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Spatial and Temporal Behavior of Soluble Manganese at the Sediment–Water Interface in the Riogrande II Reservoir in Colombia

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ABSTRACT: The behavior of manganese (Mn) at the sediment–water interface in bodies of water such as lakes and reservoirs is dependent on physicochemical factors such as pH, redox potential-Eh, organic matter, specific

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conductance, and the presence of organic and inorganic complexes. These allow the mobilization of Mn from the sediment to the water column and promote its precipitation as Mn oxyhydroxide. For the Riogrande II reservoir in Colombia (2550 m), it was found that redox potential-Eh below +350 mV is not appropriate for oxide stability. The availability and mobility of these oxides are more associated with organic complexation and desorption from sediments when the pH changes from neutral conditions to slightly acidic conditions (6.0). However, when the lower gates of the reservoir are opened during the dry season, the entry of oxygenated bottom currents most likely increases the dissolved oxygen (DO) and redox potential-Eh. Similarly, the increase in soluble Mn at the intake tower during the dry season is more associated with desorption than with reductive dissolution.

The primary objective of this study is to determine the main physicochemical factors favoring Mn remobilization from sediment to the water column and its relation to the operating mechanisms of the intake water tower of the Riogrande II reservoir.

One of the most notable results of this study is the observation that the operating mechanisms of the Riogrande II reservoir not only affect the type of water that is captured but also influence the geochemical processes at the bottom of the reservoir and in the sediment.

The results of this study highlight the influence of hydraulic processes on surface water bodies as regards the dynamics of metal remobilization, the generation of pollution into the water column, and the increasing costs of treatment and purification in reservoirs in high mountain areas in tropical countries.

KEYWORDS: Models and modeling; Hydrologic models

1. Introduction

The physicochemical conditions at the sediment–water interface in bodies of water, produced by the sedimentation of organic and inorganic material and microbial activity, define two important areas in the metal cycle. The first is an upper zone formed by the bottom of the water column; the lower zone consists of anoxic and reduced sediment and pore waters. This is because of the accumulation of minerals and organic matter and is the region where metals pass from the solid phase to the soluble phase by dissolution and desorption processes, among others (Shaw et al. 1990).

The speciation, mobility, and availability of metals and behavior of other contaminants depend on the physicochemical conditions of this matrix, such as pH, redox potential-Eh, dissolved oxygen, and organic matter (Templeton et al. 2000).

It is recognized that the release, mobility, and toxicity of metals depend on specific chemical forms and changes in environmental conditions, such as pH, redox potential-Eh, and the concentration of organic ligands. These can mobilize trace elements in the solid phase to the liquid phase and contaminate the surrounding waters (Dabrin et al. 2012; De Jonge et al. 2012).

Variations in the concentration of dissolved oxygen essentially allow four zones to be defined to understand the dynamics of metals at the water–sediment boundary. These zones include the following: (i) the oxic zone, with dissolved oxygen concentrations higher than 2 mg L^{-1} ($63 \mu\text{M}$, approximately 25% of the saturated dissolved oxygen concentration); (ii) the hypoxic zone, with oxygen concentrations between 2 ($63 \mu\text{M}$) and 0.04 mg L^{-1} ($3 \mu\text{M}$; between 25% and

0.3% of the saturated dissolved oxygen concentration); (iii) the suboxic zone, with concentrations from 0.04 to 0 mg L⁻¹ (0% to 0.3% of the saturated dissolved oxygen concentration); and (iv) the anoxic zone, with no dissolved oxygen (Rabalais et al. 1999; Trouwborst et al. 2006). Similarly, the redox potential-Eh can be used to define environments as oxidized (values > +414 mV; e.g., in sediments), slightly reduced (values between +414 and +350 mV), reduced (<+350 mV), or strongly reduced or anoxic (<-120 mV) (Rozanov 1988).

The sediment–water interface is also known as the benthic boundary layer or bottom benthic layer; it controls the exchange of solutes and particles between the sediment and water due to the dynamics related to dissolved oxygen, ammonia, hydrogen sulfide, organic material, and heavy metals, which may be soluble or in the form of phases adsorbed to surface sediments (Lorke et al. 2003).

Redox conditions in natural water are mediated by microorganisms, which in turn depend on the presence or absence of dissolved oxygen. The degradation process of organic substrates in the presence of available oxygen is known as aerobic respiration (Konhauser 2007) and is characterized by the oxidation of organic matter and the reduction of dissolved oxygen. It is also characterized by the production of CO₂, which reacts with the water and produces acidity (Hamilton-Taylor et al. 1998), thereby slightly decreasing the pH. The release of metal cations such as Mn may be due to the desorption processes, which occur as a result of ligand exchange and a decrease in the pH (Violante et al. 2010), and the formation of soluble organic complexes associated with the decomposition of organic matter (Hlavay et al. 1995). The release of transition metals such as Mn²⁺ is mainly due to the degradation of organic material, especially in oxic–suboxic layers of sediments in contact with the bottom water (Shaw et al. 1990). In addition to reducing Mn⁴⁺ oxides, the presence of H⁺ ions in the aqueous medium also affects adsorption–desorption processes and solubility (Delfino and Lee 1971).

In the Riogrande II reservoir (average altitude of 2550 m), Mn concentrations negatively affect the quality of the water resources used in Manantiales treatment plant; in order to implement the necessary controls and improve treatment, geochemical dynamics of Mn must be studied from by identifying and assessing the origin of Mn, spatiotemporal variations, and possible inorganic and organic species and determining the relations with which physicochemical conditions measured the reservoir. The principal objective of this study is to determine the main physicochemical factors favoring Mn remobilization from sediment to the water column and its relation to the operating mechanisms of the intake water tower of the Riogrande II reservoir in two climatic seasons and seven stations in order to implement geochemical modeling programs and determine environmental conditions that favor release, mobilization, or complexation of Mn and its effect on drinkable water quality.

2. Methodology

The reservoir has two purposes: energy generation and water supply. For the latter purpose, in the rainy months (March–April and October–November), the upper gate (located at 2255 m) in the intake tower is used, which is intended for the water treatment plant. In low rainfall or dry months (December–January and June–July), the lower gate, located at 2245 m, is used (Marin 2008).

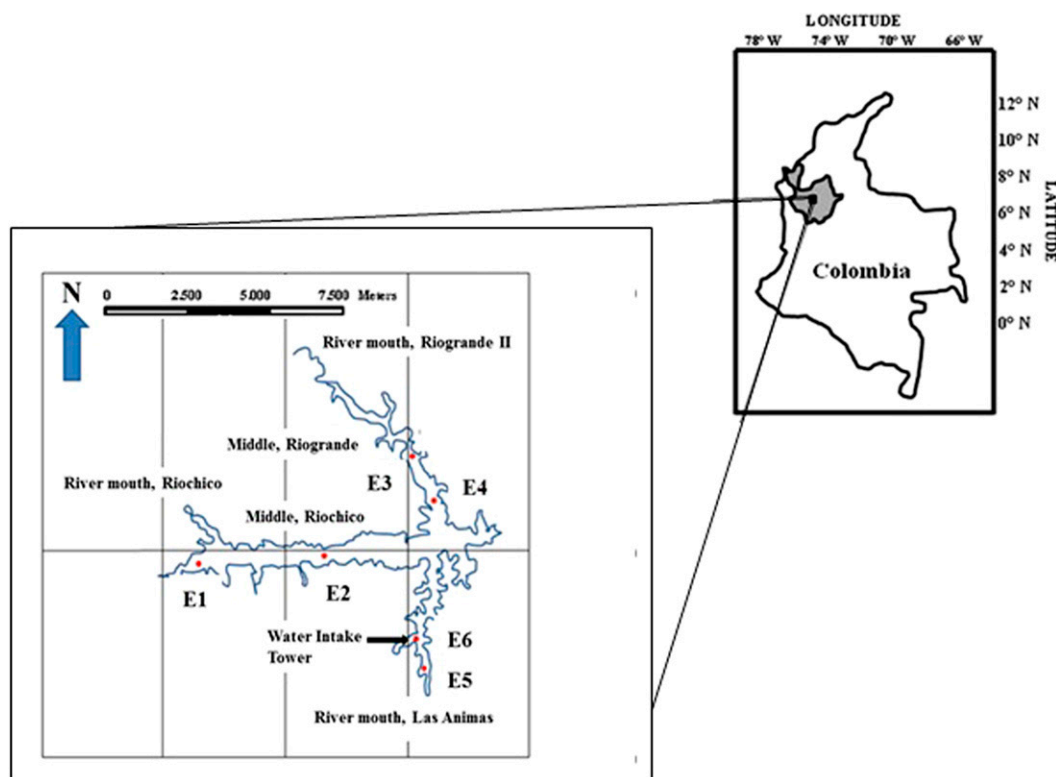


Figure 1. Shape of the reservoir and sampling sites: Rio Chico (E1 and E2), Riogrande (E3 and E4), and river mouth, Las Animas, and the intake water tower (E5 and E6).

The samples were collected in 2009 (October–November, the rainy season) and 2010 (June–July, the dry season) at six sites in the Riogrande II reservoir (Figure 1; Table 1). Sampling sites were selected according to the dominant current patterns. The sampling sites are referred to as E1 [mouth of the Rio Chico, 8 m deep, lotic conditions (i.e., moving bodies of water such as rivers)], E2 [middle of the Rio Chico, 15 m deep, semilentic conditions (i.e., slow-moving bodies of water, between river and lake conditions)], E3 (mouth of the Riogrande, 15 m deep, lotic conditions), E4 (middle Riogrande, 42 m deep, semilentic conditions), E5 (mouth of the Las Animas River, 8 m deep, lotic conditions), and E6 (water intake tower, 28 m deep, semilentic conditions).

The thermal stratification patterns in the Riogrande Riogrande II reservoir are described in Arcos (2008), Correa (2009), and Marin (2008).

Samples were obtained from the water–sediment boundary by an Ekman dredge, with supernatant water from the bottom hypolimnion covering the sediments to prevent oxidation. On the surface, Plexiglas columns were inserted vertically inside the dredge, placing the mean sediment–water boundary in the middle of the sampling points. In this way, each column had five points above the boundary in the water column and five points below the boundary in the sediment column

Table 1. Sampling stations in the reservoir Riogrande II.

Sites	Geographic location	Limnologic characteristic	Lat (°N)	Lon (°W)
E1	River mouth, Rio Chico	Lotic	6°30'21.8"	75°32'11.9"
E2	Middle, Rio Chico	Semilentic	6°30'35"	75°29'46.8"
E3	River mouth, Riogrande	Lotic	6°32'6.6"	75°28'0.4"
E4	Middle Riogrande	Semilentic	6°31'35"	75°27'42.3"
E5	River mouth, Las Animas	Lotic	6°25'37"	75°27'03"
E6	Water intake tower	Semilentic	6°27'50"	75°29'40"

(interstitial water). The column samples were sealed at the top and bottom to prevent the entry of air.

To illustrate the method used for column sampling with the Ekman dredger, the sequence of steps used is shown in Figure 2.

The column had the following dimensions (Figure 3): diameter: 2.52 cm, total length: 25 cm, material: Plexiglas, sampling points: 10, diameter of points: 0.2 cm, distance between points: 2.0 cm.

A total of six columns of samples were collected in each of the two sampling campaigns (October–November 2009 during the rainy season and June–July 2010 during the dry season). The samples were transported in polypropylene containers and stored at 4°C. In the laboratory, water and sediment samples were stored for 5 days in a dark room to allow for the reestablishment of environmental conditions. This process was repeated for each sampling point.

After the top seal was removed, an aliquot of water was taken from the highest point in the water column using a syringe that had been previously washed and rinsed in acid. The approximate volume of the samples taken from the water column was 10 mL. The same volume of a mixture of sediment and water was also extracted. After extracting the samples at each of the levels in the water–sediment columns, the pH and temperature were measured with a WTW model 330 glass electrode.

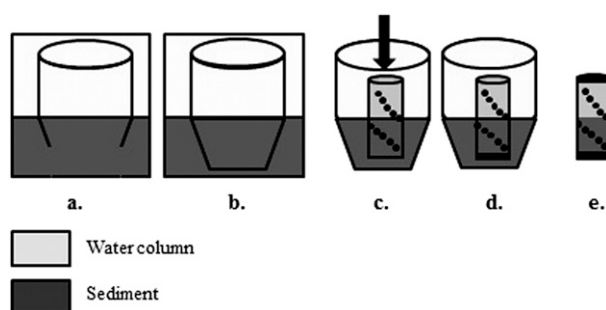


Figure 2. Column sampling sequence using the Ekman dredger. (a) Introduction of the Ekman dredge inside the sediment. (b) Collection of sediment with the Ekman dredge. (c) Introduction of the Plexiglas column inside the sediment in the Ekman dredge. (d) Sealing the bottom of the column. (e) Sealing the top of the column.

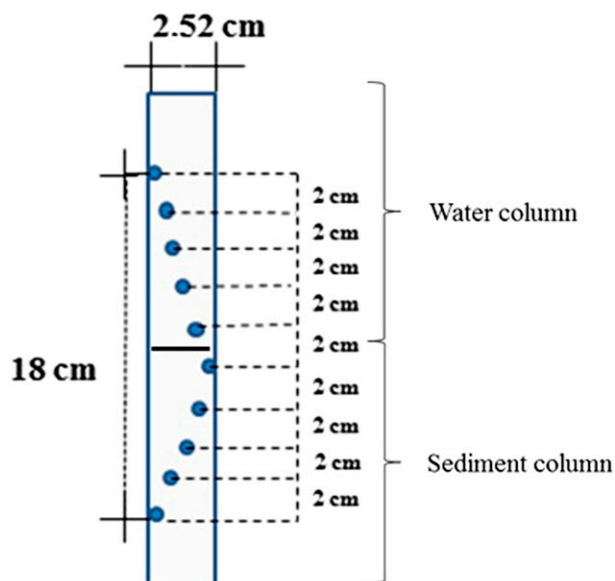


Figure 3. Sampling columns with 10 sampling points every 2 cm, each point 0.2 cm in diameter (the two central points were located 1 cm above and below the sediment–water boundary).

Water samples in each of the columns were taken in order from top to bottom, trying to minimize the effect of sampling, avoiding possible mixtures, and seeking greater independence between each of the points. The 5-day storage in total darkness for all columns tried to simulate the chemical equilibrium reached at the bottom of the Riogrande II reservoir.

It is important to explain the main limitation for this procedure in the project. Sampling each point within the columns did not allow independence between each point and could not be avoided that the different points influence each other; so, we proceeded to take samples from the top to bottom in each column to try to lessen the effects between the different points.

It was also found that the environmental conditions measured in the columns are not the same as those found in the reservoir because both water and sediments have alterations during the sampling process, the dipping of the columns into the water, and transportation. A 5-day storage in complete darkness helps to stabilize the physicochemical and microbiological balance in each column and could indicate in a certain way the processes that may be occurring at the bottom of the reservoir.

The specific conductance (SC) was measured with a WTW model 720 conductivity meter, the redox potential-Eh was measured with a WTW 330 platinum electrode, and dissolved oxygen was measured using a WTW oximeter with a Cellox cell. The soluble Mn was analyzed from samples filtered with 0.45- μm filters and then stored in polypropylene containers and preserved in acid for subsequent analysis by atomic absorption (AA). All analyses were performed in duplicate.

To evaluate the possible effect of the sampling site and depth on the parameters soluble Mn, pH, redox potential-Eh, dissolved oxygen, and specific conductance, the analysis of variance of the components was performed. The Pearson linear

Table 2. Descriptive analysis of the data of the variables analyzed in the water column and sediment water (soluble Mn, pH, redox potential, dissolved oxygen, and specific conductance) for the two periods sampled.

Type of column	Statistical results	Soluble Mn (mg L ⁻¹)	pH	Redox potential (mV)	Dissolved oxygen (mg L ⁻¹)	Specific conductance (μ S cm ⁻¹)	Sampling period
Water column	X	1.14	6.76	+36.32	3.74	173.40	Rainy period October– November 2009
	Max	2.78	7.51	+119.60	5.88	242.00	
	Min	0.38	6.05	−26.00	2.92	140.10	
	Std dev	0.63	0.35	52.59	0.76	26.83	
	CV %	55.00	5.00	145.00	20.00	15.00	
	Z	1.48	6.48	+36.03	3.44	209.35	Dry period June–July 2010
	Max	3.62	7.06	+135.00	4.52	379.00	
	Min	0.29	5.68	−57.00	1.89	61.20	
	Std dev	1.25	0.37	53.99	0.76	112.05	
	CV %	84.00	6.00	150.00	22.00	54.00	
Sediment column (sediment–water)	X	1.47	6.74	−127.22	0.41	480.83	Rainy period October– November 2009
	Max	5.89	6.98	−62.00	1.78	687.00	
	Min	0.27	6.24	−199.80	0.07	209.00	
	Std dev	1.52	0.22	37.25	0.42	170.90	
	CV %	103.00	3.00	−29.00	102.00	36.00	
	Z	2.22	6.59	−105.31	0.69	496.90	Dry period June–July 2010
	Max	9.50	7.00	−49.00	2.19	1233.00	
	Min	0.16	6.21	−185.00	0.02	202.00	
	Std dev	2.46	0.24	35.98	0.54	212.71	
	CV %	111.00	4.00	−34.00	79.00	43.00	

correlation was then used to determine whether there was a statistically significant correlation of the physicochemical factors [pH, redox potential-Eh, dissolved oxygen (DO), and specific conductance] with the response variable (soluble Mn). A variance analysis was then carried out between the Mn concentration values and the physicochemical conditions of the water ($p < 0.05$).

To evaluate the effect of each physicochemical factor on soluble Mn, a generalized linear model for the response variable was established and a significance factor of $p < 0.05$ was considered. Statistical analyses were carried out on both the water column and the sediment water (interstitial water) because they are distinct environments and are each related to soluble Mn. The testing ended with principal component analysis (PCA) in order to establish possible factors associated with geochemical processes at the water–sediment interface responsible for the behavior of soluble Mn. All measured and calculated values are presented as average (mean) values.

3. Results

For the water columns, there was no significant difference in soluble Mn between sampling seasons. The highest recorded value of 3.62 mg L⁻¹ was found at 1 cm above the sediment–water boundary in E3 in the dry season. There was no significant difference in soluble Mn between the water column and sediment water. The largest value in the sediment water was 9.50 mg L⁻¹ in E1 found at 5 cm below the sediment–water boundary in the dry season (Table 2; Figure 4). The Mn concentration was higher in the dry season, both in the water column and in the sediment water only for the site E1.

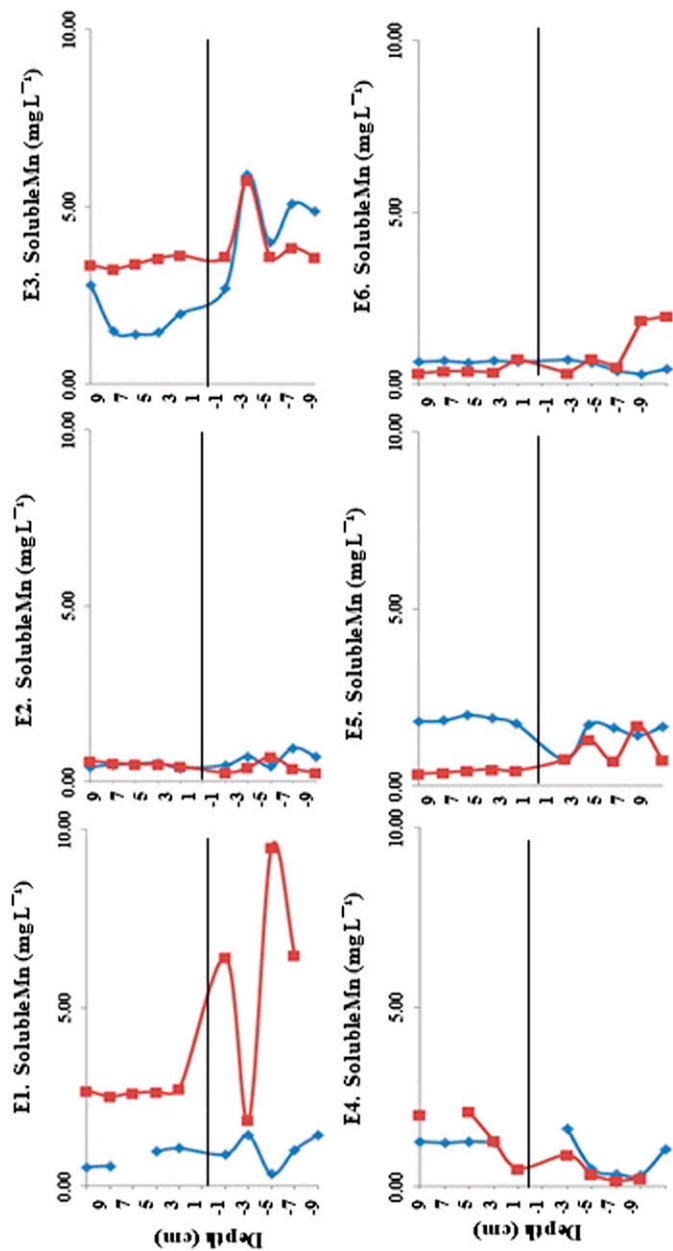


Figure 4. Soluble Mn profiles (mg L^{-1}) at the water-sediment interface at the six sites for the two seasons. Blue indicates the rainy season (October–November 2009), and red indicates the dry season (June–July 2010). The black line marks the water-sediment boundary.

When comparing the results obtained in the water column with those from the sediment water, it was found that at the reservoir input locations E1 and E3, the Mn concentration was higher in the sediment than in the water in the dry season. At E5, Mn was only higher above the sediment–water boundary in the rainy season, not in the dry season. At E2, concentrations were similar for both sampling periods, and at E4, the Mn concentration was higher in the water than in the sediment, especially in the dry season. Finally, at site E6 (water intake tower), the profiles were similar for both sampling periods (Figure 4); however, in the bottom sediment (9 cm), there were higher concentrations in the dry season compared to the rainy season.

4. pH

In the water column, the rainy season showed a higher mean pH value (6.76) compared to the dry season (6.48), but the difference was not significant. The highest value recorded (7.51) was found at 1 cm above the sediment–water boundary in the rainy season at E1, and the lowest pH (5.68) was observed at 5 cm above the sediment–water boundary at E5 in the dry season. For the sediment water, the pH was higher in the rainy season (6.74) compared to the dry season (6.59). The highest pH value was 7.0 that was found 9 cm below the sediment–water boundary at E3 in the dry season, and the lowest value was 6.21 at sites E2 and E5. In general, the pH in the water column and the sediment water was neutral to slightly acidic, averaging 6.6 (Table 2). When analyzing the profiles, E1, E2, and E5 showed a lower pH in the entire column in the dry season, while at E3 and E4, the pH profile was similar in the two seasons, and the values observed at E6 were lower in the water during the dry season and lower in the sediment water during the rainy season (Figure 5).

5. Redox potential (Eh, mV)

The water column showed a very similar redox potential-Eh in the rainy and dry seasons: +36.32 and +36.03 mV, respectively. The highest redox potential-Eh was recorded at 9 cm above the water–sediment boundary at E6, with a value of +135 mV, in the dry season. The lowest potential was observed at 1 cm above the sediment–water boundary at E1 in the dry season, with a value of –57 mV. For sediment water, the redox potential-Eh was always negative, with a mean value of –127.22 mV in the rainy season and –105.31 mV in the dry season. The highest value was –49 mV, found at 1 cm below the water–sediment boundary at E2 in the dry season, and the lowest recorded value was –199.80 mV, recorded at 9 cm below the water–sediment boundary at E1 in the rainy season (Table 2). When comparing the two columns, it can be seen that the redox conditions change from generally positive in the water column to negative in the sediment water. Furthermore, the redox potential-Eh was more negative during the rainy season.

At sites E1 and E3, the redox potential-Eh in the water column was higher and positive in the rainy season, while in the sediment water it was negative for both climatic conditions. At E2 and E4, the Eh profiles in the water column were positive in both the rainy and dry seasons. Finally, at E5 and E6, there was a greater

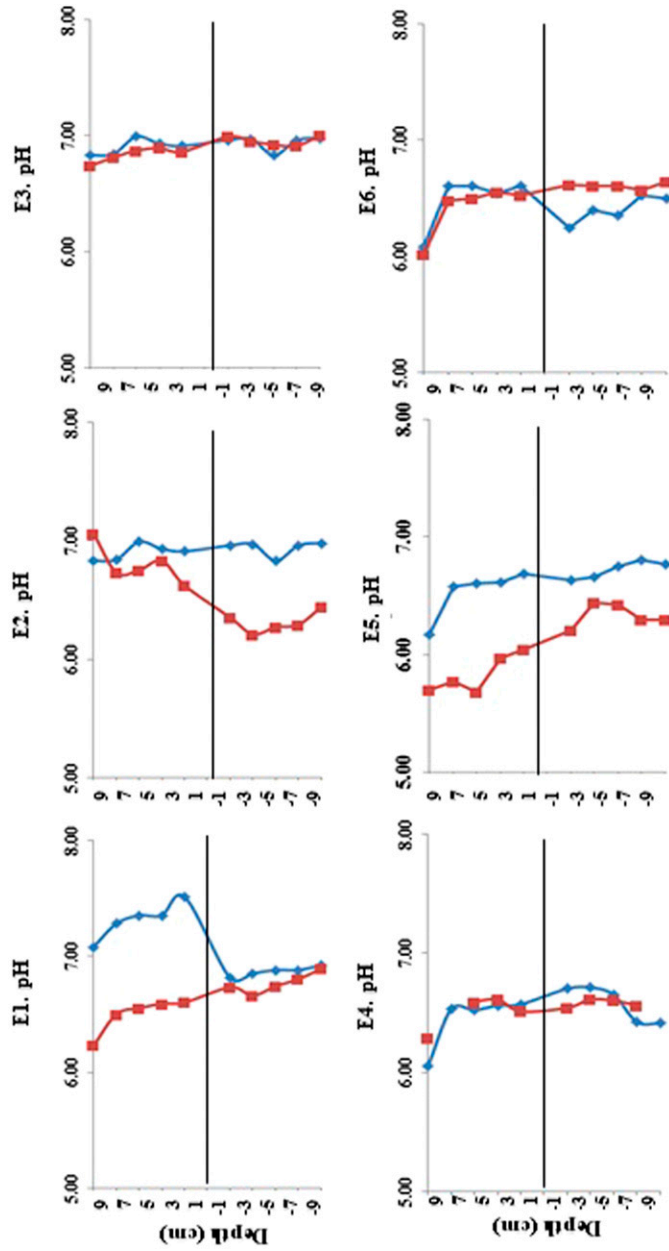


Figure 5. Profiles of pH at the sediment–water boundary at the six sites for the two seasons. Blue indicates the rainy season (October–November 2009), and red indicates the dry season (June–July 2010). The black line marks the sediment–water boundary.

positive redox potential-Eh in the dry season compared to the rainy season throughout the column (Figure 6).

6. Dissolved oxygen (mg L^{-1})

In the water column, the average DO values were 3.74 mg L^{-1} in the rainy season and 3.44 mg L^{-1} in the dry season. The highest concentration recorded was 5.88 mg L^{-1} , found at 9 cm above the sediment–water boundary at E1 in the rainy season, and the lowest value was 1.89 mg L^{-1} , measured at 3 cm above the sediment–water boundary at E4 in the dry season. Regarding the sediment water, the average for the wet season was 0.41 mg L^{-1} , and for the dry season it was 0.69 mg L^{-1} . The maximum and minimum values recorded were 2.19 mg L^{-1} at E6, measured at 1 cm below the sediment–water boundary during the dry season, and 0.02 mg L^{-1} at E1, also in the dry season, recorded at 7 cm below the interface (Table 2).

At sites E1, E2, and E4, higher concentrations of DO were obtained in the rainy season than in the dry season, and at E3, the DO concentration was similar in both seasons. At E5 and E6, the DO concentration was higher in the dry season (Figure 7).

7. Specific conductance ($\mu\text{S cm}^{-1}$)

The water columns had an SC of $173 \mu\text{S cm}^{-1}$ in the rainy season and $209 \mu\text{S cm}^{-1}$ in the dry season. The maximum value was $379 \mu\text{S cm}^{-1}$, recorded at 1 cm above the sediment–water boundary at E1, and the minimum was $61 \mu\text{S cm}^{-1}$, taken from 7 cm above the sediment–water boundary at E5, both in the dry season. The sediment water showed an SC of $481 \mu\text{S cm}^{-1}$ for the rainy season and $497 \mu\text{S cm}^{-1}$ for the dry season. The maximum value was taken from 8 cm below the sediment–water boundary at E1 in the dry season, with a value of $754 \mu\text{S cm}^{-1}$. Finally, the lowest SC was $202 \mu\text{S cm}^{-1}$, found at 1 cm below the sediment–water boundary at E2 in the dry season (Figure 8; Table 2).

At E1, there were higher values of SC in the dry season compared to the rainy season throughout the column, and at E6, there were higher values in the dry season compared to the rainy season, but only in the sediment water. In contrast, at E2, the SC profiles in the bottom of the water column and sediment column were similar for both climatic seasons, but for E5, the SC was higher in the rainy season than the dry season.

8. Statistical analysis

8.1. Water columns

For the water columns, the most approximate transformation of soluble Mn data to a normal distribution was \log_{10} . A probability distribution close to the asymptotic normal, this distribution is also called “asymptotic normality.” A distribution is said to be asymptotically normal if, as the sample size increases, the statistical distribution approaches a normal distribution. This study was considered normal

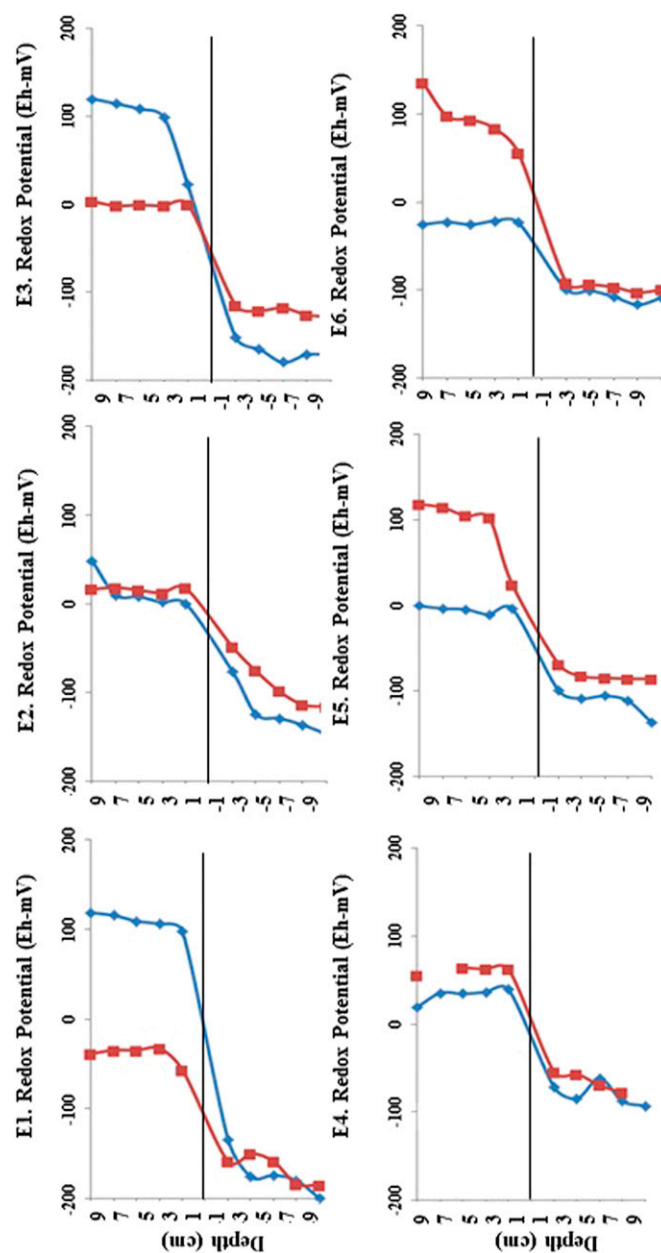


Figure 6. Profiles of the redox potential Eh (mV) at the sediment–water boundary at the six sites for the two seasons. Blue indicates the rainy season (October–November 2009), and red indicates the dry season (June–July 2010). The black line marks the sediment–water boundary.

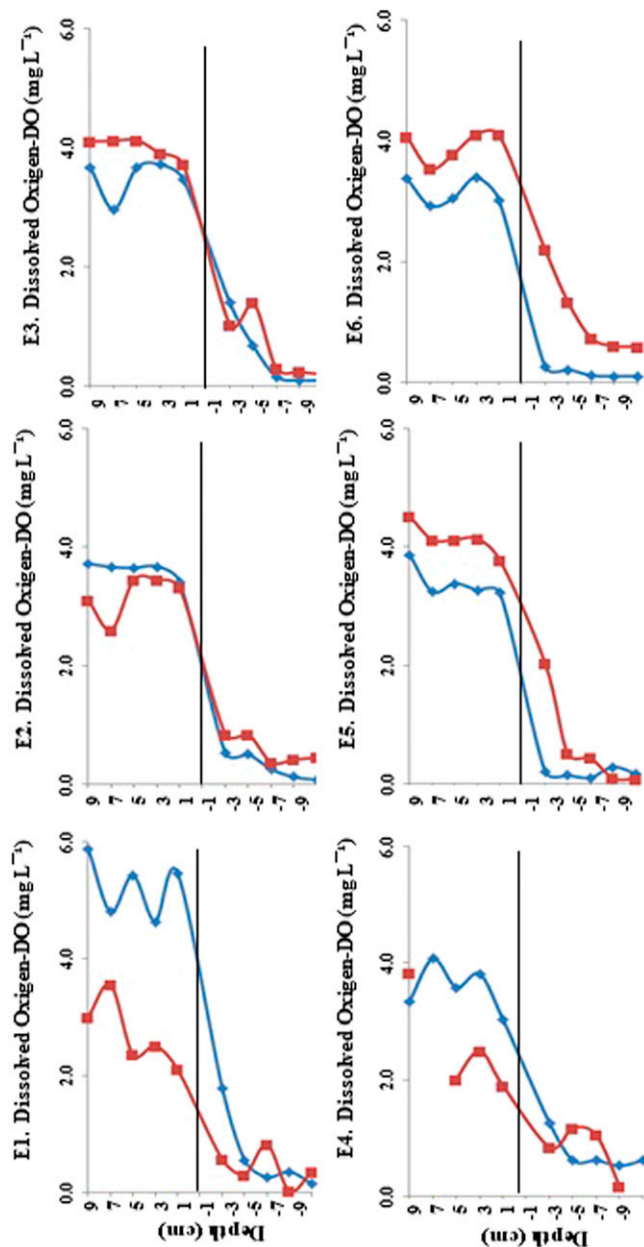


Figure 7. Profiles of dissolved oxygen (mg L^{-1}) at the sediment–water boundary at the six sites for the two seasons. Blue indicates the rainy season (October–November 2009), and red indicates the dry season (June–July 2010). The black line marks the sediment–water interface.

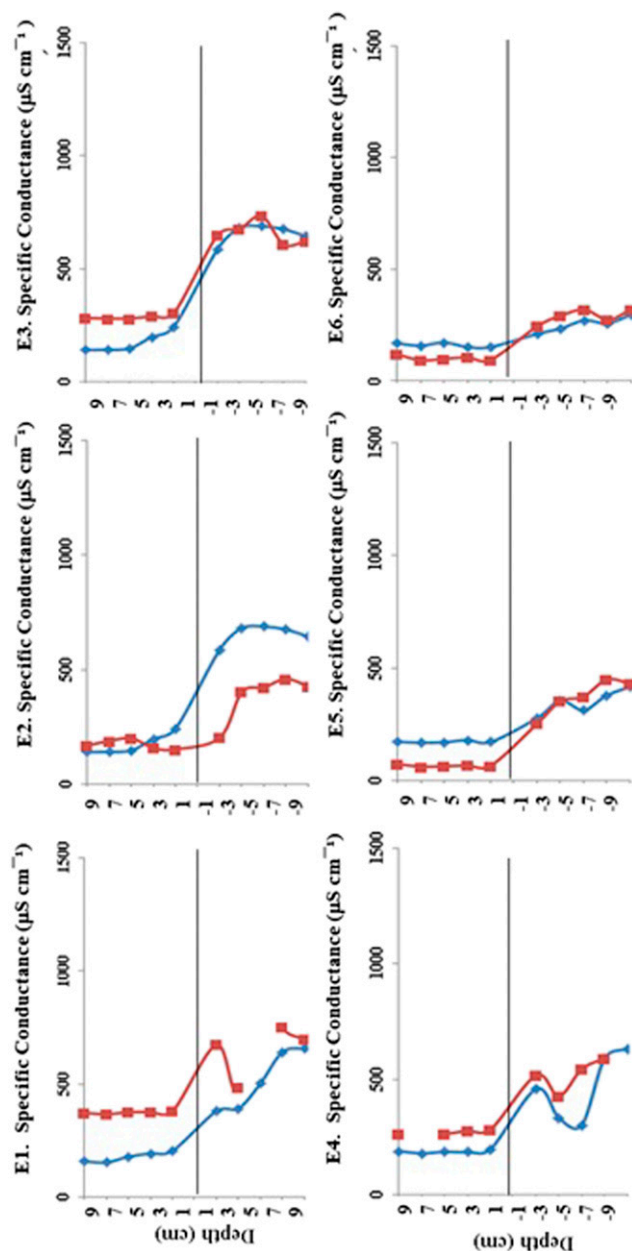


Figure 8. Specific conductance profiles ($\mu\text{S cm}^{-1}$) at the sediment–water interface at the six sites for the two seasons. Blue indicates the rainy season (October–November 2009), and red indicates the dry season (June–July 2010). The black line marks the sediment–water boundary.

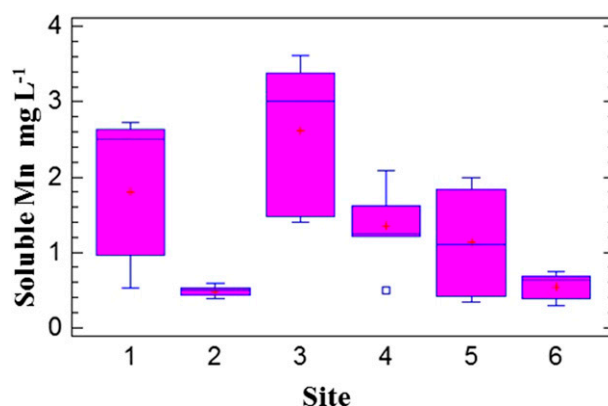


Figure 9. Box-and-whisker plot for soluble Mn (mg L^{-1}) in the water column by site.

if the asymptotic p (significance) value in the Bartlett test close to 0.5 was obtained and there was an equality of variances only for the sampling point or the height in the column ($p < 0.05$). However, the variance component analysis showed that the sampling site (E1, E2, E3, E4, E5, and E6) was the factor that most influenced the variability of soluble Mn (91.28%), compared to the sampling point (8.72%). Kruskal–Wallis analysis (a nonparametric test that establishes whether there are significant differences between three or more paired populations) was then carried out, showing significant differences among the sampling sites ($p < 0.05$), which can be seen in the box-and-whisker plot (Figure 9). Homoscedastic behavior [the statistical equality of variances of two or more populations, determined in order to proceed to analysis of variance (ANOVA)] was not observed nor were there significant differences between the two seasons (dry and rainy seasons).

To establish the relationship between the response variable (soluble Mn) and each of the physicochemical factors considered, the normal distribution and equality of variance were assessed; it was found that for the factors of pH, Eh, and DO, transformation was not necessary. For the specific conductance, data were adjusted to a \log_{10} distribution.

After accepting the asymptotic normal and homoscedastic nature of soluble Mn and the physicochemical factors, the Pearson correlation was then used. In the water column, a significant correlation ($p < 0.05$) was observed for specific conductance (0.7114) and redox potential-Eh (-0.3986). This analysis showed that physicochemical variables such as specific conductance and redox potential-Eh have the greatest influence on the behavior of the soluble Mn in the water column.

A generalized linear model was also used to assess the influence of each physicochemical factor on the Mn in the water columns, yielding a significance of $p < 0.05$. In this model, the sum of the type I squares established that with the exception of pH and DO ($p > 0.05$), the factors that best explain the variation of soluble Mn are the redox potential-Eh and specific conductance. The linear model is as follows:

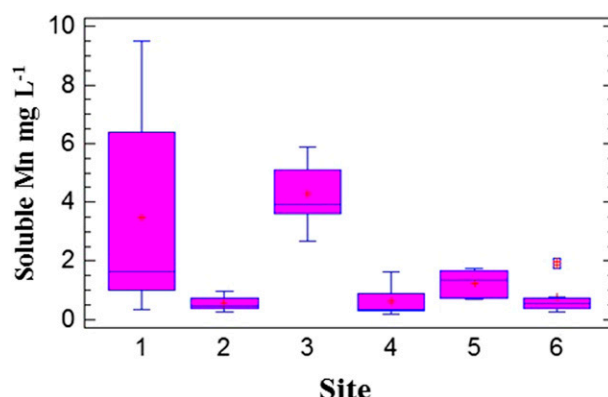


Figure 10. Box-and-whisker plot for soluble Mn (mg L^{-1}) in sediment water by site.

$$\begin{aligned} \text{soluble Mn}(\log \text{ Mn}) = & -0.38 \times \text{pH} - 0.0006 \times \text{redox potential} - \text{Eh} \\ & + 1.08 \times \text{SC}(\log \text{ SC}) + 0.03 \times \text{DO}, \end{aligned}$$

$$r^2 = 38.89\%.$$

PCA allowed two components to be established that explain 74.9% of the total variability. The first component (49.68%) shows a relationship between soluble Mn, redox potential-Eh, and SC [$0.49 \times \text{Mn mg L}^{-1} (\log \text{ Mn}) - 0.49 \times \text{redox potential-Eh} + 0.58 \times \text{SC} + 0.21 \times \text{pH} - 0.37 \times \text{DO}$]. The second component (25.22%) shows the relationship between pH and DO [$0.19 \times \text{Mn} (\log \text{ Mn}) + 0.30 \times \text{redox potential-Eh} + 0.18 \times \text{SC} + 0.72 \times \text{pH} + 0.56 \times \text{DO}$].

8.2. Sediment water

Statistical analysis of the sediment water was the same as for the water column (test of normality and equal variance). The results of ANOVA showed no significant differences for soluble Mn during the sampling period. Variance component analysis (VCA) showed that the sampling site is the factor of greatest influence on the variability of soluble Mn (77.96%), compared to the sampling point (22.04%). The Kruskal–Wallis test showed significant differences among the sampling sites ($p < 0.05$), which can be seen in the box-and-whisker plot (Figure 10).

To establish the relationship between the response variable (soluble Mn) and each physicochemical factor, the normal distribution and equality of variances was assessed. It was found that for pH and Eh, transformation was not necessary, but for DO and SC, the same transformation was performed as for the Mn (\log_{10}).

After accepting the asymptotic normal and homoscedastic nature of the soluble Mn and the physicochemical factors, the Pearson correlation was then used. In the sediment water, significant correlations ($p < 0.05$) were observed for pH (0.5326), redox potential-Eh (0.5950), and specific conductance (0.5381). This analysis showed that the pH, specific conductance, and redox potential-Eh had the greatest influence on the behavior of the soluble Mn in the sediment water.

A generalized linear model was also used to assess the influence of each physicochemical factor on the Mn in the sediment water, giving a significance of $p < 0.05$. In this model, the sum of type I squares indicated that with the exception of DO ($p > 0.05$), the factors that best explain the variation of soluble Mn are pH, redox potential-Eh, and specific conductance. The model is as follows:

$$\text{soluble Mn}(\log \text{Mn}) = -0.0073 \times \text{redox potential} - \text{Eh} - 0.33 \times \text{pH} \\ + 0.55 \times \text{SC}(\log \text{SC}) + 0.11 \times \text{DO}(\log \text{DO}),$$

$$r^2 = 36.6\%.$$

PCA allowed two components to be established that explain 76.1% of the total variability. The first component (56.26%) shows a relationship among soluble Mn, pH, redox potential-Eh, and SC [$0.47 \times \text{Mn mg L}^{-1}(\log \text{Mn}) + 0.49 \times \text{pH} - 0.51 \times \text{redox potential-Eh} + 0.48 \times \text{SC} + 0.21 \times \text{DO}$]. The second component (19.88%) shows an inverse relationship between DO and Mn ($\log \text{Mn}$) as follows: $0.14 \times \text{Mn}(\log \text{Mn}) + 0.18 \times \text{redox potential-Eh} + 0.21 \times \text{SC} + 0.24 \times \text{pH} + 0.91 \times \text{DO}$.

9. Discussion

Combined pH-Eh analysis was performed using a Pourbaix diagram (pH-redox potential-Eh diagram) for the columns at the sediment-water interface (Figure 11). It was found that the conditions at this interface during the sampling periods were within the stability field of manganous ion (Mn^{2+}). For pH, all samples fell in the range of 5.0–7.0. Although there were no significant differences between sampling periods, there was a trend toward lower pH values (near 5.0) for the entire interface in the dry season, while in the wet season there was a trend toward more alkaline pH values.

In terms of Eh, it was established that the sediment-water boundary presented reducing conditions ($\text{Eh} < +150 \text{ mV}$) in the water columns and strongly reducing conditions ($\text{Eh} < -120 \text{ mV}$) in the sediment water at sites E1, E2, E3, and E5, mainly in the rainy season (Figure 6).

Based on the dissolved oxygen levels in both the rainy and dry seasons, oxic conditions were found in the water column (Figure 7). For the sediment water, suboxic-hypoxic conditions were recorded, which were possibly anoxic beyond at a depth of 9.0 cm.

The statistical analysis showed that in the water column, soluble Mn depends on the redox potential-Eh. However, the conditions presented ($\text{Eh} < +150 \text{ mV}$) do not permit the presence of Mn oxides, so their increased mobility is likely associated with organic complexing processes. For the sediment water, as well as the redox potential-Eh, the pH was also significant for the desorption of Mn in the sediments, especially in sediments at site E6, where the pH was less than 6.5 in the rainy season.

The water-sediment boundary presented different profiles for soluble Mn at some sites and in certain sampling periods. However, this difference was only significant among different sites. In both the water column and the sediment water, the Riogrande II reservoir inflows (E1 and E3) showed the highest Mn concentrations,

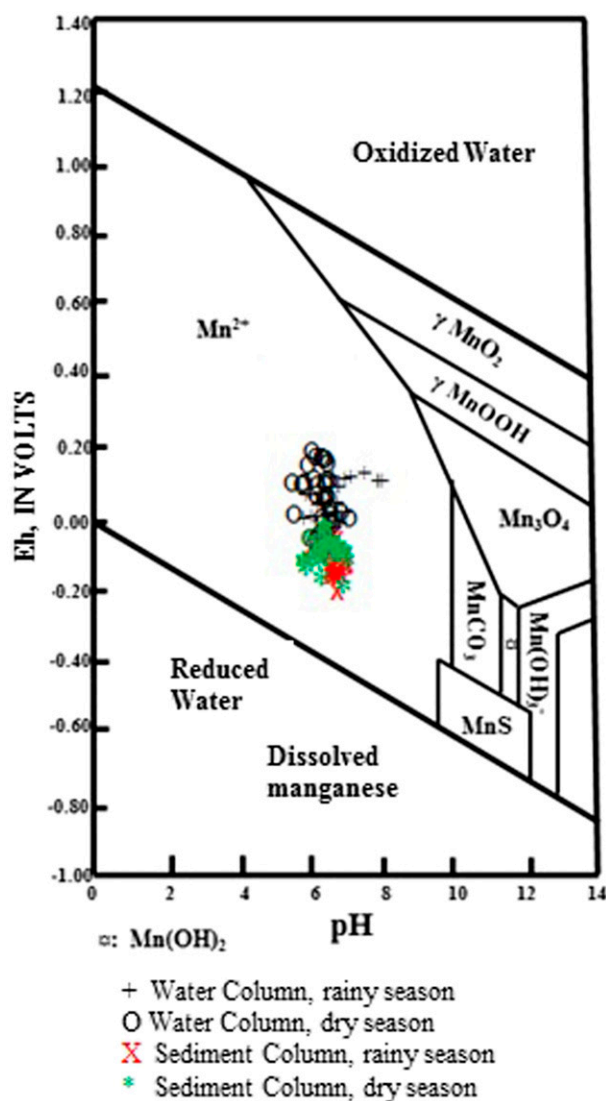


Figure 11. Pourbaix diagram for the bottom hypolimnion and sediment water of the columns at the sediment–water boundary in both climatic seasons (temperature is 25°C, HCO_3^- activity is 61 mg L^{-1} , and SO_4^{2-} is 96 mg L^{-1} , modified and adapted from Hem (1985)).

indicating that Mn enters the reservoir via the river mouth of the Rio Chico and the river mouth of the Riogrande possibly in adsorbed and particulate form.

Water columns taken from the bottom hypolimnion can be considered oxic because of the measurable oxygen concentrations. However, the organic matter present in the sediment and water column (Salazar et al. 2013) decreases the redox potential-Eh to reducing and strongly reducing conditions at the sediment–water interface. This is a result of bacterial activity, where the reduction of the oxyhydroxides of Mn and Fe favors the mobility of Mn^{2+} . Other studies have

found that reduced ions (Fe, Mn, and Zn) move from the sediment to oxidized zones as a response to redox gradients that control their solubility (Davison 1993). The release of metals may be due to processes such as desorption and the formation of soluble organic complexes associated with the decomposition of organic matter (Hlavay et al. 1995).

In the water column, DO, Eh, and pH conditions conducive to the release of Mn were observed. This clearly shows that the weather conditions associated with the rainy and dry seasons only influenced the Riogrande II reservoir, the mouth of the Rio Chico, and the mouth of the Riogrande, located away from the intake water tower (E6). The soluble Mn was greater in the dry season for both sites due to the reducing conditions. However, at the mouth of the Riogrande, the DO concentrations were greater in the dry season, which would suggest that the redox potential-Eh is not only dependent on the concentration of oxygen but also on other reduced species. The Eh values found at the sediment–water interface ($Eh < +150$ mV) suggest reduced conditions in an oxic to hypoxic environment.

The results recorded during the sampling period show that the continuous input of organic matter has established reducing conditions throughout the water column, with a redox potential-Eh of $< +250$ mV (Rozanov 1988). This is despite the presence of dissolved oxygen, especially in the epilimnion.

Where the mouth of the Las Animas River and the intake water tower (E6) sites are located, a higher Mn concentration and lower DO concentration were observed during the wet season compared to the dry season, and the conditions were more reducing. This may be due to the operating mechanisms of the reservoir: during the dry season, the lower gate of the water intake tower is opened. This causes the bottom water to contain higher concentrations of DO because when the oxygenated waters of the Las Animas River enter the Riogrande II reservoir, they are submerged by the differences in density and temperature between the epilimnion of the reservoir and the waters of the Las Animas River and are transported to the bottom of the intake tower when the lower gate is open, thereby increasing the redox potential-Eh at E5 and E6.

However, the fact that the sediment–water boundary is in reduced conditions for the two climatic seasons does not mean there is immediate remobilization. For example, Mn^{2+} may be immobilized through the formation of carbonate Mn-rhodochrosite ($MnCO_3$) adsorbed to clay minerals, carbonates, or hydroxides. Or it may be released into the water column as aqueous ions. Furthermore, the mineral phases controlling the Mn^{2+} in the sediment are rhodochrosite and MnS in strongly anoxic sediments (Kristiansen et al. 2002).

The sediment water at the mouth of the Rio Chico, the mouth of the Riogrande, the middle of the Rio Chico, middle of the Riogrande, and the mouth of the Las Animas River (E5) showed a significant increase in Mn as the redox potential-Eh became more reduced. This shows the importance of Eh in the sediment as a Mn remobilization factor, and the reducing conditions are most likely caused by microbial activity. As the organic matter is mineralized and the solid phases are reduced, reduced species are released into the water column.

The opening of the lower gate at E6 may transport oxygenated waters into the hypolimnion. This would raise the redox potential-Eh and promote the precipitation and fixation of Mn in both the water column and the sediment, especially at E6 (water intake tower). However, not opening the lower gate in the dry season would

most likely accentuate the decrease of dissolved oxygen in hypoxic and suboxic conditions and lower the redox potential-Eh, thereby increasing the release of metals from the sediments. In the absence of resuspension phenomena, whether natural or induced, the hypolimnion is a source of reduced chemical species from anoxic sediment (Mostefa and Ahmed 2012).

The boundary between the Mn^{2+} oxidation zone and reduction zone (redox potential-Eh +414 mV) is known as a redox barrier (Rozanov 1988) and was not observed in either the sediments or the first 10 cm of the water column. Therefore, at sites E1, E3, E5, and E6, the Mn^{2+} would have mainly ascended from the sediments to the water column. However, the remobilization processes of metals in sediment are complex because in addition to the degradation of organic matter, the consumption of oxidants, and desorption, other processes also participate, such as advection, diffusion, and bioturbation, which can release metals from the sediment to the water column (Lesven et al. 2008).

The pH in the water column and sediment water was lower at sites E1, E2, and E5 (not significant) in the dry season compared to the rainy season. This tendency toward acidity shown at the sediment–water interface during the dry season is likely associated with an increase in the production of CO_2 and indicates a possible relationship with aerobic bacterial growth. The increased acidity could suggest that aerobic respiration and the consequent release of CO_2 were the dominant processes (Hamilton-Taylor et al. 1998). The pH, especially at E1, E2, and E5, may be related to a higher contribution and mineralization of organic matter in the rainy season. At site E4, an increased amount of Mn was found in the water column compared to the sediment water, especially in the dry season, which may be due to advective phenomena from bottom currents that release Mn at a higher rate than diffusive phenomena.

The suboxic conditions presented in the sediment at the mouth of the Riogrande in the rainy season may be due to the combination of a slow hydraulic system and a significant organic load. As the sediment is oxidized, oxygen is consumed, yielding DO values below 0.04 mg L^{-1} . The fact that the water column presented dissolved oxygen values above 2 mg L^{-1} and pH values between 6 and 7 does not mean that the Mn oxidizes easily and precipitates. Mn has complex redox kinetics, and it is difficult for it to oxidize chemically in natural waters (Roitz et al. 2002).

The specific conductance was higher in the sediment column than the water column, indicating an accumulation of ions such as Mn^{2+} , Fe^{2+} , and possibly Zn^{2+} .

The reservoir operating mechanisms seem to promote the mobility of Mn because during the rainy season the upper gate is opened, leaving the lower levels of the reservoir without an artificial mechanism to mobilize the water in the bottom hypolimnion. This results in a lack of water movement in the central areas of the reservoir. In contrast, when opening the lower gate in the dry season, movement is generated that affects both the entrance of the mouth of the Las Animas River (E5) and the water intake tower (E6). The opening of the lower gate transports oxygenated waters into the hypolimnion in the Las Animas River, raising the redox potential-Eh and promoting the precipitation and fixation of Mn in both the water and sediment columns, especially at E6 (intake water tower). However, not opening the lower gate in the dry season would accentuate the decrease in dissolved oxygen to hypoxic and suboxic conditions and lower the redox potential-Eh, thereby increasing the release of metals from the sediment.

At sites E1 and E3, there appears to be a lesser influence from the reservoir operating mechanisms and most likely no influence from the bottom currents in the dry season. Therefore, the dissolved oxygen and redox potential-Eh are lower in this season, promoting an increased release of Mn.

The high concentrations of soluble Mn recorded in the bottom waters of the reservoir during the dry season are apparently not related to the reduction processes of Mn oxides in the hypolimnion. The study presented here did not monitor this mineral phase in sediments (Salazar et al. 2013) but rather showed the desorption processes of Mn due to the increased concentration of H^+ ions. This is most likely a result of aerobic microbial respiration related to internal currents that allow oxygen to reach the lower gate of the reservoir's intake tower in the dry season.

10. Conclusions

At the water–sediment boundary, vertical gradients of soluble Mn were observed for the mouth of the Rio Chico, the mouth of the Riogrande, and the mouth of the Las Animas River, with higher concentrations of metal in the sediment water. This demonstrates the release and diffusion of Mn from the solid phase in the sediments to the bottom hypolimnion to be a result of reductive dissolution phenomena and desorption, especially in the dry season.

This most likely also corresponds to other metals adsorbed to sulfides, such as Fe and Zn. The mouth of the Rio Chico site (E1) showed higher concentrations of Mn during the dry season in both the water column and in the sediment water. This is a reflection of the low concentrations of dissolved oxygen and therefore negative redox conditions. Such conditions may indicate significant anaerobic microbial activity because unlike sites E5 and E6 (water intake tower), E1 and E3 would not be influenced by the reservoir's operating mechanisms.

During the two sampling periods, acidic conditions were not observed in the sediments, and in most cases, the pH varied between 6 and 7. The lowest pH values are most likely the result of CO_2 production by microbial activity at the bottom, especially in the dry season.

High concentrations of DO and oxidizing conditions in the bottom hypolimnion would be the result of resuspension phenomena, either natural or caused by the operation of the Riogrande II reservoir mechanisms.

The redox potential-Eh profiles showed reducing conditions ($Eh < +350$ mV) and much reduced anoxic sediments at the bottom of some of the sediment columns, implying reductive dissolution and complexation. These conditions are caused by the anaerobic degradation of organic matter in sediments by the different bacterial communities present. It should be taken into account that the bottom has a significant amount of organic matter derived from plant material that was not removed during reservoir flooding. A change in the geochemistry of the reservoir bottom would not be expected, and dissolved metals, including Mn, would be present because of the reduction potential.

The DO presented a negative vertical gradient from the water column to the sediment water, showing oxygen depletion due to bacterial respiration in the sediment and low diffusion in the sediment. However, reducing conditions were observed in the water column, most likely indicating the predominance of reduced metal species over oxidized species.

Finally, for future research, it is necessary to evaluate the profiles of other heavy metals and their relationship to the operation of the intake water tower of the reservoir to determine if the behavior is similar to that of Mn and define measures to prevent and mitigate the migration of heavy metals from a solid phase in the sediment to the water column.

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