

Acid drainage and metal bioleaching by redox potencial changes in heavy polluted fluvial sediments.

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Abstract. Sediments from polluted urban streams act as a sink of contaminants. The high content of organic matter and sulphides makes the system appropriate for binding heavy metals. However, changes in the redox potential leads to processes in which sediments acts like a low sulphidic ore in an oxidizing environment, and could generate acid drainages. Human and not human disturbances of the sediments could derive in its oxidation catalyzed by sulphur oxidizing bacteria (SOB). This process leads to acidification and metal release. In this study we analyze the acidification potential of anaerobic sediments of polluted streams near Buenos Aires with static and kinetic methods. The results remark the necessity to consider this process before any sediment management action.

Introduction

Acid Mine Drainage (AMD) is a well documented process and the involved mechanisms are well known. Fluvial anaerobic sediments of rivers and streams that flow through urban areas are often contaminated with heavy metals. The response of such sediments to a change in redox potential is similar than a low grade sulphide ore, with the consequent possibility of AMD generation. These processes play a fundamental role in the stability and mobility of contaminants. The sediment of an urban stream can be disturbed naturally (storms, floods, etc.) or by human activities (dredging, post dredge disposal, domiciliary and industrial discharges) with consequence in the redox stability. There are numerous studies related with the interaction between heavy metals and sediments, and how these associations transform the contaminants in less bio-accessible forms [1, 2]. Typically, in undisturbed water courses with high organic loads the sediments become anaerobic. Under these conditions the activity of sulphate reducer bacteria produces high sulphide concentration and alkalinization of the environment. The heavy metals precipitate as metal sulphides or hydroxides and/or are adsorbed in the sediment matrix. The iron reducing bacteria also present in these media has the abilities of reducing the metal-ferrous oxides to the less soluble metal sulphides [1]. A change in the redox potential of the stream to more oxidizing conditions may enhance the activity of sulphur and iron oxidizing bacteria, with consequent acidification and metal release as observed in AMD processes. In this article we characterize fluvial heavy polluted sediments from Reconquista River basin (Buenos Aires, Argentina) and study the mechanism of acidification and bioleaching of metals that occurred by redox potential changes. Native consortia of iron and sulphur oxidising and reducing bacteria were the main catalyzers of the metal leaching process.

Experimental

Site description and Sampling. Reconquista River is a typical plain terrain river located few kilometers north of Buenos Aires city, which flows across areas of high population, extreme poverty

and environmental degradation. Industrial and domestic sewage loads without treatment are discharged to the river along the entire basin. Superficial samples of the sediment were taken with a core sampler among of 0–20 cm of depth. Once dredged, the cores were cut at several depths separated by 4 cm each other (samples named as “surface”, “R1”, “R2” and “bottom”), placed in plastic containers and stored at 4°C. The samples were bottled with their initial moisture content and kept saturated to maintain unaltered redox conditions during storage. Before the experiments, they were manually homogenized. Composite samples were taken with a shovel in the same sampling site (from surface to 30 cm depth), and conserved in the same conditions than above.

Sediment Characterization and Static Assays. Organic oxidizable carbon content was measured using the Walkley-Black methodology [3]. The pH was measured with a glass Cole Parmer electrode in a 1:2 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. Total sulphate was determined by turbidimetric means after H_3PO_4 extraction. A standard metal sequential extraction procedure was applied on the anoxic sediment (*BCR sequence*) [3]. The BCR sequence typically produce four fractions: fraction 1 or exchangeable; fraction 2 or Fe and Mn oxides bounded; fraction 3 or organic matter and sulphide bounded; and fraction 4 or residual. Zinc and Copper were measured in each fraction by Atomic Absorption Spectrometry (AAS)

Acid Drainage Prediction. Before sequential metal extraction, measurements of Acidity Consumption Capacity (ACC) and Acidity Potential Production (APP) were performed for acid-base balance following Förstner method [4]. Details of assumptions and calculations are described in [4,5]. If $\text{ACC-APP} < 0$, the sediment sample was considered to have a significant acidification potential [4,5].

Kinetic Assays. 15 g wet sediment were dispersed in 70 ml of modified 0K medium (low sulphate and pH 6) [5] and placed in a 150 ml flasks under constant stirring at 120 rpm. To ensure a population of sulphur oxidising bacteria, some flasks were inoculated with 1 % suspension of *Acidithiobacillus ferrooxidans* DSM 11477 [7]. In both systems two different conditions were performed. In the first condition the initial pH was set to 4.0 to enhance the activity of the acidophilic communities. In the second case the initial pH was not modified. Sulphate and zinc released to solution and pH were measured as indicated above.

Native Bacterial Consortia Isolation. Indigenous iron reducing and oxidizing bacteria, sulphate and manganese reducing bacteria and sulphur oxidizing bacteria including acidophilic ones were enriched in all the samples. The enrichment of aerobic consortia was carried out by suspending the sediment in 9K medium for iron oxidizing or 0K medium plus 1 % sulphur powder for sulphur oxidizing bacteria in agitated flasks at 25°C. Enrichment of anaerobic consortia was performed in Postgate C medium in airtight sealed vials without agitation at 30°C. Metabolic activity of consortia was studied through kinetic and stoichiometric assays and in some cases compared with collection strains.

Results and discussion

Sulphide, pH and oxydizable matter determined at different core heights and in the composite sample are showed in Table 1. The high organic matter concentration and its accumulation at the surface acts as an indicator of high organic loads in the surface water and low metabolic rate of microorganism due to the anoxic conditions. The volatile acid sulphide profiles are in the same way that organic matter, suggesting the in situ generation of sulphides by sulphate reducing bacteria. 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. The

possibility of acid drainage was studied through static and kinetic assays. Table 1 show the Forstner acid-base balance, which is negative for all the samples. That means that a significant potential for acidification of the sediment under consideration exists and heavy metals leaching to the environment is rather possible.

Table 1: Characterization of Sediments and Acid Drainage Prediction Balance.

Sample	Oxidizable Matter [%]	AVS [$\text{mg S}^{2-}/\text{Kg}$]	pH	Acid drainage prediction balance (ACC-APP _{máx})
Surface	30	452	7.3	-176
R2	15	385	7.2	-369
R3	20	309	7.3	-466
Bottom	16	24.5	7.5	-121
Composite	33	193	7.7	-180

Fig. 1 shows the concentration of Zn(II) and Cu(II) in different fractions of the sequential extractions.

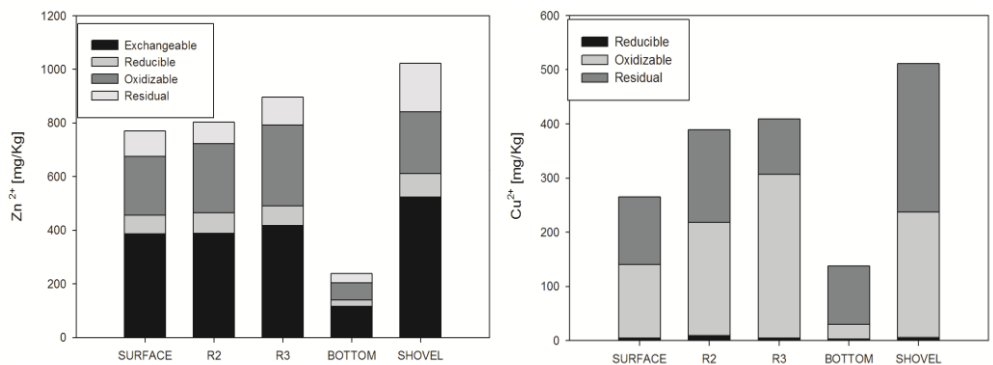


Figure 1: Characterization of the sediment: Zn(II), Cu(II) concentration

Every sample reaches values higher than the intervention value for sediment quality guidelines in several countries. Both metals trend to accumulate in the two intermediates and the more superficial layers of the core, where the organic matter and sulphides are more concentrated. The speciation of Zn(II) is mainly related to the exchangeable fraction, the most bio-accessible form, and in the second place to the organic matter and sulphide bounded form. Cu(II) is mainly related to the oxidizable fraction (sulphide and organic matter), in agreement with previous reports [5]. The concentration of this metal seems to be correlated to the amount of oxidizable matter. Fig. 2 shows the results obtained from the kinetic assays. As predicted by Forstner method, the kinetic assays confirm the acid drainage from sediments. Zn soluble concentration reached 3 ppm at day 8 witch stay constant till day 29, while the maximum leaching point was reached at 3.4 ppm at day 35. Zinc extraction profiles are in the same behavior of sulphate concentration and pH drop, suggesting a link with sulphide oxidation process. Conditioned samples showed a rise in the rates of zinc extraction, sulphate oxidation and pH drop compared with the non conditioned samples, suggesting that despite the slightly alkaline pH of the sediments, activity of acidophilic iron oxidising bacteria is the main acidification catalysis mechanism. The slightly differences between inoculated and non inoculated systems suggest the presence of native consortia of acidophilic SOB.

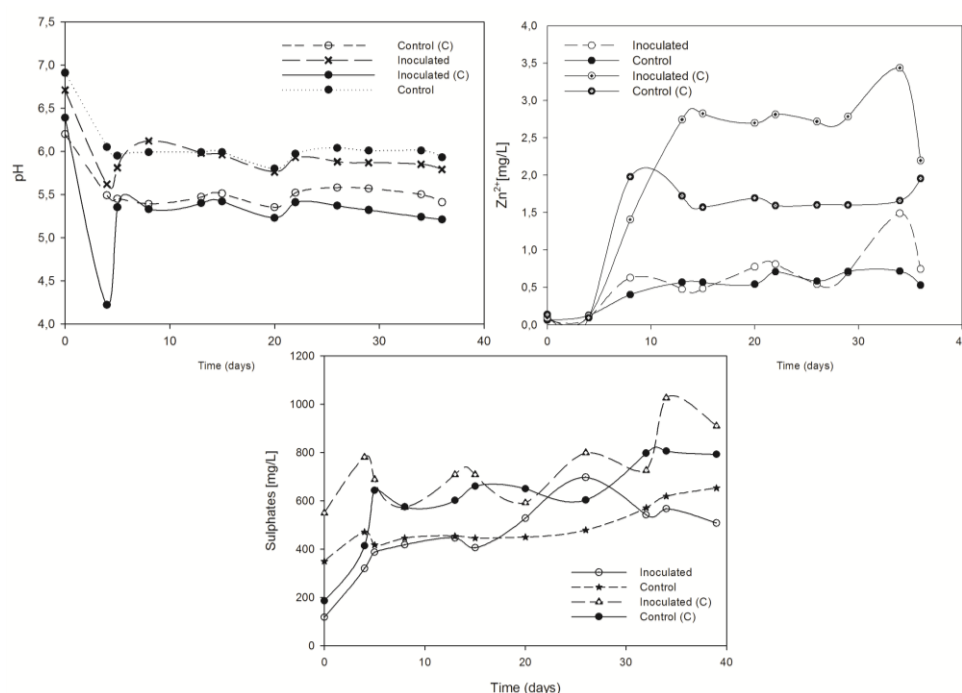


Figure 2: Kinetic assays. Measurements of pH, Zn(II) and sulphate in batch suspension systems Conditioned (C) and without conditioning. Controls have been made of the same sediment without inoculums added.

Enrichment cultures of SOB, SRB and iron oxidizing and reducing bacteria demonstrated all these activities in all the depths of the core and the composite samples. Kinetic and stoichiometric characterization of the native bacterial consortia showed both lower specific growth rates and lower yields biomass to substrate than collection strains (*Acidithiobacillus ferrooxidans* DSM11477 and *Acidithiobacillus thiooxidans* DSM11478) (Data not shown). Further molecular characterization of these consortia is under development.

Conclusions

Anaerobic polluted sediments are similar to low grade sulphidic ores and changes in the redox potential to oxidant conditions could lead to acidification and leaching of heavy metals. The main processes involved in the same way that AMD are biocatalyzed by iron and sulphur oxidizing bacteria. Knowledge of the involved processes and a accurate risk analysis are needed before any management decision on anaerobic sediments.

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