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Nitrate trends in groundwater

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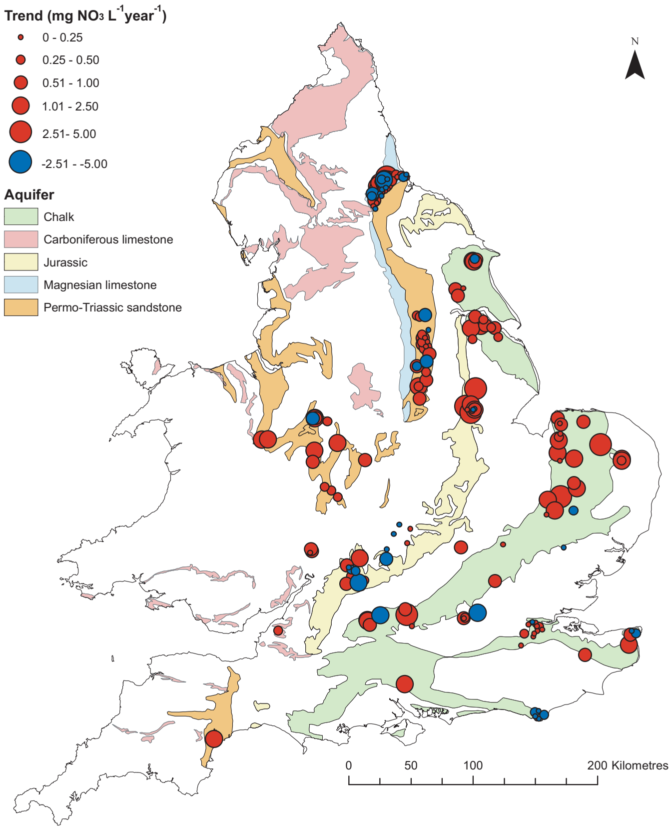
Internal Report IR/05/137R



BRITISH GEOLOGICAL SURVEY

GROUNDWATER MANAGEMENT PROGRAMME

INTERNAL REPORT IR/05/137R

Nitrate trends in groundwater

M E Stuart and D G Kinniburgh

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Foreword

This report is one of a series of published products of a study by the British Geological Survey (BGS) aimed at gaining an improved understanding of the 4-dimensional distribution of nitrate in groundwater and developing models of nitrate transport. The part of the project described here applied a methodology developed for UKWIR to evaluate trends for the large number of time series datasets held by BGS Wallingford.

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Summary

Some 450 groundwater nitrate datasets from England were examined and, where the data were suitable, trends determined. Although the datasets were not randomly selected from all possible boreholes in England, they represent a fairly broad cross-section of such boreholes. They covered a wide range of aquifers. Many of these were from working public supply wells, and the selection may therefore exclude high nitrate sources which have already been taken out of supply. Datasets from observation wells were also included, but many of these had much less available data. More than one third of the datasets were rejected for being too short (span of less than 5 years or fewer than 20 observations), too irregular or too variable. Time series in which there were obviously highly nonlinear trends were also excluded.

Trends were determined by linear regression. Tests were included for the lack of linearity, the presence of outliers, for seasonality and for possible breaks in the trend including reversals of trend. After exclusion of data where trend fitting was unsatisfactory, 309 datasets were finally selected from 191 different sites. For multi-borehole sites, median values were used to obtain the summary statistics. For these 191 sites groundwater nitrate concentrations were found to be rising at an average of 0.34 mg NO_3 L^{-1} $year^{-1}$. Average trends were greatest in the Lincolnshire Limestone aquifer (0.96 mg NO_3 L^{-1} $year^{-1}$) and lowest in the Magnesian Limestone aquifer (0.18 mg NO_3 L^{-1} $year^{-1}$). Average trends for the Chalk and Triassic sandstone aquifers were 0.38 mg NO_3 L^{-1} $year^{-1}$ and 0.44 mg NO_3 L^{-1} $year^{-1}$, respectively.

An assessment of seasonality in nitrate concentrations was also made by including a term for the month of sampling in the regression model. Significant ($p<0.05$) seasonality was found in about one third of the series tested. This showed higher concentrations during the winter months.

Breaks in a linear trend were detected by fitting a piecewise linear regression to the data with automatic detection of the break point. 21% of the time series analysed showed a significant improvement in the overall fit when such a break was included. 10.5% of these indicated an increase in trend with time and 10.5% a decrease.

The best-fitting model was used to estimate the nitrate concentration on 1 January 2000 and January 2015 for all sites. For 2000, this showed that nitrate concentrations in the major aquifers on this date were broadly similar apart from the Magnesian Limestone. The highest concentrations were in the Oolitic limestone (50 mg NO_3 L^{-1}) and the lowest in the Magnesian Limestone (8.2 mg NO_3 L^{-1}). The Chalk and the Triassic sandstone had average concentrations of 42 mg NO_3 L^{-1} and 46.3 mg NO_3 L^{-1} respectively. The average of all sites was 37.8 mg NO_3 L^{-1}. The highest nitrate concentrations were found in areas around the Wash, the Chalk of south Yorkshire/East Anglia, and the Permo-Triassic Sandstone of Yorkshire/Nottinghamshire.

By 2015 the average concentration will have increased to 43.6 mg NO_3 L^{-1}. The highest concentrations are predicted to be in the Lower Greensand (58.8 mg NO_3 L^{-1}) and the lowest in the Magnesian Limestone (12.3 mg NO_3 L^{-1}). The Chalk and the Triassic sandstone will have average concentrations of 50.5 mg NO_3 L^{-1} and 52.6 mg NO_3 L^{-1} respectively.

In 2000, 34% of sites exceeded the 50 mg/L. It is estimated that if present trends continue, 41% of groundwater sources could exceed the 50 mg/L standard by 2015.

1 Introduction

Time series of groundwater quality measured over many years often show long-term trends. They may also show evidence of seasonal behaviour. The underlying cause of these patterns may reflect, for example, long-term changes in land use, fertilizer applications, pollution history or climate.

Groundwater nitrate concentrations in many UK aquifers are high, and are often approaching or have already exceeded, statutory limits for drinking water. For this and other reasons, widespread monitoring of groundwater nitrate concentrations has been undertaken over a long period by both water companies and the Environment Agency. There is therefore a very large dataset of nitrate data suitable for analysis. This can be used to define past trends as well as to make informed estimates of future concentrations of nitrate in groundwater.

A full description of the inputs and outputs of nitrate to groundwater, as in a fully-calibrated nitrate transport model, would provide a means of predicting the future evolution of nitrate concentrations in groundwater. In the absence of this, predictions for the next 5 years or so can probably be reasonably made by assuming a continuation of existing trends. This takes advantage of the long delays and large scale of mixing inherent in most groundwater systems.

Numerous texts discuss the assessment of trends in water quality data, though most frequently these relate to trends in surface water rather than groundwater (Helsel and Hirsch, 1992; Grath *et al.*, 2001). Groundwater quality time series are inherently more damped than surface water quality series and thus often show the long-term trends more clearly.

We have developed a semi-automated methodology for trend estimation of water quality time series. This uses a range of statistical procedures, including robust estimation methods. The results are summarised in a series of tables and annotated figures that are automatically generated. All computations and graphing are carried out using scripts and so are amenable to batch execution. These scripts were originally written for the S-PLUS statistical package (Insightful Corporation, 2004) but more recently we have translated these to run in 'R', an open-source and free equivalent to S-PLUS (R Development Core Team, 2005).

This methodology was developed for, and has been applied to, various test datasets from UK water companies (UKWIR, 2003). Many of the time series examined showed a significant upward trend and some also showed evidence of seasonality. These datasets were limited in the aquifers represented and the numbers of time series examined.

Here we extend this approach by applying it to a larger number of groundwater nitrate datasets. These datasets analysed include time series from all of the major English aquifers and some minor ones. We also analyse the results in terms of the trends shown by the different aquifers. Summary statistics are used to reflect the range of trends observed on a national basis.

1.1 OBJECTIVES

The objectives of this work are to:

- Collate all time-series nitrate data held by the BGS Groundwater Management Programme. These have been collected for a large number of projects, mostly commissioned projects, and were held in different locations in a variety of formats;
- Refine and generalise the trend assessment methodology from that initially developed in projects for UKWIR and Defra;

- Analyse all of the datasets after suitable ‘data cleaning’;
- Use the datasets to illustrate the application of the statistical approach and to draw conclusions about the magnitude and nature of the trends observed in English aquifers.

2 Data description and analysis

> *"Do not attempt to build a model on a set of poor data! In human surveys, one often finds 14–inch men, 1000–pound women, students with "no" lungs, and so on. In manufacturing data, one can find 10,000 pounds of material in a 100 pound capacity barrel, and similar obvious errors. All the planning, and training in the world will not eliminate these sorts of problems. ... In our decades of experience with "messy data," we have yet to find a large data set completely free of such quality problems."*
>
> Draper and Smith (1981, p. 418)

2.1 DATA QUALITY

As the above quotation indicates, large data sets usually contain some 'messy data' which can misinform subsequent analyses. The various nitrate times series datasets available from the Environment Agency and Water Utilities are no exception. So the first job is to systematically check the data for possible errors and inconsistencies. Modern software tools can help identify 'outliers' although ultimately the decision as to whether to include or exclude a value needs additional knowledge about the data.

As time goes by and as the originators of the data become more distant from the users of the data, it becomes increasingly difficult to find and correct errors. The presumption must be to keep the data unless there are very strong grounds not to, and this is the policy adopted in this report. We have not removed any data from the datasets provided even though some of the values seem to be inconsistent with the other data for the site and time.

Differences can arise for many reasons ranging from genuine errors (incorrect data entry, wrong units, mislabelled site etc.), analytical errors (normally well-constrained) to more subtle errors, for example in sampling (insufficient purging of a borehole, periodic interference from pumping at an adjacent borehole etc). These latter errors are especially hard to locate retrospectively. Some might not even see them as 'errors' in the normal sense.

Using robust methods of data analysis, i.e. methods that give conclusions that are not strongly dependent on the presence of a certain proportion of outliers, is another approach that we explore here.

2.2 DATA COLLATION

The BGS Groundwater Management Programme now holds a considerable number of time series nitrate data. These have been collected from many projects including:

- Nitrate Sensitive Areas;
- Various projects for Anglian Water;
- Various projects for Yorkshire Water;
- UKWIR trend methodology;
- Defra identification and reversal of trends with data derived from various regional EA groundwater quality databases.

Table 2.1 Index file entry format and example

Column heading	Description
Site Code	Unique name without spaces used for individual source data files e.g. AmenCorner1
Borehole Name	Amen Corner 1 Raw
Site ID	Amen Corner
Easting	Six figure grid reference – 464250
Northing	Six figure grid reference – 365670
Data Source/BGS contact	Environment Agency NSA/AGH
Aquifer	Permo-Triassic Sandstone
Wellmaster no	SK66/26A
Start date	18/03/1976
End date	27/06/2001
Number of records	188

The sources of the data are biased towards areas in the east of England where problematic concentrations of nitrate have existed for a long time, and where monitoring programmes were consequently most frequently set up. The data available were often collected as part of a routine monitoring programme but frequently included other data collected for operational reasons, such as when an unexpected upward change had occurred. This can be seen to some extent in the frequency and regularity of sampling. Such an approach stands the danger of introducing bias into the sampling. Notwithstanding that caution, the datasets provide an important and valuable source of time series data that deserve to be analysed in a rigorous and consistent way.

An index file containing meta data about each time series was constructed. An example is given in Table 2.1. There was one such entry for each time series.

Data for each source were held in a separate Excel file and given a unique name. Sample time and dates were stored in date format in a column headed 'Date' and nitrate concentrations in columns headed 'NO3' or 'NO3-N' as appropriate. Output was always in terms of NO3.

Data units were checked carefully, as this is a common area of confusion, and corrected where necessary. The data were sorted into increasing date order. Many of the series contained multiple analyses for the same day, either simple replicates derived from merging more than one series, or separate analyses from very frequent sampling for short periods. All replicate data were deleted and the median of multiple analyses used to reduce the data to one measurement per day.

2.3 DATA ANALYSIS

An S-PLUS script was written to analyse the data in terms of long-term trends. A description of the statistical methods used is given in Appendix 1. The script also produced a series of seven diagnostic plots which were annotated to give information to aid the data analysis and interpretation. Plots 1–4 are descriptive while Plots 5–7 show the trend(s) and any seasonality. These methods were used to fit a straight line through the data by ordinary least squares regression (with unit weights), by robust regression and by a non-parametric method. The data were also tested for deviations from the underlying assumptions of the tests and for the presence of any seasonality in the data, and for a significant change in trend. The series of seven plots were produced for each time series and an overall summary file containing the most significant results was produced (Figure 2.1 and Figure 2.2).

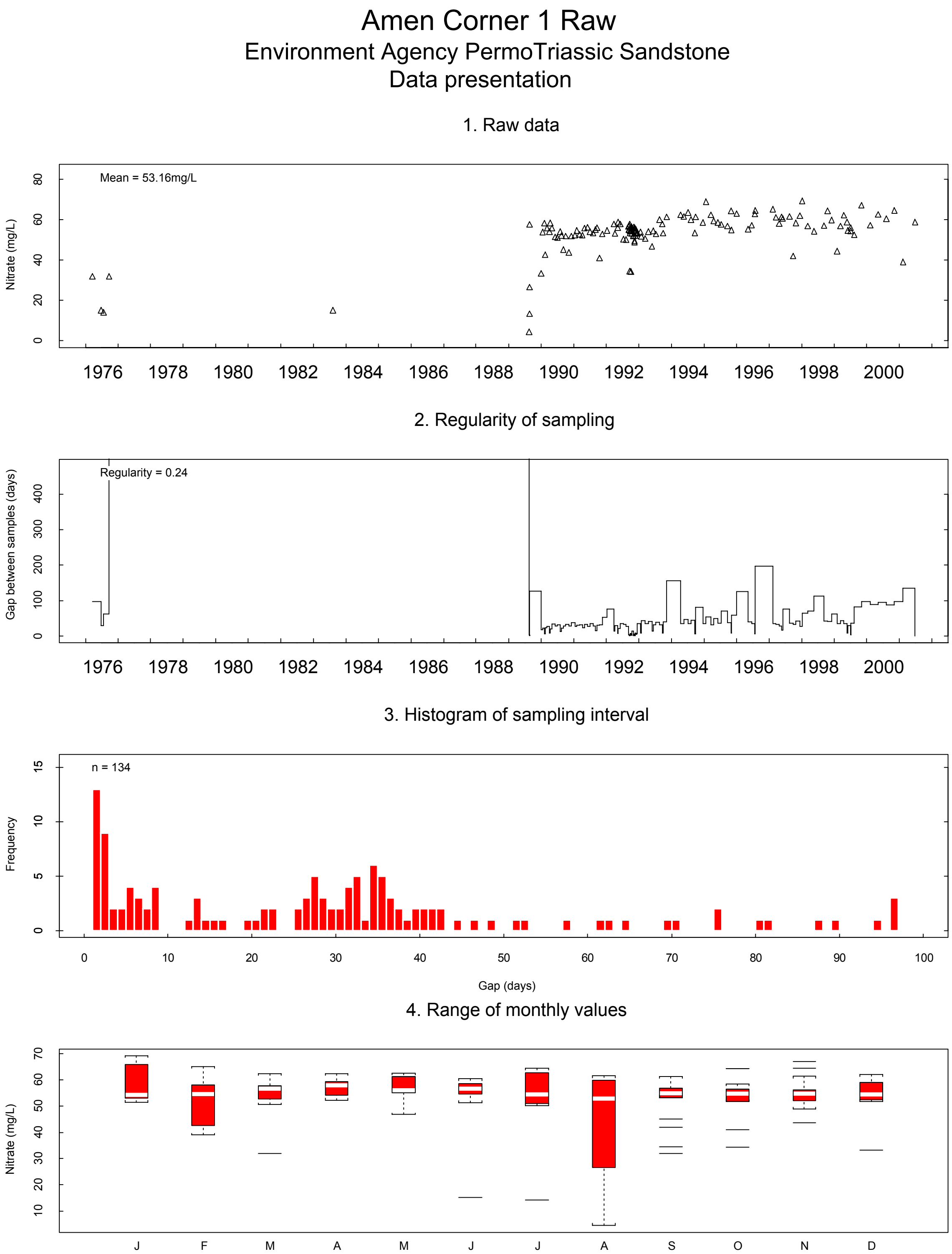


Figure 2.1 Example of Plots 1-4 for Amen Corner borehole 1.

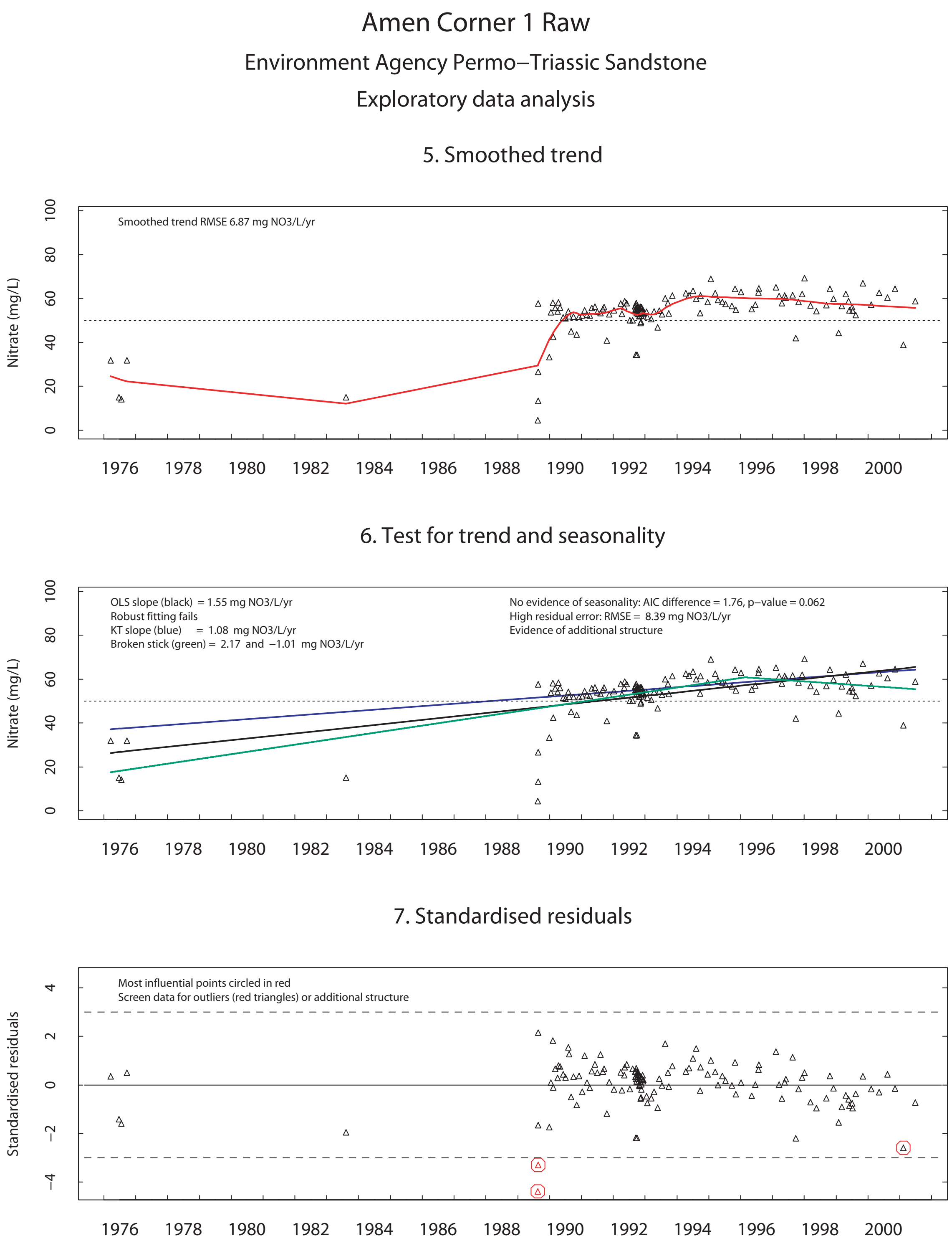


Figure 2.2 Example of Plots 5-7 for Amen Corner borehole 1.

Examples of a summary output file are shown in **Error! Not a valid bookmark self-reference.**. This initial screening was used to refine the data series selected to remove series covering very short periods and/or with very irregular sampling frequency (Table 2.3). The summary output file was also used to assess the data for a minimum time span (≥5 years) and for its regularity (≥0.2). Series from combined or mixed sources were not considered suitable for evaluating trends and seasonality and were also removed from further consideration.

Where more than one source existed at a site, the variability between the sources was assessed by calculating the median and mean concentrations and trends for each source, and their associated standard deviation and coefficient of variation.

Table 2.2 Data recorded in the summary output file

Category	**Units**	**Description**	**Examples**	
Site		Borehole name	Amen Corner 1 Raw	Aswarby Combined
Source		Data source	EA	EA
Aquifer			Permo-Triassic Sandstone-	Lincolnshire Limestone
Start		Start date	1976	1996
End		End date	2001	2001
N		Number of measurements	134	148
Regularity			0.24	1.1
Mean NO_3	mg NO_3 L^{-1}	Mean nitrate concentration	53.16	27.36
Ols slope	mg NO_3 L^{-1} $year^{-1}$	Trend using ols regression	1.55	2.29
Robust slope	mg NO_3 L^{-1} $year^{-1}$	Trend using robust regression	1.04	3.17
Sen slope	mg NO_3 L^{-1} $year^{-1}$	Trend using non-parametric method	1.08	2.62
RMSE	mg NO_3 L^{-1} $year^{-1}$		8.39	4.23
Loess RMSE	mg NO_3 L^{-1} $year^{-1}$		6.87	3.52
Seasonality		Indication of seasonality	No evidence of seasonality	Evidence of seasonality
AIC difference		Estimate of seasonality [not seasonal if zero or positive]	1.76	-26.47
Prob nonseasonal		Probability that the data are not seasonal	0.062	3.75E-06
Additional structure		Identifies irregularly noisy data for non-seasonal data	1.22	Not tested - seasonal data
Bs1	mg NO_3 L^{-1} $year^{-1}$	Slope of first part of ‘broken stick’	2.17	0
Bs2	mg NO_3 L^{-1} $year^{-1}$	Slope of second part of ‘broken stick’	-1.01	0
Ols2000	mg NO_3 L^{-1}	Estimates concentration on 1/1/2000 using trend and seasonality	63.2	32.4
Robust2000	mg NO_3 L^{-1}		62.2	29.4
Sen2000	mg NO_3 L^{-1}		62.8	30.7

Table 2.3 Selection of datasets: reasons for the exclusion of datasets from further analysis

Criterion	Number
Number of datasets with > 20 records	454
Excluded where from Jersey	13
Excluded where < 5 years data	50
Excluded where ≥ 5 years data but from combined or mixed sources	10
Excluded where ≥ 5 years data but from probable combined or mixed sources e.g. from unnumbered source with 'final' where numbered sources also present and duplicate series	14
From individual sources but with regularity <0.2	15
Number of datasets used for further analysis	352

3 Datasets

3.1 AQUIFERS AND SOURCE TYPE

The final dataset used contains sites from the major aquifers of England and Wales, and also a number of minor aquifers. These were grouped into convenient categories (Table 3.1).

Table 3.1 Aquifer groupings

Aquifer grouping	Groups and Formations
Major aquifers	
Carboniferous Limestone	
Chalk	Chalk, Upper Greensand Formation
Lincolnshire Limestone	
Lower Greensand	Lower Greensand Group
Magnesian limestone	Raisby and Ford Formations
Permo-Triassic sandstone	Sherwood Sandstone Group
Minor aquifers	
Gravels	
Lias	Lias Group
Ordovician	

Many sites contained clusters of several boreholes or springs. The number of such multiple source sites is shown in Table 3.2. Where only one dataset from a multiple source site passed the initial selection criteria, this is recorded as a single site in Table 3.2. In two cases, two boreholes at a site abstracted from different aquifers and so these were classed as two single sites. The large number of sources at one site in the Oolitic Limestone results from this site having a large number of spring monitoring points. At another site in the Lower Greensand, apparently multiple source data sets were probably all derived from the same site but given a slightly different name in the database.

Table 3.2 Summary of sources in aquifer groupings

Aquifer grouping	Total sources	Single sources	Multiple sources	Excluded sources
Gravels	3	2	0	0
Chalk	146	41	38	57
Lower Greensand	12	0	2	2
Lincolnshire Limestone	17	15	1	3
Oolitic Limestone	28	14	2	2
Lias	5	5	0	0
Permo-Triassic sandstone	90	16	28	23
Magnesian Limestone	50	50	0	0
Carboniferous Limestone	1	1	0	0
Ordovician	0	0	0	2
	352	**144**	**71**	**89**

3.2 LENGTH OF TIME SERIES, NUMBER OF SAMPLES AND THE REGULARITY OF SAMPLING

A summary of the record span, and the frequency and regularity of sampling are shown in Table 3.3. The period of record and regularity of sampling both have truncated distributions since records with 5 years or less of data and regularity of 0.2 or less were discarded following the initial screening of datasets.

Table 3.3 Summary of period, frequency and regularity of the datasets

	Minimum	Median	Maximum
Period of data (years)	5	15	43
Number of samples	21	119	1310
Frequency (samples per year)	1.1	8.8	77
Regularity	0.21	0.6	3.3

Chelvey PS in the Carboniferous Limestone has the longest record (43 years). The public supply borehole at Ogbourne St George (Chalk) has the greatest number of samples and the observation borehole at Chilton Prospect Farm has the least. Ogbourne also has the highest sample frequency and Hagley 4 in the Permo-Triassic sandstone the lowest. Warren Farm observation well is the most regular although the data have only a 6-year span with approximately monthly sampling.

Almost all the other datasets with regularity of 1.5 or more are observation wells which have approximately monthly, quarterly or 6-monthly monitoring schedules. In many cases there were long periods with no samples, often because the borehole was not being used for production. Many datasets from public supply monitoring have periods where the source had been taken out of supply for renovation of headworks, pump maintenance and borehole relining or because water quality was unacceptable. 127 (40%) of the remaining series have a regularity of less than 0.5.

Of the 352 time-series selected for trend analysis, more than one third (133) had one or more gaps in sampling of at least one year. Specifically:

- 104 had more than one gap of at least one year;
- 29 had a single gap of at least one year.

Additionally 44 had more than one year with very sparse data.

Such gaps in data are commonplace when datasets from public supply boreholes are used for monitoring purposes. Gaps in data collection are highlighted in Plot 2. An example is shown in Figure 3.1 where there was no sampling in 1984 or 1988. Although regular data are not essential for trend analysis, they do make the identification of trends more reliable and more sensitive.

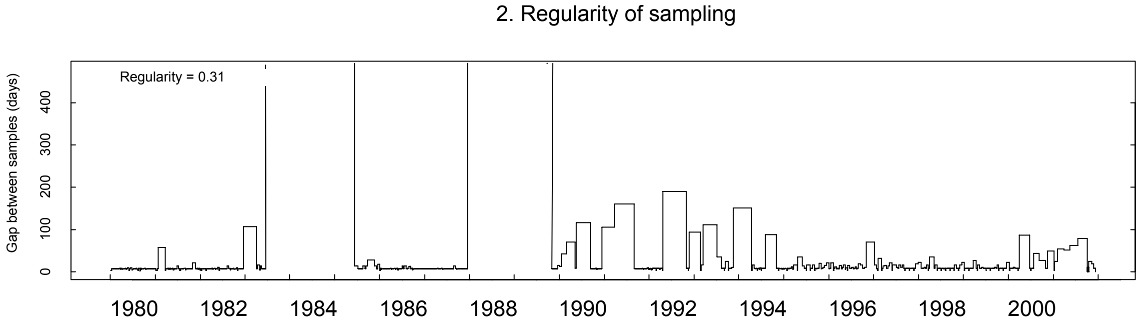


Figure 3.1 Examples of large gaps in the observation record for Thornham PS, borehole 2

3.3 SAMPLING FREQUENCY

The sampling frequency at the sites varies widely, from daily to quarterly. The patterns of sampling are clearly shown in Plot 3. These have been divided into a number of different types based on the dominant frequency of sampling (Table 3.4). Many public supply boreholes have been sampled relatively frequently, particularly when they are under investigation (Figure 3.2). A common pattern is for the sampling frequency to show predominantly weekly sampling with 14, 21 and 28-day intervals also present (Figure 3.3). Observation wells are usually sampled less frequently (Figure 3.4).

Table 3.4 Sampling frequency

Frequency	No of sources	Comment
1-10 days	46	Public supplies
Weekly	61	Public supplies
Weekly and multiples	57	Public supplies
2- weekly	11	NSA observation wells
Monthly	9	NSA observation wells
2-3 monthly	16	NSA + EA observation wells
6-monthly	46	EA observation wells
Variable	106	

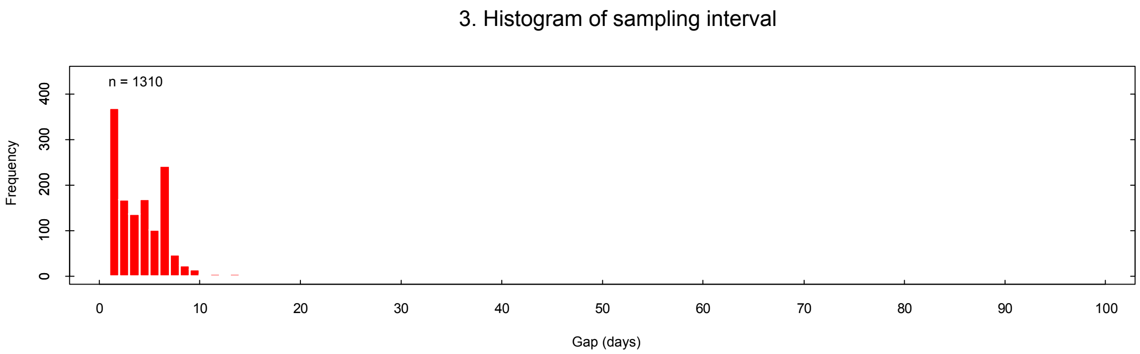


Figure 3.2 Sampling every 1-10 days at Ogbourne St George, Chalk PS over the period 1985-2002

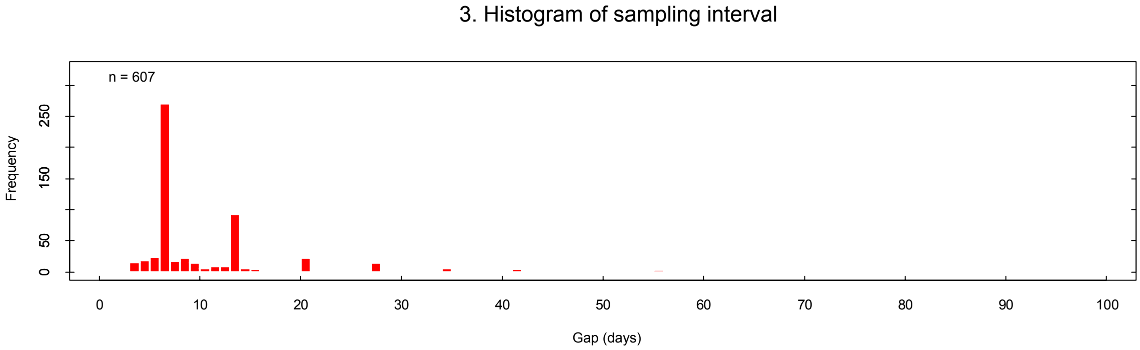


Figure 3.3 Sampling intervals of one week and multiples of a week at Kings Road, Bury PS, borehole 1 over the period 1981-2002

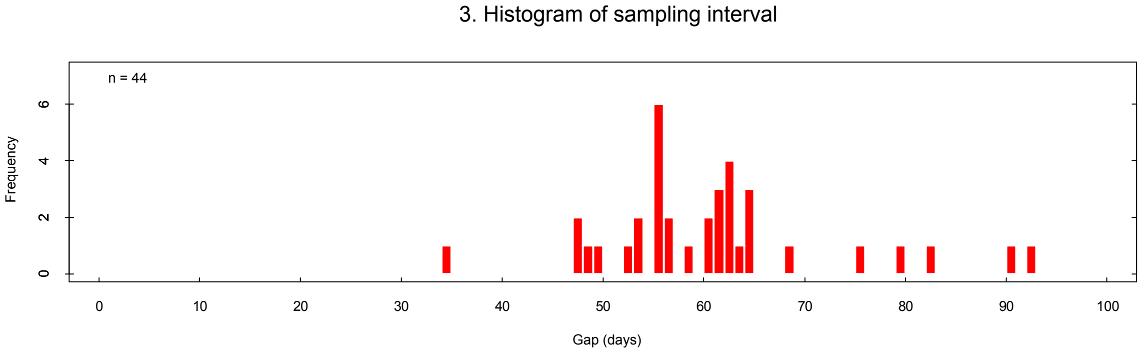


Figure 3.4 Predominantly 2-monthly sampling at Bartondale observation borehole over the period 1990-1999

4 Concentrations and trends at individual sources

4.1 THE ROBUSTNESS OF THE TREND ESTIMATES

A linear trend was fitted to the datasets using three different methods described in Appendix 1. Method 1 is the ordinary least squares (OLS) line (**black**). The second method is a robust line (**red**) fitted by an iterated re-weighted least squares (IWLS) procedure using the `rlm` procedure from S-PLUS's MASS library (method="M"). This is less sensitive to outliers than OLS. Several other robust methods are also available. Method 3 is the Kendall test (KT) slope (**blue**) which is a non-parametric slope based on ranks (using the `kendall.trend.test` method in the S-PLUS Environmental Stats module. This is also less sensitive to outliers and to serially correlated errors in the data. If the assumptions of OLS are obeyed, then all three trend lines should be similar. There are many diagnostic tests and plots to highlight possible deviations from the underlying assumptions of regression analysis.

For many of the datasets all three methods gave similar nitrate trends. The standard deviation of the mean of the three trends was <0.1 mg L^{-1} $year^{-1}$ for 49 % of the boreholes and <0.2 mg L^{-1} $year^{-1}$ for 74% of them. However, for some of the boreholes, the differences were quite large with 27 sources (5%) having a standard deviation of >0.5 mg L^{-1} $year^{-1}$.

Two situations commonly gave rise to strongly divergent trend estimates. These are where there are:

1. Highly influential points

Highly influential data points are points whose removal from the dataset would have a disproportionately large influence on the fitted trend. Such points are not necessarily wrong, but it is important to be aware of them since the fitted trend strongly depends on their correctness. 'Outliers' may be highly influential points though they are not necessarily so.

There are several statistical techniques for identifying these 'highly influential' points (and an even greater number for determining so-called 'outliers'). We use the Cook's distance approach based on the OLS fit (with or without seasonality) and use this to identify the three most influential points by putting the three points inside a red circle. This is done in Plot 7, the residuals plot (see Figure 2.2).

Figure 4.1 shows two datasets where the OLS slope differs from the other two due to a greater sensitivity to a few very influential points. The upper graph shows that the estimates of the nitrate trend range from +0.24 (OLS estimate, increasing trend) to –0.34 mg L^{-1} $year^{-1}$ (robust estimate, decreasing trend). The OLS trend is clearly strongly influenced by the two outlying points (in 1985 and 1999). These exert an unreasonably high 'leverage' on the fitted line.

There is also some evidence of seasonality though the evidence is not very strong (p=0.011). The high residual error of the OLS trend line (RMSE=5.49 mg L^{-1} $year^{-1}$) indicates a considerable amount of noise about the trend line and is in part a reflection of some outliers in the 1992–1993 period (one point is recorded as close to zero, which seems unlikely).

The OLS trend line suggests a slight downward trend whereas the other two methods indicate a slight trend upwards. The piecewise OLS regression suggests that the trend changed from strongly downward between 1994 and mid-1997 to moderately upward after that date.

The lower plot (Figure 4.1) shows a more extreme example of this effect, again with some early isolated sample points exerting a relatively large influence on the OLS trend. The trends estimated by the non-OLS methods are less influenced by these points and agree amongst themselves somewhat better.

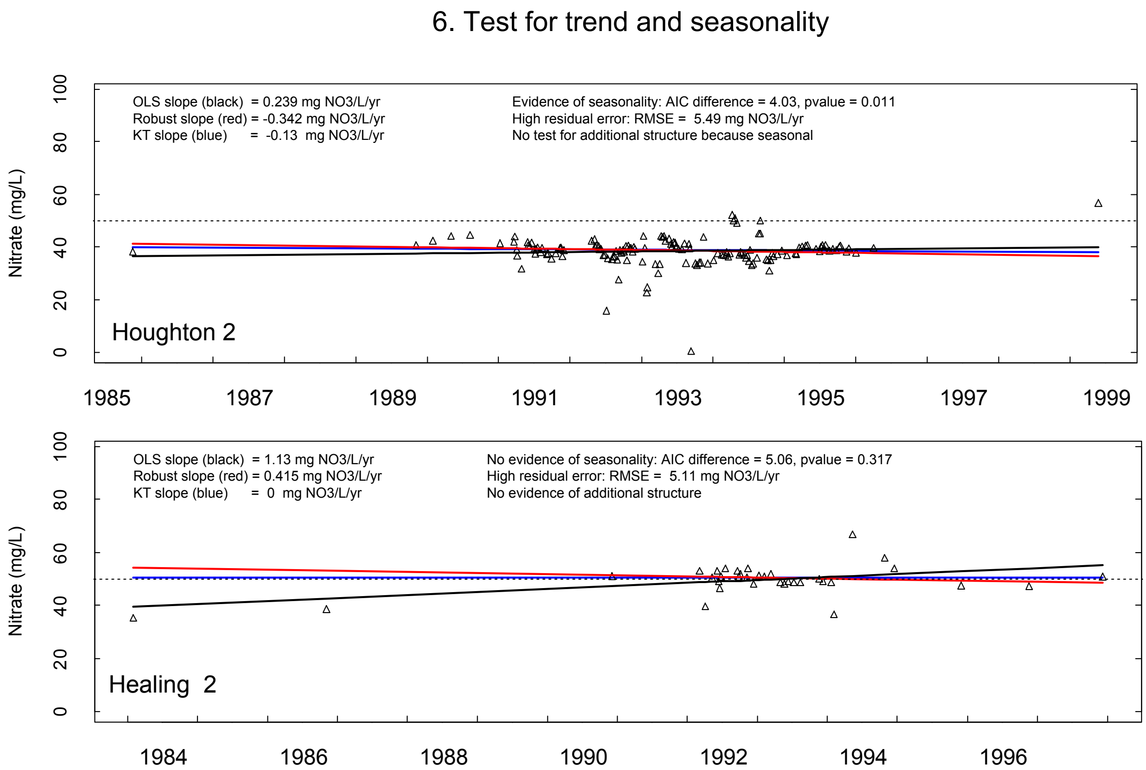


Figure 4.1 Linear trend fitting to data from public supply boreholes Houghton PS 2 and Healing PS 2, Chalk, where data density is greatest in the middle of the series

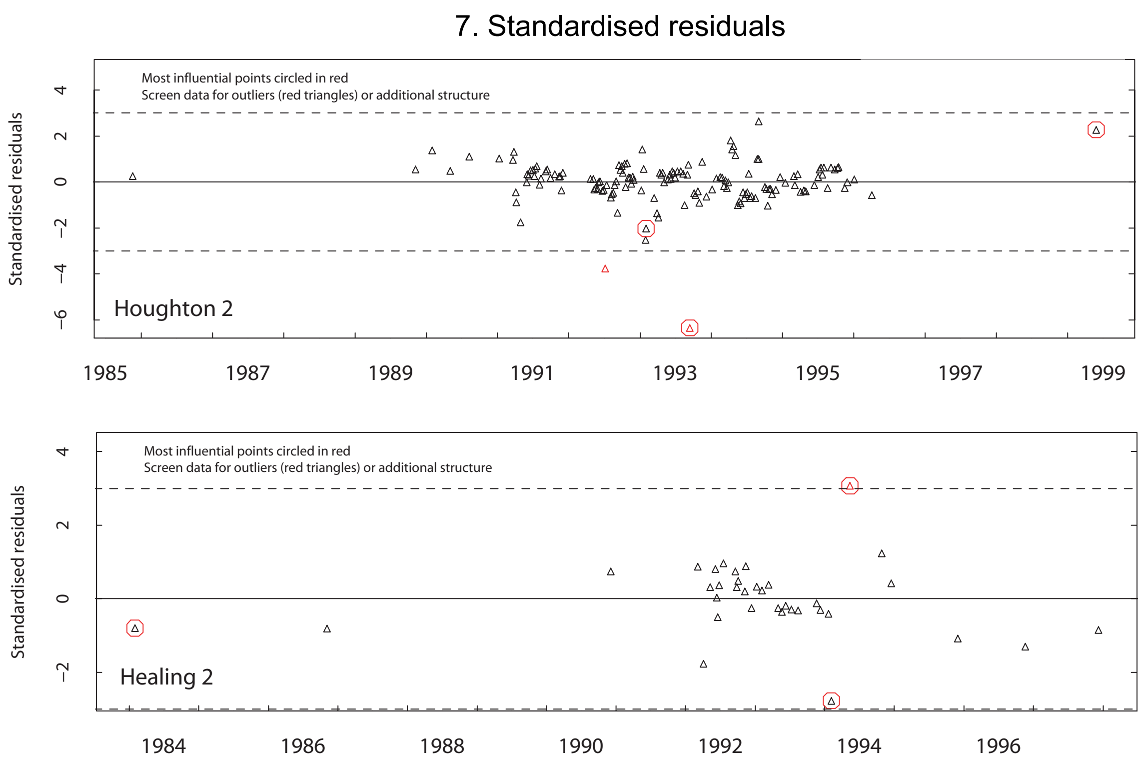
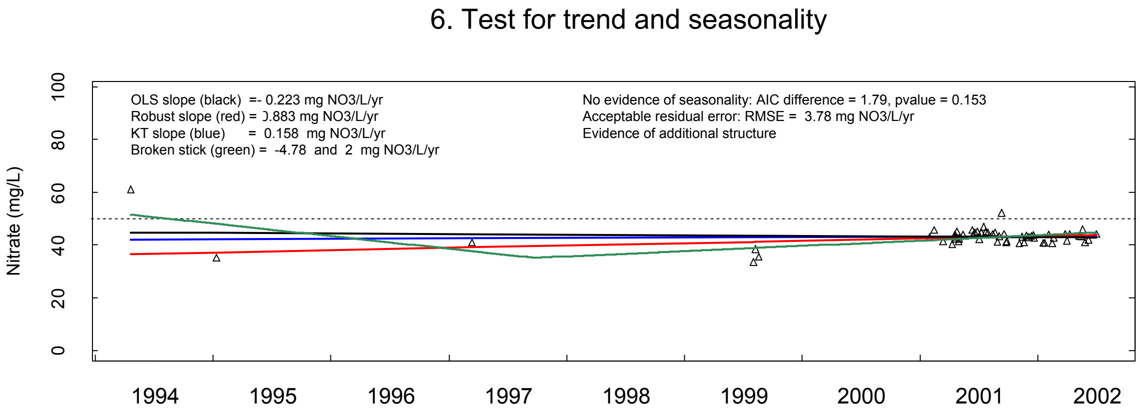


Figure 4.2 Residuals plots (Plot 7) for the two OLS fits to Houghton 2 and Healing 2 sources showing the points with a high residual error (red triangles) and the greatest influence (red circles) on the OLS fits (Figure 4.1).



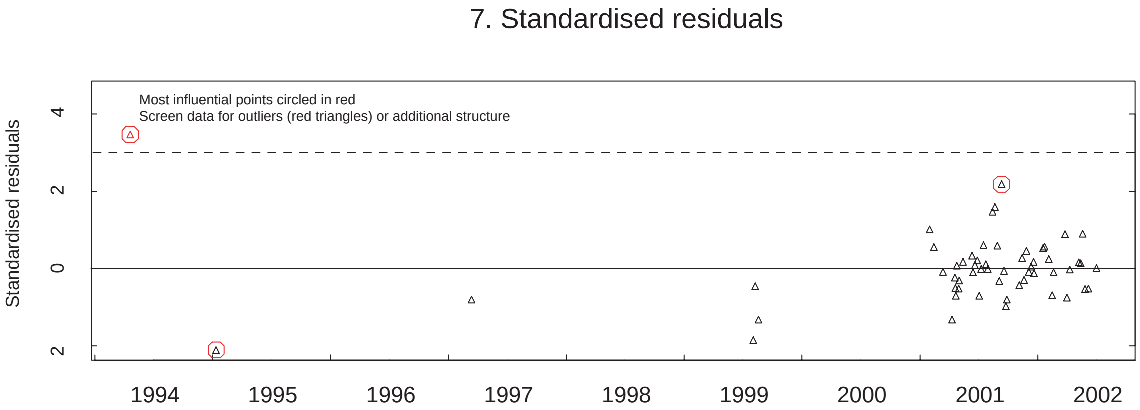


Figure 4.3 Linear trend fitting and residual plot for data from public supply borehole Lower Links PS 1, Chalk, where there is a clustering of data at one end of the series

Figure 4.3 shows another dataset where the majority of the data are clustered in a short period at one end of the series and where there is a spread of concentrations at the other end. Again these early points exert a strong influence on the fitted trends, including their direction. This can also be seen from the Residuals plot (Figure 4.3) for the two sites. The most influential points are circled in red.

2. Non-linear trends

Figure 4.4 shows an example of a non-linear trend. Nitrate concentrations in Carlton PS 3 show evidence of a distinct downturn of nitrate concentrations in 1994-1995, perhaps due to operational changes. As a result, the three methods do not agree very well. The robust estimators are less affected by this downturn. The piecewise regression or 'broken stick' line (green) does locate the change of trend. It is clear that care would be needed to use any of the three trend lines to extrapolate into the future. Even using the trend shown by the second leg of the broken stick plot would need to be made with care given the 'unexplained' nature of the change in slope. A low outlier in 1993 has not significantly affected the calculated trends because of the abundance of other data near this date.

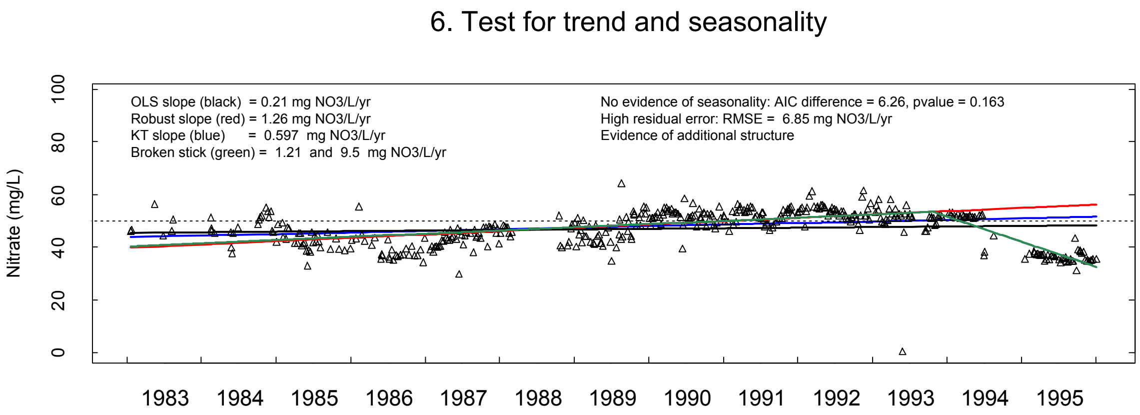


Figure 4.4 Trend fitting to data from the public supply borehole at Carlton PS 3, Permo-Triassic sandstone

Out of the 352 sites, nitrate concentrations for eight showed a peak in 2001 similar to those shown in Figure 4.5. This was assumed to be related to a particularly wet winter in 2000 – 2001. Some of these series also have a similar although smaller peak in 1995. These data were provided to the UKWIR project as examples where trend fitting was difficult. The Robust and KT methods deal very differently with such 'peak' data: the robust estimators are not greatly influenced by them, the OLS is more strongly influenced. Given that the 2000–2001 rise may be a temporary aberration, it is wise not to give it too much weight. In this sense, the robust estimators provide a better estimate of the long term, underlying trend than the OLS estimate.

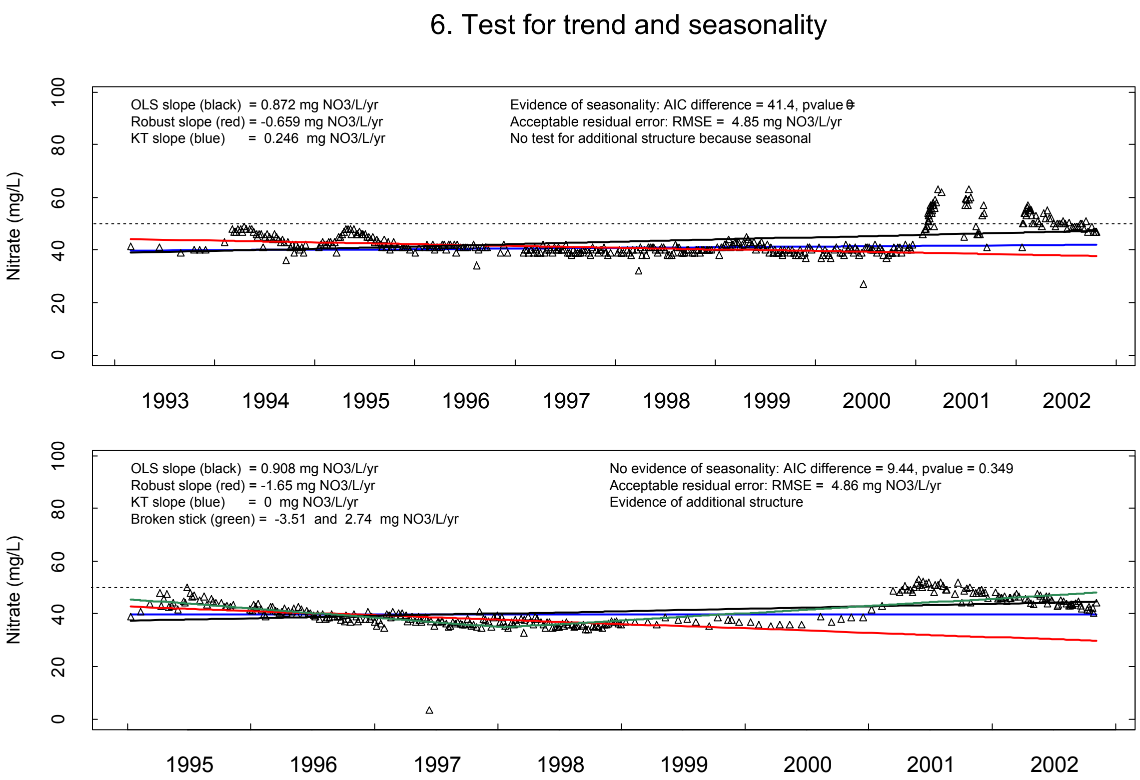


Figure 4.5 Linear trend fitting to data from public supply boreholes at Slipend and Gore which had unusually high nitrate concentrations during 2001.

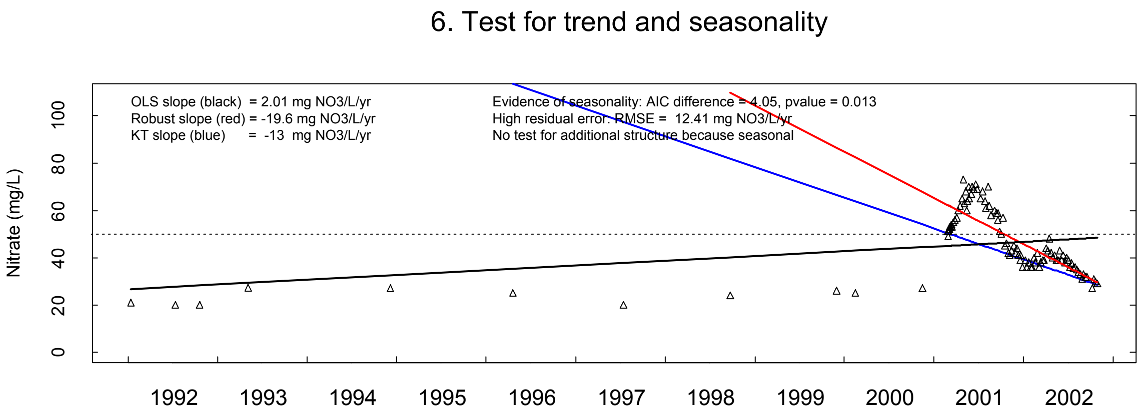


Figure 4.6 Inappropriate linear trend fitting to data from Chartridge PS.

Figure 4.6 shows time-series data from Chartridge PS which exhibits both a period of intense data collection and an anomalous peak in 2001. The Robust and KT methods define a declining trend, largely reflecting the trend seen in the 2001–2002 data, whereas the OLS approach is more influenced by the earlier 'outlier data. It is clear that the time series is not well defined by a simple linear trend. None of the trend lines captures all of the observations well. This is in part reflected by the high RMSE (12.1 mg NO_3/L/yr) of the OLS trend line as well as the residual plot (residual vs time, not shown).

4.2 CONCENTRATION

In order to compare concentrations at sources with different periods and intensity of data collection the 'concentration at 1 January 2000' was calculated for all sources using each of the three trend methods and including a correction for the calculated seasonality if present. This usually involved interpolation but in some cases involved extrapolation.

For many of the datasets, all three methods gave quite similar concentrations: 76% of individual boreholes had a coefficient of variation (CV) of < 5% and 93% of them had a CV of <10%. This indicates that the estimates were not particularly sensitive to the way that the trend line was calculated. In most cases, the trends (slopes) were quite small. For a few datasets, the differences were marked, with 10 sources having a coefficient of variation of >100%.

4.3 EXCLUSION OF DATASETS WITH POORLY-DEFINED TRENDS

The quality of the estimated trend for each source was assessed using the series of criteria shown in Table 4.1. Sources which failed two or more criteria were removed from further analysis. The RMSE and 'Additional structure' tests produced the greatest number of failures suggesting that poor fit and non-linearity are more important problems than the method of trend fitting.

For the original 352 sources the median trend was 0.37 mg L^{-1} $year^{-1}$ with an SD of 1.35 mg L^{-1} $year^{-1}$. After removal of the sources with poorly defined trends, the variability of trend between individual sources was reassessed. For the 309 remaining sources the median trend remained at 0.37 mg L^{-1} $year^{-1}$ but the SD was reduced to 0.90 mg L^{-1} $year^{-1}$.

Table 4.1 Criteria for assessing the quality of the fitted trends

	SD of individual trends	**RMSE**	**Additional structure**	**CV of modelled concentration at 1/1/2000**
Description	Variation between the three methods for estimating the trend	Error about a linear fit	Difference between a linear and loess fit	Expected concentration on Jan 1, 2000 based on the different trend estimates and procedures
Limit	≤0.5 mg L^{-1} yr^{-1}	<7.5%	≤1.2 except where seasonal	≤20%
No of datasets failing criterion	40	70	72	35
No of datasets failing 2 or more criteria				43
By aquifer	Gravel			1
	Chalk			14
	Lower Greensand			3
	Oolite			6
	Lincolnshire Limestone			4
	Permo-Triassic Sandstone			8
	Magnesian Limestone			7

4.4 CHANGES IN TREND

Broken stick plots were generated where an apparent change in trend was detected. This occurred in 40 out of the 309 sources, 19 suggesting a worsening (increasing) trend and 20 an improving (decreasing) one. In some cases, these involved a trend reversal, i.e. a change in the sign of the trend. For the majority of sources these changes were probably due to relatively short-term changes in water quality or erratic data. Examples of a possible worsening trend are shown in Figure 4.7, an end to an improving trend in Figure 4.8 and a change from a worsening trend to an improving one in Figure 4.9 and Figure 4.10.

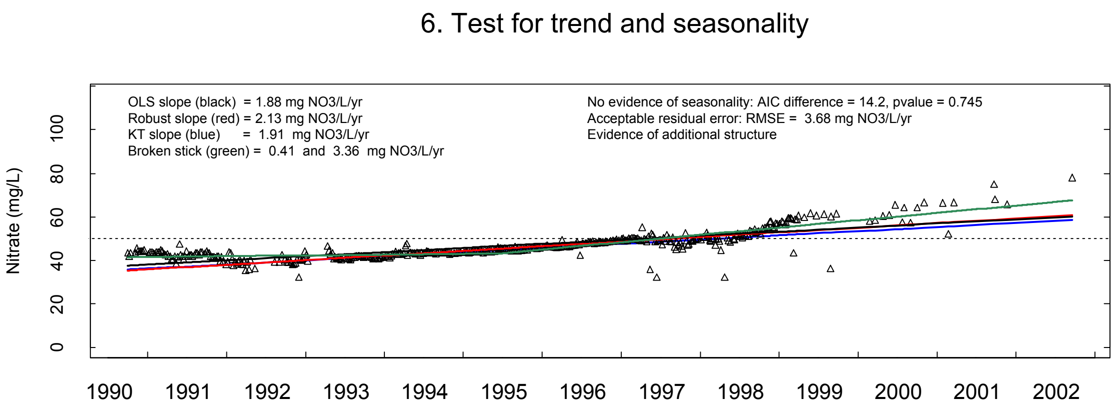


Figure 4.7 An increasingly upward trend in Charing PS borehole 2

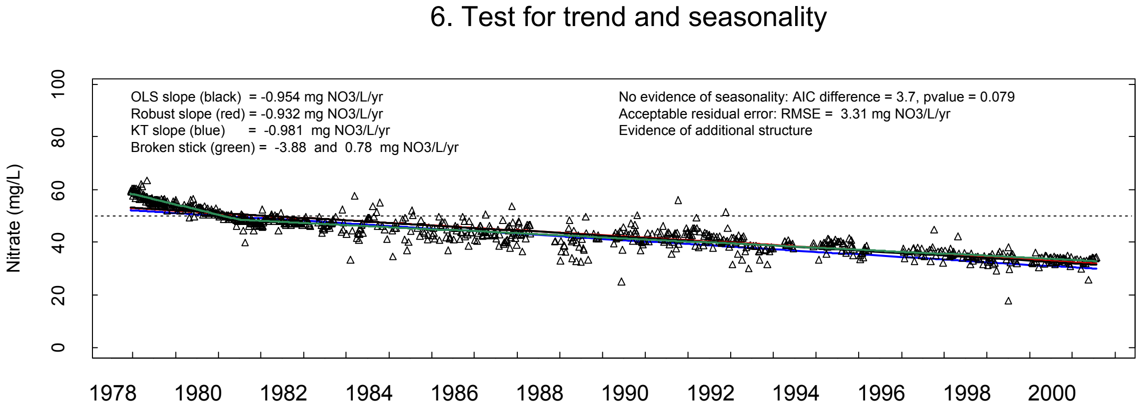


Figure 4.8 Slowing of a declining trend in Cowick PS borehole 3

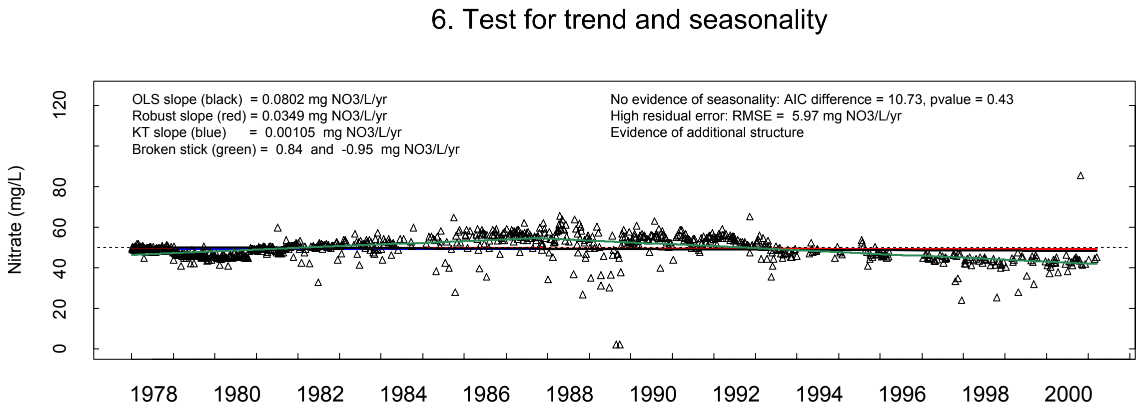


Figure 4.9 A change from a positive to a negative trend in Cowick PS borehole 1

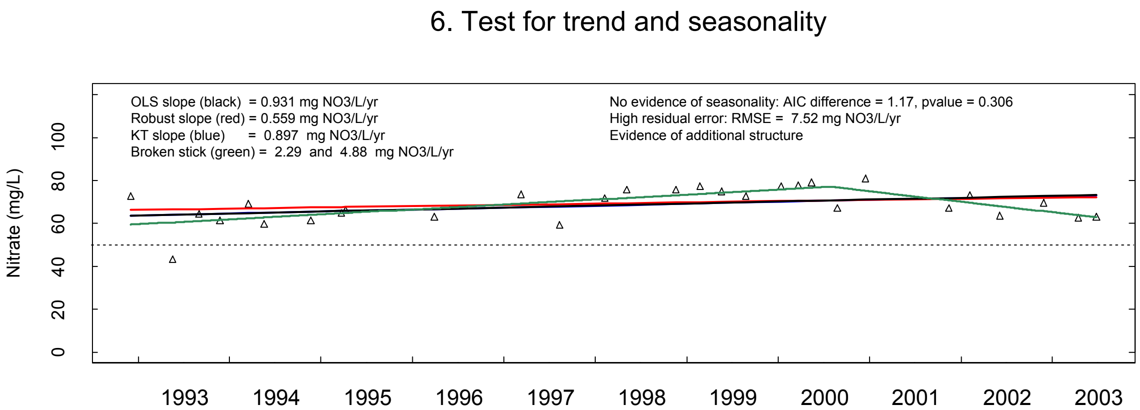


Figure 4.10 A change from a positive to a negative trend in Fossebridge spring

4.5 BETWEEN-BOREHOLE VARIATION AT A GIVEN SITE

4.5.1 Estimated mean concentration on January 1, 2000

Where there were several boreholes at a single site, the individual boreholes often showed distinctly different nitrate concentrations. The variation in the median concentration was determined for the individual sources at 66 sites that had more than one source. The median between-borehole CV was 9.6 %. 34 sites (52%) of these had CVs of <10% and 47 (72%) had CVs of <20%. Six sites had CVs of more than 50%: these were at Finningley (97%), Birchmoor (70%), Great Heck (64%), Cowick (61%), Thornham (60%) and Everton (54%).

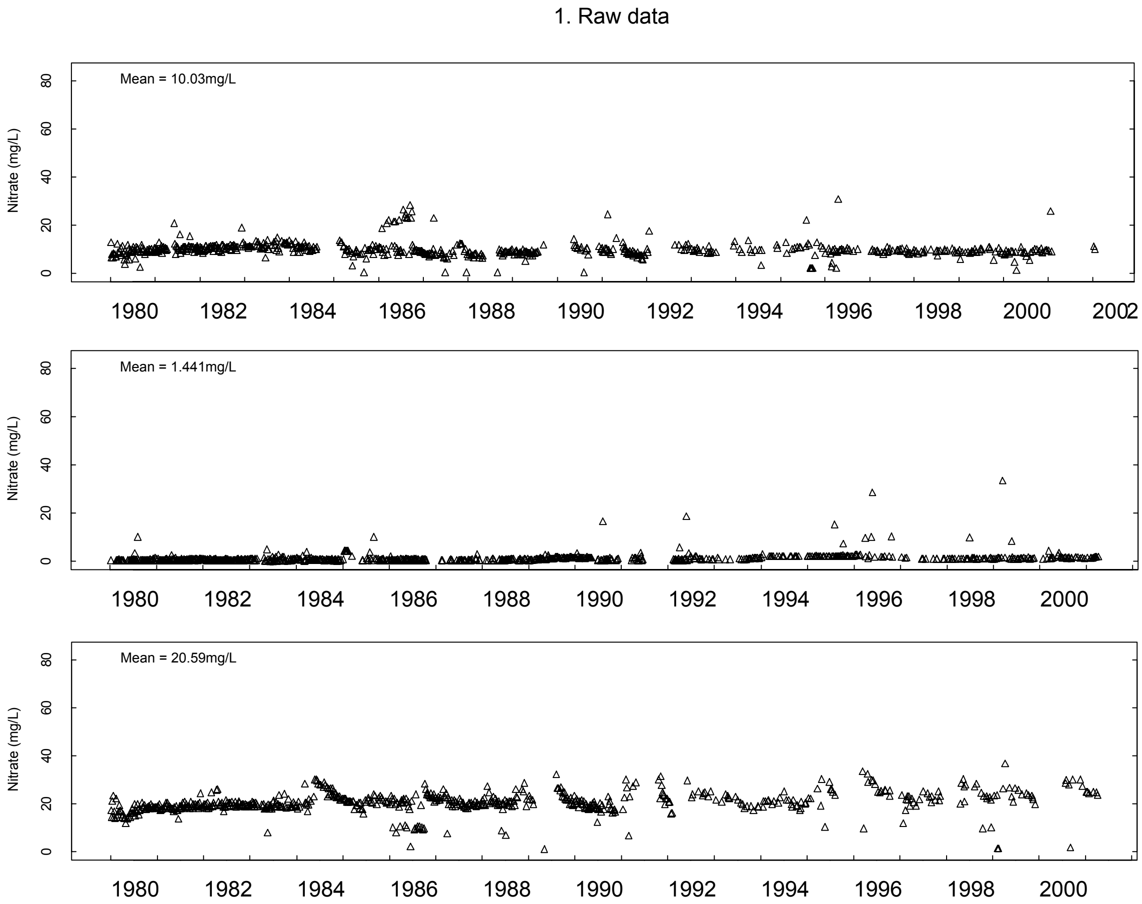


Figure 4.11 Mean nitrate concentrations for the three boreholes at Finningley PS, near Doncaster, showing the consistently different nitrate concentrations in the three boreholes.

The data for Finningley are shown in Figure 4.11. These clearly show that the three boreholes are tapping distinctly different bodies of groundwater. Of these highly-variable sites, four were in the Permo-Triassic sandstone and one was in the Lower Greensand. This could reflect local differences in the degree of denitrification taking place in the Permo-Triassic Sandstone aquifer.

The overall median predicted concentration for all sites, using median concentrations for the multiborehole sites, on January 1, 2000 was 37.8 mg L^{-1} with a CV of 66%. For concentration the between-borehole variation within sites is about 15% of the variation between sites.

4.5.2 Trend

Most sites also had variations in trend between the individual boreholes. For the 66 sites analysed with more than one source the median between-borehole SD was 0.28 mg L^{-1} $year^{-1}$, For these sites only 14 (21%) had SDs of <0.1 mg L^{-1} $year^{-1}$and 26 (39%) of <0.2 mg L^{-1} $year^{-1}$ for the median trend.

Six sites had SDs of more than 1 mg L^{-1} $year^{-1}$. These were Twelve-Acre Wood (2.7), Birchmoor (1.93), Gayton (1.54), Old Chalford (1.36), Marham (1.33) and Moulton (1.07). The data for Twelve-Acre Wood suggest that the variation at this site is due to the relatively poor estimates of trends which themselves are strongly influenced by a few data points early in the two series (Figure 4.12). In contrast, data for Birchmoor illustrate distinctly different site behaviour (Figure 4.13). At this site there was a more intensive period of sampling during 1990 and 1991 but this is not vertically aligned due to the lack of recent data for boreholes 3 and 4.

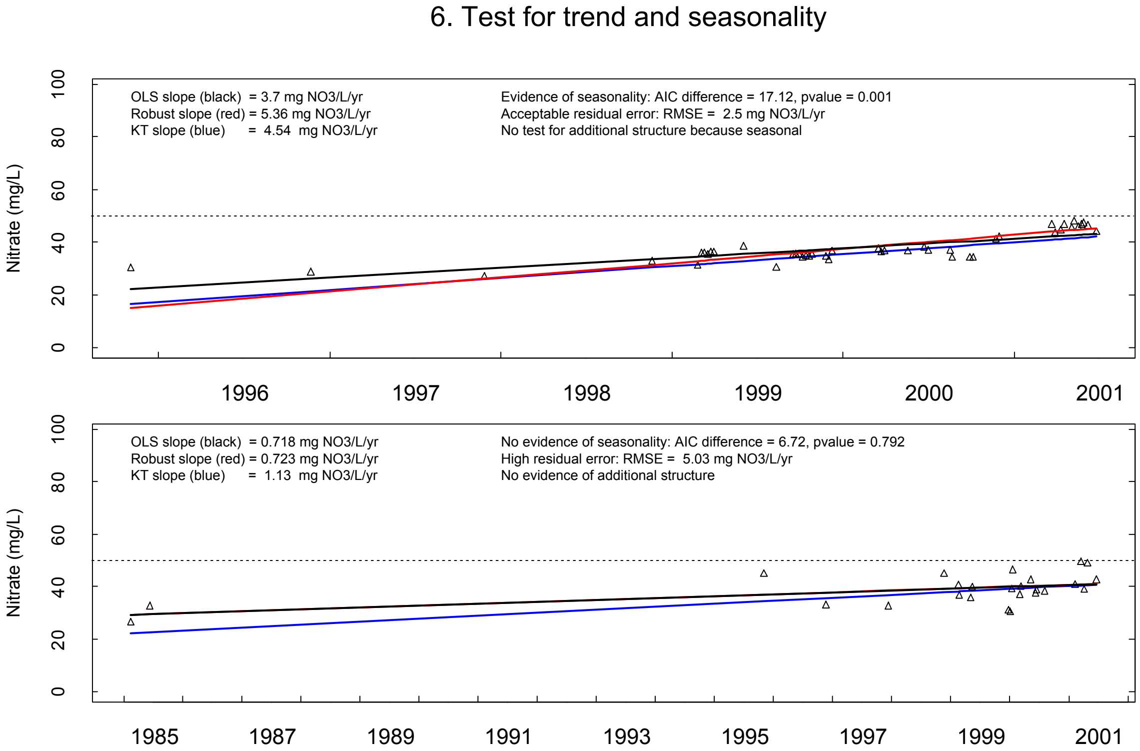


Figure 4.12 Different nitrate trends at the two boreholes at Twelve-Acre Wood PS, Chalk

All four boreholes at Birchmoor are susceptible to quite large short-term variations in nitrate concentration. While these do not, and should not, affect the longer-term trend to a great extent, they do indicate the heterogeneous behaviour of the aquifer and its sensitivity to flow paths and possibly, pumping history.

The overall median trend for all sites, using median trends for the multiborehole sites, was 0.34 mg L^{-1} $yr^{-1}$with a SD of 0.83 mg L^{-1} $year^{-1}$. Therefore for trend the between borehole variation within sites is also much greater than the variation between sites.

4.6 SITES SHOWING LITTLE BETWEEN-BOREHOLE VARIATION

There are a few sites which have clusters of boreholes showing similar mean concentrations and trends. Figure 4.14 and Figure 4.15 show two examples of these, one from the Chalk and one from the Permo-Triassic sandstone.

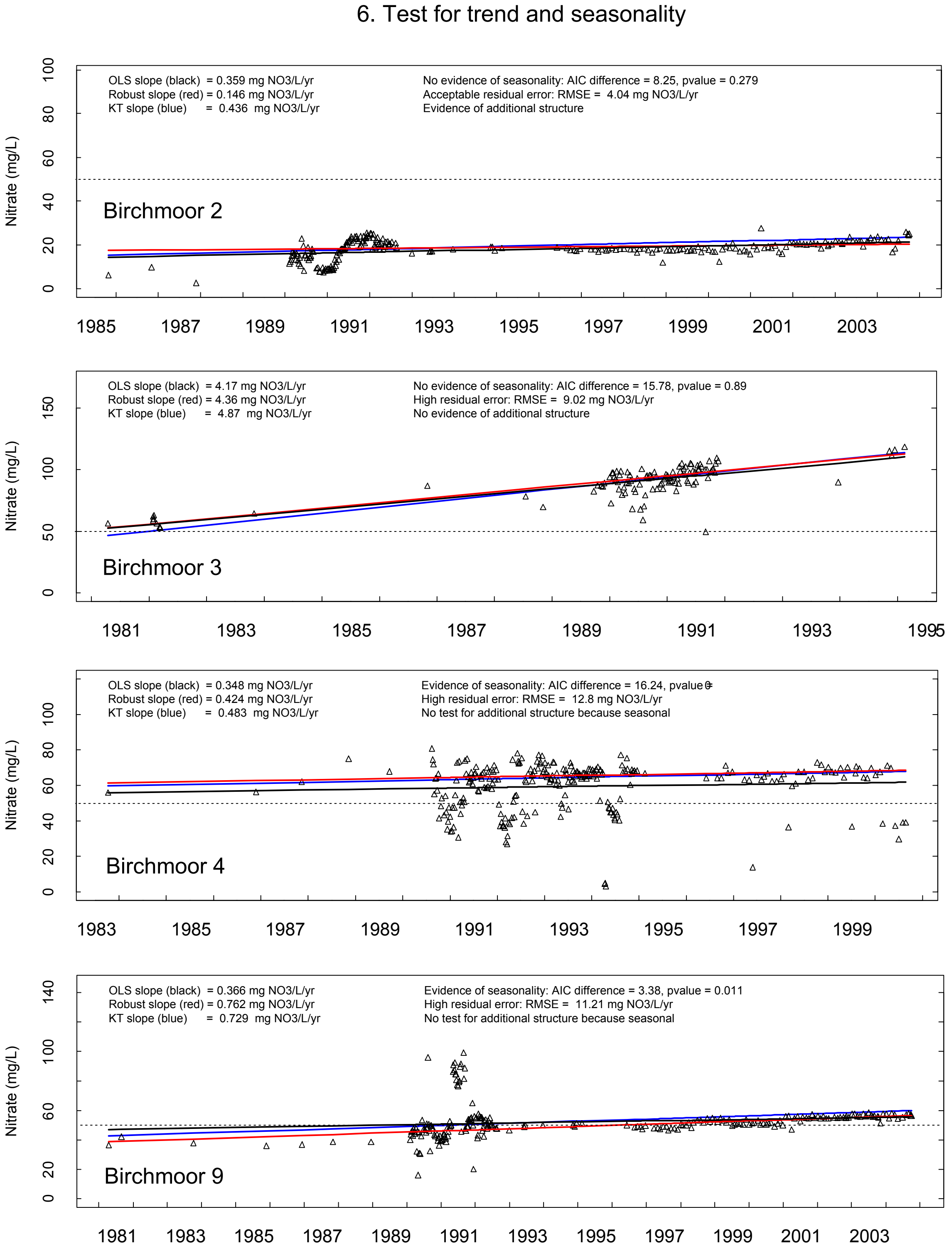


Figure 4.13 Different nitrate trends at Birchmoor PS boreholes 2,3,4 and 9, Lower Greensand (note the different timescales for the four plots)

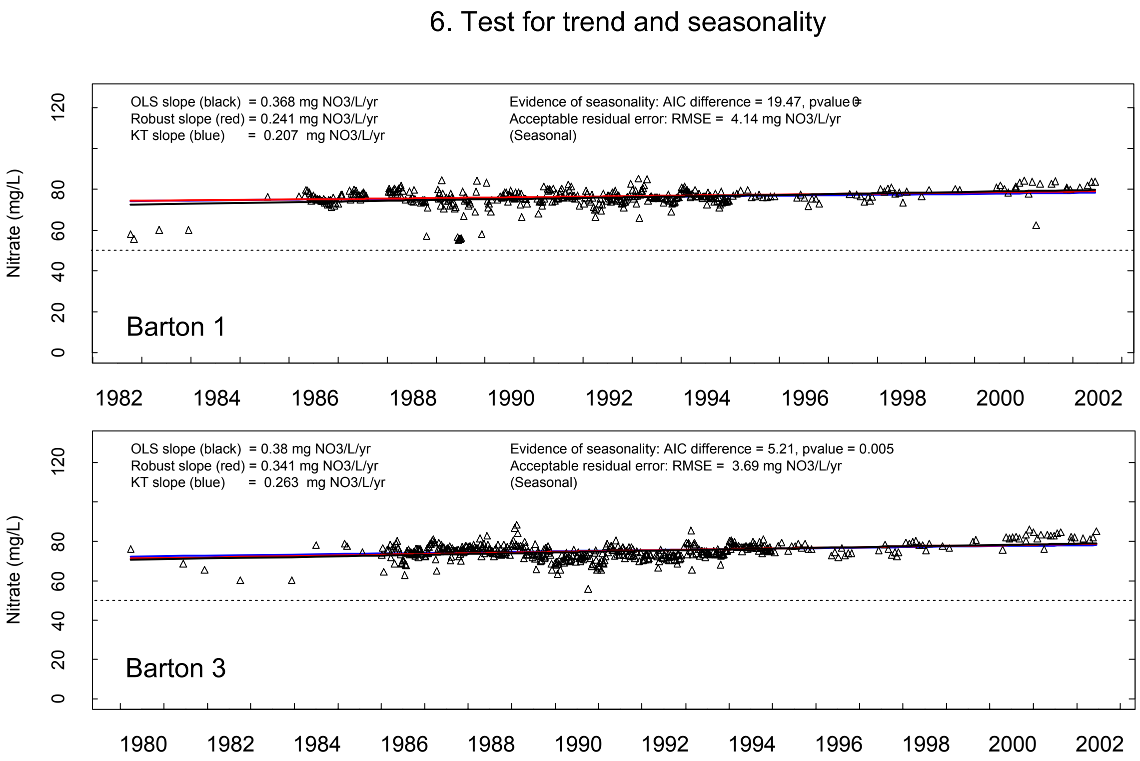


Figure 4.14 Similar mean concentrations and nitrate trends for data from Barton upon Humber PS, Chalk, boreholes 1 and 3

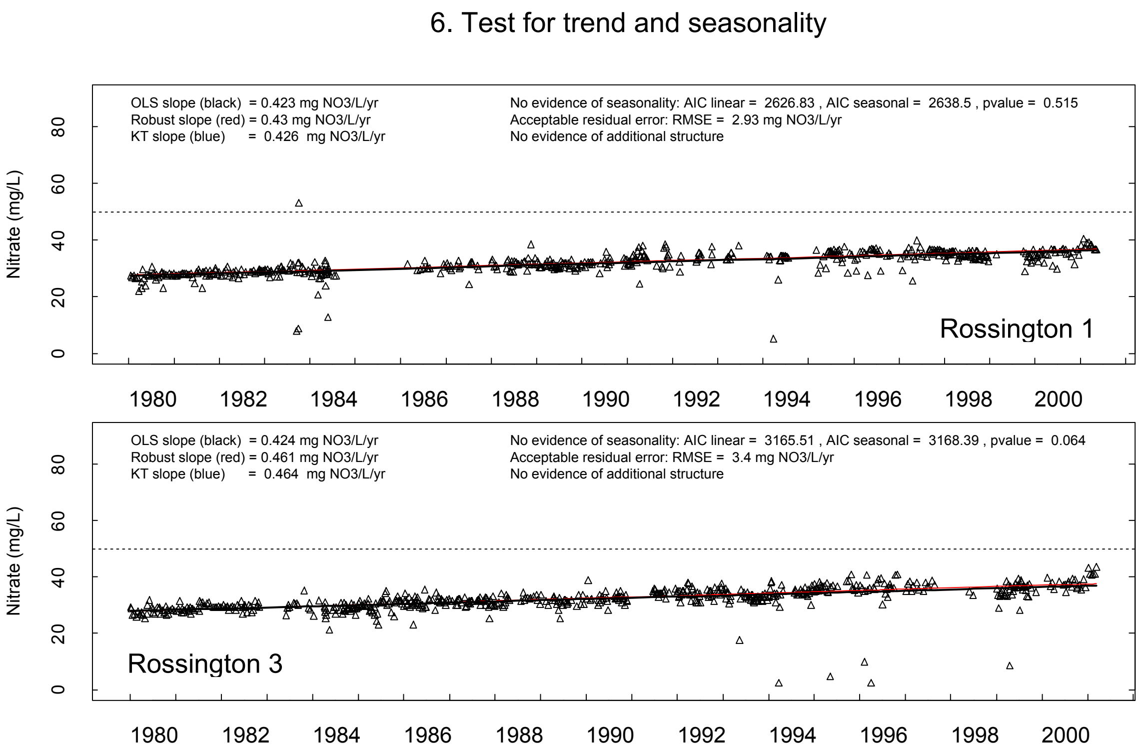


Figure 4.15 Similar mean concentrations and nitrate trends data from Rossington Bridge PS, Permo-Triassic sandstone, boreholes 1 and 2

5 Seasonality

5.1 METHOD OF DETERMINATION

Seasonality in the data is assumed to be annual and is assessed by including time as an independent variable in the regression analysis. The improvement in the OLS fit after including a term for the month of sampling was used to indicate the absence or presence of seasonality. Akaike's Information Criterion (AIC) was used to determine if the improvement was significant ($p<0.05$) (Appendix 1). The seasonal behaviour can also be conveniently visualised using a box plot with the data binned into months (Figure 5.1). This shows how the median concentration varies throughout the year and the size of the boxes also give an indication of the variability within different months. Cyclic behaviour on an annual timescale indicates seasonality though it does not necessarily have to be symmetric as in a sinusoidal pattern.

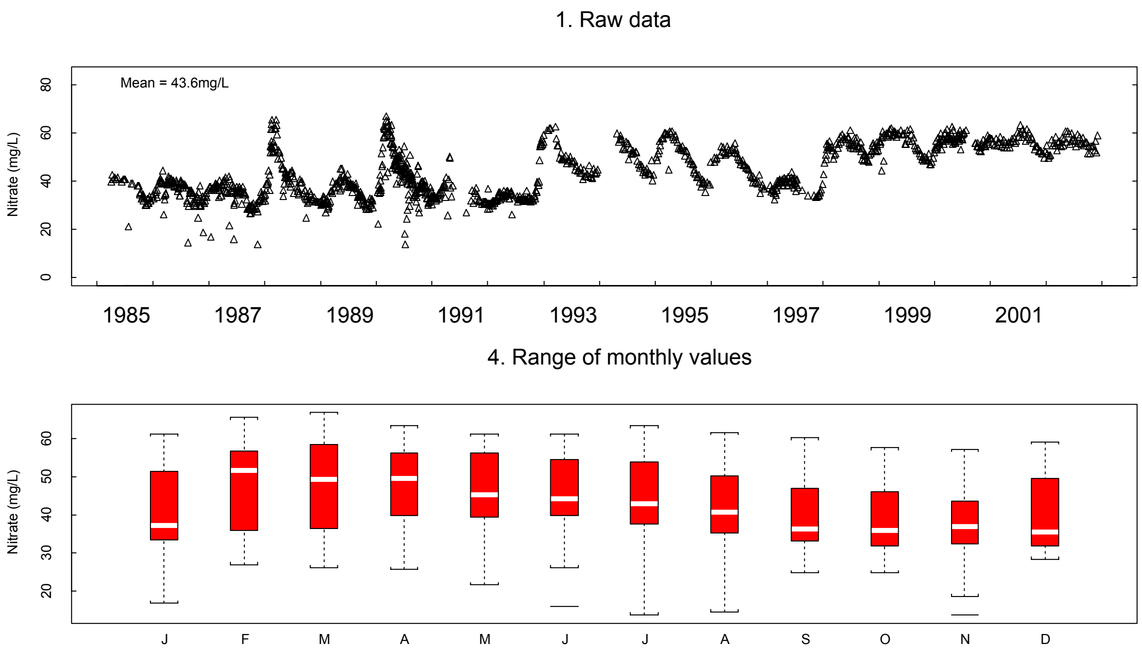


Figure 5.1 Seasonal behaviour at Ogbourne St George, Chalk.

5.2 SEASONAL BEHAVIOUR

114 individual boreholes or springs were assessed as showing seasonal behaviour out of the total sample of 309 sources. These were distributed as shown in Table 5.1 As would be expected, the Permo-Triassic sandstone is the least seasonal aquifer type although some sources within the Permo-Trias do show seasonal behaviour. Ogbourne St George (Figure 5.1), Fognam Down 2, Etton 4 and Springwell in the Chalk, Clay Hill (Figure 5.2) in the Lincolnshire Limestone, Ulnaby in the Magnesian Limestone (Figure 5.3) and one of the Old Chalford observation wells in the Oolite, showed the greatest apparent seasonal behaviour.

Table 5.1 Seasonality in different aquifers

Aquifer	No of seasonal sources	Percentage in aquifer
Gravels	1	50
Chalk	56	42
Lower Greensand	4	44
Lincolnshire Limestone	9	53
Oolitic Limestone	16	73
Lias	2	40
Permo-Triassic sandstone	9	11
Magnesian Limestone	16	37
Carboniferous Limestone	1	100

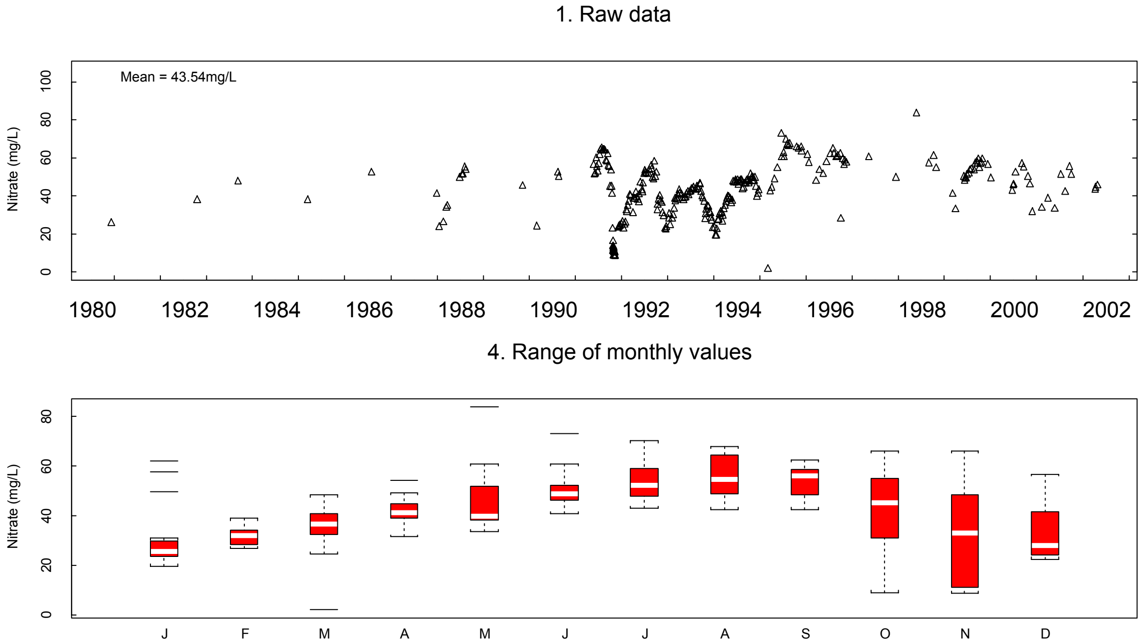


Figure 5.2 Seasonal behaviour at Clay Hill PS, Lincolnshire Limestone

Figure 5.3 clearly demonstrates that the seasonality in this data is spurious and results from a single point for January which is very different from the rest of the data. Even for the most seasonal source, the magnitude of the seasonality varies greatly from year to year. Seasonality is only clearly seen where there is frequent sampling, although it may still be detectable statistically in a dataset with intermittent sampling (Figure 5.4).

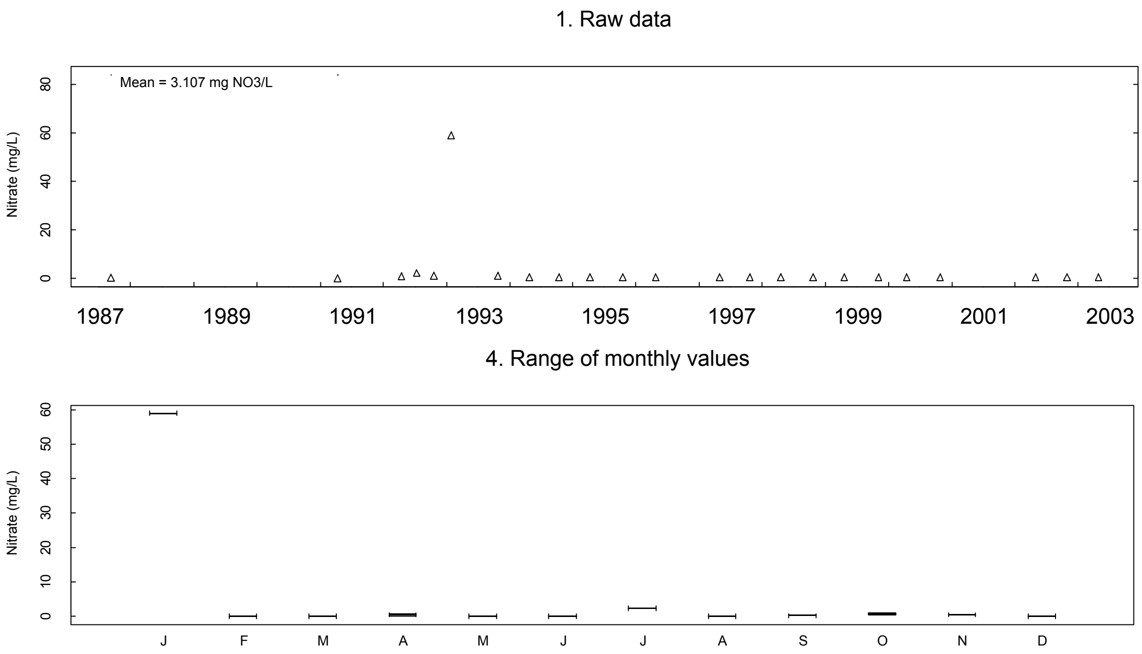


Figure 5.3 Apparent seasonal behaviour at Ulnaby monitoring borehole,

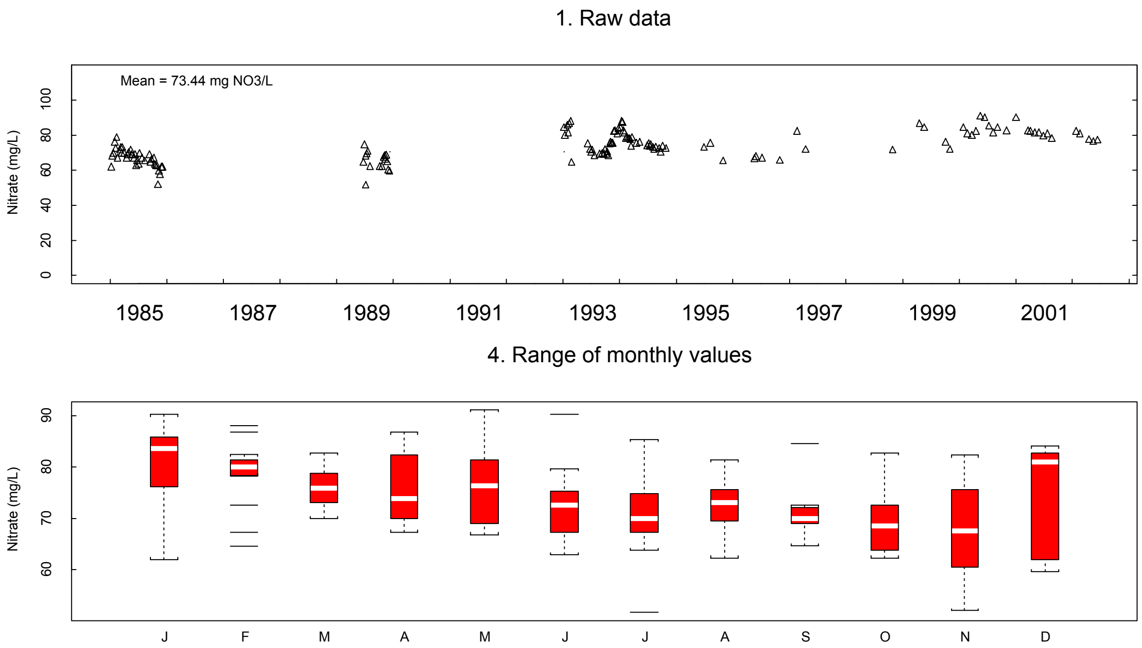


Figure 5.4 Seasonal behaviour at Barrow on Humber PS, borehole 3, Chalk

5.3 NON-SEASONAL BEHAVIOUR

Sources assessed as having the least seasonal behaviour and showing no evidence of 'additional structure' are Nutwell 3, Finningley 1, Everton 1, Hatfield Woodhouse 1, Bromsberrow 3, in the Permo-Triassic sandstone, and Bircham 3 in the Chalk. Data for Nutwell (Figure 5.5) and Finningley 1 show that these are indeed reasonably well-populated time series with very little seasonal variation.

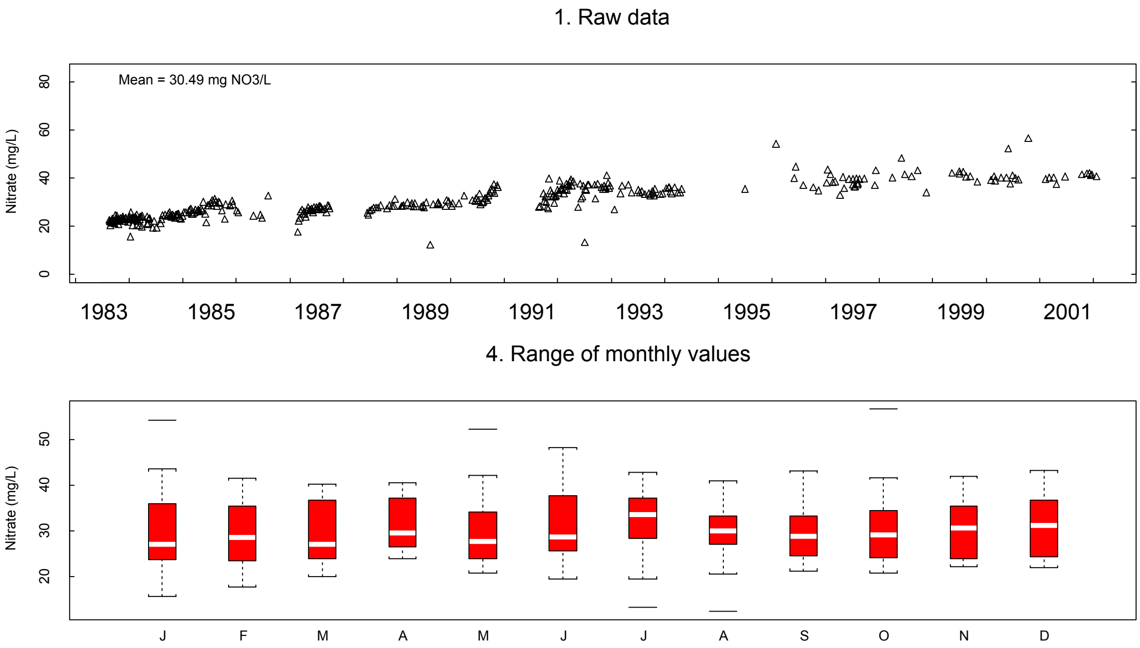


Figure 5.5 Non-seasonal behaviour at Nutwell PS, borehole 3, Permo-Triassic sandstone

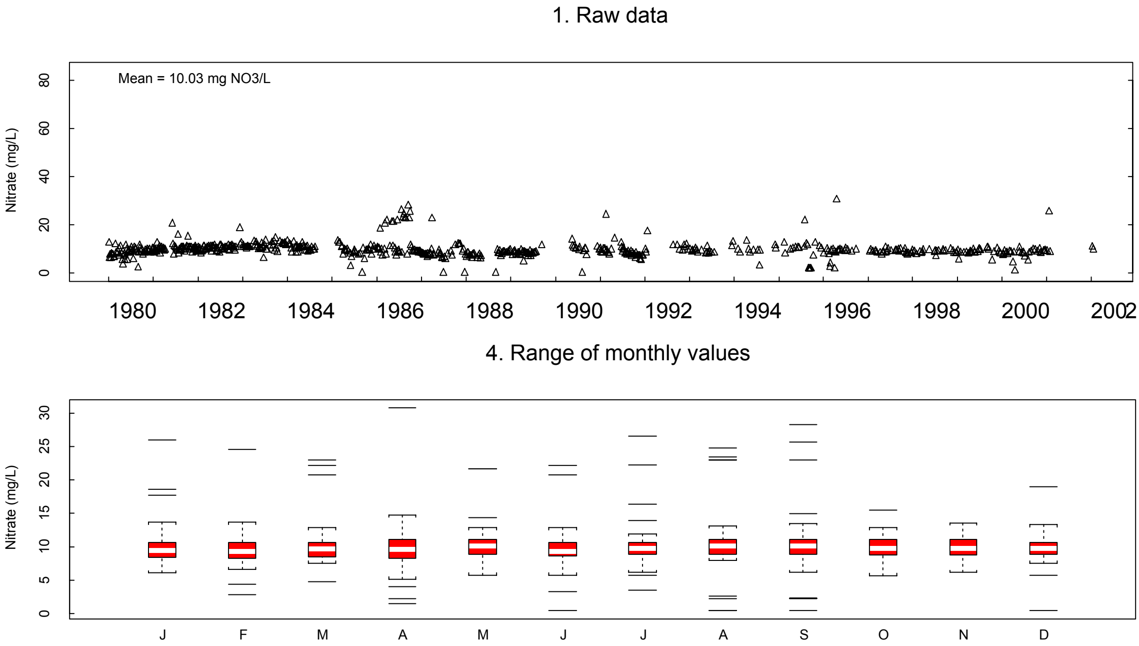


Figure 5.6 Non-seasonal behaviour at Finningley PS, borehole 1, Permo-Triassic Sandstone

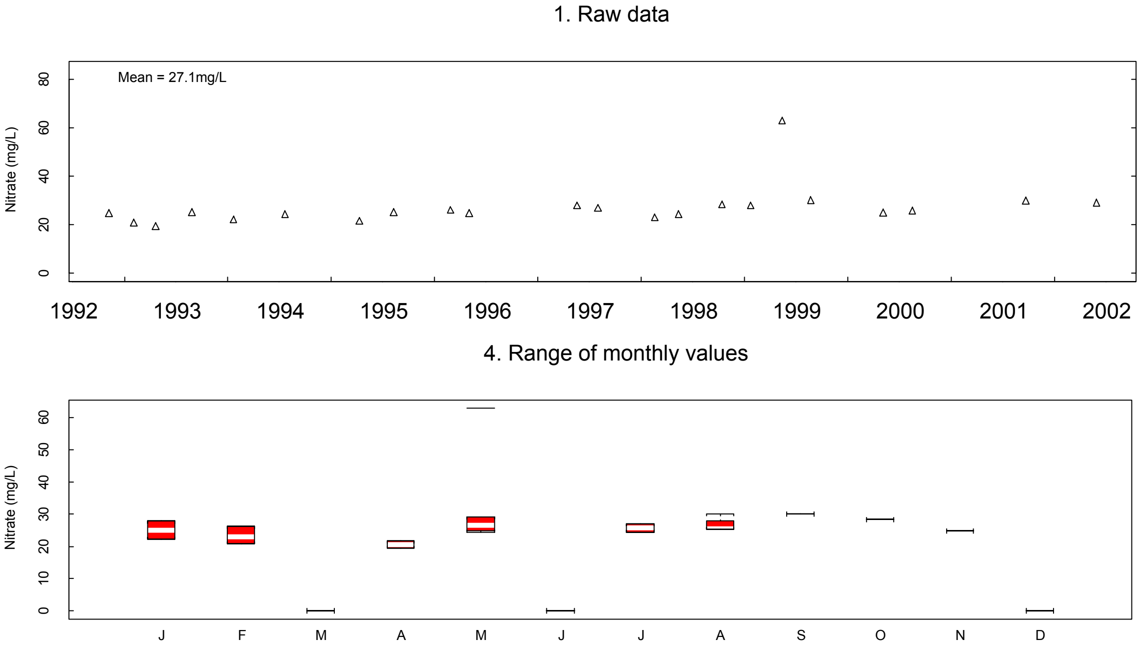


Figure 5.7 'Non-seasonal' behaviour at Mildenhall, Warren Farm observation well, Chalk

Mildenhall (Figure 5.7) in the Chalk has a low sampling frequency and the failure to detect seasonal behaviour is probably due to the lack of data for some months (March, June and December).

5.4 ADDITIONAL STRUCTURE

'Additional structure' is a term that is used here for systematic variation that falls outside that expected from a strictly linear model and which may indicate that some other model is more appropriate, e.g. a curved model. It is only estimated for non-seasonal series. If the RMSE for the linear model is greater than 1.2 times that for the loess trend line (Plot 5), then this is taken to indicate that there is likely to be some 'additional structure' present. The loess trend line tends to follow the local trend in the data irrespective of the linearity of the overall trend and so the RMSE of the loess fit largely reflects the short-term noise in the data rather than the error in the model shape.

Figure 5.8 shows the time series for Great Heck borehole 3. This clearly exhibits periodic fluctuations but which are not regular enough to be classed as seasonal. The monthly plot shows that the fluctuations are very small and there is no regular cycle. This series also shows two outliers in August and September but these are not sufficient to trigger the 'additional structure' warning as they are not part of any systematic variation.

The series for Ladywell Springs (Figure 5.9) looks at first glance to be obviously seasonal but the monthly plots show that the range of data for each month is large and again there is no regular monthly pattern.

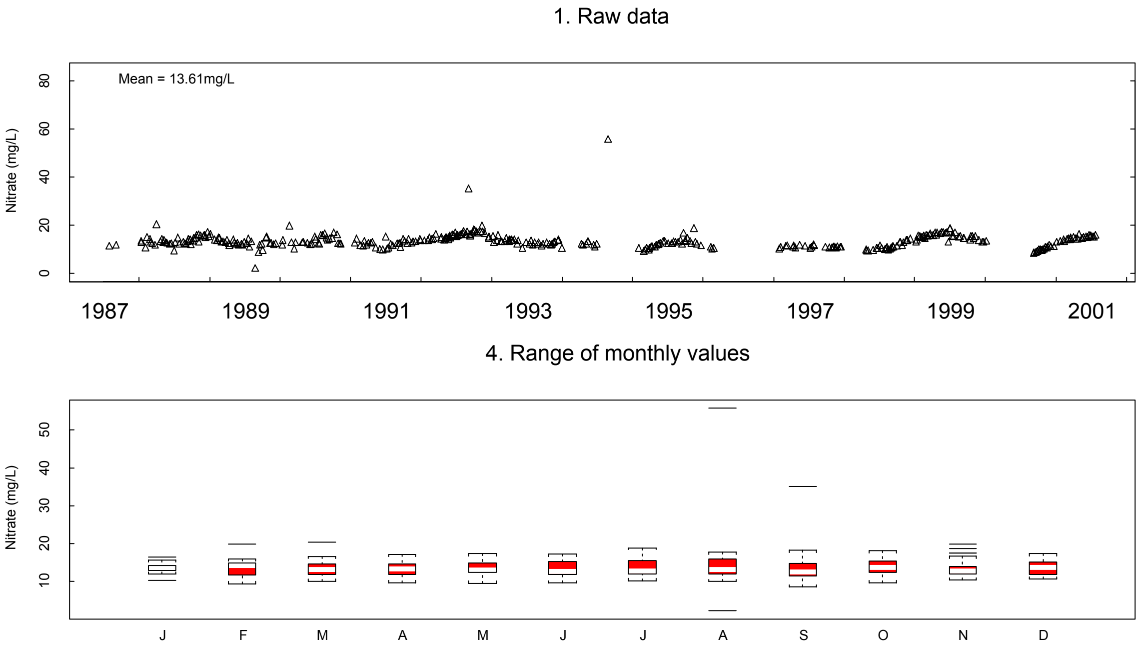


Figure 5.8 Non-seasonal behaviour at Great Heck PS, borehole 3 with evidence of additional structure

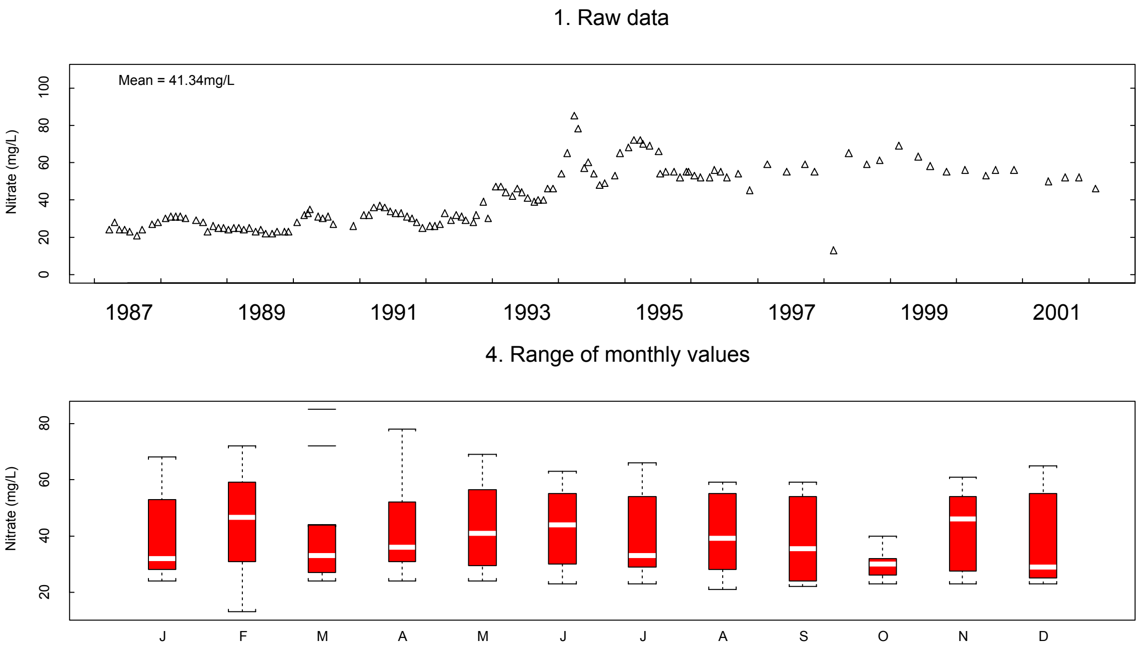


Figure 5.9 Ladywell Springs, Lincolnshire Limestone

5.5 EXCLUSION OF SITES WITH INSUFFICIENT DATA TO ASSESS SEASONALITY

Due to the clear difficulties of assessing seasonality in sources with low sampling frequency, sources with an average sampling frequency of less than 4 per year were excluded from further assessment of seasonality in Section 7.3. Of the 90 sources excluded, the majority were Environment Agency observation boreholes with the remainder being public supplies with long data gaps.

5.6 SEASONALITY AND WATER LEVELS

The relationship between nitrate trend and water levels was investigated for a small number of sources in the datasets already analysed (UKWIR, 2003). This indicated that where seasonality was significant, a relationship could often be found between the fluctuations in water level and nitrate concentration. High water levels corresponded with higher nitrate concentrations, perhaps due to a greater contribution of shallow, polluted water.

Such a simple relationship does not apply where there is a non-uniform response to rises in water level. Non-linear responses may be due to:

- Greater permeability at shallow depths resulting in a greater contribution of high nitrate water to the source and a disproportionate effect on water quality. UKWIR (2003) showed data for 'Thames A' where the variation in nitrate was largely accounted for by water level fluctuations, but where a 'smaller than usual' water level peak resulted in no nitrate peak at all.
- Lack of regular saturation of the uppermost horizons allowing high concentrations of nitrate to persist. Peak nitrate concentrations in 2001, such as those shown in Figures 4.4 and 4.5, are thought to be due to exceptional rainfall during the autumn of 2000. There will have been changes in water level in the period 1996 – 2000 but these were not mirrored by any increase in source nitrate concentration. It appears that water has to rise to some minimum level before increased nitrate concentrations become apparent at the source.

Water level information, preferably from a site close to the source of interest, provides additional information that is not necessarily captured by other available information. Specifically, although water levels tend to vary cyclically throughout the year and show few long-term trends (i.e. not a groundwater 'mining' situation with steadily declining water levels), not all years are equally wet and so the amplitude of the cyclicity in water levels as well as the peak dates tend to vary to some degree from year to year. Water level data capture this whereas simply using dates (as in fitting a sine curve of fixed amplitude) would not (Figure 5.10).

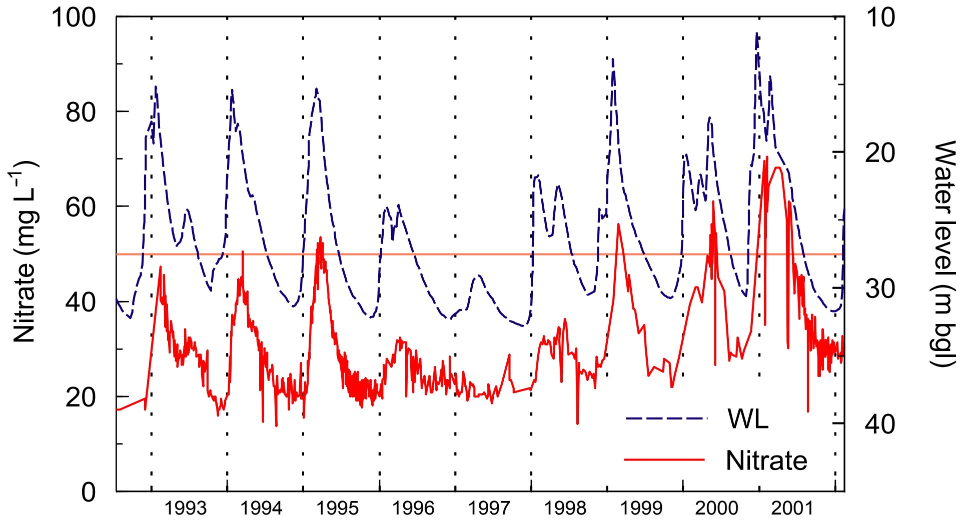


Figure 5.10 Variation of groundwater nitrate concentrations and nearby water levels (1993-2001) for Fognam Down in the Chalk aquifer ('Thames A'). Note the strong correlation between nitrate concentrations and water levels and how low water levels and low nitrate concentrations match each other even during the dry years of 1996-1997.

At this site, the high correlation between water levels and nitrate concentrations is even maintained during the dry years of 1996-1997. This points to a fundamental (process-based) connection between the two which needs further investigation. As discussed above, not all sites show such seasonality (Section 5.3) and so the use of water level data is not always of benefit.

We discuss in Section 7.2 how predictions of future nitrate concentrations can be based on both non-seasonal and seasonal models.

6 Variability at the site scale

6.1 REASONS FOR VARIABILITY

Three main reasons have been given for the different behaviour of individual boreholes at multi-boreholes sites:

- Different borehole construction – depth or cased interval allowing water from different depths (and with different quality) to enter the borehole;
- The main inflows are from a few productive horizons or fissures and these are different;
- The individual boreholes derive their water from different capture zones and the landuse history/drift cover in these is different leading to different histories of nitrate inputs.

Sites showing a high variability of either the median nitrate concentration or nitrate trend between individual boreholes are shown in Table 6.1. Most of the sites showing a large within-site variability of nitrate concentrations are in the Permo-Triassic Sandstone of south Yorkshire and Nottinghamshire whereas variable within-site trends are also found in the Chalk.

Table 6.1 Borehole sites showing high within-site variability (in descending order of their median concentration and trends; sites highlighted in **bold** are in both categories)

Site	CV median concentrations at 1/1/2000 (%)	Site	SD median trend (mg NO_3 $L^{-1}yr^{-1}$)
Finningley	97	Twelve-Acre Wood	2.70
Birchmoor	**70**	**Birchmoor**	**2.19**
Great Heck	64	Gayton	1.54
Cowick	**61**	Marham	1.33
Thornham	60	Moulton	1.07
Everton	54	Ogbourne Observation	0.99
Highfield Lane	36	Orpington	0.97
Chequer House	**33**	Houghton	0.90
Hatfield	32	**Cowick**	**0.84**
Bromsberrow	27	**Chequer House**	**0.84**

Table 6.2 sets out relevant construction details and summary information on nitrate concentration, trends and seasonality for these variable sites. For the Chalk aquifer, differences in construction and productivity could contribute to the variations seen in water quality. For example, at Houghton, different yields from the boreholes are attributed to their different acidisation histories which could suggest different inflow patterns. At Marham, the most productive boreholes, which are within a few metres of each other in the thin aquifer, have historically shown different pumped water levels.

In the Permo-Triassic Sandstone aquifer, variability could be due to quality stratification and differences in borehole construction e.g. at Bromsberrow and Highfield Lane. At Chequer House and Finningley, where borehole constructions are very similar, this must be due to differences in the individual source catchments.

Table 6.2 Construction details for sites with high inter-borehole mean or trend variability

Site	Borehole	Depth (m)	Plain casing (m)	NO_3 at 1/1/2000 (mg L^{-1})	Trend (mg NO_3 L^{-1} $year^{-1}$)	Seasonal	Aquifer
Birchmoor	2	55	24	19.6	0.36	No	Lower Greensand
	3	71	15	134	4.36	No	
	4	61	15	67.6	0.42	Yes	
	9	56	18	52.8	0.73	Yes	
Bromsberrow	1	61	18	77.4	1.29	No	Permo-Triassic Sandstone
	2	61	18	68.4	1.14	No	
	3	61	23	54.5	0.48	No	
	4	91	30	40.1	0.31	Yes	
Chequer House	2	112	26	70.4	0.73	No	Permo-Triassic sandstone
	3	104	26	43.7	-0.46	No	
Cowick	1	183	57	49.2	-0.03	No	Permo-Triassic sandstone
	2	183	69	33.0	-0.95	No	
	3	120	46	11.1	-1.71	No	
Everton	1	138	62	34.3	0.52	No	Permo-Triassic Sandstone
	3	183	27	15.3	0.48	No	
Finningley	1	148	38	9.2	-0.06	No	Permo-Triassic sandstone
	2	138	38	1.7	0.06	No	
	3	138	38	24.0	0.27	No	
Gayton	2	34		55.6	2.69	Yes	Chalk
	3	60		54.3	0.51	Yes	
Great Heck	1	132	36	41.2	1.19	No	Permo-Triassic sandstone
	2	120	37	63.3	0.43	No	
	3	120	45	13.2	-0.03	No	
Highfield Lane	1	176	78	37.9	0.60	No	Permo-Triassic sandstone
	2	175	42	42.9	0.79	No	
	3	120	50	19.8	-0.51	No	
Houghton	1	53	7	43.1	1.14	No	Chalk
	2	19	12	38.0	-0.13	Yes	
Marham	1	11	-	67.1	2.64	No	Chalk
	2	11	-	41.8	-0.44	Yes	
	3	11	-	73.2	0.92	Yes	
	5	12	8	74.1	2.06	No	
	6	11	-	74.0	2.63	No	
	8	12	-	74.8	3.31	Yes	
Moulton	2	53	9	55.4	1.79	Yes	Chalk
	3	38	9	43.7	0.28	No	
Ogbourne Obs	SF			47.6	0.49	No	Chalk
	WD			60.3	1.88	No	
Orpington	1			33.2	0.12	No	Chalk
	2			35.2	0.27	No	
	3			35.8	0.22	yes	
Thornham	1	158	33 (60)	18.3	0.49	No	Permo-Triassic sandstone
	2	183	31	6.9	0.09	No	
	3	121	60	7.3	0.18	No	
Twelve-Acre Wood	1	74	63	39.9	0.72	No	Chalk
	2	70	59	35.4	4.54	Yes	

6.2 CASE STUDIES FROM THE YORKSHIRE/NOTTINGHAM PERMO-TRIASSIC SANDSTONE

A large proportion of the sites showing most variability are situated in the Permo-Triassic sandstones of Nottinghamshire and South Yorkshire. This variability has been ascribed to the groups of factors indicated below.

6.2.1 Different borehole construction/stratified water

THORNHAM

Relining of Thornham borehole 1 has curtailed the entry of poorer quality shallow inflows through corroded casing. These inflows contributed to sporadically high nitrate concentrations during the early 1990s (Figure 6.1). Logging showed that before the relining, the coolest water was present near the base of the casing at 50 m, but that after relining, the borehole showed peak nitrate concentration at 40-42 depth indicating water movement along a low-permeability mudstone-rich or mudstone layer seen in the gamma log (Buckley, 2003). Fissuring was seen at 90 m, and above this, the dissolved oxygen concentrations were higher. Warmer, high conductivity water tends to be drawn in at the base of borehole 2 when borehole 1 is pumping. The other two boreholes have similar nitrate concentrations.

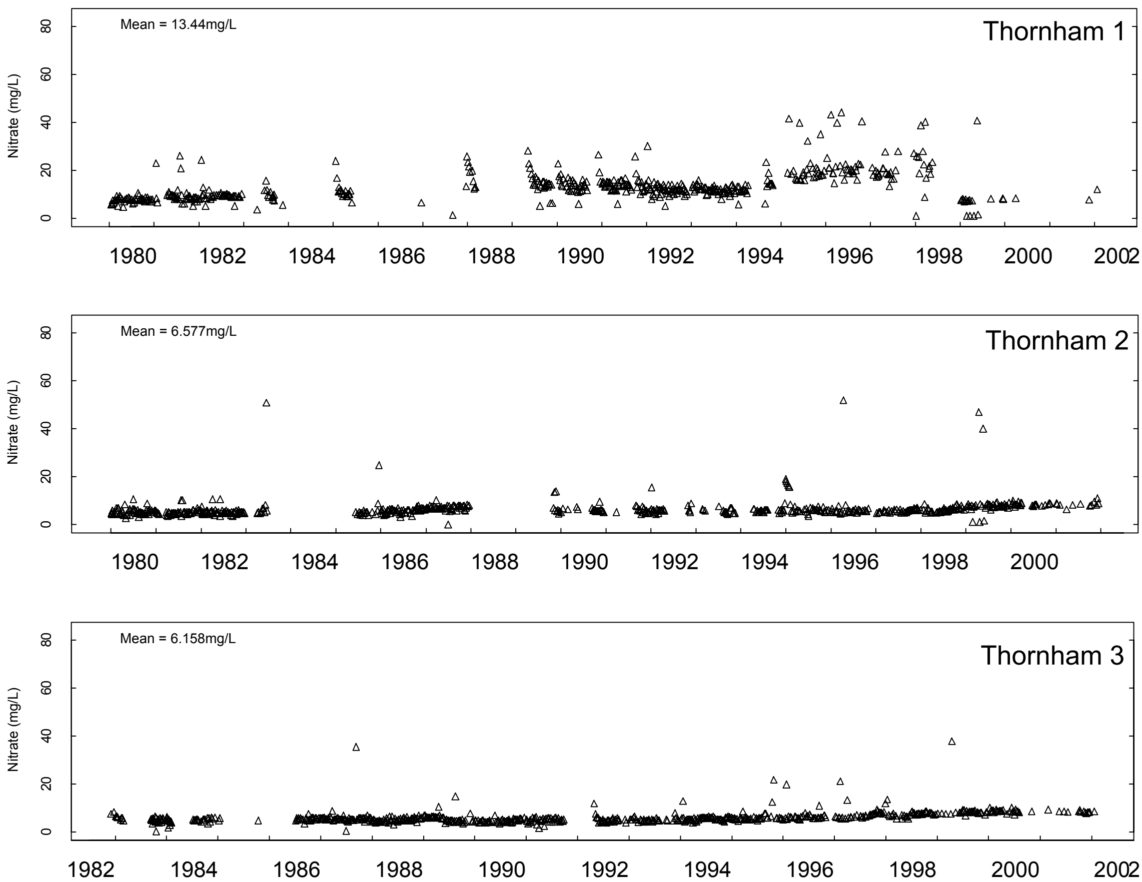


Figure 6.1 Nitrate in Thornham PS boreholes, higher concentrations in borehole 1 possibly removed by relining

CARLTON MILL LANE

This site is located in a window of sandstone outcrop surrounded by semi-permeable and impermeable drift-covered areas. Abstraction started in 1968 and the pumped water quality has deteriorated with time showing increasing nitrate concentrations and permanent hardness (Parker et al., 1985). The three boreholes have always shown consistent differences in water quality. Porewater profiles from investigation boreholes close to Mill Lane showed high concentrations of nitrate in the top part of the aquifer (up to 70 mg N L^{-1}) reducing to 10 mg N L^{-1} in the aquifer near the base of the boreholes. CCTV logging showed the importance of vertical fractures. Impeller inflow measurements showed that the permeability varied with depth between boreholes and that different boreholes pumped different concentrations due to chemical stratification within the aquifer (Buckley, 1999).

6.2.2 Impermeable drift cover in catchment

GREAT HECK

The three boreholes at Great Heck have maintained a difference in pumped quality over a long period despite their proximity. Aldrick (1984) suggested that the water quality was related to the site location close to the margin of confinement of the sandstone aquifer, so that borehole 2, the most northerly, draws the highest nitrate waters from predominantly unconfined sandstone, whereas borehole 3, the most southerly draws the lowest TDS water from the confined part of the aquifer. In 1999, the observed mean concentrations were still consistent with this interpretation and the water quality differences persisted downhole (Chilton et al. 1999). The boreholes also showed a difference in water movement within the borehole (Buckley, 1999). Logging in borehole 3 showed that 60% of the water was low-solute water moving up to the pump from below 65 m with only 40% moving down from above. In contrast, borehole 2 derived 65 % of its water from high solute water moving down. Borehole 1 had an intermediate composition. Vertical stratification and a different distribution of permeability in each hole were also factors considered to be influencing the pumped water quality.

6.2.3 Catchment landuse

AMEN CORNER

The Amen Corner site is situated on an outcrop of Permo-Triassic sandstone close to a lake. The three boreholes at this site have shown consistent differences in quality over the last 15 years. The highest concentrations of nitrate are seen in borehole 3 and the lowest in borehole 2. This is consistent with their respective catchment landuses. The catchment of borehole 2 is mainly wooded and may include part of Rufford Water, whilst that of borehole 3 is intensively arable.

HATFIELD

The Hatfield site is situated on a fault-bounded block on an outcrop of Triassic Sandstone. There were originally four boreholes operating at the Hatfield site. Nitrate concentrations were lowest in borehole 2 which abstracted from beneath the adjoining urban area and highest in borehole 4 which was closest to the arable area adjoining the other side of the pumping station. Logging in 1993 showed that the shallow groundwater contained high concentrations of nitrate consistent with the use of agricultural fertilisers (Aldrick, 1991). Boreholes 3 and 4 were progressively shut down due to high concentrations of nitrate, borehole 3 in 1990 and borehole 4 in 1993. The impact of these closures can be clearly seen in the time series plot for borehole 1 which shows the migration of high nitrate water to this borehole as a new capture zone was rapidly established (Figure 6.2).

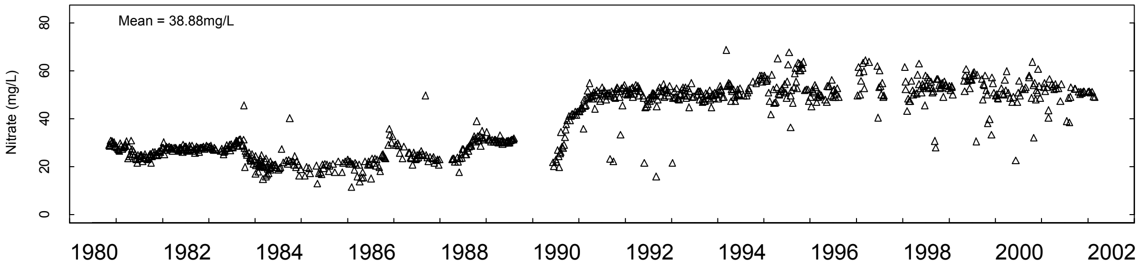


Figure 6.2 Step change in nitrate in Hatfield PS borehole 1 following closure of borehole 3 and a change in capture zone.

7 Predicting future nitrate concentrations in groundwater

7.1 INTRODUCTION

We have now analysed numerous sets of nitrate time series data, and have developed robust procedures for estimating past trends. It is natural to want to use these past trends to predict future concentrations. This can be done of course but comes with a number of 'provisos'. The main one is that the linear model being used is 'correct' and that it encompasses all significant sources of variation, both past and future. Unfortunately, since the simple linear model is an 'empirical' one and is not based on an understanding of the underlying processes, it is impossible to guarantee this.

As more components are added to the model, e.g. water levels, then more types of variability may be captured by the model and the model might reasonably be expected to cope better with future environmental changes (but of course we cannot predict future water levels either – at best we might be able to say what they might be on a statistical basis). It is always wise to try and include measurements of all-important independent variables or drivers even if the model being used is 'only empirical' (the dividing line between empirical and process-based models is not always as clear as some would like). Unfortunately, what may be important at one site may not be important at another site.

The various measures of goodness of fit give some indication of the degree to which the data fit the linear model using past data but contain no guarantee about future fits to the same model either in terms of the structure of the underlying model or its parameter values. In particular, if there is any substantial change to any of the conditions affecting nitrate concentrations, then it can be expected that the underlying model will change. This includes a change in land use and fertilizer practice, which would affect nitrate leaching, or a long-term change in climate which could affect the landuse (e.g. arable vs mixed) and the amount of recharge.

Only under a strictly 'business as usual' scenario in which all of the major drivers are stable is it reasonable to extrapolate the data to any large extent. The greater the forward prediction the less likely it is that no significant changes will have taken place. The problem of excessive nitrate leaching has been appreciated since the 1970s and various measures have been put in place specifically to control it! Statistical procedures cannot be used to anticipate or account for these changes. Only process-based models can do that. This is a major limitation of the strictly statistical approach.

Nevertheless, with this proviso in mind, it can be helpful to make modest prediction in the cases where the underlying model appears appropriate. The planning cycle for developing ways of dealing with high nitrate groundwaters in a water supply context is long and requires some anticipation of likely future concentrations. Where appropriate, we therefore use the past trends to make predictions for the next 15 years. However, predictions beyond 5 years into the future should be seen as being increasingly risky.

7.2 MAKING PREDICTIONS ABOUT FUTURE CONCENTRATIONS

Predictions should be made using the fitted linear model and specifically should take into account whether a seasonal or non-seasonal model provides the best fit. The seasonal model includes water level data; the non-seasonal model does not. Lack of seasonality was determined from the lack of a significant improvement in overall fit when the data were 'binned' on a monthly basis.

7.2.1 Non-seasonal model

The predicted concentrations were based on the fitted linear model without any water level information. A standard OLS model was used in this case although more robust models could also be used. 95% confidence intervals were calculated and are shown in Figure 7.1 as a greyed area. This reflects the uncertainty based on past behaviour and allows for the natural variation about the trend line. It gives no indication of when particularly high and low concentrations might be expected, just their probable size.

Two points should be noted in Figure 7.1:

(i) the positive deviations from the trend line tend to be larger than the negative ones

(ii) (ii) some of the deviations are larger than is normal in aquifers.

Therefore the outlying points should be carefully checked (tracing back through the laboratories if necessary) and the data eliminated if in error. As can be seen from the figure, the size of the confidence interval in the example shown is almost constant with time.

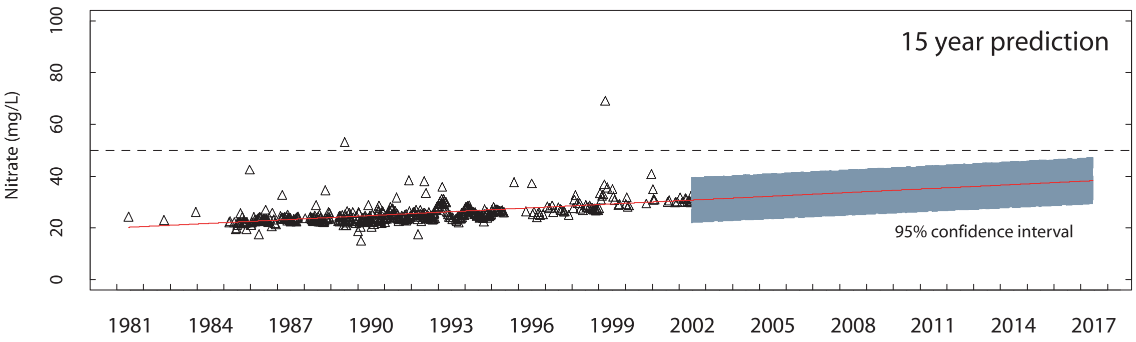


Figure 7.1 Predicted future nitrate concentrations (2002-2017) based on the past trend at Thornton 3, a Chalk site. The site does not show any seasonal effects. The red line is the fitted line and the greyed area is the 95% confidence interval.

7.2.2 Seasonal model

This is similar to the non-seasonal model except that water levels were included in the regression model. The water level data were obtained for the nearest water level monitoring borehole within a broadly similar setting (especially aquifer type). Water levels were interpolated to a daily series. The water level and nitrate data were then paired up on a daily basis and used in a multiple regression model. Future nitrate concentrations depend on the future groundwater levels which are themselves unknown. Therefore daily water levels were simulated using the average daily water levels based on the historic data. Where no data were available for a given day, this was linearly interpolated from adjacent data. This meant that each year the water level on a given day was the same, hence the repeating sawtooth pattern in Figure 7.2.

The results of such a fit are shown for Etton 4 in Figure 7.2 which shows a strong seasonal effect but little long-term trend. In this case, the seasonal fluctuations account for most of the variation observed. There is a small upward trend but it is the winter highs that approach the 50 mg L^{-1} limit.

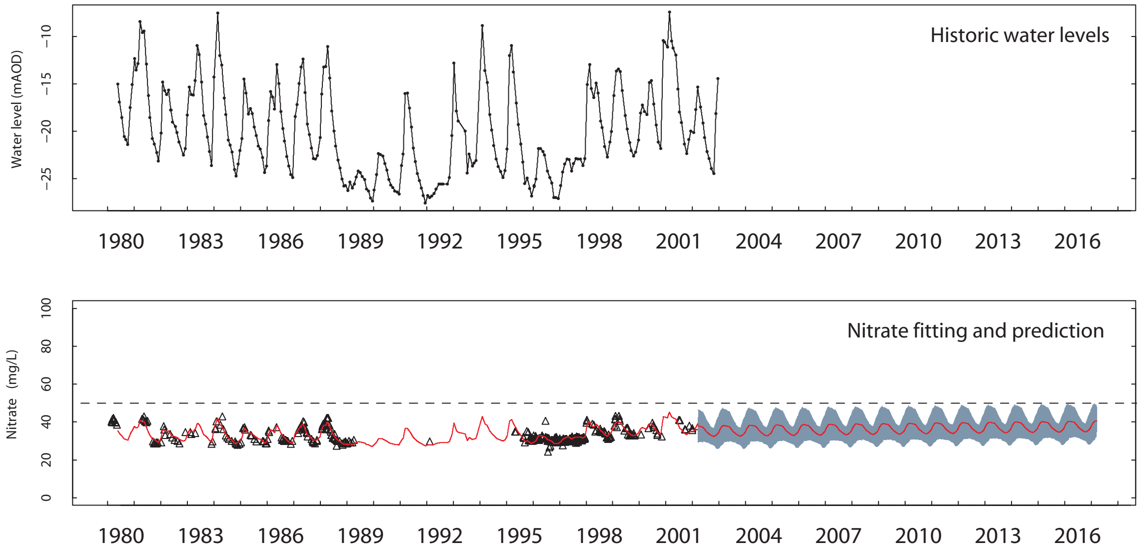


Figure 7.2 Water level fluctuations and predicted future nitrate concentrations (2002-2017) based on the past trend and seasonality at Etton 4, a Chalk site. This site shows a strong seasonal effect. The red line is the fitted line and the greyed area is the 95% confidence interval taking into account both the linear trend (which is very small) and the seasonality.

8 The national picture: general conclusions

8.1 AVERAGE CONCENTRATIONS

Accepting that in this study, areas in the east of England were disproportionately over-represented, estimated nitrate concentrations on 1 January 2000 in the Chalk, Permo-Triassic Sandstone, Oolitic limestone and the Lower Greensand aquifers were broadly similar, namely between, 42 and 50 mg NO_3 L^{-1} (Table 8.1). Concentrations were estimated from the median linear trend line through the data. Results from the small number of sites in the Lincolnshire Limestone give a somewhat lower average. This could be due to the impact of recent landuse changes in this rapidly responding aquifer or may just be due to the unrepresentativeness of the small sample set available. Results from the Magnesian Limestone aquifer give a lower average because a large proportion of the sites studied were in the confined aquifer and therefore groundwater had very low nitrate concentrations. The variation in this aquifer was greater than for the two major aquifers. The maximum and minimum values show that concentrations are extremely variable even when estimated from linear trends.

Table 8.1 Summary of estimated site nitrate concentrations at 1 January 2000 grouped by aquifer

Aquifer	**Concentration (mg NO_3 L^{-1})**			**CV (%)**	**n**
	Min	**Median**	**Max**		
Gravels	23.2	35.6	48.1		2
Chalk	0.04	42.0	78.8	37	74
Lower Greensand	38.6	49.4	60.2		2
Oolitic limestone	27.7	50.0	70.2	25	11
Lincolnshire Limestone	11.3	36.1	124	78	12
Lias	0.00	0.00	0.50	180	5
Permo-Triassic sandstone	6.45	46.3	175	57	41
Magnesian Limestone	0.35	8.2	73.1	117	43
Carboniferous limestone		32.4			1
All	0	37.8	175	66	191

The histograms in Figure 8.1 show that data from the Chalk, Permo-Triassic Sandstone and the Oolite has an approximately normal distribution whereas the Lincolnshire and Magnesian Limestones are somewhat skewed. A more detailed study of the Magnesian Limestone sites (Kinniburgh et al., 2004) showed that sources with low nitrate (<10 mg NO_3 L^{-1}) were from the confined part of the aquifer and only a few from the northern edge of the outcrop had concentrations of >50 mg NO_3 L^{-1}. The source of variability within the aquifer was predominantly related to the presence or absence of a confining drift layer.

Figure 8.2 summarises the average concentrations of nitrate for each site in the study. The highest nitrate concentrations occur in the areas around the Wash, from the Chalk of south Yorkshire and East Anglia to the Lincolnshire Limestone and the Yorkshire/Nottinghamshire Permo-Triassic Sandstone. These broadly correspond to areas of low effective rainfall and high percentage of arable land identified as at high risk from nitrate pollution by Foster et al (1986) and DoE 1986 (Figure 8.3). Concentrations in the southern Chalk are lower and generally below 50 mg NO_3 L^{-1}. There are very few datasets from the western side of England and Wales.

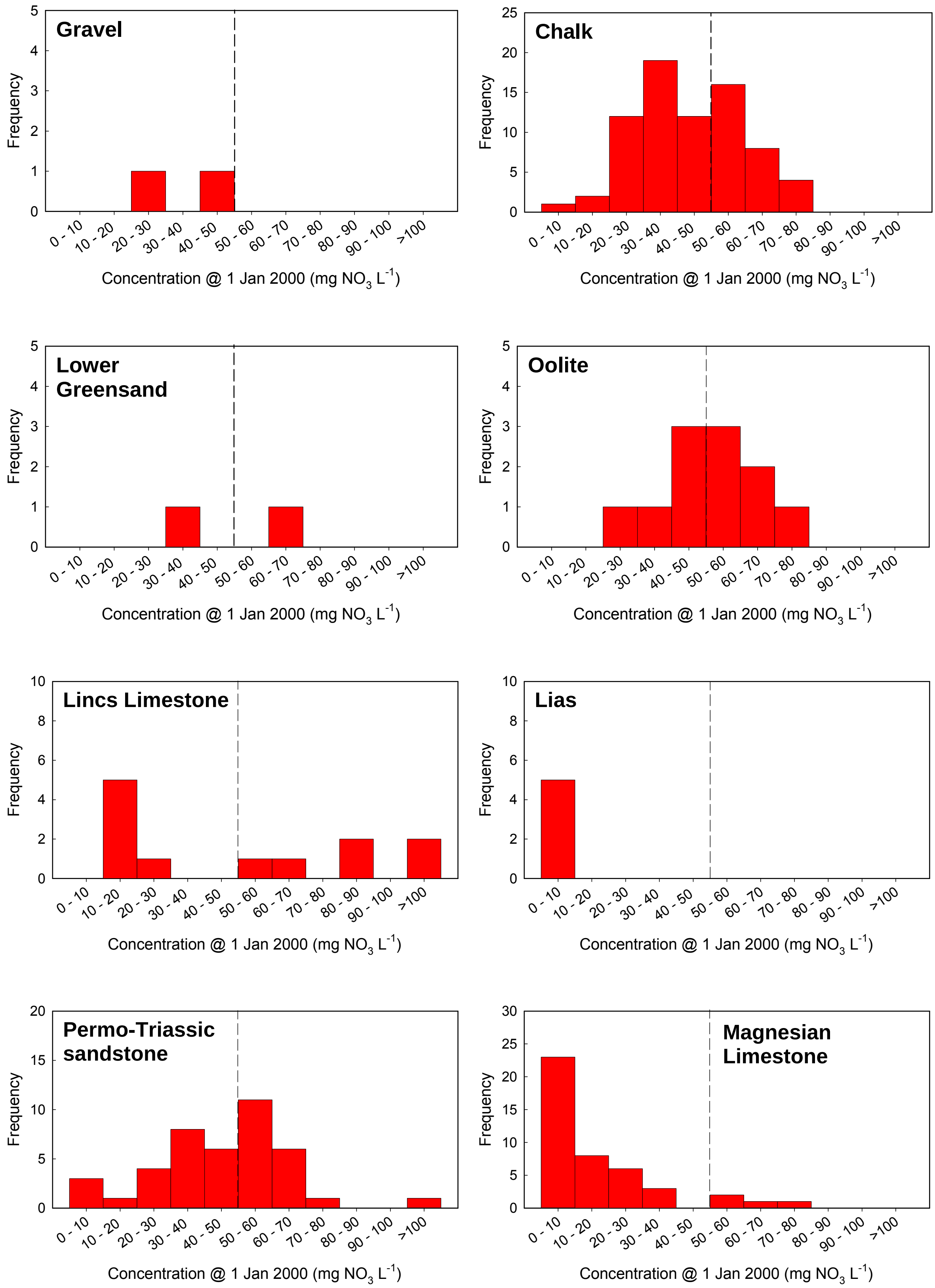


Figure 8.1 Histograms of predicted nitrate concentration per aquifer (dashed line indicates the DWL of 50 mg L^{-1}).

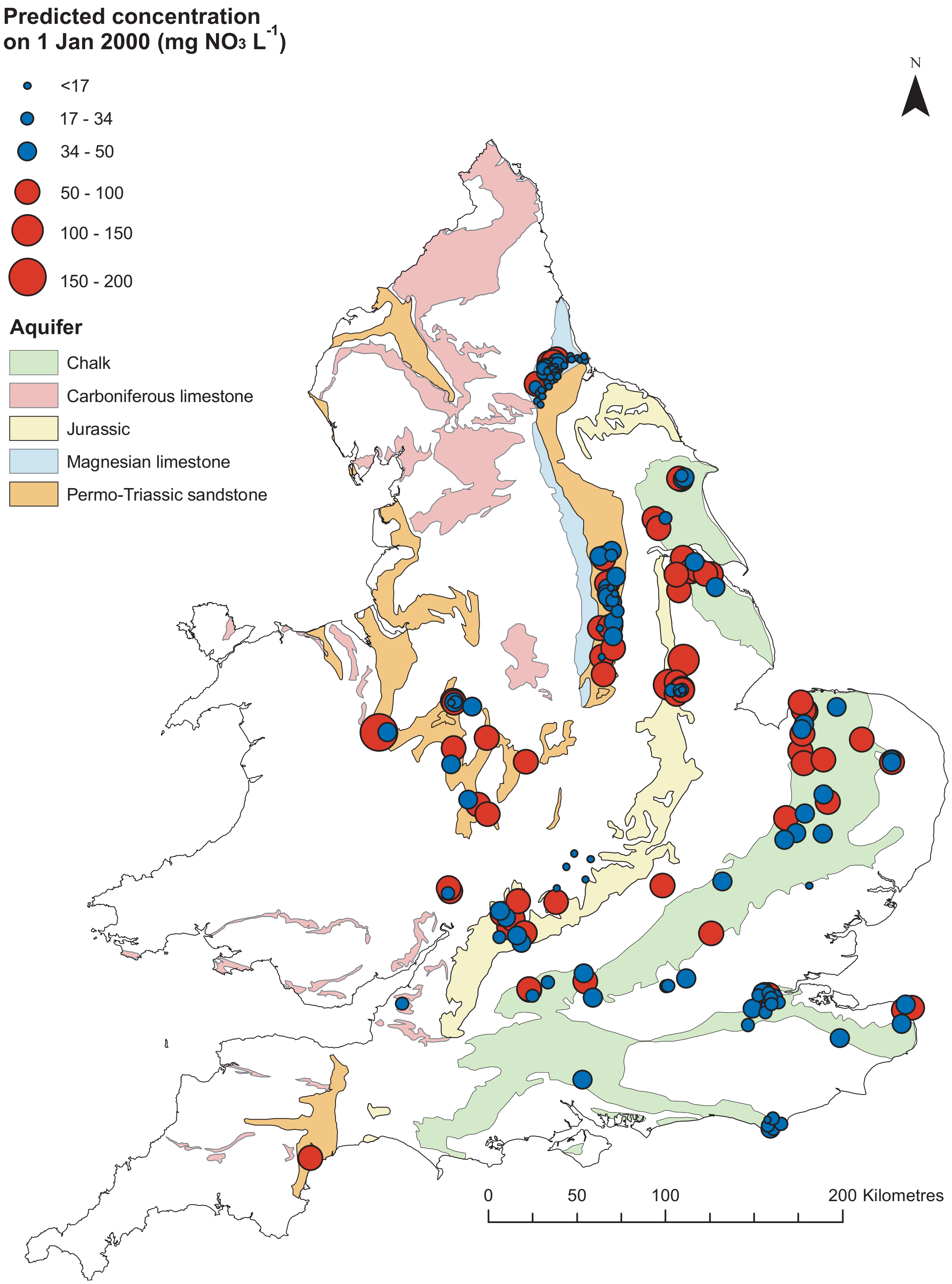


Figure 8.2 Median estimated nitrate concentration on 1 January 2000 for each site in this study. Concentrations at or exceeding the drinking water MAC shown in red.

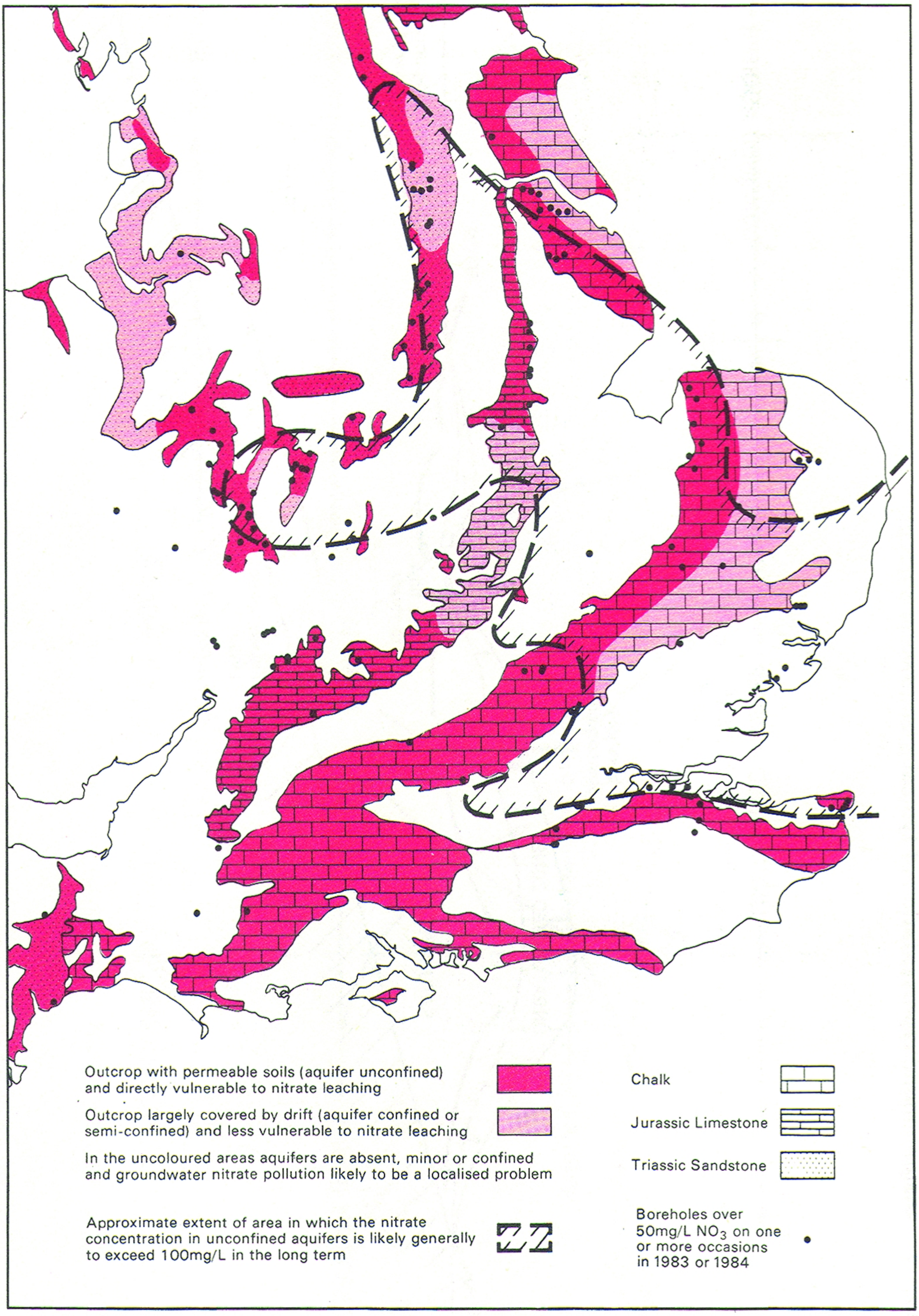


Figure 8.3 Outcrop of principal aquifers and their vulnerability to nitrate pollution (from DoE, 1986)

8.2 TRENDS

In this study, the average trend in groundwater nitrate concentrations is upwards at an overall rate of about 0.3 mg NO_3 $L^{-1}year^{-1}$ (Table 8.2). In the major aquifers (Chalk and Permo-Triassic Sandstone), the average is slightly greater (0.4 mg NO_3 L^{-1} $year^{-1}$). For individual aquifers, the steepest trend is in the Lincolnshire Limestone aquifer (0.96 mg NO_3 $L^{-1}year^{-1}$) and lowest is in the Oolitic limestone aquifer (0.05 mg NO_3 $L^{-1}year^{-1}$). The data from the Magnesian Limestone aquifer has the greatest range, reflecting the contrast between the confined and unconfined aquifer.

This estimate used all of the data available. A better estimate could perhaps be obtained by excluding data from confined sites where nitrate concentrations are low (e.g. <10 mg NO_3 L^{-1}). In this study, 32 sites have an estimated median concentration on 1 Jan 2000 of 10 mg NO_3 L^{-1} or less. These are: 3 in the Permo-Triassic sandstone, 1 in the Chalk, 24 in the Magnesian Limestone and all 5 of the Lias sites. Only the trends for the Magnesian Limestone would be significantly changed by separating the data in this way.

Table 8.2 Summary of site nitrate trends by aquifer

Aquifer	**Trend (mg NO_3 L^{-1} $year^{-1}$)**			**SD (mg NO_3 L^{-1} $year^{-1}$)**	**n**
	Median	**Max**	**Min**		
Gravels	-0.96	0.17	-2.08		2
Chalk	0.38	2.64	-1.37	0.78	74
Lower Greensand	0.6	0.62	0.57		2
Oolitic limestone	0.05	1.69	-1.27	0.86	11
Lincolnshire Limestone	0.96	3.44	-0.10	1.27	12
Lias	0.00	0.0001	-0.029	0.01	5
Permo-Triassic sandstone	0.44	1.91	-0.95	0.61	41
Magnesian Limestone	0.16	4.12	-1.02	0.83	43
Carboniferous Limestone	0.42				1
All	0.34	4.12	-2.08	0.82	191

Figure 8.4 shows histograms of the distribution of site trends in each of the aquifers. These are approximately normal for the major aquifers apart from the Lincolnshire Limestone. There are more sites with increasing trends than with decreasing trends in all aquifers.

Figure 8.5 summarises the average trends in nitrate concentration for each site in the study. The most consistent positive trends are seen in East Anglia and the highest increases at sites in the unconfined Magnesian Limestone and the Lincolnshire Limestone. Very low positive trends occur in the London area and consistently negative trends are seen in the Chalk near Eastbourne.

It might be expected that sources with the highest trends would also have the highest concentrations of nitrate. Figure 8.6 suggests that this is probably the case but that there is not a good correlation between these two variables. The outlying data are from Twelve-Acre Wood 2 and Old Chalford Springs 15, 19 and HR8. The results from Old Chalford may be influenced by recent landuse changes under the NSA scheme and may originally have had much higher positive trends.

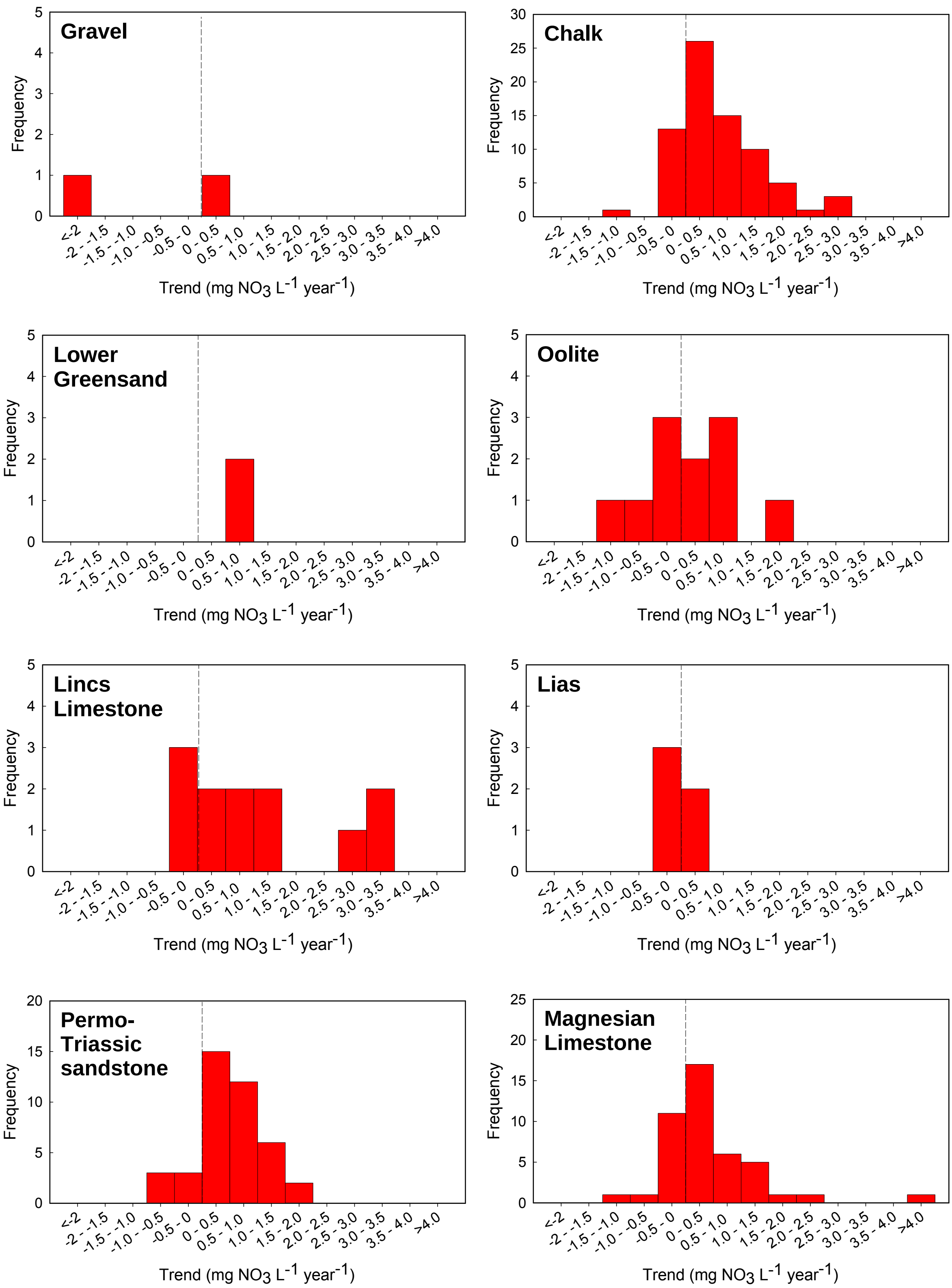


Figure 8.4 Histograms of site trend distribution per aquifer (dashed line represents no trend)

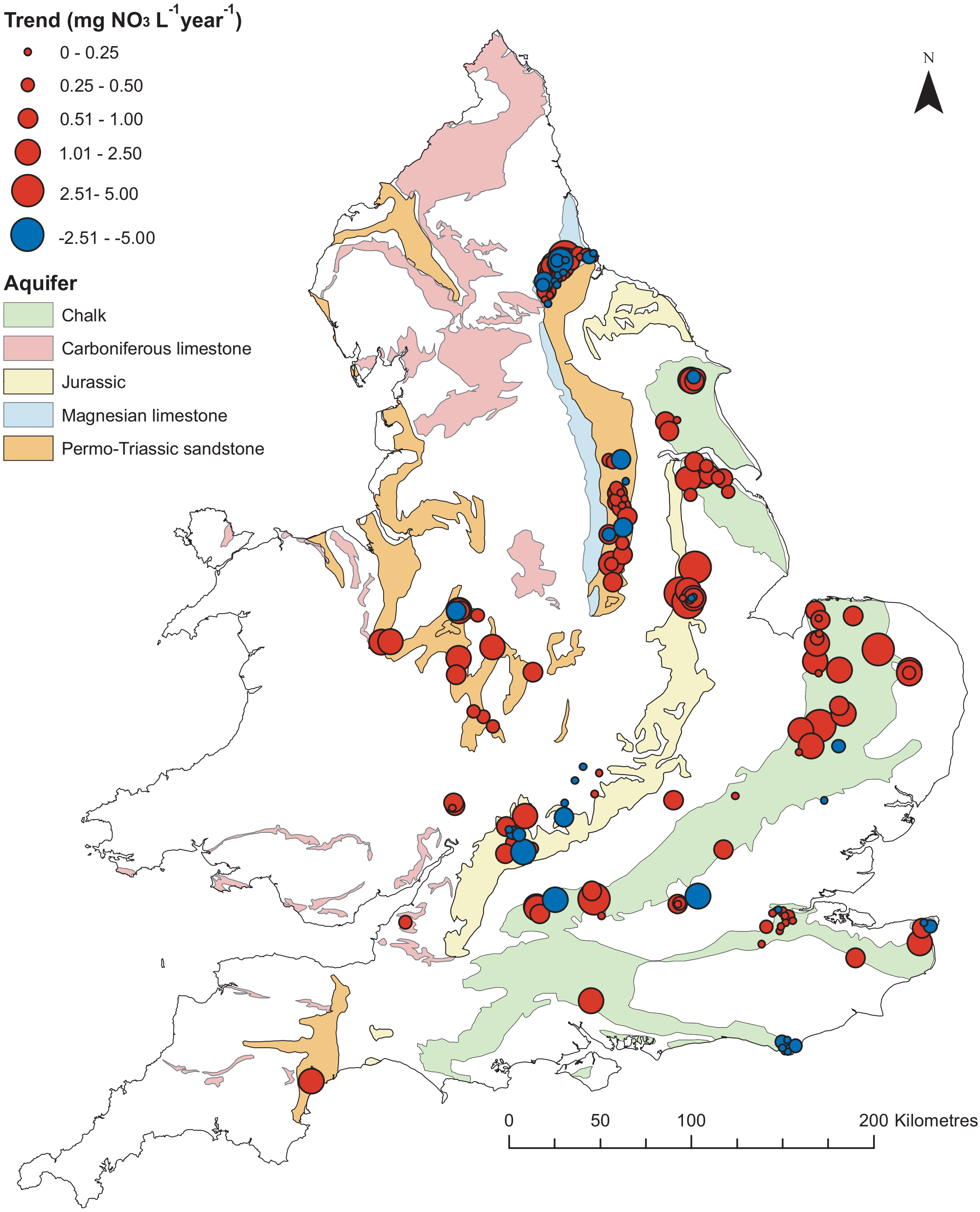


Figure 8.5 Median trends in nitrate concentration at each site in study. Positive trends in red, negative trends in blue.

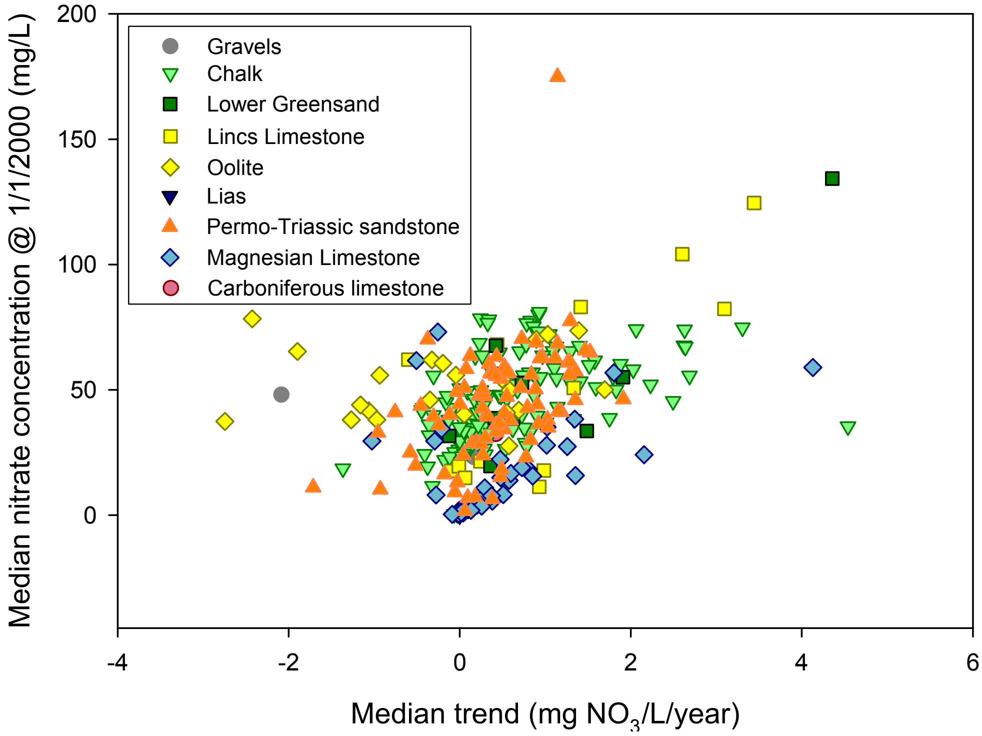


Figure 8.6 Crossplot of trend and predicted concentration per source

8.3 FUTURE CONCENTRATIONS

Table 8.3 shows the average predicted nitrate concentrations for each site in the study for January 2015, calculated by a linear extrapolation of the trends, as described in section 7.2. These show a predicted decrease in concentration in the Oolitic limestone and the gravels, and an increase in all the other aquifers. These concentrations are summarised in Figure 8.7. In this dataset, increases in concentration are most marked in the Chalk of East Anglia, Thanet and Hampshire, and the Permo-Triassic Sandstone of Nottinghamshire/Yorkshire and Cheshire.

Table 8.3 Summary of estimated site nitrate concentrations at 1 January 2015 grouped by aquifer

Aquifer	**Concentration (mg NO_3 L^{-1})**			**CV (%)**	**n**
	Min	**Median**	**Max**		
Gravels	16.8	21.2	25.6		2
Chalk	0	50.5	114	46	74
Lower Greensand	48.0	58.8	69.5		2
Oolitic limestone	8.37	41.0	75.4	44	11
Lincolnshire Limestone	14.9	47.5	176	83	12
Lias	0	0	0.07	137	5
Permo-Triassic sandstone	0	52.6	192	58	41
Magnesian Limestone	0	13.3	121	118	43
Carboniferous limestone		38.7			1
All	0	43.6	192	72	191

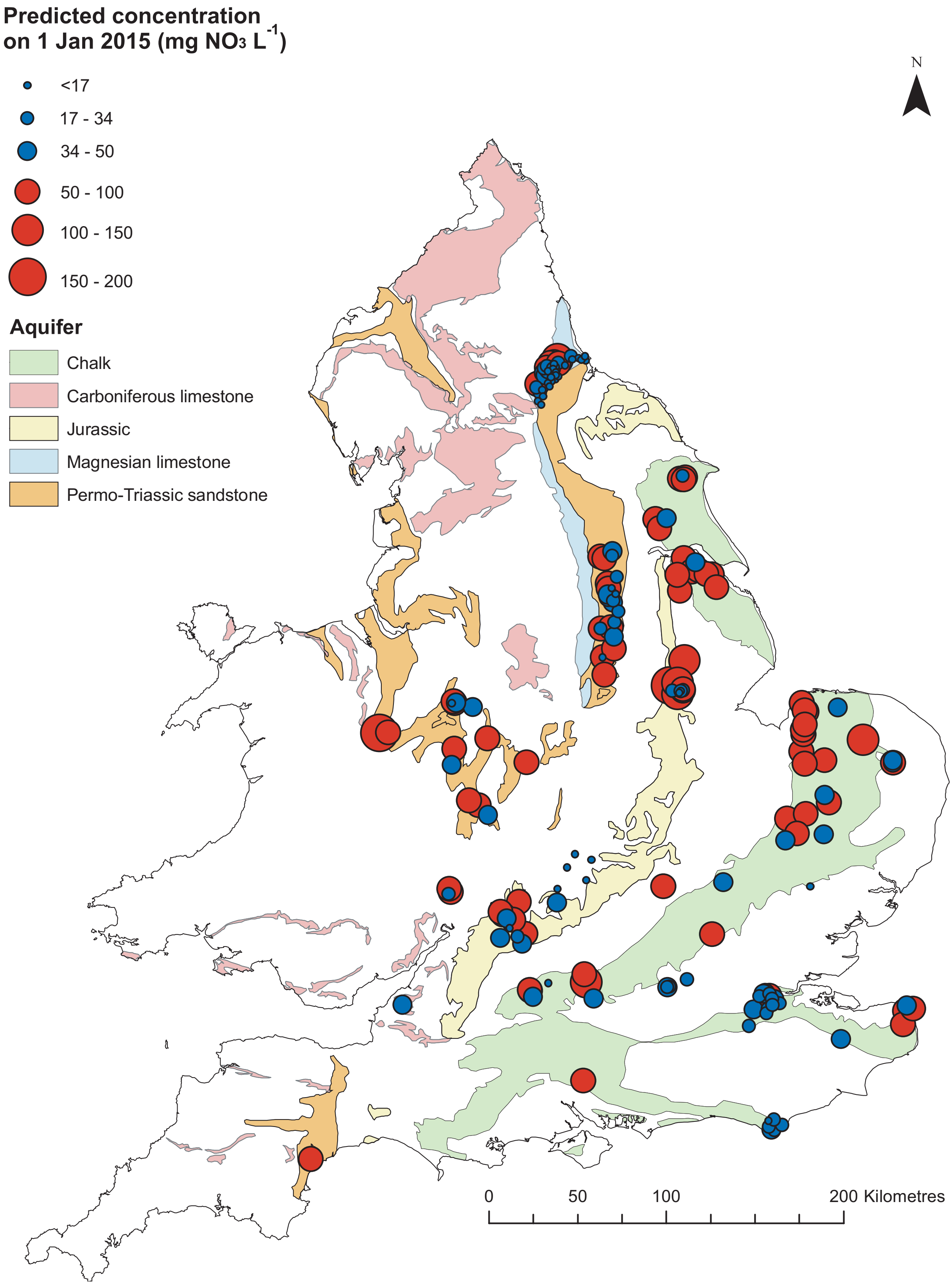


Figure 8.7 Median estimated concentrations on 1 January 2015 for each site in this study. Concentrations at or exceeding the drinking water MAC shown in red.

The predicted concentrations for 2000 show that 34% of the sites had concentrations of 50 mg L^{-1} or more (Table 8.4). The highest proportion was in the Lincolnshire Limestone. Extrapolating the trends to 2015 shows that by this time the number of sites exceeding this limit will have increased from 34% to 41%, with this increase mainly in the Chalk and the Permo-Triassic Sandstone.

Table 8.4 Sites predicted to have concentrations of nitrate exceeding 50 mg/l in 2000 and 2015

Aquifer	**2000**		**2015**		**Total number of sites**
	Sites	**%**	**Sites**	**%**	
Gravels	0	0	0	0	2
Chalk	28	38	38	49	74
Lower Greensand	1	50	1	50	2
Lincolnshire Limestone	6	54	6	45	11
Oolitic limestone	6	50	5	50	12
Lias	0	0	0	0	5
Permo-Triassic sandstone	19	46	23	59	41
Magnesian Limestone	4	10	6	14	43
Carboniferous limestone	0	0	0	0	1
Total	64	34	79	41	191

8.4 SEASONALITY

In the dataset used to evaluate seasonality, groundwater nitrate concentrations showed seasonal fluctuations at just over one third of the sites. As might be expected, the limestone aquifers (the Chalk, Jurassic and Carboniferous) were the most seasonal with only a few sites in the Permo-Triassic Sandstone showing strong seasonality. Table 8.5 shows a breakdown of these results by aquifer. The results are summarised in Figure 8.8. The most seasonal behaviour is observed in the Yorkshire and Hampshire Chalk and the Oolitic Limestone of the Cotswolds.

Table 8.5 Summary of seasonality by aquifer

Aquifer	Number of seasonal sites	Percentage of total	n
Gravels	0	0	0
Chalk	28	48	58
Lower Greensand	0	0	2
Lincolnshire Limestone	6	55	11
Oolitic limestone	5	100	5
Lias	0	0	0
Permo-Triassic sandstone	4	11	37
Magnesian Limestone	0	0	1
Carboniferous limestone	1	100	1
All	44	38	115

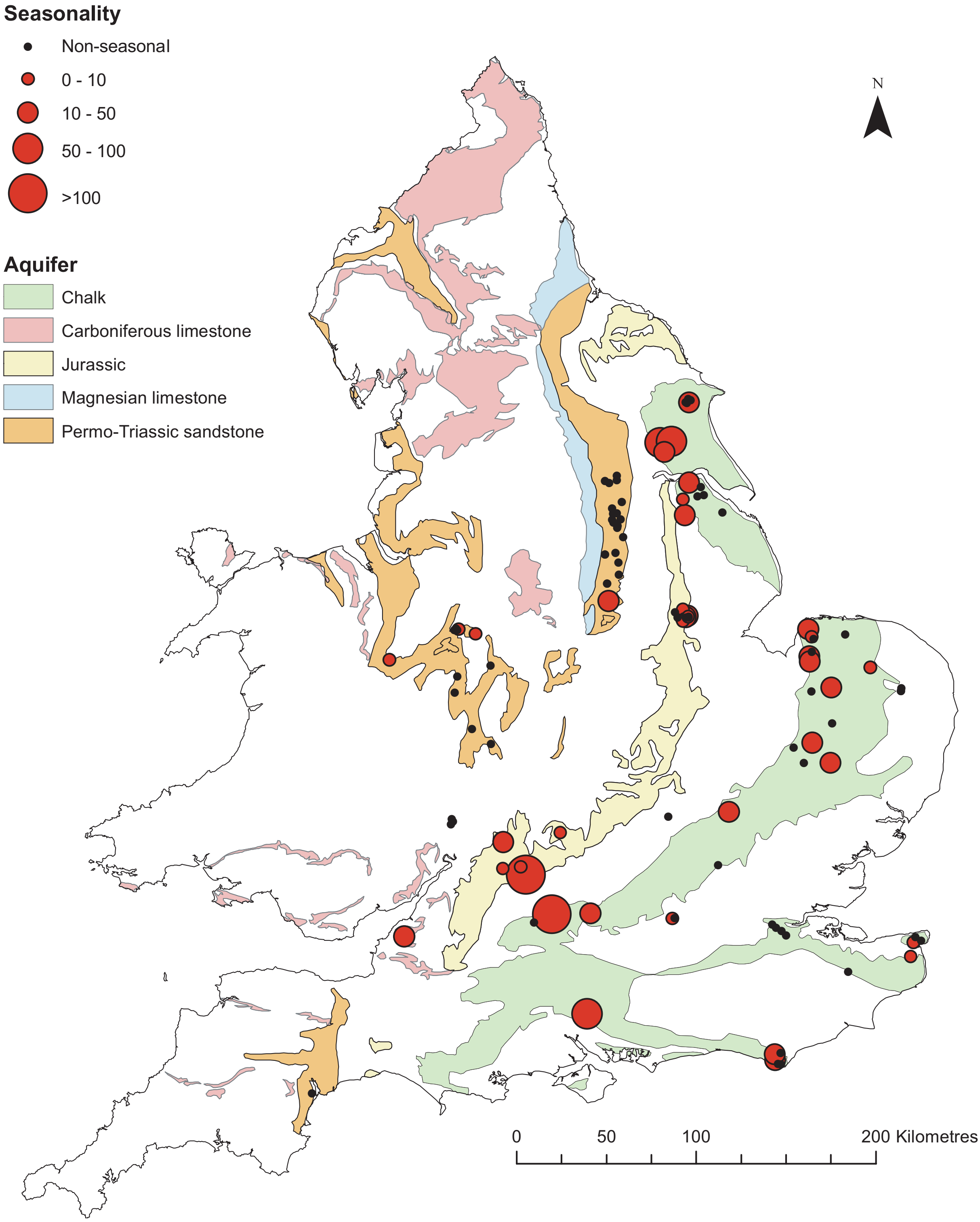


Figure 8.8 Median seasonality per site based on nitrate fluctuations

Table 8.6 shows a summary of the hydrogeological settings of the extreme members of the dataset taken from data held in the National Well Archive.

- Seasonal sites in the Chalk tend to be on outcrop along the topographic high ground close to the scarp edge where the unsaturated zone would be expected to be deepest.
- The least seasonal sites are in the Permo-Triassic Sandstone with shallow water levels, especially the Yorkshire/Nottinghamshire sandstone.

8.4.1 Seasonality in the East Anglian Chalk

The nitrate concentrations at borehole sites in the Chalk of East Anglia show a wide range of seasonal behaviour. These sites were also classified according to their geological setting and borehole construction.

Boreholes along the western margin of the Chalk, such as at Marham, only penetrate the Lower Chalk whereas those further east may penetrate the full sequence and the easternmost sites, such as Caistor, are in the Upper Chalk. Sites were also classified according to their Drift cover setting into Chalk outcrop, thin sandy drift cover, adjacent to the edge of the Till sheet and complex sites further east. Sites near the edge of the Till sheet would be expected to be subject to increased recharge from run off from the Till. Whilst this will influence nitrate trends it may not contribute to seasonality and here seasonality did not appear to be related to either of these classifications.

Assuming that seasonal fluctuations are due to rapid movement of high nitrate water at shallow depths the following factors were also considered:

- Borehole depth
- Casing depth
- Elevation as surrogate for unsaturated zone thickness
- Transmissivity

Transmissivities for at least one borehole at most of these sites were taken from Allen et al. (1998). Where only one value was found this was applied to all boreholes at a site. Where no value was found, the nearest adjacent value was used.

The plots in Figure 8.9 show that seasonality is not simply related to any of these factors. However, there could be an inverse relationship with borehole and casing depths, i.e. the greatest depths lead to the least seasonal behaviour bearing in mind that seasonality is negative. For most sites as would be expected high transmissivity leads to greater seasonality, but the site with the highest transmissivity, Two Mile Bottom 3, is not seasonal. This is a deep borehole penetrating the full chalk sequence on the outcrop near Thetford. The transmissivity in adjacent boreholes is much lower.

Table 8.6 Most and least seasonal sites identified in this study

	Site	Aquifer	Median seasonality	Height (m aOD)	WL	Setting
Most seasonal	Ogbourne	Lower Chalk	-252	151	140-155	Outcrop chalk -Dip slope
	Fairford		-123			
	Fognam Down	Chalk	-123	144		
	Springwell, Market Weighton	Chalk	-87	45		
	Twyford Well	Chalk	-84	44.8		
	Etton	Chalk	-56	38		
	Sedgeford	Middle/Lower Chalk	-45	30	21-24	Variable thickness of drift comprising broken chalk or boulder clay
	Barrow Upon Humber	Chalk	-45	11.4		Impermeable drift at wellhead 7 m clay
	Slipend	Middle/Lower Chalk	-41	69		
	Friston	Chalk	-41	35		Adits under higher ground
Least seasonal	Wellings	Permo-Triassic Sandstone	11			
	Sidway NSA	Permo-Triassic Sandstone	12			
	Clipstone Forest	Permo-Triassic Sandstone	12	98		
	Clipstone	Permo-Triassic Sandstone	13	70		
	Middledale	Chalk	14	44		
	Bednall	Permo-Triassic Sandstone	14	99	Overflowing on completion	
	Hatfield Woodhouse	Permo-Triassic Sandstone	16	3	1.5 SWL	25 ft drift sands and gravels
	Great Heck	Permo-Triassic Sandstone	16	12	-12 SWL	Impermeable drift cover in south of catchment
	Nutwell	Permo-Triassic Sandstone	17	7	5 SWL	Some silt and clay otherwise river gravels
	Everton	Permo-Triassic Sandstone	18	16		

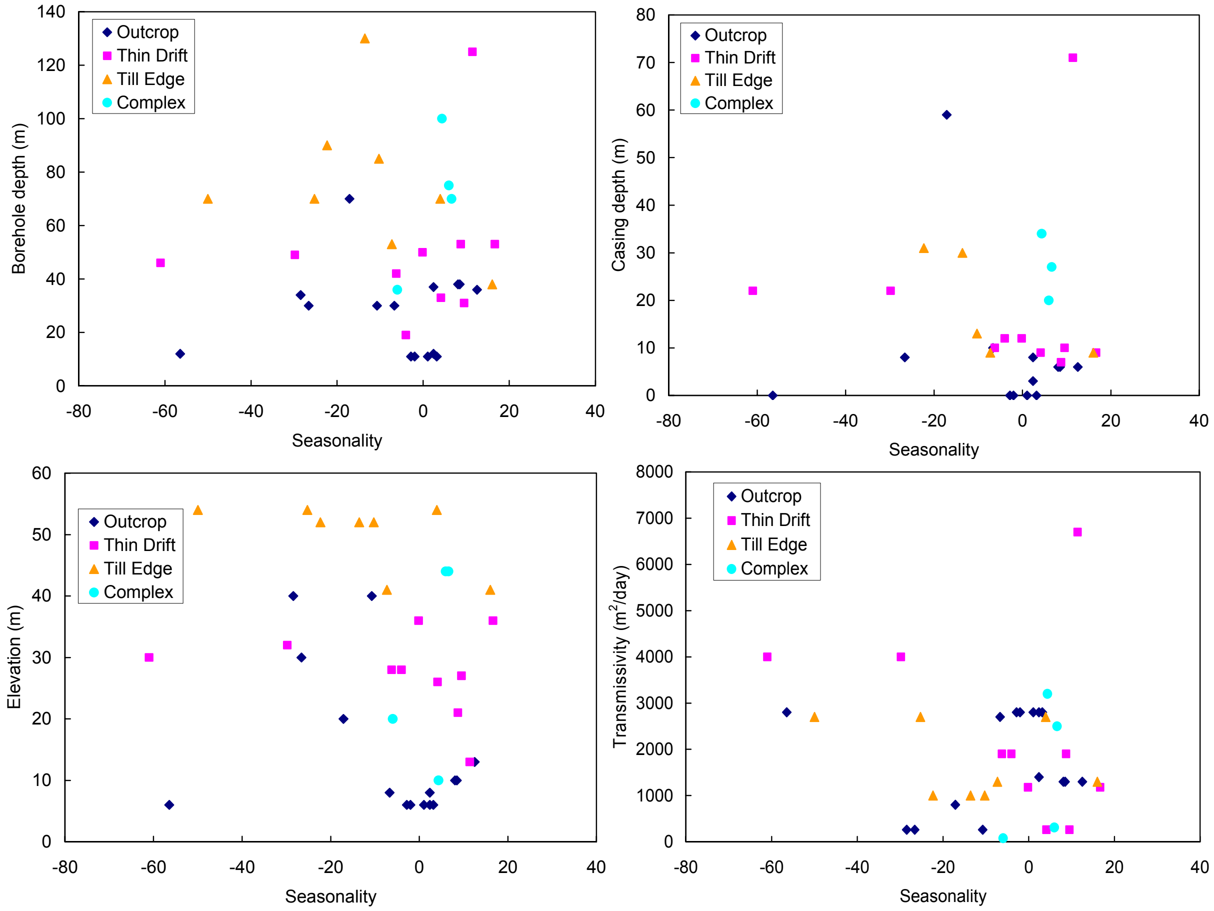


Figure 8.9 Crossplots of borehole construction details and aquifer transmissivity against seasonality for boreholes in the East Anglian Chalk

9 Conclusions and recommendations

9.1 CONCLUSIONS

We have demonstrated a methodology for nitrate trend analysis that provides useful information efficiently and rapidly and is amenable to scaling-up and full automation. The methodology provides both the theoretical framework (the statistical tests) and the way in which they are implemented (the software and the working environment). Our approach can provide tables and graphs directly for inclusion in reports and can perform 'live' analyses directly from the database. Reports can even contain live links to plot files (in Microsoft Word for example) to ensure that the latest plot is always used at print time. This ensures that the results are up-to-date and avoids the necessity of maintaining large numbers of intermediate spreadsheets and plot files. Such a structured approach is ideal for routine monitoring and reporting.

The methodology and the outputs can easily be modified to suit specific user needs, and it is relatively easy to add new tests or to modify existing ones. The exact methodology used is entirely defined by the scripts used, which because of the high-level of the R programming environment, tend to be quite short. The scripts can readily be scrutinised and are ideal for sharing with others, saving in effort but also making it possible to benefit from the 'community' development that such an approach engenders. We therefore believe the approach provides a good way of carrying out trend analysis on a national (or international) scale. It is statistically sound, open, defensible and easily updated, and provides high quality output.

The trend assessment methodology developed here was applied to the large body of time-series nitrate data held by BGS. This comprised about 450 datasets, most of them derived from external sources such as the Environment Agency (EA) and water companies. Although the datasets were not randomly selected from all possible boreholes in England, they represent a fairly broad cross-section of such boreholes. They covered a wide range of aquifers. Because many of these data were collected for specific studies of nitrate pollution, they are probably biased towards areas of high nitrate concentration. Many of these were from working public supply wells, and the selection may therefore exclude some 'high' sources which have been taken out of supply. Datasets from observation wells were also included, but many of these had much less available data. The original raw data were stored in various formats. The data were 'cleaned' to remove obvious formatting errors and stored in a consistent format.

The results highlight the importance of regular data collection for the determination of trends. More than one third of datasets were rejected for being too short, too irregular or too variable. Trends were determined by linear regression. Data were also excluded from the analysis where fitting to a linear trend was clearly inappropriate.

Tests were included for lack of linearity, the presence of outliers, for seasonality and for possible breaks in the trend including reversals of trend. After exclusion of data where trend fitting was unsatisfactory, 309 datasets were finally selected from 191 different sites for further study. For multi-borehole sites, median values were used to obtain the summary statistics.

Sometimes the data show a very distinct break indicating that the linear model provides a poor explanation of the data. This is revealed by a high RMSE (root mean square error) and for non-seasonal series, by the presence of 'additional structure'. In straightforward cases, the 'broken stick' analysis indicates the position of the break and the 'before' and 'after' trends.

This is about as far as an automated analysis can go. Ultimately it is up to the user to make some decision about what has happened to create the additional structure and how relevant the data are for using in future predictions. It may for example be best to remove some of the earlier data from the analysis on the basis that this reflects 'one off' behaviour that is unlikely to be relevant for the future, e.g. because of improved sampling methods, improved analysis or improved reporting.

Individual boreholes at multi-borehole sites often have differing concentrations and trends, and occasionally show differences in the seasonality of their response as well. This can be due to quality stratification combined with differences in borehole construction, differing main inflows or variations in landuse/drift cover in the capture zones of individual boreholes. Sites with differing concentrations are predominantly located in the Permo-Triassic Sandstone.

For the 191 sites, groundwater nitrate concentrations were found to be rising at an average of 0.34 mg NO_3 L^{-1} $year^{-1}$. Average trends were greatest in the Lincolnshire Limestone aquifer (0.96 mg NO_3 L^{-1} $year^{-1}$) and lowest in the Magnesian Limestone aquifer (0.18 mg NO_3 L^{-1} $year^{-1}$). Average trends for the Chalk and Triassic sandstone aquifers were 0.38 mg NO_3 L^{-1} $year^{-1}$ and 0.44 mg NO_3 L^{-1} $year^{-1}$, respectively.

Breaks in a linear trend were detected by fitting a piecewise linear regression to the data with automatic detection of the break point. 21% of the time series analysed showed a significant improvement in the overall fit when such a break was included. 10.5% of these indicated an increase in trend with time and 10.5% a decrease.

An assessment of seasonality in nitrate concentrations was also made by including a term for the month of sampling in the regression model. Significant ($p<0.05$) seasonality was found in about one third of the series tested. This showed higher concentrations during the winter months. As would be expected, the Jurassic Limestone and the Chalk aquifers are the ones showing most seasonality. Only a few sites in the Permo-Triassic Sandstone showed significant seasonality.

Since the time period covered by individual datasets varied, the best-fitting model using a combination of trend and seasonal behaviour was used to estimate the nitrate concentration on 1 January 2000 and January 2015 for all datasets. For 2000, this showed that nitrate concentrations in the major aquifers on this date were broadly similar apart from the Magnesian Limestone. The highest concentrations were in the Oolitic limestone (50 mg NO_3 L^{-1}) and the lowest in the Magnesian Limestone (8.2 mg NO_3 L^{-1}). The Chalk and the Triassic sandstone had average concentrations of 42 mg NO_3 L^{-1} and 46.3 mg NO_3 L^{-1} respectively. The average of all sites was 37.8 mg NO_3 L^{-1}. The highest nitrate concentrations were found in areas around the Wash, the Chalk of south Yorkshire/East Anglia, and the Permo-Triassic Sandstone of Yorkshire/Nottinghamshire.

If present trends continue, by 2015 the average concentration will have increased to 43.6 mg NO_3 L^{-1}. The highest concentrations are predicted to be in the Lower Greensand (58.8 mg NO_3 L^{-1}) and the lowest in the Magnesian Limestone (12.3 mg NO_3 L^{-1}). The Chalk and the Triassic sandstone will have average concentrations of 50.5 mg NO_3 L^{-1} and 52.6 mg NO_3 L^{-1} respectively.

In 2000, 34% of sites exceeded the 50 mg L^{-1} drinking water MAC. It is estimated that if present trends continue, 41% of groundwater sources could exceed this 50 mg L^{-1} standard by 2015.

9.2 RECOMMENDATIONS

The national picture presented here has been necessarily limited by the data available to the study. It would be much better to carry out such an analysis on a statistically-selected national dataset. This should be done in collaboration with the EA.

A key point is to clear up the degree to which the data are 'open source' in terms of use and reporting, and to whom and how acknowledgements of their origin and ownership should be made. In principle, the fewer the restrictions on data use and source identification the better.

Our approach could be compared with other approaches, e.g. the Grath et al. (2001) approach or the WRc ('Anteater') (Gunby and Ellis, 1996) and later approaches. It would be possible to possible to compare predictions from the various methods by using say pre-2000 data to predict 2005 concentrations, and then comparing with the observed 2005 concentrations.

We should explore a time series approach that takes into account the autocorrelation structure of the data. However, one of the limitations of this approach is that it ideally needs regularly spaced data (in time) and many of the historical series are far from regular in this respect.

A few UK sites have very long datasets and it would be interesting to apply the methodology to these. The methodology could readily be used to calculate trends over specific time intervals to evaluate long-term changes in trend.

The scripts used are not yet in a form suitable for 'public release', and there may be licensing issues too. These issues would need to be addressed before releasing our scripts. This needs to be explored within BGS.

The 'prediction' plots are not currently part of our existing R trend analysis script and should be extracted from the original S-PLUS scripts and incorporated into the most recent R tend analysis script.

We have not attempted a critical review of the broader literature relating to groundwater quality trend analysis. That should be done at some stage.

The methodology developed here could be applied to other chemical data, including pesticide data. This would have to address the 'less than detection limit' problem. It is now possible to do this in various ways from within the R working environment (the 'NADA' package uses statistical methods developed for the insurance industry to do this).

Our methodology could be applied to surface water data and to water level data, probably without too many modifications.

Using R (or S-PLUS) scripts allows an automated workflow. It allows the primary data to be stored in a proper database (with all the safeguards of that) and to then go straight from the database to figures and tables in reports (e.g. by live linking in a Word document). This would be ideal for producing regular reports on a large scale.

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Appendix 1 Description of the BGS/CEH approach to determining trends in groundwater nitrate time series

Setup

All the statistical tests and plots described in this Appendix were carried out and produced by S-PLUS, a powerful, modern statistical package from Insightful Corp. Similar results running essentially the same script can be obtained using the open source (and free) software called 'R' (www.r-project.org). The software runs a script (a small program) developed by BGS and CEH. You need to have both the software and the script to produce results. Other than that the script that has been developed for this trend analysis is quite general and can handle most time series, regular or irregular. It is not restricted to groundwater quality analysis though it has been designed specifically for that. The whole procedure can be run from Excel if desired but is best run from S-PLUS as a batch process. It is possible to analyse and plot more than 1000 time series per hour in this way, all without user intervention.

The plots are output as one or more postscript files. These are high quality colour plots and can easily be converted to other formats (pdf, eps, png etc) for incorporation into Word documents, spreadsheets, intranet etc.

Data input

At present, the data are read in from Excel spreadsheets although this could be easily changes to read directly from a database.

The nitrate data are stored in an Excel file containing just two columns labelled 'Date' and *determinand* where *determinand* is the name for the data given in the column below, e.g. 'NO3'. The date column contains the date of each sample in Excel date format. The determinand name is only for reference – it is not used by the script. The script assumes that the nitrate data are input as NO3 but the script can be easily adjusted to accept nitrate as NO3-N or TON. NO3-N and TON data are then transformed to NO3 units. All the plots and statistics are in terms of nitrate (NO3) no matter what the input. There can be any number of such data files, one per series.

There is also an 'index' file. This is also an Excel file which has a one line entry for each time series and gives some descriptive information about the datasets – the filename for each dataset, the full borehole name, aquifer etc. This index file also controls exactly which series are analysed and plotted.

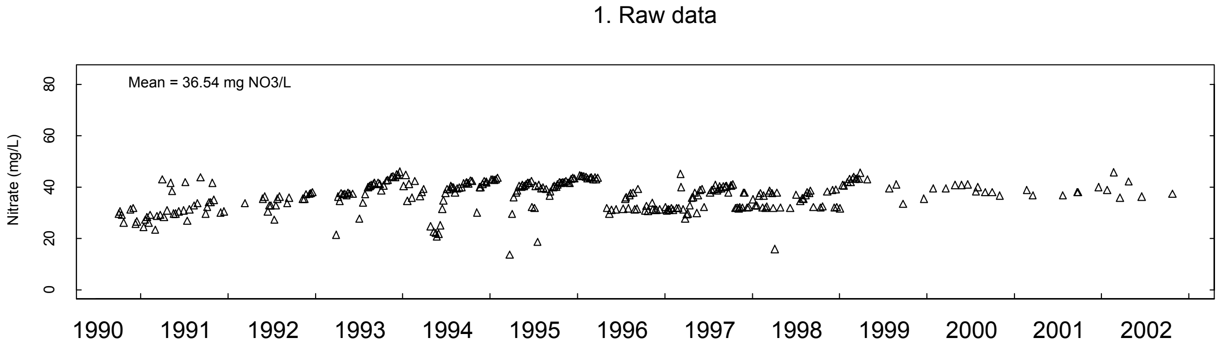
The data analysis and the plots

The data are subjected to a series of descriptive and statistical tests to determine the regularity and frequency of sampling, whether the data show a significant linear trend with time, whether there is any seasonality in the data, whether the data show any unusually large deviations from the assumptions made in the statistical tests undertaken, and whether there is any evidence for a change in trend including a trend reversal.

Below, we give a summary of the various tests undertaken and an explanation of the messages displayed on the plots.

[The main example is Charing 3 and Birchmoor 6 for broken sticks]

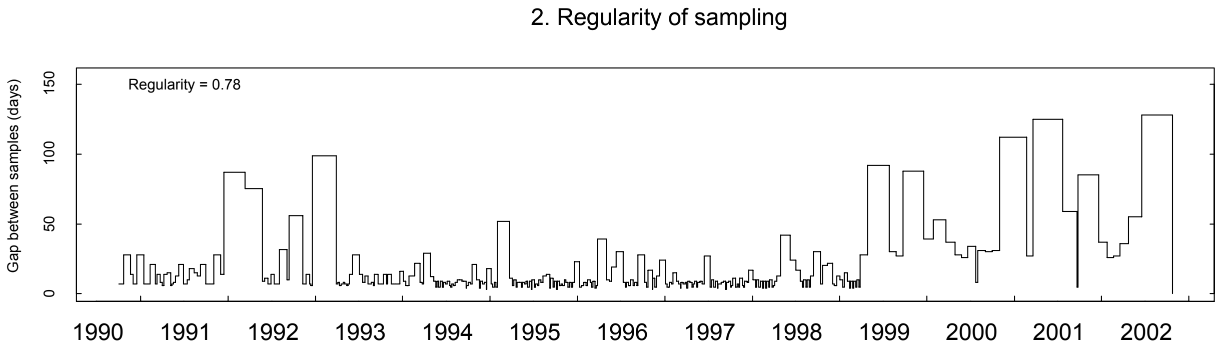
PLOT 1. RAW DATA



A simple symbol plot of the data actually used, one point per sample. There is a preliminary filter of the data so that (i) datasets with a total of 20 or less observations are discarded; (ii) where there are several observations for one day, only one value is retained for that day (the last one read in) (in practice this was not an issue here as the data had been screened to remove multiple samples per day by taking the median concentration); (iii) zero or negative values are ignored.

The inset gives the mean nitrate concentration for the selected dataset.

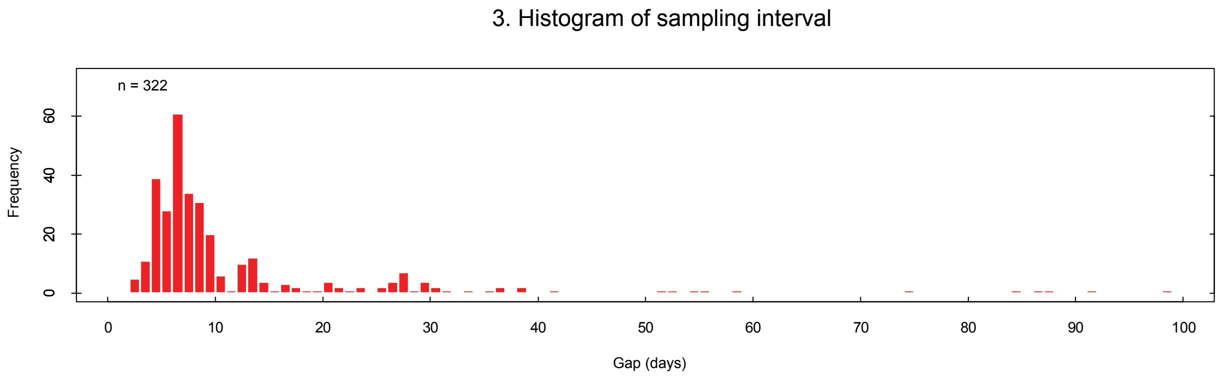
PLOT 2. REGULARITY OF SAMPLING



This plot shows the gap between successive samples and provides a rapid view of the regularity of sampling over the period covered by the time series. Regular sampling is preferable for time series analysis.

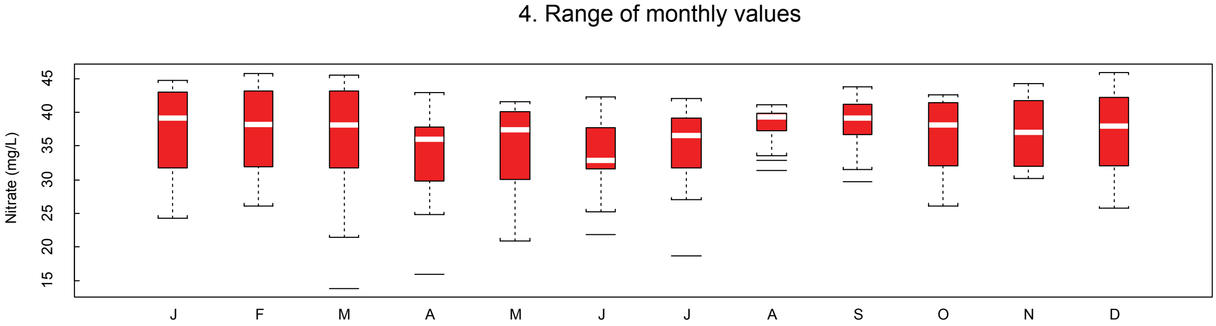
The inset gives a measure of the regularity of sampling. This is the mean/standard deviation of the gap and is therefore dimensionless. A larger number indicates a greater regularity. Generally, series with a regularity of greater than 1.0 are reasonably regular.

PLOT 3. HISTOGRAM OF SAMPLING INTERVAL



This provides a histogram (frequency) of the gap between successive samples (in days). It is easy to see whether the sampling was predominantly weekly, monthly etc from this. The inset provides the number of observations in the filtered time series.

PLOT 4. RANGE OF MONTHLY VALUES

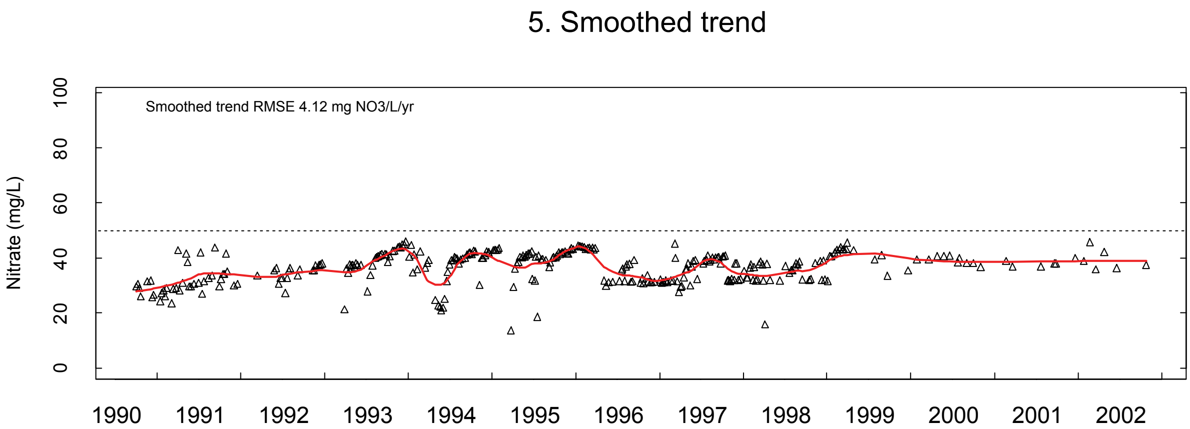


A 'box and whisker' type plot showing the range of values when all of the observations have been divided into calendar months. This type of plot provides one of the best ways of detecting seasonality visually and also gives an indication of whether the data are more variable at particular times of year, e.g. in the summer or winter months.

The white bar at the centre of the box gives the median (50th percentile) while the height of the box gives the interquartile span, i.e. from the 25th to the 75th percentile. The box therefore shows the range of half the data with the height of the box giving a measure of the tightness with which the data are packed around the median for that particular month. The white line within the box is the median and the vertical position of the line within the box gives a measure of the shape of the distribution; if the median is further from one end of the box than the other, then the distribution is skewed. A log normal distribution will have the median towards the bottom of the box. The upper whisker is drawn at the observation which is less than or equal to 1.5 times the interquartile range away from the upper quartile; the lower whisker is drawn at the observation which is more than or equal to 1.5 times the interquartile range away from the upper quartile. The whiskers therefore represent extreme values, possibly maximum and minimum values. Individual values outside this range are highlighted by horizontal lines. These outliers may deserve checking to ensure that they are valid observations.

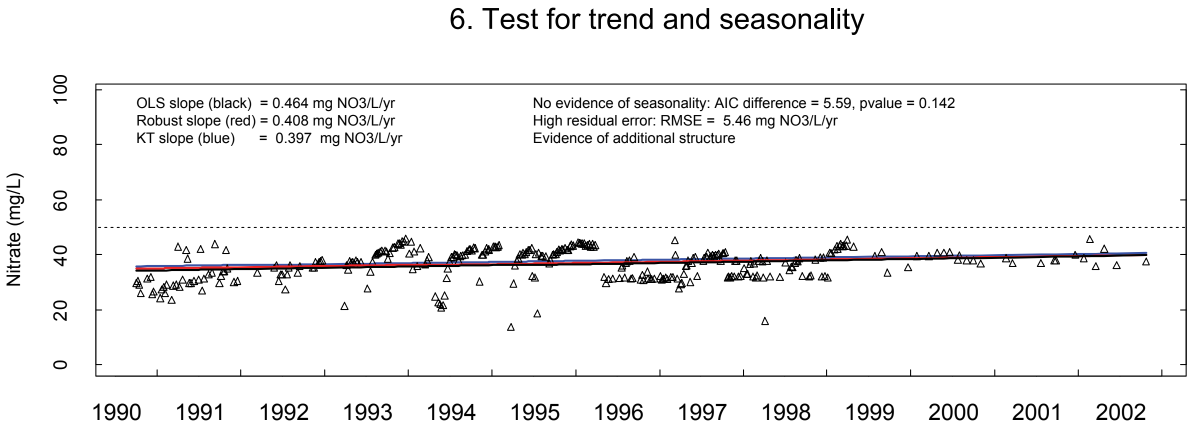
The y-scale is normally automatically adjusted to fit the data range but where there are no data for a particular month, then a placeholder of zero concentration is included and the y-range expanded accordingly. This dummy value should be ignored.

PLOT 5. SMOOTHED TREND



The red line shows the smoothed trend line calculated using a local regression (loess smoother). This attempts to follow the underlying trend in an intuitive manner. One of the critical parameters that controls the degree of smoothing is the 'span'. For the present purposes, this is set to 40/length of series (years). The larger the span, the greater the number of observations that influence the fitted line and the smoother the line becomes. If the line is too smooth, it will miss interesting excursions; if it is not smooth enough, it will tend to follow erratic 'noise'. We have found that the span defined above usually produces reasonable-looking plots.

PLOT 6. TEST FOR TREND AND SEASONALITY



This plot shows linear trend lines calculated using three different methods. These are: (i) ordinary least squares (OLS) (black line) as for example would be calculated using the simple linear regression procedure in Excel; (ii) a robust regression procedure (red line), based on a so-called M estimator that is good at rejecting spurious observations while following the overall trend, and (iii) the Kendall-tau (KT) slope (blue line), a non-parametric (rank-based) test for a monotonic trend based on Kendall's tau statistic.

A large divergence between these trends indicates that outliers or some other unexpected features are likely to be playing a significant role in determining the slopes. This provides a warning that particular care needs to be taken (i) to assess whether the outliers or other excursions reflect valid observations or are database errors of some sort, and (ii) not to over-interpret the values of the slopes since they are clearly sensitive to the assumptions made. Normally in these circumstances, one of the robust trend estimators would be a better estimate than the OLS trend.

Various tests are carried out on the results of the regression analyses to test for possible deviations from the simple linear model. These are described below.

Seasonality

A test for seasonality is carried out by comparing the OLS results with those from the model

$$y(t) = a + b*t + c*month$$

where y(t) is the nitrate concentration as a function of time, t is the date of the sample in decimal years, month is the month of the year expressed as a factor and a, b and c are adjustable parameters. Two essentially similar statistical tests are carried out to see if there has been a significant improvement in fit using the seasonal model. These two tests are: (i) the AIC (Akaike Information Criterion) for the seasonal model should be less than the AIC for the OLS model, and (ii) the reduction in the sum of squares using the seasonal model must also be significant at $p<0.05$ based on an F-test. The larger the difference in AIC and the smaller p, the greater the degree of seasonality.

This model does not impose any particular structure on the type of seasonality (sinusoidal etc) but a positive reporting of ‘seasonality’ does require that the deviations each month are replicated in the same way each year. It is not simply enough to have a fluctuating time series.

The results of these tests are shown in the top right-hand corner of the Plot 6, e.g.

Evidence of seasonality: AIC difference = −5.21, p−value = 0.005
is given when the difference in AIC is negative, and

No evidence of seasonality: AIC difference = 2.07, p−value = 0.143.
is given when the difference in AIC is zero or positive.

An alternative approach to seasonality is to link to another seasonal variable such as the depth to the water table.

Residual error

The ‘Residual error’ is a measure of the size of the deviations from the best-fitted model, be it the non-seasonal or seasonal model. The residual error is given by the RMSE (root mean square error) of the fit. This has the same dimensions as the units of measurement (mg NO_3/L/yr in the present case). A high RMSE indicates a poor fit. It is influenced by both noise about the fitted line as well as outliers. If the deviations follow a normal distribution, then 95% of the observations are expected to fall within ±2 RMSE’s of the fitted line. We consider an RMSE of more than 5 mg NO_3/L as indicating a ‘high residual error’ and less than this as indicating an ‘acceptable residual error’.

Additional structure

‘Additional structure’ is a term that is used here for the systematic variation that falls outside that expected from a strictly linear model and that may indicate that some other model is more appropriate, e.g. a curved model. It is only estimated for non-seasonal series. If the RMSE for the linear model is greater than 1.2 times that for the loess trend line (Plot 5), then this is taken to indicate that there is likely to be some ‘additional structure’ present. The loess trend line tends to follow the local trend in the data irrespective of the linearity of the overall trend and so the RMSE of the loess fit largely reflects the short-term noise in the data rather than the error in the model shape.

The message printed on Plot 6 either says something like

Acceptable residual error: RMSE = 3.15 mg NO3/L/yr
if the difference in RMSE’s is not too large, or simply

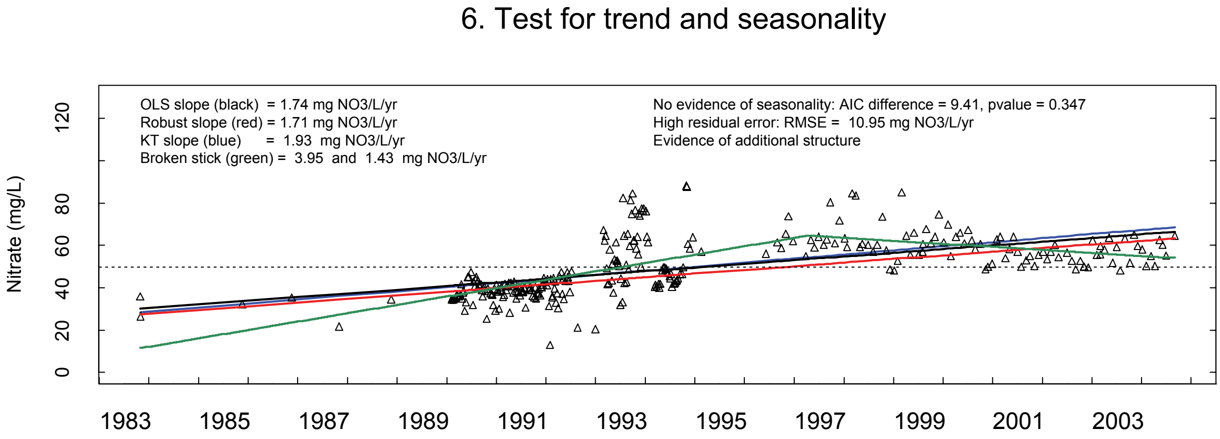
Evidence of additional structure
when there is quite a large difference. In such cases, the linear trends shown elsewhere on Plot 6 should be viewed with particular caution.

Change in trend

A piecewise linear regression model is used to see if there has been a significant change in trend over the period of the observations. This is estimated by nonlinear regression using the following function:

$$y(t) \sim a + b*t + c*(\max(0,t-d))$$

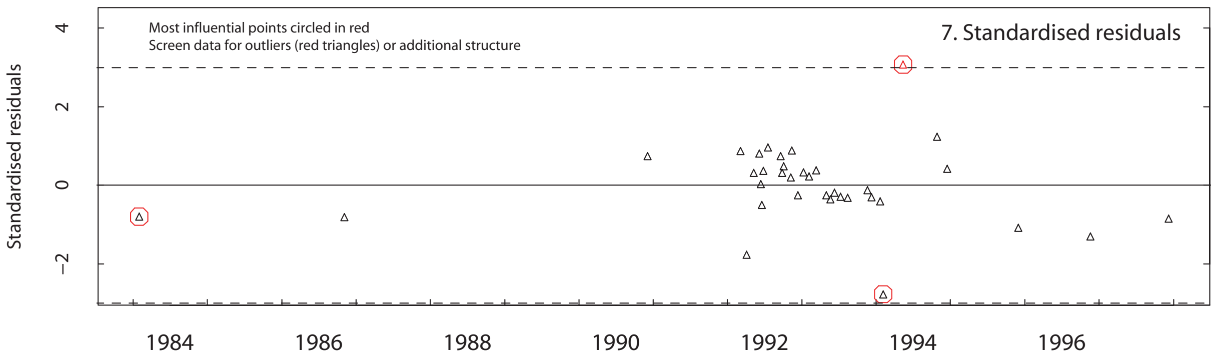
where y(t) is the nitrate concentration as a function of time, t is the date of the sample in decimal years, and d is the date at which the break occurs, also in decimal years. a, b, c and d are fitted parameters which are adjusted to minimize the residual sum of squares in y(t). The position of the break is therefore automatically located.



The results of this regression are compared against those of a single line OLS regression and where there has been a significant improvement in the overall fit, the 'broken stick' lines are drawn on the plot (green lines) and the slopes of the two segments printed on the plot.

This test does not impose any particular direction on the change, increasing-decreasing or decreasing-increasing. It will also capture cases where there have been significant increases or decreases in slope of the same direction.

PLOT 7: STANDARDISED RESIDUALS



This plot shows the standardized residuals of the best-fitting linear trend, based on the seasonal or non-seasonal model, and highlights possible 'outliers' in red. The standardized residuals are the residuals divided by the RMSE. Outliers and other forms of additional structure have absolute standardized residuals of greater than 3. When some outliers or additional structure have been identified, the message

Screen data for outliers or additional structure

is printed on the plot; otherwise nothing is printed. The residuals should not show any systematic trend about the zero line.

The three most influential points are circled in red. These have the largest Cook's distance and are the points whose inclusion changes the fitted model most. They tend to be isolated points near the ends of the series and so exert a large leverage on the fitted line. They often also have large residuals but do not always especially when a seasonal component is included. Points in months not well represented in the data can have a relatively large influence on seasonal fits and do not necessarily have large residuals. Points with a large residual error and a large influence are not necessarily incorrect and should not be automatically removed.

However, they do suggest that the linear model is not working well and that they are influencing the fit and so should be double-checked for their validity. It is unusual (and to some extent physically impossible) for the large body of water in an aquifer to change concentration rapidly with time and so outliers are inevitably suspicious and usually say something about the sampling rather than the aquifer.