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Application of the Geochemical Fractionation of Metals in Sediments for Environmental Analysis of a Water Reservoir. Case Riogrande II (Antioquia - Colombia)

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Abstract

The geochemical fractionation of metals in soils and sediments corresponds to a technique to evaluate the levels of contamination and their probability of transfer to bodies of water and biota. For environmental studies in water reservoirs, the results of geochemical fractionation added to physicochemical analysis of water, can define the environmental conditions of metal release. This chapter briefly presents the concept and some fractionation techniques, with emphasis on the BCR methodology, in conjunction with other analyzes of water from the bottom of the reservoir to evaluate the dynamics of Mn mobilization in the Riogrande reservoir in Colombia, as example of practical application of Geochemical Fractionation. The highest proportions of Mn in the sediments of the Riogrande II reservoir were found in the exchangeable fraction and associated with carbonates, however the diffraction analysis did not find carbonated phases. It was concluded that the Mn in the water of the bottom of the Riogrande II reservoir originated especially by processes of desorption of Mn, in addition to reductive dissolution of oxyhydroxides.

Keywords: geochemical fractionation, sediments, BCR protocol, metal mobility, Mn dynamics in sediment-water interface

1. Introduction

The geochemical fractionation methodology allows establishing the proportions of groups, fractions or different forms of metals associated with materials such as soils, sediments and sludge, however it is necessary to combine these results with other analyzes such as mineralogical analysis, diffractometry, geoavailability, bioaccessibility and bioavailability analysis,

for a complete environmental study. In this chapter of the book “Fractionation”, an explanation is given for the concept of Geochemical Fractionation, its importance, the BCR methodology and its application to the release of metals such as Mn in sediments, applied to the Riogrande II Water Reservoir in Colombia.

2. The problem of water contamination in reservoirs by the release of heavy metals from sediments

2.1. Metals in sediments in water reservoirs and lakes

The sediments of the reservoirs, lakes and oceans reflect a recent environmental history, since they are geological records of climatic changes, geodynamic processes, land uses and especially human activity that positively or negatively impacted the environment. The sediments are characterized by the storage of important concentrations of heavy metals and xenobiotic substances due to their high adsorbent capacity, the product of a number of functional groups that allow them to form surface complexes. However, the potential for release and contamination of water from sediments depends on: total concentrations of all substances, environmental conditions of the bottom water (pH, ORP-Eh and organic matter) and forms in which metals are found in the sediments (metals fractions).

Metals have several physicochemical properties and especially different valences, which allows them to be found in different chemical forms or fractions in solid materials such as soil, sediments and mining mud. Some of these forms or geochemical forms are more available than others; so, their release and mobilization to an aqueous phase occurs with slight changes in pH, ORP-Eh [1], temperature and electrical conductivity. The water quality of a reservoir is affected by the presence of dissolved metals and by the conditions and mechanisms of release from the soil or sediments [2], and it has been found that the physicochemical and biological properties and conditions of water quality are affected by external factors such as topography, climate and especially human activity [3], this is how, in general, the most mobile metal form, such as the interchangeable form or fraction, are related to released metals by mining or industrial activity. The sediment is normally located in the lower layer of hypolimnion, where the anoxic and reducing conditions cause several soluble compounds to increase their concentration, especially in the interstitial water through dissolution or reduction and diffuse to the lower layer of water. Temperature as the factor of thermal stratification is an abiotic factor that controls important processes for organisms, likewise it affects the physicochemical properties and other abiotic factors [4, 5]. Within the geochemical fractions or metals forms, when particles settle in a reservoir, a large part of the metal is in an adsorbed form, however in the Hypolimnion, the strongly reducing conditions can dissolve the oxides and consequently release the metals towards the water column [6].

The anaerobic zones, and specifically the deep water masses of the lakes and lagoons, present physical and chemical properties completely different to the more superficial waters, in addition to the temperature. Two of the physicochemical parameters that define ecosystem conditions correspond to dissolved oxygen as to the redox potential, which as it deepens in the water column decreases and forms two profiles similar to the temperature, with their corresponding points of inflection: oxycline and redoxcline, which can occur both in the water

column, as in the water-sediment limit, however the abrupt decrease of the potential in the redoxcline is not due to the depletion of oxygen, but due to the appearance of reducing substances such as hydrogen sulfide (H_2S), [7]. In general, in sediments under anoxic conditions, oxidizable metals forms predominate (reduced species), associated with organic and residual matter, while reducible (oxides) and interchangeable metals forms tend to be unstable and are easily solubilized [8]. Metals have a differential behavior in lentic or semilentic bodies of water where epilimnion oxygen-rich conditions predominate. It forms oxidized species (reducible metal forms), which tend to be insoluble and precipitate forming a sediment rich in oxidized solid phases (M^{3+} or M^{4+}), likewise other minerals such as clays with their negative charge, transport on their surface metals, forming complexes of external surface, which can also be submerged in the reservoir. At the bottom of the hypolimnion and sediment, the anoxic and reducing conditions, as well as biological processes, release it in the form of reduced (M^{2+}), complex and soluble species, whose oxidation process is very sensitive to heterogeneous and homogeneous catalysis, and it is dependent on pH and dissolved oxygen. This process is accelerated by the presence of microbial catalysis through different stages; it has been found that in the sediment, the movement of ions such as Mn and Fe towards the water column may be coupled with an eventual and possible H_2S formation [9, 10].

The redox conditions can influence the behavior of the trace metals in sediments and affect the proportions of the metals forms, either directly or indirectly through changes in the oxidation states of the ligands capable of complexing the metal; for example, changes in the redox conditions can cause the reductive dissolution of mineral species that have some adsorbed metals (oxyhydroxides that can be reduced and desorb metal ions): ORP-Eh values higher than +414 mV are considered oxic and oxidizing, the probability of metal release is low; ORP-Eh values between +414 and +120 mV indicate sub-toxic, moderately reducing conditions, under these redox potentials the species are controlled by the redox reactions of Mn and Fe [11], ORP-Eh between +250 and +100 mV, the metal oxyhydroxides are unstable and the process of dissolution of most metal oxides begins, and ORP-Eh values lower than -120 mV, the sediment is considered anoxic [11, 12]. If the oxidized layer is less than 5 cm, it is considered that the sediment is dominated by Mn^{2+} flow, the difference with the standard value of reduction of Mn (+526 mV), it is because this value is referenced to a pH = 7.0 and T = 25°C, while a value of +414 mV is more appropriate under environmental conditions.

2.2. Release of heavy metals and water contamination

In natural systems, the release and mobilization of metals normally occurs through soluble phases; so, the evaluation of the contamination of a soil or sediment cannot be based on its total concentration of the metal, since the potentially contaminating from metals depends on the chemical form or geochemical fraction in which the metal is found. In addition, the dissolved metal cations are subject to several mobilization or fixation processes depending on factors such as pH, ORP-Eh, presence of both soluble and insoluble organic matter, and ionic strength [13, 14]. The release, mobility and toxicity of metals depends both on the proportions of them in the geochemical fractions and the environmental conditions at the bottom of a body of water (pH, ORP-Eh, DO, OM and EC), [15–20]. However, several authors have shown the co-precipitation of some metals in the form of complexes with solid fractions [21].

The present metals in the sediments of a reservoir can eventually contaminate the water, when the physicochemical conditions of the hypolimnion and the benthic zone can produce processes such as desorption, dissolution of carbonates and reductive dissolution of oxides (Especially oxyhydroxides of Mn and Fe), mobilizing and releasing these metals, and other adsorbed: As and Cd [22]. In addition, the Mn and Fe can be mobilized as a product of the dissolution of sulfides generating H_2S , a product of the reduction of mineral sulfides such as Pyrite FeS_2 [23], or can be immobilized either by adsorption to volatile sulfides in acids (AVS: soluble FeS + insoluble FeS) under conditions of sulfate reduction [24]. However, compared to Fe, adsorption of Mn is usually much lower in AVS [25]. In the environmental studies on metals in bodies of water, the topics of [26] are very important: the determination of the distribution and concentration of elements of environmental significance in the study area, the understanding the mobility of the elements through the different environmental systems and the identification of the relationships between the geochemical behavior of these elements and their impacts on biota.

Sediments act as sinks and sources of pollutants in aquatic systems due to their variable physical and chemical properties [27]. An important aspect when using soils and sediments as a record or indicator of metal contamination is to define the degree of enrichment, both natural and anthropic, according to the concentration of a contaminating metal. The sediment can be classified as contaminated or not, according to the proportion of metal concentration in relation to non-contaminated zones, according to its enrichment compared to threshold levels and according to sediment quality guidelines (SQC), [27, 28]. Among others, the Igeo Geoaccumulation Index, the FC Contamination Factor (FC) and the EF Enrichment Factor [29] are used. To determine the relative degree of contamination, comparisons are made with threshold concentrations of standard geological materials, such factors are commonly determined to characterize the magnitude of metal contamination in environmental samples [30]. However, one of the disadvantages of these systems of environmental soil evaluation is that they are based mainly on the total concentration and not on the geochemical fractions.

Contamination by heavy metals in the soil or sediment can represent risks for humans and the ecosystem through: direct ingestion or contact with contaminated soil, food chain (soil-plant-human or soil-plant-animal-human), consumption of contaminated soil water, decrease in the quality of food, reduction of land use capacity and problems of land tenure [31]. A metal reaches a body of water in various forms: mineral particle with potential to precipitate depending on the size and hydrological dynamics of the body of water, soluble free or forming complexes and adsorbed by solid phases; the soluble form can be rapidly adsorbed by other solid phases (interchangeable fraction) and is carried to the sediments when the soluble and insoluble metallic mineral phases pass from an oxic environment to an anoxic environment (precipitation or sedimentation), remaining under a complex series of biogeochemical processes [10, 32].

In the sediment, oxides, silicates, carbonates and organic matter are deposited more or less quickly. The organic matter being initially attacked in the sediments by bacteria, oxidizing it in its order with O_2 , NO_3^- , MnO_2 , $Fe(OH)_3$, SO_4^{2-} and finally CO_2 , transforming it into oxic water bodies, whose change of redox conditions occurs very close to the water-sediment limit. That gradient is usually referred to redoxcline. The redox potential measured in sediments is basically influenced by the microbial activity in its process of degradation of organic matter, which in turn

depends on the availability and concentration of oxidizing agents [33, 34, 35]. The microbial degradation of the organic matter in the sediments is the mechanism that causes the reducing conditions, when an oxidation of the organic debris takes place, generating in the interstitial waters and base of the water column a decrease of the ORP-Eh values, whose reducing conditions can release metals such as Fe and Mn, affecting the quality of water and its potential use [6, 36].

The distribution of metals in the geochemical fractions in sediments should not be interpreted as a historical record of sedimentation, due to redox remobilization processes and the action of organisms in the upper layers of the sediment. The reducing processes under the water-sediment limit produce and release chemical compounds such as CH_4 , NH_4^+ , H_2S , Fe^{2+} and Mn^{2+} , while the oxidation of the organic matter produces HCO_3^- and NH_4^+ , in this sense the abrupt decrease of dissolved oxygen is generated not only by the oxidation of organic matter but also by the oxidation of CH_4 , NH_4^+ and HS^- [37, 38]. The models of release and mobilization of metals in the redox limit establishes a sedimentation or continuous deposition of detritus and mineral compounds from a column of hydrogen peroxide, and a source of fresh oxidized material from the upper and outer part, when this particulate material sediment and find the redox limit (oxic-anoxic region), it is reduced to its divalent forms, thus producing a point source of soluble metal in the redox limit; as the soluble metals diffuse (turbulent diffusion or molecular diffusion), up and down its point source generates two concentration profiles: an upper profile belonging to the insoluble species, caused by the gravitational accumulation of oxygen-metal hydroxides (M^{2+}), which dissolve at the redox limit and a lower profile belonging to the soluble species caused by the reductive dissolution of the solid phases of the metal, and whose concentration is higher towards the redox limit, where the migration upwards it, produces oxidation and formation of new oxidized insoluble species (**Figure 1**).

There are two basic approaches for the determination of the distribution of metals in the sediments: the theoretical one based on thermodynamic calculations that has the problem of incomplete data, and the other one is the experimental that involves a separation of fractions using a procedure or extraction sequential scheme (ESS), such as Tesier, BCR or others, these methods allow identifying phases or forms to be measured from very available to very low available [39, 40].

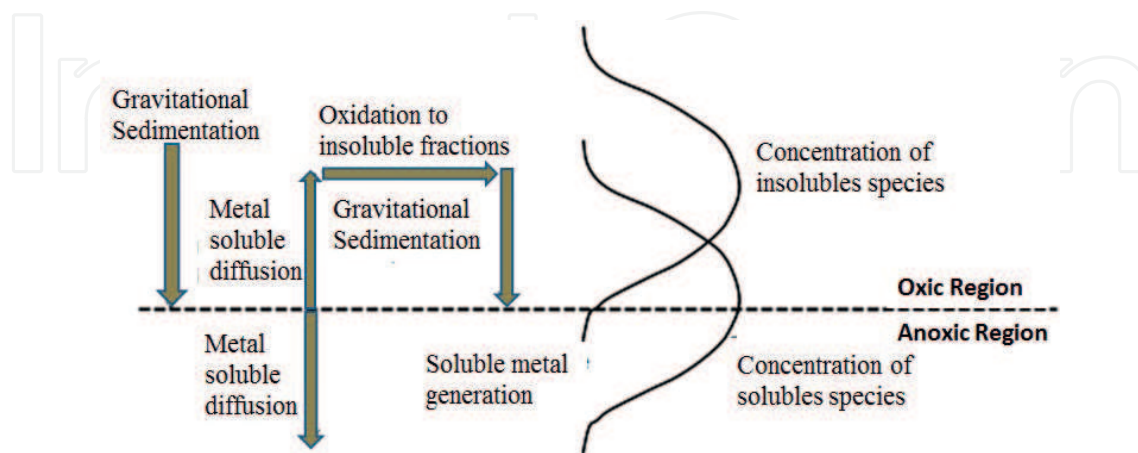


Figure 1. Conceptual model of the metals sensitive to redox processes (Mn and Fe), showing the profiles of the soluble and particulate forms. Source: adapted and modified [10].

3. Environmental study of water contamination and the advantages of the application of the geochemical fractionation methodology

3.1. Geochemical fractionation methodology

The geochemical fractionation is a laboratory process based on the application of selective chemical extractions, where the mobility of metals in soils and sediments is studied, imitating different environmental conditions or strong changes. This method or laboratory procedure is based on the rational use of a series of more or less selective reagents chosen to successively solubilize different mineralogical fractions that are believed to be responsible for retaining a large part of the trace elements [41]. Chemical extractions are used to evaluate operationally defined metal fractions, which may be related to particular chemical species, as well as to the potential mobility, bioavailability and ecotoxic phases of a sample, however, the results obtained by the extractions are dependent on the procedure applied [39, 42], so it is considered a very accurate approach to the environmental analysis of metal pollution in soils, sludges and sediments. Metals of anthropogenic origin are generally introduced into the environment as aqueous ions and inorganic complexes, which are easily adsorbed on suspended particles through weak chemical bonds to mineral grains and particles; these metals are predominantly belonging to the labile extractable fraction of the sediments [40].

In uncontaminated soils and sediments, trace metals occur mainly as relatively immobile species in silicates and primary minerals, as a result of weathering, a trace element fraction is gradually transferred to accessible forms for plants. In contaminated soils, the entrance of metals in almost all cases occurs in forms not associated with silicates. In the sediments, the situation is very similar, metallic species can exist in different forms [42]: in solution, ionic or colloidal, inorganic and organic complexes interchangeable, complexes where metals are strongly bound, insoluble mineral and organic phases and resistant secondary minerals. From a practical point of view, the geochemical fractionation of metals is achieved by sequential treatments that involve the use of chemical reagents, which are applied sequentially to a portion of the solid sample. The general applications of chemical extraction schemes are summarized in: characterization of pollution sources, evaluation of metal mobility and bioavailability and identification of metal link sites to evaluate the accumulation of metals, pollution and transport mechanisms.

In all the geochemical fractionation schemes, the extractants are applied in order to increase the reactivity to the successive fractions corresponding to forms with decreasing mobilities, most of the schemes or extraction sequences recommend the decomposition of the organic matter before the liberation of the subsequent metallic fractions [43]. Although sequential extractions are not specific to extracting the bound element from the solid fraction, they provide comparative information on metal mobility under changing environmental conditions, thus, the use of this approach can help to understand the relative contribution of metal sources and help in the prediction of trace element mobility [44]. Several extraction schemes have been designed for the determination of the forms of metals in soils and sediments, although with their limitations, sequential extraction is widely used to assess the relative importance of the

different chemical forms that may be present in soils and sediments. However, the reagents used, the times and fractions extracted depend on the objectives set out in the research projects. The geochemical fractionation protocols present a common methodology based on the successive exposure of a solid sample to extractant solutions of increasing strength and/or of different characteristics. The chemical reagents are classified according to their mode of action [45]: concentrated inert electrolytes, weak acid, reducing agents, complexing agents, oxidizing agents and strong acids.

The sequential extraction schemes seek to solubilize the following fractions (**Figure 2**):

Exchangeable fraction: the metals in this fraction are bound to sediments or soil by weak adsorption in the particles, they are species bound by weak interactions of electrostatic type and released by ion exchange processes. Changes in the ionic strength of the interstitial water affects adsorption-desorption or ion exchange processes result in the release of metals at the sediment-water, soil-water interface.

Fraction bound to carbonates: metals bound to carbonates are sensitive to changes in pH, the increase in acidity liberates metal cations, achieving the release of the metal through the dissolution of a fraction of solid material. The metal fraction recovered in the acid soluble phase is co-precipitated with carbonates, and specifically adsorbed at some sites on the surface of the clays, organic matter and oxyhydroxides of Fe-Mn.

Fraction linked to oxides of Fe-Mn or reducible fraction: metals bound to oxides are unstable under reducing conditions, these conditions result in the release of metal ions. The oxides of Mn and Fe are excellent “sweepers” of metals.

Fraction linked to organic matter or oxidizable fraction: the degradation of organic matter under oxidizing conditions can release soluble metals bound to these materials. Trace elements can be incorporated in many forms to organic matter, including living organisms, organic layers on inorganic particles and biological detritus. In sediments and soils, the organic content comprises humic substances and to a lesser degree proteins, carbohydrates, peptides, amino acids and resins, whose organic material tends to be degraded under oxidizing conditions, allowing the release of the sorbed metals.

Residual fraction: this fraction contains minerals, which may contain metals in their crystalline networks. Primary and secondary minerals contain metals in their crystalline structures, constituting the total of this fraction.

In general, the exchangeable fraction corresponds to the way in which the metal is more available for consumption by the plants and that can be released with simply changes in the ionic strength of the medium [46]. The content of metals bound to carbonates is sensitive to changes in pH and becomes mobile when the pH decreases. The fraction of metals bound to oxyhydroxides can be mobilized with the increase or reduction of oxidizing conditions in the environment; finally, the fraction associated with the residual fraction can be mobilized only as a result of long-term weathering [43]. The different schemes for the extraction of metals during geochemical fractionation are based on sequences ranging from three to five or more steps.

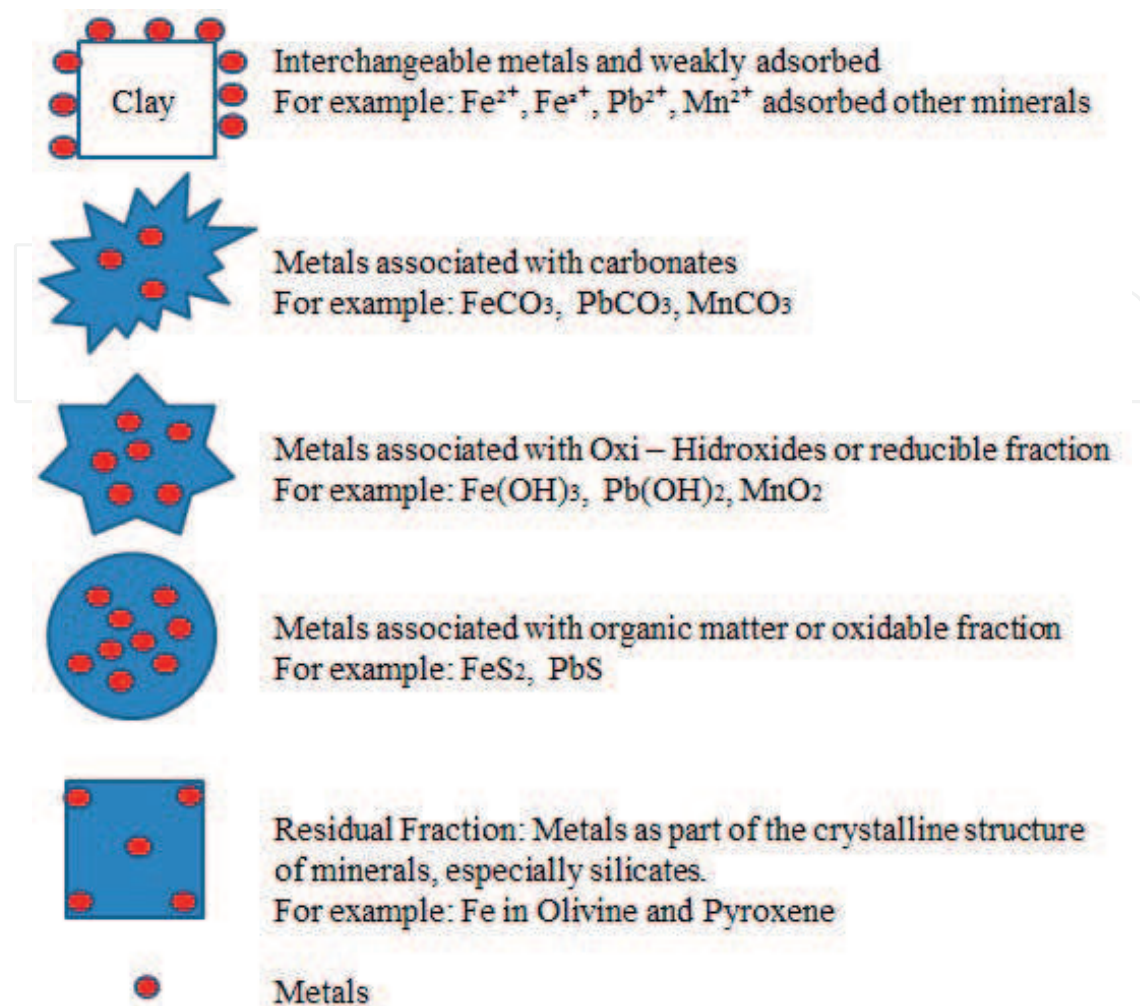


Figure 2. Metals forms or geochemical fractions of metals in sediments, soils or sludges.

3.2. The role of geochemical fractionation and the BCR methodology

The importance of geochemical fractionation or metals forms is not only to determine the groups in which metals are distributed in a soil or sediment, the most important thing is to be able to relate these results to the chemical conditions of the bottom water of a reservoir and the water of pore, and its variations in time (pH, EC, ORP-Eh and organic matter), and thus be able to infer when or under what conditions can begin to release metals. Among the established and well-known extraction schemes for metal extraction are:

3.2.1. Methodology of Tessier

It corresponds to one of the initial methodologies to establish the fractions of metals, developed in the year 1979 [47]. It determines five fractions of metals in matrices such as soils and sediments: Fraction 1: soluble in water and interchangeable, Fraction 2: associated with carbonates, Fraction 3: linked to oxides of Fe and Mn, Fraction 4: linked to organic matter and Fraction 5: residual, linked to complex oxides and silicates.

3.2.2. Methodology of bloom (emphasis on the extraction of non-volatile mercury fractions)

This methodology is very applied to mining and industrial sludge where Hg is one of the main pollutants, also determines five fractions, but with some differences: F1: soluble in water (Hg-w), F2: interchangeable (soluble in stomach acid Hg-I), F3: chelated organ (Hg-O), F4: elemental mercury (Hg-E) and F5: mercury sulfide (Hg-s) [48].

3.2.3. BCR methodology

Developed by the European Community, with the Measurement and Testing Program (BCR) [44], where several authors have defined the following fractions as the most important [40]. The BCR geochemical fractionation (European Community Reference Office—BCR), in order to determine the concentrations of metals according to their availability: BCR1: interchangeable metal, adsorbed and bound to carbonates, BCR2: metal reducible or associated with oxides, BCR3: metal associated with organic matter and sulfides and residual: mineral in silicates and other mineral phases [49].

The applied protocol in BCR Methodology [50] is:

- **Interchangeable fraction and soluble in acid, BCR1:** to 1 g of dry sediment is added 40 ml of 0.11 M acetic acid, it is stirred at 400 rpm, for 16 h. Centrifuge for 20 min at 3600 rpm, collect the supernatant for reading in AA or by ICP. The sediment is then washed with distilled water, stirring the sample with 20 ml, centrifuging 20 min at 3600 rpm, discarding the supernatant.
- **Reducible fraction, BCR2:** to the remaining sediment of the BCR1 extraction, 40 ml of 0.5 M hydroxylamine (pH = 1.5) is added, it is stirred at 400 rpm, for 16 h. It is then centrifuged 20 min at 3600 rpm, the supernatant is collected for reading in AA or by ICP. The sediment is washed with distilled water, stirring the sample with 20 ml, centrifuging 20 min at 3600 rpm, discarding supernatant.
- **Oxidizable fraction, BCR3:** to the remaining sediment of the BCR2 extraction, initially 10 ml of 8.8 M hydrogen peroxide is added, it is heated in water to 85° C for 1 h, and it is left to cool. The operation is repeated until all the organic matter is oxidized. About 50 ml of 1 M ammonium acetate is added at pH = 2.0, stirring at 400 rpm, for 16 h. Centrifuge for 20 min at 3600 rpm, collect the supernatant for reading in AA or by ICP. The sediment is washed with distilled water, stirring the sample with 20 ml, centrifuging 20 min at 3600 rpm, discarding the supernatant.
- **Residual metal:** the metallic fraction associated with the sediment after washing is considered the residual extracted with the mixture of hydrochloric acid (HCl) and nitric acid (HNO₃) in a ratio of 1:3.

The two reasons why the latter methodology was selected for the study of the mobility of Mn in the Riogrande II reservoir were the simplicity in the fractions with respect to the Tessier methodology and the existence of reference materials.

3.3. The complete environmental study for the metals in water reservoir

When the potential for water contamination is to be evaluated, based on the geochemical fractionation data of the sediments, the following analyzes are also included for the complete environmental study for the metals in water reservoir:

- Spatial time variations of the factors: pH, redox potential, electric conductivity, dissolved oxygen and temperature both in the bottom water and in the interstitial water.
- Proportions of organic matter, texture and mineralogy of the sediments using various techniques to associate mineral phases with the metals found in the fractionation.
- Experimental tests in columns with the sediments and the background water, making them vary in time especially in the pH and dissolved oxygen factors (modifying them), and evaluating the behavior of the metals in the water column.
- Analysis of soluble metals at least 50 cm above the water sediment limit and 1 m below that limit considering sampling points at least every 2 cm.
- Analysis of diffractometry with scanning electron microscopy, in order to verify the mineral phases predicted in the geochemical fractionation.

However, since a few years ago, the following three analyzes are being emphasized to assess the contamination of a metal in a soil, sediment or body of water: available fraction (corresponds especially to the BCR1 + BCR2 fractions, the extraction of the available phase is a simple extraction and can be done with: HCL 1 N-CH₃COOH 0.11 M-Na₂EDTA 0.05 M-CaCl₂ 0.01 M-NH₄NO₃ 0.1 M-Ca (NO₃)₂ 0.1 M [28, 51, 52]), bioaccessible fraction (corresponds to the fraction of the substance that once released enters an organism via ingestion, inhalation or dermal contact [53, 54], the extraction of this fraction is also simple and is generally done with: acidified 0.4 M glycine (pH = 1.5) and it is then neutralized (pH = 7.0) that would correspond to the gastric and intestinal fluid [55, 56]) and bioavailable fraction (fraction that is accumulated in vegetable and/or animal tissues [51, 52]).

4. Case study: application of geochemical fractionation in the Colombian reservoir

4.1. The Riogrande II reservoir (Antioquia-Colombia), its location and other related information

In the Riogrande II reservoir (Antioquia-Colombia) there have been concentrations of Mn that eventually affected negatively the quality of the water resource, especially due to color effects, prior to the treatment in the potabilization plant that supplies water to the city of Medellin (Colombia). In order to implement the necessary controls, it was necessary to know and analyze the geochemical dynamics of Mn from the geochemical fractionation, its relations with the physicochemical conditions of the reservoir and finally determine the conditions of

release from the sediment. The Riogrande II reservoir (6° 32.62 N, 75° 27.27 W) is located in the jurisdiction of the municipalities of Don Matías, San Pedro, Belmira, Santa Rosa de Osos and Entreríos to the North of the city of Medellín (Department of Antioquia—Colombia) [57].

4.2. Mn in the sediments of this reservoir and its significance

In natural and artificial water bodies, such as reservoirs, sediments are important in water quality, since changes in redox conditions can dissolve oxy- hydroxides of Mn and Fe, mobilizing and releasing these metals [22]. The manganese is the third element of the most abundant transition metals in the earth's crust [58], as a transition metal it gives an important behavior at the level of oxide-reduction, and it facilitates the formation of complexes, being one of the most abundant elements of the earth's crust. It is found in the ground, sediments, rocks, water and in biological products; at least a hundred minerals contain it [59]. Mn is a metal that is very sensitive to redox changes in soils and natural waters. In humid soil conditions, Mn tends to be in its reduced and mobile form. It is well-known that the concentrations of soluble forms of Mn undergo strong changes in the depth of water columns where oxygen depletion occurs, which is strongly associated to the oxidation of organic matter in sediments; therefore, organic matter plays a very important role in the control and distribution of Mn^{2+} in the interstitial water; either, as an adsorbent or as a complexing ligand [60–62].

The behavior of Mn is influenced by the acidification of the medium, with an inverse correlation between the concentrations of Mn^{2+} and the pH values. Some bodies of water with pH values ≥ 6.0 , act as sinks of Mn, while smaller values act as a source of Mn. This behavior is possibly controlled by dissolution processes of species such as Mn^{4+} and Mn^{3+} , the oxidation kinetics of Mn and the equilibrium of ion exchange [63]. Both the humic fraction and the concentrations of metal adsorbed to insoluble phases decrease as the pH decreases [64, 65]. The Mn^{2+} ion released at the bottom, forms organic complexes or the hexaquous ion $\text{Mn}(\text{H}_2\text{O})_6^{2+}$ that is very stable. When the redox conditions are adequate, a precipitate of MnO_2 (Pyrolusite) is formed; it forms incrustations even at concentrations of 0.02 mg L^{-1} . The environmental problem of Mn in reservoirs has been correlated with thermal and chemical stratification, since some bacteria use Mn^{4+} as an oxidizing agent of organic matter in its metabolic processes, reducing it to Mn^{2+} and releasing it to the water column. It has even been considered that oxide-reducing bacteria of Fe also act on manganese [66].

4.3. Application of the BCR methodology, results, discussion and conclusions

The application of BCR geochemical fractioning of Mn in the Riogrande II reservoir is presented, starting from the design of research, applied methodology, results, discussion and analysis, finally arriving at the proposed model of Mn entrance to the reservoir, the distribution of its forms in the sediment and release mechanisms towards the water column.

4.3.1. Used methodology

A sediment sampling was carried out in two different months (March and June 2008), in seven stations within the reservoir, using the Ekkman dredger and through AA, the total Mn

was determined. For the geochemical fractions, the BCR methodology was applied. The sampled stations were characterized by: E1. Rio Chico entrance: station located at the entrance of the Chico River in the reservoir, in the extreme west, depth of sampling 13 m., E2. Middle Riochico: located in the middle part of the Chico River, depth of sampling 27 m., E3. Rio Grande entrance: located at the entrance of Rio Grande, depth of sampling 12 m., E4. Middle Rio Grande: located in the middle part of Rio Grande, similar to the E2 by the amplitude of the reservoir, depth of sampling 35 m., E5. Las Animas river mouth: located at the entrance of Las Animas Creek, depth of sampling 11 m., E6. Intake Tower: located in the reservoir dam site, its importance is that in this site the water is captured by the treatment plant, depth 18 m. and E7. Dam Zone: it was located in the dam area, depth of sampling 42 m. After taking the sediment, the analyzes were carried out *in situ* by introducing the electrodes into the sediment-water mixture of factors such as: pH, dissolved oxygen, redox potential and electrical conductivity. After reading the interstitial water variables, the sediment-water mixtures of each sampled station were packed in vacuum polypropylene bags and immediately preserved in cold temperature until their arrival to the laboratory, where they were stored in the refrigerator until further analysis of Mn [67].

The analyzed factors for the water matrix (bottom hypolimnion and interstitial) were pH, dissolved oxygen, ORP-Eh potential and electrical conductivity, and in the sediment the percentage of organic matter (%OM). For the dependent variables in the sediment, were analyzed: total Mn, the Mn fractions according to the BCR protocol (interchangeable Mn and associated with carbonates, Mn associated with oxides, Mn associated with organic matter and sulfides), and the residual fraction (Mn associated with silicates). Finally, the identification of the possible mineral phases associated with Mn in some of the sediment samples was carried out by means of the analysis of X-ray diffractometry coupled to scanning electron microscopy (XRD-SEM). To the water samples of the bottom hypolimnion and interstitial water were measured pH and temperature with the WTW-model 330 equipment with a glass electrode, the electrical conductivity with the WTW-model 720 conductivity meter, the ORP-Eh potential with the WTW-model 330 equipment with a platinum electrode and dissolved oxygen with WTW brand oximeter with Cellox® cell. The organic matter (% OM) of the sediment was determined in the same way as for the soil, through the volumetric method of Black and Wlakley.

For total Mn and BCR fractions, the sediment brought from the reservoir was dried at environmental conditions for 1 week; for the total Mn, to 1 g of the dry sediment, a mixture of hydrochloric acid (HCl) and nitric acid (HNO₃) was added in a 1:3 ratio for the extraction, following the ISO 11466 protocol. The interchangeable fraction and soluble in carbonate (Mn)-BCR1) was obtained by stirring 1 g of dry sediment for 16 h with 40 ml of 0.11 M acetic acid at 400 rpm and then centrifuged, and then the supernatant was filtered, the reducible fraction (Mn-BCR2) was obtained by stirring the previous residual sediment for 16 h with 40 ml of 0.5 M hydroxylamine chloride, acidified to pH 1.5 with nitric acid, stirred at 400 rpm and subsequent centrifugation, extraction and filtration of the supernatant, for the oxidable fraction (Mn-BCR3) Initially double oxidation was performed with 20 ml of 0.88 M hydrogen peroxide for 2 h, and then agitation of the remaining sediment with 40 ml of 1 M ammonium acetate for 16 h and centrifugation, extraction and filtration of the supernatant, and finally for

the remaining residual sediment fraction, it was treated with a mixture of hydrochloric acid (HCl) and nitric acid (HNO₃) in a ratio of 1:3.

The readings for the total Mn as well as for the fractions were carried out by Atomic Absorption in a GBC Plus equipment, the detection limit (LD) was 0.01 mg L⁻¹ and the limit of quantification was 0.05 mg L⁻¹. All analyzes were performed by duplicate. As a decision rule, the efficiency of the geochemical fractionation for each sediment sample was calculated by using the percentage of recovery (% Recovery), which relates the total metal and the resultant of the sum of the fractions BCR1, BCR2, BCR3 and residual (Res), the optimal condition establishes that there should not be more than ±10% in the difference of both concentrations (100 ± 10%, [68]), this range is considered a quality standard of the extraction process.

The averages, standard deviations and the level of variability were determined by the coefficient of variation, both for the total Mn dependent variables and the Mn fractions (BCR1, BCR2, BCR3 and residual) and for the independent variables: pH, redox potential, electrical conductivity, dissolved oxygen and organic matter. To evaluate the hypothesis, the analysis of components of variance was initially started in order to determine the factors (sampling time and station) that contributed to the Mn (total and fractions), afterwards a Pearson multiple correlation was made ($p < 0.05$), to establish the physicochemical factors that have a statistically significant correlation with the response variables, moving on to an analysis of variance between the values of Mn (total, BCR1 and BCR2) and the factors: sampling, station and the physicochemical conditions of the bottom hypolimnion water and sediment ($p < 0.05$). Before proceeding with the calculations, the assumptions of the parametric statistics were corroborated, for this vector was evaluated in the matrix of the following dependent variables (Mn-Total, Mn-BCR1 and Mn-BCR2), normality was evaluated with the Shapiro Wilks (SW) Test and homoscedasticity with Bartlett's Contrast Value (β). Statistical calculations were performed in the Statgraphics Centurion XVI program with significance 0.05.

4.3.2. Results of the geochemical fractionation

The results of the total Mn (mg kg⁻¹) are summarized in **Table 1**.

Value (mg kg ⁻¹)		Location	Sampling period
Max	651,25	E1	Rainy (March 2008)
Min.	121,17	E2	
Average	407,04 ± 194,7 VC = 47,83 %	For the 7 stations	
Max	520,50	E3	Dry (June 2008)
Min	183,50	E2	
Average	334,50 ± 122,1 VC = 36,50%	For the 7 stations	
Variation between both sampling periods		In the dry period, the concentration of Total Mn was reduced by 17.82% with respect to the rainy period. However according to the CV, the difference is not significant.	

CV: coefficient of variation

Table 1. Synthesis of results of the Total Mn for the geochemical fractionation.

For both samplings, the results showed the highest concentrations in the two main entrances to the reservoir: E1 and E3, while in the middle of the Riochico, it had the lowest concentrations; when comparing these values against the considered threshold value (400 mg kg^{-1} [69]), it was found that stations E1, E3 and E4 (Middle of Rio Grande), had at least the threshold value. There were practically no significant differences between the two sampling periods. At the level of the BCR1 geochemical fraction, the results were summarized in **Table 2**.

Value (mg kg ⁻¹)		Location	Sampling period
Max	336,11	E1	Rainy (March 2008)
Min	109,78	E2	
Average	236,72 ± 79,9 VC = 33,77 %	For the 7 stations	
Max	335,94	E3	Dry (June 2008)
Min	100,00	E7	
Average	226,4 ± 91,7 VC = 40,5 %	For the 7 stations	
Variation between both sampling periods	In the dry period, the concentration of Mn-BCR1 was reduced by 4.36% compared to the rainy period. However according to the CV, the difference is not significant		

CV: coefficient of variation

Table 2. Synthesis of Mn-BCR1 results.

Similar to the Total Mn, the highest concentrations were found at the entrances to the reservoir (E1 and E3), in none of the stations and climatic periods, the threshold of 400 mg kg^{-1} was exceeded. There were practically no significant differences between the two sampling periods. At the level of the BCR2 geochemical fraction, the results were summarized in **Table 3**.

Value (mg kg ⁻¹)		Location	Sampling period
Max	79,86	E1	Rainy (March 2008)
Min	0,79	E7	
Average	30,17 = 29,5 VC = 97,68 %	For the 7 stations	
Max	68,74	E1	Dry (June 2008)
Min	12,20	E2	
Average	42,8 = 19,5 VC = 45,5 %	For the 7 stations	
Variation between both sampling periods		In the dry period the concentration of Mn-BCR2 was increased by 41.86% with respect to the rainy period. However according to your CV, the difference is not significant	

CV: coefficient of variation

Table 3. Synthesis of Mn-BCR2 results.

The reducible geochemical fraction Mn-BCR2 did not exceed 80 mg kg⁻¹, unlike the total Mn and Mn-BCR1, this fraction increased in the dry period with respect to the rainy period, but not significantly. The whole analysis of the shown fractions as a proportion, indicated a predominance of Mn in the BCR1 and BCR2 fractions, with respect to the Mn of BCR3 and residual; however, comparing both sampling times, the proportions in the dry period in stations E1, E2, E3, E4, E5 and E6 (Rio Chico, Rio Grande and Las Animas, Intake tower), exceeded the concentrations of the rainy period (Figure 3).

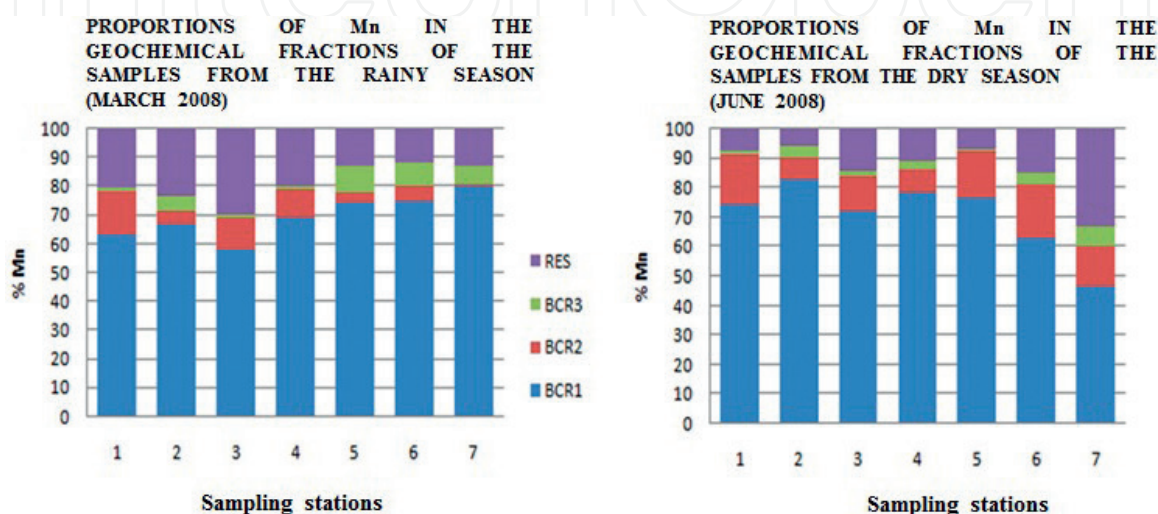


Figure 3. Proportions of the fractions of Mn in two sampling periods in seven stations. Note that the available fractions BCR1 Mn and BCR2 Mn, exceed 60% of the total Mn.

BCR1: co-precipitated, interchangeable and associated with carbonates Mn.

BCR2: reducible (associated with oxyhydroxides) Mn.

BCR3: oxidizable (Associated with sulfides and insoluble organic matter) Mn.

Res: associated with the residual fraction (silicates) Mn.

Finally, establishing the proportion of available Mn as the ratio between the sum of the BCR1 and BCR2 fractions and the Total Mn. It was found that more than 80% of the Mn of the sediment was available in the stations: E1 (Rio Chico entrance), E4 (Middle of Rio Grande), E5 (Las Animas) and E6 (Intake tower) for the dry period and E2 (Middle of Rio Chico) for the rainy period. The recovery percentage for the fractionation produced values between 80 and 90%, and indicated that the sequential extraction scheme could not solubilize the whole Mn, it was probably due to the formation of very stable organo-metallic compounds, especially in the samples taken during the rainy period. Likewise, the E2 sample (Middle of Rio Chico) presented a recovery of 135%, and could be associated with contamination during the extraction process.

4.3.3. Results-physicochemical analysis of sediment and bottom water

The results of the physicochemical analysis of two types of water in the bottom of the reservoir were compared: bottom hypolimnion water and interstitial waters (sediment water and pore water). This comparison was carried out with the purpose of identifying the changes in geochemical conditions between the water on the sediment (bottom hypolimnion) and the water under the water-sediment limit (interstitial water) and its relation with the results of total Mn and Mn in the fractions.

The results indicated an oxic bottom hypolimnion and sub-toxic interstitial water (sediment water) during the rainy period, the redox potential was more variable in the waters of the bottom hypolimnion where positive and negative redox potentials were present, compared to the same potential in interstitial waters, where the records always showed negative potentials (-128.4 mV in the rainy period and -120.3 mV in the dry period); for the sediment, the organic matter had values between 25.01% in the rainy period and 24.5% in the dry period, neutral pH in the water of the bottom hypolimnion, and more acid for the interstitial waters. The fractionation showed that more than 50% of the Mn in the sediments is present in available form (69% in the rainy period and 79% in the dry period), probably co-precipitated and adsorbed in the organic matter.

pH: the pH of both types of water (bottom hypolimnion and interstitial), presents values close to neutrality; however, while the waters of the bottom hypolimnion is practically neutral; the interstitial waters were more acidic in the rainy period.

Redox potential-Eh: the waters of the bottom hypolimnion changed significantly from positive redox potentials in the rainy period to negative values in the dry period, but always remained under reducing conditions with a maximum of $+82.5$ mV. In general, the water of the bottom hypolimnion of Riogrande II reservoir can be considered as a reducing agent, despite having positive redox potentials, and the interstitial or sediment waters can be considered as strongly reducing agent.

Dissolved oxygen (DO): in terms of dissolved oxygen, the waters of the bottom hypolimnion, maintained both oxic and hypoxic concentrations, while the sediment waters remained hypoxic. The dissolved oxygen presented a different behavior between the waters of the bottom hypolimnion and the interstitial waters. The decrease in dissolved oxygen, both in the water of the bottom hypolimnion and in the interstitial water for the dry period could be associated with a higher concentration of soluble organic matter.

Electrical conductivity (EC): first, when analyzing the values, it is found that the electrical conductivity is almost 9 times higher than the values of the hypolimnion of the bottom with respect to the interstitial waters; then, the conductivity values do not show significant variability depending on the time of sampling.

Organic matter (% OM): in the month of the rainy period, the average value in the stations was $25.01 \pm 3.9\%$ of organic matter, with a CV of 3.9%, the highest proportion was found in the

sediment of E2 with 32.28% and the minimum in E5 with 21.01%; for the dry period, the value was similar with $24.05 \pm 2.9\%$, and a CV of 12%. From the rainy period to the dry period, it was increased the % of organic matter, at stations E4 (Middle of Rio Grande), E6 (Intake Tower) and E7 (Dam Zone).

4.3.4. Results of the EDX-SEM analysis

Sediment samples taken during the rainy period were analyzed; the results showed that in the E2 station the Mn is associated with particles of Pb and calcium carbonate (**Figure 4**), in station E4 there were Zn sulfide (Characteristic of reducing conditions) and in the associated diffractogram, besides the Zn, Mn is associated with Fe within a matrix that is composed of Si, Al, C and O, probably associated with aluminosilicates and carbonates; in E6 the sample did not present evidence of Mn, only Ti within a matrix of aluminosilicates. Finally, the E7 sample shows some mineral phases associated with Mn carbonates, free spherical forms (less than $1 \mu\text{m}$), and carbonates associated with Pb that are abundant in the sediments of this station (**Figure 5**).

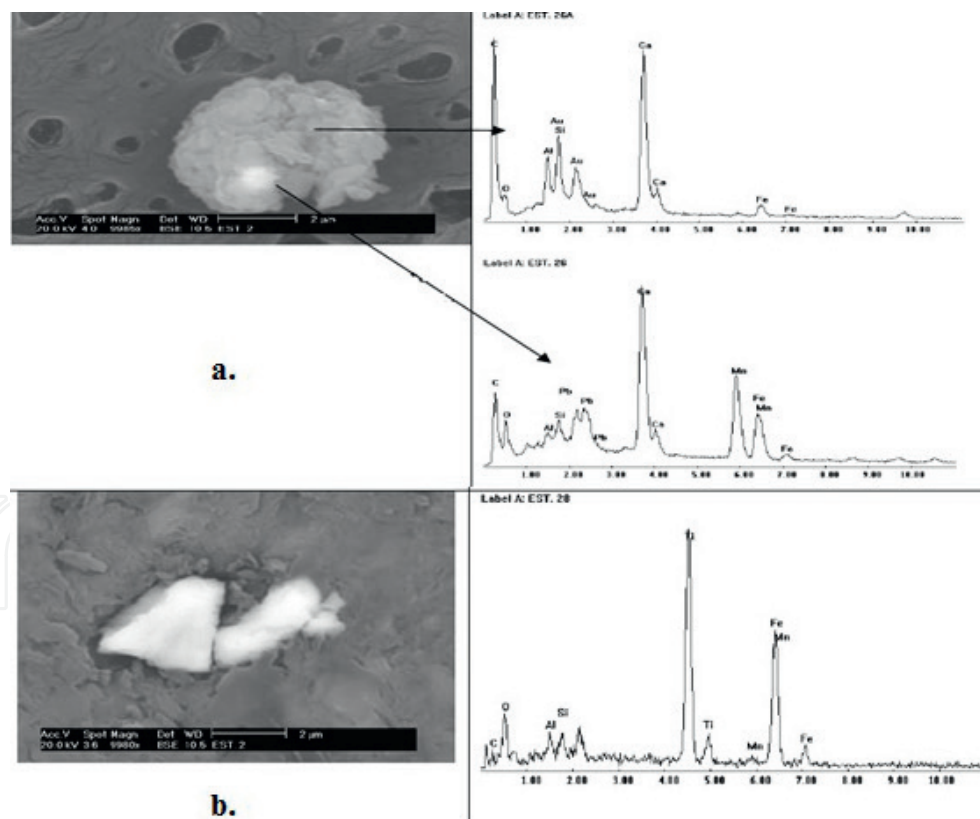


Figure 4. Image and diffractograms of the sediment in E2, observed in (a), a clear point corresponding to Pb associated with Mn and calcium carbonate, the gray part of the particle is mainly calcium carbonate. In the image (b) there are particles containing Mn associated with Ti.

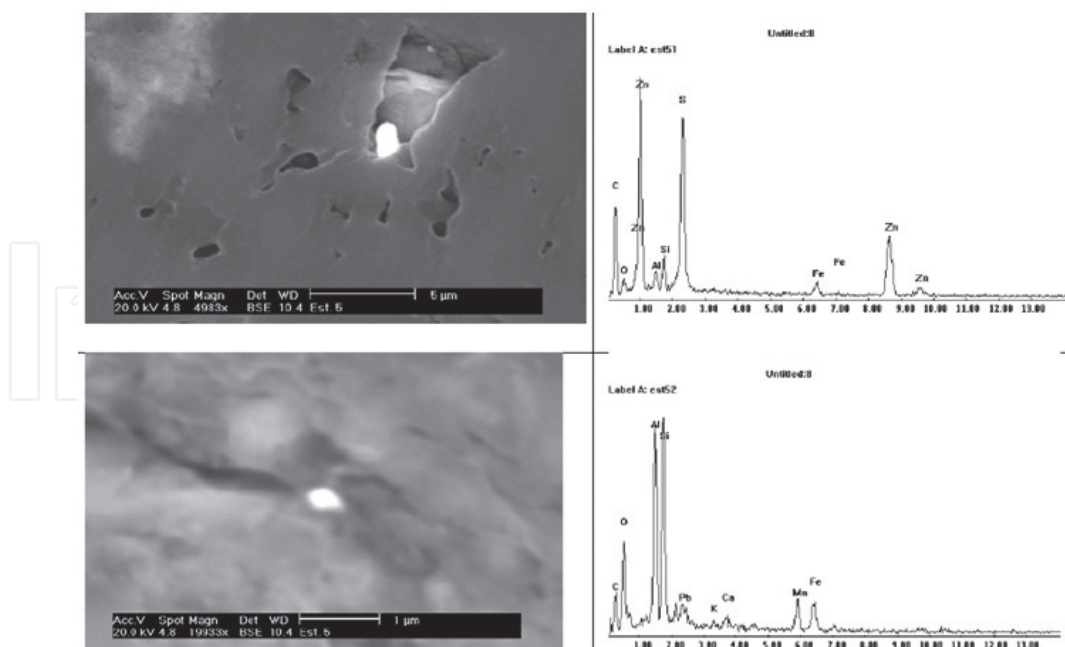


Figure 5. Images and diffractograms of the sample in E7, the particle in the image above corresponds to Pb carbonate and Mn carbonate, the diffractograms showed signal for Mn.

4.3.5. Discussion and analysis of results

- Of the geochemical fractionation and its relation with the physicochemical conditions of the bottom water and interstitial water

The entries of the Chico and Rio Grande Rivers (E1 and E3), correspond to the tributaries in which the highest concentrations of Mn reached the sediment of the reservoir, and although statistically it was not significant, there was a greater contribution at the time of rains, possibly due to an increase in the soluble and bottom charge of both streams. Conditions associated with the dry weather period could be the reason that the available fractions of Mn (MnBCR1—Interchangeable Metal and Carbonate Associated and MnBCR2—Oxyhydroxides) have been higher compared to the rainy period, possibly associated with the decrease in the redox potential during the dry period, especially in the water of the bottom hypolimnion, and could be associated with the decrease in the flow rate and a decrease in dissolved oxygen, however statistically it was not significant. The low values of redox potential, both in the bottom hypolimnion (less than 100 mV) and in the sediments (up to -150 mV), shows that in this anoxic-reducing environment, it would be changing from a post-oxic zone in the bottom hypolimnion to a sulfidic zone in the sediments [60], where Mn^{2+} , Fe^{2+} and NH_4^+ occur due to the presence of Zn sulfide in the sediments; the probability of finding oxides of Mn in this environment is minimal and the Mn found is in a reduced form, complexed and adsorbed to other mineral phases. However, no pyrite was found in the EDX-SEM analyzes, which could mean that the presence of HS- and H_2S necessary for the formation of this mineral, is below 10 cm.

- Possible causes of the release of Mn and its remobilization to the water column

One of the possible causes of the release and remobilization of Mn in the sediments of the Riogrande II reservoir were the highly reducing conditions of the sediments generated by microbial oxidation and the decrease in pH. These conditions reduce the phases of oxidized metal, releasing Mn^{2+} among other ions, which are solubilized and complexed with soluble organic matter such as fulvic acids [59]. The strongly reducing conditions in the interstitial waters remained practically the same for both sampling periods (-120 mV), and as for the pH, it went from acidic conditions (5.4) in the rainy period to almost neutral (6.7) in the dry period; however for the bottom hypolimnion waters, if there was a significant reduction in the redox potential in the dry period, without significant changes in the pH, which could suggest that the change from reducing to strongly reducing conditions in the bottom hypolimnion facilitates the remobilization of metals such as Mn.

The release of metals from the sediment of the water column may be due to processes such as the desorption and formation of soluble organic complexes, associated with the decomposition of organic matter [70], processes such as dissolution reductive metal oxides are possibly the cause of the release and mobility of Mn in the water sediment interface of the Riogrande II reservoir; however, it should be considered that the process of reducing the oxides of Mn is at the highest level in the column of water over the limit water-sediment [71]. One of the characteristics of the sediment found in the reservoir is the continuous presence of sulfides as demonstrated by the EDX-SEM analysis, it indicates strongly reducing sediment conditions during sampling; however, the presence of some carbonates in stations such as E2 (Middle of Riochico), E3 (Rio Grande Entrance) and E7 (Dam area), added to the pH values in interstitial waters, especially in the dry period, allows us to conclude that the sediments in the Riogrande II reservoir are strongly of reducing characteristics with conditions from neutral to acidic. The fractionation results indicate that although the Mn would not be found in high levels of sediment contamination, there is an environmental risk for the water quality of the reservoir due to the high proportion (more than 50%) of this metal in the more mobile fractions. (BCR1 and BCR2), especially in the dry period for E1, E3 and E4, these fractions are highly bioavailable [72]. It can be established that the Mn that enters the Riogrande II reservoir, probably makes it both soluble (organic and inorganic complexes) and insoluble (Oxyhydroxides-aluminosilicates), and when precipitated towards the bottom of the water column.

- Proposed model of Mn remobilization

Despite the presence of significant concentrations of total Mn in the sediment (values between 121.17 and 651.25 mg kg^{-1}), only Mn carbonate evidence was found in the sediment in the prey area. The results of the geochemical fractionation show that this metal is mainly in adsorbed form to other minerals, followed by Mn associated with organic matter and some oxides and hydroxides of Mn (**Figure 6**).

From the geochemical fractionation, the EDX-SEM findings and complementary studies of the sediment water interface along with geochemical modeling allowed to identify the following

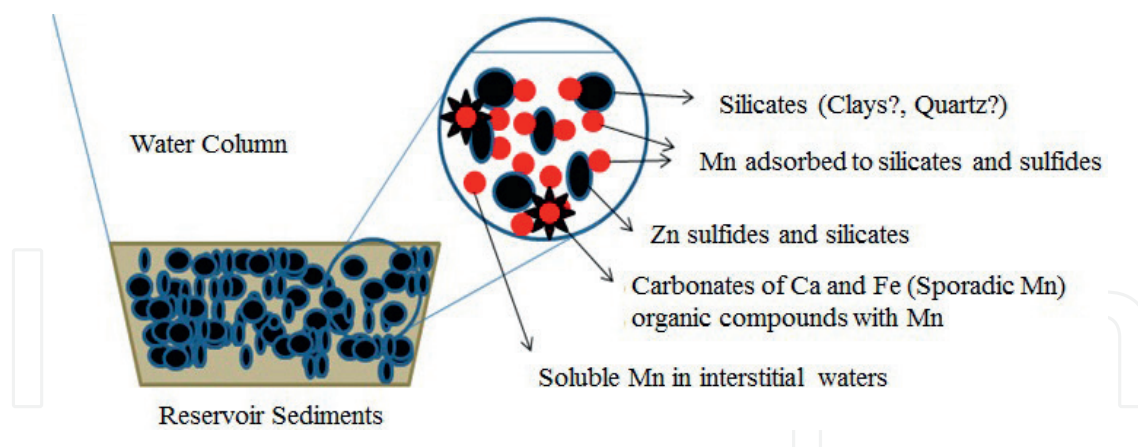


Figure 6. Probable way in which Mn^{2+} is found in the sediments of the Riogrande II reservoir in an adsorbed form, within the interstitial waters and sporadically as carbonates according to evidence from the geochemical fractionation and EDX-SEM analysis.

processes for the Mn in the Riogrande II reservoir: entrance to the reservoir in mineral form (silicates and oxides), and complex form, beginning of the reductive dissolution in terms that the oxides enter the water with reducing potentials, release in the hypolimnion of Mn^{2+} ions, adsorption of Mn^{2+} to other minerals and organic compounds, precipitation in the reservoir and finally formation of organic and inorganic complexes of Mn^{2+} in the same water column.

5. Conclusions

- The proportion of Mn available (BCR1 and BCR2) in the sediments was in a range above 50% of the total Mn in both climatic periods, which indicates that for the sediments of the Riogrande II reservoir, most of the Mn corresponds to fractions possibly adsorbed to mineral phases and organic compounds, where physical processes such as resuspensions generate chemical changes of pH, redox potential and conductivity, among others. It allows the transfer of insoluble phases with little mobility to mobile phases in the water column. This condition creates a danger to the water quality of the reservoir, because whenever there are falls of redox potential and/or the pH in the sediment water limit is lowered, reductive dissolution and desorption processes will be generated and will mobilize heavy metals towards the column of water.
- With the results and statistical analysis obtained, we accept the hypothesis about mobilization scenarios of the Mn present in the sediment to the water column, where the reducing conditions, acid pH and high conductivity increase the concentration of Mn available, product of processes of remobilization in the sediment.

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