba*, and *C. hoodii* in extremely acidic pit lakes. Nogrady and Pourriot (1995) consider *Cephalodella* one of the most taxonomically difficult genus amongst all rotifers, due to the great similarity of the phenotypes and the large number (190) of species in this genus.

In Lake Plessa-107, a coal mine lake in Germany, Lessmann et al. (1999) only found the rotifers *Cephalodella hoodii* and *Rotaria rotatoria* (Bdelloidea order) at extremely acid pH values (2.1 – 2.3) and elevated Al, Mn, and Zn. In contrast, samples from this study in moderately acid pH values (3.6 – 4.1) contained six zooplankton species, including the Rotifera *Cephalodella* sp. and Bdelloidea.

Wollmann et al. (2000) found that pH was the most important variable governing the richness of the zooplankton species in the mine lakes ML-111 (pH 2.6–2.9), ML-117 (pH 2.8–3.0), and ML-Felix (pH 3.4–3.8), with 3, 7, and 11 species, respectively. Results from this study indicate that pH (3.6–4.1) were in the same range as Lake ML-Felix, but with fewer (6) zooplankton species. Rotifers are the most pH tolerant taxa of zooplankton (Nixdorf et al. 2005), surviving in extremely acidic waters (pH < 2.8), besides being the least sensitive to metals (Jak et al. 1996).

Our investigation demonstrated that the rotifers were the most representative organisms in terms of density (17,500–77,778 ind/m³) throughout the study. According to Gladyshev and Meselson (2008), rotifers of the order Bdelloidea are extremely resistant to ionizing radiation (IR), with greater resistance and adaptation with respect to IR than other zooplankton. The ability of the Bdelloids to remain fertile after extensive DNA breakage and other damage caused by exposure to IR reflects their evolutionary adaptation, attributed to their damage repair capability or to repair protection systems, or both (Gladyshev and Meselson 2008). Raised levels of radioactivity and high concentrations of radionuclides have been detected in the Osamu Utsumi pit lake (Gomes et al. 2002; Silva et al. 2000; Veiga et al. 2000). Sheppard et al. (2005), through eco-toxicological tests applied to some freshwater invertebrates, defined that the predicted no-effect concentration (PNEC) for chemical toxicity of uranium to these organisms is 0.005 mg/L of U. Thus, the U concentrations in the lake (0.1–4.2 mg/L) could explain the higher density values of Bdelloidea.

Among the zooplanktonic cladocerans, the density of *Bosminopsis deitersi* and *Bosmina* sp. was low. *B. deitersi* is a tropical cladoceran species that has been commonly recorded in Brazilian freshwaters (Melão and Rocha 2006; Nogueira 2001) and is a sensitive indicator of polluted waters (Rocha and Güntzel 1999). Therefore, the high metal concentrations and low pH in the Osamu Utsumi pit lake could be chronically toxic to this species (Locke and Sprules 2000). Toxicity studies conducted with cladocerans have reported that concentrations of 0.8 mg/L of Mn (WHO 2004) and 1 mg/L of Zn (Sanchez-Ortiz et al. 2010) can adversely affect their growth and reproduction. Sheppard et al. (2005) have proposed a PNEC of 0.005 mg/L of U for freshwater invertebrates. The metal values in this study were, on average, 40 times the values considered toxic to cladocerans and other freshwater invertebrates, according to the authors cited above. The effects of U on the zooplankton may be due to chemical toxicity, given that the chemotoxicity of depleted uranium is much greater than its radiotoxicity (Mathews et al. 2009; Sheppard et al. 2005).

Moreover, other studies have indicated that some environmental toxicants can produce morphological abnormalities in the cladoceran *Ilyocryptus spinifer* (Elmoor-Loureiro 2004) and *Daphnia* species (Zanata et al. 2008), as possibly observed here for *Bosmina* sp. Woelfl and Whitton (2000) quantified cellular losses and deformation during fixation of planktonic organisms from acidic environments, and reported that taxonomic determination of acidic water organisms is often difficult since traditional taxonomic features such as dimensions, shape and colors may be hard to recognize reliably. According to Elmoor-Loureiro (2004), bioassays should be conducted to test the hypothesis of environmentally-induced abnormalities in zooplankton and to verify the responsible substances.

Conclusion

It is clear that potential stressors (moderately acidic pH and high concentrations of stable and radioactive contaminants) could have influenced the richness and composition of the zooplankton community in this uranium mine pit lake. However, specific causes cannot be established, but only inferred. This suggests that laboratory studies, including toxicity tests, should be carried out to assess the toxic effects caused by each isolated chemical stressor and their combined action in different pH variations. Such tests could be important in evaluating each species' ecological behavior, especially with respect to potentially toxic elements, including the stable (Mn, Al, and Zn) and radioactive (U) chemical species found in anomalous concentrations in this pit lake.

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