

# Acidification and trace metal mobility in soil and shallow groundwater on the Gngangara Mound, Western Australia

Jessica Ward<sup>A</sup>, Martin S Andersen<sup>B</sup>, Steve Appleyard<sup>C</sup> and Steven Clohessy<sup>C</sup>

<sup>A</sup>Geotechnical Engineering Department, Allan Watson Associates, Queensland, Australia.

<sup>B</sup>Water Research Laboratory, School of Civil and Environmental Engineering, University of New South Wales, Australia

<sup>C</sup>Contaminated Sites Branch, Department of Environment and Conservation, WA, Australia

## Abstract

Soil and shallow groundwater on the Gngangara Mound, Western Australia, is acidifying partially as a result of acid deposition from air pollution onto the soil. Sampling in the upper part of the saturated zone revealed a reduced pH between 3.8 and 5 at 8 of 16 sites sampled. Depth profiles show a sharp acidification front, with a higher pH of 6 below the interface. As a consequence, aluminium and trace elements (As, Cd, Pb, Cu, Zn and Ni) were released at low pH values. In the acidified zone, the Al concentration reaches 8 mg/L. The sources and controlling mechanisms behind the observed geochemistry are explored by reactive transport modelling incorporating ion exchange, surface complexation and Al-hydroxide equilibrium. These simulations estimate that the progression of the acidification front has taken place over 100 years at an average rate of 5 cm/year. Al-hydroxide dissolution and ion exchange involving Al with adsorbed Ca and Mg attenuates the progression of the front. Low pH releases trace metals from surface complexation, which accumulate by re-adsorption at the front due to the buffering mechanisms at this interface. Acidification and trace metal accumulation potentially causes severe impacts in a number of groundwater-dependent wetlands on the Gngangara Mound.

## Key Words

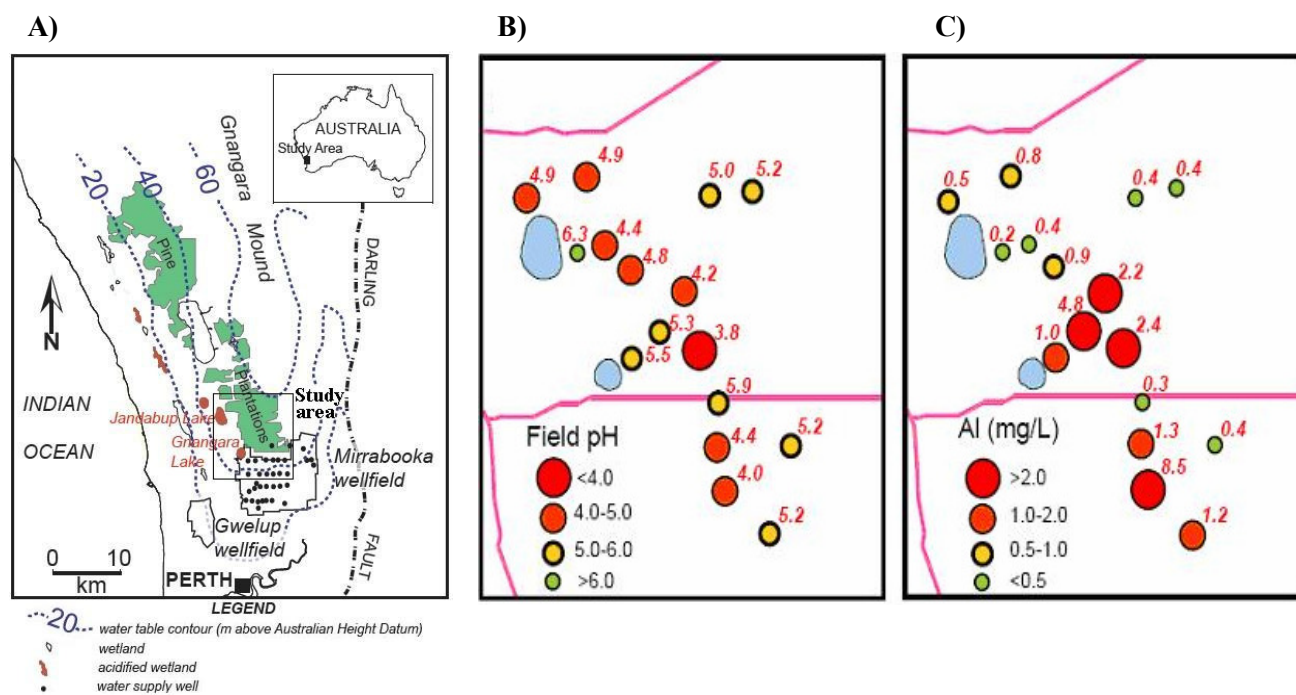
Acidification, trace metals, geochemistry, groundwater, reactive transport modelling, air pollution

## Introduction

In Western Australia, acidification has become a prominent problem in coastal areas due to unsustainable management practices, drought conditions, partially due to regional climate change, and increased industrial activity (Appleyard and Cook 2008). Investigations have focused on mechanisms related to oxidation of high contents of sulfidic material often associated with peaty coastal wetland environments. These are exposed to oxidizing conditions due to water table decline as a result of reduced rainfall and increased groundwater abstraction. However, rainfall and dry deposition may also be a source of acid especially in areas of concentrated industrial activity and high traffic density. Atmospheric emissions of anthropogenic gaseous sulphur and nitrogen oxides may have a powerful acidifying potential. The problems associated with acidification are well detailed in the literature, causing: inhibited plant growth; infrastructure corrosion and; large fish kills (White *et al.* 1997) as well as adversely impacting large habitat areas such as wetlands and woodlands (Xu 2008; van Tol *et al.* 1998). Acidification may also impact the geochemical equilibrium in soils and aquifers (Hansen and Postma 1995; Kjølner *et al.* 2004; Appleyard and Cook 2008). Deposition of acid rain may result in the gradual acidification of sediment profiles when they have a low buffering capacity. Aquifers with low alkalinity levels are particularly prone to acidification (Edmunds and Kinniburgh 1986), particularly in areas where dewatering is taking place (Swedish EPA 2002). Once sediments are acidified, increased mobility of Al as well as toxic trace elements are likely to occur (Appelo and Postma 2005). These processes are a concern in the poorly buffered soils of the Perth region where according to Appleyard and Cook (2008) an acidification front is believed to have developed in the aquifer since the beginning of the 20<sup>th</sup> century as a consequence of the increased use of fossil fuels as well as higher traffic densities. The study site, the Gngangara Mound (Figure 1A) located on the Swan Coastal Plain, is underlain by sediments of the Quaternary age as well as Bassendean sands - soils that are known to have a limited capacity for neutralising acid (Bawden 1991; Appleyard and Cook 2008). The limited content of carbonates and the progressive leaching of base cations, such as Ca and Mg, characteristic of these sediments, render these soils prone to acidification. Further to this, the release of adsorbed trace elements under low pH conditions could cause concentrations to reach toxic levels, contaminating groundwater resources and connected surface water bodies. The aim of this paper is to investigate the effects of atmospheric acid deposition on sandy aquifers. In particular the rate of acidification and the mobility of trace metals.

## Methods

Installation of wells, the sampling and the chemical analysis is described in (Appleyard and Cook 2008). The Geochemical code PHREEQC (Parkhurst and Appelo 1999) was utilised for speciation calculations; for analysing the effect on trace metal mobility in batch titrations; and finally for 1D reactive transport simulations of the downward migration of the acidification front and the associated mobility of trace metals.

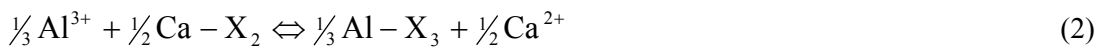


**Figure 1.** A) Location of the study area on the Gngangara Mound showing the position of water supply bores and pine plantations (green shading). Wetlands that have become periodically acidic are also depicted in red and distribution of acidity indicators at the water table near Lake Jandabup B) pH and C) dissolved Al (Appleyard and Cook 2008).

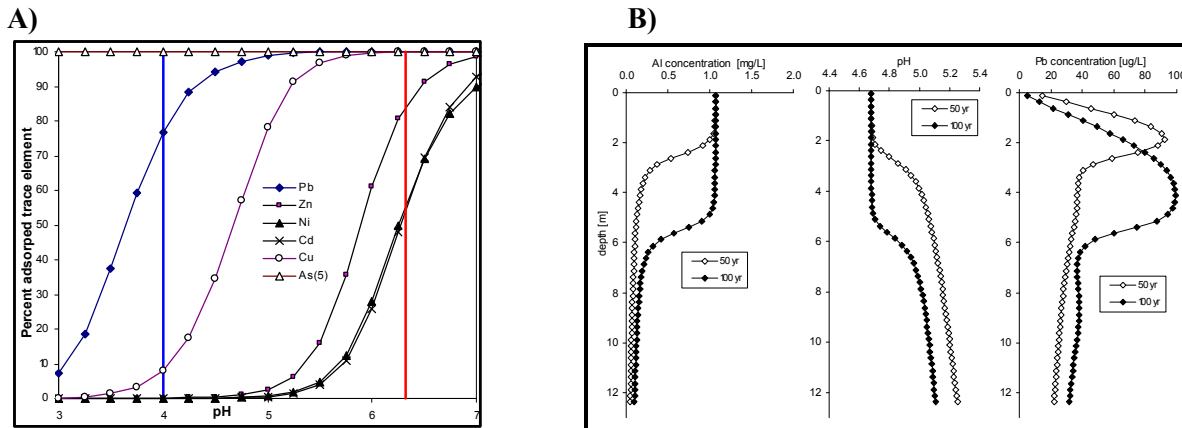
## Results and Discussion

### *Water chemistry, acidification and buffering mechanisms*

Shallow groundwater data, sampled in June 2008, reveals low pH levels ranging from 4-6 in the leached sands at the top of the Gngangara Mound aquifer (Figure 1B). The observed pH depth profiles indicate that the shallow groundwater is acidified to a depth of between 4 and 10 metres. Below this an abrupt increase in pH is delineating the acidification front (Hansen and Postma 1995; Kj  ller *et al.* 2004; Appelo and Postma 2005) where geochemical processes cause a buffering of the low pH water. Marine derived salts appear to determine the major ion water chemistry at most sites as reflected by high Na and Cl levels constituting the highest proportion of the chemical composition. Sulphate is measured at relatively high values reaching a maximum of 75 mg/L at site 2. The high mass  $\text{SO}_4^{2-}/\text{Cl}$  ratio of 3 indicates a source of sulphur in addition to marine salts. This can be explained by a number of inputs such as pyrite oxidation, air pollution or other sources. Although nano-crystalline pyrite has been identified in illuvial horizons in podsol soil profiles on the Gngangara Mound (Prakongkep *et al.* 2009), preliminary calculations suggest that there may be insufficient pyrite to account for observed levels of acidification (Ward 2009). In the acidified zone Al concentrations are quite high, whereby data at site 2 reveal it to be the most abundant cation at 21% of the total composition, reaching a level of 8 mg/L (Figure 1C) - 40 times the permissible level for Al in drinking water. Detailed mineralogy suggests that the sources of the soluble Al are the dissociation of allophane-organic complexes in illuvial horizons (Prakongkep *et al.* 2009) and the dissociation of Al-oxyhydroxide minerals according to (1). Deeper in the profile the Al concentrations decline across the acidification front corresponding to a rise in pH as illustrated in Figure 2. Speciation calculations suggest that secondary mineral equilibria with Al-containing minerals, such as gibbsite or jurbanite are controlling the pH and Al distributions. In addition, ion exchange processes involving Al, Ca and Mg (2) at the acidification front causes a reduction in Al resulting in a further rise in the pH via the coupling of equations (1) and (2).



The concentration of dissolved trace elements (Pb, Ni, Fe, Zn, Cu, Cd and As) appears to be elevated in the acidified zone, although limited data below the acidified zone makes it difficult to assess the background levels. High trace metal concentrations were measured at a site where the acidification front is particularly distinct: Cu 65; Pb 12; Ni 26 and Zn 82 (all in  $\mu\text{g/L}$ ). It appears that the trace elements, leached under low pH conditions, are accumulating at the acidification front due to the increased pH in what has been termed a geochemical trap (Kj  ller *et al.* 2004).



**Figure 2. Results of the PHREEQC modelling. A) Simulated desorption of trace elements (Pb, Ni, Zn, Cu, Cd and As) in a batch titration of a neutral (pH = 6.32, red line) groundwater sample in equilibrium with a hydrous-ferric-oxide (hfo) surface (Dzombak and Morel 1990). B) Depth profiles of dissolved Al, pH and dissolved Pb from a 1D reactive transport model combining ion exchange, mineral equilibria (Gibbsite) and surface complexation.**

#### *Reactive transport modeling of acidification and mobilization of Al and trace elements*

Simulations designed to explain the observed geochemistry at the Gngangara Mound were done in PHREEQC. Surface complexation and trace metal mobilization was investigated by equilibrating a neutral (pH = 6.32) sample with a hydrous-ferric-oxide (hfo) surface assuming the default surface oxide parameters given in PHREEQC (Dzombak and Morel 1990). Subsequently, this system is titrated from a pH of 6.32 to 3, replicating the change in pH due to acidification. This clearly illustrates almost total mobilization for Ni, Cd, Zn and Cu and significant increased mobility for Pb (Figure 2A). Arsenic (As(5)) on the contrary (assuming oxic conditions) remains completely adsorbed at these low pH values. However, Figure 2A also predicts that mobilized metals transported to the acidification front where pH increases would re-adsorb in this zone. Thus an accumulation of metals should happen with locally potentially high dissolved concentrations (Kj  ller *et al.* 2004). To further investigate the progression of the acidification front into the aquifer and reactive transport of trace metals, a 1D transport model was produced. The simulations were designed to replicate the conditions on the Gngangara Mound incorporated ion exchange, mineral equilibria with Gibbsite ( $\text{Al(OH)}_3$ ) and surface complexation. The vertical component of the groundwater flow was estimated to be 1 m/y (Appleyard and Cook 2008). Polluted precipitation with a pH of 4.3 infiltrated a model column extending to 12.5 m below the surface. Initial chemical conditions in the column were derived from uncontaminated (pH  $\sim$  6) water below the acidification front. The sediment cation exchange capacity (CEC) was set to 0.8 meq/kg (Cook *et al.* 2006). Gibbsite equilibrium was achieved with a saturation index of 1.1 obtained from speciation calculations using PHREEQC. The model overall replicates the acidification front and the observed pH (Figure 2B). The results predict the acidification front progresses down into the aquifer at a rate of approximately 5 cm/y taking between 50 and 100 years to reach its current location. However, this estimate is highly uncertain, site specific and variable depending on the local pore water velocity, buffering capacity and acid load; parameters that are not well constrained at the site. Furthermore only the modelled pH can be compared with field data since depth specific profiles of Al and trace metals do not exist. Despite this, the modelling results demonstrate, at least conceptually, the expected behaviour of trace elements as exemplified by Pb in Figure 2B where Pb is released in the acidified zone and accumulated at the acidification front due to the increase in pH and re-adsorption.

## Conclusions

Groundwater acidification at the Gngangara Mound, WA, appears to be caused by a combination of factors including pyrite oxidation, the dissociation of allophane-organic complexes and the leaching of stored acidity from historical air pollution. Modelling suggests that the pH is controlled by mineral equilibrium with unspecified Al-hydroxides whereas the progression of the acidification front is impeded by a combination of Al-hydroxide equilibrium and cation exchange involving Al with base cations (Ca and Mg). The data and the modelling indicates that the acidification causes desorption of trace elements under acidic conditions which are then accumulated at the front due to the buffering and increase in pH. The acidification and elevated trace metals not only threaten fragile eco-systems that exist on the Gngangara Mound such as wetland, woodland and lake systems, but also potential water resources for human consumption.

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