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# **Extended Abstracts**

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## title: Redox controls on the mobility of agricultural nitrogen in groundwater systems in tropical Northern Australia

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#### INTRODUCTION

Aquifer systems have long been recognised as important transport pathways for the delivery of agricultural nitrogen to surface waters (Freeze and Cherry, 1979; Johannes, 1980; Peterjohn and Correll, 1984). The distribution of nitrogen and its mobility within aquifers is highly dependent on groundwater redox conditions. Nitrogen occurs in oxidation states ranging from +5 to -3, and in aquifer systems underlying agricultural regions, nitrogen commonly exists in its most oxidized state (+5) as nitrate (NO<sub>3</sub><sup>-</sup>) (Appelo and Postma, 1999). In oxidized systems nitrate is highly mobile and can be used as a conservative tracer (Herczeg and Edmonds, 2000), however, under reducing conditions, nitrate can be highly unstable and may leave the system as N<sub>2</sub> gas or be converted to ammonium (NH<sub>4</sub><sup>+</sup>) which readily adsorbs onto mineral surfaces. These NO<sub>3</sub><sup>-</sup> reducing reactions require the presence of suitable reductants (electron donors) and the absence of oxidants (electron acceptors) stronger than NO<sub>3</sub><sup>-</sup> such as O<sub>2</sub> or some industrial pollutants (i.e. chlorinated ethenes).

The distribution of electron donors and receivers in two groundwater systems in tropical northern Australia are presented; first, the lower Burdekin, which is a coastal floodplain in northern Queensland currently under intensive irrigated agriculture; and second, the Douglas-Daly River catchment in the Northern Territory that is a region being considered for future irrigated agriculture. The geology of the two aquifer systems differ considerably with the lower Burdekin consisting of complex alluvial, deltaic and marine successions deposited during the Holocene and the Douglas-Daly a karstic aquifer system consisting of a Cambrian-Ordovician aged dolostone overlain by highly weathered Cretaceous sedimentary rocks.

#### DISCUSSION

Lower Burdekin, Queensland. The lower Burdekin floodplain aquifer is adjacent to environmentally sensitive wetlands and the World Heritage listed Great Barrier Reef (GBR) Lagoon (Furnas 2003). It currently supports 80,000 ha of largely irrigated sugarcane that uses 160–220 kg of nitrogen per hectare per year. The complex geology of the lower Burdekin aquifer has resulted in highly variable distributions of electron donors/receivers across the system that directly impacts the mobility of agricultural nitrogen. Organic rich deltaic and marine deposits host groundwater with little to no dissolved oxygen (DO), dissolved organic carbon (DOC) concentrations as high as 80 mg/l and Fe<sup>2+</sup> and  $Mn^{2+} > 1$  mg/l. Low DO and an abundance of electron donors (DOC,  $Mn^{2+}$  and Fe<sup>2+</sup>), in particular DOC, are geochemical conditions that favour nitrate attenuation (i.e. denitrification or dissimilatory nitrate reduction to ammonium) and consequently little to no nitrate has been detected in these units over a 40+ yr monitoring period. Coarse grained palaeochannel deposits that dissect the floodplain also host groundwater with high DOC concentrations; however, elevated DO (>2 mg/l) within these units decreases NO<sub>3</sub><sup>-</sup> attenuation as O<sub>2</sub> is the more thermodynamically favoured electron acceptor for DOC oxidation. In these units, NO3 concentrations >20 mg/l have been consistently recorded over the past 40 years. The connectivity of these palaeochannel units to the marine environment suggests the potential for substantial discharge of nutrients into the Great Barrier Reef Lagoon and that nitrogen loads are currently underestimated.

*Douglas-Daly, Northern Territory.* The Douglas-Daly karstic aquifer system maintains dry season flows in one of Australia's most pristine river catchments, which host unique oligotrophic ecosystems. The potential for nutrient transport through the aquifer to the Daly River is currently being assessed. Preliminary groundwater results from the current dry season (May-December 2009)

indicate a largely oxidised aquifer system that contains DOC > 10 mg/l and little to no Fe<sup>2+</sup> and Mn<sup>2+</sup>. Increases in HCO<sub>3</sub><sup>-</sup> concentrations and decreases in DO along piezometer transects toward the Daly River indicate that O<sub>2</sub> is being consumed through DOC oxidation, a process that trends toward anoxic conditions immediately adjacent to the river (<200 m). DOC levels remain high (10 mg/l), indicating a constant source of DOC, and favourable conditions for nitrate attenuation; however, further data collection and modelling is required to fully assess the potential for nitrogen transport from the aquifer to the river.

#### CONCLUSIONS

Groundwater redox conditions play a critical role in the mobility of agricultural nitrogen. Understanding current, or predicting future nitrogen distribution and mobility in aquifers in agricultural areas requires a knowledge of the spatial distribution of electron donors (i.e. OC,  $Mn^{2+}$  and  $Fe^{2+}$ ) and electron receivers, in particular dissolved oxygen (DO). In tropical northern Australia, aquifer systems exhibit relatively high groundwater DOC concentrations (DOC>10 mg/l). The presence of organic carbon or other electron donors facilitates nitrate reduction if DO levels are low (<2 mg/l); however, above this level O<sub>2</sub> behaves as the thermodynamically favoured electron acceptor over nitrate. Determining potential impacts of groundwater extraction and enhanced recharge of irrigation waters on groundwater redox conditions is of fundamental importance for predicting future water quality issues within and downstream of agricultural areas.

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