An Isotopic Study of Nitrate Pollution of Groundwater in Victoria, Australia

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SUMMARY : High nitrate (>45 mg/L NO_3) in groundwater can be hazard to human and animal health and contribute to the development of algal blooms and subsequent eutrophication of wetlands. A nitrogen isotopic study was carried out to determine the probable sources of nitrate in groundwaters of Victoria known to have high concentrations of nitrate. The results were able to distinguish between fertiliser derived nitrate from that of animal and human wastes. The results also revealed that significant fractionation of nitrogen isotopes can take place in the soil profile and interpretation with caution is warranted.

1. INTRODUCTION

Nitrate in groundwater can be hazard to human and animal health and contribute to the development of algal blooms and subsequent eutrophication of wetlands. Its presence is widespread throughout Australia and its levels overall appear to be increasing. A variety of sources of nitrate contamination are known. These include nitrogen fixing plants, termites, animal wastes, industrial and domestic wastes, sewage and fertilisers.

In Victoria, nitrate-rich groundwaters have been reported from a number of localities and include Colac, the Nepean Peninsula, Shepparton, Deer Park (Mt Derrimut), Benalla and Winchelsea (Figure 1).

A multi-isotope (N, O and H) study was carried out to determine the probable source of nitrate in groundwater in these localities.

2. SITES

Sites which included clover, industrial wastes, animal and human wastes and fertilised sources, were selected after existing databases on nitrate concentration, earlier reports and access to a suitable network of bores for collecting reliable samples. Groundwater samples were collected from Colac, Nepean Peninsula, Shepparton, Werribee, Deer Park (Mt Derrimut), Benalla, Venus Bay and Winchelsea (Fig. 1).

Hydrogeologically they are characterised by shallow aquifers (usually <20 m) which are usually unconfined and there is natural recharge or recharge induced by man (irrigation, septic tanks, etc.). Aquifer lithologies include Quaternary alluvial silt and sand (Benalla, Werribee and Shepparton), Quarternary dune sand (Nepean Peninsula and Venus Bay), Quarternary lunette silt (Winchelsea), and Upper Cainozoic basalt (Werribee, Colac and Deer Park).

2.1 Animal wastes

Nitrate pollution of groundwater from animal wastes include sources feedlots, abattoirs, pastures, etc.. A piggery near Winchelsea, about 30 km west of Geelong, Victoria, was chosen to investigate this source. Improved pastures (fertiliser-free) near Shepparton in northern Victoria used for an intensive dairy industry, were also included in this category for our investigation.

2.2 Human wastes

Septic tanks represent another important source of nitrate pollution of groundwater. Three sites were chosen. The first one is the Venus Bay area in SE Victoria, and the second one is Benalla, NE Victoria. In the latter area, Dudding (1) reported very high

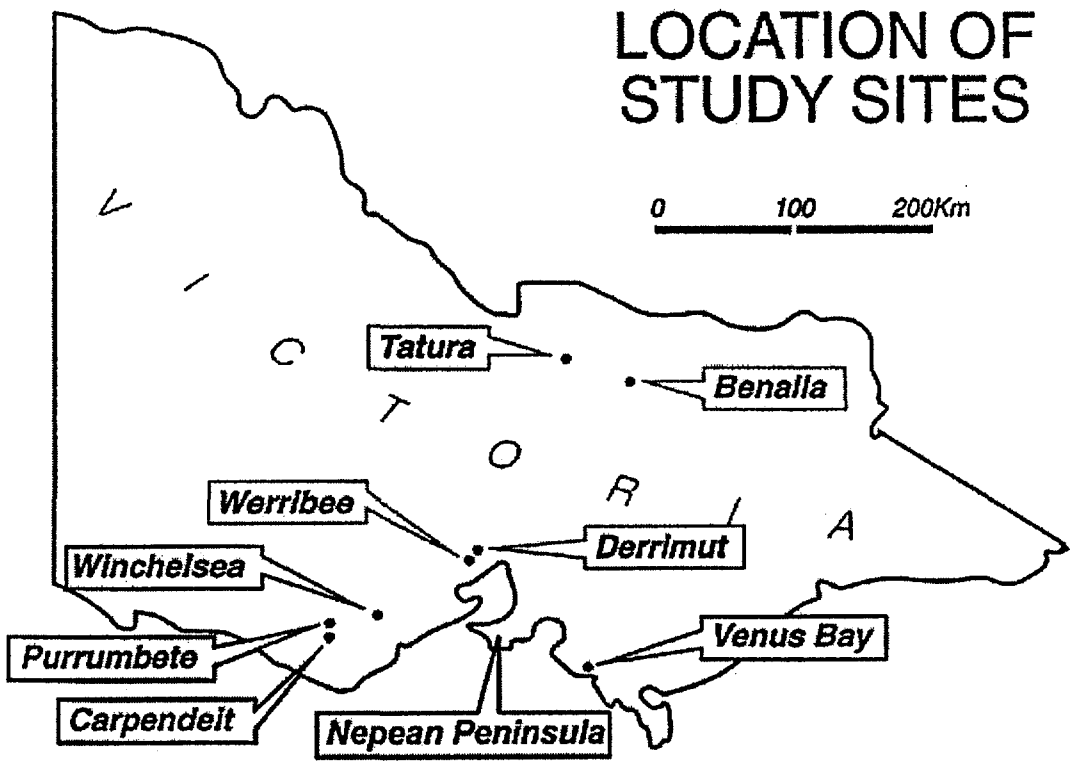

Figure 1. Locations of study sites.

levels of nitrate which he attributed to septic tanks. The Werribee Treatment Complex, located west of Melbourne, was also chosen to represent a human waste source, where three forms of land treatment of sewage are applied.

2.3 Fertilisers

The Institute of Sustainable Irrigated Agriculture, Department of Natural Resources and Environment, Victoria, Tatura, has been carrying out research on nitrate fertilisers in Tatura and Shepparton areas of northern Victoria. These sites were chosen to represent fertilisers, where urea and ammonium nitrate are applied to pastures and orchards.

2.4 Soil nitrogen

Lawrence (2) attributed the high nitrate concentrations of groundwater near Colac in western Victoria to clover. This site was chosen to represent a soil nitrogen source.

2.5 Industrial waste

The groundwaters in Mt Derrimut, Deer Park, Melbourne have been found to contain nitrate levels in excess of 300 ppm (Shugg, 3), and is believed to have originated from an ICI factory or explosives manufacturing plant, located a few kilometers north of the area.

2.6 Source unknown

High nitrate concentrations in the groundwaters of the Nepean Peninsula have been reported by Shugg (4). The source of the nitrate is unclear in these groundwaters.

3. NITROGEN IN GROUNDWATER

In groundwater nitrogen occurs as nitrate (NO_3^-), ammomium (NH_4^+), ammonia (NH_3), nitrite (NO_2), nitrous oxide (N_2O), nitrogen (N_2) and organic nitrogen.

Nitrogen transformation reactions which are important to the nitrogen isotope technique of source identification include the following:

Ammonification
$CH_2O(NH_3) + O_2 = NH_4^+ + HCO_3^-$

Nitrification
$NH_4^+ + 2O_2 = NO_3^- + 2H^+ + H_2O$

Denitrification
$4NO_3^- + 5CH_2O = 2N_2\,(g) + 5HCO_3^- + H^+ + 2H_2O$

Dissimilatory nitrate reduction
$NO_3^- + H_2O + 2CH_2O = NH_4^+ + 2HCO_3^-$

The above reactions significantly alter the nitrogen isotopic composition of the products and the reactants due to kinetic fractionation.

4. SAMPLING AND ANALYTICAL TECHNIQUES

The groundwater samples from the selected sites were collected and stored using standard techniques. Wherever possible samples were collected from contaminated and uncontaminated groundwater. The main objective of this sampling strategy within the same area was to diffrentiate between polluted and unpolluted groundwater.

Soil samples using a hand auger were collected from a nashi orchard near Tatura. Commercial fertilisers applied in this orchard were also analysed.

Nitrate and ammonium were analysed by an ALPKEM auto analyser. Samples for the determination of $^{15}N/^{14}N$ ratios were prepared by the steam distillation method of Keeney and Nelson (5). In this method inorganic nitrogen in the water samples are converted to NH_4^+ salt by steam distillation with MgO and Devarda's alloy and by titration with sulphuric acid. The ammonia is then oxidized to nitrogen gas with lithium hypobromite to determine the $^{15}N/^{14}N$ ratios in a gas source mass spectrometer. The oxygen isotope ratio ($^{18}O/^{16}O$) of the water samples were determined by the CO_2-equilibration technique. The zinc reduction technique was utilized to prepare the water samples to determine the D/H ratios. All the isotope results are presented in the standard 'δ' - notation The nitrogen isotope results are expressed with respect to atmospheric N_2, whilst the oxygen and hydrogen results are expressed with respect to V-SMOW. The results are summarised in Tables 1 and 2.

5. RESULTS AND DISCUSSION

5.1 Groundwater nitrate and ammonium

The nitrate levels ranged from less than 1 mg/L to in excess of the WHO recommended value of 45 mg/L (10mg/L $N\text{-}NO_3$). The highest levels were obtained from the industrial site at Deer Park (>50 mg/L) and fertilised areas in Tatura,

Table 1. Range of NO_3^-, NH_4^+ and $\delta^{15}N$ values of groundwaters from various source types in Victoria..

Source	NO_3^- (mg/L)	NH_4^+ (mg/L)	$\delta^{15}N$
1. Animal wastes	1.6±0.6	1.8	14.1±3.5
2. Human wastes	10.8±1.6	<1.0	11.0±1.0
3. Fertilisers	16.5±4.0	<1.0	4.8±1.3
4. Soil nitrogen	3.3±0.5	n.a.	4.9±0.9

Shepparton and Nepean Peninsula, and by septic tanks in Benalla and northern Victoria.

In the majority of the samples the ammonium levels were less than 1 mg/L. Two samples from Winchelsea had ammonium levels of 2.1 and 1.5 mg/L. This could be attributed to wastes from the piggery. An effluent sample from the Werribee sewage treatment plant had ammonium concentration of 25.7 mg/L. Since ammonium levels of groundwater at Werribee is lower than 1 mg/L, it is likely that the ammonium was converted to nitrate in the presence of dissolved oxygen.

5.2 $\delta^{15}N$ of groundwater nitrate

5.2.1 Animal wastes

The $\delta^{15}N$ values of groundwater beneath the pastures near Shepparton ranged from 9.8 to 12.1 per mil, values typical of animal wastes (Heaton, 6). The $\delta^{15}N$ values of groundwater nitrate adjacent to the piggery near Winchelsea were found to be significantly enriched. The $\delta^{15}N$ values in this locality were found to be greater than 15.0 per mil, and could be attributed to denitrification of the nitrate. The fact that denitrification is an anerobic process is supported by field measurements at Winchelsea, which showed very little dissolved oxygen in the groundwater (<2 mg/L).

5.2.2 Human wastes

The $\delta^{15}N$ values of groundwater from Benalla were also found to be enriched (9.6 to 10.9 per mil), and confirms Dudding's (1) conclusions that the source of nitrate is predominantly from septic tanks.

The $\delta^{15}N$ values of two groundwater samples from the Werribee treatment complex were 12.8 and 11.9 per mil. In contrast, the $\delta^{15}N$ values of groundwater from the outside the complex (unpolluted) were found to be significantly different (4.8 and 5.2 per mil), and probably represents the background values of the groundwater nitrate in the area.

A single sample from the Venus Bay area in SE Victoria had a $\delta^{15}N$ value of 8.8 per mil. Although the value is slightly lower than normal waste values, large variations in $\delta^{15}N$ values of wastes are sometimes seen due to the presence of significant amount of ammonium in the area under investigation (Heaton, 6). In other words, values lower than 10 per mil can be expected for nitrate derived from human or animal wastes depending on the ammonium content.

5.2.3 Fertilisers

The $\delta^{15}N$ values of groundwaters below fertilised orchards were found to be significantly enriched (4.5 to 8.2 per mil) than $\delta^{15}N$ values of fertilisers. The $\delta^{15}N$ values of fertilisers range from -4.0 to 4.0 per mil (Heaton, 6). The $\delta^{15}N$ values of fertiliser samples applied in the orchards were found to be between 0.2 and -2.9 per mil, and fall within the expected range. Also the $\delta^{15}N$ values of soil nitrate were found to be progressively enriched with depth. The $\delta^{15}N$ values of soil nitrate ranged from -0.6 per mil at 30 cm, to 2.1 per mil at 70 cm, to 3.2 per mil at 140 cm depth.

Differences in the $\delta^{15}N$ values of fertilisers, soil-nitrate and groundwater nitrate have also been reported by Flipse and Bonner (7) and Rolston et al. (8). These variations indicate fractionation of the nitrogen isotopes during nitrate migration from the surface to the water table. Ammonia volatilization of ammonium fertilisers has been found to be responsible in the increase in the $\delta^{15}N$ values of groundwater nitrate under fertilised fields of Long Island, New York (Flipse and Bonner, 7). A similar mechanism was probably operative at Tatura because ammonium nitrate fertilisers were also used at this site. Another possibility is mixing of fertiliser derived nitrate with soil derived nitrate.

5.2.4 Soil nitrogen

The $\delta^{15}N$ values of groundwaters from the Colac area range from 3.5 to 7.1 per mil. The results confirm earlier findings of Lawrence (2) who attributed the high nitrate values to nitrogen fixing by clover-rich pastures in the area.

5.2.5 Industrial source

A single analysis from the Mt Derrimut site gave a $\delta^{15}N$ value of 3.6 per mil. Due to lack of data from industrial wastes in the literature, it is difficult to comment on this single value.

5.2.6 Unknown source

The $\delta^{15}N$ values of groundwaters from the Nepean Peninsula exhibited two groups. In the first group, the groundwater samples which were collected from vegetable farms near Rosebud and Boneo, the $\delta^{15}N$ values ranged between 5 and 7 per mil, and are slightly higher than average fertiliser values. Fertilisers are regularly applied in these farms and could be the major source

of the nitrate in the groundwater. Although contribution from soil nitrogen cannot be totally ruled out. Study is in progress to discriminate the two sources at this site.

In contrast, the areas west of Rosebud, the $\delta^{15}N$ values are very enriched. The $\delta^{15}N$ values ranged from 11.2 to 11.9 per mil. The area is known to lack proper sewerage system, and most households have septic tanks. The isotope data suggests that nitrate has leaked from these septic tanks into the groundwater. The sandy nature of the unconfined aquifer in these localities could have facilitated easy transport of the nitrate into the groundwater.

5.3 $\delta^{18}O$ and δD of groundwater

Oxygen and hydrogen isotope analyses were carried out to differentiate between polluted and unpolluted groundwaters. Samples were collected from Mt Derrimut (Deer Park), Werribee and the Nepean Peninsula. Unpolluted groundwater samples (natural background) from the samples sites showed very restricted range in $\delta^{18}O$ (< -5.0 per mil) and δD(< -30 per mil) values, thereby suggesting that the isotopic composition of the meteoric water recharging these aquifers were very similar. In contrast, the $\delta^{18}O$ and δD values of groundwater samples collected from polluted sites were significantly different. (Table 2). At Deer Park the average $\delta^{18}O$ and δD values were -3.9 and -27 per mil respectively. At Werribee the the $\delta^{18}O$ and δD values were -4.8 and -27 per mil respectively. The data indicate pollution of these sites with water derived from the surface which were much more enriched in $\delta^{18}O$ and δD than the background values.

Table 2. Comparison of oxygen and hydrogen isotope data of polluted and unpolluted groundwaters in selected study sites of Victoria.

Location	Unpolluted		Polluted	
	$\delta^{18}O$	δD	$\delta^{18}O$	δD
Nepean Peninsula	-5.5	-32	-2.6	-15
Deer Park	-5.3	-33	-3.9	-27
Werribee	-5.6	-32	-4.8	-27

In the Nepean Peninsula the $\delta^{18}O$ and δD values were -2.6 and -15 per mil respectively. The significant shift in the isotopic composition in the Nepean Peninsula could be attributed to incursion of seawater into the aquifer. The $\delta^{18}O$ and δD values progressively increase towards the Port Phillip Bay.

6. CONCLUSIONS

The results obtained in this study have shown that the nitrogen isotope technique can be used effectively to differentiate nitrate pollution caused by animal and human wastes from that caused by fertilisers and soil nitrogen. Although the $\delta^{15}N$ values (-4.0 to 4.0 per mil) of nitrate derived from fertilisers are supposed to be distinct from that of soil nitrogen (4.0 to 8.0 per mil), this study has shown that due to fractionation in the soil profile, the $\delta^{15}N$ values of the nitrate derived from fertilisers could attain the $\delta^{15}N$ values of the soil nitrogen. This fractionation will be less or minimal depending on the type of sediments in the unsaturated zone. If there is little or no fractionation, the nitrogen isotopic composition of the the groundwater nitrate should be similar to the fertiliser values, and hence distinction from soil nitrogen will be possible. Research is in progress in this respect.

7. ACKNOWLEDGMENTS

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