

S, Zn, Cr, Cu AND FE CHANGES DURING FLUVIAL SEDIMENTS OXIDATION

MARÍA PÍA DI NANNO¹; GUSTAVO CURUTCHET^{1,2*} & SILVIA E RATTO³

¹ Escuela de Ciencia y Tecnología, Universidad de San Martín. Colectora Oeste de General Paz 4554. Edificio 23, INTI, San Martín (1650), Buenos Aires, Argentina

² CONICET A. Rivadavia 1971 (1033) Ciudad de Buenos Aires, Argentina;

³ Cátedra de Edafología, Facultad de Agronomía, Universidad de Buenos Aires. San Martín 4453 (1417), Ciudad de Buenos Aires, Argentina. Correo electrónico: gcuruche@unsam.edu.ar

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ABSTRACT

Acidification of dredged sediments which have been disposed on land is highly dependent on redox shifts. The aim of the present work was to assess changes in sulphur, metal speciation (Zn, Fe, Cr y Cu) and acidity caused by a polluted sediment oxidation event. Sediments were desiccated under controlled conditions and sulphide compounds (acid volatile sulphides-AVS- and sulphate), pH and neutralization potential were measured through time during 36 days. Zinc, Cu, Cr and Fe speciation (BCR metal sequential extraction procedure) were measured at the beginning of the experiment and at day 22. An acid-base equilibrium method based on the BCR procedure was employed to assess the sediment acidification risk. Some of the re-suspension experiments were inoculated with an *Acidithiobacillus ferrooxidans* strain to assess biological catalysis on sulphide oxidation. Acid-base equilibrium results indicated the sediment sample had a significant acidification potential. Oxidation increased sulphate levels (56 to 2300 mg S kg⁻¹ in the desiccation experiment with a temporal evolution adjusted by a logistic model, and a 2100 to 3000 mg SO₄⁻² L⁻¹ increase for the re-suspension experiments). Sulphide oxidation rates varied between 0 to 3.1.10⁻⁹ mg O₂ kg⁻¹ s⁻¹ for the drying sediment.

Zinc changes could be explained partially by ZnS conversion to ZnSO₄ during oxidation. Iron reduction could be attributed to an increase in Fe oxides crystallinity. Acid-base equilibrium for the sample indicated it was a potentially acid-generating material. Zinc increased its bioavailability during drying and was the only metal that appeared in significant amounts in solution during re-suspension. Land-filling with dredged sediments could present increased metals bioavailability problems despite having an important and effective neutralization potential.

Keywords. Anaerobic sediments; BCR sequential chemical extraction; desiccation; dredged sediments; fluvial sediments; heavy metals; re-suspension.

TRANSFORMACIONES DEL S, Zn, Cr, Cu y FE EN SEDIMENTOS FLUVIALES DURANTE EL PROCESO DE SECADO

RESUMEN

La evaluación de los riesgos de acidificación por deposición de sedimentos dragados en superficie es muy dependiente de los cambios generados por potencial redox. El objetivo del presente trabajo fue el de evaluar cambios en las formas de azufre, metales (Zn, Fe, Cr y Cu) y aumento de acidez generado por la oxidación de sedimentos contaminados durante un proceso de oxidación controlado. Se midió, sobre sedimentos en proceso de desecación y durante 36 días, sulfuros, sulfuros volátiles, sulfatos, pH y potencial de neutralización. A partir del día 22 se aplicó un procedimiento de extracción secuencial de Zn, Cu, Cr y Fe para evaluar el riesgo de acidificación del sedimento, incluyendo entre los tratamientos la inoculación con una cepa de *Acidithiobacillus ferrooxidans* como catalizador de la oxidación de los sulfuros. La oxidación de sulfatos aumentó de 56 a 2300 mg S kg⁻¹ con una evolución temporal que ajustó a un modelo logístico. Hubo un aumento de 2100 a 3000 mg SO₄⁻² L⁻¹ de sulfatos en el experimento de resuspensión. La oxidación de los sulfuros osciló entre 0 y 3,1.10⁻⁹ mg O₂ kg⁻¹ s⁻¹. Los cambios en el comportamiento del Zn pueden ser explicados parcialmente por la conversión de ZnS a ZnSO₄ durante el proceso de oxidación. La reducción del hierro podría ser atribuida a un aumento en la cristalinidad de los óxidos de Fe. El balance ácido-base señala que la muestra es un material con capacidad generadora de acidez. El Zn aumentó su biodisponibilidad durante el proceso de secado y es el único metal que se encuentra presente en cantidad significativa durante el proceso de resuspensión. La disposición en tierra firme de sedimentos dragados puede generar aumento de biodisponibilidad de metales más allá de su impacto en el potencial efectivo de neutralización.

Palabras clave. Sedimentos anaeróbicos, extracción secuencial (BCR), desecación, sedimentos fluviales, sedimentos dragados, metales pesados, resuspensión.

INTRODUCTION

There is a need to assess sediment/water systems in the long term to ensure their pollutant retention capability will not diminish (Salomons, 1998). Sulphur geochemistry and heavy metal research in dredged sediment derived soils is recent and shows that heavy metal adverse effects are a function of disposal conditions being Eh and pH the most important parameters (Vandecasteele *et al.*, 2002, Förstner, 2004). Many researchers have shown that pH decreases during sediment oxidation (Tack *et al.*, 1997, Borma *et al.*, 2003; Förstner, 2004). If the sediment contains sulphides their oxidation to sulphuric acid might be partially responsible for the acidification of the system. The acidification process will be a function of sulphide oxidation rates versus neutralizing rates by other compounds (Doyle, 2004).

In general, the oxygen supply will control acidity production rates. In sediments, where oxygen consumption is governed by sulphide and organic matter oxidation, the oxygen used up in sulphide sulphur oxidation can be calculated through sulphate production rates (Borma *et al.*, 2003). This parameter is called intrinsic oxidation rate (IOR, Ritchie, 1997)

Many of the oxidation reactions in sediments are catalyzed by microorganisms. Better oxygen availability enhances chemolithotrophs growth, such as those who thrive on sulphur compounds oxidation like *Acidithiobacillus ferrooxidans*, *Acidithiobacillus thiooxidans* and *Thiobacillus thioparus* (Bosecker, 1997; Lors *et al.*, 2004).

During sediment oxidation transformations in heavy metal phases can occur changes affecting their mobility and availability for plants (Singh *et al.*, 1998; Tack *et al.*, 1999). Changes from anoxic to oxic environments can release heavy metals (Hlavay *et al.*, 2004; Caille *et al.*, 2003) due to acidification and sulphide-sulphate conversion.

The aim of the present study is to assess sulphur and heavy metal speciation changes and acidity production during a polluted sediment oxidation. To achieve our goal the sediment was allowed to desiccate in controlled conditions and sulphate, acid volatile sulphides (AVS), pH, neutralization potential and Cr, Cu, Zn and Fe speciation were evaluated in a 36 days experiment. In order to try to relate metal speciation changes in the solid with their solubilization in an aqueous media, batch re-suspension experiments were also performed.

MATERIALS AND METHODS

Sampling. The sediment was sampled from Las Piedras stream which is located in 34° 45' 6.57" South and 58° 18' 47.09" West WGS 84, Buenos Aires province (Argentina). The stream is heavily polluted due to industrial effluents discharges

(paper, tannery, printing offices, slaughter houses and car wash stations). A sediment grab sample was taken in September 2006 and collected in 10 L polyethylene containers. The sample was bottled with its initial moisture content (no drying or draining was performed) and was kept saturated to maintain the anoxic conditions during storage. Before the experiments, the sample was manually homogenized and visible debris was removed.

Desiccation experiment. To assess sulphur and metal changes during the sediment drying 100 ± 3 g of the fresh sediment (57% moisture) were placed in plastic containers (7 cm height and 5 cm diameter). This resulted in a 4 cm layer of sediment. The experimental design employed was a completely aleatorized design with 18 systems (6 levels for time and three replicate systems). The systems were kept opened and at ambient temperature (20 ± 5°C). Water removal occurred by evaporation only. Periodically (days 0, 8, 15, 22, 19 and 36) sub-samples from the systems were analyzed for pH (potentiometrically, 1:2 in H₂O); neutralization potential (Ahern *et al.*, 2004); moisture (gravimetrically at 105°C until constant weight); acid volatile sulphides (AVS, ambient temperature purge and trap method with quantification by the blue methylene conversion method; Morse *et al.*, 1987) and sulphate concentration (Tack *et al.* 1997, with turbidimetric quantification). Neutralization potential is expressed as equivalent %CaCO₃.

The BCR metal sequential extraction procedure (Ure *et al.*, 1993) was performed on the sediments at the start (day 0) and after 22 days (triplicate measurements). The four sequential extraction steps use 0.11 mol L⁻¹ acetic acid (step 1: exchangeable and water-acid soluble as carbonate bound metals); 0.1 mol L⁻¹ hydroxylammonium chloride acidified with NO₃H to pH 2 (step 2: Fe and Mn oxides; reducible fraction); 8.8 mol L⁻¹ hydrogen peroxide (step 3: organic matter and sulphide bound metals; oxidizable fraction) and aqua regia (step 4: residual fraction, non silicate bound metals). As proposed by Kersten and Förstner, (1991) we used Ca from step 1, Fe from step 2 and sulphate from step 3 (from the first extraction at day 0) to calculate the Acid Producing Potential (APP) and acid consuming capacity (ACC) of the sediment samples. ACC was calculated measuring Ca concentration in the supernatant from step 1 by flame atomic absorption spectroscopy (AAS). Actual APP represented by sulphides and the maximum ferrous sulphide APP (ASC, Acid sulfide capacity) were calculated measuring sulphate from Step 3 by turbidimetric means (designated Sulphide sulphur) and Fe from Step 2 by AAS respectively. If ACC-APP < 0 the sediment sample was considered to have a significant acidification potential (Kersten & Förstner, 1991; Förstner, 2004).

Humidity levels of dry samples in the laboratory conditions varied between 4 and 6%. This means that there is enough water present from the air's humidity for the sulphide oxidation reaction to occur (Borma *et al.*, 2003). Despite this and following Borma *et al.* (2003) procedure, the systems were sprayed with 5 mL water to ensure the supply was greater than the minimum required.

All the results are expressed in a dry matter basis. Results were evaluated using variance analysis. Media comparison was performed with the Tukey test with a 5% significance level.

Re-suspension experiments. Previous work on other samples from the same site had shown a significant acidification potential with Zn release (Di Nanno *et al.*, 2007). Batch experiments were also carried out for the same sediment sample used for the desiccation experiment in order to compare the acidification and

metal release results obtained with two different methods. The experiment was carried out in 125 mL Erlenmeyer and continuously agitated on a horizontal shaker at 110 rpm and ambient temperature ($20 \pm 5^\circ\text{C}$) during 31 days. The Erlenmeyer were capped with cotton plugs in order to ensure gas exchange between the sediment and the atmosphere. The slurry for the leaching test was prepared by mixing fresh anoxic sediment with a minimum mineral media medium (iron free 9K medium) Silverman and Lundgrem 1959: $3.0 \text{ g L}^{-1} (\text{NH}_4)_2\text{SO}_4$; $0.5 \text{ g L}^{-1} \text{K}_2\text{HPO}_4$; $0.5 \text{ g L}^{-1} \text{MgSO}_4 \cdot 7 \text{H}_2\text{O}$; $0.0144 \text{ g L}^{-1} \text{CaCl}_2 \cdot 2\text{H}_2\text{O}$; $0.1 \text{ g L}^{-1} \text{KCl}$ acidified with H_2SO_4 to pH. 2.5) at a ratio of $15.0 \pm 0.5 \text{ g}$ to 70 mL leaching solution. The media employed provides N and P necessary for microbial activity. The sediment-solution ratio used ($21 \text{ g } 100 \text{ mL}^{-1}$) is recommended by the British Columbia Research Confirmation Test for rock samples with a high sulphur content (Coastech Research, 1991). Two conditions were studied: non inoculated and inoculated systems. For the inoculated systems, the *Acidithiobacillus ferrooxidans* inoculum was obtained by filtration (cells in the late exponential growth phase grown on 9K medium: Silverman & Lundgrem, 1959). The cells were re-suspended in 0K media and counted in a Thoma counting chamber with an optic microscope. Water lost by evaporation was added before sampling. For each microcosm, a 15.0 mL suspension sample was withdrawn, filtered through blue ribbon filter paper and submitted for chemical analyses (pH, sulphate, Zn, Cu, Cr, Ca and Fe). The pH of the filtrate was measured using a Cole Parmer pH electrode. Sulphate ions were quantified by a colorimetric method (Vogel, 1991). Zn, Cu, and Ca concentrations were measured by atomic absorption means. Total Cr in solution was measured

oxidizing 1.00 mL of the suspension with 2.00 mL KMnO_4 (0.02 N) and 1.00 mL H_2SO_4 (1.8M) at 100°C for 30 minutes. Afterwards the sample was discolored with sodium azide (10%) after the oxidation process and Cr concentration measured using the colorimetric diphenylcarbazide method (APHA, 1995). Fe^{2+} and total Fe were measured by the 1-10 orthophenantroline colorimetric method (Stucki, 1981).

RESULTS

The acid base account results are summarized in Table 1. The balance result is negative what indicates a significant acidification potential.

Desiccation. Desiccation results are presented in Table 2. The results show a significant pH decrease from 8.53 ± 0.09 to 7.48 ± 0.06 in 15 days. The pH decrease only occurs during the first two weeks because there are no significative differences beyond that day for that parameter. Moisture levels decrease from 51.2 ± 0.6 to $7.5 \pm 1.6\%$ during 15 days and afterwards remain constant at 4-8%. The neutralization potential of the sediments changes more gradually than pH or humidity. It decreases from 2.78 ± 0.03 to $2.02 \pm 0.17\%$ in 36 days. One of the more drastic changes was reflected in the sulphate

Tabla 1. Balance ácido-base aplicando el procedimiento de extracción secuencial de metales (BCR).

Table 1. Acid base account (BCR derived methodology).

BCR sequential leaching technique/ Kersten & Förstner method			
APP		Acid base account	
ACC (mmol kg^{-1})	ASC (mmol kg^{-1})	Sulphide sulfur (mmol kg^{-1})	ACC-APP (mmol kg^{-1})
74 ± 3	30 ± 2	140 ± 4	-96

Results are expressed as media \pm standard deviation, n=3.

Tabla 2. Evolución temporal de pH, potencial de neutralización, sulfatos, productividad de sulfatos y de sulfuros volátiles ácidos (AVS) durante el proceso de desecación.

Table 2. Temporal evolution of pH; neutralization potential, sulphate, sulphate productivity and AVS during the desiccation process.

Day	0	8	15	22	29	36
pH	$8.53 \pm 0.09 \text{ a}$	$8.04 \pm 0.14 \text{ b}$	$7.48 \pm 0.06 \text{ c}$	$7.46 \pm 0.02 \text{ c}$	$7.35 \pm 0.02 \text{ c}$	$7.46 \pm 0.01 \text{ c}$
Moisture (%)	$56.7 \pm 0.6 \text{ a}$	$28.6 \pm 1.7 \text{ b}$	$7.5 \pm 1.6 \text{ c}$	$6.58 \pm 0.7 \text{ c}$	$4.35 \pm 0.15 \text{ c}$	$5.55 \pm 0.6 \text{ c}$
Neutralization potential (% CaCO_3)	$2.78 \pm 0.03 \text{ a}$	$2.73 \pm 0.09 \text{ a}$	$2.47 \pm 0.18 \text{ ab}$	$2.33 \pm 0.09 \text{ bc}$	$2.34 \pm 0.12 \text{ bc}$	$2.02 \pm 0.17 \text{ c}$
Sulphate (mg S kg^{-1})	$56 \pm 43 \text{ a}$	$423 \pm 207 \text{ a}$	$1299 \pm 170 \text{ b}$	$2300 \pm 91 \text{ c}$	$2216 \pm 402 \text{ c}$	$2632 \pm 103 \text{ c}$
Sulphate productivity ($\text{mg SO}_4^{-2} \text{ kg}^{-1} \text{ week}^{-1}$)	—	964	2626	3003	-252	1250
AVS (mg S kg^{-1})	$127 \pm 57 \text{ a}$	$100 \pm 13 \text{ a}$	ND	ND	ND	ND

Different letters indicate significative differences ($p < 0.05$). Results are expressed as media \pm standard deviation of three replicates. ND means below detection limit ($< 2 \text{ mg S kg}^{-1}$).

concentration that increased from 56 ± 43 to 2300 ± 91 mg S kg^{-1} until day 22. Afterwards sulphate concentration in the solid reaches a plateau. Sulphide oxidation rates (IOR) measured through sulphate production reported a value of 10^{-9} $\text{mg O}_2 \text{ kg}^{-1} \text{ s}^{-1}$. AVS decreases from 163 ± 27 to <2 mg S kg^{-1} in 15 days (Figure 1).

Metal speciation results: Adding the different metal fractions from the BCR fractionation we determined the following metal contents: $173 \text{ mg Cr kg}^{-1}$; $115 \text{ mg Cu kg}^{-1}$; $364 \text{ mg Zn kg}^{-1}$ and $12000 \text{ mg Fe kg}^{-1}$. Aquaregia heavy metal contents were $158 \text{ mg Cr kg}^{-1}$; $150 \text{ mg Cu kg}^{-1}$ and $329 \text{ mg Zn kg}^{-1}$ (Table 3).

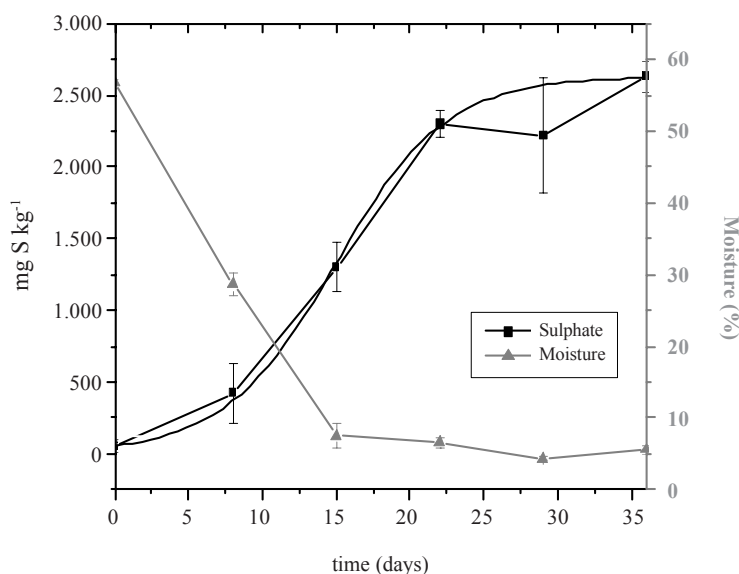


Figura 1. Evolución en el tiempo de la humedad y los sulfatos en el ensayo de desecación.

Figure 1. Moisture and sulphate evolution in time in the desiccation experiment.

Tabla 3. Especiación de metales (Zn, Cu, Fe y Cr) en sedimentos secos y frescos.

Table 3. Metal speciation (Zn, Cu, Fe and Cr) in fresh and dried sediments.

Description	%	Step 1 (acid soluble)	Step 2 (reducible)	Step 3 (oxidizable)	Step 4 (residual)
Fresh sediment (day 0)	Zn	5 ± 3	51 ± 4	10 ± 1	35 ± 5
Dried sediment (day 22)	Zn	42 ± 4	27 ± 2	3 ± 2	28 ± 5
p value	Zn	0.001	0.01	0.02	0.17
Fresh sediment (day 0)	Cu	ND	3 ± 2	31 ± 5	66 ± 4
Dried sediment (day 22)	Cu	ND	3 ± 3	5 ± 4	92 ± 10
p value	Cu	—	0.86	0.001	0.21
Fresh sediment (day 0)	Fe	14 ± 4	14 ± 1	3 ± 1	70 ± 3
Dried sediment (day 22)	Fe	3 ± 2	17 ± 3	1.0 ± 0.4	79 ± 5
p value	Fe	0.01	0.13	0.12	0.33
Fresh sediment (day 0)	Cr	ND	35 ± 5	27 ± 6	38 ± 3
Dried sediment (day 22)	Cr	ND	48 ± 6	20 ± 4	32 ± 3
p value	Cr	—	0.23	0.29	0.10

Results are expressed as media \pm standard deviation of three replicates. ND means below detection limit.

Oxidizable and reducible Zn fractions in the fresh sediments evolves into soluble ones or more labile compounds such as carbonates. Zn residual fraction does not suffer significative changes during sediment drying. Drying causes a decrease in Cu oxidizable fraction (31 % to 5%) and do not increases the other operational phases ($P < 5\%$). Fe shows no difference in speciation results, except for the first fraction that diminished with air drying. No significative differences for Cr were found between the fresh and the air dried sediment. Like for Cu, no Cr was detected in the first fraction.

Batch re-suspension experiments. It can be seen that the sediment oxidation acidified the media (between 0.8 to 1.1 pH units) in both control and inoculated systems (Figure 2a and Table 4).

Sulphate concentrations increased (2100 to 3000 mg $\text{SO}_4^{2-}\text{L}^{-1}$) and 90% of the sulphate release occurred during the first week while sulphate rate release diminished with time (Figure 2b). Sulphate rate release- calculated for the first week data only- varied between 13000 to almost 19000 mg $\text{SO}_4^{2-}\text{kg}^{-1}\text{week}^{-1}$ for control and inoculated systems respectively (see Table 4). Neither Cr nor Cu was detected during the entire re-suspension experiment (their concentration remained below 0.2 mg L^{-1}). Zn was the only analyzed heavy metal that reached high concentrations in solution- up to 5 mg L^{-1} (Figure 2c). Fe and Ca concentrations varied between $<0.3\text{--}9.0\text{ mg Fe L}^{-1}$ (Figure 2e and 2f) and $112\text{--}391\text{ mg Ca L}^{-1}$ (Figure 2d).

DISCUSSION

If we compare the neutralization potential from the Kersten and Förstner (1991) method against Ahern *et al.*

(2004) methodology we find that the first one (1.48% CaCO_3) is almost a 50% lower (see Tables 1 and 2). The Ahern method determines the neutralization potential by back titration of an excess of HCl added to 1 g dry matter of the sediment after reaction at 100°C . The drastic conditions employed increase the reacting minerals in this method.

As for the desiccation results, it can be seen that at higher humidity levels a higher pH is measured. When the sediment dries sulphide oxidation takes place and pH decreases. Despite this, pH doesn't become acid (<7) because of the effective neutralization potential content of the sample.

The neutralization potential decrease as a result of sediment desiccation has already been reported by other authors (Tack *et al.*, 1997). A neutralization potential decrease leaves the system more vulnerable against eventual pH changes. However in our case the system still has a considerable buffer capacity (more than 70% of the original equivalent carbonate content).

Sulphate reaches a constant value after day 22 may be due to oxidizable sulphides disappearance or iron hydroxide layers on the sulphide crystals that retard oxygen penetration, thus slowing down sulphide oxidation (Borma *et al.*, 2003). Sulphate concentration increases exponentially until it reaches some limiting value, so with the obtained data a model was developed that assumes a sigmoid curve adjustment ($\text{mg S kg}^{-1} = 2493[1 + 45 e^{-0.26 \text{ day}}]^{-1}$; $R^2 = 0.99$) (Figure 1). In many sediment oxidation experiments it has been found a decrease in the sulphate release rates trough time with a consequent concentration stabilization (Borma *et al.*, 2003, Tack *et al.*, 1997; Lors *et al.*, 2004).

If we compare the sulphide-sulphur amount obtained in the third step of the acid base account ($14\text{ mmol S } 100\text{ g}^{-1}$) with the maximum sulphate sulphur in the oxidized sediment ($7.2\text{ mmol S } 100\text{ g}^{-1}$) we find that there are still

Tabla 4. Resultados de los ensayos de desecación y resuspensión en estado inicial y final para el pH, variación de pH, productividad de sulfatos y comparación del IOR.

Table 4. Desiccation and re-suspension final and initial pH, delta pH; sulphate productivity and IOR comparison.

System	Initial pH (day 0)	Final pH (day 36)	Δ pH (pH units)	Sulphate productivity range (mg $\text{SO}_4^{2-}\text{kg}^{-1}\text{week}^{-1}$)	IOR (kg $\text{O}_2\text{kg}^{-1}\text{s}^{-1}$)
Desiccation	8.53 ± 0.10	7.46 ± 0.01	-1.07	0 to 3003	$0\text{--}3.1.10^{-9}$
Re-suspension	Initial pH (day 0)	Final pH (day 31)	Δ pH (pH units)	Maximum sulphate productivity (mg $\text{SO}_4^{2-}\text{kg}^{-1}\text{week}^{-1}$)	IOR (kg $\text{O}_2\text{kg}^{-1}\text{s}^{-1}$)
Control	6.0 ± 0.1	5.20 ± 0.05	-0.8	13674 ± 2050	$2.5.10^{-8}$
Inoculated	6.2 ± 0.1	5.15 ± 0.05	-1.1	18783 ± 2249	$3.4.10^{-8}$

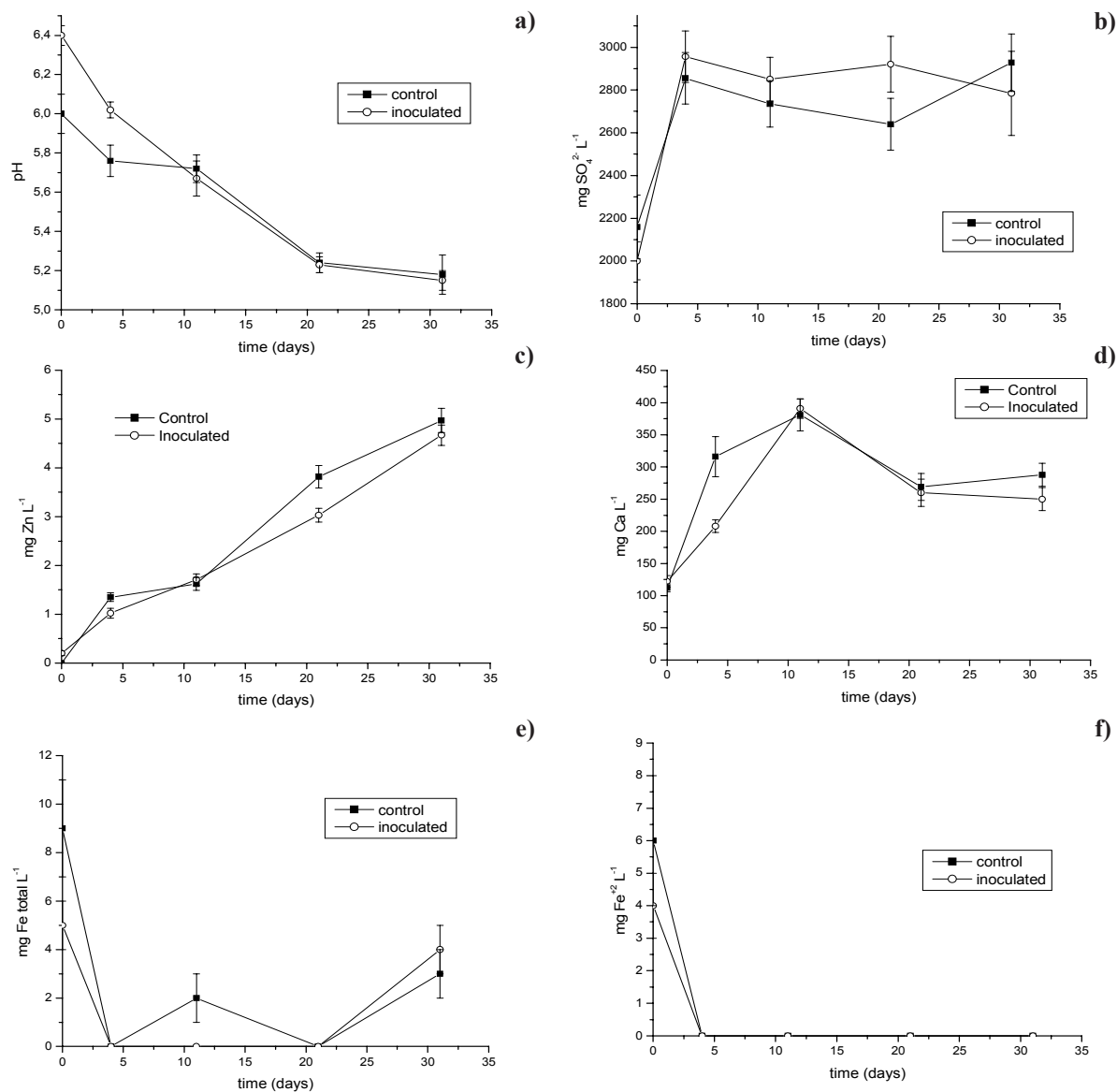


Figura 2. pH, concentración de SO_4^{2-} , Zn, Ca, Fe y Fe^{2+} en los experimentos para sistemas inoculados y testigo.

Figure 2. pH and SO_4^{2-} , Zn, Ca, Fe and Fe^{2+} concentration in the re-suspension experiment for control and inoculated systems.

remaining sulphides in the sample. But this sulphur fraction doesn't react in cold HCl and is not measured as AVS with the methodology employed in this study. This difference might be ascribed to the presence of pyrite or organic sulphur compounds more resistant to oxidation than AVS (Tack *et al.*, 1997).

When pH reaches a 7.3-7.5 value, sulphate increases in the solid are not translated into an acidification of the system (Table 2). This is explained by the sediment proton

consuming action or by the oxidation of some sulphides or organic matter that do not generate net acidity during this process.

Concerning metal speciation changes caused by drying/oxidation (see Table 4), we find that Zn increases significantly in the acid soluble phase with a concomitant decrease in the oxidizable and reducible fractions. No significant changes for the residual phase are found for none of the three studied metals as a result of the drying

process. The obtained results would indicate an increase in Zn availability due to the sediment oxidation. Our results are equivalent to the results of various others authors (Zoumis *et al.*, 2001; Zhang *et al.*, 2001). Peltier *et al.* (2005) indicated that part of the Zn that appears in the reducible fraction actually corresponds to SZn, unstable compound at pH 2 (Step 2, hydroxylamine extraction). So the actual decrease in the oxidizable fraction might be higher than what it is reported here. Zn changes could be explained partially by ZnS to ZnSO₄ conversion during oxidation and by a metal release during organic matter oxidation.

For Cu, we find that the oxidizable bound fraction diminishes in a significant way (31 to 5%). This behavior has been reported by other authors (Zhang *et al.*, 2001). Chemical and/or biochemical reactions associated to this change would be equivalent to those indicated before for Zn. Due to data dispersion and the sensitivity of the analytical method employed it wasn't possible to find an enrichment for the other operational phases. However other authors report increases in the reducible fraction upon sediment oxidation (Iorio, 1999; Zhang *et al.*, 2001).

For Fe, a significant decrease in the acid soluble fraction was found upon drying, possibly due to an increase in Fe oxides crystallisation (Hlavay *et al.*, 2004; Tack *et al.*, 1996).

Not statistically significant changes were detected for Cr as a result of the sediment oxidation during the drying process. As for Cu, the metal was not found in the acid soluble and interchangeable fraction (Step 1). Morrison *et al.* (2006) performing the metal fractionation -no residual step- on dry sediments indicate that almost no Cr was found in the first fraction but that it was mainly distributed between the second and third extracts. On land disposed sediments, Singh *et al.* (2000) report that more than the 80% of the Cr was associated to the oxidizable and residual fractions results that are consistent with ours.

Various authors have reported an increase in the more labile chemical species with sediment drying/oxidation (Baeyens *et al.*, 2003; Tack *et al.*, 1996). Land-filled calcareous dredged sediments with high organic matter and clay contents may show an appreciable bio-availability of heavy metals (Vandecasteele *et al.*, 2002; Tack *et al.*, 1999; Singh *et al.*, 1998). In the present work, changes in Fe (acid soluble fraction), Zn (acid soluble, reducible and oxidizable fractions) and Cu (oxidizable fraction) geochemical distribution were found during air drying. No changes for Cr were detected. Changes in Fe would tend to shift the metal to less labile fractions whilst for Zn its availability would increase. Our results indicate that sediment oxidation doesn't increase the availability of all the metals present in the sediment.

Sulphate rate release was much higher in the re-suspension experiment (10^{-8} kg O₂ kg⁻¹ s⁻¹) compared to the desiccation one (10^{-9} kg O₂ kg⁻¹ s⁻¹) (see Table 4). Average IOR calculated with data presented by Tack *et al.*, (1997) for polluted sediment from Belgium renders a value of $4.4 \cdot 10^{-9}$ kg O₂ kg⁻¹ s⁻¹. Borma *et al.* (2003) report IOR values for lagoon sediments from Brazil between $1.4 \cdot 10^{-11}$ and $1.3 \cdot 10^{-9}$ for a long experiment (1 year, the higher values correspond to the initial phases). Cappuyns *et al.* (2006) also find an increase in the sulphide oxidation rate for re-suspension experiments (by a factor of four). For the studied sediment and for this experimental conditions, the increase was between a factor of 4, 5 and 6 times.

The inoculation effect was demonstrated by a slightly higher maximum sulphate rate release (see Table 4). Lors *et al.*, (2004) found a higher sulphate release in biotic compared to abiotic conditions. Their result confirms that in abiotic conditions sulphide oxidation is lower (Petersen *et al.* 1997 in Lors *et al.*, 2004). In our case the control system was not sterilized-it was a not inoculated system. The sediment possibly contains indigenous microorganisms with sulphide oxidation capability.

In general, experiments indicate increased trace element availability upon aerating anoxic sediment (Caille *et al.*, 2003). In this case, neither Cu nor Cr appears in solution during the re-suspension while Zn reached high aqueous concentrations (Figure 2c). Cu is more strongly retained by various compounds present in the sediment like organic matter and Fe oxides than Zn (Tack *et al.* 1998; Lors *et al.*, 2005). Cr is usually catalogued like the less potentially leachable metal present in sediments with respect to its total content (Singh *et al.*, 2000). Fe concentration varied through time. High initial values of Fe concentration could be explained by the acid extraction media (Lors *et al.*, 2004) and the progressive increment found afterwards would be a function of the system acidification (Figure 2e). Ca appearance in solution would indicate carbonate dissolution evidencing the neutralization potential action (Figure 2d). Ca concentration lowers after 11 days. Ca y SO₄⁻² concentrations are beyond gypsum Kps what would suggest a possible precipitation of similar compounds in the systems. Gypsum precipitation has already been observed by other authors (Cappuyns *et al.*, 2006).

Comparing the results from the desiccation and the re-suspension experiments we see that Zn increased its bioavailability during both of them what indicates that it is the more potentially leachable studied metal present in the sediment.

CONCLUSIONS

Acid base account for the sample indicated the sample was a potentially acid generating material. The sediment acidified both in the desiccation and the re-suspension experiments, however sulphate productivity (sulphide oxidation rate) was higher in the re-suspension systems. Due to the effective neutralization potential of the sediment, pH didn't became acidic (<7) upon drying.

During the oxidation process important alterations in metal speciation were found. Zn increased its bioavailability during sediment oxidation caused by drying and was the only metal that appeared in significant amounts in solution during re-suspension. Fe availability was reduced upon drying. No significant changes for Cr were detected.

Recommendations and Perspectives: Land filling with dredged sediments could present increased metal bioavailability (Zn, probably Cd) problems despite having an important and effective neutralization potential.

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REFERENCES

- Ahem, CR; AE McElnea & LA Sullivan. 2004. Acid sulfate soils laboratory methods guidelines. Queensland Department of Natural Resources, Mines and Energy, Indooroopilly, Queensland, Australia.
- APHA. 1995. Standard methods for the examination of water and wastewater, 19th ed. American Public Health Association, Washington DC, USA.
- Baeyens, W; F Monteny; M Leermakers & S Bouillon. 2003. Evaluation of sequential extractions on dry and wet sediments. *Analytical and Bioanalytical Chemistry* 376: 890-901.
- Borma, L de S; M Errlich & MC Barbosa. 2003. Acidification and release of heavy metals in dredged sediments. *Can. Geotech. J.* 40: 1154-1163.
- Bosecker, K. 1997. Bioleaching: metal solubilization by microorganisms. *FEMS Microbiology Reviews* 20 : 591-604.
- Caille, N; C Tiffreau; C Leyval & JL Morel. 2003. Solubility of metals in an anoxic sediment during prolonged aeration. *The Science of the Total Environment* 301: 239-250.
- Cappuyns, V; R Swennen & A Devivier. 2006. Dredged river sediments: potential chemical time bombs? A case study. *Water, Air, and Soil Pollution* 171: 49-66.
- Coastech Research. 1991. Acid Rock Drainage Prediction Manual. Mine Environment Neutral Drainage (MEND) Program. Mend Project Report 1.16.1b. Ontario, Canadá.
- Devasahayam, S. 2006. Chemistry of acid production in black coal mine washery wastes. *International Journal of Mineral Processing* 79: 1-8.
- Di Nanno, MP. 2006. Riesgo de acidificación y liberación de metales por resuspensión de sedimentos anaeróbicos del Arroyo Las Piedras (Bs.As., Argentina). Trabajo final. Especialización en gestión ambiental en sistemas agroalimentarios. Escuela para Graduados, Facultad de Agronomía, Universidad de Buenos Aires.
- Di Nanno, MP; G Curutchet & S Ratto. 2007. Anaerobic sediment potential acidification and metal release risk assessment by chemical characterization and batch re-suspension experiments. *J Soils Sediments* 7(3): 187-194
- Doyle, M. A. 2004. Posibilidad de generación de drenaje ácido en un suelo fabricado en laboratorio conteniendo sulfuro de hierro y materia orgánica. Tesis de Maestría para optar por el Master en Ciencias e Ingeniería Civil. Universidad Federal de Río de Janeiro. Río de Janeiro, Brasil.
- Du Laing, G; DRJ Vanthuyne; B Vandecasteele; FMGTack & MG Verloo. 2006. Influence of hydrological regime on pore water metal concentrations in a contaminated sediment-derived soil. *Environmental Pollution* 147: 615-625.
- Förstner, U. 1993. Risk assessment and technological options for contaminated sediments-A geochemical perspective. Proceedings from Sediment Water Science Symposium held at Santa Barbara, USA.
- Förstner, U. 2004. Traceability of sediment analysis. *Trends in Analytical Chemistry* 23: 217-236.
- Hlavay, J; T Prohaska; M Weisz; W Wenzel & G Stingeder. 2004. Determination of trace elements bound to soils and sediment fractions. *Pure Appl. Chem.* 76: 415-442.
- Iorio, Alicia. 1999. Distribución y dinámica de las formas químicas de Cu en relación con Fe y Mn en un Natracuol de la Pampa deprimida. Tesis de Maestría. Facultad de Agronomía, Universidad de Buenos Aires.
- Kersten, M & U Förstner. 1991. Geochemical characterization of the potential trace metal mobility in cohesive sediments. *Geo-Marine Letters* 11: 184-187.
- Lors, C; C Triffreau & A Laboudigue. 2004. Effects of bacterial activities on the release of heavy metals from contaminated dredged sediments. *Chemosphere* 56: 619-630.
- Morrison, H; V Vicente-Beckett. Chemical sequential extraction of estuarine sediments of central Queensland. (2006). http://www.association.cqu.edu.au/cqusa_new_site/cqusa%20site/aafash/Menu/Site/ps0/2002%20Papers/HelenMorrison.pdf
- Morse, JW; FJ Millero; JC Cornwell & D Rickard. 1987. The chemistry of hydrogen sulphide and iron sulphide systems in natural waters. *Earth Science Review* 24: 1-42.
- Peltier, E; A Dahl & JF Gaillard. 2005. Metal speciation in anoxic sediments: when sulfides can be construed as oxides. *Environ. Sci. Technol.* 39: 311-316.
- Price, W. 1997. Draft Manual. Guidelines and Recommended Methods for the Prediction of Metal Leaching and Acid Rock Drainage at Minesites in British Columbia (Prediction Manual). Reclamation Section, Energy and Minerals Division. Ministry of employment and investment. British Columbia, Canadá. 143 págs.

- Ritchie, I. 1997. Optimization of biooxidation of bioheaps. *In: Biomining: Theory, microbes and industrial processes*. Douglas Rawlings (ed). Springer Verlag. Germany. 302 pag.
- Salomons, W. 1998. Biogeodynamics of contaminated sediments and soils: perspectives for future research. *Journal of Geochemical Exploration* 62: 37-40.
- SENES Consultants Limited. 1994. Review of waste rock sampling techniques. Prepared for Energy Mines and Resources. Canadian Centre for Mineral and Energy Technology (CANMET), MSL Division. Mine Environmental Neutral Drainage (MEND) Project 4.5.1. Canadá.
- Silverman, MP & D.G Lundgren. (1959). Studies on the chemotrophic iron bacterium *Ferrobacillus ferrooxidans*: I. An improved medium and harvesting procedures for securing high cell yields. *J. Bacteriol.* 77: 642-651.
- Singh, SP; LQ Ma; FMG Tack & MG Verloo. 2000. Trace metal leachability of land-disposed dredged sediments. *Journal of environmental quality* 29: 1124-1132.
- Singh, SP; FM Tack & MG Verloo. 1998. Heavy metal fractionation and extractability in dredged sediment derived surface soils. *Water, Air, and Soil Pollution* 102: 313-328.
- Smolders, AJP; M Moonen; K Zwaga; E.C.H.E.T Lucassen; LPM Lamers & JGM Roelofs, 2006. Changes in pore water chemistry of desiccating freshwater sediments with different sulfur contents. *Geoderma* 132: 372-383.
- Stucki, W. 1981. The quantitative assay of minerals for Fe+2 and Fe+3 using 1-10-phenantroline: II A photochemical method. *Soil Sci. Soc. Am.* 45: 638-641.
- Tack, FM; WJJ Callewaert & MG Verloo. 1996. Metal solubility as a function of pH in a contaminated, dredged sediment affected by oxidation. *Environmental pollution* 91: 199-208.
- Tack, FM; F Lapauw & MG Verloo. 1997. Determination and fractionation of sulphur in a contaminated dredged sediment. *Talanta* 44: 2185-2192.
- Tack, FMG; SP Singh & MG Verloo. 1999. Leaching behavior of Cd, Cu, Pb and Zn in surface soils derived from dredged sediments. *Environ Pollut.* 106:107-114.
- Tack, FMG; SP Singh & MG Verloo. 1998. Heavy metal concentrations in consecutive saturation extracts of dredged sediment derived surface soils. *Environmental pollution* 103: 109-115.
- Ure, AM; Ph Quevauviller; H Muntau & B Griepink. 1993. Speciation of heavy metals in soils and sediments. An account of the improvement and harmonization of extraction techniques undertaken under the auspices of the European communities. *Int. J. Environ. Anal. Chem.* 51: 135-151.
- Vandecasteele, B; B De Vos & FMG Tack. 2002. Heavy metal contents in surface soils along the Upper Scheldt river (Belgium) affected by historical upland disposal of dredged materials. *The Science of the Total Environment* 290: 1-14.
- Vogel, AT. 1961. A textbook of quantitative inorganic analysis including elementary instrumental analysis. Third edition. Longman, London.
- Zhang, S; S Wang & X Shan. 2001. Effect of sample pretreatment upon the metal speciation in sediments by a sequential extraction procedure. *Chemical Speciation and Bioavailability* 13: 69-74.
- Zoumis, T; A Schmidt; L Grigorova & W Calmano. 2001. Contaminants in sediments: remobilisation and demobilisation. *The Science of the Total Environment* 266: 195-202.