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The effects of preload surcharge on arsenic and aluminium mobilization in pyritic sediment

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ABSTRACT: The preload technique is employed in geotechnical engineering to improve the shear strength and load-carrying capacity of saturated fine-grained sediments. The technique is based on transient flow of pore water in response to excess pore pressure build-up in the sediment pores under surface surcharge. In pyritic sediment, the preload has an additional advantage of suppressing pyrite oxidation and associated acidity through obstruction of atmospheric oxygen influx. The resulting DO depletion creates severely reduced conditions within the sediment, which may be favourable for the mobilization of toxic metals. This study investigated the mobilization of As and Al in a pyritic sediment under preload surcharge. The objectives were to establish the effects of redox changes under preload surcharge on the mobilization of arsenic and aluminium. It was demonstrated that the severely reduced conditions beneath the surcharge was conducive for As mobilization. However, the abundant supply of iron minerals in pyrite-rich sediment provided natural attenuation of As through sorption onto the iron minerals. For Al, the dissolution was found to be pH dependent with minimum concentration of Al in the pore water occurring around pH 4.5. Imposition of surcharge was accompanied by pH increase with potential increase in Al mobilization into the pore waters. The study outcome shows that the preload technique over pyrite-rich sediment is not a mere physical phenomenon. It has geochemical consequences to be taken into consideration.

1 INTRODUCTION

Pyritic sediments occur commonly in marine deposits and in waterlogged conditions within sedimentary deposits (Hurtgen et al., 1999, Wildman et al., 2004, Bolton et al., 2006). These sediments are associated with acidic leachate from pyrite oxidation, which occurs when the sediment is exposed to aqueous oxygen. The dissolution of phyllosilicate clay minerals is markedly boosted in the resulting acidic environment, leading to the release and proliferation of hydrolysable, heavy or light and alkali earth metal ions such as Al(III), Fe(II/III), Mg(II), Ca(II), Pb(II), K^+ and Na^+. In high concentrations, these metal ions may invariably pose serious toxicity problem to the environment. Infrastructural developments in pyritic sediment environment have been on the increase in recent times, due principally to shortage of other suitable lands in prime locations in cities around the world (Karikari-Yeboah and Gyasi-Agyei, 2000).

This has necessitated frequent use of the preload technique for ground improvement. The technique is based on induced consolidation through transient flow of pore water out of the sediment, due to the creation of hydraulic gradient in response to the application of surface surcharge. Pyritic sediments are characterized by oxic zone, overlying an anoxic region with distinct redox interface. The application of surface surcharge interrupts oxygen supply to the sediment, leading to oxygen depletion, transformation of the previously oxic zone into reduced environment and the creation of severely reduced conditions within the sediment, as the dissolved oxygen is used up by microorganisms for metabolic activities. Consequently, pyrite oxidation and associated acidic leachate are suppressed (Karikari-Yeboah and Addai-Mensah, 2014, Karikari-Yeboah et al., 2014). However, the reduced conditions so created beneath the surcharge may be conducive for mobilization of toxic metals, including arsenic and aluminium. This study involved field testing and laboratory analyses of pyrite-rich sediment hydrogeology, Pore water geochemistry and solid-phase speciation. Improvement in the groundwater quality through carbonate dissolution and decrease in acidity through the suppression of pyrite oxidation (Johnston et al., 2009) and natural attenuation of arsenic (Carrero et al., 2015) have been demonstrated. However, increase in aluminium concentration was also observed in the severely reduced environment.

2 MATERIALS AND METHODS

2.1 *The study Site*

The study site is situated at Murwillumbah, in the northern New South Wales (NSW), Australia (Figure 1). The original site topography comprised isolated hills rising to reduced level RL 38.60 (Australian Height Datum, AHD), with low-lying areas of pyrite-rich sediment at RL 0.9 m to RL 1.2 m (AHD) at the bottom of the hills. During an infrastructure development, a section of the low-lying area was placed under preload and permanent surcharge. The surcharge thicknesses varied between 9.0 and 16.2 m. The low-lying area with the imposed surcharge is, herein, referred to as the surcharged area (SA).

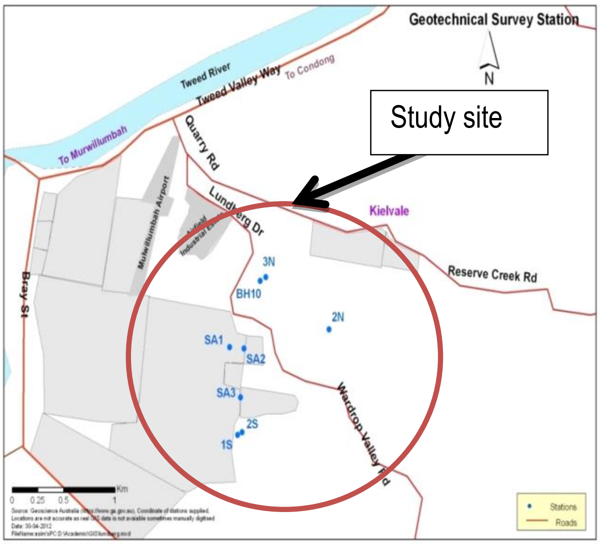

Figure 1: Locality Plan

2.2 *Methodology*

2.2.1 *Fieldwork*

Soil samples were obtained from boreholes across the study site. Several boreholes were established within the original sediment (OS) and at the surcharged area. Samples were collected at close depth intervals with 50 mm diameter (U50) and 0.5m long, thin-wall steel tubes. The sample tubes were sealed at both ends immediately upon withdrawal from the ground, and kept in iced compartment, en route to the laboratory, where they were immediately refrigerated pending laboratory analyses. Standpipes were installed in the boreholes for in-situ water quality monitoring. Dissolved oxygen (DO), electrical conductivity (EC), salinity, oxidation reduction potential (ORP), pH, and temperature were monitored with in-situ calibrated standard instrument. Measurements were taken using a TPS 90FL-MV field/lab analyzer with a 20-metre length cable. The field measurements extended over a period of two years. Target parameters were determined simultaneously at the various depths.

2.2.2 *Elemental Analyses*

The elemental analyses targeted the determinations of metal concentrations in pore water and soil samples. Pore water samples were extracted by the pressure exertion and centrifugal extraction procedures. The sediments were loaded into tightly sealed centrifugation tubes, which were filled and capped under inert atmospheric conditions. Pore water metal concentrations were measured using a Perkin Elmer Optima 7300 DV ICP-OES. Calibration and certified standards were made in 1% nitric acid solution. The acid extractable metal content of soil samples was measured in the digest liquor of soil samples. 200 mg of dry soil was digested with 3 ml of 70% nitric acid and 9 ml of 32% HCl. The mixture was then filtered through Whatman paper followed by 0.45 µm PTFE membranes. The filtrate was subsequently analysed by ICP-OES as described above. The acid generating potential of the soil samples was assessed using the NAG test method[1]. Briefly, 2.5 g of dried and pulverised (<75 µm) soil sample was treated overnight at room temperature with 250 ml of 15% hydrogen peroxide, followed by boiling for 2 hrs. The sample was cooled and filtered and the filtrate titrated with the appropriate concentration of sodium hydroxide solution to pH 4.5 and pH 7 (where the NAG pH was < 7). As and Mn were read in axial-view. Raw spectra were processed using the multicomponent spectral fitting (MSF) algorithm with WinLab 32 (Ver. 4.0) software. Arsenic was speciated as As (III), As(V), monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA). Separation of arsenic species was achieved using an Agilent 1100 liquid chromatography module equipped with a Hamilton PRP-X100 anion exchange column. Detection was achieved using an Agilent 7500c ICP-MS. Arsenic was quantified using the m/z 75 ion with Agilent ChemStation software.

3 RESULTS AND DISCUSSION

The water table was intercepted at the original sediment (OS) at depths within 0.5 m below the ground surface at normal times, and above the ground surface during periods of peak and prolonged rainfalls. At the surcharged area (SA), it rose into the surcharge material in response to the total stress increase. Dissolved oxygen (DO), pH, temperature, Eh, EC and salinity profiles in the Murwillumbah sediment have been reported elsewhere (Karikari-Yeboah et al., 2014). Redox partitioning of the sediment environment has been confirmed, with the redox interface at or around RL -1.2 m. The reduced level at the ground surface was RL 0.9. Table 1 is a summary of the monitored parameters.

Table 1: Summary of physico-chemical properties

Parameter	Oxic Zone (OS)	Anoxic Zone (OS)	SA
DO (%Sat)	0 to 26	0	0
pH	4	7	8 to 9
Temp (ºC)	19 to 22	20	21
Eh (Mv)	200 to 600	100	200
EC (μS/cm)	1200	6000	1200
Salinity (ppm)	800	3800	600

In the original sediment, DO was completely depleted at and below the redox interface. The pH was around 4 in the oxic zone and 7 in the anoxic zone. Temperature was highest at 22 ºC within the top 1.0 m of the original sediment, but fell with depth to a minimum value of 19 ºC at the redox interface. In the anoxic zone, the temperature was kept uniform at 20 ºC. Eh was highest within the oxic zone of the original sediment but dropped significantly at or immediately beneath the redox interface. The electrical conductivity and salinity were low in the oxic zone, but experienced significantly increase immediately below the redox interface. At the surcharge area, the pH ranged between 8 and 9 beneath the surcharge. The temperature was kept uniform around 21 ºC. Eh, EC and salinity were all significantly lower beneath the surcharge. These changes have impacted on the speciation of toxic metals, including As and Al, in the sediment. The measured arsenic concentrations in the sediment and in the pore water are summarized in Table 2 (a & b). Total As concentrations in the sediment were generally higher in the reducing environments of the anoxic zone of the original sediment and beneath the surcharge, compared to the levels in the oxic zone of the original sediment. There was no significant difference in the measured concentrations in the pore waters. Published literature indicates that arsenic is generally present in reduced environment as As (V), with adequate supply of organic matter and strongly reduced environment as the major contributory factors for its mobilization (Acharyya and Shah, 2006, Aggarwall et al., 1991). A reductive dissolution mechanism involving hydrated iron oxide was proposed by Acharyya and Shah for the release of arsenic into ground water. Consequently, the strongly reduced environments in the anoxic zone of the original sediment, and beneath the surcharge, would be expected to complete the necessary conditions for the mobilization of arsenic in the sediment environment. However, in pyrite-rich sediment, arsenic mobilization has been noted to be controlled by As (V) sorption onto schwertmannite (Burton et al., 2009). Consequently, the low As concentration levels observed, with values below detection limits, confirm the roles of iron as effective removal of As in acidic sediment (Burton et al., 2009, Carrero et al., 2015).

Table 2a: Arsenic concentrations in pore water

Parameter	Oxic Zone (OS)	Anoxic Zone (OS)	SA
Total As	0.006-0.021	0.007-0.015	< 0.02
As (III)	0.001	0.01-0.002	< 0.005
As (V)	0.005-0.021	0.009-0.015	< 0.005

Table 2b: Arsenic concentrations in sediment

	Depth (RL)	Total As (mg/kg)
Oxic Zone - OS	0.2	8.4
	-0.8	5.3
Anoxic Zone - OS	-1.8	7.5
	-2.8	8.5
SA	0.02	4.2
	-1.56	9.2
	-3.06	7.8

Aluminium occurs in sediments as water soluble, and particulate matter in the form of exchangeable and secondary mineral phases (Yvanes-Giuliani Yliane et al., 2014). Its partitioning and dissolution in the sediment and into the pore waters were controlled by the sediment chemical characteristics, including the pH, salinity, total organic matter, represented by total organic carbon, and presence of other metals such as Fe (Yvanes-Giuliani Yliane et al., 2014, Upadhyay, 2008, Carrero et al., 2015). The typical range of Al in soils is 1% to 30 % (10,000 to 300, 000 mg/kg) (US-EPA, 2003). The levels encountered in the Murwillumbah sediment were in the range of 20 to 25 mg/kg in the pore water, and 100 to 120 mg/kg as particulate matter in the soil (Figure 2). In the soil, Al concentration levels were quite similar in the original sediment and beneath the surcharge.

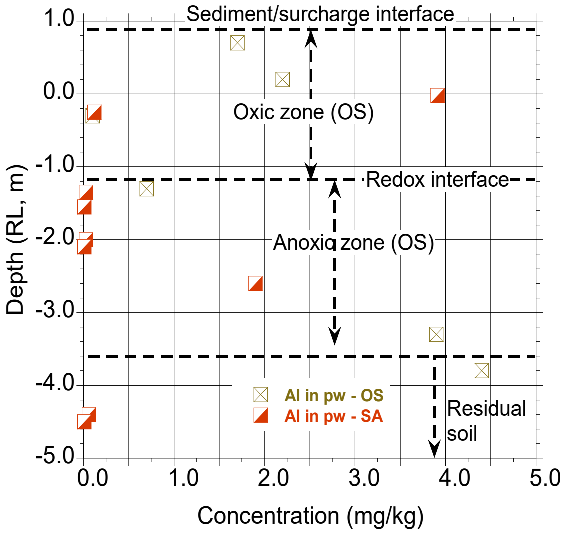

Figure 2a: Al concentration–depth profiles - pw

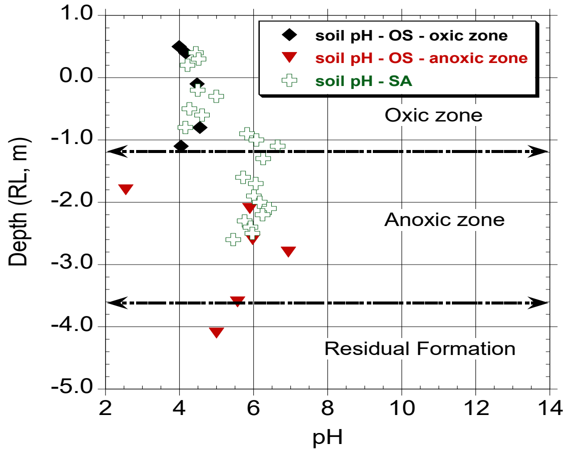

Figure 4: Sediment pH profile – OS & SA

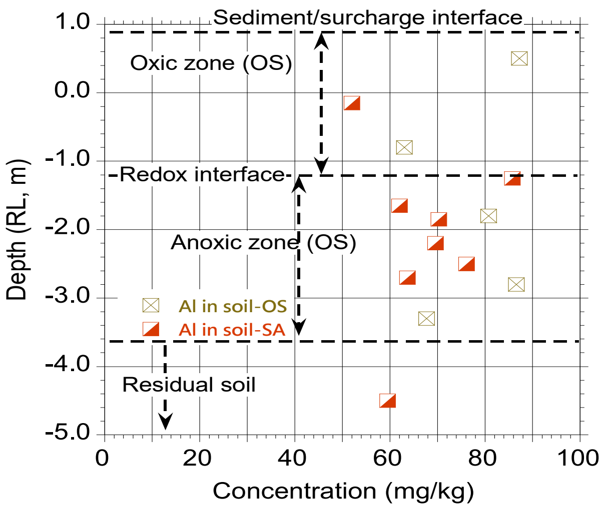

Figure 2b: Al concentration–depth profile - soil

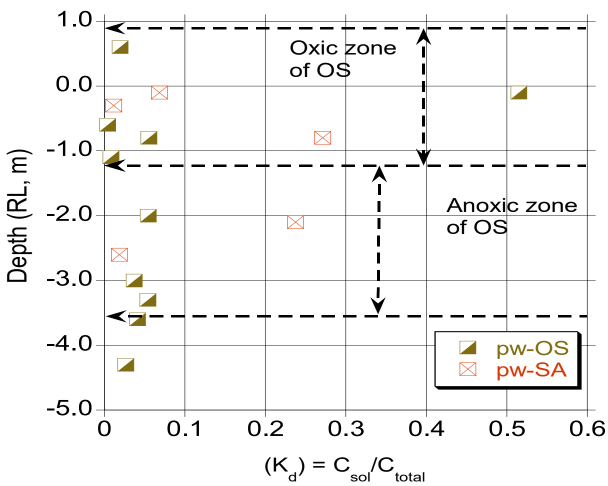

Figure 3: K_p with depth: OS and SA

In the pore waters, however, the concentration levels were far greater at and immediately beneath the redox interface in the original sediment, and beneath the surcharge.

The concentration levels in the pore water were less than the levels in the soil. The difference reflected the proportionate soluble and particulate aluminium that were present in the sediment. A solid–solution partitioning coefficient (K_p) (Fig. 3) (Upadhyay, 2008) can be established to described the dissolution in the various redox zones. K_p is defined here as $Kp = C_{sol}/C_{total}$, where C_{sol} was the Al concentration in the pore water (mg/kg) and C_{total} was the sum of the concentrations in the pore water and in the particulate phase. In the original sediment, dissolution was more active at and below the redox interface, with up to 0.1 of the total aluminium going into solution. Up to 0.3 of the total aluminium went into solution beneath the surcharge. Al dissolution into the pore water was noted to be pH dependent. It decreased with pH increase in the oxic zone of the original sediment, up to pH of about 4.5, at depth of RL -1.0. Thus, maximum concentration of Al in the sediment and minimum concentration in the pore water occurred around the redox interface RL -1.2 (Fig. 2) at pH of about 4.5 (Fig. 4). Similar pH conditions have been reported by others (Carrero et al., 2015, Yvanes-Giuliani Yliane et al., 2014). At pH of 4 and 7 that existed in the oxic and anoxic zones of the original sediment, Al concentration in the pore water would had been at about the minimum levels in the oxic zone, and would had been on the increase in the anoxic zone.

The application of surcharge, accompanied by pH increase, would have triggered further increase in Al mobilization into the pore water. As the re-course of Figure 3 shows, the dissolution factor beneath the surcharge was more than double that in the original sediment. Figures 5, 6 and 7 show the effects of organic carbon, Fe and Cl on the dissolution of Al in pore water.

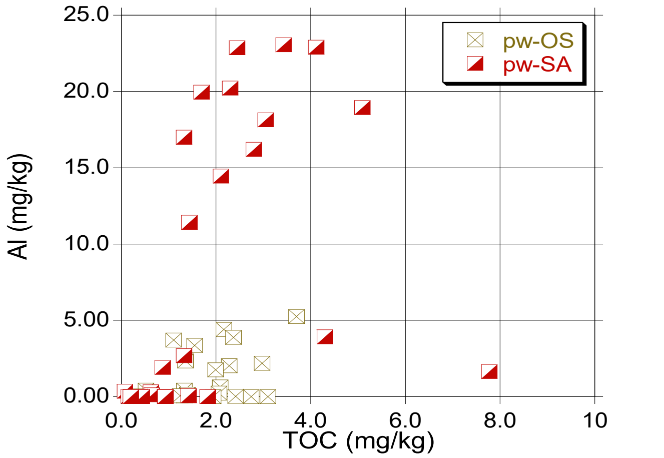

Figure 5: Al concentration versus Total organic carbon (TOC) concentration in pore water–OS & SA

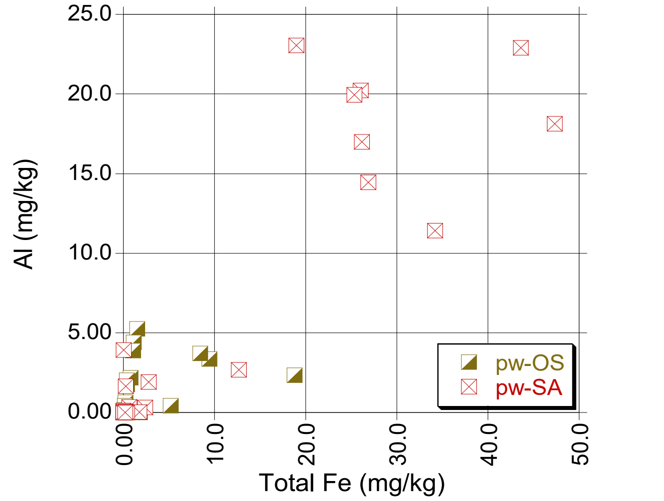

Figure 6: Al concentration versus total iron (Fe) concentration in pore water – OS & SA

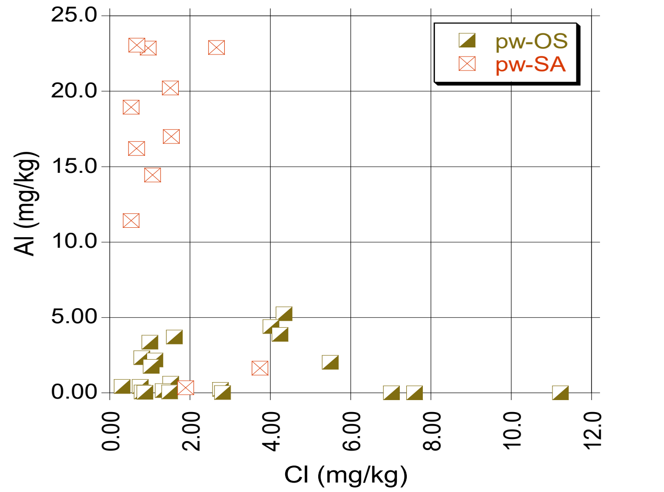

Figure 7: Al concentration versus chloride (Cl) concentration in pore water – OS & SA

Al concentration in the pore water generally remained high until a concentration level of TOC, Fe and Cl reached a certain level, and then decreased thereafter. The same trend was also observed beneath the surcharge. The phenomenon can be ascribed to the formation and precipitation of complexes. The same trend was also observed beneath the surcharge.

4 CONCLUSIONS

The effects of surcharge on the dissolution of As and Al into the pore waters of pyritic sediment have been investigated. The results demonstrate reduced As concentration in the original sediment and beneath the surcharge. This may be associated with high concentration of iron minerals and their consequent precipitation, and favoured As (V) removal from pore waters through sorption onto the iron minerals surfaces, leading to natural attenuation of As contamination in the sediment environment.

The increase in pH associated with imposition of surcharge appeared to favour the dissolution of Al into the pore water. Al in pore water is associated with the weathering of phyllosilicate clay minerals of the host formation and dissolution of the reactive, water-soluble portions. The dissolution process is mediated by pH, presence of adequate organic matter and other metallic ions. Al concentration in the pore water increased with decrease in pH in the oxic zone of the original sediment, with minimum concentration occurring around pH of 4.5. Thereafter, the concentration in the pore water increased with increase in pH. In the oxic zone, the pH was typically around 4 to 4.5. Consequently, Al concentration in the pore water would have been around its lowest levels. The imposition of surcharge and the associated pH increase would have triggered further mobilization of Al into the pore water.

Al concentration in the pore water also appeared to be affected by the concentrations of organic matter, total Fe and chloride in the sediment.

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