# Biocatalysed acidification and metal leaching processes in sediments of polluted urban streams

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**Abstract:** Sediments of fluvial streams are a sink for pollutants such as heavy metals and organic recalcitrant compounds. In anoxic conditions, sulphide generation and alkalinisation cause precipitation of heavy metals. The redox potential of the system could change to higher values, mainly owing to oxygen exposition generated by anthropogenic disturbances of the sediment such as dredging operations. Knowledge about the mechanisms involved is fundamental to assess the risk of acid generation and rise in heavy metals bioavailability. In this paper, the characterisation and assessment of acidification risk of sediments of a contaminated stream near Buenos Aires was carried out by static and kinetic assays. Speciation of heavy metals was determined after metal sequential extraction procedure. Also, re-suspension of sediments assay in batch mode, with and without *Acidithiobacillus ferrooxidans* inoculum, was carried out to assess the chemical changes that occur at oxygen exposure, verifying the acidification and heavy metal release processes.

**Keywords:** sediment acidification; acid generation risk; metal leaching; biocatalysed leaching processes; polluted urban streams.

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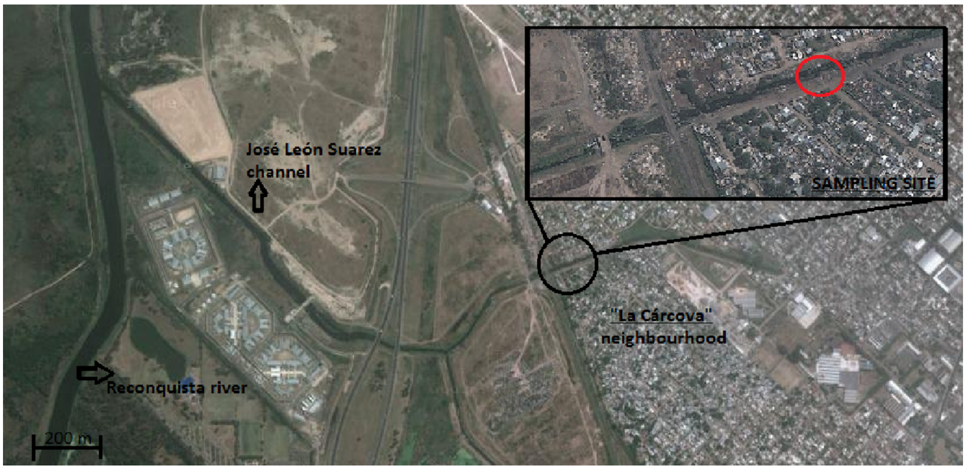
## 1 Introduction

The Reconquista is one of the more polluted rivers in Argentina and is emblematic of environmental problems. This river receives contributions from storm sewers and streams that run across zones of high population density and serious environmental problems (hyper-degraded territories). Many of the tributaries of this basin receive domiciliary and industrial contaminating loads. One of them is the José León Suarez channel studied in this paper. This stream runs tubing as a rainwater collector and leaves open at 'La Cárcova' neighbourhood situated approximately 4.5 km upstream of its drainage at the Reconquista river as can be seen in Figure 1. This neighbourhood has characteristic of extreme poverty, lack of drinking water services, sewer and energy, and its population is highly exposed to contaminants carried by the channel and those that sediments accumulate.

To maintain the runoff and the depth of the stream, periodic works of dredging with the following disposition of the sediment in areas close to the river bank are carried out (Curutchet et al., 2012). This practice is not recommendable without taking in consideration certain risk factors, such as acidification and releasing of metals, which can lead to an increment in the bioavailability of contaminants with its resultant impact to the biota. Sediments of the stream act as a sink for toxic substances like heavy metals and organic pollutants and, consequently, dredged materials often contain those pollutants over safe limits (Di Nanno et al., 2007). Remobilisation of sediment-associated contaminants can occur during natural events, such as storms and floods, or during human activities such as dredging and dredge disposal (Eggleton and Thomas, 2004). This paper explores some aspects of the processes that arise during sediment suspension and the transfer of contaminants from sediment to biota.

**Figure 1** Sampling site location in J.L. Suarez district at Buenos Aires province, Argentina (see online version for colours)



*Source*: Google maps

There are numerous studies related to heavy metals interacting with sediments and how this association may reduce the bio-availability of these contaminants (Cappuyns, 2006; Hatzinger and Alexander, 1995; Teuchies, 2011). Two groups of bacteria are critical on the regulation of the processes involved in the immobilisation and mobilisation of metals from sediments (Di Nanno et al., 2009): the sulphate-reducing bacteria (SRB), whose respiration requires sulphate as terminal electron acceptor generating large amounts of sulphides, and sulphur oxidising bacteria (SOB), chemoautotrophics that catalyse the reverse process, the aerobic oxidation of reduced sulphur compounds including sulphides. Under anaerobic conditions, the formation of insoluble metal sulphides is favoured, which are also deposited in the sediments (Förstner, 2004). Changes in redox potential to an oxygenated condition, as in a dredging or re-suspension, promote several oxidation reactions generally catalysed by SOB (Bosecker, 1997; Lors et al., 2004). The oxidation of anaerobic sediments can produce sulphide conversion to sulphate with consequent acidification and metal release risk.

Under this context, it is very important to include the monitoring of certain indicating parameters of potential risks in sediments of contaminated basins. Therefore, the objective of this work is to characterise and determine the risk of acidification and liberation of metals from J.L. Suarez channel sediments.

## 2 Experimental

### 2.1 Site description and sampling

Since J.L. Suarez channel is open to the sky until its drainage at the Reconquista river, it combines practically all of the typical elements of a hyper-degraded area: informal occupation of the plain of flooding, high demographic density, extreme poverty, industrials and domestic non-covered loadings and the presence of multiple irregular landfills and garbage accumulations (Curutchet et al., 2012).

Two seasonal samplings in May (sample I) and August (sample II) of the year 2011 were taken. Superficial 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. Before the experiments, the samples were manually homogenised.

### 2.2 *Sediment characterisation and static assays*

A standard metal sequential extraction procedure was applied on the anoxic sediment (BCR sequence; Ure et al., 1993). The sediments, saturated in water, were stored up 1 week at 4°C before the extraction. Briefly, the four-step sequential extraction was performed as follows:

*Step 1*: Exchangeable and water-acid soluble like carbonate bound metals. 1.00 g of sediment was gently stirred overnight with 40 $cm^3$ of 0.11 mol $dm^{-3}$ acetic acid. The supernatant was separated by centrifugation and stored at 4°C. The same procedure was applied in all the steps.

*Step 2*: Iron and manganese oxides. The solid obtained in step 1 was stirred overnight with 20 $cm^3$ of 0.10 mol $dm^{-3}$ hydroxilammonium chloride solution, acidified at pH 2.0 with $HNO_3$.

*Step 3*: Organic matter and sulphide bound metals. 10 $cm^3$ of 8.8 mol $dm^{-3}$ hydrogen peroxide was incorporated to the solid obtained in step 2. The suspension was manually stirred during short intervals and kept at 23°C for 1 h. Then, the temperature was raised to 85°C and the system was periodically stirred for another 1 h. The volume was reduced to 3.0 $cm^3$ by evaporation at 100°C and the procedure was repeated one more time. The concentrated system was stirred overnight with 50 $cm^3$ of 1.0 mol $dm^{-3}$ ammonium acetate solution acidified at pH 5.0 with acetic acid.

*Step 4*: Residual fraction, non silicate-bound metals. The solid obtained in step 3 was gently stirred during 1 h with 15 $cm^3$ of aqua regia. The solid was separated by filtration through white ribbon filter paper (Whatman 589/2) and thoroughly washed with distilled water.

In all the cases, the final volume of supernatant was adjusted to 50.0 $cm^3$.

Cadmium, zinc, copper and chromium were measured in each fraction by Atomic Absorption Spectrophotometry.

### 2.3 *Acid consuming capacity (ACC) and acid producing potential (APP)*

Acid consuming capacity (ACC) was calculated by measuring calcium concentration in the supernatant obtained from step 1. $Ca^{2+}$ was determined by EDTA titration with 1% murexide in NaCl as indicator. Maximum acid producing potential (APP), represented by sulphides and the maximum ferrous sulphide (available sulphide capacity (ASC)), were calculated by measuring $SO_4^{2-}$ from step 3 (designated as sulphate from sulphide; Vogel, 1961) and total Fe from step 2. If ACC-APP < 0, the sediment sample was considered to have a significant acidification potential (Förstner, 2004; Kersten and Förstner, 1991).

Sulphate was measured by turbidimetry and total iron by Atomic Absorption Spectrometry.

### *2.4 Oxidisable organic carbon (OOC) and acid volatile sulphides*

Oxidisable organic carbon (OOC) content was measured using the Walkley-Black methodology (Walkley and Black, 1934). The pH was measured with a glass Cole Parmer electrode in a 1 : 2 g $cm^{-3}$ suspension with distilled water. Moisture content was determined gravimetrically at 105°C until constant weight.

Acid volatile sulphides (AVS) content was measured using the purge and trap method (Morse et al., 1987). This method consists in the addition of HCl acid to a sediment sample, purging with $N_2$ gas and trapping the emitted $H_2S$ in a 0.5 mol $dm^{-3}$ NaOH solution. The sulphide content of the solution was determined colorimetrically at 670 nm using the blue conversion methodology (Tabatabai, 1982). Calibration solutions were daily prepared from $Na_2S.9H_2O$ (Merck). AVS content was measured within 48 h of sediment arrival at the laboratory. AVS is an operational definition and it does not correspond to a single mineral structure, since different minerals may be present in the samples as for example: mackinawite, greigite, amorphous iron sulphide and compounds dissolved in the pore water (Förstner, 2004; Richard and Morse, 2005). Total sulphur was determined using a LECO analyser (CS200 model). Non-volatile sulphides (pyrite like sulphides; Sand, 2001) were determined by subtracting the values of total sulphate and AVS from the total sulphur value. Total sulphate was determined by turbidimetric means after $H_3PO_4$ extraction (Tack et al., 1996).

### *2.5 Kinetic assays*

The acid base account is a guide to whether the sample considered will generate acidic drainage. To study the rates of acid generation or neutralisation potential consumption, kinetic tests were performed by re-suspension experiments.

Re-suspension of sediments in batch mode was carried out to study the chemical changes that occur at oxygen exposure. It was performed by suspending 15 g of wet sediment in 70 $cm^{-3}$ of 0 K medium (Di Nanno et al., 2007; Silverman and Lundgrem, 1959) contained in a 150 $cm^{-3}$ flasks under constant agitation at 120 rpm. The sediment-solution ratio used (21 g: 0.1 $dm^{-3}$) is recommended by the British Columbia Research Confirmation Test for rock samples with a high sulphur content (Di Nanno et al., 2007; Coastech Research, 1991). To ensure a population of sulphur oxidising bacteria, some flasks were inoculated with 1% suspension of *Acidithiobacillus ferrooxidans* (Di Nanno et al., 2007; Coastech Research, 1991). The inoculum of *A. ferrooxidans* was obtained from cells cultured in 9 K medium, recovered in the late exponential growth phase (Di Nanno et al., 2007) by filtration through a 20-µm cellulose acetate filter. The cells were re-suspended in 0 K media and counted in a Thoma counting chamber with an optic microscope. Sample takeover with previous addition of the water of evaporation was achieved periodically, as tracking of pH, sulphates and metals released too.

## 3 Results and discussion

### 3.1 Heavy metals speciation in sediment

Table 1 shows the results of sequential extraction of Cd, Cu, Cr and Zn in the two samples. It is useful to compare these results with reference values. In Argentina, there are no reference values for fresh water sediment contamination and guidelines for other countries such as Holland or USA are commonly used. There is a proposal of Argentine Water National Institute (INA, 1998) for the Parana-Paraguay waterway but without legal application. The guidelines for Holland and INA are included (Tables 2 and 3).

Tables 2 and 3 show the sediment quality guidelines for Holland and those employed by the Argentine National Institute for water for the Parana-Paraguay waterway.

As expected in heterogeneous and complex systems, the results showed differences between samples, but the observed values for total concentration of each metal are in the same order in both samples. The highest difference is for copper, which shows near 5 fold higher in sample II than sample I. The speciation of the metals is in agreement with their affinities for sulphides and organic matter. Copper and chromium are mainly in fraction 3 (associated to organic matter and sulphides) and zinc is in fraction 1 (interchangeable, associated to clays) and fraction 4 (the excess of zinc is recovered in the last fraction). Similar results were found in other systems (Akinci and Guven, 2011; Zhang et al., 2001; Zoumis et al., 2001).

**Table 1** Fractions of metals of sequential extraction (BCR)

| *Sample I* (*Autumn*) | *Cadmium* (mg/kg) | *Chromium* (mg/kg) | *Copper* (mg/kg) | *Zinc* (mg/kg) |
|---|---|---|---|---|
| Fraction 1 | 0.26 | 1.04 | 1.02 | 239 |
| Fraction 2 | 0.4 | 6.83 | 27.0 | 106 |
| Fraction 3 | ND | 22.4 | 27.6 | 5.47 |
| Fraction 4 | 2.18 | 16.0 | 3.29 | 1029 |
| *Total* | *2.84* | *46.3* | *58.9* | *1274* |
| *Sample II (Winter)* | | | | |
| Fraction 1 | 4.39 | 1.55 | 16.4 | 774 |
| Fraction 2 | 2.93 | 0.79 | 4.23 | 613 |
| Fraction 3 | 4.06 | 58.1 | 199 | 81.3 |
| Fraction 4 | ND | 57.3 | 95.2 | 229 |
| *Total* | *11.4* | *118* | *315* | *1697* |

**Table 2** Sediment quality guidelines for Holland. All the concentrations are expressed in mg kg$^{-1}$

| *Holanda. Sediment Quality guidelines* (*2006*) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| *Metals/metalloids of interest* (mg kg$^{-1}$) | *As* | *Cu* | *Cd* | *Cr* | *Hg* | *Ni* | *Pb* | *Zn* |
| Target value | 29 | 36 | 0.8 | 100 | 0.3 | 35 | 85 | 140 |
| Intervention value | 55 | 190 | 12 | 380 | 10 | 210 | 530 | 720 |

**Table 3** Sediment quality guidelines employed by INA at the complementary studies on the Paraguay-Paraná project. All the concentrations are expressed in mg $kg^{-1}$. Pollution levels indicate final disposition alternatives

| *Substance* | *Level 1* | *Level 2* | *Level 3* |
|---|---|---|---|
| As | 3 | 9 | 33 |
| Cd | 0.6 | 0.9 | 10 |
| Zn | 100 | 271 | 540 |
| Cu | 28 | 50 | 110 |
| Cr | 26 | 55 | 110 |
| Ni | 16 | 35 | 75 |
| Pb | 23 | 42 | 250 |

Not polluted: ≤ level 1

Mildly polluted: level 1 < sediment ≤ level 2

Moderately polluted: level 2 < sediment ≤ level 3

Very polluted: > level 3

Comparing the obtained results (Table 1) with the reference values (Tables 2 and 3), it is clear that the heavy metals pollution level in the sediments is very high. Cu, Cd, Cr and Zn are above level 3 (very polluted) of the INA reference and above the intervention level of the Holland reference in sample II. Zn is above level 3 in sample I too and Cu, Cd and Cr are between levels 2 and 3 (moderate polluted). The José León Suarez channel is a pluvial collector, with domestic discharges, and this strong pollution by heavy metals is unexpected and indicates industrial discharges upstream.

Table 4 shows the organic matter and volatile sulphides concentration in samples 1 and 2.

**Table 4** Initial sediment characterisation

| | *Moisture* (%) | *pH* | *Oxidisable carbon* (%) | *AVS* (mmol S $kg^{-1}$) |
|---|---|---|---|---|
| Sample I | 55.3 | 7.80 | 25 | 9.2 |
| Sample II | 57.1 | 7.23 | 50 | 5.9 |

The very high content of organic matter in the sediments is mainly due to sewage discharges from the neighbourhood and other close residential zones without sewer collection service. The high organic load trends to sediment very quickly and is incorporated to the sediments (Curutchet et al., 2012). The nature of this kind of discharges causes strong variations in the loads and in the concentrations of organic matter and sulphides in sediments. The environment becomes anoxic and the stabilisation of organic matter by anaerobes as SRB is slow, leading to accumulating of organic matter and sulphides in the sediment (Caille et al., 2003). Organic matter and sulphides have a crucial role in the regulation of the speciation of the metals in the sediment, and their oxidation may lead to acidification and metal release processes. Some of the chemical reactions that can lead to these kinds of processes are:

$$MS + 2O_2 \rightarrow M^{2+} + SO_4^{2-} \quad (1)$$

$$MS + 2O_2 + 2H_2O \rightarrow M(OH)_2\,(s) + SO_4^{2-} + 2H^+ \quad (2)$$

$$FeS_2 + 15/4\ O_2 + 7/2\ H_2O \rightarrow Fe(OH)_3 + 2SO_4^{2-} + 4H^+ \quad (3)$$

$$2Fe^{2+} + 2H^+ + ½\ O_2 \rightarrow 2Fe^{3+} + H_2O \quad (4)$$

$$Fe^{3+} + 3\ H_2O \rightarrow Fe(OH)_3\,(s) + 3\ H^+ \quad (5)$$

$$S + 3/2\ O_2 + H_2O \rightarrow SO_4^{2-} + 2H^+ \quad (6)$$

M in equations (1) and (2) stands for different divalent metals. The rate of reactions 1, 2, 3, 4 and 6 is enhanced by microbial catalysis by SOB (Bosecker, 1997; Di Nanno et al., 2007; Lors et al., 2004).

Analysis of the acidification process is discussed in the following paragraph.

## *3.2 Acidification risk after redox potential changes*

Table 5 displays the risk prediction parameters (Förstner, 2004) calculated from the results obtained by sequential extraction of metals and the determination of different kinds of sulphur.

**Table 5** Acid drainage prediction by Kersten and Förstner (1991) method

| | *ACC* (mmol Ca kg$^{-1}$ × 0.5) | *ASC* (mmol Fe kg$^{-1}$) | *APP S-sulphur* (mmol S kg$^{-1}$) | *Máx. APP* | *Balance: ACC-APP* |
|---|---|---|---|---|---|
| Sample I | 76 | 20.3 | 81.8 | 102 | –26.1 |
| Sample II | 125 | 19.2 | 138 | 158 | –32.7 |

The fraction of calcium was determined from the first step. It corresponds to the highest value of ACC, which has to be multiplied by the stoichiometric factor of 0.5, which is the redox relation among $FeS_2$ and $CaCO_3$. The APP is determined by the quantity of $SO_4^{2-}$ present in solution after the third step of metal sequential extraction. These sulphates came from the reaction of metal sulphides that resist the previous stages of extraction. To determine the maximum APP, it should be considered both the reservoir of FeS types and the maximum potential of production of ferrous sulphides, like $FeS_2$ type. This potential maximum capability of production of sulphides is named available sulphur capacity (ASC). ASC value corresponds to the available $Fe^{3+}$ to form mineral sulphides measurable as the total Fe present in the reducible fraction (step 2).

For both samples, the value of maximum APP (present-day APP plus ASC) is superior to ACC value (Table 4). It means that a significant potential for acidification of the sediment under consideration exists and, in consequence, heavy metals leaching from the sediment and its release to the water body is possible.

In both samples, the sulphide determined in the Förstner Method (APP) is much higher than the sulphide determined as AVS. This can be due to the large presence of sulphides like pyrite type that contribute to create a great quantity of acidity as consequence of its oxidation (Rawlings, 2002). This postulate was confirmed with the determination of total sulphur, by subtracting acid volatile sulphides (%) and total sulphates (%) correlated to the sediment at the value of total percentage, giving a higher value for the sample II for acid insoluble sulphides (pyrite type ones).

Kinetic assays results are shown in Figures 2 and 3, where pH changes and release of zinc to the solution occurred in the re-suspension experiments. Four different conditions were tested for both samples: with and without *A. ferrooxidans* inoculation and with and without conditioning of the initial pH. Both situations are recommended to ensure the optimal conditions for oxidation of reduced sulphur compounds (Di Nanno et al., 2007, 2009; Lors et al., 2004).

**Figure 2** (a) pH variation and (b) Zn release to solution vs. time of samples I and II with their controls. Culture conditions: 0 K medium pH 2.5, 22°C, 122 rpm

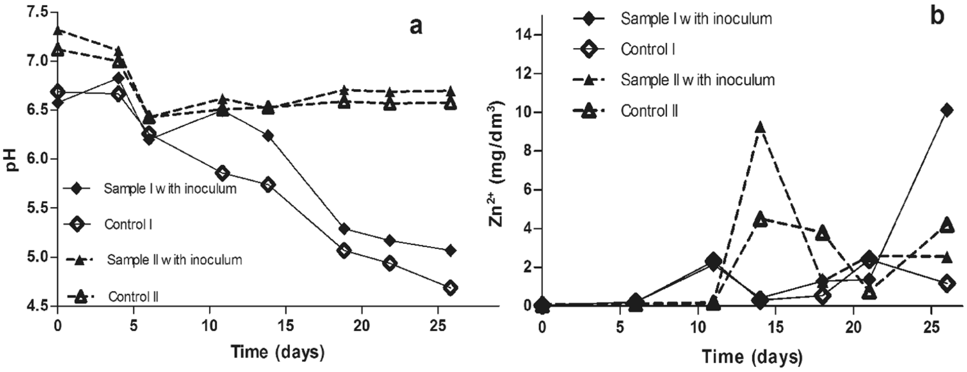
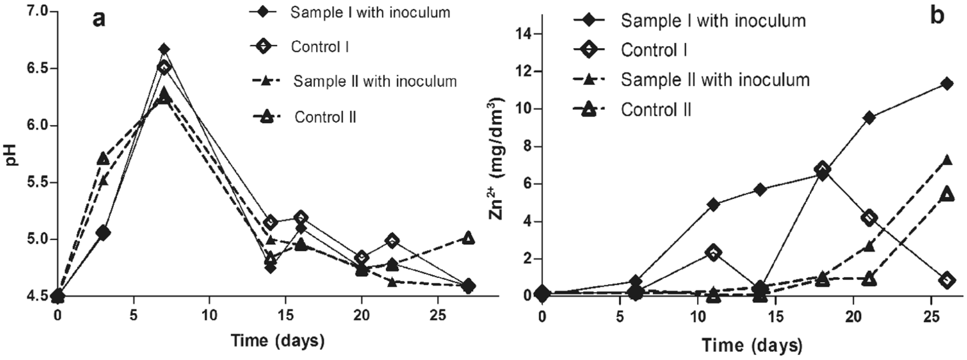


**Figure 3** (a) PH variation and (b) Zn release to solution vs. time of the samples I and II with their controls: 0 K medium pH 2.5, 22°C, 122 rpm



## 3.3 Systems without initial conditioning of pH

Figure 2(a) shows the evolution of pH in non-acidified inoculated samples (samples I and II), and in the corresponding non-inoculated controls (controls I and II). Both samples displayed fast acidification during the first 5 days, with a decrease in pH close to one unit. In the following days, sample II reached a plateau while acidification continued in sample I until the pH reached the 4.5–5.0 range. The differences between inoculated and not inoculated systems were very low (less than 0.5 pH units between sample I and control I at the end of the experiment), being the inoculated system faster than the not inoculated. These results show that sediment oxidation causes acidification. Sulphate concentration in the re-suspension systems (data not shown) rises from 700 mg $dm^{-3}$ to 1500 mg $dm^{-3}$ in all conditions, suggesting that acidification is partially due to sulphide oxidation. Organic matter oxidation is another possible acidity generation reaction. It has been previously noted that acidification in land-disposed sediments is related not only to sulphide oxidation but also to organic matter decomposition (Caille et al., 2003; Eggleton and Thomas, 2004; Gambrell, 1991).

The slight difference between inoculated and control systems was attributed to the presence of indigenous bacteria. The importance of indigenous bacteria such as *Acidithiobacillus thiooxidans* and *Thiobacillus thioparus* in batch re-suspension systems has been demonstrated previously (Lors et al., 2004). Gómez and Bosecker (1991) have isolated *A. ferrooxidans* and *A. thiooxidans* strains from polluted sediments containing metals and organic compounds, and from these sediments we isolated consortia with iron and sulphur oxidation capabilities (data not shown). Further experiments are needed to demonstrate and characterise these bacteria.

Figure 2(b) shows the evolution of $Zn^{2+}$ in solution. The release of zinc to the solution showed some differences between inoculated and not inoculated systems. Although both samples did not showed pH differences, in the inoculated system (sample I) the concentration of $Zn^{2+}$ rose markedly at day 25, while in the not inoculated sample (control I) zinc values in solution remain very low. This may be due to *Acidithiobacillus ferrooxidans* catalysis of zinc sulphide oxidation that, as was demonstrated, can occur at pH near neutrality without acidification of the medium (Di Nanno et al., 2007; Lors et al., 2004). The further drop in the concentration of zinc in solution may be due to precipitation of hydroxides or adsorption to the solid phase. Taking into account the main species of zinc observed in this experimental conditions (Caille et al., 2003), zinc in solution reaches concentration values around the expected saturation concentration for $Zn(OH)_2$ and phenomena of dissolution and re-precipitation of $Zn(OH)_2$ could explain the instability of zinc concentration.

### 3.4 Systems with initial conditioning of pH

Figure 3(a) shows the evolution of pH in samples previously acidified at pH 4.5. In all the samples, the evolution of pH showed a fast initial rise from 4.5 to 6.5, followed by a diminution to pH 5.0 or lower. No difference between inoculated and not inoculated systems was observed. Figure 3(b) shows the evolution of $Zn^{2+}$ concentration. By comparing Figure 3(a) and (b), it can be noticed that zinc extraction showed a rise in parallel with the pH drop. In sample I, the inoculated system showed a typical pattern of a bioleaching process and reaches values of 12 $mg/dm^3$. The not inoculated sample (control I) displayed important zinc extraction but with a more disperse pattern. In sample II, both systems show high zinc extraction following a typical kinetic of an acid extraction system based in biocatalysed acid production.

## 4 Conclusions

The sediments at the José León Suarez canal act as a sink for contaminant accumulation. The high organic load is responsible for the typical anaerobiosis characteristics of the system with important formation of sulphides and accumulation of organic matter. The heavy metals level is in many cases above the standards values (Paraguay Paraná waterway and Holland lists), so these sediments could be classified as a system with high level of contamination. Such contamination values suggest discharges of industrial effluents upstream of the sampling zone. The speciation of Zn, Cu and Cr in the sediments is in agreement with their affinities for organic matter and sulphides. In case of a change in the redox potential of the system (as in a dredging operation), the risk of metal liberation and acidification of the stream was confirmed in static and dynamic assays. This kind of operations should be done under carefully control dredging conditions, with an adequate disposition of the sediments to avoid heavy metal leaking to running water or to the aquifers.

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