The use of peepers to sample pore water in acid sulphate soils

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Summary

Serious environmental impacts of acidic drainage from acid sulphate soils in coastal areas are the result of the interactions between the hydrologic cycle, land use and drainage management, and pore water chemistry. In this study, *in situ*, diffusion-controlled dialysis profile samplers, or peepers, were used to examine pore water chemistry of acid sulphate soils in a coastal, sugarcane-producing area in Eastern Australia. The peepers sampled pore water at 20-mm intervals over a 1.0-m length, permitting excellent resolution of the sharp transitions in pore water chemistry that occur around a soil profile's iron sulphide oxidation front. Comparison of peeper profiles with soil water profiles extracted from soil samples by centrifuging, illustrated the advantages of peepers over conventional soil water sampling techniques in unconsolidated, sulphidic soils. For conventional sampling, the low permeability, gel-like, unoxidized soil samples had to be frozen then thawed before water could be extracted by centrifuging. Peeper profiles of species not involved in redox reactions agreed well with those from centrifuged soil extracts. Redox sensitive species, however, were in poorer agreement because of the lengthy soil sample preparation and extraction procedures required for extraction by centrifuging. The approximately 6-day equilibration time required for peeper sampling allows them to follow monthly or seasonal changes in pore water chemistry in acid sulphate soils due to variations in climate, and land use and management.

Introduction

Throughout the world, coastal lowlands are under increasing development pressures for agricultural, aqua-cultural, urban and resort expansions. In many of these lowlands, Holocene acid sulphate soils were deposited in floodplains, embayments, mangrove swamps and salt marshes during and following the last major sea level rise. Drainage from acid sulphate soils can have major adverse impacts on soil water, groundwater and downstream water quality. These impacts include decreases in crop production, fish mortality and outbreaks of fish diseases, and accelerated corrosion of concrete, iron, steel and aluminium infrastructures. The selection of land and water management strategies that minimize or eliminate these impacts requires an understanding of management-induced changes in lowland and floodplain hydrology and the accompanying, dramatic alterations in soil-water chemistry. Accurate sampling of soil-water chemistry in acid sulphate soils is difficult because of:

- the rapid, major changes in pore-water chemistry due to oxidation of reduced sulphur species that occur over small depth intervals;
- the reactive, reduced and oxidized species that can be altered by sampling; and
- the hydraulic conductivity of the unoxidized sulphidic soil layer is less than $0.01 \text{ mm hour}^{-1}$ so that *in situ* or laboratory pore water extraction methods are too slow.

In situ dialysis samplers, commonly called peepers (Hesslein, 1976), have the potential to overcome these difficulties. In this work we investigate the use of peepers compared with centrifuging, so as to sample the spatial distribution of redox sensitive pore water in an unconsolidated acid sulphate soil profile.

Pore water sampling

Widely-used pore water extraction systems include centrifugation, pressure filtration of sliced sediment cores, ceramic-cup suction samplers, and *in situ* dialysis sampling (Adams, 1994; Bufflap & Allen, 1995).

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The extraction of pore waters from sediment cores is the traditional methodology. However, there are problems with this technique. Pore water concentrations obtained through sample centrifugation appear dependent on time and speed of rotation (Carignan *et al.*, 1985). Pressure filtration or core squeezers usually require several manipulations of the sediment, increasing the possibility of sample oxidation, sample dissolution or contamination (Adams, 1994; Montgomery *et al.*, 1996). Core-squeezing can also give erroneously high species' concentrations due to temperature changes and the pressure-induced mechanical breaking of soft particles with subsequent release of ions (Bertolin *et al.*, 1995). Ceramic cup suction extractors are expensive, difficult to operate in soils with a large silt and clay content, and have a poor sampling resolution (Teasdale *et al.*, 1995). In reduced marine sediments, the oxidation of samples is a major problem when analysing reduced soils and waters (Loder *et al.*, 1978).

The advantage of the *in situ* techniques over the other methods is the elimination of possible temperature- and pressure-induced artifacts, and minimization of potential redox variations and solid-solution interactions (Azcue *et al.*, 1996).

Diffusion dialysis samplers or 'peepers' (Figure 1) were developed to sample pore waters and quantify *in situ* interactions between lake sediments and overlying waters (Hesslein, 1976). In the peeper technique, dissolved constituents from interstitial pore water or free water bodies diffuse through a semi-permeable membrane into deionized water in the peeper chambers. Past studies include for trace metal analysis (Carignan *et al.*, 1985), nutrient dynamics (Viel *et al.*, 1991), the determination of oxygen gradients (Adams *et al.*, 1992), diagenetic processes

(Marnette *et al.*, 1993) VOCs (Vroblesky & Campbell, 2001) and perchlorate (Tan *et al.*, 2005).

The peeper technique does have disadvantages, which include membrane breakdown and the time necessary for the peeper chamber to come to equilibrium by diffusion with the surrounding soil-solution. Other disadvantages include profile averaging and phase shifts, where the peak in pore water concentration is coincident between peeper cells (Harper *et al.*, 1997). The diffusive equilibrium in thin films (DET) and diffusive gradient in thin films (DGT) gel techniques are used to obtain high resolution profiles of trace-metals in sediment pore waters (Harper *et al.*, 1997, 1999).

Despite the disadvantages, the reported simplicity of the peeper technique (Carignan & St Pierre, 1994) and its sampling resolution makes it an attractive option for field studies of acid sulphate soils or other water logged soft soil where large changes in dissolved species can occur over small depth intervals.

Peeper equilibration time

Reported equilibrium times of peepers similar to that used in this study vary from 3 to 20 days (Carignan, 1984; Bufflap & Allen, 1995). Equilibration time is determined by porosity of the sediment, the area to volume ratio of sampler compartments, diffusion coefficients of the ions of interest, temperature, degree of adsorption to the solid phase, and dissolution of the solid phase (Carignan *et al.*, 1985; Azcue *et al.*, 1996). Teasdale *et al.* (1995) related the time dependence of concentration of a species in the peeper chamber, C_t , to the physical characteristics of the peeper:

$$C_t C_0^{-1} = 1 - \exp(-k_m 2AtV^{-1}), \quad (1)$$

where C_0 is the undisturbed concentration of the species in the pore waters adjacent to the membrane, k_m is a species membrane mass transfer coefficient (LT^{-1}), V is the volume of the peeper chamber (L^3), A is the surface area of the chamber (L^2), and t is peeper insertion time (T). While calibration of peeper equilibration time is recommended, most common dissolved species approach equilibration in about 10 days with peepers having $VA^{-1} = 10$ mm. The calculated equilibration time of the peepers used here from Equation (1) is 6 days.

A further problem concerning sampled volume and peeper equilibration time arises from the difference in densities between the initially fresh water in the peeper chambers and the surrounding pore waters (Grigg *et al.*, 1999). This may produce density-driven mass flow that causes the convection of water up the face of the peeper. Such flows are possible when peepers are inserted into sandy sediments with pore water salinities approaching seawater. The occurrence of these unstable flows can be estimated from the porous material Rayleigh number, N_{Ra} , (Wooding, 1964) with:

$$N_{Ra} = \frac{\Delta\rho g k L}{D_s \mu} = \frac{\Delta\rho K L}{\rho_s D_s}, \quad (2)$$

Figure 1 Schematic diagram of peepers used in this work showing the plexiglass body, cover plate and dialysis membrane. Dimensions are given in the text.

where $\Delta\rho$ is the difference between the density of pore water in the sediment (ρ_s) and that of the fresh water (ρ_f) in the peeper chamber (ML^{-3}), g is acceleration due to gravity (LT^{-2}), k is the intrinsic permeability of the sediment (L^2), L is a characteristic physical dimension, here taken as the length of the peeper (L), D_s is the diffusion coefficient of dissolved species in the sediment (L^2T^{-1}), μ is the dynamic viscosity of the pore water solution ($\text{M}(\text{LT})^{-1}$) and $K = kg\rho_s\mu^{-1}$ is the hydraulic conductivity of the sediment to pore water (LT^{-1}).

Density-driven convection is expected to be significant when the Rayleigh number exceeds the critical stability limit for saturated porous materials of about 40 (Lapwood, 1948; Wooding, 1964; Elder, 1967). In this work, the maximum value expected for $\Delta\rho\rho_s^{-1}$ around the oxidized zone in acid sulphate soils is 2.9×10^{-5} (about 0.05 for seawater-fresh water), K for the reduced soil in this study is less than 10^{-10} ms^{-1} , L is 1 m and D_s for the major chemical species, Na^+ and Cl^- , is about 8 to $13 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ (Li & Gregory, 1974; Boudreau, 1996). These values give a range for the Rayleigh number of 0.002 to 0.006, four orders of magnitude less than the critical stability limit. Density-driven convective mixing, due to peeper insertion is therefore not a problem here. Grigg *et al.* (1999) examined pore-water convection induced by peeper emplacement and derived a Péclet number (Pe), which is the ratio of diffusive to convective time scales. In this case $\text{Pe} = 0.3$, which indicates that convection is not a significant issue and thus the period that was employed for peeper equilibration is sufficient. The peepers were used in fine mud and gel-sediments in this study, which are seen as appropriate sediment to prevent convection (see Grigg *et al.*, 1999). However, in strongly oxidized soils, peat layers and coarse sandy soils, where K could vary between 10^{-4} to 10^{-8} (White *et al.*, 2003), convection will be a problem, and longer equilibration times are needed.

The flux of solutes to the peeper cell is a function of diffusive transport with a degree of supply from the diffusive phase. Harper *et al.* (1997) have modelled peeper equilibrium times for buffered, diffusive and partial resupply, for ions in the pore water solution. In the case of the buffered and partial resupply, equilibrium (99%) times are < 50 hours, but for the diffusion only case > 56 days (Harper *et al.*, 1997). The underlying assumption of the Péclet number (Pe) (Grigg *et al.*, 1999) is that the pore waters are not buffered or resupplied from the sediment grains and thus represents the worst-case scenario. Based on the above estimates of equilibrium times the peepers were allowed to equilibrate for 14 days, 2.3 times longer than predicted by Equation (1). The objective of this work is to assess the applicability of peepers for sampling pore waters in acid sulphate soils. A key problem with the sampling and analysis of these soils is that much of the pore water chemistry is redox dependent and significant sampling artifacts can be caused by using traditional techniques. The secondary object is to examine the soil pore concentration profiles in acid sulphate soils.

Materials and methods

Field site

The study site was the 4.5 km^2 , drained, sugarcane catchment of McLeod's Creek, a right-bank tributary of the Tweed River, New South Wales, Australia ($28^\circ 30'\text{S}$, $153^\circ 30'\text{E}$). The soil at the floodplain site is a remarkably uniform Thiosonic Fluvisol (FAO, 1998), with at least 9 m of unconsolidated sulphidic (pyrite concentration 25 mg kg^{-1}), Holocene estuarine deposits, overlying stiff Pleistocene clays (Wilson, 1999). A peat layer of variable thickness, up to 0.3 m, overlays the sulphuric horizon ($\sim 0.7 \text{ m}$), which contains approximately 50 tonnes of sulphuric acid per hectare throughout the former backswamp (Smith *et al.*, 2003).

Peepers

The unit and preparation. Figure 1 is a schematic diagram of the peepers that were used in this study. The total length of the peeper is 1200 mm and the sampling section is 1000-mm long, 80-mm wide and 15-mm thick. Fifty horizontal chambers, 60-mm wide and 10-mm in height were milled into a 10-mm thick sheet of plexiglass. These chambers have a volume-to-membrane area of 6 mm. Chambers were separated by 10 mm of plexiglass, which allows the profile to be sampled at 20-mm vertical resolution. Inert polysulphone membranes (pore size of $0.45 \mu\text{m}$), resistant to bacterial degradation over the peeper equilibration time (14 days), are placed over both faces of the milled sheet. These are secured with two 2.5-mm thick cover plates with slots to match those of the solution chambers.

Peepers and PVC cylinders used for transporting peepers were initially cleaned with P-free detergent, soaked in $\sim 1.2 \text{ M}$ HCl for 2 weeks and then rinsed with deionized water. The peeper chambers were filled with Milli-Q[®] deionized water by immersing the peeper body with one membrane attached in a deoxygenated water bath. The other polysulphone membrane was then placed over the water-filled compartments; the cover plates were placed on the membrane and screwed in place with stainless steel screws. The assembled peepers were placed in the PVC transport cylinders, filled with deoxygenated Milli-Q[®] deionized water, and N_2 was bubbled through the cylinder for 72 hours. The deoxygenated cylinders were then sealed with gas-tight screw caps for transport to the field.

Peeper pore water sampling

Pore water sampling was carried out at the beginning of the wet season, December 1996, 1 month after the harvest of a ratoon sugarcane block. Prior to the insertion of the peepers, soil profile descriptions were made on samples that were collected with a bucket auger and soil gouge. Soil colour, morphology, *in situ* pH, reaction to 30% (volume) hydrogen peroxide and the position of the watertable were noted (Table 1). From these

descriptions, the oxidation front, the boundary between the sulphuric and sulphidic layers (−0.55 m Australian Height Datum (AHD), where 0 m AHD approximates m.s.l.), was determined to identify at which elevation the peepers were to be inserted.

For peeper insertion, a new hole, close to that used for the profile description, was augered to a depth approximately 100 mm above the intended position for the top peeper chamber. The peeper was then removed from the deoxygenated water-filled transport cylinder, a rope was attached to the peeper for later extraction, and the peeper was pushed into the soil at the bottom of the augured hole. The total time for this operation was less than 2 minutes, which minimized oxygen contamination. Three peepers, D, E and F, were placed in the soil at 0.5 m apart to minimize equilibrium times. This is greater than the recommended 0.16 m (see Harper *et al.*, 1999). Two of the peepers, D and E, were duplicates positioned to straddle the oxidation front. The third, F, was inserted 0.47 m below the other two in order to examine the deeper profile. The depths to which peepers were placed and the elevation of the ground surface were surveyed relative to AHD. Water table

depth at insertion was 0.2 m below the ground surface at +0.26 m AHD.

Peeper pore water collection

After equilibration, peepers were removed rapidly and soil adhering to the peeper faces was rinsed off with de-ionized water. The content of the peeper chambers was sampled by tilting the peeper slightly from horizontal and piercing the membrane with a digital micro-pipette and withdrawing a predetermined volume (4.5 ml). The peeper chambers were sampled from the anoxic to the oxic end and the operation of peeper removal, rinsing and sampling was completed within 15 minutes. No iron oxy-hydroxide stains were visible on the membrane or the peeper body or in the chambers before or after sampling.

Samples were injected into cleaned tubes (prewashed with ~1.6 M HNO₃ solution followed by a triple rinse with Milli-Q® deionized water), the pH measured and redox sensitive species and trace metals were preserved with 3 ml of 0.05 M HNO₃ (solution pH < 2). Solution samples, blanks and random

Table 1 Representative profile description of the McLeod's Creek study site

Depth m from surface	Elevation AHD ^a	pH ^b	Peroxide reaction ^c	Colour	Description
0–0.1	0.41	4.33	0	10YR2/1	Black organic topsoil
0.1–0.2	0.31	4.47	0		Watertable at 0.2 m., black organic topsoil
0.2–0.3	0.21	4.3	0	10YR4/3 (80%) 10YR2/1 (20%)	Black/brown, start of iron mottles, organic
0.3–0.4	0.11	4.15	0	7.5YR5/1 (60%) 7.5YR5/6 (30%) 7.5YR6/8 (10%)	Brown, iron mottles, slight jarosite
0.4–0.5	0.01	4.13	0		Brown, iron mottles, slight jarosite
0.5–0.6	−0.09	4.16	0		Brown/grey, iron mottles, jarosite
0.6–0.7	−0.19	3.9	0		Brown/grey, iron mottles
0.7–0.8	−0.29	3.85	0		Brown/grey, iron mottles
0.8–0.9	−0.39	3.78	0		Brown/grey, iron mottles
0.9–1.0	−0.49	4.21	x		Brown/grey, iron mottles
1.0–1.1	−0.59	6.01	xxx	2.5Y4/2	Grey, iron stained roots
1.1–1.2	−0.69	6.2	xxx		Grey, iron stained roots
1.2–1.3	−0.79	6.39	xxx		Grey, iron stained roots
1.3–1.4	−0.89	6.45	xxx		Grey, no iron stains
1.4–1.5	−0.99	6.5	xxx	5Y4/1	Blue grey mud
1.5–1.6	−1.09	6.55	xxx		Blue grey mud
1.6–1.7	−1.19	6.6	xxx		Blue grey mud
1.7–1.8	−1.29	6.71	xxx		Blue grey mud
1.8–1.9	−1.39	6.7	xxx		Blue grey mud
1.9–2.0	−1.49	6.77	xxx		Blue grey mud
2.0–2.1	−1.59	6.79	xxx		Blue grey mud
2.1–2.2	−1.69	6.8	xxx		Blue grey mud

^aAHD = Australian Height Datum (c. 0 m mean sea level).

^b*In situ* pH by direct insertion of spear-point probe.

^cStrength of reaction to 30% (wt) peroxide.

0 = no reaction, x = slight reaction, xxx = strong reaction.

tubes were refrigerated in the field in a portable cooler and stored at 4°C until analysis, which was completed within 2 weeks of sampling. No filtering of the samples was necessary because of the nominal 0.45 µm pore size of the peeper membranes.

Soil sampling, centrifugation and laboratory soil water extraction

A soil core was collected for determination of bulk density (wax block method) and gravimetric moisture content; the profile is shown in Figure 2. In order to compare peeper soil water profiles with soil water extracted from the soil by centrifugation, three undisturbed soil cores were collected. The cores were sampled using a Russian D-section corer from locations adjacent to the peepers (within 0.5 m) directly after the peeper pore water sampling was complete. The cores were wrapped tightly in 100% clear polyethylene film and sealed in a plastic bag and placed in a car fridge (< 4°C). The cores were sectioned in the laboratory into 40-mm increments using a knife and a tape measure, 3 days after sampling, and attempts were made to centrifuge (2000 g) the samples. Although the soils contain up to 80% by volume of water, because of the extremely low hydraulic conductivity of the gel-like reduced soil, this centrifugation procedure proved impossible. The sectioned cores were placed in shaking tubes, frozen in a standard freezer and then thawed, after which soil water was easily extracted by centrifuging the samples at 2000 g for 7 minutes. Aliquots of the centrifuged pore water were filtered (0.45 µm) and used for analysis.

Soil and peeper pore water analyses

Elemental concentrations in peeper pore water and core soil water samples were determined using an Inductively Coupled

Plasma Optical Emission Spectrometer (ICP-OES, Perkin and Elmer Optima 3000, Waltham, MA, USA) and an Activon Cl⁻ ion electrode (pH-ISE meter, 9455) at the School of Geography laboratories, University of New South Wales. Redox-sensitive, 'reactive' and trace metal species were measured by ICP-OES included S, Al, Fe, Mn, and Si. Major ions measured included Ca, Mg, Sr, Na, K, and Li.

Results and discussion

Comparison with centrifuged soil samples

The accuracy of the analytical analysis was checked by the charge balance technique.

$$\text{E.B.} = (\Sigma \text{cations} - \Sigma \text{anions}) / (\Sigma \text{cations} + \Sigma \text{anions})^{-1} \times 100. \quad (3)$$

Pore water samples and extracted soil water samples had charge balance errors that were less than 5%. Despite our best efforts, the peeper cells were misaligned by 20 mm between Peepers D and E and the soil core samples were also misaligned by a similar error. Figure 3 shows the concentration of Si and Fe in the collected pore waters. It is evident that differences between the methods are due to technique rather than soil spatial variation. The variation in concentration in each of the methods is probably due to sampling misalignment and could be further reduced. The 1:1 agreement between the measured conservative species (Figure 3) in each of the sampled core pore waters and peeper pairs indicates that the soil spatial variability is not affecting the results. Figure 4 shows the comparison between selected species' profiles from peeper E and from soil core B. The peeper profiles of the general 'background' species, mostly those with monotonic increasing concentrations with decreasing elevation, Cl, Na, K and Ca values (as well as Mg and Sr values, not shown) are in good agreement with those obtained by the centrifuge technique. The S profiles also show reasonably good agreement. However, peeper profiles for the species with sharp maxima, Fe, Si and Li in Figure 4 (also Mn, data not shown) have concentration maxima up to three times those found from centrifuged samples. The results for Al (not shown) were in better agreement with maximum values but in poorer agreement in the reduced part of the profile. The results suggest that the length of time required for sample preparation in the centrifuged soils permitted oxidation of dissolved Fe²⁺, thereby producing iron precipitates, which is consistent with the findings of Loder *et al.* (1978), and also there has been coprecipitation of Si, Mn and Li (Kato, 1969; Nriagu, 1978). Iron precipitates, such as amorphous iron oxyhydroxide, are efficient scavengers of metals and other ions and the use of standard soil extraction techniques causes the precipitation of iron. This will result in a non-representative soil solution devoid of or with substantially less metal content.

Figure 2 Profiles of bulk density, ρ_b , t m⁻³, and volumetric water content, θ_v , m³ m⁻³ at the study site. The watertable was at approximately -0.3 m AHD (about 0.7 m below the soil surface).

Figure 3 Comparison of mean and standard deviations of Fe and Si profiles for the peepers D and E and soil cores B and C. Elevation is metres (AHD) and the relationship of the Na^+ concentration measured by peepers (D, E, and F) and soil extraction.

Figure 4 Comparison of profiles of species measured using peeper E (open points) with those measured from soil water samples profile B extracted by centrifuging frozen then thawed soil samples (solid points). Elevation is metres (AHD) and concentrations in mg litre^{-1} .

Figure 5 Comparison of species profiles in acid sulphate soil under high watertable conditions determined from three spatially separate peepers (D, E, and F). Elevation is metres (AHD) and concentrations in mg litre⁻¹.

The number of manipulations and the length of time required for soil freezing, thawing and centrifuging increases the likelihood of the alteration of the sample chemistry by oxidation during pore water extraction. Loder *et al.* (1978) found that up to 75% of the ferrous iron present in the pore waters was removed by as short as a 12 minutes exposure to the laboratory atmosphere. In our study, up to 80% of the total iron was removed from the samples with $\text{pH} < 5.5$. Winger *et al.* (1998) found that centrifuging and vacuum extraction produced similar concentration profiles to those obtained by peepers. But the sediment that was used in their experiment was obtained some days earlier, stored at $\sim 4^\circ\text{C}$ and the extraction and dialysis was performed in the laboratory, not in the field. Any oxidation would have therefore probably occurred prior to the extraction. The agreement between the two sampling techniques used in our study for non-reactive species indicates that the peeper technique does produce reliable estimates of *in situ* pore water composition. The disagreement for the more reactive species illustrates the comparative advantages and simplicity of the peeper technique for sampling pore water species that are redox-dependent. The use of a glove box with an inert atmosphere during field extraction and pore water preservation might have improved the recovery of species that are redox reactive. In general, there is a good correspondence between the three separate profiles and the use of peepers to investigate pore water chemistry is an appropriate strategy for acid sulphate soils.

Spatial variation in peeper profiles

Figure 4 shows a comparison between the three separate pore water peeper profiles, D, E and F. The peeper sampling interval of 20 mm provides excellent resolution of the marked vertical changes in species concentrations, which occur around the oxidation front. The three sets of peeper profiles correspond closely, and the 0.47 m deeper peeper profile, F, overlaps well with the other two.

The impact of sulphide oxidation ($\text{FeS}_2 + 15/4\text{O}_2 \rightarrow \text{Fe}(\text{OH})_3 + 2\text{SO}_4^{2-} + 4\text{H}^+$) on pore water chemistry is evident in Figure 5. Above the oxidation front, pH is < 5.5 and the weathering of pyrite releases iron and protons, and acid weathering of the aluminosilicates contributes aluminium and silica to the soil solution. Lithium is also present in the soil solution and probably is also due to the clay mineral weathering. The variation of the iron, aluminium and lithium profiles could be due to inherent soil variability and phase shift between the peepers (Figure 5). In the sulphuric horizon, gypsum is probably forming and consuming soluble Ca^{2+} and SO_4^{2-} and potassium is also being removed from the soil solution into precipitated iron minerals (e.g. jarosite). Differences in maximum concentrations of Al^{3+} , Fe^{2+} and Li^+ for individual profiles do occur around the oxidation front, where there are steep gradients in species concentrations. The profiles in Figure 5 fall into three categories: species with

a pronounced concentration maximum (H^+ , Fe^{2+} , Al^{3+} , Si^{4+} and Li^+); species with a broad maximum, (S^{2-} , Ca^{2+} and Mn^{2+}); and species with monotonic increasing concentrations with decreasing elevation (Cl^- , Na^+ , K^+ and Mg^{2+}). The profiles of Fe and Li with plumes extending in the sulphidic horizon indicate a downward diffusion. The sulphidic horizons at many acid sulphate soil sites in eastern Australia are characterized by gel-structure. The gel is thixotropic and the clays are arranged in a house of cards structure (White *et al.*, 2005). The diffusion of divalent cations into the gel has important implications for the stability of the house-of-cards structure through the change in the double layer of the colloids. This may lead to structural instability and ingress of oxygen and further oxidation.

Conclusions

We have shown here that the use of *in situ*, diffusion-controlled, dialysis profile samplers, or peepers, is relatively straightforward in acid sulphate soils or indeed any soft soil environment. Peepers can resolve the spatial variations in pore-water concentrations that occur over small distances around the sulphide oxidation front in these soils. Comparison of peeper results with conventional pore-water extraction from soil samples showed the difficulty of using conventional extraction by centrifugation in these soils. Samples with volumetric water contents close to 0.8 had to be frozen then thawed before water could be extracted. The concentration profiles of 'background' species measured with peepers were in good agreement with profiles determined by centrifuging soil samples after freezing. Agreement for redox-active species was poorer, which we attribute to the number of manipulations and the length of time required for preparation and centrifugation of soil samples.

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