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## Mass balances in a dam that receives mine drainage

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### Abstract

This work focuses in a small reservoir named The Santa Ana dam that receives abandoned mine drainages since 200 years ago. The presence of calcite in fractures of local rocks maintains an alkaline pH in all the mass water. Oxygenation condition inside reservoir is almost constant. According to the bathymetry, the mass balance displays a variation of properties which are seasonally controlled by hydrological events. High loads of elements were detected in solution during dry season (November 2015): sulfates present a load of 11,378.65 tons, confirming that main inlets in the reservoir are mine drainages. The Arsenic has a similar behavior: a greater load in solution during dry season, with 9.85 tons compared with other periods (less or equal to 0.5 tons). The greatest loads of iron and manganese are present in rainy season (20.43 and 9.15 tons respectively). This suggests the existence of a mobilization of precipitated minerals on the channel that feeds the mass water and reach the bottom of the reservoir where reducing conditions are dominant, favoring their release to the aqueous phase. Oxygen concentration decreases by half between the seasons due to organic matter oxidation. This trend continued in November, because quantities in solution were very high.

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### 1. Introduction

Mining and processing of sulphide ore generates great amounts of material which produce severe impacts on water resources. Metal sulphide deposits contain significant amounts of economically important metals such as: Au and Ag which can also be found as native elements; however, metals such as Cu, Ni, Zn, Pb are present<sup>1</sup>. Sulphide minerals are main sources of potentially toxic elements, including: As, Se, Cd, Sb and Hg and in some cases of acidity, being pyrite the main source. Abandoned mine works in this region generate leachates with high

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concentrations of solutes, mainly sulfates, about  $1,000 \text{ mg/L}^2$  and potentially toxic substances (PTS) in higher concentrations.

Balance of solutes produced through sulphides oxidation can be used to estimate rates of the processes and estimate a hydric balance<sup>3</sup>. Comparing this information with laboratory studies and the baseline, is possible to define the intensity of quality affectation. The dissolved constituents in natural waters are released through geochemical weathering facilitated by microbial processes<sup>3</sup>. PTS are transported in aqueous or particulate phase.

Affectations of mine drainages will be reflected in: high concentrations of metals and metalloids, pH (according mineralogy), and content of sulfates. This situation will be observed in the currents of rivers, streams, lakes, which are affected by mine drainage.

For the spatial and temporal variations of properties of source waters, regular monitoring programs are required to estimate the available volume considering drinkable water<sup>4</sup>. Monitoring water quality is a useful tool not only to assess the impacts of pollution sources but also to ensure efficient management of water resources<sup>5</sup>. This work focuses on the spatial and temporal description of the chemistry of a small reservoir ( $50,000 \text{ m}^3$ ) in Guanajuato city (Figure 1). The reservoir receives drainage of at least 5 abandoned mines, and there is a plan to expand the storage volume and use for population supply.

## 2. Material and methods

### 2.1 Sampling strategy

The study was developed during the period of December 2014 until November 2015 during four dates: December 2014 (I), February 2015 (II), September (III) and November (IV). Water samples were collected considering the effect of the reservoir geometry in the parameters to be measured. The different sampling points considered can be appreciated in Figure 1, the body of reservoir was divided by segments from 0-7, with 0 being in dam; sampling points are located in the changes of direction in the flow of the reservoir. At each point, samples were collected both at surface and depth to compare variations between oxic-anoxic environments.

### 2.2 Water sampling and analyses

Samples were collected in polyethylene high-density bottles previously washed with diluted nitric acid and rinsed three times with distilled water. Also, at the site bottles were rinsed three times with sampled water. Samples were filtered by Whatman No 4, and alkalinity was determined by volumetry with 0.1 N sulphuric acid. Sulphides,  $\text{Fe}^{2+}$ , and  $\text{Mn}^{2+}$  was quantified by spectrophotometry with a Hach DR-2800 equipment. A 50 ml aliquot of each sample was filtered with Millipore membranes of  $0.22 \mu\text{m}$  pore size and acidified ( $\text{pH} = 2$ ) with a drop of concentrated  $\text{HNO}_3$  for cation and arsenic analysis in Atomic Absorption.

### 2.3 Hydrodynamical model

To consider aspects as residence time and the mix of different mass water: storage volume and runoff divided in baseflow (with an important component of mine drainage) and storm runoff, the CE-QUAL W2<sup>6</sup> code was used. The adaptation of the code considers a rain-runoff model and the description of bathymetry. Figure 1 is a representation of the geometry of the reservoir.

## 3. Results and discussion

In Table 1 measured values are presented. Electric Conductivity (EC) shows higher values at the entrance of the dam as well as at depth, near the sediments, and is possible to detect a trend of decreasing of EC along the reservoir. Sulfates are present at greater concentration at the inlet and surface, while depth has very low values.

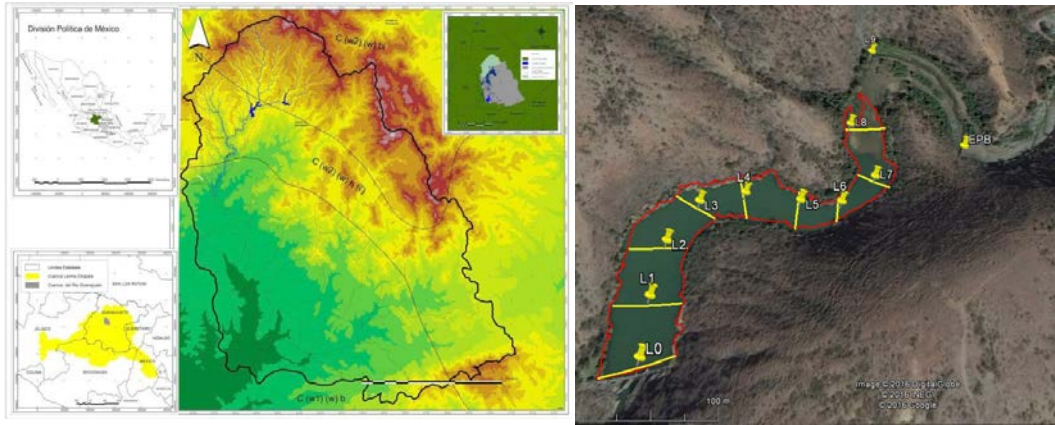


Figure 1. Location of study area.

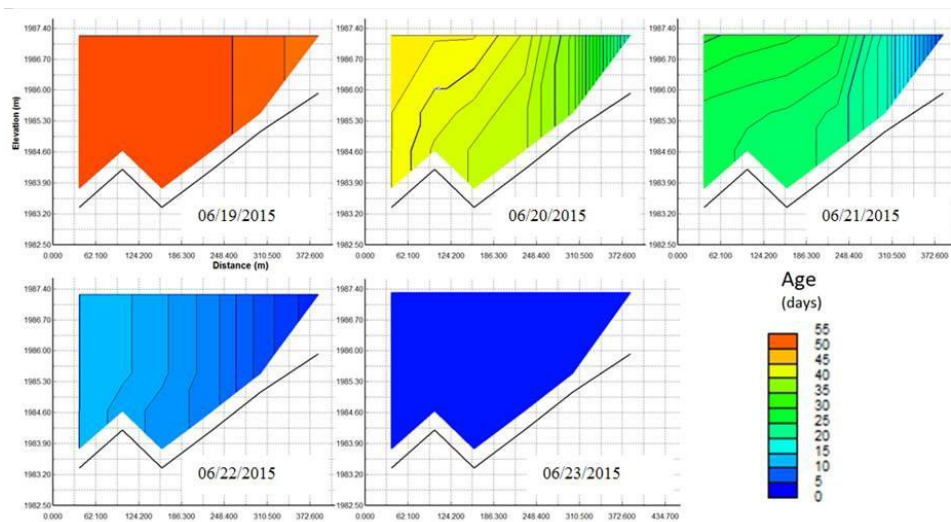


Figure 2. Representation of residence time of mass water inside the reservoir.

Table 1. Maximum permissible limits of parameters analyzed.

Analyzed parameters	Maximum Permissible Limit NOM-127 <sup>7</sup>	Average (maximum and minimum)	Standard Deviation	% samples exceeding the maximum permissible N=50
pH	6.5 - 8.5	8.56 (10.02-7.46)	0.592	30
Electric Conductivity	1200 $\mu$ S/cm	665 $\mu$ S/cm (940-360)	201.7	0
Fe	0.3 mg/L	1.68 mg/L (12.7-0)	2.97	35
Mn	0.15 mg/L	0.23 mg/L (2.1-0)	0.40	21.7
SO <sub>4</sub> <sup>2-</sup>	400 mg/L	219 mg/L (557.13-24)	135.63	7
NO <sub>3</sub> <sup>-</sup>	10 mg/L	7.3 mg/L (22-0)	7.15	27
S <sup>2-</sup>	0.05 mg/L	0.107 mg/L (0.980-0)	190.3	33.33
As	0.025 mg/L	0.008 mg/L (0.034-0)	9.5	8.3

Table 2. Mass balance of some parameters (in tonnes) according to the bathymetry of the reservoir and sampling periods.

	I (Dec 2014, N=19)	II (Feb 2015, N=9)	III (Sept 2015, N=11)	IV (Nov 2015, N=11)
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O <sub>2</sub>	306.12	311.21	159.16	151.12
Fe	11.65	3.70	20.43	9.84
Mn	2.49	5.53	9.15	3.50
SO <sub>4</sub>	9122.3	14430	1940.2	11378.65
As	0.52	0.37	0.23	9.85
Ca	4913.8	7188.12	7970.14	5997.53

Table 2 display a mass balance representation derived from measured values and bathymetry. Is possible to appreciate that oxygen diminishes by half (that means periods I and II have dissolved oxygen concentrations of 9.5 mg/L and decrease to 5 mg/L in periods III and IV). The reservoir has a considerable level of sediments and high organic matter content (10.6%-1.6% an average of 5.8%) and consumes dissolved oxygen.

These observations suggest that sulphate-reduction processes can be occurring. Fe and Mn was find at high concentrations at depth. Sulfates are present in greater concentration at the inlet and surface, while depth has very low values, this can be explained because under reducing conditions this species is transformed to sulphides, which is ratified with a high presence of sulfides in the bottom and practically null in surface. Nitrates are mostly presented in depth and are observed in a greater amount in rainy season. Arsenic is seen in higher concentrations at inlet and at depth, possible reason for this is its liberation from oxides that reduces at sediment conditions.

#### 4. Conclusions

Geochemical processes occurring in a water body are controlled by several factors which interact with each other. The study reservoir contains a relatively small mass of water, the presence of oxygen is high, with a relatively short residence time (60 days to hours, accord Figure 2). Although the oxygen reaches the sediments, it is consumed quickly by the organic matter and a reducing environment generates, which favors the mobility of As, Fe and Mn.

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