



Isotopic evidence for nitrate sources and controls on denitrification in groundwater beneath an irrigated agricultural district

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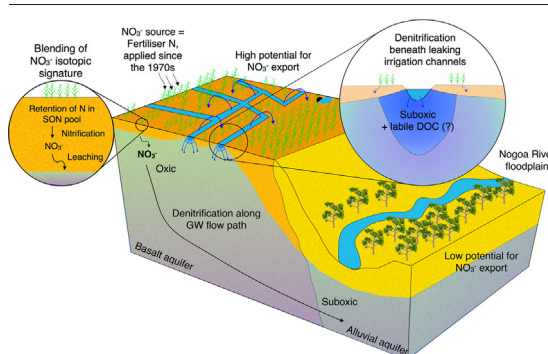
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HIGHLIGHTS

- Groundwater NO_3^- in an irrigated agricultural district was studied using isotope tracers.
- Groundwater NO_3^- is linked to modern irrigation practices commencing in the 1970s.
- NO_3^- is derived from N fertilisers which was previously retained in the SON pool.
- Denitrification is a key feature of the groundwater system.
- A conceptual model for district-scale NO_3^- production and attenuation is discussed.

GRAPHICAL ABSTRACT



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ABSTRACT

The application of N fertilisers to enhance crop yield is common throughout the world. Many crops have historically been, or are still, fertilised with N in excess of the crop requirements. A portion of the excess N is transported into underlying aquifers in the form of NO_3^- , which is potentially discharged to surface waters. Denitrification can reduce the severity of NO_3^- export from groundwater. We sought to understand the occurrence and hydrogeochemical controls on denitrification in NO_3^- -rich aquifers beneath the Emerald Irrigation Area (EIA), Queensland, Australia, a region of extensive cotton and cereal production. Multiple stable isotope (in H_2O , NO_3^- , DIC, DOC and SO_4^{2-}) and radioactive isotope (^3H and ^{36}Cl) tracers were used to develop a conceptual N process model. Fertiliser-derived N is likely incorporated and retained in the soil organic N pool prior to its mineralisation, nitrification, and migration into aquifers. This process, alongside the near absence of other anthropogenic N sources, results in a homogenised groundwater NO_3^- isotopic signature that allows for denitrification trends to be distinguished. Regional-scale denitrification manifests as groundwater becomes increasingly anaerobic during flow from an upgradient basalt aquifer to a downgradient alluvial aquifer. Dilution and denitrification occurs in localised electron donor-rich suboxic hyporheic zones beneath leaking irrigation channels. Using approximated isotope enrichment factors, estimates of regional-scale NO_3^- removal ranges from 22 to 93% (average: 63%), and from 57 to 91% (average: 79%) beneath leaking irrigation channels. In the predominantly oxic upgradient basalt aquifer, raised groundwater tables create pathways for NO_3^- to be transported to adjacent surface waters. In the alluvial aquifer, the transfer of NO_3^- is limited both physically (through groundwater-surface water disconnection) and chemically (through denitrification). These observations underscore the need to understand regional- and local-scale hydrogeological processes when assessing the impacts of groundwater NO_3^- on adjacent and end of system ecosystems.

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1. Introduction

Excess nitrate (NO_3^-) in groundwater, especially if subsequently discharged to surface waters, is a global environmental problem that continues to threaten aquatic ecosystems (Adimalla et al., 2021; Burrow et al., 2010; Gu et al., 2013; Mateo-Sagasta et al., 2017; Rabalais, 2002; Spalding and Exner, 1993; Vitousek et al., 1997). The recent enhancement of NO_3^- in groundwater is in large part due to diffuse pollution from intensive agriculture (Foster, 2000; Kendall et al., 2007). In Australia, the issue of N pollution is pertinently demonstrated within the World Heritage-listed Great Barrier Reef (GBR), which continues to be affected by land-based N runoff that manifests in the eutrophication and acidification of many coral reef ecosystems (Bell, 1992; Brodie et al., 2012; Great Barrier Reef Marine Park Authority, 2019). The Fitzroy Basin drains the largest area ($\sim 142,000 \text{ km}^2$) of the GBR catchments. Prior to the development of agriculture, it has been estimated that only 1700 t/year total N (TN) was exported from the Fitzroy Basin to the GBR (Kroon et al., 2012). It is now estimated that approximately 15,000 t/year TN is exported from the Fitzroy Basin. This is the highest proportional increase in TN loads of all GBR catchments (Kroon et al., 2012). Currently, the Fitzroy Basin accounts for approximately 20% of TN delivered to the GBR (Bartley et al., 2017), making it a key target for implementing improved N management practices.

The Emerald Irrigation Area (EIA) is of particular note for potential groundwater-surface water NO_3^- transfer in the Fitzroy Basin. Irrigated cropping, particularly cotton farming, is widespread throughout the EIA. These crops rely on the application of N fertiliser to enhance crop yield. Fertiliser application rates for fully irrigated cotton in the Fitzroy Basin average 296.9 kg N/ha, which is lower than the industry average 335.9 kg N/ha (Cotton Research and Development Corporation, 2018). However, these rates are still higher than amounts recommended by research, which indicates that application rates exceeding 200–240 kg N/ha do not improve lint yield (Macdonald et al., 2018). Nitrogen management is made more complex given the variable Central Queensland climate. N-based fertilisers, such as urea and urea ammonium nitrate are the most widely used fertilisers in the region (Australian Bureau of Statistics, 2018). The application of manure to cotton crops in the EIA is not as widespread, with only approximately 50% of cotton farmers using manure (chicken, cow, feedlot, and pig manure) for fertilisation in Central Queensland (Roth Rural, 2016). Application rates are lower and highly variable, ranging from 1 to 20 t/ha of manure which is roughly equivalent to 5–20 kg N/ha based on manure type (Roth Rural, 2016). Historical data indicate that NO_3^- occurs in EIA aquifers at varying concentration, reaching as much as 29 mg/L N (Queensland Government, 2020), suggesting that excess N from inorganic fertiliser and/or manure is migrating to EIA aquifers. Despite these historical measurements, the relative contributions from inorganic fertilisers and manure to groundwater NO_3^- , as well as the aquifer-scale hydrogeological controls on its distribution, have not been studied in the EIA. Elucidating the sources and controls on these processes provides the knowledge required to improve land and groundwater management practices in the EIA. This also advances our understanding of both catchment- and basin-wide NO_3^- sources and their potential impacts to downstream ecosystems such as the GBR.

Denitrification attenuates NO_3^- in groundwater (Böttcher et al., 1990; Postma et al., 1991; Trudell et al., 1986), and therefore could play an important role in controlling the magnitude of NO_3^- loads exported from the EIA. The removal of NO_3^- via denitrification in groundwater is predominantly observed under anaerobic conditions with sufficient electron donors (Rivett et al., 2008). Many studies have shown strong hydrological controls on groundwater denitrification, especially redox boundaries that occur along hydraulic gradients (Clague et al., 2015; Hinkle et al., 2007; Stenger et al., 2018; Tesoriero et al., 2000; Tesoriero et al., 2007; Tesoriero and Puckett, 2011). Hyporheic zones tend to be sites for denitrification because of the anaerobic conditions, presence of electron donors, and occurrence of microbial communities that promote denitrification (Böhlke et al., 2009; Harvey et al., 2013).

Like many agricultural districts situated in semi-arid climates, the EIA is equipped with water infrastructure that enables intensive cultivation. Much of the irrigated cropping in the area has been exclusively sustained by water from Fairbairn Dam, whose construction was completed in 1972 to form Lake Maraboon. Irrigation water is distributed via an irrigation channel network, the majority of which was built by 1979 (Geddes et al., 2019). Seepage from these earthen channels, combined with deep drainage from crop irrigation and land clearing, have enhanced groundwater infiltration into EIA aquifers. This has resulted in rising groundwater levels and decreased unsaturated zone thickness (Pearce and Hansen, 2007). Many studies have shown that these processes can alter groundwater flow paths and prevailing geochemical conditions (e.g., Böhlke, 2002; Pulido-Bosch et al., 2018; Scanlon et al., 2008, 2009; Stewart and Aitchison-Earl, 2020). By extension, the alteration of hydrogeochemical conditions caused by irrigation in the EIA could have a strong influence on groundwater NO_3^- cycling. For instance, groundwater mounding can enable evaporation near the groundwater surface, which concentrates dissolved salts and NO_3^- in remaining groundwater (Pulido-Bosch et al., 2018). Waterlogging also enhances mineralisation rates in soil profiles, transforming organic forms of N into more soluble and mobile forms of oxidised N, such as NO_3^- (Scanlon et al., 2008, 2009). Leakage from irrigation infrastructure, such as channels and dams, can further enhance groundwater recharge and distort groundwater flow paths (Fernald and Guldán, 2006; Harvey and Sibray, 2001; Kendy and Bredehoeft, 2006). Locally, irrigation channel leakage can change the geochemical conditions of aquifers via their recharge to groundwater. This renders them conducive to biologically mediated processes such as denitrification (Fernald and Guldán, 2006).

It is well-documented that the isotopes of NO_3^- ($\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{18}\text{O}-\text{NO}_3^-$) can assist in identifying probable NO_3^- sources, in addition to detecting the occurrence of denitrification and/or dilution in groundwater systems (Aravena and Robertson, 1998; Aravena et al., 1993; Carrey et al., 2021; Kendall et al., 2007; Widory et al., 2004). Additional isotopic tracers, such as $\delta^{13}\text{C}$ in dissolved inorganic and organic carbon (DIC and DOC) and $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ in sulfate, have been used to trace the co-fractionation of the electron donors (organic C and reduced Fe) in denitrification processes (Otero et al., 2009; Puig et al., 2017; Valiente et al., 2018; Vitória et al., 2008). $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ in sulfate are additionally useful as a proxy for detecting fertiliser signatures in groundwater, especially because the $\delta^{15}\text{N}$ signatures of different NO_3^- sources have considerable overlap (Xu et al., 2016).

In addition to stable isotopes, radioactive tracers such as tritium (^3H) have been used to determine whether concentrations of NO_3^- are related to modern anthropogenic activities (Böhlke and Denver, 1995; Clague et al., 2015; Erostate et al., 2018; Koh et al., 2010; McMahon and Böhlke, 2006; Pastén-Zapata et al., 2014; Stenger et al., 2018). These tracers have also been used to estimate the timeframe over which denitrification persists based on apparent groundwater residence times (Hinkle et al., 2007). The utility of radioactive isotope tracers potentially extends beyond that of being robust indicators of groundwater age. For example, the $^{36}\text{Cl}/\text{Cl}$ ratio is a useful tool to study salt origins and transport processes in younger groundwater, such as halite dissolution and evapotranspiration (Cartwright et al., 2006). To our knowledge, $^{36}\text{Cl}/\text{Cl}$ ratios have not been explicitly used to study N pollution but may have utility in resolving the mobilisation/mixing of solutes from the unsaturated zone. For example, Cl^- and NO_3^- increases in aquifers receiving enhanced recharge prompted by land use change (e.g., Scanlon et al., 2008).

Considering the above, the aim of this study is to investigate NO_3^- sources and its transport and fate across the EIA groundwater system. To address these issues, we combine geochemical (major ion), stable isotope ($\delta^2\text{H}-\text{H}_2\text{O}$, $\delta^{18}\text{O}-\text{H}_2\text{O}$, $\delta^{15}\text{N}-\text{NO}_3^-$, $\delta^{18}\text{O}-\text{NO}_3^-$, $\delta^{13}\text{C}-\text{DIC}$, $\delta^{13}\text{C}-\text{DOC}$, $\delta^{34}\text{S}-\text{SO}_4^{2-}$ and $\delta^{18}\text{O}-\text{SO}_4^{2-}$) and radioactive isotope (^3H and ^{36}Cl) tracers to:

1. identify the source (s) of groundwater NO_3^- ;
2. determine the hydrogeological controls on denitrification and how this may have been altered by irrigation practices; and
3. evaluate the potential for NO_3^- export from the aquifers of the EIA.

2. Study area

2.1. Location and climate

The EIA ($\sim 150 \text{ km}^2$) is located on both the western and eastern banks of the Nogoa River, which intersects the township of Emerald, in the Lower Nogoa sub-catchment of the Fitzroy Basin, Queensland, Australia (Fig. 1). It is located in a hot semi-arid climate (BSH; Peel et al., 2007). The mean January and July maximum temperatures at Emerald Airport (site number 035264) are 34.6°C and 23.4°C , respectively, with the average rainfall for the same months being 83.0 mm and 16.6 mm, respectively (Australian Bureau of Meteorology, 2021). The mean annual precipitation (1992–2021) is 544 mm/year whilst evaporation ranges between 2000 and 2400 mm/year. Rainfall is strongly seasonal, with 74% falling in the summer months between October to March.

Fig. 1 presents the location of 24 groundwater and 4 surface water sampling sites used for this study. The groundwater sample locations are referred to as NogGW1 to NogGW24. These sites are located within and adjacent to the EIA, covering an area of $\sim 408 \text{ km}^2$ (see Fig. 1). Surface

water samples are referred to as sites NogSW1, NogSW2, NogSW3 and NogSW5. Further details on sample collection are outlined in Section 3. Groundwater samples were confined to the existing QLD Department of Natural Resources, Mines and Energy groundwater monitoring network. These monitoring wells provide both good spatial and depth sampling coverage of the different hydrogeological units in the study area.

2.2. Hydrogeology

Within the EIA, the oldest outcropping formation is the Late Permian Freitag Formation comprising interbedded clastic sedimentary rocks that are exposed at Fairbairn Dam (lithic sandstone, siltstone, coal, and carbonaceous shale; Fielding and McLoughlin, 1992; Power, 1966). The Freitag Formation is underlain by the Early Permian Aldebaran Sandstone (sandstones, conglomeratic sandstones, conglomerates, and coal; Dickins and Malone, 1973), which is intersected by deeper groundwater monitoring wells with screens below 30 m (NogGW16 and 17).

The Permian sedimentary sequences are overlain by fluvial and lacustrine sediments of the Emerald Formation (unconsolidated to semi-

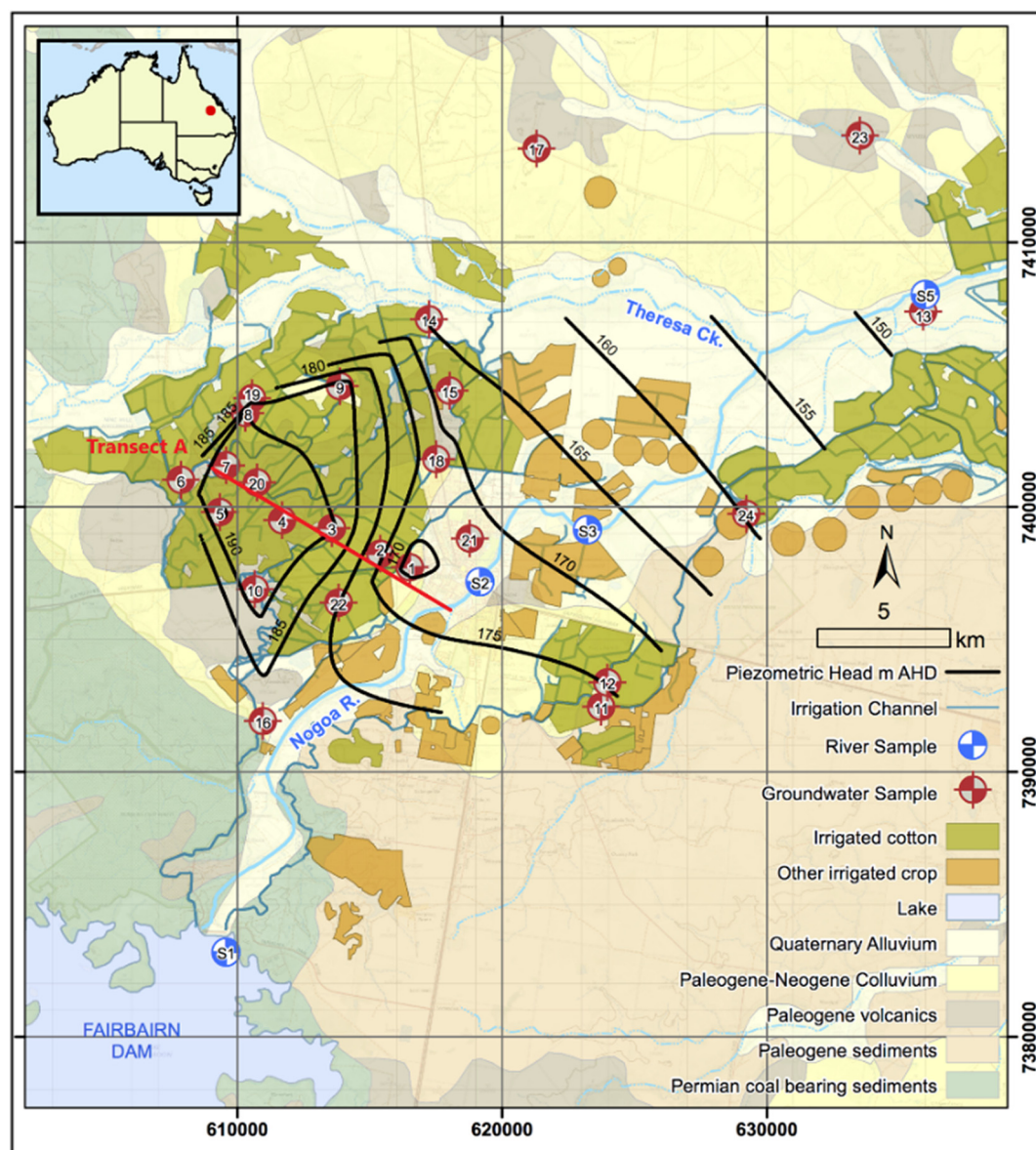


Fig. 1. Map of the study area, including groundwater sampling sites and irrigation channels used for crop irrigation in the EIA. Piezometric head data is interpolated using the Natural Neighbour algorithm over the study area to highlight the hydraulic gradient. Transect A is indicated in red. The locations of river sampling sites (designated with an “S”) are also indicated.

unconsolidated claystones, siltstones, sandstones with minor interbedded basalt) deposited throughout the Paleocene and Oligocene (Day et al., 1983). These sedimentary rocks have low permeability and poorly developed fracture networks, resulting in low groundwater extraction yields. The sedimentary aquifer is therefore not exploited for irrigated agriculture (Pearce and Hansen, 2007). Only one monitoring well screening this aquifer was sampled in this study (NogGW24) due to a lack of intersecting groundwater monitoring wells.

The preceding sedimentary sequences are overlain by basalts and trachytes, most likely emplaced during the Oligocene based on dating of regional volcanics (Jones et al., 2018). These volcanics form an unconfined aquifer, with groundwater resources contained within weathered and fractured zones that are hydraulically connected (Pearce and Hansen, 2007; Webb and McDougall, 1967). Most monitoring wells sampled in this study are screened within a localised basalt flow that is exposed on the western bank of the Nogoa River. This exposure forms a topographic high that has weathered to form dark cracking clay soils (McDonald and Baker, 1986). The soils on the basalt are typically less than 1 m deep, making the underlying aquifers vulnerable to anthropogenic pollution from irrigated cropping practices.

From the Miocene to Late Pleistocene, a paleo-valley was carved through these rocks and filled with unconsolidated colluvial and alluvial sediments (coarse sands and gravels with varying amounts of clay). The distribution of these sediments follows the drainage system of the Nogoa River and its tributaries, forming a floodplain that varies in width from less than 100 m to 6 km either side of the riverbanks (Tucker et al., 2003).

A prominent feature of the EIA is that groundwater is not pumped for irrigation. Instead, irrigation waters are sourced exclusively from dam water distributed via irrigation channels. Groundwater recharge occurs via a combination of rainfall, crop irrigation and irrigation channel water leakage (discussed further in Section 2.3), with no input from irrigation return flows because groundwater is not used for crop irrigation. Groundwater recharged in the upgradient basalt aquifer flows in an easterly direction into the downgradient alluvial aquifer. Transect A traces south-easterly groundwater flow over a portion of the study area (Fig. 1) and is used later in the Discussion to demonstrate the behaviour of NO_3^- as groundwater flows from the basalt aquifer into the alluvial aquifer.

2.3. The EIA irrigation channel network

An important hydraulic feature of the EIA is the surface irrigation channel network that distributes the water used for irrigated agriculture (see Fig. 1). This network originates 19 km upstream of Emerald at Fairbairn Dam ($1.3 \times 10^9 \text{ m}^3$ capacity), which supplies water for irrigation by controlling flows to the channel network. In the absence of any surface runoff and precipitation, the flows of the channel networks and Nogoa River are entirely controlled by water releases from Lake Maraboon through Fairbairn Dam (Tucker et al., 2003). In total, the channels and pipelines supplying water for irrigation in the EIA extends for over 126 km and can distribute irrigation water to an area of approximately 15,000 ha (Fairbairn Irrigation Network, 2019). The Selma Channel System supplies water to the western bank of the Nogoa River and the Weemah Channel System supplies water to the eastern bank of the Nogoa River. A surface drainage system of over 144 km in length is in place to provide off-farm drainage (Sunwater, 2012).

The construction of the Selma and Weemah Channel Systems elevated groundwater levels in the EIA because many channels were not internally lined. In the absence of regional groundwater abstraction, the water table has risen between 1.7 and 21 m (6 m on average across sites sampled in this study) on both banks of the Nogoa River. Analysis of groundwater hydrographs indicates that groundwater levels have steadily risen since the 1980–1990s (Queensland Government, 2020). On the western bank of the Nogoa River, the potentiometric head data indicate that the increase in recharge – the result of both enhanced areal recharge (crop irrigation) and point recharge (irrigation channel leakage) – has increased the natural hydraulic gradient. Recently, portions of the channel network have been

internally lined to limit leakage and restore natural groundwater levels (Sunwater, 2020). As a result, the geochemistry of the groundwater that is affected by irrigation channel leakage may represent transient geochemical signals. Given the strong influence that irrigation channels have had on groundwater, the presence of leaking irrigation infrastructure may be an important factor to consider when interpreting groundwater NO_3^- cycling in the EIA.

3. Methods

3.1. Sample collection

Twenty-two groundwater monitoring wells and two privately-owned wells of varying depths were sampled in October and November 2018 (Fig. 1). Fifteen monitoring wells are screened in the Cenozoic basalt aquifer at depths between 6 and 29 m. These monitoring wells are located on the western bank of the Nogoa River where the most intensive irrigated cropping occurs. Five monitoring wells and one private well are screened in the alluvial aquifer at depths between 13 and 20 m. These monitoring wells are located within the Nogoa River floodplain, to the east of the Cenozoic basalt aquifer. The remaining two wells (one private and one monitoring well) are screened in the weathered Cenozoic sedimentary rock aquifer at depths ranging from approximately 30 m in the private well to 95 m in the monitoring well. These are located on the periphery of the main irrigated cropping practices of the EIA. Monitoring wells with screens less than 30 m in depth were sampled with a 12 V Proactive impeller pump, with the pump intake placed approximately 1 m above the screen. Deeper wells were sampled with a bladder pump using low-flow methods (Iverach et al., 2017). During this procedure, the pump was placed approximately 10 m below the groundwater level with a drop tube positioned within the screened interval. Both privately-owned wells were sampled from a pump outlet because these wells are sealed. Sample collection procedures for each chemical analyte are provided in Supplementary Material 1.

During the groundwater sampling campaign, auxiliary surface water samples were taken from Nogoa River (sites NogSW1, NogSW2, NogSW4 and NogSW5; Fig. 1). These samples were acquired using a peristaltic pump and prepared and analysed using the same sampling techniques as the groundwater samples. The chemistry of the surface water samples is not the focus of this study but is used to infer groundwater-surface water mixing processes in the study area. Measurements obtained from these surface water samples are broadly consistent with those collected during a two-year surface water monitoring campaign conducted by our research group in the Lower Nogoa sub-catchment. These point-in-time samples thus provide an adequate representation of surface water inputs into EIA aquifers.

3.2. Chemical analyses

Total alkalinity concentrations were determined in the field by titration using a HACH digital titrator and external pH meter. Fe^{2+} and HS^- ion concentrations were determined using a HACH DR890 portable colorimeter. $\text{NH}_3\text{-N}$ concentrations were measured on a HACH DR3900 Spectrophotometer using the HACH Method 10,205. Samples for cations were analysed using inductively coupled plasma atomic emission spectroscopy (ICP-AES) at ANSTO. Samples for anions were analysed using ion chromatography (IC) at ANSTO. The charge balance error for the measured major ion concentrations did not exceed 5%. Total dissolved solids (TDS) were calculated as the sum of all major ions.

Samples for $\delta^2\text{H-H}_2\text{O}$ and $\delta^{18}\text{O-H}_2\text{O}$ were analysed using an established method on a cavity ring-down spectroscopy (CRDS) on a Picarro L2130-i analyser at ANSTO. These values are reported as ‰ deviations from the international standard V-SMOW (Vienna Standard Mean Ocean Water) and results have a precision of $\pm 1\text{‰}$ for $\delta^2\text{H}$ and $\pm 0.15\text{‰}$ for $\delta^{18}\text{O}$. Samples for $\delta^{13}\text{C-DIC}$ were also analysed at ANSTO using a Delta V Advantage mass spectrometer, and a GasBench II peripheral. The results are reported as ‰ deviations from International Atomic Energy Agency (IAEA)

secondary standards that have been certified relative to the international standard V-PDB (Vienna Pee Dee Belemnite) for carbon with a precision of $\pm 0.3\text{‰}$. DOC samples were analysed at UC-Davis Stable Isotope Facility, USA using a total organic carbon (TOC) analyser connected to a PDZ Europa 20–20 IRMS using a GD-100 Gas Trap interface. Results were corrected based on laboratory standards calibrated against National Institute of Standards and Technology (NIST) Standard Reference Materials. Samples for $\delta^{34}\text{S}\text{-SO}_4$ and $\delta^{18}\text{O}\text{-SO}_4$ were analysed using a Carlo Erba 1108 elemental analyser and TC-EA pyrolyser (for the $\delta^{18}\text{O}$), both coupled to a Thermo Finnigan Delta Plus XP Spectrometer at University of Barcelona (CCiTUB). Values are reported as ‰ deviations from the international standard Cañon Diablo Troilite (CDT), and the analytical error (2σ) is $\pm 0.3\text{‰}$ for $\delta^{34}\text{S}\text{-SO}_4$ and $\delta^{18}\text{O}\text{-SO}_4$. Values obtained for the international standard NBS-127 were $\delta^{34}\text{S}$: $20.3 \pm 0.1\text{‰}$, and $\delta^{18}\text{O}$: $9.3 \pm 0.2\text{‰}$. Samples for $\delta^{15}\text{N}\text{-NO}_3^-$ and $\delta^{18}\text{O}\text{-NO}_3^-$ analysed on an autosampler / PreCon / GasBench II assembly coupled to a Finnigan Delta Plus Advantage IMRS, using the bacterial denitrification method (Sigman et al., 2001) at IsoLab at the University of Washington, USA. Long-term precision (1σ) for $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ was $\pm 0.3\text{‰}$ and $\pm 0.5\text{‰}$, respectively.

Samples for ^3H were analysed using established liquid scintillation methodologies at ANSTO as outlined in Cendón et al. (2014). The ^3H concentrations are expressed in tritium units (TU) with an average combined standard uncertainty of ± 0.05 TU and quantification limit of 0.04 TU. $^{36}\text{Cl}/\text{Cl}$ and $^{36}\text{Cl}/^{37}\text{Cl}$ ratios were measured by accelerator mass spectrometry (AMS) using the ANSTO 6MV SIRIUS Tandem Accelerator as outlined in Wilcken et al. (2017).

4. Results

Table S2-1 (Supplementary Material 2) presents the physicochemical, major ion and isotope results for EIA groundwater. Auxiliary geochemical data obtained for Lake Maraboon and the Nogoa River, collected at the same time as the groundwater sampling campaign, are also provided in Table S2-1.

To aid the description and discussion of results, the EIA groundwater samples are differentiated into three clusters and referred to as the following:

1. **pre-irrigation** groundwater samples, which are located on the periphery of the main irrigated cropping practices of the EIA and have screened intervals in the deeper portions of the aquifers in the study area;
2. **mixed** groundwater samples, which include most samples collected in the main irrigation district of the EIA; and
3. **leakage-dominated** groundwater samples, which are in proximity (< 1 km) to leaking irrigation channels.

The differentiation of these groundwater samples has been undertaken to streamline the discussion of the results based on trends in the data, and is not the focus of this study. To ensure that the categories are sufficiently capable of describing NO_3^- dynamics in the EIA, the statistical validity of these clusters was assessed using agglomerative hierarchical clustering (see Supplementary Material 3). The agglomerative hierarchical clustering was used to objectively organise the data into groups based on their $\delta^2\text{H}\text{-H}_2\text{O}$, $\delta^{18}\text{O}\text{-H}_2\text{O}$, $\delta^{13}\text{C}\text{-DIC}$, ^3H , $^{36}\text{Cl}/\text{Cl}$ and NO_3^- compositions (which form the basis of our data interpretation). Dissimilarities (and by analogy similarities) between groundwater sample compositions were measured using squared Euclidean distances according to Ward's method and classified using a dendrogram (e.g. Lambrakis et al., 2004; Swanson et al., 2001). There was good agreement between the derived statistical clusters and those interpreted, indicating that these clusters are statistically viable representations of processes affecting the cycling of NO_3^- in the EIA groundwater system.

4.1. Physicochemistry and major ions

Across all groundwater samples, temperature varied between 24 and 30 °C, pH was between 5.5 and 8.2, TDS between 395 and 3747 mg/L, and dissolved oxygen (DO) ranged from 0.1 to 6.4 mg/L. Dissolved NO_3^-

concentrations ranged from <0.02 to 24.39 mg/L N. Nine samples had concentrations that exceeded the WHO maximum guideline value of 10 mg/L N NO_3^- for drinking water (WHO, 2011). Seventeen groundwater samples had concentrations that exceeded the Australian/New Zealand long-term trigger value for NO_3^- in irrigation water of 5 mg/L N NO_3^- (ANZECC/ARMCANZ, 2000). Two samples had detectable NO_2^- concentrations (0.03 mg/L N NO_2^- in both samples). Two samples had detectable NH_3 concentrations (0.11 and 0.34 mg/L N NH_3). The surface water samples from Lake Maraboon and Nogoa River did not have any detectable NO_3^- .

The deep *pre-irrigation* groundwater samples had no detectable NO_3^- but had detectable NH_3 (reaching a maximum 0.34 mg/L N NH_3). These samples had low DO (0.12 to 0.20 mg/L) and variable TDS (1033 to 1554 mg/L). The *mixed* groundwater cluster consists of Na- HCO_3 and Ca- HCO_3 type groundwater associated with the Cenozoic basalt aquifer on the western portion of the study area. These samples had variable DO (0.19 to 6.43 mg/L), TDS (521 to 1734 mg/L) and NO_3^- (<0.02 to 24.39 mg/L N). Groundwater from the Cenozoic basalt aquifer flows east to mix with the groundwater in the alluvial aquifer, which is classified as Na-Cl type groundwater. This groundwater has higher TDS (>3000 mg/L) and lower DO (<0.6 mg/L) and NO_3^- (<0.02 to 9.46 mg/L N). The *leakage-dominated* groundwater samples had low TDS (395 to 649 mg/L) and NO_3^- (<0.02 to 1.83 mg/L N), and were mostly suboxic (<0.5 mg/L DO).

4.2. H_2O stable isotopes

H_2O stable isotope compositions across all EIA groundwater samples ranged from -34.4 to $+0.9\text{‰}$ for $\delta^2\text{H}\text{-H}_2\text{O}$ and -5.2 to $+1.2\text{‰}$ for $\delta^{18}\text{O}\text{-H}_2\text{O}$ (Fig. 2a). The most depleted groundwater samples were from the deeper *pre-irrigation* groundwater systems on the periphery of the main irrigated cropping practices of the EIA. Their $\delta^2\text{H}$ and $\delta^{18}\text{O}$ compositions ranged from -34.4 to -28.6‰ and -5.2 to -4.6‰ , respectively. These compositions plot near the global meteoric water line (GMWL; Craig, 1961). The *mixed* groundwater samples plot to the right of the GMWL on an evaporation trendline extending from the *pre-irrigation* groundwater to the *leakage-dominated* groundwater samples (notably GW10 and 15; $\delta^2\text{H}$ from -0.4 to $+0.9\text{‰}$ and $\delta^{18}\text{O}$ from $+0.8$ to $+1.2\text{‰}$). In Fig. 2a, the evaporation trendline was extended to include those H_2O stable isotopic compositions of Lake Maraboon and Nogoa River ($\delta^2\text{H}$ from $+7.57$ to $+11.32\text{‰}$ and $\delta^{18}\text{O}$ from $+2.20$ to $+2.86\text{‰}$). The slope of this evaporation trendline (~ 5.5) is consistent with those reported elsewhere in eastern Australia (Hollins et al., 2018; Iverach et al., 2017).

4.3. ^3H activities

^3H activities ranged from 0.05 to 1.55 TU (average: 0.60 TU). The lowest ^3H activities (0.05 to 0.10 TU) were measured for the *pre-irrigation* groundwater (Fig. 2b). In contrast, the highest ^3H activities (0.85 to 1.55 TU) were recorded for *leakage-dominated* groundwater samples. These higher activities approach those measured in Lake Maraboon and Nogoa River (1.82 to 1.99 TU). The *mixed* groundwater samples had ^3H activities between these two extremes, ranging from 0.16 to 1.1 TU.

To determine tracer-based ages for EIA groundwater, ^3H input from modern groundwater recharge were estimated. To do this, a composite ^3H rainfall record was calculated based on ^3H records from Brisbane, Queensland (extending from the 1960s to 2012), Charleville, Queensland (2006 to 2017), other southern hemisphere records for rainfall prior to 1962 (Morgenstern and Taylor, 2009). The effect on ^3H due to distance from the coastline was also taken into account. A loess best-fit was used to smooth the composite record. The resulting ^3H input from rainfall in the EIA was estimated to be 1.73 TU, which is within the range for ^3H in rainfall predicted by Tadros et al. (2014) for the study area (1.6 to 2.0 TU). This estimate is similar to ^3H activities in Lake Maraboon and the Nogoa River (1.82 to 1.99 TU).

Assuming the average input ^3H for modern groundwater recharge is 1.7 TU, the *mixed* and *leakage-dominated* groundwater samples (which all have quantifiable ^3H) have tracer-based ages of less than ~ 75 years (based on

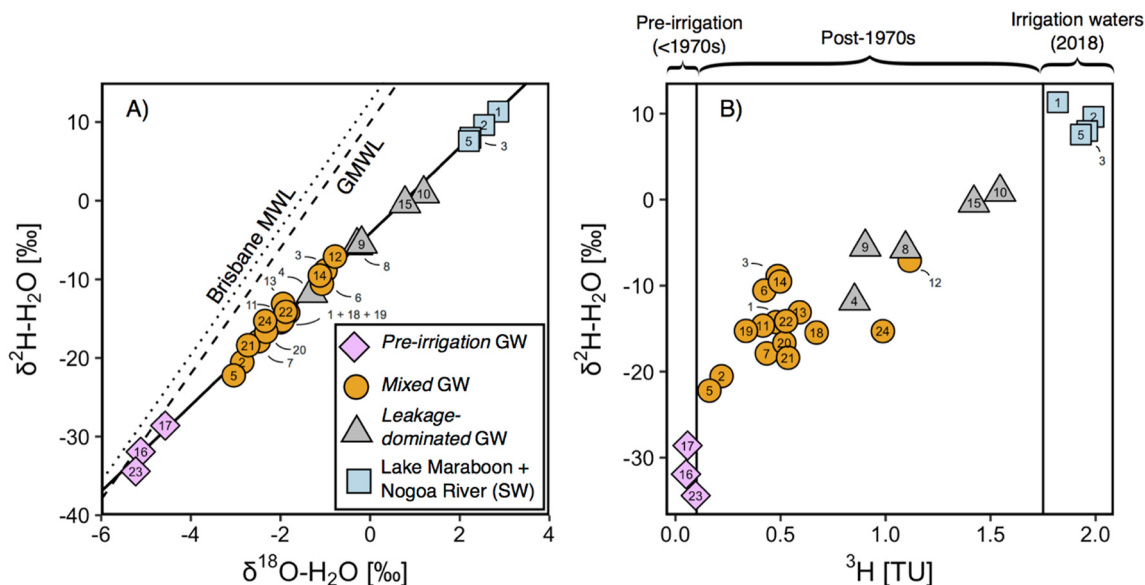


Fig. 2. a) $\delta^2\text{H-H}_2\text{O}$ and $\delta^{18}\text{O-H}_2\text{O}$ compositions of the different groundwater clusters in the EIA. The global meteoric water line (GMWL; Craig, 1961) and the Brisbane MWL (Hollins et al., 2018) are indicated by the dashed and dotted black lines, respectively. All groundwater samples plot on an evaporation line (solid line) with the equation $\delta^2\text{H} = 5.47 \times \delta^{18}\text{O} - 4.16\text{‰}$ ($r^2 = 0.99$, $p < 0.001$). b) ^3H versus $\delta^2\text{H-H}_2\text{O}$ in the different groundwater groups in the EIA.

radioactive decay). However, a further age constraint can be placed on these samples because they show variable degrees of mixing with infiltrating irrigation channel water (Fig. 2a and b). This indicates that these groundwater locations have received recharge from water originating from the mid-1970s when the first irrigation channels were constructed in the EIA, placing their tracer-based ages to less than ~40–50 years. This timeframe is consistent with deep drainage infiltration rates estimated for the EIA (0.7 to 7.7 m/year; Shaw and Yule, 1978), considering the depth of screens for these monitoring wells (9.3 to 29.6 m below ground surface; mbgs). In contrast, the deeper *pre-irrigation* groundwater samples with low ^3H activities (<0.05 TU) have tracer-based ages of more than ~40–50 years, which pre-dates any irrigation practices in the EIA.

4.4. $^{36}\text{Cl}/\text{Cl}$ ratios

$^{36}\text{Cl}/\text{Cl}$ ($\times 10^{-15}$) ratios ranged from 72.8 to 170.0. *Pre-irrigation* groundwater samples had low $^{36}\text{Cl}/\text{Cl}$ ratios (72.8 to 90.8), while the *mixed* groundwater samples had variable ratios (72.8 to 146.5). *Leakage-dominated* groundwater samples had elevated $^{36}\text{Cl}/\text{Cl}$ ratios (142.2 to 170.0), which approach, and at times exceed, those measured for Lake Maraboon and Nogoa River (109.6 to 159.2). Given that the measured ^3H activities pertain to young tracer ages in EIA groundwater, an estimation of groundwater “age” using $^{36}\text{Cl}/\text{Cl}$ ratios – which require considerably longer groundwater residence times due to the half-life of ^{36}Cl (301,000 years) – is not justified. Instead, these ratios are used to trace the mobilisation of solutes in the young EIA groundwater, as well as to trace the input of modern $^{36}\text{Cl}/\text{Cl}$ -rich water.

4.5. $\delta^{15}\text{N-NO}_3^-$ and $\delta^{18}\text{O-NO}_3^-$

$\delta^{15}\text{N-NO}_3^-$ signatures ranged from +1.9 to +19.6‰ and $\delta^{18}\text{O-NO}_3^-$ ranged from +4.2 to +24.8‰. Neither the *pre-irrigation* groundwater samples, nor Lake Maraboon and Nogoa River, had detectable NO_3^- concentrations. Therefore, no isotopic signatures were attainable for these samples. The *mixed* and *leakage-dominated* groundwater samples had similar variations in their isotopic composition.

4.6. $\delta^{34}\text{S-SO}_4^{2-}$ and $\delta^{18}\text{O-SO}_4^{2-}$

$\delta^{34}\text{S-SO}_4^{2-}$ ranged from +3.9 to +15.4‰ and $\delta^{18}\text{O-SO}_4^{2-}$ ranged from +9.6 to +19.0‰. *Pre-irrigation* groundwater samples had $\delta^{34}\text{S-SO}_4^{2-}$

compositions ranging from +9.0 to +9.5‰, and $\delta^{18}\text{O-SO}_4^{2-}$ ranged from +10.5 to +11.6‰. *Mixed* groundwater samples had $\delta^{34}\text{S-SO}_4^{2-}$ compositions ranging from +3.9 to +15.4‰, and $\delta^{18}\text{O-SO}_4^{2-}$ ranged from +9.6 to +17.6‰. The *leakage-dominated* groundwater samples had $\delta^{34}\text{S-SO}_4^{2-}$ compositions ranging from +4.7 to +8.8‰, and $\delta^{18}\text{O-SO}_4^{2-}$ ranged from +15.4 to +19.0‰. These $\delta^{18}\text{O}$ compositions are notably higher than the vast majority of those in the *mixed* groundwater cluster (barring GW7). No isotopic signatures were attained for Lake Maraboon and Nogoa River during this sampling campaign.

4.7. HCO_3^- and $\delta^{13}\text{C-DIC}$

HCO_3^- concentrations ranged from 31.5 to 925.1 mg/L and $\delta^{13}\text{C-DIC}$ compositions ranged from −15.2 to −8.6‰. In the lower pH groundwater samples (pH < 6.4), HCO_3^- concentrations were low (31.5 to 276.8 mg/L) and $\delta^{13}\text{C-DIC}$ signatures were depleted (−15.2 to −13.1‰). For the remaining circum-neutral groundwater, $\delta^{13}\text{C-DIC}$ compositions extended from c. −13‰ (mostly *mixed* groundwater) to −8‰ (mostly *pre-irrigation* and *leakage-dominated* groundwater samples). Lake Maraboon and Nogoa River HCO_3^- concentrations ranged from 164.3 to 176.9 mg/L and $\delta^{13}\text{C-DIC}$ compositions ranged from −6.6 to −3.5‰.

4.8. DOC and $\delta^{13}\text{C-DOC}$

DOC concentrations ranged from 0.37 to 3.25 mg/L but were typically between 0.37 and 1.5 mg/L. $\delta^{13}\text{C-DOC}$ compositions ranged from −32.6 to −17.2‰, yet most samples had compositions between −28 to −25‰. There were no clear distinctions in the DOC content and $\delta^{13}\text{C-DOC}$ signature across the three geochemical clusters. In Lake Maraboon and Nogoa River, DOC concentrations ranged from 5.2 to 5.5 mg/L and $\delta^{13}\text{C-DOC}$ compositions ranged from −24.9 to −24.1‰.

5. Discussion

5.1. Groundwater recharge sources and distribution of NO_3^-

The *pre-irrigation* groundwater in the study area is characterised by low ^3H activity, $^{36}\text{Cl}/\text{Cl}$ ratios, and non-evaporated water stable isotopes, representing natural recharge signatures (Fig. 2a and b). The lack of NO_3^- in these groundwater samples might be explained by the absence of NO_3^-

contamination, and/or complete removal of NO_3^- via denitrification given the suboxic conditions. Although the latter cannot be confirmed via the use of NO_3^- isotope data, it is likely that this groundwater cluster contains natural background NO_3^- concentrations given their depth, lack of evidence for evaporation and tracer-based ages (> 40 – 50 years). Detectable, yet minor, $\text{NH}_3\text{-N}$ concentrations may be of natural origin.

The tendency of the *mixed* groundwater samples to trend towards the water stable isotopic (Fig. 2a) and ^3H (Fig. 2b) composition of surface water samples suggests that they are a mixture of modern recharge water sources (i.e., evaporated irrigation waters sourced from Lake Maraboon) and *pre-irrigation* groundwater. The stable water isotopic enrichment in the *mixed* groundwater samples is not likely the result of in-situ evaporation given the depth of the groundwater sampling. Instead, elevated ^3H activity and enrichment in ^2H and ^{18}O in the *mixed* groundwater samples is most likely derived through mixing with infiltrating evaporated irrigation waters which have atmospheric ^3H signals and enriched ^2H and ^{18}O . NO_3^- concentrations in these samples were broadly dependent on whether they were in the upgradient Na-HCO_3^- type waters of the basalt aquifer (lower TDS, and higher DO and NO_3^-), or the downgradient Na-Cl type waters of the alluvial aquifer (higher TDS, and lower DO and NO_3^-). This is reflected in the

moderate negative correlation between NO_3^- and TDS ($r^2 = 0.60$, $p < 0.001$; Fig. 3a) and moderate positive correlation between NO_3^- and DO ($r^2 = 0.50$, $p < 0.005$; Fig. 3b). This suggests that the distribution of NO_3^- is in part controlled by processes that occur over the regional flow paths implied by the hydraulic gradient.

All samples containing detectable NO_3^- in the *mixed* cluster had ^3H activities above quantification limits (0.05 TU; Fig. 3c), suggesting NO_3^- is derived from modern anthropogenic sources. Interestingly, $^{36}\text{Cl}/\text{Cl}$ ratios were positively correlated with NO_3^- concentration in this groundwater cluster ($r^2 = 0.69$, $p < 0.001$; Fig. 3d). One possible explanation for this may be that the variation in $^{36}\text{Cl}/\text{Cl}$ ratios reflect the incorporation of Cl (and other salts) from the unsaturated zone into the saturated zone following the introduction of irrigation in the EIA (Scanlon et al., 2008, 2009). Prior to the mid-1970s, this Cl likely accumulated over millennia in the unsaturated zone in the form of dispersed halite resulting in lower $^{36}\text{Cl}/\text{Cl}$ ratios. The dissolution and subsequent mobilisation of old chlorides following cultivation may have resulted in a decline in the $^{36}\text{Cl}/\text{Cl}$ ratio along the groundwater flow path. After modern NO_3^- -rich water with elevated $^{36}\text{Cl}/\text{Cl}$ ratios was introduced to the system post-1970s, a simultaneous increase in NO_3^- and $^{36}\text{Cl}/\text{Cl}$ was possibly established in more-recently

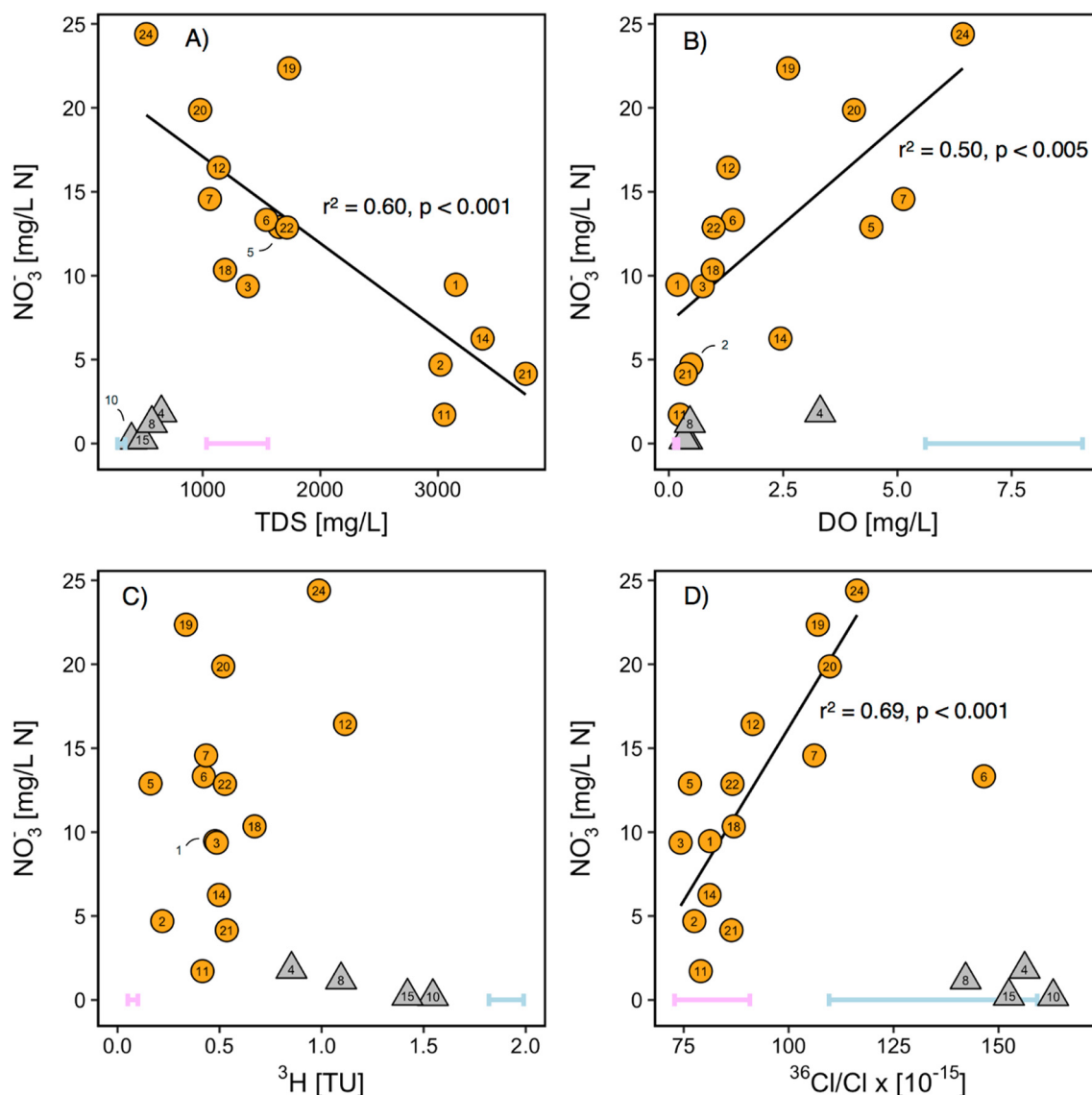


Fig. 3. NO_3^- (mg/L N) plotted against a) TDS, b) DO, c) ^3H , and d) $^{36}\text{Cl}/\text{Cl}$ ratios. In panel d), one sample (GW6) was removed from the linear regression. Note that *pre-irrigation* groundwater values are indicated by a range (in violet) because NO_3^- concentrations were below detection limit. Similarly, surface water samples are indicated by a range (in light blue). Symbols are as in Fig. 2.

recharged groundwater. There does not appear to be simultaneous isotopic enrichment in water stable isotopes as salinity increases (Fig. 4a), which is consistent with the origin of salinity being from the dissolution of pre-existing unsaturated zone salts rather than recent evapo-concentration. Moreover, NO_3^- concentrations do not appear to have been increased via evapo-concentration (Fig. 4b).

The *leakage-dominated* groundwater cluster samples have H_2O stable isotope, ^3H and $^{36}\text{Cl}/\text{Cl}$ ratios that range from those of the *mixed* groundwater towards those of Lake Maraboon and Nogoa River (Fig. 2a and b). The elevated ^3H and $^{36}\text{Cl}/\text{Cl}$ ratios in these samples indicate that they have been influenced more heavily at a local scale by modern irrigation supply channel leakage than the *mixed* groundwater samples (Fig. 3c and d). Plots of NO_3^- vs TDS and DO (Fig. 3a and b) show the behaviour of NO_3^- in the groundwater at these sample locations is distinct from the *mixed* groundwater cluster: they have low NO_3^- and TDS and are mostly suboxic (<0.5 mg/L DO). This suggests that localised modern surface water input via irrigation supply channel leakage dilutes and, potentially, attenuates NO_3^- at these locations. Indeed, the dilution effect of irrigation supply channel leakage on both TDS and NO_3^- on this groundwater cluster can be seen in Fig. 4. The possibility of denitrification is explored further in Section 5.3.

Overall, the mixing trends shown in Fig. 2b indicate that there is a continuum of mixing between recharge sources in the EIA (rainfall, crop irrigation and irrigation channel leakage), and that this is a modern process occurring within the past 40–50 years. The different groundwater clusters show varying degrees of mixing across the different recharge sources, with the *leakage-dominated* groundwater samples displaying the greatest degree of mixing with irrigation surface waters. The evaporated irrigation supply channel waters, which originate upstream from Lake Maraboon, have low NO_3^- contents. These irrigation waters are therefore unlikely to contribute to NO_3^- loads via leakage, but rather dilute underlying groundwater.

5.2. Identifying NO_3^- sources

The potential anthropogenic sources of NO_3^- include inorganic fertilisers and manure, which have recent (post-1970s) and widespread application across the EIA. Fig. 5a and b show the $\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{18}\text{O}-\text{NO}_3^-$ values for both the *mixed* and *leakage-dominated* groundwater samples in relation to potential NO_3^- isotopic source signatures (derived from Xu et al., 2016 and references therein). Although a wide range of $\delta^{18}\text{O}-\text{NO}_3^-$ signatures have been reported for different NO_3^- sources via nitrification in the literature (ranging from -10 to $+15\text{‰}$; Xu et al., 2016 and references therein), the measurement of $\delta^{18}\text{O}-\text{H}_2\text{O}$ permits further refinement of signatures of

NO_3^- derived from nitrification. During nitrification, one atom of oxygen from each of H_2O and dissolved O_2 is incorporated into the NO_2^- molecule during the first step (Buchwald et al., 2012; DiSpirito and Hooper, 1986; Hollocher, 1984), and one atom of oxygen from H_2O is incorporated into the NO_3^- molecule in the second step (Kumar et al., 1983). It has been noted, however, that various kinetic isotopic fractionation effects occur during both steps (Buchwald and Casciotti, 2010; Casciotti, 2009; Casciotti et al., 2010; Granger and Wankel, 2016). Therefore the $\delta^{18}\text{O}$ signature of the product NO_3^- do not always reflect the isotopic composition of H_2O and O_2 in a 2:1 ratio (Snider et al., 2010). Nonetheless, in keeping with most groundwater NO_3^- studies (e.g., Minet et al., 2017; Osaka et al., 2010; Paredes et al., 2020; Valiente et al., 2018), in this paper the expected $\delta^{18}\text{O}-\text{NO}_3^-$ compositions derived via the nitrification of NH_4^+ fertilisers and manure is approximated using Eq. (1), after Mayer et al. (2001):

$$\delta^{18}\text{O}-\text{NO}_3^-_{\text{estimate}} = 2/3 \cdot \delta^{18}\text{O}-\text{H}_2\text{O}_{\text{sample}} + 1/3 \cdot \delta^{18}\text{O}-\text{O}_2_{\text{atmosphere}} \quad (1)$$

where $\delta^{18}\text{O}-\text{NO}_3^-_{\text{estimate}}$ is the expected $\delta^{18}\text{O}-\text{NO}_3^-$ composition of the groundwater sample, $\delta^{18}\text{O}-\text{H}_2\text{O}_{\text{sample}}$ is the measured $\delta^{18}\text{O}-\text{H}_2\text{O}$ composition of the sample, and $\delta^{18}\text{O}-\text{O}_2_{\text{atmosphere}}$ is the $\delta^{18}\text{O}$ composition of atmospheric O_2 ($+23.5\text{‰}$; Kroopnick and Craig, 1972).

The expected $\delta^{18}\text{O}-\text{NO}_3^-$ composition for nitrification derived using Eq. (1) for the *mixed* and *leakage-dominated* groundwater samples ranged from $+4.3$ to $+7.3\text{‰}$ and $+7.0$ to $+8.6\text{‰}$, respectively. Although these results are interpreted with caution, when compared to the individual measured $\delta^{18}\text{O}-\text{NO}_3^-$ signatures, nine *mixed* and three *leakage-dominated* groundwater samples had $\delta^{18}\text{O}-\text{NO}_3^-$ compositions exceeding those derived from Eq. (1) (Fig. 6). This suggests possible enrichment via denitrification.

Those samples containing nitrified NO_3^- had $\delta^{15}\text{N}-\text{NO}_3^-$ signatures ranging from $+1.9$ to $+9.9\text{‰}$, which plot in the fields for both nitrified NH_4^+ fertiliser and soil organic nitrogen (SON; Fig. 5a and b). The dominant fertilisers applied to EIA crops are NH_4^+ -based, which explains the tendency of data to plot towards this isotopic source field.

Due to the significant overlap in $\delta^{15}\text{N}-\text{NO}_3^-$ signatures of NH_4^+ fertiliser and SON, the contribution from the nitrification of reduced SON is challenging to resolve. Prior to cultivation and irrigation commencing in the EIA, SON was presumably derived from fixed N_2 that was incorporated into soil and plants. However, this natural source of soil NO_3^- alone does not account for the elevated groundwater NO_3^- concentrations in EIA aquifers. During microbial immobilisation, inorganic N is reincorporated into the SON pool and N is retained in the soil profile as organic N (Wells

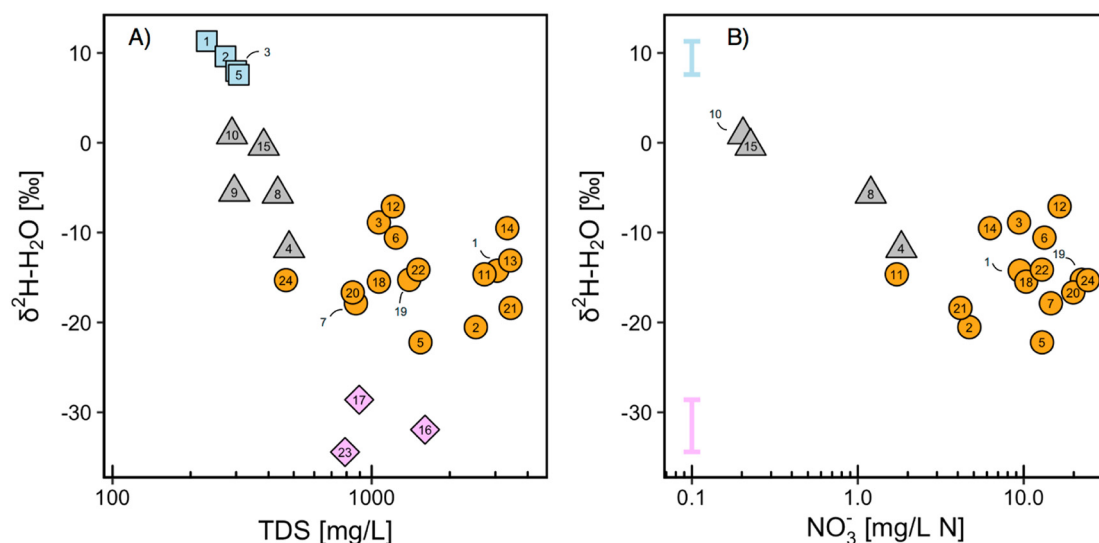


Fig. 4. $\delta^2\text{H}-\text{H}_2\text{O}$ plotted against a) TDS and, b) NO_3^- concentration in the groundwater and surface water samples. Similar observations are made for $\delta^{18}\text{O}-\text{H}_2\text{O}$. In b), pre-irrigation groundwater samples and surface water samples are plotted as a range for demonstrative purposes, as these samples did not contain detectable NO_3^- concentrations. Symbols are as in Fig. 2.

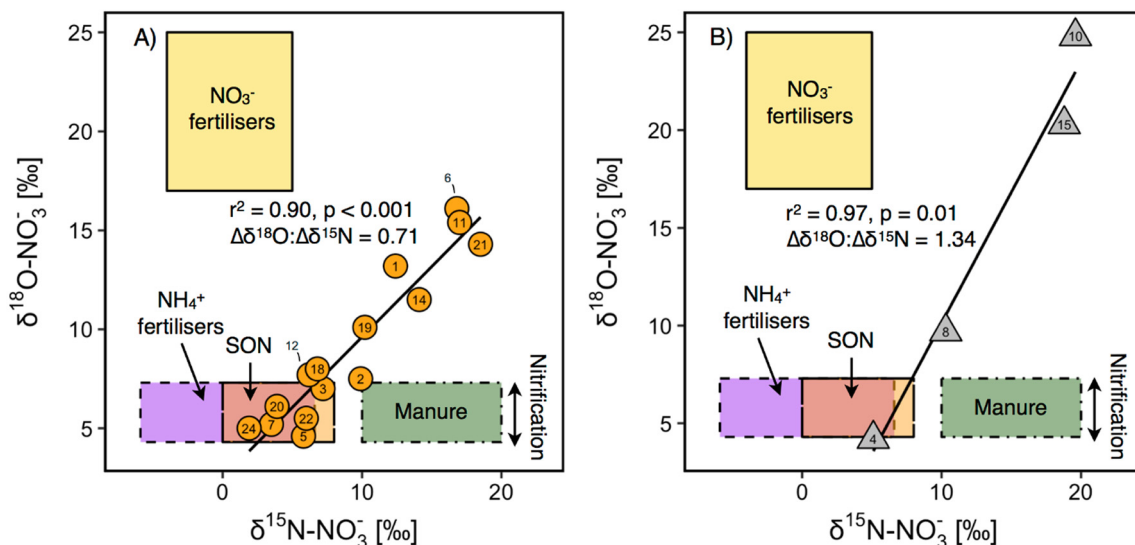


Fig. 5. Dual NO_3^- isotope plots for the a) mixed and b) leakage-dominated groundwater samples. The range of $\delta^{18}\text{O}$ composition of these sources (apart from NO_3^- fertilisers) was limited to those expected via nitrification assuming the NO_3^- incorporated O atoms from H_2O and atmospheric O_2 in a 2:1 ratio as in Eq. (1) (Mayer et al., 2001). Note that the field for sewage-derived NO_3^- is not provided, as the groundwater locations sampled in this study were not proximal to any possible sewage sources. Symbols are as in Fig. 2.

et al., 2015). Several authors have postulated that NO_3^- derived from fertilisers is not directly leached to groundwater. Instead, it is retained in the soil-plant system prior to its subsequent mineralisation and re-oxidation during nitrification (Mengis et al., 2001; Somers and Savard, 2009; Stewart and Aitchison-Earl, 2020). This process is known as mineralisation-immobilisation-turnover (Mengis et al., 2001), and has been shown to alter and homogenise $\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{18}\text{O}-\text{NO}_3^-$ compositions in groundwater (Kloppmann et al., 2018). In addition, waterlogging can enhance microbial activity in the soil zone causing increased rates of mineralisation of SON (Scanlon et al., 2008). Waterlogging is well-documented in the EIA (Department of Natural Resources Queensland, 1998; Silburn et al., 2013; Yule, 1997), meaning this could also play an important contributing factor during this turnover process. Thus, it is plausible that prior to being leached to groundwater, fertiliser-derived NO_3^- is retained in the SON pool where its isotopic composition is homogenised, resulting in the isotopic signatures shown in Fig. 5. It is only after its subsequent mineralisation and nitrification that it is leached to EIA aquifers.

It must also be noted that volatilisation may occur during the surface application of NH_4^+ fertilisers. This process enriches the residual NH_4^+ , which is then transferred to the NO_3^- during nitrification (Vitória et al., 2005). Thereby, the measured $\delta^{15}\text{N}$ signatures of NO_3^- derived from NH_4^+ -based fertilisers which have undergone volatilisation can verge towards those of manure (Valiente et al., 2018). The occurrence of volatilisation in the EIA is well-documented (Weier, 1994), and therefore could be responsible for the apparent vergence of $\delta^{15}\text{N}-\text{NO}_3^-$ signatures towards more enriched NO_3^- sources such as manure.

$\delta^{34}\text{S}-\text{SO}_4^{2-}$ and $\delta^{18}\text{O}-\text{SO}_4^{2-}$ signatures in the mixed and leakage-dominated groundwater samples lend further credibility to a fertiliser source of NO_3^- in the EIA. In Fig. 7a, the $\delta^{34}\text{S}-\text{SO}_4^{2-}$ and $\delta^{18}\text{O}-\text{SO}_4^{2-}$ compositions plot in the same range typical for fertiliser-derived sulfate (Cravotta, 2002; Finlay and Kendall, 2007; Otero et al., 2007; Rees et al., 1978; Vitória et al., 2004, 2008). They also roughly plot on a mixing line between fertiliser-derived and seawater SO_4^{2-} , suggesting a minor contribution from seawater SO_4^{2-} via rainfall deposition. It is noteworthy, however, that the pre-irrigation groundwater cluster also plots in a similar field, and therefore the signatures cannot be adequately separated from natural background signatures. Nonetheless, the observed signatures are significantly more enriched than those expected for the oxidation of sulfides (Vitória et al., 2008), and the $\delta^{18}\text{O}-\text{SO}_4^{2-}$ signatures are more elevated than would be expected for manure (Cravotta, 2002; Otero et al., 2009) and soil organic matter (Finlay and Kendall, 2007).

Collectively, the $\delta^{15}\text{N}-\text{NO}_3^-$, $\delta^{18}\text{O}-\text{NO}_3^-$, $\delta^{34}\text{S}-\text{SO}_4^{2-}$ and $\delta^{18}\text{O}-\text{SO}_4^{2-}$ data indicate the source of NO_3^- in EIA groundwaters is most likely the nitrification of fertilisers and less so from manure. The contribution of NO_3^- fertilisers, as well as the occurrence of additional processes such as volatilisation could not be ruled out by the trends apparent in Fig. 5.

5.3. Evidence for denitrification using NO_3^- isotopes

During denitrification, as the NO_3^- concentration decreases, there is a simultaneous increase in both $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of the residual NO_3^- . Many groundwater studies have shown that denitrification results in $\Delta\delta^{18}\text{O}-\text{NO}_3^-:\Delta\delta^{15}\text{N}-\text{NO}_3^-$ ratios ranging from 0.5 to 0.8 (e.g., Aravena and Robertson, 1998; Baily et al., 2011; Böhlke et al., 2006; Bourke et al., 2019; Cey et al., 1999; Minet et al., 2017; Singleton et al., 2007), which deviate substantially from the ratio of ~ 1 expected for bacterial denitrification (Sigman et al., 2005). Granger and Wankel (2016) showed that $\Delta\delta^{18}\text{O}-\text{NO}_3^-:\Delta\delta^{15}\text{N}-\text{NO}_3^-$ ratios < 1 arise when

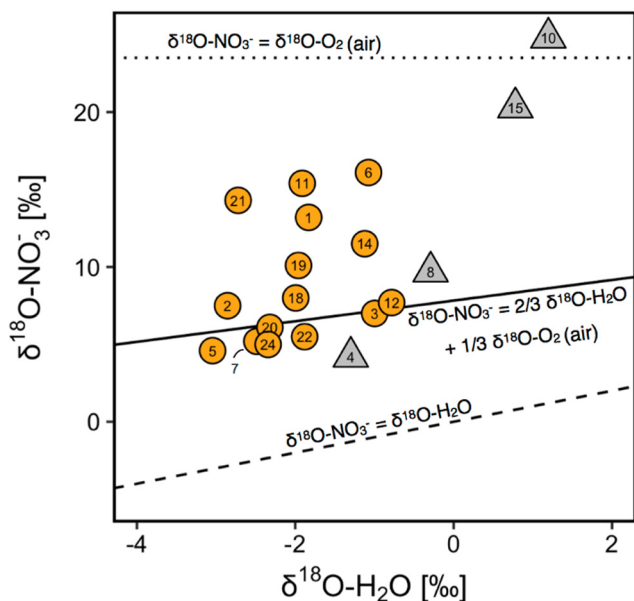


Fig. 6. $\delta^{18}\text{O}-\text{NO}_3^-$ vs. $\delta^{18}\text{O}-\text{H}_2\text{O}$ for EIA groundwater samples. Symbols are as in Fig. 2.

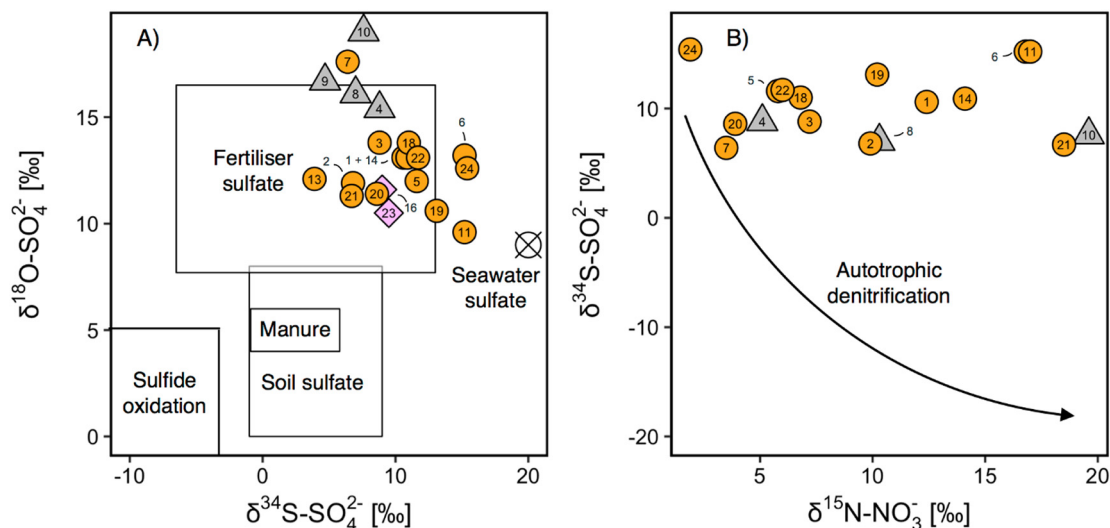


Fig. 7. a) $\delta^{34}\text{S-SO}_4$ versus $\delta^{18}\text{O-SO}_4$. The range of values for the different SO_4^{2-} sources indicated were taken from references in-text. b) $\delta^{34}\text{S-SO}_4$ versus $\delta^{15}\text{N-NO}_3^-$. The expected trend for autotrophic denitrification is indicated by an arrow after Hosono et al. (2014). Symbols are as in Fig. 2.

NO_2^- derived from denitrification is re-oxidised to NO_3^- by incorporating atoms of oxygen from ambient H_2O with depleted $\delta^{18}\text{O-H}_2\text{O}$. In contrast to freshwater systems, ratios equal to or greater than 1 have been reported for marine systems (Buchwald et al., 2015). This is attributed to elevated rates of NO_2^- re-oxidation relative to NO_3^- reduction and the incorporation of O atoms with enriched $\delta^{18}\text{O-H}_2\text{O}$ values (Casciotti et al., 2013).

In the *mixed* groundwater samples, there was a strong positive linear correlation between $\delta^{15}\text{N-NO}_3^-$ and $\delta^{18}\text{O-NO}_3^-$ ($r^2 = 0.90$, $p < 0.001$; Fig. 5a), indicating the occurrence of denitrification (Mariotti et al., 1988). $\Delta\delta^{18}\text{O-NO}_3^- : \Delta\delta^{15}\text{N-NO}_3^-$ increased at a ratio of 0.71, which were in a similar range to previously reported ratios for groundwater denitrification. This suggests that denitrification may have been superimposed by concurrent nitrification, with the produced NO_3^- incorporating atoms of oxygen from ambient H_2O with depleted $\delta^{18}\text{O-H}_2\text{O}$ (as shown by Granger and Wankel, 2016). Plots of $\delta^{15}\text{N-NO}_3^-$ and $\delta^{18}\text{O-NO}_3^-$ vs $\ln(\text{NO}_3^-)$ (Fig. 8a and b) showed moderate to weak to moderate linear correlations ($r^2 = 0.49$ and 0.32 , respectively, $p < 0.05$). Estimated isotope enrichment factors (ϵ) calculated using a simplified Rayleigh equation (Mariotti et al., 1988) were -5.2‰ for $^{15}\epsilon$ and -3.2‰ for $^{18}\epsilon$.

Similarly, *leakage-dominated* groundwater samples showed a strong positive linear correlation between $\delta^{15}\text{N-NO}_3^-$ and $\delta^{18}\text{O-NO}_3^-$ ($r^2 = 0.97$, $p = 0.01$; Fig. 5b), indicating the occurrence of denitrification. $\Delta\delta^{18}\text{O-NO}_3^- : \Delta\delta^{15}\text{N-NO}_3^-$ increased at a ratio of 1.34, which is greater than typically reported values for groundwater denitrification. Plots of $\delta^{15}\text{N-NO}_3^-$ and $\delta^{18}\text{O-NO}_3^-$ vs $\ln(\text{NO}_3^-)$ (Fig. 8a and b) showed strong linear correlations ($r^2 = 0.98$ and 0.97 , respectively, $p < 0.05$), with isotope enrichment factors of -6.1‰ for $^{15}\epsilon$ and -8.2‰ for $^{18}\epsilon$. Importantly, because these samples plot along a straight line in Fig. 8, this suggests that the isotopic enrichment of NO_3^- in these samples is caused by denitrification, rather than dilution or mixing of different NO_3^- sources (Mariotti et al., 1988). The deviation of the $\Delta\delta^{18}\text{O-NO}_3^- : \Delta\delta^{15}\text{N-NO}_3^-$ ratio from 1 also suggests that the simultaneous re-oxidation of NO_2^- occurs concurrently to NO_3^- reduction in this groundwater cluster. However, in contrast to the *mixed* cluster, NO_2^- re-oxidation to NO_3^- likely incorporates O atoms with enriched $\delta^{18}\text{O-H}_2\text{O}$ originating from evaporated surface waters. There was indeed a strong positive linear correlation between $\delta^{18}\text{O-NO}_3^-$ and $\delta^{18}\text{O-H}_2\text{O}$ for the *leakage-dominated* groundwater ($r^2 = 0.98$, $p < 0.01$), suggesting that the NO_3^- has derived part of its $\delta^{18}\text{O-NO}_3^-$ signature from isotopically enriched $\delta^{18}\text{O-H}_2\text{O}$ (see Fig. 6). Similar trends indicating partial reduction/re-oxidation processes

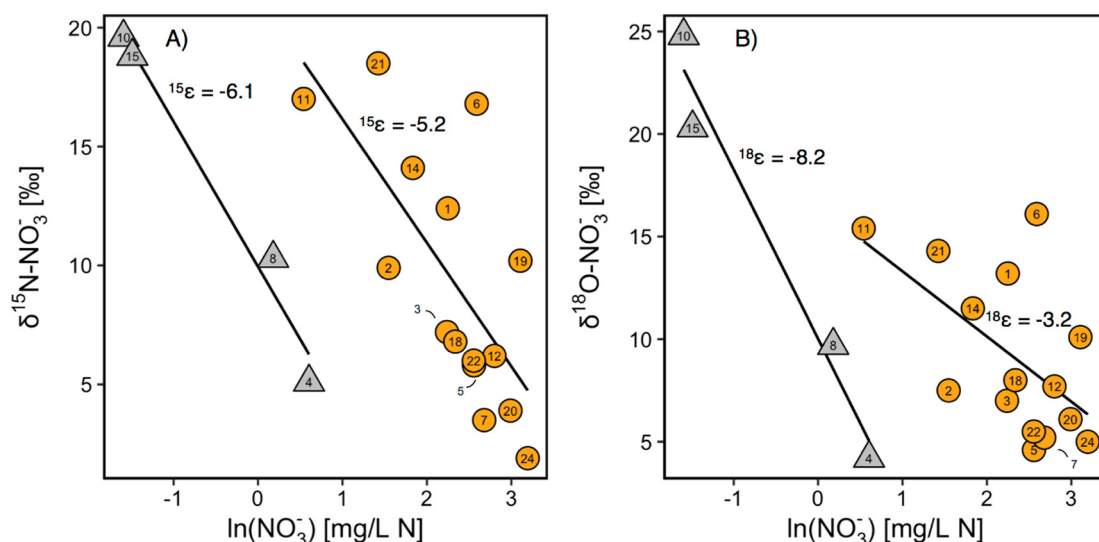


Fig. 8. $\delta^{15}\text{N-NO}_3^-$ and $\delta^{18}\text{O-NO}_3^-$ plotted against the natural logarithm of the NO_3^- concentration in mg/L N for the *mixed* and *leakage-dominated* groundwater clusters. Associated enrichment factors (ϵ) are indicated next to each regression line. Symbols are as in Fig. 2.

were observed for $\delta^{18}\text{O-SO}_4^{2-}$ in this groundwater cluster ($r^2 = 0.95$, $p < 0.05$), lending further support for partial reduction/re-oxidation process occurring in these locations. Collectively, these trends suggest that suboxic hyporheic zones have been created beneath leaking irrigation supply channels. These locations likely represent zones of enhanced exchange between surface water and groundwater, creating favourable conditions for denitrification to occur (Fernald and Guldán, 2006).

In view of the multiple lines of evidence suggesting the presence of denitrification in our study area, we used the estimated enrichment factors to calculate the percentage of denitrification for both the *mixed* and *leakage-dominated* groundwaters. This approach is outlined in Ostrom et al. (2002) and Otero et al. (2009), wherein Eq. (2) is used to quantify the percentage of denitrification in the groundwater samples:

$$\begin{aligned} \text{DEN (\%)} &= \left[1 - \frac{[\text{NO}_3]_{\text{residual}}}{[\text{NO}_3]_{\text{initial}}} \right] \times 100 \\ &= \left[1 - e^{(\delta_{\text{residual}} - \delta_{\text{initial}}/\epsilon)} \right] \times 100 \end{aligned} \quad (2)$$

To quantify the percentage of denitrification, an initial $\delta^{15}\text{N-NO}_3^-$ composition must be assumed when $^{15}\epsilon$ is used in the calculation (Ostrom et al., 2002; Otero et al., 2009). For the *mixed* groundwaters, NogGW24 was selected as this corresponds to the location that had the highest NO_3^- and DO concentrations, and lowest $\delta^{15}\text{N-NO}_3^-$ signature (+1.9‰), and thus was the most likely to correspond to nitrification-derived NO_3^- . Similarly, NogGW4 ($\delta^{15}\text{N-NO}_3^- = +5.1\text{‰}$) was selected for the *leakage-dominated* groundwater cluster. Excluding NogGW24 and NogGW4, the extent of denitrification ranged from 22 to 93% (average: 63%; median: 64%) in the *mixed* groundwaters, and from 57 to 91% (average: 79%; median: 89%) in the *leakage-dominated* groundwaters (Table S2-1). Refinement of estimated enrichment factors and, by extension, the amount denitrified, would be possible with more rigorous temporal studies and/or from the installation of multi-piezometer networks in the EIA.

5.4. What are the hydrogeochemical controls on denitrification?

5.4.1. Dissolved oxygen

$\delta^{15}\text{N-NO}_3^-$ compositions in the study area increase with decreasing DO regardless of groundwater cluster (Fig. 9a), suggesting that DO is an overarching control on denitrification in the EIA groundwater system. A similar trend is evident in the $\delta^{18}\text{O-NO}_3^-$ data (data not shown). NogGW19, which clearly contained denitrified NO_3^- ($\delta^{15}\text{N-NO}_3^- = +10.2\text{‰}$; $\delta^{18}\text{O-NO}_3^- = +10.1\text{‰}$), had a DO concentration of 2.6 mg/L, which represents an approximate limit below which denitrification occurs. The most denitrified

samples were those with suboxic DO concentrations (<0.5 mg/L), reinforcing the strong DO control on denitrification.

5.4.2. Groundwater flow path

Analogous to the strong DO control on denitrification in the *mixed* groundwaters, there was a strong positive linear correlation between $\delta^{15}\text{N-NO}_3^-$ and TDS ($r^2 = 0.83$, $p < 0.001$, NogGW6 excluded as an outlier; Fig. 9b). This indicates that denitrification tended to follow the flow path as the groundwater incorporated solutes and became progressively anaerobic. The groundwater flow path control on denitrification within the *mixed* groundwaters was confirmed by examining the geochemistry of groundwaters downgradient along Transect A as it flows from the upgradient basalt aquifer to the downgradient alluvial aquifer (shown in Fig. 1). Along this transect, DO and NO_3^- concentrations progressively decrease alongside the hydraulic gradient, while $\delta^{15}\text{N-NO}_3^-$, $\delta^{18}\text{O-NO}_3^-$, % denitrified and TDS increase (Fig. 10), highlighting the strong influence of groundwater flow duration on denitrification.

In contrast, there was no relationship between TDS and $\delta^{15}\text{N-NO}_3^-$ in the *leakage-dominated* groundwater cluster, and the groundwater flow path had little effect on denitrification (Fig. 9b). This suggests that denitrification in the *leakage-dominated* groundwaters were primarily controlled by suboxic hyporheic zone processes occurring near leaking irrigation channels, as opposed to over the regional hydraulic gradient.

5.4.3. Electron donors (C and S)

The groundwater samples with circum-neutral pH showed a mixing trend between DIC with near-atmospheric $\delta^{13}\text{C}$ composition (a first end-member; c. -8‰; Clark and Fritz, 1997) and DIC with $\delta^{13}\text{C}$ compositions c. -12‰ (a second end-member; Fig. 11a). The first end-member with higher $\delta^{13}\text{C}$ values likely reflects modern dissolved CO_2 within infiltrating surface waters. The mixing of this surface water with groundwater is most pronounced in the *leakage-dominated* groundwater samples (Fig. 11a). The second $\delta^{13}\text{C}$ end-member of c. -12‰ may reflect naturally-occurring processes, such as the weathering of silicate minerals with soil CO_2 , or *leakage-dominated* overprinting from the weathering of pedogenic carbonates. Thus, $\delta^{13}\text{C}$ compositions of -12‰ likely reflect pre-irrigation groundwater signatures, with the subsequent enrichment in $\delta^{13}\text{C}$ -DIC reflecting modern input of DIC from irrigation waters.

There was no clear decreasing trend in $\delta^{13}\text{C}$ -DIC when plotted against $\delta^{15}\text{N-NO}_3^-$ in the *mixed* and *leakage-dominated* clusters (Fig. 11b), possibly because the natural weathering and mixing with modern waters containing elevated proportions of atmospheric CO_2 have overprinted any evidence of heterotrophic denitrification. In the *mixed* groundwater samples, there was only a weak negative correlation between NO_3^- and HCO_3^- ($r^2 = 0.37$;

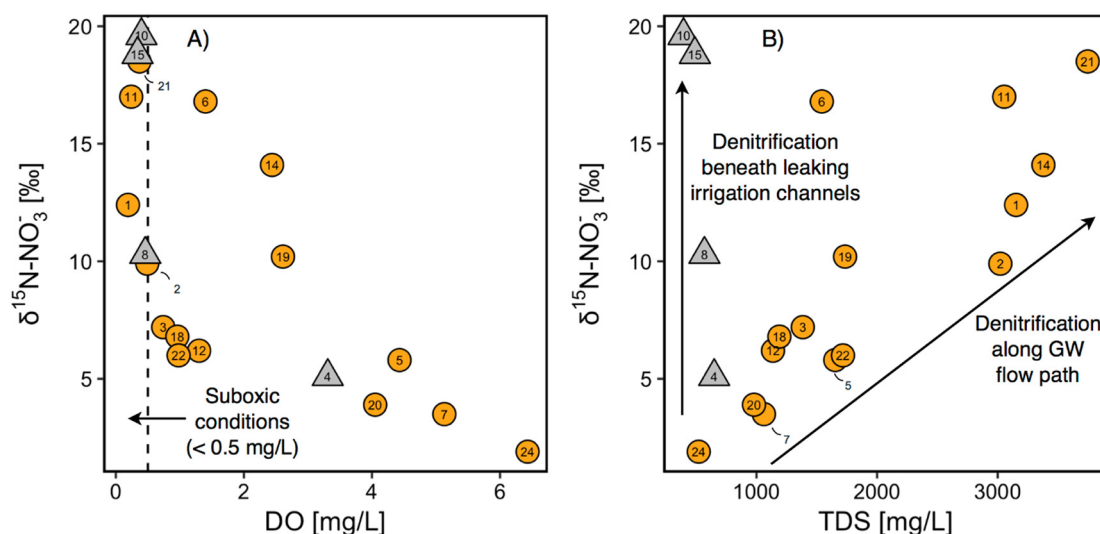


Fig. 9. a) $\delta^{15}\text{N-NO}_3^-$ plotted against DO. Suboxic conditions (<0.5 mg/L DO) are indicated by the dashed line. b) $\delta^{15}\text{N-NO}_3^-$ plotted against TDS. Symbols are as in Fig. 2.

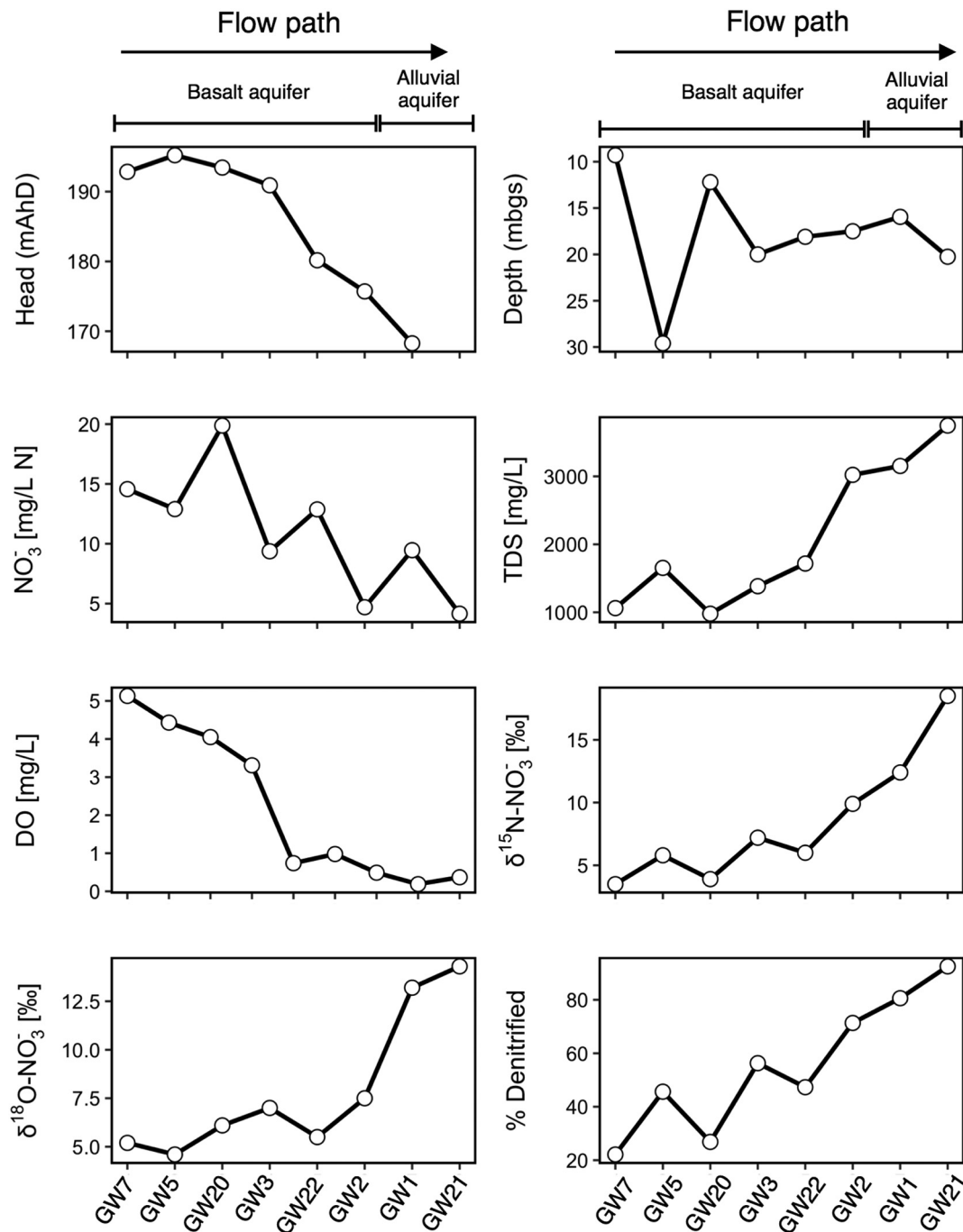


Fig. 10. Geochemical evolution of *mixed* groundwater samples taken along Transect A as it flows from the oxic basalt aquifer into the suboxic alluvial aquifer. Denitrification progresses along the flow path. Note: NogGW21 was sampled from the pump outlet, and therefore piezometric head could not be determined.

$p < 0.05$; Fig. S4-1a in Supplementary Material 4). Similarly, there were only weak positive correlations between $\delta^{15}\text{N-NO}_3^-$ and HCO_3^- ($r^2 = 0.37$, $p < 0.05$; Fig. S4-1b in Supplementary Material 4), further confirming the lack of insight that inorganic C can provide into the denitrification process in the *mixed* groundwater cluster. Interestingly, there was a strong positive correlation between NO_3^- and HCO_3^- ($r^2 = 0.95$, $p < 0.05$; Fig. S4-2a in Supplementary Material 4) and a strong negative relationship between $\delta^{15}\text{N-NO}_3^-$ and HCO_3^- ($r^2 = 0.96$, $p < 0.05$; Fig. S4-2b Supplementary Material 4) in the *leakage-dominated* cluster. These relationships are seemingly at odds with heterotrophic denitrification (a decrease in NO_3^- and increase in $\delta^{15}\text{N-NO}_3^-$ should coincide with increasing HCO_3^-). One possible explanation for this

relationship is that the extent of denitrification is directly related to the magnitude of irrigation channel leakage at these locations. That is, denitrification occurs most at locations receiving high amounts of irrigation channel waters that have low HCO_3^- content. Further research is required to determine the spatial effect of irrigation leakage on denitrification in the EIA groundwater system.

There was no relationship between DOC concentration and $\delta^{15}\text{N-NO}_3^-$, nor between $\delta^{13}\text{C-DOC}$ and $\delta^{15}\text{N-NO}_3^-$ in the *mixed* and *leakage-dominated* groundwater clusters (Fig. S4-3 Supplementary Material 4). This suggests that the dissolved C fraction was not consumed during denitrification. The lack of a clear link between DOC and denitrification, however, is

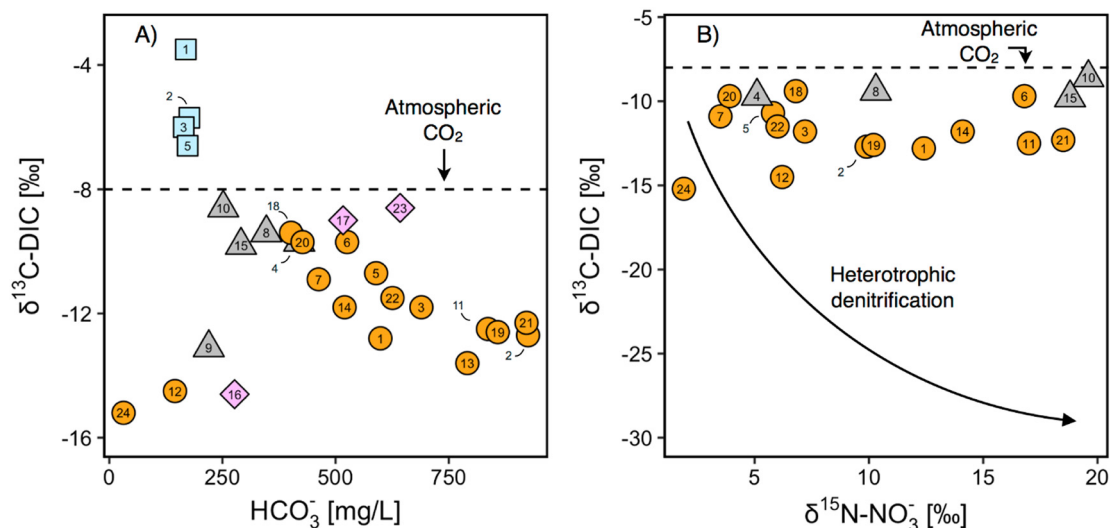


Fig. 11. a and b) $\delta^{13}\text{C-DIC}$ plotted against $\delta^{15}\text{N-NO}_3^-$ and HCO_3^- . Note that $\delta^{15}\text{N-NO}_3^-$ data was unattainable for the pre-irrigation groundwater samples and for the modern irrigation waters (Lake Maraboon and Nogoa River). Note that the y-axis scale is changed in b). Symbols are as in Fig. 2.

consistent with the findings of Hinkle et al. (2007), who found dissolved C fractions were less significant in denitrification compared to solid phase OC contained within the aquifer matrix. Nonetheless, three groundwater samples (GW9, 10 and 15), which all belong to the leakage-dominated cluster, had DOC concentrations exceeding 2 mg/L. This could indicate that DOC was contributed via the infiltration of irrigation channel waters, which have higher DOC contents ranging from 5.2 to 5.5 mg/L. The NO_3^- in GW10 and GW15 were also highly denitrified. Although this DOC may not be directly consumed during the denitrification process, the elevated DOC content suggests that the hyporheic zones created beneath the leaking irrigation channel may act as a pathway for labile OC into the groundwater system where it can act an electron donor (Harvey et al., 2013; Hinkle et al., 2001).

There was no significant relationship between $\delta^{15}\text{N-NO}_3^-$ and $\delta^{34}\text{S-SO}_4$ (Fig. 7b), suggesting autotrophic denitrification did not occur in the study area (Hosono et al., 2014; Otero et al., 2009; Pauwels et al., 2010; Vitòria et al., 2008). Furthermore, the positive $\delta^{34}\text{S-SO}_4$ and $\delta^{18}\text{O-SO}_4$ compositions of all EIA groundwater samples greatly exceed those expected for sulfate derived from sulfide oxidation during autotrophic denitrification (Vitòria et al., 2008).

Considered collectively, there was no conclusive evidence of an electron donor control on denitrification in the EIA groundwater system. Overprinting from increased recharge render it difficult to rule out the occurrence of heterotrophic denitrification in the absence of other geochemical data. However, there is some evidence to suggest that hyporheic zones near leaking irrigation channels provide the necessary C for heterotrophic denitrification.

5.5. Conceptual model and management implications

A conceptual model is shown in Fig. 12 that captures the origin and fate of NO_3^- across the EIA groundwater system. Fertiliser-derived N is likely retained in the SON pool prior to its mineralisation and subsequent nitrification, after which it is leached to underlying groundwater. Within the groundwater system, denitrification is strongly related to DO availability. At a regional-scale, this manifests in denitrification along the groundwater flow path as it becomes progressively more oxygen-depleted and incorporates solutes. At a local-scale, denitrification occurs in suboxic hyporheic zones beneath leaking irrigation supply channels, independent of the regional groundwater flow.

What is the potential for NO_3^- export from the aquifers of the EIA? Waterlogging from rising shallow groundwater tables has previously been reported in the extensively irrigated fields overlying the basaltic soils in the EIA. This is managed using tile and surface drainage to nearby tributaries

(Department of Natural Resources Queensland, 1998; Sunwater, 2012; Yule, 1997). Irrigation farm drainage water in the EIA has been found to consistently exceed Australian environmental guidelines for TN concentrations (Department of Natural Resources Queensland, 1998). The elevated groundwater NO_3^- concentrations measured in this study indicate that the shallow groundwater therefore remains an important transport mechanism for NO_3^- export to surface waters, and more so under high rainfall or flood conditions. Although denitrification was detected in hyporheic zones beneath leaking irrigation channels, it is currently unknown to what spatial extent this may occur throughout the EIA. Thus, denitrification should not be relied upon to attenuate groundwater NO_3^- at a regional-scale in this aquifer.

In contrast, standing water levels in the monitoring wells in the alluvial aquifers underlying the Nogoa River remain below 10 m, despite water levels having also risen ~5 m since the 1980s. Aside from the EIA, groundwater levels in the Lower Nogoa sub-catchment are mostly disconnected from overlying fluvial systems (typically between 10 and 20 mbgs; Pearce and Hansen, 2007; Queensland Government, 2020), making regional-scale groundwater-surface water discharge in the Nogoa River alluvial floodplain under current groundwater levels unlikely. Nonetheless, if groundwater levels continue to rise, the alluvial aquifers risk becoming hydraulically connected. This could become an important pathway for NO_3^- discharge into the Nogoa River and surrounding tributaries. Indeed, groundwater discharge from the alluvial aquifer has been documented in localised instances further east (downstream) of the study area (SLR Consulting Australia, 2020). However, such groundwater expressions have not been documented on a region-scale. Thus, catchment-wide transfer of groundwater NO_3^- from the alluvial aquifer can be considered less important than in the basalt aquifer, especially given that denitrification persists as groundwater flows into this aquifer.

While groundwater N may reflect past practices, considered collectively, groundwater management in the EIA should focus on:

1. improved irrigation water management, including the lowering of shallow groundwater tables of the basalt aquifer. This may have the benefit of decreasing mineralisation rates in soil profiles and decrease the rate at which solutes are mobilised to the groundwater system. Furthermore, lowering groundwater levels in this aquifer would decrease the rate at which water levels rise in the adjacent alluvial aquifers, albeit with a degree of time lag; and
2. improved N fertiliser use-efficiency, to reduce the amounts of anthropogenic N reaching these aquifers via deep drainage. Current attempts to re-line leaking irrigation channels (Sunwater, 2020) will likely assist in lowering shallow groundwater tables.

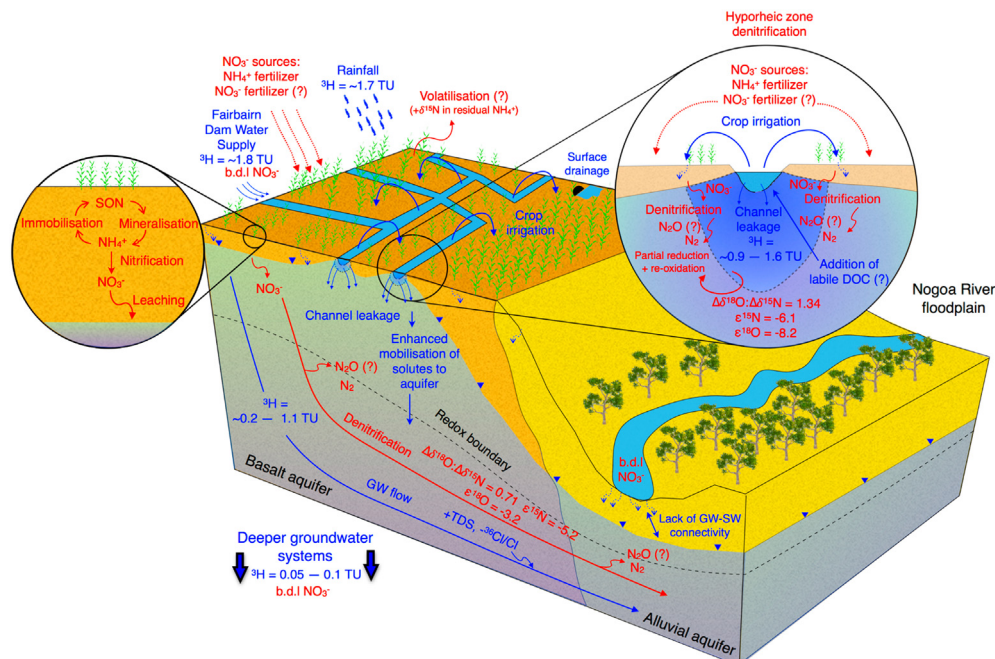


Fig. 12. Conceptual diagram (not to scale) of the processes leading to regional-scale denitrification and hyporheic zone denitrification beneath leaking irrigation channels. Processes relating to N are shown in red, and hydrological processes indicated in blue. b.d.l.: below detection limit.

6. Conclusion

We applied multiple stable and radioactive isotope tracers to elucidate the sources and hydro-geochemical controls on groundwater NO_3^- cycling in the EIA. Our isotopic data are consistent with a fertiliser source of groundwater NO_3^- , which is likely retained in the SON pool (via microbial immobilisation) prior to being mineralised and nitrified. This NO_3^- is delivered to EIA aquifers following the beginning of modern irrigation practices in the mid-1970s. NO_3^- isotopes indicate that denitrification is a prominent feature of the EIA groundwater system. Denitrification manifests progressively as groundwater flows from the upgradient oxic basalt aquifer to the downgradient suboxic alluvial aquifer. In locations where groundwater is hydraulically connected to leaking irrigation channels, dilution and denitrification occurs in electron donor-rich suboxic hyporheic zones. This process acts independently of the regional groundwater flow. Denitrification is not likely to be coupled to sulfide oxidation. However, evidence for organic matter oxidation during denitrification could not be decoupled from the strong isotopic influence of infiltrating irrigation waters and natural weathering processes. Importantly, the application of both ^3H and ^{36}Cl to identify zones of channel leakage, as well as regional mixing processes, was critical for enabling the de-coupling of local- (hyporheic zones beneath leaking irrigation channels) and regional-scale (groundwater flow path) denitrification.

The ability to successfully characterise (with strong statistical significance) denitrification and associated enrichment factors using NO_3^- isotopes in the EIA is noteworthy. This is likely due to the blended isotopic signature of groundwater NO_3^- resulting from the immobilisation of NO_3^- in the SON pool prior to migration to the groundwater system, in addition to there being a single predominant N source (N fertiliser) to EIA groundwater. To further confirm the role of SON retention in soils, more detailed studies into SON content and the isotopic signature of both SON and different crop types are required in the EIA. Further studies are also needed to confirm the potential role of organic C in denitrification processes in these aquifers.

In the predominantly oxic upgradient basalt aquifer, raised groundwater tables have created pathways for NO_3^- to be transported to adjacent rivers and tributaries. In contrast, in the alluvial aquifers of the Nogoa River floodplain, the transfer of NO_3^- is limited both physically (through

groundwater-surface water disconnection) and chemically (through denitrification along the groundwater flow path) in the study area. The lowering of groundwater levels in the basalt aquifers and limiting future groundwater table elevation in the alluvial aquifers, are thus important steps in minimising the export of NO_3^- from EIA groundwaters. A unified approach focused on improving water use and fertiliser use efficiency in the EIA is therefore needed to minimise any risk of fertiliser use on adjacent and end of system ecosystems.

CRediT authorship contribution statement

Experimental conceptualisation and design was carried out by DIC, BFJK and SJH. Fieldwork and in-field geochemical analyses were conducted by all authors. Data analysis was primarily undertaken by SJH, with guidance from DIC and BFJK. The manuscript was written by SJH with input from all authors. Funding for the research was obtained by DIC and BFJK.

Declaration of competing interest

The authors declare that they have no conflict of interest.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2021.152606>.

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