



Research article

Nitrate dynamics in groundwater under sugarcane in a wet-tropics catchment

Jim Stanley^{*}, Lucy Reading

Queensland University of Technology, 2 George St, Brisbane City, 4000, QLD, Australia



ARTICLE INFO

Keywords:

Groundwater
Nitrate
Sugarcane
Tropics
Sulphate
Denitrification
Soil chemistry
Environmental chemistry
Water geochemistry
Contaminant transport
Geochemistry
Environmental science

ABSTRACT

The transport of nitrogen (N) to groundwater and surface water in the form of nitrate (NO_3^-), as a by-product of the application of N-rich fertilisers, has been studied extensively. Yet, in the catchments adjacent to the Great Barrier Reef (GBR) in tropical north Queensland, Australia, NO_3^- transport in groundwater is not regularly monitored. An assessment of groundwater chemistry in the Liverpool Creek catchment of Queensland's wet-tropics region was conducted by regular sampling and analysis of groundwater over 12 months, through wet and dry seasons. A distinct spatial variability in groundwater chemistry was observed; groundwater aquifers with very low dissolved oxygen (DO) and NO_3^- consistently displayed relatively higher concentrations of sulphate (SO_4^{2-}), sulphur (S^{2-}) and ferrous iron (Fe^{2+}) and low concentrations of dissolved organic carbon (DOC) (<2 ppm). Combined with averaged measured redox potential (Eh) of <250 mV, this indicates certain regions of the catchment have conditions favourable for removal of NO_3^- via autotrophic denitrification (DN), while other groundwater aquifers retained NO_3^- concentrations just above the acceptable trigger limits defined in regional water quality guidelines. Observations indicate that the naturally heterogeneous structure of the coastal alluvium contributes to the distinct variability in groundwater chemistry over small distances, with NO_3^- concentrations influenced by a combination of DN, lateral shallow drainage and potential adsorption to clay surfaces within the alluvial sediments.

1. Introduction

Understanding the transport and dynamics of agricultural dissolved nitrogen in groundwater aquifers is of global importance, particularly in tropical regions where the world's major producers of sugarcane are located. In these countries, annual nitrogen fertiliser use per hectare of cropland has shown an increase of 14.6 Mt over the last 15 years (2002–2017) (FAO, 2019). This continues to contribute excess NO_3^- concentrations in groundwater which exceed acceptable health and environmental limits (Ratchawang and Chotpantarat, 2019). It is estimated that $56 \pm 6\%$ of global terrestrial nitrogen contamination is produced in these tropical regions, while >25 % of the world's river basins discharge more reactive nitrogen ("fixed" nitrogen, in the form of NO_3^- and NH_3) than they receive (Lee et al., 2019). From 2009 to 2017, Australia's own annual nitrogen fertiliser use per hectare of cropland increased from 850 kt to 1090 kt (FAO, 2019). In tropical regions the situation is particularly challenging, where higher rainfall promotes rapid loss of dissolved inorganic nitrogen (DIN) through leaching (Robinson et al., 2011). Agricultural development in wet tropical catchments abutting the GBR marine ecosystem poses a significant

environmental hazard to inshore coral reef communities and marine water quality, via input from terrestrially derived sediments and nitrogen (Thorburn et al., 2011; Hunter and Walton, 2008; Hutchings et al., 2005). Thirty percent of total nitrogen inputs to Great Barrier Reef (GBR) ecosystems is derived from river runoff (Devlin and Brodie, 2005), with sugarcane cropping being a major contributor (DSITI, 2016).

Global research has demonstrated how broad scale agricultural practices directly influence the concentration and transport of contaminants in groundwater aquifers (Bohlke, 2002; Rajmohan and Elango, 2005; Koh et al., 2007; Kellner et al., 2015; Amano et al., 2016; Lwimbo et al., 2019; Reading et al., 2019). In recent decades there has been increased interest in assessing the environmental impacts of broad scale sugarcane farming, particularly in relation to the transport of nitrate (NO_3^-) (Mitchell et al., 2009; Davis et al., 2013; Thorburn et al., 2011; Rasiah et al., 2003, 2013). NO_3^- has been identified globally as a widespread contaminant in groundwater and surface waters, following the application of nitrogen-rich agricultural fertilisers (Appelo and Postma, 2010; Hiscock and Bense, 2014; Zhou et al., 2016; Shukla and Saxena, 2018; Reading et al., 2019). Although considered an essential plant

^{*} Corresponding author.

E-mail address: j5.stanley@qut.edu.au (J. Stanley).

nutrient in soils, NO_3^- becomes a pollutant once it is leached below the root zone and occurs in undesirable concentrations (Tate, 2000; Zhou et al., 2016; Juntakut et al., 2019).

Several studies examining the occurrence of NO_3^- and its potential removal via denitrification (DN) in north Queensland's wet and dry tropics have focused outside the Liverpool Creek catchment, in the Tully, Burdekin, Mulgrave-Gordonvale and upper Johnstone River catchments (Mitchell et al., 2009; Thorburn et al., 2011; Connor et al., 2012; Rasiah et al., 2013; Connolly et al., 2015). These studies show that factors influencing NO_3^- retention and transport are complex and can be highly variable between catchments. Where deep (1 m to >10 m) Fe-rich soil profiles under sugarcane are present, there can be sufficient anion exchange capacity (AEC) to adsorb and retain NO_3^- in soil profiles (Rasiah et al., 2003). In some instances, localised geochemical properties indicate high potential for reducing NO_3^- via DN in oxygen-deprived groundwater (Thayalakumaran et al., 2007). This study set out to examine whether these same factors and processes are important in the Liverpool Creek catchment, where the heterogeneity of the coastal alluvium results in a highly variable sedimentological structure beneath the sugarcane plantations.

2. Site description

The physiography of coastal plains in the South Johnstone river basin, in the wet tropics of north Queensland (Figures 1 and 2), consists of low, flat to undulating surfaces of thick alluvium (>30 m deep), swampy lagoon deposits and Pleistocene age dune deposits and beach ridges (Hair, 1990; DSITI, 2013). These are bounded to the west by irregular, northerly-trending coastal ranges which are typified by dense rainforest coverage, steep mountain sides, waterfalls and perennial flowing streams. Hair (1990) observed that most of these mountainous areas adjacent to the plains have low fracture development and limited groundwater storage potential. The area is characterized by intensive sugarcane plantations, but irrigation has not been traditionally required in the region and plantations rely exclusively on seasonal rainfall. Periodic flooding is a feature which can affect sugarcane crop yields.

The major rivers and water courses drain separate catchments within the basin and discharge to the coastline. Hair (1990) noted that approximately 50% of the coastal alluvium is composed of clay, while sand and gravel beds are of limited thickness (commonly 2–3 m) and limited areal extent. This heterogeneity can make lithological correlation between groundwater bores problematic, even when the distance

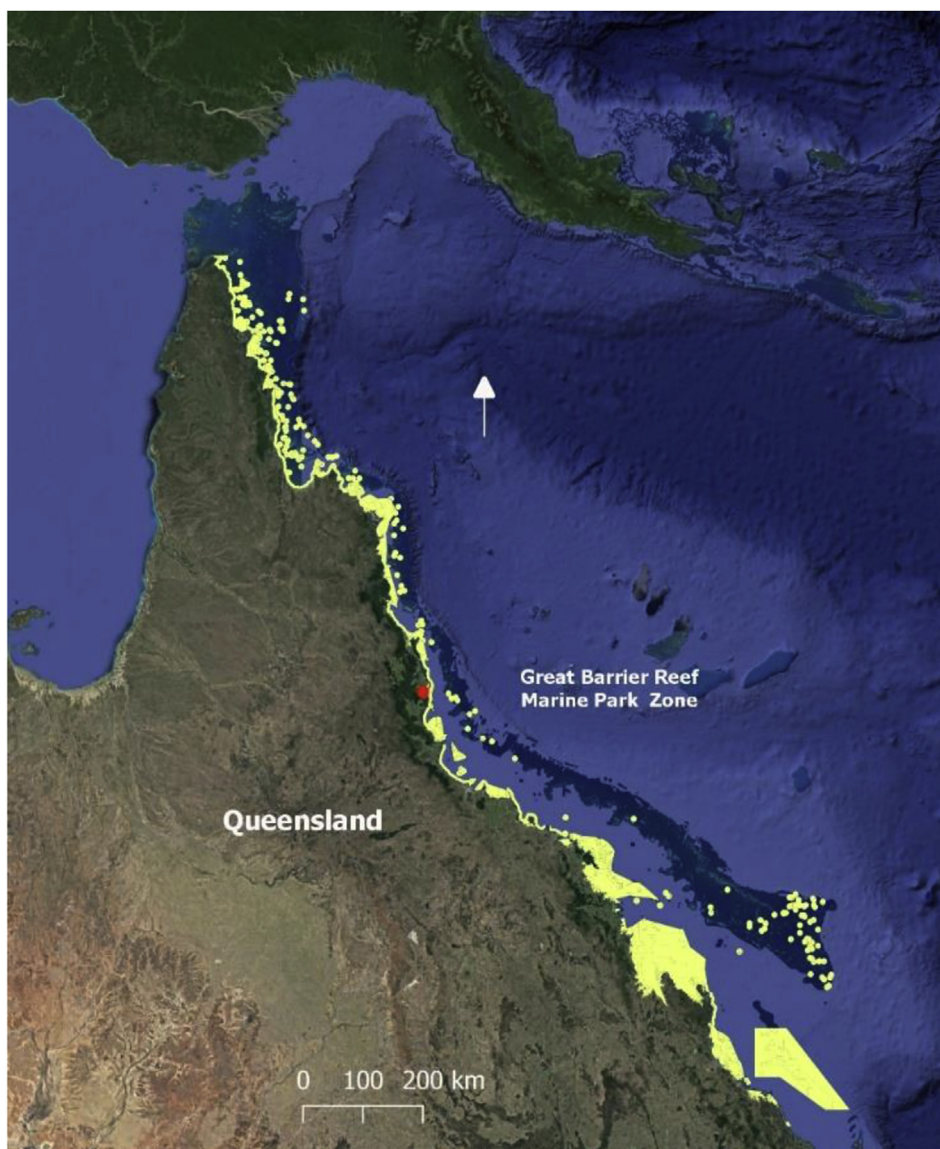


Figure 1. Map showing the location of study (red dot) in northern Queensland. Yellow polygons indicate extent of Great Barrier Reef marine zones (Queensland Government, 2020). (Source: Esri, Digital Globe, GeoEye, EarthStar Geographics, CNES/Airbus CS, USDA, USGS, AeroGRID, IGN and the GIS user community).



Figure 2. Location map displaying Silkwood region in the Liverpool Creek catchment, South Johnstone River basin, north Queensland, Australia. Red boundary indicates extent of major Johnstone Rivers basin catchment. Dotted blue lines indicate locations of North and South Johnstone River and Liverpool Creek, in respective catchments. (Source: QGIS 3.6).

between them is small. QDPI (1995) reported that testing of monitoring bores in the region recorded a maximum pumping rate of typically less than 3 L/s and rarely exceeded 8 L/s, reflecting the claybound nature of the alluvium and discontinuity of aquifer material.

Within the South Johnstone river basin is the Liverpool Creek catchment surrounding the town of Silkwood. The creek is a perennial stream with a length of 55 km draining a catchment of ~ 320 km² (DSITI, 2013). The catchment alluvium is composed of heterogeneous, clay-rich quaternary sediments, derived from weathering of rock formations which are exposed as topographic highs close to the coastline (DSITI, 2013). Historical groundwater bore report data indicates a significant heterogeneity and discontinuation of alluvial aquifer material in the Silkwood region, within the Liverpool creek catchment. Murtha (1986) classified several soil types in the South Johnstone catchment as poorly drained soils formed on alluvium, most common being the *Bulgun* series hydrosol soil type. However, the only available data on sediment below the soil profile (>2 m below ground level (BGL)) is lithology descriptions from historical bore reports and these do not provide any quantitative mineralogical information about the alluvium in the catchment.

Fifteen groundwater-monitoring bores owned and operated by the Queensland Government's Department of Natural Resource, Mines and Energy (DNRME) are currently in use in the South Johnstone catchment for water-level monitoring and groundwater chemistry analysis. These are typically sampled for analysis only annually or biannually, so detailed historical information regarding any seasonal fluctuations in groundwater chemistry and standing water levels (SWLs) was lacking.

The DNRME's "Paddock-To-Reef" (P2R) research program operates a project situated at a sugarcane plantation paddock near Silkwood, in the South Johnstone River basin, which is owned and managed by MSF Sugar Pty Ltd. The focus of the P2R paddock research is quantifying seasonal loss versus uptake of soil nitrogen, to improve fertiliser application management. The Queensland Government's technical report of studies conducted at the research paddock from 2014 to 2017 provides important paddock-scale data on DIN transport in crop soil, shallow groundwater drainage (≤ 1 m below ground level (BGL)) and surface-water runoff (DNRME, 2017).

3. Methods and materials

3.1. Location

The wet tropics region in the location of the Johnstone Rivers basin is characterized by intensive sugarcane plantations, tropical climate (average monthly temperatures ranging from 24 °C to 31 °C; BOM, 2019) and high annual rainfall (3383.3 mm/y; DSITI, 2013).

To examine seasonal changes in groundwater chemistry, eight groundwater monitoring bores within the Liverpool Creek catchment were selected for regular (monthly/bi-monthly) sampling from September 2017 to September 2018 (Figure 3). Six of these bores are owned and operated by the DNRME (Table 1).

Bores 183021 and 183022 were installed in July 2017 on the site of the DNRME's P2R research paddock. Bore installation was completed using a Boart Longyear Sonic LX 600 Drill Rig which recovered intact sediment cores in 1 m lengths. Site observations showed very dense clay layers overlying and underlying aquifer material of fine-to-medium clayey-sand. Fourteen sediment samples were collected from the extracted core sections, corresponding to various depths in bores 183021 and 183022. Samples were collected from below 3 m depth. The distance between bores 183021 and 183022 is approximately 270 m.

Rainfall measurement data was provided from a rain gauge owned and operated by DNRME, installed near the location of bore 183021. The rain gauge used a 2 mL tipping method to accurately record timing of rainfall. A Heron™ electric dip-meter was used to record the standing water level (SWL) at each bore before pumping. A Proactive Mega-Monsoon™ 12 v submersible peristaltic pump was used to extract water from each bore and each bore was purged of 3 x volume to remove static bore water before sampling to ensure accurate sampling of aquifer water. Measurements of groundwater quality parameters were recorded at each bore using a calibrated WTW™ portable multimeter: electrical conductivity (EC μ S/cm), dissolved oxygen (DO mg/L), pH and temperature (°C). Samples intended for laboratory analysis of cations were preserved with HNO₃ (to <2 pH). In accordance with Geoscience Australia and Queensland Government guidelines, groundwater samples intended for major ion analysis were filtered through 0.45 μ m polytetrafluoroethylene

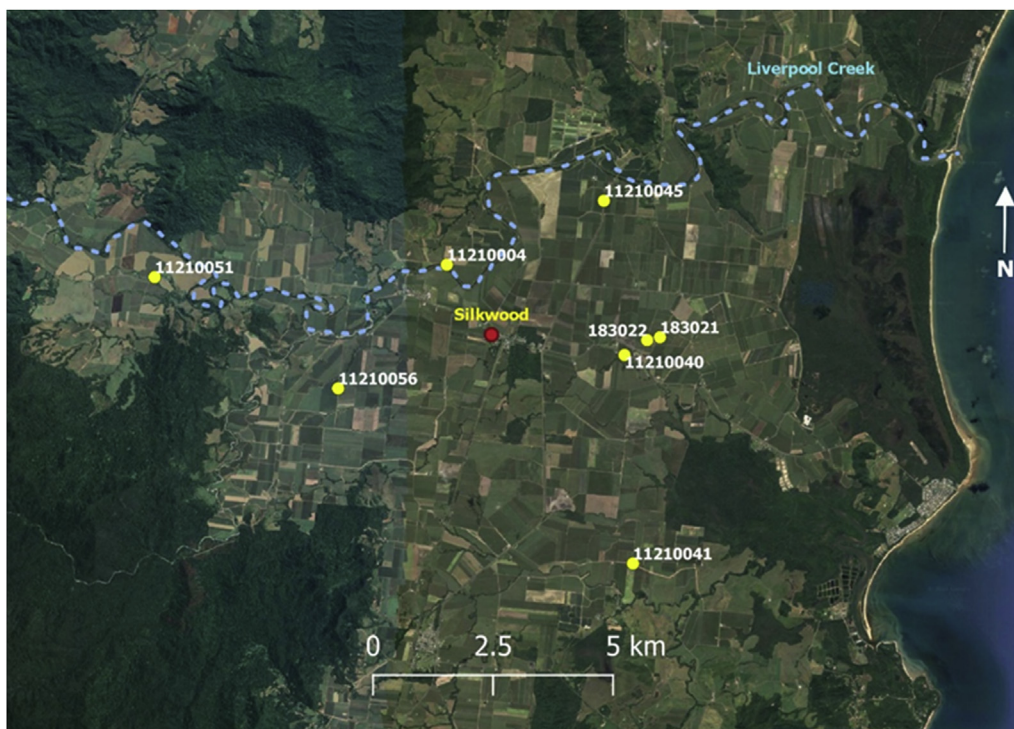


Figure 3. Map displaying Silkwood region and location of groundwater bores sampled for groundwater analysis. (Source: QGIS 3.6).

Table 1. Bore registration numbers (RN), aquifer depth and lithology of bores sampled for analysis. All displayed depths are in metres (m). (Data sourced from historical DNRME bore reports).

Registration Number	Bore Depth	Screen Depth	Aquifer depth	Aquifer Material
11210004	10.00	6.00–9.00	6.00–9.50	Clayey, coarse, gravelly sands.
11210040	10.54	6.50–9.50	5.00–8.00	Clayey, silty, fine/coarse sand; clay
11210041	34.00	17.10–19.10	17.00–21.00	Clay, silt, fine/coarse sand.
11210045	48.00	38.40–40.40	38.40–40.40	Fine/medium quartz, decomposed metamorphics, gravel, clay.
11210051	66.70	10.50–12.50	11.80–13.80	Medium sand to fine gravel.
11210056	42.00	31.70–33.70	31.70–33.70	Metamorphics (basement rock)
183021	14.00	8.80–11.80	9.00–11.00	Medium/coarse clayey sand, fine quartz (~4–5 m).
183022	15.00	9.00–12.00	9.00–11.00	Fine/medium clayey sand, fine quartz (~2 mm).

filters. All samples were kept at refrigerated temperatures (<4 °C). To ensure quality control, duplicate samples were collected at each site as well as field blanks using deionised water.

3.2. Laboratory methods

Field samples were immediately transported to the Queensland University of Technology's Central Analytical Research Facility (CARF) for laboratory analysis. Analysis of cations in groundwater samples was completed using Inductively Coupled Plasma Optical Emission Spectroscopy (PerkinElmer Optima ICP-OES). Analysis of anions was completed using Ion Chromatography (Thermo Scientific Dionex D211 RFIC Ion Chromatograph). Analysis of NO_3^- and nitrite (NO_2^-) concentrations was conducted on filtered samples using a Thermo Scientific Gallery Automated Chemistry Analyser. Sediment samples from extracted cores were analysed for quantitative mineralogical composition by X-Ray Diffraction (XRD), using a PANalytical Multi-Purpose Diffractometer. Analysis of total organic carbon (TOC) was conducted on unfiltered samples using a Shimadzu TOC-V Analyzer and TNM-1 Measuring Unit. Where the results of laboratory analysis indicated specific sample contamination, data from identified sample was omitted from further analysis.

3.3. Statistical data analysis methods

Statistical analysis of groundwater major ion chemistry was conducted using Minitab software (© Minitab Inc., 2017), through principal component (PC) analysis (standard correlation matrix method) and cluster analysis (combined correlation coefficient distance and complete-linkage (hierarchical) clustering method). The data was first tested for normality and standardised using z-score transformation (Hoshmand, 2017). The analyses combined the total groundwater data from all observations at all groundwater sites during the 12-month research period.

4. Results

4.1. Groundwater levels and rainfall

Regular measurements of groundwater levels from each bore show that SWLs responded noticeably to rainfall events (Figure 4). SWLs display a clear decline during a dry period (December 2017–January 2018) and increase following significant rainfall events (February–March 2018). Bores 11210041 and 183021 recorded SWLs above ground level in the wet season, with bore casings overflowing. Bore 11210004 ran dry in December 2017, with SWL falling below 10 m depth. These

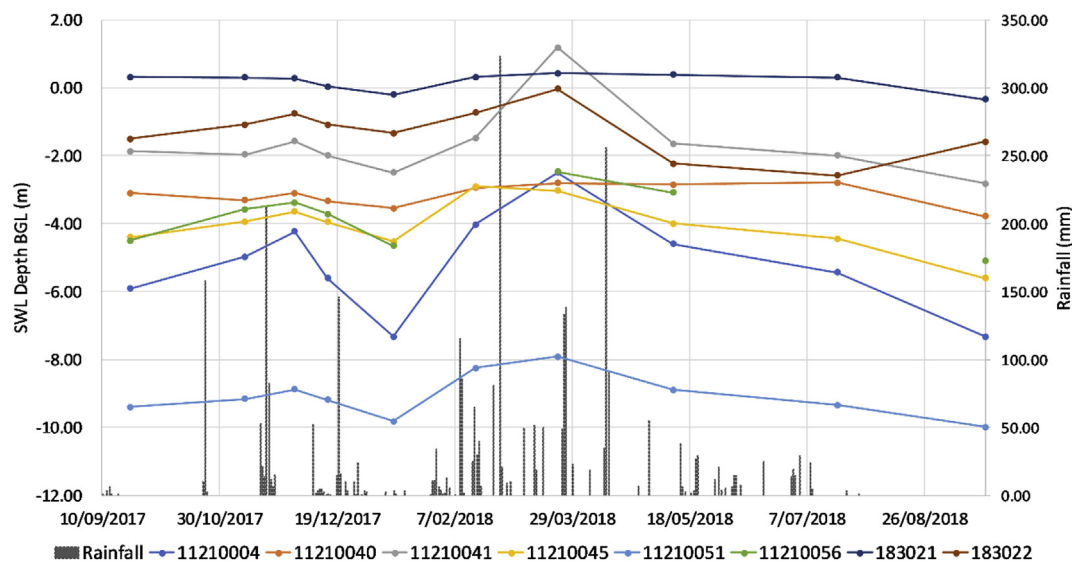


Figure 4. Measured SWLs from groundwater bores 2107-2018 (using dip-meter) and rainfall data from DNRME rain gauge located near bore 183021.

observations indicate rapid recharge and aquifer response to rainfall. Bore 1210056 was inaccessible in February and May 2018 due to paddock conditions.

4.2. Groundwater chemistry

Temperature and pH values remained consistent across all sites throughout the research period. The overall average pH of 5 indicates a moderately-acidic groundwater environment while measured groundwater temperatures across all sites were consistently ~ 26 °C. A summary of measured water chemistry and water quality parameters is presented in Figure 5 (A-F) and Figure 6. The focus of this paper is groundwater chemistry relating specifically to DN and the activity of NO_3^- . The most significant chemical trend observed in the groundwater analysis was a distinct relationship between measured concentrations of DO, NO_3^- , SO_4^{2-} and Fe^{2+} . Previous environmental studies have identified the relationship between these parameters as highly relevant and indicative of DN in catchments characterised by intensive agriculture (Rasiah et al., 2003; Thayalakumaran et al., 2007; Jahangir et al., 2012; Jessen et al., 2017). Therefore, the groundwater chemistry data is presented and discussed with a specific focus on these parameters.

The sites with consistently low DO displayed low NO_3^- and relatively higher dissolved SO_4^{2-} and Fe^{2+} (bores 11210045, 183021 and 183022; Figure 5B–5D). These sites all consistently recorded Eh values < 250 mV (Figure 5A). Figure 5 shows bores 11210056 and 11210040 represented in coloured markers to highlight the fluctuating nature of their chemistry over the study period.

4.3. Statistical analysis

Statistical analysis of groundwater chemistry shows distinct groupings and chemical relationships based on bore site and chemical variables. Figure 7 displays a score plot of the PC analysis, with groupings based on chemistry of each bore site. There is a distinct main grouping for bores 11210004, 11210040, 11210041 and 11210051. Bore 11210045 (yellow triangle markers) appears distinct from the other bores. Bores 183021 and 183022 also cluster separately.

The most significant calculated coefficients (Eigenvectors) based on chemical variables were S^{2-} (0.387), DO (-0.384), NO_3^- (-0.382) and SO_4^{2-} (0.375) for Principal Component 1 (PC1) and Mg^{2+} (0.467), Ca^{2+} (0.460), Na^+ (0.389), K^+ (0.347), and Fe^{2+} (-0.338) for Principal Component 2 (PC2). The grouping of data points in Figure 7, based on groundwater bore sites, shows the principal variables contributing to the

variance in data for bores 183021 and 183022 were S^{2-} , SO_4^{2-} and Fe^{2+} . For bore 11210045, the principal influential variables were Mg^{2+} , Ca^{2+} , Na^+ and K^+ . DO and NO_3^- are principal influences on the variance in data for the main cluster of bores (11210004, 11210040, 11210041 and 11210051) as are Mg^{2+} , Ca^{2+} and, to a lesser degree, Fe^{2+} .

Cluster analysis based on major chemistry variables shows a high degree of similarity between S^{2-} and SO_4^{2-} (97.10 %) (Figure 8). These both cluster with Fe^{2+} (77.25% similarity) separately from the other major ions, indicating a strong relationship between these variables. Similarly, DO and NO_3^- show a strong similarity (86.34%), indicating a correlation between these variables.

4.4. Sediment analysis

Sediment cores were collected in 1-metre lengths during installation of bores 183021 and 183022. The sediment cores were composed mostly of very dense, blue-grey clay. Aquifer material extracted from 9–12 m BGL was sandy, clayey silt with some coarse quartz grains (≤ 5 mm diameter). Muscovite was also observed frequently throughout.

Field observations showed that pale yellow and red-brown mottling occurred commonly in the cores after extraction (Figure 9).

XRD analysis on sediment samples from bores 183021 and 183022 revealed the dense clays to be mostly kaolinite (Figure 10). The aquifer material composed sand, clay and silt was > 85 weight % quartz. The weight % abundance of muscovite/illite appears to correlate with weight % of kaolinite. This may be indicative of the chemical weathering process of muscovite/illite to kaolinite (Islam et al., 2002; Ekosse, 2010). Fe-oxide minerals are present throughout the sediments, including amorphous (non-crystalline) minerals ranging from 1.3 to 27.3 weight % (Figure 9).

5. Discussion

5.1. Groundwater chemistry: NO_3^-

The Queensland Government's water quality objectives for protecting aquatic ecosystems in the Johnstone River basin (coastal floodplains) permit NO_3^- concentrations of up to 4 mg/L for shallow groundwater aquifers (< 15 m depth) and up to 13 mg/L for moderate depth groundwater (15–40 m depth) (DEHP, 2014). The measured NO_3^- concentrations in groundwater samples from all bores remained within these limits, except for bores 11210004, 11210041 and 11210051 (Figure 5). NO_3^- concentrations ranged from below detection limits (0.02 mg/L) to a

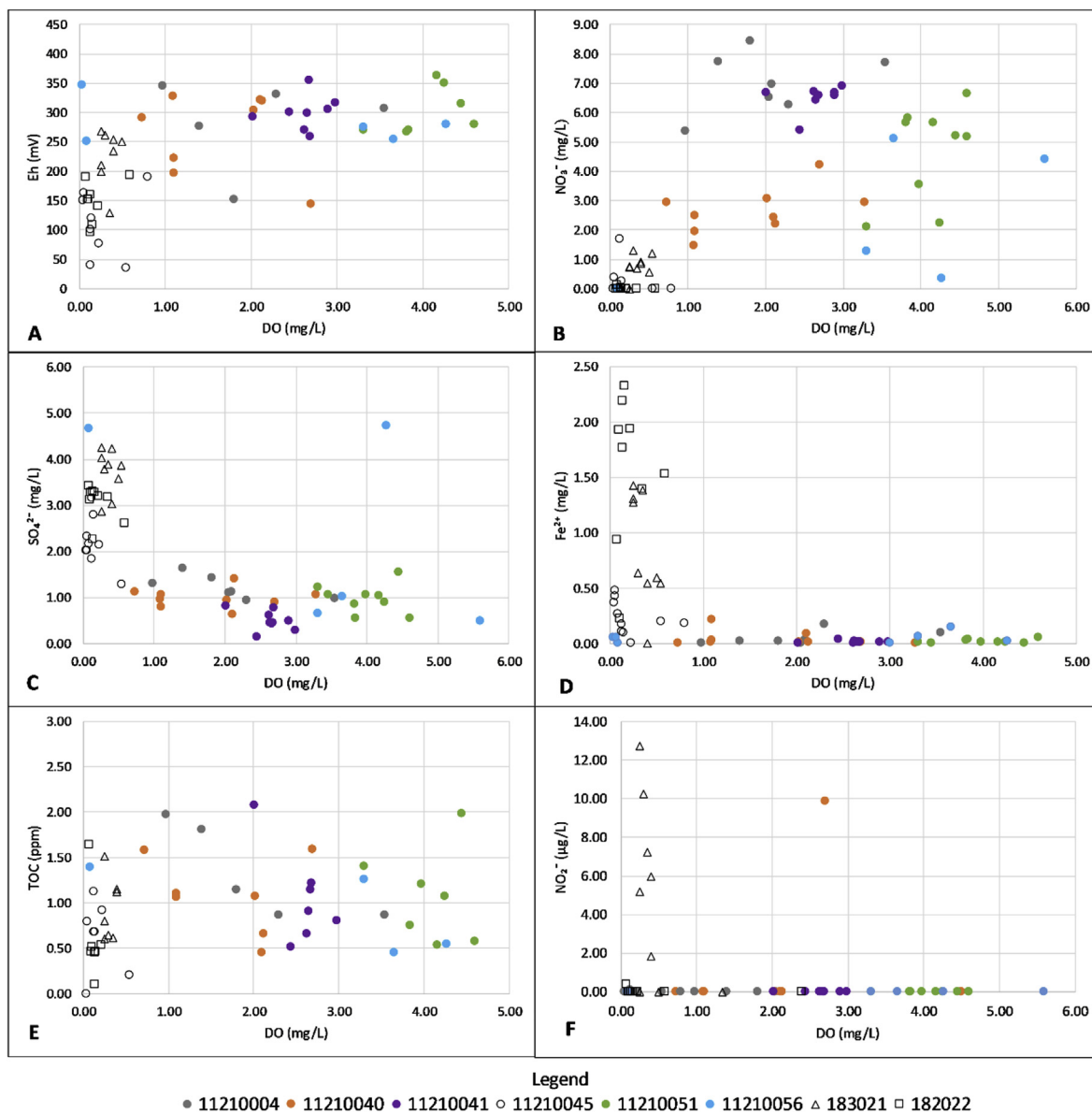


Figure 5. Displaying the activity of the major chemical redox parameters in relation to DO availability (including redox potential (Eh) and measured concentrations of NO₃⁻, NO₂⁻, SO₄²⁻, Fe²⁺ and TOC).

maximum value of 8.43 mg/L measured from bore 11210004 in February 2018. Some bores displayed a slight increase in NO₃⁻ concentrations following rainfall events in February and March (bores 11210004, 11210045, 183021 and 183022) while bores 11210040 and 11210051 experienced a decline in NO₃⁻ concentrations at the same time.

Bores 11210004 and 11210041 recorded the highest average NO₃⁻ concentrations across this study period (6.87 mg/L and 6.51 mg/L, respectively). Both these bores recorded rapid SWL responses to recharge from rainfall (Figure 4), indicating the shallow alluvium in these locations has greater potential for rapid infiltration of surface water. Examination of the historical bore installation report of bore 11210041 shows that the groundwater aquifer is overlain with ~13 m of silty, fine-coarse sand and clay, indicating higher potential hydraulic conductivity. Hence, localised variations in clay content throughout the catchment may contribute to greater infiltration and transport of NO₃⁻ to groundwater aquifers.

5.1.1. Total organic carbon

Overall TOC concentrations in groundwater remained <3 mg/L (Figure 5). There appeared a weak relationship between rainfall and

TOC, with some increase in TOC concentrations in groundwater following the periods of high rainfall in February and March. For example: TOC concentrations in bore 11210004 before rainfall events in February ranged from 0.87 to 1.41 mg/L and following February ranged from 1.15 to 2.60 mg/L. Similarly, TOC concentrations in bore 11210045 before rainfall events in February ranged from below detection limits to 0.35 mg/L and following February ranged from 0.68 to 1.13 mg/L. However, measured TOC in groundwater across all sites remained consistently within the range expected of pristine, unpolluted aquifers (0.1–4 mg/L) (Regan et al., 2017), regardless of aquifer depth. This indicates that a major amount of soil-derived TOC is being removed or consumed before deep infiltration to groundwater can occur. It is possible that the low permeability of the clay, as observed at the site of bores 183021 and 183022, can create a barrier to deep infiltration of chemical species like DO, NO₃⁻ and TOC to deep drainage. However, there are specific knowledge gaps regarding the amount of TOC actually being produced in the soil biochemical processes, which prevents the calculation of a representative TOC soil-water balance.

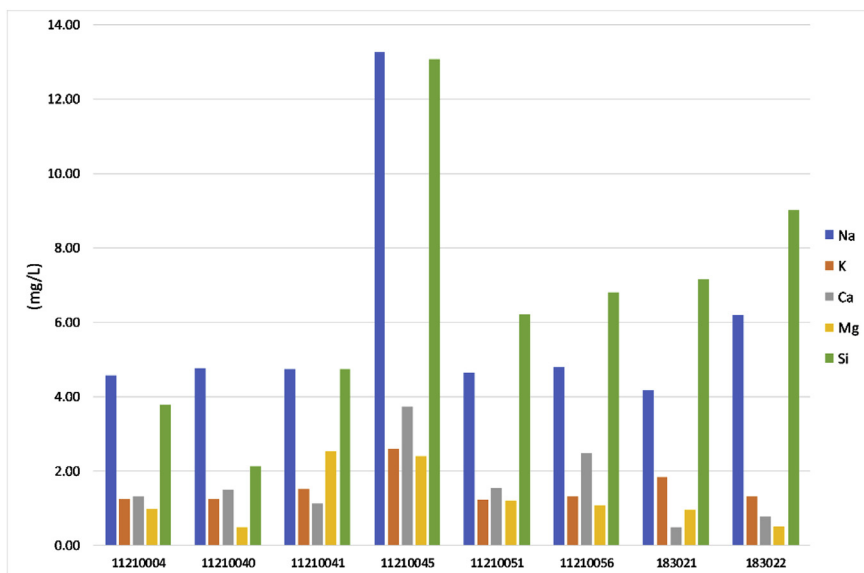


Figure 6. Calculated average concentrations of measured major cations at each groundwater bore site (2017–2018).

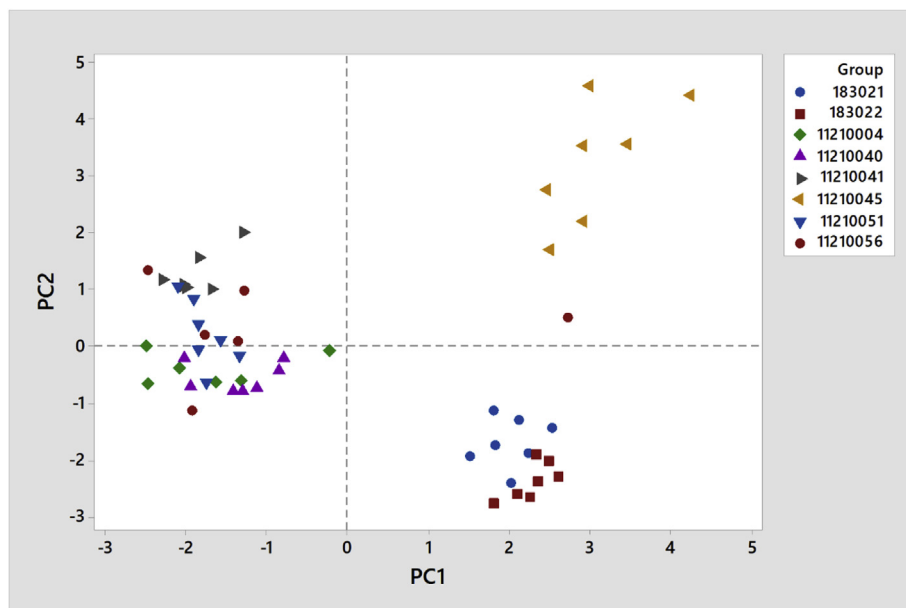


Figure 7. Groundwater chemistry (major ions) PC analysis score plot. Data point identification is based on bore site (“Group”).

5.1.2. Denitrification potential

Groundwater chemistry analysis showed a relationship between DO and NO₃ concentrations (Figure 5). Bores 11210004, 11210041 and 11210051 displayed the highest DO and NO₃ concentrations while bores 11210045, 183021 and 183022 consistently displayed the lowest DO and NO₃ concentrations. Bore 11210045 was essentially anoxic throughout the year (<0.5 mg/L DO). *Thayalakumaran et al. (2007)* observed this relationship in their study of groundwater in the sugarcane-dominated lower Burdekin catchment, ~ 190 km south of the Liverpool Creek region. They recorded that NO₃ concentrations were strongly correlated to DO concentrations and also negatively correlated to Fe²⁺ concentrations, which ranged from <2 mg/L to >15 mg/L. The high Fe²⁺ in groundwater contributed to higher potential for NO₃ reduction via autotrophic DN with Fe²⁺ as a key electron-donor. This inverse relationship between Fe²⁺, NO₃ and DO is also apparent in the groundwater chemistry analysis from this study (Figure 5), with bores lower in DO and NO₃ displaying higher Fe²⁺.

Other studies have shown Fe²⁺-rich groundwaters low in NO₃ also linked to elevated SO₄²⁻ concentrations (*Mariotti et al., 1988; Korom, 1992; Jessen et al., 2017*). The potential for NO₃ reduction via autotrophic DN in anaerobic saturated environments is well documented (*Böttcher et al., 1990; Hiscock et al., 1991; Jahangir et al., 2012; Burghate and Ingole, 2014; McAleer et al., 2017*). In locations where DO is unavailable as an electron-donor, bacteria may utilise inorganic geochemical sources like Mn²⁺, Fe²⁺, S²⁻ or sulphide minerals (e.g. pyrite; FeS₂) (*Korom 1992; Zhang et al., 2015*). DN reactions which utilise these common inorganic electron-donors often result in the production of Fe³⁺ and SO₄²⁻ (*Cardoso et al., 2006; Appelo and Postma, 2010; Ishii et al., 2016*). This could explain the observed negative correlation between DO & NO₃ and Fe³⁺ & SO₄²⁻. Figure 5 also shows that groundwater at sites 11210045, 183021 and 183022 was consistently within Eh conditions favourable for DN to occur (<250 mV; *Korom, 1992; Jahangir et al., 2012*).

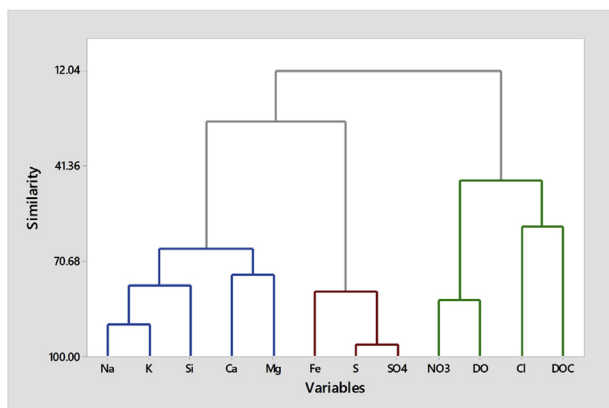
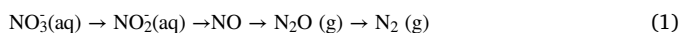


Figure 8. Groundwater chemistry cluster analysis dendrogram (to 3 clusters as defined by blue, red and green) of chemical variables in all groundwater samples.

Environmental NO_2 commonly exists in trace level concentration (Appelo and Postma, 2010) but can be used as an indicator of DN if occurring in relatively elevated concentrations. This is due to it occurring as a metastable intermediate species of DIN during the DN process (Eq. 1; Appelo and Postma, 2010):



NO_2 concentrations across the catchment remained low ($<0.02 \mu\text{g/L}$) (Figure 5). However, bore 183021 consistently displayed measurable NO_2 concentrations as well as consistently lower NO_3 . These NO_2 concentrations peaked in February 2018 during the onset of higher rainfall ($12.75 \mu\text{g/L}$), coincident with the only other significant NO_2 measurement in the nearby bore 11210040 ($9.89 \mu\text{g/L}$). This also coincided with a marked decline in redox potential in bore 11210040 (from 305 mV to 145 mV) and a decline in DO concentrations in both bores. Overall, the groundwater chemistry data indicates that autotrophic DN potential is high in specific groundwater aquifers where DO and DOC concentrations are consistently low and electron-donors in the form of Fe^{2+} and S^{2-} are available.

5.2. Groundwater chemistry: spatial variation

Analysis of the measured groundwater data shows variability in groundwater chemistry across the catchment (Figures 5, 6, 7, and 8). Half

of the sites displayed similar chemical grouping (bores 11210004, 11210040, 11210041 and 11210051), but bores 11210045, 183021 and 183022 were noticeably distinct from this group (Figure 7).

While the groundwater chemistry of most sites remained within a stable range of concentrations over the study period, bore 11210056 displayed distinct fluctuations (Figure 5); DO concentrations fluctuated in bore 11210056 from 0.04 to 5.60 mg/L (with a noticeable positive correlation with rainfall events in February/March 2018); NO_3 concentrations fluctuated from 0.70 to 6.42 mg/L and SO_4^{2-} concentrations ranged from 0.65 to 5.68 mg/L. Similarly, DO concentrations in bore 11210040 fluctuated over the study period from 0.73 to 3.28 mg/L (Figure 5). However, in contrast to bore 11210056, these showed a negative correlation with rainfall events, with bore 11210040 also recording a decrease in redox potential in February following rainfall (from 305 to 145 Eh). This highlights the localised variability of chemical conditions within the alluvium; some local groundwater aquifers may be recharged with dissolved oxygen from precipitation, whereas recharge may contribute to reducing conditions in other groundwater aquifers.

The grouping of chemical variables in the results of the cluster analysis (Figure 8) can be interpreted as displaying various processes influencing groundwater chemistry within the catchment. On one hand, the chemical variables are indicative of lithological factors such as the mineralogy of the alluvium and parent rock materials (blue cluster; Na^+ , K^+ , Si^{4+} , Ca^{2+} and Mg^{2+} with $>77\%$ similarity). A clear correlation is observed between DO and NO_3 (green cluster; at $>80\%$ similarity), whose presence is derived solely from meteoric and surface processes, as is DOC. Between these are the variables whose concentration is influenced by specific redox conditions; a combination of the variable availability of subsurface oxygen and geochemical influences from clay mineral surfaces (red cluster; Fe^{2+} , S^{2-} and SO_4^{2-}). This is supported by the PC analysis (Figure 7), which characterises these clusters of variables in a similar way, highlighting their spatial influence on groundwater chemistry.

Interestingly, cluster analysis indicates a clear separation between Na^+ and Cl^- (Figure 8). It may be expected that a stronger statistical link between Na^+ and Cl^- would be observed due to the influence of seawater-derived NaCl in coastal precipitation, which would result in a calculated Na^+/Cl^- ratio = 1 (Hounslow, 1995). But there are other potential sources of both Na^+ and Cl^- . A calculated Na^+/Cl^- ratio of <1 was found for all groundwater bores in the study except 11210045. This can be expected in groundwater from agricultural areas with Cl^- input from Muriate of Potash (MOP; KCl; potassium chloride) (Bohlke, 2002). MOP is a commonly used fertiliser on sugarcane plantations, with a

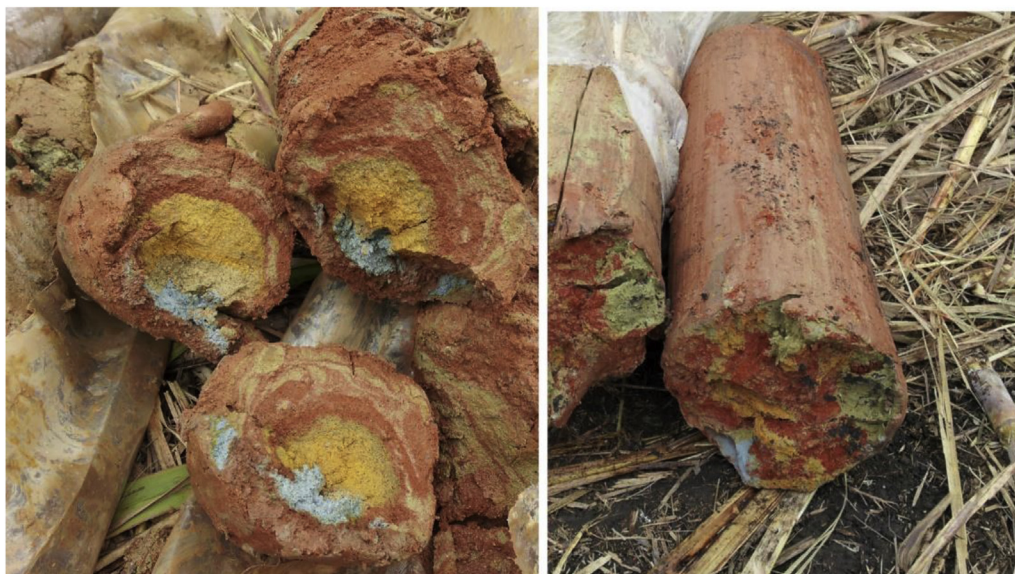


Figure 9. Extracted sediment cores from the paddock location of groundwater bores 183021 and 183022. The figure displays cores removed from 4-5 m BGL.

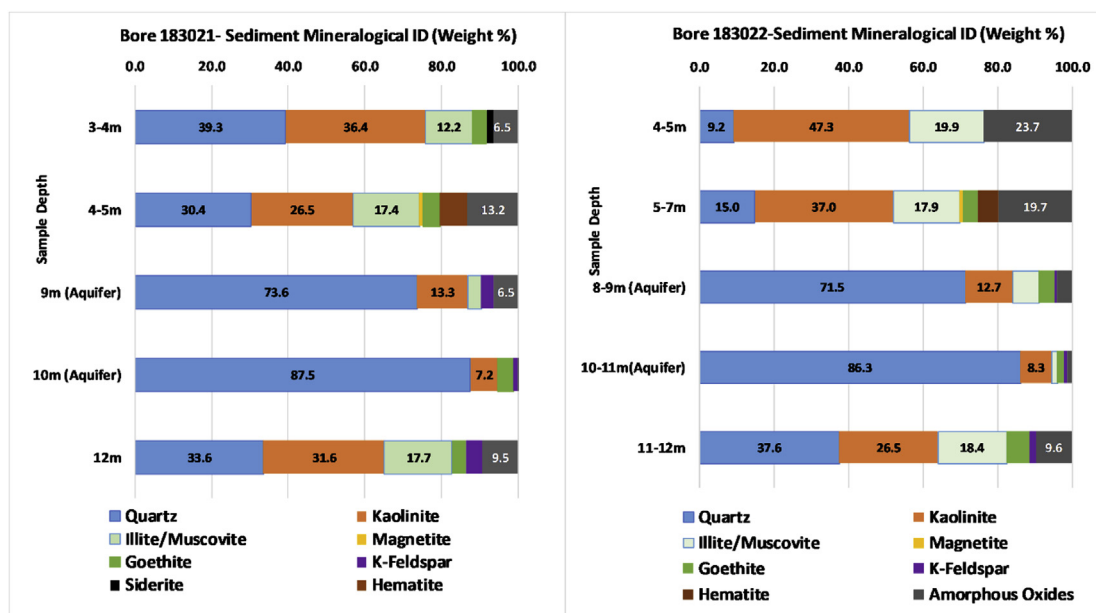


Figure 10. XRD analysis showing identified mineralogy (in weight %) corresponding to specific depths for bores 183021 and 183022. Higher weight % values of quartz correspond to location of aquifer material at 9–11 m BGL.

typical K^+/Cl^- content ratio of $\sim 50/50$ (Di Bella et al., 2013; Calcino et al., 2018) and was applied at a known rate of 100 kg K^+ /ha (2014–2016) at the site of bores 183021 and 183022 (Masters et al., 2017). This may explain the correlation between Cl^- with the surface-derived variables DO, NO_3^- and TOC (Figure 8.)

The calculated Na^+/Cl^- ratio from the measured groundwater chemistry data of bore 11210045 was >1 , indicating a Na^+ source other than NaCl (Hounslow, 1995). This is most likely derived from the weathering of silicate minerals such as plagioclase feldspar ($NaAlSi_3O_8$) in the decomposed metamorphic rock aquifer material, also contributing higher dissolved Na^+ , K^+ , Si^{4+} (Figure 6) (Appelo and Postma, 2010).

5.3. Sediment mineralogy and SO_4^{2-}

Sediment cores extracted from the installation of bores 183021 and 183022 revealed very dense clays overlying and underlying the silty, clayey-sand aquifer material found at 9 m BGL. Cores extracted from depths down to 5 m displayed distinct colouration from Fe^{2+} and S^{2-} oxidation (Figure 9). This is consistent with rapid aeration of Fe-sulphides, producing the pale-yellow pigment of Jarosite ($KFe_3(SO_4)_2(OH)_6$), while Fe-oxides goethite ($FeOOH$) and hematite (Fe_2O_3) produce a distinct red colouration (Nordstrom, 1982; Lynn and Pearson, 2000).

XRD analysis shows kaolinite as the dominant clay mineral within the unconsolidated alluvium, with Fe-oxide minerals present, including goethite ($FeO(OH)$) and “amorphous” oxide minerals without identifiable crystalline structure (Figure 10). Clay minerals, amorphous oxides and hydroxides are amongst the most common adsorbents in subsurface environments (Hounslow, 1995). Kaolinite clay is known to be characteristic of heavily weathered, tropical environments and makes a suitable anion exchanger of both SO_4^{2-} and NO_3^- (Hounslow, 1995; Eash et al., 2016). This is due to its variable-charge when H^+ ions are accepted on the edges of the plate-like kaolinite crystal structure during the dissolution of hydroxyl ions (OH^-) in lower pH environments (Eash et al., 2016). This explains the observed high AEC of acidic *Bulgun* soils in the South Johnstone River basin and their ability hold S^{2-} and SO_4^{2-} (Schroeder et al., 2007).

The Fe-oxides present in the subsoil environment may be inhibiting the transport of soil-derived organic carbon to groundwater aquifers, as organic carbon has a high capacity for adsorption to hydrous Fe-oxides

(Luider et al., 2003). It is a possibility, therefore, that a combination of adsorption and low permeability/infiltration is also contributing to the lower TOC and NO_3^- concentrations in groundwater within the catchment, where zones of heavy kaolinite clays are present.

Sulphide minerals are not common among the geological parent material in the Liverpool Creek catchment and although sulphur oxidation was apparent in sediment cores during the installation of bores 183021 and 183022, XRD analysis on sediment samples did not reveal the presence of any sulphide minerals (Figure 10). Historical data indicates that some seawater intrusion may occur in the coastal sediments near the inlet of Liverpool Creek, but there has been no evidence of seawater intrusion (which would supply S^{2-}) into the alluvial aquifers (DSITI, 2013). This raises a question: what is the major source of sulphur in the catchment soils and groundwater? Precipitation is a source of atmospheric SO_4^{2-} but there is scarce accurate data available regarding the amount of deposition of SO_4^{2-} from rainfall in Australia. In their study on NO_3^- and SO_4^{2-} in soil profiles under sugarcane in the South Johnstone River catchment, Rasiyah et al. (2003) concluded that the SO_4^{2-} content preceded current land use and was most likely derived from retention of historical SO_4^{2-} in precipitation. However, no isotopic analysis was performed for source determination (e.g. $\delta^{18}O-SO_4^{2-}$) and the conclusion regarding rainfall input was drawn mainly from calculations based on observations from a study conducted in New South Wales (Ayers and Manton, 1991) and assumed complete retention of SO_4^{2-} over ~ 6000 years.

Most of the S^{2-} present in productive agricultural soils usually comes from decomposed soil organic matter (Tabatabai, 1984; Schlesinger, 1991; Schroth et al., 2007). The biologically-catalysed oxidation of sulphur in soil organic matter (SOM) produces SO_4^{2-} and under anoxic conditions, sulphur and SO_4^{2-} is transformed to H_2S (Fuentes-Lara et al., 2019). However, the biochemical processes of sulphur activity in agricultural soils is very complex; overall, the abundant forms of sulphur in soils as a result of microbial redox activity includes S^{2-} , SO_4^{2-} , SO_3^{2-} (sulphite) and $S_2O_3^{2-}$ (thiosulphate) (Schroth et al., 2007; Fuentes-Lara et al., 2019).

Sugarcane also requires sulphur application in relatively large amounts (25 kg S/ha/year) for plant structure and growth (Schroeder et al., 2007). Elemental S^{2-} is a common component in sugarcane fertilisers (Boswell and Friesen, 1993; Calcino et al., 2018), with studies showing that S^{2-} application improves nitrogen-use efficiency

(Bologna-Campbell et al., 2013). Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) contains 12–18% sulphur (Calcino et al., 2018) and is known to be used in the South Johnstone region as a soil ameliorant. The research conducted by Masters et al. (2017) for the DNRME's P2R project in the Liverpool Creek catchment (on the location of bores 183021 and 183022) describes the fertiliser framework for the plantation paddock utilised N-rich fertiliser coated with elemental S^{2-} from 2014 to 2016, at rates of 94 kg N/ha and 110 kg N/ha. Given the known high AEC of the *Bulgun* soils, fertilisers and soil conditioners cannot be ruled out as major sources of S^{2-} in the catchment. Further detailed research may prove whether their widespread application may actually be beneficial for enhancing autotrophic DN potential in tropical regions of high AEC soils by providing a suitable inorganic replacement for organic carbon in anaerobic groundwater zones.

6. Conclusion

Over the course of this twelve-month study, groundwater in the Liverpool Creek catchment area of the South Johnstone consistently displayed NO_3^- concentration mostly within the limits of official environmental guidelines. While it is likely that a large percentage of NO_3^- is lost from the catchment through surface runoff and shallow drainage, observations from this study indicate that anion adsorption on clay surfaces may also contribute to NO_3^- reduction. This reduces the potential for groundwater aquifers to provide a NO_3^- contaminant pathway to the GBR marine zone. Similarly, soil-derived organic carbon is either consumed by biological soil processes or adsorbed by Fe-oxides before deep infiltration to groundwater. Moreover, the observed relationship between NO_3^- , DO, TOC, SO_4^{2-} and Fe^{2+} cannot be overlooked as a probable indicator of autotrophic DN by anaerobic microorganisms in specific areas of the catchment, given appropriate redox potential conditions. Further research focussing on the identification of microbiological species present in groundwater may provide a more quantitative assessment of DN potential in both shallow and deep groundwater aquifers. It is also likely that decaying organic matter from sugarcane crops and anthropogenic input from fertilisers and soil conditioners enriches the concentration of S^{2-} and SO_4^{2-} in the catchment. An indirect consequence of this may be an increased potential for autotrophic DN in anaerobic groundwater aquifers.

Declarations

Author contribution statement

Jim Stanley: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Lucy Reading: Conceived and designed the experiments; Contributed reagents, materials, analysis tools or data.

Funding statement

This work was supported by the Queensland Government's Queensland Reef Water Quality Program.

Data availability statement

Data associated with this study has been deposited at Mendeley Data under the accession number <https://doi.org/10.17632/RT6X6362YX.1>.

Declaration of interests statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

Acknowledgements

This research project was made possible by funding from the Queensland Government's Queensland Reef Water Quality Program. Thanks to staff from DNRME and MSF Sugar Pty Ltd for their assistance.

References

- Amano, H., Nakagawa, K., Berndtsson, R., 2016. Groundwater geochemistry of a nitrate-contaminated agricultural site. *Environmental Earth Sciences* 75 (15).
- Appelo, C., Postma, D., 2010. *Geochemistry, Groundwater and Pollution*, second ed. A.A.Balkema.
- Ayers, G.P., Manton, M.J., 1991. Rainwater composition at two BAPMoN regional stations in SE Australia. *Tellus B: Chem. Phys. Meteorol.* 43 (5), 379–389.
- Böhlke, J., 2002. Groundwater recharge and agricultural contamination. *Hydrogeol. J.* 10 (1), 153–179.
- Bologna-Campbell, I., Franco, H., Vitti, A., Faroni, C., Costa, M., Trivelin, P., 2013. Impact of nitrogen and sulphur fertilisers on yield and quality of sugarcane plant crop. *Sugar Tech* 15 (4), 424–428.
- <http://www.bom.gov.au/>, 2019.
- Boswell, C., Friesen, D., 1993. Elemental sulfur fertilizers and their use on crops and pastures. *Fert. Res.* 35 (1–2), 127–149.
- Böttcher, J., Strebel, O., Voerkelius, S., Schmidt, H., 1990. Using isotope fractionation of nitrate-nitrogen and nitrate-oxygen for evaluation of microbial denitrification in a sandy aquifer. *J. Hydrol.* 114 (3–4), 413–424.
- Burghate, S., Ingole, N., 2014. Biological denitrification – a review. *J. Environ. Sci. Comput. Sci. Eng. Technol.* 3 (1).
- Calcino, D., Schroeder, B., Panitz, J., Hurney, A., Skocaj, D., Wood, A., Salter, B., 2018. *Australian Sugarcane Nutrition Manual*.
- Cardoso, R., Sierra-Alvarez, R., Rowlette, P., Flores, E., Gómez, J., Field, J., 2006. Sulfide oxidation under chemolithoautotrophic denitrifying conditions. *Biotechnol. Bioeng.* 95 (6), 1148–1157.
- Connolly, N., Pearson, R., Loong, D., Maughan, M., Brodie, J., 2015. Water quality variation along streams with similar agricultural development but contrasting riparian vegetation. *Agric. Ecosyst. Environ.* 213, 11–20.
- Connor, S., Nelson, P., Armour, J., Hénault, C., 2012. Hydrology of a forested riparian zone in an agricultural landscape of the humid tropics. *Agric. Ecosyst. Environ.* 180, 111–122.
- Davis, A., Thorburn, P., Lewis, S., Bainbridge, Z., Attard, S., Milla, R., Brodie, J., 2013. Environmental impacts of irrigated sugarcane production: herbicide run-off dynamics from farms and associated drainage systems. *Agric. Ecosyst. Environ.* 180, 123–135.
- Devlin, M., Brodie, J., 2005. Terrestrial discharge into the Great Barrier Reef Lagoon: nutrient behaviour in coastal waters. *Mar. Pollut. Bull.* 51 (1–4), 9–22.
- Di Bella, L., Stacey, S., Benson, A., Royle, A., Holzberger, G., 2013. An assessment of controlled release fertiliser in the Herbert cane-growing region. *Int. Sugar J.* 115 (1380), 868–872.
- Department of Environment and Heritage Protection (DEHP), 2014. *Johnstone River Basin Environmental Values and Water Quality Objectives*. Queensland Government.
- DSITI, 2013. *Conceptualisation of Groundwater System for Lower Johnstone River Basin: Final Report*. Queensland Department of Science, Information Technology, Innovation and the Arts, Brisbane.
- DSITI, 2016. *Land Use Summary 1999–2015: Wet Tropics NRM Region*. Department of Science, Information Technology and Innovation, Queensland Government.
- Eash, N., Sauer, T., O'Dell, D., Odoi, E., Bratz, M., Harpstead, M., 2016. *Soil Science Simplified*, sixth ed. Wiley Blackwell, Hoboken, New Jersey.
- Ekosse, G., 2010. Kaolin deposits and occurrences in Africa: geology, mineralogy and utilization. *Appl. Clay Sci.* 50 (2), 212–236.
- FAO, 2019. *World Fertilizer Trends and Outlook to 2022*. Rome.
- Fuentes-Lara, Laura Olivia, Medrano, Julia, Perez-Labrada, Fabian, Rivas, Erika, 2019. From elemental sulfur to hydrogen sulfide in agricultural soils and plants. *Molecules* 24.
- Hair, I.D., 1990. *Hydrogeology of the Russell and Johnstone rivers alluvial valleys, north Queensland*, geological survey of Queensland record. Geological Survey of Queensland.
- Hoshmand, A. Reza, 2017. *Statistical Methods for Environmental & Agricultural Sciences*, 2nd. Taylor and Francis.
- Hiscock, K., Bense, V., 2014. *Hydrogeology*. John Wiley and Sons.
- Hiscock, K., Lloyd, J., Lerner, D., 1991. Review of natural and artificial denitrification of groundwater. *Water Res.* 25 (9), 1099–1111.
- Hounslow, A., 1995. *Water Quality Data*. Lewis Publishers.
- Hunter, H., Walton, R., 2008. Land-use effects on fluxes of suspended sediment, nitrogen and phosphorus from a river catchment of the Great Barrier Reef, Australia. *J. Hydrol.* 356 (1–2), 131–146.
- Hutchings, P., Haynes, D., Goudkamp, K., McCook, L., 2005. Catchment to reef: water quality issues in the Great barrier reef region—an overview of papers. *Mar. Pollut. Bull.* 51 (1–4), 3–8.

- Ishii, S., Joikai, J., Otsuka, S., Okabe, S., 2016. Denitrification and nitrate-dependent Fe(II) oxidation in various *pseudogulbenkiania* strains. *Microb. Environ.* 31 (3), 293–298.
- Islam, M., Stuart, R., Risto, A., Vesa, P., 2002. Mineralogical changes during intense chemical weathering of sedimentary rocks in Bangladesh. *J. Asian Earth Sci.* 20 (8), 889–901.
- Jahangir, M., Johnston, P., Khalil, M., Richards, K., 2012. Linking hydrogeochemistry to nitrate abundance in groundwater in agricultural settings in Ireland. *J. Hydrol.* 448–449, 212–222.
- Jessen, S., Postma, D., Thorling, L., Müller, S., Leskelä, J., Engesgaard, P., 2017. Decadal variations in groundwater quality: a legacy from nitrate leaching and denitrification by pyrite in a sandy aquifer. *Water Resour. Res.* 53 (1), 184–198.
- Juntakut, Pongpun, Snow, Daniel D., Haacker, Erin M.K., Ray, Chittaranjan, 2019. The long term effect of agricultural, vadose zone and climatic factors on nitrate contamination in Nebraska's groundwater system. *J. Contam. Hydrol.* 220, 33–48.
- Kellner, E., Hubbard, J., Ikem, A., 2015. A comparison of forest and agricultural shallow groundwater chemical status a century after land use change. *Sci. Total Environ.* 529, 82–90.
- Koh, D., Ko, K., Kim, Y., Lee, S., Chang, H., 2007. Effect of agricultural land use on the chemistry of groundwater from basaltic aquifers, Jeju Island, South Korea. *Hydrogeol. J.* 15 (4), 727–743.
- Korom, Scott F., 1992. Natural Denitrification in the Saturated Zone: A Review. *Water Resources Res.* 28, 1657–1668.
- Lee, M., Shevliakova, E., Stock, C., Malyshev, S., Milly, P., 2019. Prominence of the tropics in the recent rise of global nitrogen pollution. *Nat. Commun.* 10 (1).
- Luider, C., Peticrew, E., Curtis, P., 2003. Scavenging of dissolved organic matter (DOM) by amorphous iron hydroxide particles Fe(OH)₃(s). *Hydrobiologia* 494 (1-3), 37–41.
- Lynn, W., Pearson, M., 2000. The color of soil. *Sci. Teach.* 67 (5), 20–23.
- Mariotti, A., Landreau, A., Simon, B., 1988. 15N isotope biogeochemistry and natural denitrification process in groundwater: application to the chalk aquifer of northern France. *Geochem. Cosmochim. Acta* 52 (7), 1869–1878.
- Masters, B., Tahir, N., Fries, J., Mortimore, C., Enderlin, N., Armour, J., 2017. Paddock-scale water quality monitoring of nitrogen fertiliser management practices in sugarcane cropping. Queensland Government.
- McAleer, E., Coxon, C., Richards, K., Jahangir, M., Grant, J., Mellander, P., 2017. Groundwater nitrate reduction versus dissolved gas production: a tale of two catchments. *Sci. Total Environ.* 586, 372–389.
- Mitchell, A., Reghenzani, J., Faithful, J., Furnas, M., Brodie, J., 2009. Relationships between land use and nutrient concentrations in streams draining a 'wet-tropics' catchment in northern Australia. *Mar. Freshw. Res.* 60 (11), 1097.
- Murtha, G., 1986. Soils of the Tully-Innisfail Area, North Queensland. [Glen Osmond, S. Aust.]. Commonwealth Scientific and Industrial Research Organization.
- Nordstrom, D., 1982. Aqueous pyrite oxidation and the consequent formation of secondary minerals. In: Kittrick, J., Fanning, D., Hosner, L. (Eds.), *Acid Sulfate Weathering*. Soil Science Society of America, Madison, Wisconsin.
- Queensland Department of Primary Industries (QDPI), 1995. Overview of water resources and related issues: the Southern Wet Tropics region. Queensland Government, Brisbane, Queensland.
- Rajmohan, N., Elango, L., 2005. Nutrient chemistry of groundwater in an intensively irrigated region of southern India. *Environ. Geol.* 47 (6), 820–830.
- Rasiah, V., Armour, J., Menzies, N., Heiner, D., Donn, M., Mahendrarajah, S., 2003. Nitrate retention under sugarcane in wet tropical Queensland deep soil profiles. *Soil Res.* 41 (6), 1145.
- Rasiah, V., Armour, J., Nelson, P., 2013. Nitrate in shallow fluctuating groundwater under sugarcane: quantifying the lateral export quantities to surface waters. *Agric. Ecosyst. Environ.* 180, 103–110.
- Ratchawang, S., Chotpanarat, S., 2019. Nitrate contamination in groundwater in sugarcane field, suphan buri province, Thailand. *Int. J. Recent Technol. Eng.* 8 (1S), 239–242.
- Reading, L., Bajracharya, K., Wang, J., 2019. Simulating deep drainage and nitrate leaching on a regional scale: implications for groundwater management in an intensively irrigated area. *Irrigat. Sci.* 37 (5), 561–581.
- Regan, S., Hynds, P., Flynn, R., 2017. An overview of dissolved organic carbon in groundwater and implications for drinking water safety. *Hydrogeol. J.* 25 (4), 959–967.
- Robinson, N., Brackin, R., Vinall, K., Soper, F., Holst, J., Gamage, H., Paungfoo-Lonhienne, C., Rennenberg, H., Lakshmanan, P., Schmidt, S., 2011. Nitrate paradigm does not hold up for sugarcane. *PLoS One* 6 (4), e19045.
- Schlesinger, W., 1991. *Biogeochemistry: an Analysis of Global Change*. Academic Press Inc, San Diego, California.
- Schroeder, B., Wood, A., Moody, P., Panitz, J., Benn, J., 2007. *Soil-specific Nutrient Management Guidelines for Sugarcane Production in the Johnstone Catchment*. BSES Ltd.
- Schroth, A., Bostick, B., Graham, M., Kaste, J., Mitchell, M., Friedland, A., 2007. Sulfur species behavior in soil organic matter during decomposition. *J. Geophys. Res.: Biogeosciences* 112 (G4) n/a-n/a.
- Shukla, S., Saxena, A., 2018. Global status of nitrate contamination in groundwater: its occurrence, health impacts, and mitigation measures. *Handbook of Environmental Materials Management*. Springer International Publishing.
- Tabatabai, M., 1984. Importance of sulphur in crop production. *Biogeochemistry* 1 (1), 45–62.
- Tate, R., 2000. *Soil Microbiology*. John Wiley, New York, N.Y.
- Thayalakumaran, T., Bristow, K., Charlesworth, P., Fass, T., 2007. Geochemical conditions in groundwater systems: implications for the attenuation of agricultural nitrate. *Agric. Water Manag.* 95 (2), 103–115.
- Thorburn, P., Biggs, J., Attard, S., Kemei, J., 2011. Environmental impacts of irrigated sugarcane production: nitrogen lost through runoff and leaching. *Agric. Ecosyst. Environ.* 144 (1), 1–12.
- Zhang, H., Wang, H., Yang, K., Chang, Q., Sun, Y., Tian, J., Long, C., 2015. Autotrophic denitrification with anaerobic Fe²⁺ oxidation by a novel *Pseudomonas* sp. W1. *Water Sci. Technol.* 71 (7), 1081–1087.
- Zhou, J., Gu, B., Schlesinger, W., Ju, X., 2016. Significant accumulation of nitrate in Chinese semi-humid croplands. *Sci. Rep.* 6 (1).