Hydric halitic sulfuric soils in secondary salinised landscapes of Southwest Western Australia

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Abstract

Rising water-tables due to clearing of native vegetation in the south-west of Western Australia (WA) have been recognised as causing secondary salinisation of landscapes with impacts mostly considered to be due to increased salt accumulation and water-logging. Much of the shallow saline groundwater rising to the surface has recently been recognised as being acidic ($pH<4.5$) posing an additional threat. We report on the first broad survey to characterise lake and wetland sediments under the influence of increased regional acidic saline groundwater discharge in the agricultural zone of WA (covering an area 300 x 100 km). This investigation found that soil $pH_{field}<4$ in shallow horizons (<15 cm) of most profiles along with total actual acidity was marginally less than those common in other Acid Sulfate Soils (ASS) with sulfuric materials. Deeper horizons tended to have higher pH, with less total actual acidity, but with sometimes significant occurrences of alunite, although with few indications of secondary minerals characteristic of sulfuric materials such as jarosite and schwertmannite. Most sulfuric materials contained only minor evidence of sulfidic materials being present within the profiles and this was generally in horizons overlying sulfuric horizons containing alunite minerals. We suggest that external acidity sources such as discharge of acidic groundwater via water-table rise or deep drains to lakes and floodplains has led to the formation of sediments with a chemistry similar to those of Acid Sulfate Soils where acidity originates within the profiles.

Key Words

Saline acidic sediments, inland acid sulfate conditions, alunite, salinised soils

Introduction

Rising water-tables due to clearing of native vegetation in the south-west of Western Australia (WA) have long been recognised to be the cause of widespread secondary salinisation of landscapes (e.g. Hatton *et al.* 2003). The effects of rising saline water-tables are recognised by increased accumulation and mobility of salts in surface soil profiles and increased waterlogging (Hatton *et al.* 2003). Much of the shallow saline groundwater in salinised valley floors in the south-west of WA has been recently recognised as being acidic ($pH<4.5$) posing an additional threat to these landscapes (Shand and Degens 2008). The effects of this groundwater discharge on the formation of various types of hydric soils (after USDA-NRCS 2010) in playas and claypans is not certain and may lead to the formation of conditions similar to those of acid sulfate soils (ASS). ASS with sulfidic materials (or potential ASS materials) may have formed in previous waterlogging under saline conditions (Fitzpatrick and Shand 2008). These carry implications for the management of such waters, particularly since there is the risk of impacts of acidity on aquatic ecosystems compounding the existing impacts of salinisation (Shand and Degens 2008). We report on results of the first broad scale survey of these secondary salinised hydric halitic soils (Fitzpatrick and Shand 2008) influenced by acidic saline groundwaters in low lying landscapes covering an area of over 50,000 km^2.

Methods

A broad survey of shallow soil profiles in secondary salinised lakes containing acidic ($pH<4$) waters during the final stages of drying (identified in Shand and Degens 2008) was conducted across the central part of the Western Australian agricultural zone (Figure 1). Representative pits were dug in twelve lakes and shallow (<30 cm) horizons, colours, textures, mottling and major inclusions were described and field $pH_{1:1water}$ determined. Sampling depth was constrained by shallow water-tables, silcretes and the focus on horizons most likely to influence overlying water quality. Samples were collected from each horizon, sealed in ziplock bags and frozen on-site for transport to the laboratory for analysis of basic soil properties ($pH_{1:5\ water}$, electrical conductivity or $EC_{1:5\ water}$, organic C and carbonate C), major and minor elements by XRF, mineralogy by quantitative XRD (PANalytical X'Pert Pro Multi-purpose Diffractometer) and ASS properties. The latter analyses included analysis of sulfide-S using the chromium reducible S (S_{Cr}) method (Australian standard ASS method 22B Ahern *et al.* 2004) and total actual acidity determined by titration to pH 6.5 (Australian standard ASS method 23F; Ahern *et al.* 2004). Only selected results are presented here.

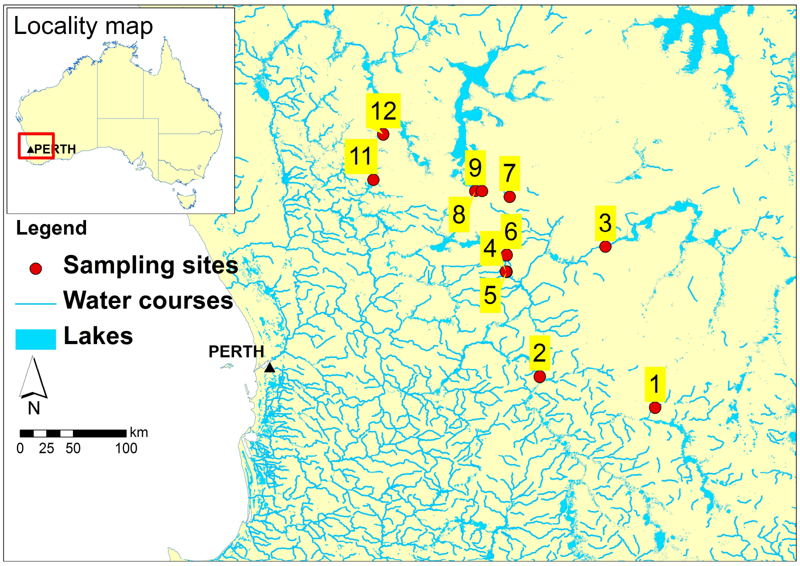

Figure 1. Location of playas and clay pans sampled across secondary salinised landscapes in the Western Australian agricultural zone

Results

Most profiles exhibited horizons with pH<4.5 with some as low as 3.6 and all were hypersaline with EC generally exceeding 9 dS/m (Table 1). Total actual acidity could be as much as 109 moles H^+/tonne, although most were less than 45 moles H^+/tonne (Table 1). Shallow horizons were frequently halitic crusts commonly overlying soft silts with deeper horizons consisting of red or grey clays (Figure 2; Table 1).

All soil profiles were dominated by kaolin clays and contained at least one horizon with alunite (>9%; Table 1). Some sites contained horizons with up to 68% alunite. Most profiles did not contain detectable schwertmannite or jarosite, with only one profile (site 8) containing jarosite (up to 7%). Significant concentrations of salts such as halite, gypsum and bassanite (suspected to be formed during oven drying for sample analysis) also occurred in all profiles. There were no carbonate minerals in any of the profiles.

Sulfidic material (Isbell 1996) occurred mostly in near surface layers in some lakes, although only a few contained evidence of pyrite of any significance. Pyrite, evident by analysis of chromium reducible S, was generally not detected (<0.005%S) or less than 0.01% S in the profiles at most sites. Where present at >0.01%S, pyrite was evident in either thin (<2 cm) surface or near surface horizons (<5 cm) at up to 0.6%S, although most occurrences were 0.01 to 0.04%S. These horizons also tended to contain the greatest concentrations of organic C within the profile and were prominent in formerly vegetated or lakes sited within the main flow path of floodways.

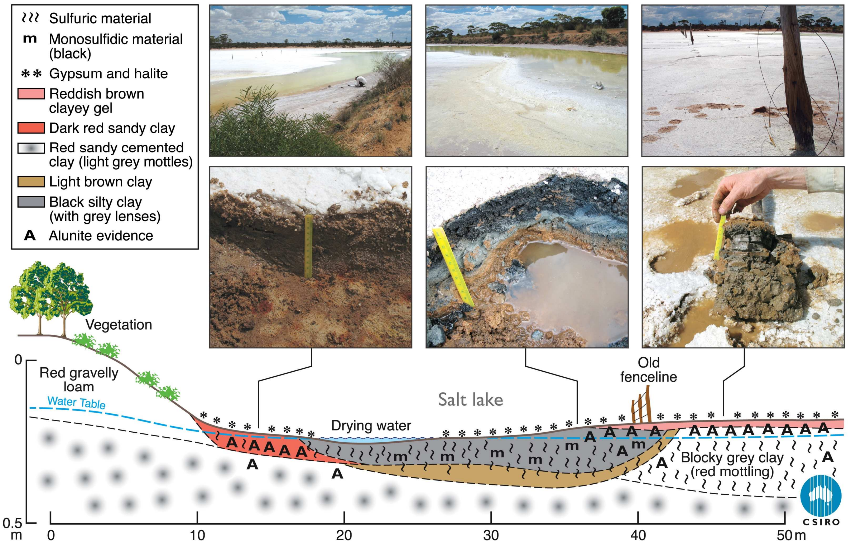

Figure 2. Typical hydric halitic sulfuric soil sequence (Site 3 is the profile on the far right)

Table 1. Selected profiles illustrating common acidic soil chemistry and mineralogy of secondary salinised soils in playas and claypans (indicated in Figure 1)

Site	Hydrology & vegetation	Depth (cm)	Soil horizon description	pH[1]	EC[1] (dS/m)	%S_{Cr}[2]	TAA[3] (mole H^+/tonne)	Alunite[4] (%)
3	Terminal non-vegetated playa	0-1	Halitic crust	3.8	126	<0.01	5	<1
		1-2	Red-brown silty gel	3.9	126	<0.01	27	3
		2-15	Grey clay, red/brown mottles	3.9	62	<0.01	51	18
		15-25	Red cemented clay, grey mottles	4.4	14	<0.01	16	5
4	Terminal formerly non-vegetated playa	0-1	Halitic crust	4.4	127	<0.01	0	5
		1-1.5	Red-brown gypsic silt	4.0	73	<0.01	38	7
		1.5-3	Dark brown clay	3.8	47	<0.01	66	20
		3-15	Grey clay	3.8	23	<0.01	35	68
		15-20	Light grey clay	3.8	22	<0.01	35	60
6	Flow through non-vegetated playa, secondary salinised	0-3	Gypsic sand	4.7	20	<0.01	23	<1
		3-6	Greenish grey silt	4.3	27	0.02	53	<1
		6-7	Gypsic pan	N/A	N/A	N/A	N/A	<1
		7-13	Grey silt (soft)	4.4	14	0.04	32	3
		13-17	Red-brown clayey silt	4.1	13	<0.01	44	16
		17-21	Olive yellow sand	4.7	9	0.01	24	6
		21-36	Grey silty clay	4.2	16	0.03	45	26
7	Terminal formerly vegetated clay pan, secondary salinised	0-12	Halitic crust	*1.9*[5]	N/A	N/A	N/A	<1
		12-15	Brown gypsic silt	3.6	53	0.01	N/A	5
		15-15.5	Light-brown sand	N/A	N/A	N/A	N/A	<1
		15.5-19	Grey brown sandy clay, dark-brown mottles	4.7	26	0.03	31	18
		19-25	Dark-grey brown sandy clay	5.2	20	<0.01	16	28
		>25	Indurated clay	N/A	N/A	N/A	N/A	N/A
8	Flow through non-vegetated playa, secondary salinised	0-1	Gypsic yellow-brown silt	3.9	45	0.27	96	<1
		1-3	Very-soft dark-grey silt	4.7	50	0.06	47	<1
		3-5	Dark-grey clayey silt, black mottles	5.1	28	0.01	26	2
		5-9	Soft grey silt	5.1	25	0.02	24	12
		9-15	Red silty clay	4.5	17	<0.01	38	19
10	Terminal formerly vegetated clay pan, secondary salinised	0-2	Halitic crust	*2.4*[5]	N/A	N/A	N/A	N/A
		2-3	Yellow-brown black mottled gel	3.8	63	0.06	N/A	<1
		3-7	Soft black silt	4.0	56	<0.01	55	<1
		7-11	Soft brown silt	3.8	43	<0.01	109	9
		11-40	Dark-grey brown sandy clay	4.3	15	<0.01	52	4
		40-45	Grey-brown sandy clay	4.2	18	<0.01	58	6
12	Flow through formerly vegetated clay pan, secondary salinised	0-0.03	Yellow-brown gel, grey mottles	5.4	76	<0.01	2	<1
		0.03-1	Black silt	5.6	58	0.08	0	3
		1-5	Black clayey silt	5.6	35	0.61	0	5
		5-15	Firm grey sandy clay	4.8	10	<0.01	11	11
11	Flow through formerly vegetated clay pan, secondary salinised	0-0.03	Yellowish-red gel	4.8	53	<0.01	42	2
		0.03-2	Black silty clay with grey mottles	5.7	25	0.04	0	4
		2-5	Grey clay with red mottles	6.5	19	<0.01	0	3
		5-20	Brownish grey clay, red-brown mottles	6.1	19	<0.01	0	8

[1]Soil pH and EC (electrical conductivity). [2]S_{Cr} = Cr reducible sulfur (Ahern *et al.* 2004). [3]Titratable Actual Acidity (Ahern *et al.* 2004). [4]Alunite as a proportion of minerals by quantitative XRD. [5] pH in italics measured *in situ* using WTW spear point pH probe.

Conclusions

The acidic saline lake sediments present characteristics similar to those of inland ASS but are commonly much more saline (halitic) and usually do not contain iron oxyhydroxysulfate minerals common in sulfuric materials in ASS or inland ASS such as jarosite or schwertmannite (Fitzpatrick and Shand 2008). This may reflect the acidity source being predominantly saline groundwaters with the pH ranging from 3 to 4.5, which can contain high concentrations of aluminium (Shand and Degens 2008). Iron can also occur in high concentrations (Shand and Degens 2008), which would be expected to precipitate as jarosite or schwertmannite in some lakes (given groundwater pH; Long *et al.* 1992). Other iron minerals were also notably absent in any detectable concentrations in the sediment profiles.

Although traces of sulfides (as indicated by chromium reducible S) occur in surface and sub-surface sediments of some lakes and wetlands, contemporary sulfide oxidation is not believed to be the main source of acidity. Sulfides may have completely oxidised but recent drying or exposure of the sediments is unlikely to have occurred because these lakes have experienced increasing waterlogging as a result of rising groundwater over the past 50–100 years and have not experienced contemporary drought conditions occurring elsewhere in Australia. Furthermore, the concentrations of alunite in some places (up to 68%) suggest oxidation of significant concentrations of sulfides (almost two orders of magnitude greater than sulfide concentrations presently occurring) or that acidity had concentrated within the profiles by way of discharge of acidic saline groundwater over significant periods of time. This contrasts with evidence of that most lakes were not continuously influenced by acidic saline groundwater and secondary salinised, with vegetation being evident prior to recent rises in watertables.

Accumulations of significant concentrations of alunite in subsurface sediments may be residual from previous exposures of lake sediments to acidic conditions in previous climate regimes. This probably occurred under climate variations during the Quaternary geological period, which caused periodic expansion and contraction of groundwater discharge areas in the landscape, of which the playas are regarded as remnants of this activity (George *et al.* 2008). Although alunite has been identified in primary salinised lakes in Victoria (Long *et al* 1992) and southern WA (McArthur *et al* 1991, Bowen and Benison 2009), the present study indicates that these also occur in secondary salinised wetlands and lakes. Evidence that some lakes were vegetated prior to secondary salinisation (Table 1) and accumulations of sulfides in shallow horizons indicate that recent alkaline conditions may have prevailed. These appear to be experiencing re-acidification. The origin of the acidity in these sulfuric soils is complex and needs further work to clarify whether pyrite had any role in this.

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