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## **Study of physicochemical changes of polluted sediments from Reconquista river basin (Argentina) after remediation processes**

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**Abstract:** The physicochemical properties of sediments and their ability to retain pollutants are affected by both contamination and remediation processes. The aim of this study is to determine structural and physicochemical changes in real sediment contaminated with metals, subjected to bioleaching processes in a previous study. The sediment contaminated with heavy metals and samples of the same sediment treated with different heap leaching tests were used. They were characterised by potentiometric titrations, electrophoretic mobility, organic matter (OM), nuclear magnetic resonance (NMR), volatile solids and sulphides. For contaminated and treated sediment samples, the results of OM, sulphides, volatile solids to 600°, potentiometric titrations and zeta potential values depended on the bioleaching treatment performed previously. The contaminated sediment sample without any bioleaching treatment presented the greatest amount of OM and sulphides. Moreover, metal adsorption isotherms were performed. The contaminated sediment without bioleaching treatment was the one with the highest adsorption capacity. The baseline sample did not present a noticeable adsorption capacity. This study indicates the importance of the contribution of OM and sulphides to sediments and structural and physicochemical studies after remediation treatments.

**Keywords:** sediments; remediation; physicochemical properties.

**Reference** to this paper should be made as follows: Olivelli, M.S., Simpson, M.J., Porzionato, N.F., Fernández, M.A., Torres Sánchez, R.M. and Curutchet, G. (2018) 'Study of physicochemical changes of polluted sediments from Reconquista river basin (Argentina) after remediation processes', *Int. J. Environment and Health*, Vol. 9, No. 1, pp.36–49.

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This paper is a revised and expanded version of a paper entitled ‘Study of physicochemical changes of a polluted sediment from Jose Leon Suarez, after remediation processes’ presented at *II Congreso Internacional de Ciencia y Tecnología Ambiental y II Congreso Nacional de la Sociedad Argentina de Ciencia y Tecnología Ambiental*, Buenos Aires, Argentina, 1–4 December, 2015.

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## 1 Introduction

Sediments play a major role in the fate of pollutants in water courses, as they function as a sink for pollutants in the environment. Owing to the increased agricultural and industrial activities, and the uncontrolled rise of population, mainly in peripheral neighbourhoods without sewage collectors, the contamination of sediments in urban water courses has greatly increased in the last years. As a consequence, pollutants are deposited in soils and sediments, affecting their functions and the whole ecosystems (Alvarenga et al., 2012; Porzionato et al., 2016).

Numerous studies have been developed, where the application of techniques for remediation of contaminated sediments for both heavy metals and recalcitrant organic compounds was evaluated (Subirés-Muñoz et al., 2011). For instance, soil washing using water, acids, basic solutions, organic solvents, non-toxic cations, complexing agents or oxidative/reductive agents was employed (Subirés-Muñoz et al., 2011).

Whereas, owing to the high iron oxides content in soils and sediments, remediation based on Fenton type reactions were also developed for the degradation of organic pollutants, including hydrocarbons (Yap et al., 2011; Laurent et al., 2012; Romero et al., 2011).

Both pollution and remediation processes affect the physicochemical properties of sediments (Favas et al., 2011) changing their structure and therefore their physicochemical and biological properties. Therefore, it is essential to acknowledge how their properties are affected by pollution and remediation processes for the conservation of these soils and sediments in order to prevent their future degradation.

Leaching, bioleaching or *ex situ* washing piles (*bioheaps*) (Mesania and Jennings, 2000; Kathiravan et al., 2011; Begum et al., 2012; Peng et al., 2009) techniques stand out in their use to remediate soils contaminated with heavy metals. The structure and composition of a sediment are the main characteristics that determine its ability to retain contaminants and therefore the fate of pollutants in the environment (Chrastnya et al., 2012). However, there is a significant lack of studies that evaluate the resulting conditions of the sediments after application of the remediation processes. As examples of modification of soils and sediments after treatments, the addition of acid or basic solutions for metal leaching can produce pH and redox potential modification (Lindsay, 1979), as well as alterations in the iron oxides or mineral constituents (Macdonald et al., 2004; Favas et al., 2011). Other properties that can be modified include, interactions with metals (Sparks, 2005), water movement (Sirguy et al., 2008), cationic exchange and amount of organic matter (OM) (Chrastnya et al., 2012). Moreover, in sites highly exposed to pollution (as highly polluted rivers and basins), modifications in substrate properties would cause that subsequent pollutants adsorption to the solids might not be efficient enough (Covelo et al., 2007).

Therefore, the objective of this study is to determine structural and physicochemical changes in a contaminated sediment that was subjected to different degree of bioleaching processes in a previous study (Porzionato et al., 2014b); in order to evaluate its potential recovery and/or reuses after treatment. Sediment samples contaminated with heavy metals from a sewage channel (tributary of the river Reconquista) from Jose Leon Suarez in Buenos Aires, Argentina, and samples of that sediment previously treated by different bioleaching tests were used. The structural characterisation was performed by nuclear magnetic resonance (NMR), ATD-TG and zeta potential analysis. The physicochemical properties were assayed by OM content, sulphides, metals adsorption capacities and potentiometric titration.

## 2 Materials and methods

### 2.1 Samples used

For this study, different kinds of sediment samples were used: a contaminated sediment sample (1); this same sample after remediation processes (3) and a sediment sample without contamination (2). Details about each sample are given below.

- 1 Samples from a contaminated sampling site, described in detail in a previous work from Porzionato et al. (2014a) (contaminated samples – defined as *without treatment* – *WT* along the text), belong to Jose Leon Suarez channel sampling site (34°31'20.0"S 58°35'28.1"O). This channel combines industrial and domestic non-

covered loadings and the presence of multiple irregular landfills and garbage accumulations (Curutchet et al., 2012).

- 2 Samples from upstream *without contamination* were studied in order to establish the baseline for all characterisations (sample from the same basin). These samples were obtained from the Ingeniero Roggero reservoir (34°41'03.8"S 58°51'26.8"O), an area much less polluted than the José León Suarez channel (Porzionato et al., 2016) and defined along the text as the *baseline* sample.

For obtaining both kinds of samples, surface composite samples of the sediment were taken with a shovel (0–20 cm). Once dredged, the collected samples were placed in plastic containers and stored at 4°C. The samples were bottled with their initial moisture content (no drying or draining was performed) and kept saturated to maintain the anoxic conditions during storage.

- 3 Fractions of the *WT* sample were subjected to different bioleaching tests in a former study (Porzionato et al., 2016).

All the different bioleaching treatments were applied using bioleaching heap systems compiled into polyethylene terephthalate (PET) reactors of 12-cm height and 6-cm diameter. For all systems, first a conditioning step, using 5% (w/w) of perlite addition to the sludge, was achieved to improve drainage and aeration. Then, the electron source for sulphur-oxidising bacteria (SOB) was added as elemental sulphur in the mixture in different amounts (different bioleaching treatments: 1%, 2%, 5%, w/w). Whereas, the last system was dusted superficially using 5% (w/w) of elemental sulphur. After the conditioning step, 100 g (dry weight) of conditioned sediment was used in each system, and the bulk density was 280 g L<sup>-1</sup>.

The conditioning described led to the following samples in this work:

- Without the adding of elemental sulphur; Sample A.
- 1% of elemental sulphur added to the mixture; Sample B.
- 2% of elemental sulphur added to the mixture; Sample C.
- 5% of elemental sulphur added to the mixture; Sample D.
- 5% of elemental sulphur just dusted superficially; Sample E.

All the systems were inoculated with a mixture of *A. ferrooxidans* (DSM 11477) and *A. thiooxidans* (DSM 11478) previously suspended in 0 K medium, as SOB inoculum. The irrigation methodology was achieved in two stages as indicated elsewhere (Seidel et al., 2004). The aim of the first stage or acidification step was primarily to promote the acidification generated by the oxidation of sulphides and elemental sulphur by the bacteria, while in the second step or washing step, the aim was to drag all the soluble metals that have been released into the microenvironment. Bioleaching tests were performed by duplicate and no differences were found between duplicates.

## 2.2 *Samples characterisation*

The Walkley–Black methodology (Gelman et al., 2012) was used to determine the content of oxidisable organic carbon by oxidation of carbon by the dichromate ion. Excess dichromate ion is then back titrated with ferrous ion. Acid volatile sulphide

(AVS) content was measured using the purge and trap method (Morse et al., 1987). AVS is an operational definition, and it does not correspond to a single mineral structure, since different minerals may be present in the sample as MS sulphide type (M denotes bivalent metals like Fe(II), Zn(II), etc.). The sulphide content of the trap solution was determined colorimetrically at  $\lambda = 670$  nm using the methylene blue conversion methodology (Tabatabai, 1982). Prior to that process, an estimate of the quantity of carbonates in the sample was arrived at by means of the Kemess fizz rating method (Di Nanno et al., 2007). The concentration of Cu and Zn extraction from each sample was measured by determination of Cu and Zn in the leached liquor by atomic absorption spectrophotometry (AAS) in a previous work (Porzionato et al., 2016).

Total volatile solids were determined gravimetrically by calcination at 600°C.

Additionally, in a previous work (Porzionato et al., 2016), the BET analysis of specific area of the sediment before and after bioleaching showed a diminution of the specific area proportional to the degree of treatment reached; and the XRD patterns indicated the presence of mineral phases such as feldspar, silicates and several clays in the WT sample, while the treated ones also showed iron oxides, calcium sulphates and/or iron sulphates.

### 2.3 *Metals' adsorption capacity*

Metals' adsorption capacities were determined as the maximum adsorption capacity by performing adsorption isotherms for Cu(II), Zn(II) and Cr(III) at pH 5 and 3, for each metal. The value reported as the maximum adsorption capacity was obtained from the maximum value obtained in the experiments.

The amount of wet sample that contained 50 mg of dried weight was added to 50 ml of each metal solution, the pH was adjusted to pH 3 or 5 and sample and flasks were agitated overnight. Remnant metals in the supernatant were measured by atomic absorption spectrometry (AAS).

### 2.4 *Total proton exchange*

Total proton exchange was determined on suspensions of 0.3% (w/v) of each sample by potentiometric titrations as the amount of HNO<sub>3</sub> 0.02 M consumed by the suspension to reach pH 3.8 from the initial pH around 7–8. The experiments were performed by duplicate.

### 2.5 *Zeta potential*

The zeta potential was determined with a Brookhaven 90Plus/Bi-MAS equipment, in the respective mode, operating at:  $\lambda = 635$  nm, 15 mW solid state laser, scattering angle 90°, temperature 25°C and using KCl 10<sup>-3</sup> M as inert electrolyte.

### 2.6 *Solid-state <sup>13</sup>C NMR analysis*

Prior to analysis, the whole sediments were repeatedly treated with 10% hydrofluoric acid (HF) to remove paramagnetic compounds and minerals and to enhance the signal-to-noise ratio. After HF treatment, all samples were rinsed five times with deionised water to remove excess HF and then freeze dried. Solid-state cross-polarisation magic angle

spinning (CP-MAS)  $^{13}\text{C}$  NMR spectra were acquired on a Bruker BioSpin Avance III 500 MHz NMR spectrometer equipped with a 4-mm H-X MAS probe. Samples were prepared by packing 100 mg into a 4-mm zirconium rotor which was then closed with a Kel-F cap. Ramped-amplitude (ramp) CP with pulse phase modulated (TPPM) decoupling in conjunction with fast MAS to avoid sideband overlap was used to obtain  $^{13}\text{C}$  NMR spectra. The acquisition parameters were as follows: MAS spinning rate of 13 kHz, ramp-CP contact time of 1 ms and a 1 s recycle delay. NMR spectra were processed using a zero filling factor of 2 and line broadening of 50 Hz. Chemical shifts were assigned based on previously published data (Simpson et al., 2011).

### 2.7 Thermal analysis

Differential thermal analysis (DTA) and thermogravimetric (Tg) experiments were carried out using a Rigaku Thermo plus EVO instrument. Samples of 10 mg were placed in an aluminium pan and heated from 30°C to 1000°C, at a scanning rate of 10°C/min in air atmosphere with a gas flow rate of 40 mL/min.

## 3 Results and discussion

In previous experiments, it was determined the metal extraction capacity as the bioleaching efficiency for each sample in the *bioheaps* (Porzionato et al., 2014b). Samples D and E showed the highest percentages of Cu (10% and 43%, respectively); and Zn extraction (45% and 70%, respectively). Sample C presented a very low Cu extraction, but 40% Zn extraction was observed. While samples A and B, did not present any bioleaching.

Table 1 shows results from the total volatile solids, AVS, total proton consumption and OM for each sample. The sample WT was the sample that presented the highest values for OM and AVS. For the *bioheap*-treated samples, the OM content, AVS, total volatile solids and total proton consumption were related to the type of bioleaching treatment under which the sample was subjected.

**Table 1** Total volatile solids<sup>a</sup>, AVS<sup>a</sup>, organic matter<sup>a</sup> (OM) and total proton consumption for each sample

	% total volatile solids ( $m_{\text{volatiles}}/m_{\text{sediment}}$ )	OM %C ( $m_{\text{C}}/m_{\text{sediment}}$ )	AVS (mg/kg)	$m_{\text{eq}} \text{H}^+/\text{g sample}$
Baseline	3.8 ± 1.1	1.4 ± 0.3	nd	0.4 ± 0.1
WT	23.4 ± 2.6	14.4 ± 0.3	222 ± 5	1.2 ± 0.2
A	16.4 ± 2.3	8.6 ± 0.3	46 ± 6	0.5 ± 0.2
B	16.7 ± 1.9	7.7 ± 0.3	48 ± 1	0.3 ± 0.1
C	15.5 ± 3.1	9.2 ± 0.1	65 ± 1	0.3 ± 0.1
D	19.5 ± 2.9	8.4 ± 0.1	85 ± 6	0.2 ± 0.1
E	14.9 ± 1.7	8.0 ± 0.1	nd	0.3 ± 0.2

nd: non detected.

<sup>a</sup>total oxidised compounds.

Samples that presented a better Cu and Zn extraction, as samples C, D and E, showed a lower value for OM content, AVS and total proton consumption compared to the WT sample.

The magnitude of the decrease of these parameters, compared to the WT sample values, could not be correlated to the amount of elemental sulphur in the samples; and therefore, the decrease of these parameters could not be correlated to the amount of metals extracted.

Despite sample B did not show a noticeable leaching, the values for OM or AVS were lower than those values obtained for samples C, D and E. Lower values, compared to WT samples, are explained in terms of the irrigation method applied in the bioheap treatment. In all bioleaching processes, oxidative steps are occurring in order to release the retained metals. These oxidative processes caused the oxidation of the OM and sulphides, causing also, a significant decrease in the available sites for binding protons/cations. The baseline sample presented the lowest value for all the parameters analysed with the exception of the total proton consumption that was similar to the value found for the WT sample.

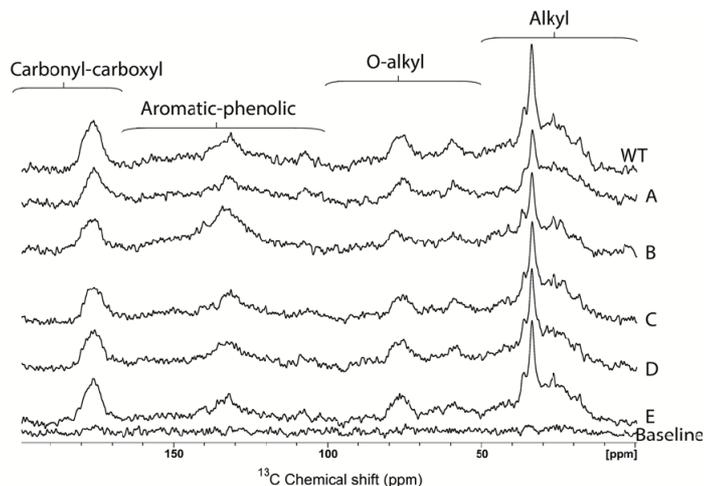
For characterisation of the OM in each sample after the bioleaching treatments, NMR analysis was performed.

Figure 1 shows the NMR spectra of OM of each sample. Owing to its low carbon content and corresponding low signal/noise ratio, a NMR spectrum for the baseline sample could not be obtained. NMR analysis did not show different peaks, but differences in the peaks intensities among samples were observed. These results indicated that all samples have the same type of functional groups, regardless that, differences in the amount of OM were found (Table 1). To establish differences in the relative proportion of the functional groups of each sample, the integration for NMR chemical shift regions was calculated (Table 2). Samples WT, A, B and E were the samples that presented the highest proportion of carboxyl and carbonyl groups. These functional groups play a major role in pollutants retention processes in soils and sediments (Lindsay, 1979). Meanwhile, samples C and D showed a high proportion of alkyl groups with respect to the other samples. Therefore, the bioleaching processes were not only affecting the amount of OM but also it was causing a selective oxidation of the OM present in the sediment samples. Notwithstanding, the total proton consumption was not directly related to the proportion of carbonyl and carboxyl groups because all samples (with the exception of the samples WT and A) presented similar proton consumption values, but the proportion of functional groups among samples were different.

**Table 2** Main different functional groups types percentages, in sediment samples

Sample	% Alkyl (0–50 ppm)	% O-alkyl (50–110 ppm)	% Aromatic-phenolic (110–165 ppm)	% Carboxyl-carbonyl (165–215 ppm)
Baseline	nd	nd	nd	nd
WT	38	25	23	14
A	36	27	25	12
B	34	16	39	11
C	50	21	22	7
D	49	22	21	8
E	41	23	21	15

nd: not detectable due to low carbon content.

**Figure 1** Solid-state  $^{13}\text{C}$  nuclear magnetic resonance (NMR) spectra of the HF treated samples

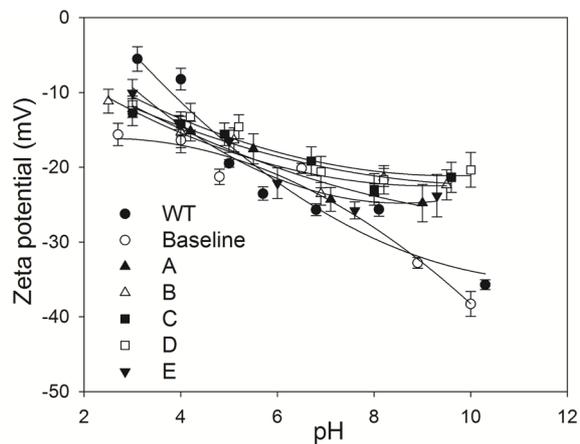
Comparing the functional groups proportion obtained in this study with literature data, it was found that this OM from sewage pollution (adsorbed to the mineral clay fraction), presented similar functional groups to those found in non-polluted soils and sediments (Simpson et al., 2005; Simpson and Simpson, 2012).

Figure 2 shows the zeta potential curves as a function of the pH of the samples. Among all the pH values analysed, similar zeta potential values were found for all samples, from  $-10$  to  $-40$  mV. However, between pH 2 and 5, the baseline and the WT sample had the highest and lowest negative zeta potential value, respectively. Associating these observations with the OM content (Table 1), it could be an OM adsorption on the particles which in turn could shift the slipping plane of the double electric layer decreasing the negative zeta potential of the mineral particles. This indicates that the OM still would not be subjected to processes of humification, since the presence of, for example, humic and fulvic acids (or other anionic organic molecules) increase the surface negative charge of the mineral fractions (Furukawa et al., 2009; Marco-Brown et al., 2012). However, the selective oxidation observed in Table 2, where the labile fraction is firstly oxidised enriching the sample in alkyl groups, could be evidencing the beginning of the generation of some recalcitrant compounds as humic substances. This is related to the total proton consumption that did not show an increase in samples with bigger OM content, particularly in bioleached samples. Also, the quantitative differences obtained from OM and NMR results, are not correlated to the zeta potential data.

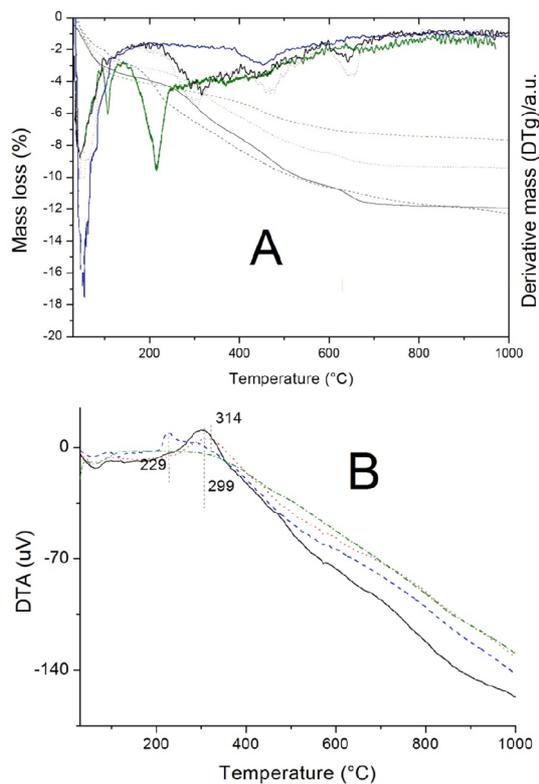
To attain a more exhaustive analysis of the OM present in the sediment samples and its association with the mineral fraction, Tg-DTg and DTA studies were performed and plots showed in Figure 3(A) and (B), respectively. From the Tg plots (Figure 3(A)) a continuous mass loss between 29 and 700°C was found for all samples, while DTg plots indicated several mass-loss steps. The first mass loss (4.14; 3.74; 2.92% and 4.04% for baseline, WT, samples A and D) before 200°C was attributed to the evaporation of adsorbed water, with and endothermic peak at 78°C. A significant mass loss (3.52; 7.98; 6.21% and 8.34% for baseline, WT, A and D samples) between 200 and 600°C, was assigned to combustion of OM and the dehydroxylation reactions of the clay minerals present as was determined in previous work (Porzionato et al., 2016). Particularly, the

combustion of OM showed an exothermic peak (Figure 3(B)) (at 299; 314; 229°C for WT, A and D samples) which is not encountered for the baseline sample in agreement with the NMR and zeta potential results.

**Figure 2** Zeta potential of indicated samples (see online version for colours)



**Figure 3** (A) Tg/DTg and (B) DTA curves for following samples (see online version for colours)



Lines indicated (full-black) WT; (dash-dot-green) Baseline; (dot-red) Sample A and (dash-blue) Sample D.

The adsorption capacity of metals (Zn, Cu, Cr) in the sediment samples was determined. Adsorption isotherms of Cu(II), Zn(II) and Cr(III) at pH 3 and 5 were performed. Table 3 represents maximum adsorption values obtained from each metal isotherm at the pH indicated. The WT sample was the one that had a higher adsorption capacity, with values in the range of 11–30 mg metal g<sup>-1</sup> sediment. On the other hand, samples A, B and E, exhibited a metals adsorption capacity in a range of 3–14 mg metal g<sup>-1</sup> sediment. These metal adsorption data can be correlated with the percentage of types of functional groups (Lewis base group), contained in these samples. Samples with a higher proportion of carboxyl–carbonyl groups showed higher metals adsorption values. However, the study of the lower negative zeta potential values of sediment samples did not explain this higher adsorption capacity. Although the negative zeta potential values of the samples was lower than the baseline one, metals adsorption affinity per unit of mass was much greater. This underlines the importance of the different association of sewage pollutants with the mineral fraction in sediments as an important influence in controlling metal retention.

**Table 3** Maximum Cu(II), Zn(II) and Cr(III) adsorption capacities of, at pH 3 and pH 5

<i>mg metal/g sample</i>	<i>Zn pH 3</i>	<i>Zn pH 5</i>	<i>Cu pH 3</i>	<i>Cu pH 5</i>	<i>Cr pH 3</i>	<i>Cr pH 5</i>
Baseline	nd	nd	nd	nd	nd	nd
WT	11 ± 1	16 ± 1	13 ± 2	25 ± 3	15 ± 2	27 ± 2
A	3 ± 1	12 ± 1	nd	12 ± 3	6 ± 1	14 ± 1
B	nd	9 ± 1	nd	8 ± 2	nd	10 ± 1
C	nd	4 ± 1	6 ± 1	12 ± 2	nd	12 ± 1
D	6 ± 1	nd	nd	2 ± 1	nd	nd
E	nd	1 ± 0	1 ± 0	9 ± 2	2 ± 1	12 ± 2

nd: non detectable.

Those samples with stronger bioleaching of metals present in the sediment were the samples that had lower adsorption capacity and in this case, this parameter indeed was associated to the amount of elemental sulphur added initially to the samples in the previous experiments; being the samples with the highest amount of elemental sulphur, the samples with the lowest adsorption capacity (D and E). The decrease in the adsorption capacity is related to the lower content of OM and sulphides and can also be correlated to the lower BET specific area (Porzionato et al., 2016). Furthermore, although the baseline sample exhibited total proton consumption similar to the treated samples, and a greater negative zeta potential value at the pH studied; it did not present a greater adsorption capacity than treated samples. This may be due to its low OM content and sulphides, confirming that the interactions of the studied metals with OM and sulphides are the most important associations when assessing the fate of pollutants in an aquatic environment. This study indicates that the metal extraction by bioleaching treatments, affects the number of available sites for proton exchange due to the oxidation of the OM and sulphides, causing a loss in its subsequent ability to retain metals. Therefore, it is important to study and characterise both sediments undergoing remediation processes in the laboratory as non-contaminated sediments (baseline), before adapting processes to a

larger scale or *in situ*, in order to make decisions regarding the disposition of the resulting solids or to determine future uses.

#### 4 Conclusions

Samples that showed greater bioleaching in the bioheaps developed prior to this study, were those that exhibited lower values for OM content, total proton consumption, sulphide content and a lower proportion of carbonyl–carboxyl groups, as this last parameter could be analysed by NMR studies. Results indicated that treatments using *bioheaps* affected the content and quality of the OM in the sediment affected as well, the presence of sulphides and exchangeable sites for the retention of metals. Therefore, the subsequent metal adsorption capacity of the *bioheaps* treated sediments was influenced by OM content, sulphide content and the proportion of carbonyl–carboxyl groups.

In addition, this study indicated that the OM and sulphides input to a non-contaminated (pristine) sediment is performed during the course of the Reconquista river along the entire basin. Furthermore, structural and adsorption capacity of the resulting solids after remediation treatments, study would help to determine whether they can be reinstated in their natural environment.

#### Acknowledgement

The authors acknowledge the CONICET PIO 4022/14 and UNSAM proyect “Dialogo entre las Ciencias” for the financial support. N.F. Porzionato and M.S. Olivelli thanks CONICET for the scholarships given to PhD students. M.S. Olivelli also thanks the awarded scholarship “Financiamiento Parcial para Estadías Breves en el Exterior Becarios Postdoctorales-CONICET”. G. Curutchet, R.M. Torres Sánchez and M.A. Fernández are researchers of CONICET. M.J. Simpson thanks the Natural Sciences and Engineering Research Council (NSERC) of Canada for support via a Discovery Grant.

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