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Articles

Using subsurface flow wetlands with *Phragmites Australis* as a bioremediation alternative for surface sources affected by acid drainage from coal mines

Uso de humedales de flujo subsuperficial con *Phragmites australis* como alternativa de biorremediación de fuentes superficiales afectadas por drenajes ácidos de minas de carbón

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Abstract

Mining generates environmental impacts such as Acid Mine Drainage (AMD). The Cali River is one of the main water resources in the city of Santiago de Cali, Colombia and it is affected by drainage from abandoned mines, which reach the Cali River through the Las Minas brook. As bioremediation alternatives, the use of subsurface flow wetlands coupled with a limestone-based pretreatment was assessed in this study. The research methodology was structured in two stages: a) physicochemical monitoring of Las Minas brook waters, and b) treatment system operations. For these purposes, four systems were evaluated: 1) Wetlands with plants (WL1), 2) Limestone + WL1 (LS + WL1), 3) Wetlands without plants (WL2) and 4) Limestone + WL2 (LS + WL2). The results revealed that the water from the Las Minas brook presents characteristics similar to AMD (pH: 2.4-4.0; acidity: 1 303.2 mg/l ± 139.2; iron: 715.3 mg/l ± 70.6; sulfate: 1 134.5 mg/l ± 314.6) and affects the Cali River mainly owing to the increase in iron, aluminum, and the presence of ferric hydroxide precipitates. In addition, limestone-based treatment systems achieved greater efficiencies, and the LS + WL1 configuration is recommended. All systems were able to reduce the affluent acidity from 31 to 52 %. Furthermore, the average iron removal efficiencies achieved were between 54 and 67 %; sulfates between 16 and 35 %, nickel between 25 and 50 %, and aluminum between 0 and 73 %. However, manganese could not be removed.

Keywords: Acid mine drainage, bioremediation, constructed wetland, limestone, passive treatment.

Resumen

La minería genera impactos ambientales como drenajes ácidos de minas (DAM). El río Cali es uno de los principales recursos hídricos de la ciudad de Santiago de Cali, Colombia, y está afectado por los drenajes procedentes de minas abandonadas que llegan a través de la quebrada Las Minas. Como alternativas de biorremediación se evaluó el uso de humedales de flujo subsuperficial, además de piedra caliza como pretratamiento. La metodología de la investigación se estructuró en dos etapas: a) caracterización fisicoquímica del agua de la quebrada y b) operación de los sistemas de tratamiento. Se evaluaron cuatro sistemas: 1) humedal con especie vegetal (H1); 2) piedra caliza + H1 (PC + H1); 3) humedal sin especie vegetal (H2), y 4) piedra caliza + H2 (PC + H2). Los resultados mostraron que el agua de la quebrada Las Minas presenta características similares a DAM (pH: 2.4-4.0 unidades; acidez: 1 303.2 mg/l ± 139.2; hierro: 715.3 mg/l ± 70.6; sulfatos: 1 134.5 mg/l ± 314.6), y afecta al río Cali principalmente por el incremento del hierro, aluminio y presencia de precipitados de hidróxido férrico. Se observó que los sistemas de tratamiento que emplearon PC lograron mayores eficiencias; es recomendable la configuración PC + H1. Todos los sistemas lograron reducir la acidez del afluente en un rango promedio de 31 y 52 %, y se alcanzaron eficiencias de remoción promedio de hierro total entre 54 y 67 %; sulfatos entre 16 y 35 %; níquel entre 25 y 50 %, y aluminio entre 0 y 73 %. No se logró remover manganeso.

Palabras clave: drenaje ácido de mina, biorremediación, humedal construido, piedra caliza, tratamiento pasivo.

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Introduction

At the worldwide level, the coal mining industry reports an annual production of 7.269 million tons with China accounting for the highest production (44.6%) followed by India (9.7%) and the United States (9.2 %). In addition, countries such as Australia (29.2 %), Indonesia (27.7

%), Russia (12.8 %), and Colombia (6.2 %) represent the main coal exporters in the world (IEA, 2018).

In Colombia, the participation of the mining sector in the economic and social development of the country is reflected in its contribution to the Gross Domestic Product (GDP) (DANE, 2018; ACM, 2018), the generation of more than 2.5 trillion pesos in royalty resources, and contributions that are later converted into infrastructure works and benefits for the different regions of the country (ANM, 2019).

Although mining activities generate economic benefits, they also bring serious environmental impacts, being Acid Mine Drainage (AMD), one of the most pressing issues associated with both active and abandoned or poorly closed mines around the world (Kefeni, Msagati, & Mamba, 2017; Pat-Espadas, Loredo-Portales, Amabilis-Sosa, Gómez, & Vidal, 2018; Naidu *et al*., 2019). Abandoned or closed mines can continue generating AMD perpetually owing to the exposure of sulfurous material on the surface, releasing metallic ions and sulfuric acid into the environment (Sheoran & Sheroran, 2006; Obreque-Contreras Pérez-Flores, Gutiérrez, & Chávez-Crooker, 2015; Kefeni *et al*., 2017; Skousen, Ziemkiewicz, & McDonald, 2019).

AMDs generates a loss of biodiversity, accumulation of toxic substances in plant roots, habitat alterations by metallic precipitates, nutrient cycle alterations, contamination of surface and groundwater sources, deviation of natural riverbeds, deforestation, soil contamination, and visual impacts, among others (Skousen *et al*., 2019; Naidu *et al*., 2019).

AMD formation arises from exposure to the atmosphere of pyrite and other sulfur minerals. In this case, oxygen, and oxidizing bacteria and water oxidize these materials, causing the formation of sulfates, and the release of sulfuric acid and different heavy metals (Fe, Co, Pb, Ni, Mn, Cd, Al, Cu, Zn) (Pat-Espadas *et al*., 2018; Moodley, Sheridan, Kappelmeyer& Akcil, 2017; Kefeni *et al*., 2017). In general, AMDs can present low pH, high acidity, and high concentrations of iron, sulfates, and heavy metals, depending on the mineral deposits that originate them (Akcil & Koldas, 2006; Sheoran & Sheoran, 2006).

The chemical transformation of pyrite (FeS_2) to form AMD can be simplified through the following reactions, from where ferric hydroxide ($Fe(OH)_3$) known as “yellow boy” originates (Gaikwad & Gupta, 2007):

$$4\,FeS_2 + 15\,O_2 + 14\,H_2O \rightarrow 4\,Fe\,(OH)_3 \downarrow + 8\,H_2SO_4 \quad (1)$$

$$2\,FeS_2 + 7\,O_2 + 2\,H_2O \rightarrow 2\,Fe^{2+} + 4\,SO_4^{2-} + 4\,H^+ \quad (2)$$

$$4\,Fe^{2+} + O_2 + 4\,H^+ \rightarrow 4\,Fe^{3+} + 2\,H_2O \quad (3)$$

$$4\,Fe^{3+} + 12\,H_2O \rightarrow 4\,Fe\,(OH)_3 \downarrow + 12\,H^+ \quad (4)$$

$$FeS_2 + 14\,Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \quad (5)$$

AMD is generated by the exposure of pyrite, which reacts with oxygen to generate ferric hydroxide and sulfuric acid (Equation 1). Sulfide oxidizes to form sulfate, releasing ferrous iron (Fe^{2+}) (Equation 2). As a result, Fe^{2+} is transformed into ferric iron (Fe^{3+}) (Equation 3) under acidic pH values. The hydrolysis of iron and other metals occurs in the fourth reaction, causing the precipitation of different metals (Equation 4). Finally, in the last reaction, ferric iron oxidizes both pyrite and the other trace elements (Equation 5). The formation of ferric hydroxide precipitates depends on the pH level as they will only be formed if the pH level exceeds 3.5. The production of AMD is cyclical and self-propagated, and the reaction does not stop until the Fe^{3+} and the other metals are completely depleted (Gaikwad & Gupta, 2007).

AMD treatments can be conducted through active and passive treatments. Active treatments include the addition of alkaline chemicals, such as $Ca(OH)_2$, CaO, $NaOH$, Na_2CO_3, and NH_3. However, these treatments can be expensive and can require equipment and dispensing facilities that typically operate for decades (Skousen *et al*., 2019). Alternatively, the operation and maintenance costs associated with passive treatments are low, and these treatments include surface and subsurface flow wetlands, anoxic limestone drainage, vertical flow wetlands, open channels, or limestone beds (Sheoran & Sheoran, 2006; Moodley *et al*., 2017; Pat-Espadas *et al*., 2018; Skousen *et al*., 2019). In addition, they are the most appropriate treatments for abandoned or remote mines with active AMD flows (Clyde, Champagne, Jamieson, Gorman, & Sourial, 2016).

Different studies have proven the feasibility of treating AMD using alkaline media (Shim *et al*., 2015; Tolonen, Sarpola, Hu, Rämö, & Lassi, 2014; Labastida *et al*., 2019). Therein, limestone is regarded as one of the least expensive alkalinity sources with 75 to 100 % neutralization potential (Skousen *et al*., 2019).

Within this context, wetlands are considered a long-term bioremediation technology, whose efficiency depends on factors such as the chemical characteristics of AMD, its degree of acidity, the concentration of toxic metals, and the combination of the support medium with organic materials (Pat-Espadas *et al*., 2018; Sekarjannah, Wardoyo, & Ratih, 2019).

These systems constitute a microorganism-plant consortium that promotes bacterial oxidation processes, traces element fixation, and the precipitation and absorption of metals such as iron, manganese, arsenic, aluminum, copper, zinc, cadmium, selenium, nickel, and lead (Johnson & Halberg, 2005b; Pozo-Antonio, Puente, Lagüela, & Veiga, 2017; Pat-Espadas *et al*., 2018). These studies report Fe removal efficiencies at between 67 and 98.4 %; Zn between 79 and 98 %; Cu between 10 and 92 %; Mn at 98.4%; Al at 98%; Ni at 88.5 %, and Pb at 90 % (Nyquist & Greger, 2009; Pat-Espadas *et al*., 2018).

Few authors have assessed the combined use of wetlands and limestone-based chemical treatments, who reported metal removal efficiencies of up to 99 % (Al, As, Cd, Co, Cu, Fe, Mn, and Ni), zinc removal efficiencies at 67.5 %, and sulfates at 60%. Moreover, pH increases from 2.6 to 9.5 (Lagos & Geo, 2011; Tolonen *et al*., 2014; Gandy, Davis, Orme, Potter, & Jarvis, 2016) resulting in a potential neutralization option for AMD acidity, reducing sulfates, and eliminating dissolved metals (Mayes *et al*., 2009; Kefeni *et al*., 2017).

In the city of Santiago de Cali, Colombia, the Cali River is one of its main water and landscape resources. It is used as a supply source for 17.1 % of the population (approximately 500 000 inhabitants) and an ecological and tourist corridor within the city. This river is currently being impacted by the Las Minas brook, which receives acid drainage from abandoned coal mines through runoff and infiltration. However, the impact exerted on water quality by brook waters is unknown, and there are no physicochemical characterizations. Hence, the results from this research study are of great interest to the community and environmental regulatory entities.

This research identified the main physicochemical variables affecting the water quality of Las Minas brook. In addition, a passive treatment based on limestone and subsurface flow wetlands was used as a bioremediation alternative for mitigating the impacts caused by AMD (Lañas & Cuenca, 2018).

Materials and methods

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The study area was delimited to the left bank of the Cali River at the exact discharge point of the Las Minas brook, at coordinates 3° 27′ 15.36′′N and 76° 32′ 48.12′′W, in the city of Santiago de Cali, Colombia (Figure 1). The methodology was structured in two stages: 1) physicochemical characterization of the waters from the Las Minas brook and 2) treatment system commissioning and operation.

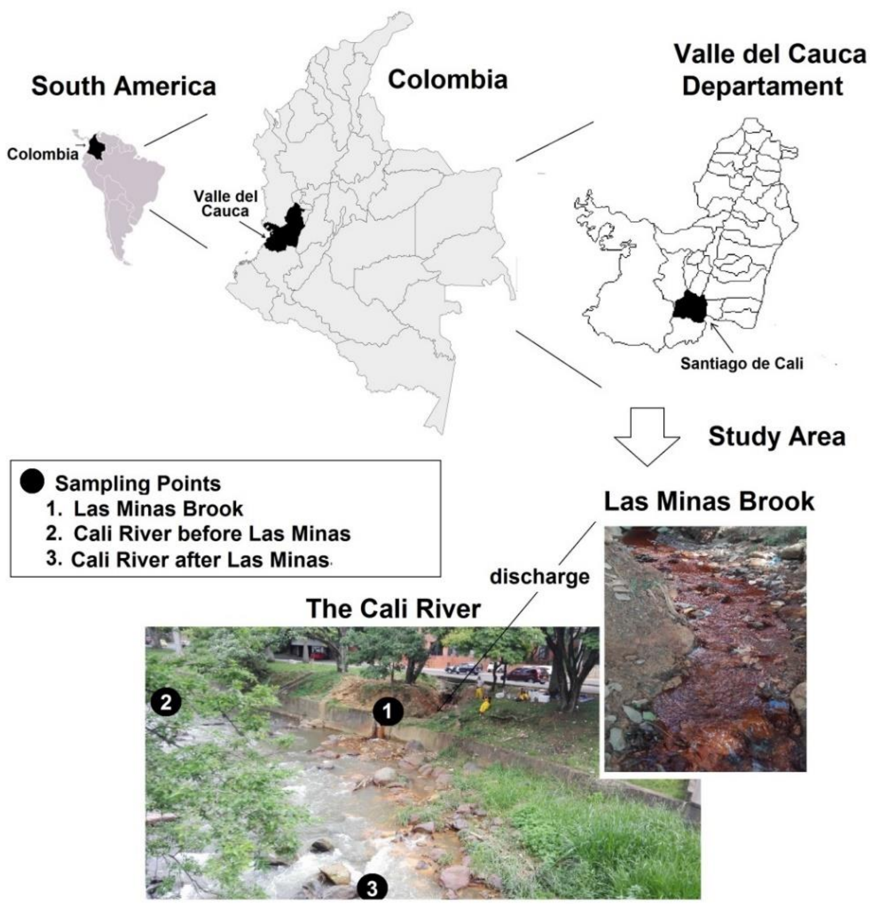

Figure 1. Study Area and Water Quality Sampling Points.

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Physicochemical Characterization of the Waters from the Las Minas Brook

Two 24-hour composite sampling runs were conducted under different climatic conditions in 2018. The first sampling run took place during the dry season with a specific episode of rain, and the second sampling run was conducted during the transition season with the presence of rains. During these runs, the waters from the Las Minas brook (point 1) and the Cali River were monitored before discharge (point 2) and after discharge (point 3) from the brook (Figure 1).

During the samplings, the brook flow was volumetrically gauged, and the pH (SM 4500-H+B), temperature (SM 2550 B), and conductivity (SM 510B) were measured onsite according to the Standard Methods (SM) (APHA, AWWA, & WEF, 2012). Samples were taken for the measurement of physicochemical variables, such as chemical oxygen demand (SM 5220C), biochemical oxygen demand (SM 5210B), total, suspended, dissolved, and settleable solids (SM 2540B, SM2540D, and SM2440F), total alkalinity (SM2320B), acidity (SM 2310B), total Kjeldahl nitrogen, ammonia nitrogen, nitrates, nitrites, chlorides, boron, total phosphorus and sulfates (SM 4500); potassium, sodium, total iron, cadmium, copper, lead, manganese, and magnesium (SM3111B); calcium and aluminum

(SM3111D); mercury (SM3112B); chromium (SM3111D), and arsenic (SM3114C).

Treatment system commissioning and operation

From the physicochemical water characterization results for the Las Minas brook, the physicochemical variables that reported the highest concentrations were selected as response variables for treatment system assessment.

Here, two treatment configurations were evaluated. The first consisted of a subsurface flow wetland and the second consisted of a subsurface flow wetland coupled with limestone. In addition, two control treatments were formed in order to determine the effects from limestone and plants on the system efficiency. Table 1 lists the experimental units used. All wetlands flows were horizontal.

Table 1. Description of the experimental units.

Experimental unit	**Acronym**	**Description**	**Total useful volume***
Treatment 1	WL1	Subsurface Flow Wetland with Plants (*Phragmites Australis*)	120 liters
Treatment 2	LS + WL1	Limestone + Subsurface Flow Wetland with Plants (*Phragmites Australis*)	180 liters
Control 1	WL2	Subsurface Flow Wetland without Plants	120 liters
Control 2	LS+WL2	Limestone + Subsurface Flow Wetland without Plants	180 liters

*Useful wetland dimensions: Length: 0.80 m; width: 0.3 m, and Height: 0.5 m.

In the wetlands with plants, we used *Phragmites Australis* owing to its high resistance to low pH values (Mayes *et al*., 2009; Guo, Ott, & Cutright, 2014). For these purposes, six plants with average height of 60 cm were planted in each wetland. In all experimental units, the support materials used were a 4-cm-high gravel bed with an average diameter of 2–3 cm placed at the bottom of the unit, and a ballast bed (river sand) of approximately 46 cm height with an average diameter of 0.05–0.5 cm.

The limestone treatment units operated at a Hydraulic Retention Time (HRT) of 17 h (Watzlaf, Schroeder, Kleinmann, Kairies, & Nairn, 2004) and a useful volume of 60 L. The granulometry of the limestone ranged from 1 to 2 in. Regarding the wetlands, they operated at an HRT of 2 days (Fernando, Ilankoon, Syed, & Yellishetty, 2018) and a useful volume of 120 l.

Figure 2 displays the experimental setup and describes the treatment systems. As it can be observed, a 500-liter storage tank was used, thus allowing the treatment systems to operate in continuous flow. The raw water flowing into the systems was collected from the Las Minas brook every two days and transported in 20-liter plastic containers to the storage tank.

Figure 2. Experimental Setup Schematics.

Considering that the plants were of adequate size and data collected throughout the six months of operation were sufficient to conduct the comparative system performance analysis, their operation lasted 180 days. In this period, variables such as pH (SM 4500-H+B), conductivity (SM 510B), and total acidity (SM231) were measured three times a week. In addition, variables such as total, suspended, and dissolved solids (SM 2540B, SM2540D), sulfates (SM 4500), total iron (SM3111B), Fe^{3+} (SM3111D), Fe^{2+} (difference total Fe–Fe^{3+}), nickel (SM3113D), manganese (SM3111B), and aluminum (SM3111D) (APHA *et al*., 2012) were measured once a week.

Results and discussion

Physicochemical characterization of the Las Minas Brook

Table 2 summarizes the results obtained during the sampling and characterization sessions at the three monitoring points. The average flow measured at the Las Minas brook was 1.9 L/s for the first sampling run and 2.0 L/s for the second run.

Table 2. Physicochemical characterization of the waters from the Las Minas Brook.

Variable	Unit	Sampling Run 1*: Sampling Point			Sampling Run 2*: Sampling Point			Reported AMD Values
		Las Minas	Cali River before Las Minas	Cali River after Las Minas	Las Minas	Cali River before Las Minas	Cali River after Las Minas	
pH Level	-	1.6-3.3	7.3-7.9	6.9–7.8	3.8–4.4	6.2–7.9	6.1 – 7.7	0.5– 5.0 (1) (2) (3) (4) (5)
Conductivity	µs/cm	2 610–2 730	231–363	175–406	1 940-2 510	190 - 380	120 – 280	1 400 – 2 405 (1) (5)
Temperature	°C	18.9-25.8	18.5 – 25.9	18.3-24.1	18.4-25.4	18.5–24.7	18.3–24.7	-
Acidity	mg/l $CaCO_3$	`	`	`	288	<20	<20	-
Total Alkalinity	mg/l	<10.0	101.36	85.34	<10.0	56.05	45.92	-
COD	mg/l	<2.0	7.73	<2.0	<2.0	3.41	2.51	-
DBO_5	mg/l	<2.0	3.71	<2.0	<2.0	<2.0	<2.0	4.25 (2)
Total Solids	mg/l	3 105	350	325	3 435	165	1 300	1 347 (5)
Total Dissolved Solids	mg/l	3 025	180	170	3 374	142	1 271	1 347 (5)
Settling Solids	mg/l	0.8	0.9	0.1	< 0.1	0.3	0.8	-
Total Suspended Solids	mg/l	170	155	80.0	23	28	61.0	-
Total Nitrogen	mg/l	< 5.0	12.42	< 5.0	< 5.0	< 5.0	< 5.0	-
Ammonia Nitrogen	mg/l	< 0.5	< 0.5	< 0.5	2.33	0.78	0.56	-
Nitrates	mg/l	1.2	4.67	4.01	0.89	1.53	1.18	-
Nitrites	mg/l	0.016	< 0.015	< 0.015	< 0.015	< 0.015	< 0.015	-
Total	mg/l	100.67	37.29	39.26	1.3	0.37	0.36	-

Phosphorus								
Sulfates	mg/l	1 745	41.9	23.63	1 755	<5.0	< 5.0	500 – 7 532 (2) (3) (4) (5) (6)
Total Iron	mg/l	55.4	3.28	5.13	1.53	0.43	0.47	2.6 – 1 052 (1) (2) (3) (4)
Potassium	mg/l	2.8	1.55	1.19	3.23	3.43	1.84	3 – 32 (1) (3)
Sodium	mg/l	12.12	8.45	6.1	11.86	6.15	3.57	14 (1) (4)
Calcium	mg/l	297.5	166.2	181	49.83	12.7	9.22	1 - 4(3)
Magnesium	mg/l	71.35	14.06	11.63	93.4	8.06	5.85	385(3) 392(4)
Manganese	mg/l	11.28	< 0.01	< 0.01	13.08	0.01	< 0.01	0.02 – 998 (1) (3) (4) (5)
Chlorides	mg/l	8.74	8.74	3.89	14.43	6.32	4.05	32.2 (1)
Aluminum	mg/l	9.59	0.81	2.66	0.15	0.21	0.23	11.3 – 532 (1) (2) (3) (4) (5)
Boron	mg/l	< 0.137	< 0.137	< 0.137	< 0.5	< 0.5	< 0.5	-
Arsenic	mg/l	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	1 257(4)
Cadmium	mg/l	< 0.006	< 0.006	< 0.006	< 0.006	< 0.006	< 0.006	362(4)
Copper	mg/l	0.02	0.02	0.03	< 0.01	< 0.01	< 0.01	0.03–1.44(2)
Chrome	mg/l	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	-
Mercury	mg/l	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	-
Nickel	mg/l	0.24	0.01	0.01	< 0.01	< 0.01	< 0.01	0.388 – 96 (2) (4)
Lead	mg/l	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.01 – 130 (2) (3) (4)

* Dry season with a specific episode of rain

** Transition season with the presence of rains. AMD: Acid Mine Drainage

(1) Batty and Younger (2004)

(2) Several authors cited by Pat-Espadas *et al*. (2018)

(3) Shim *et al*. (2015)

(4) Torres *et al*. (2018)

(5) Cadorin, Carissimi y Rubio (2007)

(6) Fernando *et al*. (2018)

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The Las Minas brook water presented acid characteristics with low pH level values (1.6–4.4), high conductivity (1 940–2 730 μs/cm), and a high concentration of compounds, such as sulfates, total dissolved solids (TDS), iron, calcium, magnesium, manganese, aluminum, and nickel when compared with data measured in the waters of the Cali River.

The pH, sulfates, TDS, iron, and manganese values at Las Minas brook denote the high impact caused by acid drainage from the abandoned mines in the upper part of the basin reporting concentrations similar to AMD values (Johnson & Hallberg, 2005b; Kefeni *et al*., 2017; Fernando *et al*., 2018; Labastida *et al*., 2019; Neculita & Rosa, 2019), which are characterized by pH values ranging from 0.5 to 5.0, and a sulfate concentration exceeding 400 mg/l (Pat-Espadas *et al*., 2018).

Furthermore, the presence of iron in water is typical of acidic water from coal mines (Cadorin *et al*., 2007). Here the iron found in the waters from the Las Minas brook may be Fe^{3+}, which releases a large amount of acidity, thus accounting for the acidic characteristics of AMD (Gaikwad & Gupta, 2007; Moodley *et al*., 2017) and confirming that its origin is caused by the constant exposure of pyrite to the atmosphere due to inadequate mine closures.

The COD and BOD_5 results, as well as the low content of substances such as sodium, chlorides, phosphorus, nitrogen, nitrites, and nitrates, reflected minimal contributions from organic matter on the creek, indicating the absence of domestic discharges and a predominance of inorganic contamination associated with AMD.

In Colombia, Resolution 631-2015 (Ministerio de Ambiente y Desarrollo Sostenible, 2015) specifies, among others, the permissible liquid discharge limits for the mining sector. Although these regulations are not applicable to the Las Minas brook because it is a water body, the water quality of the brook well exceeds the pH (6.0–9.0), total iron (2.0 mg/l), sulfates (1 200 mg/l), and total suspended solids (50 mg/l) limit established therein.

Still, the chemical quality of the Cali River downstream from the Las Minas brook discharges was not significantly affected, reporting only an increase in iron and aluminum. This is due to the great dilution capacity of the Cali River since its flow rate (average 4 000 l/s) is considerably higher that the flow rate of the brook (2 l/s). However, the impact is evidenced in the different colors observed in the water and aesthetic characteristics of the Cali River (Figure 3). This situation is owing to the formation of ferric hydroxide precipitates ("yellowboy") (Gaikwad & Gupta, 2007; Kefeni *et al*., 2017) as a result from the increased pH level in the water (> 3.5 units) and presence of dissolved oxygen in the Cali River (6.8-7.03 mg/l) (DAGMA, 2018).

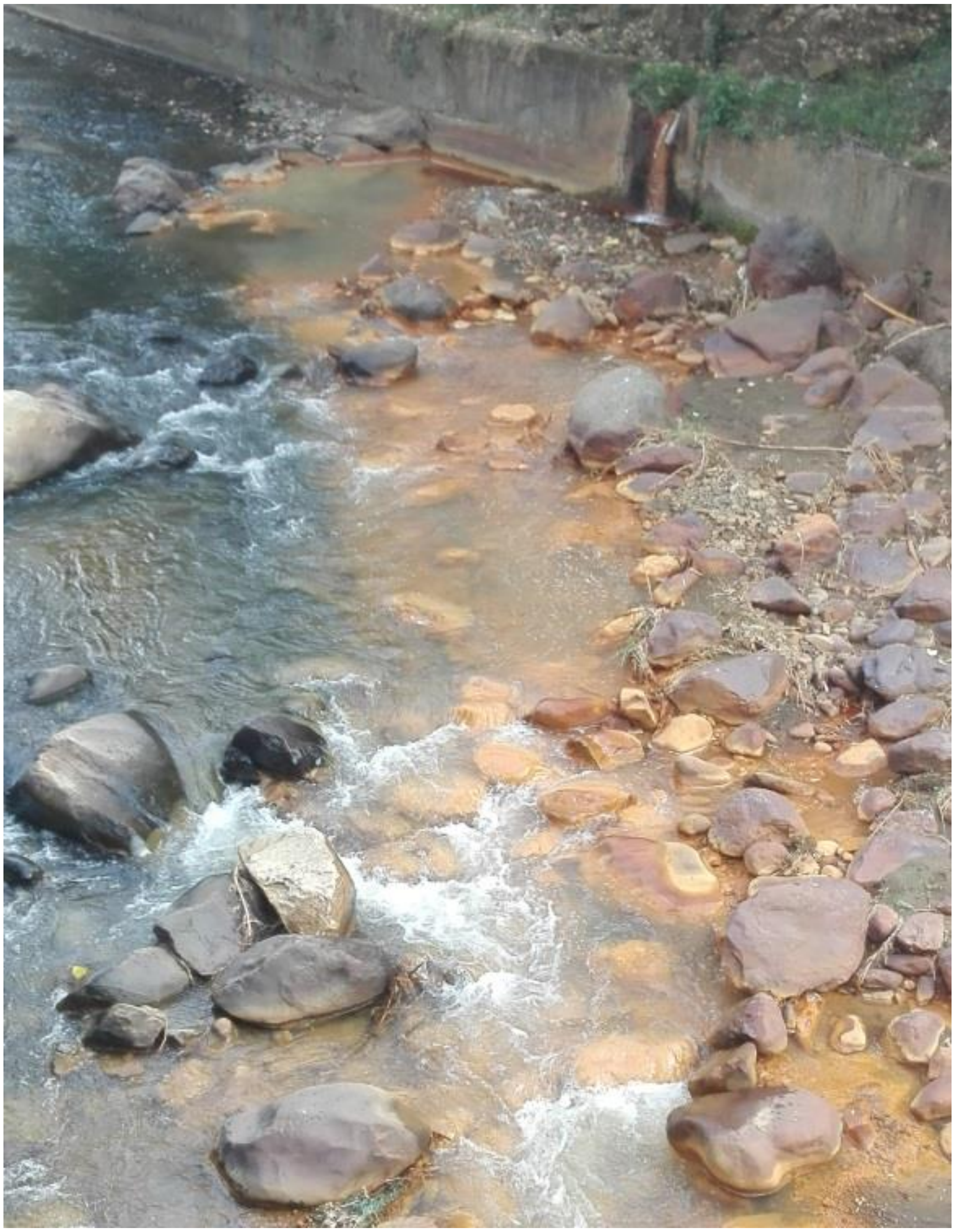

Figure 3. Color Changes observed in the Cali River.

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The results from the sampling sessions evidenced the Las Minas brook is strongly affected by acid drainage runoff and infiltration from abandoned coal mines, which means brook waters have similar characteristics as AMD. This serious impact on the brook has affected the natural ecosystems causing stress and reducing biodiversity and preventing its waters from being used in domestic or industrial contexts (Johnson & Hallberg, 2005a), in addition to the direct effects on Cali River water quality.

Treatment system commissioning and operation

Table 3 denotes the average characteristics measured in raw water extracted from the Las Minas brook during treatment system operation.

Table 3. Variation of the Physicochemical Characteristics of Raw Water extracted from Las Minas creek.

Variable	*n*	Units	Mean ± standard deviation	Minimum	Maximum
pH level	48	Units	-	2.38	4.02
Total acidity	41	mg/l	1 303.2 ± 139.2	960	1 620

Conductivity	48	µS/cm	1 890.41 ± 433.51	920	2 410
Total solids	13	mg/l	3 211.7 ± 329.6	2 338	3 580
Total dissolved solids	13	mg/l	3 026.3 ± 335.2	2 303	3 380
Total suspended solids	13	mg/l	163.5 ± 140.7	5	418
Sulfates	13	mg/l	1 134.5 ± 314.6	752	1 696
Total iron	6	mg/l	715.3 ± 70.6	635	845
Fe^{3+}	13	mg/l	542 ± 110.0	362	750
Fe^{2+}	6	mg/l	124.3 ± 165.2	0	387
Nickel	13	mg/l	0.4 ± 0.06	0.25	0.48
Manganese	13	mg/l	9.4 ± 1.17	7	11.1
Aluminum	13	mg/l	16.8 ± 1.69	12.2	17.9

n: Number of samples.

The raw water characteristics were similar to those obtained during the sampling runs, with low pH levels and high content of acidity, sulfates, iron, nickel, aluminum, manganese, and dissolved solids (94%). The variation of these characteristics throughout the study confirms their high similarity with the AMD generated by the pyrite and sulfide mineral oxidation reactions (Gaikwad & Gupta, 2007).

During treatment system operation, both the treatments (WL1 and LS+WL1) and the controls (WL2 and LS+WL2) improved their raw water pH (median: 3.17 units) and acidity (median: 1 310 mg/l) levels, as shown in Figure 4.

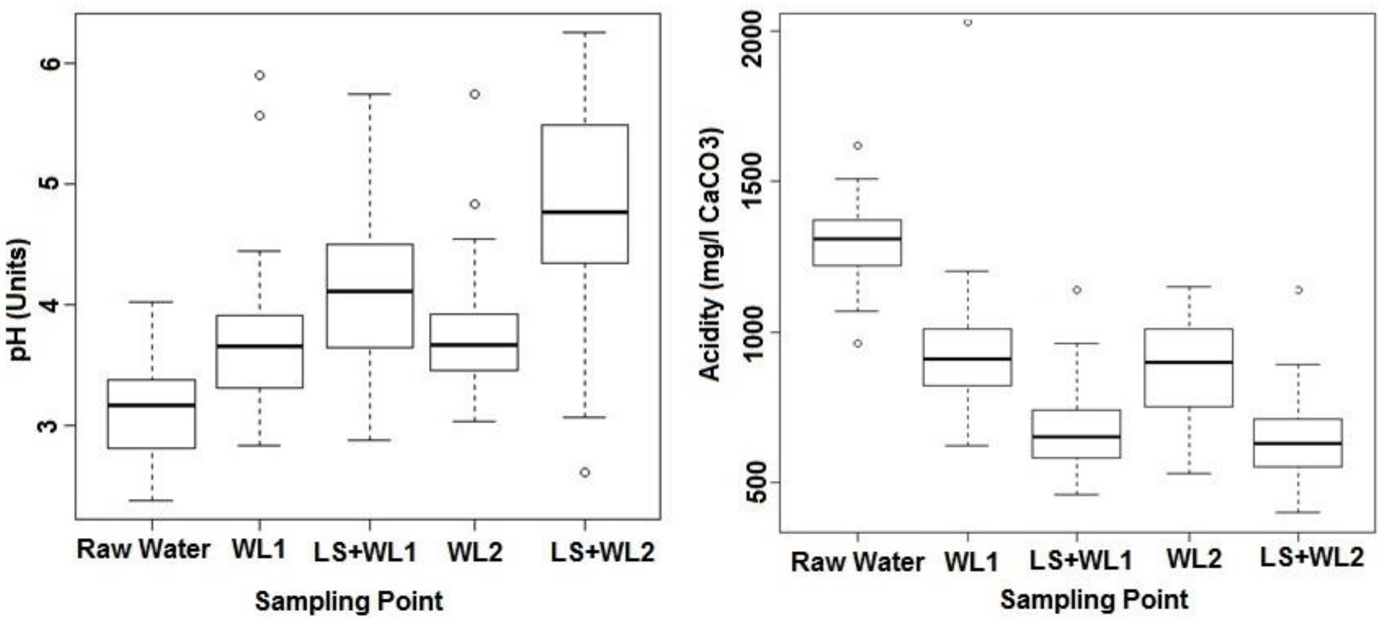

Figure 4. pH and Acidity Variation during treatment system monitoring**.**

Although the WL1 treatment (wetland with plants) managed to improve the characteristics of the treated effluent by slightly increasing its pH level (median: 3.7; maximum: 4.4) and reducing its acidity (median: 910 mg/l) by an average of 31%, it was not as efficient as the limestone-based systems (LS+WL1 and LS+WL2) reached maximum pH values of 5.7 (LS+WL1) and 6.3 (LS+WL2), in addition to an average acidity reduction of 50% and 52%, respectively. This could be because limestone fosters a higher pH level by reacting with AMD acidity, thus favoring the formation of bicarbonate (Gandy *et al*., 2016; Pat-Espadas *et al*., 2018).

Here, WL1 behavior was similar to the control WL2 (wetland without plants) demonstrating that plants did not exert much effect on these variables and within the support medium, adsorption and carbonate contribution phenomena were favored owing to the clay material from the ballast (Sheoran & Sheoran, 2006; Skousen *et al*., 2019). Although plant roots prevent pH reduction, its favorable effect is reduced as the plants grow, being perceived at longer system operation times when this effect was overshadowed by the supporting materials (Nyquist & Greger, 2009; Pat-Espadas *et al*., 2018).

Regarding the other tracking variables, Table 4 lists the results obtained during the treatment system operation. The conductivity and concentration of solids (total, dissolved, and suspended) showed similar reductions in all systems. Conductivity decreased on an average from 3 to 10 %, total and dissolved solids between 19 and 26 %, and suspended solids between 21 and 77 %.

Table 4. Results from treatment system monitoring variables.

Variable	Units		Treatment		Control (without plants)	
			WL1	**LS + WL1**	**WL2**	**LS + WL2**
Conductivity $n = 48$	µS/cm	Mean	1 769.8	1 827.9	1 705.4	1 708.3
		Min	1 040	1 040	950	970
		Max	2 440	2 420	2 150	2 240

		SD	358.03	367.8	327.6	329.3
Total Solids $n = 13$	mg/l	Mean	2 489.8	2 519.1	2 446.8	2 381.5
		Min	1 220	1 290	1 400	1 094
		Max	3 596	3 398	3 110	2 940
		SD	772.3	715.3	620.4	539.3
Total Dissolved Solids $n = 13$	mg/l	Mean	2 446.5	2 451.8	2 408.1	2 253.7
		Min	1 210	1 269	1 380	1 910
		Max	3 527	3 310	2 980	2 870
		SD	757.7	664.3	606.4	511.9
Total Suspended Solids $n = 13$	mg/l	Mean	44.1	76.3	37.4	129.3
		Min	3	10	5	69
		Max	290	296	132	234
		SD	76.01	76.7	40.7	48.7
Sulfates $n = 13$	mg/l	Mean	951	1 039.1	739.9	851.3
		Min	259	447	237	480
		Max	1 667	1 605	1 034	1 275
		SD	357.3	441.3	357.3	284.1
Fe^{3+} $n = 13$	mg/l	Mean	263.23	176.12	277	194.01
		Min	109	86.6	113	42.08
		Max	453	298	431	291
		SD	113.04	60.09	108.44	74.6
Fe^{2+} $n = 6$	mg/l	Mean	30.9	53.95	12.35	68.33
		Min	0	0	0	0
		Max	199	144	81	164
		SD	93.25	64.84	64.91	66.79

Total Iron *n* = 6	mg/l	Mean	303.37	234.72	326.85	275
		Min	79.2	42.3	87.1	207
		Max	496	333	488	348
		SD	156.85	100.72	144.33	50.32
Nickel *n* = 13	mg/l	Mean	0.3	0.3	0.3	0.2
		Min	0.157	0.176	0.196	0.077
		Max	0.473	0.398	0.41	0.346
		SD	0.102	0.063	0.079	0.079
Manganese *n* =13	mg/l	Mean	10.81	12.12	11.3	10.16
		Min	5.16	5.81	4.91	3.66
		Max	16.5	18.5	18.4	14.7
		SD	3.43	3.53	4.01	2.94
Aluminum *n* = 13	mg/l	Mean	23.5	11.9	20.2	4.49
		Min	8.47	4.03	9.76	0.18
		Max	51.6	22.4	34.2	19.8
		SD	11.22	4.73	7.79	5.47

WL1: wetland with plants

LS + WL1: Limestone + wetland with plants

WL2: wetland without plants

LS+WL2: Limestone + wetland without plants

The treatment systems also removed from 16 to 35 % of sulfate concentrates with the WL2 and LS+WL2 controls being slightly more efficient than the others. We expected that limestone would contribute to increasing sulfate removal efficiencies owing to the increase in pH and alkalinity (Nyquist & Greger, 2009) and because it is considered as one of the conventionally used treatments for improving sulfate removal and metal precipitation; however, as reported by Fernando *et al*. (2018), conventional methods (lime, limestone, and wetlands) often fail to reach the expected efficiencies. Hence, it is highly recommended to evaluate other processes (i.e., electrocoagulation, ion exchange, adsorption, precipitation, or filtration).

Regarding the iron variable, which was assessed as total iron, Fe^{3+} and Fe^{2+}, the ferric ion Fe^{3+} species prevailed in all systems, since a higher pH level (> 3.5 units) contributes to the formation of ferric hydroxide (Gaikwad & Gupta, 2007). Iron concentrations in the treated effluents showed average total iron removals between 54 and 67 %; between 45 and 90 % for Fe^{2+} species, and between 49 and 67 % for Fe^{3+}. Figure 5 details the behavior of the predominant Fe^{3+} species in raw water and effluents treated throughout the study.

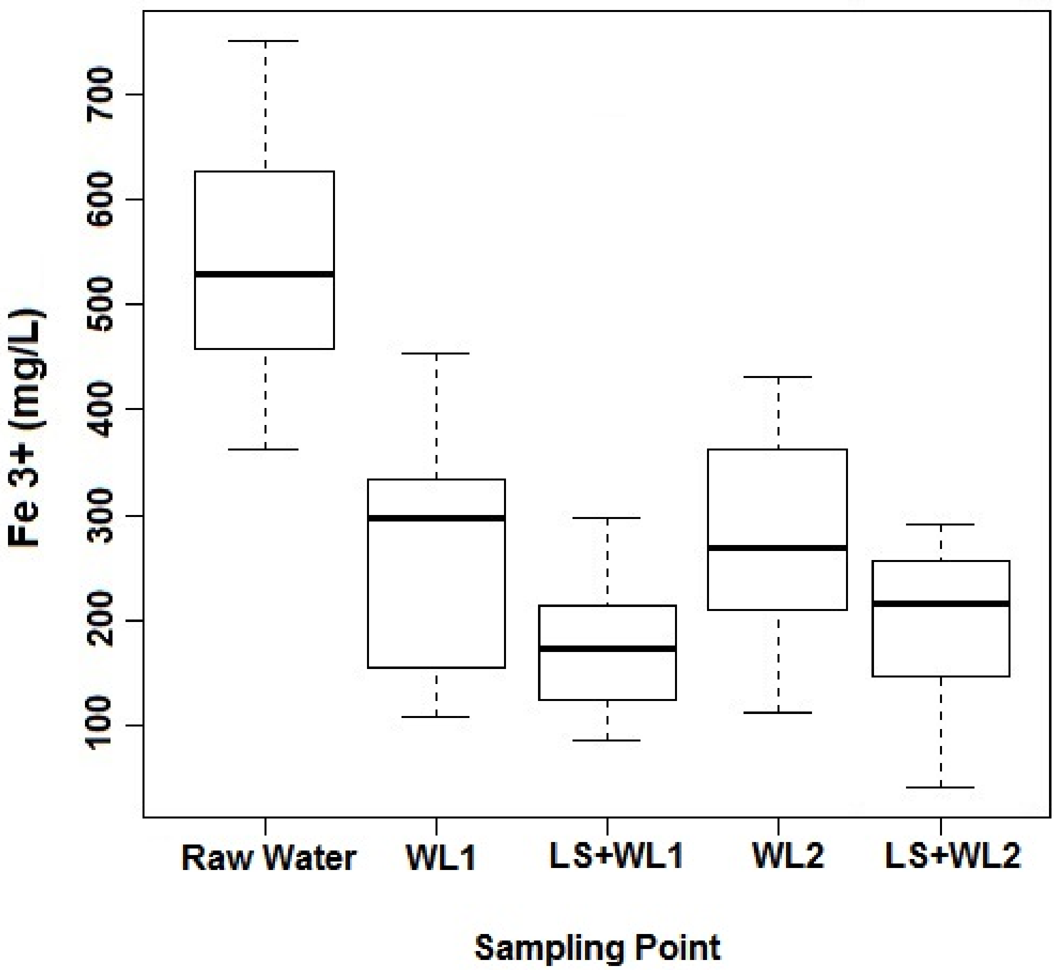

Figure 5. Variation of the Predominant Iron Species (Fe^{3+}) during treatment system operation.

The treatment with the best iron removal performance was the LS+WL1, followed by the LS+WL2, indicating that the limestone (LS) pretreatment favored the precipitation of Fe^{3+} as the pH increases. This was reflected in the external $Fe(OH)_3$ precipitate coating formed on the limestone (Skousen *et al*., 2019), which can later be removed by sedimentation and filtration processes. The best performance achieved by LS+WL1 indicates that the plants possibly contributed to improving iron removal efficiencies through absorption processes (Sheoran & Sheoran, 2006).

Regarding the removal of Ni, Al, and Mn, removal efficiencies were low for nickel and aluminum, and practically zero for manganese. Figure 6 denotes the behavior of these variables throughout the study. The best removal efficiencies were achieved by LS-based systems (Ni: 25%–50% and Al: 29%–73%), mainly LS+WL2. This behavior is because the LS+WL2 control reached the highest pH values or that removal processes were favored by iron oxide co-precipitation (Sheoran & Sheoran, 2006).

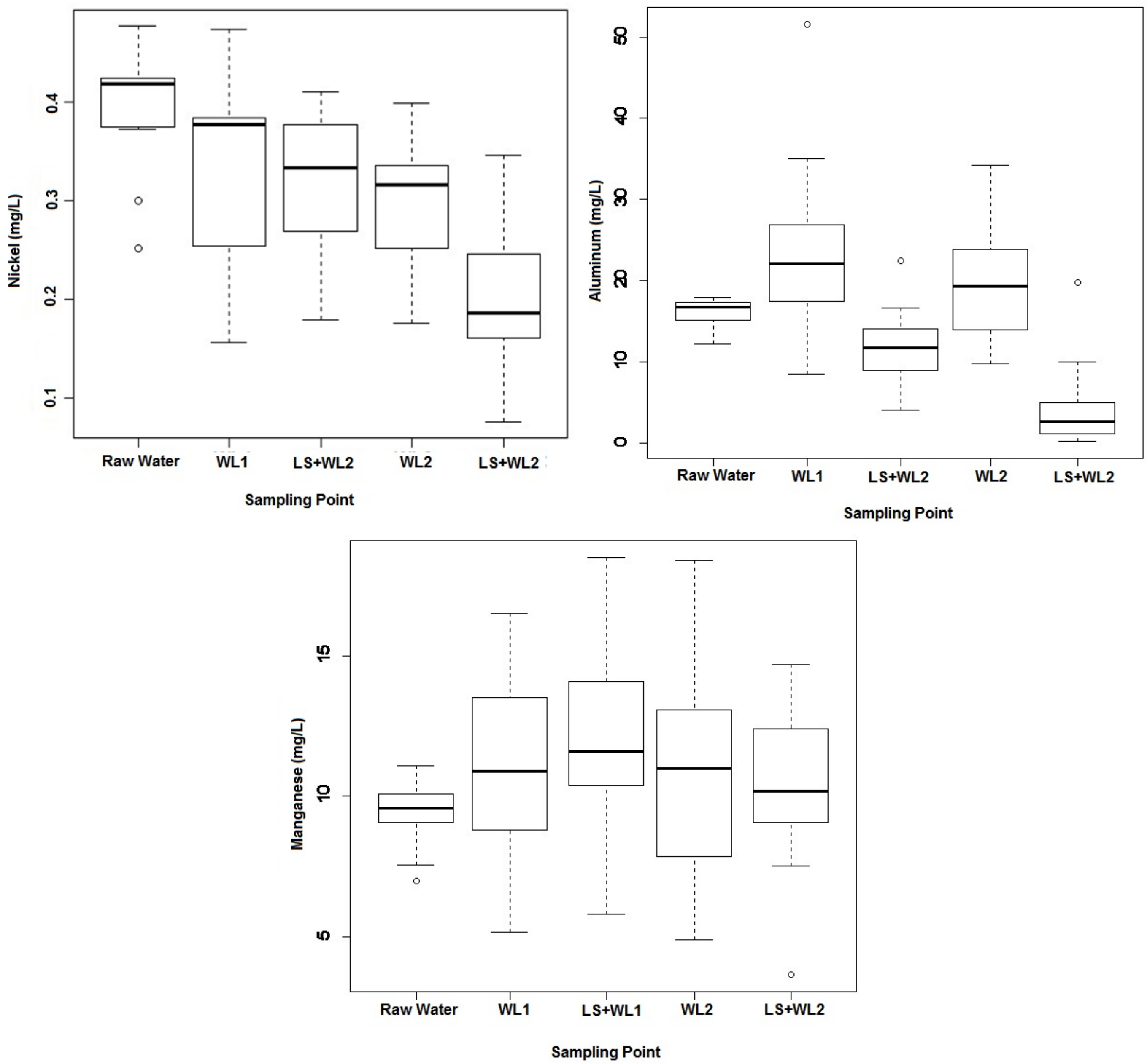

Figure 6. Nickel, aluminum, and manganese variation during treatment system monitoring.

The highest nickel and aluminum removal efficiencies were reported in the LS systems, possibly because different wetland metal removal mechanisms are strongly influenced by pH (Nyquist & Greger, 2009). For manganese, sufficiently high pH values (> 8.0) are required for its removal (Sheoran & Sheoran, 2006; Torres *et al*., 2018), a condition that did not occur in any of the treatments systems. Instead, some removal issues were evidenced for the manganese found in system sediments (Neculita & Rosa, 2019).

Furthermore, during the study, it was observed that plant development in terms of height and number of stems was similar in all systems, proving no signs of affectation owing to low pH values. This behavior is possibly owing to the resilient nature of *Phragmites Australis* as reported by some authors (Guo *et al*., 2014; Pat-Espadas *et al*., 2018).

Alternatively, plants apparently did not affect the metal-removing capabilities of the different systems. However, longer system operation times may have demonstrated the removal mechanisms exerted by the plants used (Nyquist & Greger, 2009).

By way of synthesis, the global results of the study indicated that, although subsurface flow wetlands (WL1) favored acidity reduction, increased pH levels, and removed compounds such as iron and sulfates, the highest efficiencies were achieved through limestone pretreatments. In addition, the high resistance of plants against the acid characteristics of the tributary was observed. Conversely, the efficiencies reached in the study were not sufficient to remove the main pollutants found in the Las Minas brook waters (Fe, Sulfates, Ni, Al, and Mn).

Therefore, we recommend assessing other pretreatment options, hydraulic retention times, and support media that can foster higher pH levels and provide carbon (Sheoran & Sheoran, 2006), in addition to considering that limestone can lose effectiveness over time (Shim *et al*., 2015).

Conclusions

The results revealed that the Las Minas brook is impacted by AMD, which generates low pH levels (2.4–4.0) and high levels of acidity (1 303.2 mg/l ± 139.2), iron (715.3 mg/l ± 70.6), sulfates (1 134.5 mg/l ± 314.6), aluminum (16.8 mg/l ± 1.7), manganese (9.4 mg/l ± 1.2), and nickel (0.4 mg/l ± 0.06) and low pH values (1.6–4.4), characteristics similar to those found in AMD.

All the treatment systems evaluated were able to improve the pH and acidity characteristics of the tributary, achieving maximum increases in pH levels between 4.4 and 6.3, and an average acidity decrease between 31 and 52 %, with the systems that used limestone being deemed more efficient (LS+WL1 and LS+WL2). However, higher pH values (> 8.0) that promote better removal efficiencies for metals, sulfates, and manganese could not be achieved.

The treatment systems showed average removal efficiencies of total Fe between 54 and 67 %, sulfates between 16 and 35 %, nickel between 25 and 50 %, and aluminum between 0 and 73 %. It was not possible to remove manganese and, instead, certain removal issues were such that even increased manganese concentrations in the effluents.

Limestone pretreatments favored the removal efficiencies of the treatment systems and, although the plants used did not seem to have any effect on the system efficiency, the configuration that exhibited the best performance was the LS+WL1 treatment.

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