

EXPERIMENTAL RESULTS ON SULFUR AND SALT FLUX FROM AN INLAND SULFIDIC SYSTEM- THE LOVEDAY BASIN

Sue Welch¹, Gabby Yates¹, Andrew Higgins¹, Luke Wallace¹, Dirk Kirste^{1,3}, & Sara Beavis²

¹Department of Earth and Marine Sciences

²Centre for Resource and Environmental Studies, The Australian national University, Canberra ACT 0200, CRC LEME

³Department of Earth Sciences, Simon Fraser University, Burnaby, BC Canada

INTRODUCTION

The Loveday Basin was a natural flooded wetland adjacent to the River Murray. Prior to the installation of locks along the river, the basin would have experienced annual exchange of both water and salts with the river and groundwater. Installation of locks raised the river base water levels and altered hydrologic regime of the basin (Walter, 2005). Starting in the early 70's, the site was used as a disposal basin for saline irrigation water. This has led to an increased salinization of the area and accumulation of sulfidic sediments, and severe land and water degradation of the site. Several years ago the site was decommissioned as a disposal basin and is now targeted for remediation.

Previous work on the site has shown that there are significant stores of total sulfur and salts contained within the water and sediments in the basin, both of which pose environmental problems (Lamontagne et al., 2004; Wallace et al., 2005; Welch et al., 2005). Total sulfur is concentrated in the upper 40 cm of the sediment, and occurs predominately as gypsum, though pyrite and FeS are abundant within the peds and particularly in the partially infilled cracks between the peds in the wetter parts of the basin (Lamontagne et al., 2004; Wallace et al 2005). The concentration and accumulation of reduced S species is controlled by the extent of flooding and by organic content of the sediments. Jarosite, a partial oxidation product of pyrite, is present in the drier parts of the basin, especially along the edges in sandy areas, and in the southern half of the basin, indicating that at least parts of the site may contain sulfuric materials (i.e. actual acid sulfate soils).

The surface water and shallow ground water measured over the three sampling trips, Dec 2004-Aug 2005 had a salinity that was one to three times that of seawater (Welch et al., 2005). Salt crusts, predominately gypsum, cover the surface of the dry parts of the basin and affect surface structure of the peds. The salts also affect the sediment structure, resulting in increased shrinkage from the surface to the interior of the peds and increased shrinkage downprofile (Beavis et al., 2006). Salts are concentrated at the surface, and decrease with depth, reflecting the recent history of the site as a saline disposal/evaporite basin. Estimates of salt stores range from 10's to 100's mg salt per gram of sediment.

The purpose of this work is to determine the sulfur and total salt flux from the sediments under different conditions. Specifically, experiments were designed to investigate if flooding and flushing the basin (removing buffering capacity) would result in accelerated pyrite oxidation and acidification. Previous experimental studies from the site (Beavis et al., 2005; Welch et al., 2005) showed that salt release in slurry experiments was rapid, within ~ 1 day. Total S flux was dominated by gypsum dissolution for sediments collected from the upper part of the sediment profile even though pyrite was abundant ~ 1 wt%. Sediments from lower in the profile had a much lower total salt and sulfur release to solution, and the stoichiometry of the solution ($\text{Ca}/\text{SO}_4 \ll 0.4$ wt/wt) indicated that at least some of the sulfur in solution did not originate from dissolving gypsum. None of these slurry experiments ever became acidic, even after a year.

METHODS

Slurry experiments were conducted to determine the total salt and sulfur flux from the sediments. Bulk samples were collected from different locations and different depths within the basin to obtain representative samples. Sediments were homogenized by mixing, and 10 g of wet sample was placed into a 120 ml bottle. For the first set of experiments samples were prepared in triplicate, for the second set of experiments (acidic conditions) experiments were done in duplicate. 100 ml of Milli-Q water was added to each bottle, the slurry was shaken to disaggregate the sediments. Bottles were placed on an orbital shaker so that the slurry was well mixed and to allow for oxygenation. Solutions were sampled periodically over three days to determine the 'initial salt flux'. After this, the supernatant was removed, and 100 ml of fresh solution was added. The solutions were Milli-Q water, 4 mM HCl (pH ~ 2.4) to simulate sediment reactivity acidic conditions, and 10 mM FeCl₃ to 1 mM HCl to simulate the affect of iron oxidizing microbes under extremely acidic conditions. All solutions were filtered with a 0.45 µm filter. Solution pH and EC were measured with Orion pH and EC

meters that were calibrated with standard solutions. Ferrous iron was measured on small volume samples using a modified ferrozine method after Stookey (1970). Major cations and total S (predominately SO_4^{2-}) was measured on the ICP-AES. Chloride concentration was estimated by the difference in charge balance between major cations and sulfur (sulfate) by ICP-AES. Selected sediments were also analysed by Scanning Electron Microscopy and light microscopy to confirm the mineralogy.

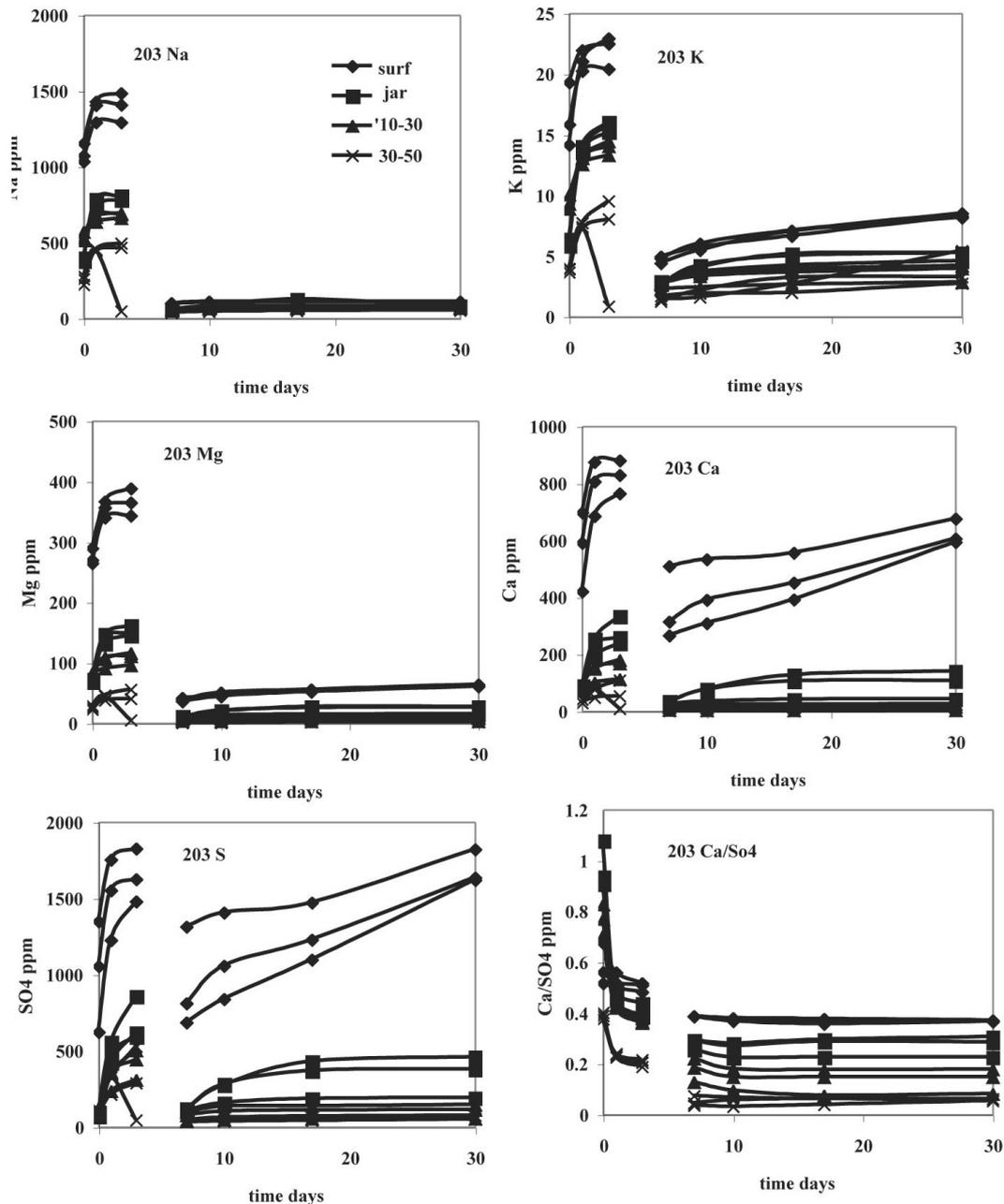


Figure 1: Major ion concentrations and Ca/SO₄ ratio from slurry experiments with samples from site 203. The break in the curves represents removal of the initial water and replacement with fresh water

RESULTS AND DISCUSSION

Slurry experiments were conducted with sediments collected from site 203, 401, and 602. Site 203 is on the northern side of the basin ~ 100 m north of the causeway in the intermittently flooded zone, the ped structure at the surface is not well developed. The site has jarosite mottles below the surface. Site 401 is on the southern side of the basin and has abundant jarosite. Site 602 is at the southernmost end of the basin, and has a much sandier texture. The sediments at the surface had a cracked crust that was the result of recent rainfall. The surface here was covered with snail shells.

In the initial stages of the experiments, there was a rapid release of salts to solution within the first day of the experiments, and then concentrations did not change substantially over the next two days (Figure 1). The

composition and concentration of salts depended on location and depth. Highest salt concentrations were leached out of the surface sediments, particularly at site 203 which experiences periodic wetting and drying. Salt content in the initial leaches ranged from ~ 20 to 80 mg/g from the surface sediments and ~10 to 30 mg/g in deep sediments at the three sites. The total salt content was dominated by Na and Cl though the ratios of the major ions were variable depending on location and depth. At site 203, the Ca/SO₄ mass ratio was close to that expected for gypsum dissolution, Ca/SO₄ ranges from ~ 0.37 to 0.5, indicating that gypsum is the likely source of the sulfur. In all the other sediments, the Ca/SO₄ ratios in the initial leaches are < 0.4, suggesting the S flux is not predominately due to gypsum dissolution. The total sulfur in solution could be from (i) dissolved sulfate in the pore water, (ii) dissolution of jarosite, or (iii) most likely from the oxidation of the iron sulfide phases during the experiments.

After 3 days the solution was replaced, to simulate flushing of the basin, and fresh water was added to the sediments. In the second leach, major ion concentrations increased much more slowly with time. Total salt concentrations in solution at the end of the second leach (30 days) were a factor of 5 to 10 lower than for the first leach (Table 1). The ratios of major ions in the second leach were significantly different than for the first leach, Mg/Na and Ca/Na much higher, indicating that salt release was controlled by dissolution of sparingly soluble salts and silicate minerals and possibly by ion exchange reactions with clays. The Ca/SO₄ second leach was highest in the surface samples, usually close to that expected for gypsum, and then decreased with depth. The high Ca/SO₄ ratio in surface sediments indicates that the total S flux out of the sediments is still dominated by gypsum dissolution, inspite of the high reduced ferrous sulfide content in these sediments. The Ca/SO₄ ratio generally decreases with depth suggesting that a major source of sulfur may be from oxidation of pyrite.

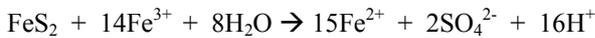
Table 1: major ion concentrations at the end of the first and second water leaches

	<i>time</i>	<i>total salt</i>				
		<i>mg/g sed</i>	<i>Ca/S</i>	<i>1000Sr/Ca</i>	<i>Ca/Na</i>	<i>Mg/Na</i>
203 surf	3	77.39	0.50	21.40	0.59	0.26
203 surf	30	26.33	0.37	14.86	5.69	0.38
203 jar	3	36.06	0.40	15.97	0.35	0.19
203 jar	30	6.63	0.27	11.01	1.21	0.28
203 10-30	3	27.17	0.37	17.74	0.23	0.16
203 10-30	30	2.87	0.14	15.70	0.22	0.10
203 30-50	3	17.62	0.20	17.70	0.18	0.10
203 30-50	30	1.94	0.06	18.18	0.06	0.04
401 cr	3	28.56	0.28	73.33	0.17	0.17
401 cr	30	22.04	0.34	21.51	5.10	0.53
401 top	3	54.65	0.31	35.55	0.18	0.14
401 top	30	19.75	0.33	18.58	4.13	0.53
401 10-25	3	28.18	0.20	22.86	0.20	0.11
401 10-25	30	5.88	0.18	17.74	0.83	0.27
401 bped	3	22.51	0.16	24.66	0.12	0.09
401 bped	30	3.14	0.09	22.09	0.21	0.10
602 0-2	3	3.14	0.09	22.09	0.21	0.10
602 0-2	30	2.64	0.13	72.09	0.12	0.10
602 1-10	3	11.27	0.04	53.33	0.04	0.04
602 1-10	30	1.82	0.13	67.29	0.08	0.30
602 10-30	3	12.13	0.02	65.53	0.01	0.02
602 10-30	30	1.56	0.12	85.26	0.13	0.32
602 30+	3	10.33	0.02	69.37	0.01	0.01
602 30+	30	2.75	0.17	86.42	0.06	0.08

The pH of these experiments ranged from ~ 4 to near neutral. Sediments that had jarosite were acidic in both the first and second leach. However, in most of the experiments the pH remained near neutral even though pyrite and FeS occurs in the sediments and the stoichiometry of the reaction indicated that these were oxidizing.

The second set of experiments was conducted to determine if inducing acidic or extremely oxidizing conditions would effect total S and salt release from the sediments. While most of the sediments in the basin are well buffered, there are acid hot spots that could spread with continued wetting and drying cycles. Pyrite oxidation should be catalyzed by either addition of acid or ferric iron, so, in the second set of slurry experiments 100 ml of either 4 mM HCl, or 10 mM FeCl₃ (pH ~ 2) was added to the sediments after the initial water leach, and solution composition was measured over time as reaction with the sediment occurred. Solution pH in the HCl treatments ranged from near neutral for surface sediments to slightly acidic (pH ~ 3 to 4) in the deeper sediments. In the FeCl₃ treatment, all solutions were acidic, ranging from pH ~ 2 up to 5.

The total salt content in the supernatant in the HCl treatments was similar to that of the water treatment for all the sediments tested, concentrations were at most ~ a factor of two greater in the acid than in water (Figure 2). The effect was most apparent from the deeper sediments, where there was less total salt released overall and insufficient buffering capacity to neutralize the acid added. The cation concentrations in the supernatant in the FeCl₃ treatments however were 2 to 20 times higher than for either the water or HCl experiments. Ferrous iron was also present in solution, suggesting that pyrite is being oxidized via the following reaction:



Although the cation release to solution was greater in the HCl and FeCl₃ treatments than for the reaction in water, these acid solutions had minimal impact on pyrite oxidation. The total sulfur flux to solution was at most a factor of two greater in acid than in water (Figure 2)

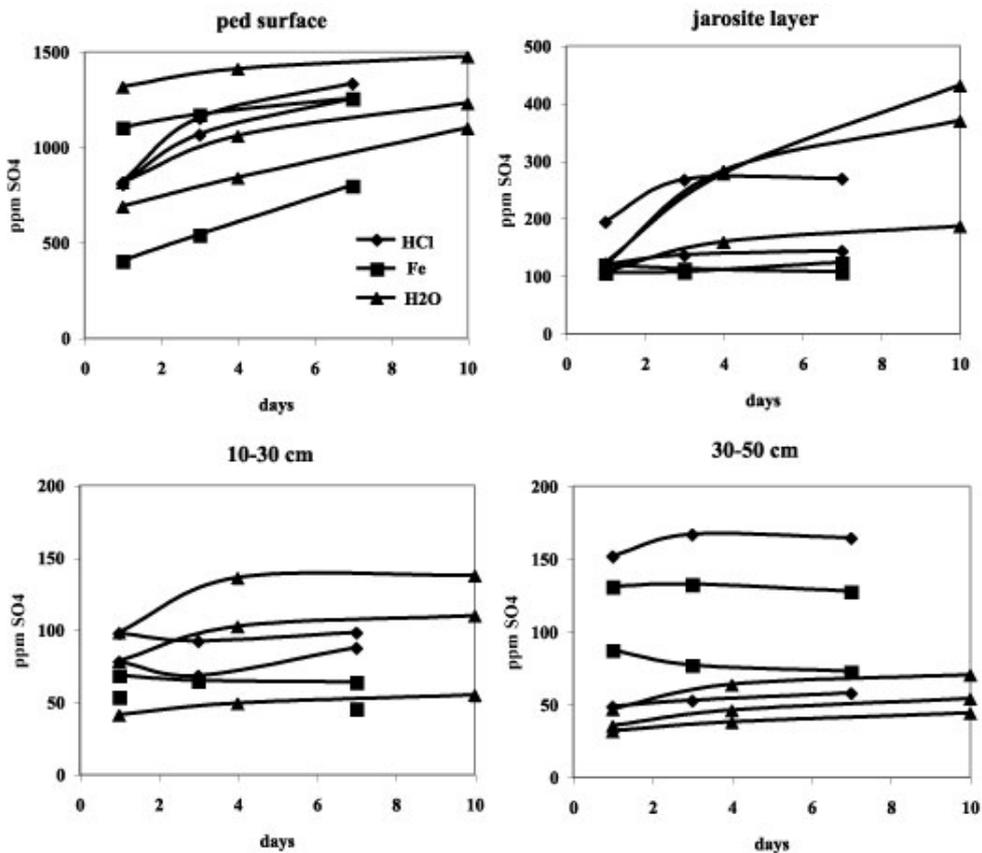


Figure 2: total S concentrations in slurry experiments from site 203

CONCLUSIONS

Based on the slurry experiments, it is unlikely that the site will develop sulfuric materials (i.e. actual acid sulfate soils). Although pyrite is abundant in the basin, especially in the near surface sediments, the sediments generally contain significant buffering capacity to limit the rapid oxidation of pyrite. Total sulfur flux from in the slurry experiments increased by only a factor of two under these extreme conditions. As long as the system remains closed, i.e., net alkalinity is not removed from the system, the basin is not likely to become acidic.

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