Nitrogen species distribution in groundwater: A review of historical data with recent sampling in the Gippsland, Victoria (Australia)

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Abstract
In agricultural regions diffuse pollution by nitrate is considered one of the main causes of groundwater quality deterioration. For agricultural systems that are pasture based, the input loads (e.g. fertiliser, cow dung and urine) can result in loss of nutrients. Hence, shallow groundwater aquifers in agricultural areas are susceptible to nitrate contamination from losses of N by leaching. A review of historical data, together with recent sampling, was carried out in the Gippsland region of Victoria to map distribution of N-species in shallow aquifer systems. This review revealed that there is limited routine monitoring of nitrate in groundwater. Nevertheless, based on the limited historical spatial and temporal groundwater chemistry data available, the concentrations of nitrate and ammonium are generally below Australian water quality (ANZECC) limits in the shallow unconfined aquifer in West Gippsland. However, localized clusters of values higher than the ANZECC limit exist in alluvium near Mitchell River, East Gippsland. In all confined deep aquifer samples the concentrations were found to decrease further. An analysis of groundwater chemistry could not identify a correlation between land use or soil and the concentrations of groundwater nitrate and total nitrogen. Only shallow piezometer samples at Willow Grove, West Gippsland suggested high nitrate reductions under intensely grazed dairy soils. Site-specific piezometer studies would be required to determine the depth of influence below the soil zone for reduction of nitrate to acceptable concentrations.

Key Words
Agriculture, dairy, nitrates, land use

Introduction
Widespread pollution of groundwater due to 20th century agricultural intensification has been of major concern in the developed world (e.g. Europe and USA) for several decades and is generating concern in Australia (Dillon et al., 1991; Wilcock et al., 2011; Ladson, 2012). Loss of nitrate is particularly difficult to manage, as the anion is highly mobile, non-reactive and readily leaches through soil to contaminate the underlying groundwater. Nitrate leached to groundwater can remain and be discharged to environmentally sensitive surface waters long after leaching losses have decreased. Balancing the demands for agriculture and clean water requires understanding the routes by which nitrate enters the surface-ground water system and how long it takes to get there. This paper reviews historical data and reports recent groundwater chemistry studies carried out in the Gippsland region of Victoria (145.4-149.9 ˚E and 36.8-39.1 ˚S). The research forms part of a program to quantify below root zone and groundwater nitrogen pathways and loads under dairy agriculture in the Gippsland region.

Methods
Study area description
The agricultural production of the Gippsland region of Victoria represents a large portion of the export and contribution to the state's economy. The area extends from Warragul (100 km east of Melbourne) to the eastern tip of Victoria at Mallacoota, enclosing parts of two natural resource management regions (Yates et al., 2015). The region can be broadly described as a coastal sedimentary basin comprising seven catchment areas (Figure 1). An overview of the area geology and hydrogeology have been compiled from available maps, Groundwater Atlas and Victoria Aquifer Framework (SKM, 2009).

Data sets
Existing State Observation Bore Network (SOBN) groundwater data for the Gippsland region was collated and mapped to show the spatial distribution of nitrogen species (nitrate, nitrite, total nitrogen) in groundwater. This dataset (including basic bore information, water levels and total dissolved solids, TDS)

was compiled from the Victorian Water Measurement Information System (WMIS). In addition, twenty-four bores were selected from the existing network and sampled in December 2015 to analyse for chemical constituents of the groundwater. These bores were mainly from the dairy areas in West Gippsland.

The WMIS database comprising 129 bores within West Gippsland and 30 bores in East Gippsland with details on EC, total or bicarbonate alkalinity, TDS, NO_3-N or NO_3^- and NO_2^- combined as N or total nitrogen (TN). Fifty-five percent of these bores access the upper aquifer system (mostly Haunted Hills Formation and Alluvium). Stratigraphic analyses indicate the upper aquifer system in Table 1 form a connected unconfined aquifer, including the Boisdale aquifer (Nuntin Clay), which allow leakage into the aquifer system (Yates et al., 2015). Also, a recent study demonstrated inter-aquifer mixing in the Latrobe Valley (Cartwright et al., 2012).

Field and Analytical methods
Electrical conductivity (EC), dissolved oxygen (DO), and pH values were measured directly in the field during the December 2015 sampling. Samples were filtered (0.45 µm) and stored at a temperature of ~4 ºC. The groundwater samples were analysed at the Centre for Applied Sciences, DEDJTR Macleod, , Victoria. These samples were analysed for inorganic constituents: ammonium (NH_4^+), nitrite (NO_2^-) and nitrate (NO_3^-). Nitrate and nitrite were determined using an ion chromatograph DIONEX DX 500 (detection limit was 0.05 mg/l for nitrate and 0.01 mg/l for nitrite) whilst the ISO (1997) standard method was used for the analysis of NH_4^+.

Results and discussion
The 129 bores in West Gippsland had NO_3-N concentrations ranging from 0.1 to 20 mg/l and 85% of these were < 1 mg/l NO_3-N. The 30 bores from East Gippsland had concentrations ranging from 0.02 to 99.4 mg/l (as NO_3-N). Only 20 % of these bores were above the Australian water quality (ANZECC) permissible limit of 10 mg/l. These bores were mostly shallow and screened in Alluvium.

The NO_3-N concentrations in the Gippsland region groundwater varied considerably from East Gippsland to West Gippsland (as shown in Figure 2), although the chemistry data was limited both spatially and temporally. Table 1 shows the summary statistics of nitrate-nitrogen distribution by aquifers and TN concentrations. Bores with nitrite-nitrogen levels < 0.01 mg/l are not presented in the table. To show the temporal variation of nitrate, the concentration levels in groundwater were grouped by season. The seasonal influence is distinct with autumn and spring having higher nitrate concentrations. Wetter soils are prone to nitrate reduction, as they typically provide restricted oxygen availability and sufficient electron donors (Follett, 2008).

In the measured data (December 2015 sampling), maximum nitrate (NO_3^-) concentrations reached up to 18 mg/l in groundwater (Figure 2) and were predominantly greatest in bores screened in the upper aquifer (Haunted Hills and Quaternary). The median concentrations were 9.2 and 9.5 mg/l for Haunted Hills and Quaternary respectively. This is in contrast to the Upper Latrobe Group (median 1.0, mean 1.9 mg/l) and Thorpdale Volcanics (median 1.0, mean 3.5 mg/l), indicating a heterogeneous distribution of nitrate concentration ranges (by aquifers). Nitrite concentrations were near or below the detection limit of 0.01 mg/l in the study area. Ammonium concentrations were generally low (<0.5 mg/l) in all the unconfined aquifer bores. However, one bore was found to have 2.64 mg/l NH_4-N, probably due to mineralisation in the Haunted Hills (Cartwright et al. 2012).

Both WMIS data and measured data showed very low nitrate concentrations in shallow groundwater in the west Gippsland catchments. In all confined or deeper aquifers groundwater bore samples, the concentrations were found to decrease further compared to shallow groundwater (bores with screen <25 m). An analysis of groundwater chemistry could not identify a correlation between land use or soil and the concentrations of groundwater nitrate and total nitrogen. However, shallow nested piezometers (1-3 m) sampled at Willow Grove (West Gippsland, location shown in figures 1 and 2) over 3-years (2003-2005) on a dairy farm showed concentrations of nitrate and total nitrogen that suggest the possibility of high nitrate reduction rates under intensely grazed dairy soils.

The shallower piezometers (1 m depth) have relatively higher concentrations (up to 36 mg/l as NO_3) as compared to its nested pair (at 3 m depth) showing nitrate concentration <1 mg/l. The ratio of nitrate and TN of the deeper piezometers to the shallower ones is high (4 to >10). When the concentrations (NO_3 and TN) were plotted against water level in the piezometers, three groups emerged; the relatively shallow piezometers and higher water table combination have nitrate concentrations more than 3 times as high as the deeper piezometers. It is clear from these limited results that N-load from the land surface has less impact with depth and that transformation processes through the soil profile is possible in the context of the dominant land use. This study equally showed that prolonged wetness (or wetter soils), which are prone to nitrate reduction chemically, may be caused by a slowly permeable layer within the soil profile (e.g., perch-grey soils) or by the presence of a shallow groundwater table. Field studies in anoxic aquifers have shown that denitrification potential is inversely correlated with the permeability of the soil material (Rivett et al. 2008, Lasagna et al. 2016).

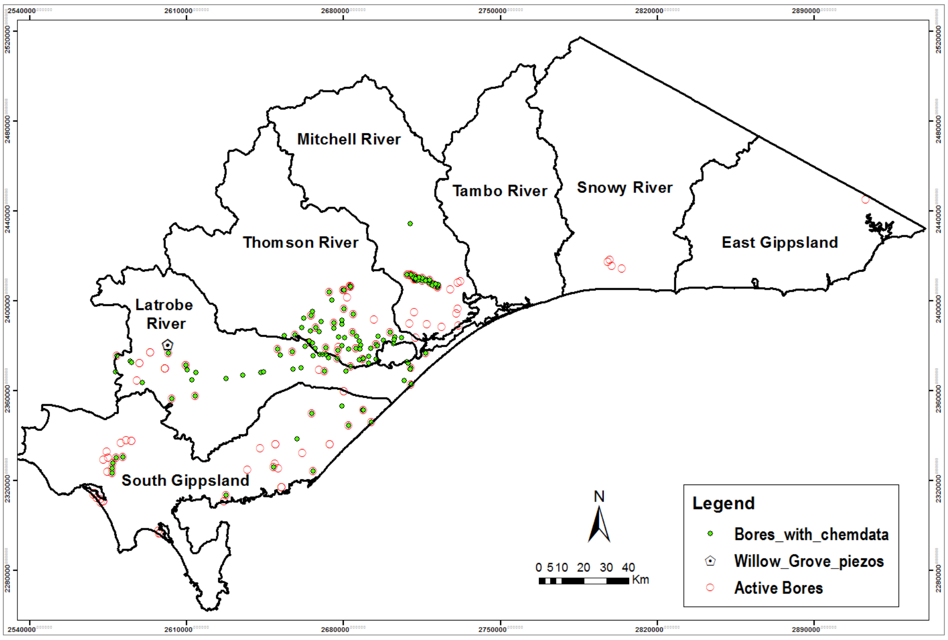

Figure 1: Map of the Gippsland Basin with SOBN distribution across the catchments used in the study.

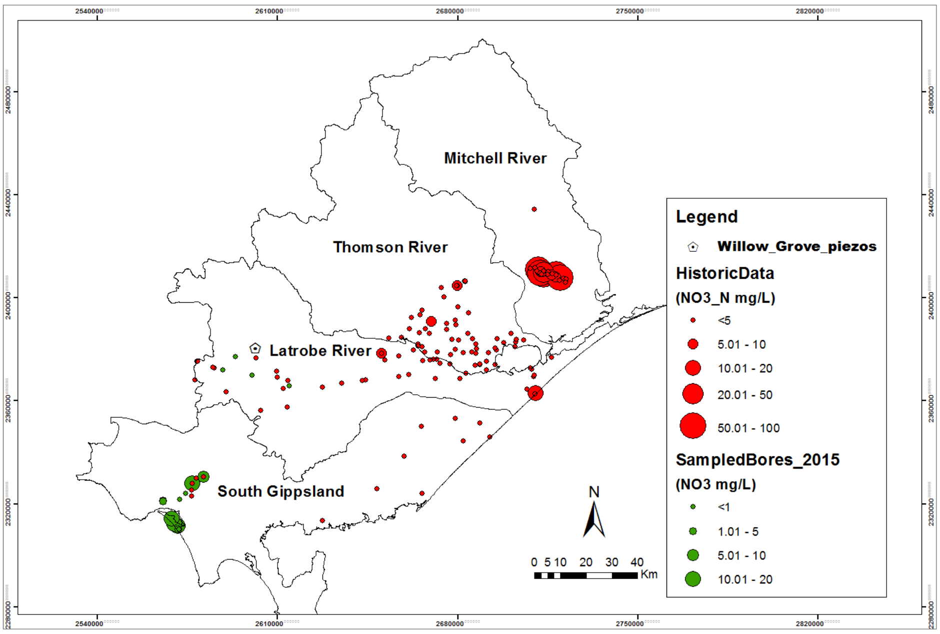

Figure 2: Spatial distribution of nitrate in Gippsland from historical and sampled data
(Note the different measurement units for nitrate: milli-equivalent of compound N is equivalent to 62 mg when expressed as NO_3^-).

Table 1. Summary statistics of nitrogen concentrations in groundwater in the Gippsland

AQUIFER SYSTEM	NITRATE-NITROGEN (mg/l)				TOTAL NITROGEN (mg/l)			
	(Count)	(Min)	(Max)	(Mean)	(Count)	(Min)	(Max)	(Mean)
Upper Aquifer System	**86**	**0.02**	**99.4**	**6.0**	**30**	**0.1**	**36**	**3.2**
Alluvium	27	0.03	99.4	10.7				
Haunted Hills	45	0.02	90.0	4.5	24	0.1	36	2.4
Nuntin Clay	3	0.15	0.5	0.3	1	3.3	3.3	3.3
Quaternary	9	0.05	7.0	0.9	5	0.2	30	7.1
Unknown	2	0.15	20.0	10.1				
Mid Aquifer System	**34**	**0.01**	**2.9**	**0.4**	**14**	**0.1**	**5**	**1.2**
Balook	5	0.15	0.5	0.4	4	0.3	3.4	1.6
Boisdale	12	0.01	2.9	0.4				
Boisdale	11	0.01	0.9	0.3	9	0.1	1.4	0.6
Latrobe Valley	3	0.09	2.1	1.1				
Yallourn	3	0.15	0.3	0.2	1	5	5	5.0
Lower Aquifer System	**36**	**0.01**	**4.1**	**0.4**	**3**	**0.1**	**0.1**	**0.1**
Childers	3	0.02	0.0	0.0				
Latrobe Group	14	0.01	1.6	0.2				
Older Volcanics	6	0.01	0.0	0.0				
Seaspray Sand	1	0.19	0.2	0.2				
Thorpdale Volcanics	2	0.01	3.5	1.8	1	0.1	0.1	0.1
Unknown	2	0.01	4.1	2.0				
Upper Latrobe	7	0.15	1.7	0.4	1	0.1	0.1	0.1
Upper Latrobe	1	0.15	0.2	0.2	1	0.1	0.1	0.1
Basement Aquifer System	**3**	**0.01**	**2.3**	**0.8**				
Strzelecki	3	0.01	2.3	0.8				
Grand Total	**159**	**0.01**	**99.4**	**3.4**	**47**	**0.1**	**36**	**2.4**

Conclusion

There was variation in the concentrations of dissolved N-species in the groundwater within the Gippsland study area (from West to East) based on historical WMIS and recently measured data. But there was no identifiable large spatial variability in the nitrate concentrations in West Gippsland. However, relatively higher levels (>50 mg/l NO_3-N) were found in the alluvial aquifers near the Mitchel river, where infiltration of surface runoff to groundwater appears to occur. Hence, the unconfined/semi-confined aquifers at the eastern side around the Mitchells Plain alluvium are very vulnerable to contamination by nitrogen species. Groundwater chemistry data was limited, both spatially and temporally, and it does not appear that groundwater from the different aquifers in the central part of the Gippsland Basin can be differentiated based on the distribution of nutrients and general major ion chemistry. This may be because the bores were not specifically designed for either detecting the nutrient impact or for water quality studies. This may also explain why the regions of intense dairying in South Gippsland do not appear to show impacts on the groundwater nitrate concentrations. Although recent groundwater sampling in the south-western Gippsland recorded concentrations within the lower nitrate range of the historic (WMIS) data, piezometers within a previously established dairy farm have concentrations close to the ANZECC guideline limits. These results suggest that land use practices in these areas be frequently monitored to ensure nitrogen losses to groundwater do not have a detrimental impact. Analysis of monitored N-species concentrations with isotopic compositions under various land uses and environmental conditions would inform an evaluation of nitrogen loading in the landscape.

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