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WATER QUALITY AND TOXICITY OF RIVER WATER DOWNSTREAM OF THE URANIUM MINING FACILITY AT POÇOS DE CALDAS

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ABSTRACT

The uranium mining site of Poços de Caldas consists of open mine pit, tailings, waste rock dumps and an acid rock drainage problem, which has the potential to impact upon freshwater of the Ribeirão das Antas catchment. The high level of manganese (value of 1.8 mg/L) contained in the discharge water (DW) is an important factor affecting the water quality of the river (water quality criterion for aquatic life for Mn is 0.1 mg/L). Water quality criteria (WQC) are used for regulatory purpose and intended to define concentrations of chemicals in water that are protective of aquatic life and human health. WQC is a standard, although it is recognized that in some instances these criteria may be overprotective as metal bioavailability and hence toxicity is dependent on water chemistry. The toxicity assessment of WD was performed by bioassays with *Dapnhia similis* and *Ceriodaphnia dubia* as bioindicators. As DW showed no toxicity to the organisms and the chemical analysis and dose assessments pointed U and Mn as the most important metals for water toxicity, the U and Mn toxicities were evaluated in the DW spiked with U and Mn. Acute uranium toxicity (48 h immobilisation test) for *Daphnia similis* was determined as a LC50 value (concentration that is toxic to 50% of test organisms) around 0.05-0.06 mg/L, value close to the one found for effects on reproduction, a 7 day LOEC (lowest observed effect concentration) of 0.062 mg/L for *Ceriodaphnia dubia.* The value of NOEC (no-observed effect concentration) for U was 0.03 mg U/L, which is higher than the concentration corresponded to the authorized dose limit for ^{238}U (0.004 mg/L) and higher than the uranium WQC (0.02 mg U/L). The manganese concentration in the DW is lower than the found value of LC50 (11.5 mg/L), LOEC (10 mg/L) and NOEC (5 mg Mn/L).

1.INTRODUCTION

Acid mine drainage (AMD) is recognized as the most serious environmental pollution problem facing the mining industry. Mining activities inadvertently accelerated physical weathering of pyrite by grinding up the ore and placing the waste residues in tailings impoundments. The initiating reaction in the geochemical processes of generating acidic waters is a complex combination of chemical and bacterial action, mainly with pyrite to form sulphuric acid. Subsequently, the formed acidic mine water leaches metal from the contacted ore and in consequence metals are mobilized and may contaminated groundwater and downstream water bodies. The AMD composition is an outcome of local hydrology, geology, and geochemistry. Acid mine drainage (AMD) represents significant environmental and financial liability for the mining industry.

The Poços de Caldas region is characterized by the occurrence of radioactive anomalies and bauxite associated with fluorite, pyrite and oxide of manganese. The uranium mining activities generated tree sources of acid drainage: a mine pit and two waste rock dumps. In order to decrease the containing of metals, fluorite and radionuclides in the acidic water, the drainage from waste rocks are pumped to a unit of chemical treatment in which by addition of $Ca(OH)_2$ the acidic drainage is neutralized to pH 10-11. After the solid settlement in tailing dams the liquid overflow is released into the Antas River.

The impact of the mining site and the enhancement of metal concentrations in the nearby surface water has been the subject of extensile studies; a compilation of these studies is cited by Fernandes et al., 2008 [1]. Prado (1994) stated that the main contaminants of concern in Antas River were manganese, fluorite and uranium, which concentration values exceeded the water quality criteria (WQC) established by CONAMA [2]. Antas River is the strategic water resource for the Poços de Caldas city. Although the river water is mainly used for crop irrigation and for cattle watering, sometimes it has been used for water supply of the city.

Water quality criteria are used in regulatory programs to ensure that the quality of natural waters will achieve their desire use [3]. Typically the criteria are derived based on calculations of a statistical distribution of laboratory ecotoxicity data, for acute exposure conditions (short-term) and for chronic exposure conditions (long-term). The data set is plotted in a normal probability plot and the 5 th percentile is used for setting the protection limits, as an attempt to offer a level of protection of 95% for all species [4]. Most of the compiled data are from aquatic invertebrates, which are a very sensitive species widely used in ecotoxicological testing. As a number derived for regulatory purpose, the established limits do not consider specific characteristics of water, although it is recognized that the best practice would be to derive site-specific water quality standard [3].

The need for site specific criteria arises from observation that metal bioavailability and hence toxicity is dependent on water chemistry, mainly to the concentration of free ions in solution [5]. Hence toxicities of metal bound into colloidal, particulate and complexed forms are assumed to be less than those of the aquo-ionic forms. Another way in which water's chemistry affect the toxicity of metals is contributing to reduce metal uptake and toxicity through competition for surface binding sites, e.g. the metal toxicities decrease with the water hardness. Many metals are toxic to organisms due to their ability to hinder the organism uptake of essential metals, as Ca and Na. Consequently, high levels of Ca and Na in water decreases the blockade of ions by toxic metals. In a review, Sheppard et al. (2005) showed that the sensibility of organisms to uranium depends on several environmental parameters such as alkalinity, (due to the complexation of uranyl ion with carbonates), and hardness (due to its competition with calcium and magnesium) [4]. There is also evidence that manganese toxicity is higher in soft water conditions (25 mg calcium carbonate/litre) than in harder conditions. On the other hand, it was reported that manganese can protect organisms against the effect of more toxic metals [6].

Taking into account the effect of water chemistry over the metal toxicities, this research addresses to evaluate the level of contamination in the Antas River downstream the uranium mining site, to assess the chemical species of key metals within water and to evaluate the toxicity of the water to the aquatic invertebrates, *Daphnia similis* and *Ceriodaphnia dubia.* These bioindicators were used to assess the ecotoxicological level of U and Mn in the discharge water of the site.

2. METHODOLOGY

2.1. Sampling and parameter analysis

Water samples were collected at the point of mining discharge on four occasions during 2008 (March, June, September and December). Physical-chemical parameters (pH, Eh, temperature, and electrical conductivity) were measured in the field. For other determinations, about 4 L were sampled: 1 L in a polyethylene bottle for alkalinity determination, 20 mL for major cations and 500 mL for anion determinations. Samples for cation determinations were filtered with a filter of 0.45 μm, connected to a syringe, and stored in a polyethylene centrifuge tube. The solution was acidified with 0.1 mL 65% concentrated Ultrapure HNO_3. For uranium determination 2 liters of sample were filtered by a Millipore membrane (0.45 μm). In addition, water was sampled in 200 ml amber glass bottles for dissolved organic carbon (DOC). Samples for alkalinity determination as well samples for anion and DOC determination were stored at 4 °C until their analysis.

The acidic aliquot was analyzed for major cations and metals by inductively coupled plasma atomic emission spectrography (ICPOES). Alkalinity was determined by titration with H_2SO_4. Uranium was determinated spectrophotometrically. Anions were determined by classical methods: chloride (Volhard's argentometric method), sulfate (turbidimetry) and fluorine (by selective electrode), nitrate (cadmium/copper column) and phosphate by the ammonium molybdate/ascorbic acid method [7]. Organic carbon was measured using high temperature catalytic combustion (Shimadzu TOC Analyser).

2.2. Ecotoxicity tests

Twenty-five litres of the discharge point water was collected in five 5 L polyethylene containers. The samples were stored at 4 °C and immediately transported to a laboratory in Poços de Caldas. At the laboratory the samples were stored at -5°C and transported to Rio de Janeiro city, where remained frozen until the tests. Ecotoxicity tests were performed in acute exposition (24–48 h), with *Daphnia similis* and chronic exposition with *Ceriodaphnia dubia*

(7 days) according to NBR 12713 [8] and to NBR 13373 [9], respectively. These tests were performed in triplicate.

For assessing the uranium ecological level, DW was spiked with a standard of uranyl hexahydrate in 0.3% nitric acid solution (1.04 $g.L^{-1}$). Uranium acute toxicity was studied in solutions with initial concentrations of 10 $mg.L^{-1}$, 5 $mg.L^{-1}$ and 0.5 mgL^{-1}, pH 7. The organisms were exposed to increasing dilution factors DF of these spiked samples (DF=1, 2, 4, 8). As effect was observed only for the uranium concentration solution of around 0.5 mg/L, more two bioassay tests were carried out with two solutions of uranium concentration of 0.5 mg/L and 0.4 mg/L. Chronic toxicity was examined from 0.0325 $mg.L^{-1}$ to 0.5 $mg.L^{-1}$ of U in DW-pH 7. In order to eliminate differences in nitrate concentrations associated with uranium spikes, for all tests conditions including controls, nitrate was adjusted to 2.5E-05 mM [10].
Manganese tests were carried out with solutions spiked with a solution of chloride of manganese (20 g. L^{-1}). Acute and chronic tests were performed at concentrations ranging from 1.25 to 20 $mg.L^{-1}$.

The studied ranging of concentrations for both uranium and manganese were set taking into account the reported levels responsible for observed effects. For Mn the literature report levels for acute toxicity varies between 0.8 and 350 $mg.L^{-1}$ [6] and for uranium the levels of concentrations which caused chronic and acute effects varies between 0.01 to 100 $mg.L^{-1}$ [11].

The value of LOEC (lowest observed effect concentration) and the value of NOEC (no-observed effect concentration) were obtained by the Steels many-one rank test using the TOXSTAT statistic software version 3.3 [12]. The program SPEARMAN estimated the LC50 values using the Trimmed Spearman-Karber Method [13].

2.3. Geochemical speciation modelling

To provide information on metal bioavailability in the DW, the speciation of U and Mn was predicted using the MINEQL+ geochemical speciation code, version 4.5 (Environmental Research Software, Hallowell). The input parameters were based on measured physicochemical data (i.e. pH, pe (electric potential, calculated by dissolved oxygen concentration value), temperature, and ion concentrations, table 1). Metal complexation with dissolved organic carbon (DOC, humic substance) in the DW was performed using the approach % HA=0.01 DOC. In order to assess the chemical speciation the values of the minimum detectable concentration were divided by two.

3. RESULTS

3.1. **Water chemistry data**

The results of the measured parameter in field, major cation and anion, toxic metal and radionuclide analysis are shown in table 1.

Table 1. Physicochemistry of DW, encompassing national water quality criteria for protecting freshwater biota established by CONAMA [13].

PARAMETER	MARCH	JUNE	SEPTEMBER	DECEMBER	WQC
Temperature (ºC)	24	17	21	25	
Conductivity (µScm^{-1})	148	181	519	168	
pH	6.8	5.9	6.7	6.2	**6-9**
Dissolved Oxygen (mg/L)	10	9.4	6.3	7.7	**>6**
Eh (mV)	289	-	300	220	
Organic Carbon (mg/L)	ND	ND	6.9	2.2	
Na (mg/L)	0.7	0.9	1.3	1.1	
K(mg/L)	2.4	2.2	4.0	3.5	
Ca(mg/L)	19.5	19.1	103.8	37.1	
Mg(mg/L)	0.67	0.59	0.76	0.62	
Al(mg/L)	0.11	0.10	<0.05	<0.05	**0.1**
Mn(mg/L)	1.65	1.22	1.41	0.60	**0.1**
Fe (mg/L)	0.21	<0.05	<0.05	0.06	**0.3**
Ba(mg/L)	0.018	0.018	0.058	0.051	**0.7**
Si(mg/L)	1.81	2.42	1.65	2.75	
Cr(mg/L)	<0.001	<0.001	0.0020	< 0.001	**0.05**
Cu (mg/L)	<0.04	<0.04	<0.04	<0.04	**0.09**
Zn (mg/L)	0.042	0.088	0.023	0.124	**0.18**
Cd (mg/L)	<0.0002	0.0004	<0.0002	<0.0002	**0.001**
Hg (mg/L)	<0.0005	<0.0005	<0.0005	<0.0005	**0.0002**
Pb (mg/L)	<0.001	<0.004	0.0020	< 0.004	**0.01**
As (mg/L)	<0.003	<0.003	<0.003	<0.003	**0.01**
Ni (mg/L)	<0.001	<0.001	<0.001	< 0.001	**0.025**
U (mg/L)	0.0039	0.0027	0.0062	0.0009	**0.02**
Ra-226 (Bq/L)	0.024	0.028	0.032	0.024	
Ra-228 (Bq/L)	<0.03	0.04	0.04	0.02	
Pb-210 (Bq/L)	0.03	0.07	0.05	0.05	
Cl (mg/l)	0.65	1.52	3.68	0.65	**250**
SO_4^{-2} (mg/L)	49.7	64.3	245.4	75.3	**250**
$CO^{-2}{}_3$ (mg/L)	<1.0	<1.0	<1.0	<1.0	
F^{-1} (mg/L)	1.27	0.69	1.82	1.55	**1.4**
$NO^{-1}{}_3$ (mg/L)	<0.05	0.12	<0.05	0.08	**10**
$PO^{-3}{}_4$ (mg/L)	<0.075	<0.075	<0.025	<0.025	

ND=not determined

The CONAMA guidance values for Al, Cu and Fe are established for dissolved concentrations, whereas for Cu, Ba, Cd, Pb, Cl, Cr, F, Mn, Hg, Ni, SO_4 and U the limit values are established for the total concentrations. As no significant differences between dissolved and total concentrations for any parameter were observed, the values reported in table 1 regard to dissolved concentrations. With respect to Mn and F, the data confirm the prior observation reported by Prado [2]. The levels of Mn are higher than the CONAMA limit value for all studied period. In fact, water data from background points showed that the waters of this region have a natural level of Mn (median 0.2 mg/L) higher than the CONAMA limit. For uranium, a potential pollutant from the mining site, the levels were lower than the CONAMA and CNEN authorized limit (0.004 mg/L). Fluoride and aluminum presented levels higher than the maximum limit value (for Al in March, and for F^{-1} in June and December).

Considering the water quality index adopted by IGAM (Instituto Mineiro de Gestao das Aguas) [14], the water quality of the Antas River at DW point was considered good (March, June and December) and excellent (September).

3.2. Ecotoxicity tests

The speciation of the river water at the point of effluent discharge (DW) using MINEQL pointed out Mn^{2+} (87%) and $UO_2(HPO_4)$ (99%) as the main species of Mn and U in the water, in spite of the low concentration of phosphate in the water. Even though the concentration of phosphate would not be considered, only 6% of U would be present as the free ion UO_2^{2+} specie. Most of uranium would form complexes with fluorite (62%) and carbonate (13%). Considering that according to the free ion activity model the metal toxicity varies as a function of free metal concentration, Mn would be the most toxic metal in the water.

The DW tests for toxicity showed absence of acute and chronic toxicities to the organisms. The spiked DW acute test for uranium pointed LC50 value (concentration that is toxic to 50% of test organisms) around 0.05-0.06 mg/L (48 h immobilisation test) for *Daphnia similes*, Figure 1. This value is close to the one found for effects on reproduction: a 7 day LOEC (lowest observed effect concentration) of 0.062 mg/L for *Ceriodaphnia dubia* (Figure 2). This LOEC value is lower than the data range (0.5 to 3.5 mg/L) found by Poston et al. [15] for *D. magna* and than the LOEC value found by Kuhne et al. [16] for *Ceriodaphnia dubia* (3.91 mg/L). The value of NOEC (no-observed effect concentration) for U was 0.03 mg U/L, which is higher than the corresponded concentration to the authorized dose limit for U-238 (0.1 Bq/L=0.008 mg/L) and higher than the uranium water quality criteria (WQC) (0.02 mg U/L).

The manganese concentrations in the DW (0.6 to 1.65 mg/L) are lower than the found value of LC50 (11.5 mg/L), LOEC (10 mg/L) and NOEC (5 mg Mn/L). The LC50 value is lower than the range values reported in literature for *Daphnia magna* (16-19.5 mg/L) [17].

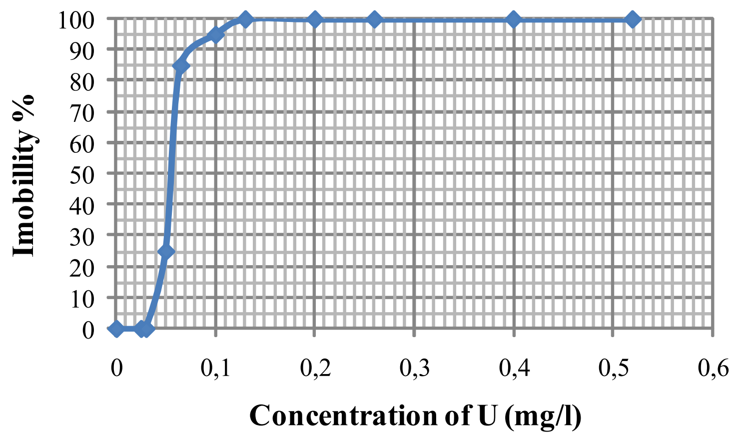

Figure 1. Concentration reponse plots showing the toxicity of uranium in water of discharge to *Daphnia similis* (acute test)

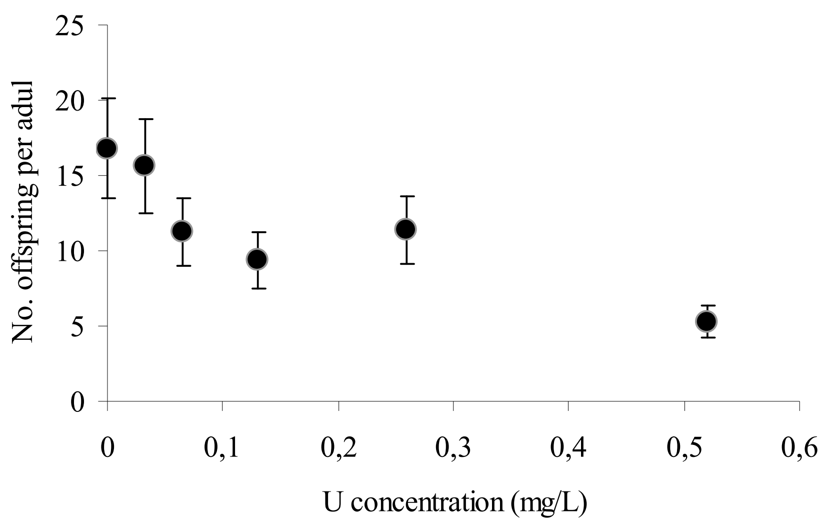

Figure 2. Effect over reproduction of spiked uranium DW using *Ceriodaphnia dubia*.

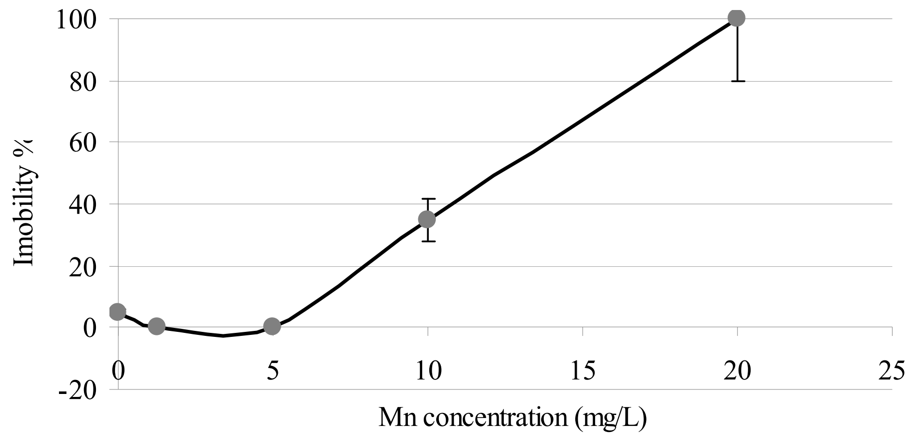

Figure 3. Ecoxicity test results for the Mn spiked DW using *Daphnia similis*-acute tests.

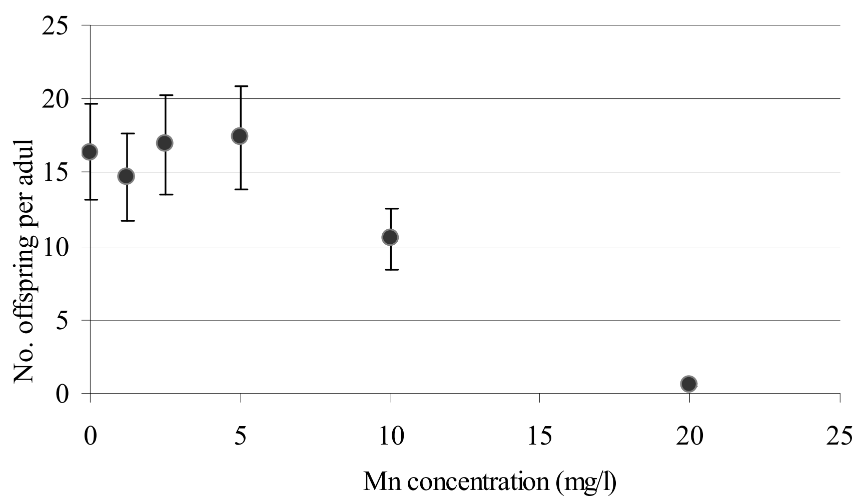

Figure 4. Effect over reproduction of spiked manganese DW using *Ceriodaphnia dubia*

4. CONCLUSION

Discharge water from the Poços de Caldas mining site is not toxic to *Daphnia similis* and *Ceriodaphnia dubia* which were investigated in this study. Based on DW water chemistry data, the calculated water quality index adopted by IGAM pointed out a good to excellent water quality. Mn, F and Al might be considered the main pollutant for the river water. Taking into account the free ion theory, Mn^{2+}, the main present specie of Mn (87%), would be available for the biota and may be toxic. In spite of the presence of relatively elevated concentration of Mn in the DW, its concentration in water is still very low when compared to the NOEC (5 mg Mn/L) value found in this research. The uranium NOEC value (0.03 mg/L) is higher than the median value of the uranium concentration in the DW (0.0033 mg/L) and than the authorized limit by CNEN (0.008 mg/L).

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