Dissolved inorganic carbon in coastal acid sulfate landscapes

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Abstract

An acid sulfate soil landscape was investigated to understand the pattern of dissolved inorganic carbon (DIC). Drainage water was measure in situ for DIC using a novel conversion methodology. Sediments and soils were collected and used in an incubation experiment to induce oxidation. Temporal and spatial variations in DIC and stable isotope ($^{13}C_{DIC}$) concentration were found to exist between the groundwater and surface water. This demonstrated a hydrologic boundary between the surface water located in the drainage system and the underlying groundwater. Lab-based atmospheric equilibration studies of groundwater showed temporal decreases in pH, Fe(II), alkalinity, and, DIC with an associated increase in $^{13}C_{DIC}$ when compared to non-acid sulfate impacted waterbodies. The loss of DIC was demonstrated to follow first-order kinetics.

Key Words

Dissolved inorganic carbon, acid sulfate soil, carbon efflux

Introduction

Understanding the control of carbon fluxes from terrestrial ecosystems is of interest due to their contribution to the global carbon cycle. Several important studies have focused on the transfer of CO_2 between the atmosphere, soils, and vegetation. However, there is limited information on the links between hydrology and the biogeochemical processes that may regulate CO_2 fluxes. The overall contribution of the outgassing of CO_2 from surface waters is recognised as a significant component of the terrestrial carbon efflux. Drainage waters from coastal acid sulfate landscapes have elevated metal concentrations, which upon hydrolysis generates additional acidity (Green *et al.* 2006). We have previously shown that variable flow events in drainage systems of acid sulfate landscapes results in variable discharge of metals (Macdonald *et al.* 2007). Studies on gaseous emissions from terrestrial acid sulfate landscapes have provided a detailed understanding of gaseous emissions (Macdonald *et al.* 2004a; Kinsela *et al.* 2007) and shown the importance of acid sulfate soils as carbon emitters (Denmead *et al.* 2008). At the same instance, metal oxidation and hydrolysis in acid sulfate waters are increasingly well understood, however, the relationship between metal oxidation, hydrolysis and carbon flux has yet to be determined.

The acidification of drainage water should result in a drive of equilibria to CO_2* ($CO_{2(aq)+}H_2CO_3$). The degassing of the CO_2 component should be accompanied by an enrichment in ^{13}C as ^{12}C is preferentially lost. It is not known precisely how these processes operate under different hydrologic regimes and varying sediment/soil geochemistry in acid sulfate landscapes. It is the aim of this work to produce an accurate in situ measurement technique for the quantification of DIC and measure diurnal flux between soils and sediments and the overlying waters. By investigating biogeochemical processes in situ and under laboratory controlled conditions, an understanding of the interrelationship between metals, acidity and carbon was established.

Methods

Study Site

The study area is Black's Drain a subcatchment (520 ha) of the Tweed River, in northern New South Wales (28°18'S, 153°31'E), eastern Australia. Originally, the subcatchment was a poorly drained backswamp, but today is extensively drained and the predominant floodplain landuse is currently sugarcane production. The climate of the Tweed Valley is humid and subtropical with a summer-dominant (November-March) average annual rainfall at neighbouring Murwillumbah is 1682 mm. The site is characterised by acid sulfate soils which dominate the floodplain (at 325 ha or 93%), and produce acidic, metal-rich discharge (see Macdonald *et al.* 2007). The soils are characterised by an A1 horizon that is an organic clay loam with 5% organic C, pH ~4-6, and 65% porosity. The A2 horizon is strongly acidic (pH <4), while the reduced subsoil B horizon is 85% clay, pH ~6.5.On average, acid sulfate soil within the region contains the equivalent of 50-70 tonnes of soluble H_2SO_4/ha within the sulfuric horizon (Macdonald *et al.* 2004b).

One drain sampling point at upstream and downstream locations of Black's Drain was selected based on the findings of Macdonald *et al.* (2007) for water quality and Collins *et al.* (2009) on iron oxide composition. The upstream site is dominated by discharge from acid sulfate soil, whilst the downstream site is a mix of acid sulfate discharge and tidal water from the adjoining Tweed River.

DIC analysis

An CO_2/H_2O infra-red gas analyser (LI-840, LI-COR Biosciences) was modified to measure DIC concentration in situ following conversion of aqueous DIC to $CO_{2(g)}$. The procedure involved the uptake of 10 ml of drainage water by peristaltic pump and addition of perchloric acid (0.5 ml) in a sealed line for conversion of DIC to $CO_{2(g)}$. The evolved $CO_{2(g)}$ passes through a hydrophobic membrane into a gas line and is analysed by infra-red. The $CO_{2(g)}$after passing through the infra-red is trapped in a molecular sieve which is preserved for 13C analysis and transported back to the lab. ^{13}C and ^{12}C isotopes were measured using a GV Instruments Isoprime ratio mass spectrometer. Samples were collected every 6 hours for a 72 hour period. For each DIC sample a corresponding sample was taken for field pH, Fe(II)/Fe(III), EC, DO, and a sample preserved with HNO_3 for determination of metals (ICP-OES and ICP-MS).

Sediment/Soil dispersion and incubation

Soils and sediments were collected from the drain bottom at depth of 0.5 m AHD (monosulfide enriched), and from drain edges (at 1.2 m AHD and above drain water height on the drain bank) adjacent to the DIC measurement locations. Samples of unoxidised sediment (potential acid sulfate soil) and groundwater were sampled (at a depth of 1.2 AHD metres (2.5 metres depth the ground surface) and 15 metres perpendicular from the drain) and sealed in airtight containers. Additional to this, an organic rich surface soil was collected from the sugar cane cropping zone to investigate organic additions. All samples were chilled to 3ºC. Triplicate 50 g samples were homogenised in 200 ml of MQ water and allowed to oxidise under a controlled environment in a sealed incubation chamber for a period of 72 hours. The incubation chamber included comprised a sealed vessel, inlet and outlet for pressurised high-purity oxygen to pass and a magnetised stirring bar to allow for continual mixing. At 4-hour intervals a sample was withdrawn via syringe and analysed for DIC and metal concentrations (as above). A 5 L sample of Tweed River water was collected from 5 km upstream of the Tweed River, beyond the extent of acid sulfate soil presence and used as a non-acid sulfate impacted water body control sample.

Results

The characteristics of the drainage water from upstream (acid sulfate impacted) and downstream (tidal Tweed River impacted) are presented in Table 1. Evident are an increase in concentration of DIC and Eh in the downstream water as a result on estuarine Tweed River water entering the drainage system. Upstream beyond the limits of tidal reach, alkalinity and DIC are depleted. The loss of DIC in the upstream waters as $CO_{2(g)}$ is driven by the oxidation and hydrolysis of metals derived from the surrounding acid sulfate soils. A time-series plot of the soil and sediment suspension data (Figure 2) shows an exponential decline. The same trend in decline also applied to the sampled 'groundwater', which followed a pattern similar to the unoxidised potential acid sulfate soil over the 72-hour experiment. The reaction mechanism for exponential decreases in DIC concentration over time is governed by first order kinetics:

$$\mathrm{Ln}f = \ln(C_t / C_o) = - kt \qquad (1)$$

where f is the fraction of residual DIC since the start of the DIC transformation, C_t is the residual concentration of DIC at time t, C_o is the concentration of DIC at the start to the experiment and k is the rate constant. A decrease in Fe(II), alkalinity and pH have been reported in studies conducted on drain sediments collected at this location same (Burton *et al.* 2006). However, this is the first instance where DIC has been measured and shown to decrease.

Table 1. Characterisation of drainage waters from acid sulfate soils (BD = Below Detection Limit).

	pH	EC (dS/m)	Alk ($CaCO_3$ mg/L)	DO (mg/L)	Eh (mV)	SO_4^{2-} (mg/L)	Fe(II) (mg/L)	^{13}C (‰)	DIC (mM C/L)
Upstream	2.8 – 4.8	4.5 – 5.2	0 – 0.8	4.0 - 5.7	280 - 360	20 - 32	1.2 – 4.3	BDL - 0.1	0 – 0.6
Downstream	5.5 - 6.6	0.7 – 1.6	28 – 37	5.2 – 7.3	410 - 430	360 - 390	0.1 - 1.7	-1 - 1	0.8 - 1.2

The $^{13}C_{DIC}$ in the drainage water as with the DIC concentration was dependant upon the acidity generated via the hydrolysis of metals from the acid sulfate soil. The same result could be repeated in the monosulfide incubation experiment where $^{13}C_{DIC}$ decreased over the 72-hour incubation time. The unoxidised potential acid sulfate soil had an increase in $^{13}C_{DIC}$ over the incubation period. This was due to buffering capacity of the small amount of carbonate present in the estuarine deposited material. Overall the shift in $^{13}C_{DIC}$ is controlled by the isotopic fractionation, which is dependent upon whether DIC transformation and potential loss occurs by equilibration or kinetic processes. A discontinuity existed between the drainage water and the underlying groundwater that appears to confirm the assumption that hydraulic conductivity is exceedingly low in these landscapes.

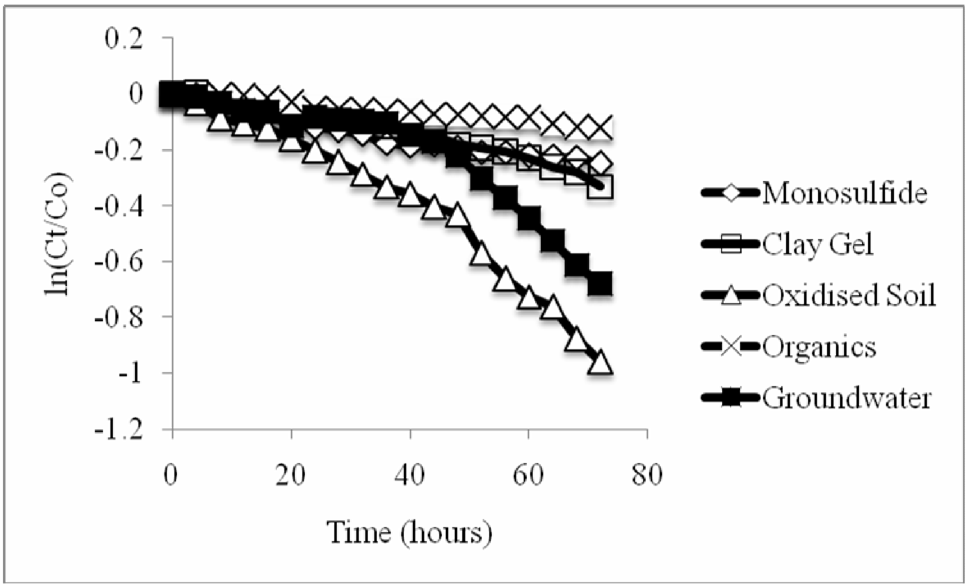

Figure 1. Results from the oxidation experiment presented as a actual to initial DIC concentration.

At the pH and alkalinity levels of the upstream acid sulfate waters it can be assumed the all DIC exists as CO_2*. However, the tidal water which enters the drainage system has a higher pH and DIC will be dominated by HCO_3^- and as expected has an enrichment of $^{13}C_{DIC}$. It can be suggested that the continuous loss of DIC associated with the mixing of estuarine tidal waters and acid sulfate soil discharge water, is subject to kinetic isotopic fractionation effects. In these acid sulfate discharge waters, the extent of HCO_3^- dehydration to $CO_{2(aq)}$ is controlled by the HCO_3^- concentration relative to the concentration of protons produced by Fe(III) hydrolysis. It is likely that subjected to repeated cyclic precipitation and dissolution of Fe(III)/Fe(II) will typically exhaust the pool of DIC in drainage systems. Such a cyclic nature at this same site has been considered by Collins *et al.* (2009).

Conclusion

Monosulfide sediments and groundwaters exposed to atmospheric conditions had high rates of CO_2 loss. Such loss may explain the depleted nature of DIC in discharge waters from acid sulfate landscapes. The hydrolysis of metals during the oxidation of sulfidic sediments generates a loss of DIC which can be modelled to follow first order kinetics. It is more difficult to understand $^{13}C_{DIC}$ processes in acid sulfate discharge waters; however an enrichment process does occur in the studied samples and may follow a kinetic loss mechanism.

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