Element Behaviour in Inundated

Actual Acid Sulfate Soils, East Trinity, Cairns

Thesis submitted by

John Douglas Broughton
BSc(Hons)

in March 2008

for the degree of Doctor of Philosophy

in the School of Earth and Environmental Sciences

James Cook University

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Statement of Contributors

The project was supported by a scholarship from the School of Earth Sciences, James Cook University. Project supervision was provided by Bernd Lottermoser. Field support was provided by the Queensland Acid Sulfate Soils Investigation Team. Particular thanks go to Michelle Martens, Doug Smith and the QASSIT technical staff who greatly assisted with the work at East Trinity.

Plants collected as part of the project were identified by staff at the Queensland Herbarium. Processing of plant samples was assisted by Dawn Rowan at the Department of Primary Industries Mareeba research station.

Acknowledgements

The project was largely funded by grants from the Far North Queensland Natural Resource Management Board Pty Ltd, the Queensland Government's funding the Smart State program and James Cook University's graduate research scheme. Special thanks go to Dr Paul Nelson and Dr Lex Cogle for their support in securing the Natural Resource Management grant.

This research is proudly supported by the Queensland Government's Growing the Smart State PhD Funding Program and may be used to assist public policy development. The State of Queensland accepts no responsibility for decisions or actions resulting from any information supplied. The views and information contained in the research do not necessarily represent the view or opinions of the Queensland Government and carry no endorsement by the Queensland Government.

ABSTRACT

Actual Acid Sulfate Soils (AASS) undergoing inundation with seawater were examined for: 1) element distributions; 2) element mobilisation during seawater inundation; 3) the fate of elements mobilised during inundation; and 4) element phytoavailability. Seawater inundation is a potential method of ameliorating the acidic soil conditions and on-going release of elements in toxic concentrations frequently associated with AASS. The key research question to be answered by the study was:

> *What are the effects of seawater inundation on the distribution, hosting, fate and phytoavailability of elements in actual acid sulfate soils?*

Elements examined were Al, As, Co, Cr, Cu, Fe, Mn, Na, Ni, Pb, Sc, V and Zn. Barium, Ga, Nb, S, Ti, and Zr were also frequently determined to assist with interpretation of geochemical processes in the ASS. This project focused on the behaviour of elements in selected soil profiles and sites at East Trinity, north Queensland. A statistical description of Acid Sulfate Soils (ASS) properties and quantitative modelling of the element losses and gains for the entire East Trinity site were beyond the scope of the project.

The study site was the Firewood/Magazine Creek catchment of East Trinity. East Trinity is a 900 ha parcel of coastal lowland opposite Cairns city on Trinity Inlet in North Queensland. In the 1970s, East Trinity was reclaimed ostensibly for sugar cane production using a 7.2 km bundwall and one-way floodgates. The site contained large areas of Potential ASS (PASS) that oxidised and acidified during the reclamation to form AASS. AASS is PASS that has acidified (due to oxidation) to a soil pH of less than four. PASS typically has near neutral soil pH values. Widespread AASS formation led to extensive vegetation death on the site and the discharge of drainage waters with high loads of Al, Fe and Zn. Frequent fish kills were reported in creeks receiving waters from the AASS. In 2000, the Queensland State Government acquired the site with a view to rehabilitation. The ASS rehabilitation method selected used repeated seawater inundation of the AASS and management of water quality with lime dosing.

Seawater inundation of AASS theoretically neutralises the soil acidity of, and stops further oxidation/starts reduction in, the AASS. By neutralising soil acidity and stopping oxidation/starting reduction, seawater inundation addresses the acidity and element mobilisation issues that are the source of the environmental harm associated with AASS. However, seawater inundation also has the potential to cause a second event of element mobilisation because of the formation of reducing conditions in the previously oxidised AASS.

The geochemistry of seawater Inundated AASS (IAASS) had not been documented in the literature. Thus, a geochemical characterization of IAASS was developed based on the following principles: 1) IAASS formed from AASS, and both IAASS and AASS formed from PASS; therefore IAASS and AASS should contain similarly low concentrations of elements (e.g. Co, Mn, and Zn) that are lost during PASS oxidation; 2) IAASS would have a near neutral soil pH, because soil acidity would be neutralised by seawater inundation; and 3) IAASS would be enriched in Na (particularly in the water-soluble and exchangeable fractions) compared to AASS, because of increased contact with seawater. Using these principles, ASS matching the proposed properties was identified in an ASS profile taken from a seawater inundated area of the Firewood Creek catchment.

The geochemistry of the AASS, IAASS and PASS from Firewood Creek was dominated by Si, Al and Fe. Comparison of the ASS compositions with ANZECC and ARMCANZ (2000) sediment quality and the NEPC (1999) soil quality guidelines identified environmentally significant concentrations of As (> EIL, ISQG-Low), Ni (> ISQL-Low) and V (> EIL).

Isocon Analysis (IA) was used to identify element enrichment/depletion in an inundated (IAASS containing) and a non-inundated (AASS containing) ASS profile. IA used the immobile elements Ba and Ti to establish the isocon relationship between altered and parent samples. Cobalt, Mn, Ni and Zn were extensively depleted from both ASS profiles, likely during PASS oxidation. Sodium was depleted in the dry ASS profile and enriched in the wet ASS profile. Iron was depleted from the middle sections of both ASS profiles, with the depletion in the wet ASS profile being more extensive. The probable cause of the increased depletion of Fe in the wet ASS profile was extended periods of reducing conditions caused by more extensive seawater inundation. Copper and Pb displayed similar behaviour to Fe, suggesting they were associated with Fe in the ASS, likely by sorption onto oxidised Fe phases.

Examination of element hosting using two Sequential Extraction Procedures (SEPs) identified reductive dissolution as the geochemical process responsible for Fe depletion in the IAASS. The two SEPs were the Geological Survey of Canada (GSC) SEP and the Modified BCR (MBCR) SEP. Iron was largely hosted by the reducible fraction in the AASS (i.e. oxides). In the IAASS, the size of the Fe reducible fraction was smaller by a third compared to the AASS. This indicated that Fe in the IAASS was mobilised by the reductive dissolution of Fe oxides during inundation. A combination of seawater inundation and organic matter likely generated reducing conditions in the inundated ASS profile and was hence the probable cause of the reductive dissolution of the oxidised Fe phases.

The Fe mobilised from the IAASS was transported by egressing soil-waters and precipitated in the drains servicing the inundated areas. The Fe that precipitated from the egressing waters flocculated

as chemical sediments in the drains. The drain sediments consisted of Fe precipitates in various states of oxidation/reduction. The geochemistry of the drain sediments was variable, but uniformly dominated by Fe, Si, Al and LOI. The mineralogy was largely crystalline and amorphous Fe oxides and detrital silicates. Trace element concentrations in the drain sediments were generally low compared to the ASS. Arsenic was the only trace element that demonstrated substantial enrichment. Comparison of the drain sediment geochemistry with the ANZECC and ARMCANZ (2000) sediment guidelines identified environmentally relevant concentrations of As, Cu and Ni. More than 75 % of the drain sediments sampled contained more As than the ISQG -Low, and the largest value from the drain sediments exceeded the ISQG-High. Copper and Ni concentrations in the drain sediments were also greater than the ISQG-Low values in more than 25 % of samples.

The drain sediments were found to be a potential source of rapid acidification and element release in the Firewood Creek catchment. Soil pH (pH_F) and oxidised soil pH (pH_{FOx}) values indicated that the drain sediments rapidly acidified on oxidation, likely because of sulfide oxidation and Fe hydrolysis. Examination of element hosting and pH_F and pH_{FOx} data from the drain sediments indicated that the greatest threat with regard to element mobilisation was oxidation. This was because oxidation and the resultant acidification of the drain sediments would cause the release of elements from both the oxidisable fraction and the acid extractable fraction.

Sediments from the mouth of Firewood Creek were found to have increased their concentration of As, Fe, Ni and Pb between July 2002 and April 2004. This period coincided with increased seawater inundation of the Firewood-Magazine Creek catchment. This indicated that more extensive seawater inundation of the Firewood Creek catchment caused an increase in the transfer of As, Fe, Ni and Pb from the ASS to the mouth sediments.

Plant samples growing in the IAASS were collected for element bioavailability assessment. Species collected were the mangrove fern *Acrostichum speciosum* and the grass *Paspalum vaginatum*. Comparison of element concentrations in the stems from the *Acrostichum speciosum* samples collected from IAASS with the background samples showed larger median concentrations of Co, Cr and Zn. Median concentrations of Cu and Zn were higher in the stems *Paspalum vaginatum* from the IAASS than the background locations. This indicated that Co, Cr, Cu and Zn were potentially more phytoavailable in the IAASS.

Comparison of element concentrations in the stems of *Paspalum vaginatum* with the NRC (1980) animal feed guidelines identified Al concentrations toxic to cattle (> 1,000 ppm), horses and pigs (> 200 ppm). However, the toxic Al concentrations did not appear to be related to AASS inundation.

The research showed that seawater inundation was rehabilitating AASS in the Firewood-Magazine Creek catchment on East Trinity. This was demonstrated by the near neutral soil pH values of IAASS. However, Fe was mobilised during AASS inundation. The mobilised Fe contributed to the formation of chemical sediments in the drains servicing areas of IAASS. Furthermore, inundation of the Firewood Creek catchment may have increased the concentration of As, Fe, Ni and Pb in mouth sediments of Firewood Creek.

Based on the findings of the project, it is recommended that controlled seawater inundation (i.e. inundation to a constant elevation) of Firewood Creek be maintained and closely monitored. Inundating the AASS of Firewood-Magazine Creek catchment to a constant elevation will continue the rehabilitation of the AASS, as well as mitigate the risk of oxidation of the drain sediments. Plants should be monitored for element concentrations. Site management should include minimising wild and domestic animal exposure to toxic element concentrations from plants growing in the areas of AASS inundation. Finally, the mouth sediments of Firewood Creek showed increased concentrations of elements mobilised during seawater inundation of AASS. Monitoring of the sediments of Firewood Creek should be conducted to assess the changes in the element concentrations of the sediments during the rehabilitation.

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LIST OF ACRONYMS AND ABBREVIATIONS

[*x*]	Concentration of element *x*
AAC	Advanced Analytical Centre
AASS	Actual Acid Sulfate Soils
AES	Atomic Emission Spectroscopy
ANZECC	Australian and New Zealand Environment and Conservation Council
ARD	Acid Rock Drainage
ARMCANZ	Agriculture and Resource Management Council of Australia and New Zealand
ASS	Acid Sulfate Soils
BCR	Bureau Communautaire de Référence (Community Bureau of Reference, BCR in French)
BCR-SEP	Bureau Communautaire de Référence - Sequential Extraction Procedure
bgl	Below ground level
DPI	Department of Primary Industries, Queensland Government
DTPA	Diethylenetriaminepentaacetic acid
EDDS	Ethylenediamine-N,N'-disuccinic acid
EDTA	Ethylenediaminetetraacetic acid
EIL	Ecological based Investigation Limit
GSC-SEP	Geological Survey of Canada - Sequential Extraction Procedure
IA	Isocon Analysis
IAASS	Inundated Actual Acid Sulfate Soils
ICP	Inductively Coupled Plasma
IR	Isocon Ratio
ISQG-H	Interim Sediment Quality Guideline – High
ISQG-L	Interim Sediment Quality Guideline – Low
JCU	James Cook University
LOI	Loss On Ignition
MBCR-SEP	Modified BCR - Sequential Extraction Procedure
MS	Mass Spectroscopy
NEPC	National Environment Protection Council
NR and W	Natural Resources and Water, Queensland Government Department of
OES	Optical Emission Spectroscopy
PASS	Potential Acid Sulfate Soils
QASSIT	Queensland Acid Sulfate Soil Investigation Team
R%D	Relative Percentage Difference
SEP	Sequential Extraction Procedure
SRM	Standard Reference Material
XRD	X-Ray Diffractometry
XRF	X-Ray Fluorospectroscopy
$\Delta\%_{SRM}$	Percentage difference from SRM value