

SULPHUR GEOCHEMISTRY IN THE SEDIMENTS OF A NATURAL TROPICAL WETLAND

Alfaro-De La Torre M. Catalina¹, Pérez-Castillo F. Virginia¹, Briones-Gallardo Roberto², Medellín-Milán Pedro³; ¹Facultad de Ciencias Químicas; ²Instituto de Metalurgia; ³Agenda Ambiental, Universidad Autónoma de San Luis Potosí, México

ABSTRACT

In freshwater wetlands, the degradation of organic sulfur from plants residue may result in higher sulfate concentration in the overlying water column. The influence of plant activities may therefore modify the distribution of sulfur between the solid and aqueous phases.

Understanding the biogeochemistry of sulfur (S) in a wetland is important because elevated sulfate levels may contribute to phosphorus release from soils, a process termed “internal eutrophication”. Even though the above processes are well understood from a theoretical standpoint, the extent to which they may occur in a tropical wetland located in Central Mexico is unknown, especially the influence of S on P cycling. In this work, S (SO_4^{2-} , $\Sigma[\text{HS}^-]$) in sediment and porewater were determined over 1.5 year additionally to phosphorus, iron and other parameters to understand the contributions of S on the mobility of P.

In this study, we found high sulfate concentrations (2.0-19.9mM) and low Fe concentrations in porewater (< 25 μM). The determination of diffusion flux using Fick's law and diffusion coefficient at the interface water-sediment indicates that sulfates flows from sediment to the water column. Modeling with MINEQL, sulfides predict these are controlled by the formation of $\text{FeS}_2(\text{s})$ or $\text{MnS}(\text{s})$ since there are saturation conditions concerning these solid phases. Thus, we proposes that in the wetland, the presence of sulfides is controlled by the dissolution of the solid phases that are mobilized from sediments to water and the production via sulfate reduction. Several authors have indicated that sulfides produced from sulfate reduction promote the formation of iron sulfides and decrease the potential of absorption of phosphorus and the potential of release of phosphorus from sediments.

Keywords: Sulfate Reduction, Phosphorus, Eutrophication, Tropical Freshwater Wetland

INTRODUCTION

Significant sulfate reduction occurs in eutrophic lakes [1]. This process is controlled by the sulfate concentration however this aspect is poorly known in the sediments of shallow systems. Sulfate concentrations are delivered from groundwater discharges in wetlands. However, the degradation of organic sulfur from plants residue may also result in higher sulfate concentration in the overlying water column in freshwater wetlands [2]. The influence of plant activities may therefore modify the distribution of S between the solid and aqueous phases. Sulfate reduction to sulfides can mobilize P bound to Fe impacting eutrophication in freshwater ecosystems [3]. This process is known as “internal eutrophication” and refers to the sulfate reduction and iron sulfides formation leading to a lower availability of Fe for P binding [1].

Few reports have documented the effects of high concentrations of sulfate on the eutrophication process in wetlands. However, those systems with high organic matter concentrations could be affected

through the sulfate reduction increasing the release of iron bound-P.

Understanding the biogeochemistry of sulfur (S) in freshwater wetlands is important because elevated SO_4^{2-} levels may contribute to P release from sediment. This paper presents preliminary results of sulfate and sulfides in sediment porewater from a tropical wetland located in central Mexico also the dissolved iron fluxes through the water-sediment interface to understand the contributions of S on the mobility of P.

METHODS

The study was done in the tropical wetland “Ciénega Tamasopo” located in Central Mexico (Figure 1) [4]. Water inputs come from springs in the upper part of the basin (twelve have been characterized) and rainwater. Wetland supply water for agriculture (sugar cane) and population (15 towns with less than 250 inhabitants are located around). In addition, this wetland is affected by wastewater discharges. Water column depth varied between 0.3m and 1.2m (September – November, 2012).

Vegetation is abundant, ~68% of the wetland area and is dominated by hydrophyte plants (floating as *Nymphaea goudotiana*, submerged as *Elodea* sp. and emergent as *Typha* sp., and *Cladium* sp.). Vegetation acts as a filter of sediments however the plant abundance increased by 10% in the last decade indicating that some process are affecting the eutrophication in this lake.

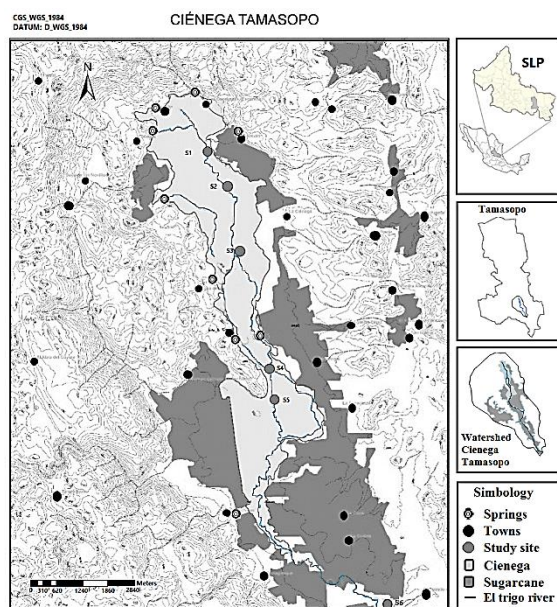


Fig. 1. Location of the wetland “Ciénega de Tamasopo” SLP, Mexico and the sampling sites (S1-S5). Processed with data from INEGI (1999).

Water and Sediments Sampling

Two sediment cores were collected with a gravity sampler (Wildco 2404-A14) at each of five sampling sites (S1 to S5, Figure 1) on November 2010 at zones not covered by plants. Sediments were cut in 0.5, 1 and 2 cm slices, preserved at 4 °C and oven dried (60 °C, 12 h) in the laboratory.

Acrylic porewater samplers (1 cm vertical resolution peepers; comprising two columns of 4 mL cell) were deployed (3 peepers; left in place for two week) on May 2012 and November 2012 to collect porewater and overlying water. Peepers were deaerated with N₂ for a minimum of 15 days prior to filling the cells with deionized water and covering them with a hydrophilic cellulose acetate membrane (0.2 µm). Upon retrieval, peepers were sampled immediately for the measurement of pH and total dissolved concentrations of sulfide ($\Sigma[\text{HS}^-]$), Fe, Ca, and anions (NO_3^- , SO_4^{2-} , PO_4^{3-}).

Analyses. Sub-samples (0.1 - 0.5 g) of homogenized sediments were acid digested (HNO_3 , HClO_4 and HF ;

Fortin et al., 1993) to determine Ca and Fe, by Atomic Absorption Spectrophotometry with Flame (AAS-F; SpectrAA Varian220FS) or with Graphite Furnace (AAS-HG; SpectrAA Varian 220). Phosphorus was determined by the molybdenum blue method [5]. Reference sediment sample (TH-2, National Water Research Institute) was used for Fe, Ca and P and the recovery was 96.3, 104.4, 71% respectively; a laboratory control sample was analyzed for the water measurements.

In water, sulfides were determined by the Cline method [6]; anions (sulfate, nitrate and total dissolved phosphate) by ion chromatography (Dionex HPLC-IC 2500) and metals by Atomic Absorption Spectrophotometry with Flame (AAS-F; SpectrAA Varian220FS) or with Graphite Furnace (AAS-HG; SpectrAA Varian 220). All pH were measured within 10 - 30 min in the field with an electrode (IQ 150 pH meter). Samples and field blanks were stored to 4 °C in dark during their transportation to the laboratory.

RESULTS AND DISCUSSION

The concentration of the substances determined in porewater at S1 to S5 are shown on Table 1 as average values to give a concentration magnitude. It is interesting to note that Fe concentrations were lower at sites S3 to S5 located at the lower part of the wetland (see Fig. 1) in November 2012; sulfate concentrations were also the highest at those sites.

Total dissolved phosphates in porewater were below the detection limit of the analytical method used ($3 \times 10^{-6} \text{ M}$; ionic chromatography) and varied from non-detectable to $1.36 \mu\text{M}$ in November 2012, and, from 0.63 to $12.7 \mu\text{M}$ in May 2012 in water flowing into the wetland from springs. At the same sites, sulfates varied from 0.14 to 1.34 mM, these concentrations are lower than those determined in porewater (Table 1) suggesting that springs support with some sulfates but the most important sources should be organic matter from plants in the wetland; chlorophyll was determined at the surface of the water column at sites were porewater and sediments were collected and varied from 0.001 to $0.035 \mu\text{g}/\text{m}^3$ in May 2012 and $<0.01 \mu\text{g}/\text{m}^3$ in November 2012.

The chemical behavior of Fe can be linked to the sulfur redox process and in this case, the metal concentration could be undetectable in reducing environments with production of sulfide. In general, the lowest concentrations of Fe in porewater were determined at depths with sulfides production, which suggests that Fe could be controlled by its precipitation with sulfide.

Table 1. Concentrations of total dissolved sulfides ($\Sigma[\text{HS}^-]$), sulfates $[\text{SO}_4^{2-}]$ calcium (Ca) and iron (Fe) determined in porewater samples collected from the wetland "Ciénega de Tamasopo".

Sampling site / Date	S1 (n=15)	S2 (n=15)	S3 (n=15)	S4 (n=15)	S5 (n=15)
Total dissolved sulfides ($\Sigma[\text{HS}^-]$; μM)					
May 2012	0 – 250	0 – 266	0 – 146.5	N. D.	0 – 278.1
November 2012	0 – 263.6	0 – 242.9	1.3 – 305.3	0 – 264.1	1.05 – 244.5
Sulfates (mM)					
November 2012	2.0-5.4	5.7-7.0	4.8-8.8	3.7-19.8	2.1-19.9
Nitrates (μM)					
November 2012	0 – 131	17.3 – 264.3	12 – 278	0 – 1.93	0 – 74.5
Calcium (mM)					
May 2012	6.21 ± 0.84	7.44 ± 1.49	6.41 ± 0.71	N.D.	2.26 ± 1.69
November 2012	4.79 ± 1.12	5.99 ± 0.86	5.88 ± 1.46	5.18 ± 0.89	6.30 ± 0.62
Iron (μM)					
May 2012	5.52 ± 8.19	6.37 ± 6.56	13.95 ± 2.53	N.D.	8.27 ± 5.26
November 2012	6.33 ± 5.64	6.71 ± 5.37	2.99 ± 5.70	1.13 ± 1.80	0.70 ± 0.89

N.D. means no determined

In November 2012, Fe concentrations were determined from non-detectable to less than 10 μM at sites S3 to S5; interestingly sulfates showed the highest concentrations at sites S4 and S5. The chemical model MINEQL v4.5 was used to estimate the solid and dissolved species present in the physico-chemical conditions in the wetland. To do this, we used $3 \times 10^{-6} \mu\text{M}$ for dissolved phosphates.

Modeling suggests supersaturation conditions with respect to CaCO_3 and predicts that the origin of phosphates in porewater could be the dissolution of hydroxyl-apatite $[\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2(\text{s})]$; this mineral has been reported in wetlands [7]. Studies on calcareous lakes indicated that the formation of hydroxyl-apatite is produced by precipitation or co-precipitation of o-PO_4^{3-} in calcite crystals, or co-adsorption on CaCO_3 precipitates [8]. Calcite and hydroxyl-apatite are dissolved together, but its dissolution rate depends among other factors on the degree of oversaturation of both and the decrease of pH [9]. In the wetland, pH decreased at the sediment – water interface from 8 to 6.5 in the majority of sites.

After the MINEQL modeling, dissolved sulfides are controlled by the formation of $\text{FeS}_{2(\text{s})}$ or $\text{MnS}_{(\text{a})}$ since there are saturation conditions concerning these solid phases. Production of sulfides from the sulfate reduction can influence the cycle of the Fe favoring the reduction of Fe(III) in compounds such as phosphates of hydroxides where phosphates are absorbed [9-10]. As a result, concentrations of sulfides can control the concentration of iron, which remains at low levels in water due to the formation of compounds as FeS_2 in the sediment, while the immobilized phosphate is released and can be used by plants and bacteria.

Production of dissolved total sulfides $\Sigma[\text{HS}^-]$ in porewater was recorded under the water-sediment interface specially in May 2012 (dry season), where the water column is shallow with respect to the rest of the year (0.3 – 1.2 m). Sulfates decreased at depths of sulfide production. However, sulfate concentrations were not depleted in the sediments, only a fraction of sulfates is consumed in the production of sulfides since the concentrations of both substances are not of the same magnitude (Table 1); the degradation of organic matter mediated by sulfate reduction has been described in aquatic sediments (Beck et al., 2008). This process is probably one of the most important in the sediments of the "Ciénega Tamasopo" and control the dissolved iron concentrations. The impact of sulfate reduction and iron sulfides precipitation in the sediment of the wetland is not very clear from the information we have until now. Mobilization of P was not evident from the porewater profiles since the concentrations were below the detection limit.

Figure 2 shows the concentration profiles with depth of total P, Fe and Ca in the sediments; the highest concentrations of P seem to be at sites with the lower Fe concentrations (see S2 and S3) and follow more or less a similar shape as Ca. We intended a correlation between P and Fe or Ca and results suggested a correlation with Fe at site S2 and S3 and with Ca at S1, S4 and S5. However the results are not very conclusive. Table 2 shows the diffusion fluxes of Fe, sulfides and sulfates at the sediment – water interface. The results suggest a diffusion of Fe (sites S2 and S3) and sulfates (all sites except S3) from the water column to the sediments and sulfides from the sediment to the water column. The fluxes support that sulfates are reduced to sulfides but not completely.

Depth (cm)

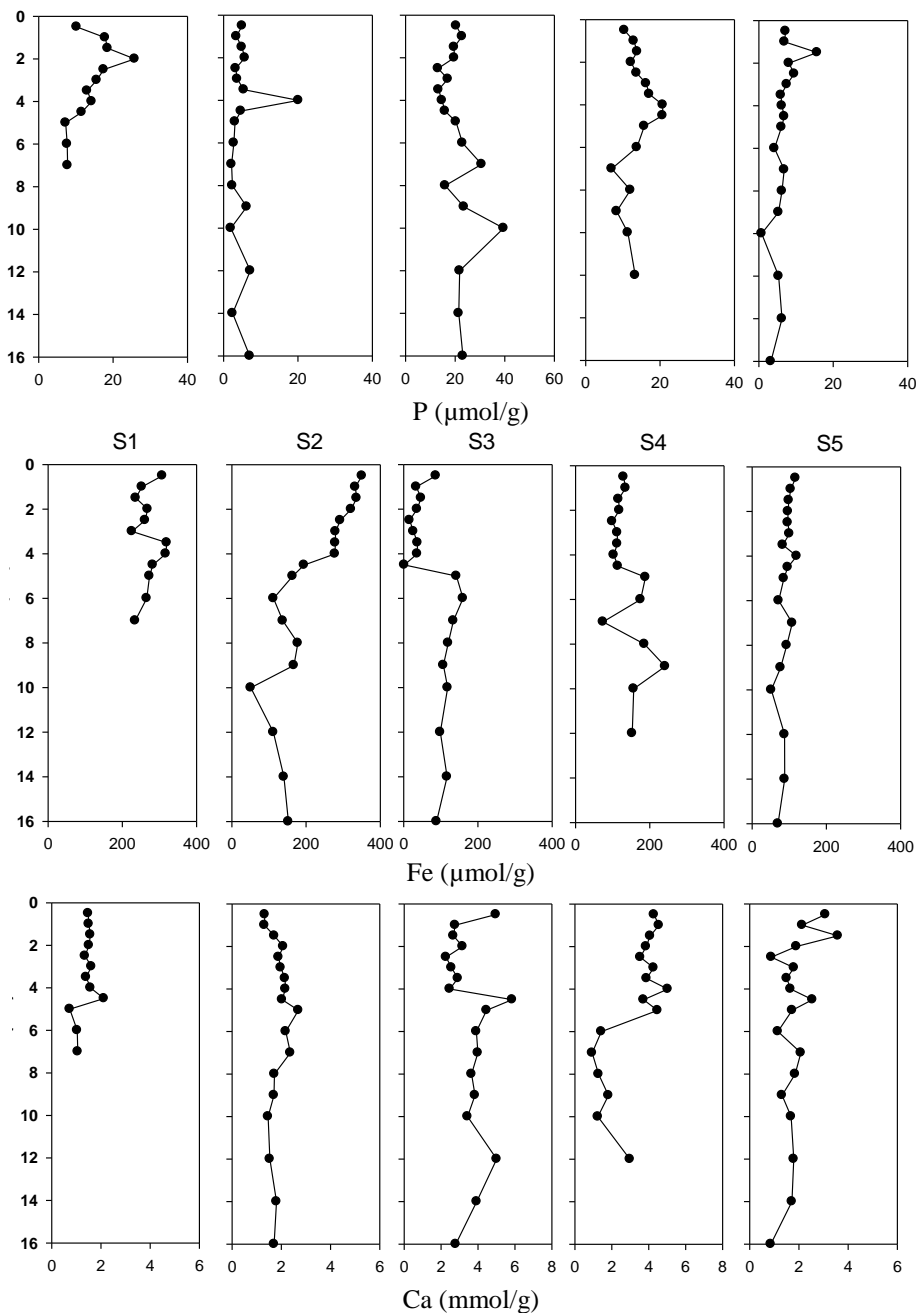


Fig. 2. Sediment concentration profiles with depth of total P, Fe and Ca determined in November 2010.

CONCLUSIONS

The mineralization of organic matter in the sediments of the wetland “Ciénega de Tamasopo” proceed importantly through the sulfate reduction. Production of sulfides is explained by the reduction of sulfates and the concentrations in porewater are controlled by the precipitation of Fe sulfides. Chemical modelling suggest that P is controlled by its

precipitation with Ca and the relation with the S cycle is not evident to support an internal eutrophication via the sulfate reduction.

Table 2. Diffusion flux of Fe, $\Sigma[\text{HS}^-]$ y SO_4^{2-} calculated in porewater in November 2012.

Site	Fe ($\mu\text{M}/\text{cm}^2\cdot\text{d}$)	$\Sigma[\text{HS}^-]$ ($\mu\text{M}/\text{cm}^2\cdot\text{d}$)	SO_4^{2-} ($\text{mM}/\text{cm}^2\cdot\text{d}$)	ΔZ (cm)
S1	0.08 ± 0.62	13.18 ± 6.17	-0.209 ± 0.067	4
S2	-1.09 ± 1.41	0.46 ± 0.47	0.072 ± 0.025	3
S3	-0.20 ± 0.22	37.44 ± 47.68	-0.773 ± 0.418	2
S4	0.04 ± 0.06	38.26 ± 3.02	-0.211 ± 0.240	6
S5	0.16 ± 0.27	69.02 ± 5.88	-3.526 ± 1.375	3
$D_{\text{Fe}} = 7.2 \times 10^{-6}$ $D_{\text{Ca}} = 7.93 \times 10^{-6}$ $D_{\Sigma[\text{HS}^-]} = 1.3 \times 10^{-5}$ $D_{\text{SO}_4} = 1.1 \times 10^{-5}$ $J_D (\text{SO}_4^{2-})$ calculated with $\Delta Z = 3$ cm in S1-S2 and $\Delta Z = 2$ cm in S3-S5. (+) The flow is from sediment to water column and (-) the flow is from water column to the sediment.				

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