Acidity fluxes following rewetting of sulfuric material

W. S. Hicks[A], N. Creeper[**B**], J. Hutson[C], R. W. Fitzpatrick[B], S. Grocke[B] and P. Shand[B]

[A]CSIRO Land and Water, GPO Box 1666 Canberra ACT, Australia, Email warren.hicks@csiro.au
[B]CSIRO Land and Water, Private Bag No. 2, Glen Osmond SA, Australia
[C]School of Chemistry, Physics and Earth Sciences, Flinders University, GPO Box 2100 Adelaide SA, Australia

Abstract

We selected two sites with soil materials of clay and sand and used mesocosms to study the effect of rewetting sulfuric material with sea water and fresh water. The materials behaved differently due to different water seepage rates and acid stores. The water seepage rate was low for the clay soil (0.8×10^{-3} m/d) compared to the sandy soil ($8–15\times10^{-3}$ m/d). Initial acid flux rates were higher (0.1–0.2 mol/m^2/d) compared to long term rates (0.007–0.014 mol/m^2/d). For the clay soil, the low seepage rate and higher stored acidity resulted in a net flux of solutes from the soil to the water column. In contrast, the higher seepage flux of the sandy material resulted in a flux of water and solutes from the water column into the soil profile, displacing acid pore water deeper into the soil profile. However there is a residual acid flux into the water column probably due to the ongoing and slow dissolution of residual acid oxidation products. In both materials, sea water mobilised more acidity. Comparing the measured flux and calculated advective and diffusive fluxes highlighted the importance of solid phase reactions such as dissolution and surface exchange reactions.

Key Words

Acid sulfate soil, Lower Lakes.

Introduction

The Murray-Darling Basin is currently experiencing the worst drought conditions in recent record. The Lower Lakes (LL) are under extreme stress from a combination of low water levels, salinity increases and the exposure of acid sulfate soils (ASS; Fitzpatrick *et al*. 2008a). The most significant risks are likely to occur during reflooding of sulfuric materials, largely due to potential mobilisation of acidity and trace elements made available during previous oxidation of sulfidic soils. The transport and fate of acidity and bioavailable metals is poorly understood in these systems. The complexities in the local geology, soil type and landscape position means that metal mobilisation characteristics are likely to be site specific, and also be governed by re-wetting scenarios. The aim of our study was to determine acid fluxes upon rewetting sulfuric material.

Methods

We selected two sites in L. Alexandrina: (a) Boggy Ck. where sulfuric materials have formed in the sandy clays of drier areas; and (b) on the south side of Pt. Sturt peninsula where sulfuric materials formed in sands. The materials at these sites provided a contrast in soil physical and chemical properties and are considered representative end members of materials likely to be encountered in the lake. The location of the experiment sites is shown in Figure 1. Soils were described and classified using the Australian Soil Classification (ASC; Isbell 1996) and assigned to a class using the key developed for the Atlas of Australian Soils (Atlas; Fitzpatrick *et al.* 2008b). The soil at the Boggy Ck. site is a sulfuric cracking clay soil (Atlas) and according to the ASC a Redoxic Sulfuric Bleached-Vertic Hydrosol. The soil texture varies from a sandy clay loam in the top 0.03 m through fine sandy clay to light clay from 0.2 to 0.38 m, then a fine clayey sand to the limit of sampling at 1.8 m. The soil at the Pt Sturt site is a sulfuric soil (Atlas) and according to the ASC a Redoxic Sulfuric Acidic Hydrosol. The texture is sand to 0.6 m then sandy clay to the limit of sampling at 1.6 m. We also measured soil physical parameters including porosity, bulk density and seepage rate. The clay soil bulk density from 0–0.05 m was 0.88 t/m^3 and from 0.05–0.5 m it was 1.28 t/m^3. Porosities were 0.67 and 0.52 respectively. Seepage rates were very low and rates were similar for both treatments at 0.8×10^{-3} m/d. In the case of the sandy soil, the bulk density was uniform from 0.03–0.65 m at 1.53 t/m^3 with a porosity of 0.42. Seepage rates ranged from $8–15\times10^{-3}$ m/d for the fresh water and sea water treatments respectively.

At these sites we trialled rewetting of the sulfuric material using fresh water (River Murray water) and sea water treatments. Treatments were replicated and carried out in mesocosms set one metre into the soil. For each treatment, one mesocosm was installed with redox electrodes in the water column and at various depths below the surface and soil solution samplers. Dialysis chamber samplers (Batley *et al.*1993) were used to capture a snapshot of soil solution at 0.01 m resolution to ~0.30m bgl 28 days after rewetting.

Seepage rate was calculated from the amount of water supplied to maintain a constant mesocosm water depth, rainfall and class A pan evaporation. No local measurements of evaporation have been available since 2003 and interpolated data from Silo Data Drill (Jeffrey *et al.* 2001) was used. Evaporation values ranged from 0.8–6.8 mm/d. A comparison of measured and interpolated evaporation values from 1987–2003 showed that for the time of year covering the period of investigation, the difference between measured and interpolated values is ±0.2 mm/d. The net acidity flux to the mesocosms was estimated from the alkalinity change (after accounting for inputs and outputs). The diffusive and advective flux of 'acidic' cations (H^+, Al^{3+}, Fe^{2+}, and Mn^{2+}) was calculated using the flux equation $F_{z=0} = F_d + F_a + F_s$ where d, a and s are the diffusive, advective and solid phase fluxes (Stumm and Morgan 1996) and parameterised using soil physical data and data from the dialysis chambers. Fluxes of individual cations were calculated and summed to determine the total flux. These values were compared with the measured fluxes.

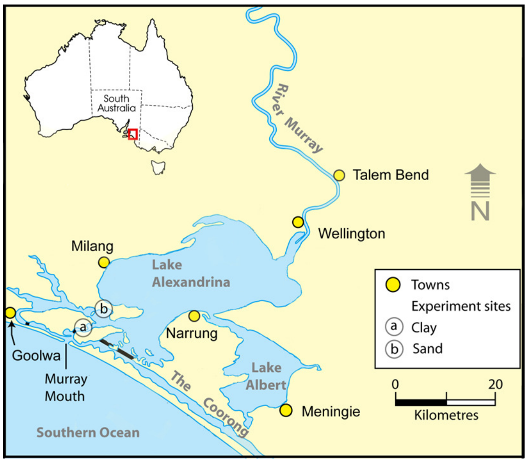

Figure 1. Location map of the study sites.

Results

Flux measurements

The initial acidity flux rate was higher for all sites, soils and treatments. The flux rate for the seawater treatments was also higher (Figure 2). This agrees with laboratory studies (Simpson *et al.* 2009) which found higher concentrations of toxic metals and metalloids in the overlying water for soil corer-reactors and sea water. A possible explanation for the difference between the fresh and sea water treatments is that an initial filling and saturation of the soil profile with the high ionic strength sea water resulted in the acidic cations in efflorescences on the surface, in precipitates, on exchange sites and weakly bound to metal oxides in the near surface being dissolved or displaced directly into the water column. These mobilised acidic cations consume alkalinity and cause an initial sharp drop in alkalinity. This is consistent with the smaller initial change in alkalinity for the fresh water treatment where the initial acid input is likely to be limited to the dissolution of surface efflorescences and sparingly soluble acidic oxidation products in the near surface.

At Pt. Sturt, the higher seepage rate means the water column alkalinity was relatively stable with a small initial decrease likely due to the dissolution of surface efflorescences followed by a later increase due to evapoconcentration. However when alkalinity inputs and seepage losses are taken into account there is a small acidity flux into the water column of 0.007(±0.001) mol $H^+/m^2/d$. For the sandy soil there is a net flux of solutes into the soil profile. This can be observed in the $Cl:SO_4$ ratio (Figure 3). At 0.2 m bgl, the ratio has increased and is approaching the supply water value. For pore water at 0.2 m bgl at 0.5 and 1.0 m bgl, the ratios are decreasing and are approaching the starting value for the water from 0.2 m bgl. This indicates a net flux of solutes from the water column into the soil profile and that the shallow pore water is being displaced by piston flow deeper into the soil profile. Despite the evidence of piston flow, changes in the moisture characteristics of the soil prior to flooding may alter subsoil rewetting characteristics. Additionally the experiment design means that lateral flow was prevented by the tank walls until 1 m bgl. Despite the advective flux of surface water into the soil profile, the pH of the pore water at 0.2 m bgl remains acid with a pH of ~ 3 and an acidity of ~1 mmol H^+/L for the fresh water treatment and 3 mmol H^+/L for the sea water treatment. In both cases the major component of the acidity at 0.2 m bgl is H^+ (Figure 4) although there is some contribution from Al and Fe in the case of the sea water treatment. The source of these ions is unclear but it is likely that they result from the dissolution of sparingly soluble acid oxidation products.

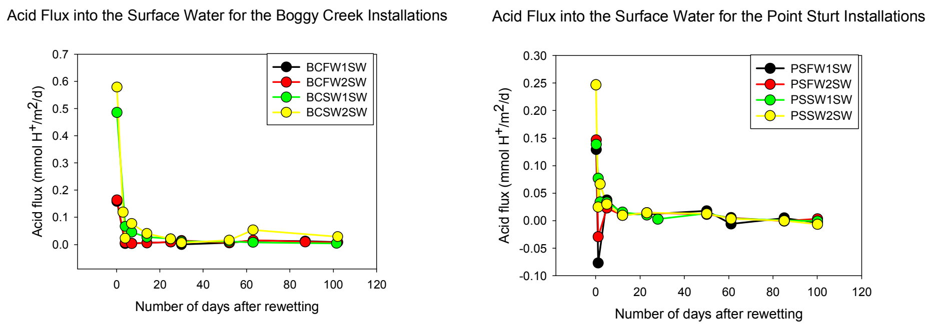

Figure 2 Acid flux rate

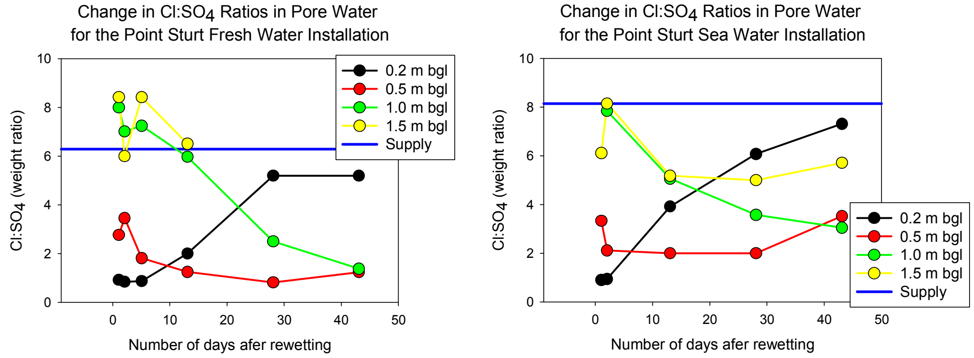

Figure 3 Time series for Cl:SO$_4$ ratios

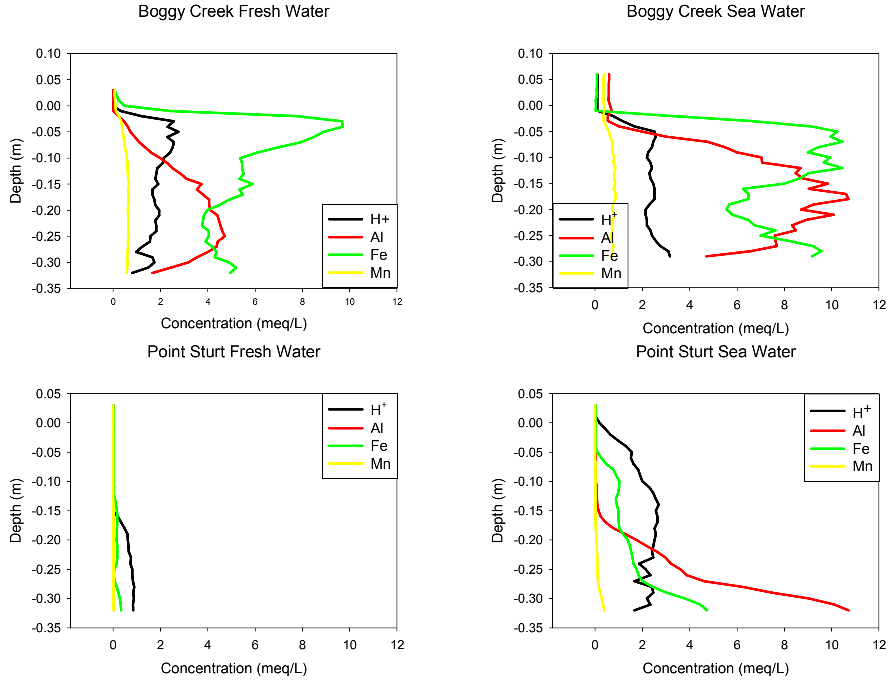

Figure 4 Dialysis chamber profiles for 'acidic' cations

Flux calculations

Examination of the dialysis chamber profiles shows that the major contributors to the acid flux differ between sites. For the clay soil, Fe is the major contributor to the acid flux, whereas for the sandy soil the H$^+$ is the major contributor (Figure 4). For the clay soil, values for the measured flux rates are two orders of magnitude greater in the case of the initial flux rate and up to an order of magnitude greater for the longer term flux rate. In the case of the sandy soil the net advective + diffusive flux is from the water to the soil, whereas the measured flux is a small flux from the soil to the water column (Table 1). These differences are probably due to the last term in the flux equation, the flux due to solid phases. The solid phase acidity stored in the exposed ASS of the LL is present in a number of forms in both the dry soil and in the unsaturated and saturated zones. In the solid phase, these include sparingly soluble 'acidic' oxyhydroxide and oxyhydroxy sulfate minerals that can accumulate as concentrated surface precipitates as well as more diffusely in the bulk soil. Acidic cations also exist adsorbed to oxides and on cation exchange sites. The precipitates have different solubilities and dissolution rates (e.g. see Bigham and Nordstrom 2000) so that the acid flux on rewetting will have a number of sources that vary in their difficulty to identify and measure. While surface reactions and exchange with iron oxyhydroxides have been incorporated into models (see Appelo and Postma 2005) in general the ability to reliably predict such solid phase flux terms is limited.

Table 1 Calculated and measured flux rates (mol $H^+/m^2/d$). Negative values indicate flux from the soil to the water column and positive values flux from the water column to soil.

Location	Calculated			Measured	
	Acid	Alkalinity	Net		
Boggy Ck.				Day 1	Day 7+
Fresh water	-1.5×10^{-2}	2.2×10^{-3}	-1.3×10^{-3}	$-1.61\pm0.02\times10^{-1}$	$-10\pm1\times10^{-3}$
Sea water	-1.1×10^{-2}	2.1×10^{-3}	-8.5×10^{-3}	$-5.3\pm0.5\times10^{-1}$	$-14\pm1\times10^{-3}$
Pt. Sturt				Day 1	Day 5+
Fresh water	-5.4×10^{-4}	3.6×10^{-2}	3.5×10^{-2}	$-1.38\pm0.09\times10^{-1}$	$-7\pm1\times10^{-3}$
Sea water	-6.1×10^{-4}	2.1×10^{-2}	2.0×10^{-2}	$-2.8\pm0.3\times10^{-1}$	$-7\pm1\times10^{-3}$

Conclusion

The acidity stored in the exposed ASS is present in a number of forms in both the dry soil and in the unsaturated and saturated zones. In the solid phase, these include sparingly soluble oxyhydroxide and oxyhydroxy sulfate minerals that can accumulate as concentrated surface precipitates as well as diffusely in the bulk soil. Acidic cations also exist adsorbed to oxides and on cation exchange sites. Following rewetting this acidity can be transported into the water column or the soil profile. The precipitates have different solubilities and dissolution rates so that the acid flux on rewetting will have a number of sources that vary in their difficulty to identify and measure. While the decrease in water column alkalinity provides a simple direct measure of the net acid flux to the water column, predictive models will require information on solid phase and surface reactions for which the exchange isotherms, cation exchange parameters and solubility terms needed are poorly characterised. Additionally redox changes will 'dissolve' iron oxyhydroxides and alter these reactions. van Breemen (1975) produced a conceptual model of these processes in ASS however further research is still required for incorporation of these processes into predictive numerical models.

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