Nitrate and ferrous iron concentrations in the lower Burdekin aquifers: assessing denitrification potential

Thabonithy Thayalakumaran[1], Philip B. Charlesworth[1,2], Keith L. Bristow[1,2], Renate J. van-Bemmelen[3] and Jasmine Jaffrés [4]

[1]CSIRO Land and Water and [2]CRC for Irrigation Futures, PMB Aitkenvale, Townsville, QLD 4814, Australia. Email: thabo.kumaran@csiro.au
[3]Aquatic Eco-Technology at Hogeschool Zeeland in Vlissingen, The Netherlands.
[4] Department of Mathematical and Physical Sciences, James Cook University, Townsville, Qld 4811, Australia.

Abstract
The lower Burdekin is one of Australia's premier irrigation districts with more than 80,000 ha of sugarcane and other crops. Because it is located adjacent to the Great Barrier Reef Lagoon, there is strong interest in understanding the fate of nitrogen applied as fertiliser. Natural denitrification is increasingly recognised for its ability to reduce nitrate concentrations in groundwater and we therefore analysed water samples for a range of constituents (nitrate, ferrous iron, dissolved oxygen, redox potential, pH) from 57 monitoring bores to investigate the denitrification potential of the lower Burdekin aquifers. Nitrate concentrations ranged from <0.1 to 14.4 mg/L NO_3-N (three times the ANZECC environmental standard of 5 mg/L). Ferrous concentration varied from 1 to 360 mg/L, dissolved oxygen was < 2 mg/L, redox potential varied from -120 to +235 mV, and pH ranged from 5.9 to 7.6. Elevated nitrate levels were observed in 16% of the bores located mostly in the Home Hill area. These areas also had low ferrous levels. High ferrous levels were found mostly in the Ayr area and at shallow depths. The data in general showed an inverse relationship between nitrate and iron, and between nitrate and ammonium. Furthermore, undetectable amounts of nitrate were measured in the nested bores located along the coast. These geochemical conditions favour the presence of ferrous iron and a reduced environment conducive to denitrification. These results suggest that denitrification is one of the mechanisms involved in reducing the amount of nitrate in the lower Burdekin aquifers and hence reducing the potential for nitrate to move from the groundwater into the near-shore marine environment.
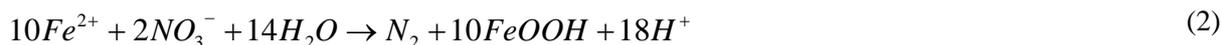
Key Words
Geochemical conditions, Eh, DO, DNRA, DOC

Introduction
Contamination of groundwater by nitrate is a widespread problem in agricultural areas such as the lower Burdekin in the north Queensland where 80, 000 ha is under irrigated surgarcane and other crops. Nitrate concentrations above the Australian New Zealand Environment and Conservation Council (ANZECC) guideline for long-term environmental sustainability (5 mg NO_3-N/L) have been reported in 49 out of the 397 sample bores in the Burdekin region (Weir 1999). Also, during 2000-2002, sampling of ten farmer production bores in the Delta found nitrate levels from 1 to 12 mg/L NO_3^--N (Charlesworth and Bristow 2004). As this area overlies major groundwater supplies and is close to environmentally sensitive wetlands, waterways and the Great Barrier Reef Lagoon (GBR), its impacts on the water quality are under increasing scrutiny. Consequently, there has been increasing interest in understanding any natural processes that utilise the groundwater nitrate and conditions that enhance the processes. While denitrification has been intensively studied with respect to surface water/sediment interfaces, soil environments and waste water treatment processes (Barton et al. 1999) it has in recent years been recognised for its ability to eliminate or reduce nitrate concentrations in groundwater (Postma et al. 1991; Korom 1992).

Denitrification is a microbially mediated process where nitrate is converted to N_2 gas when O_2 becomes limited. While organic carbon is the most preferred electron donor as it yields the most energy to bacteria (Starr and Gillham 1993) other reduced inorganic substrates such as ferrous or pyrite (Postma *et al*. 1991) have been reported as electron donors in nitrate reduction process. Nitrate is used as an electron acceptor by the bacteria only in the saturated zone. Following equations describe the denitrification process using different electron donors,

$$5C + 4NO_3^- + 2H_2O \rightarrow 2N_2 + 4HCO_3^- + CO_2 \qquad (1)$$

$$10Fe^{2+} + 2NO_3^- + 14H_2O \rightarrow N_2 + 10FeOOH + 18H^+ \qquad (2)$$

The N_2 gas produced from denitrification processes remains in solution until the groundwater discharges to surface-water and equilibrates with the atmosphere. Measurement of excess N_2 in groundwater, electron donors and other geochemical conditions can give an indication of whether an aquifer has potential for natural denitrification, and to some extent, the fate of nitrate in groundwater can be predicted. While there has been ample observational evidence of iron in groundwater of the lower Burdekin in certain areas including yellowish-red deposits around pump outlets, and some measurements on the distribution of iron (Kelly 1974) in groundwater, no studies have linked iron and/or dissolved organic carbon (DOC) and hydrogeochemical conditions with the nitrate in the groundwater. The objective of this study was to determine the potential for denitrification in the Burdekin aquifer and the effect this might have on the amount of nitrate likely to reach the GBR lagoon.

Methods

The lower Burdekin is located approximately 90 km southeast of Townsville in north Queensland. The Burdekin River Delta aquifer comprises sedimentary deposits extending upto 100 m deep and overlies a predominantly granitic basement. The nature of sedimentation is very complex comprising a mixture of interbedded gravel, sand, silt, mud and clay. The groundwater system in the lower Burdekin is generally considered to be unconfined, due to the presence of sandy to loamy soils and the discontinuous nature of underlying clay layers (Brodie *et al*. 1984). Groundwater flows generally from the south to the north based on potentiometric surface maps. Water loss from the aquifer is through discharge to the sea and river, pumping for irrigation and evaporation. Fertiliser nitrogen recommendation for sugarcane in the Burdekin is 160-220 kg of N/ha/yr and is usually applied as urea in a single operation at the start of the season (April-October).
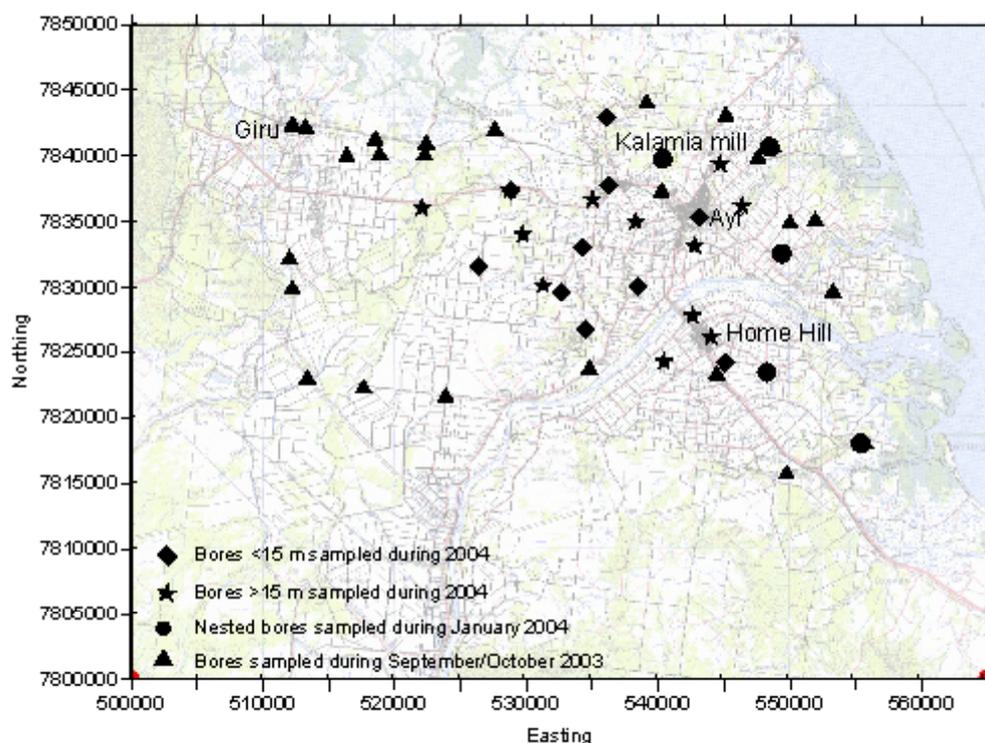

Figure 1. Sampling locations during September/ October 2003 and in January 2004

Groundwater sampling of monitoring bores installed by the Queensland Department of Natural Resources Mines and Energy was performed in two different periods, one during September/October 2003 and the other during January 2004. In the first period, 28 single and 2 nested bores were sampled and during January 2004, 22 single and 5 nested bores were sampled (Figure 1). Most of the chosen bores were confined to areas planted sugarcane. The depth of the bores varied from 5.4 m to 88.5 m. Water samples were withdrawn from bores using a stainless steel submersible pump with a Teflon discharge line. Purging of a bore continued until either three bore volumes had been pumped out or until the pH had

stabilised. Redox potential (Eh), pH, dissolved oxygen (DO) and electrical conductivity (EC) were measured using electrodes in a flow cell, and water samples were collected with little exposure to the air. Sub-samples were collected from each bore for ferrous iron, total dissolved iron, nitrate, ammonium, DOC, cations and anions after filtering with a 0.45 μm filter. Samples were preserved in ice packs and transported to the lab for analysis.

Results and Discussion

Distribution of nitrate, ferrous iron and DOC in groundwater

The depth to water table, below ground level (bgl), ranged from 0.96-10.5m. There was a tendency for shallow water tables to occur near the coast and deeper water tables inland in both sampling times. Although the nitrate concentrations in the majority of the bores were below the ANZECC levels for long term environmental sustainability values as high as 14.4 mg of NO_3^--N/L were measured. During the September/October 2003 sampling period, only 25% of the bores showed NO_3^--N levels higher than 0.1 mg/L, with three bores above 5 mg/L. In contrast, 77% of the single bores yielded concentrations higher than 0.1 mg/L in January 2004 (Figure 2). There were five single bores which have NO_3^--N values above 5 mg/L. Elevated nitrate levels were mostly observed in the Airville-Homehill area. This applied to both sampling periods. Brodie *et al* (1984) and Weier (1999) also reported a similar spatial distribution but the magnitude of the concentrations they reported were higher.
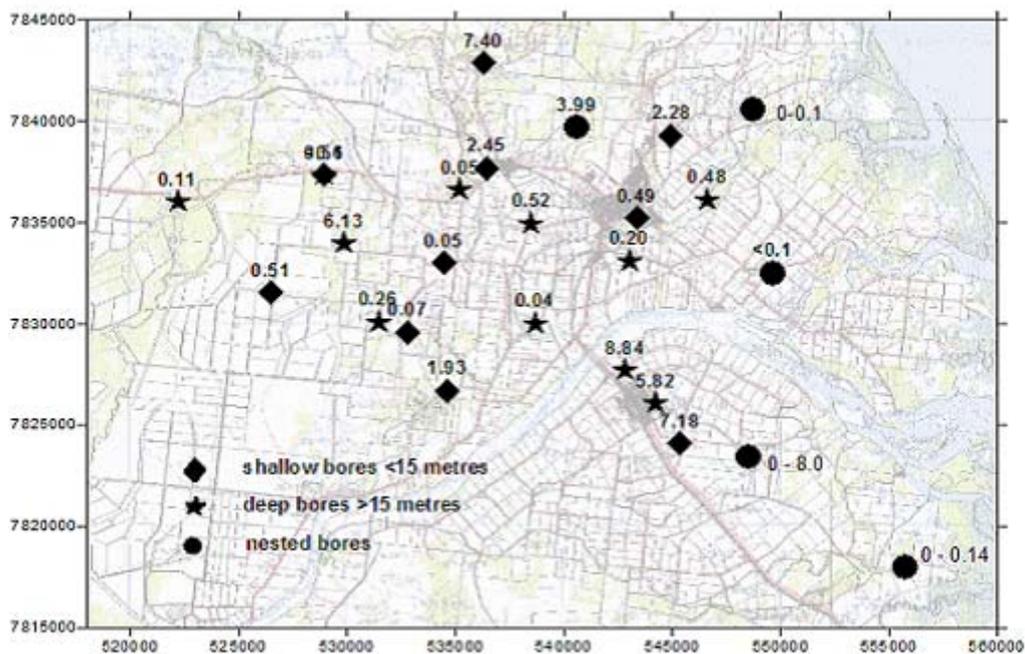

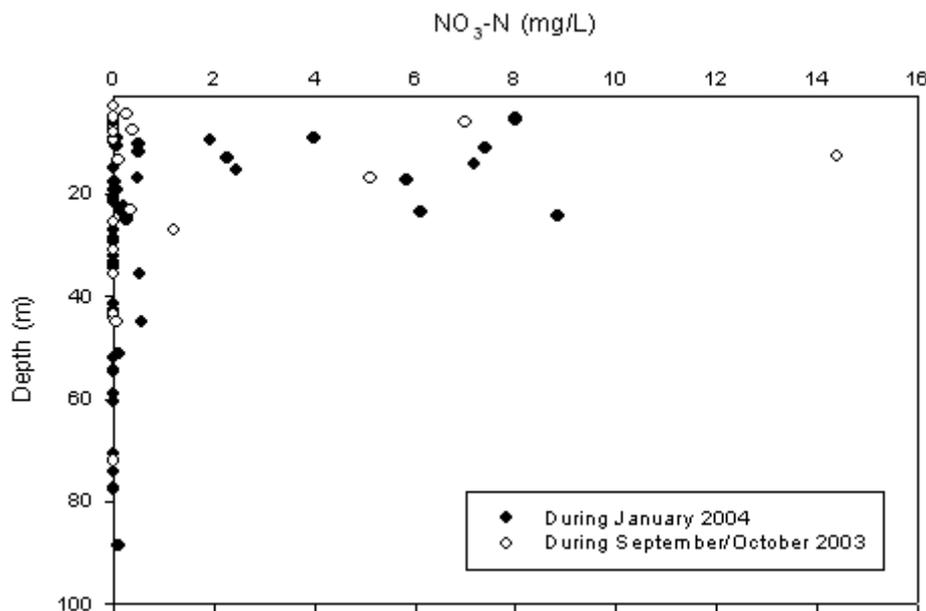**Figure 2. Spatial distribution of NO_3-N$^-$ (mg/L) in the lower Burdekin during January 2004**

Figure 3. NO$_3$-N$^-$ concentrations in mg/L at different depths

The vertical distribution of nitrate concentration revealed different trends between sampling periods. In the first sampling period not many bores showed higher nitrate levels at shallow depths (< 30 m) while six of the 28 sampled bores had values more than 5 mg NO$_3$-N$^-$ /L in the second sampling (Figure 3). The observed differences in the vertical nitrate concentration profile with time could be related to fertiliser applications and subsequent irrigations. It is worth noting that different bores were sampled during the two periods. A steady decline in nitrate concentrations from the wet season to the dry season has been noted previously by Brodie *et al.* (1984). Elevated nitrate concentrations occurred mostly in bores located in areas where water table depths ranged between 2 and 6 m. Similar patterns have been observed with nitrate levels highest near the water table and decreasing to below detection with depth both at this site by Brodie *et al.* (1984) and at other sites by Trudell *et al.* (1986) and McLarin *et al.* (1999). With the exception of one shallow pipe located in Ayr, none of the nested bores had concentrations above 0.1 mg/L irrespective of the sampling time. The nested bores were mostly located along the coast. Nitrite concentrations were below detection or negligible (<0.1 mg/L) in all of the bore samples. Concentrations of NH$_4^+$ reached 8.1 mg/L in the September/October sampling period while lower concentrations (maximum of 3.6 mg/L) were measured in bores sampled during January 2004. Its distribution showed no particular spatial or vertical trend, but nested bores showed higher values.
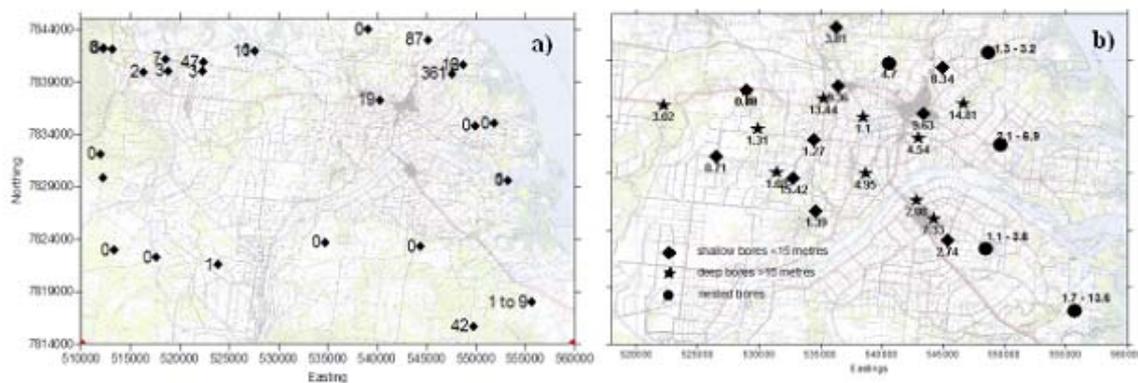

Figure 4. Distribution of ferrous iron (mg/L) in the Lower Burdekin groundwater
a) during September/October 2003 b) January 2004
The distribution of ferrous iron in the aquifer during the two sampling periods is shown in Figure 4 with values ranging from 0 to 361mg/L. The bores sampled during September/October 2003 had very high concentrations which may be related to the particular location of the bores. While we have only limited data at this stage, there is some evidence of spatial trends with high ferrous concentrations in the Kalamia Mill and Ayr areas. These results are consistent with the findings of Kelly (1974). Elevated ferrous levels

were also observed in the Giru-Barratta area where concentrations of 3.02 - 15.42 mg/L were measured. Ferrous levels were below 2 mg/L in the Airville - Home Hill area.It is worth noting that elevated nitrate concentrations were observed in these areas. In general, elevated nitrate concentrations were not found in bores along the coast where elevated ferrous concentrations were common. As shown in Figure 5 ferrous iron concentrations were quite variable but tend to be higher in bores less than 20 metres deep, compared to deep bores (>55 metres deep) where the concentration ranged between 1.22 and 3.20 mg/L. The spatial and vertical trends in ferrous iron concentrations were consistent in both the sampling periods. Ferrous concentration in the nested bores ranged from 1.15 to 13.5 mg/L, and with the exception of one bore, there was no distinct vertical pattern. This could be influenced by the fractured nature of the aquifer materials and the prevailing geochemical conditions.

The DOC levels in the lower Burdekin aquifer were very high and variable both spatially and vertically. It ranged from 4 mg/L to 82 mg/L. One reason for these high levels could be the movement of sugar juices lost during harvest moving to deeper depths and entering the shallow groundwater systems. These high DOC concentrations in groundwater are also not that surprising when compared with the DOC concentration of 260 mg/L in the first runoff water from one of the sugar cane farms. A conservative estimation of Rayment in 2000 reported 0.13 tonnes of sucrose-C/ha/yr (0.33 tonnes of sucrose/ha/yr) loss to the soil/water environment during cane harvest. It is likely that the elevated levels of DOC in the lower Burdekin aquifer degrade with ferric iron as the terminal acceptor and results in the production of reduced soluble ferrous iron in anaerobic situations.
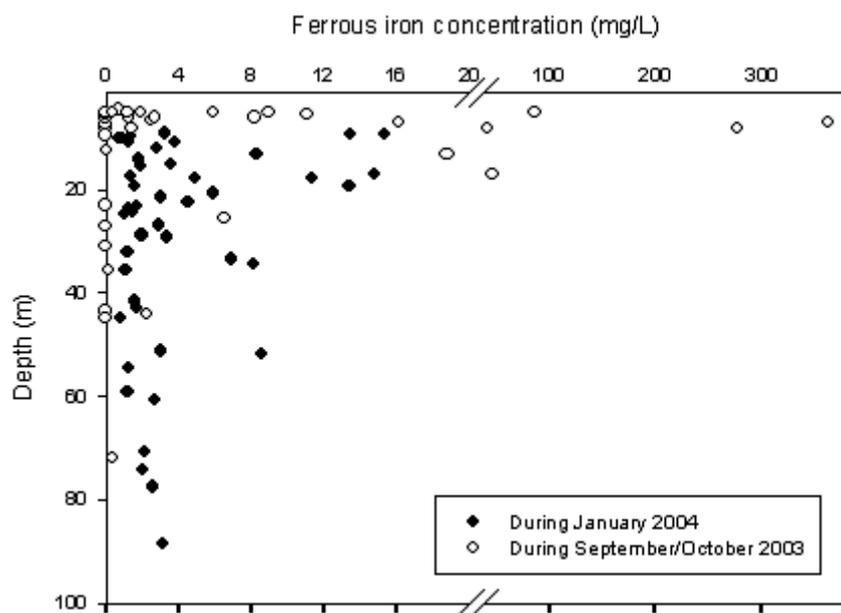

Figure 5. Ferrous concentrations at different depths during September/October 2003 and in January 2004.

Other geochemical conditions
In most bores, the DO concentrations were below 1 mg/L in both sampling periods. Although the concentration varied considerably at shallow depths it decreased with the water table depth. In the nested bores DO concentrations did not show the decreasing trend with depth as reported by others (Kelly, 1997). They were however, all below 0.7 mg/L meaning that anoxic conditions prevailed in the groundwater.

Eh varied between -120 and 235 mV, with little evidence of trends with increasing depth. In the bores sampled, DO varied from 0.1 to 6 mg/L between an Eh of 0 and 235 mV but was <1 mg/L below 0 mV. Elevated NO_3^--N concentrations occurred in groundwater at Eh values between 37 and 235mV, and NO_3^--N was largely undetectable with Eh less than 0. In contrast to the NO_3^--N profile, elevated ferrous concentrations (>4 mg/L) occurred in groundwater with Eh below 0 mV and a DO concentration lower than 1 mg/L.

Denitrification potential

Nitrate is a redox-sensitive species and it would be expected that loss of nitrate due to reduction or denitrification will be accompanied by changes in other redox species, changes in geochemical conditions, and the production of reduced forms of nitrogen (Puckett and Cowdery 2002). As such, an evaluation of the dominant species of the major redox-active elements including oxygen, iron, manganese, sulphur, carbon, and nitrogen together with the geochemical conditions can provide clues to the potential of the aquifer for denitrification. As discussed earlier the DO concentration varied widely however, only 2 of the groundwater samples had values greater than 2.0 mg/L, indicating favourable conditions. DO levels of less than 2.0 mg/L was reported to be favourable for denitrification (Korom 1992). Furthermore, the Eh values from -120 to + 235mV tend to support the existence of favourable reduced conditions for denitrification in the aquifer.

A plot of nitrate versus ferrous iron or ammonium for samples taken shows the relationship between these parameters; the presence of one is usually marked by the absence of the other (Figure 6). The observed negative correlations between nitrate and iron or ammonium suggest that the nitrate in the groundwater is being consumed. This could be one of the reasons for little change observed in nitrate concentration in 90% of wells monitored in the Burdekin region (Thorburn *et al.* 2003). It appears that two processes are involved, one relating to ferrous and the other to high ammonium levels. As discussed earlier bacteria use iron in its reduced ferrous form as an electron donor to reduce nitrate in the absence of dissolved oxygen.
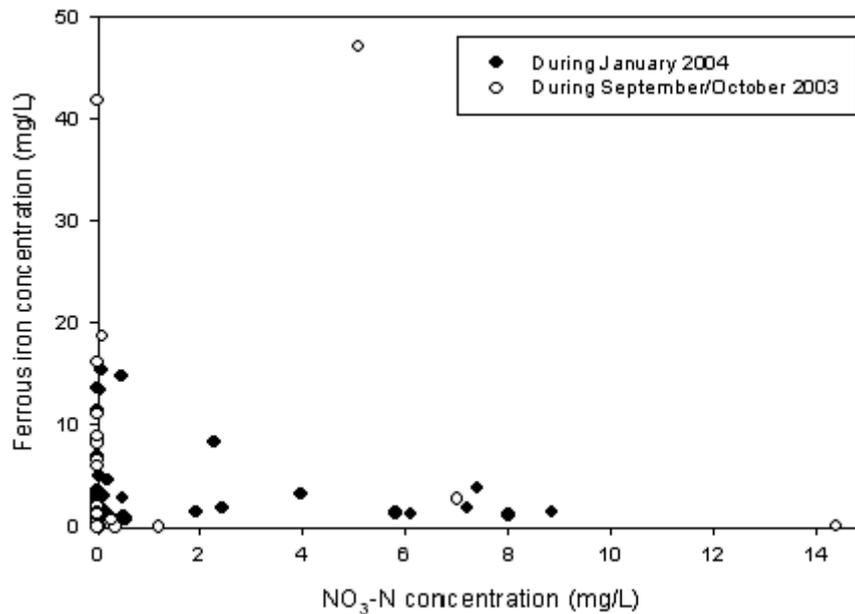

Figure 6. NO$_3^-$-N concentration versus ferrous iron concentration

Based on the stoichiometry of denitrification in equation (2), at the median NO$_3$-N concentration of 0.51 mg/L at least 10.2 mg/L of ferrous iron are required. It appears that the ferrous iron available is not enough for denitrification across the entire area of the lower Burdekin however, the higher amounts of ferrous iron found in the Kalamia mill-Ayr area indicates that this area has good potential for denitrification. A map showing potential areas for denitrification in the lower Burdekin was prepared with reference to the ferrous iron concentrations used by the Minnesota Pollution Control Agency (1999) to define nitrate sensitive areas. Figure 7 shows areas of low and high potential for denitrification at shallow (a) and deep depths (b). The map suggests that the shallow groundwater has potential for denitrification in most of the areas compared to the deep groundwater.
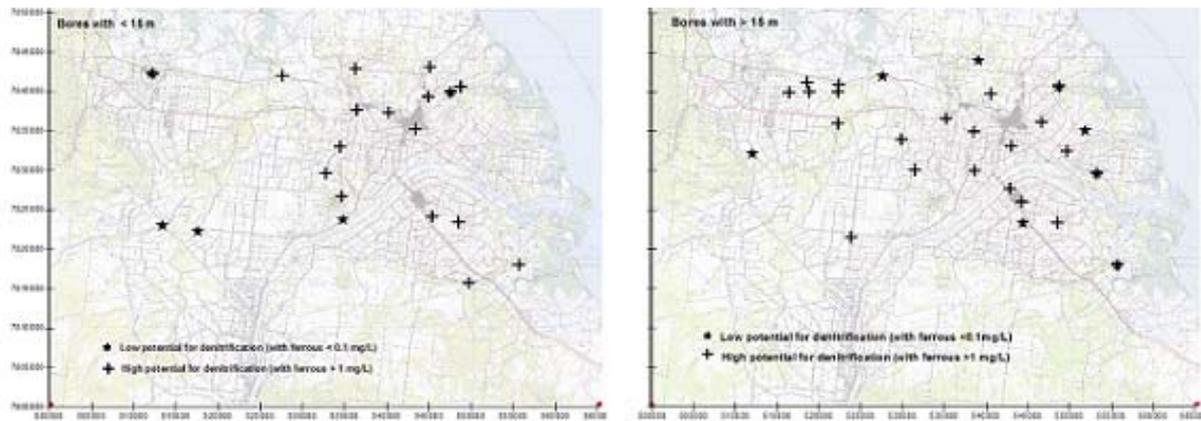
Figure 7. Map showing areas of low and high potential for denitrification in the lower Burdekin

The existence of low nitrate concentrations in bores with high levels of ammonium, and the reduced environment in the groundwater suggest that Dissimilatory Nitrate Reduction (DNRA) could be occurring (Figure 8). Ammonium (NH_4^+) is the end product of DNRA, which is a process that can temporarily remove nitrate as long as NH_4^+ does not come in contact with aerobic environments (Korom 1992; Tesoriero *et al.* 2000). DNRA appears more in salt marshes and in strongly anoxic marine sediments (Postma *et al.* 1991). Marine deposits are present within the Burdekin aquifer which seems to support the existence of dissimilatory denitrification processes.
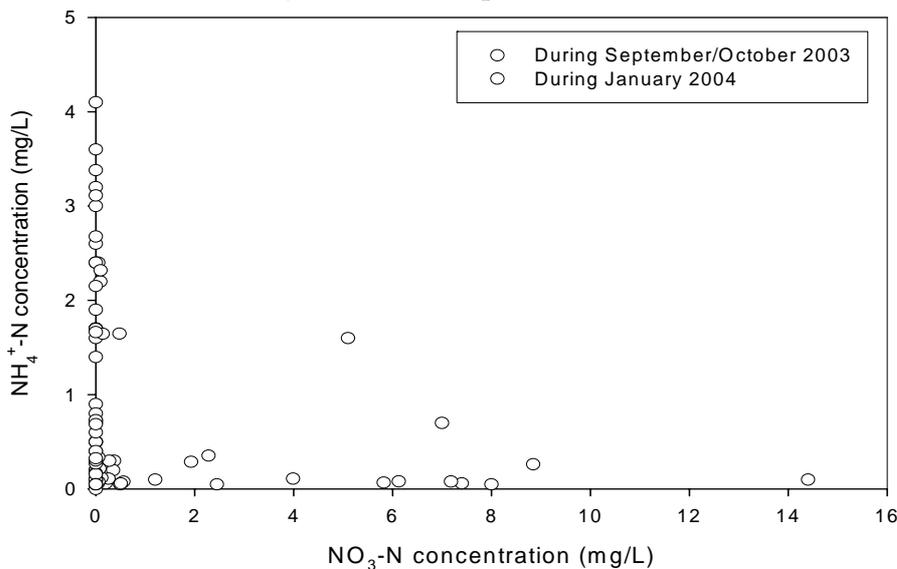

Figure 8 NO_3^--N concentration versus NH_4^+-N concentration

There was no consistent pattern of high nitrate concentrations associated with low DOC concentrations. Considering DOC as the most preferred electron donor and given the stoichiometry of 1:1.25 (molar basis) between nitrate and DOC required for denitrification processes (Korom, 1992), the range of DOC (4 to 82 mg/L) measured in the groundwater is enough to denitrify a large amount of nitrate at a depth of < 30 m. It means that we should not expect nitrate at this depth. The fact that we do suggest that either biological constraints exist or that the denitrification rate is slow. While beneficial on the point of view of promoting denitrification, the high DOC loading to the aquifer increases the weathering rates of iron and manganese oxides.

Conclusion
Given the spatial variation in nitrate concentrations and the fact that the nitrate input is not constant with time, it is difficult to determine the extent of nitrate reduction which has taken place within the aquifer. However, the measured values of DO, Eh and pH which can be used to characterise the geochemical conditions of the aquifer, are near the upper threshold levels given in the literature to support the

denitrification process. Also, the negative correlation between nitrate and the levels of ferrous iron indicates that there has been at least some denitrification. The presence of higher NH_4^+ in places where the nitrate is lower and, vice versa suggests the occurrence of DNRA. Furthermore, higher levels of ferrous iron found both in Ayr-Kalamia Mill areas and near the coast indicate that these areas have potential for removing nitrate from the groundwater. High levels of DOC with a wide spatial distribution indicates that the whole area has the potential for denitrification. More studies are required in order to quantify the amount of nitrate loss from the aquifer due to denitrification and to delineate nitrate insensitive or potential denitrification depths.

The map presented in this paper is a first step towards identifying those areas of the lower Burdekin with most potential for denitrification. Although generalized, it is a valuable start in helping determine the fate of nitrate entering the groundwater. This information is important in helping to understand the complexities of the floodplain and in enabling resource managers to better target their management practices.

Acknowledgement

References

Barton, L., McLay, C.D.A., Schipper, L.A., and Smith, C.T. (1999) Annual denitrification rates in agricultural and forest soils: a review. *Australian Journal of Soil Research*, **37**, 1073-1093.

Brodie, J.E., Hicks, W.S., Richards, G.N., and Thomas, F.G. (1984) Residues related to agricultural chemicals in the groundwaters of Burdekin river delta, North Queensland. *Environmental Pollution*, **8**(7), 187-215

Charlesworth, P. B., and Bristow, KL. (2004) Sustainable Management of the Burdekin Groundwater System, *Final report to the National Program for Sustainable Irrigation*. (CLW 32), CSIRO, Townsville.

Korom, S.F. (1992) Natural denitrification in the saturated zone: A review. *Water Resources Research,* **28**, 1657-1668

Kelly, G.J. (1974) Iron in Burdekin irrigation waters, *Proc.Qld Soc. Sugar Cane Technol.*, **41**, 27-35.

Kelly, W.R., (1997) Heterogeneities in ground-water geochemistry in a sand aquifer beneath an Irrigation field, Journal of Hydrology **198**, 154-176, U.S.A.

McLarin, W., Bekesi, G., Brown, L., and McConchie, J. (1999) Nitrate contamination of the unconfined aquifer, Manakau, Horowhenua, New Zealand, *Journal of Hydrology* (NZ) **38**(2): 211-235, s.l,

Minnesota Pollution Control Agency, (1999) Estimating ground water sensitivity to nitrate contamination', Environmental outcomes division Ground water monitoring & assessment program.

Postma, D., Boesen, C., Kristiansen, H., and Larsen, F. (1991) Nitrate reduction in an unconfined aquifer: Water chemistry, reduction processes, and geochemical modeling. *Water Resources Research,* **27**, 2027-2045

Puckett, L.J., and Cowdery, T.K. (2002) Transport and fate of nitrate in a glacial outwash aquifer in relation to ground water age, land use practices, and redox processes. *Journal of Environmental Quality,* **31**(3), 782-796

Rayment, G.E., (2000) Water quality in sugar catchments of Queensland. Department of Natural Resources and Mines, Natural Resource Sciences, and CRC for Sustainable Sugar Production, 80 Meiers Road, Indooroopilly QLD 4068

Starr, R.C., and Gillham, R.W. (1993) Denitrification and organic carbon availability in two aquifers. *Ground water*, **31**(6), 934-947

Tesoriero, A.J., Liebscher, H., and Cox, S.E. (2000) Mechanism and rate of denitrification in an agricultural watershed: Electron and mass balance along groundwater flow paths. *Water Resources Research,* **36**(6), 1545-1559

Thorburn, P.J., Biggs, J.S., Weier, K.L., Keating, B.A. (2003) Nitrate in groundwaters of intensive agricultural areas in coastal Northeastern Australia. *Agriculture, Ecosystems and Environment*, **94**, 49-58.

Trudell, M.R., R.W. Gillham, and Cherry, J.A. (1986) An in-situ study of the occurrence and rate of denitrification in a shallow unconfined sand aquifer. *Journal of Hydrology*, **83**, 251–268.

Weier, K., (1999) The quality of groundwater beneath Australian sugarcane field. CSIRO Tropical Agriculture, St. Lucia, 1999.