Development of a Methodology for Selection of Determinand Suites and Sampling Frequency for Groundwater Quality Monitoring

National Groundwater and Contaminated
Land Centre Project NC/00/35

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March 2003

Research Contractor:
British Geological Survey

Environment Agency
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National Groundwater and Contaminated Land Centre Project
NC/00/35

Publishing Organisation:
Environment Agency
Rio House
Waterside Drive
Aztec West
Almondsbury
Bristol BS12 4UD
Tel: 01454 624400 Fax: 01454 624409

ISBN: 1857 05864X

Dissemination status
Internal: Released to Regions and Areas
External: Public Domain

Statement of use
This report summarises existing approaches to groundwater quality monitoring, reviews additional monitoring techniques and describes the statistical optimisation of monitoring frequency. A technical framework for sampling frequency and determinand selection within the national framework is described to facilitate the Environment Agency to meet the requirements of its statutory duties including those of the WFD.

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National Groundwater & Contaminated Land Centre Project NC/00/35

EXECUTIVE SUMMARY

Groundwater quality monitoring in the Regions of the Environment Agency (the Agency) has long suffered from a recognised lack of consistency which makes national reporting of the state and trends in groundwater quality very difficult. This was addressed for the National Rivers Authority (NRA), the predecessor of the Agency, in 1994 by the British Geological Survey (BGS) in a project which developed a national strategy for more effective monitoring, assessment and reporting of groundwater quality. Since that report and until recently, however, no nationally co-ordinated strategy had been implemented by the Agency, partly because of a lack of clearly specified statutory requirements for monitoring, but mainly because of limited organizational resources. The effectiveness of groundwater quality monitoring has not improved overall and, most importantly, has not significantly enhanced the capacity of the Agency to meet its increasing information needs at national level and its broader obligations within Europe. The project described here is intended to address part of this deficiency and forms an element of a new national strategy. The overall project objectives were to develop a practical, cost-effective and scientifically-based framework for determinand suite selection and sampling frequency for groundwater quality monitoring in England and Wales.

The recent review of current monitoring undertaken by Environmental Simulations International (ESI, 2001a) also forms part of the Agency's overall national strategy. This shows that the variation in practices across the country remains great. Regions have implemented none, some or all of the recommendations of the previous study independently and in inconsistent ways. What has changed, however, is that the drivers for groundwater monitoring have become both more numerous and more individually demanding, specifying monitoring requirements more clearly than before. This applies particularly at the European level, with the Water Framework Directive (WFD), the Nitrate Directive, the Groundwater Action Programme and the European Environment Agency's Monitoring and Information network (EUROWATERNET).

Sampling frequency in the regions remains highly variable, but averages once to twice per year. Exceptions are South West, where a much fewer number of sampling points (giving inadequate density of coverage) are sampled approximately six times per year, and Thames, whose groundwater monitoring programme is more fully developed, and where the average is about four times per year. The wide variation in determinand groupings and suites between Agency Regions was also highlighted. Since 1994 the value of field determinations has become broadly accepted by the regions, and all now routinely carry out at least some field determinations. Major ion concentrations are measured in all regions, together with some metals, and the greatest variability comes with respect to organic compounds and pesticides.

The study has reviewed practice elsewhere. In Europe, sampling frequencies for national groundwater monitoring range from once every two years to 4-6 times per year, with annual or six monthly sampling being the most common. Determinand selection is also characterized by significant variability, reflecting a range of both national objectives and commitment of resources to monitoring. It has been more difficult to find out about the criteria and the decision making process by which these programmes were arrived at and such information has not been obtained.

The project has reviewed the current availability and applicability of field chemistry methods, *in-situ* measurement techniques, novel analytical tools such as the ELISA method and the potential for the use of indicators has also been reviewed. While there has been rapid

technological development of in-situ measurement capability, changes in groundwater quality are not normally on a time-scale for which such frequent data are required. Interest in the possibility of using indicator determinands to represent groundwater quality is high, but thus far it has been difficult to identify indicators which would perform this function cheaply and effectively. The potential for the use of boron and zinc, which are currently not widely measured in groundwater by the Agency, as indicators of urban impact has been identified.

The published statistical approaches to the optimization of sampling frequency were considered. An autoregressive moving average model was applied to long-term datasets from selected Chalk, Sherwood Sandstone and Great Oolite sources to calculate the variance of the sample mean and confidence intervals. The confidence interval around mean concentrations was large for all datasets tested, approximately 25% when sampling weekly and increasing to 50% when sampling monthly. The confidence interval is strongly dependent on the variance, and datasets characterized by large variance should be sampled more frequently. Highly seasonal data should also be sampled more frequently. These two conclusions point towards more frequent sampling in the Chalk and Jurassic limestones than in the Sherwood Sandstone. Existing trends, either positive or negative, could be detected at all of the sampling frequencies tested, ranging from weekly to six-monthly.

The proposed approach to determinand selection and sampling frequency takes account of all of the factors which influence these choices. The philosophy adopted here retains a framework which allows for more frequent sampling in aquifers in which groundwater flow is more rapid and less frequent in aquifers with slower movement. It also builds in a less frequent requirement for sampling in confined aquifers than in unconfined aquifers, reflecting the greater degree of protection from pollution, slower water movement and less rapid hydrochemical change in confined aquifers. It follows but simplifies the approach put forward by the BGS in 1994, by dropping the UK distinction between Major and Minor aquifers, as this is considered unlikely to be compatible with the methodology for definition of groundwater bodies set out in the WFD.

The approach proposed here has an important innovation in that the philosophy governing the framework for determinand selection also has a fast and slow dimension, but in this case defined by the anticipated response of the hydrochemical conditions. This is because experience shows that major ion chemistry in groundwater bodies is likely to be more stable than many of the determinands indicative of human impacts. Therefore, from an information needs perspective, a strong case can be made for measuring pollutants or pollutant indicators more frequently than the components of major ion hydrochemistry. The information-needs approach developed here caters for the requirements of the water quality manager, rather than the capabilities and historical practices of laboratories.

The recommended approach to determinand selection takes as its starting point the set of core parameters and indicative list of pollutants defined by the WFD. This comprehensive list is intended to form the basis for the surveillance monitoring which the WFD will require every six years. The proposed strategy then allows for selected determinands to be measured in responsive or unresponsive sets, representing firstly those pollutant determinands which may change more rapidly and secondly the components of inorganic hydrochemistry and the less common pollutants. The former are less variable and the latter less likely to reach groundwater. These two sets are then further divided into standard and selective determinand sets, the former of which would be measured at all groundwater monitoring sites and the latter would be selected on the basis of similar land use criteria to those which the Agency is developing to aid monitoring site selection, augmented if necessary by a degree of local knowledge within each region, and the results of the characterisation and impact assessment of groundwater bodies to be carried out under the Water Framework Directive.

The recommended framework suggests four inorganic and eight organic analytical suites and a microbiological suite classified as responsive or unresponsive and standard or selective according to land use. This framework provides sets of suites for operational (more frequent) and surveillance (less frequent) monitoring requirements. These are combined in the strategic framework with a sampling frequency matrix of slow and fast, confined and unconfined aquifers to give recommended operational measurement frequencies ranging from quarterly (fast outcrop), twice a year (slow outcrop and fast confined) to annual (slow confined). The corresponding recommended unresponsive measurement frequencies range from annual, through once every three years to once every six years.

The recommended framework was tested against existing analytical datasets for three selected areas in southern England, the Colne-Lee catchments north of London, the Oolite of the Cotswolds between Cheltenham and Oxford, and the Chalk of Central East Anglia. The proposed methodology was shown to be generally successful by comparing for each monitoring site the organic suites derived in the recommended strategy with observed positive detections at that site. Given the scale of complexity of land use in southern England, for many monitoring sites most categories are represented within close proximity. Taking the reasonable radii of 1 km around each site, and a 10% land use threshold, then most suites are required at most sites. If a 3 km radius is used, then suite selection approaches the full precautionary position of analysing for everything everywhere. Testing of the method in an area of northern or western England with less mixed land use would be expected to produce a more selective outcome in terms of suites.

Where suites were predicted but not observed, this may be because the proposed suites are more comprehensive than current regional practices. In total, a very small number of determinands were detected although not predicted, and these emphasise the need for an additional element of local knowledge of potential pollutant sources which are not directly predicted from the land cover map. The spreadsheet comparisons could also be used to assist in interpreting monitoring results. Where determinands are consistently observed but not predicted from land use, then further investigation of local pollution sources may be required.

The testing has also shown that the geographical information system (GIS) and spreadsheet approach developed would allow the land-use criteria to be applied to the entire regional or national networks quickly and consistently. Structuring the land-use methodology at the beginning would allow subsequent revision of the network, changing the radius around the sites and the land use threshold, updating the underlying land use data (a new CEH land cover map is due), or changing the analytical suites to embrace new determinands. Fears amongst some regional Agency staff that the land-use approach would be unduly burdensome have proved groundless and, because the GIS approach is easy to apply, it is recommended that it be applied on a site-by-site basis, rather than as a broader regional land use definition of suites.

There are clearly potential roles for the rapid, semi-quantitative screening methods being developed by the Environment Agency's National Laboratory Service (NLS). While it is probably not yet ready to be used extensively to replace components of operational monitoring, it could have a role to play even at its present stage of development in detecting priority hazardous substances and in assisting in determinand selection for regions which currently have less existing monitoring data. Further work on the development of screening methods is therefore fully justified.

KEY WORDS

Groundwater; monitoring; methodology; Water Framework Directive; frequency, determinand.

Contents

List of Tables

List of Figures

Glossary of Terms

The following terms have been used with specific meanings during the discussion of monitoring strategy

Responsive	Used in this report to describe determinands which may change rapidly in response to human impacts
Unresponsive	Used in this report to describe determinands which are not likely to change rapidly in response to human impacts
Standard	Used in this report for a determinand suite measured at all monitoring points
Selective	Used in this report for a determinand suite measured at monitoring points only where a particular land-use occurs in the catchment
Determinand	Chemical or physicochemical parameter which can be measured in an analytical laboratory
At risk	Defined under the WFD as groundwater bodies at risk of failing to achieve good chemical status under Article 4 and Annexe V
Surveillance monitoring	Defined under the WFD as monitoring of a comprehensive range of parameters at least once per six years to supplement and validate the impact assessment procedure and to provide information for use in the assessment of long-term trends both as a result of changes in natural conditions and through anthropogenic activity
Operational monitoring	Defined under the WFD as monitoring of a limited range of parameters undertaken at least annually in periods between surveillance monitoring for groundwater bodies defined as being 'at risk'
Reference network	Used by Chilton and Milne (1994) to describe monitoring points selected from the national network giving broad coverage of the major aquifers at a greater sampling frequency to meet the objectives of trend observation and baseline data provision

1. INTRODUCTION

1.1 Background

Groundwater quality monitoring in the Regions of the Agency has long suffered from a lack of consistency, which, among other resulting problems, makes national reporting of the state of groundwater very difficult. Recognising this, in 1994 BGS was contracted by the then NRA to review the monitoring of both groundwater levels and quality, and to make recommendations for national strategies for each, which would lead to more effective monitoring. However, until recently, no nationally driven and co-ordinated implementation plan had been developed by the Agency. This was because of the lack of well-defined statutory requirements, limited organisational resources and other priorities for those limited resources. Regions have, therefore, implemented none, some or all of the recommendations independently and in inconsistent ways. This has not necessarily improved the effectiveness of groundwater quality monitoring overall and, most importantly, has not significantly improved the capacity of the Agency to meet its increasing information needs at a national level and its broader obligations at a European level.

Aware of the increasing drivers for water quality monitoring, the Agency undertook a strategic review of its information needs and monitoring (Lytho, 1998), which identified an increasing requirement for co-ordinated monitoring to meet current and future statutory duties. The review also highlighted information gaps requiring improved monitoring, including:

- the quality of standing waters and groundwaters;
- reliable data on the quantities of priority contaminants released into the environment;
- their flux through the environment and concentrations in soil, water, sediments and biota;
- the extent and severity of contaminated land.

A new national groundwater monitoring strategy was prepared to enable the Agency to fulfill its statutory duties properly, and to replace the existing inconsistent approach to monitoring in England and Wales. As part of the process of developing the strategy, a further review of current groundwater quality monitoring has confirmed the degree of regional variation in the determinands measured and frequency of measurement. A number of different determinand suites are used within the Agency, and in some cases these have been derived from surface water monitoring and are not wholly appropriate for groundwater. Because of these inconsistencies, the Agency is still unable to report adequately at a national scale on the state of the groundwater environment, and the project described here is intended to address this deficiency. Whilst a rigid standardization of approaches across the Agency, given the considerable range of aquifers, pollutant sources and groundwater development across the Regions, may be unrealistic, a consistent framework leading to a degree of convergence is clearly desirable.

1.2 Drivers for monitoring

Since the time of the 1994 BGS study, there have arisen much more clearly defined drivers for co-coordinated monitoring of, and consistent information about, groundwater quality.

These include new European Directives, national statutory duties and the Agency's own initiatives, as summarised in Table 1.1.

The stated primary objectives of the national groundwater quality monitoring strategy are to comply with statutory and non-statutory national and European commitments by:

- providing objective, reliable and comparable information at the national level;
- defining baseline groundwater conditions, in both currently used aquifers and those as yet to be used, so the Agency can determine their suitability for future use and the potential impact of permitted discharges;
- determining trends in groundwater quality and quantity, against the identified baseline, resulting from natural causes, from the impact of diffuse pollution sources and from changes in the hydraulic regime to enable the development of strategies that ensure resource protection, but allow continued use;
- providing a three-dimensional picture of groundwater quality within aquifers where suitable boreholes exist;
- providing early warning of groundwater pollution, particularly in outcropping aquifer recharge areas and other sensitive areas, such as wetlands;
- identifying links between groundwater systems, surface water systems and terrestrial systems (land use) to support a truly integrated approach to river basin management.

Other objectives of the strategy should be to improve understanding of solute transport through British aquifers in a similar way to the BGS project Natural Baseline Quality in British Aquifers and analogously to the USA National Water Quality Assessment (NAWQA) scheme (see Section 2.4 of this report).

1.3 Statutory duties for the Agency to monitor groundwater quality

To support development of the Agency Strategy, ESI provided an interpretation of the statutory duties on the Agency to monitor groundwater quality in their earlier review of current monitoring in the Agency's regions (ESI, 2001a). This interpretation is largely based on the requirements of the WFD which encompasses most of the other relevant legislation and is on the whole the most specific with regard to the details of the monitoring required. The WFD requires a comprehensive and coherent overview of groundwater chemical status under Annexe V, 2.4.1. For groundwater bodies identified as being 'at risk' the frequency of sampling should be at least annual for operational monitoring with potentially more comprehensive surveillance monitoring every six years.

The Nitrate Directive requires the monitoring of freshwater over a period of a year to be carried out at least every four years, except for those stations where the nitrate concentrations in all previous samples have been below 25 mg/l and no new factors likely to increase the nitrate content have appeared. In this case monitoring need only be repeated every eight years.

Monitoring is also required by other legislation, such as the Water Resources Act 1991, the Environmental Protection Act 1995, the Groundwater Regulations 1998 and the Groundwater Directive but these specify the required output not the detail of monitoring.

Table 1.1 Drivers for monitoring of groundwater quality

Drivers	Requirements
The European Level:	
Groundwater Action Programme & Eurowaternet	Development of integrated planning methodology for groundwater. Monitoring of water quality and quantity and establishment of a thorough and reliable basis of information on the state of the aquatic environment.
Water Framework Directive & proposed Groundwater Daughter Directive	River Basin Management Plans to protect and enhance aquatic ecosystems. Protection and restoration of identified groundwater bodies to good groundwater status. Definition of groundwater bodies and statutory monitoring and reporting to detect changes in chemical composition from indirect discharges.
Nitrate Directive	Routine collection of groundwater quality monitoring data, and use for designation, review and re-assessment of Nitrate Vulnerable Zones.
Groundwater Directive (80/68)	Transposed into UK legislation through the Groundwater Regulations 1998.
The National Level:	
Environmental Protection Act 1990, Environment Act 1995, Water Resources Act 1991, Groundwater Regulations, 1998	Consideration of the impact of substances and activities on all environmental media. Monitor the extent of pollution in controlled waters, including groundwater.
Water Resources Act 1991	Collate and publish information on actual and prospective water resources.
Groundwater Regulations 1998	Ensure ‘requisite’ groundwater surveillance to ensure background concentrations of List I and II substances and the potential impacts of discharges to groundwater are monitored. Good understanding of baseline groundwater conditions from which impacts can be identified.
The Agency itself:	
Environmental Strategy for the Millennium and Beyond (EA, 2000)	Nine themes identified, in eight of which understanding groundwater plays a key role, most significantly in: • delivering integrated river basin management; • managing our water resources; • conserving the land; • regulating major industries.
Environmental Vision (EA, 2000) for Contribution to Sustainable Development	Expands and reformulates these themes:

1.3.1 Surveillance monitoring

The objectives of surveillance monitoring under the WFD are to:

- supplement and validate the impact assessment procedure;
- provide information for use in the assessment of long-term trends both as a result of changes in natural conditions and through anthropogenic activity.

The WFD requires Member States to provide a comprehensive and coherent overview of groundwater chemical status (Annexe V, article 2.4.1). Groundwater chemical status is determined by conductivity and concentrations of pollutants. The WFD specifies that the following set of core parameters shall be monitored in all selected groundwater bodies:

- oxygen content;
- pH value;
- conductivity;
- nitrate;
- ammonium.

The WFD also requires that monitoring shall be focussed on determinands that are indicative of the pressure and impacts to which each groundwater body is assessed as being ‘at risk’. An indicative list of pollutants is provided in Annex VIII of the WFD as follows:

- organohalogen compounds and substances which may form such compounds in the aquatic environment;
- organophosphorus compounds;
- organotin compounds;
- substances and preparations, or the breakdown products of such, which have been proved to possess carcinogenic or mutagenic properties or properties which may affect steroidogenic, thyroid, reproduction or other endocrine related functions in or via the aquatic environment;
- persistent hydrocarbons and persistent and bioaccumulable organic toxic substances;
- cyanide;
- metals and their compounds;
- arsenic and its compounds;
- biocides and plant protection products;
- materials in suspension;
- substances which contribute to eutrophication (in particular nitrate and phosphate);
- substances which have an unfavourable influence on the oxygen balance and can be measured using parameters such as Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD) etc.

Although ‘indicative’, this comprehensive and complex list would be very expensive to accommodate in total. It is not specifically targeted at groundwater and indeed groups such as the organotin compounds, endocrine disrupters, materials in suspension and factors related to the oxygen balance are more likely to apply to surface waters. For groundwater, further criteria and selectivity to focus on actual or potential risks to groundwater bodies will be required, and the approach to determinand selection outlined in Chapter 5 addresses this requirement.

1.3.2 Operational monitoring

For groundwater bodies 'at risk' operational monitoring shall be undertaken in the periods between surveillance monitoring programmes in order to:

- establish the chemical status of all groundwater bodies or groups of bodies determined as being at risk;

- establish the presence of any long-term, anthropogenically induced upward trend in the concentration of any pollutant.

The frequency of operational monitoring shall be sufficient to determine the impacts of relevant pressures but at a minimum of once per annum. For bodies not 'at risk' only an initial characterization is specified and monitoring is not defined.

1.3.3 Priority substances

Priority substances discharged to surface water are covered under Article 16 (3) of the WFD. It is anticipated that discharges to groundwater will be covered under the Groundwater Daughter Directive. The requirements for monitoring of these substances are as yet to be decided, but will need to be incorporated into the Agency's monitoring strategy in the future.

1.4 Project objectives

The overall objective of the project was to develop a practical, cost-effective and scientifically based framework for determinand suite selection and sampling frequency for groundwater quality monitoring in England and Wales. In achieving this overall objective the project:

- investigated and identified specific statutory and other requirements for groundwater quality monitoring with respect to determinand suites and frequency of measurement;

- reviewed previous studies and recommended approaches to determinand selection and monitoring;

- identified where improved techniques and methodologies (sampling and analysis) were required and also identified the potential use of *in situ* monitoring devices;

- developed a recommended approach for selection of determinand suites and frequency of monitoring of groundwater;

- considered the implications of introducing the recommended approach in terms of practicality (sampling and analysis) and the ability of the Agency to adopt the approach, as well as cost.

Spatial distribution and density of sampling points, vertical quality considerations and sampling methods are also integral components of monitoring strategy design. Although these fell outside the scope of the present project, the BGS view is that these components should not be treated separately but incorporated together so that their interrelationships can be adequately taken into account in the overall design.

1.5 Scope of report

This report addresses the first four points above. These are described as:

Task 2 – Review of Existing Approaches,

Task 3– Development of Approach, and

Task 4 – Evaluation of Proposed Methodology, in the Agency's Terms of Reference.

Thus, following this brief introduction and background, Chapter 2 firstly summarises very briefly the current situation in England and Wales as described by ESI (2001a). It then provides relevant information which BGS has been able to obtain on existing experience with groundwater quality monitoring elsewhere in Europe and in the USA. There is a brief discussion of monitoring techniques, including the value of field determinations, the increasing usage of *in situ* techniques and the growing interest in the potential for indicator determinands for groundwater quality assessment. Chapter 4 describes the statistical work undertaken in relation to the optimisation of sampling frequency. The approach recommended by the BGS project team is outlined in Chapter 5, discussion and evaluation of the approach is given in Chapter 6 and the conclusions in Chapter 7, with a list of the references consulted at the end of the report.

The remaining point in section 1.4 is addressed by the plan for implementation of the recommended framework – Task 5 – which is described separately in a confidential report to the Agency.

2. EXISTING APPROACHES

2.1 The Environment Agency Regions

2.1.1 Monitoring points

Data in this section are taken from the recent ESI report (ESI, 2001a), which shows that the Agency's monitoring network is currently made up principally from the following types of monitoring point:

- privately owned abstraction boreholes;
- Environment Agency observation boreholes;
- water utility operated public water supply boreholes;
- a small number of springs.

The numbers of each are shown in Table 2.1. Except for North East Region the number of Agency-owned and sampled monitoring points is very small. Substantial proportions of the remainder are privately owned supplies, particularly in North East and North West Regions.

From the viewpoint of the present project, the most important aspect of Table 2.1 is the high degree of variation in the proportion of sampling currently carried out by the Agency itself. In North East and South West, all sampling is undertaken by Agency staff, and in North West all by the Agency's contractor, including the sampling from water utility groundwater sources. In Anglian, Thames and Wales it is about half, in Midlands about one third and in Southern only 3% (Table 2.1). This is important because where the Agency is responsible for collecting and analysing samples it can control sampling frequency and determinand selection. The remaining sites are water utility sampled and analysed. The Agency receives data from these points but has less control over sampling frequency and determinand selection.

2.1.2 Frequency of sampling

The data provided in Table 2.1 can be used to indicate an approximate mean sampling frequency for Agency collected samples for each of the regions. It is accepted that this can only be an indicator since frequency may vary considerably from one point to another. This appears to be between 1 and 3 times per year for regions except Thames, where the frequency is greater, and South West, where it is much greater but the total number of points is small.

2.1.3 Determinand selection

The different regions use differently defined determinand suites for sample analysis. A full listing is given in Appendix B of the ESI report (ESI, 2001b). Figure 2.1 shows a summary of the frequency of measurement of generalized suites of compounds for the Agency regions. This suggests that major ion concentrations are measured by all regions, and field chemistry and at least some metals are generally also determined. The pattern for the minor ions, pesticides, organics and TOC is much more uneven. None of the regions analyse for bacteria.

Table 2.1 Frequency of monitoring per Agency Region

Region	Number of monitoring points				Percentage sampled and analysed by the Agency	Total analyses by the Agency (per year)	Reported frequency of sampling (number per year)	Mean sampling frequency by the Agency
	The Agency	Private	Water Utility	Total				
Anglian	21	142	204	367	44	302	Variable	1.9
Midlands	0	103	242	345	29	278	Variable	2.7
North East	77	314	36	427	100	666	2	1.7
North West	1	250	100	351	100	700	2	2
South West	0	32	11	43	100	288	Variable	7
Southern	0	9	307	316	3	9	1	1
Thames	0	189	288	477	40	865	Variable	4.6
Wales	6	109	103	218	53	115	Variable	1

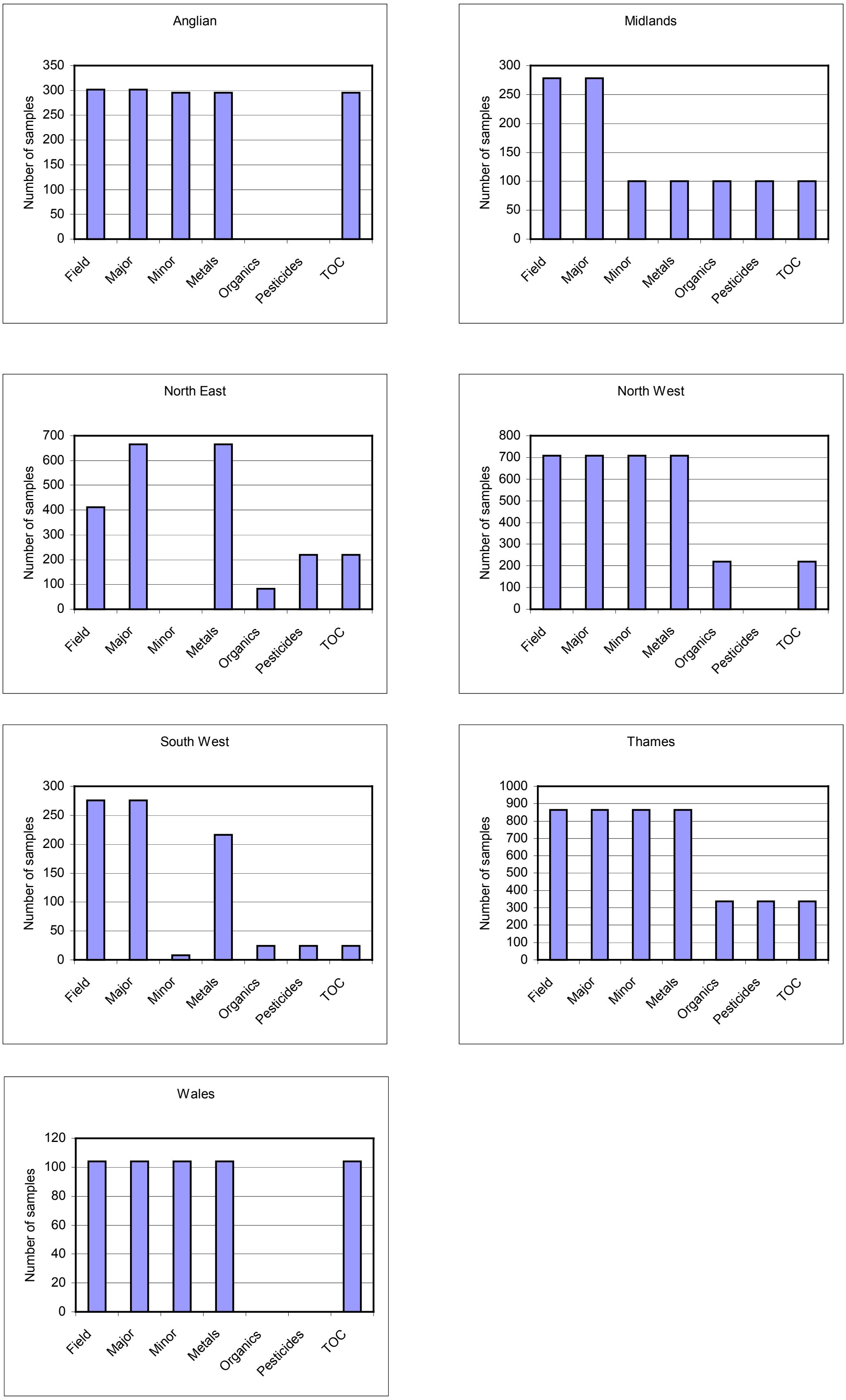

Figure 2.1 Summary of number of samples analysed by each region per year by determinand group (data from ESI, 2001a)

2.1.4 Costs of analysis

All of the Agency's samples are analysed by the Agency's NLS. This uses specific charge rates depending on the suite of analytes chosen. A summary of this is given in Table 3.3 of the ESI report (ESI, 2001a). The costs of individual analytical suites obtained from discussion between ESI and staff from the NLS and listed in Section 6.3 of ESI (2001c). The assumptions used to derive such 'typical' suites are not given. These costs are quoted at the commercial rate for external analyses and are therefore higher than those charged by the NLS for internal samples within the monitoring programme. These costs were used by ESI for scoping the cost impact of a number of scenarios of varying proportions of sample collection and analysis by the Agency and third parties.

Analytical costings supplied to BGS by NLS for the present project are shown in Table 2.2. These are broken down into the standardised determinand suites proposed in Section 5.2.2 of this report.

Table 2.2 Summary of NLS costs for various determinand suites

Suite	Cost/sample (£)
Anions (excluding alkalinity and sulphate)	8
Metals (and sulphate)	35
Non-standard inorganics (assuming all 7 determinands)	41
ONP pesticides	85
OCP pesticides	80
Acid herbicides	45
Uron/urocarb pesticides	25
Non-standard pesticides (assuming 4 determinands)	100
Phenols	45
VOCs	45
PAHs	25
Microbiology	35

2.2 The water utilities

Monitoring is usually carried out within water utilities for both operational and regulatory reasons. Most utilities have undertaken very much less raw water sampling at the individual point of abstraction than was the case before privatization because this is not explicitly required of them for regulatory purposes. The frequency of monitoring is therefore generally in line with that required under the supply regulations for point of supply, that is treated water in the distribution system. The current relevant regulations are the Water Supply (Water Quality) Regulations 1989, its subsequent amendments, the Water Supply (Water Quality) Regulations 2000 and the Water Supply (Water Quality) (England) Regulations 2000. These require the monitoring of untreated (raw) water only for new sources and those which have not been used for more than six months. New Drinking Water Inspectorate (DWI) regulations, planned to commence in 2003, are likely to specify an increased focus on source based (raw water) analysis.

The amount and types of laboratory analysis currently performed on the waters therefore vary considerably. All companies surveyed by ESI have targeted suites for specific boreholes, including, for example, for iron and nitrate (ESI, 2001b). A small survey reported for UK Water Industry Research (UKWIR 2000) for a different subset of water utilities indicated that the majority of determinands are measured on average weekly or monthly with bacteria, turbidity, temperature, taste and odour, and conductivity carried out more frequently. Reporting arrangements between the Agency and the utilities are described in ESI (2001b).

2.3 Europe

2.3.1 Member states

This section has been summarised from Groundwater Monitoring in Europe (European Environment Agency, 1996) and supplemented with information supplied by personal contacts in relevant organizations. Sampling frequencies varied from monthly to biennially and are summarised in Table 2.3. Monitoring is carried out for a wide range of purposes from status determination to saline intrusion and pollutant detection.

The investigated determinands varied between the monitoring systems (Table 2.4). They were adapted to national circumstances but could not be compared on a European level at the time of the report. The total number of investigated determinands varied between 15 and 106 and even the number of determinands in the basic programme ranged between 14 and 51. The determinands observed were divided into five groups:

- physicochemical determinands, such as pH, conductivity, temperature;
- major ions including nitrite and ammonium;
- heavy metals;
- pesticides, herbicides and insecticides;
- chlorinated solvents.

All participating countries determined physicochemical determinands and major ions. The variety in monitoring for the last two groups was particularly high, for both numbers of compounds and frequency.

2.3.2 EUROWATERNET

The European Environment Agency's (EEA) monitoring and information network for inland water resources (EUROWATERNET) is designed to provide the EEA with information that it needs to meet the requirements of the European Commission, other policy makers, national regulatory bodies and the general public (EEA, 1998). This information includes:

- the status of Europe's inland water resources, quality and quantity (status and trends assessments);
- how this status relates and responds to pressures on the environment.

Table 2.3 Summary of frequency of monitoring of groundwater quality networks in the EU

Country		Purpose	Frequency (times/yr)
Austria	(	Status, trends, identification of polluted areas, remediation	4
	(	Transboundary management	12
Denmark	(	Status in relation to land use and point sources	2-4
	(	Specific suites	0.5
Finland		Status	6
France		Status, trends, reinforcement of policy, optimizing action	0.5-4
Germany		Organized at regional (Länder) level, public water supply status, pollution and landuse impacts, trends	1-6
Greece		Exploitation for irrigation	3
Ireland		Status, trends, drinking water resources, pollutant detection	-
Netherlands	((	Status, trends, evaluation of corrective actions, environmental quality, enforcement of regulations, response to emergencies	1
Norway	(	Basic	1-2
	(	Soil and water acidification, precipitation chemistry	12
Portugal		Saline intrusion, nitrate, groundwater status	1-4
Spain	(	Basic Rainfall pattern, irrigation, fertilizer application	2-4
	(	Specific factors e.g. saline intrusion in coastal zones	Very frequently or continuously
Sweden		Status, threat and impact of anthopogenic loading	2-6

Table 2.4 Summary of determinand selection for water quality monitoring in the EU

Country	Programme	Standard suite (number of determinands)	Specific suites	Other
Austria	1 year of wide range followed by 5 years with standard suite plus selected specific determinands	Temp, pH, SEC, DO_2, nutrients, TOC, DOC (34)	Heavy metals, hydrocarbons, pesticides, PAH, metabolites, selected on regional usage and probability of occurrence, rolling replacement	Radon, radium, tritium, O18, MTBE, endocrine disruptors
Denmark	Not stated	pH, hardness, temp, major ions, NO_3, NH_4, heavy metals (51)	Chlorinated hydrocarbons, pesticides	
Finland	Not stated	(28)		
France	Not stated	Not stated		
Germany	Regionally based	Various (24-43)		
Greece	Not stated	Not stated		
Ireland	Not stated	Not stated		
Italy	Not stated	(26)		
Netherlands	Not stated	Basic determinands (23)	Heavy metals, industrial organic pollutants, pesticides	
Norway	Not stated	(14)		
Portugal	Not stated	(15)	-	
Spain	Not stated	Temp, pH, SEC Major ions, NO_2, NH_4, COD (14)	Minor ions, heavy metals, organic matter, hydrocarbons, phenols, pesticides as required	
Sweden	Not stated	(24)		

Monitoring frequency

A two-step approach is recommended:

1. Periodical characterization of each important groundwater body including construction and representativeness of the monitoring station(s), anthropogenic pressures on the aquifer etc;
2. Initial and surveillance monitoring of the groundwater quality of each important groundwater body on a repeating five-year cycle:
    - in the first year quality should be monitored at least twice for all important groundwater bodies, taking into account seasonal variations and aquifer characteristics which require a higher frequency;
    - during the following four years monitoring should be carried out at least annually for groundwater bodies where significant anthropogenic pressure or impacted water quality has been detected during the initial characterization or surveillance monitoring, taking into account seasonal variations and aquifer characteristics which require a higher frequency;
    - the sampling schedule should relate to the infiltration or recharge regime of the groundwater body and to seasonal variations in the use of pollutants.

Determinands

Determinand selection is clearly based on that originally recommended for the UK (Chilton and Milne, 1994, see section 2.5) and is shown in Table 2.5. The initial monitoring should give a first overview and characterization of the content of both natural constituents and anthropogenically-induced pollution. It shall contain at least the bold marked determinands of Group 1 in Table 2.5 and all other determinands of Groups 1 and 2 which could be of relevance to assessment of anthropogenically-induced pollution. The surveillance monitoring follows the initial monitoring and should include all Group 1 determinands and all other determinands where significant deviations from the background occur.

2.4 The USA

In 1991 the United States Geological Survey (BGS) began full-scale implementation of the National Water-Quality Assessment (NAWQA) programme. The first cycle of sampling aimed to examine the quality of ground and surface water resources in 60 major hydrogeological basins (study units) covering about 60% of the contiguous United States. The study units were divided into three groups to be intensively studied in 9-year cycles on a rotational schedule. Each group was intensively studied for three years followed by six years of low-intensity assessment. Landuse studies were one component of each assessment. The main aim was to evaluate the status of groundwater (Table 2.6).

Cycle II has been planned to focus more on improving understanding of processes and trends, with less effort being directed towards status (Table 2.7), but the change in government in the US is predicted to result in significant reduction in funding for organizations such as USGS.

The details of determinand selection are not yet available but current draft information is consistent with a policy of oversampling until robust criteria have been established (Table 2.8).

Table 2.5 Determinands specified for EUROWATERNET

Group	Class	Determinands
1	Descriptive determinands	**pH, EC, DO** Temperature
	Major ions	**Ca, Mg, Na, K, Cl, NH_4, NO_3, NO_2, HCO_3, SO_4** PO_4, TOC
2	Heavy metals	As, Hg, Cd, Pb, Cr, Fe, Mn, Zn, Cu, Al, Ni. Choice depends partly on local pollution source as indicated by land-use framework
	Organic substances	Aromatic hydrocarbons, halogenated hydrocarbons, phenols, chlorophenols. Choice depends partly on local pollution source as indicated by land-use framework
	Pesticides	Choice depends partly on local usage, land-use framework and existing observed occurrences in groundwater
	Additional determinands	Choice depends partly on the results of analysis of pressures on groundwater

Determinands in **bold** are minimum suite

Table 2.6 USGS sampling strategy for NAWQA

Programme	**Aims (secondary aims)**	**Frequency**		**Criteria**
NAWQA Cycle I	Status, (evaluation of trends, understanding factors governing water quality)			
NAWQA Cycle II	Evaluation of trends, understanding factors governing water quality, (status)	Three categories of frequency	Decadal	All wells
			Biennial	Selected based on access and known information
			Seasonal	Selected based on access and known information

Table 2.7 Themes for Cycle II, NAWQA

Theme type	Theme
Status	Resources not previously sampled Drinking water resources Contaminants not previously sampled
Trends	Trends and changes in status of resource Response to urbanization Response to agricultural management practices
Understanding	Sources of contaminants Transport processes: land surface to and within groundwater Transport processes: land surface to and within streams Transport processes: Groundwater/surface water interactions Effects on aquatic biota and stream ecosystems Extrapolation and forecasting

Table 2.8 USGS determinand selection in NAWQA Cycle II (draft)

Category	**Strategy**	
Decadal	All determinands	Including microbiology, age dating, redox status
Biennial	All determinands	Including microbiology, age dating, redox status
Seasonal	Selected determinands	Field determinands, major ions, seasonally fluctuating determinands, locally used pesticides, local point sources

2.5 BGS Approach in the 1994 report

In their 1994 report BGS proposed a tiered or hierarchical approach in which a sampling network of three levels and scales was to be differentially targeted at the monitoring objectives agreed with the NRA at the time (Chilton and Milne, 1994). This approach defined a basic set of determinands, grouped into inorganic and organic parameters (Table 2.9). The most important purpose of the National Network was to provide knowledge of the spatial distribution of groundwater quality. Selected points formed a Reference network which gave broad coverage of the Major aquifers only, to meet the objectives of trend observation and baseline data provision. The third tier was to address objectives related to a range of pollution issues on a local or site scale. While the tiered approach was strongly endorsed by the NRA as meeting its national needs and international obligations at that time, it has not been carried through into national strategy by the Agency.

2.5.1 Determinands

It was felt to be essential to have a standardized national framework for determinand selection that could be mutually agreed by all regions and also applied by the water companies to the analysis of raw water samples. A basic set of determinands was selected (Table 2.9). Further subdivision of this was required to give a flexible framework within which regions could choose which metals, pesticides and other organic compounds to analyse for. It was proposed to do this on a land-use basis, and a draft list relating determinand choice to simplified major land-use categories was proposed.

2.5.2 Frequency

The recommendations made in 1994 for sampling frequencies and determinand suites are shown in Table 2.10. It was considered that, as a general principle, all determinands should be measured in the National Network at some time. Suites 1 to 6 inclusive would be analysed. Subsequently the major ion and land-use specific determinands would be analysed at reasonably frequent intervals, whilst the full suites of minor ions and organic pollutants would be re-analysed regularly but less frequently.

Frequencies for the Reference network were approximately twice those suggested for the National Network in recognition of the role of the Reference network sites in providing high quality time series data to meet the objectives of trend detection and baseline definition. The suggested frequencies also took account of the variation in aquifer characteristics. This combination of different targeted suites and frequencies was designed to allow monitoring effort to be realistically focussed on those determinands which are likely to cause the main problems while allowing the broad range of monitoring necessary to meet the objectives of spatial distribution and early warning.

Table 2.9 Determinand suites for water quality assessment in BGS approach (Chilton and Milne, 1994)

Suite		Determinands
1.	Field parameters	Temperature, pH, DO, (EC)
2.	Major ions	Ca, Mg, Na, K, HCO_3^-, Cl^-, SO_4^{2-}, PO_4^{3-}, NH_4^+, NO_3^-, NO_2^-, TOC, EC, ionic balance
3.	Minor ions and List II substances	Choice depends partly on local pollution sources as indicated by land-use framework
4.	Organic compounds	Aromatic hydrocarbons, halogenated hydrocarbons, phenols, chlorophenols. Choice depends partly on local pollution sources as indicated by land-use framework
5.	Pesticides	Choice depends in part on local usage, land-use framework and existing observed occurrences in groundwater.
6.	Bacteria	Total coliforms, faecal coliforms

Table 2.10 Sampling frequencies and determinand suites in BGS approach (Chilton and Milne, 1994)

Network	Aquifer	Condition		Determinand suites					
				1. Field	2. Major	3. Minor	4. Organic	5. Pesticides	6. Bacteria
Reference	Major					Determinands targeted at specific land-uses at same frequency as major ions, others at:			
		slow flow	unconfined	< . . . . .twice yearly . .. . >		< . . . . annually . . . . >			
		slow flow	confined	< . . . . . . .annually. . . . . . >		< . . . . every two years . . . .>			
		fast flow	unconfined	< . . . . . .quarterly. . . . . . >		< . . . . twice yearly . . . .>			
		fast flow	confined	< . . . . .twice yearly. . . . . >		<. . . . . annually . . . .>			
National	Major					Determinands targeted at specific land-uses at half frequency as major ions, others at:			
		slow flow	unconfined	no	twice yearly	< . . . . every two years . . . . >			
		slow flow	confined	no	annually	<. . . .. every five years . . . .>			
		fast flow	unconfined	no	quarterly	< . . . . annually . . . .>			
		fast flow	confined	no	twice yearly	<. . . . . every two years . . . .>			
	Minor	alluvium		no	quarterly	< . . . . annually . . . . >			
		others		no	twice yearly	<. . . . . every two years . . . .>			
Local	Landfills			monthly	quarterly	< . . . . site specific . . . . >			
	Others			< . . . . site specific . . . . >					

2.6 The ESI Approach

As already summarised in section 2.1, ESI were commissioned to review and report on the current status of groundwater quality monitoring in the Agency regions (ESI, 2001a). Additionally they were required to identify the resources required by the Agency to implement the developing groundwater strategy. For this purpose, ESI used the approach proposed by the Agency's National Groundwater and Contaminated Land Centre (NGWCLC). This adapted the original BGS determinand classification, taking recommendations from the EUROWATERNET approach, in order to make estimates for the cost implications of implementation of the strategy. The sampling frequencies used by ESI are also similar to those of the earlier BGS approach, but without the distinction between Major and Minor aquifers (ESI, 2001c). Their revised approach is summarised in Tables 2.11 and 2.12.

Table 2.11 Determinand suites proposed by NGWCLC for water quality assessment

Suite		Determinands
Standard	Field parameters	Temperature, pH, DO, EC
	Major ions	Ca, Mg, Na, K, HCO_3^-, Cl^-, SO_4^{2-}, PO_4^{3-}, NH_4^+, NO_3^-, NO_2^-, TOC
	Additional	Specified target determinands identified during initial characterization which show concentrations above the background (e.g. specific contaminants)
Selective	Heavy metals	As, Hg, Cd, Pb, Cr, Fe, Mn, Zn, Cu, Al, Ni
	Organic compounds	Aromatic hydrocarbons, halogenated hydrocarbons, phenols, chlorophenols, MTBE.
	Pesticides	Land-use, environment and property (e.g. mobility) dependent
	Additional	Other target determinands, other List II substances and microbiological contaminants

Table 2.12 Sampling frequencies proposed by NGWCLC for water quality assessment

Aquifer	Flow type	Condition	Determinands	
			Standard	Selective
Major/Minor	Slow	Outcrop	6 monthly	every 2 years
	Slow	Confined	annually	Every five years
	Fast	Outcrop	3 monthly	Annually
	Fast	Confined	6 monthly	every 2 years

3. MONITORING TECHNIQUES

3.1 The use of field determinations

Field chemistry provides several important advantages over laboratory analysis in the interpretation of hydrochemical data and can be considered as essential. It can provide:

- a more rapid measurement of determinands which are sensitive to changes in chemistry due to degassing, ingassing or temperature such as dissolved oxygen and redox potential;
- an additional Quality Assurance (QA) check for conductivity in cases of sample contamination or misidentification;
- a rapid indication at the time of sample collection of major changes in groundwater composition.

Changes in the concentration of chemical species during the collection, transport and shelf life of groundwater samples prior to laboratory analysis are the major potential sources of error or bias in laboratory-analysed samples. These chemical changes are commonly caused by changes in the partial pressure of carbon dioxide (CO_2) gas and water sample temperature. A number of studies have documented the effects of CO_2 degassing on groundwater samples (Wallick, 1977, Schuller, 1981, Shaver, 1993) with significantly decreased concentrations of H^+ (leading to higher pH), Ca^{2+} and HCO_3^- being demonstrated.

The inclusion of oxygen status in the list of required determinands in the WFD suggests that some field analysis will be inevitable. Table 3.1 shows a summary of the advantages and practical disadvantages of various field techniques. There are many published field methodologies (e.g. Cook *et al.,* 1989; Walton-Day *et al.,* 1990; White *et al.,* 1990). There have also been a number of concerns expressed about the reliability of field analysis data and difficulties with Quality Control (QC) and QA issues. The use of field determinations also has considerable implications for the time required to visit individual sites and therefore of staff resources and overall costs. Particular issues which would need to be addressed are consistency of approach between the Agency regions, training of sample collection personnel and health and safety. It may also be difficult to achieve a consistency of approach between Agency and water utility sampling.

The use of field determination of unstable parameters is however strongly recommended and would require the development for the Agency by the NLS of suitable protocols to do this Such protocols would also need to deal with the issues of field instrumentation, sample filtration, preservation of samples for laboratory analysis and the time interval between sampling and analysis.

3.2 *In-situ* techniques

A number of *in-situ* (or on-line) techniques have been developed, mainly for the real-time monitoring of wastewater quality or for surface water intake for public supply (Table 3.2). There has also been recent interest in turbidity and particle counting and size analysis related to the difficulties of assessing the risk to groundwater supplies from *Cryptosporidium* oocysts (Hall and Croll, 1997; Gregory, 1998; UKWIR, 2000).

Table 3.1 Evaluation of field chemistry determinands and techniques.

Determinand	Application	Field techniques	Advantages	Disadvantages
Dissolved oxygen	• Changes in the redox status of the aquifer • Control on mobility of metals • Influence on microbial activity and hence to contaminant fate	• Potentiometric (oxygen-sensitive polarographic membrane electrode)	• Simple • Reliable	• Needs flow through cell • May be slow
		• Titrimetric (Winkler) using iodine and thiosulphate	• Reliable	• Higher detection limit
		• Colorimetric (ampoule kit using Rhodazine-D)	• Simple • Rapid • Low detection limit	• Expensive for large number of determinations • Semiquantative
Temperature		• Digital thermometer	• Simple • Inexpensive	
pH	• Limited direct value for monitoring but may change on degassing/ aeration of sample	• Potentiometric	• Inexpensive • Simple	
Redox potential (Eh)	• Changes in the redox status of the aquifer • Control on mobility of metals • Influence on microbial activity and hence to contaminant fate	• Potentiometric (platinum electrode)	• Avoids direct measurement of redox sensitive species	• Needs flow through cell • May be slow • Not always reliable due to electrode contamination or exposure to high dissolved oxygen • Not responsive to all reactions
Electrical conductivity (EC)	• Rapid indication of bulk changes to quality • QA check on laboratory analyses and sample contamination	• Potentiometric (conductivity cell)	• Simple	• Less accurate than laboratory test
Alkalinity	• Part of major ion suite and may change	• Digital titrator		• Requires relatively large volume of

	on degassing/ aeration of sample		filtered sample
Qualitative observations	- Olfactory - Turbidity	- Observation	- Non-quantitative

Table 3.2 Examples of on-line monitoring techniques for water quality

Class	Determinand	Technique	Limit of detection	Reference
General	Tubidity	Light scattering	<0.1 NTU	Gregory, 1998
	Particle size counting	Electrozone sensors Optical sensors		Gregory, 1998
	Conductivity			
Nitrogen species	Nitrate Nitrite	Sequential injection and spectrophotometry	<0.05 mg/l <0.05 mg/l	Lapa *et al,* 2000
Global organic determinands	BOD COD TOC	Biosensors, optical sensors, electronic noses		Bourgeois *et al,* 2001
Pesticides	Acid herbicides	Solid phase extraction / liquid chromatography	< 1µg/l	Drage *et al*, 1998
	Triazines and phenyl urea herbicides	FIIAA		Kramer, 1998

FIIAA = flow injection immunoaffinity analysis

These techniques are designed to detect very rapid changes in the monitored water and are clearly able to produce very large amounts of data. They may be important in karstic environments, particularly with regard to bioparticles, and for depth profiling. However, they may have less applicability to the timescales required for the assessment of baseline conditions and long-term trends required under the WFD where a rapid data turnaround is not required. Many of the techniques, for example some of those described by Bourgeois *et al* (2001), are still in the development stage and are considered as novel. It is also considered that these techniques are probably too expensive to use other than for special intensive investigations.

3.3 Laboratory techniques

3.3.1 Test kits

ELISA (Enzyme-linked immuno-sorbent assay)

ELISA is an analytical method which relies on the specific interaction between antibodies and antigens to measure a variety of substances. A target compound is detected by an antibody which binds only to that substance. The binding efficiency can be designed to permit measurements below the picogram level (Van Emon and Mumma, 1990). The technique therefore allows for a rapid analysis of large sample sets at relatively low cost. Immunoassays can be either a qualitative or quantitative test but are currently used primarily as a screening technique. They are well suited to this since it is very rare for them to give a false negative (Barbash and Resek, 1996).

ELISA methods provide a comparatively inexpensive way to detect the presence of one or more analytes in a particular class but they may not detect particular individual compounds within the class of interest. Interference effects arise from unknown levels of related parent compounds and metabolites. ELISA has been used for the analysis of the major crop herbicides in the USA both as a quantitative tool and as a screening method to reduce sample load for conventional analysis (Barbash and Resek, 1996). In a study of herbicide migration into the Chalk aquifer, Gooddy *et al* (2001) found that the advantages of ELISA rather than solid phase extraction (SPE) followed by High-Performance Liquid Chromatography (HPLC) separation with Ultra Violet (UV) detection is that a considerably smaller volume of water is required for analysis.

ELISA methods are available for the compounds or groups of compounds shown in Table 3.3. Kits are available for commonly found pesticides in UK groundwaters, such as atrazine, chlorotoluron, diuron, isoproturon, mecoprop and 2,4-D. An example of typical specifications of an atrazine test is shown in Table 3.4.

Table 3.3 Pesticides with published ELISA methods

Group	Compounds with published ELISA method
Triazine herbicides	Atrazine, cyanazine,
Carbamate insecticides	Aldicarb, carbaryl, carbofuran, methiocarb, methomyl, propoxur
Phenoxyalkanoic herbicides	2,4-D, mecoprop
Urea herbicides	Fluometuron, isoproturon, metsulfuron
Organophosphorus insecticides	Chlorofos ethyl, chlorpyrifos,
Acetanilide herbicides	Acetochlor, alachlor, alachlor ESA metolachlor,
Dinitroanaline herbicides	Trifluàlin,
Organochlorine compounds	Chlorothalonil, cyclodienes, DDT (triclopyr)
Bipyridyl herbicides	Paraquat
Imidazolinone herbicides	Imazaquin, (imazapyr)
Amino acid derivative herbicide	(Glyphosate)

from: www.cee.vt.edu/program_areas/environmental/teach/smprimer/immuno, www.ks.cr.usgs.gov/kansas/reslab/elisa, McMahon 1993, Abad *et al.* 1999, Walker *et al.* 2000, Alcocer *et al.* 2000, Maestroni *et al.* 2001, Pennington *et al.* 2001.

3.3.2 Analytical limits of detection

The WFD does not specify suitable limits of detection for groundwater parameters. The greatest difficulties in defining such limits are related to the detection limits for pesticides. Under the Drinking Water Directive the current Maximum Admissible Concentration for individual compounds is 0.1µg/l and for total pesticides is 0.5µg/l. The obligation to be able to analyse for such compounds in water to sufficiently low concentrations to ensure that the limit is met has led to the rapid development of suitable techniques for most pesticide compounds.

Table 3.4 Specifications for an ELISA test kit for atrazine

Determinand	Specification
Limit of detection (µg/l)	0.03
Range (µg/l)	0 – 2.5
Degree of cross-reaction where atrazine = 100 %	Propazine 35.7 Promethyn 29.4 Simazine 16.6 Atrazine desethyl 2.9 Non-triazine <0.001

For surface waters the criteria for ecological status include physico-chemical criteria as shown in Table 3.5. These clearly specify that synthetic organic pollutants must be quantified by the most advanced analytical techniques in general use. It would therefore be reasonable to assume that such techniques will be required for groundwaters. A suitable technique should be able to detect at least one order of magnitude below the appropriate detection limit. For example, for pesticides, methods with analytical limits of detection of 0.01µg/l or less would be required.

3.4 Indicators

An intriguing and much discussed possibility is the prospect of using a limited set of indicator determinands to represent groundwater quality. This concept is attractive because of its potential for savings in analytical costs and its consistency with the use of indicators in surface water monitoring for the establishment of indices. The possibility of using indicators more widely has been considered by BGS (Edmunds, 1996) and was also reviewed in the preparation by UN Economic Commission for Europe (ECE) of Guidelines on Transboundary Monitoring (1999), in which the BGS project team leader participated. It is, however, more difficult to choose suitable indicators for groundwater quality than surface water, and the combination of the Agency's multiple monitoring objectives and the broad statutory framework outlined above both imply the need for extensive suites of determinands.

Indicators have two roles:

- to indicate which other pollutants may be present;
- to indicate the source of the pollution.

Barbash and Resek (1996) were not able to identify any useful candidates in a review of the use of other solutes as indicators of pesticide occurrence in groundwater potentially affected by agrochemical use. They found that nitrate concentrations were generally unreliable predictors of pesticide concentration apart from in a few cases, although the likelihood of detecting pesticides in groundwater does increase with increased nitrate concentration in some cases. The lack of satisfactory correlation may depend on the very different rates of migration in the subsurface of nitrate and many pesticides compounds, and the ready reduction of nitrate in the absence of oxygen whereas pesticides tend to be recalcitrant.

Table 3.5 Physico-chemical criteria for ecological status in surface waters from Water Framework Directive

Determinand	Status		
	High	Good	Moderate
General	Physico-chemical elements correspond totally or nearly totally to undisturbed conditions. Nutrient concentrations remain within the range normally associated with undisturbed conditions. Temperature, oxygen balance and transparency do not show signs of anthropogenic disturbance and remain within the range normally associated with undisturbed conditions.	Temperature, oxygenation conditions and transparency do not reach levels outside the ranges established so as to ensure the functioning of the ecosystem and the achievement of the values specified for the biological quality elements. Nutrient concentrations do not exceed the levels established so as to ensure the functioning of the ecosystem and the achievement of the values specified for the biological quality elements.	Conditions consistent with the achievement of values specified for the biological quality elements.
Specific synthetic pollutants	Concentrations close to zero and at least below the limits of detection of the most advanced analytical techniques in general use.	Concentrations not in excess of the standards set in accordance with the procedure detailed in section 1.2.6 without prejudice to Directive 91/414/EC and Directive 98/8.	Conditions consistent with the achievement of values specified for the biological quality elements.
Specific non synthetic	Concentrations remain within the range normally	Concentrations not in excess of the standards set	Conditions consistent with the

pollutants	associated with undisturbed conditions.	in accordance with the procedure detailed in section 1.2.6 without prejudice to Directive 91/414/EC and Directive 98/8.	achievement of values specified for the biological quality elements.

Tritium was found to be a potentially useful indicator for waters recharged before the 1950s where no pesticides were detected in water which lacked detectable tritium, but was of limited utility for more recent waters.

The presence of one or more pesticides at detectable levels was also found to be associated with an increased likelihood that other pesticides will be present, for areas of the USA where a restricted range of crops were rotated.

Ideal marker species for particular activities were defined by Rivers *et al.* (1996) as having the following characteristics:

- present only in one recharge source;
- detectable in both groundwater and in recharge source water;
- present in water which indicates recharge from a specific source.

In reviewing the impact of urban areas on groundwater quality Lerner and Barrett (1996) compared the concentrations of a range of inorganic determinands in the rural and urban parts of the area centred on Coventry. Those with the largest ratios (Figure 3.1), especially chloride, zinc and boron, were considered to be the most useful indicators of urban influence, although they might not identify the precise source of pollution. Similar concentrations of boron in Birmingham groundwaters appeared to be due to the use of boric acid in metal working (Ford and Tellam, 1994), and were also associated with chromium and nickel. In a study of the urban geology of the Wolverhampton area, samples from the urban part of the Triassic sandstone aquifer showed strong positive correlations between chloride, nitrate and boron as compared to rural. The urban areas also had elevated concentrations of heavy metals (Hooker *et al.,* 1999).

Elsewhere it is possible that high boron will result from domestic sewage pollution and be associated with a different range of pollutants. For Nottingham, Barrett *et al.* (1999) suggested that faecal indicator bacteria and nitrogen speciation had potential as marker species. Viruses are also more commonly distributed than previously thought (Powell *et al.,* 2001). It therefore seems reasonable to include boron, selected trace metals and faecal bacteria as well as nitrogen species in a programme of operational monitoring.

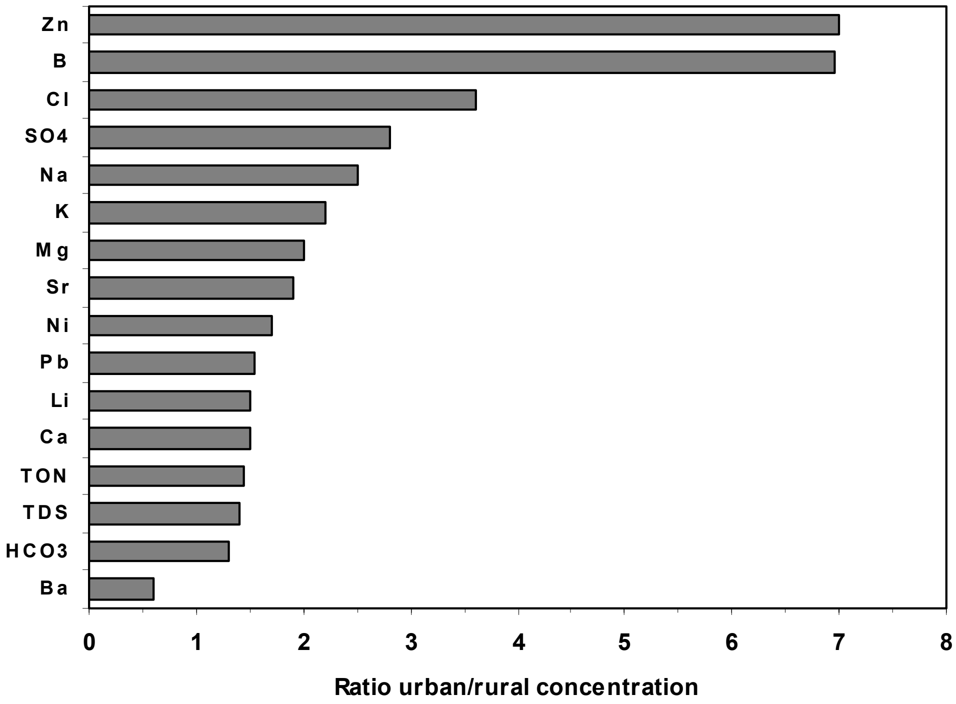

Figure 3.1 Ratio of various inorganic species in groundwater beneath urban and rural parts of the Coventry area (Lerner and Barrett, 1996)

In principle, relying on one pollutant to indicate the presence of others must be dangerous since groundwater systems are potentially very fractionating and, in addition, pollutant sources are not always sufficiently uniform in composition to be sure one pollutant will always be associated with another. However, the use of species to indicate sources of pollution is common to many contamination studies and raises the possibility of using diagnostic parameters which are not necessarily themselves directly important as pollutants.

4. APPLICATION OF STATISTICS TO MONITORING FREQUENCY

4.1 Statistical approach

In the literature, statistical techniques have been applied to monitoring design for network optimisation and to test whether sampling frequency is adequate to detect specified changes in concentration. Only the second is of concern here, and was partly investigated by Water Research Centre (WRc) (Clark, 1992) in their earlier review of groundwater monitoring for the NRA.

To determine the optimal measurement frequency, the relationship between estimation uncertainty and measurement frequency is one of the key issues. Sampling frequency can be optimised with respect to several aspects of a dataset relating to groundwater quality evolution. The most important aspects are:

- influence of sampling frequency on the accuracy of the estimation of the mean concentration of a chemical determinand;

- influence of the sampling frequency on the ability to detect a trend in a dataset and the accuracy with which this trend is estimated.

Both aspects were investigated with respect to one observation point in the following sections. Recently, relevant research was carried out on the simultaneous optimisation of sampling frequency taking into account more observation points and their spatial dependence. Within a groundwater body selecting specific sites with higher sampling frequencies while most other sites are less frequently sampled seems intuitively efficient and cost effective. However, combining sampling frequency and spatial dependence was not within the scope of the project. The possible desirability of developing tiered networks to meet the multiple objectives of monitoring was also suggested by BGS in the 1994 study.

For the statistical analysis the following approach was taken:

- identification of characteristics in groundwater quality data series which are likely to influence optimal sampling frequency (e.g. seasonality, trends, variance, observation period);

- selection of existing datasets of chemical determinands provided by the Agency, for which these characteristics are clearly observed;

- estimation of optimal sampling frequency by applying a direct statistical method or by applying statistical measures on sub-sets generated by assuming different sampling frequencies from highly sampled datasets.

4.2 Techniques applied for statistical analysis

The techniques used are only described in brief in this paragraph. In Appendix 1 a detailed description of the applied techniques is given and reference to the specific literature is made.

4.2.1 Influence of sampling frequency on the accuracy of calculation of the mean

The accuracy of the estimated mean is of high importance since it will allow determination of whether a measured concentration is within the natural range or must be seen as exceptionally high. A direct approach was applied to establish a relationship between sampling frequency and accuracy of the mean based on a method described by Loftis and Ward (1980). This method was applied to all the test datasets.

4.2.2 Influence of sampling frequency on trend detection in a dataset

No direct method to establish a relationship between trend detection, accuracy of this trend and sampling frequency is available from the literature; therefore a practical approach was taken. Subsets based on different sampling frequencies were taken from the original datasets in which a trend was present and non-parametric statistics (Mann-Kendall test) were applied to estimate the slope of the trend and the accuracy of the slope in the selected subsets. Additionally, the variability of the slope and the width of the confidence interval around the slope were evaluated using different subsets of the original datasets with the same sampling frequency.

4.3 Datasets selected for the analysis

The datasets consisting of time series data for different determinands in different aquifers were provided by the Agency. A selection of the data available was carried out based on the following criteria:

- adequate length of the dataset;
- more or less constant sampling interval;
- characteristics of the dataset: presence of seasonality, outliers, trends.

The time series were chosen so that they represent a maximum variety in characteristics of groundwater quality data. The number of cases modelled was limited by the availability of the data and the allocated time.

The selected datasets are listed in Table 4.1 and presented graphically in Appendix 1 together with the autocorrelation graphs which indicate the presence of seasonality. Two datasets were selected for the Jurassic Limestone. These datasets are for the same spring (Old Chalford) and consist of total oxidised nitrogen (TON) and chloride measurements respectively. For these two datasets the influence of the sampling frequency on the detection of monotonic trend was evaluated. The TON dataset selected from the Chalk (Ogbourne) showed a high seasonality and was analysed both including and excluding the seasonality. One TON dataset (Armthorpe 2) was selected for the Sherwood Sandstone. For all the datasets the influence of the sampling frequency on the confidence limits around the mean were calculated and interpreted. Two of the datasets showed a clear trend: in the Armthorpe 2 dataset an upward trend was visible while in the Old Chalford TON dataset a downward trend was suggested.

Table 4.1 Characteristics of the data selected for statistical analysis.

	Name	Aquifer type	Determinand	Length	Sampling frequency	Remarks
1	Old Chalford Spring no 11	Great Oolite Jurassic Limestone	TON	10 years	Approx every 14 days	Spring data
2	Old Chalford Spring no 11	Great Oolite Jurassic Limestone	Chloride	10 years	Approx every 14 days	Spring data
3	Ogbourne (UKPGWU 1035)	Chalk	TON	10 years	Irregular, mostly less than 7 days	
4	Ogbourne (UKPGWU 1035)	Chalk	TON	10 years	Irregular, mostly less than 7 days	Deseasoned data
5	Armthorpe 2	Sherwood Sandstone	TON	9.5 years	Irregular, mostly less than 7 days	

4.4 Results

All the results were obtained using the following software packages: Excel (Microsoft) and Splus2000 including the Splus Environmental Statistics addin (Insightfull).

4.4.1 Influence of the sampling frequency on the width of the confidence limits around the mean

The results are listed in Table 4.2 and the graphs for the different datasets are shown in Figures 4.1 to 4.5. As a rapid overview the percentage increases in confidence intervals for different sampling frequencies (weekly, monthly, 6 monthly) are shown in Figure 4.6.

The following observations can be made:

- The width of the confidence limits is large in comparison to the mean concentration and depends strongly on the variance of the dataset. For most of the sampling frequencies the width of the confidence interval exceeds half of the mean concentration;

- For the strongly seasonal dataset of the Chalk (Ogbourne), increasing the sampling interval leads to a steep increase in the width of the confidence interval from around 27 % of the mean when sampling at a weekly interval to 82% of the mean concentration when sampling at 6 months intervals;

- When the seasonality is removed from the Chalk data, not only does the trend in increasing width of the confidence interval seem to remain, but also the percentage increases are similar. This indicates that, although the datasets show a seasonal pattern at first sight, this pattern might be extremely difficult to eliminate statistically;

The increase in the width of the confidence limits with decreasing sampling frequency is minimal for the time series with little seasonality. For example for the Armthorpe dataset the width of the confidence interval decreases by only 2 % of the annual mean when the sampling frequency is increased from 6-monthly to weekly. The shape of the curve indicates that when one wants to reduce the width of the confidence interval significantly, very frequent sampling (probably every few days) will be necessary.

Table 4.2 Results of the analysis of influence of sampling frequency on width of the confidence limits around the mean

	Old Chalford Spring no 11	Old Chalford Spring no 11	Ogbourne UKPGWU 1035	Ogbourne UKPGWU 1035 (deseasoned)	Armthorpe 2
Aquifer Type	Great Oolite, Jurassic	Great Oolite, Jurassic	Chalk	Chalk	Sherwood Sandstone
Determinand	Total oxidized N (mg/l)	Chloride	Total oxidized N (mg/l)	Total oxidized N (mg/l)	Total oxidized N (mg/l)
Type of ARMA* model fitted	ARMA(1,1)	ARMA(1,1)	ARMA(2,0)	ARMA(2,0)	ARMA(2,0)
Mean concentration	13.33	25.38	9.499	9.499	12.18
Variance	3.439	20.89	5.459	4.687	0.750
Correction for seasonality	-	-	-	Yes	-
Correction for outliers	-	-	-	-	2 outliers excluded
Correction for trends	-	-	-	-	-
Confidence Interval (weekly sampling)	n.a.	n.a.	2.60	2.26	3.19
	n.a.	n.a.	27 %	24 %	26 %
Confidence Interval (monthly sampling)	7.075	17.11	4.85	4.25	3.34
	53 %	67 %	51 %	45 %	27 %
Confidence Interval (6 monthly sampling)	7.203	17.3	7.87	7.12	3.38
	54 %	68 %	82 %	75 %	28 %

*ARMA – Auto-regressive moving average model

n.a.: - not applicable

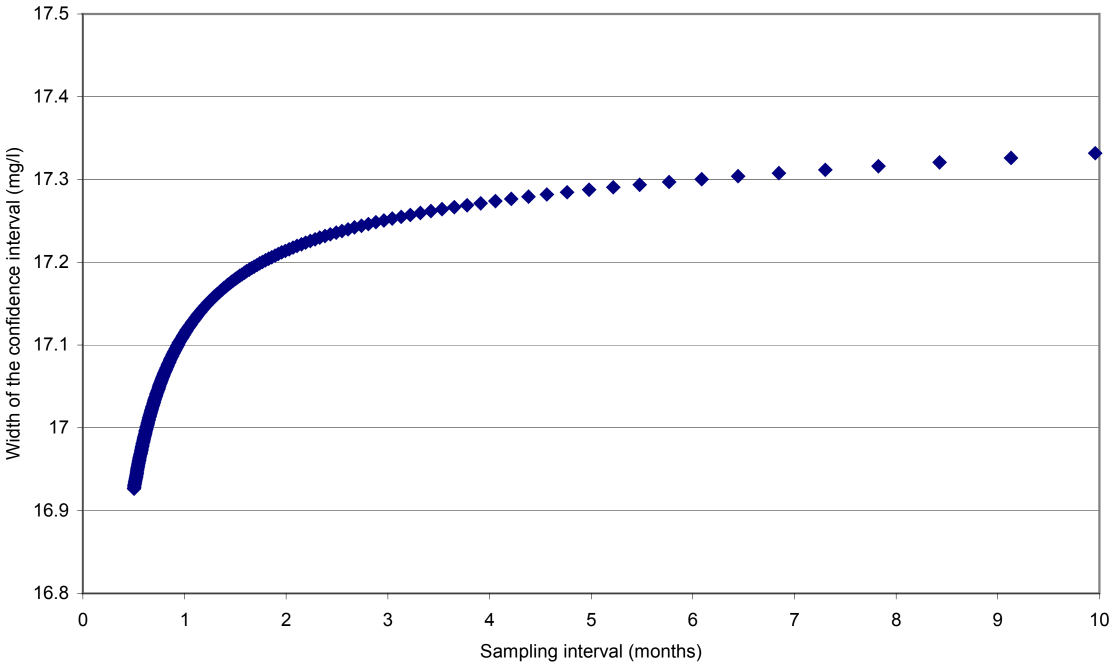

Figure 4.1 Chloride data for Old Chalford Spring 11 (Jurassic Limestone); width of the confidence interval around the mean as a function of sampling frequency

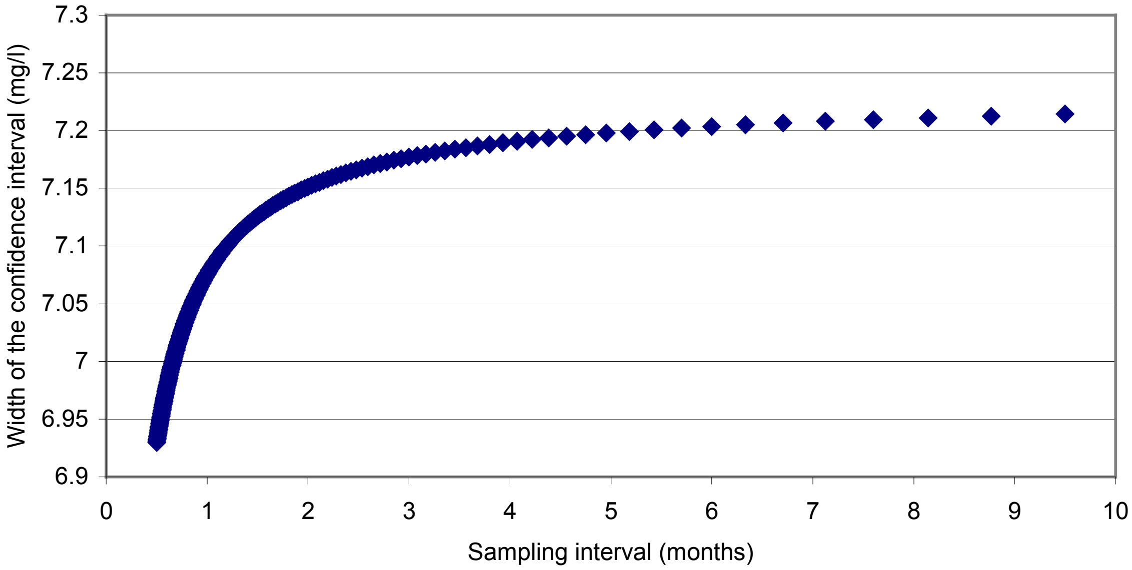

Figure 4.2 TON data for Old Chalford Spring 11 (Jurassic Limestone); upper: autocorrelation graph (lag=2 weeks); lower: width of the confidence interval around the mean as a function of sampling frequency

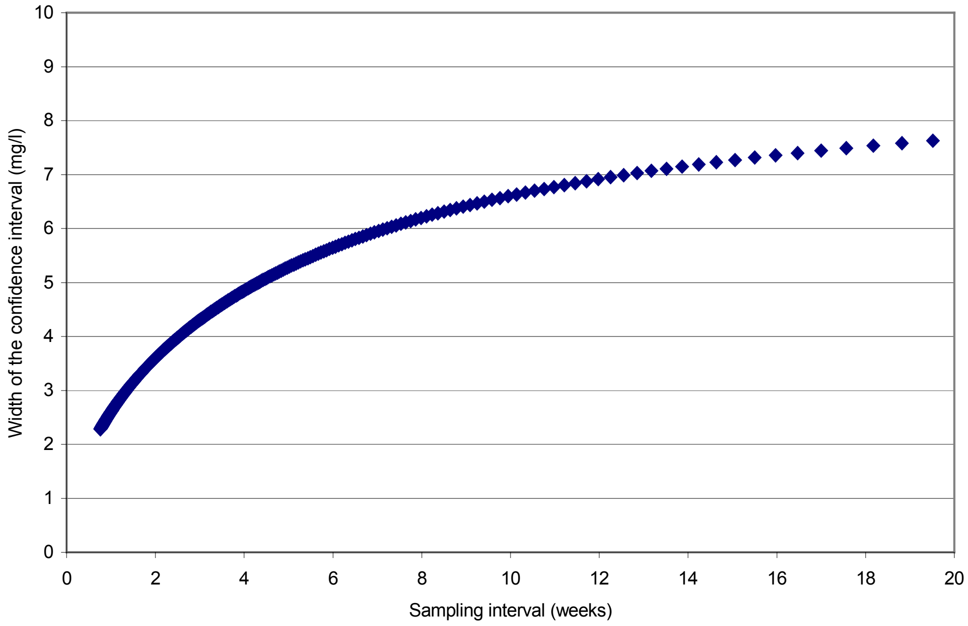

Figure 4.3 **TON data for Ogbourne (UKPGWU1035, Chalk): width of the confidence interval around the mean as a function of sampling frequency**

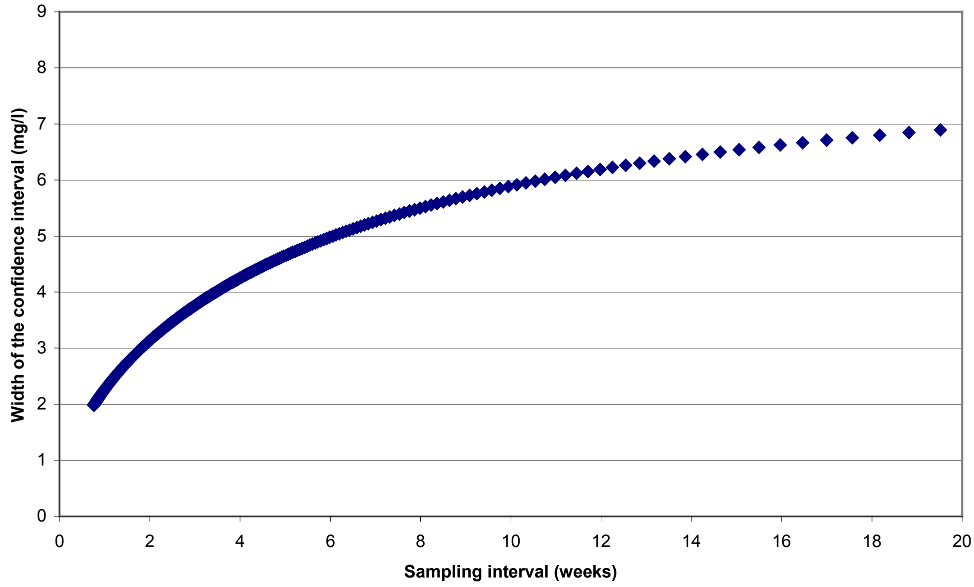

Figure 4.4 **TON data for Ogbourne (UKPGWU1035, Chalk) whereby the seasonality was eliminated; width of the confidence interval around the mean as a function of sampling frequency**

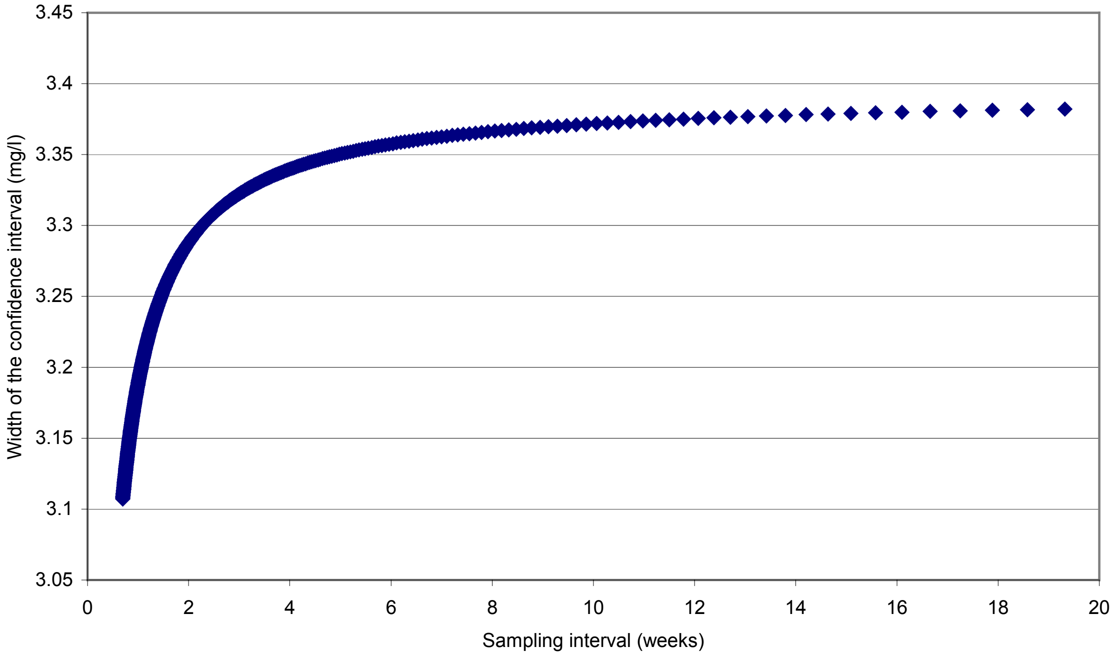

Figure 4.5 TON data for Armthorpe 2 (Sherwood Sandstone); width of the confidence interval around the mean as a function of sampling frequency

4.4.2 Influence of the sampling frequency on the detection of an existing trend

The results for the Mann-Kendall test analysis are shown in Figure 4.7 for the Old Chalford Spring TON dataset and Figure 4.8 for the Armthorpe 2 dataset. The width of the confidence intervals of the slope expressed as the percentage of the slope for both datasets are shown in Figure 4.9.

The following observations can be made:

- In both cases the choice of sampling interval does not influence the detection of the presence of a positive or negative slope;

- The slope can change significantly depending on the sampling frequency, the trend can become more or less steep when the sampling interval increases;

- When using different subsets from the same dataset with the same sampling frequency, the width of the confidence interval varies more in the case of the Armthorpe 2 dataset than for the Old Chalford Spring 11 TON dataset;

- Also the shape of the curve relating the width of the confidence intervals of the slope to the sampling interval is different in the two cases: while for the Armthorpe data a steady increase in confidence interval width can be observed, for the Old Chalford 11 data a plateau is reached at a sampling interval of around 10 weeks;

- The width of the confidence interval of the slope increases quickly with decreasing sampling frequency: for both datasets a value of over 100% is reached when the sampling interval increases to 3 months.

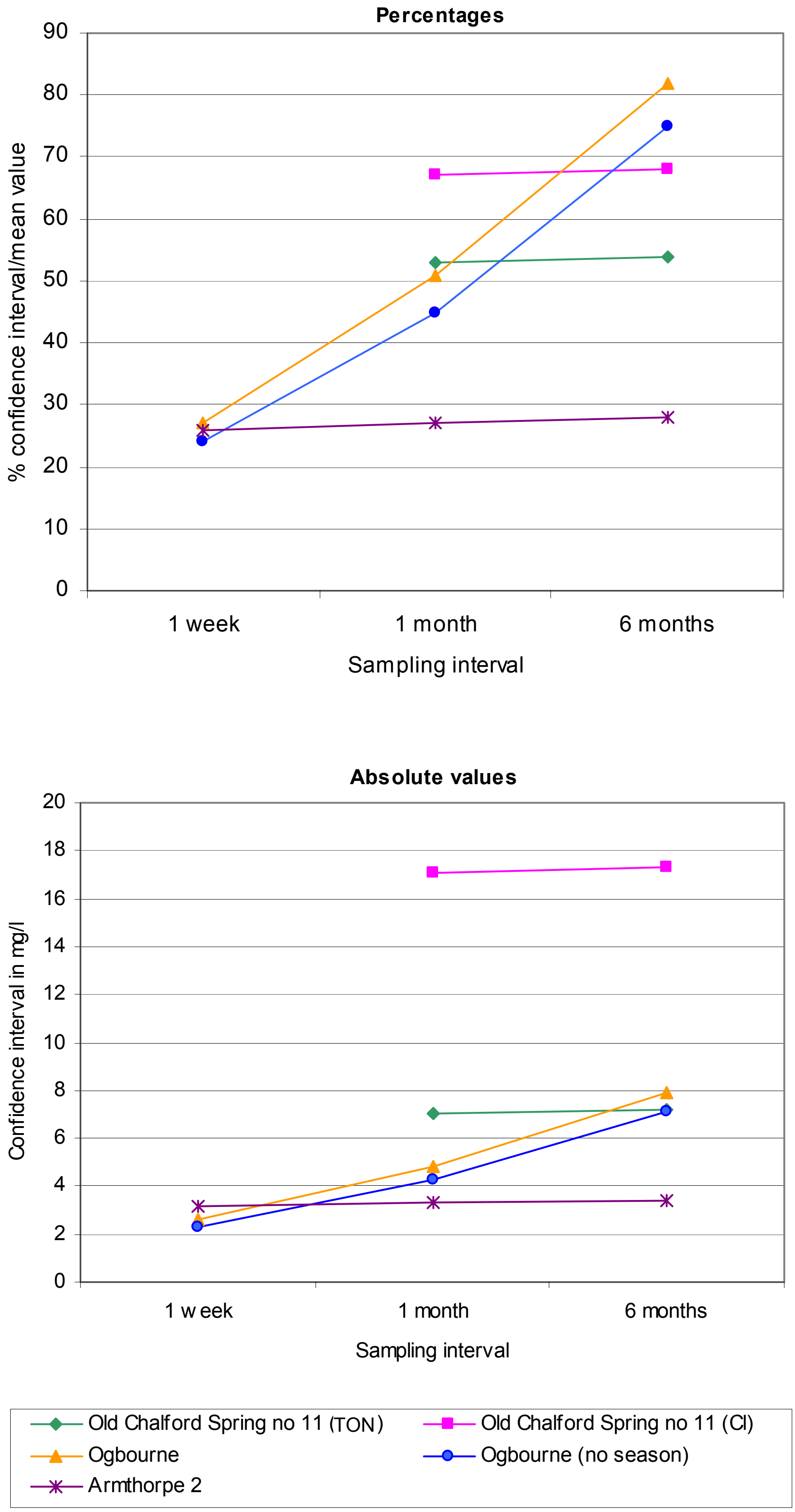

Figure 4.6 Width of the confidence interval for all the datasets for a weekly, monthly and 6 monthly sampling interval; upper: expressed as the percentage of the mean concentration; lower: absolute values in mg/l

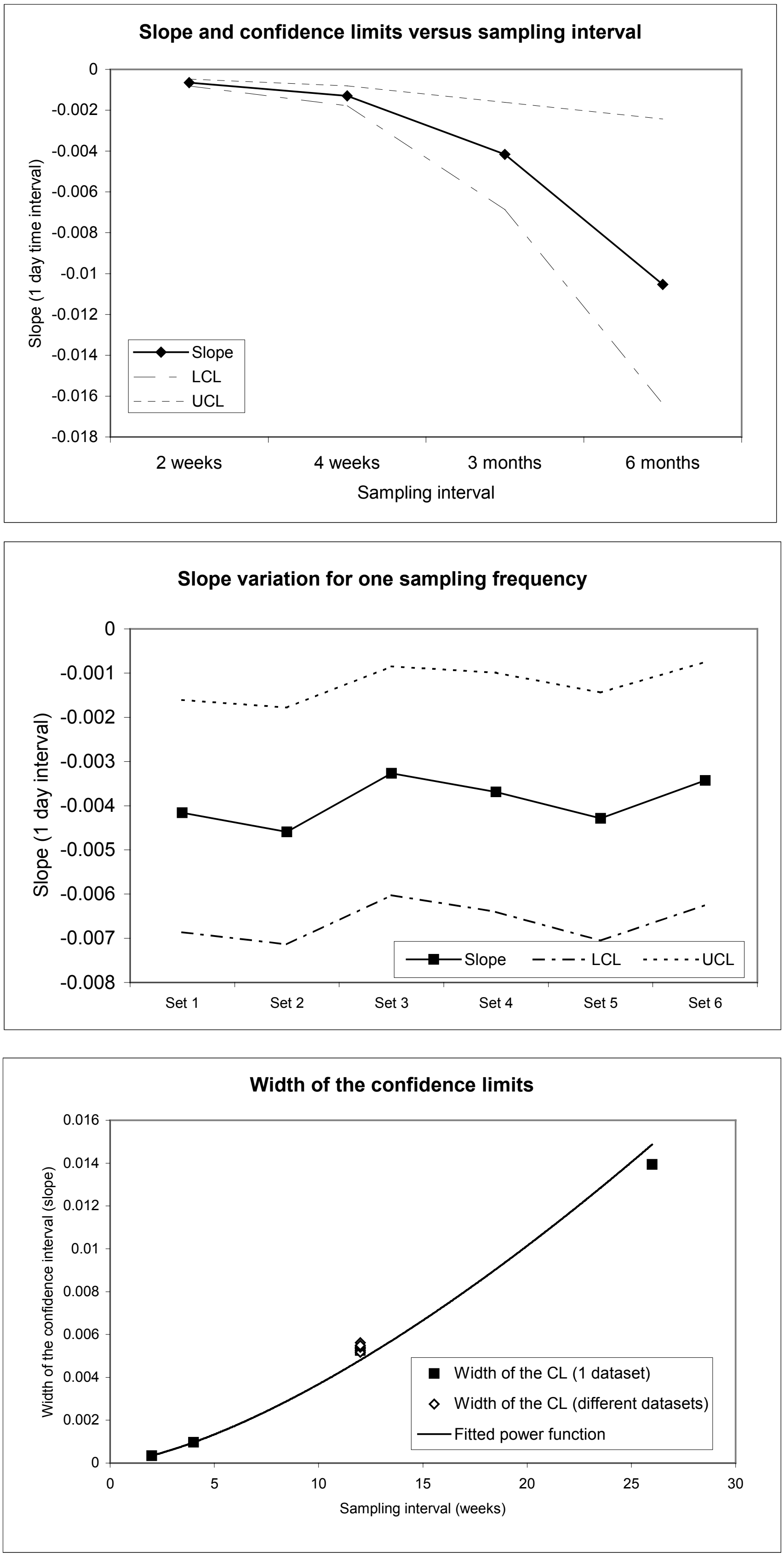

Figure 4.7 TON data for Old Chalford Spring 11 (Jurassic Limestone); upper: slope and confidence limits versus sampling interval; middle: slope variation for one sampling frequency; lower: width of the confidence interval versus sampling interval

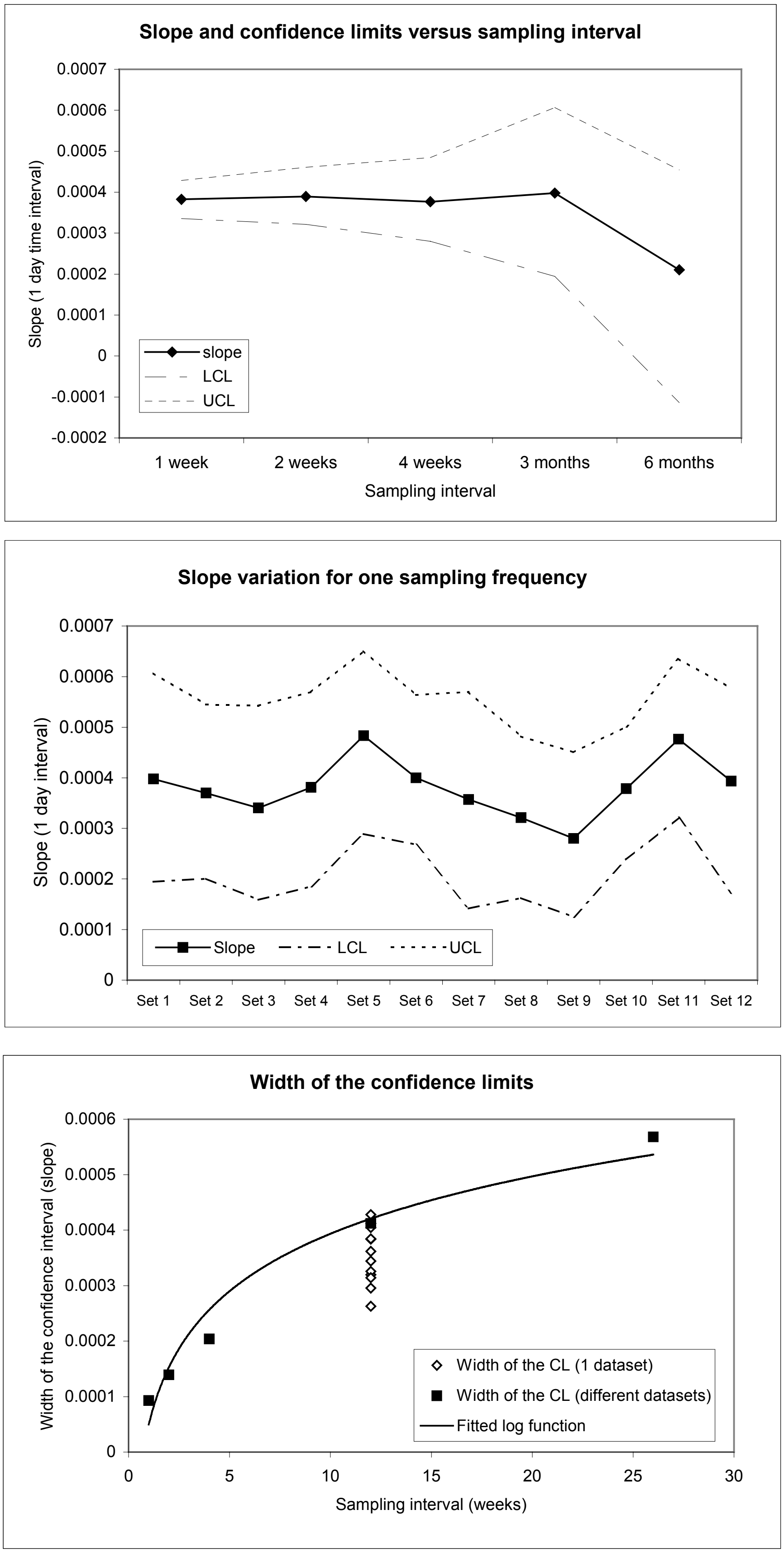

Figure 4.8 TON data for Armthorpe 2 (Sherwood Sandstone); upper: slope and confidence limits versus sampling interval; middle: slope variation for one sampling frequency; lower: width of the confidence interval versus sampling interval

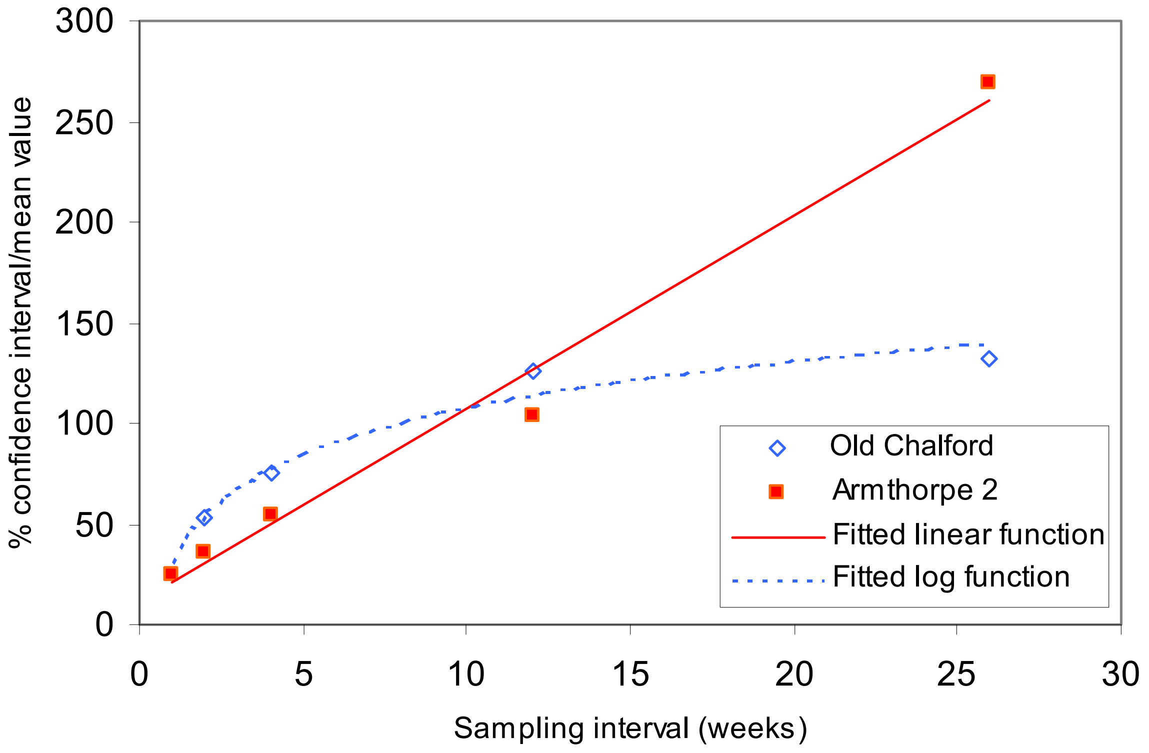

Figure 4.9 Width of the confidence interval of the slope of a detected linear trend expressed as the percentage of the slope

4.5 Conclusions

The following conclusions are based on the limited number of datasets used for this analysis only. It is possible that, when using other datasets, these conclusions will have to be revised since it is unclear how representative these datasets are. It is however expected that these conclusions can act as general guidelines when assessing optimal sampling frequencies.

4.5.1 Confidence in the mean concentration

- The confidence interval around the mean concentrations for all tested datasets appears to be large: approximately 25% when sampling weekly, increasing to 50% in most cases when sampling monthly.

  This means that exceptionally high concentrations can only be identified as such when they are at least 25% higher than the mean concentration in the case of weekly sampling and more than 50% higher in the case of monthly sampling.

- The confidence interval around the mean concentration is strongly dependent on the variance of the dataset. If datasets are characterised by a large variance, the chosen sampling frequency should be greater than for datasets characterised by a small variance.

  This means that when datasets show a large variation in measured concentrations an exceptionally high concentration will be much more difficult to identify and will require higher sampling frequencies.

- When the dataset shows a strong seasonality the increase in width of the confidence interval around the mean is substantial for lower sampling frequencies and highly seasonal data should therefore be sampled more frequently.

  Wells in seasonally influenced aquifers (e.g. unconfined, shallow, highly fractured aquifers) should be sampled more frequently to obtain the same reliability with respect to the mean concentration (and to identify very high concentrations).

4.5.2 Detection of trends

- In the analysed datasets it was possible to detect an existing positive or negative linear trend using all the tested sampling frequencies (ranging from weekly to 6 monthly).

  Even if datasets are sampled with a low sampling frequency it is still likely that a trend will be detected.

- The confidence limits around the slope of a linear trend in a dataset increase quickly with lower sampling frequencies: a monthly sampling frequency is necessary to guarantee that the width of the confidence interval of the slope is smaller than half the value of the slope.

  The accuracy of the slope of the trend is very low for low sampling frequencies; to obtain a reasonable accuracy monthly sampling seems to be necessary.

4.5.3 Implications for sampling frequency

The analysis showed that to be able to draw conclusions from the datasets with high accuracy more frequent sampling than quarterly is necessary. It is, however, not possible to apply such high sampling frequencies to all observation points in a groundwater body because of practical and budgetary constraints. Ideally, on the scale of a groundwater body, one could make a selection of observation points sampled at a sufficiently high frequency (e.g. monthly) to obtain accurate results, while the remaining observation points are sampled at lower frequencies. Preferably, such an approach should be developed incorporating spatial aspects of the observation point distribution. An alternative approach to the reliable detection of trends on a national basis would be to establish a small reference network of key monitoring points, which would be sampled monthly, as referred to in Section 5.3.

5. DEVELOPMENT OF APPROACH

5.1 Philosophy of approach

The guiding principles of the philosophy adopted here are that a national framework for sampling frequency and determinand selection should have a sound technical basis in hydrogeological and hydrochemical principles. At the same time, it should be realistic in terms of the Agency's present and anticipated capacity for implementation.

The principal factors which influence choices of sampling frequency and determinand selection are common to all types of groundwater quality monitoring, as confirmed by the review of existing approaches outlined in Chapter 2. These factors are (Chilton and Milne, 1994):

Determinand selection:	objectives, water uses, water quality issues, statutory requirements, costs.
Sampling frequency:	objectives, hydrogeological characteristics (residence times) hydrology (seasonal influences), statistical considerations, costs.

While the inevitable balance between the broad, multiple objectives outlined in Chapter 1 and limited funding is likely to be the most critical, each of these factors may have varying priority and be given different weight according to local circumstances.

The philosophy adopted here embraces or responds to all of the factors outlined above. Sampling frequency and determinand selection are closely linked in a framework which allows for more frequent sampling in aquifers in which groundwater is judged to move more rapidly and are more likely to be affected by seasonal quality variations, i.e. those with high hydraulic conductivity and low effective porosity, and less frequent sampling in 'slow' aquifers. It also envisages a lesser requirement for sampling in confined than unconfined aquifers, which reflects the greater degree of protection from pollution as well as the slower movement and less rapid hydrochemical change. This approach follows that put forward in the previous BGS study (Chilton and Milne, 1994). It is, however, simplified by dropping the distinction between Major and Minor aquifers, which is considered unlikely to be compatible with the approach to the definition of groundwater bodies set out in the WFD.

The present recommendations, however, have one important innovation, in that the philosophy governing the framework for determinand selection also derives from 'fast' and 'slow' criteria, but in this case defined by the anticipated response of the hydrochemical conditions. Experience shows that the major ion chemistry in groundwater bodies is likely to be more stable than many of the determinands indicative of human impacts which may, for example, be subject to seasonal influences reflecting both sources (agricultural usage) and pathways (recharge conditions). From an information needs perspective, therefore, a strong case can be made for measuring pollutants or pollutant indicators more frequently than the components of the major ion hydrochemistry. This 'information needs' approach is potentially in conflict with, and would need to be adapted to, the more traditional and usually laboratory-based determinand suite selection. The latter has tended to start with the easier, long-established determinands of water chemistry and been extended gradually to incorporate more difficult and costly pollutant determinands. The information needs approach caters for and is driven by the requirements of the water quality manager, rather than by the capabilities and capacities of the laboratories. It is relevant to note that the approach to determinand selection used by the water companies often has many similarities in being strongly oriented towards specific information needs.

While the decision-influencing factors themselves remain as they were, the legislative context is significantly more specific in terms of determinands but only a little more so in terms of frequency than that which confronted the NRA in 1994. The philosophy adopted here has been to take the provisions of the WFD and to develop a national framework for determinand selection and sampling frequency from that, as described below. While the other national and European drivers and objectives (Chapter 1) are not to be ignored, it is considered that the evolving implementation by Member States of their obligations under the WFD are likely to become increasingly dominant in shaping national groundwater monitoring programmes.

5.2 Determinand selection

5.2.1 Classification of determinands

The starting points for classification of determinands are taken to be the set of core parameters defined in the body of the WFD and the indicative list of pollutants provided in Annex VIII of the WFD. These parameters and groups are displayed in a simplified way in the left hand column of Table 5.1, and form the broad guidance on pollutants which should be considered for the surveillance monitoring at six yearly intervals required by the WFD. The remainder of the table is divided into 'responsive' and 'unresponsive' columns, representing respectively those pollutant determinands which may change more rapidly in response to pressures on the aquifer, either because they are source-specific or more mobile, and the components, including much of the inorganic hydrochemistry, which are less variable. The approach selects from the main list and moves to the right across the table, into the responsive column, those determinands that may require more frequent monitoring. Both the responsive and unresponsive columns are then further divided into 'standard' and selective' determinand sets, the former of which are to be measured at all groundwater monitoring sites and the latter are to be selected on the basis of land use criteria or other pressures (as discussed below) or from existing monitoring information.

For example, the major cations are likely to be stable in typical UK aquifers whereas boron and trace metals have been identified as indicators of urban or industrial pollution. Hence the 'major metals' are classified as unresponsive and 'minor metals' as responsive. 'Minor metals' are also classified as selective as they are expected to be typical of urbanised or industrial areas. Other potential indicators are also responsive, atrazine, nitrate species and chloride (salinity), as are some volatile organic compounds (VOCs) and organophosphorus pesticides. Pesticides and VOCs, other than atrazine, are classified as selective since they depend on land-use. All other parameters have been classified as unresponsive, with organohalogen compounds, organotin compounds, the broad, carcinogen /endocrine disruptor class, cyanide and phenols being selective.

Table 5.1 thus represents the technical basis of an information needs approach to address primarily the requirements of the WFD. It does, however, raise a number of problems and requires further elaboration to render it 'user-friendly' and easily applicable in the field by monitoring staff or those designing monitoring programmes. Firstly, the pollutants and pollutant groups listed in Annex VIII of the WFD are not specific to groundwater. Secondly, some groups are very broad and need a degree of risk-based selection within them, which takes account of existing occurrence of pollutants in groundwater. Thirdly, this scheme needs to be checked to ensure that it addresses the drivers other than the WFD. Fourthly, it is potentially in conflict with the more traditional, laboratory-based groupings of determinands currently employed, and for practical and cost reasons needs some degree of rationalization. The following sections provide this further elaboration of the classification in Table 5.1 and address these problems, to arrive at a process of determinand suite selection that can be readily applied to groundwater quality monitoring in England and Wales.

Table 5.1 Classification of Water Framework Directive core parameters, indicative pollutants and other compounds of concern

	Unresponsive		Responsive	
	Standard	Selective	Standard	Selective
WFD				
Dissolved oxygen	●			
pH	●			
Electrical conductivity			●	
Nitrate			●	
Ammonium			●	
Salinity			●	
WFD Annex VIII				
Organohalogen compounds		○		○
Organophosphorus compounds				●
Organotin compounds		●		
Carcinogens, mutagens		●		
Endocrine disruptors		●		
Persistent hydrocarbons		●		
Cyanides		●		
Metals (major)	●			
Metals (minor)				●
Arsenic	●			
Biocides		○	atrazine	○
Phosphate	●			
COD, BOD	●			
Suspended material				
Other common concerns				
MTBE			●	
BTEX			●	
Phenols		●		
Major anions	●			

Key: ● = single classification ○ = split classification

5.2.2 Standardised determinand suites

The overall analytical resources available are a key constraint in the selection process, as stated in Section 5.1. It is essential for the Agency to be able to focus its limited resources on the most critical determinands in relation to its information needs. Analysis of determinands which are either unlikely to occur or unlikely to change rapidly often does not represent the best use of limited funds. However, this must be balanced against the need for good background data and early warning of new pollutants. The national strategy recommended by BGS in 1994 addressed the need for selectivity by using land use as a surrogate for, or representation of, anticipated water quality issues and pollution sources (Chilton and Milne, 1994). Discussions with colleagues in some countries (particularly the Netherlands) have suggested unease about this approach and a desire to adopt the precautionary principle, aided by more adequate funding of monitoring, to err on the side of less selectivity. However, the UK land use approach to aid determinand selection has been endorsed by the European Environment Agency in the proposals for EUROWATERNET (European Environment Agency, 2000), and is recommended again here.

Whatever the strategic rationale involving hydrochemical responsiveness and land-use influences, the practicalities of performing analyses in the laboratory provide a strong steer on the choice of determinand suites. The majority of determinands analysed in modern, major water-analysis laboratories, including those of the Agency's NLS, are now measured using instrumentation capable of performing multi-determinand procedures. There is a significant fixed cost inherent in measuring any one determinand, arising from the time and materials required to run the analytical procedure. However, the additional marginal cost incurred by simultaneously measuring any other determinands that the method is capable of detecting is negligible or even nil. In such circumstances there is no cost advantage in determining only one or a few determinands, and potentially considerable information benefit in using the full scope of a given technique.

From a practical point of view, it is therefore highly desirable to base standard determinand suites on the groupings which can be obtained from a single instrument run in the laboratory, rather than on considerations of usage or perceived likelihood of detection. The suites proposed, after discussion with the National Laboratory Service, are shown in Table 5.2 and a full listing of the determinands allocated to each suite is given in Appendix 2. These are based on groups of determinands which can be measured in a single instrument run rather than the conventional anions, cations etc. It is likely that these suites will need to be reviewed and updated periodically in the light of continuing analytical development, changing industrial and agricultural practices and future legislative requirements. Suites I1 to I3 cover the main inorganic groupings; suites O1 to O7 relate to standard analytical procedures for measuring the majority of organic determinands of concern. Suite M1 contains standard microbiological determinands. These are not derived directly but are considered to be indicators of pressure on groundwater. Suites I4 and O8 are exceptional; they contain a number of individual determinands which are often difficult to analyse and which may require special single-analyte methods, but which have been grouped together as a convenient shorthand. It is strongly recommended that all regions should use the same national set of analytical suites and identification codes.

Total organic carbon (TOC) has not been included in the standard suites, although it is recognised that TOC can be useful in some circumstances as a quick and relatively cheap test which provides an empirical measure of gross organic contamination.

Table 5.2 Proposed analytical suites

Suite	Suite name	Examples of suite members
I1	Field	Alkalinity, DO, (Eh?), pH, SEC,
I2	Anions and ammonium	Ammonium, chloride, nitrate, nitrite, phosphate
I3	Metals	Boron, cadmium, calcium, iron, manganese, sodium, zinc,
I4	Special inorganics	Arsenic, mercury, selenium, cyanide, fluoride
O1	ONP pesticides	Atrazine, simazine, terbutryn, malathion, diazinon
O2	OCP pesticides	Lindane, PCBs, permethrin, trifluralin
O3	Acid herbicides	2,4-D, bentazone, bromoxynil, chlopyralid, mecoprop
O4	Uron/urocarb pesticides	Chlortoluron, diuron, isoproturon, methabenzthiazuron
O5	Phenols	Chlorophenols, phenols
O6	VOCs	Benzene, chloroform, MTBE, tetrachloroethene, trichloroethene, xylene
O7	PAHs	Fluoranthene
O8	Special organics	Carbendazim, chlormequat, cypermethrin, glyphosate, metamitron
M1	Microbiology	Total coliforms, faecal coliforms, faecal streptococci

For a full list see Appendix 2

The main thrust of the ‘information needs’ strategy is then achieved by applying hydrochemical responsiveness and land-use considerations to each of the suites as a whole. The suites are first classified into responsive/unresponsive and standard/selective using the parameters identified in Table 5.1. This is shown in Table 5.3. The occurrence of a single ‘responsive’ or ‘standard’ determinand in a given suite is sufficient to cause the whole suite to be classified accordingly. Classification is straightforward for most of the determinands, although it should be noted that carcinogens and endocrine disruptors cannot easily be classified into suites, as they are both large groups of compounds with many different chemical properties. Many of the other groups contain carcinogenic compounds. Endocrine disruptors pose a greater problem because of the range of substances implicated (Environment Agency, 1998a). Suite I4, which contains a number of determinands which may have to be analysed separately, is anomalous in having both standard (As) and selective (other special metals) elements.

Thus suites I1 and I2 are classified as standard, I3 as responsive to take account of the use of boron, zinc and other suite members potentially acting as urban indicators, and I4 is selective apart from arsenic. The organic suites are all selective apart from O1, to take account of the ubiquity of atrazine, and O6 similarly for Methyl tertiary butyl ether (MTBE) and Benzene toluene xylene (BTEX).

Operational monitoring under the definition of the WFD can be considered to be equivalent to the more frequent monitoring for the responsive determinands. Surveillance monitoring will automatically encompass all operational monitoring and therefore include both responsive and

Table 5.3 Derivation of analytical suites from classification in Table 5.1

	Unresponsive		Responsive	
	Standard	Selective	Standard	Selective
WFD				
Dissolved oxygen	I1			
PH	I1			
Electrical conductivity			I1	
Nitrate			I2	
Ammonium			I2	
Salinity			I2	
WFD Annex VIII				
Organohalogen compounds		O5		O6
Organophosphorus compounds				O1, O2
Organotin compounds		Not relevant to groundwater		
Carcinogens, mutagens		Large non-specific group		
Endocrine disruptors		Large non-specific group		
Persistent hydrocarbons		O7		
Cyanides		I4		
Metals (major)	I3			
Metals (minor)	I3			I3
Arsenic	14			
Biocides		O3,O4,O8	O1	O2
Phosphate	I2			
COD, BOD		Not relevant to groundwater		
Suspended material		Not relevant to groundwater		
Other common concerns				
MTBE			O6	
BTEX			O6	
Phenols		O5		
Major anions	I2			

unresponsive determinands. The classifications shown in Table 5.3 can therefore be expressed in terms of suite selection for both operational and surveillance monitoring (Table 5.4). Suite M1 does not appear in Table 5.3, but is shown in Table 5.3 as an operational standard suite to act as an indicator for impact of wastewater infiltration.

5.2.3 Application of land-use criteria to suite selection

It is proposed to use land-use criteria to aid in the choice of appropriate selective suites. The Agency is using a land-use approach to assist in groundwater monitoring network design and these data have been used as the starting point. It is accepted that these data represent modern land-use and that this may be very different from land-use at the date of recharge, which can be some hundreds of years for the Triassic sandstone. Based on the 25m digital *Land Cover Map of Great Britain* produced by the Centre for Ecology and Hydrology (© Natural

Table 5.4 Allocation of analytical suites to operational and surveillance monitoring

Suite	Surveillance		Operational	
	Standard	Selective	Standard	Selective
I1	✓		✓	
I2	✓		✓	
I3	✓			✓
I4	✓(As)	✓		
O1	✓		✓	
O2		✓		✓
O3		✓		
O4		✓		
O5		✓		
O6	✓		✓	
O7		✓		
O8		✓		
M1	✓		✓	

Environment Research Council), the Agency's NGWCLC has begun to re-classify all the data by consolidating the original CEH classes into five classes to be used in ensuring adequate representation of the various land cover types in the distribution of monitoring points over aquifers or groundwater bodies. These classes are: arable, managed grassland, forestry and woodland, semi-natural vegetation and urban.

Comparison with the original classes developed by BGS in 1994 suggests that urban might be further sub-divided into urban/suburban housing areas and industrial areas, woodland might be divided to take account of orchards and plantations because of their specific associated pesticides and, for the same reason, major sheep-farming areas could be identified within both managed grassland and semi-natural vegetation. However, some of these additional sub-divisions cannot easily be derived from what is essentially an ecologically-focused classification by CEH, and require local knowledge and/or the use of OS maps.

An indication of common pesticides associated with these land-use categories is shown in Table 5.5. No particular problems have been identified for natural woodland or semi-natural vegetation other than sheep. There will be other pesticides used with localised application which will need to be added to these core compounds on a regional or local basis. A good example of this is the pesticides associated with wool processing detected by the Agency in central northern England (Environment Agency, 1998b).

This approach can be extended to the other analytical suites and the selection of appropriate suites from a consideration of land use is shown in Table 5.6. Neither managed woodlands nor sheep are easy to determine from CEH land-use and topographic cover. However both of these categories are at least partially covered in suite O1, which forms part of the operational monitoring and therefore will always be included.

Table 5.5 Proposed specific pesticides for land-use categories

Pesticide	Class	Arable	Managed grassland	Managed woodlands	Urban	Sheep	Amenity
Atrazine	H	✓*		✓			
Simazine	H	✓		✓			
Bentazone	H	✓					
Chloridazon	H	✓					
Chlormequat	GR	✓					
Chlorotoluron	H	✓					
Clorothalonil	F	✓					
Dichlorprop	H	✓					
Flutriafol	F	✓					
Isoproturon	H	✓					
Linuron	H	✓					
Metamitron	H	✓					
Propachlor	H	✓					
Terbutryn	H	✓					
Bromoxynil	H	✓					
2,4-D	H	✓	✓				✓
MCPA	H	✓	✓				✓
MCPB	H	✓	✓				✓
mecoprop-P	H	✓	✓				✓
Dicamba	H	✓	✓				✓
Dichlobenil	H						✓
Diuron	H				✓		✓
Imazapyr	H				✓		✓
Cypermethrin	I					✓	
Diazinon	I					✓	
Flumethrin	I					✓	
propetamphos$^+$	I					✓	

* atrazine is used on maize, which is a crop that is mainly associated with dairy farms and may therefore be represented best in the grassland category rather than arable.

$^+$ propetamphos is no longer approved for sheep dipping but is still detected in surface waters.

Key: H = herbicide, F = fungicide, GR = growth regulator, I = insecticide
Arable includes horticulture, Amenity = railways, airfields, etc

There is a clear role for the POPPIE (Prediction of Pesticide Pollution in the Environment) model currently being developed by the Agency to inform the selection of pesticide compounds for monitoring. This model incorporates a number of different databases including landuse and pesticide usage as well as climate, soil type and depth to groundwater. The model is designed to produce predictive pesticide concentrations in infiltration to groundwater on a 2 km × 2 km grid, and likelihood of detection in groundwater, based on the presence of an aquifer, and major groundwater sources, such as boreholes or springs.

Table 5.6 Selection of suites from landuse criteria

Suite	Land use					
	Arable	Managed grassland	Managed woodlands	Urban	Sheep	Amenity
I3				✓		
I4				✓		
O2	✓					✓
O3	✓	✓		✓		✓
O4	✓			✓		✓
O5				✓		
O7				✓		
O8	✓				✓	

A system of review to identify newly developed compounds which should be included in the determinand suites needs to be put in place, coordinated with any required analytical development work in the NLS.

A basic assumption implicit in this approach is that sites selected for inclusion in the network have been screened to show the absence of point source pollution, for example from landfills or local historical industrial pollution. Overall the land cover approach will provide an initial pass assessment but it will probably need to be augmented by a considerable input of local knowledge to arrive at the final list of determinands.

5.2.4 Priority substances

The draft allocation of priority to hazardous substances discharged to water under the WFD is shown in Table 5.7. The precise monitoring requirements for groundwater have yet to be decided at a European level, but will need to be incorporated into the Agency's monitoring strategy. The majority of these substances are already covered by the proposed determinand suites. The NLS presently has specific methods available for octyl- and nonyl-phenols, and phthalates which could be applied where necessary. Other substances not already covered could be detected by the semi-quantitative screening offered by the NLS (Section 5.2.5).

5.2.5 The role of screening

The NLS are able to offer and are continuing to develop semi-quantitative screening methods for organic compounds which could include many of the determinands of interest. This could potentially have several roles in the monitoring process:

- to inform the choice of surveillance determinands;
- to aid choice of land-use selective determinands;
- to identify the presence of priority hazardous substances;
- to replace operational monitoring.

Table 5.7 Priority substances identified under the WFD

Priority hazardous substances	Priority substances subject to review to priority hazardous substances	Priority substances
1. Brominated diphenylether (only pentabromobiphenylether) 2. Cadmium and its compounds 3. C10-13-chloroalkanes 4. Hexachlorobenzene 5. Hexachlorobutadiene 6. Hexachlorocyclohexane 7. Mercury and its compounds 8. Nonylphenols 9. Pentachlorobenzene 10. Polyaromatic hydrocarbons (PAHs) 11. Tributyltin compounds 12. Trichlorobenzenes 13. Simazine 14. Trifluralin	1. Anthracene 2. Atrazine 3. Chlorpyrifos 4. Di (2-ethylhexyl) phthalate (DEHP) 5. Diuron 6. Endosulfan 7. Isoproturon 8. Lead and its compounds 9. Naphthalene 10. Octylphenols 11. Pentachlorophenol	1. Alachlor 2. Benzene 3. Chlorfenvinphos 4. 1,2-Dichloroethane 5. Dichloromethane 6. Fluoranthene 7. Nickel and its compounds 8. Trichloromethane

The screening protocol could be particularly useful in the detection of priority hazardous substances such as chloroalkanes, phthalates, pentachlorobenzene and possibly the diphenyl ethers shown in Table 5.7, none of which are included in the proposed determinand suites. This list of hazardous substances is likely to be expanded in the future and the screening approach may prove to be of particular value in this area. At the present state of method development it is considered that the last role would not be appropriate since it may not be possible to achieve an acceptable limit of detection for all determinands. Nevertheless, screening would be useful particularly for regions which have less existing monitoring data to aid determinand selection during setting up of the monitoring process.

5.3 Sampling frequency

The next step is to put together the hydrochemical responsive and unresponsive classifications with the important hydrogeological factors to produce an overall framework for sampling frequency. The aquifer classification follows that originally proposed and detailed in Chilton and Milne (1994) and taken forward into the sampling frequencies shown in Table 2.12. If trend analysis were the only objective, then the statistical work described in Chapter 4 would suggest that very frequent sampling might be required. However for a multi-objective programme the frequencies shown in Table 5.8 are recommended. In the ‘slower’ confined aquifers, sampling for the less responsive determinands is suggested to be at the six-year interval of the WFD, whereas at outcrop in more rapidly responding aquifers, quarterly sampling for the more responsive determinands is recommended. The matrix in Table 5.8 thus takes due account of the practicalities imposed by the financial resources likely to be available, but also allows aquifers subject to seasonal variations to be adequately sampled. Further, within both the responsive and unresponsive determinand groupings, provision is made for the use of ‘standard’ and ‘selective’ determinands. These would be measured at the frequencies given in Table 5.8, but with the standard ones everywhere and the selective ones according to land use.

If necessary the aquifer response ‘speed’ could be assessed using the aquifer response time (*ART*) approach:

$$ART = \frac{x^2}{ST}$$

where x = a representative distance, T = transmissivity and S = storage coefficient (Oakes and Wilkinson, 1972). Karst systems would need to be dealt with at a regional or local level.

These frequencies fully conform to the requirements of the WFD with operational monitoring being at least annual and all sites subject to surveillance monitoring at least once every six years. They are also broadly consistent with the requirements of EUROWATERNET

Table 5.8 Matrix of sampling frequencies for differing aquifer and chemical determinand response behaviours

			Hydrochemical determinand	
			Unresponsive	**Responsive**
Hydrogeology	**Slow**	**Outcrop**	3 years	6 monthly
		Confined	6 years	Annual
	Fast	**Outcrop**	Annual	Quarterly
		Confined	3 years	6 monthly
			Surveillance	**Operational**

although on a six rather than five year cycle.

To enable overall long-term trends to be confidently observed, one possibility would be to establish a third tier of sites designed to be broadly representative of regional groundwater quality. This would be equivalent to the reference network recommended by Chilton and Milne (1994). For example, this tier could comprise about 25 sites selected from the national network and sampled for a very limited suite of determinands at monthly intervals, in addition to the routine operational and surveillance monitoring. The choice of determinands would be site-dependent and might include nitrate, pesticides, VOCs, trace metals, boron or other indicators.

5.4 Practical and logistical optimization

A summary flow chart of the decision process is shown in Figure 5.1. From this it is clear that although the classification processes may appear complex the final outcome is reasonably simple. The operational suites are measured relatively frequently (Frequency 2) and all suites except those excluded on land-use criteria are measured less frequently.

Although the matrices of determinands and sampling frequencies suggested in Tables 5.4 and 5.8 have been designed to meet the requirements of the WFD, there may be valid reasons for adapting these choices before implementing the strategy. Reducing the range of determinands or the sampling frequencies is perhaps unlikely to be acceptable because the tables arguably represent the minimum monitoring requirements of the WFD, and hence reduction in monitoring may lead to non-compliance. Increasing the scale of monitoring will not fall foul of the WFD but, in general, such an increase must necessarily also increase the cost of monitoring, through additional sampling or more laboratory analysis. Nevertheless, some expansion of the monitoring may be justified. There may be over-riding strategic or political considerations for collecting additional data. Local knowledge and issues may lead to refinement of the data collection. The cost increases associated with additional monitoring may be marginal. Or perhaps, in practice, the variation in a standard field or laboratory procedure to collect only a subset of the usual data may cost more than routine completion of the full procedure and generating the additional ‘unnecessary’ data.

Assuming the suggested frequencies are taken as a minimum the following factors may need to be considered as flexible options in tailoring monitoring to local or regional needs:

- As has been discussed, where multi-determinand laboratory analytical techniques are used there may be no advantage in determining only part of the standard suite. If more elements are being determined, then it may be pointless not to report the data. Conversely, reporting the full suite may in some circumstances generate additional QC and calibration overheads, which could be avoided if only one or two elements were reported;

- When major metal cations are determined, it can be advantageous also to determine the major anions, because the combination allows an ionic balance calculation to be used as an analytical consistency check;

- Where certain pollutants have a high public profile, it may be appropriate to monitor them more frequently than is hydrogeologically necessary in order to prevent criticisms of inaction or mistaken perception of risk. For example, although endocrine disruptors may be detected in some surface waters, they are less commonly so in groundwaters; yet Agency assurances may not be persuasive without firm data.

Taking account of these and similar factors to modify the minimum framework presented here would lead to a final optimized strategy suitable for implementation. It should be remembered, however, that the resulting strategy should not be regarded as unchangable. Whereas the underlying theoretical recommendations would remain the mandatory minimum requirement unless there were changes in the strategic and legislative framework, the detail of implementation may need to be reviewed, for example, if new analytical techniques or equipment change the laboratory capabilities. Implementation should also allow flexibility for adjustment in the monitoring pattern to meet particular local needs. Similar driving forces for enhanced monitoring may apply at site-specific level as well as nationally. For example:

- A site with a particularly good long-term monitoring history may be worth monitoring more regularly than is technically necessary in order to preserve the integrity and

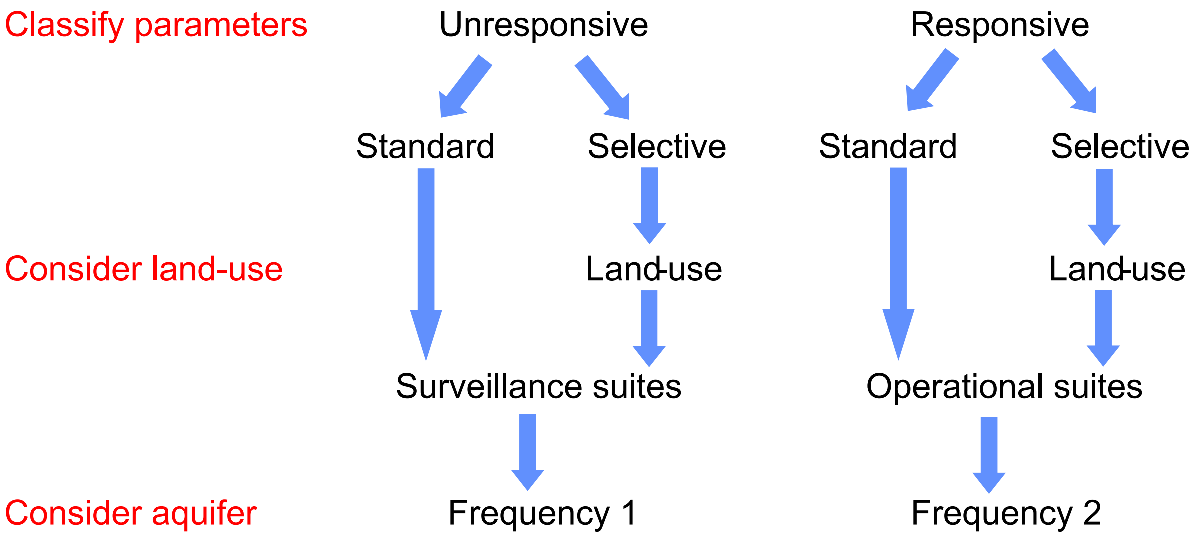

Figure 5.1 Flow chart summarising determinand and frequency selection

continuity of the time series.

- A site close to a specific known point-source pollution threat may need monitoring for additional determinands not included for the broader land-use category.

These cases would inevitably involve additional monitoring, augmenting the requirements of the main national strategy. Given that there are such circumstances to be taken into account, the Agency should consider setting up a team to work with local Agency hydrogeologists to set up local practices which will satisfy national needs.

The proposed methodology would benefit from further development taking into account spatial and sampling method issues. This should include the 3-D aspects of quality distributions (Chilton and Milne, 1994) and the 4-D issues associated with pumping well water sampling. Appreciating and understanding vertical variations in groundwater quality (which have often been observed in the UK's principal aquifers), the effects of pumping and the age of groundwaters become particularly important for interpretation of the monitoring results. Overall integration of these would allow a sounder hydrogeological basis for the data which is lacking due to the limited scope of the present project.

6. EVALUATION OF METHODOLOGY USING EXISTING DATASETS

6.1 Approach

The effectiveness and practicality of the proposed strategy for establishing monitoring regimes were assessed by comparing the recommendations of the strategy with existing monitoring data. This enabled an evaluation of the methodology, as specified by Task 4 in the Project Terms of Reference. The stepped approach detailed in Chapter 5 was applied, to determine the theoretical appropriate choice of determinand suites to be analysed at each sampling point. Existing monitoring data were then manipulated to establish which determinands were indicated as necessary to be monitored, based on the current knowledge of groundwater quality. Comparing the two sets of recommended determinands allowed identification of any inconsistencies between the suggested approach and the known situation.

The allocation of analytical suites and hydrogeological responsiveness of determinands is made at a national strategic level. In this evaluation, the tables of suites and determinands derived in the previous section were used without modification. Consequently, the first step in applying the strategy to a local or regional scale is consideration of land-use for the area in question. Assessment of land-use for each sampling point was carried out by a rapid GIS procedure described in Section 6.2 below. The identified land-use was then used as a tool to indicate the required monitoring suites predicted by the methodology.

Analysis of existing monitoring data focused on results for organic parameters, partly because these represent many of the major concerns about groundwater quality, but mainly because in the proposed strategy the use of organic determinand suites is much more heavily related to variations in land-use than the use of inorganic suites. Using the data for organic determinands therefore provides a more searching test of the approach. All positive determinations (i.e. reported as above detection limits) of organic determinands were extracted from the analytical datasets supplied by the Agency and allocated to the proposed analytical suites to give the second set of monitoring suites predicted by the known data. The two sets of suites were then compared as described in Section 6.3.

Three study areas were selected for the analysis, chosen on the basis of their land-use patterns and on the availability of suitable, extensive sets of existing monitoring data. The three aquifers concerned are:

- the Chalk of the Colne and Lee river catchments, north of London (Thames Region);
- the Oolite of the Cotswolds, between Cheltenham and Oxford (Thames Region);
- the Chalk of central East Anglia (Anglian Region).

The areas in Thames Region both show highly variable land-use and can be considered to be representative of the more complex areas of the UK. The Colne-Lee area in particular has a very high population density and extensive urban areas. In contrast, the area in East Anglia is more representative of intensive agriculture, with a clear emphasis on arable cultivation. The influence of land-use on choices of determinands might therefore reasonably be expected to be different between the Anglian and Thames Region areas. Comparison with a study area from the northern or western parts of England and Wales, where other land-uses would be dominant, was considered desirable. However, no areas could be identified that had sufficiently extensive existing Agency monitoring data of comparable quality to those available for the three areas used.

6.2 Land-use classification

Land-use classifications used during the analysis were derived from the digital *Land Cover Map of Great Britain* produced by the Centre for Ecology and Hydrology (© Natural Environment Research Council). The original classes of the data were aggregated, as detailed in Table 6.1, to give eight new classes corresponding to the land-use categories used in Chapter 5. The bare ground category was retained as it was thought it could be useful to delineate large car parks and similar. Areas where there were no data appeared to be due to unusual land-uses. One such area in the present study corresponded to a large glasshouse. The data were also smoothed to remove noise from <5 contiguous 25 m pixels.

Table 6.1 Original and aggregated CEH data classes

Aggregated classification	CEH classification
Arable	Tilled land
Managed grassland	Mown/grazed turf
Forestry & woodland	Scrub/orchard Deciduous Coniferous Felled forest
Semi-natural	Grass heath Meadow/verge/ semi-natural Rough/marsh grass Open shrub moor Dense shrub moor Bracken Dense shrub heath Upland bog Ruderal weed Lowland bog Open shrub heath
Urban	Suburban/rural development Urban
Water	Sea/estuary Inland water Beach and coastal bare Saltmarsh
Bare ground	Inland bare ground
No data	Unclassified

For simplicity during this preliminary analysis, land use was considered for fixed radius areas around each monitoring point, with no distinction being made between abstraction and observation boreholes or springs, and no account being taken of groundwater flow, gradient or capture zone. Analysis was carried out for zones with both 1 km and 3 km radii around each monitoring point, so that an indication of the effect of spatial scale could be obtained.

Once the original land-use data had been smoothed and the classes aggregated, the simplified data were overlain, using a GIS system, onto a map of the monitoring borehole locations. The GIS system was then used to define the 1 km and 3 km zones around each point and count the number of pixels of each land-use type occurring within each zone. In addition, for the Thames region (where the data were available) further GIS layers, showing the locations of railways, airfields, petrol filling stations and landfill sites were analysed. Occurrences of these amenity functions within a zone were identified and flagged. The full results were output to a spreadsheet, where the data were matched with the analytical suites according to the strategy given in Chapter 5. A given analytical suite was considered to be required when the occurrence of a given land-use as a percentage of the whole zone exceeded a threshold percentage. The level of the threshold could be varied to assess the sensitivity of the suite selection to small fractions of land-use.

The scope of these analyses is represented visually in Figures 6.1–6.6 which show maps of the three study areas coloured according to the land-use classifications. Two maps are presented for each of the areas, the Colne-Lee valleys (Figures 6.1 and 6.2), the Cotswolds (Figures 6.3 and 6.4) and Central East Anglia (Figures 6.5 and 6.6). The first of each pair shows the full land-use of the whole area and enables visualization of the regional pattern and dominant uses. The second of each pair shows only the 3 km zones (with the 1 km zones inset) immediately surrounding each of the monitoring points, together with the main rail and river networks.

The analysis procedure proved to be very efficient. Once the main GIS and spreadsheet framework had been established, the process could be repeated for large areas, and even nationally if required, very quickly. It was possible to vary the main criteria and thresholds very easily, and recalculate the effect within a few minutes.

The results highlight the contrast in regional land-use (Table 6.2). As would be expected, the data demonstrate that the Cotswold and Anglian study areas are much more agricultural, with much higher proportions of arable land, than is the Colne-Lee area. Conversely the Colne-Lee area shows heavier urbanisation. The data also highlight the complexity of land-use patterns in all the areas considered. For example, although at a 20% threshold almost 90% of the zones in central East Anglia include arable land use, there are also 62% with semi-natural areas, and 25% with urban areas. Clearly many zones include multiple land-uses, even within a 1 km radius and with moderately high (i.e. 20 %) thresholds. When the criteria are tightened so that smaller incidences of each land-use are considered significant then the picture becomes even more complex: at a 10% threshold three different land-use types each occur in over 70% of the Colne-Lee sites. A clearer picture is obtained using a very crude threshold of 50 %, when the distinction between the arable and urban areas becomes sharp, but such a high threshold would mean that smaller land-uses would not be taken into account when deriving the individual site monitoring regimes. The correct level of the threshold is a matter for consideration. The level must be set so that land-uses giving rise to genuinely significant potential impacts on groundwater quality influence the strategy, but minor fragments of land-use classes do not have a disproportionate influence.

Table 6.2 Summary indication of variation in land-use for the three case study areas. Upper figures represent the percentage of sites where the given land-use occurs at greater than specified threshold coverage within a 1 km radius of the boreholes. Lower figures give average proportions of each land-use across all zones of each study area.

Aquifer area	Threshold %	Arable	Managed grassland	Wood-land	Semi-natural	Urban	Bare
			% of sites affected by land-use				
Colne-Lee Chalk	10	74	31	32	86	84	4
(78 sites)	20	49	5	5	71	49	1
	50	4	0	0	1	25	0
Cotswold Oolite	10	100	58	22	96	32	1
(72 sites)	20	94	22	4	44	8	0
	50	31	0	1	0	0	0
Anglian Chalk	10	99	9	14	92	47	0
(620 sites)	20	88	1	6	62	25	0
	50	50	0	1	1	1	0
			average % of land-use per site				
Colne-Lee Chalk		23	9	8	25	32	1
Cotswold Oolite		43	13	8	20	9	0
Anglian Chalk		49	5	6	25	13	0

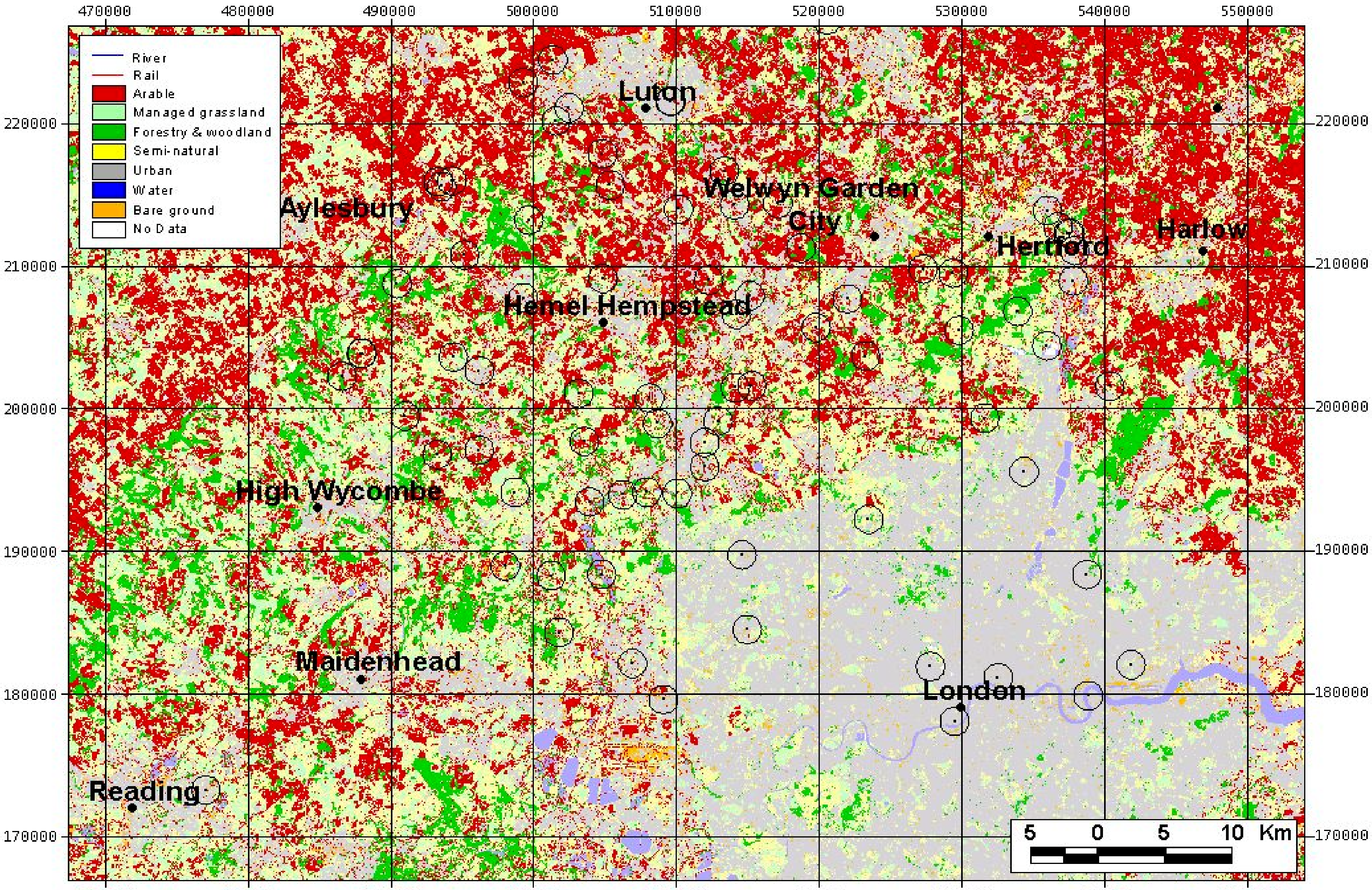

Figure 6.1 Simplified land-use mapping for the Colne-Lee valley area, showing the locations (1 km radii) of Environment Agency monitoring boreholes in the Chalk aquifer

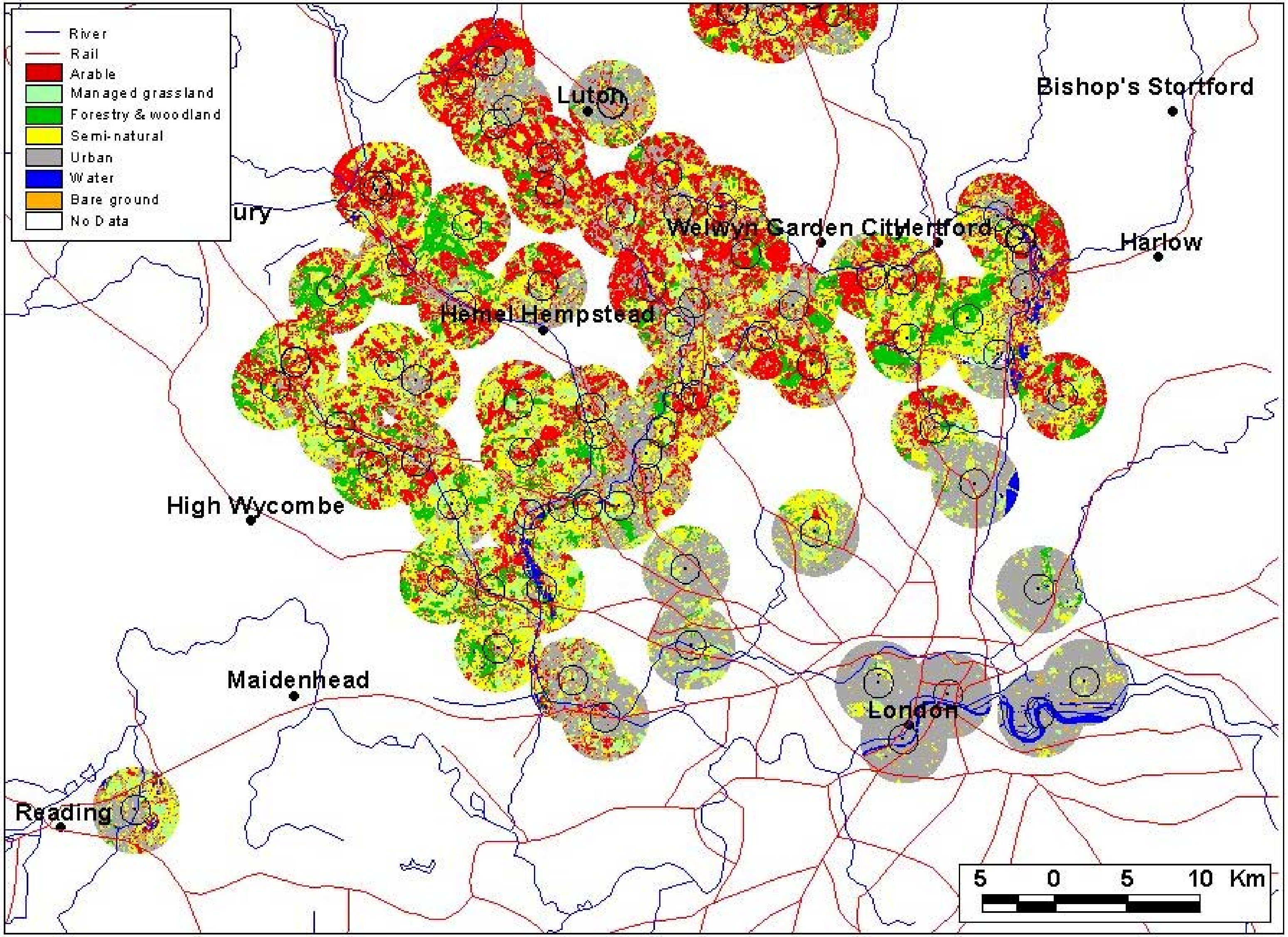

Figure 6.2 Land-use data for 3 km (and inset 1 km) radius surrounds for monitoring boreholes in the Chalk of the Colne-Lee valleys.

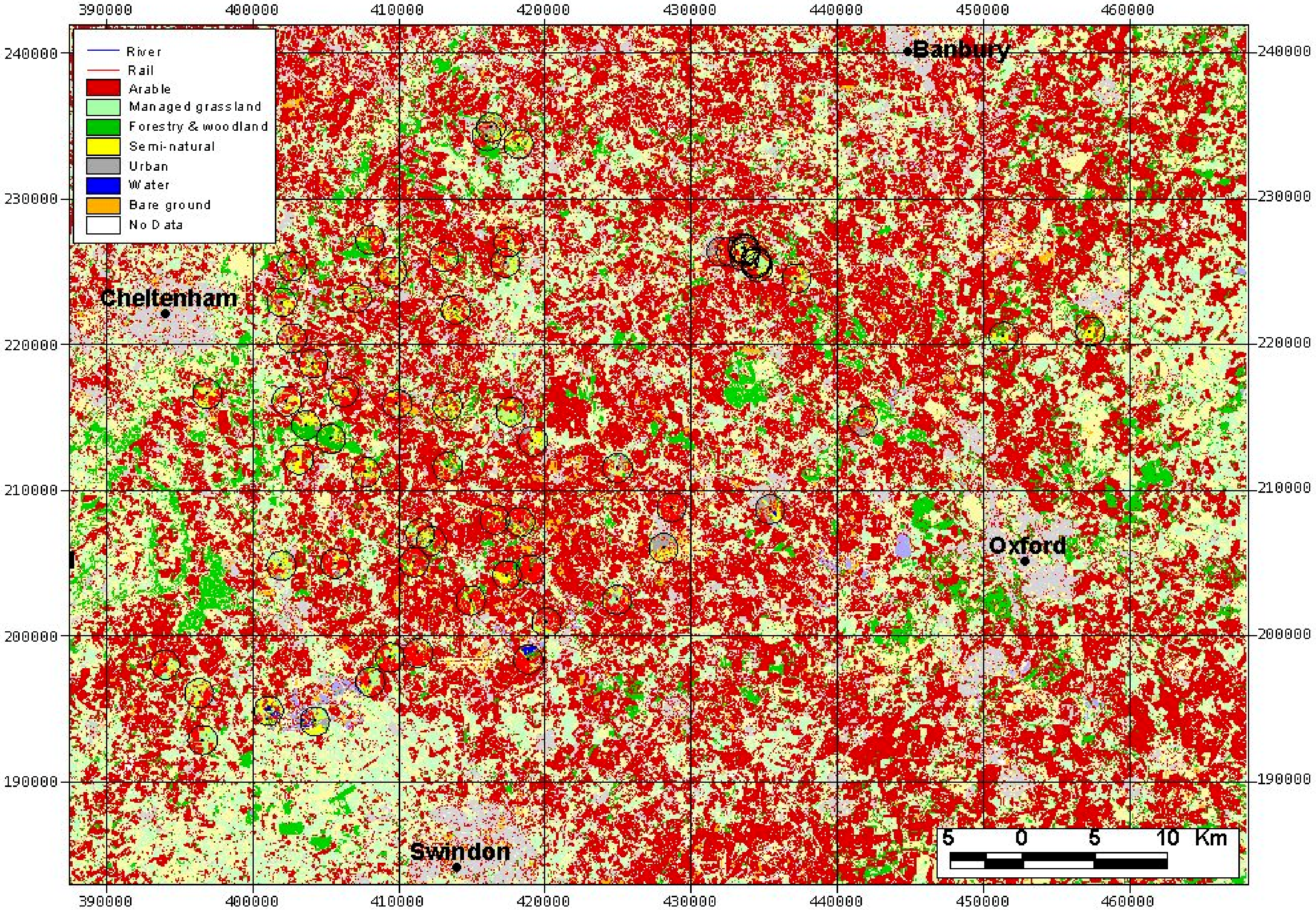

Figure 6.3 Simplified land-use mapping for the Cotswolds area, showing the locations (1 km radii) of Environment Agency monitoring boreholes in the Oolite aquifer

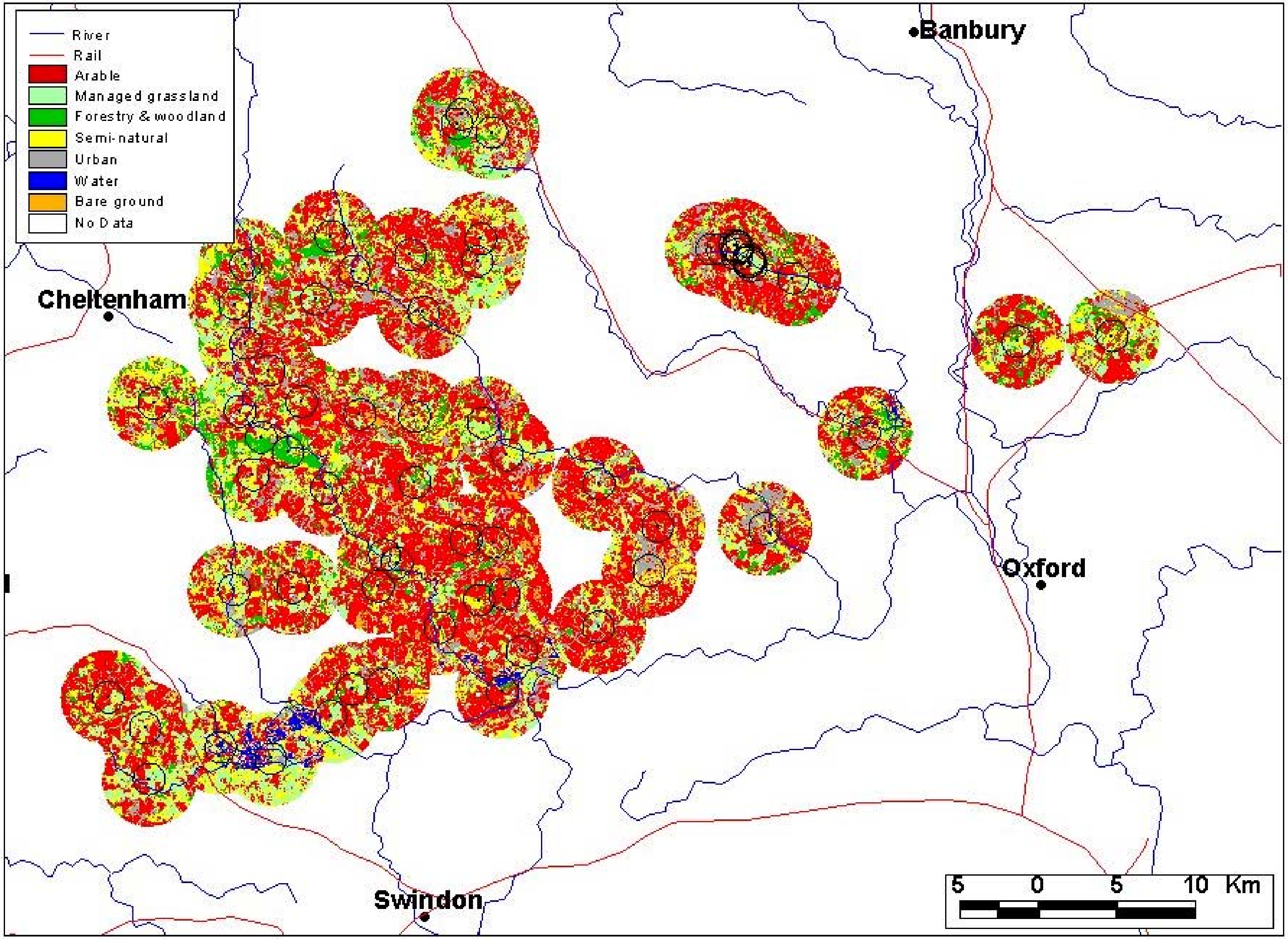

Figure 6.4 Land-use data for 3 km (and inset 1 km) radius surrounds for monitoring boreholes in the Cotswold Oolite.

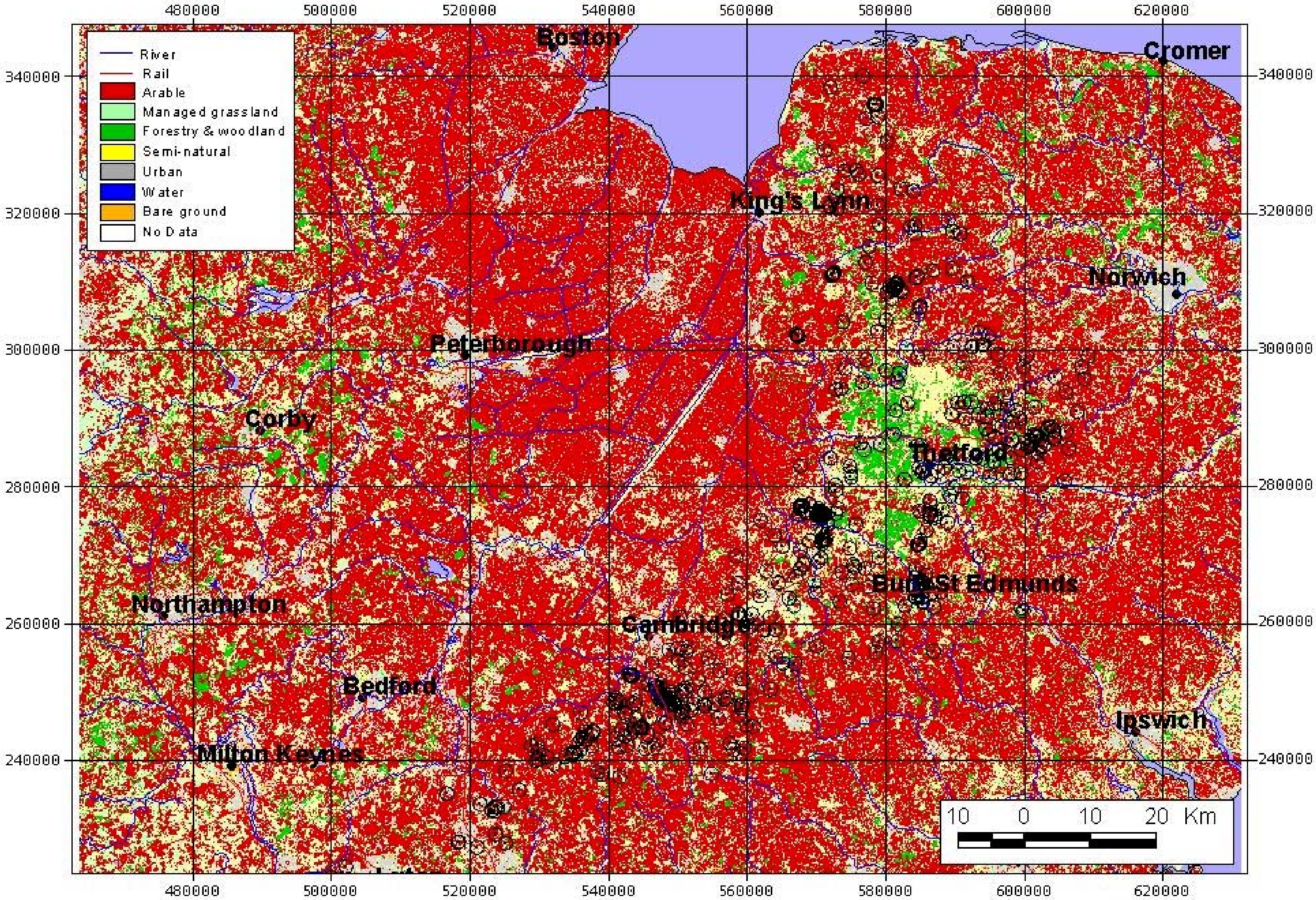

Figure 6.5 Simplified land-use mapping for central East Anglia, showing the locations (1 km radii) of Environment Agency monitoring boreholes in the Chalk aquifer

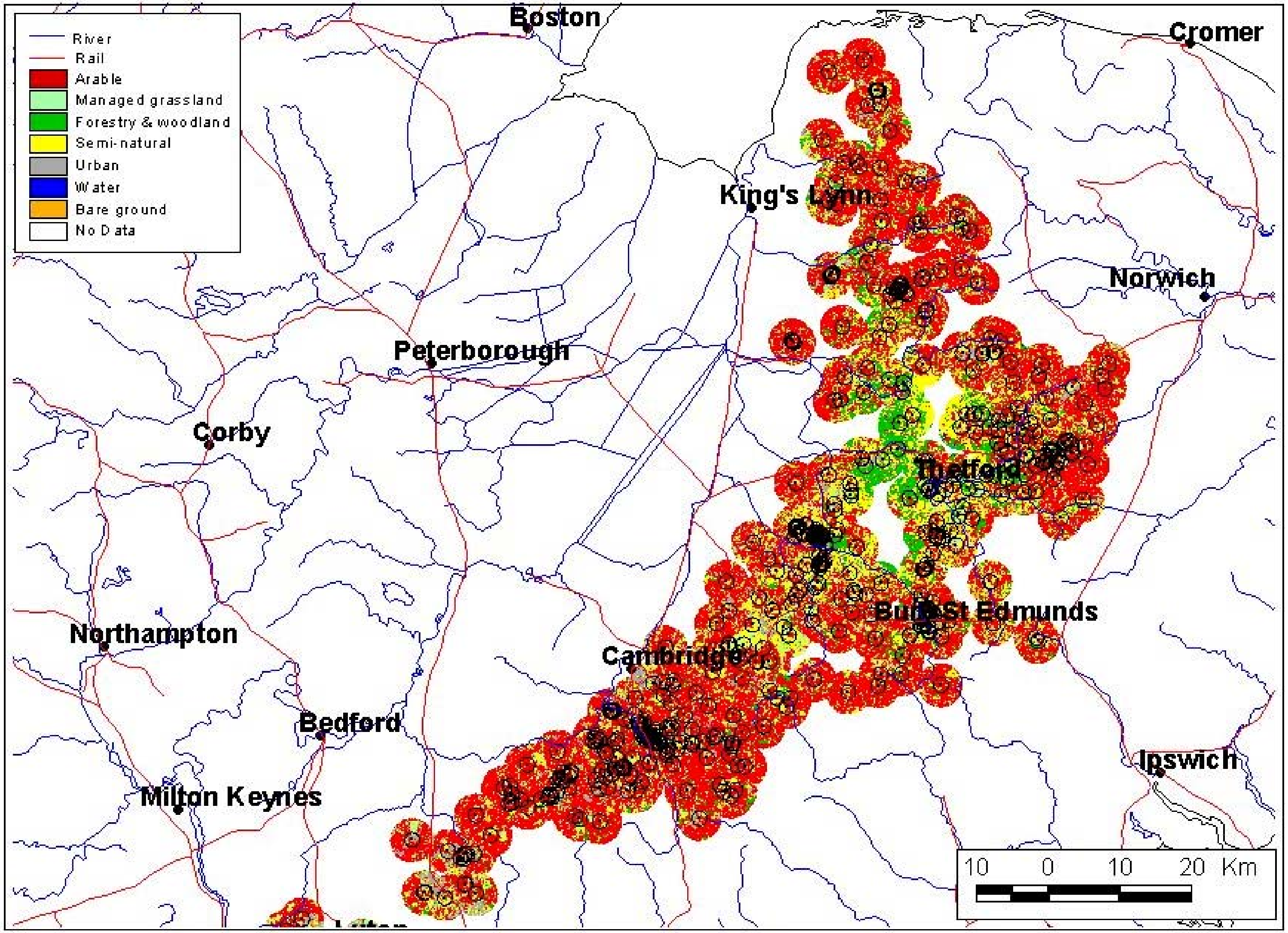

Figure 6.6 Land-use data for 3 km (and inset 1 km) radius surrounds for monitoring boreholes in the Chalk of central East Anglia.

Figure 6.7 Example section of evaluation analysis comparing efficacy of determinand suites indicated by proposed strategy against existing groundwater quality monitoring data. See main text for full explanation.

				SUCCESS?									LAND-USE									ANALYTICAL RECORD							
No	**Site**	**Easting**	**Northing**	**O1**	**O2**	**O3**	**O4**	**O5**	**O6**	**O7**	**O8**		**O1**	**O2**	**O3**	**O4**	**O5**	**O6**	**O7**	**O8**		**O1**	**O2**	**O3**	**O4**	**O5**	**O6**	**O7**	**O8**
CL01	Reading, Adwest Steering	477050	173290	LU	ok	ok	LU	LU	ok	LU	LU		🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥			🟥	🟥			🟥		
CL02	Great Missenden	491020	199500	ok	ok	ok	ok	LU	ok	ok	LU		🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥		🟥	🟥	🟥	🟥		🟥	🟥	
CL03	Woodrow, Keeper's Cottage	493280	196820	LU	LU	ok	LU	LU	ok	LU	ok		🟥	🟥	🟥	🟥	🟥	🟥	🟥					🟥			🟥		
CL04	Amersham PS	496220	197120	ok	LU	ok	LU	ok	LU	ok	LU		🟥	🟥	🟥	🟥		🟥	🟥	🟥		🟥		🟥				🟥	
CL05	Gerrards Cross: Bulstrode PS	498040	189000	ok	LU	ok	ok	LU	ok	ok	ok		🟥	🟥	🟥	🟥	🟥	🟥	🟥			🟥		🟥	🟥		🟥	🟥	
CL06	Chalfont St Giles PS	498730	194160	ok	LU	ok	ok	LU	ok	ok	LU		🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥		🟥		🟥	🟥		🟥	🟥	
CL07	Gerrards Cross PS	501260	188320	ok	LU	ok	ok	LU	ok	LU	LU		🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥		🟥		🟥	🟥		🟥		
CL08	Iver Heath, Pinewood Studio	501810	184330	LU	LU	ok	LU	ok	ok	ok	LU		🟥	🟥	🟥	🟥		🟥		🟥				🟥			🟥		
CL09	Chorleywood PS	503580	197730	ok	ok	ok	ok	LU	ok	LU	LU		🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥		🟥	🟥	🟥	🟥		🟥		
CL10	Mill End PS	503950	193490	ok	LU	ok	ok	LU	ok	ok	LU		🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥		🟥		🟥	🟥		🟥	🟥	
CL11	South Harefield, Blackford PS	504800	188420	ok	ok	ok	ok	LU	ok	LU	LU		🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥		🟥	🟥	🟥	🟥		🟥		
CL12	Batchworth PS	506280	193990	ok	LU	ok	ok	ok	ok	LU	LU		🟥	🟥	🟥	🟥		🟥	🟥	🟥		🟥		🟥	🟥		🟥		
CL13	Hillingdon Hospital	506940	182160	LU	LU	ok	LU	LU	LU	LU	LU		🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥				🟥					
CL14	Rickmansworth, Tolpits PS	507970	194180	ok	ok	ok	ok	LU	ok	LU	ok		🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥		🟥	🟥	🟥	🟥		🟥		🟥
CL15	Watford, The Grove PS	508710	199000	ok	LU	ok	ok	LU	ok	ok	ok		🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥		🟥		🟥	🟥		🟥	🟥	🟥
CL26	Enfield, Parkview Nursery	531650	199360	LU	**AR**	LU	ok	ok	LU	LU	ok		🟥		🟥			🟥	🟥				🟥						
CL27	Midland Bank, Poultry	532590	181170	LU	ok	LU	LU	LU	ok	LU	ok		🟥		🟥	🟥	🟥	🟥	🟥								🟥		
CL28	Enfield, GE Thorn	534400	195600	LU	ok	LU	LU	LU	ok	LU	ok		🟥	🟥	🟥	🟥	🟥	🟥	🟥				🟥				🟥		
CL29	Whipps Cross Hospital	538800	188400	LU	LU	LU	LU	LU	LU	LU	LU		🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥									
CL30	Greenwich, Pioneer BH	538900	179900	LU	**AR**	LU	LU	LU	LU	LU	ok		🟥		🟥	🟥	🟥	🟥	🟥				🟥						
Totals	ok			155	68	97	107	387	375	396	31																		
	LU			616	699	674	664	359	396	374	740																		
	AR			0	4	0	0	25	0	1	0																		
	Indicated												771	757	767	765	379	771	396	743		155	62	93	101	45	375	23	3
	Not-indicated												0	14	4	6	392	0	375	28		616	709	678	670	726	396	748	768
	Total			771	771	771	771	771	771	771	771		771	771	771	771	771	771	771	771		771	771	771	771	771	771	771	771

6.3 Comparison with existing monitoring data

A sample section of the large spreadsheet used for evaluating the methodology is shown in Figure 6.7. The analysis comprised three main stages. The stages are illustrated here using site CL08, at Iver Heath in the Colne-Lee area, as an example.

1. *Allocation of analytical suites according to the proposed methodology.*

The land-use data for CL08 show that, for the criteria used in this evaluation (10% land-use density threshold; 1 km radius), four land-uses occur within the zone around the borehole: arable, grassland, woodland and semi-natural. There were no amenity uses intersecting the zone. From Table 5.6 it can be seen that the existence of arable land requires that suites O2, O3, O4 and O8 be analysed during surveillance monitoring, managed grassland also requires O3, whereas woodland and semi-natural land-uses have no specific organic analytical suites associated with them. In addition, suites O1 and O6 are standard suites (Table 5.4), required for all sites. Thus on the basis of the proposed strategy, for site CL08:

- suites O1, O2, O3, O4, O6 and O8 should be analysed;
- suites O5 and O7 are not required.

The required suites are identified by filled boxes in the ‘land-use’ section of Figure 6.7.

2. *Identification of known groundwater quality issues using existing data records.*

The available data for groundwater quality analyses of water from the CL08 borehole show that several organic contaminants have been recorded, at above detection limit concentrations, at some time over the duration of the record. These were, dichlorprop, MCPA, mecoprop, tetrachloromethane, trichloroethene, trichloromethane (and unspecified trihalomethanes). The listings in Appendix 2 show that the first three of these would all be analysed as part of the proposed O3 “acid herbicides” analytical suite, while the latter three would all be part of the O6 “VOCs” suite. Therefore, on the basis of the existing data, to be sure of identifying all previously known groundwater quality problems:

- suites O3 and O6 should be analysed.

The required suites are shown by filled boxes in the ‘analytical record’ section of Figure 6.7.

3. *Comparison of the strategy and evidence based suites.*

The land-use and analytical record datasets were compared suite by suite, to yield the results shown in the ‘success?’ section of Figure 6.7. Three results were possible:

- ‘ok’ – where both approaches made the same recommendation for a given suite.
- ‘LU’ – where the suite is invoked by land-use criteria but none of the component compounds were detected in the analytical record.
- ‘AR’ – where a compound was detected in the analytical record but the corresponding suite was not indicated by the land-use criteria.

The ‘ok’ result could mean either that neither method indicated the need for the suite to be analysed, or conversely that the historical record demanded it and the land-use predictions correctly identified the need. Although at opposite ends of the spectrum, both scenarios represent a success for the methodology, so the ‘ok’ result is shown in green. The ‘LU’ result is shown in orange as it represents a warning: the land-use criteria indicate that compounds from the suite may pose a threat, even though none have so far been detected. Most seriously, the 'AR' result, shown in red, represents an alarm, where the land-use approach has failed to pick up a known problem.

For the example site CL08:

- suites O3 and O6 were both detected and predicted, hence the result was 'ok'
- suites O5 and O8 were neither predicted nor detected, hence again the result was 'ok'
- suites O1, O2, O4 and O7 were suggested by the land-use strategy, although no compounds have been detected, hence the result was 'LU'.

The evaluated methodology was thus successful for site CL08. All the previously known groundwater quality problems would have been detected by the regime of organic analytical suites derived from the strategy, and the strategy further suggested that some suites were necessary precautions even though there is currently no evidence of any problems.

6.4 Success and applicability

The results of the evaluation for all sites in the three study areas are summarised at the bottom of Figure 6.7. It is immediately clear from the summary of the 'Land-use' section that for most sites the complex land-use patterns observed mean that many analytical suites are identified as being required. Even with the relatively moderate criteria of 1 km zones and 10 % land-use threshold, most suites are required at most sites. If the zones around the monitoring points are extended to 3 km the picture moves even closer to the fully precautionary position of analysing for everything everywhere.

The least frequently required organic suites were O5 and O7 (Phenols and PAHs) which were indicated in approximately half of all the sites (using 1 km radius). In the strategy these two suites are associated exclusively with urban and amenity land-uses, and hence were not required in wholly rural zones. In the light of this, it is possible to consider the use of land-use based choice of analytical suites at a much broader scale. Instead of considering the detailed land-uses classes on a site-by-site basis a single strategic land-use decision could be made at a regional scale. For example it could be argued that the Colne-Lee valley area as a whole was predominantly urban and suburban, but with significant arable and wooded land in the suburban areas. All sites in the area would then be monitored for all the suites associated with those land-uses. In contrast perhaps North Yorkshire would be considered to be mainly arable, with significant sheep-farming and almost no urban areas; all sites in North Yorkshire would then be monitored according to those land-use classes. This approach would simplify the overall monitoring regime significantly, but would need to be very carefully considered because, as the analysis here shows, land-use across much of Britain is complex and variable. Although a certain type of land-use may represent only a small proportion of a regional area, it may nevertheless be a significant source of particular contaminants.

There are a considerable number of 'LU's shown in the 'Success?' section of Figure 6.7 indicating that the proposed methodology recommended analysis of determinands and suites which have not been proven to be occurring above detection limits. At first sight, this may appear to suggest that the proposed methodology is over-prescriptive, requiring unnecessary analysis. There are strong arguments against this. Firstly, if there are reasonable grounds to suspect that, because of the prevalent land-uses, certain determinands could in theory pose a threat, then it will be necessary for the Agency to be able to demonstrate that the threat has been addressed or contained. It can only do so by carrying out regular monitoring, even if the determinand levels are shown to be below detection limits.

Second, there are three reasons for there being no previous record of a pollutant at a site:

(i) the pollutant is not present in the system or is below the detection limit;

(ii) the pollutant is in the system but has not reached the monitoring point;

(iii) there are no analyses in the test dataset for that pollutant.

It should be remembered that the proposed standard analytical suites discussed here are more extensive than any of those used in current Regional monitoring practices. Hence, it is possible that some determinands are present in groundwater, but have not been looked for. The current analysis, based on existing analytical data, would necessarily be unable to identify such occurrences. Monitoring using the proposed suites may result in more positive detections.

More dangerous are the small number of 'AR's found for suites O2, O5 and O7. These determinands were detected in groundwater, but the proposed strategy would not have looked for them. A more detailed analysis of the data shows that these are due to detection of:

- pesticides (O2-OCP pesticides, mainly γ-HCH, some trifluralin) at four highly urban sites in and around London;
- several polyaromatic hydrocarbons (O7-PAHs) at a single site in East Anglia where urban land-use was not indicated;
- phenols (O5) in the Oolite at sites mainly to the east of Cheltenham, and at a dozen sites distributed across central East Anglia. The source of these is not clear;
- phenols (O5) at North Mimms in the Colne-Lee valley.

The inclusion of phenols (O5) for rural areas perhaps derived from wood preservatives would have reduced the number of ARs with a consequent increase in sample numbers. These occurrences do however emphasise how the major local land-uses will not necessarily predict all possible contamination. Minor land-use, point sources or movement of contaminants from outside the immediate zones may have some effect. This highlights the need for the inclusion of local/site -specific issues to increase confidence in the monitoring data.

Overall, the proposed methodology was generally successful in defining a monitoring programme which includes most of the determinands which have shown detectable concentrations in the analytical record. The number of failures to catch contamination was small given the large number of determinands and sites considered. This indicates that there is scope for using the land-use approach to choice of analytical suites as a valid part of the complete monitoring strategy. The evaluation has shown that with a properly established GIS system, once the system is established it would be possible to apply the land-use approach to the entire monitoring network, in a consistent way, fairly quickly. Structuring the system well during the development and establishment would also allow subsequent revision or development of the network, such as changing the radius of the borehole zones, updating the underlying land-use data, or changing the allocation of determinands or suites, to be carried out very easily. It is recommended that, because the GIS approach which has been developed is relatively easy and efficient, the land-use analysis should be applied on a site-by-site basis, rather than by using a broad regional definition of suites.

The effects of changing the parameters of the methods should be explored and adjustments made as appropriate. This could include an investigation of the suggested simplification of land-use. Risks with such simplification can be seen, for example, from a rural but large industrial site which might be associated with a large flux of pollutant.

It is clear, however, that the land-use criteria cannot be infallible. The system must therefore be used as a tool to aid monitoring design, rather than a definitive statement of monitoring requirements. The recommended main analytical suites could be augmented as required by using the screening analyses discussed elsewhere. Screening should identify any additional contamination threats (the red 'AR' alarms in this analysis) and allow the monitoring manager to add the necessary extra analytical suites for some sites where needed. As in other aspects of the strategy, the core recommendations of the proposed methodology should be augmented on the basis of local knowledge or need, taking into account the likely impact on costs.

The proposed approach provides a significant amount of flexibility which could be brought in as experience is gained. Data need to be collected on the performance of the scheme, for example by undertaking a complete analysis every few years at a random selection of sites.

7. CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

The monitoring of groundwater quality has often been the poor relation of surface water monitoring, and in this respect the UK is no exception. Groundwater quality monitoring in the regions of the Environment Agency has long suffered from a lack of consistency which, among other problems, makes national reporting on the state of and trends in groundwater quality very difficult. This has been recognized for some years, and was addressed for the NRA by BGS in a 1994 project which developed a national strategy for more effective monitoring, assessment and reporting of groundwater quality. Since that report and until recently, however, no nationally co-ordinated strategy had been implemented by the Agency, partly because of a lack of clearly specified statutory requirements for monitoring, but mainly because of limited organizational resources. The effectiveness of groundwater quality monitoring has not improved overall and, most importantly, has not significantly enhanced the capacity of the Agency to meet its increasing information needs at national level and its broader obligations within Europe. The project described here addresses part of this deficiency and forms an element of a new national monitoring strategy which is being developed by the Agency.

A recent review of current monitoring undertaken by ESI for the Agency (ESI, 2001a) showed that variation in practices across the country still remains great. Regions had implemented none, some or most of the recommendations of the previous study independently and in inconsistent ways. What has changed, however, is that the drivers for groundwater monitoring have become both more numerous and more individually demanding, specifying monitoring requirements more clearly than before. This applies particularly at the European level, with the WFD, the Nitrate Directive, the Groundwater Action Programme and EUROWATERNET. The Agency therefore needs guidance on establishing a framework for determinand selection and sampling frequency, and this is the objective of the present study.

From the implementer’s point of view, it is difficult to consider sampling frequency in isolation. The combination or product of the number of monitoring points and sampling frequency provides the sampling and analytical workload for an organisation responsible for monitoring. Thus, from the review undertaken by ESI, present sampling frequency in the regions is highly variable, but can be said generally to average once to twice per year. Exceptions are South West, where a much smaller number of sampling points (giving inadequate density of coverage) are sampled more like six times per year, and Thames, whose groundwater monitoring programme has long been more fully developed, where the average is about four times per year.

The study reviewed practice elsewhere, where possible. Looking at the present picture in Europe, sampling frequencies in national groundwater monitoring range from every two years to 4-6 times per year, with annual or six monthly sampling being probably the most common. However, while it has been possible to obtain this basic factual information, it has been more difficult, even from personal contacts, to find out about the criteria and the decision making process by which these frequencies were arrived at. For the present study, this background, including other options which may have been considered and rejected for technical or financial reasons, would have been helpful. However, the development processes are not documented in the same way as the outcome and such information could not be obtained.

The wide variation in determinand groupings and suites between Agency regions was highlighted and documented in detail by ESI. The most important conclusions to be drawn are that the value of field determinations has become broadly accepted by the regions, and all now routinely carry out at least some field determinations. Major ion concentrations are measured in all regions, together with some metals, and the greatest variability comes with respect to organic compounds and pesticides. The European picture is also characterized by significant variability, reflecting a range of both national objectives and commitment of resources to monitoring.

The project has reviewed the current availability and applicability of field chemistry methods, in-situ measurement techniques, novel analytical tools such as the ELISA method and the potential for the use of indicators. While there has been rapid technological development of in-situ measurement capability, changes in groundwater quality are not normally on a time-scale for which such frequent data are required. Interest in the possibility of using indicator determinands to represent groundwater quality is high, but thus far it has been difficult to identify indicators which would perform this function as cheaply and effectively as is the case with DO, BOD, COD and suspended solids for rivers. However, boron and zinc, which are presently not widely measured in groundwater by the Agency have been identified as potential indicators of urban inputs.

The BGS team has reviewed the published literature for statistical approaches to the optimization of sampling frequency. An autoregressive moving average model has been used to calculate the variance of the sample mean and confidence intervals, using long-term datasets from selected Chalk, Sherwood Sandstone and Great Oolite sources. The confidence interval around mean concentrations is large for all datasets tested, approximately 25% when sampling weekly and increasing to 50% when sampling monthly. The confidence interval is strongly dependent on the variance, and datasets characterized by large variance should be sampled more frequently. Highly seasonal data should also be sampled more frequently. These two conclusions point towards more frequent sampling in the Chalk and Jurassic limestones than in the Sherwood Sandstone. Existing trends, either positive or negative could be detected at all of the sampling frequencies tested, ranging from weekly to six-monthly. A monthly sampling frequency is necessary to guarantee that the width of the confidence interval of the slope is smaller than half the value of the slope. If trend detection were the only objective, then such a frequency would be advisable, but for the multiple objectives of national groundwater quality monitoring then monthly sampling is not considered appropriate or cost effective.

7.2 Discussion

The proposed approach to determinand selection and sampling frequency takes account of all of the factors which influence these choices. The philosophy adopted here retains a framework which allows for more frequent sampling in aquifers in which groundwater flow is more rapid and less frequent in aquifers with slower movement. It also builds in a less frequent requirement for sampling in confined aquifers than in unconfined aquifers, reflecting the greater degree of protection from pollution, and generally slower water movement and less rapid hydrochemical change in confined aquifers. It follows, but simplifies, the approach put forward by BGS in 1994, by dropping the UK distinction between Major and Minor aquifers, as this is considered unlikely to be compatible with the methodology for definition of groundwater bodies set out in the WFD.

The approach proposed here has an important innovation in that the framework for determinand selection also has a fast and slow dimension, but in this case defined by the anticipated response of the hydrochemical conditions. This is because experience shows that major ion chemistry in groundwater bodies is likely to be more stable than many of the determinands indicative of human impacts. From an information needs perspective, therefore, a strong case can be made for measuring pollutants or pollutant indicators more frequently than the components of major ion hydrochemistry. The information needs approach developed and recommended here caters for the requirements of the water quality manager, rather than the capabilities and historical practices of the laboratories. In this sense, the approach is closer in its intention to, but more structured in its design than, that adopted by the water companies.

The recommended approach to determinand selection takes as its starting point the set of core parameters and indicative list of pollutants defined by the WFD. This long and comprehensive list is intended to form the basis for the surveillance monitoring which the WFD will require every six years. The proposed strategy then allows for selected determinands to be measured in responsive or unresponsive sets, representing firstly those pollutant determinands which may change more rapidly and secondly the components of inorganic hydrochemistry and the less common pollutants. The former are less variable and the latter less likely to reach groundwater. These two sets are then further divided into standard and selective determinand sets, the former of which would be measured at all groundwater monitoring sites and the latter would be selected on the basis of similar land-use criteria to those which the Agency is developing to aid monitoring site selection, augmented by a degree of local knowledge within each region. A land-use based approach is considered important to assist in focusing the very costly pesticide analysis to those compounds that are most likely to occur, and again mirrors existing, but less formal, practice in the water utilities.

In order to facilitate field and laboratory programmes and to simplify the selection process, the determinands have been grouped into a number of suites on the basis of analytical method. Where one member is required the whole suite will be determined at similar cost. Thus, the recommended framework envisages four inorganic, eight organic analytical suites and one microbiological suite, each classified as responsive or unresponsive and standard or selective according to land-use. This provides sets of suites for operational (more frequent) and surveillance (less frequent) monitoring requirements. These are combined in the strategic framework with a sampling frequency matrix of slow and fast, confined and unconfined aquifers to give recommended operational measurement frequencies ranging from quarterly (fast outcrop), to twice a year (slow outcrop and fast confined) and annual (slow confined). The corresponding recommended unresponsive measurement frequencies range from annual, through once every three years to once every six years.

The recommended framework was tested against existing analytical datasets for three selected areas in southern England. These were the Colne-Lee catchments north of London, the Oolite of the Cotswolds between Cheltenham and Oxford (both Thames Region) and the Chalk of central East Anglia (Anglian Region). The proposed methodology was shown to be generally successful by comparing the organic suites derived in the recommended strategy with observed positive detections at each monitoring site. Given the scale of complexity of land use in southern England, for many monitoring sites most categories are represented within close proximity. Taking the reasonable radii of 1 km around each site and a 10% land use threshold, then most suites are required at most sites. If a 3 km radius is used, then suite selection approaches the full precautionary position of analysing for everything everywhere. Testing of the method in an area of northern or western England with less mixed land use would produce a more selective outcome in terms of suites.

Where suites were predicted but not observed, this may be because the proposed suites are more comprehensive than current regional practices. In total, a very small number of parameters were detected although not predicted. These were pesticides from suite O2 at several urban sites in north London, polyaromatic hydrocarbons (O7) and phenols (O5). These emphasise the need for an additional element of local knowledge of potential pollutant sources which are not directly predicted from the land cover map. The spreadsheet comparisons can also be used to assist in interpreting monitoring results. Where determinands are consistently observed but not predicted from land use, then further investigation of local pollution sources may be required. These determinands would probably be picked up by other elements of the groundwater body risk assessment and characterisation process.

The testing has also shown that the GIS and spreadsheet approach developed would allow the land-use criteria to be applied to the entire regional or national networks quickly and consistently. Structuring the land-use methodology at the beginning would allow subsequent revision of the network, changing the radius around the sites and the land use threshold, updating the underlying land use data (a new CEH land cover map is due), or changing the analytical suites to embrace new determinands. Concerns that the land-use approach would be unduly burdensome have proved groundless and, because the GIS approach is easy to apply, it is recommended that it be applied on a site-by-site basis, rather than as a broader regional land use definition of suites.

The recommended approach represents the minimum monitoring considered to be sufficient to comply with the requirements of the WFD. Local or site-specific issues, or other factors can be used to augment the monitoring as required.

There are clearly potential roles for the rapid, semi-quantitative screening methods being developed by the Agency's NLS. Whilst it is probably not yet ready to be used extensively to replace components of operational monitoring, it could have a role to play even at its present stage of development in detecting priority hazardous substances and in assisting in determinand selection for regions which currently have less existing monitoring data. Further work on the development of screening methods is therefore fully justified.

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APPENDIX 1. TECHNIQUES APPLIED TO THE STATISTICAL ANALYSIS AND GRAPHICAL PRESENTATION OF THE DATASETS

1.1 Influence of sampling frequency on the accuracy of calculation of the mean

1.1.1 Review of methodology

Literature specifically on statistical optimisation of sampling frequency is scarce. This contrasts strongly with literature on statistical analysis of existing data. A review on aquatic monitoring programme design is given in Dixon and Chiswell (1996), in which reference is made to optimisation of sampling frequency. In more recent works time-series analysis methods seem to be the preferred approach. A summary of the most relevant publications is listed.

Clark (1992)

The following calculations are discussed:

- a calculation of the number of samples necessary to obtain a future estimate of the mean with a predefined precision;
- a calculation to detect change in the mean concentration of two series of data from the same borehole.

This approach is somewhat crude in that it does not take into account the fact that the groundwater quality data represent time series which are characterised by seasonality, scatter and autocorrelation. These calculations also assume that the data are normally distributed.

Loftis and Ward (1980)

A method is selected to optimize sampling frequencies in order to achieve reasonable small and uniform confidence interval widths about annual sample means or sample geometric means of water quality constituents.

The major steps consist of: elimination of the seasonality if present, calculation of the variance of the remaining correlated noise, fitting an autoregressive moving average model (ARMA-model) to the historic data record, calculating the values of the theoretical autocorrelation functions $\rho(n)$, calculating the variance of the sample mean and calculating the variance of the sample mean and the confidence intervals.

Ahn & Salas (1997)

The parameters of the underlying ARIMA models fitted for the series sampled at a given arbitrary time interval h are obtained as a function of h and as a function of the model parameters for the series sampled at a unit time interval. This is accomplished by linking the derived variances and autovariances at the two sampling scales. This method is developed for several simple ARIMA type models (low-order). Using this method a sampling interval for a predefined allowable noise variance can be calculated.

This method is in comparison to the previous method numerically much more complex and requires a solver for non-linear equations. The method is also developed for groundwater head data and therefore likely to be based on data sampled with a very high sampling frequency (daily measurements). These sampling frequencies are very rare for groundwater quality data. It is unclear if applying this method for data which have much lower sampling frequencies would affect the reliability of the results.

1.1.2 Description of the method applied for this study (Loftis and Ward, 1980)

The following steps were undertaken:

1) **Interpolation of the datapoints**

Time series analysis requires datasets with a constant sampling interval. With real datasets this is almost impossible to achieve. Linear interpolation has been carried out to obtain a constant sampling interval. Interpolations over long unsampled periods were avoided.

2) **Assessing the seasonality of the data**

Seasonality of time series can be assessed using the autocorrelation plot. In non-seasonal data the autocorrelation reduces with increasing lag. In seasonal data at certain lags the autocorrelation increases. These lags are an indication for the presence of seasonality.

3) **Eliminating the seasonality of the data**

Depending on the results one wants to obtain, one can take out the seasonality in the dataset and apply statistical methods on the residuals (what is left of the dataset when the seasonality is removed). There are many different ways of removing seasonality from time series data; two examples are applied here:

1. Fitting and subtracting a sinusoidal function to the dataset. This function was suggested by Loftis & Ward (1980) and has a period of 1 year:

   $Y(t) = A(\cos wt+C)$

2. Averaging the values for each month and subtracting the appropriate average from each month

4) **Fitting an autoregressive – moving average model (ARMA-model) to the historic dataset.**

In each case 5 ARMA models were fitted: ARMA(1,0), ARMA(0,1), ARMA(1,1), ARMA (2,0), ARMA (0,2). The maximum likelihood method was used for the optimization. The ARMA-model ultimately used was based on the AKAIKE-criterion which takes into account both optimal fit and degrees of freedom.

5) **Calculating the values of the theoretical autocorrelation function associated with the fitted ARMA process.**

The calculation of the values of the theoretical autocorrelation function is described in Box & Jenkins (1976).

6) **Calculating the variance of the sample mean based on the theoretical autocorrelation function.**

The variance of the sample mean was calculated as described in Loftis and Ward (1980):

$$\operatorname{var}(\bar{X}) = \frac{\sigma_z^2}{k^2}\left[k + 2\sum_{n=1}^{k=1}(k-n)\rho(n)\right]$$

where:

k: number of samples

σ_z^2: variance of the remaining correlated noise

$\rho(n)$: lag n autocorrelation coefficient

The minimum sampling interval for which the calculation was executed was the sampling interval from the original dataset itself, the maximum sampling interval was the length of the dataset.

7) **Calculating the width of the confidence intervals around the annual mean**

The width of the 95 % - confidence interval is calculated based on:

$$\left\{\bar{X} - \left(K_{\frac{\alpha}{2}}\right)\left[\operatorname{var}\left(\bar{X}\right)\right]^{1/2}, \bar{X} + \left(K_{\frac{\alpha}{2}}\right)\left[\operatorname{var}\left(\bar{X}\right)\right]^{1/2}\right\}$$

where:

$\bar{X}$: the sample mean

$\operatorname{var}\left(\bar{X}\right)$ the variance of the sample mean

$K_{\alpha/2}$: the standard normal deviate corresponding to a probability of $\alpha/2$, (α=0.05)

The width of the confidence interval is then plotted against the sampling frequency for which it was calculated for a large range of sampling frequency starting from the actual sampling frequency of the dataset to a sampling frequency based on only one sample for the total length of the observation period.

1.2 Influence of sampling frequency on trend detection in a dataset

1.2.1 Review of methodology

In an existing dataset there are two types of method for detecting a trend depending on the distribution of the observations:

1. When the observations are normally distributed a curve (linear, exponential, etc) can be fitted to the dataset and the indication of goodness of fit/width of the confidence limits is a measure for the presence/absence of a trend.

2. When the assumption that the data are normally distributed is not met, one has to use non-parametric tests. The Mann-Kendall test tests for the presence of a monotonic trend (Hollander and Wolfe, 1973). When using the Theil/Sen estimator also the slope of a linear trend and the confidence limits of this slope can be calculated. In the case the data show seasonality the Mann-Kendall test can be performed to test for a monotonic trend within each season based on Kendall's tau statistic, and optionally compute a confidence interval for the slope across all seasons.

The published statistical methods describing trend analysis of time series are applicable to existing datasets. We are not aware of any significant publications evaluating methods which describe the influence of sampling frequency on trend detection, and which could be used for this project. Therefore an approach was developed for the project based on the application of the Mann-Kendall test on subsets of the selected datasets.

1.2.2 Description of the method applied

The evaluation of sampling frequency on the ability to detect a trend in the dataset was tested using the Mann Kendall test for linear trend. The Mann Kendall test is a non parametric and does not require the datasets to be normally distributed.

This test returns the slope of the best fitted linear trend to the dataset using the Theil/Sen estimator and the confidence limits at the 95% confidence interval using Gilbert's modification of the Teil/Sen method (Hollander & Wolfe, 1973).

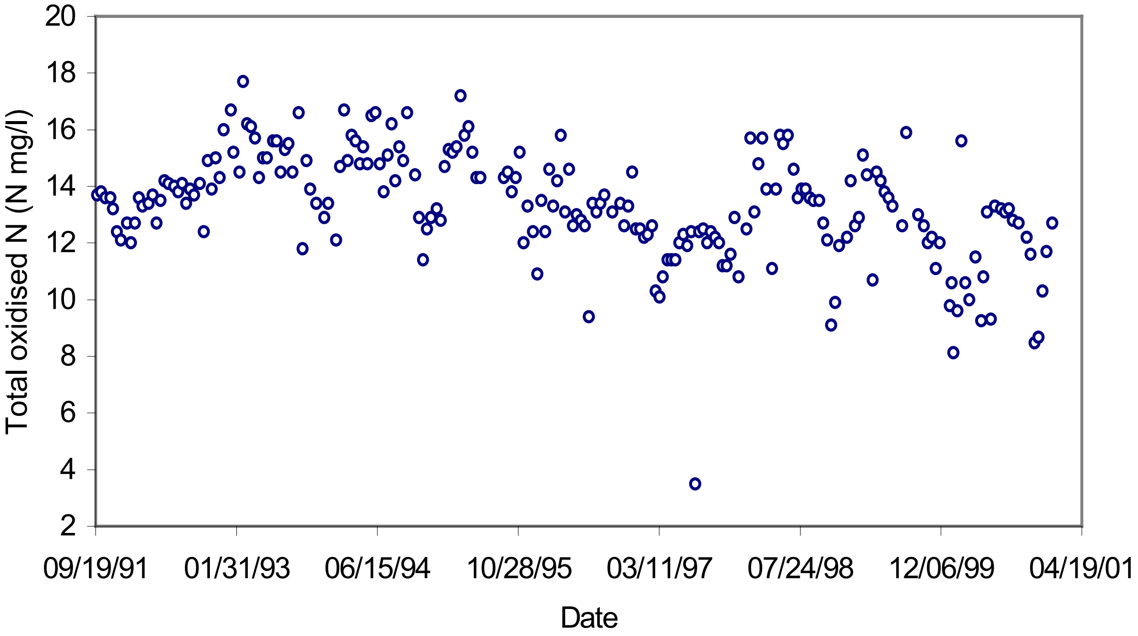
Two aspects were evaluated during the analysis based on subsets of the datasets, selected using different sampling frequencies:

- the influence of the sampling frequency on the slope;
- the influence of the sampling frequency on the confidence limits of the slope.

Additionally, the variability of the slope and the width of the confidence interval around the slope were evaluated using different subsets of the original datasets with the same sampling frequency.

1.3 Graphical presentation of the datasets used for the statistical analysis

Original data



Interpolated data

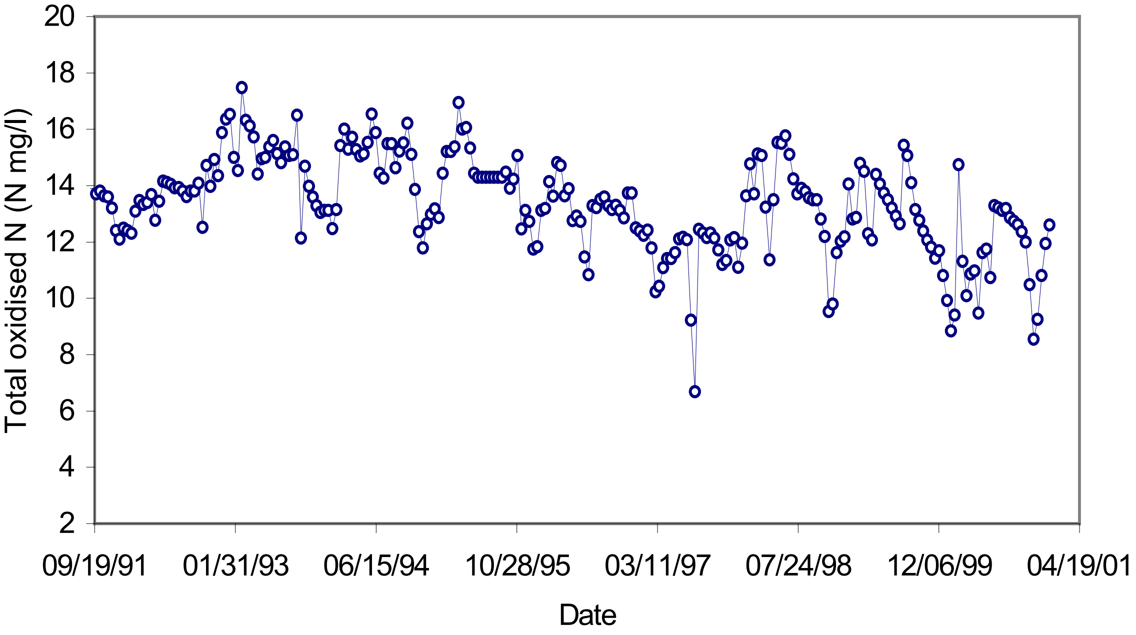
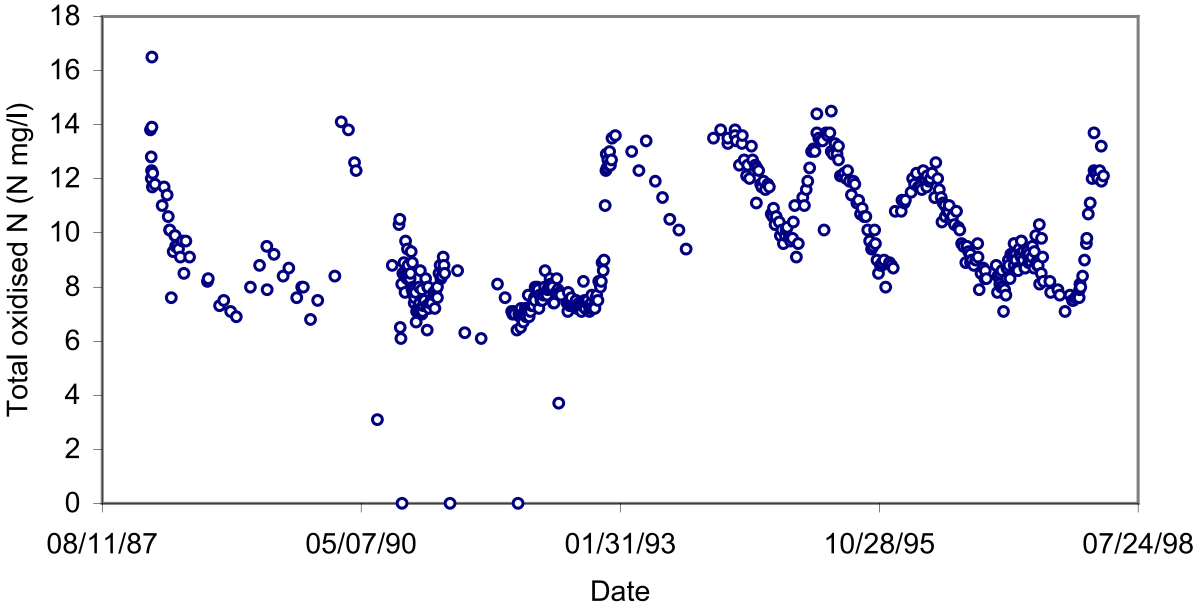


Figure A.1 TON data for Old Chalford Spring 11 (Jurassic Limestone); upper: original data; lower: interpolated data on 2 weekly intervals

Original data



Interpolated data

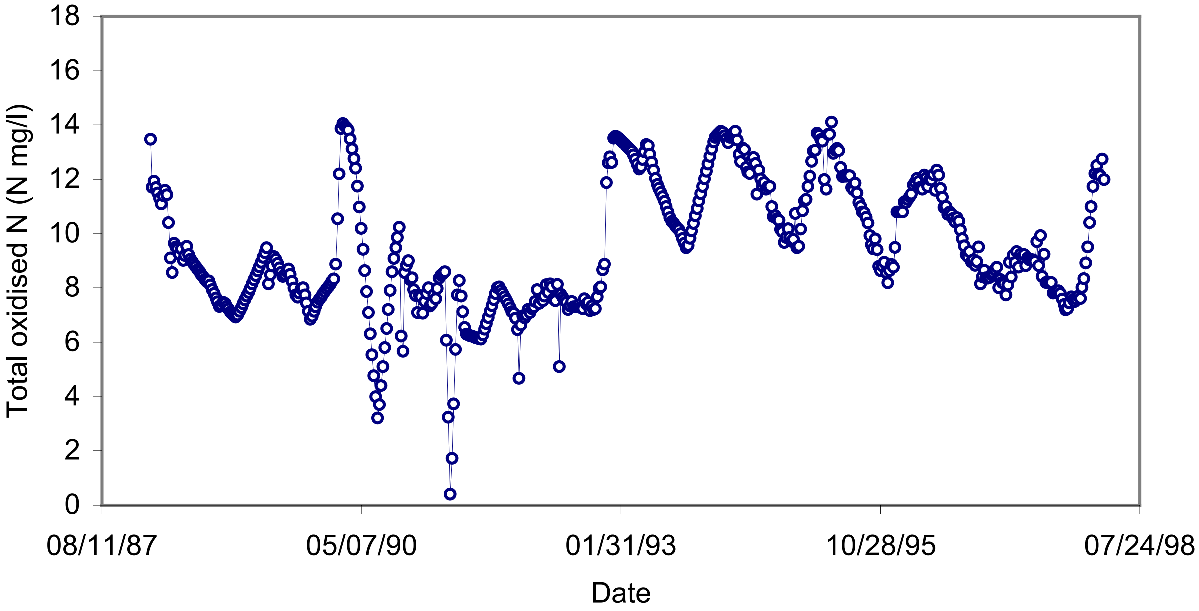
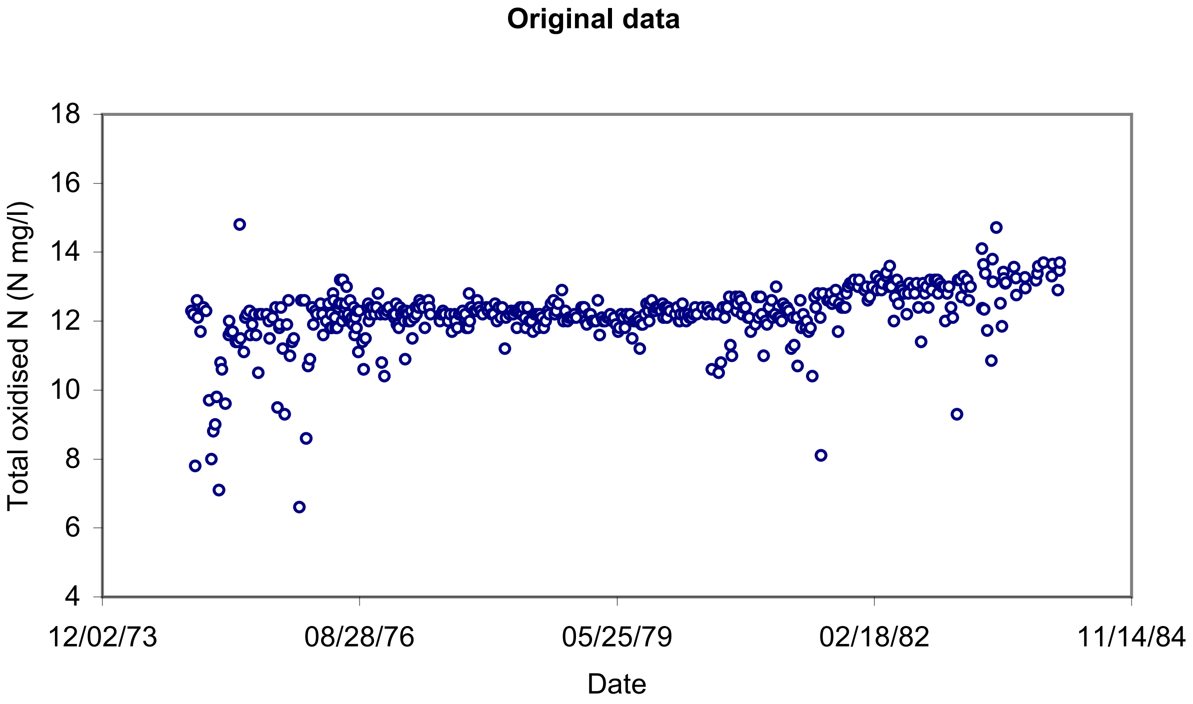


Figure A.2 TON data for UKPGWU1035 (Ogbourne, Chalk); upper: original data; lower: interpolated data on weekly intervals



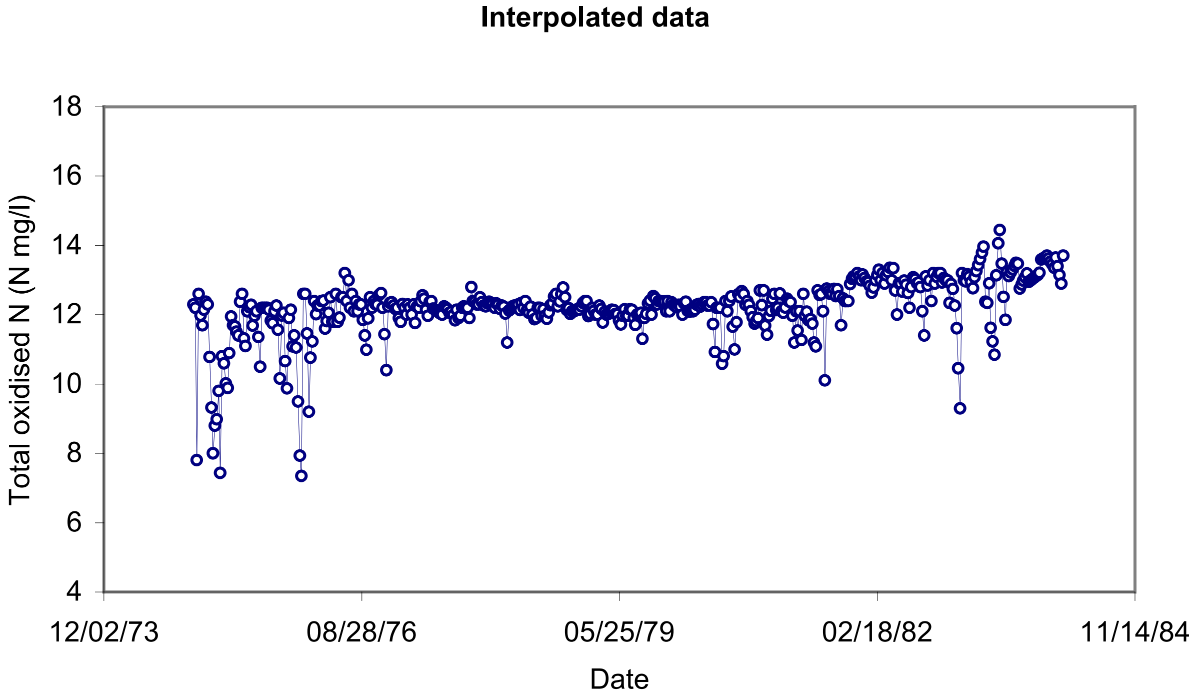


Figure A.3 TON data for Armthorpe 2 (Sherwood Sandstone); upper: original data; lower: interpolated data on weekly intervals

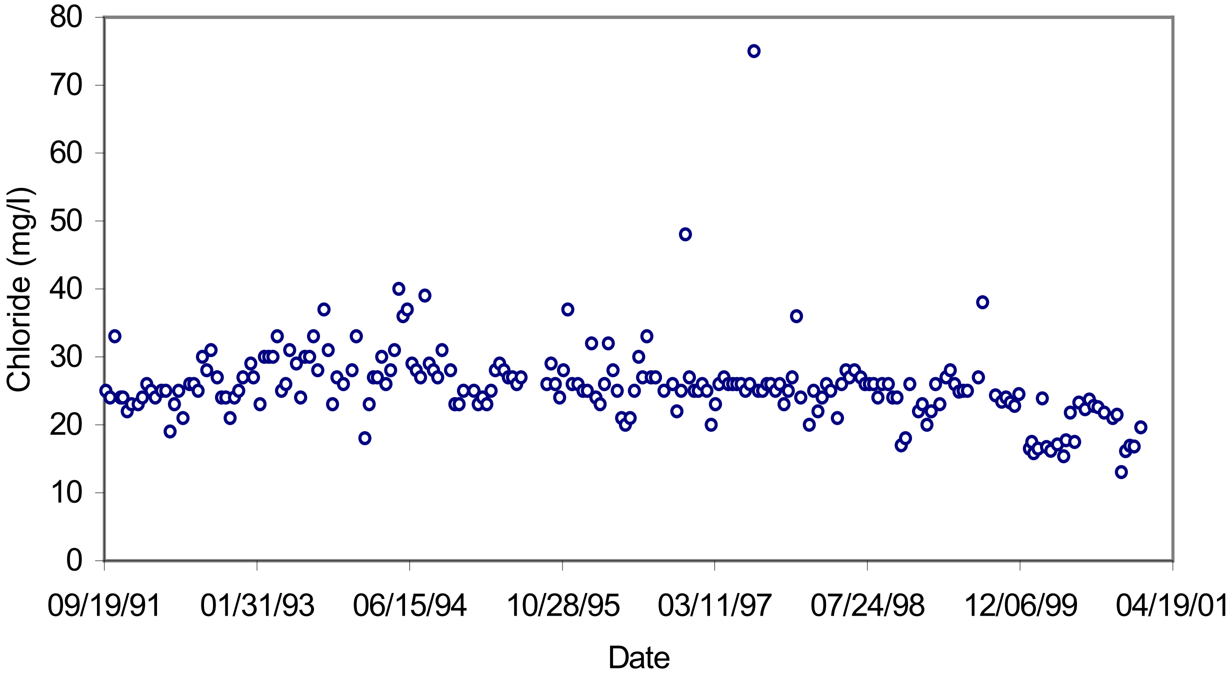


Figure A.4 Chloride data for Old Chalford Spring 11 (Jurassic Limestone)

1.4 Autocorrelation diagrams to assess the presence of seasonality in the datasets

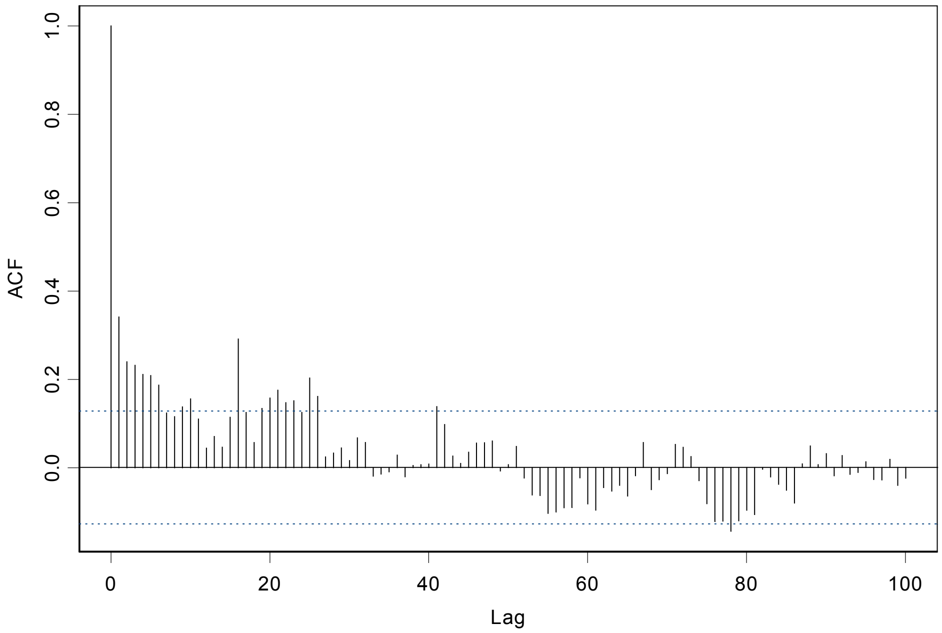


Figure A.5 Chloride data for Old Chalford Spring 11 (Jurassic Limestone), autocorrelation graph (lag=2 weeks).

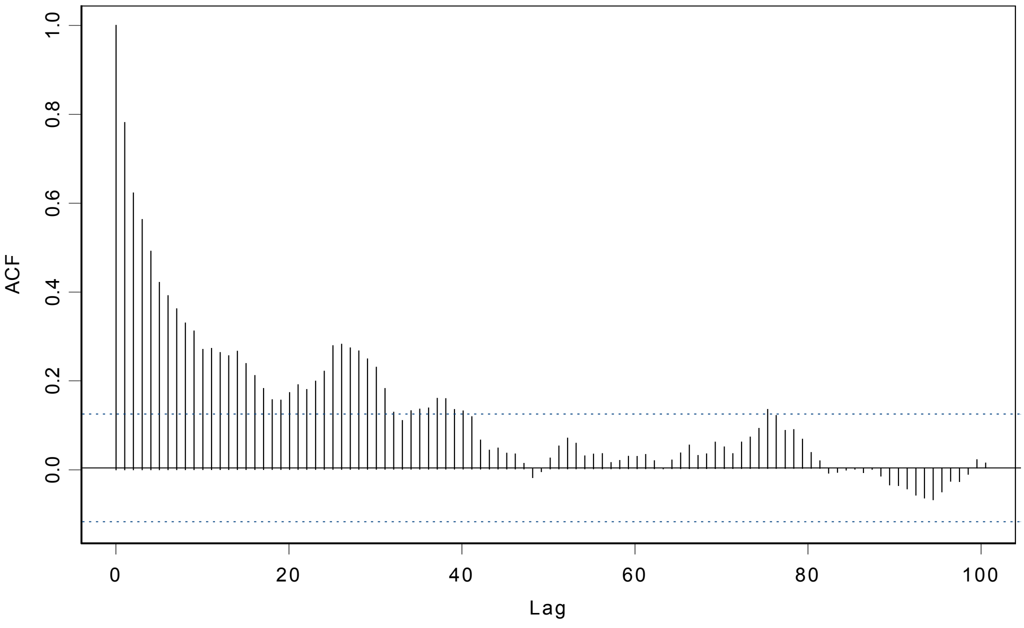


Figure A.6 TON data for Old Chalford Spring 11 (Jurassic Limestone); autocorrelation graph (lag=2 weeks).

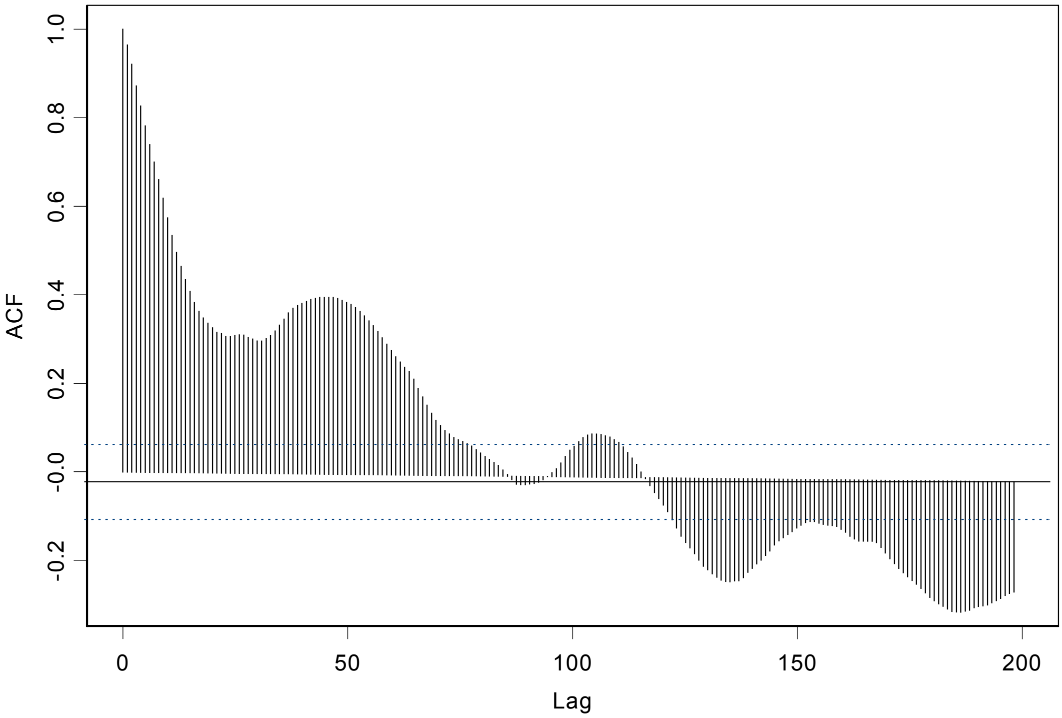


Figure A.7 TON data for UKPGWU1035 (Ogbourne, Chalk); upper: autocorrelation graph (lag=1 week).

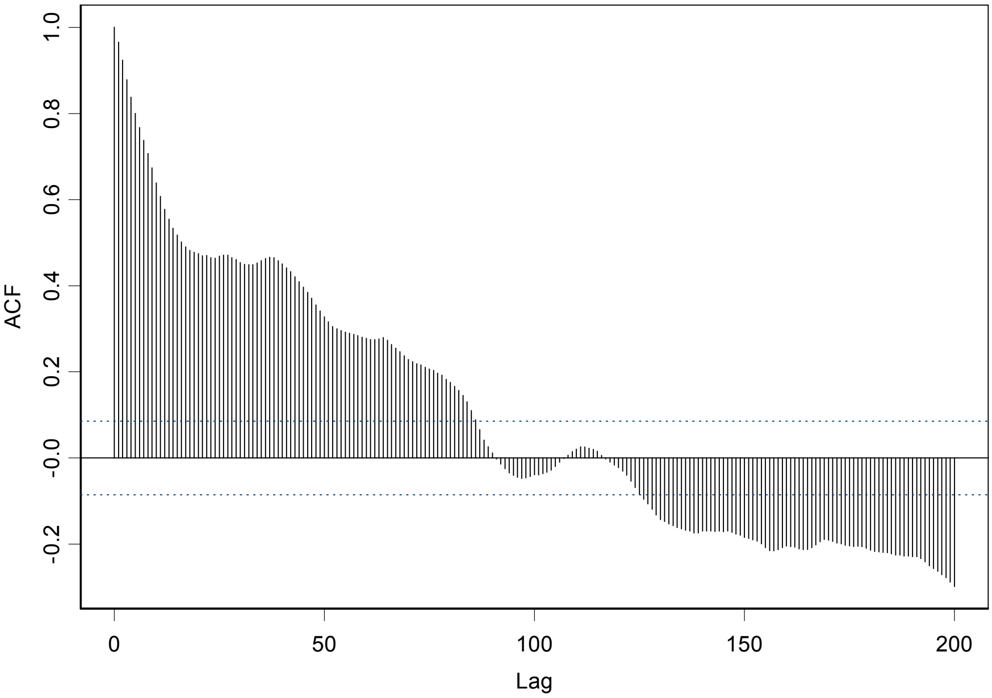


Figure A.8 TONdata for UKPGWU1035 (Ogbourne, Chalk) whereby the seasonality was eliminated; autocorrelation graph (lag=1 week).

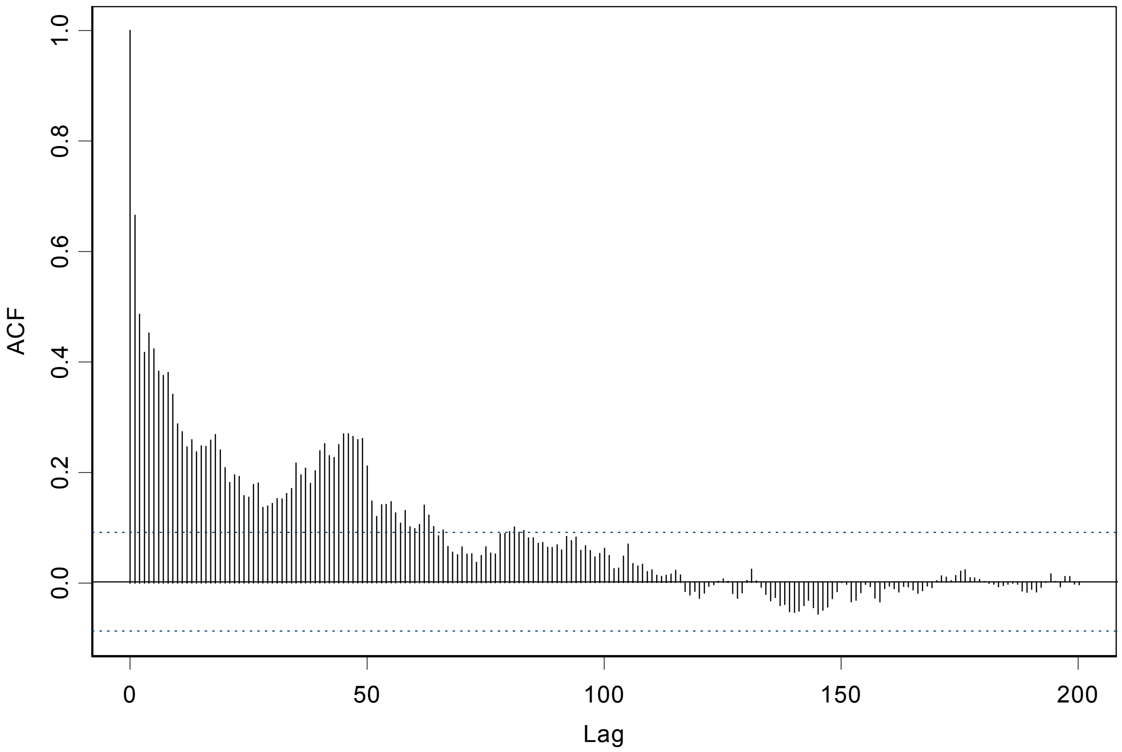


Figure A.9 TONdata for Armthorpe 2 (Sherwood Sandstone); autocorrelation graph (lag=1 week).

Appendix 2 - Recommended Analytical suites

I1	I2	I3	I4	O1	O2	O3	O4	O5	O6	O7	O8	G1	M1
Field	**Anions and Metals**	**Dissolved Metals (Filtered)**	**Special inorganics**	**ONP pesticides**	**OCP pesticides**	**Acid herbicides**	**Urons/urocarbs**	**Phenols**	**VOCs**	**PAHs**	**Special organics**	**Dissolved gases**	**Microbiology**
DO	Ammonium	Iron	Antimony	Atrazine	1,2,3 Trichlorobenzene	2,3,6 TBA	Carbetamide	4-Chloro-3-methylphenol	Benzene	Benzo(a)pyrene	Chlormequat	Methane	Faecal coliform
pH	Chloride	Manganese	Arsenic	Atrazine Desethyl *	1,2,4 Trichlorobenzene	2,4 D	Chloridazon	Chlorophenol-2	Bromodichloromethane	Benzo(b)fluoranthene	Cypermethrin	Carbon dioxide	Faecal Streptococci
SEC	Nitrate		Mercury	Atrazine Desisopropyl*	1,3,5 Trichlorobenzene	2,4 DB	Chloroxuron	Chlorophenol-3	Bromoform	Benzo(ghi)perylene	Flumethrin		Total coliforms
Temp	Nitrite		Selenium	Azinphos-Ethyl	2,3,5,6 Tetrachlorothioanisole	2,4,5 T	Chlortoluron	Chlorophenol-4	Carbon tetrachloride	Benzo(k)fluoranthene	Metamitron		
	TON		bromate	Azinphos-Methyl	2,3,5,6 Tetrchloroanailine	Benazolin	Diuron	Cresol-m	Chloroform	Fluoranthene	Carbendazim		
	Orthophosphate		Bromide	Bendiocarb	Aldrin	Bentazone	Isoproturon	Cresol-o	Dibromochloromethane	Indeno(123-cd)pyrene			
	Silica		Cyanide	Bupirimate	Chlordane cis	Bromoxynil	Linuron	Cresol-p	Dichlorobenzene -1,2	Naphthalene			
	Total Hardness		Fluoride	Carbophenothion	Chlordane trans	Chlopyralid	Methabenzthiazuron	Dichlorophenol- 2,4	Dichlorobenzene -1,3	Total PAHs			
	Alkalinity			Chlorfenvinphos	Chlorothalonil	Dicamba	Monolinuron	Dichlorophenol-2,5	Dichlorobenzene -1,4				
	pH (Lab)			Chlorpyriphos-ethyl	Chlorpropham	Dichlorprop	Monuron	Dichlorophenol-2,6	Dichloroethane-1,1				
	TOC			Chlorpyriphos-methyl	DDE OP	Fluoroxypyr	Phenmedipham	Pentachlorophenol	Dichloroethane-1,2				
	Aluminium			Coumaphos	DDE PP	Imazapyr		Phenol	Dichloroethane-1,2 cis				
	Barium			Cyanazine	DDT OP	Ioxynil		Trichlorophenol-2,4,5	Dichloroethane-1,2 trans				
	Beryllium			Desmetryn	DDT PP	MCPA		Trichlorophenol-2,4,6	Ethyl benzene				
	Boron			Diazinon	Dichlobenil	MCPB		Xylenol-2,3	MTBE				

Cadmium	Dichlorvos	Dieldrin	Mecoprop	Xylenol-2,4	Styrene
Calcium	Dimethoate	Endosulphan I	Trichlopyr	Xylenol-2,5	Tetrachloroethane-1,1,1,2
Chromium	Ethion	Endosulphan Ii		Xylenol-2,6	Tetrachloroethane-1,1,2,2
Cobalt	Ethofumesate	Endrin		Xylenol-3,4	Tetrachloroethene
Copper	Fenchlorphos	HCH Alpha		Xylenol-3,5	Toluene
Iron	Fenitrothion	HCH Beta		Total Phenols	Trichloroethane-1,1,1
Lead	Fenpropimorph	HCH Delta			Trichloroethane-1,1,2
Magnesium	Fenthion	HCH Gamma			Trichloroethene
Manganese	Flutriafol	Heptachlor			Xylene-m
Nickel	Fonofos	Heptachlor epoxide			Xylene-o
Potassium	Iodofenphos	Hexachlorbenzene			Xylene-p
Silver	Iprodione	Hexachlorobutadiene			
Sodium	Irgarol 1051	Isodrin			
Strontium	Malathion	Methoxychlor			
Sulphate*	Metalaxyl	PCB 101			
Vanadium	Metazochlor	PCB 105			
Zinc	Mevinphos	PCB 118			
Total metals	Naproamide	PCB 138			
	Parathion-methyl	PCB 153			
	Parathion-ethyl	PCB 156			
	Pirimicarb	PCB 180			
	Pirimiphos-methyl	PCB 28			

Pirimphos-ethyl

Prochloraz

Promethryne

Propazine

Propetamphos

Propyzamide

Simazine

Terbutryn

Triazophos

Trietazine

PCB 52

Permethrin-cis

Permethrin-trans

Propachlor

TDE OP

TDE PP

Tecnazene

Trifluralin