OVERVIEW OF ACID SULFATE SOIL PROPERTIES, ENVIRONMENTAL HAZARDS, RISK MAPPING AND POLICY DEVELOPMENT IN AUSTRALIA

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SUMMARY
This paper presents information on the nature, distribution and impacts of both coastal and inland acid sulfate soils (ASS) in Australia. It overviews factors associated with formation of pyrite and sulfuric acid in these complex soils and the key impacts this has on a wide range of environments. Three case studies have been selected to illustrate the properties and impacts of ASS, ranging from two characterized sites in coastal tropical north Queensland and temperate (Mediterranean) South Australia to an inland ASS site in the Mount Lofty Ranges, SA. The paper outlines the National Strategy (National Working Party on Acid Sulfate Soils, 2000) to manage coastal ASS around Australia and the priorities for future research that has been identified by the National Committee on Acid Sulfate Soils (NatCASS). Acid sulfate soils and sediments (ASS) containing sulfidic materials (pH > 4 with pyrites), sulfuric horizons (pH < 4 with oxyhydroxysulfates of Fe and Al) and monosulfidic black ooze (pH > 4 with monosulfides) are currently developing in a wide range of landscapes across Australia, often in association with areas undergoing salinisation. Oxidation of sulfidic materials and monosulfidic black ooze following the lowering of water tables or soil disturbance is contributing to degraded saline seepages and poor stream water quality.

PROPERTIES AND ENVIRONMENTAL HAZARDS

Acid sulfate soils are saline soils or sediments containing pyrite, which once drained (as part of land management or development measures), become acidic and release large amounts of acidity and other contaminants to the environment. The source of acid sulfate problems is pyrite, FeS_2, which when oxidised produces sulfuric acid that brings the soil pH below 4, sometimes even below 3. Each mole of pyrite yields 4 moles of acidity and the overall equation for the oxidation of pyrite is:

$$FeS_{2(s)} + {}^{15}/_{4}O_{2(g,aq)} + {}^{7}/_{2}\ H_2O \rightarrow Fe(OH)_{3(s)} + 4H^{+}_{(aq)} + 2SO_4{}^{2-}{}_{(aq)}$$

Identified impacts from acidity causes: (i) minerals in soils to dissolve and liberate soluble and colloidal aluminium and iron, which may leak into drains, streams and floodwaters killing vegetation and aquatic life (acidic waters rich in metals, deoxygenated waters, fish kills, fish disease and localised losses of fish and aquaculture production); (ii) acidification and arsenic contamination of groundwater aquifers; and, (iii) damage to infrastructure such as roads, concrete and steel pipes, buildings, housing estates, tourism assets, bridges and culverts constructed on ASS. Drainage of peaty acid sulfate soils also results in the substantial production of greenhouse gases, carbon dioxide and N_2O (Hicks *et al.* 2002).

Development and primary industries around Australia are facing a $10 billion legacy of acid sulfate soils (National Working Party on Acid Sulfate Soils 2000). Public recognition of this serious problem has been reflected in government legislation in NSW, Queensland and South Australia. As well, there is much support from local government and industries to develop statutory requirements for rehabilitation.

COASTAL ASS

Coastal ASS occur in tidal floodplains where sources of sulfates, iron and other salts originate from seawater and estuarine sediments, which are less than 5 metres above sea level (AHD < 5 m). These soils form due to waterlogged conditions from the interaction of seawater and abundant organic material. Potential ASS materials or sulfidic materials (Soil Survey Staff 1999) are characterized by the development of pyrite, which precipitates because of strongly reducing conditions. Excluding seawater from these materials causes sulfide oxidation that produces sulfuric acid (pH commonly between 2.5 and 3.5) and the formation of bright yellow mottles of jarosite $[KFe_3(SO_4)_2(OH)_6]$ (i.e., sulfuric horizon development according to Soil Survey Staff 1999).

IDENTIFICATION AND RISK MAPPING OF COASTAL ASS

In Australia, coastal ASS occupy an estimated 40,000 km^2, which potentially contains over one billion tonnes of sulfuric acid underlying coastal estuaries and floodplains near where the majority of the Australian population lives (White *et al.* 1997, National Working Party on Acid Sulfate Soils 2000). When left undisturbed potential ASS material remains relatively benign.

Since the 1990s the demand to study coastal ASS has lead to the establishment of acid sulfate soils mapping programs, training programs on identification and management and policy development to regulate use of these high-risk soils. These activities are most advanced in the States of New South Wales (Naylor *et al.* 1995) and Queensland (Ahern *et al.* 1998, Department of Natural Resources 2000) and include the establishment of advisory committees and acid sulfate soil specific planning policies/regulations, technical management guidelines and training programs. For management purposes, classification of ASS takes into account the thickness and severity of acid sulfate soil horizons present. These specify sulfide content, lime requirement and an assessment of risk based on proposed volume of soil disturbance (Dear *et al.* 2002). This information is used to develop comprehensive, technically valid soil management plans. More recently an inventory and web-based maps of ASS risk classes covering the entire South Australian coastline was developed from the vegetation mapping of saltmarsh habitats, field inspection and laboratory analyses from the 70 sites. This information was used to construct a web-based map, with attached soil database, indicating the risk of acid sulfate soil development should the soil profiles be disturbed. The profiles were also classified using a "user-friendly" system, the Australian Soil Classification, US Soil Taxonomy and the FAO World Reference Base. The risk classes were associated with treatment categories, based on recent management guidelines developed in Queensland (Dear *et al.* 2002).

EAST TRINITY CASE STUDY IN TROPICAL NORTH QUEENSLAND

The 1975 drainage of a tropical estuarine wetland at East Trinity, north Queensland (near Cairns), by construction of a bund wall and floodgates left adjacent undrained soils in their original condition allowing paired measurements and samples to be taken. The results of this study demonstrate several environmental consequences of drainage and the formation of actual ASS (Hicks *et al.* 2002). Hicks *et al.* (2002) identified wetland drainage as a significant source of carbon dioxide emission with a 20 y average emission rate of 150 t CO_2-e ha^{-1} y^{-1}. Drainage also resulted in massive acidification with about 110 ha having an average pH of 3.4 at 0.5 m below ground level and a 20 y average acid production rate of $7x10^5$ moles H^+ ha^{-1} y^{-1}. The site is discharging water that contains concentrations of aluminium, iron and zinc considered deleterious to aquatic ecosystems. Considerable stored acidity remains on the site. The activity of aluminium is controlled by the solubility of various aluminium hydroxy sulfates. Seasonal reduction of iron results in increased sulfuric acid intensity. However, the pH is too low for any decrease in acidity by carbonate formation and the system not sufficiently reducing for sulfate reduction to occur. This net result is seasonal cycling between iron oxidation states.

BARKER INLET CASE STUDY SITES IN TEMPERATE (MEDITERRANEAN) SOUTH AUSTRALIA

At Gillman, near Adelaide, bunds constructed across mangrove swamps nearly 50 years ago cut off tidal flushing and drained areas resulting in the formation of ASS. Detailed work in the Gillman and St Kilda (degraded mangroves) areas (Thomas *et al*. 2003) and broader investigations along the South Australian coastline (Merry *et al.* 2003) have indicated several aspects where temperate (Mediterranean) South Australian ASS differ from those observed in the north-eastern states:

- Presence of large quantities of calcite ($CaCO_3$) in most soils;
- Presence of large quantities of gypsum ($CaSO_4$) in several soils;
- Evidence that C cycling and turnover may differ in mangrove soils because of the high concentration of sapric material in these soils, which is more finely divided and reactive than the coarser, "fibric" materials observed in tropical areas, where organic carbon decomposition rates are much faster. It is thought that the "sapric" materials in these South Australian soils form from the detritus of seagrass and mangroves in the Gulf St Vincent (Fitzpatrick *et al*. 1993);
- The presence of eutrophied mangrove soils that result in mangrove decline. The intense reducing conditions (i.e. low redox potential or Eh values to -600 mv) occurring in potential ASS where mangrove dieback is present in the St Kilda area may be the result of increased nutrient loads (eutrophic conditions). These soil processes and materials must be better understood if effective approaches to management are to be developed.

INLAND ASS

Acid sulfate soils can also form under modern freshwater conditions in inland settings, especially in the higher rainfall (> 500 mm per annum) Mediterranean environments of Australia where locally extreme changes in hydrology and geochemistry have occurred (Fitzpatrick *et al.* 1996). These inland acid sulfate soils develop as a result of contemporary land clearing, excess discharge of saline groundwater and erosion to form unsightly discharge areas, with eroded "iron ochre scalds". A model has been developed to illustrate the pedological, biogeochemical and mineralogical processes involved. Pyrite framboids form in sulfidic materials following reduction of sulfate-rich groundwaters in saline seeps. When these sulfidic soils are eroded and exposed to air, pyrite is oxidised producing sulfuric acid, which dissolves soil minerals and leads to the precipitation of the following minerals: (i) natrojarosite and jarosite in clay-rich layers; (ii) sideronatrite, tamarugite, halite and gypsum in sandy layers; and, (iii) ferrihydrite (red), schwertmannite (orange) and amorphous/pseudoboehmite-like (white) precipitates in stream waters. These processes cause less permeable, Fe-rich layers to form in discharge areas and explains the mechanisms that lead to degraded soils, erosion and poor water quality (Fitzpatrick & Self 1997).

MOUNT LOFTY RANGES CASE STUDY SITES IN TEMPERATE (MEDITERRANEAN) SOUTH AUSTRALIA

A case study is presented for specific soil, geomorphologic and biogeochemical processes that occur mostly in saline seeps where sulfate-rich saline groundwater discharge is evident in Mount Lofty Ranges, South Australia (Fitzpatrick *et al.* 1996). Secondary sulfides, iron oxyhydroxides and oxyhydroxysulfates form or transform relatively rapidly in these soils. The relative proportions and nature of these iron minerals depends critically on the soil solution biogeochemical conditions, in particular, Eh, pH and ionic concentrations. Colour, form, crystallite size and concentration of substituted cations (e.g., As and Pb) in iron minerals can be used quantitatively as indicators of specific soil processes (Fitzpatrick & Self 1997). Because specific types of pedogenic minerals are formed or altered by changes in hydrology, geochemistry and evapotranspiration, they can be used to infer where and to what degree soils have been influenced by current land use changes. As well as being environmental indicators, the geochemical composition of these mineral precipitates also indicates that they are a geochemical sampling medium for the detection of mineral deposits (Skwarnecki *et al.* 2002).

IDENTIFICATION AND RISK MAPPING OF INLAND ASS

The toposequence (soil landscape cross-sections) is used as a basis for constructing mechanistic models of soil-regolith and water processes that explain and predict the processes giving rise to a range of complex and poorly understood inland ASS in catchments. The toposequence is suitable for constructing such mechanistic models of spatial and temporal soil-regolith changes in ASS, because each of the vertical and lateral changes can be linked to hydrological and biogeochemical processes (Fitzpatrick *et al.* 1996). Two types of soil-water-landscape process models have been constructed to describe: (i) current inland ASS processes; and, (ii) chronology or Holocene history in the development of inland ASS (i.e., environmental reconstruction). These soil-water-landscape models, using the toposequence approach, have been used to: (i) generate maps at catchment and regional scales using GIS (Fitzpatrick *et al.* 1999, 2002); and, (ii) produce practical soil-landscape and vegetation field keys for Landcare groups that details land use options to prevent the irreversible spread of ASS conditions (Fitzpatrick *et al.* 2003).

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