CHAPTER 3. TREND ANALYSIS OF HISTORICAL DATA

3.1. INTRODUCTION

As outlined in earlier sections, there have been significant resources directed towards the assessment of nitrate contamination of groundwater in the South East region. An important aspect of this study was the assessment of the degree to which groundwater nitrate concentration data can be used to inform natural resource managers. Although it is tempting to focus upon the collection of further ground water samples, every effort should be made to maximise the use of historical data. This is needed as not only is the data unique, in that it can not now be reproduced, it is often that each data record represents the expenditure of tens, or in some cases hundreds, of dollars in salaries and analytical costs. Considering that much of the data has been collected by state government agencies, there is an obligation upon researchers and natural resource managers to maximise the use of this historical data to better inform decision making.

However the use of historical data is often complicated by an absence of information giving context to the data records. This uncertainty in reliability of the data discourages the consideration of many historical datasets. Ideally, the assessment of groundwater trends should be based upon long term records, however these records are often not available within South Australia. The determination of trends in groundwater nitrate concentrations is further complicated because of the variability of nitrate concentrations over short distances and therefore the inappropriateness of using single data points for extrapolation (Exner and Spalding 1990).

Groundwater quality data for the study area has been collated through specific projects (MacKenzie and Stadter 1981, Schmidt, et al. 1998), for ongoing ambient water quality monitoring, and for quality control for reticulated water supplies. The work by MacKenzie and Stadter (1981) and Schmidt and his colleagues (1998) reported on much of the available data to that time. These two projects were different in that the project by Schmidt and his colleagues was intended to report at the regional scale, whereas the work by MacKenzie and Stadter was focused upon the Coonawarra area. Neither study attempted to assess any temporal trends in nitrate concentrations in groundwater. The identification of water quality trends is an important aspect for understanding of the environmental processes that influence nitrate concentrations in groundwater. Knowledge of longer term changes in groundwater quality is also important for natural resource managers to assess the effectiveness of management responses.

This chapter reports upon the degree to which historical groundwater quality data can be used to determine temporal trends of nitrate contamination in the region.

3.2. METHODS

3.2.1 Collation of Existing Datasets

Access to historical data can be difficult due to the non-digital nature of many older datasets, and the poor data management methods that have been adopted in the past. Fortunately, considerable work had already been undertaken in the region to collate, in a digital form, the majority of nitrate related groundwater data. It was possible to access the original dataset that was the basis for the work by Schmidt and his colleagues (1998), and an updated dataset from the work reported by MacKenzie and Stadter (1981). Additional water quality data was also sourced from the State Government maintained database systems SAGEODATA (borehole database maintained by the Department for Water, Land and Biodiversity Conservation; DWLBC) and EDMS (surface and groundwater quality database maintained by the Environment Protection Authority; EPA). All digital data available to June 2004 was collated from these sources.

Additionally, all available local records for the 2085 bores within the study area (hardcopy and microfiche) held by the EPA and the DWLBC were accessed to identify water quality data that had not been included in the above studies.

Unsuccessful attempts were made to source any historical data from the laboratories likely to have undertaken much of the analysis for water quality; namely AMDEL and the Australian Water Quality Centre (AWQC; then called the State Water Laboratory). AMDEL, being a commercial institution, only retained laboratory results for seven years. Although the AWQC may retain hardcopies of relevant analyses these could not be incorporated as there had been no standard referencing of sample locations. Given the extent of hardcopy records within the AWQC laboratories, it was considered impractical to initiate an individual review of all their archived groundwater results.

3.2.2 Data Reliability

Data reliability is a key concern for the use of historical data. Microfiche water quality records existed for 309 of the bores considered for this study. Digital data records replaced microfiche during the 1990s, and any water quality analysis undertaken since the early 1990s would have been entered into digital databases, with hard copy laboratory reports not always retained.

Even though the use of digital databases were adopted in the early 1990s, there have been attempts to incorporate earlier historical data into the SAGEODATA system.

Where historical records were available within digital databases, it was necessary to determine the reliability of the water quality values. During collation of the water quality data, sources were documented where identified (e.g. hardcopy laboratory reports). Where disagreement existed between water quality data, for the sample location and time, between datasets, the original laboratory result was used. This disagreement mainly occurred where departmental documentation either rounded water quality values, or errors were made with conversion between units.

Due to data integrity concerns, particularly with the digital datasets, water quality results were collated for well sites up to 20 kilometres outside the study area. This process was undertaken to expand the opportunity for cross-referencing digital data and hardcopy records. Later, this dataset was reduced to the study area to reflect the focus of this research. Therefore the discussion throughout the data review sections may refer to the total collated data or the data within the study area.

3.2.3 Special Aspects of Historical Hardcopy Reports and Data

Collation of historical groundwater data followed a reasonably simple approach of data entry from hardcopy records. However, considerable difficulties were encountered with collating the historical data into a consistent and reliable format.

Many of the sampling reports prior to the 1980s reported water quality differently to the current standards. For instance, laboratory reports prior to 1962 reported concentrations as grains per gallon, and it was therefore required to convert these values to milligrams per litre. The conversion factor used was 14.25, based on there being 4.546 litres per gallon, and 64.799 milligrams per grain (Madison 1996). Nitrate concentrations were reported as both nitrate and nitrogen; nitrate concentrations as nitrogen (as N) have been used throughout this thesis.

In addition, many of the laboratory reports prior to the 1970s did not report the actual concentration of nitrate in groundwater. For 106 out of 117 water quality reports for analysis undertaken prior to 1973, nitrate concentrations were reported as “Present”, “Trace” or “Nil”. A review of the archived laboratory reports identified that the classification of “Trace” was less than 20 mg/L (as NO_3), and therefore the classification “Present” was an indication that the nitrate concentration was greater than or equal to 20 mg/L (as NO_3). This correlation of classified data to concentrations was also used by Harvey (1979) in his study.

The determination of the nitrate concentration appropriate for the “Nil” term was problematic as there was no documentation able to be sourced that indicated the laboratory detection limit for nitrate analysis at that time. Although the collated data showed reported nitrate concentrations during this early period as low as 4 mg/L (as NO_3), Harvey (1979) believed that the “Nil” classification represented 5 mg/L (as NO_3). In the absence of other information, the assumption by Harvey has been adopted for this study. This conversion from qualitative to quantitative data was undertaken for 73 nitrate records within the study area.

During data collation it was identified that many data reports did not contain detail on the sample collection date. Almost all reports included a date that the laboratory received the samples, or the date that the report was produced, and in some cases this date was the only date available. In these cases the date of the analysis was used in the dataset. This does not impact significantly on the data quality for this study, but may be relevant for future studies that investigate seasonal variability.

3.2.4 SAGEODATA data

SAGEODATA is the database used for the storage and management of water quality data collected by the DWLBC. This dataset contained a large number of records of water quality for bores within the study area, and is the primary repository for water quality data across the region. Although a considerable amount of data was easily available from this database, there were a number of issues identified in respect to its reliability.

During data collation it was identified that the concentration values for (particularly) nitrates within the data extracted from SAGEODATA was often significantly different from microfiche or other hardcopy records. Although the SAGEODATA database reports all nitrate concentrations as nitrogen (i.e. as N) with the units being milligrams per litre, other researchers have identified that some of the values are in fact milliequivalents per litre (H. King, EPA, pers. comm. 2005).

In order to confirm this, the available nitrate concentration data was reviewed to identify all of those duplicate results where one of the data sources was from SAGEODATA. This identified a consistent relationship between the data within SAGEODATA and the laboratory (or other) reported sources of data. This allowed the conversion of records into a standard unit of measure for later analysis.

As a first step, an assessment was undertaken of the data provided by SAGEODATA for the combined concentration of nitrate and nitrite (as N). Although these records did not represent the older datasets, (the reporting of NOx only appears in SAGEODATA for the study area from 1987), these were more common in the 1990s. It was important that these were also verified. All 69 SAGEODATA NOx concentrations were within 0.3 mg/L of a reference hardcopy value. This variation is considered to be negligible, and arguably within the accuracy of the sampling and analytical method. It is therefore considered that there is a high degree of confidence of the NOx concentrations sourced from SAGEODATA.

The review of nitrate concentration data from SAGEODATA identified that the relationship to reference values was more complex. A comparison of 128 SAGEODATA records with other records gave the ratio of the reported concentrations shown in Figure 3.1.

Figure 3.1 indicates there was no consistent relationship between the SAGEODATA values for any period except after 1996. After 1996 the project of Schmidt and his colleagues (1998) established consistency in data analysis and data entry in the region and therefore there is confidence in this later period of the data. While there are some outliers in Figure 3.1, there are three main groupings for the ratio (excluding the ratio of 1 after 1996).

Through further investigation it was identified that these ratio groupings were the result of the following situations;

- **Ratio of 4.3 to 4.5.** It is suggested that nitrate values in this grouping

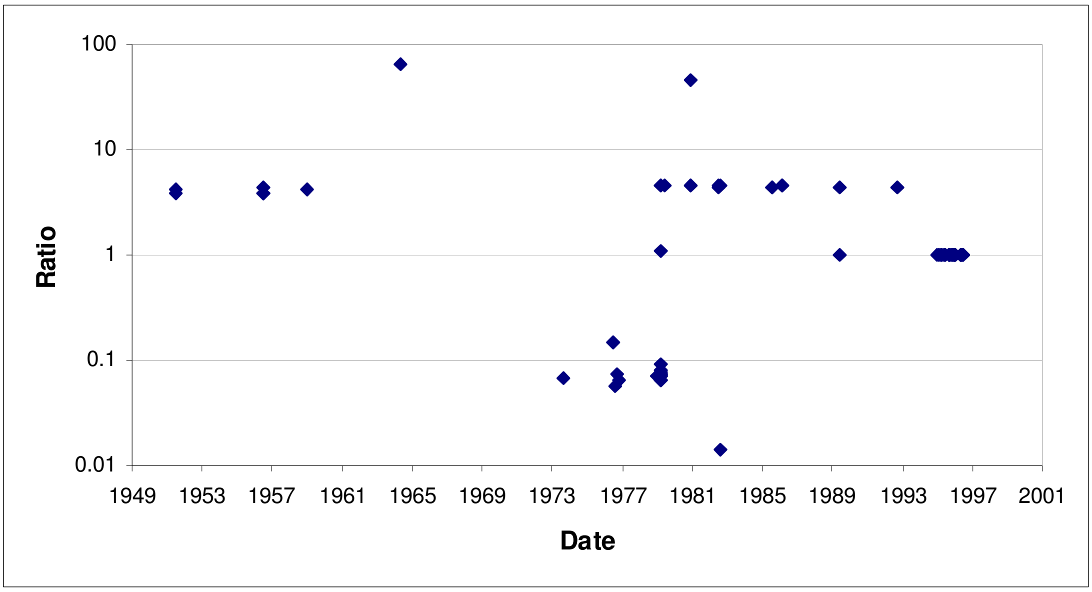


Figure 3.1: The ratio of historical SAGEODATA NO_3-N values against sourced hardcopy values

were as NO_3 but reported as N. The conversion between these two units is 4.4286, and it is likely that the variability is the product of typographic and rounding of values (this is relevant to the following two ratio groups as well). Reporting of nitrate concentrations as NO_3 was common in Australia until the late 1990s. This was confirmed through a review of the available laboratory reports.

- **Ratio of 4.4 to 5.1.** All of the values compared prior to 1960 displayed a ratio within this range. A review of available laboratory reports identified that nitrate concentrations were actually reported as NO_3 in grains per gallon (gr/G), however the variability in the range (4.4 to 5.1) is greater than for the other two ratio groupings. A possible explanation for this is that the original values in grains per gallon were rounded to the nearest integer before being entered into the database. A rounding the values reported in the laboratory records resulted in a significantly narrower ratio range of 4.44 to 4.47 (consistent with the ratio of the above group). It was not possible to confirm if this data entry approach had occurred, and it would not be possible to take account for it in those records where laboratory reports were unavailable. Given the narrow range of the recalculated comparison records, it appears that these values were entered as NO_3 yet reported as N in mg/L.

- **Ratio of 0.06 to 0.08.** It is suggested that these data values represent nitrate concentrations that have been entered as NO_3 in milliequivalents per litre (meq/L), but reported as N in mg/L. This explanation is likely as many of the laboratory results reviewed as part of this project reported in meq/L during the 1970s, and the conversion ratio between these two forms (NO_3 in meq/L to N in mg/L) is 0.07143.

These three explanations describe the nature of nitrate values stored within SAGEODATA, and there is some temporal consistency with the data. For instance, in June 1979 there was a clear change to the reported data ratio, with values changing from being entered as nitrate (as NO_3) in meq/L to being entered as NO_3 in mg/L. However, the date of change to meq/L as a data entry method was not as easy to identify, as there is a period of approximately 14 years between which there were available records with both paper and digital records for comparison (Figure 3.1).

As much of the historical data within SAGEODATA contains values for more than one analyte, it was possible to individually assess other water quality results and determine whether results were entered as meq/L. Given the magnitude of the difference between results displayed as meq/L, this identification was not difficult when comparing concentrations such as chloride and calcium.

The review has identified that the historical nitrate concentration data stored within SAGEODATA was not stored in a consistent manner, although the following was identified;

- Nitrate and nitrite (as N) in mg/L values are in correct units.
- Nitrate (as N) in mg/L values since May 1995 are in correct units.

- Nitrate (as N) in mg/L values between July 1979 and April 1994 are actually nitrate (as NO_3) in mg/L.
- Nitrate (as N) in mg/L values between November 1973 and June 1979 are actually nitrate (as NO_3) in meq/L.
- Nitrate (as N) in mg/L values between May 1959 and November 1973 may be in either nitrate (as NO_3) in meq/L or nitrate (as NO_3) in gr/G and require individual checking.
- Nitrate (as N) in mg/L values prior to April 1959 are in nitrate (as NO_3) in mg/L.

The application of these assumptions to the SAGEODATA was undertaken, however each conversion result was individually checked to ascertain the likely validity of the resulting value. As indicated in Figure 3.1, there were two occasions where the nitrate (as N) value within SAGEODATA during the 1980s appeared accurate and did not require conversion. In this situation, the resulting corrected concentration will be low, and difficult to identify as inappropriately converted. In other situations, such as where a result during the mid 1970s was in nitrate (as NO_3 mg/L), but the assumption was that the value is in nitrate (as NO_3 meq/L), then the resulting converted value is very high and easily identified. Seven records of 1955 appeared to have been entered as nitrate (as NO_3 mg/L), and therefore were converted appropriately.

Once duplicate values were removed from the combined datasets, these conversions were applied to 36 water quality records within the collated dataset; with only 25 of these records were for bores within the study area.

3.2.5 Dealing with Data Duplication

The collation of the historical water quality data required a variety of manual processes to combine the different datasets into a single data table. The initial data collation was expected to have duplicated data, as the data assessed in previous studies, particularly MacKenzie and Stadter (1981) and Schmidt and his colleagues (1998), was also collected from the historical data and the databases.

Given that there were minor variations in dates reported in publications and those dates on corresponding laboratory reports, it was not possible to automatically identify all of the duplications. It was therefore necessary to individually review each bore's results and remove duplicates of water quality data. As previous publications had only reported nitrogen concentrations, this manual review was only necessary for nitrogen related water quality results.

3.2.6 Dealing with Non-Detection and Qualitative Values

The combined water quality dataset included 41 records (out of a total of 916 records within the study area) where nitrate concentrations were reported as less than, presumably, the level of detection. Although these records are important in understanding the water quality in the study area, there is a difficultly with including these records within any statistical analysis of the data. The clear preference is for these records to continue to be reported as "Less than" in order to reflect the uncertainty of the values, and this information is therefore retained and used where possible.

However, for some interpretation methods it was necessary to convert such values to an estimated concentration based upon the referenced level of detection. Given the small proportion of these records, and the low level of detection for all of the values (0.22 mg/L to 0.1 mg/L), the choice of any option for these values was not considered to bias any of the subsequent conclusions. An acceptable approach is to adopt for these records a value equivalent to half of the referenced detection limit (ANZECC and ARMCANZ 2000), and although this approach is not ideal, it will minimise the possible bias that may occur with other estimation techniques (Keith 1991).

A further conversion that was required was the estimation of concentration values from the qualitative results reported during the 1960s and 1970s ("Present", "Trace" and "Nil"). As already discussed, a review identified that these classifications were equivalent to ‘Greater than 20 mg/L (as NO_3)’, ‘Less than 20 mg/L (as NO_3)’ and ‘Less than 5 mg/L (as NO_3)’ respectively.

In an effort to minimise the bias in the dataset, the following conversion approach was adopted for the different qualitative descriptions;

- Those records of “Present” were assigned a nitrate (as NO_3) concentration of 20 mg/L.
- Those records of “Trace” were assigned a nitrate (as NO_3) concentration of half the threshold value of 20 mg/L (i.e. 10 mg/L).
- Those records of “Nil” were assigned a nitrate (as NO_3) concentration of half the estimated detection threshold of 5 mg/L (i.e. 2.5 mg/L).

It is considered that the adoption of this approach for the 73 records within the study area where qualitative data exists is the most appropriate given the circumstances. However this estimation of concentration must be considered in drawing conclusions based upon the data.

3.2.7 Confidence in Accuracy of Historical Data

A further issue identified during the data collation phase is the differing levels of confidence placed on nitrate results stored within the different databases. Schmidt and his colleagues (1998) incorrectly reported the approach of Harvey (1979) in collating historical groundwater quality data in the region by stating that Harvey had excluded water quality data prior to 1970 due to his view that the analytical method was considered unreliable. While Harvey had recognised that a variety of analytical methods had been used for analysing nitrate in groundwater during the 1960s-1970s (a zinc reduction method, a copper activated cadmium reduction method, an automated cadmium/copper column reduction method and a UV absorption method), he did not make any judgement regarding the impact that these changing methods may have had on the analytical results, and continued to report on the available nitrate concentrations.

Harvey did however exclude data prior to 1 January 1960 from his study (calculating the median nitrate concentrations in each Hundred area) because there were concerns that the sampling methodology may not have been collecting representative groundwater concentrations (e.g. inadequate purging, sample preservation) and because nitrate analysis was rarely undertaken anyway.

Although recognising the approach adopted by Harvey (1979), the historical data prior to 1960 was not excluded from the present dataset. Although there was the need to carefully consider their interpretation, the data was included in an attempt to identify any possible trends.

The concern with data reliability within the collated dataset is also highlighted by the recent decision by the Department for Water, Land and Biodiversity Conservation to suspend the service it has been providing since 1996 for the free analysis of nitrate in water samples from newly constructed bores. This step has been taken in response to concerns that inadequate quality controls were being applied to sample collection and preservation (G. Harrington, DWLBC, pers. comm. 2005). While quality control processes for older samples has been discussed above, this decision also questions the confidence that can be placed in data collected for new bores. Reliability ratings are not included for nitrate data within the SAGEODATA system.

Although these issues of data reliability are raised with these two main sections of data (prior to 1960 and new bores post 1996), the data was not excluded from the dataset analysis. Trend analysis did take these issues into account however.

3.2.8 Collation of New Data

During August and September 2003 field samples were collected from 74 bores throughout the study area as part of this project. Sampling was directed towards those bores that had previously reported concentrations above 10 mg/L. Consistent sampling locations were considered preferable for assessing temporal trends in nitrate concentration.

Not all of the 121 bores initially identified for sampling were able to be sampled. This was due to a number of reasons, and although gaining access to the bores was an issue in some cases, generally landowners provided considerable assistance (and time) to assist in locating bores. In a number of instances, bores were not able to be located due to their destruction, particularly as a result of vineyard development.

Groundwater samples were collected in accordance with the Murray-Darling Basin Groundwater Quality Sampling Guidelines (MDBC 2002). All bores were purged of at least three bore-volumes prior to samples being collected. At unequipped bores, groundwater was pumped for purging and sampling using a 3.5hp centrifugal suction pump, with sample collection as close as possible to the surface of the unconfined aquifer. The physical and chemical water quality parameters (pH, temperature and electrical conductivity) were monitored during purging using a YSI6000 water quality instrument (YSI Incorporated, Yellow Springs, Ohio, USA) until they were considered stable.

Water samples were collected in 1.25 litre plastic sample bottles (high density polyethylene; HDPE) for analysis for nitrogen concentration. Filtered samples (using disposable 0.45 µm filters) were also collected into 500 ml HDPE sample bottles.

All sample bottles were washed prior to sampling with Xtran-300 detergent and rinsed with deionised water to avoid contamination. Where samples were collected from unequipped bores, all sampling and pumping equipment was decontaminated with water which had a residual chlorine concentration above 0.2 mg/L to kill any potential iron bacteria and prevent cross-contamination of bores.

Samples were packed into ice-filled transport containers and couriered to Deakin University overnight. The unfiltered samples were analysed for total nitrogen (Alkaline Persulphate Digestion); Method 4500-NB and C (APHA

1998), and oxidised nitrogen (Automated Cadmium Reduction/Colorimetric); Method 4500-NO3-I (APHA 1998) at the Water Quality Laboratory, Deakin University, Warrnambool. This laboratory is NATA accredited for these analytical methods.

3.3. RESULTS

As a result of the collation of historical records, and the additional collection of further samples in 2003, a dataset of 916 records of nitrate related data was assembled for 477 bores within the study area. This number of data points, and the period over which the data was collected is significantly greater than that previously reported (MacKenzie and Stadter 1981, Schmidt, et al. 1998; Table 3.1).

3.3.1 Forms of Nitrogen in Groundwater

The water quality data (Appendix 2) shows that nitrogen is predominately present within groundwater in the form of nitrate ions.

There were 180 results for nitrite in groundwater samples with 147 of these being below detection limits (although detection limits ranged from 0.005 to 0.025 mg/L as N). Only eight samples reported nitrite concentrations above 0.1 mg/L as N, with the highest reported concentration being 0.67 mg/L as N. The drinking water guideline value for nitrite is 0.91 mg/L as N (NHMRC and ARMCANZ 1996).

There were 36 ammonia results, all of which were below 0.9 mg/L as N, with 32 of these being below 0.1 mg/L as N. There is no health based drinking water guideline set for ammonia although an aesthetic guideline level of 0.5 mg/L as N has been adopted (NHMRC and ARMCANZ 1996).

Generally, the concentrations of organic forms of nitrogen in groundwater are low throughout most of the study area. There were 67 groundwater samples

Table 3.1: The collated groundwater nitrate records and sources for the study area

Source of Data	Number of nitrate sampling records
Archived results from DWLBC Microfiche	433
SAGEODATA	185
Miscellaneous laboratory results located from EPA files	76
Data collected as part of this study	74
Schmidt and his colleagues (1998)	56
MacKenzie and Stadter (1981) with updated records	29
EDMS	28
Survey undertaken by Emmett (unpublished)	21
Miscellaneous records and reported results from EPA files	8
Survey undertaken by Harvey (unpublished)	6
Total number of records	**916**

analysed for Total Kjeldahl Nitrogen (TKN; measurement of ammonia and organic nitrogen concentrations), with the majority (60) of the samples having concentrations below 0.9 mg/L as N. Of the remaining samples, all but one are from bore 702302854, which has displayed elevated TKN (1.56 to 3.4 mg/L as N) intermittently since analysis for TKN was recommenced in 1996. This bore location has been reviewed and the bore is considered inadequately protected from surface water entry. It is highly likely that the elevated TKN values are the result of organic-nitrogen entering the bore via surface water flow. The concentrations reported are not considered to reflect surrounding groundwater quality. The other bore reporting an elevated TKN result is 702302800. One sample in 1999 of 1.81 mg/L as N is well above the other four samples for this bore collected between 1996 and 2000 of less than 0.21 mg/L. Similarly, there is little protection from surface water inflow into this bore, and the elevated level is likely to be the result of the transport of surface-derived organic matter directly into the bore.

Relative to the other forms of nitrogen, nitrate concentrations in groundwater are generally elevated across the study area, and have attracted the greatest focus for analysis. This study reports on the nitrate concentrations in the study area and assesses additional detail from the historic data that may suggest possible sources, pathways or temporal trends of nitrate in groundwater.

3.3.2 Non-random nature of nitrate data

This background describes the limitations of statistical analysis of these datasets, highlighting the need to consider data reliability. The main issue relating to the nitrate data assembled through this research is that, with respect to a number of factors, the data cannot be considered to be a random sample set of the unconfined aquifer.

The first aspect that is recognised is that a majority of the dataset is collated from a number of independent projects undertaken within the study area over discrete time periods. Figure 3.2 illustrates the clustering of nitrate results-reflecting the collection periods. This means that the assessment of temporal trends in nitrate concentration is not a simple process.

Nitrate concentrations in groundwater have been shown to display positively skewed leptokurtic distributions (i.e. dominated by a large proportion of very low concentrations). This is not unusual for environmental quality assessment (Helsel 1990). This characteristic is reflected in the histogram of the nitrate concentrations for the study area shown in Figure 3.3. An assessment of the distribution of the data using the Kolmogorov-Smirnov test reinforces that the distribution is significantly non-normal ($D(916)=0.20$, $p<.05$), and this limits the application of parametric analysis tools to the data (Field 2005).

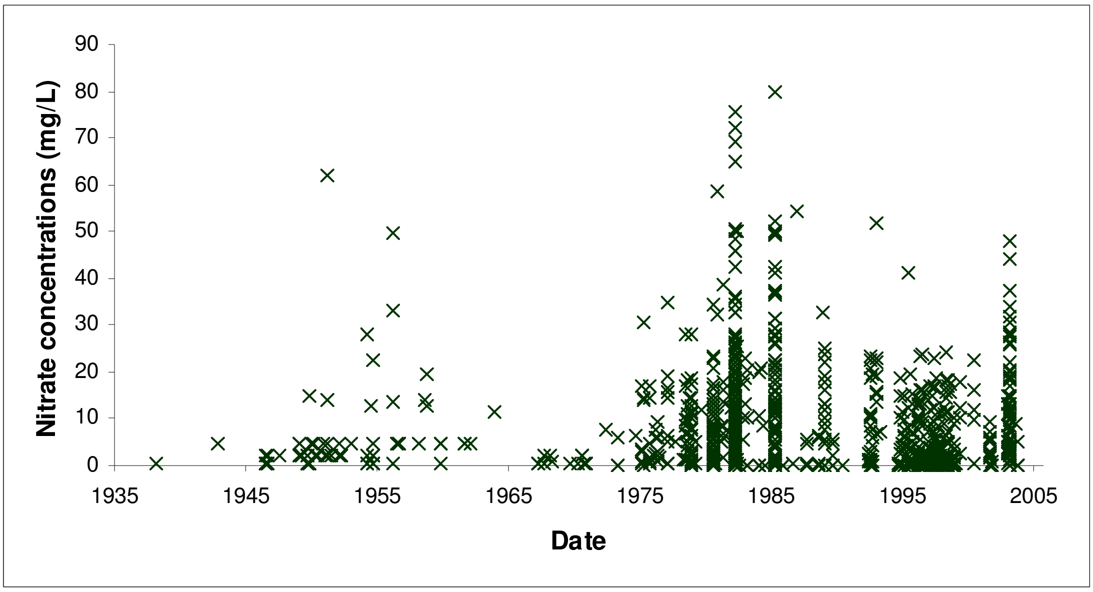


Figure 3.2: **A presentation of the non-random temporal distribution of nitrate results for the study area**

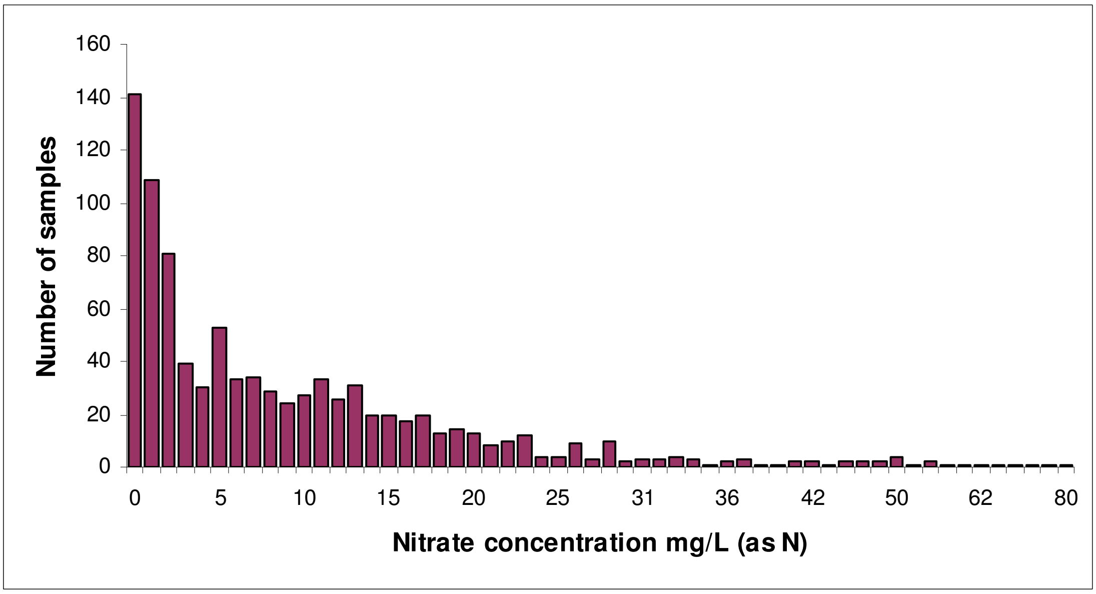


Figure 3.3: **The histogram of nitrate concentrations showing the dominance of low concentration values**

Another issue identified is that the collated dataset showed bias towards the resampling of bores with an elevated nitrate concentration (greater than 10 mg/L). Figure 3.4 illustrates that bores with low nitrate concentrations (less than 10 mg/L) are generally not included in repeat sampling events.

Conversely, bores displaying higher nitrate concentrations are generally those resampled. This practice introduces a bias within the available dataset of sites displaying elevated nitrate concentrations, and also means that records within the dataset are not independent of each other.

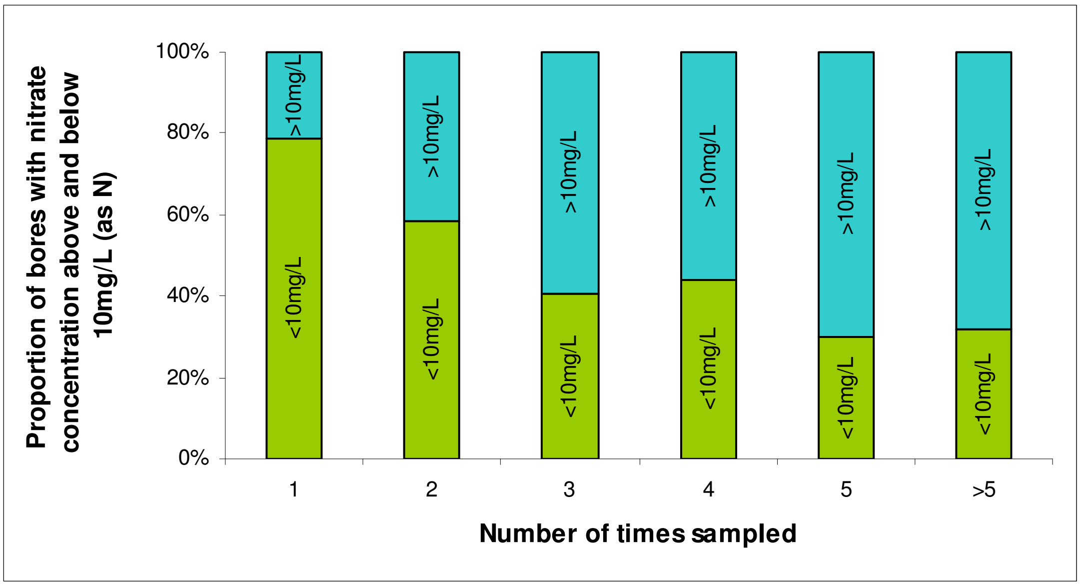


Figure 3.4: Proportion of bores with a maximum nitrate concentration above or below 10 mg/L against the number of times the bores are sampled

Although the data collated remains valid, that is it is still useful for assessing groundwater condition and groundwater quality changes, this tendency for resampling to be biased towards higher concentration bores does need to be considered in interpretation of the datasets. As previous water quality studies within the region have been 'snap-shot' or condition studies, the approaches adopted to incorporate multiple nitrate concentration results for a single bore have included using the latest value (Dillon 1988) or the median value of the samples (Harvey 1983). For this study the combination of temporal data was considered undesirable as it could disguise trends within the dataset. However trend analysis had to take into account that the data in any one year may be biased towards higher concentrations due to the preference for resampling bores with elevated concentrations.

The third issue that was considered in respect to the collated dataset was that the sampling locations (i.e. the bore locations) are not randomly distributed throughout the study area, but are sited for convenience, or to fill potential data gaps. In most cases the data collected and collated as part of this study was from bores not necessarily located and constructed for monitoring purposes. This situation can impact on the representativeness of the data as the locations of bores may tend to be close to activities and landuses that may locally impact upon nitrate concentrations in groundwater. As an example, domestic bores tend to be close to houses, and in the study area this also means that they are close to potential nitrate sources (e.g. septic tanks and fertilised lawns). Also farm bores are often in close proximity to stock watering points. Animal wastes at these locations are also likely to impact upon local nitrate concentrations in groundwater. Applying the results of groundwater sampling from these types of bore locations to the whole of the study area therefore presents some difficulties.

These limitations of the collated data are identified at this stage in order to provide some context to the manner in which an assessment of the data was undertaken. The non-random nature (spatial and temporal) of the data is likely to be reflected in many other areas where groundwater data has been collected.

3.3.3 Trends of Nitrate in Groundwater

Where nitrate data did not exist, but oxidised nitrogen data did, the assumption was made that the concentration of nitrite was zero (which is supported from the discussion in section 3.3.1).

After conversion, there were 916 nitrate records for the study area for 477 different boreholes, ranging from October 1938 to April 2004. The sample records from the database are included as Appendix 2.

For a variety of reasons, including the non-normalised distribution of the data, the use of statistical analysis methods that assume random sampling were not appropriate for summarising the dataset as a whole. Further, assessing yearly variations in data was not considered to produce useful results as the variation in the number of samples each year produced potentially misleading results where only a small number of samples were collected.

3.3.4 Yearly Classification of Nitrate Data to Identify Trends

The historical data was grouped into multi-year periods in order to reduce the sensitivity of the analysis to small sample sizes. However this grouping means that the ability to identify short-term variations is lost. Nitrate concentrations may vary considerably over seasonal or other short term periods, and the identification of these variations may provide insight into the source and transport of nitrate to groundwater within the study area. An investigation into these shorter term variations is described later in this chapter.

Multi-year periods covered a maximum of 10 years, with later groupings of five years as a result of the greater number of water quality records (Table 3.2). Mean nitrate concentrations using the multi-year periods of Table 3.2 have high standard error values resulting from the non-normal distribution of the nitrate concentration data. This data is also displayed as Figure 3.5, with the standard error of each mean shown.

Three issues were identified during this analysis;

1) Nitrate concentrations reported for the 2000-2004 multi-year period indicate the sampling bias inherent in this research. Bores for this sampling were specifically chosen because previous studies have reported elevated nitrate concentrations (as the samples were originally collected for nitrogen isotope analysis).
2) The choice of the multi-year periods in Figure 3.5 was subjective (in an effort to balance the number of samples within each reporting period). It is unclear whether this has impacted on the summarised data.

Table 3.2: **The mean groundwater nitrate concentrations for each multi-year period**

Multi-Year Period	Number of Samples	Mean Nitrate concentration (mg/L)	Standard Error
1938-1949	17	2.0	0.4
1950-1959	50	6.9	1.4
1960-1969	13	3.2	0.8
1970-1979	98	6.8	0.7
1980-1984	265	11.9	0.8
1985-1989	113	14.6	1.4
1990-1994	42	9.0	1.6
1995-1999	219	5.3	0.4
2000-2004	99	11.0	1.1

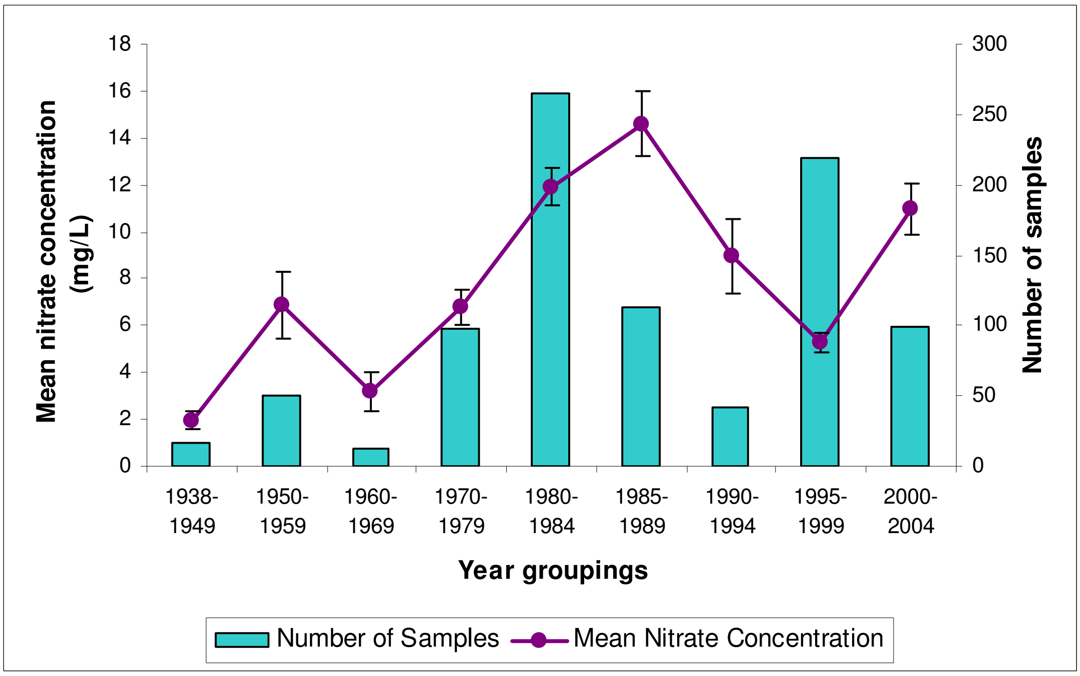


Figure 3.5: **The mean groundwater nitrate concentrations and standard errors for each multi-year period**

3) Statistical analysis of the data needed to take into account its non-normal distribution. Schmidt and his colleagues (1998) found their data was approximately log-normally distributed, and therefore converted all nitrate data prior to analysis (dependant t-test). The collated data for this study remained non-normally distributed after log-normal transformation ($D(56)=0.15$, $p<.05$). A non-parametric test was therefore used for further assessment.

A combined approach was adopted whereby a running mean of the percentage (or proportion) of grouped nitrate concentrations were calculated across all of the collated data. The approach classified the nitrate concentrations into five groups adapted from the classification groups used by Schmidt and his colleagues (1998). These were revised to improve their relevance to the collated dataset (particularly the lowest classification which was 0 to 4.5 mg/L to account for the descriptive classification used in early analysis).

The classification groupings used were for nitrate concentrations;

- less than 4.5 mg/L;
- greater than or equal to 4.5 mg/L, but less than 10 mg/L;
- greater than or equal to 10 mg/L, but less than 15 mg/L;
- greater than or equal to 15 mg/L, but less than 20 mg/L;
- greater than or equal to 20 mg/L.

Due to the relatively small number of samples in some years, and the arbitrary nature of choosing temporal calculation periods (such as calendar years), the percentage of the historical groundwater samples in each of the classification groups were calculated across a running five year period. Although other summarising periods (1 year, 2 years, and 10 years) were reviewed, the five year period was adopted as this minimised large fluctuations in the dataset that were due to the sensitivity of small sample sizes during some periods. It was identified that even with this five year calculation period, there were periods where there were few records available, and therefore the calculated percentage was over-sensitive to nitrate concentrations in individual records. The calculated percentages have not been presented where there were less than 25 sample records across any five year period (such as for the period between 1954 and 1974).

Figures 3.6 to 3.10 illustrate the variation in the proportion of nitrate samples in the study area over the period of the dataset.

Figure 3.6 illustrates the percentage of those records that have nitrate concentrations less than 4.5 mg/L. This classification group is generally the largest classification group, but also displays considerable variation over time. Between the mid 1980s and the late 1990s the percentage of samples less than 4.5 mg/L increased from approximately 30% to 60%. The very early records of nitrate concentration are heavily weighted towards these low concentrations.

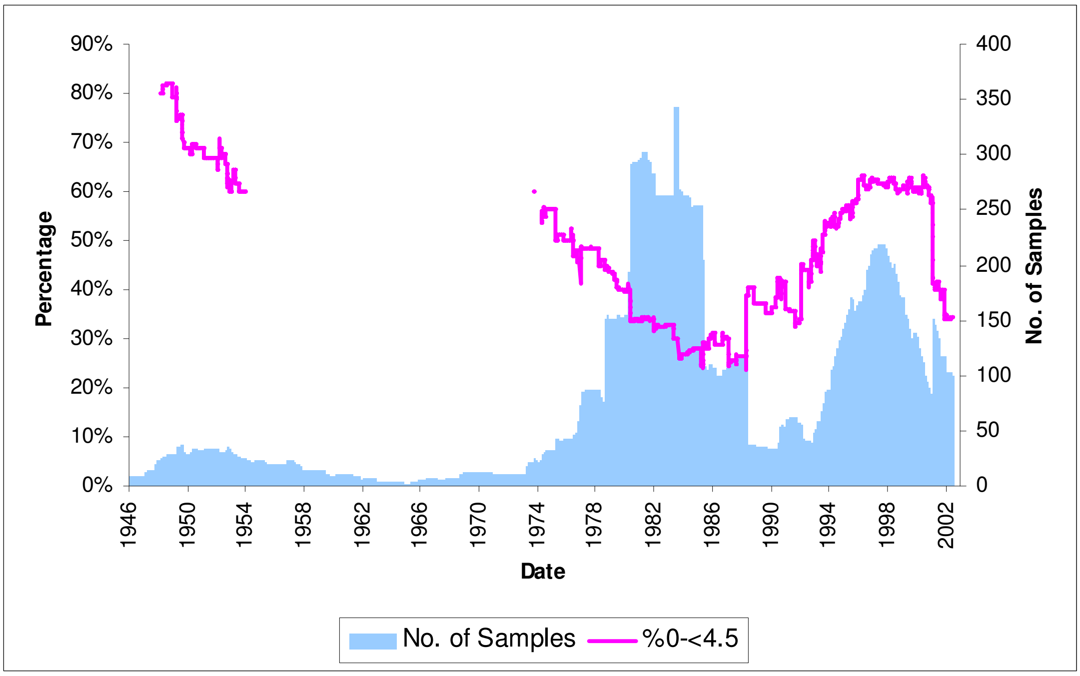


Figure 3.6: The percentage of records having a nitrate concentration less than 4.5 mg/L for a running five year averaging period (n≥25)

The percentage of samples in the classification grouping 4.5 mg/L to less than 10 mg/L (Figure 3.7) displays some variation over time, but has generally remained within 10-30%. This includes during the very early period of sampling in the area. The considerable variability in the percentage of less than 4.5 mg/L samples (Figure 3.6) is not reflected in this grouping.

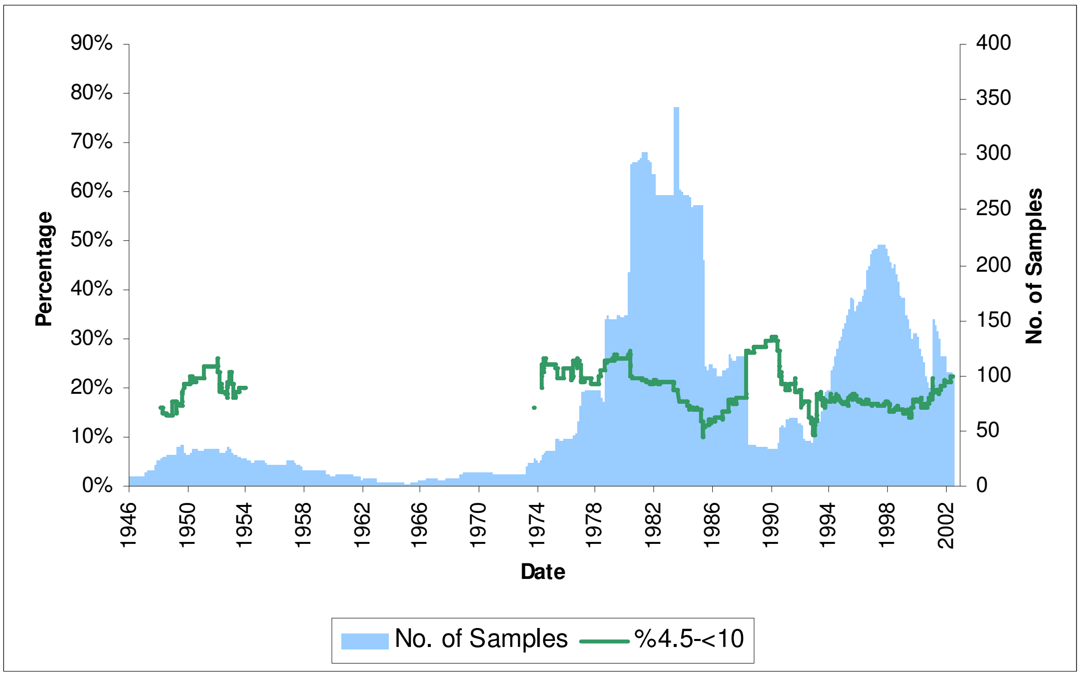


Figure 3.7: The percentage of records having a nitrate concentration greater than or equal to 4.5 mg/L but less than 10 mg/L for a running five year averaging period (n≥25)

Similarly, the percentage of records with nitrate concentrations between 10 mg/L (inclusive) and 15 mg/L has little apparent trend (Figure 3.8). The nitrate concentrations reported for this group are generally between 10 and 20% of all records, although percentages calculated for the 1950s are lower.

The percentage of samples in the 15-20 mg/L range (Figure 3.9) does not display any discernable trend since 1974, with the percentage being consistently between 6 and 14% during this period. There were no records of samples having nitrate concentration within this range in the period 1938-1959.

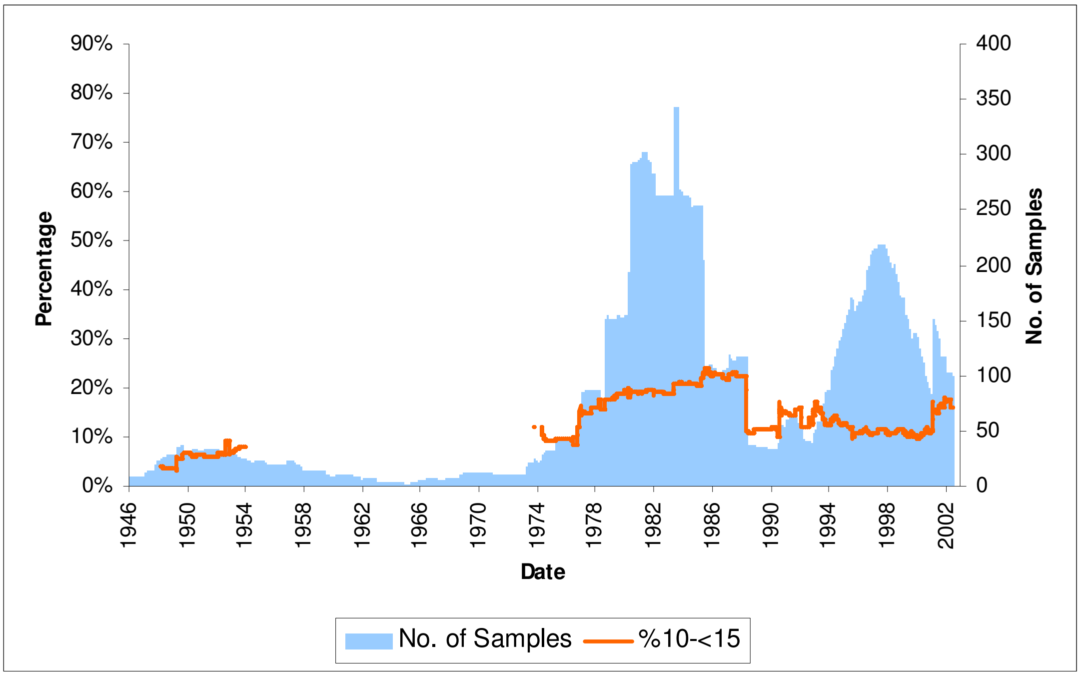


Figure 3.8: **The percentage of records having a nitrate concentration greater than or equal to 10 mg/L but less than 15 mg/L for a running five year averaging period (n≥25)**

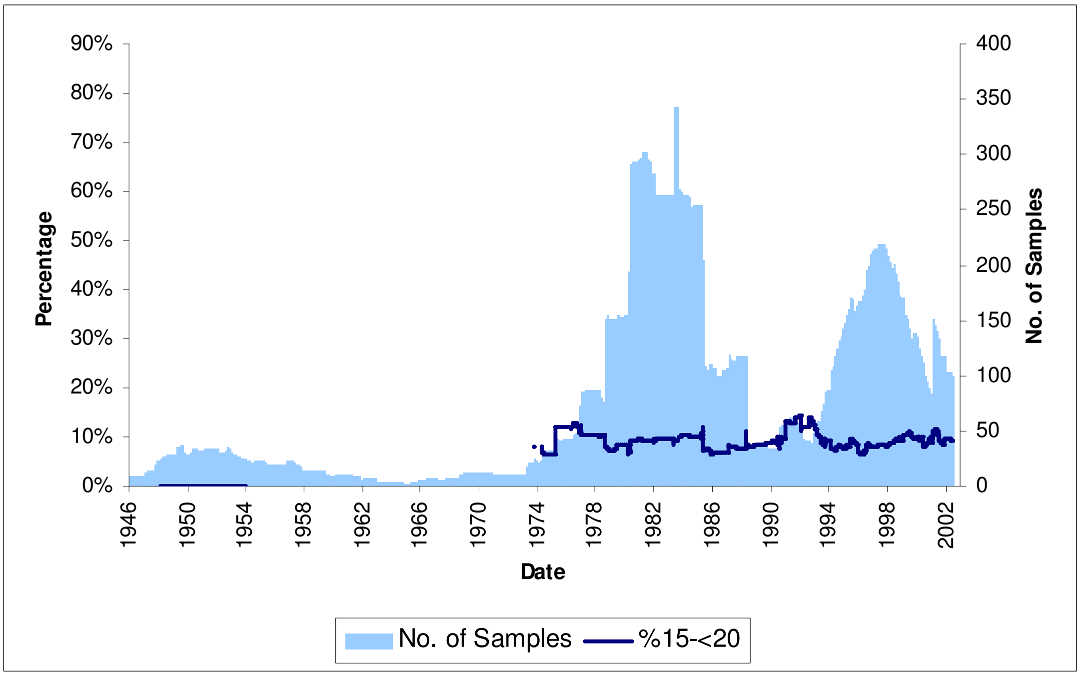


Figure 3.9: **The percentage of records having a nitrate concentration greater than or equal to 15 mg/L but less than 20 mg/L for a running five year averaging period (n≥25)**

Figure 3.10 displays considerable variation in the percentage of samples whose nitrate concentrations exceeded 20 mg/L. The variability in percentages corresponds (negatively; r^2=0.76) with the variability in the percentage of concentrations less than 4.5 mg/L for the entire period. It is suggested that the net change in percentages are between these two extreme class groupings. This figure also highlights the effect of the targeted sampling program undertaken as part of this study during 2003.

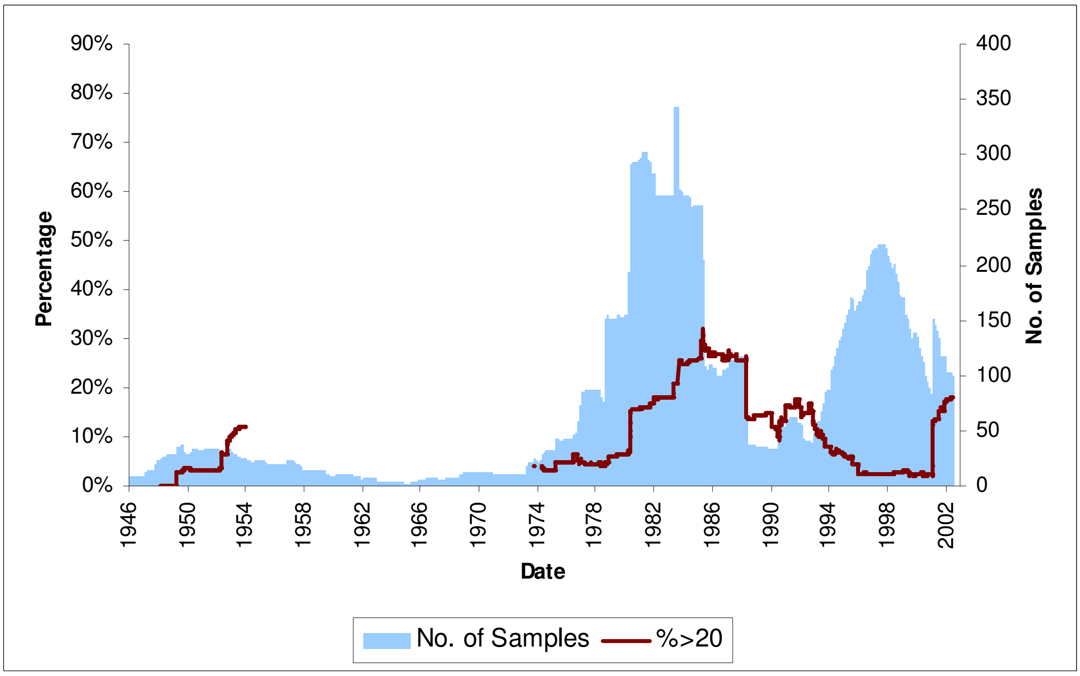


Figure 3.10: The percentage of records having a nitrate concentration greater than or equal to 20 mg/L for a running five year averaging period (n≥25)

The corresponding changes in the proportion of samples above 20 mg/L and below 4.5 mg/L may indicate an overall reduction in nitrate concentrations within the study area. The magnitude of the effects of bias from non-random resampling of bores was considered in a simplified classification based upon the proportion of samples above or below 10 mg/L; (the protection level for potable groundwater in South Australia (EPA 2003)). The difference in this analysis is that the bias of resampling is removed as only the first record for each bore is considered. Figure 3.11 illustrates the proportions for both a running five and ten-year averaging.

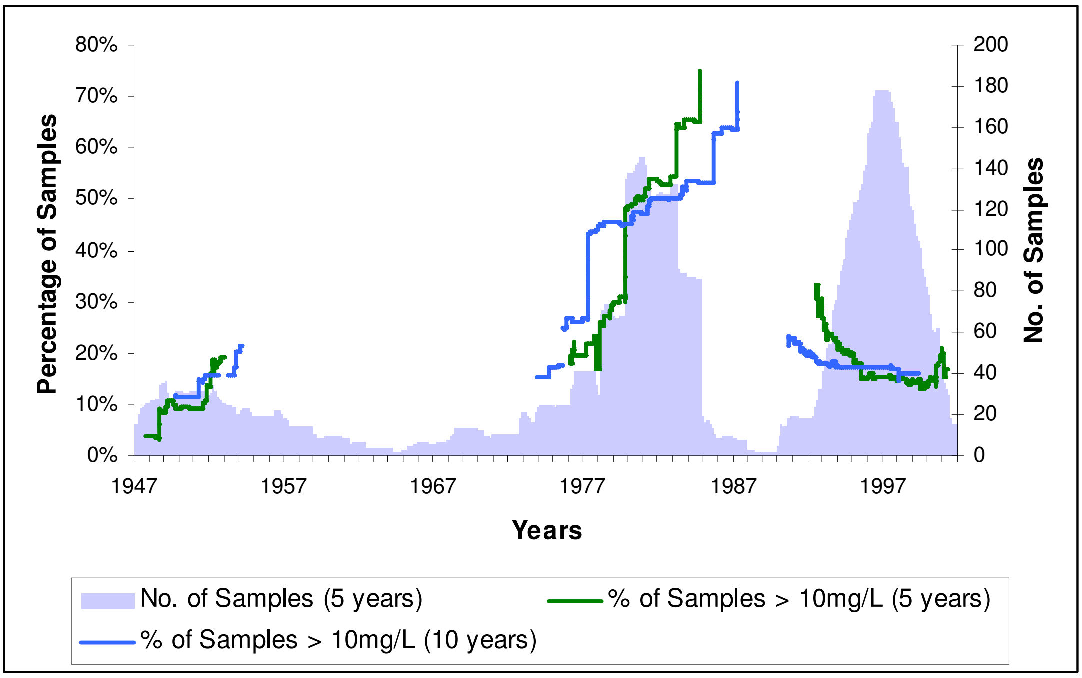


Figure 3.11: The percentage of records having a nitrate concentration greater than 10 mg/L for a running five year (n≥25) and ten year averaging periods (n≥50) using first bore record only

The modelled results presented in Figure 3.11 show general agreement between the two averaging periods. The chart also indicates that there has been a substantial reduction in the proportion of new bores registering above 10 mg/L from around 50% in the early 1980s to approximately 20% by the year 2000.

3.3.5 Nitrate Trends in Selected Bores

The assessment of the historical grouped nitrate data reports that trends in groundwater quality were present, however there are a number of limitations affecting the confidence of the conclusions. Increased confidence can occur where there exists water quality results at the same sample points over an extended period of time. This was not the case with the bulk of the data, with many (313 out of 477) of the bore locations only having one nitrate record. However, there were 21 bores within the study area that had multiple sampling records that were considered as candidates for assessing trends.

These were identified based upon criteria that;

- They had been sampled on at least five occasions;
- The samples had been collected over at least a ten year period;
- At least one of the nitrate concentrations reported in the bore was above 3 mg/L (this was chosen as the bores with nitrate concentrations consistently below this would not contribute substantially to any trend analysis).

The 21 bores meeting this criteria and used in the assessment are presented in Appendix 3 along with the illustration of individual nitrate trends.

Temporal variability in the nitrate concentrations for these bores showed no consistent pattern. Bore 702302854 displayed a major reduction in nitrate concentrations over the period of sampling, but there did not appear to be any consistent trends across all of the bores.

Nitrate concentrations within the study area may vary seasonally or over a longer time. Large variations in the nitrate concentrations from these wells are reported. For instance bore 702302993 has varied from <0.5 mg/L to 10.4 mg/L and back to 1.5 mg/L within 15 years. Some variations may be due to combinations of inconsistent sampling, changing analytical methodologies or data entry or data control problems, or may be due to dilution or intermittent sources of nitrate to the aquifer. Given that some of the bores display large variations, it is also possible that the variations may be due to local impacts at the boreholes.

Nitrate concentrations across all of these bores were combined to identify any underlying trend in groundwater nitrate concentrations. This process required the linear interpolation of nitrate concentrations between sampling events for each bore, and so must be considered in that context. At a daily interval time-step, the mean and median nitrate concentration was calculated from the interpolated nitrate concentrations (Figure 3.12). The assessment illustrates that there has been a slight decrease in the mean nitrate

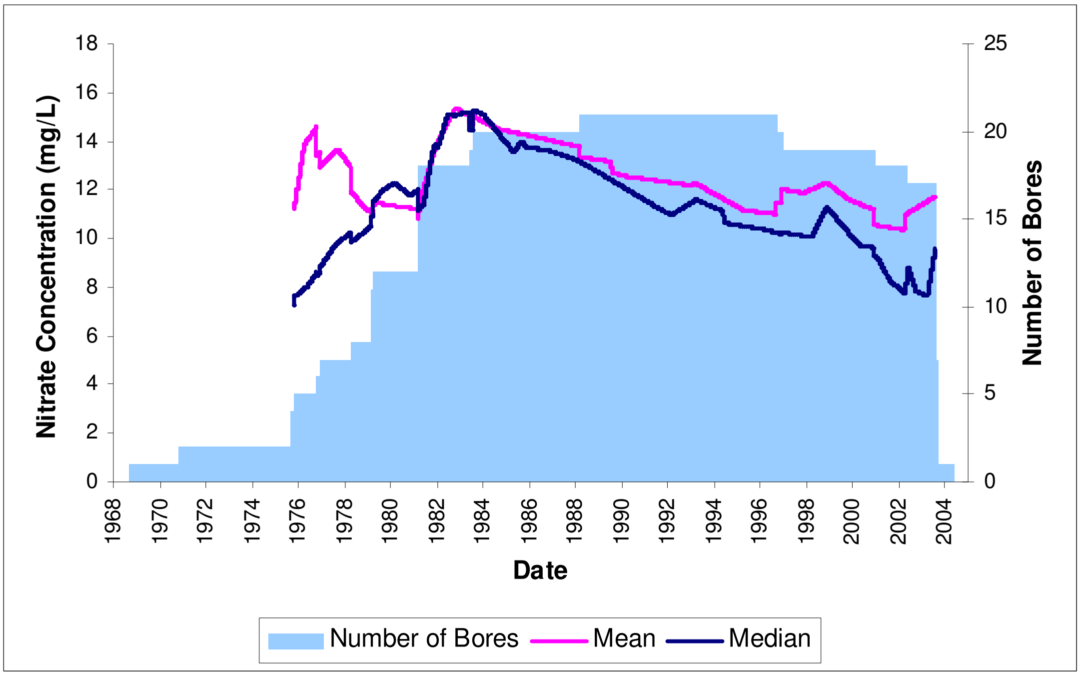


Figure 3.12: The change in mean and median nitrate concentrations over time for those bores with repeated sampling (n≥5)

concentration across the boreholes, with a more pronounced decrease in the median concentration, since 1984.

A further assessment was also undertaken to combine the individual trends from each of the bores (i.e. the slope of nitrate concentrations over time). As above, this approach used the linear interpolation of the nitrate concentrations from discrete sampling dates for each bore (Appendix 3). The model calculated on a daily time step the sum of the slopes of all nitrate concentration trends for the wells, and derives a cumulative sum (therefore the cumulative sum starts at zero). This approach was pursued so that the calculations were not dominated by changes in the higher concentrations of some bores (i.e. the slope of the change is used instead of the quantity of change).

This modelling outcome is presented in Figure 3.13, and indicates that, based upon these 21 bores, there were elevated nitrate concentrations in groundwater in the early 1980s, however since this time, there has been a

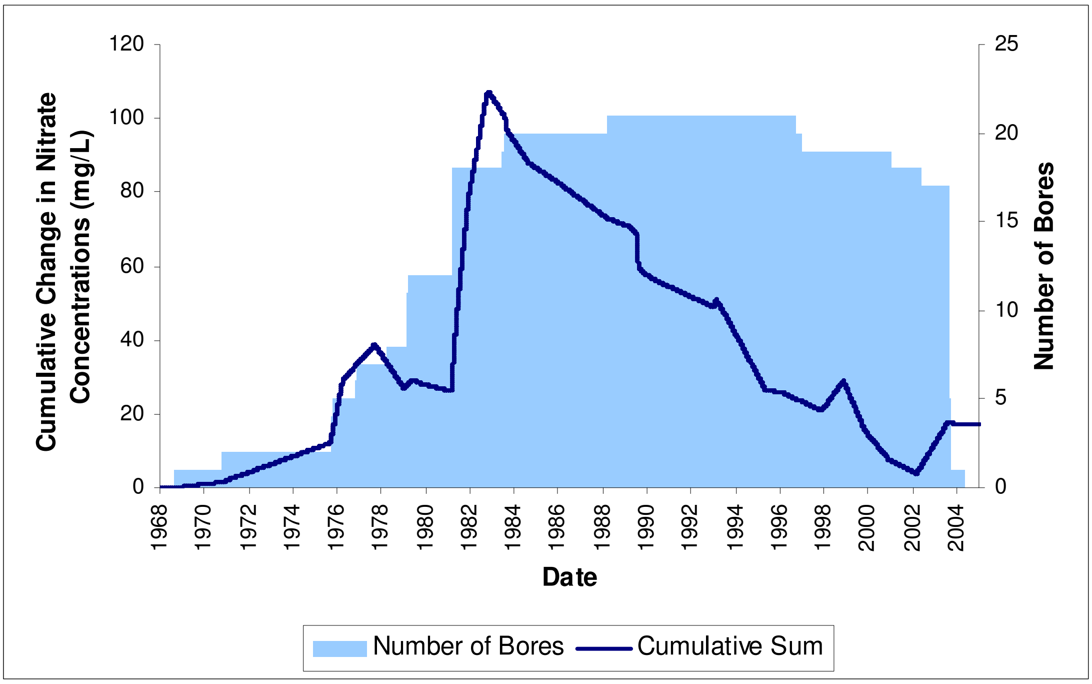
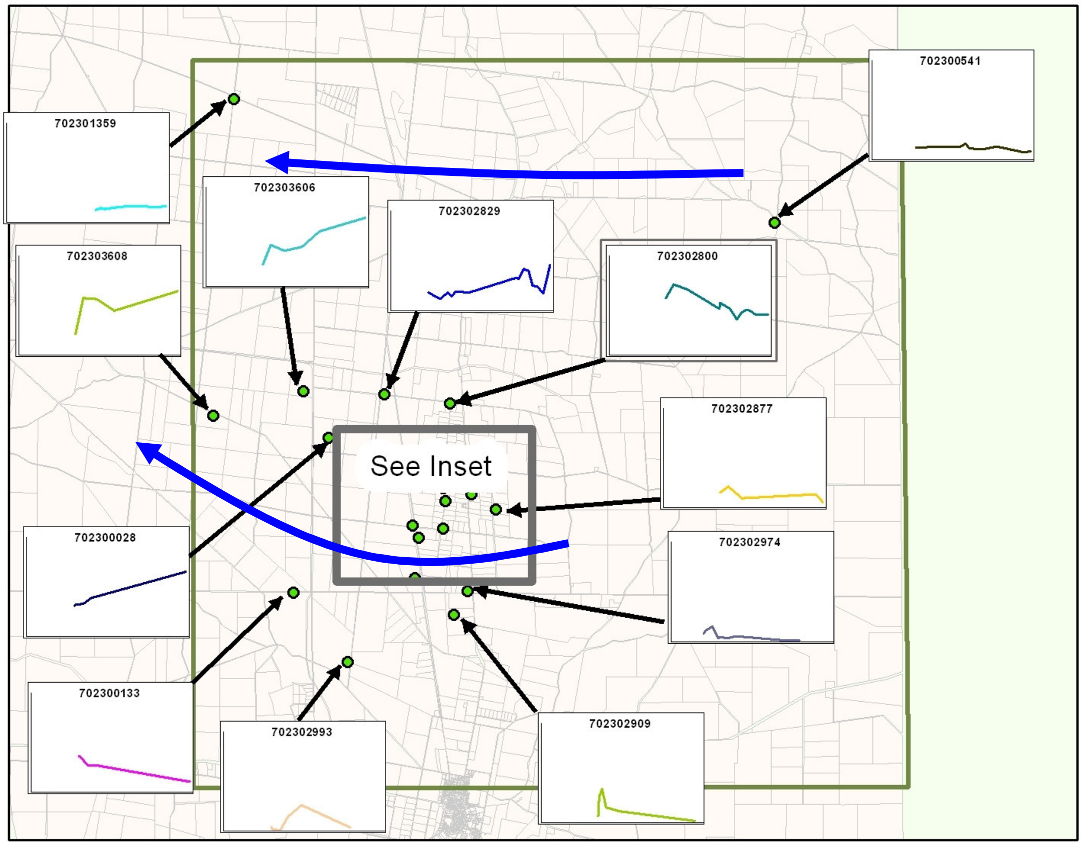


Figure 3.13: The cumulative slope of change in nitrate concentration over time for those bores with repeated sampling (n≥5) indicating an overall trend in nitrate concentrations

steady decrease in nitrate concentration across the study area. This outcome agrees with the previous assessments of the entire groundwater nitrate dataset.

It is also suggested that changes in the size or position of the nitrate plume delineated by MacKenzie and Stadter (1981) and Schmidt and his colleagues (1998) could also result in some bores displaying increasing concentrations of groundwater nitrate, while others displayed decreasing or stable concentrations (Appendix 3). Figure 3.14 shows the locations of the 21 bores across the study area and their individual trends of nitrate concentration.

This assessment suggests that there is a spatial association of the broad trends of nitrate concentrations within the study area, with increasing trends corresponding to groundwater flow and broad-acre cropping and irrigations



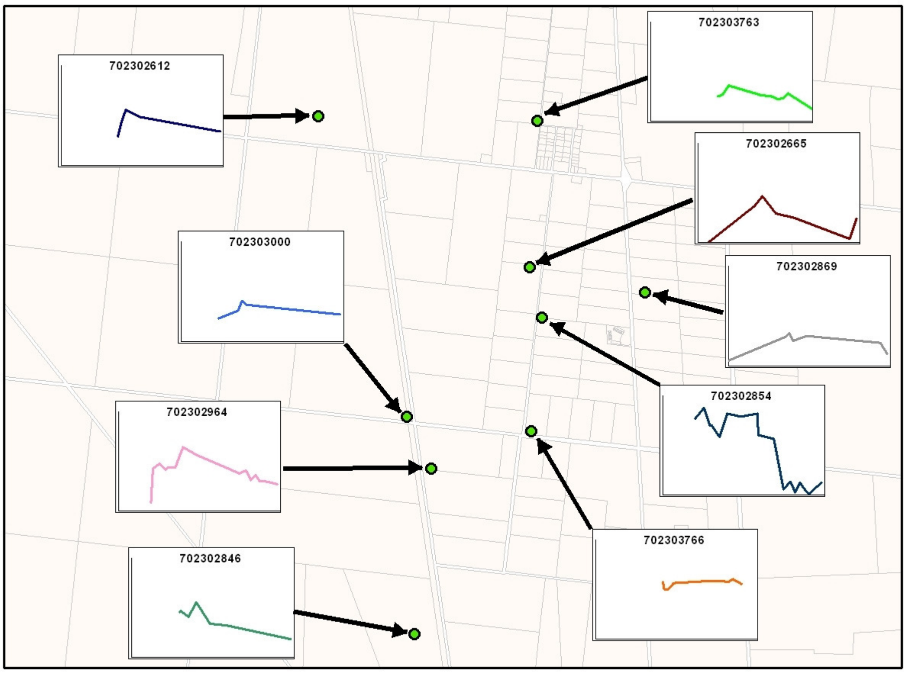


Figure 3.14: The location and individual nitrate concentration trends over time for wells with longer term data, with inferred groundwater flow direction

(groundwater flow direction is shown on Figure 3.14; see Figure 1.4 for generalised landuse descriptions). The methods here do not allow further investigation of this relationship, and it is suggested that this potential association may better be determined through spatial modelling of temporal nitrate concentration changes.

A review was also undertaken to confirm that the observed variations in nitrate concentrations were independent of concentration changes for other major ions in the groundwater to provide confidence that the observed variability was not the result of groundwater mixing.

Chloride was chosen to normalise the nitrate data due to the conservative behaviour of this ion (Clark and Fritz 1997). If the ratio of nitrate to chloride concentrations remained constant while the concentration of nitrate decreased, then the reduction in nitrate concentrations suggested by the above analysis may actually be the result of dilution.

Data was available for 186 sampling events from 98 bores where both nitrate and chloride had been analysed. To avoid the difficulties associated with the reliability of the historical data, only data since 1 January 1970, or for SAGEODATA since 1 January 1982, was used for this assessment.

Figure 3.15 shows the ratio of nitrate to chloride against nitrate concentrations.

This graph shows that the ratio of nitrate to chloride ions increases as nitrate concentrations increase, indicating that variation in nitrate concentrations are independent of the chloride cycle in the groundwater. There are three outliers in this graph that are the result of unusually low chloride concentrations in those three samples, however the correlation coefficient still suggests a strong relationship.

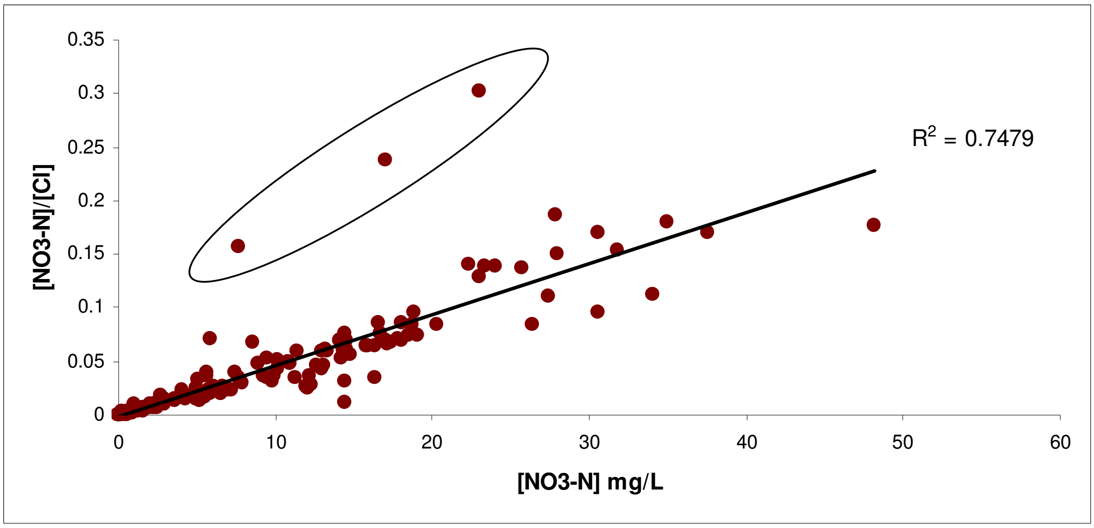


Figure 3.15: Variation of the ratio of nitrate ions to chloride ions with nitrate concentration. Circled points are considered outliers.

3.4. DISCUSSION

3.4.1 Data Reliability – Data Management

Collation and interrogation of the historical water quality data identified a series of limitations with the existing SAGEODATA data. Although the numerical values have been generally correct, their true concentration units are often not those reported by the SAGEODATA database. Almost all nitrate units prior to the 1980s within the study area are incorrect. Without access to the hardcopy records of the laboratory reports, it is likely that this serious data quality issue would not have been identified.

Although it appears that this fault has been recognised by staff that have experience with the database, the data continues to be made available to the public through internet browser services.

There are also considerable amounts of historical groundwater data that cannot be located. During this investigation it was found that a large number of records were not contained within centralised data management systems. Table 3.1 illustrates that only 213 of the 916 nitrate records collated for the study area were sourced from the SAGEODATA and EDMS systems. This suggests that much of the historical data has not been entered into a managed database system, and therefore there is considerable risk of loss. With the exception of the microfiche, departmental records were not consistently managed in accordance with accepted document management systems. Many of the files appeared incomplete, and there were few occasions where the hardcopy laboratory reports could be located for those records accessed from the SAGEODATA system.

The amount of data able to be collated for this study is significantly greater than that previously considered (Harvey 1979, MacKenzie and Stadter 1981, Schmidt, et al. 1998). An unknown amount of the collected data remains missing.

3.4.2 Data Reliability – Representative Nature

As previously discussed, Harvey (1979) excluded nitrate data collected prior to 1 January 1960 due to his concern that sampling errors meant the data may not have been reliable. Harvey (1979) did accept groundwater nitrate data collected after 1960. Although issues such as holding times and sampling methodology may have changed by this time, this assumption cannot be corroborated with departmental documentation.

During the investigation, it was not possible to locate the sampling documentation that would now be considered essential for providing confidence in the analytical results. Documentation detailing sampling events (including purging, depths of samples, decontamination methods), chain of custody reports, sampling preservation, sample storage methods or analytical methods could not be located for almost all samples. This absence of sampling documentation has recently been identified as reducing the level of confidence that can be placed in historical water quality data collected within the region (GHD 2005).

It is also recognised by government scientists that much of the nitrate sampling has not occurred in a manner consistent with acceptable groundwater sampling methods (H. King, EPA, pers. comm. 2005). The recent decision by the Department for Water, Land and Biodiversity Conservation to cease free nitrate analysis on water samples reflects a concern that there were little controls placed upon the collection and storage of samples prior to analysis.

Resolution of these data quality issues is difficult. A conservative approach to exclude all data that was not accompanied by quality control documentation would necessitate the exclusion of all data with the exception of the recent EDMS data and the data collected as part of this study. Clearly this is not a desirable outcome and it is preferable that the data is considered in a manner that reflects the confidence in its accuracy.

Although purging of bores has been undertaken as part of the sampling program for a considerable period (at least 20 years), aspects such as equipment decontamination, sample preservation and analysis within the required holding times are not consistently applied. In the instance of incorrect preservation methods, the reported nitrate concentration values may either under estimate or over estimate the groundwater nitrate concentration.

To some degree, the reported nitrate concentrations within the study area are likely to be influenced as much by the non-random nature of the location of boreholes (and the proximity to point-sources such as septic tanks) as the deficiencies in the sampling methodology. The absence of a standardised sampling methodology adds a level of uncertainty to be combined with the other aspects of uncertainty applied to the data (such as bore construction or bore location), and not a single reason to exclude the data from consideration.

The level of protection of the boreholes from the ingress of surface contamination also needs to be considered. Many of the sampled bores within the study area have very little well head protection. Although some of the bores have been constructed for the purpose of groundwater sampling and have been protected accordingly, many of the bores associated with windmills, or other monitoring bores are not adequately protected (Figures 3.16 to 3.17). This inappropriate design is suggested as contributing to the elevated results for TKN in bore 702302800 which allows ingress of surface-derived organic material into the borehole.

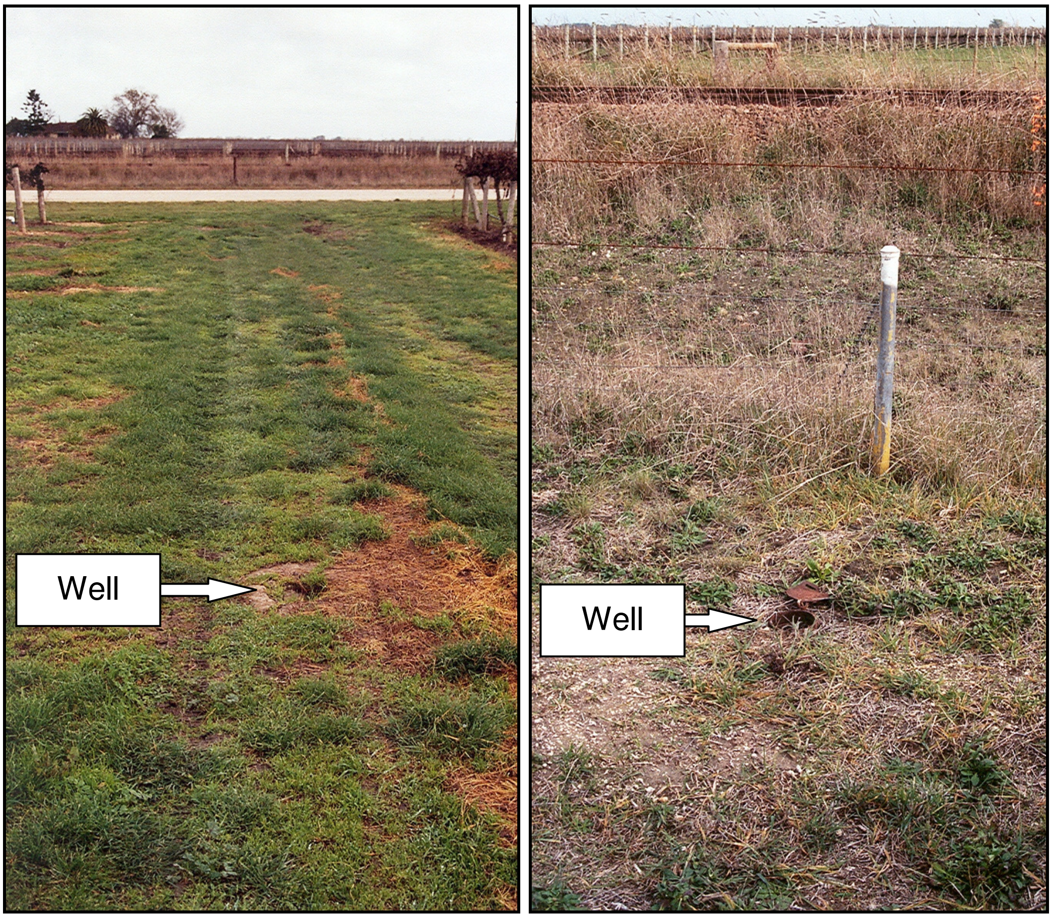


Figure 3.16: The unprotected well head for bore 702302964 (left), and lockable well cap (but at surface level) for bore 702303000 (right)

It is apparent from this study that the manner in which groundwater samples are collected, stored, analysed and reported by government departments requires urgent attention to reduce the potential for similar issues of data reliability to be raised in the future regarding data currently being collected.

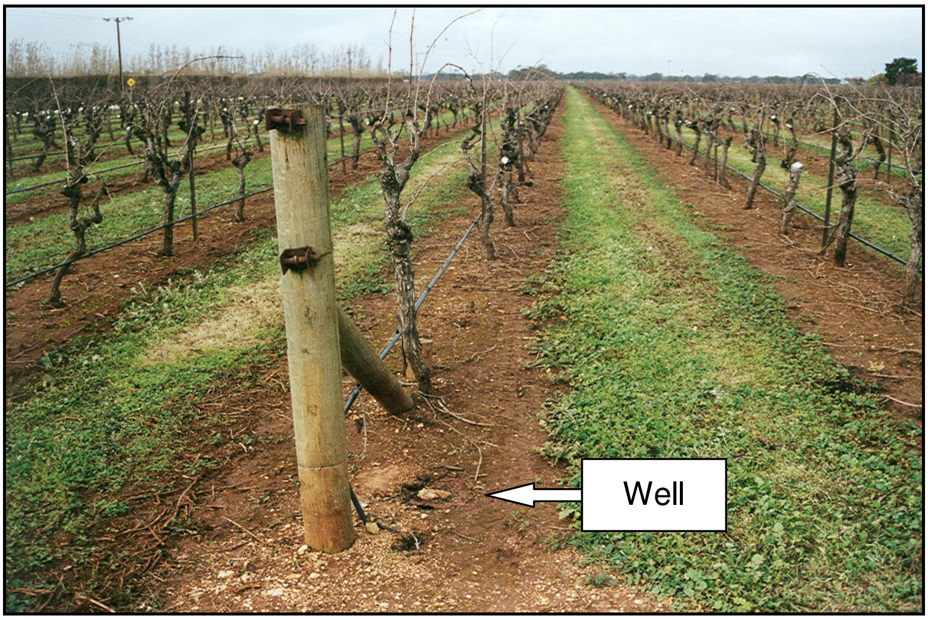


Figure 3.17: Poor well head protection for bore 702302800 (a tin cap and rock)

The research has shown that although the collated data is extensive, it may not be representative of the ambient groundwater quality of the study area. The location, timing and recurrence of sampling are shown to introduce bias into the dataset that needs to be considered in any assessment process.

3.4.3 Historical Nitrate Trends

Given the issues relating to data reliability, considerable caution must be applied to the interpretation of historical groundwater data. This study has applied a number of methods to investigate any trends or agreement between methods.

The historical nitrate data does not display a normal distribution and therefore the application of parametric statistical methods was not appropriate. Three non-parametric methods (ten year groupings, five-year running class percentages and combined assessment of trends in particular bores) all indicated that nitrate concentrations in groundwater increased until the mid 1980s, but have decreased since then. As this behaviour is reflected in the bores with longer term data as well as the whole dataset it cannot be simply a result of the dominance of samples from new bores during the mid 1990s.

The assessment of nitrate concentrations against chloride concentrations further suggests that the observed changes are not simply due to dilution but represent actual changes in the mass of nitrogen within the groundwater. The investigation also found that nitrate has consistently been the main form of nitrogen in groundwater in the study area.

The percentage of nitrate samples in different concentration classes provides further evidence that the increase in nitrate concentrations and the subsequent decrease is heavily influenced by the percentage of very high (>20 mg/L) or very low (<4.5 mg/L) records. Generally, the relative proportion of samples between these extremes (i.e. 4.5 mg/L to 20 mg/L) has remained constant throughout the period where data has been available.

Averaging the rate of change in nitrate concentrations across a series of bores with longer term data further suggested that there was a decreasing trend in nitrate concentrations since the early 1980s. The map of individual trends in the nitrate concentration in boreholes (Figure 3.14) indicates a spatial patterning in the change in nitrate concentration across the study area.

3.4.4 Summarising of Historical Nitrate Data

An objective of this study was to recommend an acceptable reporting method for historical nitrate concentrations that could be readily applied for consistency in reporting. There have been a variety of regional studies of nitrate levels in groundwater (Waterhouse 1977, Harvey 1979, Dillon 1988, Schmidt, et al. 1996, Schmidt, et al. 1998), however only the study by Dillon (1988) reported upon temporal trends.

Three main modelling methods were applied and provided different levels of detail. No one method can be recommended however, as the most appropriate methodology will depend upon the objective of any review.

The mean nitrate concentration for discrete decades had the advantage of being easy to calculate, however the data was not made up of random samples of the population (i.e. groundwater). Further, the mean nitrate concentration was significantly influenced by the tendency of the dataset to have multiple records for those boreholes with higher nitrate concentrations. These characteristics of the dataset suggest that it is inappropriate (and of little value) to test for differences between means of discrete decades.

The use of concentration ranges is more appropriate for this type of dataset, as it addresses the concern that the data is not normally distributed. In addition, the classification ranges avoid the need to assign arbitrary concentration values to categorical concentration records (e.g. 'less than' records). The application of classification ranges is also insensitive to very high nitrate concentrations, and on a study area or regional scale can provide a more realistic account of the nitrate concentrations in groundwater. The relative proportion of the records in each group can be used as a measure of the success of management and government policies.

There are a number of difficulties that remain with this approach, and this includes the standardisation of classification ranges to allow comparisons across time or space. The classifications utilised in this study were chosen to reflect the nature of the dataset. Comparison with other regions that use different classification ranges will be difficult. Within the South East region the classification ranges should provide sufficient resolution to nitrate trends in groundwater. There will be occasions where further sub-division of the classification ranges may be necessary, for example the separation of the classification range 0-4.5 mg/L into two classes would still be possible as long as the main classification boundaries are not altered.

A further difficulty with this method is that it is sensitive to preferential resampling of bores having high nitrate concentration. Assessment was undertaken that demonstrates that the broad trends are unaltered (Figure 3.11), however it is not recommended that this bias be discounted in the consideration of trending analysis.

Nitrate trends in individual bores that had longer term data provided good evidence of the change in nitrate concentration, and avoided the difficulties of the non-random nature of the larger dataset. Inconsistencies in the timing of sampling was addressed through the summation of the trends of individual bores, and the resulting trend supported the general assessment identified in the other methodologies.

The review of individual boreholes which have a historical dataset appears to be the most valuable approach for assessing nitrate trends in groundwater in the region. Although it only uses a small fraction of the dataset (173 records out of the total of 916), the results have a higher degree of relevance to summarising trends. As indicated by Figure 3.14, the summation of the data from these bores should take into account the spatial distribution of the bores.

3.5. CONCLUSIONS

Collation of the dataset has identified a number of quality control issues that limit the confidence that can be applied to the assessment of water quality within the study area. These issues need to be considered carefully to allow effective management of the data and to ensure that further expenditure on sample collection, analysis and reporting provides reliable information.

Analysis of the study area's data suggests that the groundwater nitrate concentration reached a peak concentration in the mid 1980s and has subsequentially decreased. This assessment however does not provide any reason for this change in concentrations. Comparison of nitrate and chloride concentrations indicates that the change in nitrate concentration is due to a change in nitrate mass in the groundwater rather than dilution effects.

The change in nitrate concentration could be the result of changing landuse practices and it is unclear as to whether this is consistent across the study area. An assessment of spatial variability of groundwater nitrate concentrations is reported in Chapter 5.