National Institute
for Public Health
and the Environment

Report 680100006/2008
B. Fraters et al.

A new compliance checking level for nitrate in groundwater?

RIVM report 680100006/2008

A new compliance checking level for nitrate in groundwater?
Feasibility study on monitoring the upper five metres of groundwater.

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This study was carried out on the instructions and at the expense of the Ministry of Housing, Spatial Planning and the Environment and the Ministry of Agriculture, Nature and Food Quality in the context of project 680100, National Monitoring Programme for the Effectiveness of the Minerals Policy.

Abstract

A new compliance checking level for nitrate in groundwater?
Feasibility study on monitoring the upper five metres of groundwater

Changing the compliance checking level for nitrate in groundwater in sand region from the upper metre to the upper five metres of groundwater has not proven to be to be expedient. The motivating factor for this change is the opportunity it would offer to comply with the objectives of the EU Nitrates Directive and the Water Framework Directive without unnecessary restriction of the total nitrogen application standards. This change in the compliance checking level lacked expediency because the current nitrate concentration in the upper five metres of groundwater in soils vulnerable to nitrate leaching failed to show a decrease. The nitrate concentrations decrease in depth in the upper five metres of groundwater in other soils. But the upper metre of groundwater also flows via run off and shallow subsurface flow (for example, via tile-drains) to surface waters, and transports nitrate and other nitrogen compounds. For this reason, water-quality objectives for surface waters have to be taken into consideration as well. For the other soils, nitrate concentrations decrease by 15 to 40% in the upper five metres of groundwater in moderately vulnerable sandy soils and 30 to 100% in slightly vulnerable sandy soils.

Key words: compliance checking level, nitrate, shallow groundwater, denitrification, surface waters

Rapport in het kort

Een nieuwe toetsdiepte voor nitraat in grondwater?
Eindrapport van het onderzoek naar de mogelijkheden voor een toetsdieptemeetnet

Het verlagen van de toetsdiepte voor nitraat in het grondwater in zandgebieden van de bovenste meter van het grondwater naar de bovenste vijf meter, blijkt niet opportuun. Het verlagen van de toetsdiepte wordt gezien als mogelijkheid om aan de doelstellingen van de Nitraatrichtlijn en de Kaderrichtlijn Water te kunnen voldoen, zonder de landbouw onnodig scherpe gebruiksnormen op te leggen. Een verlaging is niet opportuun, omdat bij de nitraatuitspoelingsgevoelige (“droge”) gronden, op basis van de beschikbare gegevens, geen afname van de nitraatconcentratie in de bovenste vijf meter van het grondwater kan worden aangetoond. Bij de overige gronden neemt de nitraatconcentratie wel af tussen één en vijf meter onder de grondwaterspiegel, maar is er meestal sprake van uit- en afspoeling van nitraat en andere stikstofverbindingen naar het oppervlaktewater. De kwaliteitsdoelstellingen voor het oppervlaktewater moeten daarom ook in beschouwing worden genomen. Voor de neutrale gronden (matige natte en matige droge gronden) bedraagt de afname van de nitraatconcentratie in de bovenste vijf meter van het grondwater 15 tot 40% en voor de natte gronden 30 tot 100%.

Trefwoorden: toetsdiepte, nitraat, bovenste grondwater, denitrificatie, oppervlaktewater

Preface

On the authority of the Ministry of Housing, Spatial Planning and the Environment (VROM) and the Ministry of Agriculture, Nature and Food Quality (LNV), the National Institute for Public Health and the Environment (RIVM), Alterra and TNO Built Environment and Geosciences carried out a study to investigate whether lowering the compliance checking level on sandy soils would be appropriate and scientifically responsible, and if so, how this should be implemented.

The study, which in the first instance was carried out solely by the RIVM, had a strongly iterative character. It started in late 2004 with a preliminary study at 50 existing National Groundwater Quality Monitoring Network (LMG) multi-screen wells. The first set-up for the field study was based on this preliminary study. This led to a survey and selection of drilling and sampling methods for the field study (Van Elzakker and Gast, 2006). The progress made was continually discussed in a consultative group and with the commissioning parties. The consultative group consisted of Wim Post (Geo Delft), Hans Peter Broers (TNO) and Gerard Velthof (Alterra). At the end of April 2005 a workshop was organized in which the results were discussed and the ideas for a field study assessed. The involved ministries, provinces, other research institutes, environmental organizations and the agricultural business community were invited to attend this workshop. The workshop resulted in the expansion of the field study with a study into the denitrifying capacity of the subsoil at the bore hole locations. Since then, Alterra and TNO have also been involved as commissionees. The field study was largely carried out in July 2005 and will be reported on by Van Elzakker et al. This report contains a synthesis of the mentioned sub-studies stated and a desk study.

The authors would like to thank Stan Smeulders and Renske van Tol, from the Ministry of VROM, and Edo Biewinga and Cindy van den Boom, from the Ministry of LNV, for supervising this study. The authors are also grateful to Martin van Rietschoten (Ministry of LNV) for his comments and valuable suggestions regarding the draft version of the summary. Finally, we are indebted to those participating in the field study in July 2005 and all the field and laboratory staff at the RIVM Laboratory for Environmental Monitoring.

Dico Fraters, Leo Boumans, Bernard van Elzakker, Lou Gast, Jasper Griffioen,
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22 May 2006

This report was published in Dutch in 2006. For the benefit of an international workshop it has been translated to English. We would like to thank the translators of the University of Amsterdam and Mariëlle van Vliet of Royal Haskoning for the main part of this work.

The authors, 13 May 2008

Guide to the report
This report is a technical scientific report, some sections of which will be difficult to follow without a certain amount of prior knowledge. Given the importance of the report to the discussion of whether or not a monitoring network should be set up for the upper five metres

of groundwater, it ought, in principle, to be readable for everyone. In order to provide everyone with sufficient information without prejudicing the report's scientific character, a comprehensive summary has been included that should meet the requirements of a broad target group.

Contents

Summary

Conclusion

Research was carried out to investigate whether lowering the compliance checking level for nitrate from the upper metre of groundwater to the upper five metres would enable compliance with the Nitrates Directive under less stringent policies on fertiliser use. Contrary to the expectations at the start of the study, it appears that nitrate concentrations do not significantly decrease within the first five metres of the groundwater in dry sandy soils vulnerable to nitrate leaching. For these soils, lowering the compliance checking level would not be beneficial. In other sandy soil types there is a decrease in nitrate concentrations with depth. However, in these soil types surface and subsurface transport of nitrate and other nitrogen compounds occurs towards surface waters.

In neutral soils (moderately vulnerable to nitrate leaching) nitrate concentrations decreased by 15 to 40% within the first five metres of groundwater. In wet soils with very limited vulnerability to nitrate leaching nitrate concentrations decreased by 30 to 100% within the first five metres. Wet soils, and some neutral soils, need to be drained to make them suitable for agricultural purposes. Due to this drainage considerable surface and subsurface run-off occurs, transporting nitrate and nitrogen compounds to nearby surface water. Nitrate concentrations around 50 mg l^{-1} (equivalent to 11.3 mg l^{-1} nitrate-nitrogen) in the upper metre of groundwater result in surface water concentrations three or four times as high as the Dutch nitrogen target of 2.2 mg l^{-1}.

Routine measurements, such as used in monitoring programmes and networks, are not sufficient to ascertain whether a decrease in nitrate levels is caused by denitrification (break down of nitrate). It is also not possible to establish the link between denitrification and the increase of undesirable by-products (e.g. sulphate and heavy metals) by using routine measurements. Due to the large spatial variation in nitrate concentrations in the upper metre of groundwater, the differences in changes in nitrate concentrations within the first five metres of groundwater, the heterogeneity of soil geo-chemical characteristics, variation in soil fertilisation with nitrogen, and variation in precipitation, the trends yielded by routine measurements are not sufficiently clear for a sound interpretation.

Introduction

In the past two decades, Dutch agriculture has been subject to increasingly stringent policies regarding fertiliser use (methods, amount and period of application). From the late 1980's, the use of animal manure has seen increasing limitations. This started with the prescription of maximum levels for the use of phosphate with animal manure. From 1998 onwards, the nitrogen surplus was regulated by limiting the use of nitrogen fertiliser (artificial fertiliser and animal manure) via a mineral accounting system (MINAS). Within this system the nitrogen surplus (the difference between farm import and exports of nitrogen) was regulated in the form of a farm gate balance. As of the start of 2006 the Dutch mineral legislation has been adapted to comply with the Nitrates Directive. Within the new system, the use of animal manure, the total nitrogen fertilisation and the total phosphate fertilisation are limited using application standards. These standards are being increasingly tightened.

The Dutch government and the European Commission have agreed that the application standards for 2009 should lead to compliance with the threshold value of 50 mg l^{-1} nitrate in groundwater. This agreement is the result of negotiations with the European Commission regarding the implementation of the EU Nitrates Directive via the Third Dutch Action Programme (2006-2009) and the Derogation decision. Within the Nitrates Directive, if the threshold value for groundwater is exceeded, steps must be taken to mitigate the problem. In addition, European Member States must comply with the Water Framework Directive (WFD) in 2015. Within the WFD, a lasting good ecological potential must be achieved for surface waters. One of the aspects that threaten the ecological potential of surface waters is eutrophication caused by excessive leaching of nutrients via run-off and shallow groundwater. The depth at which compliance to the threshold value should be checked in groundwater is not defined in existing European policy and legislation.

Within the Nitrates Directive the use of animal manure is limited to 170 kg of nitrogen per hectare. After negotiations with the European Commission the Netherlands obtained a derogation for animal manure of 250 kg ha^{-1} (2005/880/EU).The derogation applies only to farms with at least 70% grassland area. The Netherlands has assured the European Commission that the derogation will not have a negative effect on nitrate levels in groundwater. To monitor this the Commission requires that the Netherlands measures nitrate levels on at least 300 farms that make use of the derogation and annually informs the European Commission of the results.

One of the principles of the Third Dutch Action Programme is that the threshold value of 50 mg l^{-1} will not be exceeded in the upper groundwater. In the period 2000-2002 this threshold was exceeded on 80% of the farms in the sandy soil region where measurements were taken in the upper metre of groundwater. In the coming years until 2009, the application standards included in the new Fertiliser Act that came into force in 1 January 2006 will be gradually tightened in order to comply with the threshold value.

In 2004 the Fertiliser Act that was applicable at this time was evaluated. In the ensuing discussions with the Dutch Lower Chamber, the Minister for Agriculture, Nature and Food Quality committed himself to a study on the possibilities for lowering the compliance checking level for nitrate for the sandy regions. The aim of the study was to allow the Ducth government to make a go-no go decision on whether to lower the compliance checking level for nitrate. The draft monitoring guidelines composed by the European Commission leave room for such a decision. In the guidelines, which have never formally been adopted, the following is said about compliance checking level:

"Both shallow and deep groundwater should be included in the monitoring network …. For example, both the upper and lower parts of the aquifer that are connected to the soil should be sampled, as the upper parts (the first five metres of the saturated zone) will tend to respond quickest to changes in agricultural practice, …".

In the Third Dutch Action Programme 2006-2009 the Netherlands has indicated that as part of the next evaluation of the Fertiliser Act in 2007 research will be carried out to investigate the possibilities for lowering the compliance checking level. Aside from the question whether nitrate concentrations are less likely to be exceeded at a lower compliance checking level, the study focuses on the feasibility and the environmental effects of lowering the compliance checking level. The Lower Chamber has been informed that the current compliance checking level is part of a package of agreements with the European Commission, and that research

results may lead the Dutch government to negotiate with the European Commission regarding a change in compliance checking level.

Goal and delineation of the study

The goal of the study is to gather information on which the Dutch government can base decisions on whether to lower the compliance checking level and how this can be justified to the European Commission and put into practice.

The present study has been carried out to fulfil this goal and follows on from an earlier study carried out by Boers et al. in 2004. This earlier study investigated (a) whether regions where denitrification takes place in the saturated subsoil without adverse (environmental) consequences can be accurately designated and (b) at what depth compliance to the threshold value for nitrate (50 mg l^{-1}) should be tested. The results of this study indicated that it is not feasible to designate such areas as there is insufficient information on the extent to which denitrification occurs within different parts of the sandy regions. A large mapping and measuring effort would be required in order to be able to designate areas where denitrification occurs with sufficient accuracy. Broers et al. also suggest that lowering the compliance checking level should only be considered for those areas where groundwater quality does not directly influence surface water quality (areas with little run-off). Furthermore, the study concludes that the compliance checking level should not be lowered to more than 10 metres.

In accordance with the draft monitoring guidelines of the European Commission the present study is restricted to the upper five metres of the groundwater. In the Netherlands, on a national scale, there is no existing monitoring network of the upper five metres of groundwater. The national monitoring programme for the effectiveness of the minerals policy (LMM) is used to monitor the quality of the first metre of groundwater; the national groundwater quality monitoring network (LMG) is made up of permanent wells with well screens at 10 m and at 25 m below the surface. On average, 10 m below the surface corresponds with approximately 7.5 m below the groundwater table.

The present study limits itself to the sandy regions of the Netherlands. For clay and peat soils, lowering the compliance checking level is undesirable. The nitrogen load to surface waters in these areas comes mainly from surface run-off and leaching through shallow groundwater flow. As the objectives for nitrate in surface water are even stricter than for nitrate in groundwater, the nitrate concentration in the first meter of groundwater needs to be lower than 50 mg l^{-1} if the objectives for surface water are to be met.

Research question and set-up of research

The goal of the study has been translated into the following research question: Is it beneficial to change the compliance checking level for nitrate in groundwater and if so, what are the prerequisites when designing a network to monitor at a different depth?

Based on this research question, seven sub-questions were defined that further elaborate on scientific, technical and instrumental aspects. Two field studies (incorporating laboratory trials) and a desk study were carried out in order to answer these sub-questions. The field studies focused mainly on the technical and instrumental questions, while the results of the desk study were mainly used to answer the scientific questions.

Answers to the sub-questions

Sub-question 1: Does the nitrate concentration decrease with depth in agricultural lands in the sandy regions? If so, what is the extent of this decrease and are there differences between regions?

There is no indication that nitrate levels decrease with depth in the dry sand regions (see for example figure S1). Data from studies performed in 2004 and 2005 support this conclusion. In a number of wells (mainly in dry sand) the nitrate concentration increased with depth. In the neutral and the wet sandy regions, the nitrate concentration did decrease on average within the first five metres of the groundwater column. The extent of the decrease varied between 15 and 40 % in the neutral areas and between 30 and 100% in the wet areas.

Based on these results, changing the compliance checking level for nitrate in the dry sand areas will not result in easier compliance with the threshold value for nitrate (50 mg l^{-1}). Lowering the compliance checking level in neutral and wet sandy regions could increase compliance with the threshold value. Therefore, it is important to establish if this decrease is due to denitrification and if so, whether this denitrification leads to any adverse environmental effects.

Nitrate levels increased with depth in some years and decreased with depth in others (Figure S1). The general trend is that the soils where the most marked decrease with depth was measured (the wet soils) had the lowest nitrate concentration in the first meter of the groundwater. The soils with the highest concentration in the upper meter of groundwater (dry soils) showed, on average, no decrease in nitrate concentration with depth.

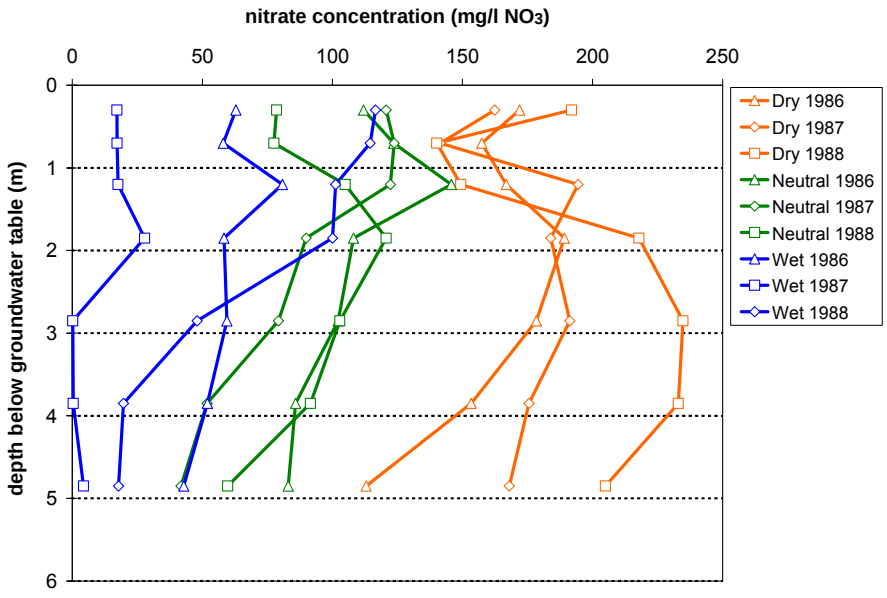

Figure S1 Development of the average nitrate concentration for three drainage classes (wet, neutral and dry) in the upper five metres of groundwater on dairy farms in the sandy regions of the Netherlands (data from 1986 to 1988).

Sub-question 2: If the nitrate concentration decreases within the upper five metres, can this be attributed to denitrification, or are there other causes for this decrease?

In neutral and wet sandy soils, the nitrate concentration does drop between the first and fifth metre of the groundwater column. This decrease is probably partly due to denitrification. However, we expect that a number of other causes also contribute to this decline, such as hydrological aspects (interfering soil layers), regional upward seepage from underlying water layers, and drainage of part of the precipitation surplus to nearby surface waters.

If a decrease in nitrate concentration is caused by factors other than denitrification, then the nitrate may simply be transported to another part of the groundwater or to the surface water. Alternatively, when the decrease is caused by a temporary variation in precipitation, the decrease will also be temporary. If there is an interfering soil layer between the first and fifth meter of groundwater, then the deeper groundwater in the fifth meter may have originated from precipitation in another area (not on the agricultural land) and subsequently have moved via horizontal transport to the agricultural land. In this case a decrease with depth does not indicate denitrification, and the nitrate-rich groundwater from the agricultural land will also move elsewhere. If denitrification does occur, then the capacity for this process within the soil may be limited by availability of energy sources for the process.

Sub-question 3: If denitrification occurs, to what extent does this process lead to adverse environmental effects such as an increase in the levels of sulphate or heavy metals, or increasing hardness of the water?

It was not possible to quantify the increase in other substances as a result of denitrification. Because of the heterogeneity of the subsoils in the Dutch sandy regions, there is considerable spatial variation in the rate of denitrification and in the effects that denitrification has on other aspects of groundwater quality.

If the compliance checking level for nitrate were to be lowered, and this led to less need for stricter application standards for nitrogen fertiliser, then more nitrate would occur in the groundwater and more denitrification could occur. This could lead to an increase in the products of denitrification, including sulphate and heavy metals. Other studies have demonstrated such increases. However, the present study yielded insufficient data to quantify the problem for Dutch sandy soil regions.

Sub-question 4: In the clay and peat regions, lowering the compliance checking level in order to be able to apply less strict application standards would lead to insufficient reduction of the nitrate load to surface waters. To what extent does this apply to the sandy soil areas?

If the compliance checking level for sandy soils is lowered then concentrations exceeding 50 mg l^{-1} will be accepted in the first meter. This implies allowing higher concentrations in the drain water. This will lead to nitrate concentrations in tile drain water exceeding 11.3 mg l^{-1} nitrogen (the objective used to support the derogation). Surface water concentrations may be three or four times as high as the target value of 2.2 mg l^{-1} nitrogen.

For clay and peat regions the target values for groundwater are partly based on the targets for surface water because the surface water is largely fed by run-off and leaching via shallow groundwater flow. In the sandy region, surface water must also comply with the European targets. Certain sandy areas (the wet areas and some neutral areas) are drained using tile

drains and ditches. The drainage water is discharged into the surface water and in this way nitrate is also released into the surface water.

The results demonstrate that in a drained area with a concentration of 50 mg l^{-1} in the upper metre of the groundwater (equivalent to 11.3 mg l^{-1} nitrogen) the Dutch nitrogen target level for surface water (2.2 mg l^{-1}) will generally be exceeded in the ditches. The nitrogen target level for surface water is based on preventing eutrophication. In general, the nitrate concentration in ditches in drained farmland is approximately 35% lower than the nitrate concentration in the upper metre of groundwater, see Figure S2. With a nitrate concentration of 50 mg l^{-1} (11.3 mg l^{-1} nitrate-nitrogen) in the groundwater, the concentration in the ditches will be approximately 7.3 mg l^{-1} nitrogen, a level three or four times as high as the target value for surface waters. In addition to nitrate-nitrogen, ditches also receive ammonium-nitrogen and organic-nitrogen.

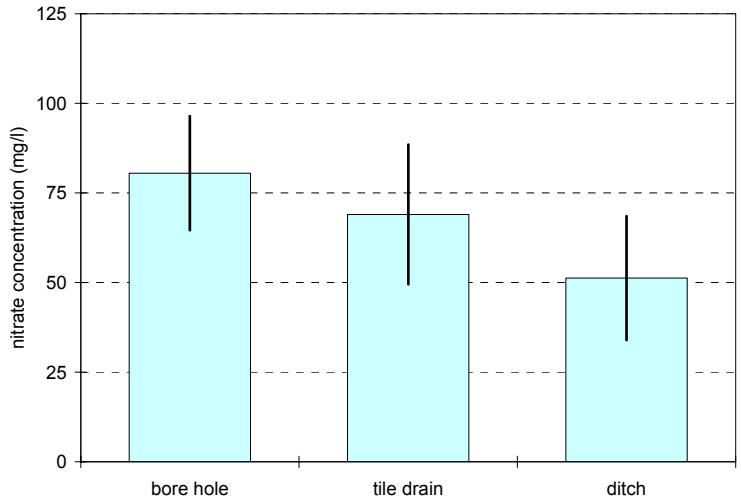

Figure S2 Average nitrate concentration in groundwater (bore hole), tile drain water and ditchwater on 24 farms in the sandy regions of the Netherlands (data from winter 2004-2005). The vertical lines indicate the range within which the average nitrate concentration is located with 95% certainty.

It is preferable to install permanent wells with several screens in the field. Several screens are a prerequisite to make up for the fact that some screens may not yield any water after placement. This lies in the fact that screens can be placed in impermeable soil layers or they can silt up with fine soil particles from the groundwater. Wells should be placed within the agricultural property. When wells are placed outside the farmland, the risk exists that the groundwater sampled has infiltrated outside the field, even if the direction of groundwater flow in the subsoil has been accounted for. Manual drilling methods are unsuitable as the desired depth below the groundwater table cannot always be attained manually.

Sub-question 5: : Regardless of how complex, is it feasible to measure the nitrate concentration at a depth of five metres in the saturated zone, or can the average nitrate concentration in the first five metres be determined?

If the compliance checking level is lowered, monitoring data on nitrate will also be needed to check compliance. It is possible to routinely measure nitrate concentrations at a number of

depths in the first five metres of the saturated zone. Such measurements cost more than those in the top level of groundwater.

If possible, permanent multi-screen wells should be installed inside the plots. A number of screens are needed, as no groundwater can be sampled with some of them, e.g. because the screen is in a relatively impermeable stratum or because it has silted up with fine particulate matter. The wells should be installed inside the plots, as with wells outside the plots there is a risk of sampling groundwater which comes partly from elsewhere. Even if the groundwater flow direction has be taken into account when installing wells of this kind. Manual techniques are not suitable: the desired depth below the groundwater table cannot always be achieved with manual drilling.

Sub-question 6: Regardless of how complex, is it feasible to measure the extent to which denitrification occurs, whether it is sustainable, and whether the process produces undesirable by-products?

It is not feasible to measure the extent to which denitrification occurs, the sustainability or whether undesirable by-products (e.g. sulphates, heavy metals) result using routine measurements such as those used in monitoring programs or networks. Using a combination of existing non-routine methods it is possible to determine the extent of denitrification and the presence of undesirable by-products at specific locations. One unavoidable uncertainty is that other soil processes may produce the same undesirable compounds, so that the extent to which denitrification leads to a deterioration in groundwater quality cannot be accurately established.

The compliance checking level can only be lowered if nitrate levels decrease due to denitrification and this process does not lead to an increase in other undesirable compounds (e.g. sulphates and heavy metals). It is therefore important to establish via measurements that any decrease in nitrate concentrations can be attributed to denitrification and that this process does not result in undesirable by-products.

There are methods to measure groundwater composition and thus gain insight into the current groundwater quality and the historical shifts therein. However, these measurements cannot irrevocably prove that a decrease in nitrate concentrations is due to denitrification, nor do they provide information on the future groundwater quality or the sustainability of denitrification. There are chemical and biological analyses available to measure the denitrification capacity of the subsoil, which may also yield insight into the sustainability of denitrification. The choice of the most suitable type of measurement depends on the research question at hand.

Sub-question 7: Regardless of how complex, is it feasible to measure whether the groundwater at five metres depth has the same origins (infiltrated at the same place) as the groundwater in the first metre?

It is not feasible to measure whether groundwater at five metres depth has the same origins as groundwater in the first metre, or at least not using routine measurements in a monitoring program or network. By using a combination of methods currently not used in routine programs it is possible to determine whether groundwater at five metres depth infiltrated at the same place as groundwater in the upper metre of groundwater.

Instead of denitrification, a decrease in nitrate concentrations may be due to nitrate-rich water flowing off horizontally and being replaced by cleaner water from elsewhere. This results merely in displacement of the problem. In order to discount this possibility, it is necessary to establish whether the groundwater at five metres depth infiltrated at the same place as the groundwater in the upper metre.

Points of consideration

At what level should compliance be checked?

This study focussed on changes in nitrate concentrations within the upper five metres in order to test whether lowering the compliance checking level within the first five metres would be beneficial. If the compliance checking level were to be lowered, the question still remains to which depth. Compliance checking can occur just in the fifth meter, or by taking the average of measurements in the first five metres of groundwater. This second option fits in better with the draft monitoring guidelines of the Nitrates Directive. However, this brings about only approximately half of the decrease in nitrate concentrations (if such a decrease even exists).

Designation of infiltration areas

Within the sandy regions, we distinguish infiltration areas and artificially drained areas. In artificially drained areas run off and leaching of nitrogen to surface waters occurs via the soil surface and shallow groundwater flow. This is not the case in infiltration areas, where nitrate tends to be transported vertically into deeper soil layers. This study distinguishes between dry (nitrate vulnerable soils), neutral and wet soils. For these soil types, changes in nitrate concentrations with depth have been examined. The dry soils are situated in the infiltration areas and the wet soils in the artificially drained areas. It is not clear whether neutral soils are fully situated in the artificially drained areas or whether they also occur in infiltration areas. It may be technically feasible to establish this, but the resulting designation would not necessarily be useable in practice.

Sustainability of denitrification

This study did not measure the sustainability of denitrification in the subsoil (the period of time during which denitrification may sufficiently limit nitrate concentrations in the subsoil). No data are known on the sustainability of denitrafication in the subsoil on a national scale or within the scale of the sandy regions.

1. Introduction

1.1 Nitrate in the soil and groundwater

1.1.1 Nitrate and the nitrogen cycle

Nitrogen is an essential element for both plant and animal. It takes many forms. Figure 1.1 shows a diagram of its most important forms and their interrelationships. Plants are able to take up nitrogen from the soil, primarily in the form of nitrate (NO_3^-) or ammonium (NH_4^+). Some plant species can also take up nitrogen by means of nitrogen binding, a process that is realized by microbes living in symbiosis with these plants. Nitrate and ammonium are inorganic nitrogen compounds. Ammonium is a cation that can adsorb to soil particles. In solution it is in equilibrium with dissolved ammonia (NH_3). The acidity of the soil affects this equilibrium. In alkaline soils (pH $\geq$ 7) ammonium will rapidly evaporate as ammonia gas. In the upper layers of most sandy soils, ammonium in solution will rapidly be converted into nitrate (nitrification), because this environment contains sufficient oxygen. Ammonium concentrations in the upper groundwater are therefore usually low (< 2 mg l^{-1}). Nitrate is an anion that dissolves easily in water and does not bind to soil particles. As a result, nitrate will easily leach out to the groundwater. In the soil and groundwater, nitrate can be converted into various other forms, including nitrogen gas. The conversion of nitrate into nitrogen gas, known as denitrification, is described in more detail in Appendix 1.

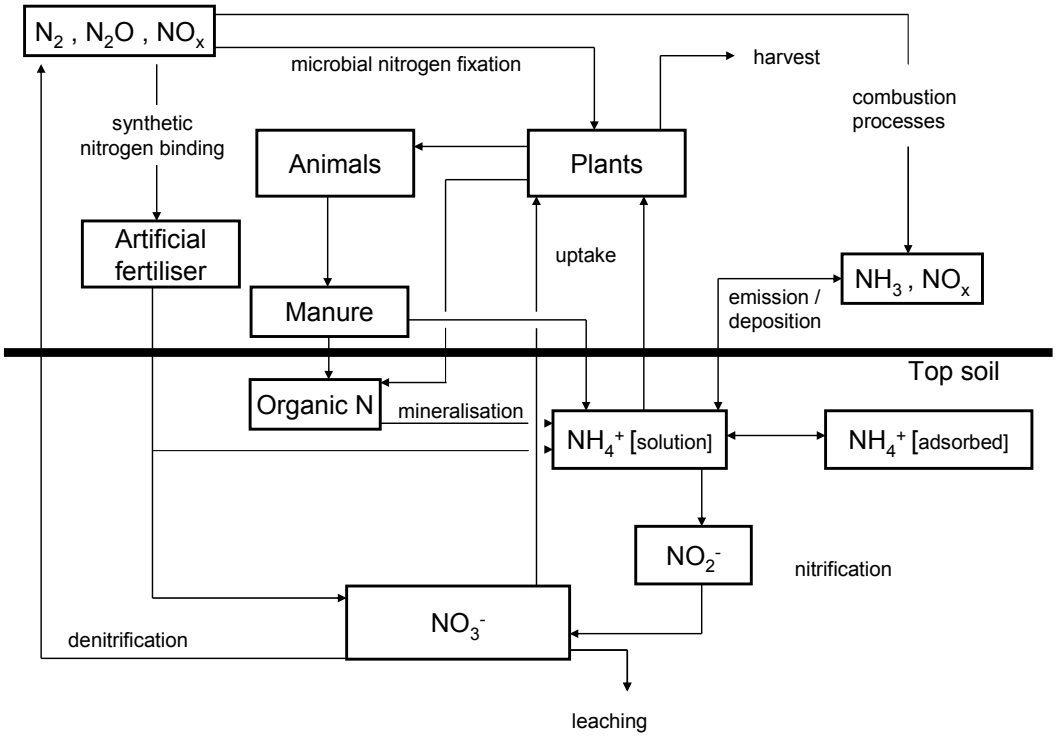

Figure 1.1 Simplified diagram of the soil nitrogen cycle.

For an extensive discussion of the current knowledge of the behaviour of nitrate in the subsoil, see chapter 3 of the compliance checking level report by Broers et al. (2004). A number of relevant aspects are discussed briefly below.

1.1.2 Soil type, nitrate leaching and nitrogen compounds

Soil properties, such as type and draining capacity, determine the leaching of nitrate from the soil to ground and surface water to a large extent (Schröder et al., 2005, Fraters et al., 2004). Nitrate concentrations in the upper groundwater of farms in sand, clay and peat regions in the Netherlands vary, see Figure 1.2, though this cannot be attributed to differences in the use of nitrogen. The lower nitrate concentrations in clay soils than in sandy soils and the almost total absence of nitrate in peat soils are attributed to the fact that more denitrification takes place in these soil types. This is partly a result of their structure and partly of their higher organic content. The soil type also affects the ammonium concentrations, which are, by nature, higher in peat soils than in clay and sandy soils.

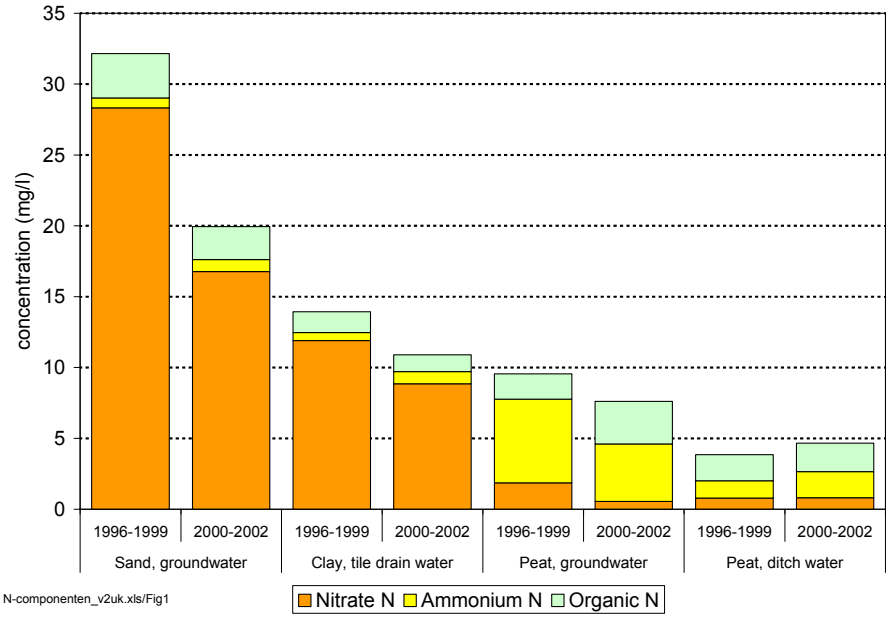

Figure 1.2 Nitrogen concentrations in water on farms in the sand, clay and peat regions of the Netherlands for the periods 1996-1999 and 2000-2002 (Fraters et al., 2004)

1.1.3 Groundwater level and nitrate

Large variations can also be found between nitrate concentrations at measuring locations on sandy soils that cannot be attributed to the differences in nitrogen use. Boumans et al. (1989) showed that differences between average groundwater levels and seasonal fluctuations in these levels could be the cause of such differences. The difference in groundwater level development in a year and the difference between the average (mean) highest (MHG) and mean lowest groundwater level (MLG) are recorded in a system of groundwater table classes (Gts). Eight groundwater table classes have been distinguished plus a few subclasses (Gt I through Gt VIII), see Locher and De Bakker (1993). Gt I indicates high average groundwater levels and Gt VIII indicates low average groundwater levels. Boumans et al. (1989) found, for example, that the upper metre of the groundwater in a soil with Gt II had only 5% of the nitrate measured in a soil with Gt VIII at the same level of fertilization. Willems et al. (2005a) showed recent results and discussed the effects of the decrease in groundwater levels.

Based on research carried out in the period 1992-1995 on 100 farms in sandy areas, these Gts were grouped in three drainage classes on the basis of the MLG and MHG (Fraters et al., 1997, Boumans et al., 1997), see Table 1.1. This study and the analyses of data from later years showed that this aggregation resulted in the best explanation of the differences in nitrate concentrations. Willems et al. (2005a) used a slightly different classification (three groups), the distinction between wet and neutral being based on the MHG instead of the MLG. The Gts IV and V/V* then switch classes.

Table 1.1 Characteristics of the different drainage classes

Drainage class	Groundwater table class (Gt)	MHG (cm below surface level)	MLG (cm below surface level)
Wet	I, II, II*, III, III*, IV	< 40 / > 40	< 120
Neutral	V, V*, VI	< 80	> 120
Dry	VII, VIII (formerly VII*)	> 80	> 120

The reason that less nitrate is measured in the upper metre of groundwater in soils in the wet drainage class than in that of the dry soils is probably caused by more denitrification. This higher denitrification activity in wet soils is caused by two factors. The first is the naturally higher organic content in wet soils than in dry; this organic content provides an energy source for denitrification. The second factor that plays a role here is the combination of the decrease in the organic content with depth and high groundwater levels in wet soils compared to the low groundwater levels in dry soils.

If the groundwater level is high, as is the case with wet soils, it is more likely that denitrification will take place than with a low groundwater level. This is because the layers saturated with water, in the case of a high groundwater table, contain more organic matter and oxygen deficiency therefore arises more quickly. Anoxia is another requirement for denitrification. Moreover, wet soils usually contain more organic matter over the whole depth profile than dry soils. Wet soils, and some neutral soils, are less suited to agriculture naturally. These soils are usually drained by digging ditches to improve their agricultural properties. Tile-drains may also be placed in the subsoil for the same purpose. Some of the precipitation surplus is discharged via these ditches and drains and does not infiltrate into deeper groundwater layers. Nitrate is also transported along with this water in the direction of the surface water. The upper metre of groundwater in these soils will therefore be older, on average, than that in drier soils. This means that there has also been more time for denitrification to take place. There is no information available as to the extent to which this also affects the decrease in the nitrate concentration with depth.

1.1.4 Regional differences in subsoil and water quality

The quality of the groundwater at depths below the first metre shows regional differences. Reijnders et al. (2004), for example, shows that in shallow groundwater (10 m below surface level) in the sand region in Noord-Brabant there are marked differences between the nitrate and sulphate target value exceedances at the Peelhorst and the Slenk, see Figure 1.3. These differences are related to geochemical properties of the subsoil.

Van Beek et al. (2002) grouped the drinking-water catchments that use groundwater as their source according to various types of vulnerability, see Figure 1.4. This vulnerability is

determined based on the chemical properties of the soil, as manifested in the chemical composition of the groundwater, see Table 1.2.

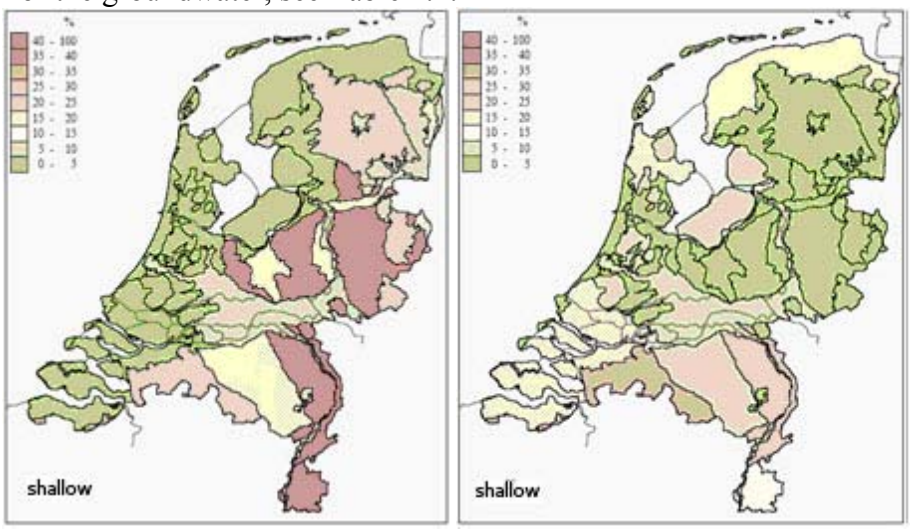

Figure 1.3 Nitrate (left) and sulphate (right) in the shallow groundwater of the Netherlands in 2000. Percentage of observations that exceed the target value for each ecological district (Reijders et al.., 2004)

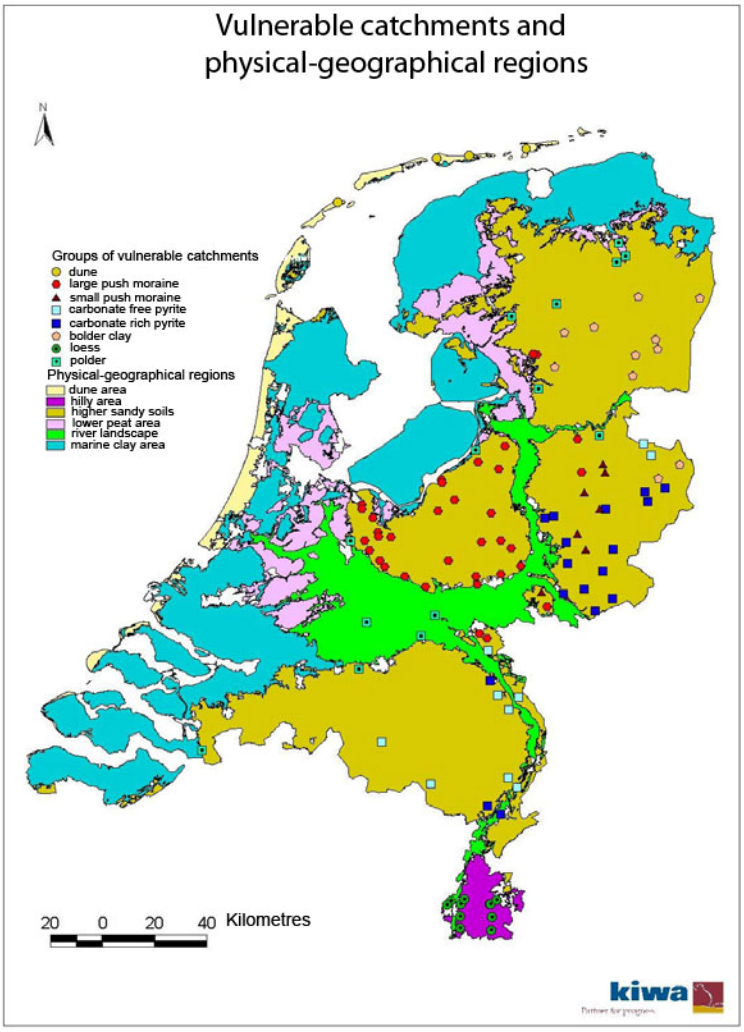

Figure 1.4 Location of vulnerable groundwater catchments classified according to group (Van Beek et al.., 2002).

Table 1.2 Classification of groups of vulnerable catchments (from Willems et al., 2002, based on Van Beek et al. 2002)

Group	Agricultural influence[1]	Effects of fertilization	Region
Carbonate-free pyrite	++	NO_3, SO_4, Ni	East Noord-Brabant, North Limburg
Carbonate -rich pyrite	++	SO_4, Hardness	Regions include Achterhoek, Twente
Large push-moraine	+	NO_3	Regions include also the Veluwe, Utrechtse Heuvelrug
Small push-moraine	++	NO_3, SO_4, Hardness	Widespread in sand region
Boulder clay	+	Hardness	Drenthe
Loess	++	NO_3, SO_4, Hardness	Zuid-Limburg
Dunes	-	-	The West Frisian Islands
Polder	+	Hardness	Widespread

[1] - = no influence; + = light/moderate influence; ++ strong influence

The effects given in Table 1.2 are partly the indirect effects of nitrate leaching, also termed 'a shift in the problem'. A shift in the problem refers to the increase in the concentration of substances in the groundwater as a result of denitrification in the subsoil below the root zone. Denitrification in the root zone takes place by the decomposition of organic matter, nitrogen (N_2) and carbon dioxide (CO_2) being formed. The N_2 and CO_2 can partially escape into the atmosphere. If the denitrification occurs deeper in the profile, below the groundwater table, the system is closed to gas exchange. This may lead to an increase in acidity (lowering of pH). As a result, silicates and carbonates (if present) dissolve, so that the concentrations of elements such as Ca, Mg, K and Na increase[1]. Pyrite-like compounds can also oxidize due to denitrification, causing the concentrations of sulphate (SO_4) and of heavy metals to increase, see Appendix 1. Incidentally, the greenhouse gas, laughing gas (N_2O), is also produced by denitrification (Bouwman et al., 2002).

1.1.5 Development of the nitrate concentration with depth

A comparison of nitrate concentrations in the upper metre of the groundwater with those at greater depths shows that the concentrations decrease with depth, see Figure 1.5. The percentage observations with a nitrate concentration higher than 50 mg l^{-1} decease markedly with depth. Appendix 3 gives the data for the different geomorphological areas in the sand regions.

There may be various causes for this decrease. According to Broers et al. (2004), the following points may play a role here, either individually or in combination:

1. The age of groundwater usually increases with depth; in infiltration areas, groundwater at a depth of more than 10 metres infiltrated at the soil surface, on average, 10-15 years before.
2. Roughly speaking, the use, and in turn, leaching of, fertilizers from the root zone showed an upward tendency between 1950 and 1990; deeper and older groundwater frequently still has a lower nitrate concentration as a result.
3. From a certain depth in the saturated zone, denitrification occurs due to the presence of organic matter, sulphides and/or siderite.

[1] If no gas exchange can take place during denitrification of nitrate with organic matter in a calcium-bearing subsoil and the acidity (pH) of the groundwater is initially lower than 7.0, the pH can rise. In this case, calcium will be deposited and the concentrations of calcium and magnesium will decrease and, in turn, the hardness.

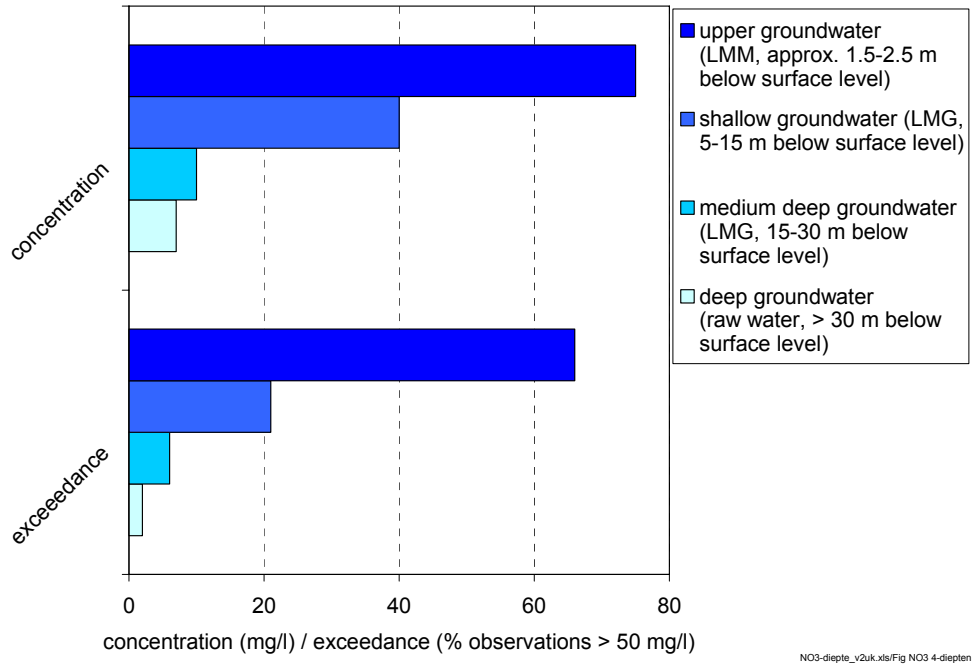

Figure 1.5 Development of nitrate concentration with depth and the percentage observations that exceed the EU value of 50 mg l^{-1} in the groundwater in the sand region used for agricultural purposes in the Netherlands; average value for the period 2000-2002 (Source: Fraters et al., 2004). The data on deep groundwater concern raw water at drinking water catchments. This water does not solely originate from agricultural plots.

Finally, there may still be a technical problem in the specific case of wells installed outside agricultural plots. In order to prevent disruption of operations and to enable easy access to the wells for sampling, permanent wells for sampling of groundwater are usually installed outside plots. The water in the upper screen in a well has, in the past, infiltrated to the surface at a different spot from the water in the lowest screen. It does not make any difference whether the well is installed inside or outside the plot, because in the water-saturated zone the water does not flow vertically downwards but partially also horizontally, see Figure 1.6. Thanks to this horizontal component, the wells do not have to be in the plot, certainly not if the screens are installed at greater depths below the groundwater table. In the event that, due to local conditions, the well is some distance away from the plot, the upper screen could collect water from the edges of the plot, or worse, from outside the property (road verge). This also applies if there are interfering layers in the subsoil. Comparisons of the measurements for the first and fifth metre do not therefore tell us anything about the processes taking place in the soil. On the basis of a study using mini-screen wells installed along the road, six in a sandy region and five in a clay region, Boumans and Van Duijvenbooden (1985) concluded that the quality down to several metres below the groundwater table was determined by the water running off the road.

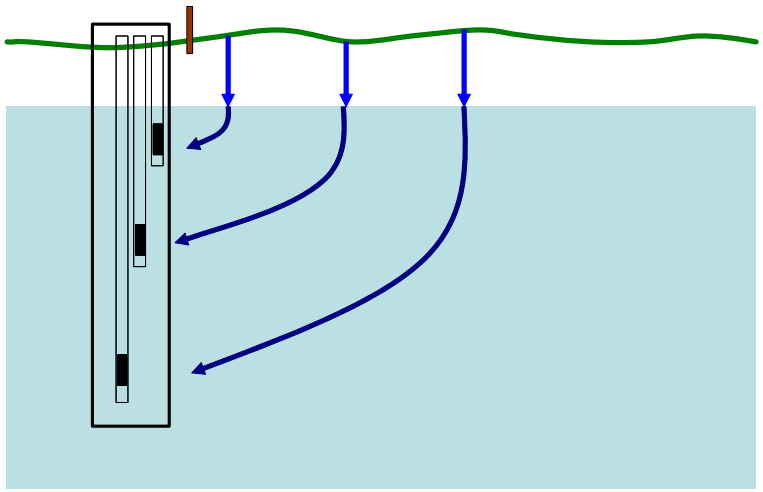

Figure 1.6 Diagram of groundwater sampling with multiple screen wells next to an agricultural plot.

1.2 Background to the study

The agricultural community in the Netherlands is increasingly confronted with regulations regarding the use of fertilizers. The regulation of the use of livestock manure was started in the late 1980s by means of standardization of the maximum amount of phosphate that could be applied with livestock manure (Ministry of Agriculture, Nature and Food Quality, LNV, 2001, 1997, 1993). From 1998 the use of nitrogen fertilizer and livestock manure was regulated by standards for nitrogen surpluses (LNV, 2001, 1997). As of January 2006 the system was changed and another was introduced entailing the use of application standards for nitrogen, phosphate and nitrogen-based livestock manure (LNV, 2005).

The objective of this legislation is (in time) to meet the objectives of both the EU Nitrates Directive (EU, 1991) and the Water Framework Directive, WFD (EU, 2000). One of the objectives of both of these directives is that the nitrate concentration in groundwater and surface water remains below 50 mg l^{-1}, or if it is higher, that it decrease to below this concentration. Neither of the directives indicates how the groundwater is to be sampled to check whether it meets the environmental quality objectives.

The Nitrate Directive does give provisions setting out the measures to be taken to realize this quality objective. These include the requirement that member states limit the amounts of livestock manure applied to a maximum rate of nitrogen of 170 kg ha^{-1} per year. In late 1999 the Dutch government declared the intention to ask the European Commission to allow a higher nitrogen application than 170 kg ha^{-1} per year with livestock manure, the so-called derogation request. The correspondence with the European Commission, including that substantiating the derogation (Willems et al., 2000), indicated repeatedly that the quality objective for nitrate will be realized in the recently-formed groundwater. The point of departure in deriving the mineral accounting system (MINAS) surplus standards for nitrogen (Van Eck, 1995), the substantiation of the derogation (Schröder, 2005; Willems et al., 2000) and the application standards in the new system (Schröder et al., 2004, Van Dijk, 2005) has

always been that the nitrate objective of 50 mg l^{-1} will be achieved in the upper metre of the groundwater[2].

The evaluation of the intended application standards system for 2006 and thereafter, carried out in 2004, showed that for approximately 20% of Dutch farmland the measures would be inadequate for realizing the 50 mg l^{-1} nitrate objective (Netherlands Environmental Assessment Agency, MNP, 2004). Evaluation of the MINAS system and the intended tightening of regulations had already yielded a similar conclusion (MNP, 2002), particularly for areas vulnerable to leaching. That report suggests checking compliance levels of nitrate concentrations in groundwater in recharge areas in deep groundwater instead of upper groundwater, a precondition being that the other groundwater quality parameters are also monitored here. In its report of 2004 based on a study implemented by TNO and RIVM (Broers et al., 2004), the MNP concludes that there is still insufficient information available at a regional level to lower the compliance checking level for nitrate. According to the report, there is a lack of information on both the sustainability of the denitrification process and its harmful side effects (such as the release of sulphate, heavy metals or hardness). Furthermore, altering the compliance checking level would entail a change in the policy followed so far.

The Draft Guidelines for the Monitoring Required under the Nitrates Directive (EU, 2003) appear to provide an opening for a different compliance checking level. These guidelines state that:

> *"Both shallow and deep groundwater should be included in the monitoring network […] For example, both the upper and lower parts of the aquifer that are connected to the soil should be sampled, as the upper parts (the first five metres of the saturated zone) will tend to respond quickest to changes in agricultural practice, …".*

In the National Groundwater Quality Monitoring Network (LMG), however, the depth at which samples are taken fall outside the upper five metres. The first screens, which are located 8-10 m below the surface in the sandy areas are, on average, 6.5-8.5 m below the groundwater table. These data cannot therefore be used for the study into the decrease of the nitrate concentration in the upper five metres. The quality of the groundwater between one and five metres below the groundwater table has so far not been monitored on a national scale, see section1.3.

In 2004 the Fertilizer Act that was applicable at this time was evaluated. In the ensuing discussions with the Dutch Lower Chamber, the Minister for Agriculture, Nature and Food Quality committed himself to a study on the possibilities for lowering the compliance checking level for nitrate for the sand region (see Appendix 2). The Lower Chamber has been informed that the current compliance checking level is part of a package of agreements with the European Commission, and that scientific research results may lead to negotiations with the European Commission regarding a change in compliance checking level.

The present study has been carried out to fulfil this goal and follows on from an earlier study carried out by Boers et al. in 2004. This earlier study investigated (a) whether regions where

[2] Fertilizer recommendations have been used as basis for the nutrient application standards for agriculture and horticulture since 2006, but the application norm will be tightened in the period up to and including 2009. When deriving application standards for grassland in the sandy areas, the nitrate concentration in the upper metre of the groundwater had to remain below 50 mg l^{-1}. The total nitrogen concentration for the clay and peat areas could not exceed 11 mg l^{-1} in the drain and ditch water respectively.

denitrification takes place in the saturated subsoil without adverse (environmental) consequences can be accurately designated and (b) at what depth compliance to the threshold value for nitrate should be tested. The results of this study indicated that it is not feasible to designate such areas as there is insufficient information on the extent to which denitrification occurs within different parts of the sand region. A large mapping and measuring effort would be required in order to be able to designate areas where denitrification occurs with sufficient accuracy. Broers et al. (2004) also suggest that lowering the compliance checking level should only be considered for those areas where groundwater quality does not directly influence surface water quality (areas with little run-off). Furthermore, the study concludes that the compliance checking level should not be lowered to more than 10 metres. It also indicates that it would be advisable to keep the monitoring depth for the Nitrate Directive the same as existing monitoring depths in the Netherlands, unless there are pressing reasons for choosing a different one. The reason put forward for this was that a different monitoring depth would not only entail costs for a design study and the installation of new (permanent) monitoring screens, but also the annual operating costs. The following section gives an overview of the existing groundwater monitoring networks in the Netherlands.

1.3 Measuring groundwater quality

The groundwater quality in the Netherlands is monitored at different depths. The LMG was set up (LMG; Van Duijvenbooden, 1987) in the early 1980s to obtain a picture of the general quality of the groundwater in the Netherlands and changes in this quality. Since 1984 measurements have been taken at around 360 locations throughout the Netherlands at two depths, 8-10 metres and 23-25 metres below the surface. There is an additional measuring point at 13-15 m below the surface to enable sampling in the event that the groundwater level is very low. Up to and including 1998 all the wells were sampled annually at each of these depths. After an evaluation in that year (Wever and Bronswijk, 1998) the decision was made to reduce the measuring frequency to once in two or four years at those wells or depths at which the water quality changes were negligible. A recent overview of the results can be found in Reijnders et al. (2004). This report also incorporates the data from the Provincial Groundwater Quality Network (PMGs). The PMGs supplement the LMG, their objective being to produce a picture of the groundwater quality and quality changes at provincial level for the drawing up and evaluation of provincial policy. A recent overview of the scope of the PMGs is given in Appendix 1 of the Guidelines for monitoring groundwater for the WFD (Verhagen, 2005).

In addition to these general groundwater quality monitoring networks there are monitoring networks with special objectives that include the groundwater quality. These are (a) the impact monitoring networks the objectives of which are to show the effects of policy and/or water quality measures and (b) the monitoring programmes of the water boards in which the quality of the water pumped up (raw water), which serves as source for the drinking water production, is monitored.

These impact monitoring networks examine the water most clearly affected by the measures, the quality of which can no longer be altered by uptake by crops or vegetation. The sampling of the groundwater in these networks is therefore limited to the upper metre of the groundwater. There are two national monitoring networks, the Minerals Policy Monitoring Programme (LMM), that focuses on obtaining a picture of the impact of the minerals policy

on the water quality3 on farms (Fraters and Boumans, 2005), and the Trend Monitoring Network Acidification (TMV), which focuses on the changes in water quality in natural areas. Besides these national monitoring networks there are also the Provincial Monitoring Networks for Soil Quality (PMBs) which monitor the water quality on both farms and natural locations; see Westerhof et al. (2005) for an overview. The PMBs are intended for the making and evaluation of provincial policy, as are the PMGs.

The situation sketched above shows that there is no network for monitoring the quality of the groundwater of the upper five metres on a national level or for the sand region. Incidental measurements have, however, been taken in the past (see for example Boumans and Van Duijvenbooden, 1985; Broers et al., 2004).

1.4 Goal and delineation of the study

The policy question that must be answered is whether it is possible to lower the compliance checking level, if so how, and whether this is a responsible move. This question will have to be answered by the policy makers.

The goal of the study is to gather information on which the Dutch government can base decisions on whether to lower the compliance checking level. The policy question was therefore translated into the following research question: Is it opportune to change the compliance checking level for nitrate in groundwater and designe a programme or network and if so, what are the prerequisites when designing a programme or network to monitor at a different depth?
A number of aspects will have to be examined here, such as whether a lowering of the compliance checking level will contribute to the realization of the objectives of the European environmental directives without requiring far-reaching tightening of the application standards.

The study must therefore verify whether a lowering of the compliance checking level means that tightening of the application standards can be avoided. The underlying question is: does the nitrate concentration decrease with depth within the first five metres of the groundwater. Whether the European directives (Nitrate Directive, Water Framework Directive, Groundwater Directive) can be met despite the lowering of the compliance checking level must also be examined. The risk of a lowering of the compliance checking level (and, in turn, a less far-reaching tightening of the application standards) entailing a shift or transfer of the nitrate problem will also have to be looked at. The question of whether a possible decrease in nitrate concentration is caused by denitrification, and if so, whether the denitrification is sustainable and leads to a shift in the problem, that is, an increase in concentrations of other substances (for example heavy metals and sulphate) or not will have to be checked. The stocks of organic matter and pyrite, both energy sources for denitrification, in the subsoil are finite. The depletion of these energy sources means that denitrification can no longer take place and nitrate concentrations will increase in the groundwater at greater depths. If denitrification is not the cause of the decreasing concentrations, the true cause must be sought and whether this leads to problems elsewhere. Finally, whether leaching and run off of nitrogen is the cause of a shift to the surface water must also be examined.

[3] A large number of inorganic parameters are determined in the water samples; in addition to the nutrients (N, P and K) the general macronutrients (Ca, Fe, Mg, Cl , SO_4) and heavy metals (such as As, Cd, Cu, Cr, Ni and Zn) are also measured

The aspect of the political feasibility of a policy change of this kind or a costs and benefits analysis remains outside the scope of this study and may possibly be included in the next evaluation of the Fertilizer Act in 2007. The question of how the results of a new compliance checking level monitoring network could be used in the discussion on application standards is not handled here, either; see the compliance checking level report by Broers et al. (2004, pg. 57 et seq.) for this.

The present study is limited to the sand region of the Netherlands. For the clay and peat regions, lowering the compliance checking level is undesirable. The nitrogen load to surface waters in these regions comes mainly from surface run-off and leaching through shallow groundwater flow. As the objectives for nitrate in surface water are stricter than for nitrate in groundwater, the nitrate concentration in the first metre of groundwater in clay and peat soils needs to be lower than 50 mg l^{-1} if the objectives for surface water are to be met (see Broers et al., 2004). As regards the depth, the study is limited to the upper five metres of the groundwater, because this ties in with the text of the EU Draft Guidelines for the Monitoring Required Under the Nitrates Directive (EU, 2003) mentioned earlier.

Part of the question concerns the best form for a monitoring network if the compliance checking level is lowered. Part of the study therefore focuses on the technical possibilities and feasibility of monitoring the quality of the groundwater at greater depths.

1.5 Set-up of the study and structure of the report

The research question was split up into a number of sub-questions to facilitate answering it. The sub-questions are as follows:

1. Does the nitrate concentration decrease with depth in agricultural lands in the sand region? If so, what is the extent of this decrease and are there differences within the region?
2. If the nitrate concentration decreases within the upper five metres, can this be attributed to denitrification, or are there other causes for this decrease?
3. If denitrification occurs, to what extent does this process lead to adverse environmental effects such as an increase in the levels of sulphate or heavy metals, or increasing hardness of the water?
4. In the clay and peat regions, lowering the compliance checking level in order to be able to apply less strict application standards would lead to insufficient reduction of the nitrate load to surface waters. To what extent does this apply to the sand areas?
5. Regardless of how complex, is it feasible to measure the nitrate concentration at a depth of five metres in the saturated zone, or can the average nitrate concentration of the upper five metres be determined?”
6. Regardless of how complex, is it feasible to measure the extent to which denitrification occurs, whether it is sustainable, and whether the process produces undesirable by-products?
7. Regardless of how complex, is it feasible to measure whether the groundwater at five metres depth has the same origins (infiltrated at the same place) as the groundwater in the first metre?

The study was carried out in steps and consisted of various sub-studies, implemented as field, laboratory and desk studies. Each of chapters 2 up to and including 6 handles a field or laboratory study. The objective and set-up of these successive studies are described, the

results presented and discussed and conclusions given. The results and conclusions are used to answer the sub-questions in chapter 7. In addition to the research results, the substantiations of the answers to the sub-questions are supported by the desk studies. These desk studies were not limited to reproducing the findings of others but the available underlying data was analysed anew. Detailed information on these previously-published studies and the reprocessing of the data are included in Appendix 10, insofar as cannot be referred to existing literature. Finally, chapter 8 summarizes the answers to the sub-questions and the research question is answered. A number of points of consideration are also given.

The following field and laboratory studies were carried out for this research:

- In December 2004 a preliminary study was carried out at special LMG wells. Groundwater from different depths can be sampled using these wells. This research is discussed in chapter 2.
- In the second half of 2005 research was carried out into the development of the nitrate concentration in the first five metres of the groundwater and its influence on the other aspects of water quality at four dairy farms participating in the LMM. chapter 3 discusses this research.
- Besides the above, a comparative study was also carried out on the four LMM farms. Implementation and water quality aspects of four methods of sampling the first and fifth metres of the groundwater were tested. chapter 4 deals with this study.
- Soil samples originating from the layers in which the upper five metres of groundwater is located at the research locations on the four LMM farms were tested for their denitrifying capacity. One study focused on both the microbial aspects and the physical-chemical aspects. The former study was carried out by Alterra and is handled in chapter 5. The second was carried out by TNO and is discussed in chapter 6.

2. Research in LMG multi-screen wells

2.1 Introduction

In 1985 a multi-screen well was installed in the vicinity of 50 LMG wells to enable research into the quality of the shallow and upper groundwater. A multi-screen well is a well containing various screens at different depths below the groundwater table, see Figure 1.6 and Figure 2.1. A detailed description of the boreholes was made for all the wells during installation. The wells have never been used for research or monitoring, because after their installation, the decision was made to carry out research into the quality of the upper metre of the groundwater (see for example the research described by Boumans, 1990).

Figure 2.1 A multi-screen well next to a field (left) and the taking of samples (right).

The field study at the LMG multi-screen wells was a limited study that was carried out in December 2004. Its objective was twofold. Firstly, it served as a preliminary study in which 16 reference wells were to be selected. In the follow-up study the sampling methods were to be tested at these wells in a comparative study (see chapter 4). Secondly, the study served to obtain additional information on the development of the nitrate concentration with depth. After the completion of the study it became apparent that only this latter objective was still relevant. In the original set-up, the sampling methods to be tested were to be limited to methods that worked with temporary boreholes. In the spring of 2005 discussions with the consultative group and commissioning authorities made clear that sampling methods with permanent wells also had to be included in the field study. Given that sampling methods of this kind are generally accepted, there was no longer any need for a follow-up study with the multi-screen wells.

2.2 Set-up of the study

The study consisted of mapping and photographing all the multi-screen wells and a once-only sampling from all the screens. The water samples were analysed in the field and the parameters tested were acidity (pH), electrical conductivity (EC) and nitrate concentration (Nitrachek colour comparison). The precise methods used will be described in more detail in

an RIVM report (Fraters et al., in preparation). A total of 44 of the 50 wells could be traced and were still functioning. Of these, 29 are representative for agricultural land and the other 15 for natural areas. Table 2.1 shows an overview of the precise distribution of the wells according to soil type, soil use and drainage class[4]. Figure 2.2 indicates the location of the wells.

Table 2.1 Distribution of the 44 LMG multi-screen wells according to soil type[1], drainage class and land use.

	Reclaimed peat soil		Sandy soil			
	Neutral	Wet	Dry	Neutral	Wet	Total
Agricultural	2	4	9	9	5	29
Natural			9	6		15
Total	2	4	18	15	5	44

1 Within the sand region wells have been placed in sandy soils that were peat soils before reclaiming and other sandy soils.

[4] Three drainage classes were distinguished: wet, neutral and dry. These classes were based on a grouping of groundwater table classes (Gts). The Wet class includes the Gts I through IV, the neutral class, the Gts V, V* and VI and the dry class, the Gts VII and VIII (= VII*), see section 1.1.3.

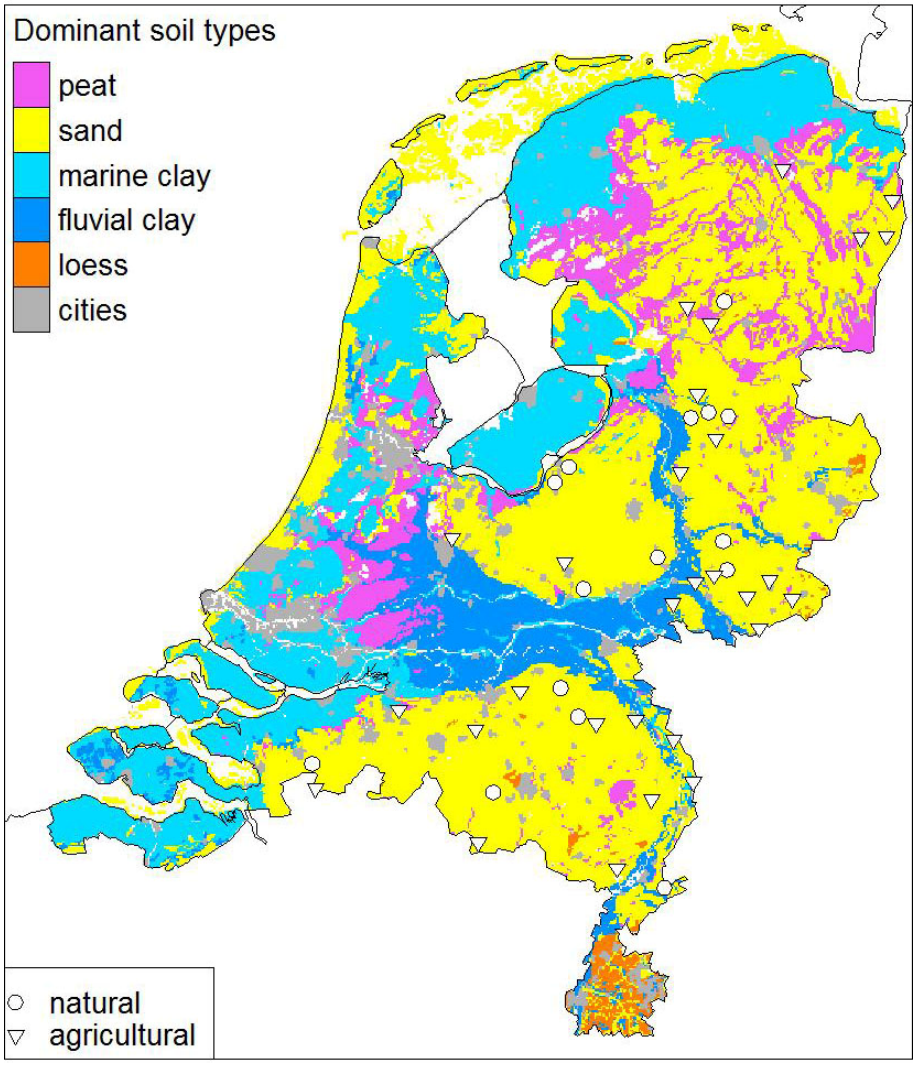

Figure 2.2 Overview of the locations of the 44 multi-screen wells in the sandy areas; background is a simplified soil map of the Netherlands.

2.3 Results

The development of the nitrate concentration with depth in the multi-screen wells varies greatly and there are large differences between wells, see for example Figure 2.4. At four of the wells it was not possible to sample groundwater at the screen or screens at the upper and/or the fifth metre. The average nitrate concentration in the first metre of the groundwater at the other 25 wells was 58 mg l^{-1}. The concentration in the fifth metre was 73 mg l^{-1} (26% higher). The average concentration in the upper five metres was 63 mg l^{-1}. For soils with a dry drainage class (dry soils: Gts VII and VIII) the nitrate concentration at five metres below the groundwater table was on average twice as high as the concentration in the first metre, see Figure 2.3. In the soils with a neutral drainage class (neutral soils: Gts V, V* and VI) there is an average decrease of 13%. Figure 2.3 shows that the nitrate concentration varies greatly, particularly in the neutral soils (there is a large difference between the lower and upper limit of the 95% confidence interval of the average). In the soils with a wet drainage class (wet soils: Gts I through IV) the average decrease is 31%, but in these soils the nitrate concentrations in the first metre are on average already low.

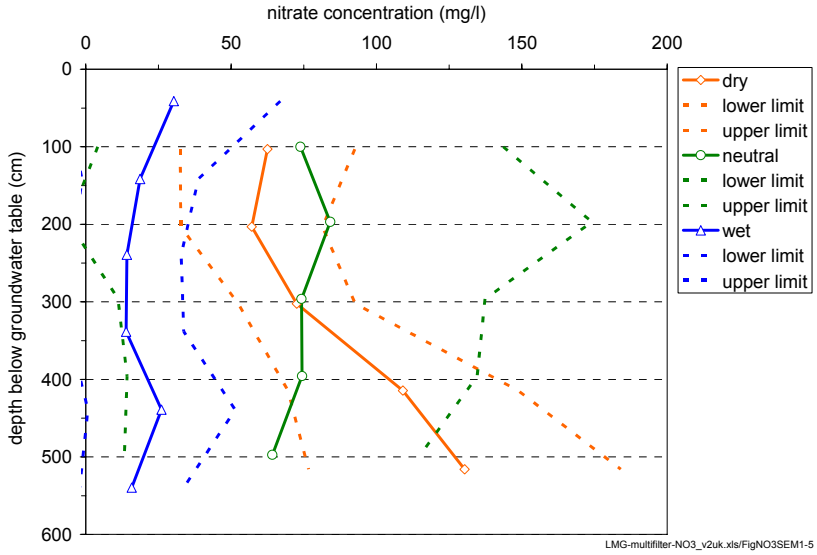

Figure 2.3: Development of the average nitrate concentration with depth below the groundwater table next to agricultural plots in sandy areas in 2004 for the three drainage classes: wet (Gts I through IV, 7 wells), neutral (Gts V, V and VI, 10 wells) and dry (Gts VII and VIII, 8 wells). The dotted lines show the 95% confidence interval of average values.*

The number of wells with an increase or decrease for each drainage class is given in Table 2.2; the development at the four wells for which there were no measurements were also looked at. It is clear that for dry soils, most profiles show an increase, see also Figure 2.4.

Table 2.2 Change in the nitrate concentration with depth in the 29 LMG multi-screen wells next to agricultural plots in sandy areas in 2004 for the three drainage classes: wet (Gts I through IV), neutral (Gts V, V and VI) and dry (Gts VII and VIII).*

Change	Dry	Neutral	Wet	Total
Increase	7	2	1	10
None	2	6	5	13
Decrease	0	3	3	6
Total	9	11	9	29

The nitrate concentrations in the nine wells with a dry drainage class vary in the first metre from less than 10 mg l^{-1} to more than 250 mg l^{-1}, see Figure 2.4. The nitrate concentrations at most wells increase, but the pattern varies greatly.

Most wells with a neutral or wet drainage class do not show any change (Table 2.2). The nitrate concentrations are low at both the higher and the lower levels. The higher nitrate concentration in the first metre of the neutral soils compared with that for dry soils (Figure 2.3) is caused by three neutral locations with high nitrate concentrations in the first metre, see Figure 2.5. These three wells are also responsible for the decrease in the nitrate concentration with depth in the neutral soils. More than half of the wells (six out of eleven) contain hardly any nitrate, if any, (< 10 mg/l) over the whole depth.

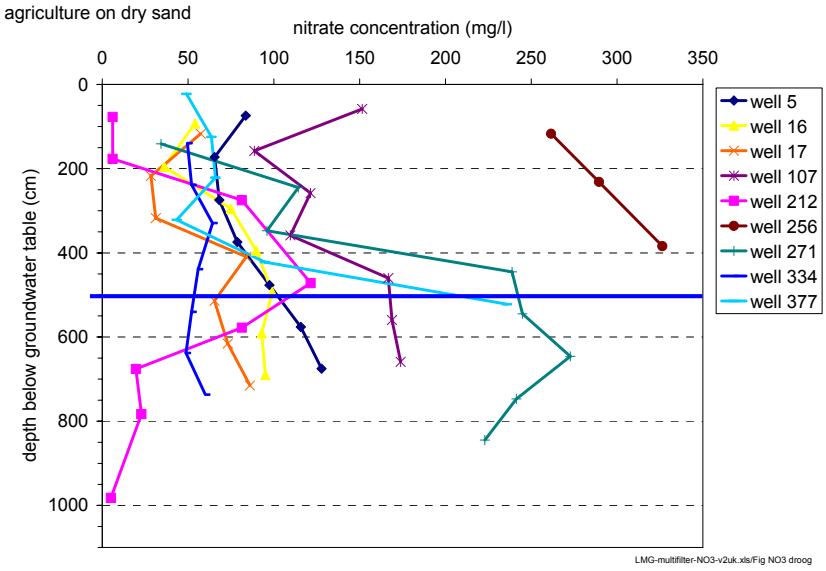

Figure 2.4 Development of the nitrate concentration with depth below the groundwater table at nine multi-screen wells on sandy soils with a dry drainage class (Gts VII and VIII).

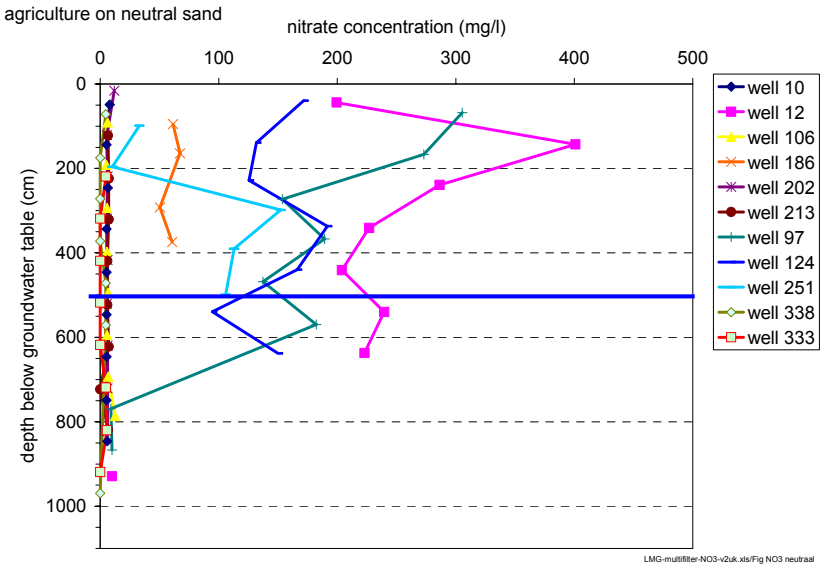

Figure 2.5: Development of the nitrate concentration with depth below the groundwater table at eleven multi-screen wells on sandy and reclaimed peat soils with a neutral drainage class (Gts V, V and VI).*

2.4 Discussion

The nitrate concentration in the fifth metre in the wet soils is on average 31% and in neutral soils on average 13% lower than in the first metre. There is no difference between the average nitrate concentration of the first metre and the upper five metres of the groundwater in the neutral soils in this study so that lowering the compliance checking level and having to monitor the concentration of nitrates in the upper five metres will not alter the situation. For the wet soils the difference in this case will be about the same (34%) as the decrease between the first and fifth metre. This decrease means that it might be interesting to test the deeper groundwater for the wet soils. However, the shift in problems (increase in other substances)

to the groundwater or to the surface water (leaching and run-off of nitrogen) would then also have to be looked at. Research on nitrate levels in ditch and drain water (see section 7.4) shows that some of the decrease can be related to leaching. Based on the available data it is not possible to make a reliable determination of how much of the decrease in nitrate is due to denitrification. For the dry soils there is an increase of 109% with depth. The average concentration in the upper five metres is 38% higher than in the first metre. Checking groundwater at greater depths in these soils does not, therefore, appear worthwhile.

An increase in the nitrate concentration with depth, as observed in the dry soils, may seem strange. Both the formation of nitrate in the saturated subsoil and desorption are not relevant. The increase with depth can partially be related to the fact that the deeper groundwater is older (from previous to the current minerals policy) or to horizontal transport of groundwater from nitrate-richer plots (see also section 1.1.5).

Suppose that nitrate does not denitrify and every year the precipitation surplus amounts to 300 mm. In a standard sandy soil without interfering layers in an infiltration area the groundwater will leach by a metre annually. The age difference between the first and fifth metres will then be four years. If in this period the nitrogen applied is reduced, which thus reduces the leaching to the groundwater, the nitrate concentration at the top will be lower than at the bottom. In the period 1995-2002 the nitrogen applied and the average nitrate concentration in the upper metre of the groundwater in the sandy areas, corrected for precipitation effects, did indeed decrease (Fraters et al., 2004).

If the amount of nitrate that leaches into the groundwater annually (in kg) remains constant in time, the nitrate concentration could decrease as a result of an increase in the average annual precipitation surplus. Dilution will then take place. In this case, too, the nitrate concentration will increase with depth. The annual amount of precipitation in the 1990s varied from just under 600 mm to more than 1200 mm. The dilution factor can therefore differ by a factor of two.

Another possible explanation for the measured development of the nitrate concentration with depth is the presence of an interfering layer or layers between the first and fifth metres. The groundwater would then be unable to flow vertically, but would flow horizontally. The groundwater at five metres below the groundwater table therefore comes from elsewhere (another plot). If this is (or was in the past) a more heavily fertilized plot, the nitrate concentration at a depth of five metres could be higher.

These three factors can lead not only to a higher but also a lower nitrate concentration. A decrease in the nitrate concentration does not therefore mean that denitrification is, by definition, taking place.

In the period 1995-2002 the nitrogen surplus decreased and the precipitation surplus increased. These two factors both facilitate an increase in the nitrate concentration with depth. Interfering layers could not have played a role in this study because no such layers were observed when the wells were installed.

Finally, there may be a technical problem, as described in section 1.1.5, in connection with well locations outside the farm plots. The question of whether the nitrate concentration in the upper screen gives a good picture of the nitrate concentration in the upper metre in the plot cannot be answered with a simple yes or no. As Figure 2.3 shows, the upper screens are

located on average at about one metre below the groundwater table in the neutral and dry soils and a certain amount of horizontal transport will therefore have taken place.

2.5 Conclusions

There was on average a 26% higher nitrate concentration in the fifth metre of the groundwater than in the first metre at the 25 LMG locations on agricultural plots.

The development of the nitrate concentration with depth is different for soils with a dry drainage class than for soils with a neutral or wet drainage class. With the dry soils (soils vulnerable to nitrate leaching) a large increase of 109% is seen in the nitrate concentration with depth in the upper five metres of the groundwater. This increase could be caused by the decrease in the nitrogen load, the increase of the precipitation and because these wells are not on the plot but next to it.

For the neutral and wet soils, there is a decrease in the nitrate concentration with depth of 13% and 31%, respectively. But the percentage does not tell us very much, particularly in case of wet soils, because the nitrate concentration is already low in the first metre; on average 30 mg l^{-1} for the seven wells.

For the locations examined in this study, checking the nitrate concentration against the nitrate objective in the upper five metres of the groundwater instead of in the upper metre would only has certain prospects for the wet soils. Checking at five metres below the groundwater table could also be beneficial for the neutral soils. The fact that the decrease is due to denitrification and not to leaching or horizontal transport and that the denitrification does not result in any undesirable environmental effects would, however, first have to be demonstrated.

3. Water quality study on farms

3.1 Introduction

The objective of this part of the field study was to examine the change in the nitrate concentration in the upper five metres of the groundwater using measurements taken in the plot.

The study consisted of a preliminary location study, the drilling of the boreholes, sampling, measuring and chemical analysis for the water quality study and the implementation of these operations for the comparison of sampling methods (chapter 4) and the denitrification study (chapters 5 and 6). The implementation of the field study is described in more detail in Van Elzakker et al. (2007). The following section gives a brief summary of the set-up of the study.

3.2 Set-up of the study

3.2.1 Selection of farms and locations, and the location study

Four farms, plus one as back-up, were selected from the LMM participants that, on the basis of their location, would be sufficiently typical for the differences that can be found in sandy areas, see Figure 3.1. The nitrate concentrations measured in previous years at the farms had to average more than 25 mg l^{-1} (see Table 3.1) and farms participating in the 'Cows and Opportunities' project (C&O) were given preference. The reason for this preference is that these farms had experience with research and that additional information is available about them. There were no C&O participants available in the central sandy area so a typical LMM farm was selected to represent this area.

A preliminary geological study was carried out by TNO Built Environment and Geosciences for all five farms. Series of groundwater level data were also supplied for piezometric wells in the vicinity of the farms, including the mean highest groundwater level (MHG) and mean lowest groundwater level (MLG) calculated from these data for these wells.

The preliminary geological study was based on descriptions of bore holes in the vicinity of the farms and what is known about the area by the TNO regional expert and provides insight into the occurrence of the lateral continuity of clay/loam layers or layers with a coarse texture (soil layers and coarse sand layers) in the shallow subsoil (to 10 metres below MLG).

The study was carried out at four selected dairy farms in the four different sandy areas of the Netherlands (north, central, east and south), see Table 3.2, and three different types of groundwater catchment areas according to the classification drawn up by Van Beek et al. (2002), see Figure 1.4.

Table 3.1 Nitrate concentrations (mg l^{-1}) in the upper metre of the groundwater on the farms selected for the field study in the period 1999-2004.

	1999	2000	2001	2002	2003	2004	mean
Maarheze	-[1]	82	112	93	67	64	84
Nieuweroord	-	51	35	24	12	27	30
Nutter	129	94	81	75	69	88	89
Spankeren	-	116	-	-	36	-	76
Stand by	84	82	94	94	63	78	82

[1] '–' means that no groundwater samples were taken

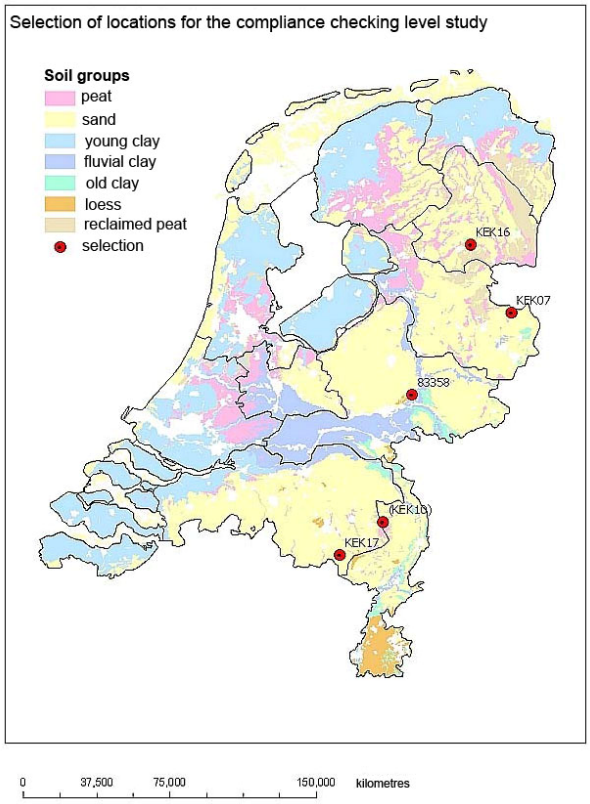

Figure 3.1 Farms selected for the field study. The back-up farm is shown between brackets. The farms are located at Spankeren (83358), Nutter (KEK07), Maarheeze (KEK17) and Nieuweroord (KEK16), and the back-up farm at Ysselsteyn (KEK10).

The RIVM has drawn up an MLG map for each farm using information provided by TNO, the surface level information and the data on groundwater levels in the sampling wells during sampling in previous years.

Four locations were selected for each farm, three of which were supposed to be typical of soils with a neutral or dry drainage class and one for soils with a wet drainage class. For this use was made of the MLG maps drawn up, maps with the nitrate concentrations measured in previous years and, for the C&O farms, recent measurements of the groundwater class (Gt)

for the locations at which the groundwater is sampled. It was not always possible to realize the intended distribution of locations for each farm over the drainage classes, see Table 3.2. The choice of the locations was determined on the basis of accessibility, the absence of cattle and the presence of visibility lines so that the location could be located easily at a later date.

Table 3.2 Characteristics of the four dairy farms and the numbers of locations for each drainage class; wet (Gts I through IV), neutral (Gts V, V and VI) and dry (Gts VII and VIII).*

Farm	Code	Sandy area	Soil type	Type[1]	Wet	Neutral	Dry
Maarheze	57E	South	Sand	Large push-moraine	1	3	-
Nieuweroord	17D	North	Reclaimed peat soils	Boulder clay	-	2	2
Nutter	28F	East	Sand	Carbonate-free pyrite	-	1	3
Spankeren	33G	Central	Sand	Carbonate - free pyrite	1	-	3

[1] Type of groundwater catchment area (Van Beek et al., 2002), see section 1.1.4.

3.2.2 Soil sampling and description

The soil samples required for profile description and denitrification measurements were collected prior to installing the screens. The screen depths are in fact dependent on any interfering layers, the presence of which can partly be determined by studying the soil profiles. The soil cores were brought up with the Aqualock method and collected in half PVC gutters of a metre in length, see Appendix 4. After the samples were photographed and described they were sealed in with another half gutter. These ‘cylinders’ were finally wrapped in plastic foil and labelled in a similar way as the bottles for the water samples. Subsequently they were transported to Bilthoven within 24 hours and stored there in a refrigeration cell at approximately 4 ºC until they were transported to TNO Built Environment and Geosciences for a precise description of the cores and the follow-up study, see Appendix 4. Descriptions of the cores were also drawn up by Utrecht University for the spots at which temporary screens were installed using the Van der Staay method.

3.2.3 Groundwater sampling

The groundwater was sampled for the first time in July 2005, see Table 3.3. All the available methods were tested during this round. See chapter 4 for more details and a description of the sampling method. The groundwater was also sampled immediately after installation at the permanent wells. The installation of permanent wells disturbs the subsoil such that the composition of the groundwater could be affected. The closure of the wells above the screens was not optimal at the time, either, because the bentonite used for the sealing had not yet fully expanded. For this reason, these wells were sampled again in August and in the period from the end of November to the beginning of December 2005. In the first round in July and the third round in November – December the upper groundwater was also sampled at every location using the LMM method.

Table 3.3 Sampling dates at the four dairy farms in 2005

Farm	Code	Region	Round 1	Round 2	Round 3
Maarheeze	57E	South	20-28 July	10-11 August	12-19 December
Nieuweroord	17D	North	14-15 July	4 August	6 December
Nutter	28F	East	18-19 July	8 August	30 November – 1 December
Spankeren	33G	Central	11-12 July	3 August	22 November

The groundwater was sampled using a peristaltic pump. The samples were filtered (0.45 μm) and acidified (pH < 2) with HNO_3 (for analysis for total P, metals and other cations), H_2SO_4 (for analysis for total N, NO_3, NH_4, ortho-P and Dissolved Organic Carbon [DOC]) or not acidified (for analysis for Cl, SO_4), and refrigerated (< 4 °C) and kept in the dark until the chemical analysis. The series 'metals and other cations' includes the elements Al, As, Ba, Cd, Ca, Cr, Fe, K, Cu, Pb, Mg, Mn, Na, Ni, Sr, Zn. During sampling in the field, the unfiltered samples were analysed for acidity (pH), electrical conductivity (EC) and oxygen concentration and filtered samples for the nitrate concentration (Nitrachek colour comparison).

3.3 Results

The soil structure of the sedimentary deposits in which the upper five metres of the groundwater is found at the four farm locations is heterogeneous, see Figure 3.2. chapter 6 gives a detailed description of the soil structure at the farms. A brief sketch of the most important characteristics is given here. The sediments at most of the locations consist of sand with thin clay and/or loam layers in it. The locations at Nieuweroord and one location at Nutter (28F0473) and Spankeren (33G0414) are exceptions. The sediments here consist primarily of loam containing (thin) sandy layers. At the location 33G0412 the bottom of the deposit consists of gravel layers. Peat layers occur at a number of locations (57E0335, 57E0338 and 33G0414). A layer of (organic-rich) detritus[5] occurs in the sediments at two locations at Spankeren (33G0413 and 33G0415). The locations at Spankeren contain carbonate, the others do not. The carbonate contains siderite ($FeCO_3$). Two of the locations at Maarheeze may contain layers in which some pyrite occurs (57E0335, 57E0338) in addition to a few other reactive iron compounds. Most layers in the sedimentary deposits at the Nutter locations contain varying amounts of reactive iron in the form of glauconite and, possibly, iron oxides. Location 28F0473 is the only one to contain some pyrite at the bottom of the sedimentary deposits. The locations at Nieuweroord do not contain any reactive iron with the exception of one sample from location 17D0200. Pyrite does not play an important role in the denitrifying capacity of the sediments at Nieuweroord.

This report presents only the results of the groundwater sampling from the second and third rounds. The results for the permanent wells from the first round appear to have been influenced by the installation (Elzakker et al., 2007). The reader should realize that the study was carried out at a very limited number of locations, there being a link between the farms and the drainage classes. The sections below present only those quality parameters relevant to this report. For a full overview, please see the abovementioned report.

[5] organic residues of decayed, decomposed plants and animals

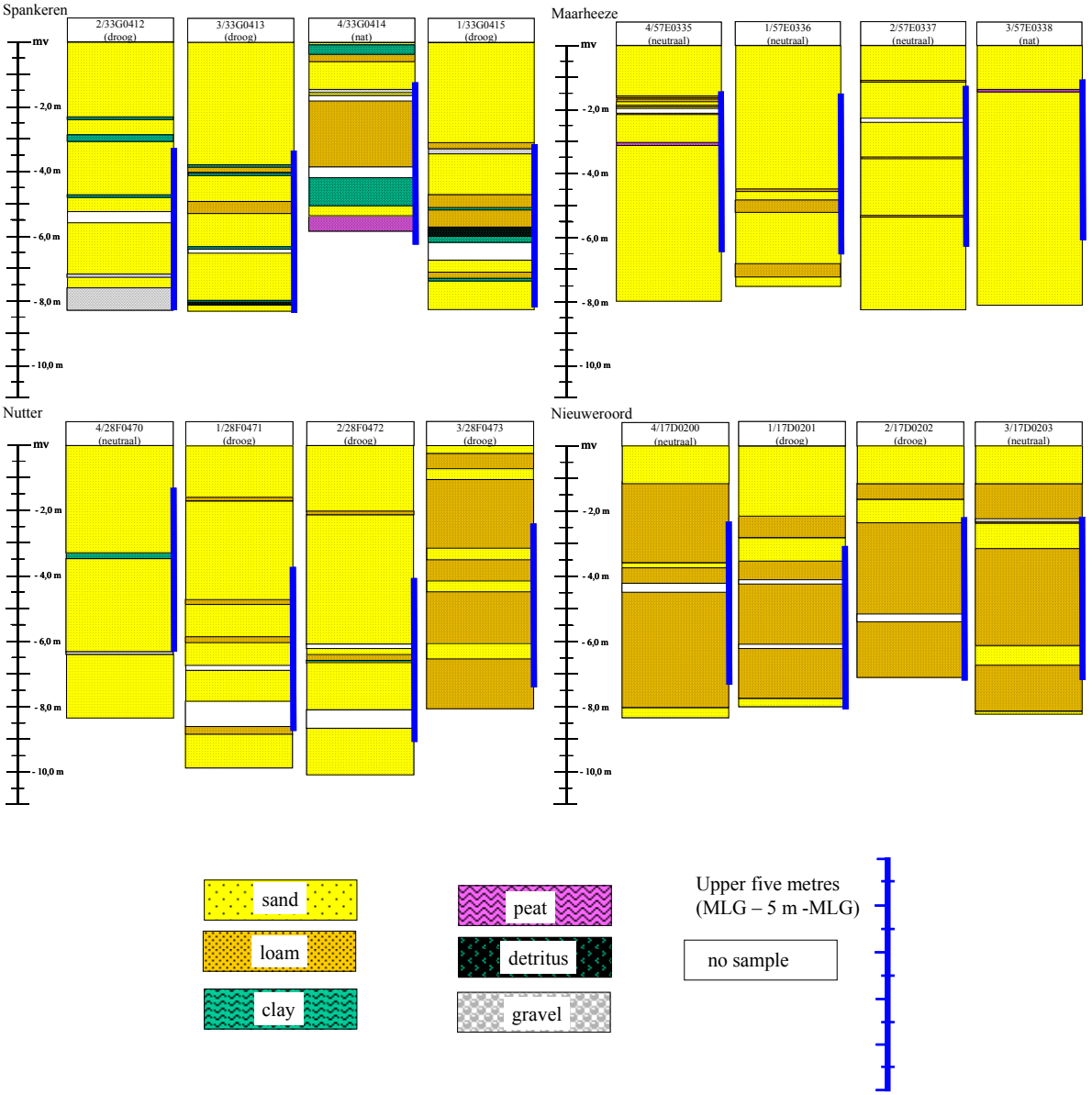

Figure 3.2 Simplified diagrams of the soil layers from MLG to five metres below MLG for the locations examined at the four dairy farms, based on the description of the subsoil by TNO, and of the topsoil by Utrecht University. For more details, see section 6.3. Top left Spankeren (33G), top right Maarheeze (57E), below left Nutter (28F) and below right Nieuweroord (17D).

Table 3.4 shows the average nitrate concentrations for the first and fifth metres of the groundwater column for each drainage class for each round. Only locations at which both depths were sampled have been included in the calculation. Comparison of the first metre with the fifth metre (first at an average of 46 cm below MLG and fifth at an average of 464 cm below MLG) shows that the nitrate concentration at five metres below MLG is on average 20% lower than in the first metre (12 mg l^{-1}, standard error 20 mg l^{-1}) in the second round. In the third round this difference is 8% (4 mg l^{-1}, standard error 20 mg l^{-1}). Given the small number of wells and the variation in the concentrations measured, these differences are not significant.

For the dry soils, there is, in fact, no decrease with depth; the decrease of 2 mg l^{-1} in round 2 and increase of 6 mg l^{-1} in round 3 were not significant. The decrease in the neutral soils met 39% in the second and 28% in the third round are, likewise, not significant and can furthermore be almost fully attributed to the observations from a single farm (Maarheeze).

The results of the nitrate measurements at the individual locations at each farm in round 3 have been included in Figure 3.3. This is the round for which most measurements are available. Furthermore, the influence on the water quality by the installation of the permanent wells had almost disappeared by the time this round took place (Van Elzakker et al., in preparation). The results of the second round are shown in Figure 5.1 in chapter 5.

Table 3.4 Nitrate concentrations (average and standard error) at approximately 1 and 5 metres below MLG for each drainage class for each round[1].

Drainage class	Round	Number of locations[2]	Depth	Depth below MLG (cm)	Nitrate (mg l^{-1})	Standard error
Dry	2	4 (8)	1	75	78	11
			5	451	76	10
	3	5 (8)	1	57	81	10
			5	466	86	9
Neutral	2	4 (6)	1	75	75	9
			5	452	46	13
	3	6 (6)	1	7	46	7
			5	480	33	6
Wet	2	2 (2)	1	75	0.3	0.5
			5	472	0.1	0.3
	3	2 (2)	1	-8	0.9	0.8
			5	457	0.0	*

[1] Concerns averages of all measurements for each location for each depth.
[2] Number of locations for which data was available for both depths. The number of locations at which wells were installed is shown between brackets. The extra locations in the third round are all at Nieuweroord.

The results clearly show that the upper groundwater at the farm on reclaimed peat soil (Nieuweroord) contains very little nitrate, if any, despite the fact that the locations at this farm are classified as being in a neutral or dry drainage class. The locations with a dry drainage class at the other farms (three at Spankeren and one at Nutter) show both a decrease (28F0472 and 33G0413) and an increase (33G0412 and 33G0415) with depth. The locations with a neutral drainage class at Maarheeze (57E) show a decrease, the location at Nutter (28F0470) on the other hand, an increase.

The concentrations of dissolved organic matter (DOC) in the upper five metres of the groundwater show large differences between the farms, see Figure 3.4. The highest concentrations occur at Maarheeze, with an average of about 50 mg l^{-1} in the upper metre for both measuring rounds, while at Nieuweroord this figure is only 18 mg l^{-1} and at the two other farms less than 10 mg l^{-1}. The DOC concentration in the fifth metre at Maarheeze is on average 10 mg l^{-1}, and much lower than in the first metre. There is no clear decrease at the other farms.

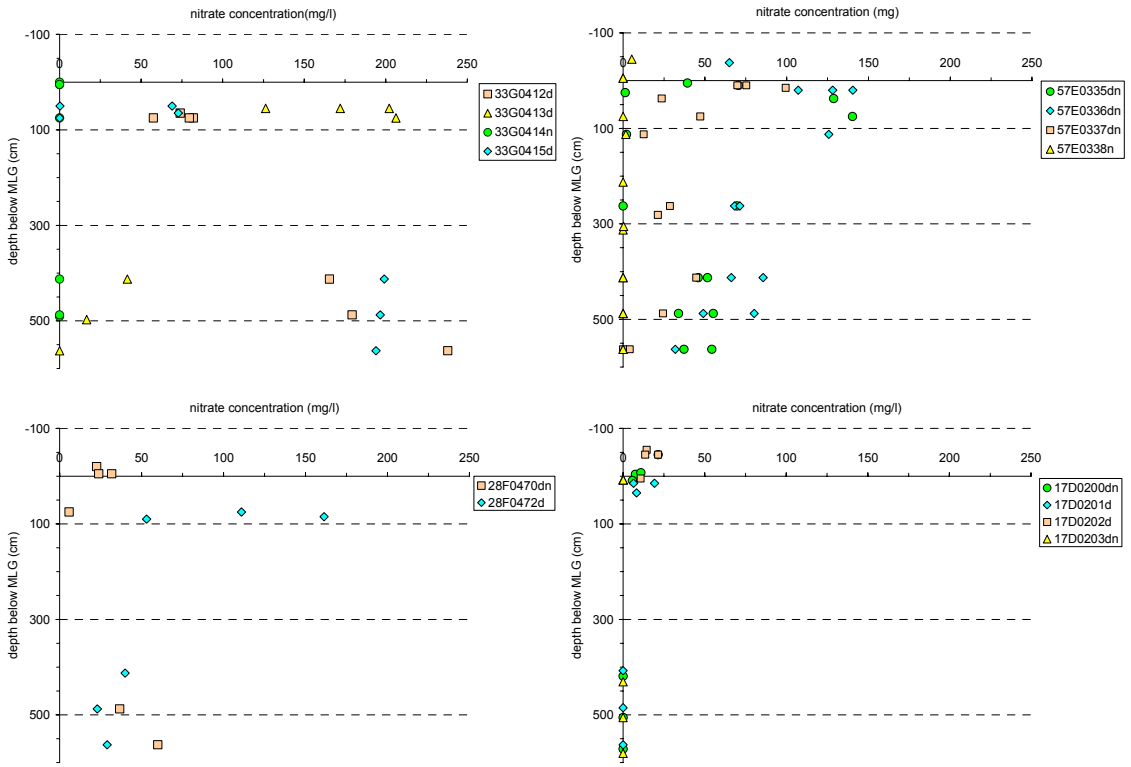

Figure 3.3 Nitrate concentrations at various depths at the four dairy farms for sampling round 3. Top left Spankeren (33G), top right Maarheeze (57E), bottom left Nutter (28F) and bottom right Nieuweroord (17D).
Drainage classes: d = dry, dn = neutral, n = wet.

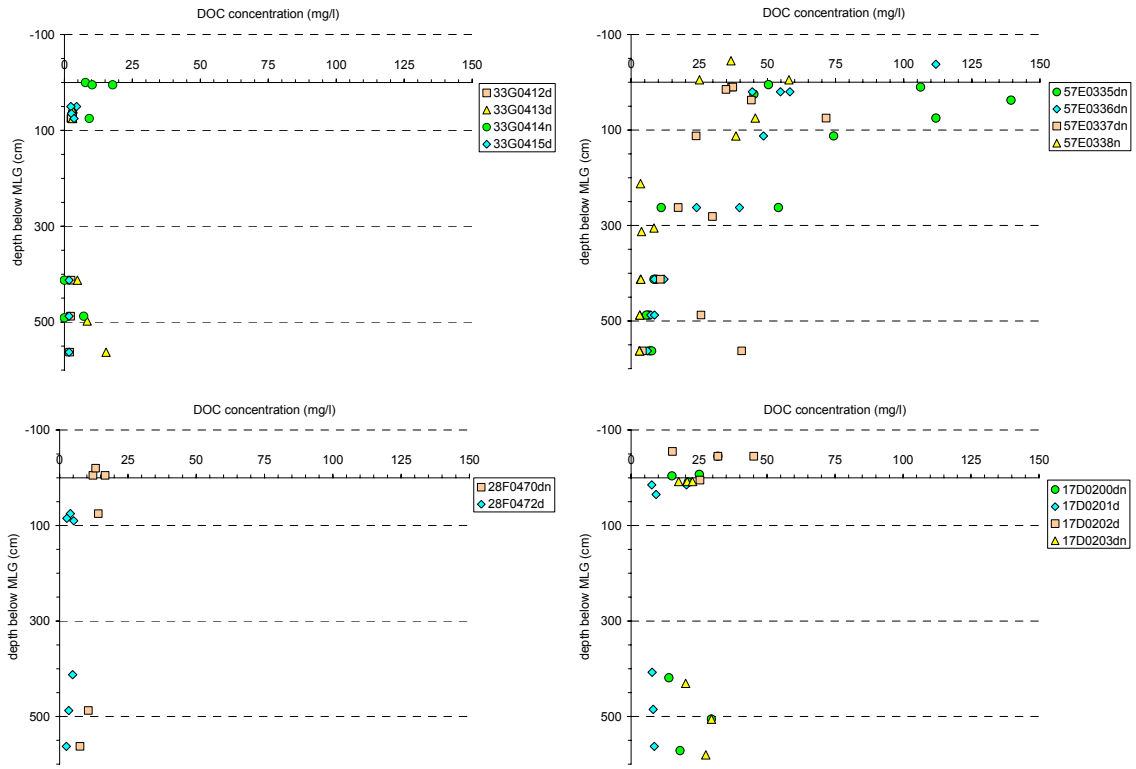

Figure 3.4 DOC concentrations. For explanation, see text for Figure 3.3.

The ammonium concentrations are low (< 2 mg l^{-1}) in the groundwater at Spankeren and Nutter, see Figure 3.5, which is normal for sandy soils. Higher ammonium concentrations (> 2 mg l^{-1}) occur in the profiles at Nieuweroord. There are also high ammonium concentrations in the upper metre of the wet profile 57E0338 at Maarheeze.

The chloride concentrations do not appear to show any differences between the first and fifth metres, with the exception of location 33G0413, see Figure 3.6. A markedly higher chloride concentration is visible at location 33G0413 at five metres below MLG in the third round. There was no difference in the second round. There is a 30-cm-thick clay-loam layer from about 60 cm below MLG in this profile, and there are also clay and loam bands at greater depths (see Figure 3.2).

The iron concentrations are low at the locations at Spankeren, Nutter and Maarheeze (< 5 mg l^{-1}), with the exception of the wet location 57E0338 (more than 20 mg l^{-1} at the top and between 10 and 15 mg l^{-1} at the bottom), see Figure 3.7. Three of the four locations at Nieuweroord have relatively high iron concentrations, particularly at five metres below MLG (between 10 and 30 mg l^{-1}). There was no significant difference in the iron concentration between the first and fifth metre in either round, see Table 3.6.

The sulphate concentrations in the first and fifth metres for the different drainage classes in rounds 2 and 3 are given in Table 3.5. On average, the locations with wet and dry drainage classes show a higher sulphate concentration at five metres below MLG, but the increase compared with the first metre is not significant in any of the cases and is small in the dry drainage class (19% in the second round and 3% in the third round). This is also clearly visible in Figure 3.8 at the locations at Spankeren. At the locations with a neutral drainage class, the increase with depth is significant in both rounds (the 95% confidence interval for the average of 112% in round 2 is 31-193%, and that for the average of 98% in round 3 is 15-182%). The locations at Maarheeze illustrate this, Figure 3.8.

Table 3.5 Sulphate concentrations (average and standard error) at approximately 1 and 5 metres below MLG for each drainage class for each round.

Drainage class	Round	Number of locations[1]	Depth	Depth below MLG (cm)	Sulphate (mg l^{-1})	Standard error
Dry	2	4 (8)	1	75	94	48
			5	451	112	27
	3	5 (8)	1	57	49	9
			5	466	51	5
Neutral	2	4 (6)	1	75	64	18
			5	452	137	8
	3	6 (6)	1	7	42	5
			5	480	83	11
Wet	2	2 (2)	1	75	44	43
			5	472	119	58
	3	2 (2)	1	-8	33	24
			5	457	46	9

[1] Number of locations for which data was available for both depths. The number of locations at which wells were installed is given in brackets. The extra locations in the third round are all at Nieuweroord.

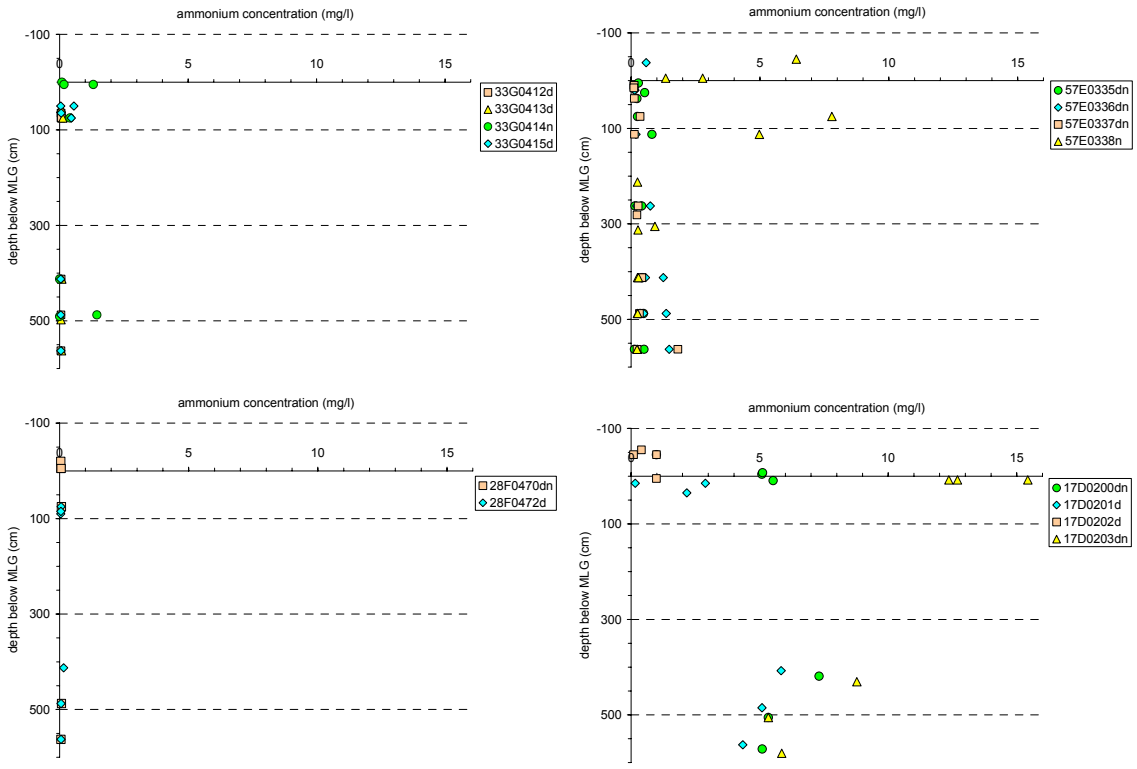

Figure 3.5 Ammonium concentrations at different depths at the four dairy farms for sampling round 3. Top left Spankeren (33G), top right Maarheeze (57E), bottom left Nutter (28F) and bottom right Nieuweroord (17D).
Drainage classes: d = dry, dn = neutral, n = wet.

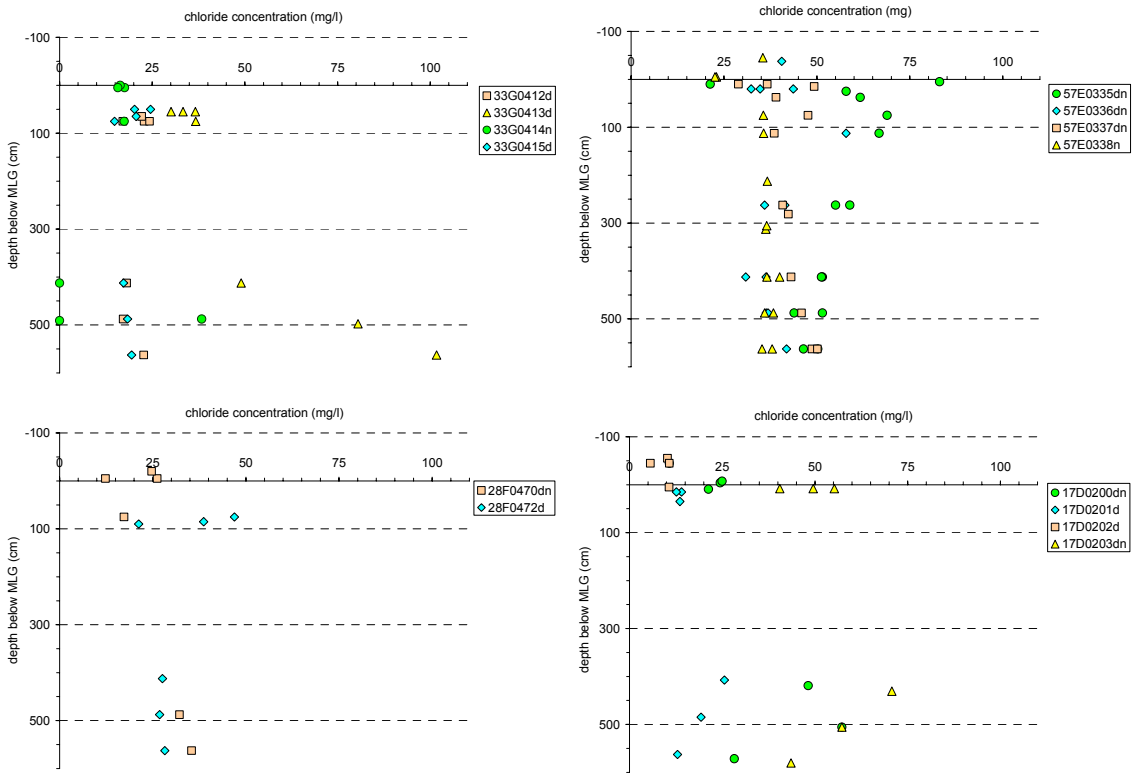

Figure 3.6 Chloride concentrations. For explanation, see text for Figure 3.5

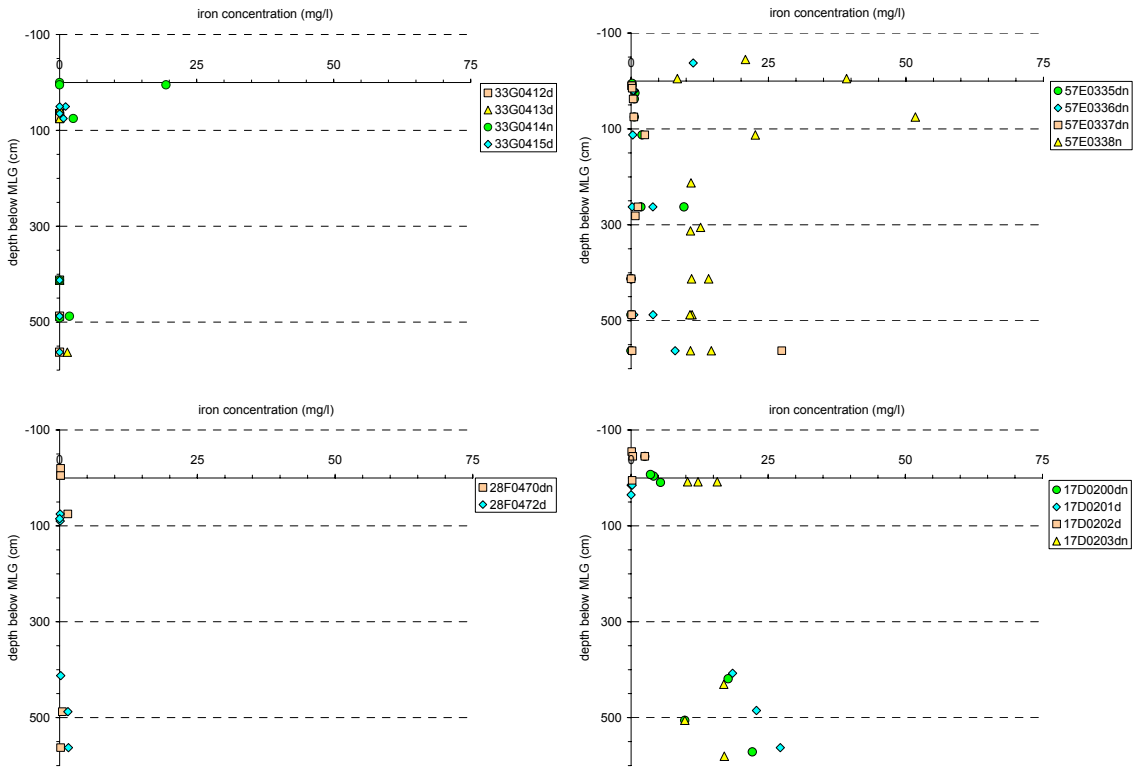

Figure 3.7 Iron concentrations at different depths at the four dairy farms for sampling round 3. Top left Spankeren (33G), top right Maarheeze (57E), bottom left Nutter (28F) and bottom right Nieuweroord (17D).
Drainage classes: d = dry, dn = neutral, n = wet.

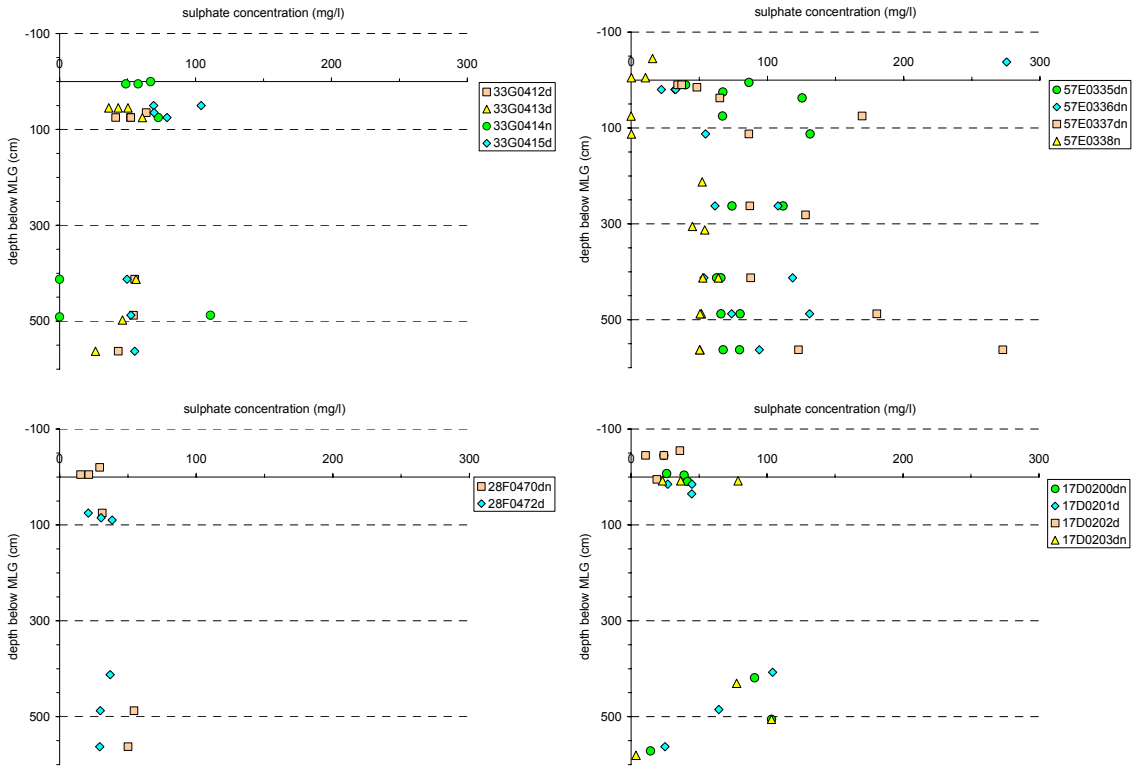

Figure 3.8 Sulphate concentrations. For explanation, see text for Figure 3.7.

The calcium and magnesium concentrations, which jointly determine the hardness of the water, are lower in the fifth metre than in the first metre of the groundwater in the soils with a neutral or wet drainage class but the difference is not significant. There is an increase in the soils with a dry drainage class but this is not significant, either. Only the magnesium concentration in the second round is significantly higher in the fifth than in the first metre (2-59%) in these soils.

A notable point is that the dry location 33G0413 at Spankeren, which shows a clear decrease in the nitrate concentration with depth (see Figure 3.3), also shows a noticeable increase in calcium (Figure 3.9) and magnesium concentrations (Figure 3.10). Conversely, the dry location 28F0472 at Nutter, which also shows a decrease in the nitrate concentration, shows a decrease in the calcium and magnesium concentrations rather than an increase. The subsoil of the locations at Spankeren contain carbonate as opposed to the subsoil of the locations at the other farms, see section 6.3.

The locations with a neutral drainage class at Maarheeze (57E), which show a decrease in the nitrate concentration with depth, also show a decrease in the calcium and magnesium concentrations.

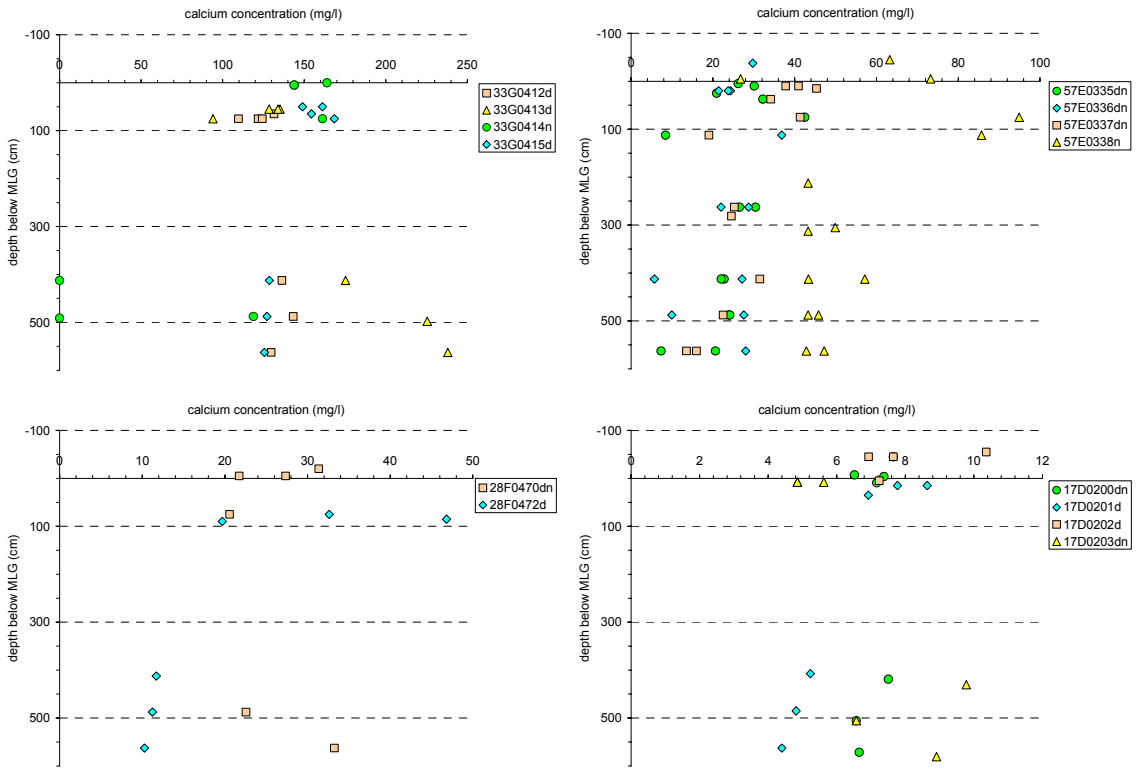

Figure 3.9 Calcium concentrations at different depths at the four dairy farms for sampling round 3. Top left Spankeren (33G), top right Maarheeze (57E), bottom left Nutter (28F) and bottom right Nieuweroord (17D).
Drainage classes: d = dry, dn = neutral, n = wet.

The concentrations of trace elements (arsenic, cadmium, chromium, copper, nickel and zinc) are on average lower in the fifth metre than in the first metre, see Table 3.6. At this point, however, it must be said that the results for the majority are not significant due to the large variation and the small number of observations. The nickel concentration for the neutral

drainage class is, however, considerably higher in the fifth metre than in the first metre; 32 µg l^{-1} versus 9 µg l^{-1} in the second round and 23 µg l^{-1} versus 9 µg l^{-1} in the third round. These differences are not significant due to the large variation, see Figure 3.11. At location 33G0413 (decrease in nitrate, increase in DOC, chloride, calcium and magnesium) too, the nickel concentration was higher lower down than at the top. The profile contains pyrite but has a relatively high potential denitrification between 566 and 588 cm below surface level (Appendix 8). The results for the other metals for each farm are shown in figures in Appendix 7.

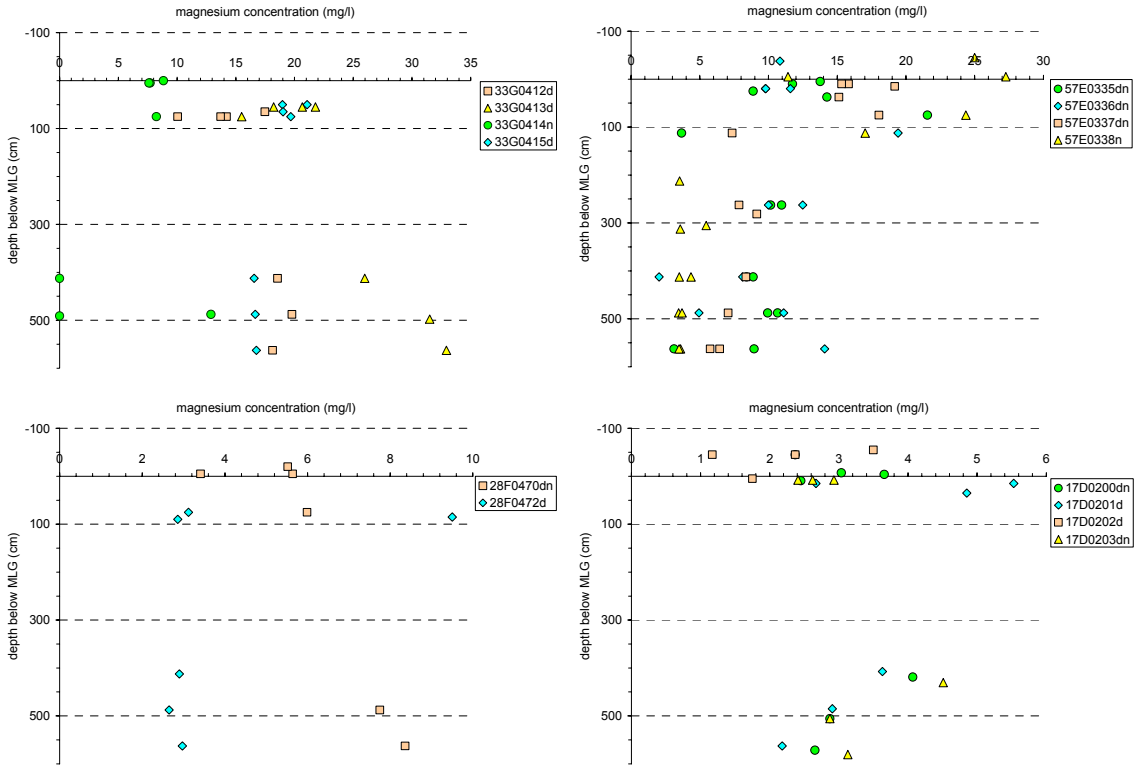

Figure 3.10 Magnesium concentrations at different depths at the four dairy farms for sampling round 3. Top left Spankeren (33G), top right Maarheeze (57E), bottom left Nutter (28F) and bottom right Nieuweroord (17D).
Drainage classes: d = dry, dn = neutral, n = wet.

Table 3.6 Differences in the concentrations of a number of trace elements (µg l^{-1}) and iron (mg l^{-1}) between the first and fifth metres below MLG for each drainage class for each round[1].

Drainage	Round	Arsenic	Cadmium	Chromium	Copper	Nickel	Iron	Zinc
Dry	2	-1.3	-0.08	-0.7	+0.1	-0.9	+0.9	-2.9
	3	+0.0	-0.15	-1.4	-2.2	-2.2	+2.3	-33
Neutral	2	-1.2	-0.57	-2.6	-17	+23	+2.9	-4.5
	3	-0.4	-0.32	-1.3*	-17*	+14	+0.5	-44
Wet	2	-2.7	-0.01	+0.8	+0.1	-1.5	-7.7	+0.6
	3	-4.5	-0.02	-0.6	-2.7	-4.3	-7.2	-15

[1] A negative number means a lower concentration at a depth of five metres than at one metre, a positive number, a higher concentration at five metres than at one metre.
* The significant differences ($p < 0.05$) are marked with *.

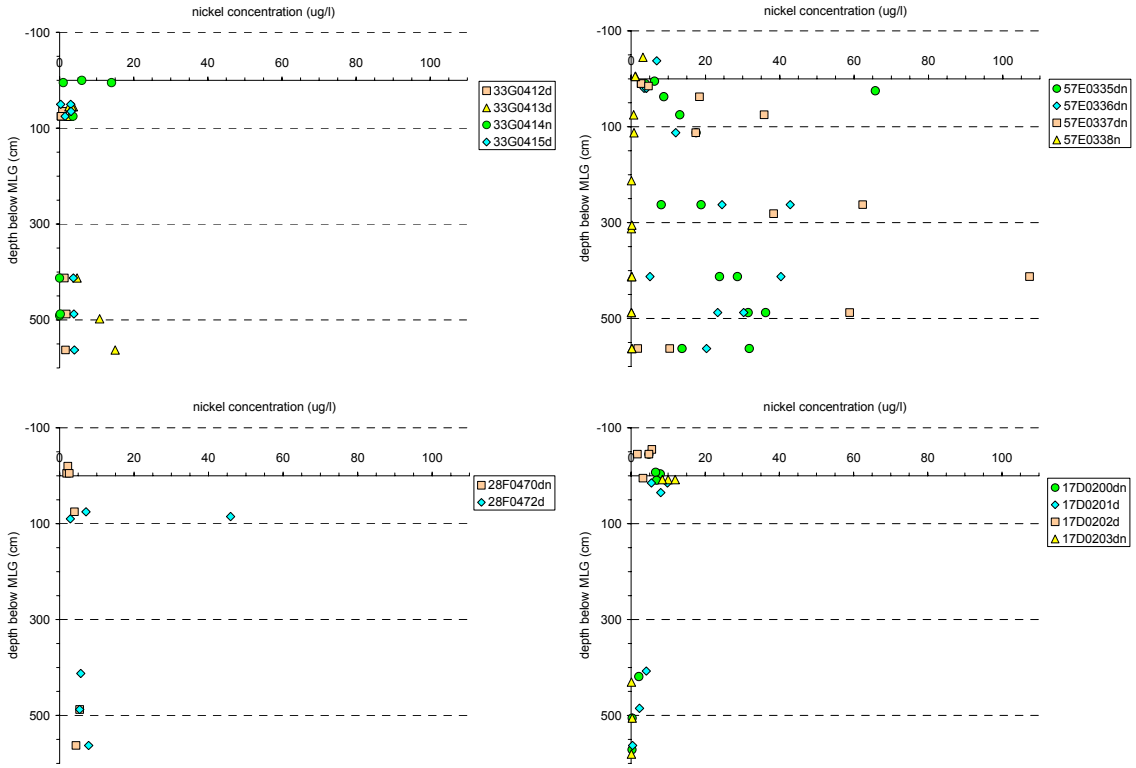

Figure 3.11 Nickel concentrations at different depths at the four dairy farms for sampling round 3. Top left Spankeren (33G), top right Maarheeze (57E), bottom left Nutter (28F) and bottom right Nieuweroord (17D).
Drainage classes: d = dry, dn = neutral, n = wet.

3.4 Discussion

If the study makes one thing clear, it is that the subsoil of the sandy areas in the Netherlands is highly heterogeneous. Even if we only take a very rough look at the structure of the sediments, there is at least one aberrant (non-sandy) layer at every location. In most cases, the locations at any one particular farm also vary from one another in terms of the structure of the upper part of the aquifer. A notable point is that the locations at Spankeren (situated in the vicinity of the large push-moraine, see Figure 1.4) contain carbonate, which is atypical for this area (Van Beek, 2002). The same applies to the lack of pyrite at the locations at Nutter (area with carbonate-free pyrite). As a result, large differences can arise within short distances in groundwater flow and whether denitrification occurs or not.

The nitrate concentrations are (not-significantly) lower in the fifth metre than in the first metre. There are differences between drainage classes as was the case in the previous study. On average, the soils with dry classes do not show a decrease, and those with neutral classes do, although this is not significant. The soils with a wet class do not contain any nitrate in either the first metre or the fifth.

If the annual precipitation surplus remains constant and the downwards water movement amounts to one metre per year, and we assume that the soil profile is homogeneous and that denitrification does not occur, then Table 3.1 can be converted into a nitrate-depth profile, see

Figure 3.12. In this situation the nitrate concentrations at the bottom will be higher than those at the top, because the nitrate concentration in the upper metre decreased in the period 1999-2004.

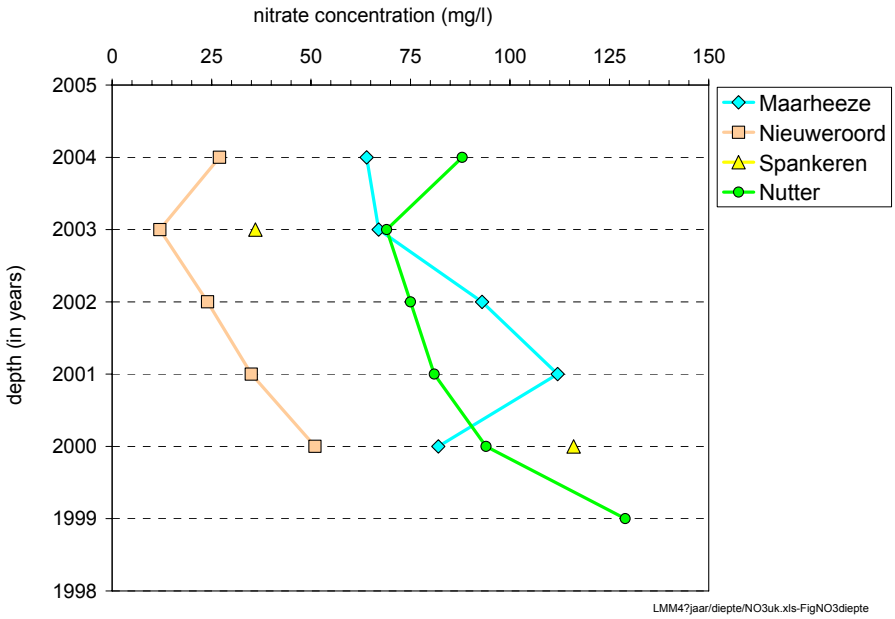

Figure 3.12 Graph of the nitrate concentration in the upper metre of the groundwater at the four LMM farms in the period 1999-2004 against depth. Assuming that nitrate leaches out a constant rate of one metre per year and that no denitrification occurs, the year 2000 gives the nitrate concentration at approximately five metres below the groundwater table.

It is not possible to give a detailed explanation of the differences between the first and fifth metres for each location, given that there are various inconsistencies. For example, there is a layer of detritus in the fifth metre at location 33G0413, see Figure 3.2. The presence of this organic matter could be the reason for the lower nitrate concentrations in the fifth metre at the location, see Figure 3.3. There is no such layer in the profile at location 28F0472, but there is still a decrease. There is a detritus layer in the upper five metres of the groundwater at location 33G0415, but the nitrate concentration increases nevertheless.

The presence of peat or detritus layers in the profile appear to have little, if any, effect on the concentration of DOC, see Figure 3.4. The profiles 33G0414 at Spankeren and 57E0335 at Maarheeze with peat layers and the profiles 33G0413 and 33G0415 at Spankeren with a detritus layer mentioned earlier do not have markedly higher DOC concentrations. The first three metres of groundwater at Maarheeze do have relatively high DOC concentrations compared with the other three farms. This also applies for the locations without peat layers in the first five metres of the groundwater (57E0336 and 57E0337).

chapters 5 and 6 discuss the link between organic matter, DOC and denitrification. The measurements presented here show that the presence of layers rich in organic matter in the subsoil do not by definition mean lower nitrate concentrations.

High ammonium concentrations are often found in peat soils, particularly in groundwater below the first metre (Willems and Fraters, 1995). A notable point is that high ammonium concentrations (> 2 mg l^{-1}) occur between MLG and five metres below MLG in profiles at

Nieuweroord without peat layers and that the ammonium concentrations are lower in the wet profile 33G0413 at Spankeren and the neutral profile 57E0335 at Maarheeze with peat layer, see Figure 3.5. The wet profile 57E0338 at Maarheeze, with a peat layer at the top, does have high ammonium concentrations in the upper metre. The locations in Nieuweroord do not have peat layers in the layers above MLG either (Van Maarseveen, 2005). The ammonium may originate from residues of peat deposits present in these reclaimed peat soils in the past. The detritus in the profiles 33G0413 and 33G0415 at Spankeren does not have any effect on the DOC concentration or on the ammonium concentration.

The fact that the nitrate concentrations five metres below the groundwater table can be higher than at a depth of a metre has already been discussed section 2.3. It appears plausible given the development of the nitrate concentration in the upper metre of the groundwater over time (Figure 3.12). The higher concentrations at five metres at the locations 33G0412 and 33G0415 could also be a consequence of discontinuity in the subsoil; that is, gravel layers at five metres at location 33G0412 and clay and loam layers between the first and fifth metres at location 33G0415. But this would then also apply to the lower concentrations at five metres at the dry locations 33G0413 and 28F0472 (Nutter), where clay and loam layers also occur between the first and fifth metres. Whether this causes discontinuity in the downwards groundwater flow at ‘plot scale’ is not certain. Location 33G0413 is the only one to give an aberrant chloride concentration at a depth of five metres (only in the third round, see Figure 3.6), which could indicate a different water type. The chloride concentrations for the other locations did not substantiate this. The same applies to the hardness (calcium and magnesium concentrations), and to a lesser extent to the nickel concentration, which are higher at a depth of five metres than in the first metre at location 33G0413. An increase in both of these parameters is, however, contradictory because in carbonate-rich soils the acidity will be such that nickel will be deposited.

The conditions in the upper groundwater at Nieuweroord indicate a highly reduced (anoxic) environment (high DOC, iron and ammonium concentrations). For these reasons, nitrate was not expected in the groundwater at these spots, and was, indeed, not found. The wet location 57E0338 (Maarheeze) shows a similar picture. There is no nitrate in the upper metre at wet location 33G0414 (Spankeren), but the average DOC, ammonium and iron concentrations are also low.

The increase in the sulphate and nickel concentrations with depth in the soils with neutral drainage classes at Maarheeze (Figure 3.8 and 3.11) in combination with the nitrate concentration decreases ascertained above (Figure 3.3) could indicate denitrification by iron sulphides in a carbonate-free environment.

The concentrations of the other metals decrease with depth. This corresponds with findings from an earlier study in which the concentrations of these metals also decreased with depth (Fraters et al., 2001).

3.5 Conclusions

The heterogeneity of the subsoil at the four farms is such that large differences can arise as to whether or not denitrification takes place and how denitrification affects the water quality within short distances (within a particular farm).

The nitrate concentration in the fifth metre is on average 20% (second sampling) and 8% (third sampling) lower than in the first metre (not significant) for the 16 locations at the four LMM dairy farms.

For the soils with a dry drainage class there is no decrease in the nitrate concentration with depth; for the soils with a neutral class there is an average (non-significant) decrease of 31%.

The decrease in the nitrate concentration with depth in the neutral soils appears to lead to detrimental effects a problem shift; that is, the sulphate concentration doubles (this is significant) and the nickel concentration triples (non-significant).

The development of the nitrate concentration cannot be attributed unequivocally to a single process based on the results of this study because various factors could be responsible for the development.

4. Comparison of sampling methods

4.1 Introduction

The objective of this part of the field study was to test methods for sampling the upper five metres of groundwater under field conditions and to compare the methods with one another in terms of the technical aspects of the implementation and the quality. Soil samples were also taken for the denitrification study.

The study consisted of the installation of screens for groundwater sampling, the sampling of the groundwater, measurement and chemical analyses of the groundwater samples and the sampling of soil for the denitrification study. The implementation of the field study is described in more detail in Van Elzakker et al. (2007). The following section briefly summarizes the set-up (section 4.2) and the results (section 4.3) of the study.

The following technical aspects (section 4.3.1) were looked at: is the method easy or complex, are cheap, simple materials needed or do expensive machines have to be used, how likely is the installation of a screen at the required depth to be successful, how well do the screens function and do they continue to function (only for the permanent wells), is equipment left in the subsoil, what are the costs in the short and long term, are there any particular advantages or disadvantages. The chemical analyses (section 4.3.2) were compared to see whether they yielded comparable results, and the methods using permanent wells were looked at to see whether there was development in the water quality over time.

The most important difference between the sampling methods is whether screens are installed permanently or temporarily. Permanent screens will facilitate the sampling of groundwater in the years to come with little effort. Because the groundwater level can vary from year to year, the location of a permanent screen also varies with respect to the groundwater level, which is a disadvantage if the intention is to sample the upper five metres of the groundwater. This drawback can, however, be overcome by varying the screen length and installing several screens.

4.2 Set-up of the study

4.2.1 Groundwater sampling methods examined

In the first instance, three methods for sampling the upper five metres of the groundwater were selected for testing under practical conditions (Elzakker and Gast, 2006). A fourth method was added at a later date (Direct Wells). Two of the methods used screens for extracting groundwater installed on a temporary basis and two used screens installed permanently. Besides in rounds 1 and 3 the standard LMM method was also used. It could, however, only be used for taking samples from the upper metre of the groundwater.

The study was carried out at 16 locations that were spread out over four dairy farms that participated in the LMM. The selection of the farms and the locations, and the soil

characteristics and groundwater quality at these locations are described in the previous chapter.

Three of the four methods were used at each of the 16 locations. One method (the Continuous Multichannel Tubing method, CMT) was only used at the four locations at Maarheeze. Besides these methods, standard LMM sampling was carried out. A few characteristics of these methods are given in Table 4.1.

Table 4.1 Characteristics of the selected sampling methods and their applications.

Method	Code	Type[1]	Organization carrying out the sampling	Number of locations	Screens/ location	Rounds[2]
Van der Staay	US	Manual, temporary bore holes	Utrecht University	16	2	1
Extending point	EU	Mechanical, temporary bore holes	Eijkelkamp	16	2-3	1
Direct Wells	ED	Mechanical, permanent wells	Eijkelkamp	16	4	1, 2, 3
Continuous Multichannel Tubing (CMT)	EC	Mechanical, permanent wells	Eijkelkamp	4	7	1, 2, 3
LMM	RL	Manual, temporary bore holes	RIVM	16	1	1, 3 [3]

[1] The mechanical drilling methods concern only the SonicSampDrill (Sonic) used by the company Eijkelkamp (see Appendix 4).
[2] Number of the round, see Table 3.3 for sampling data for each round.
[3] In round 1, one bore hole was made at each location; in round 3, three bore holes were made at each location.

Each location was marked in advance. The Direct Wells were installed at the spots marked. All other bore holes were drilled within a metre of the marked spot.

4.2.2 Sampling of the groundwater

With the temporary methods (US and EU) a screen of a length of 50 cm was placed 25 cm and 450 cm below the current groundwater table.

For the permanent ED method, a screen of a length of 100 cm was placed 25 cm below MLG. In addition, three screens of a length of 25 cm were placed at 400 cm, 475 cm and 550 cm below MLG. For the EC method, three screens of a length of 25 cm were placed at 50 cm above MLG, 25 cm below MLG and 100 cm below MLG instead of a single screen of a length of 100 cm at 25 cm below MLG. The deeper screens were placed in the same manner as for the ED method. For the EC method, another screen was also placed at 250 (300) cm below MLG.

If a clearly aberrant soil layer was ascertained, an additional sampling was carried out above this layer (temporary methods) or a screen was placed above it (permanent methods). For the

purposes of this study, an interfering layer was defined as a layer that meets the following criteria:

1. The soil type is not sand or peat, for example clay, clay/loam, boulder clay, gravel, etc.
2. The aberrant layer begins more than two metres below the reference level, that is, the current groundwater level in the case of temporary screens and the MLG in the case of permanent screens.
3. The layer stretches out to at least the edge of the plot. This condition lapses if the layer is thicker than 50 cm; if this is the case, the layer in question is an interfering layer, regardless.

4.3 Results

4.3.1 General technical aspects of the implementation

The Sonic vibratory method combined with Aqualock enables the determination of the soil texture first and then, depending on the results, the placing of the screen. The Aqualock usually works well but it does have a few disadvantages (compacting of the soil, puddling, etc.). Alternatives were not examined.

Installing a well finish device directly above the permanent well and below the top soil (to enable sampling) is possible from the practical point of view. The disadvantage is that the well has to be dug up every time new samples are taken. Finishing on the plot edge is also possible, practically speaking. It is, however, not known whether this would present problems with, for example, silting up of the tubes, over a period of time. Whether a difference in analytical results can be expected between samples taken at the plot edge and immediately above the well, in view of, for example, a difference in tube length of approximately 20 metres is not known either. Comparative measurements using both methods have not (yet) been carried out.

4.3.2 Technical aspects of the groundwater sampling

During the third sampling round in late 2005 it became apparent that not all the permanent wells (ED, EC) installed were still operational. One well (17D0203) was totally destroyed by the laying of drainage pipes on the plot. At another well (57E0338) the well finish device at the edge of the plot was damaged during mowing of the banks of the ditch. It was still possible to sample this well directly in the field. In 2006 two wells (17D0201 and 17D0202) were lost because the plot in which they were located was excavated.

Screen installation was only a problem when the Van der Staay method (US) was used, see Table 4.2. Deeper screens could not always be placed because it was not possible to drill down to the intended depth by hand every time.

Between 58 and 82% of the screens placed at about five metre below the MLG yielded enough water for sampling in the successive rounds, see Table 4.3. Possible reasons for delivering too little, or no, water are discussed in section 4.4.

Table 4.2 Overview of the number of screens planned and actually placed at each location and for each sampling method and the numbers of water-yielding screens for each round[1], sampling method and location.

	number of screens to be placed				number of screens placed				number of screens that yielded water							
									round 1				round 2		round 3	
farm/location	**EC**	**ED**	**EU**	**US**	**EC**	**ED**	**EU**	**US**	**EC**	**ED**	**EU**	**US**	**EC**	**ED**	**EC**	**ED**
Nieuweroord																
17D0201		4	2	2		4	2	2		2	2	2		2		2
17D0202		4	2	2		4	2	1		0	0	1		0		1
17D0203		4	2	2		4	1	1		3	1	0		3		0
17D0200		4	2	2		4	1	1		3	1	0		3		3
Nutter																
28F0471		4	2	2		4	2	1		2	1	1		2		0
28F0472		4	2	2		4	2	1		4	0	0		4		3
28F0473		4	2	2		4	2	1		0	0	1		0		0
28F0470		4	2	2		4	2	1		4	0	1		4		3
Maarheeze																
57E0336	7	4	2	2	7	4	2	2	4	3	2	2	4	3	5	2
57E0337	7	4	2	2	7	4	2	2	6	1	2	2	6	2	4	2
57E0338	7	4	2	2	7	4	2	2	6	4	2	2	6	4	7	4
57E0335	7	4	2	2	7	4	2	2	6	4	1	2	6	4	7	4
Spankeren																
33G0415		4	2	2		4	2	2		0	2	1		3		3
33G0412		4	2	2		4	2	2		4	1	2		4		4
33G0413		4	2	2		4	2	2		4	1	2		4		4
33G0414		4	2	2		4	3	1		2	3	1		2		2
sum	**28**	**64**	**32**	**32**	**28**	**64**	**31**	**24**	**22**	**40**	**19**	**20**	**22**	**44**	**23**	**37**
% compared with those to be placed					**100**	**100**	**97**	**75**	**79**	**63**	**59**	**63**	**79**	**69**	**82**	**58**
% compared with those actually placed									**79**	**63**	**61**	**83**	**79**	**69**	**82**	**58**

[1] Methods: EC = Continuous Multichannel Tubing (CMT); ED = Direct Well; EU = Extending point; US = Van der Staay (see Table 2.3 for characteristics).
Non-placement of wells means that the required depth could not be reached by drilling, or that the extraction of groundwater was deemed impossible based on the soil samples bored out (upper screen in the EU method at 2 locations at Nieuweroord).

Table 4.3 Overview of the number of screens planned and actually placed at each location and for each sampling method and the numbers of water-yielding screens for each round[1], sampling method and location for the deep screens (about five metres below MLG).

	number of screens to be placed				number of screens placed				number of screens that yielded water: round 1				round 2		round 3	
farm/location	**EC**	**ED**	**EU**	**US**	**EC**	**ED**	**EU**	**US**	**EC**	**ED**	**EU**	**US**	**EC**	**ED**	**EC**	**ED**
Nieuweroord																
17D0201		3	1	1		3	1	1		2	1	1		2		2
17D0202		3	1	1		3	1	0		0	0	0		0		0
17D0203		3	1	1		3	1	0		3	1	0		3		0
17D0200		3	1	1		3	1	0		3	1	0		3		3
Nutter																
28F0471		3	1	1		3	1	0		2	0	0		2		0
28F0472		3	1	1		3	1	0		3	0	0		3		3
28F0473		3	1	1		3	1	0		0	0	0		0		0
28F0470		3	1	1		3	1	0		3	0	0		3		2
Maarheeze																
57E0336	3	3	1	1	3	3	1	1	2	2	1	1	2	2	2	2
57E0337	3	3	1	1	3	3	1	1	3	1	1	1	3	1	2	1
57E0338	3	3	1	1	3	3	1	1	3	3	1	1	3	3	3	3
57E0335	3	3	1	1	3	3	1	1	3	3	0	1	3	3	3	3
Spankeren																
33G0415		3	1	1		3	1	1		0	1	1		2		2
33G0412		3	1	1		3	1	1		3	0	1		3		3
33G0413		3	1	1		3	1	1		3	1	1		3		3
33G0414		3	1	1		3	2	0		1	2	0		1		1
sum	**12**	**48**	**16**	**16**	**12**	**48**	**17**	**8**	**11**	**32**	**10**	**8**	**11**	**34**	**10**	**28**
% compared with those to be placed					**100**	**100**	**106**	**50**	**92**	**67**	**63**	**50**	**92**	**71**	**83**	**58**
% compared with those actually placed									**92**	**67**	**59**	**100**	**92**	**71**	**83**	**58**

[1] Methods: EC = Continuous Multichannel Tubing (CMT); ED = Direct Well; EU = Extending point; US = Van der Staay (see Table 2.3 for characteristics).

The pros and cons of each of the methods were listed based on the findings during the preparations for the study, the placing of and sampling from the screens and the closure of the wells after sampling. These pros and cons are discussed below.

Van der Staay (US)

The advantages of the Van der Staay method are as follows:

1. relatively simple;
2. little equipment is required;
3. the method generates knowledge about the soil texture to the depth reached by drilling;
4. no equipment (screens or tubes) is left in the soil;
5. relatively cheap;
6. the screens placed all yielded sufficient water for a sampling.

The disadvantages of the Van der Staay method are as follows:

1. only 50% of the deep screens could be placed because the planned depth could not be reached by manual drilling;
2. hard physical work.

Sonic with Extending Point Method (EU)

The advantages of the Extending point method are as follows:

1. the required depth is always rapidly and successfully reached with the Sonic;
2. in principle groundwater sampling is always possible, if no groundwater can be sampled at the required depth, another depth can be chosen relatively quickly from which to get water (40% of the deep UPM screens, five metre below MLG, did not yield any water during the study);
3. no equipment (screens and tubes) is left in the soil.

The disadvantages of the Extending point method are as follows:

1. heavy equipment is required for the drilling (Sonic equipment + tractor);
2. the drilling (heavy work) and the sampling (accurate/clean work) are carried out by the same person; these are two different disciplines that are difficult for one person to combine in the field;
3. the construction (screen gauze) is vulnerable during the opening of the screen (extending the point);
4. the construction (with O rings) is not optimum but can be improved;
5. the screen gauze may be too coarse;
6. in connection with the above point: connection of the pump to the screen via the conical connection point should be made before the screen is released, because the falling shut of the formation against the screen and shooting up of soil above the connection point can hinder the connection of the pump (it is not known how often this occurred in the course of the study).

Sonic with Direct Wells (ED)

The advantages of the Direct Wells placed using the Sonic vibratory method are as follows:

1. the required depth is always rapidly and successfully reached with the Sonic;
2. the use of a permanent screen means that successive samplings are cheap;
3. the sampling can be separated from the drilling/placing of screens (these are two different disciplines that are difficult for one person to combine in the field).

The disadvantages of this method are as follows:

1. heavy equipment is required for the drilling (Sonic equipment + tractor);
2. a bore hole has to be drilled for every screen to be placed;
3. it is possible to make a mistake with screen depths due to the repeated changing of the drill casing lengths between placing the various screens on drilling locations;
4. of the deep screens placed (about five metres below MLG) ‘only’ 67% (round 1), 71% (round 2) and 58% (round 3) respectively, yielded water; approximately 30% of the screens placed were therefore placed ‘for nothing’.

Sonic with CMT (EC)

The advantages of the CMT placed using the Sonic vibratory method are as follows:

1. the required depth is always rapidly and successfully reached with the Sonic;
2. up to seven screens can be placed in one bore hole;
3. the use of a permanent screen means that successive samplings are cheap;

4. compared with the other methods, this is the most accurate method for determining the average water quality from the upper five metres (there are, after all, seven screens);
5. mistakes with screen depths are not possible because the whole construction with screens is visible at surface level prior to installation;
6. the sampling can be separated from the drilling/placing of screens (these are two different disciplines that are difficult for one person to combine in the field).

The disadvantages of this method are as follows:

1. heavy equipment is required for the drilling (Sonic equipment + tractor);
2. the method is relatively expensive;
3. with CMT, 30% of the screens are placed for nothing (90% of the deep screens placed at Maarheeze yielded water; with the deployment of the CMT at the other three farms in this research this percentage would be comparable with that of the Direct Wells, that is, approximately 70%);
4. the preparation of the CMT above ground level is fairly laborious.

4.3.3 Comparison of analytical results

The results of the chemical analysis of the groundwater samples are compared by dividing up the sampling methods according to whether they used a:

A. permanent or temporary screen;
B. manual or mechanical drilling method.

In addition, any differences that may arise in the analytical results could be due to:

- the reference depth used for placing the screen (MLG for the permanent screens versus the current groundwater level for the temporary screens);
- the lengths of screens used.

Re A Permanent versus temporary screen

The nitrate concentrations measured with the upper screen of the Direct Wells (ED) in round 1 are always lower than concentrations measured with the methods using screens placed temporarily, that is, the Van der Staay (US, manual), LMM (RL, manual) and Extending point (EU, mechanical), see Figure 4.1. Only the screens at a comparable measuring depth (with the top at 20 to 30 cm below MLG) are taken into consideration here. The sulphate concentrations measured with the ED in round 1 are, however, practically always higher than the concentrations measured with the temporary methods (US, RL and EU), see Figure 4.2.

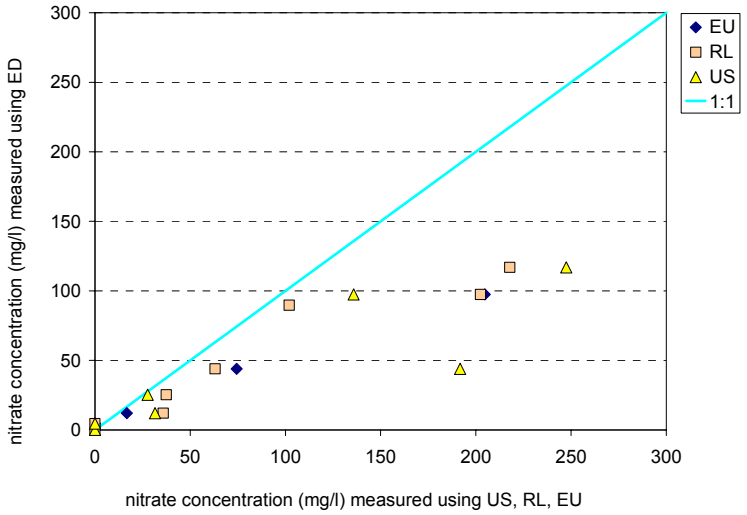

Figure 4.1 Nitrate concentrations measured in the upper screen of the Direct Wells (ED) compared with the concentrations measured in the upper screens placed using the temporary bore hole methods Van der Staay (US), LMM (RL) and Extending point (EU). Data for round 1, top of the screen 20-30 cm below MLG.

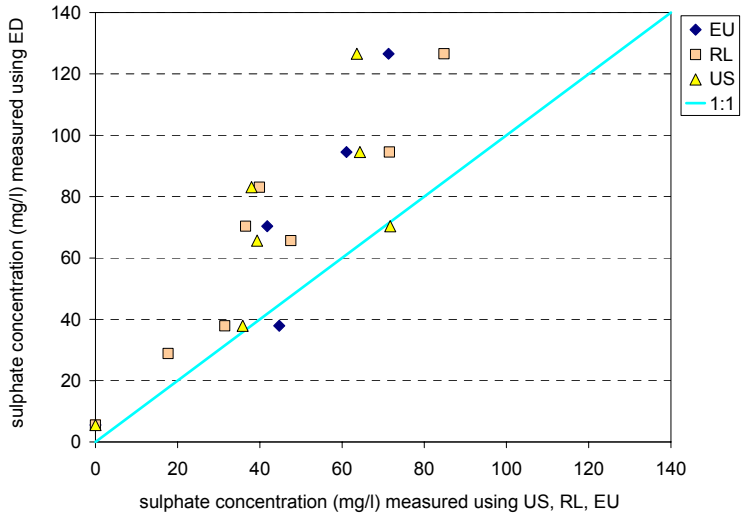

Figure 4.2 Sulphate concentrations measured in the upper screen of the Direct Wells (ED) compared with the concentrations measured in the upper screens placed using the temporary bore hole methods Van der Staay (US), LMM (RL) and Extending point (EU). Data for round 1, top of the screen 20-30 cm below MLG.

During the third sampling round, the LMM method was also used at locations with permanent screens where groundwater could be sampled (13 of the 16 locations). Three LMM bore holes were drilled at each location. Figure 4.3 shows a graph of the nitrate concentration measured in the upper ED screens against the average nitrate concentration measured using the LMM method. The measurements for nitrate taken with the Direct Well and the LMM method in round 3 do not differ systematically.

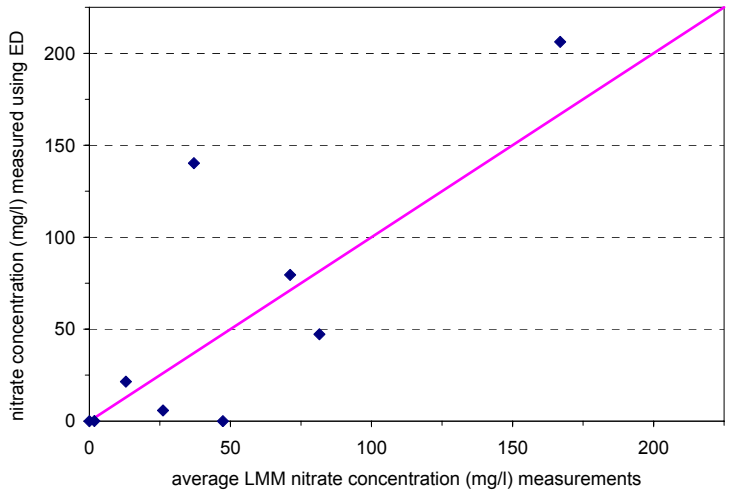

Figure 4.3 Nitrate concentrations measured in the upper screen of the Direct Wells (ED) compared with the concentrations measured in the upper screens placed using the temporary LMM bore hole method. Data for round 3, three LMM measurements for each ED well.

Figure 4.4 shows a graph of the sulphate concentrations measured using the Direct Well method against the average sulphate concentration measured using the LMM method in round 3. Apart from a single exception, the sulphate concentration measured in round 3 using the Direct Well method also corresponds well with the measurements obtained using the LMM method (average of three bore holes).

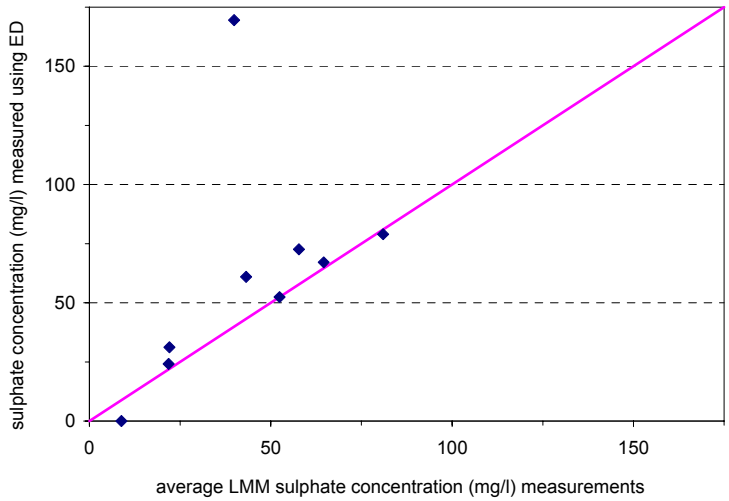

Figure 4.4 Sulphate concentrations measured in the upper screen of the Direct Wells (ED) compared with the concentrations measured in the upper screens placed using the temporary LMM bore hole method. Data for round 3, three LMM measurements for each ED well.

The nitrate and sulphate measured with the upper screen of the Direct Well during round 1 deviates from the measurements with comparable screens placed using temporary methods, but this difference is no longer visible in round 3.

Re B Manual versus mechanical drilling method

The sulphate concentrations measured at the deeper screens (about five metres below MLG) placed using the Van der Staay method are practically all lower than those measured with both temporary and permanent screens placed sonically (ED, EC and EU methods), see Figure 4.5. Except for one or two exceptions, the sulphate concentrations measured at the deeper screens placed using the EC method decrease still further in rounds 2 and 3, see Figure 4.6

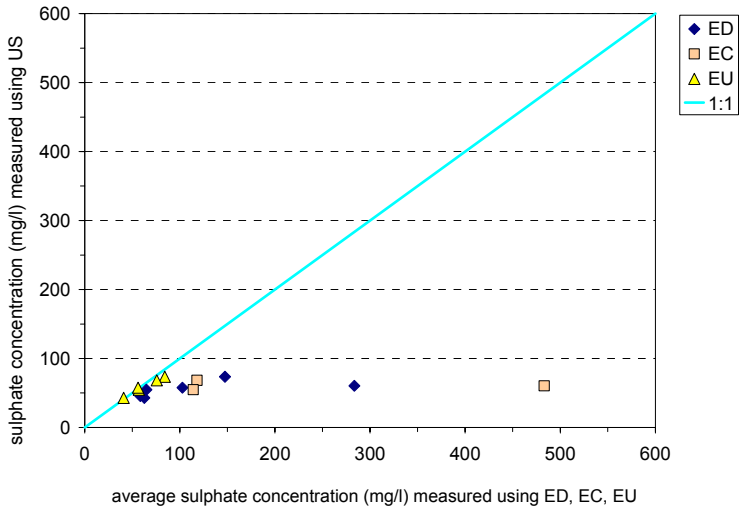

Figure 4.5 Sulphate concentrations measured at the deep screen placed using the Van der Staay method (US) compared with the concentrations measured at the deep screens placed using the SonicSampDrill, CMT (EC), Direct Well (ED) and Extending point (EU). Data for round 1.

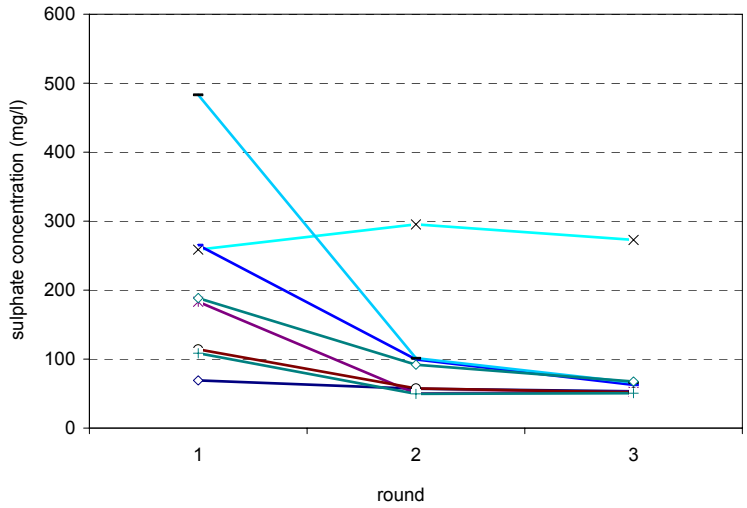

Figure 4.6 Sulphate concentrations measured at the deep CMT (EC) screens placed using the SonicSampDrill for three sampling rounds.

A decrease in the sulphate concentration is also visible at the deeper ED screens, but this is not as large, see Figure 4.7.

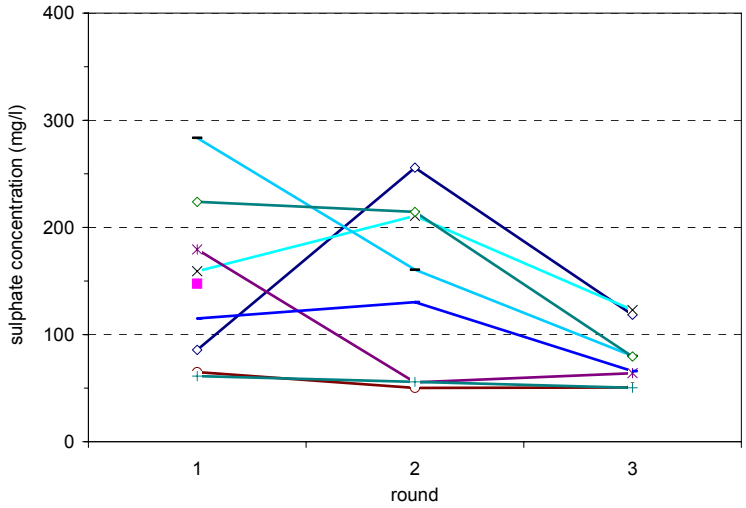

Figure 4.7 Sulphate concentrations measured in the deep Direct Well (ED) screens placed with the SonicSampDrill for three sampling rounds.

Differences in the measured water qualities are visible between the EC and ED methods in round 1 for the shallow and deep screens for both nitrate and sulphate, see Figure 4.8 and 4.9.

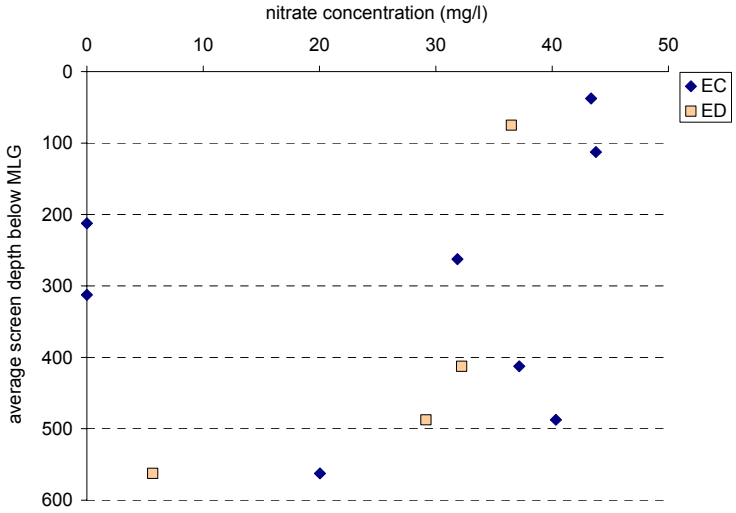

Figure 4.8 Nitrate concentrations measured at the Direct Well (ED) and CMT (EC) screens placed using the SonicSampDrill for the first sampling round at Maarheeze.

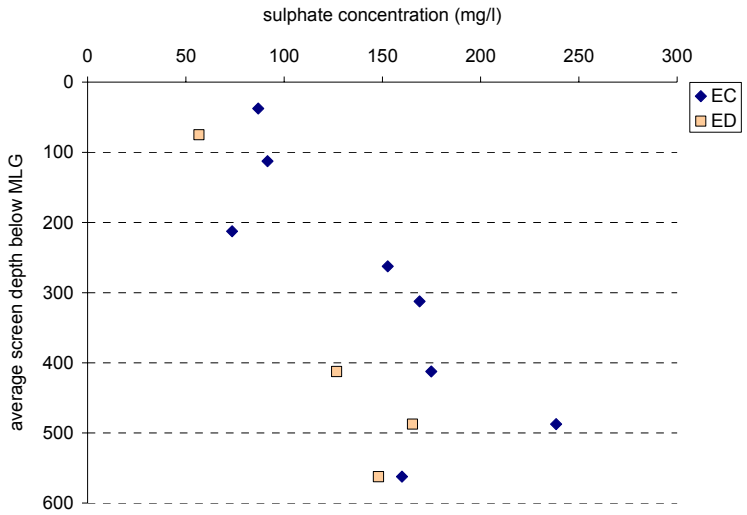

Figure 4.9 Sulphate concentrations measured at the Direct Well (ED) and CMT (EC) screens placed using the SonicSampDrill for the first sampling round at Maarheeze.

However, after a time the same measurements are obtained for the water quality with the two methods (EC and ED), both for the shallow and the deep screens, see Figure 4.10 and 4.11 for the nitrate and sulphate concentrations measured during round 3 at Maarheeze.

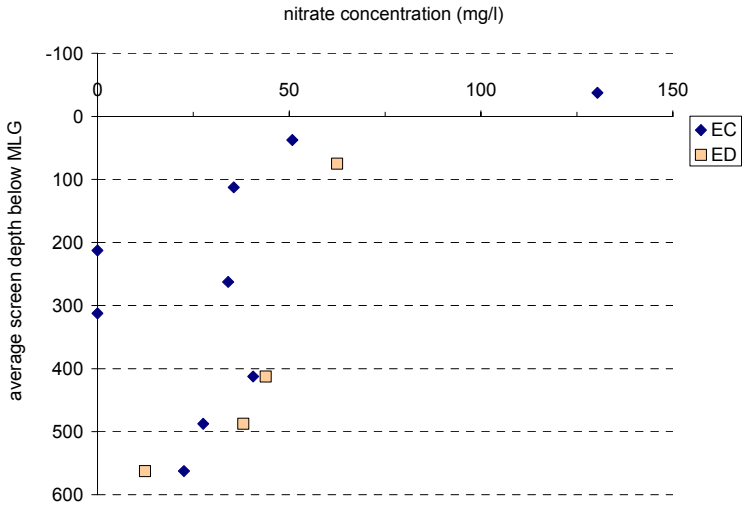

Figure 4.10 Nitrate concentrations measured at the Direct Well (ED) and CMT (EC) screens placed using the SonicSampDrill during the third sampling round at Maarheeze.

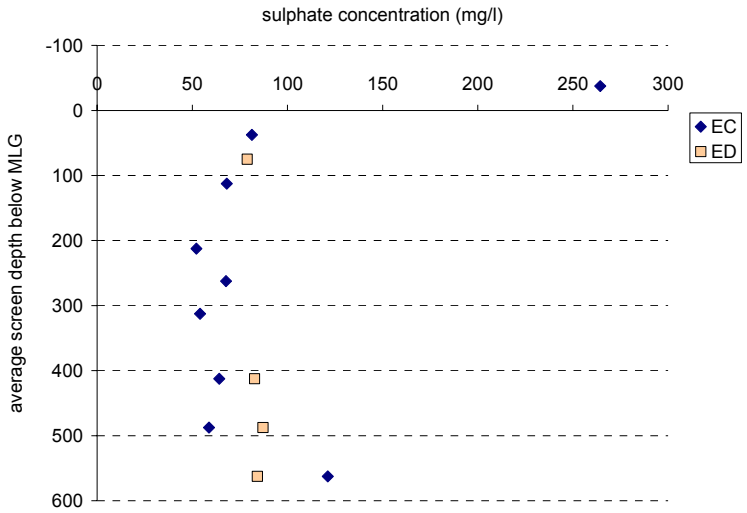

Figure 4.11 Sulphate concentrations measured at the Direct Well (ED) and CMT (EC) screens placed using the SonicSampDrill for the third sampling round at Maarheeze.

4.4 Discussion

4.4.1 Technical aspects of implementation

Because it is not always possible to reach the required depth manually, screens cannot be placed at every depth for sampling of the groundwater. The Van der Staay alternative was therefore dropped. The probability of reaching the required depth of five metres below the groundwater table was too low (50% during the study).

Screens can always be placed at the required depths with the mechanical methods, although sampling of the groundwater is not always successful. This may be due to the fact that the screens are located in layers that are not very permeable or that they silt up rapidly due to the presence of fine material. The Sonic with extending point (UPM) method guarantees that water samples can always be obtained. If no water is pumped up, it is relatively easy to drill further and try again. In addition, no equipment is left in the soil and the method does not influence the situation because the farmer does not have to adapt his activities as he might do in the case of permanent wells. In this sense, the UPM is comparable with the LMM method.

Apart from the fact that the UPM still has to be further optimized, the combination of drilling and direct sampling is highly disadvantageous. Drilling and sampling are two different disciplines each requiring precision of a different kind and therefore the deployment of employees with different skills. Furthermore, the Sonic cannot be deployed efficiently because it is not being used while samples are being taken. This could be solved by using more UPMs, and separate teams for drilling and sampling. After the tube has been pulled up (screen is released) the drilling team moves on to drill elsewhere and the sampling team can get started. Practical problems may arise here if the Sonic has to be put back to pull the tube out of the soil again (correct positioning). Moreover, at least three employees would be required for this approach (two for drilling, one for the sampling), making this method very expensive.

For the placing of permanent screens, the Sonic with CMT method is preferable to the Direct Wells method because with the Sonic method seven screens can be placed at the same time after a single drilling. Sampling using these screens (with or without mixing) yields a more reliable picture of the average groundwater quality of the upper five metres of the groundwater than using four screens, as is the case with the Direct Wells. The nitrate profiles measured sometimes show an extremely varied development between one and five metres below the groundwater table (see chapter 3). Furthermore, the likelihood of at least some of the screens yielding water is greater with seven screens than with four. An alternative would be to install seven Direct Wells, but this would entail drilling seven bore holes and the installation of the well finish device would be more laborious. The configuration of the CMT above ground practically excludes any mistakes with screen depths; the further optimization of the whole implementation is possible and should be realized.

The loss of wells must be taken into account in the case of the permanent wells. During the study, it became apparent that, despite the subsoil finishing of the wells, one in 16 was lost within six months due to activities in the soil. It is known that this will, at least, increase to three in 16 wells (almost 20%) within 1.5 years of installation. What is more, changes in ownership of the plots on which the wells are located and/or changes in the land usage in the medium term must also be taken into account. Such changes might mean that it is no longer possible to sample the groundwater from certain wells or they may become less suitable for the intended objective.

If the age of the water is also relevant or, for other reasons, sampling of the groundwater has to be carried out using a submersible pump, the types of permanent wells now installed may not be suitable. Further investigation is therefore required with regard to these points.

4.4.2 Water quality aspects

The cause of the lower nitrate concentrations and the higher sulphate concentrations measured at the upper screen samples of the Direct Wells (ED) method compared with the concentrations in comparable screens placed using the temporary methods in the first sampling round is not immediately obvious. The difference is no longer visible in round 3. In this latter round the only measurements available are measurements taken using the LMM method (RL); there are none available for the Van der Staay (US) or Extending point (EU) methods. However, the RL measurements from the first round also deviate markedly from the ED measurements. The RL and US methods are both manual methods, but this cannot be the explanation since the EU screens were placed with the Sonic Drill, as were the ED screens.

The sonic drilling could, however, cause the mobilization of sulphate if one looks at the results of the measurements taken at the deeper screens. The effect is greater for the CMT (EC) than for the ED methods. This could perhaps be caused by the larger diameter of the drill pipe used in the EC method. Given that the same drill pipes are used for the EU method as for the ED method, the effect there should be the same, but only measurements from the first round are available for this method. The US method does not affect the results, or at least, it affects them less than the methods with the screens placed sonically.

4.5 Conclusions

The manual drilling and placing of screens at five metres below the groundwater table is not a good option because it is often impossible to reach the required depth.

The manual placing of screens results in less impact on the water quality than the methods in which screens were placed using the SonicSampDrill.

If more than one sample is to be taken of the groundwater at five metres below the groundwater table, it is advisable to install permanent wells.

The water quality is affected in permanent wells installed using the SonicSampDrill and tests will have to be carried out to examine whether the results are representative of the water quality.

The CMT method is the most reliable method because seven screens can be placed at once. Any confusion regarding screen depth is excluded and at 30% falling-out, there are still sufficient screens for sampling.

With permanently-installed wells within plots, the possibility of a high percentage (10-20%) of replacements annually as a result of irregular deep tillage and/or changes in ownership or usage must be taken into account.

The tested methods are not appropriate for groundwater sampling for the determination of the age of the groundwater or other analyses for which a degassing-free sampling is needed.

The pros and cons of the sub surface diversion of sampling tubing to the side of the plot are still not sufficiently clear. In order to reach a decision, a comparison of the sampling at the plot edges and directly above the wells will have to be carried out and the experience of others (abroad) will also have to be looked at.

5. Potential denitrification

5.1 Introduction

The nitrate concentrations in the groundwater decrease with depth. Various factors may, however, play a role in this decrease (see section 1.1.5). Denitrification, that is, the conversion of nitrate to nitrogen gas (see Appendix 1), may be a significant cause. By taking samples from the sedimentary deposits over the entire depth in which we are interested from the standpoint of the groundwater quality changes, we can test whether denitrification occurs in these sedimentary deposits if nitrate is added. This is termed potential denitrification. If denitrification does not occur, this could mean that substrate needed for the conversion of nitrate into nitrogen gas (reductors) are not present. It may also mean that there is no microbial activity in the subsoil, for example, due to the absence of this type of microbes or the lack of activity of those that are present. If this is the case, other causes must be sought for the decrease in nitrate concentrations.

The potential denitrification (a biological indicator for denitrification, see Appendix 1) was determined by Alterra. Alterra also carried out an extraction of the soil samples using a calcium chloride solution. A number of compounds in the extract were determined in order to try to identify possible causes of potential denitrification, or its absence.

The possible presence of reductors in the subsoil was looked at in another sub-study (see Chapter 6).

5.2 Set-up of the study

5.2.1 Sampling and pretreatment

Soil samples were taken by the RIVM. A description of the method is given in section 3.2.2 and Appendix 4.

The samples for which the potential denitrification was determined, were selected by TNO. For analyses for organic carbon fractions (C) TNO took 1 cm above and 1 cm below a specific depth. More soil was required for the determination of the potential denitrification. Because there was only a single drilling core available each time, the layer of 11 cm above and the layer of 11 cm below the layer sampled by TNO was taken. For example, a depth of 500 cm below surface level means that TNO analysed the layer 499-501 cm for C fractions and Alterra, the layers 488-499 and 501-512 cm for potential denitrification. The whole layer is shown in section 5.3, but a layer of 2 cm is therefore missing from the measurements in the middle of the soil column. The samples supplied by TNO to Alterra were split into two parts. The water content was determined and a $CaCl_2$ extraction was carried out to determine other compounds, including N, on one part of the samples. The remaining part of the soil samples was stored in a refrigerated cell and the potential denitrification was determined from a series of 40 samples.

5.2.2 Determination of the potential denitrification

The potential denitrification is determined by means of anaerobic incubation at 20 ^{o}C in a nitrate-enriched medium using the acetylene inhibition technique (Velthof and Oenema, 1995; Velthof, 2003). Acetylene inhibits the conversion of nitrous oxide (N_2O) to N_2, as a result of which the easily measurable N_2O is the only end product of denitrification (Yoshinari et al., 1977). The N_2O is determined with a Bruel and Kjaer photoacoustic gas monitor (Velthof and Oenema, 1995) after 1, 2 and 3 days. The method in which the potential denitrification is determined by means of N_2O production with acetylene inhibition corresponds with the method in which the potential denitrification is determined by measuring the decrease in nitrate concentration in the soil during incubation (Zwart, 2003). The detection limit of the method using acetylene inhibition is lower than the method based on nitrate decrease. Furthermore, the acetylene inhibition method is faster, cheaper and can be carried out on a smaller soil sample. One uncertainty with the use of the acetylene inhibition method is the effect of acetylene on *Thiobacillus denitrificans*, a bacterium that is able to use pyrite as energy source for denitrification. A study by Dalsgaard and Bak (1992) with a specific strain of *Thiobacillus denitrificans* showed that acetylene did not inhibit the reduction of N_2O. It is not clear whether this occurs frequently with *Thiobacillus denitrificans*.

All the determinations were carried out at the Soil Quality laboratory at Wageningen UR.

The determination of the potential denitrification was carried out in a period of five days. On day 1 fresh soil was weighed out into 500-ml-incubation bottles, corresponding with 100 grams of dry soil. The water content was determined by means of drying at 105 ^{o}C. The bottles with soil were subsequently incubated for one day at 20 ^{o}C. This was carried out to raise the activity of the bacteria, given that the samples had been stored in a refrigerated cell. On day 2 the soil samples were wet with water and subsequently 5 ml of a KNO_3 solution was added (0.086 *M* NO_3), such that the nitrate content of the soil solution amounted to approximately 1.2 g l^{-1} (more than 300 mg N per kg soil). The solution was well mixed through the soil. All the soil samples were saturated with water and incubated as 'slurry' (the final water content amounted to 0.20-0.35 g water per gram of wet soil). The bottles were then flushed with N_2 to create anaerobic conditions. The bottles were sealed with a septum cap and 25 ml of acetylene (C_2H_2) was added, so that the C_2H_2 concentration in the headspace amounted to approximately 5% (v/v).

On days 3, 4 and 5 the N_2O concentration of the headspace of the bottles was measured. The average measuring time for each sample was 3.5 minutes and after each sample the gas analyser was flushed with N_2. After the last measurement on day 5, the volume of the headspace was determined by the difference in weight between the bottle with soil only and the bottle with soil filled with water. The N_2O concentration measured in the headspace was corrected for the N_2O in the supply and discharge tubes and the content of the gas analyser:

[1] $$N_2O_{cor} = (N_2O_m*(volume_{bottle} + volume_{analyser}) - N_2O_{analyser}* volume_{analyser})/volume_{bottle}$$

in which

N_2O_{cor} = the corrected N_2O concentration in the headspace of the bottle in µl l^{-1}

N_2O_m = the measured N_2O concentration in the headspace of the bottle in µl l^{-1}

$N_2O_{analyser}$ = the N_2O concentration of the air in the analyser that is blown into the headspace of the bottle (this is the N_2O concentration of the previous measurement) in µl l^{-1}

$volume_{bottle}$ = volume of the headspace of the bottle with soil in litres.
$volume_{analyser}$ = internal volume of the analyser and the volume of the supply and discharge tubes in litres (was 70 ml in this study)

The N_2O production in µg nitrogen per kg of soil per day is calculated from the increase in the corrected N_2O concentrations in the headspace between two points in time, the time between two measurements, the volume of the headspace and the amount of soil:

[2] N_2O production = $(N_2O_{t2} - N_2O_{t1})$ * $volume_{bottle}$ /$molar_{N2O}$ * molecular $weight_{N2O}$/soil/time

in which
N_2O production = the N_2O production in µg N kg^{-1} dry soil day^{-1}
N_2O_{t2} = the corrected N_2O concentration in the headspace of the bottle at point in time 2 in µl l^{-1}
N_2O_{t1} = the corrected N_2O concentration in the headspace of the bottle at point in time 1 in µl l^{-1}
$volume_{bottle}$ = volume of the headspace of the bottle with soil in litres.
$molar_{N2O}$ = the molar volume of N_2O in l mol^{-1} (1 mol = 22.4 l at 20 ^oC)
molecular $weight_{N2O}$ = the molecular weight of N_2O-N (28 g per mol N_2O as N)
soil = amount of dry soil in kg
time = time between the two measurements in days

The potential denitrification (µg kg^{-1} dry soil day^{-1} as N) is the maximum daily N_2O production measured in the three days. The potential denitrification differs sometimes during the three days but there is no clear pattern. There is therefore no indication that the potential denitrification increases in the period of three days, which would indicate adaptation of bacteria and increasing denitrification activity.

5.2.3 Soil analyses after $CaCl_2$ extraction of soil samples

Besides the potential denitrification analyses, other analyses were also carried out. To this end, the soil samples were dried at 40 ^oC, extracted for two hours at 20 ^oC with 0.01*M* $CaCl_2$ (ratio: 3 grams soil in 30 ml 0.01*M* $CaCl_2$ solution; Houba et al., 2000). The NO_3, NH_4, total N and soluble organic C (SOC) levels in the extracts were determined in accordance with the procedures described by Houba et al., 2000). The level of soluble organic N (SON) was calculated from the difference between the total N and inorganic N (NO_3 + NH_4). The pH of the extract was also determined.

The results of the analyses with $CaCl_2$ extraction were expressed by the laboratory in mg per kg of dry soil. However, the soil samples originated from layers that were saturated with water so that it was to be expected that water ran out of the samples when they were taken, and during transportation and pretreatment. This leads to underestimates of the actual levels if the levels are expressed as weights per kg of dry soil. Given that the soil moisture contents are known, the concentrations can be converted into mg per litre of soil water. The data are therefore expressed in this way.

5.3 Results and discussion

5.3.1 General

The results of measurements taken in the topsoil by Assink et al. (2005), using the same method, at two of the farms are shown in Table 5.1 to enable the interpretation of the potential denitrification of the samples from the subsoil. The potential denitrification decreases greatly with depth. This is due to the distribution of biodegradable organic matter. New and easily-degraded organic matter is added at the top of the soil profile in the form of manure and crop residues.

Table 5.1 Potential denitrification in μg kg^{-1} soil day^{-1} (as N) in the topsoil at various plots on the farms at Maarheeze and Nieuweroord (Assink et al., 2005).

Soil layer (cm)	Maarheeze					Nieuweroord	
	12 grass	1AB grass	11 maize	13 maize	7B maize	p2 grass	p3 grass
0-20	60886	28618	12632	35897	20395	40763	47124
20-40	20334	7618	139	6383	17931	16991	12344
40-60	2171	1708	125	133	9823	16443	3999
60-80	65	24	18	180	75272	2752	161
80-100	27	22	16	26	461	112	42

5.3.2 Nitrate concentration in the groundwater

Figure 5.1 shows the nitrate concentrations calculated from the $CaCl_2$ extraction results. These nitrate concentrations (referred to as 'soil moisture' in the figure) are compared with the nitrate concentration measured in the groundwater (referred to as 'groundwater'). It must, however, explicitly be stated that this is a different methodology than the analyses of the groundwater by the RIVM. Firstly, it concerns an extraction with a salt solution, as a result of which cations (such as ammonium) are extracted from the adsorption complex. More organic carbon and nitrogen could also go into solution because of this. The effect of this extraction on nitrate, an anion, may be limited. Secondly, the detection limit is much higher and the accuracy much lower with the analyses using soil extraction than those using direct analyses of the groundwater. The results of the direct analyses of the groundwater will be compared with those of the soil extractions.

The results from the nitrate concentrations calculated from the extraction usually correspond well with those from the measurements in the groundwater. Most profiles show a considerable variation in nitrate concentration with depth. If denitrification is the only process influencing the nitrate concentration in the subsoil, the nitrate concentration decreases with depth. The varying nitrate concentrations with depth indicate that other factors, besides denitrification, play a role. These other factors may include differences in fertilization and weather between different years (years with a lot of or little leaching), and the hydrology (horizontal transport of nitrate). Given that the nitrogen added to agricultural land has been reduced during recent years because of the manure policy, the possibility that the nitrate concentration in the recent groundwater is lower than that in the older groundwater cannot be excluded, see for example Figure 3.12.

Based on the nitrate profiles shown in Figure 5.1, we can conclude that it will be difficult to show that denitrification in the subsoil leads to the decrease in the nitrate concentration in the groundwater with this set of data. The following sections present the potential denitrification results and relate them to the development of nitrate concentration with depth.

5.3.3 Potential denitrification

Tables 5.2 through 5.5 contain the results of the measurements of potential denitrification. Appendix 8 gives all the results of the measurements for each location. The highest potential denitrification is found in the Spankeren profiles (Table 5.3) and the Maarheeze profile, 57E0338. The potential denitrification in peat layers is usually high (profiles 33G0414, 570E0335 and 570E0338). Potential denitrification can, however, not be demonstrated in most soil layers. Of the 140 samples, 111 have a potential denitrification of < 5 μg kg^{-1} day^{-1} as N, 18 samples have a potential denitrification of 5-100 μg kg^{-1} day^{-1} and 11 samples had a potential denitrification of >100 μg kg^{-1} day^{-1} as N. The highest potential denitrification (4013 μg kg^{-1} day^{-1} as N in a peat layer in profile 33G0414) is much lower than the potential denitrification measured in the topsoil (Table 5.1). These results indicate clearly that in most soil layers there is no energy source for denitrifying bacteria (biodegradable organic matter or inorganic energy sources such as pyrite) and/or that there are no active denitrifying bacteria present.

An indicative calculation was made to obtain an idea of how much nitrate can denitrify at a specific potential denitrification. To this end, use was made of the model concept of Heinen et al. (2005), in which the "actual" denitrification is calculated from the potential denitrification and reduction functions for temperature, nitrate concentration and anoxia. A layer of 10 cm with a potential denitrification of 5 μg kg^{-1} day^{-1} (as N) can denitrify about 0.6 kg NO_3-N per year (see footnote for assumptions made in these calculations[6]). If groundwater with a nitrate concentration of 100 mg l^{-1} as NO_3-N remains in this layer for one year, the concentration after one year is still 98 mg l^{-1} as NO_3-N. With a potential denitrification of 250 μg kg^{-1} day^{-1} as N all the nitrate present will denitrify in one year. With lower nitrate concentrations the denitrification will be lower. The potential denitrification in a soil layer will certainly have to be at least 50-100 μg kg^{-1} day^{-1} as N in order to lead to a marked decrease in the nitrate concentration.

A high potential denitrification activity was determined in layers containing no nitrate in profile 33G0414 from Spankeren (Appendix 8). Apparently the adaptation of bacteria to nitrate (as a result of which it takes a little while before denitrification starts) does not play a role in this profile. It is not clear whether this is generally applicable and conclusions can therefore not be drawn about the presence of an energy source in soil layers in which no potential denitrification can be determined.

[6] assumptions made (based on Heinen et al., 2005): temperature in the subsoil is 10 °C, the denitrification at 10 °C is equivalent to 50% of that at 20 °C. The denitrification at 100 mg l^{-1} NO_3-N is equivalent to 50% of that at the nitrate concentration during the determination of the potential denitrification (>300 mg l^{-1} as N). The bulk density is 1350 kg m^{-3} and the porosity 30%. It is assumed that the groundwater is anaerobic.

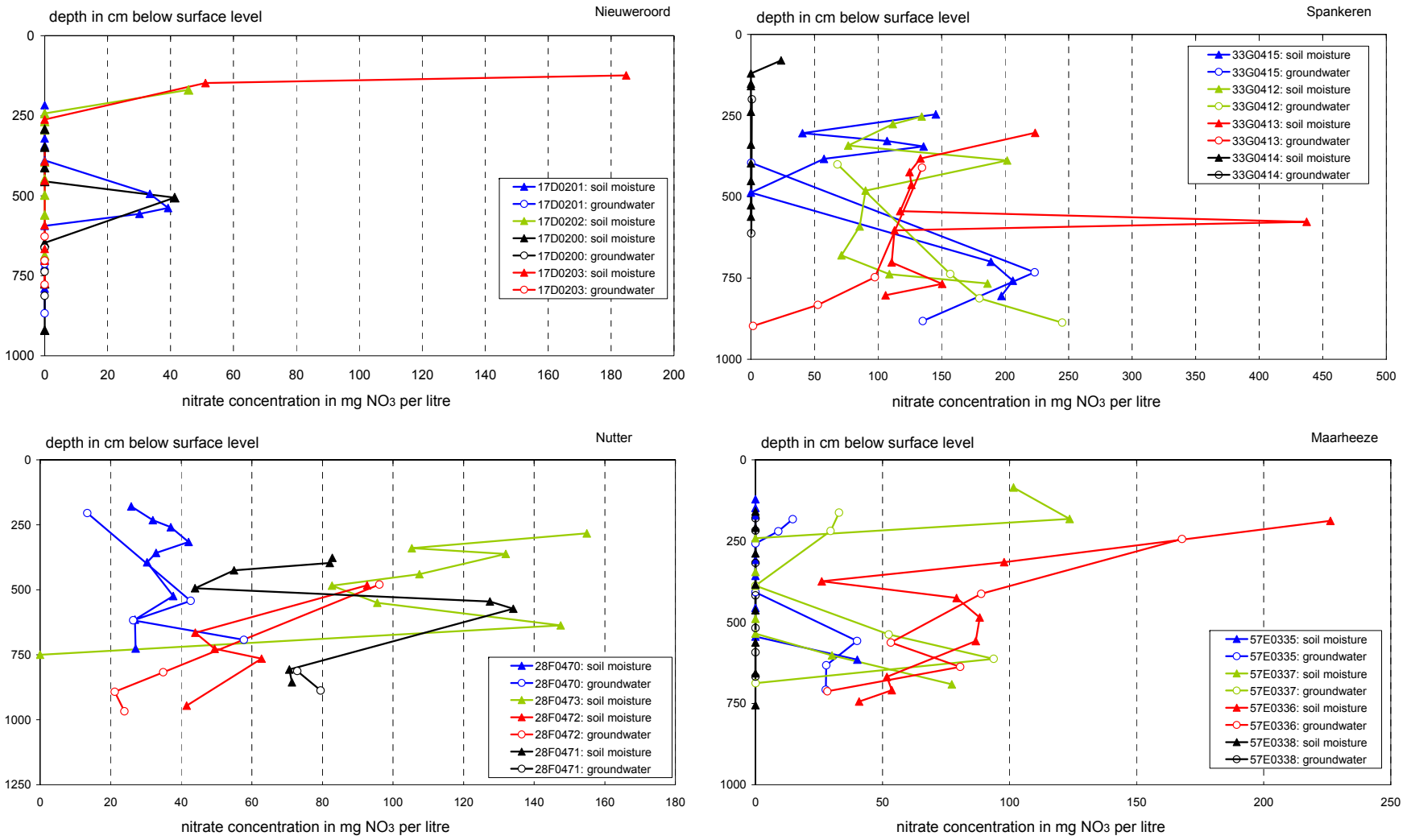

Figure 5.1. Nitrate concentrations in soil moisture (calculated from the 0.01M $CaCl_2$ extraction results) and in the groundwater (results from the second measuring round) on the x axis against the depth below the surface level on the y axis. Note the differences in the x axis (nitrate concentration) between the four diagrams of Figure 5.1.

Table 5.2 Potential denitrification (DNP) in the soil profiles for Nieuweroord.

17D0201		17D0202		17D0200		17D0203	
layer cm below surface level	DNP N µg/kg/day	layer cm below surface level	DNP N µg/kg/day	layer cm below surface level	DNP N µg/kg/day	layer cm below surface level	DNP N µg/kg/day
206-228	0	158-180	0	113-135	0	113-135	0
310-331	0	232-254	0	137-159	0	137-159	0
354-332	0	258-278	0	251-273	0	251-273	0
379-400	0	283-305	0	281-303	0	382-404	0
483-505	0	384-405	0	337-359	0	442-464	0
528-548	76	437-459	0	401-423	0	581-603	0
548-565	0	487-509	0	444-466	0	655-677	0
583-605	0	549-571	0	495-517	0	692-714	0
679-701	0	675-697	0	636-658	0	763-785	0
708-730	0			764-786	0		
779-801	0			909-931	0		

Table 5.3 Potential denitrification (DNP) in the soil profiles for Spankeren.

33G0415		33G0412		33G0413		33G0414	
layer cm below surface level	DNP N µg/kg/day	layer cm below surface level	DNP N µg/kg/day	layer cm below surface level	DNP N µg/kg/day	layer cm below surface level	DNP N µg/kg/day
235-257	5	242-264	0	292-314	0	69-91	14
293-315	118	265-287	0	371-393	3	109-131	16
317-339	2	331-353	0	413-435	0	141-163	0
334-356	80	377-399	1	452-474	0	148-170	0
372-394	9	470-492	562	533-555	15	227-249	621
476-498	117	580-602	0	566-588	852	328-350	1425
689-711	1	669-691	0	592-614	32	386-408	0
747-769	0	727-749	0	691-713	12	440-462	120
794-816	2	756-778	0	757-779	0	515-537	331
				792-814	36	550-572	4013

Table 5.4 Potential denitrification (DNP) in the soil profiles for Nutter.

28F0470		28F0473		28F0472		28F0471	
layer cm below surface level	DNP N µg/kg/day	layer cm below surface level	DNP N µg/kg/day	layer cm below surface level	DNP N µg/kg/day	layer cm below surface level	DNP N µg/kg/day
168-190	0	272-294	0	472-494	0	366-388	0
221-243	0	329-351	0	654-676	0	386-408	0
248-270	0	351-373	3	716-738	0	414-436	0
305-327	0	429-451	0	754-776	0	483-505	2
347-369	18	473-495	0	935-957	0	534-556	0
383-405	0	539-561	0			562-584	0
513-535	0	626-648	20			796-818	0
604-626	2	739-761	0			845-867	0
715-737	67						

Table 5.5 Potential denitrification (DNP) in the soil profiles for Maarheeze.

57E0335		57E0337		57E0336		57E0338	
layer cm below surface level	DNP N µg/kg/day	layer cm below surface level	DNP N µg/kg/day	layer cm below surface level	DNP N µg/kg/day	layer cm below surface level	DNP N µg/kg/day
110-132	6	74-96	0	177-199	0	148-170	113
137-159	0	171-193	0	304-326	0	198-220	284
160-182	0	230-252	1	363-385	0	277-299	88
237-259	0	334-356	0	414-436	0	373-395	51
297-319	45	376-398	0	474-496	0	452-474	1
346-368	0	478-500	0	547-569	0	551-573	0
445-467	0	524-546	0	657-679	0	646-668	1
533-555	0	591-613	1	698-720	0	744-766	0
604-626	0	680-702	0	733-755	0		

5.3.4 Relationship between potential denitrification and nitrate concentration in the groundwater

It is assumed that potential denitrification is an indicator for denitrification in the groundwater. If no other factors influence the nitrate concentration, the nitrate concentration in the groundwater above a soil layer with a significant potential denitrification is higher than the nitrate concentration in the groundwater below this soil layer. Figure 5.2 shows a graph of the potential denitrification against the difference in nitrate concentration between the layers above and below the layer for which the potential denitrification has been determined.

The figure shows that there is no relationship between the potential denitrification and the difference in nitrate concentration. The negative values indicate that the nitrate concentration sometimes increases with depth, as shown in Figure 5.1. As we already concluded when discussing Figure 5.1, it is not possible to show that denitrification in the subsoil leads to a decrease in the nitrate concentration in the groundwater for the soil profiles in this study.

5.3.5 Relationship between potential denitrification and soil properties

Figure 5.3 shows that there is no relationship between the amount of soluble organic carbon (C) and the potential denitrification, despite the fact that some soil layers contain relatively high levels of soluble organic C. The soluble organic C in the subsoil is apparently already degraded to the extent that the remaining part is very difficult for denitrifying bacteria to degrade. In the topsoil, on the other hand, the potential denitrification is related to the levels of soluble organic C, particularly in grassland (Velthof, 2003). Soluble organic C in the subsoil is therefore not an indicator for biodegradable organic matter and, consequently, not for the denitrifying capacity of the subsoil.

Denitrification can affect pH. Denitrification in which organic matter is used as energy source can lead to alkalization, see Appendix 1, equation [5]. Denitrification in which pyrite is fully oxidized can lead to acidification; see Appendix 1, equation [2] and [3]. In profile 17D0201 from Nieuweroord the pH of the only soil layer with a significant potential denitrification is higher than the other soil layers, see Appendix 8. This could indicate increased denitrification activity. This is, however, not visible in other profiles with soil layers with a significant potential denitrification. There are no strong decreases in pH visible that could point to pyrite oxidation, either. The pH in the soil is usually related to the type of sediments and the presence of carbonate. The development of pH with depth is therefore not an indicator for denitrification in the profiles examined.

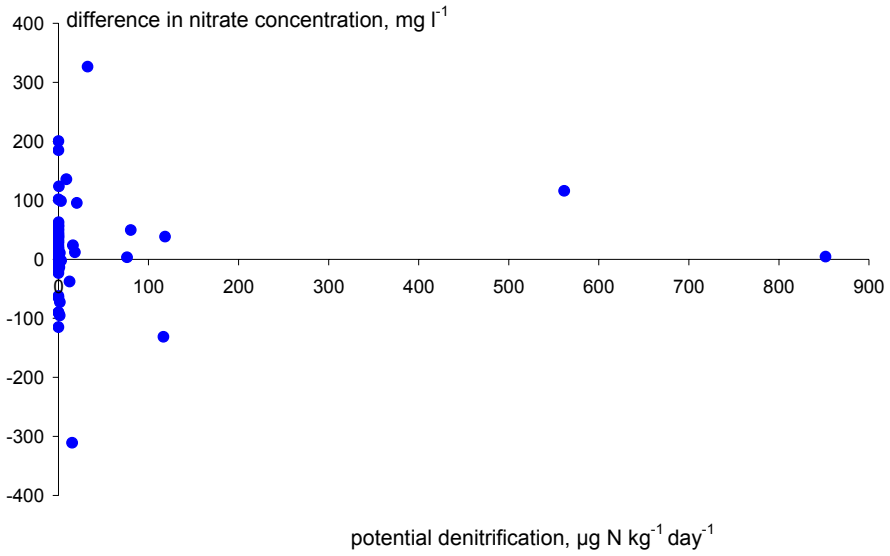

Figure 5.2 Relationship between the potential denitrification (x axis) and the difference in nitrate concentration between the layer above and the layer below the layer in which the potential denitrification has been determined (y axis). The figure includes only the layers in which nitrate was present in the layer above the layer in which the potential denitrification has been determined. Negative values mean that the nitrate concentration increases with depth.

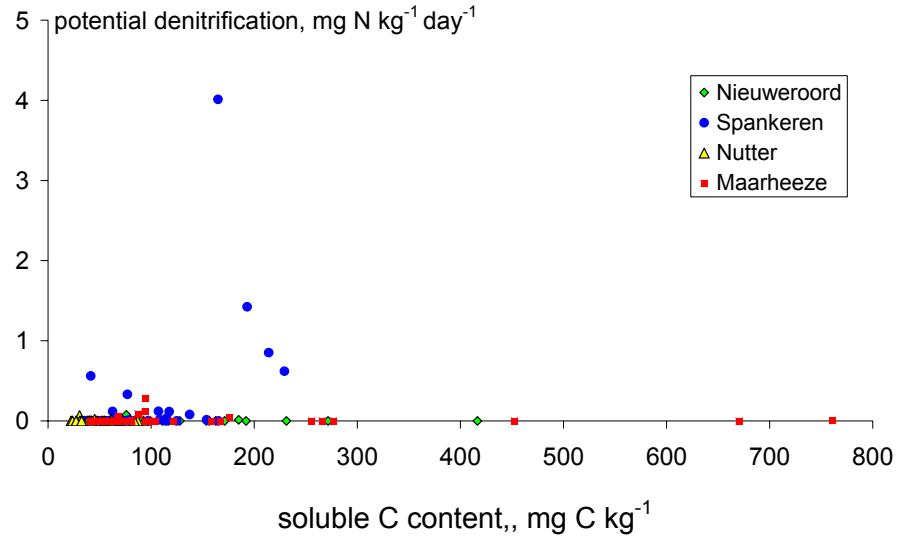

Figure 5.3. Relationship between the soluble carbon content (determined in 0.01M $CaCl_2$; x axis) and the potential denitrification (y axis).

5.4 Conclusions

Most of the soil profiles in this study show a considerable variation in nitrate concentration with depth. This indicates that factors other than denitrification, such as differences in fertilization and weather in different years, and the hydrology, determine the development of nitrate concentration. Because nitrate concentration does not decrease with depth, it is not possible to establish a clear relationship between potential denitrification and nitrate concentration in the groundwater.

Only a slight potential denitrification, if any, can be demonstrated in most of the soil layers in the profiles examined. This means that there is no energy source (such as biodegradable organic matter or pyrite) present in these soil layers for denitrifying bacteria and/or no active denitrifying bacteria present.

No relationship can be demonstrated between potential denitrification and the development of nitrate concentration with depth.

The level of soluble organic carbon (C) in the subsoil and the development of the acidity (pH) with depth are not related to potential denitrification in the profiles examined.

Based on the measurements of potential denitrification, it cannot be demonstrated that denitrification in the subsoil leads to a decrease in nitrate concentration in the groundwater for the soil profiles in this study. This is due to the large fluctuations of nitrate concentrations with depth. The low potential denitrification in many of the profiles does, however, indicate that denitrification will not lead to a marked decrease in the nitrate concentration of the groundwater in these profiles.

Based on this study, no conclusions can be drawn on the usefulness of potential denitrification as a method for demonstrating that denitrification leads to a decreasing nitrate concentration in groundwater with depth.

6. The presence of reactive components in the soil as a factor in the denitrification of nitrate

6.1 Introduction

Nitrate concentrations in groundwater decrease with depth, but various factors can be involved here (see section 1.1.5). Denitrification, the conversion of nitrate into nitrogen gas (see Appendix 1), can be a major cause. By taking samples from the soil across the entire range of depths where we are interested in groundwater quality changes we can ascertain whether substances required for the denitrification of nitrate are present there. If such substances, also known as 'reductors', are absent, or only present in small quantities, denitrification is unlikely to occur and other reasons for the decrease in nitrate levels need to be considered.

The presence of reductors, however, does not necessarily mean that denitrification will occur, as this also requires an active microbial population. This is examined in another study (see Chapter 5).

6.2 Design of the study

The study was carried out at the TNO laboratory, using soil samples taken by the RIVM (National Institute for Public Health and the Environment) from four farms participating in the National Programme for Monitoring the Effectiveness of Minerals Policy (LMM) at the 16 locations where permanent wells have been installed for groundwater sampling (see section 3.2.1). The method used to obtain the soil samples is described in section 3.2.2 and Appendix 4.

The physical and chemical characterization of the soil (an indicator of the presence of organic matter and pyrite, among other things) was carried out by TNO Built Environment and Geosciences. Before being analysed the samples were dried and sieved to 2mm. The gravel content was not determined separately.

For X-ray fluorescence (XRF) analysis, sub-samples of 10 grams were ground and then pressed with wax into tablets. These were then used to analyse main and trace elements on an ARL9400 with an Rh tube. Full matrix correction was used for main elements (SiO_2, TiO_2, Al_2O_3, Fe_2O_3, MnO, MgO, CaO, Na_2O, K_2O, P_2O_5, S) , and the Compton-scatter method for trace elements. The XRF was calibrated using approximately 100 certified geological reference samples. Three reference samples were added to each batch of 50 analyses to determine the precision (0.5-1% relative standard deviation) and accuracy (1-5% relative standard deviation).

The contents of organic matter and carbonate were determined by thermogravimetric analysis using a LECO TGA 601. From each sample a sub-sample of approximately 4 grams was taken and placed in a ceramic cup. Analysis comprised automatically measuring the weight loss from a sample when continuously raising the temperature by 1ºC per minute. The weight

loss was measured every 2 minutes using this TGA technique (20 samples per run). When this was complete, temperature profiles were calculated, averaging five measurements in each case. Finally the weight loss in the temperature range 105-350ºC (unstable organic matter), 350-550ºC (stable organic matter), 550-620ºC (siderite, $FeCO_3$ and water from clays) and 620-800ºC (Ca-carbonate) was calculated.

The total carbon, organic carbon and sulphur were measured using a LECO SC DR 134 elementary analyser (CS). For this purpose approximately 0.2 grams of dried sample was placed in an oven in an oxygen atmosphere at 1450ºC. This oxidizes and breaks down all the organic and inorganic carbon to CO_2. To analyse the amount of organic carbon, carbonate was first removed using 1N HCl: 1-2 ml HCl was carefully dripped onto the sample on a hot plate (80ºC) until the reaction visibly ceased. Reduced sulphur compounds and sulphates decompose to form SO_2. The concentration of gas escaping was analysed using an infrared cell. Calibration was carried out using precisely weighed quantities of pure $CaCO_3$ and Ag_2S. The inorganic carbon content (carbonate-C) can be calculated by deducting the organic carbon content from the total carbon content.

As the carbon content of a large proportion of the samples was around or below the detection limit of the LECO CS analyzer, the carbon content of a number of samples was also ascertained using a Carlo Erba NA 1500 CNS analyzer. For this analysis the sample weight ranged from 10 to 30 mg, depending on the nature of the sample and the expected content. As a result of the low weight of these samples they had to be ground and homogenized in a Herzog grinder. Using a sample changer, the dried samples, some pre-treated with HCL, were placed in the combustion tube, where combustion took place in the presence of oxygen and the catalysts chromium oxide (Cr_2O_3) and silvered cobalt oxide ($AgCo_3O_4$). The combustion gases CO_2, N_2, N_xO_y, H_2O and the remaining O_2 elute through a heated quartz tube filled with Cu wire, where all the oxides of nitrogen are reduced to N_2. Water was absorbed on magnesium perchlorate. The N_2 and CO_2 were then separated on a Hayesep Q column and detected with the aid of a Hot Wire Detector (HWD).

Finally, the ground samples that had been analysed using the Carlo Erba were measured at higher weights on the LECO SC DR134.

Particle size analysis was carried out using a Malvern 2000 Mastersizer. This technique is based on the correlation between the scatter angle of a laser beam and particle size. Approximately 5 grams of sample is placed in a ultrasonic bath, which is connected to the measuring cell placed in front of the laser. The suspended sample is pumped through the cell for 5 minutes. The scattered light and the straight beam fall on a lens, which distributes the light over the detector. The lens causes Fourier transformation of the various light rays, forming a diffraction pattern in the focal plane of the lens. In the focal plane is a detector with 52 concentric sectors that catches the scattered light. The particle size distribution can then be calculated based on the distribution, using the Fraunhofer Approximation.

In a Pollut-Eval analysis approximately 80 milligrams of sediment is heated to 650ºC in an inert atmosphere (programmed pyrolysis). The temperature is set to rise by 5ºC per minute after the oven has been kept at 105ºC for 5 minutes. The hydrocarbons released are measured using a Flame Ionization Detector (FID). The CO and CO_2 released during the heating process are measured constantly using an infrared cell. A description of the method is found in Appendix 6.

The geochemical parameters were determined using XRF, TGA, CS and Pollut-Eval. Some of these can be used as a direct measure of reactivity; others have to be calculated. Table 6.1 gives an overview of the parameters relevant to this report and how they were determined. The formulae for reactive iron ($Fe_{reactive}$) and reactive (degradable) organic carbon (Q2/(Q2+Q3) can be found in Appendices 5 and 6.

Table 6.1 Overview of relevant parameters and method of determination.

Parameter	Method of determination	Notes
SiO_2 (%)	XRF	Measure of sand content
Al_2O_3 (%)	XRF	Measure of clay/lutum
D50	Malvern	Measure of lutum/clay
Particle size distribution	Malvern	
Organic matter (%)	TGA	Measure of reactivity of organic matter
Total organic matter (%)	CS after decalcification	Presence of organic matter
Carbonate (%)	TGA, CS	
Siderite (%)	TGA	Weight loss 550-620ºC
S_{total} (%)	CS, XRF	Measure of pyrite content
$Fe_{reactive}$ (%)	Fe_2O_3 (XRF) adjusted for Fe in clay using Fe_2O_3 - Al_2O_3(XRF)/4, then converted to % Fe[1]	
$Fe_{reactive\ non\text{-}pyrite}$ (%)	Calculated from $Fe_{reactive}$ and S_{total}[2]	Measure of iron present in iron hydroxides, siderite or glauconite
(Q2/(Q2+Q3)	Pollut-Eval	Possible measure of reactivity of soil organic matter

[1] See Huisman and Kiden (1998) and Huisman (1998).

6.3 Results

6.3.1 Introduction

This section describes the geological and geochemical properties of the sediment samples. Wherever possible it is described for each LMM farm or each group of four bores. If there are major differences between the four drillings these will be mentioned. Appendix 9 gives an overview of the main results of the chemical and physical measurements for each location (drilling).

6.3.2 Nieuweroord, Drenthe (map sheet 17D)

The drill cores ran from 100-200 cm below ground level to 600-800 cm below surface level. The formation drilled into is the Gieten Member of the Drenthe Formation. At the base of the drilling 10-30 cm of the Delwijnen Member of the Boxtel Formation was drilled into in some cases. The texture is predominantly loam, with sand intervals in some drillings. The material is often slightly gravelly. The Delwijnen Member is sand throughout. The upper layer of the Gieten Member is olive green and slightly humic; the lower layer is brown and very humic.

The particle size (50 percentile) in the 17D drillings ranges from 130 to 200 µm, with an average of 175 µm (Figure 6.1). Interestingly, there was no difference in particle size between the sandy and the more clayey samples (Al_2O_3 percentages > 6%). Compared with the other drillings, the sediments in the 17D drillings have a limited range of particle sizes. The sediments consist almost entirely of quartz and an increasing percentage of clays in the more aluminium-rich samples (with SiO_2 percentages very constant at around 90%: Figure 6.2).

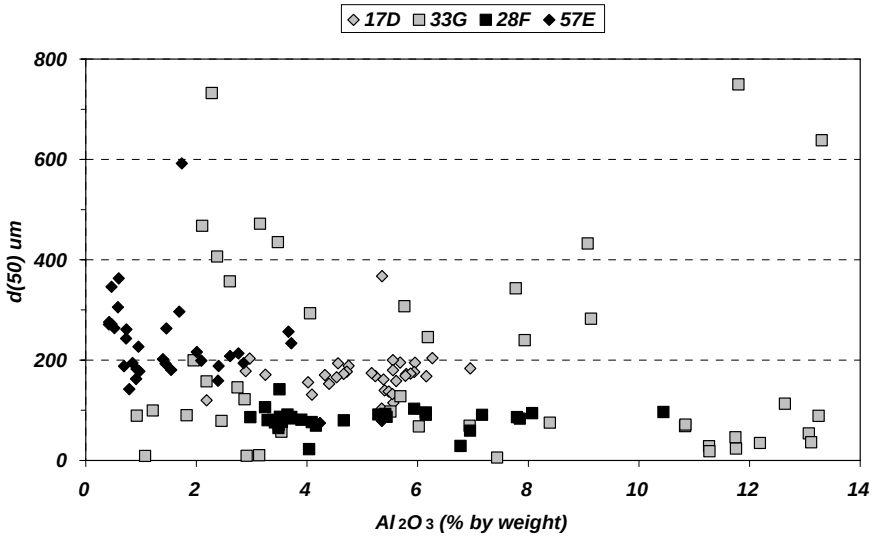

Figure 6.1 Particle size variation with Al_2O_3 content in the drillings examined shows that there are hardly any clays at these locations on the four farms; 17D = Nieuweroord, 33G = Spankeren, 28F = Nutter, 57E = Maarheeze.

The sulphur content (S) is very low, except for two or three samples which contained 0.2-0.3% S. Pyrite does not therefore play a major role in denitrification capacity at these locations. The samples are also carbonate-free. If the iron content (Fe) is adjusted for reactive Fe, there is no reactive Fe present, with the exception of one sample from drilling 17D0200, which contained 7.6% reactive Fe.

A total of 10 samples had an organic carbon content (TOC) above the detection limit, ranging from 0.1 to 0.60% by weight. The higher values were found mainly at the base of the drillings and in the clayey samples (> 6% Al_2O_3).

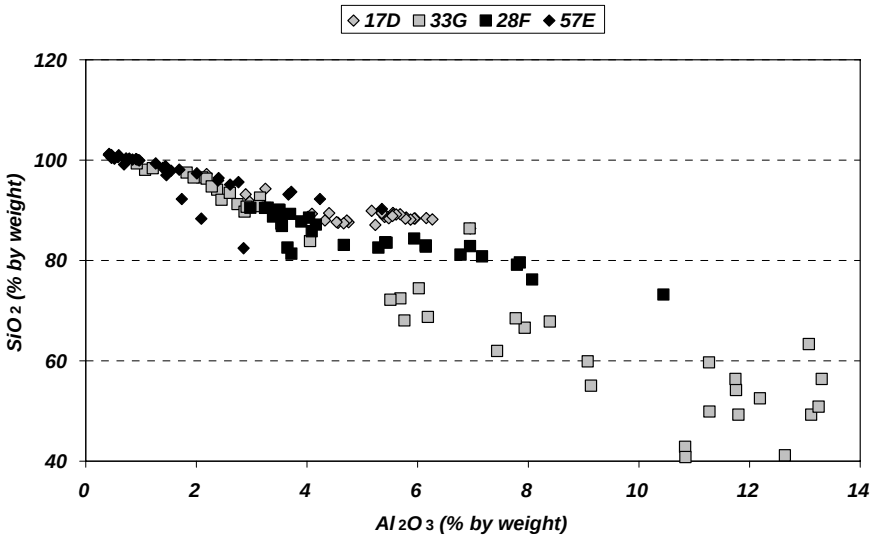

Figure 6.2 The sediments from drillings 17D and 57E consist almost entirely of quartz (SiO_2 percentages > 85%) and those from drillings 33G and 28F also contain clays and loam in addition to the quartz sands (the SiO_2 percentage of Dutch clays is approximately 50%); 17D = Nieuweroord, 33G = Spankeren, 28F = Nutter, 57E = Maarheeze.

6.3.3 Nutter, Overijssel (map sheet 28F)

The drill cores started at depths of 40-470 cm below surface level. The base of the drillings is between 800 and 1000 cm below surface level. The sampled material is from the moraine deposits of the Dongen Formation, apart from shallow material (<60 cm below surface level) which comes from the Boxtel or Drenthe Formations. The texture is predominantly extremely fine sand, sometimes with a 10-20 cm layer of loam or clay. Drilling 28F0473 is predominantly loam instead of sand. The colour is usually olive green, with regular shallower orange patches. Most of the samples contain a little glauconite, but some have only a trace of this mineral whereas a few contain a lot.

The particle size (50 percentile) ranges from 20 to 100 µm, with an average of 80 µm (Figure 6.1). The 50 percentile of the particle size up to 6% Al_2O_3 displays hardly any variation. The SiO_2 content at 4% Al_2O_3 is around 90%, and at higher Al_2O_3 values (6% and over) around 80% (see Figure 6.2). Interestingly, the XRF analysis revealed high contents of K_2O and reactive Fe in the samples from Nutter (28F, in Figs. 6.3 and 6.4), caused by the presence of glauconite.

The sulphur content was below 0.02%, except for the two deepest samples from drilling 28F0473, which contained 0.25 and 0.6% S. Pyrite does not therefore play any role in denitrification capacity at these locations, except for the base of drilling 28F0473. There is little or no carbonate in the soil: CaO is below 0.5%, and the TGA did not show any weight loss between 650 and 800ºC. The content of reactive Fe is high, at 0.75-4%, and this is not pyrite Fe. Reactive Fe is most likely to occur in the glauconite, then perhaps in iron oxide, but we cannot rule this out on the basis of the current data. Siderite ($FeCO_3$) is almost certainly not present, as no weight loss was found in the TGA between 550 and 620ºC.

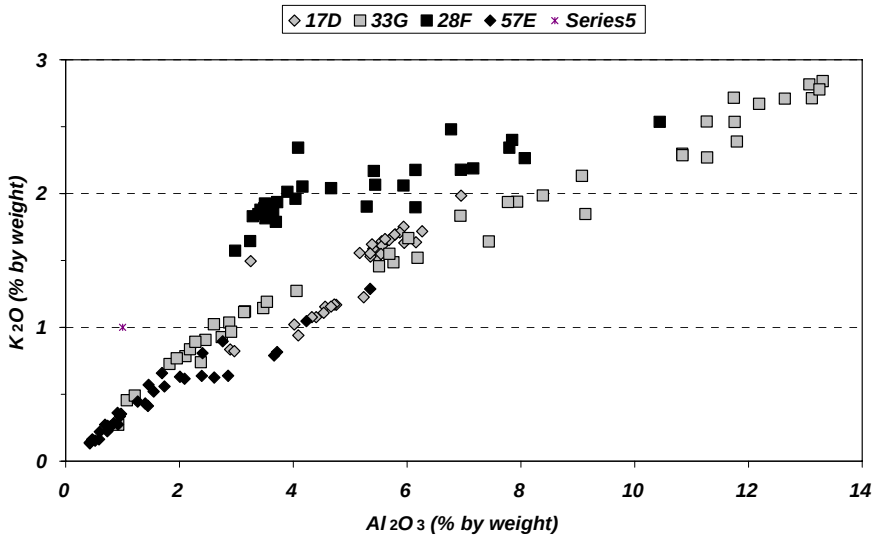

Figure 6.3 The sands and loams in drillings 28F have a much higher K_2O content than in the other drillings. At approximately 3% Al_2O_3 the K_2O/Al_2O_3 ratio in the sediments of drillings 33G changes; 17D = Nieuweroord, 33G = Spankeren, 28F = Nutter, 57E = Maarheeze.

The organic carbon content is extremely low, with only four samples having a level above the detection limit of 0.1% by weight.

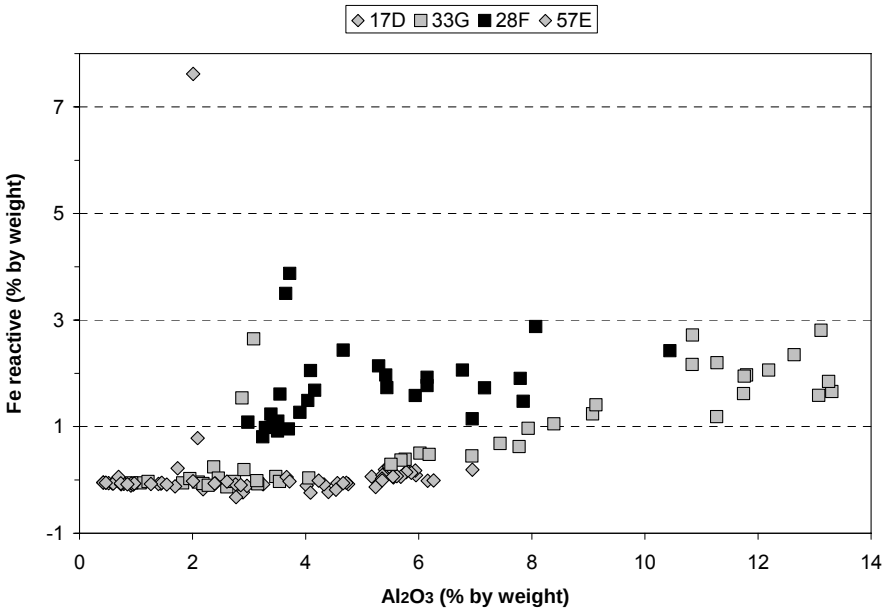

Figure 6.4 Plot of reactive Fe against Al_2O_3: only the samples from drillings 33G and 28F have a higher content than 0.5%; 17D = Nieuweroord, 33G = Spankeren, 28F = Nutter, 57E = Maarheeze.

6.3.4 Spankeren, Gelderland (map sheet 33G)

The drillings at this location are the most diverse in terms of geological and geochemical properties (Figs. 6.1, 6.3, 6.4 and 6.5). In three of the four drillings the first 200-300 cm was not sampled and the base of the drilling is slightly deeper than 800 cm below surface level. In one drilling (33G0414) the sample was taken from just below surface level to 585 cm below

surface level (see Figure 3.2). In the case of the three deeper drillings the top portion down to 350-500 cm below surface level is from the Boxtel Formation and the lower portion from the Kreftenheije Formation: the latter is frequently from the Zutphen Member. In the shallow drilling we find first the Boxtel Formation down to 29 cm below surface level, then the Wijchen Bed of the Kreftenheije Formation down to 154 cm below surface level, then another thin stratum from the Boxtel Formation down to 165 cm below surface level, and from 185 cm to the base of the drilling the Kreftenheije Formation again, with the Zutphen Member in the deepest part.

The colour of the soil in drillings 33G0412 and 33G0413 is mainly brown and the soil consists predominantly of sand or gravel with a few thin clay layers. Drillings 33G0415 is also predominantly sand, with varying brown colours. The Zutphen Member, from 474 to 729 cm below surface level, contains a highly stratified interval with loam, clay and dark brown detritus. The detritus is rich in organic matter. This layer was also densely sampled geochemically. The soil type of the Boxtel Formation is usually sand, but also frequently clay, loam or gravel. The soil type in the Kreftenheije Formation is sand (or gravel) except in the case of the Wijchen Bed or Zutphen Member, as with drilling 33G0415: in these deposits the soil type is diverse.

The shallow drilling 33G0414, which does not contain much of the Boxtel Formation, consists of brown clay or loam down to 61 cm below surface level, then light yellowish brown sand down to 165 cm below surface level; from 185 to 505 cm below surface level greenish grey loam or clay is found (a portion was not sampled); below this is a 36 cm interval of light grey sand, and the last 45 cm consists of dark brown peat.

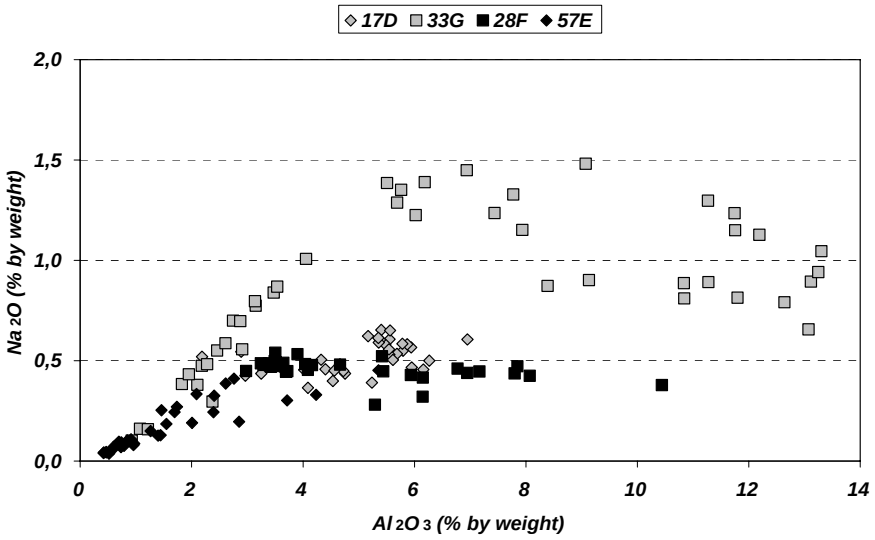

Figure 6.5 The sediments in drillings 33G have a much higher Na_2O content than those from the other drillings. The Al_2O_3 trends are the same, however; 17D = Nieuweroord, 33G = Spankeren, 28F = Nutter, 57E = Maarheeze.

The particle size (50 percentile) in the sand layers is highly variable, ranging from 70 to 700 µm (Figure 6.1). The sand fraction consists of quartz and sodium feldspars (high Na_2O content in sands with an Al_2O_3 content up to 4% by weight: Figure 6.5). The thin clay layer consist of silt and clay, and the amount of clay can vary widely with the same Al_2O_3 content

(Figure 6.6). The SiO_2 content is determined not only by the amount of silt and clay in a sample (Figure 6.2) but also by the amount of carbonate. The carbonate as it were dilutes the silicious minerals in the soil and is removed prior to particle size analysis. It is only present in the drillings on the Spankeren farm (33G); there is none in the other drillings. The Na_2O content is also particularly high in the clay layers. Lastly, the clays in 33G have a high K_2O content (Figure 6.3). Macroscopically no micas were found, so the high K_2O content of the clays can only be due to a high percentage of illite in them.

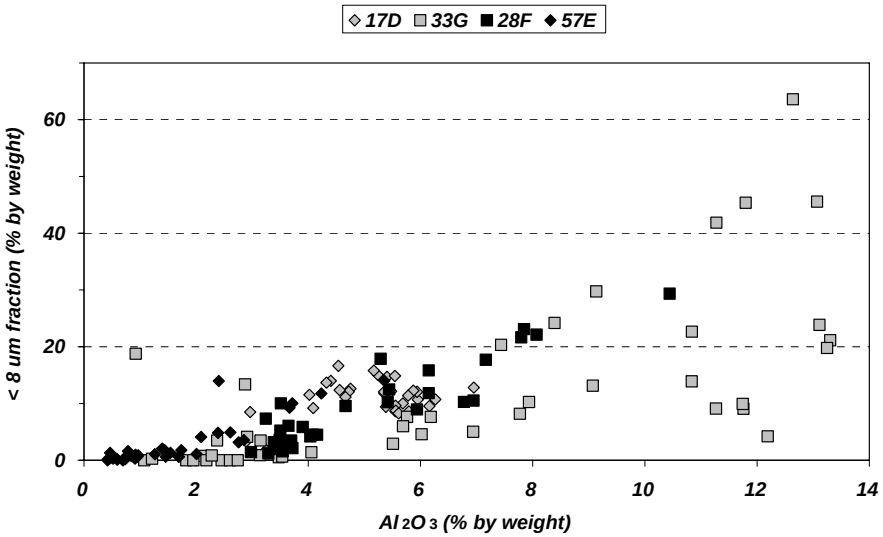

Figure 6.6 Variation in lutum content (<8 µm fraction) with aluminium. Samples with an aluminium content lower than 3% contain hardly any clays. Comparisons between the Laser Particle Sizer (LPS) and the pipette method indicate that an LPS fraction <8 µm corresponds to a <2 µm pipette fraction (Konert and Vandenberghe, 1997).
17D = Nieuweroord, 33G = Spankeren, 28F = Nutter, 57E = Maarheeze.

The soil is predominantly low in sulphur, which rules out the presence of pyrite. Major exceptions are an interval from 474 to 620 cm below surface level in drillling 33G0415 with detritic material, clay and loam, and from 250 cm below surface level to the base of drilling 33G0414, where 2% S occurs in the peat of the lowest 45 cm; most of this, however, is likely to be organic sulphur.

The soil is predominantly calciferous and the proportion of carbonate is generally 15-30%, but with higher values of up to 40%. The carbonate occurs in both Boxtel and Kreftenheije. Samples containing carbonate also have reactive iron (0.50-2% Fe), and this is not pyrite Fe. Reactive Fe is most likely to occur in siderite, then perhaps in iron oxide. The presence of siderite can also be deduced from the TGA profiles, as a weight loss was measured between 550 and 620ºC. Samples containing less than 7% Al_2O_3 have little or no reactive Fe (see Figure 6.4). A few samples do not conform to this general pattern.

The sands in these drillings are low in organic carbon, with only two samples having a content above the detection limit. In the clayey, peaty intervals (479-620 cm below surface level in 33G0415) the organic carbon content ranges between the detection limit of the method of analysis used (<0.1%) and 40% by weight.

6.3.5 Maarheeze, North Brabant (map sheet 57E)

The top of the drill cores was at 50-150 cm below surface level and the base approximately 800 cm below surface level. The formation sampled is the Boxtel Formation; in the case of drilling 57E0338 the top portion, from 134 to 405 cm below surface level, lies in the Singraven Member. The soil type is very fine to moderately coarse sand, with the occasional thin layer of less than 10 cm very sandy loam or amorphous peat. Drilling 57E0336 contains two thicker loam layers of 40 cm. The colour is predominantly light brown, sometimes with light olive, light grey or white, apart from the first metre of drilling 47E0338, which is very humic and dark brown.

There is hardly any clay in these samples. The drillings consist almost entirely of quartz, with a clay content below 5% (Figure 6.6). The median particle size ranges from 100 to 400 μm (Figure 6.1).

The sulphur content is below the detection limit, except in the samples from the first few metres of drilling 57E0338 and one sample from drilling 57E0335 which is rich in organic matter. The sulphur content here is merely a few tenths of a percent. There is little or no carbonate in the soil: the CaO content is below 0.5%, and the TGA did not show any weight loss between 620 and 800°C, ranging from 0.01 to 0.5%. There is no reactive Fe present, except in the two sulphurous samples: here about half of the reactive Fe can be attributed to sulphides, assuming pyrite (FeS_2) as the sulphide phase.

These clastic sediments contain little organic carbon, except for one soil sample from drilling 57E0335 and two from 57E0338: these three samples contain several percent of organic carbon. The samples with the higher organic carbon content also have a higher sulphur content.

6.4 Discussion

6.4.1 Chemical properties

The low sulphur contents and the chemometric calculations indicate that there is hardly any pyrite in the sediments from the four farms in the study, so denitrification due to pyrite oxidation probably plays no significant role.

The TGA analyses and the chemometric calculations show that there is a lot of siderite in the Spankeren subsoil, so denitrification due to siderite oxidation could be a factor here (Weber et al., 2001).

The high Fe_2O_3 and K_2O contents and the particular green colour of the sediments from the Nutter drillings indicate that these sediments contain a lot of glauconite. Whether glauconite is a potential reductor of nitrate is discussed below.

6.4.2 Methods of analysing TOC

The analyses show that, except for an interval that is locally richer in organic matter (the Zutphen Member in 33G0415), the content of organic matter in the subsoil at the locations examined is very low. Most of the sediments have a TOC content below 0.1%. The LECO CS analyzer has a detection limit of 0.1%, whereas 0.05% is required. Lower than 0.05% is not feasible, as at least 50 grams needs to be ground and homogenized to obtain a

representative sample, given the particle size of the sediments. As the sediments with the lowest TOC contents consist almost entirely of quartz, they have to be ground in a hard grinding vessel. This is made of wolfram carbide, and C is released from the vessel when grinding the quartz sediments. It is estimated that a few dozen mg per kg of C in the ground sediment comes from the grinding vessel.

Figure 6.7 compares the results from 50 samples in the study analysed using the LECO CS (dual samples of 2.5g) and the Carlo Erba CN (maximum sample 10-30 milligrams). As Figure 6.7 shows, the results from the two techniques are very much in agreement. The Carlo Erba detection limit (<0.05%) is much lower than that of the LECO CS analyzer. For the Carlo Erba all the samples have to be ground and homogenized because of the small sample size, but for the LECO CS only if the TOC content is below 0.1%. The consequence of grinding and homogenizing the samples is that CS analysis is more expensive, by about 30 Euros. Moreover, a minimum sample of 100 grams is required to carry out all the analyses needed for geochemical characterization (XRF, particle size, TGA and CS).

The organic carbon content of the sediments from the four farms in the study – except for the organically rich intervals in Spankeren – is around the detection limit (0.1% organic C) of the LECO CS analyzer used.

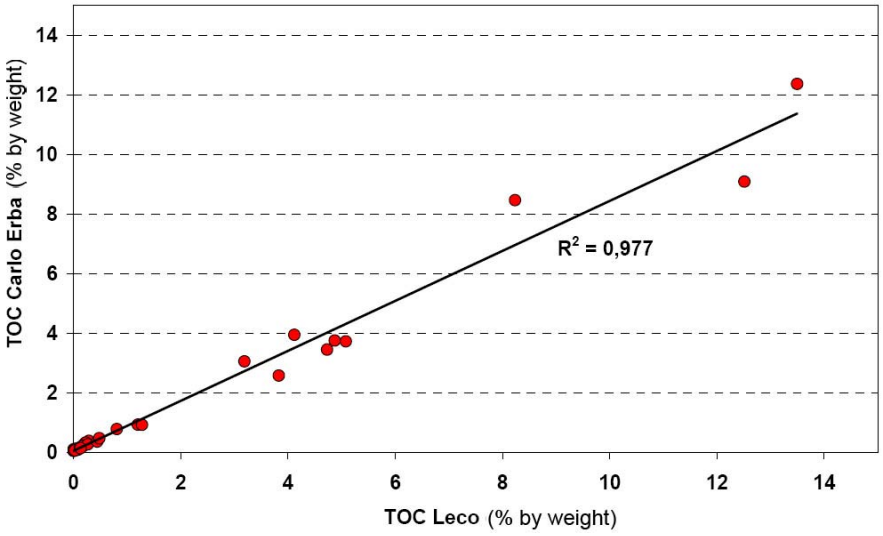

Figure 6.7 Comparison between the organic carbon contents found using the LECO CS and Carlo Erba. The samples were ground, and dual samples were used for the measurements on the LECO CS.

6.4.3 Proportion of degradable organic matter

What is important is not only the absolute content of organic matter but also whether it is suitable for microbially mediated degradation. Based on these differences and the experiments by Cuypers et al. (2002), for the purposes of this report it is assumed that soil organic matter (SOM) condensed in a TGA profile (105-800ºC) is more stable at higher temperatures (Appendices 1 and 6).

Further examination of the TGA analyses shows that the weight loss between 105 and 550ºC is greater than can be attributed to SOM, based on the results of the CS analysis (Figure 6.8). The organic matter content of the soil can be estimated by multiplying the organic carbon

content (TOC) by the ratio of soil organic matter (SOM) to the organic carbon (TOC) found in the soil. In Dutch soils this can range from 1:1 to 2:1 (Hieltjes and Breeuwsma, 1983; Van den Berg, 1998), so the SOM:TOC ratio should be between 2:1 and 1:1. As Figure 6.8 shows, the weight loss from 105 to 550ºC is more than twice the TOC content, indicating that a large proportion of the loss must be from a source other than SOM. The sulphur content is generally very low, so weight loss due to conversion of pyrite cannot be the cause.

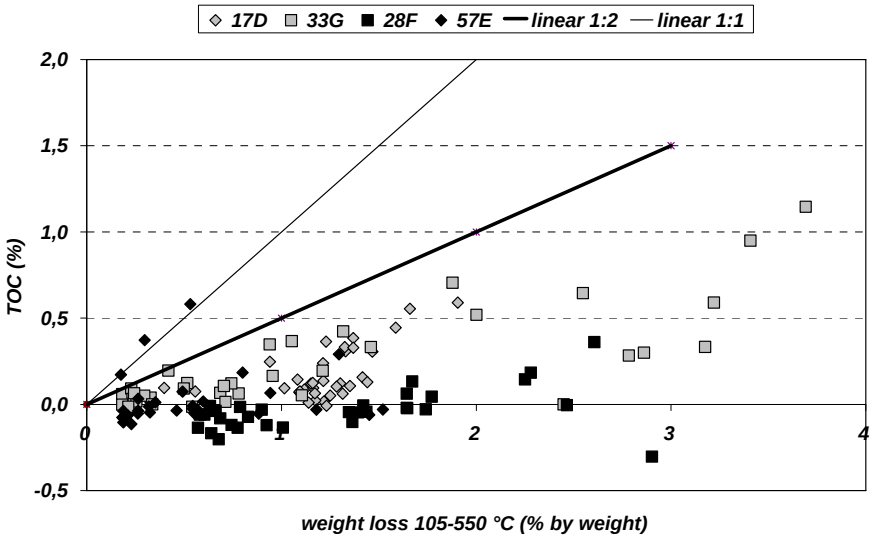

Figure 6.8 Weight loss from 105 to 550ºC in relation to TOC content compared with linear ratios between TOC and SOM
17D = Nieuweroord, 33G = Spankeren, 28F = Nutter, 57E = Maarheeze.

The cause of the weight loss is probably structurally bonded water lost from clayey minerals (Breeuwsma, 1996) in the 105-550ºC temperature range, assuming that the Fe content in the samples in the form of iron oxide is negligible.

In Figure 6.9 we looked to see whether the weight loss found from 105 to 550ºC could be attributed to loss of water from clayey minerals by comparing the loss with the Al_2O_3 content, taking the latter to be the measure of the amount of clays. As Figure 6.9 shows, there is a reasonable correlation between the Al_2O_3 content and the weight loss from 105 to 550ºC. Based on this positive correlation we must conclude that the TGA cannot be used on these sediments with a very low TOC content to estimate the thermal stability, hence the biogeochemical reactivity, of the organic matter. The approach adopted by Cuypers et al. (2002) is therefore not suitable for poor sandy soils with a low organic carbon content.

The feasibility of an alternative approach using the Pollut-Eval was determined for a selection of 20 samples. A Pollut-Eval measures the hydrocarbons released on the pyrolysis of organic matter as a function of oven temperature. The detector only measures the hydrocarbons released, so unlike the TGA it is insensitive to any water that is released.

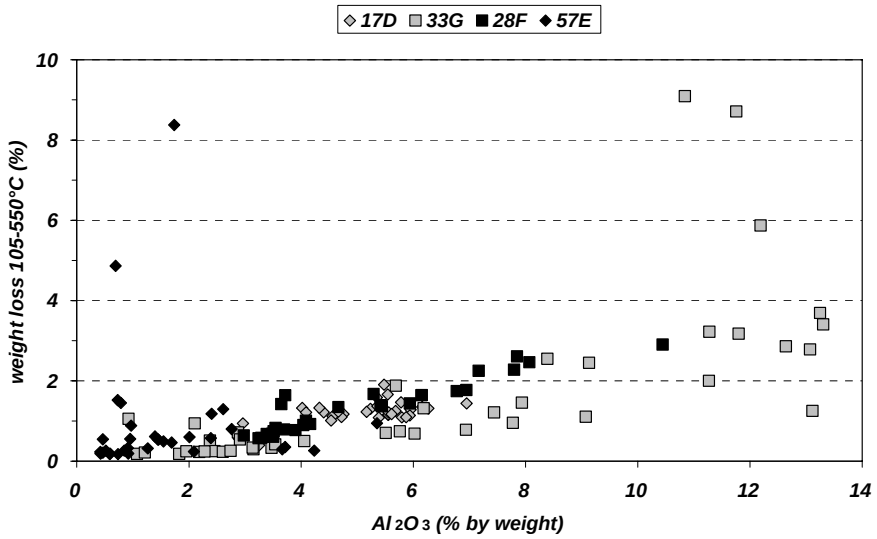

Figure 6.9 The correlation between Al_2O_3 content as a measure of clay content and weight loss from 105 to 550ºC. 17D = Nieuweroord, 33G = Spankeren, 28F = Nutter, 57E = Maarheeze.

As already pointed out, the hypothesis is that organic matter that pyrolizes at lower temperatures could be available first for biological degradation. The decisive factor in the reactivity is the ratio between the unstable (105-350 ºC) and stable (> 350 ºC) fraction, which is defined here as fraction Q2, based on the Pollut-Eval parameters Q2 and Q3 (see Appendix 6). Figure 6.10 shows this reactivity parameter for a number of samples selected on the basis of their TOC content. The differences between the soil samples were not particularly great, varying between 0.17 and 0.35.

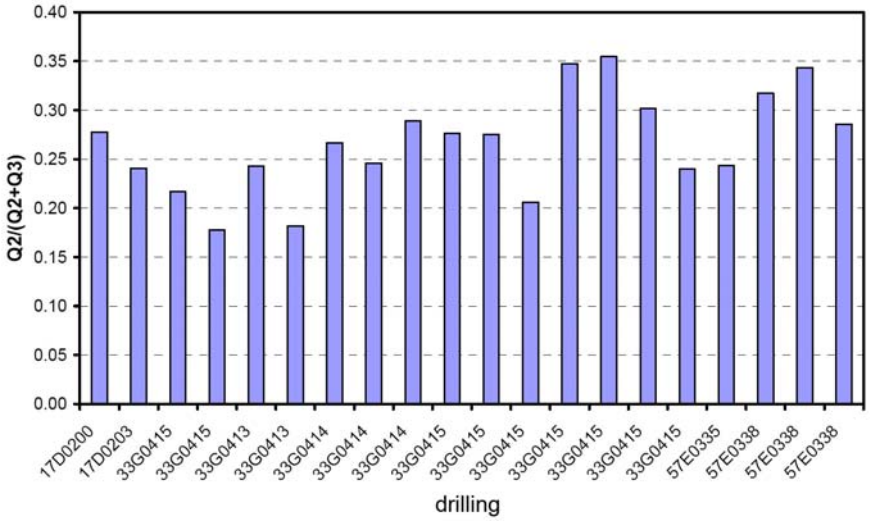

Figure 6.10 Reactivity of organic matter calculated from the Pollut-Eval results for a selected number of samples. The reactivity is based on thermal stability. 17D = Nieuweroord, 33G = Spankeren, 28F = Nutter, 57E = Maarheeze.

How significant the differences in Figure 6.10 are needs to be examined by:

- carrying out the test on a larger number of samples
- analysing the same samples several times

A related measure of reactivity could be the total percentage of pyrolizable organic matter, which can be calculated by normalizing the sum of Q0-Q3 for TOC content. Figure 6.11 shows the result of this computation. The fraction varies widely, from under 0.05 to 0.40. This is the first indication that the reactivity of these soil samples differs.

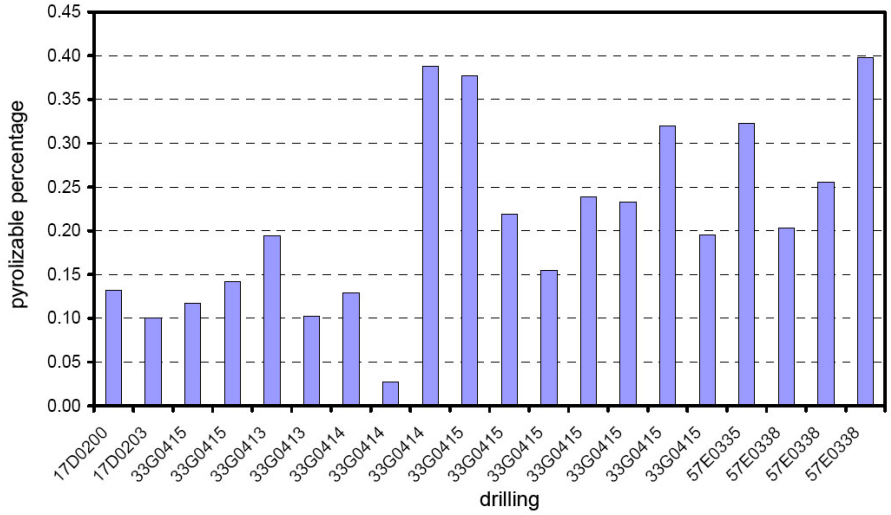

Figure 6.11 Percentage of pyrolizable organic matter calculated from the Pollut-Eval results for a selected number of samples. 17D = Nieuweroord, 33G = Spankeren, 28F = Nutter, 57E = Maarheeze.

As Figure 6.12 shows, the percentage of organic matter that can be pyrolized using the Pollut-Eval is independent of the total percentage of organic matter. This could mean that the reactivity potential is also independent of the TOC content. Where the TOC content is low the method needs to be modified, as the Pollut-Eval does not give good results on a TOC content lower than approximately 0.5%.

As already pointed out, the hypothesis is that only the organic matter that can pyrolize at lower temperatures is available for biological degradation. The Pollut-Eval analyses suggest that only 0.17-0.35 of the total organic carbon content of the sediments is available for biological degradation. This means that less than half of the already very low organic carbon content is suitable for biological degradation, hence the denitrification potential of the sediments examined must be very low, as shown by the DNP experiments described in chapter 6.

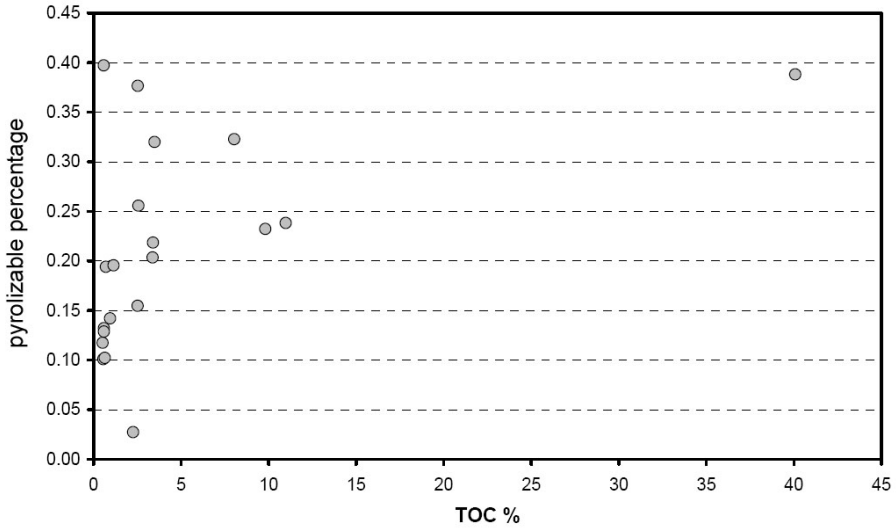

Figure 6.12 Percentage of pyrolizable organic matter in relation to quantity of organic matter. The figure does not indicate a clear correlation between the two parameters. 17D = Nieuweroord, 33G = Spankeren, 28F = Nutter, 57E = Maarheeze.

6.4.4 Comparison of geochemical properties and water quality

In the sediments examined the method used revealed the presence of pyrite in only a few cases, which means that denitrification via pyrite oxidation does not take place at the locations studied.

The groundwater nitrate profiles display fluctuations that are difficult to interpret. Figure 6.13 shows depth profiles of the nitrate concentration in the groundwater in round 2, the organic carbon content (TOC) and potential denitrification (DNP) at all locations. We note that there is no nitrate in the groundwater at any of the Nieuweroord locations, the Maarheeze location 57E0338 and the Spankeren location 33G0414, which suggests that all the nitrate there is reduced in the first metre. The nitrate concentrations in the $CaCl_2$ extractions in the Nieuweroord drillings are also lower than on the other three farms (see Appendix 8).

At the Maarheeze locations 57E0335 and 57E0337 the nitrate concentration in the first five metres drops to zero, then increases to over 50 mg l^{-1} below this depth (see Figure 5.1). At location 57E0336 the concentration falls from over 150 mg l^{-1} to approximately 50 mg l^{-1} at a depth of 550 cm, remaining more or less constant at a greater depth. Locations 33G0415 and 33G0412 in Spankeren display more or less the same pattern as the deeper screens in Maarheeze; there is no data available on the shallow screens at these locations, though the results of $CaCl_2$ extraction indicate that nitrate is present there. On the Nutter farm nitrate concentrations are only available at two locations, in both the first and the fifth metre, ranging between 5 and 20 mg l^{-1}.

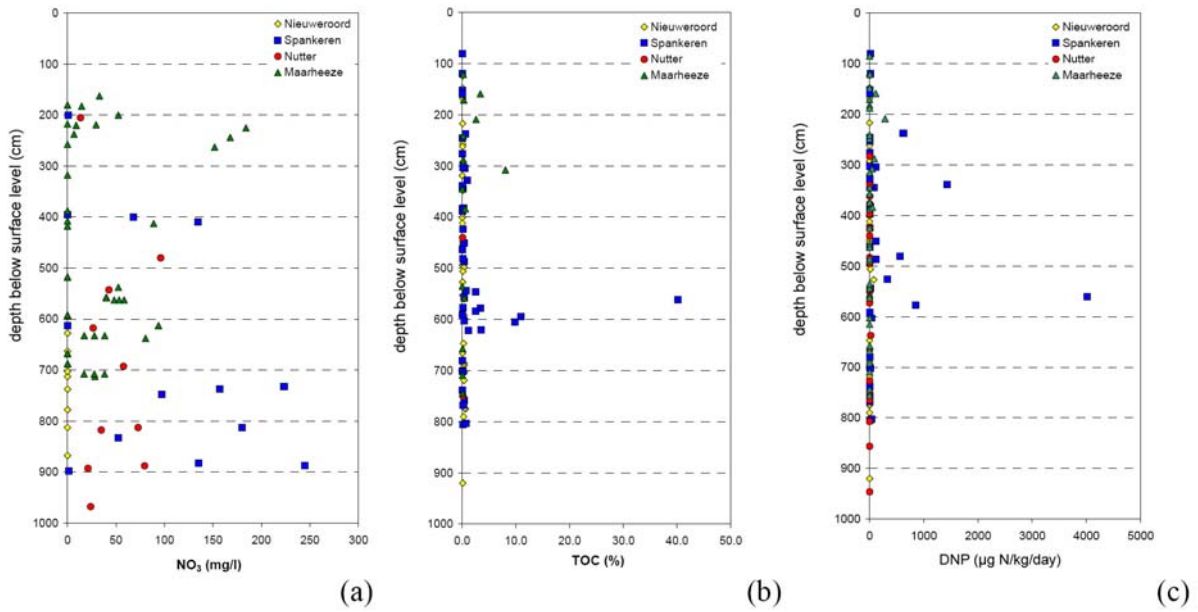

Figure 6.13 Nitrate concentration in the groundwater, round 2 (a), organic carbon content (TOC) (b), and potential denitrification (DNP) (c) on the four farms in relation to depth.

The TOC content is very low, and where it is significantly higher than the detection limit of 0.10%, potential denitrification is also found in those intervals. In Spankeren higher TOC contents are found in the peat/clay interval (33G0413) at a depth of between 500 and 650 cm below surface level. A higher potential denitrification rate is also found in this interval. Above this interval (depth 400 cm below surface level) a nitrate concentration of 120 mg l^{-1} is found, and below it (depth approximately 800 cm below surface level) a concentration of around 100 mg l^{-1}. The nitrate concentration in 33G0413, however, only starts to fall at this depth (see Figure 5.1). No potential denitrification and no TOC was found in this interval. Nor was any decrease in the concentration of dissolved organic carbon (DOC) with depth found in these samples; on the contrary, there was an increase (see Figure 3.4).

Of the groundwater profiles measured, only those measured in 57E336, 57E337 and 57E335 (Maarheeze) show a clear decrease in nitrate concentration in the shallow screens. In 57E336 and 57E337 nitrate ceases to be present at a depth of 400 cm below ground level (Figure 5.1). In 57E335 a sharp decrease in nitrate concentration is found in the samples taken at 350, 450 and 550 cm below surface level. In the groundwater in these three drillings the decrease in concentration appears to go hand in hand with the decrease in DOC concentration (cf. Figs. 3.3 and 3.4). The correlation between nitrate and DOC concentration is weak (-0.69 where p = 0.08: see Figure 6.14) and does not provide direct evidence that DOC plays a major role in denitrification.

Dutch research to date has not systematically studied the role of the leaching of dissolved organic matter in the occurrence of denitrification in the deeper subsoil. In principle this could be a sustainable process with no adverse environmental effects. There are some indications that this process could play a role in groundwater (unpublished TNO study).

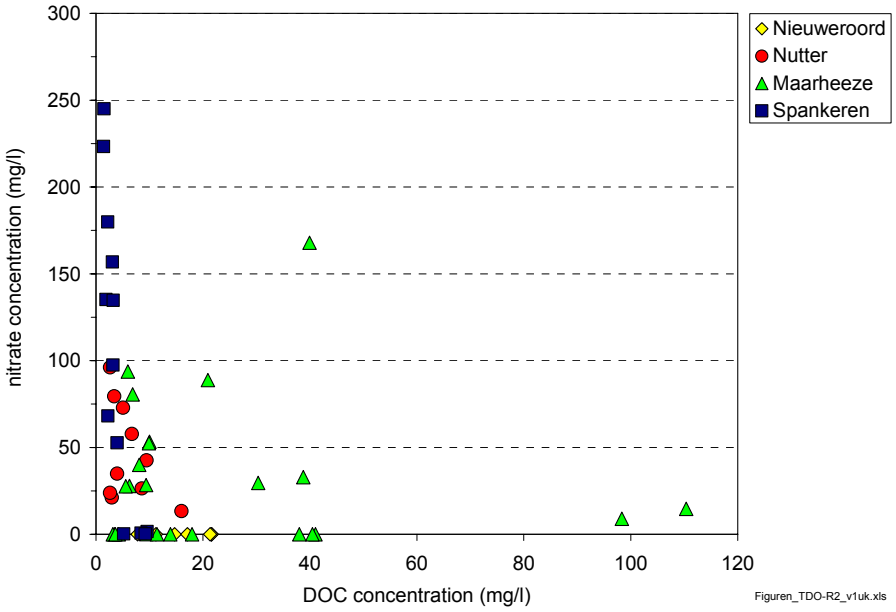

Figure 6.14 Relationship between nitrate concentration and DOC concentration in groundwater at the four LMM dairy farms (round 2 measurements)

The nitrate profiles in Spankeren and Nutter do not show any systematic decrease with depth, which indicates that the organic matter in the subsoil at the Nutter and Spankeren locations does not cause nitrate reduction. The subsoil sediments at these two farms are not generally representative of the Pleistocene sands. An interesting point here is that no sands e.g. from the Dungen Formation had hitherto been analysed by TNO. The nitrate profiles also suggest that siderite and glauconite do not play a role in denitrification at these locations.

6.5 Conclusions

The analyses show that, except for an interval that is locally richer in organic matter (the Zutphen Member in 33G0415), the content of organic matter in the subsoil at the locations examined is very low. Most of the sediments have a TOC content below 0.1%.

In this study we assume that only the organic matter that can pyrolize at lower temperatures is available for biological degradation. The Pollut-Eval analyses suggest that only 0.17-0.35 of the total organic carbon content of the sediments is available for biological degradation. This means that less than half of the already very low organic carbon content in the sandy sediments is suitable for biological degradation, hence the denitrification potential of the sediments examined must be very low, as shown by the DNP experiments described in chapter 5.

The sediments examined only displayed the presence of pyrite in a few cases, which means that denitrification via pyrite oxidation does not take place, or not significantly, at the locations studied.

The nitrate profiles in Spankeren and Nutter do not show any systematic decrease with depth, and they suggest that both siderite present at Spankeren and glauconite at Nutter do not play a role in denitrification at these locations.

Organically rich intervals having a higher potential denitrification rates (chapter 5), have no effect on nitrate concentration in the groundwater below and above these intervals.

The approach to determe the fraction of degradable organic matter adopted by Cuypers et al. (2002), is not suitable for poor sandy soils with a low organic carbon content.

7. Answers to the sub-questions

7.1 Nitrate concentration in relation to depth

Sub-question
The first sub-question is: 'Does the nitrate concentration in groundwater under agricultural lands in the sand region decrease with depth in the first five metres of the saturated zone? If so, what is the extent of this decrease and are there differences between areas?'

Lowering the compliance checking level is pointless if nitrate concentration does not decrease with depth.

Results and discussion
The results of the 2004 and 2005 studies are unclear. At the 25 locations in the National Groundwater Quality Monitoring Network (LMG) the nitrate concentration was on average 26% higher in the fifth metre of groundwater than the first metre (chapter 2). The 16 locations at the four dairy farms participating in the National Programme for Monitoring the Effectiveness of Minerals Policy (LMM), on the other hand, displayed 8% and 20% (not significant) lower nitrate concentrations on average in the fifth metre in the two sampling rounds respectively (chapter 3).

Both studies do however show that changes in nitrate concentration in relation to depth differ between soils in the drainage class 'dry' and the 'neutral' or 'wet' class (see Table 7.1). In the case of soils in the 'dry' class – soils that are dry or prone to nitrate leaching – no decrease in nitrate concentration with depth was found in the first five metres of groundwater. The large increase with depth in the LMG wells could be due partly to the fact that these are not on the plot but just outside it (for an explanation see section 7.5). In the case of the neutral and wet soils nitrate concentrations do decrease with depth, but in the wet soils in particular the percentage is not informative, as the nitrate concentration is already low in the first metre, on average 30 mg l^{-1} in the case of the seven LMG wells and 1 mg l^{-1} in that of the two locations on the LMM farms.

It is unclear at present whether, were the compliance checking level to be lowered, the checking level would be set at five metres below the groundwater table or the average nitrate concentration for the first five metres would have to meet the nitrate target of 50 mg l^{-1}. In the latter case the difference vis-à-vis checking the first metre would usually be smaller (see right-hand side of Table 7.1). In the case of the LMM dairy farms, where measurements take place almost entirely in the first and fifth metre, the effect would quite simply be a halving. In the case of the LMG wells the average nitrate concentration in the first five metres is based on all the screens between the groundwater table and five metres below it: because of the erratic changes in nitrate concentration in relation to depth here there would be no halving. The pattern emerging from these studies is in accordance with the findings of previous research, discussed below.

Table 7.1: Percentage difference[1] in nitrate concentration between the first and fifth metre of groundwater (left) and the first metre and the average of the first five metres for three drainage classes[2]

	Difference between 1st and 5th metre			Difference between 1st and average of first 5 metres		
Study [3]	Dry	Neutral	Wet	Dry	Neutral	Wet
LMG	+109	-13	-31	+38	0	-34
LMM (2)	-3	-39	-66	-1	-19	-33
LMM (3)	+7	-28	-100	+3	-14	-50

[1] A + means a higher concentration in the fifth metre or across the entire range of depth than in the first metre; a – means a lower concentration.
[2] The three drainage classes are based on a combination of groundwater step classes (see section 1.1.3): wet = GWS I-IV; neutral = GWS V, V* and VI; dry = GWS VII and VIII.
[3] LMG: 25 multi-screen wells adjacent to agricultural plots (chapter 2); LMM: monitoring locations on agricultural plots at LMM farms (chapter 3); (2) = round 2 with results for 10 locations; (3) = round 3 with results for 13 locations.

Intensive research into the variations in nitrate concentrations in space and time was carried out at ten dairy farms in the sand region at the end of the 1980s (Boumans, 1990; Boumans et al., 1989; see Appendix 11.2). Reanalysis of the data from some 85 wells indicates that the average nitrate concentration in the fifth metre was between 15% and 43% lower than in the first metre during the 1986-88 period. The average nitrate concentration in the first five metres (measured at seven depths) varies from one year to another, from an average of 2% higher to 5% lower than the average in the first metre.[7] This study also shows that there is a big difference between soils in the drainage classes ‘wet’ and ‘dry’, with soils in the ‘neutral’ class occupying an intermediate position (see Figure 7.1).

In the case of the dry soils the nitrate concentration in the last metre is 1% higher than in the first metre. Here again there are differences from one year to another: whereas in 1986 the concentration at the base was 2% lower, in 1987 it was 14% higher and in 1987 as much as 18% higher (see Figure 7.2). In the case of the neutral soils the average decrease is 42% (decreases of 23%-66%) and in that of the wet soils 66% (29% and 85%). Here again there were major differences from one year to another. The study shows that there can also be major differences in changes with depth within a drainage class, and that changes with depth in a well can differ from one year to another (for details see Boumans, 1990).

[7] The nitrate concentration in the first metre was calculated by averaging the results from the top two screens (length 20 cm); the concentration in the fifth metre was taken to be equal to that in the bottom screen (length 50 cm); and the concentration in the first five metres was calculated by averaging the results from all the screens.

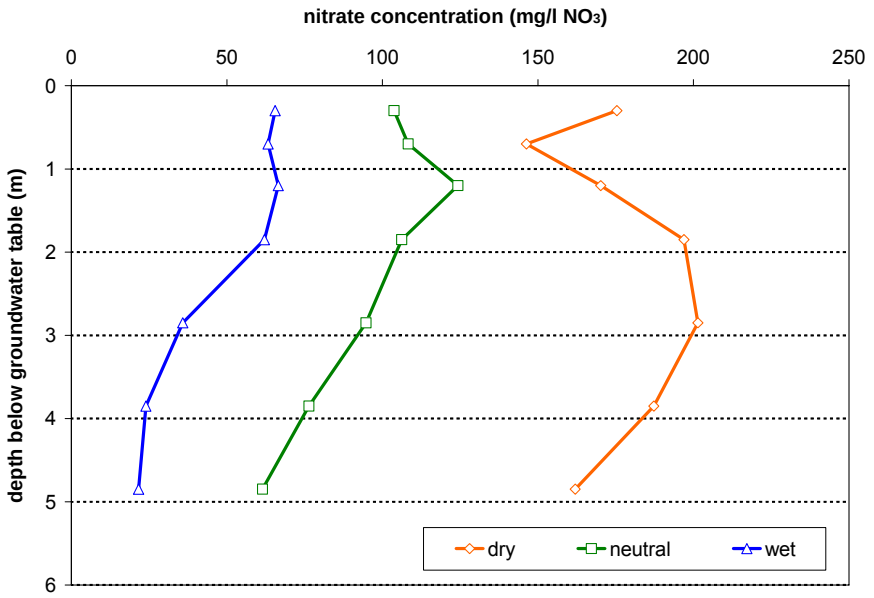

Figure 7.1: Changes in average nitrate concentration with depth in the first five metres of groundwater under dairy farms in the sand region, average over the 1986-88 period, for three drainage classes, wet (Gts I-IV), neutral (Gts V, V and VI) and dry (Gts VII and VIII).*

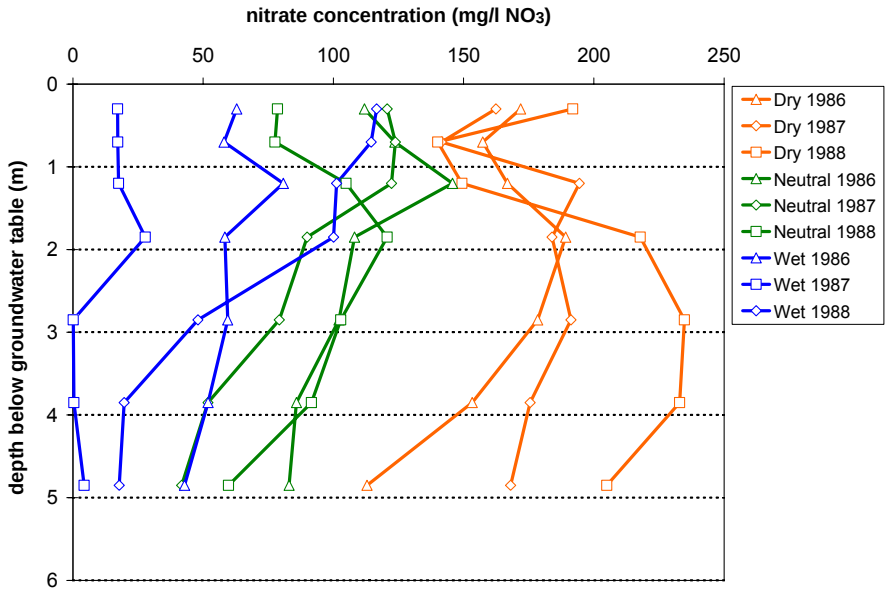

Figure 7.2 Changes in average nitrate concentration with depth in the first five metres of groundwater under dairy farms in the sand region, 1986-88 period, for three drainage classes, wet (Gts I-IV), neutral (Gts V, V and VI) and dry (Gts VII and VIII).*

At De Marke (in 1990, dairy farm) and Wedde (in 1992, arable farm), in addition to the first metre of groundwater samples were also taken at a depth of 1.5-2.5 metres below the groundwater table: an average decrease in nitrate concentration of 48% was found at Wedde and 4% at De Marke (see Table 7.2). The dairy farm situated in the eastern sandy region has neutral and dry soils. The arable farm is situated in the northern sandy region; the drainage class and precise nature of the soils (sandy soils or reclaimed peat soils) is unknown.

Table 7.2: Nitrate concentration in the first and third metre of groundwater and the decrease with depth at two farms in the sand region. The standard error is shown in brackets.

Farm	Year	Number of locations	0-1 m – GWL	1.5-2.5 m – GWL	% decrease
Wedde (arable)	1991	92	23 (2.1)	12 (1.2)	48
De Marke (dairy)	1990	130	194 (15)	186 (15)	4

TNO research at De Marke in 2001 shows that on that farm the change in nitrate concentration with depth in the first five metres of groundwater corresponds to the change in nitrate concentration over time in the first metre (see references in Broers et al., 2004, p. 29): in other words, there are no indications that denitrification takes place in the first five metres of groundwater. Only under five metres below the groundwater table is the nitrate concentration lower than might be expected from historical data on the first metre of groundwater. This decrease is attributed to denitrification, as the subsoil has enough denitrification capacity and mathematical modelling shows that it is only at a greater depth that the origin of the groundwater comes from elsewhere.

Other TNO research in intensive livestock farming areas in North Brabant (see reference in Broers et al., 2004, p. 34) indicates that nitrate concentration does decrease with depth, but only below the first five metres of groundwater. This is partly an age effect, but the decrease is attributed largely to denitrification by pyrite.

Boumans and Van Duijvenbooden (1985) reported finding a clear pollution front in shallow groundwater below sandy soils in various cases 6-8 metres below surface level, whereas this was not detected in the top screen of the nearby LMG wells (8-10 m below surface level). This study too shows little if any decrease in nitrate concentration in the first five metres.

Conclusion
In the case of nitrate vulnerable (‘dry’) soils all the data point to the fact that, on average, nitrate concentration does not decrease in the first five metres of groundwater. An increase in nitrate level with depth was found in some wells. In the case of the other soils a decrease in nitrate concentration was found between 1 and 5 metres below the groundwater table: the decrease was 15-40% in the case of the neutral (moderately wet and moderately dry) soils and 30-100% in that of the wet soils.

This means that lowering the compliance checking level for nitrate vulnerable soils would have no effect on the nitrate concentration. If the checking level for the other soils were to be lowered, the nitrate target of 50 mg l^{-1} could be met with less strict application standards, but lowering the checking level for these soils only makes sense if the decrease is related to denitrification and the denitrification does not cause some other environmental problem, e.g. an increase in other undesirable substances (see sub-questions 3 and 4).

7.2 Causes of the decrease in nitrate concentration

Sub-question
The second sub-question is: ‘If the nitrate concentration decreases within the upper five metres, can this be attributed to denitrification, or are there other causes for this decrease?’

If there are causes other than denitrification, the problem could occur elsewhere, or the decrease in nitrate concentration with depth is due e.g. to variation over time in nitrogen load or rainfall. If the latter is the case, the decrease with depth will be temporary. It should also be noted that that capacity of the soil to denitrify nitrate may be finite, if the required energy sources (organic matter or pyrite) run out.

Results and discussion

The decrease in nitrate concentration with depth found in this study can be attributed to a combination of factors, as already described in part by Broers et al. (2004):

1. The age of the groundwater usually increases with depth: groundwater below a depth of 10 metres in infiltration areas will have been infiltrated 10-15 years ago on average, and 5-10 years ago on average at a depth of 5 metres. Leaching of fertilizers increased between 1950 and 1987, with the result that nitrate concentrations in deeper and older groundwater are often lower. Between 1987 and 1990 and after 1995 the use of nitrogen fertilizers – hence leaching – gradually reduced, so nitrate concentrations in the first five metres can be higher five metres below the groundwater table than in the first metre.
2. Below a certain depth in the saturated zone denitrification is caused by the presence of organic matter, sulphides and/or reactive iron.
3. There can be impermeable soil layer (clay and loam layer) in the subsoil between the first and fifth metre of groundwater, or conversely at a depth of five metres there can be a highly permeable layer (in gravelly and coarse sandy sediments), with the result that the origin of the water at a depth of five metres may be different from that of the first metre. As we are now looking at farming locations, the water there at a depth of five metres may come from other farming locations or other land uses (e.g. nature areas). If it comes from other farming locations, the nitrate concentration will be sometimes higher and sometimes lower than if the water actually came from the location under consideration. On the other hand, if the water comes from a location with a different land use the nitrate concentration will almost always be lower. Nitrate concentrations in the upper metre of groundwater are lower on average in the case of other land uses than in case of agricultural land. As a result, if there is an interfering soil layer, on average the nitrate concentration will be lower at a depth of five metres than in the first metre.

In the case of the dry soils there would seem to be an increase rather than a decrease in nitrate concentration with depth. This may be related to point 1 above, but it may also be partly due to technical limitations (see section 7.5). The decrease in nitrate concentration with depth in the other sandy soils is usually likely to be due to a combination of denitrification, the presence of interfering soil layers and the relatively older age of the groundwater at a depth of five metres than in the dry soils. As a result of the artificial drainage of agricultural soils in these areas by means of ditches and drainage pipes, only part of the precipitation surplus is likely to infiltrate to a greater depth. The annual downward water movement will therefore be much less than a metre, so it will take longer for the groundwater to reach a depth of five metres. The artificial drainage also causes more leaching into surface water, which can result in too high nitrate levels in surface water (see section 7.4).

The study conducted at the four LMM dairy farms in 2005 looked at soil properties that allow denitrification to occur. Samples were taken from the soil layer in which the first five metres of groundwater flow. The study also looked at the extent to which the microbial population of these layers was able to denitrify nitrate. The results of these studies, as reported in chapters 5 and 6, do not provide an answer to the sub-question. The nitrate concentrations in the first

metre are already low at the locations in the drainage class ‘wet’ (2) and those with reclaimed peat soils (4). In the case of the other locations (8) for which measurements on the first and fifth metre are available the pattern varies. We may conclude that, in general, the soils examined have little pyrite or organic matter in the subsoil. Three of the eight soil profiles did however display thin peat or detritus layers that were rich in organic matter, but this did not always result in a lower nitrate concentration in the fifth metre, although significant potential denitrification rates were usually found in these layers. This indicates that these layers contain organic matter that is available as an energy source to denitrify bacteria. Tests for the proportion of degradable organic matter were inconclusive, however. Lastly, at some locations siderite or glauconite was found which could serve as an energy source for denitrification, although it did not appear to have any effect on the nitrate concentrations at these locations.

Nor was it possible to prove, based on potential denitrification rates, that denitrification in the subsoil results in a reduction in nitrate levels, (a) because little or no potential denitrification was found in most soil layers and (b) because nitrate concentrations displayed large variation with depth.

Almost all the profiles contain thin clay and/or loam layer that could in principle mean that the lower nitrate concentrations are due to the origin of the water at a depth of five metres below the groundwater table being different from that in the first metre. The uniform changes in chloride concentrations with depth, however, would seem to rule out this conclusion. The increase in sulphate and nickel concentrations with depth in the profile in the drainage class ‘neutral’, and in water hardness in a profile in the ‘dry’ class, indicate that denitrification could play a part here, but this conflicts with the finding that the profiles contain hardly any pyrite and have low potential denitrification rates.

If there are causes other than denitrification, the problem could occur elsewhere, or the decrease in nitrate concentration with depth is due e.g. to variation over time in nitrogen load or rainfall. If the latter is the case, the decrease with depth will be temporary. It should also be noted that that capacity of the soil to denitrify nitrate may be finite, as the stocks of organic matter and/or pyrite can run out.

An interfering layer could mean that the origin of the upper layer and the lower layer of groundwater is different: e.g. the first metre could be leached from an agricultural plot and the fifth metre could be old seepage water infiltrated with a low nitrate concentration prior to 1950. If this is the case, nothing can be said about the effect of farming practice on nitrate concentrations at a depth of five metres.

Conclusions

The soils in the drainage classes ‘wet’ and ‘neutral’ have lower nitrate concentrations at a depth of five metres below the groundwater table than in the first metre of groundwater. This decrease is probably partly due to denitrification, though other factors could also be involved, e.g. hydrology (interfering layers), regional seepage of groundwater from the deeper subsoil and discharge of some surplus rainfall to surface water. The change in the nitrogen load, particularly in the period following the mid-1990s, complicates the interpretation of the nitrate concentrations found with depth.

7.3 Consequences of denitrification

Sub-question
The third sub-question is: 'If denitrification occurs, to what extent does these process lead to adverse environmental effects such as an increase in the levels of sulphate or heavy metals, or increasing hardness of the groundwater?'[8]

Lowering the compliance checking level, hence applying less strict application standards, would mean more nitrate leaching into the groundwater below the first metre. In certain soils this could result in higher denitrification and an increase of the levels of other substances.

Results and discussion
In the groundwater on the four LMM dairy farms there are only a few locations which display a decrease in nitrate concentrations. As discussed in the previous section, the soil chemistry and soil biology investigation of the capacity of the soil to denitrify nitrate did not provide a clear answer to whether or not denitrification occurs. In other words, there is no hard evidence that the decrease found is due to denitrification; there are merely indirect indications that denitrification could play a role, such as an increase in sulphate concentration, water hardness and nickel concentration. This implicitly presupposes that there is a shift in the problem.

As the results of the field work were inconclusive, the data on the first metre of groundwater (LMM) and the shallow groundwater at a depth of 10 metres below ground level (LMG) were compared. The comparison clearly showed that the nitrate concentrations were lower at a depth of 6.5-8.5 m below the groundwater table than in the first metre of groundwater. No differences were found between drainage classes (see Appendix 3). The question is whether these lower nitrate concentrations in the shallow groundwater resulted in higher concentrations of other substances. The data do not show any increase in water hardness, sulphate or heavy metals with depth (see Appendix 10). Reijnders et al. (2004) investigated whether there were changes over time in the levels of a large variety of substances in the shallow and medium-depth groundwater. No increase or decrease over time was observed in substances such as sulphate and heavy metals (As, Cd, Cr, Cu, Ni, Pb and Zn) in the sand region (1984-2000 period) or nitrate (it was only possible to detect changes >10%).

This does not mean that there are no adverse environmental effects, but it is clear that they cannot be shown to occur using the data from the national monitoring networks. Regional and local research, however, has shown that such effects occur (see e.g. Van Beek et al., 2002; Broers et al., 2004).

It should be noted that there are other processes that cause an increase in levels of the displacement substances concerned. Farming adds Ca, Mg, K, Na and SO_4 to groundwater and plants also add CO_2. Mineralization of organic matter in the subsoil also creates CO_2, which can dissolve minerals (see also section 1.1.4). These Ca, Mg, K and Na cations can also dislocate one another and heavy metals from the adsorption complex, with the result that

[8] The chemical reactions that take place in the subsoil where denitrification occurs can cause soil minerals to be dissolved, resulting in an increase in concentrations of sulphate, heavy metals, calcium and magnesium, which could cause the standards for these substances in drinking water to be exceeded.

they end up in the groundwater. Lowering of the groundwater table in historically wet areas (dehydration) can cause pyritic compounds to oxidize with oxygen, and atmospheric deposition also adds SO_4 and NO_3 to the groundwater. The deposition of SO_4 in particular used to be higher in the past. It is difficult to distinguish between (a) denitrification and (b) other causes of elevated concentrations (Reijnders et al., 2004; Van Beek et al., 2002; Broers et al., 2004). Only detailed research at a location, as carried out at one time by TNO and RID, can prove the shift in problem.

This study did not look at the effects of changing the compliance checking level on the emission of N_2O. If lowering the checking level results in higher application standards, more nitrous oxide will also be emitted.

Conclusions
It was not possible to quantify the problem of the increase in other substances (adverse environmental effects) due to denitrification. The heterogeneity of the subsoil in the Dutch sand region is such that there can be large differences in the occurrence or non-occurrence of denitrification and the type of effect denitrification has on water quality over short distances (within a farm).

Lowering the compliance checking level, hence applying less strict application standards, would mean more nitrate leaching into the groundwater below the first metre. In certain soils this could result in higher denitrification and an increase of the levels of other substances. Various detailed studies have indeed shown adverse environmental effects of this kind, but there is insufficient data to quantify the effects in the first five metres of groundwater in the sand region.

7.4 Consequences for surface water

Sub-question
The fourth sub-question is: ‘In the clay and peat regions, lowering the compliance checking level in order to be able to apply less strict application standards would lead to insufficient reduction of the nitrate load to surface waters. To what extent does this apply to the sandy soil areas?’

Wet soils, and some of the neutral soils, are by nature less suited to agriculture. In order to use them more effectively they are usually drained by digging ditches and sometimes laying drainage pipes in the subsoil. Some of the precipitation surplus is carried away by the drains and ditches, along with the nitrogen leached from the topsoil.

Results and discussion
To answer the sub-question we need to use results from previous research. There are four studies available that determined nitrate concentrations in both the first metre of groundwater sampled in temporary boreholes (well water) and by collecting drainage water. Two studies also measured nitrate concentrations in ditch water.

One of the two last-mentioned studies looked at two farms participating in the ‘Koeien en Kansen’ (sustainable dairy farming) project in the sand region (see Appendix 11.4). The average nitrate concentration in the well water was lower than 50 mg l^{-1} on one farm and higher on the other (see Figure 7.3). The nitrate concentration in the drainage water was

somewhat lower than in the well water (20%) on the first farm but higher (75%) on the second farm. The levels in the ditch water were lower than in the drainage water on both farms (30-35%). Although there were differences from one year to another, this pattern was true in almost every year (see Figure 7.4).

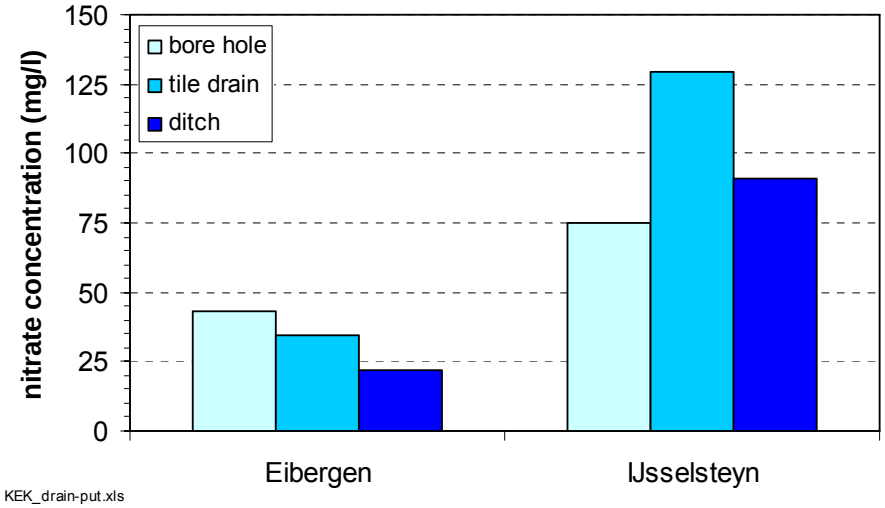

Figure 7.3 Nitrate in the first metre of groundwater sampled from open boreholes (well) and by collecting drainage water (tile drain) and in the ditch water (ditch) on two farms participating in the 'Koeien en Kansen' project. Average nitrate concentrations in the 1999-2004 period.

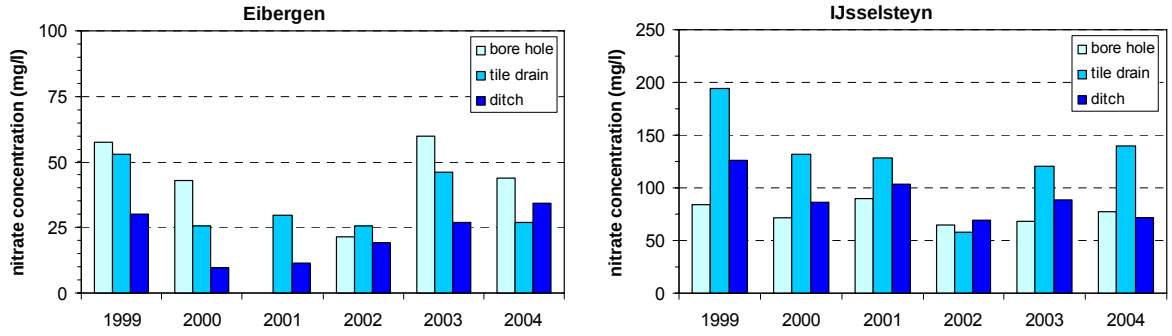

Figure 7.4 Nitrate in the first metre of groundwater sampled from open bore holes (well) and by collecting drainage water (tile drain) and in the ditch water (ditch) in the 1999-2004 period on the farms at Eibergen (left) and IJsselsteyn (right).
Note the differences in the nitrate axes in the left and right figures.

The higher concentration in the drainage water than in the well water could be related to the different sampling periods for the two types of water: the well water was sampled in the summer, the drainage and ditch water in the winter. Research in the clay regions shows that nitrate concentrations in groundwater are lower in summer than in winter (Fraters et al., 2001; Nillesen, 2002). This may be due to the fact that the nitrate level in groundwater decreases in the summer as a result of denitrification, only to increase again in the winter as a result of replenishment with young, nitrate-rich groundwater.

The soils at both of the farms mentioned above are predominantly in the drainage class 'neutral' (Gts V and VI; see Table 7.3). Run-off and leaching into surface water also play a major role on farms of this kind.

Table 7.3: Drainage class distribution (%) at the two farms participating in the 'Koeien en Kansen' project

	Dry	Neutral	Wet
Eibergen	0	87	13
IJsselsteyn	0	100	0

Well water, drainage water and ditch water have been sampled at a group of 25 farms since winter 2004-05 (see Appendix 11.4). Provisional data from the first sampling are now available (see Fig 7.5). The nitrate concentration in the drainage water is 13% lower than in the well water, but the difference is not significant (the 95% reliability range is from -7% to 32%). The nitate concentrations in the ditch water were 35% lower than in the well water (14-57%). The soils on the farms are on average 14% in the drainage class 'dry', 54% 'neutral' and 32% 'wet'. Well water was sampled on all the plots, including those without drainage.

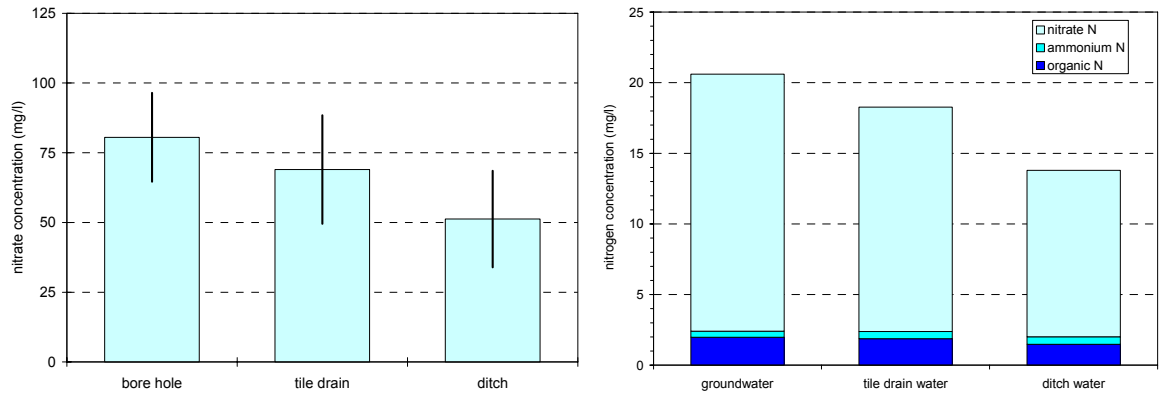

Figure 7.5 Average nitrate concentration (left) and nitrogen concentration (right) in well, drainage and ditch water on 24 farms in the sand region in winter 2004-05. The vertical line in the columns on the left of the figure shows the 95% reliability range for average nitrate concentration.

Eight of the farms were also sampled the previous summer (2004). The average nitrate concentration in the well water was 34% higher in the winter than in the preceding summer. This is probably due to rising nitrate levels since 2003 caused by a relatively dry period.[9] The average nitrate concentrations on farms in the sand region in the summer increased from 52 mg l^{-1} in 2003 to 74 mg l^{-1} in 2004 and 79 mg l^{-1} in 2005.

A 1987 study of two dairy farms gave a somewhat different picture (see Figure 7.6: unpublished data from the study by Boumans et al., 1989). On these farms the nitrate concentrations were markedly lower in the drainage water than the well water. They have

[9] In years with lower precipitation surplus about the same quantity of nitrate (in kilograms) is leached, so the concentrations are higher.

somewhat more soils in the drainage class ‘wet’ (27-47%; the remaining soils are in the ‘neutral’ class), and the well and drainage water were both sampled during the winter, with about a month between the two samplings. The figures are less reliable than the recent ones, as only one measurement was carried out on each farm. The number of drainage water samples at Bavel was limited (Holten: 89 wells and 34 drainage pipes; Bavel: 61 wells and 4 drainage pipes).

A similar study was carried out at three arable farms in 1989 (RIVM, unpublished data). The farm at Nieuwlande was sampled again in 1990. There was one round of sampling a year; the precise sampling dates are not known. The numbers of samples are shown in Table 7.4. In most cases the nitrate concentration in the drainage water did not appear to differ that much from that in the well water (30% lower to 20% higher) except during the 1989 sampling round at the Nieuwlande farm, when the nitrate level in the drainage water was only 10% of that in the well water (see Figure 7.7).

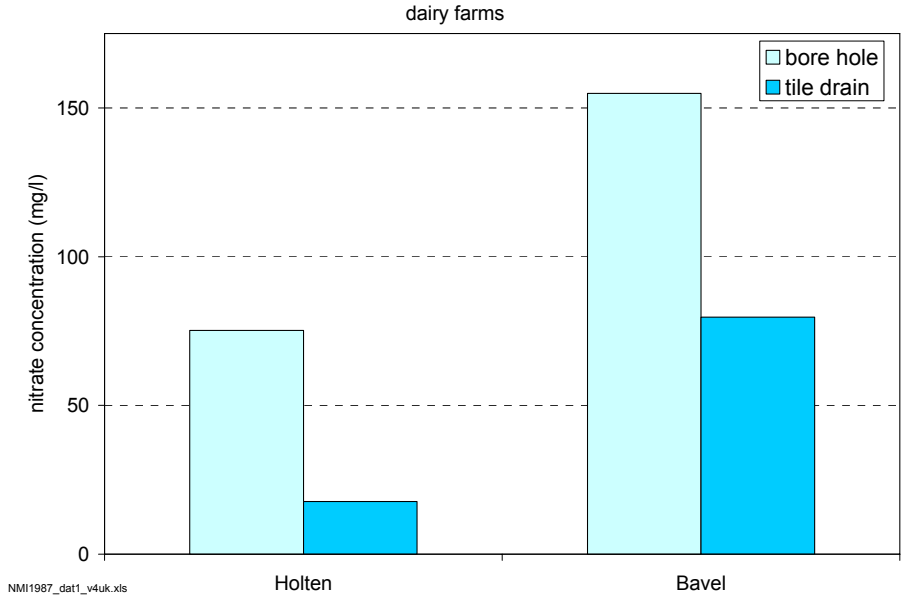

Figure 7.6 Nitrate in the first metre of groundwater sampled from open boreholes (well) and by collecting drainage water (tile drains) on two dairy farms in 1987.

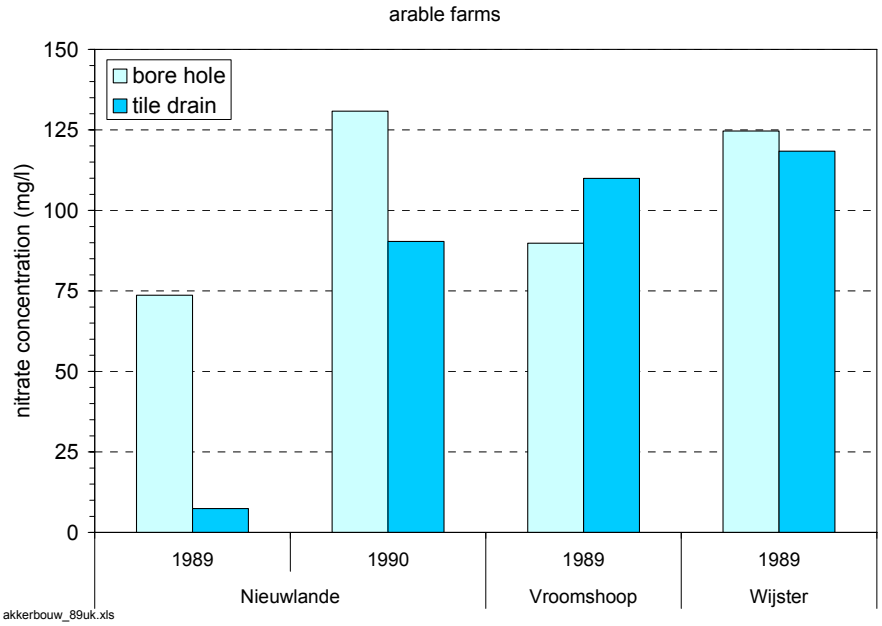

Figure 7.7 Nitrate in the first metre of groundwater sampled from open boreholes (well) and by collecting drainage water (tile drains) on three arable farms in 1989 and 1990.

Table 7.4: Numbers of samples of well water and drainage water per round on the three arable farms in Figure 6.8

	Nieuwlande		Vroomshoop	Wijster
	1989	1990		
Well water	44	88	39	21
Drainage water	49	37	54	112

To sum up, average nitrate concentrations in drainage water on farms in the drained areas of the sand region were approximately 15% lower than those measured in the first metre of groundwater in the winter in open boreholes. In relation to the nitrate concentration in the top level of groundwater in the summer, the levels in the drainage water in winter could be higher. As the above examples show, soils in the drainage class ‘neutral’ can also be drained, and the ‘drained areas’ are not confined to the wet soils.

The study shows that at a nitrate concentration in the first metre of groundwater of 50 mg l^{-1} (equivalent to 11.3 mg nitrate nitrogen per litre), the nitrogen standard for surface water will generally be exceeded in the *ditches* in these drained areas. The nitrogen standard (Maximum Permissible Risk) for surface water to prevent eutrophication is 2.2 mg nitrogen per litre. On farms in the sand region the average nitrate concentration in the ditches is 35% lower than in the first metre of groundwater (well water; see Figure 7.5). At a nitrate concentration of 50 mg l^{-1} in the top level of groundwater the nitrate nitrogen concentration in the ditch water would be 7.3 mg l^{-1} N, more than three times as much as the standard for surface water. In addition to nitrate nitrogen, ammonium nitrogen and organic nitrogen also end up in the ditch water (see Figure 7.5 right).

The derogation for the clay regions is based on the principle that the total nitrogen concentration in the *drainage water* must not exceed 11.3 mg l^{-1}. The average nitrate concentration in the drainage water in the sand region is approximately 15% lower than in top

level of groundwater (see Figure 7.5 left). At a concentration of 11.3 mg l^{-1} nitrate nitrogen (N) in the groundwater 9.6 mg l^{-1} nitrate nitrogen leaches from the drains. In addition to nitrate, the drainage water contains an average of 2-3 mg l^{-1} ammonium nitrogen and organic nitrogen (N) (see Figure 7.5 right), amounting to a total nitrogen concentration in the drainage water of just over 11.3 mg l^{-1}.

Conclusions
Lowering the compliance checking level in the drained areas of the sand region would mean permitting nitrate concentrations of over 50 mg l^{-1} in the first metre of groundwater, and thus indirectly permitting a higher nitrogen load on surface water than in the case of compliance checking in the first metre. This would result in a nitrogen concentration in the drainage water of over 11.3 mg l^{-1} (on which to base the derogation) and the nitrogen standard for surface water of 2.2 mg l^{-1} would be exceeded by more than a factor of 3-4.

7.5 Measuring nitrate at a depth of five metres

Sub-question
The fifth sub-question is: ‘Regardless of how complex, is it feasible to measure the nitrate concentration at a depth of five metres in the saturated zone, or can the average nitrate concentration in the first five metres be determined?’

If the compliance checking level is lowered, monitoring data on nitrate will also be needed to check compliance.

Results and discussion
Sampling groundwater five metres below the groundwater table cannot be done using a simple manual technique, as is done in the LMM. It can however be done mechanically, either using temporary boreholes or by installing permanent wells.

Using temporary boreholes to sample groundwater at a greater depth only makes sense for one-off measurements. The results of the field study on the LMM farms, however, indicate that mechanically inserted screens can affect measured water quality. If sampling is to be repeated it is more cost-effective to install permanent wells. The advantage is that they can first be flushed out a few times over a period of time to neutralize the effect of installing on water quality. The disadvantage of permanent wells is that they are susceptible to damage, could hamper the work of the land user or could influence his behaviour (for example, he might modify his practice in the vicinity of the well, with the result that the water in the top screens is not representative of the effects of normal farming practice on water quality). With permanent wells it is not easy to use the groundwater table as a reference level, as groundwater levels fluctuate not only during the year but also from one year to another. For the purpose of the study it was therefore decided to take the mean lowest groundwater level (MLG) as the reference level. Lastly, installing a permanent well on a plot requires the cooperation of the user/owner over a number of years.

If it is decided to install permanent wells there are two options: (a) the well can be placed just outside the plot, taking account of the groundwater flow direction; (b) it can be placed inside the plot, in which it will need to be covered underground to prevent inconvenience to the land user. From the practical point of view placing it outside the plot has substantial advantages. If sampling only needs to take place at greater depths (five metres or more below the

groundwater table) any interference between the first and fifth metre will be no worse than in a well placed inside the plot. The first metre could then be sampled using temporary manual boreholes inside the plot. If both the first and fifth metre, and possibly intermediate layers, are to be sampled using the same well, it should be placed inside the plot. A comparison of the results from wells outside the plots (LMG multi-screen wells) with those from wells inside the plots (on LMM dairy farms) raises questions about the results from the LMG wells. The concentrations measured in the water in the top screen in wells outside the plots may have been affected by water other than water from the plot, so it may not be a good indication of the quality of the first metre of groundwater on the plot.

Where wells are placed inside the plot there is also the option of running the pump tubes underground to the perimeter of the plot. It is unclear as yet how well this system works in the long term. It may limit where wells can be placed, as the tubes must not be too long, so as to reduce the risk of their becoming damaged or blocked. Before deciding to use permanent wells with tubes running to the perimeter it would be advisable to pay a visit to our Danish colleagues and a Danish groundwater station, as the Danes have some years' experience of similar methods.

The study showed that changes in nitrate concentration with depth can be highly erratic. As a result, a difference in nitrate levels between the first and the fifth metre in a particular well does not tell us very much about the average nitrate concentration in the five metres in the well or changes over time in that well, and nothing about the situation at similar locations. To overcome this problem, monitoring needs to take place at a number of locations in an area with a homogeneous combination of soil and land use on which we wish to draw conclusions. It is advisable to install a number of screens in the range of depths under consideration so as to gain some idea of the changes in nitrate concentration with depth.

Installing a number of screens is also advisable for a technical reason: research shows that with the methods and screen materials currently in use it is impossible to obtain samples from some 30% of screens (as no groundwater can be pumped up).

The sampling methods tested in the study are suitable for measuring nitrate concentrations in the first five metres, but during the study it became clear that additional measurements might be needed, e.g. to measure the effects of denitrification and check the origin of the water at a depth of five metres. One method for determining denitrification could be to determine the quantity of nitrogen gas dissolved in the groundwater (see the next section).

Conclusions

It is possible to routinely measure nitrate concentrations at a number of depths in the first five metres of the saturated zone. Such measurements cost more than those in the top level of groundwater.

If possible, permanent multi-screen wells should be installed inside the plots. A number of screens are needed, as no groundwater can be sampled with some of them, e.g. because the screen is in a relatively impermeable stratum or because it has silted up with fine particulate matter. The wells should be installed inside the plots, as with wells outside the plots there is a risk of sampling groundwater which comes partly from elsewhere. Even if the groundwater flow direction has be taken into account when installing wells of this kind. Manual techniques are not suitable: the desired depth below the groundwater table cannot always be achieved with manual drilling.

7.6 Measuring denitrification and effects

Sub-question
The sixth sub-question is: 'Regardless of how complex, is it feasible to measure the extent to which denitrification occurs, whether it is sustainable, and whether the process produces undesirable by-products?'

Lowering the compliance checking level is an option in those situations where nitrate in the groundwater is broken down by denitrification and no harmful substances such as sulphate or heavy metals are released. This is why it is important to establish from measurements that any decrease in nitrate is actually due to denitrification and that there are no adverse environmental effects.

Results and discussion
There is a need for information on the occurrence of denitrification in the first few metres of the saturated zone. Below we discuss various approaches in terms of measuring techniques and usefulness.

Groundwater composition
Denitrification is a reaction whereby not only nitrate disappears but sulphate (SO_4) or bicarbonate (HCO_3-) also appears in solution. Follow-up reactions can also take place as a new carbonate equilibrium develops. The occurrence of denitrification cannot therefore be established solely from the behaviour of nitrate. The problem is that the concentrations of the substances concerned are also determined by other reactions or sources. When analysing the data on a national scale this causes insuperable problems, though on a regional basis identical behaviour can be expected and it should be possible to establish a connection of this kind.

Measurements of groundwater composition, in particular NO_3, SO_4, Fe and alkalinity or HCO_3, provides information on the historical occurrence of denitrification. The amount of denitrification between the groundwater table and the sampling depth can be determined for a certain volume of groundwater by means of a mass balance approximation, especially if a number of samples are taken along a flow line.

Degradable organic matter
There are a number of ways of determining the quantity of degradable organic matter. This study examined the suitability of the pyrolysis method. The general expectation is that the chemical stability of a soil sample when pyrolized will be indicative of the microbial degradability of the organic matter (OM). Pyrolizable OM thus provides an indirect indication of denitrification capacity, as it shows the quantity of unstable OM. The relationship between organic chemical composition and denitrification capacity has not yet been demonstrated.

An alternative is to extract organic matter selectively: methods of doing this are described in the literature. There are also methods involving measuring CO_2 during incubation. We are not aware of these methods being used on denitrifiable OM. The potential denitrification rate is also an indicator of the degradability of the organic matter: this indicator is discussed below.

The role of the dissolved organic matter (DOM) leached from the first metre of groundwater as an energy source for denitrification is unclear. There are some indications that this could play a role, but there is no convincing evidence.

Pyrite
There is sufficient field evidence that denitrification due to pyrite oxidation occurs in parts of the Netherlands. The pyrite content can readily be measured by a simple overall soil analysis. In the case of sediments in aquifers the general expectation is that pyrite will be the iron sulphide present, rather than other more soluble iron sulphides (measured as acid volatile sulphides). These more soluble iron sulphides are however likely to occur in surface water sediments. In the case of soil that is rich in organic matter an adjustment has to be made for organic sulphur. This can be achieved using another relatively simple analysis combined with an assumption as to the C:S ratio of the OM.

Potential denitrification
Incubation experiments provide information on the occurrence of denitrification and the maximum rate under laboratory conditions. This measurement gives a direct indication of the possible occurrence of denitrification in the soil and is also an indicator of capacity. If no potential denitrification is found there will be no denitrification and denitrification will not be the cause of any lower nitrate concentrations found.

Dissolved nitrogen gas (N_2)
In addition to the traditional substances dissolved in groundwater, dissolved gases can be analysed. Nitrogen gas is the end-product of denitrification and also occurs in the atmosphere. The concentration of nitrogen gas over and above the amount in equilibrium with air is a measure of the amount of denitrification that has taken place, assuming no degasification has occurred and the gas dissolved in the groundwater flows along with it. This is a reasonable assumption as long as the total gas pressure is lower than the hydrostatic pressure (Blicher-Mathiessen et al., 1998). If the total gas pressure is higher, degasification can occur: this can be adjusted for by looking at the noble gases present in the air. The N_2 concentration provides information on the amount of denitrification that has occurred upstream in a certain volume of groundwater. No groundwater samples need to be compared to determine this quantity. Degasification complicates measurement and is a realistic proposition if the original nitrate concentration was high (a few hundred mg per litre).

The study did not examine this method. How promising it is would need to be investigated before using it on a regular basis.

Isotope investigation (N, S en C)
In addition to analysing the concentrations of ions present in the solution, the isotopic composition of many ions can be measured. Isotope geochemistry often tells us about the origin of the ions dissolved in the water. Mass balance approximations enable hydrogeochemical reactions to be quantified to a greater or lesser extent. This method complements traditional water analysis and can provide more information on the occurrence of reactions.

In the case of denitrification it is possible in principle to measure the isotopic composition of NO_3, SO_4 and HCO_3. Then additional information can be obtained from e.g. B isotopes. Like its general composition, the isotopic composition of groundwater can provide information on the historical occurrence of denitrification. Using isotope measurements, the

amount of denitrification between the groundwater table and the sampling depth can often be determined much better by means of a mass balance approximation, especially if (as in the case of macro groundwater composition) a number of samples are taken along a flow line.

Allowance needs to be made for the fact that other processes can also affect the isotopic composition, and the composition of inorganic fertilizer and animal manure are also different. As additional methods these might provide more information, but the pros and cons should be investigated before using them.

Conclusions
It is not possible, using routine monitoring such as that carried out in a monitoring network or monitoring programme, to determine with sufficient reliability how much denitrification is occurring and whether it is sustainable and does not cause adverse environmental effects. Using a combination of methods not currently used on a routine basis it is possible, however, to determine the occurrence of denitrification and any adverse effects at specific locations, though this would increase the cost of monitoring substantially. Another problem is that there are other processes that can cause deterioration of water quality.

7.7 Determining the origin of water at a depth of five metres

Sub-question
The seventh and final sub-question is: ‘Regardless of how complex, is it feasible to measure whether the groundwater at five metres depth has the same origins as the groundwater in the first metre?’

Determining the origin of groundwater at a greater depth is important, as we need to be able to rule out the possibility that the decrease in nitrate concentration with depth is due to clean water coming in from elsewhere, e.g. old seepage water, in which case denitrification is ruled out. In a situation of this kind it could also be the case that the problem is being shifted to surface water.

Results and discussion
Conclusively proving that the origin of the groundwater at a depth of five metres below the groundwater table is the same as that of the groundwater in the first metre is not likely to be easy in practice.

Homogeneous sandy soils going down to a great depth under agricultural land are rare in practice. At all the 16 locations on the four LMM dairy farms the sediments containing the first five metres of groundwater includes one or more clay and/or loam layers, which could interfere with the downward flow of the water; or there was a gravel layer, which might mean that a lot of the water comes from elsewhere. The situation in the LMG multi-screen wells was better, containing relatively more homogeneous sandy sediments.

When abnormal soil layers of this kind occur the question is whether they interfere wholly or partly with downward flow within the plot. The fact that the water cannot drop vertically is not a problem: even in a completely homogeneous soil the water at a depth of five metres below the groundwater table has not infiltrated at precisely the same location at surface level as that in the first metre of groundwater (see Figure 1.6).

Preliminary geological investigation combined with a description of the material sampled at the location of the well can provide information on the probability of abnormal layers present having a more than local effect on the flow of water.

The results of a wide-ranging chemical analysis of the water – especially if it has been sampled at a number of depths in the first five metres of groundwater – can provide an indication of discontinuity in the flow of water, i.e. to what extent changes in water quality are not due to processes such as denitrification occurring in the soil.

A physical, chemical and biological characterization of the soil layers can also provide valuable information to explain changes in water quality with depth. Based on the results of investigations of this kind it is possible to check whether changes in water quality with depth are due to the soil chemistry and biology, i.e. not to the water having a different origin.

Augmenting the tests carried out on groundwater with specific measurements can have added value. By establishing whether denitrification has taken place based on N_2 measurement it may be possible to show that the lower nitrate concentration is unlikely to be due to sampling water that has come from elsewhere. Similarly, determining the age of the water can help to show that the water five metres below the groundwater table is indeed likely to have the same origin. Adding these tests would however require a different type of well from those tested on the plots.

Conclusions
It is not possible, using routine monitoring such as that carried out in a monitoring network or monitoring programme, to determine the origin of the deeper groundwater at all the monitoring locations with sufficient reliability. Using (a combination of) methods not currently used on a routine basis it is possible, however, to determine at specific locations that the groundwater at a greater depth comes from the same plot as the top level of groundwater.

8. Conclusions and considerations

8.1 Conclusions when answering the sub-questions

The following conclusions were drawn when answering the sub-questions:

Sub-question 1: 'Does the nitrate concentration in groundwater under agricultural lands in the sand region decrease with depth in the first five metres of the saturated zone? If so, what is the extent of this decrease and are there differences between regions?'

In the case of nitrate vulnerable ('dry') soils all the data point to the fact that, on average, nitrate concentration does not decrease in the first five metres of groundwater. An increase in nitrate level with depth was found in some wells. In the case of the other soils a decrease in nitrate concentration was found between one and five metres below the groundwater table: the decrease was 15-40% in the case of the neutral (moderately wet and moderately dry) soils and 30-100% in that of the wet soils.

This means that lowering the compliance checking level for nitrate vulnerable soils would have no effect on the nitrate concentration. If the checking level for the other soils were to be lowered, the nitrate target of 50 mg l^{-1} could be met with less strict application standards, but lowering the checking level for these soils only makes sense if the decrease is related to denitrification and the denitrification does not cause some other environmental problem, e.g. an increase in other undesirable substances (see sub-questions 3 and 4).

Sub-question 2: 'If the nitrate concentration decreases with depth, can this be attributed to denitrification, or are there other causes for this decrease?'

The soils in the drainage classes 'wet' and 'neutral' have lower nitrate concentrations at a depth of five metres below the groundwater table than in the first metre of groundwater. This decrease is probably partly due to denitrification, though other factors could also be involved, e.g. hydrology (interfering layers), regional seepage of groundwater from the deeper subsoil and discharge of some participation surplus to surface water. The change in the nitrogen load, particularly in the period following the mid-90s, complicates the interpretation of the nitrate concentrations found with depth.

Sub-question 3: 'If denitrification occurs, to what extent does this process lead to adverse environmental effects such as an increase in the levels of sulphate or heavy metals, or increasing hardness of the groundwater?'

It was not possible to quantify the problem of the increase in other substances (adverse environmental effects) due to denitrification. The heterogeneity of the subsoil in the Dutch sand region is such that there can be large differences in the occurrence or non-occurrence of denitrification and the type of effect denitrification has on water quality over short distances (within a farm).

Lowering the compliance checking level, hence applying less strict application standards, would mean more nitrate leaching into the groundwater below the first metre. In certain soils this could result in higher denitrification and an increase of the levels of other substances. Various detailed studies have indeed shown adverse environmental effects of this kind, but there is insufficient data to quantify the effects in the first five metres of groundwater in the sand region.

Sub-question 4: 'In the clay and peat regions, lowering the compliance checking level in order to be able to apply less strict application standards would lead to insufficient reduction of the nitrate load to surface waters. To what extent does this apply to the sandy soil areas?'

Lowering the compliance checking level in the drained areas of the sand region would mean permitting nitrate concentrations of over 50 mg l^{-1} in the first metre of groundwater, and thus indirectly permitting a higher nitrogen load on surface water than in the case of compliance checking in the first metre. This would result in a nitrogen concentration in the drainage water of over 11.3 mg l^{-1} (on which to base the derogation) and the nitrogen standard for surface water of 2.2 mg l^{-1} would be exceeded by more than a factor of 3-4.

Sub-question 5: 'Regardless of how complex, is it feasible to measure the nitrate concentration at a depth of five metres in the saturated zone, or can the average nitrate concentration in the first five metres be determined?'

It is possible to routinely measure nitrate concentrations at a number of depths in the first five metres of the saturated zone. Such measurements cost more than those in the top level of groundwater.

If possible, permanent multi-screen wells should be installed inside the plots. A number of screens are needed, as no groundwater can be sampled with some of them, e.g. because the screen is in a relatively impermeable stratum or because it has silted up with fine particulate matter. The wells should be installed inside the plots, as with wells outside the plots there is a risk of sampling groundwater of which comes partly from elsewhere. Even when the groundwater flow direction has also be taken into account when installing wells of this kind. Manual techniques are not suitable: the desired depth below the groundwater table cannot always be achieved with manual drilling.

Sub-question 6: 'Regardless of how complex, is it feasible to measure the extent to which denitrification occurs, whether it is sustainable, and whether the process produces undesirable by-products?'

It is not possible, using routine monitoring such as that carried out in a monitoring network or monitoring programme, to determine with sufficient reliability how much denitrification is occurring and whether it is sustainable and does not cause adverse environmental effects. Using a combination of methods not currently used on a routine basis it is possible, however, to determine the occurrence of denitrification and any adverse effects at specific locations, A problem is that there are other processes that can cause deterioration of water quality.

Sub-question 7: 'Regardless of how complex, is it feasible to measure whether the groundwater at five metres depth has the same origins as the groundwater in the first metre?'

It is not possible, using routine monitoring such as that carried out in a monitoring network or monitoring programme, to determine the origin of the deeper groundwater at all the monitoring locations with sufficient reliability. Using a combination of methods not currently used on a routine basis it is possible, however, to determine at specific locations that the groundwater at a greater depth comes from the same plot as the top level of groundwater.

8.2 Overall conclusion

The research question is: 'Is it beneficial to change the compliance checking level for nitrate in groundwater and if so, what are the prerequisites when designing a network to monitor at a different depth?'

Lowering the compliance checking level for nitrate in groundwater in the sand region from the first metre to the first five metres of groundwater, so as to meet the targets in the Nitrates Directive or the Water Framework Directive, would not be opportune, as in the case of nitrate vulnerable ('dry') soils the data available do not substantiate a decrease in nitrate concentration in the first five metres of groundwater. In the other soils the nitrate concentration does decrease between one and five metres below the groundwater table, but there is usually leaching and run-off of nitrate and other nitrogen compounds into surface water.

The decrease in nitrate concentration is 15-40% in the case of the neutral (moderately wet and moderately dry) soils and 30-100% in that of the wet soils, but there is leaching and run-off of nitrate into surface water in the wet soils and to some extent in the neutral soils. In these generally drained soils even a nitrate concentration of 50 mg l^{-1} (equivalent to 11.3 mg of nitrate nitrogen per litre) in the first metre of groundwater will cause the nitrogen standard for surface water of 2.2 mg of nitrogen per litre to be exceeded by a factor of 3-4 on average.

It is not possible, using routine monitoring such as that carried out in a monitoring network or monitoring programme, to determine whether the decrease in the wet and neutral soils is due to the presumed desirable breakdown of nitrate (denitrification) and whether water quality deterioration is due to an increase in the level of other substances (adverse environmental effects), because of the wide spatial variation in nitrate concentrations in the first metre of groundwater, the wide variation in changes in nitrate concentration with depth, the wide variation in the properties of the topsoil and subsoil (e.g. the capacity for breaking down nitrate), and the wide spatial and temporal variation in the soil nitrogen load and rainfall.

8.3 Considerations

Compliance checking level

The study looked at the decrease in nitrate concentration with depth in the first five metres of groundwater. In the debate on the compliance checking level it remained an open question whether lowering the level would mean checking – instead of in the first metre of groundwater – in the fifth metre below the groundwater table or the first five metres (i.e. the average nitrate concentration in the groundwater between the groundwater table and five metres below it). The latter would be more in line with the formulation in the draft guide on Monitoring for the Nitrates Directive but only produces about half the decrease in nitrate concentration (if there is one).

Defining infiltration areas

Within the sand region there is a difference between infiltration areas and drained areas. In the drained areas leaching and run-off to surface water takes place via shallow groundwater flows, unlike in the infiltration areas. The study distinguished between nitrate vulnerable ('dry') soils, neutral soils and wet soils. It examined whether there is a decrease in nitrate concentration with depth in these soils. The dry soils are situated in the infiltration areas, the wet ones in the drained areas. Whether all or part of the neutral soils are in drained areas or whether part of them are in infiltration areas is not known. It might be possible technically to ascertain this, but we do not know whether it would make sense to do so in practice.

Sustainability of denitrification

The study did not look at the sustainability of denitrification, i.e. how long denitrification in the subsoil can continue. As far as we know there are no data available to estimate this, either on a national scale or on the scale of the sand region.

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Appendix 1 Denitrification

Denitrification is the microbial process whereby nitrate and nitrite (NO_2-) in the soil are converted into the gaseous nitrogen compounds N_2, N_2O and NO_x. Denitrification only takes place in anaerobic (oxygen-free) conditions in the soil. The groundwater level and fluctuations in it are a factor in the frequency with which such conditions occur. The main energy source for denitrifying bacteria is readily degradable organic matter. In addition to organic matter, some bacteria can also use inorganic compounds as an energy source, e.g. the iron sulphide (FeS_2) present in pyrite. Glauconite [$(K,Na)(Fe^{3+},Al,Mg)_2(Si,Al)_4O_{10}(OH)$], siderite ($FeCO_3$) or adsorbed iron are other potential energy sources or reductors of nitrate.

The process whereby nitrate is converted into molecular nitrogen involves a number of steps:

[1] $NO_3^- \Rightarrow NO_2^- \Rightarrow NO \Rightarrow N_2O \Rightarrow N_2$

Denitrification reactions are usually microbially controlled, but whether the reaction takes place depends on the presence of reactive phases (energy sources) in aquifers (degradable organic matter, pyrite and siderite).

Reactive ferrous phases

Pyrite

In the case of iron sulphides such as pyrite two reduced compounds are involved, Fe(II) and S(-I), both of which can be oxidized by nitrate. In the incomplete oxidation of pyrite only S(-I) is oxidized by nitrate:

[2] $14\ NO_3^- + 5\ FeS_2 + 4\ H^+ \Rightarrow 7\ N_2 + 10\ SO_4^{2-} + 5\ Fe^{2+} + 2\ H_2O$

The reaction consumes acid and releases sulphate. In the complete oxidation of pyrite the Fe(II) mobilized is also oxidized:

[3] $5\ Fe^{2+} + 14\ NO_3^- + 12\ H_2O \Rightarrow ½\ N_2 + 5\ Fe(OH)_3 + 9\ H^+$

Siderite

The reduction of nitrate by Fe(II) in siderite takes places as follows:

[4] $2\ NO_3^- + 10\ FeCO_3 + 14\ H_2O \Leftrightarrow N_2 + 10\ FeOOH + 8\ H_2CO_3 + 2\ HCO_3^-$

Unlike in the case of denitrification by pyrite, Fe always has to precipitate as an oxide (cf. equations 2 and 4). Denitrification by siderite can be distinguished from denitrification by organic matter by the much larger amount of inorganic carbon produced (TIC: H_2CO_3 + HCO_3^-). The main difference from denitrification by pyrite is that no sulphate is produced.

Glauconite

Iron that is structurally bonded in silicate or sulphate minerals is redox reactive (Hansen et al., 1996; Ernstsen et al., 1998; Kostka et al., 1999; Rivas Perez, 2005). This is also true of

the iron in glauconite. High Fe_2O_3 and K_2O contents and a particular green colour of sediments indicate that these sediments contain a lot of glauconite. Fanning et al. (1989) have established that the Fe(II)/Fe(III) ratio between the oxidized and reduced glauconitic zones ranges from 0-0.2 to 0.35. We also know that Fe(II) is redox reactive with nitrate or nitrite (Sorensen and Thorling, 1991; Nielsen and Nielsen, 1998; Ratering and Schnell, 2001; Straub et al., 2001). It is therefore legitimate to ask whether glauconite is a potential reductor of nitrate.

Organic matter

The redox reaction for the denitrification of organic matter is:

[5] $4\ NO_3^- + 5\ CH_2O \Rightarrow 2\ N_2 + 4\ HCO_3^- + H_2CO_3 + 2\ H_2O$

Here the composition of organic matter is simplified to CH_2O.

What is important, however, is not only the absolute concentration of organic matter but also whether it is suitable for biological degradation. There are a number of ways of determining the degradability of organic matter. In the case of topsoil this is often done by measuring the amount of CO_2 produced during aerobic or anaerobic incubation.

Based on the experiments by Cuypers et al. (2002), for the purposes of the TNO study (see chapter 6) it was assumed that bulk organic matter (BOM) condensed in a thermogravimetric profile (105-800ºC) is more stable at higher temperatures. The hypothesis, then, is:

> *Organic matter that generates hydrocarbons at lower temperatures is available first for biological degradation. In other words, thermal stability is a measure of reactivity.*

This means that the weight loss in a TGA profile between 105 and 350ºC should be due to the unstable organic matter, and the loss between 350 and 550º from stable organic matter.

Potential denitrification

The study carried out by Alterra determined the potential denitrification rate of the subsoil (see chapter 5). Potential denitrification is the maximum denitrification that can occur in field conditions at 20ºC. It is defined here as the denitrification during the incubation of soil at 20ºC with a surplus of nitrate under anaerobic conditions (Focht, 1978; Bijay-Singh et al., 1988).

Differences in potential denitrification rates between soil samples are due mainly to differences in the availability of the energy source. In the topsoil the potential denitrification rate is related to the amount of degradable organic carbon (C) (Burford and Bremner, 1975). In the subsoil pyrite can also be used as an energy source. Other factors besides the presence of an energy source can result in different potential denitrification rates, e.g. pH, salt concentration and the presence of toxic compounds (e.g. heavy metals).

For denitrification to take place there must be active denitrifying bacteria in the soil. These are always present in the topsoil, and the literature shows that they are also present in the subsoil (at 1.5-10 m) (Lind and Eiland, 1989; McCarty and Bremner, 1992; Sotomayor and Rice, 1996; Yeomans et al., 1992). We cannot rule out the possibility that there will sometimes be no active population of denitrifying bacteria in the deep subsoil. This will be

the case, for example, in soil strata that have never contained nitrate (e.g. because all the nitrate has been denitrified in higher strata). In these strata it may be that no potential denitrification can be shown to occur during a brief incubation, even though an energy source is present. Research by Hartog (2003) has shown that denitrifying bacteria in samples from the saturated zone where there is no nitrate need an adaptation period of a month to reach full denitrification. The potential denitrification rate found during a brief incubation is thus an indicator of the presence of an energy source and/or active denitrifying bacteria.

There is not much likelihood that the denitrification rate under field conditions is the same as the potential denitrification rate, as one of the controlling factors (oxygen, temperature and nitrate) is usually limiting. If no potential denitrification can be shown to occur there will be no denitrification taking place under field conditions either.

Appendix 2 Undertakings to the House of Representatives on Compliance Checking Level

Source: Horeman et al. (2005)

No.	Subject	Description	Source	Date
1.	Compliance checking level	'Lowering the compliance checking level from the current one is only possible if it can be proved scientifically that there would be no harmful consequences. I shall ensure that the 2007 evaluation provides a sound scientific account of the possibilities and consequences of lowering it, so that they can be taken into account when laying down the standards for 2008 and subsequent years. This will also link up with the implementation of the Water Framework Directive and the new Groundwater Directive.'	House of Representatives, 2003-2004 session, 28 385, No. 34	8 June 2004
2.	Compliance checking level, derogation, LMM	'Mr Oplaat has asked about the monitoring technique and monitoring depth. The National Programme for Monitoring the Effectiveness of Minerals Policy (LMM) monitors in the same way as is done in other countries. The network needs to be modified to take advantage of the 250 kg derogation. Also after an initial derogation period, as the agreement in Brussels was that the derogation standard should be dependent on the evaluation of the results. With this in mind, the number of monitoring points is to be dramatically augmented with 300 dairy farms.'	House of Representatives, 2003-2004 session, 28 385, No. 38	12 July 2004
3.	Compliance checking level	'As stated at the meeting of the Parliamentary Standing Committee and the Minister(s) on 31 August, based on the evaluation of the Fertilizers Act in 2007 the Netherlands will decide whether it is possible to lower the compliance checking level for sandy soils, and if so, how.	House of Representatives, 2003-2004 session, 28 385, No. 43	23 September 2004

4.	Balance fertilization (phosphate), compliance checking level	'The aim is to achieve balance fertilization in the case of phosphate by 2015. The Commission is not prepared to derogate from the agreements at present. The agreements on the matter – this also applies to monitoring depth – are part and parcel of the package. The aim, however, is to produce sufficient scientific evidence from the next evaluation to justify amendments.'	House of Representatives, 2003-2004 session, 28 385, No. 44	19 October 2004
8.	Compliance checking level	'We are currently examining what lowering the monitoring depth would mean and to what extent it could be done in the current monitoring network. […] We are working on this at present. We shall take this into account when updating the monitoring programme and in the evaluation. […] To sum up, we are monitoring, we are examining whether it is possible. If it makes sense we shall do it. If it does not make sense we shall not.'	Senate, Proceedings 2004-2005, No. 34, pp. 1605-14	13 September 2005
16.	Compliance checking level, nitrogen application standards for arable land and horticulture	'The National Institute for Public Health and the Environment is currently carrying out an exploratory study which will provide the basis for a forthcoming study to answer the question of whether it makes sense to check for compliance with the 50 mg standard at a greater depth, and if so, how best to carry out this check. The study should produce results for the evaluation of the Fertilizers Act in 2007, where they can play a role in deciding on nitrogen standards for arable farming and horticulture from 2008.'	House of Representatives, 2004-2005 session, 29 930, No. 6	5 April 2005

Appendix 3: Nitrate concentrations in top-level and shallow groundwater by ecodistrict

The nitrate concentration in the sand region decreases markedly with depth (see Figure 1.5 in chapter 1). The average nitrate concentration in groundwater under agricultural land was 75 mg l^{-1} in the first metre of groundwater, on average at 1.4 m below ground level, in the 2000-2002 period. In the medium-deep groundwater from agricultural plots the concentration in the same period was only 10 mg l^{-1}. Not only the concentration but also the number of observations that exceed the EU limit of 50 mg l^{-1} decreases with depth from over 65% to approximately 6% (see Figure 1.5).

Nitrate concentrations in the Dutch subsoil can differ substantially from one region to another (Broers et al., 2004). Allowance needs to be made for the fact that there can also be regional differences in nitrate concentrations in the first metre. Figure 3.1 shows the average nitrate concentrations in upper most and shallow groundwater under agricultural land in the sand region by geomorphological region.

With an average groundwater level of approximately 1.4 m below surface level, then, the nitrate concentration in the first metre of groundwater was compared with that in the stratum between approximately 6.4 and 8.4 m below the water table. As for that depth the analysis only included observations from the 2000-2004 period with water less than 25 years old, it is not so likely that the decrease is due to cleaner infiltration water from the period when farming was less intensive. On average this will be rainwater that infiltrated the soil during the 1985-95 period.

The difference between the nitrate concentrations in the top level of groundwater and the shallow groundwater is in the order of 50% on average. In the former high moorland and the stream valleys nitrate has virtually disappeared from the shallow groundwater, whereas on the perimeter of the push-moraines higher concentrations are found in the shallow groundwater than in the top level. We find a similar pattern in the dry soils (Gt VII and Gt VIII: see Figure B3.2), the neutral soils (Gt V and Gt VI: see Figure B3.3) and the wet soils (Gt I t/m Gt IV: see Figure B3.4).

The link between the nitrate concentrations in the top level of groundwater and the shallow groundwater is indirect, as they were not measured at the same locations. In this study, moreover, the change in the first five metres is important, and the observations in the shallow groundwater fall outside this (6.4-8.4 m below the groundwater table on average).

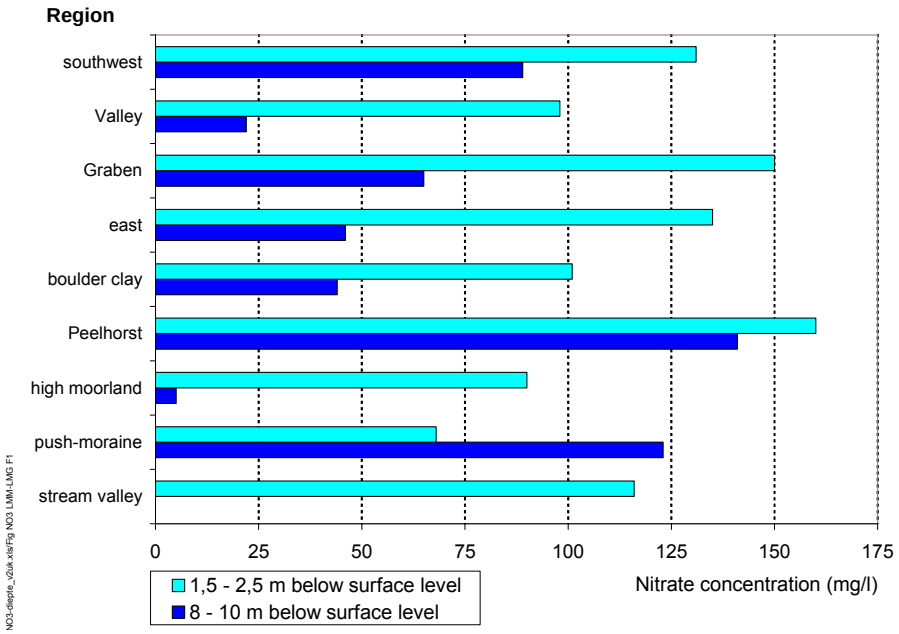

Figure B3.1: Nitrate concentrations in the top level of groundwater (1992-2003, approximately 295 farms) and shallow groundwater (2000-2004, approximately 100 wells) under agricultural land in the various geomorphological regions in the sand region of the Netherlands.

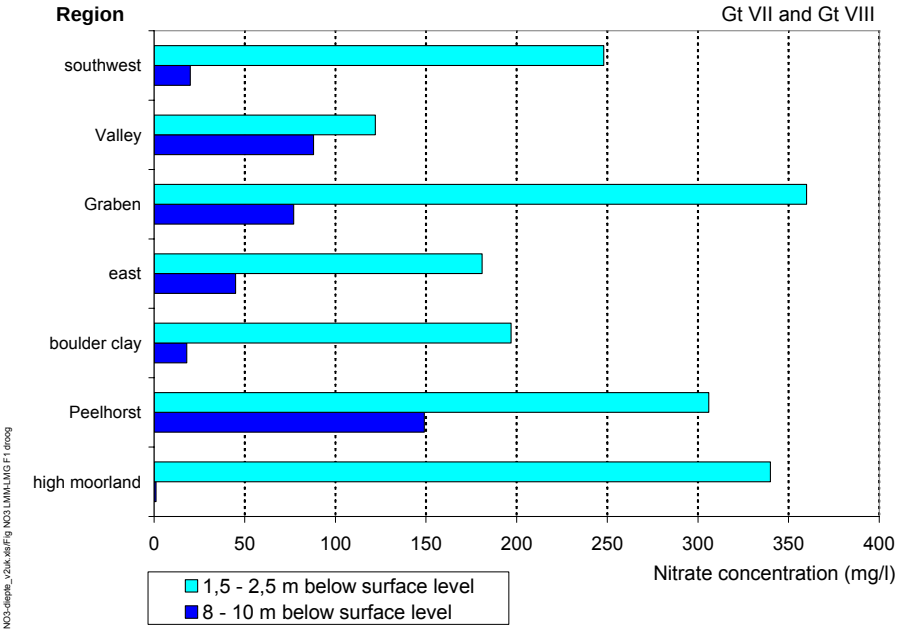

Figure B3.2: Nitrate concentrations in the top level of groundwater (1992-2003, approximately 295 farms) and shallow groundwater (2000-2004, approximately 100 wells) under agricultural land with dry soils (Gts VII and Gts VIII) in the various geomorphological regions in the sand region of the Netherlands.

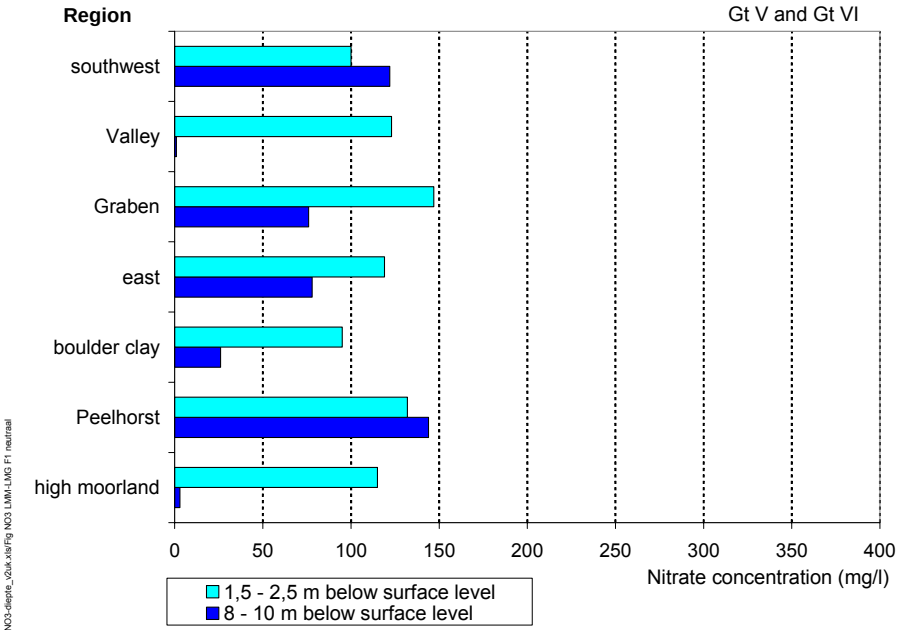

Figure B3.3: Nitrate concentrations in the top level of groundwater (1992-2003, approximately 295 farms) and shallow groundwater (2000-2004, approximately 100 wells) under agricultural land with neutral soils (Gts VII and Gts VIII) in the various geomorphological regions in the sand region of the Netherlands.

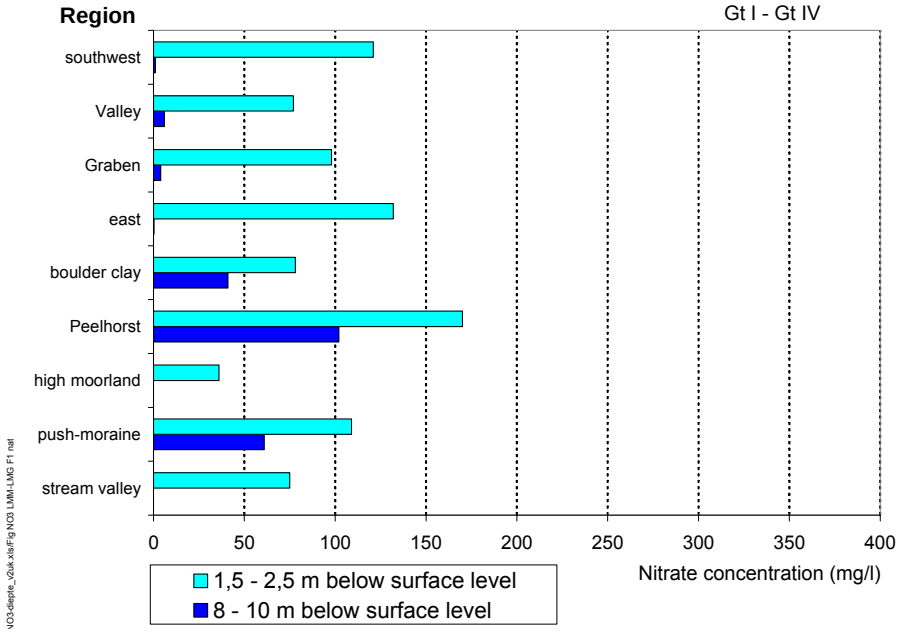

Figure B3.4: Nitrate concentrations in the top level of groundwater (1992-2003, approximately 295 farms) and shallow groundwater (2000-2004, approximately 100 wells) under agricultural land with wet soils (Gts VII and Gts VIII) in the various geomorphological regions in the sand region of the Netherlands.

Appendix 4: Drilling method and bore description

Drilling method

The vibration drilling was carried out by Eijkelkamp/Giesbeek using the method described below.

The heart of the sonic drilling system consists of two excentres driven by high-speed hydromotors. The high-frequency vibrations generated are transferred efficiently to the drilling rods. The vibration causes the soil directly surrounding the drive cone and casing to behave like a fluid. This process reduces friction so that the Sonic equipment swiftly penetrates sandy, gravelly and clay soils.

The AquaLock is a patented sampling method that really becomes effective when used in combination with the Sonic drilling module. The sampler (2, 3 or 4 m long) is lowered to the target depth at the same rate as in the lost cone method. During penetration a piston is held down by filling the interspace in the AquaLock sampler with water, so a drilling cone is not needed. Once the target depth is reached, the water is allowed to escape to the rods above. The sonic vibration cuts a good-quality core, with only the outer layer of 1-2 mm visibly influenced by the vibration. Samples can be taken e.g. in clay and in coarse gravelly sand. For the next sample the sampler can be lowered through the predrilled borehole and reopened at the desired depth. The drilling rod has to be inserted and removed each time, but sampling is very fast and easy using this method. Water is finally used to extrude the sample from the sampler into a sample gutter, foil or stainless steel tube (VOCs).

Bore description

Filing information on subsoil structure starts with ascertaining the properties of the soil strata, data which is obtained from drillings. A written description of the samples taken is essential, therefore. Where information is stored digitally we find that the properties observed can only be used effectively if the descriptions are standardized. First and foremost this means standardizing the terms in common use, starting with the classification of soil types. NEN standards 209/210 and 213 were used for this in the past. These were amended to some extent by the Stiboka classification (De Bakker and Schelling, 1966), which laid down standards for clay, loam and peat as well as sand. NEN 5104 combines the two classifications.

This document also gives values for certain properties that do not apply to SBB5.1 but to bore descriptions already entered in the TNO-NITG Geological Information Databank (‘DINO’).

The full report on the standard bore description can be found at the following URL:
http://dinolks01.nitg.tno.nl/dinoLks/about/dataTypes/bor/resources/sbb51.pdf

Appendix 5: Calculating the amount of reactive iron

In order to calculate the amount of reactive iron in a sediment, first an adjustment has to be made for the iron present in the silicate fraction of the sediment. The silicate fraction in Dutch sediments comprises mainly quartz, feldspars and clayey minerals. When making the Fe adjustment we assume that the quartz and feldspars do not contain any iron and that the clayey minerals are in the lutum fraction. As Figure B4.1 shows, the sediments examined here with an aluminium content of below 3% contain hardly any lutum. Above the 3% aluminium level the clay content of Dutch sediments rises linearly with aluminium (Huisman and Kiden 1998, Figure 6.6 in chapter 6). When calculating reactive Fe only sediments with an aluminium oxide content of above 3% are adjusted for Fe in clay using the formula Fe_2O_3 - Al_2O_3 (XRF) / 4 then converted to % Fe.

Figure 6.4 shows the reactive iron that remains after this adjustment in relation to Al_2O_3. It shows that drillings 28F and 33G differ markedly from the other drillings: only samples from drillings 28F and 33G contain over 0.5% reactive Fe.

‘Pyrite Fe’ is calculated by assuming that all the S is present as FeS_2 and stoichiometrically converting this to ‘pyrite Fe’. ‘Non-pyrite reactive Fe’ is then calculated as the difference between ‘reactive Fe’ and ‘pyrite Fe’. Non-pyrite Fe can in fact comprise both Fe(hydr) oxides such as siderite and, in the sediments examined here, also glauconite. As there is hardly any sulphur present in the drillings, no plots of ‘pyrite Fe’ or ‘non-pyrite reactive Fe’ were made, which means that hardly any measurable quantities of pyrite were found at the three locations. The consequence is that little if any nitrate is reduced by oxidation of pyrite.

Appendix 6: Calculating the amount of reactive organic matter

According to Cuypers et al. (2002) the differences between the amorphous and condensed soil organic matter (SOM) are as follows:

- Condensed SOM is less polar than amorphous SOM.
- Condensed SOM contains more aromatics than amorphous SOM.
- SOM subjected to a higher degree of diagenesis is more condensed than the original material.
- Following NAOH extraction or oxidation SOM is more condensed than the original material.
- Humic acids are more condensed than fulvic acids.
- Coal and charcoal are specific condensed components of SOM.

Based on these differences and the experiments by Cuypers et al. (2002), for the purposes of this study it is assumed that SOM condensed in a thermogravimetric (TGA) profile (105-800ºC) is more stable at higher temperatures than amorphous SOM. The hypothesis is that organic matter that generates hydrocarbons at lower temperatures could be available first for biological degradation. In other words, thermal stability is a measure of reactivity.

This means that the weight loss in a TGA profile between 105 and 350ºC should be due to the unstable organic matter, and the loss between 350 and 550º from stable organic matter. The organic matter is combusted in the presence of added oxygen.

Instead of weight loss, a Pollut-Eval measures the hydrocarbons released on the pyrolysis of organic matter as a function of oven temperature. The detector only measures the hydrocarbons released, so unlike the TGA it is insensitive to any water and sulphur oxide that are released. The second difference is that the organic matter does not combust but is heated in a nitrogen atmosphere of 105-600ºC. In a Pollut-Eval analysis approximately 80 milligrams of sediment is heated to 650ºC in an inert atmosphere (programmed pyrolysis). The temperature is set to rise by 5ºC per minute after the oven has been kept at 5C for 105º minutes. The hydrocarbons released are measured using a Flame Ionization Detector (FID). The CO and CO_2 released during the heating process are measured constantly using an infrared cell.

Figure B6.1 shows a typical ‘pyrogramme’ resulting from a Pollut-Eval analysis. It is divided into four temperature ranges (Q0-Q3). The ratio between the four calculated values (areas) characterizes the type of organic matter. Petrol, for example, will have a high Q0 value, whereas diesel pollution will have a higher Q1. The sum of Q0, Q1 and Q2 can be taken as the unstable organic matter content (105-350ºC) and Q3 as the stable organic matter content (>350ºC).

The decisive factor in the reactivity is the ratio between the unstable (105-350ºC) and stable (>350ºC) fraction, which is defined here based on the Pollut-Eval parameters Q2 and Q3.

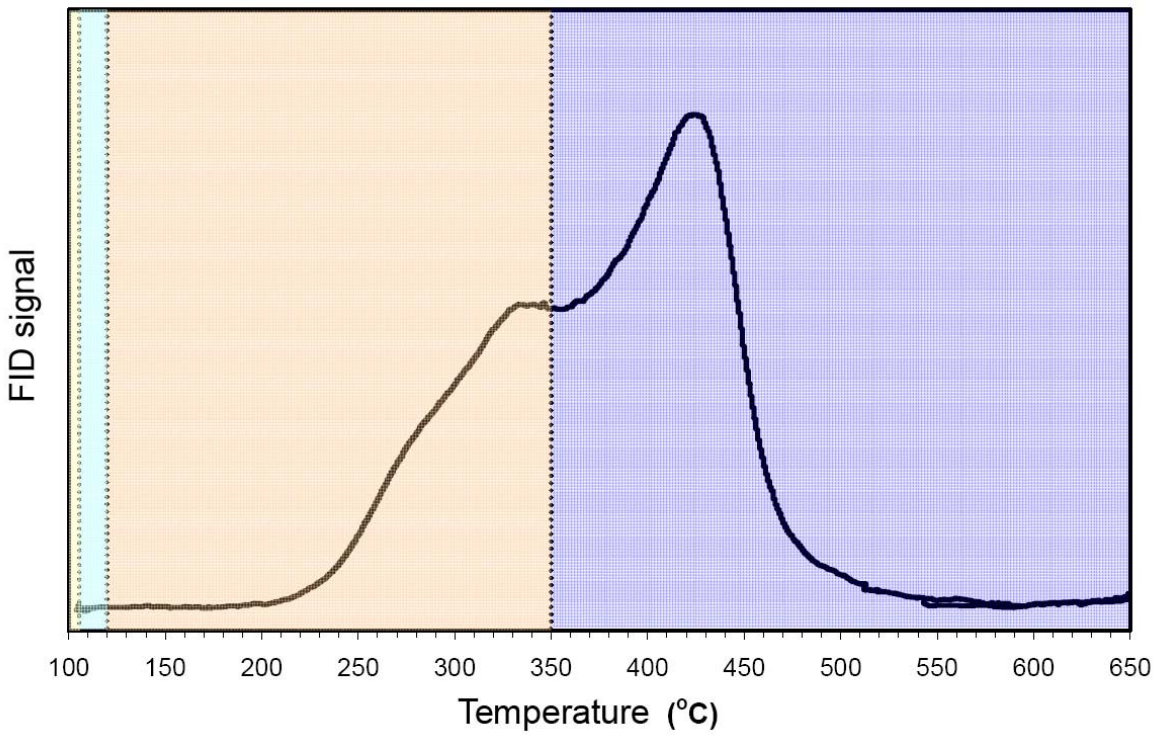

Figure B6.1 Example of a Pollut-Eval pyrogramme. The vertical dotted lines show the Q0, Q1, Q2 and Q3 areas, with Q0 the amount of hydrocarbons released at 105ºC (isotherm); Q1 is the amount of hydrocarbons released between 105ºC and 120ºC; Q2 is the amount between 120ºC and 350ºC; and Q3 is the amount of hydrocarbons released from the pyrolysis of organic matter between 350ºC and 650ºC.

Appendix 7: Concentrations of trace elements

The figures below show the concentrations of a number of trace elements in the first five metres of groundwater on the four dairy farms in the preliminary study. Results of the third round. These are the elements not included in the main report, namely arsenic, cadmium, chrome, copper, nickel and zinc.

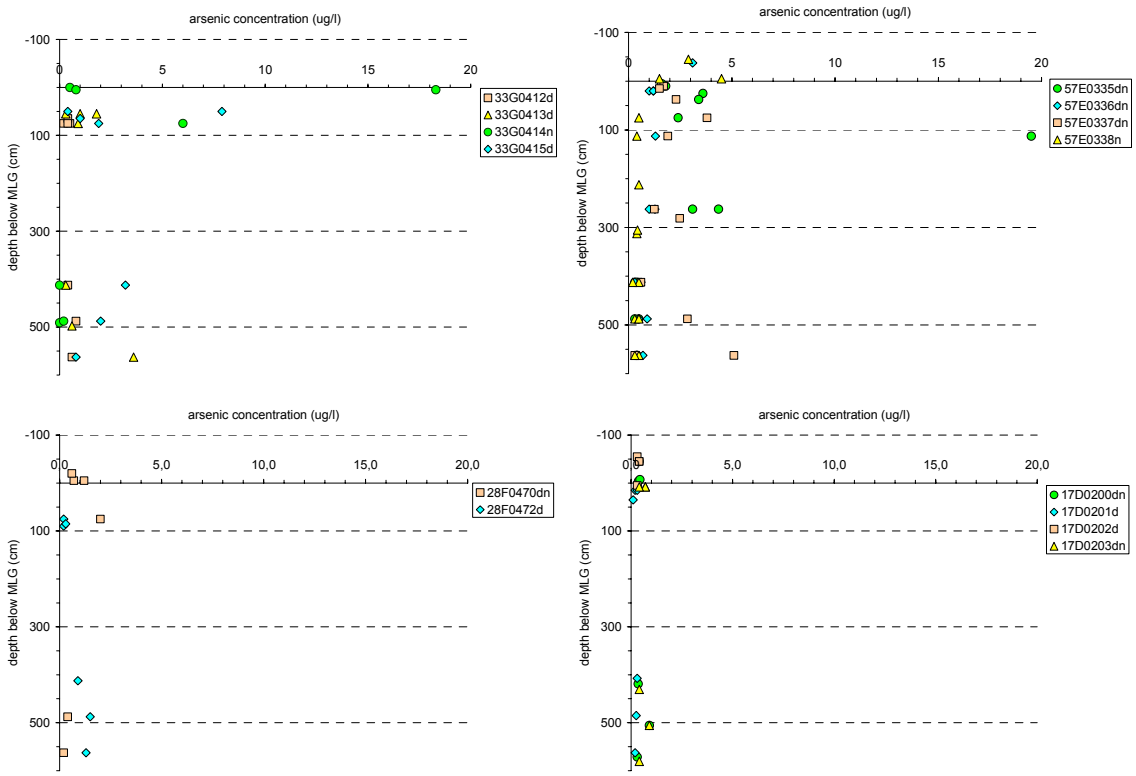

Figure B7.1 Arsenic concentrations at various depths on the four dairy farms in sampling round 3. Top left Spankeren (33G), top right Maarheeze (57E), below left Nutter (28F) and below right Nieuweroord (17D).
Drainage classes: d = dry, dn = neutral, n = wet.

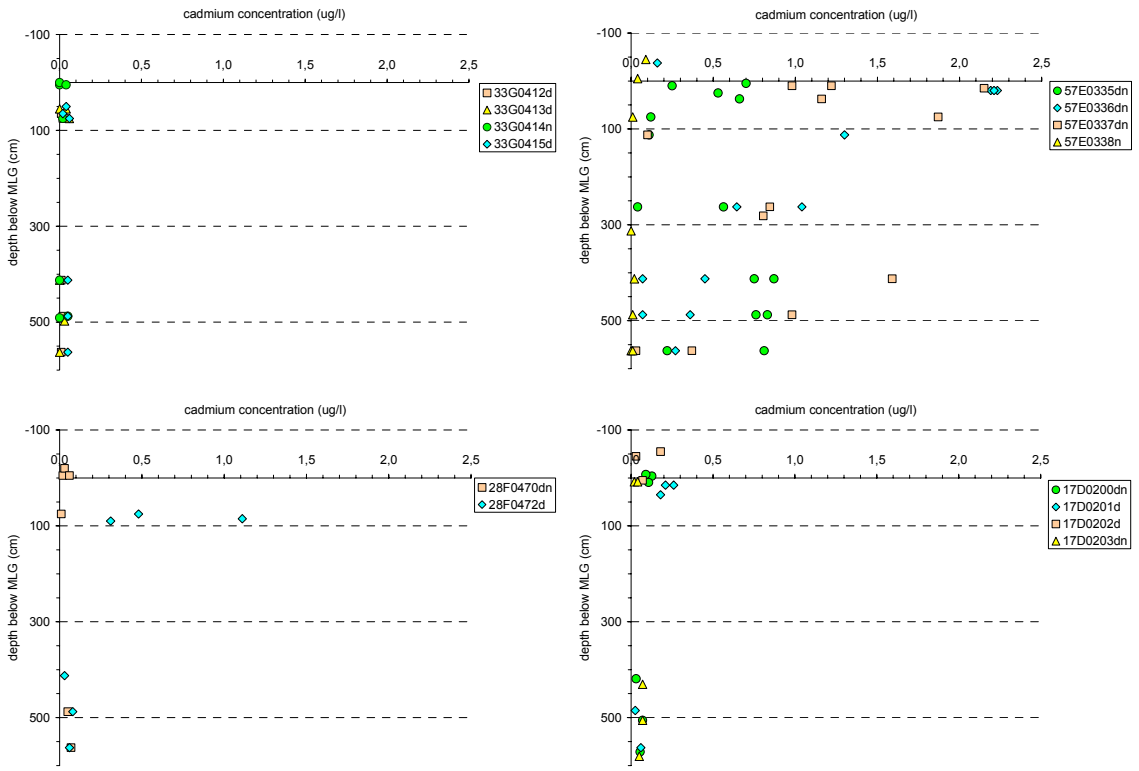

Figure B7.2 Cadmium concentrations at various depths on the four dairy farms in sampling round 3. Top left Spankeren (33G), top right Maarheeze (57E), below left Nutter (28F) and below right Nieuweroord (17D).
Drainage classes: d = dry, dn = neutral, n = wet.

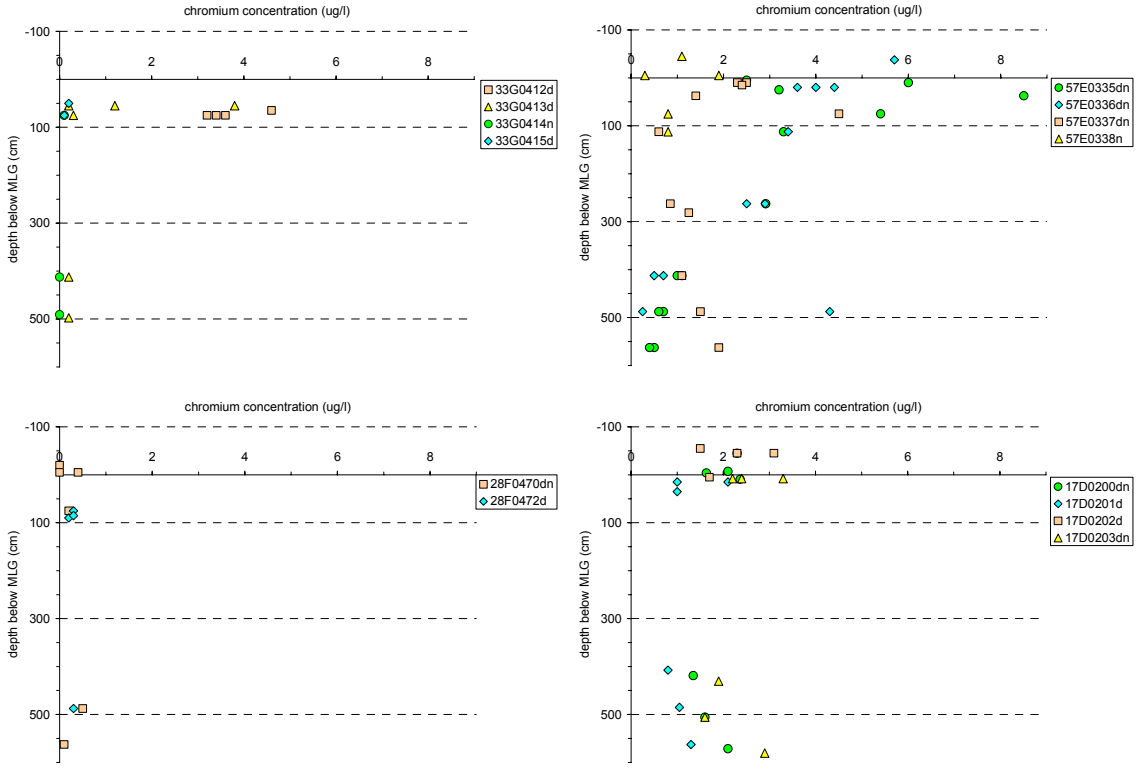

Figure B7.3 Chromium concentrations. For an explanation see the text for Figure B7.2.

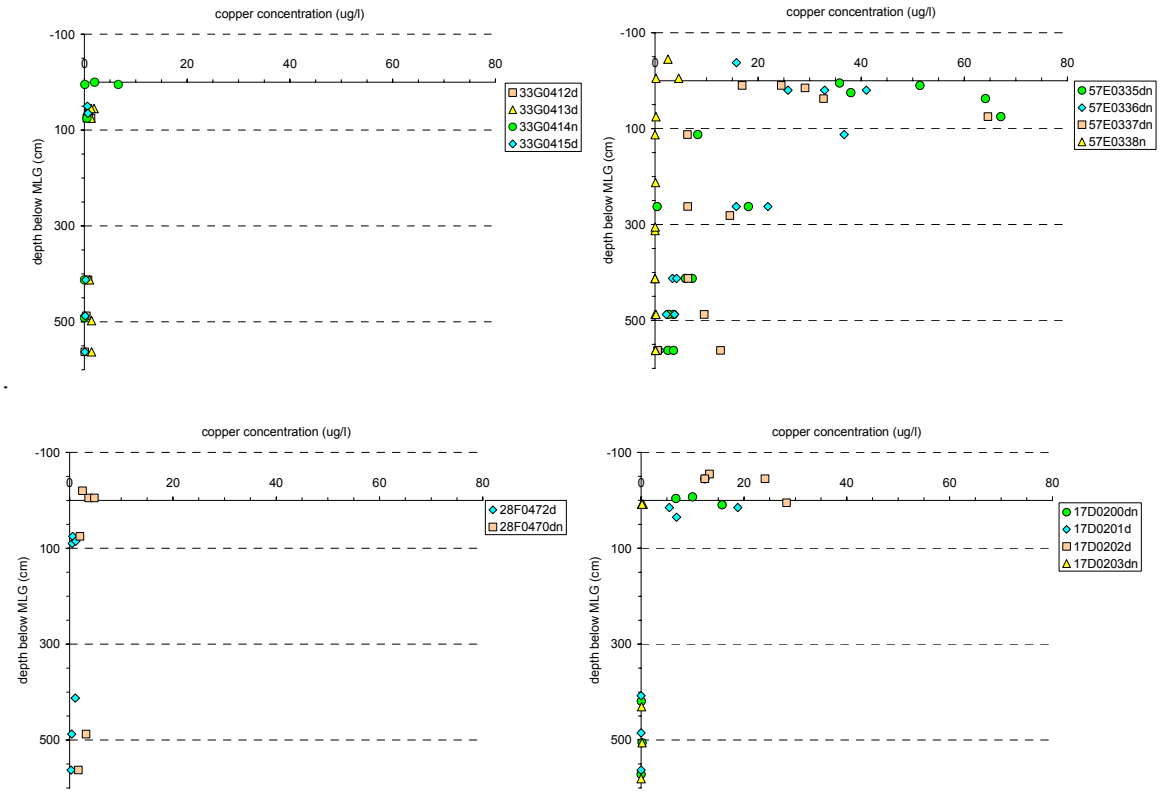

Figure B7.4 Copper concentrations at various depths on the four dairy farms in sampling round 3. Top left Spankeren (33G), top right Maarheeze (57E), below left Nutter (28F) and below right Nieuweroord (17D).
Drainage classes: d = dry, dn = neutral, n = wet.

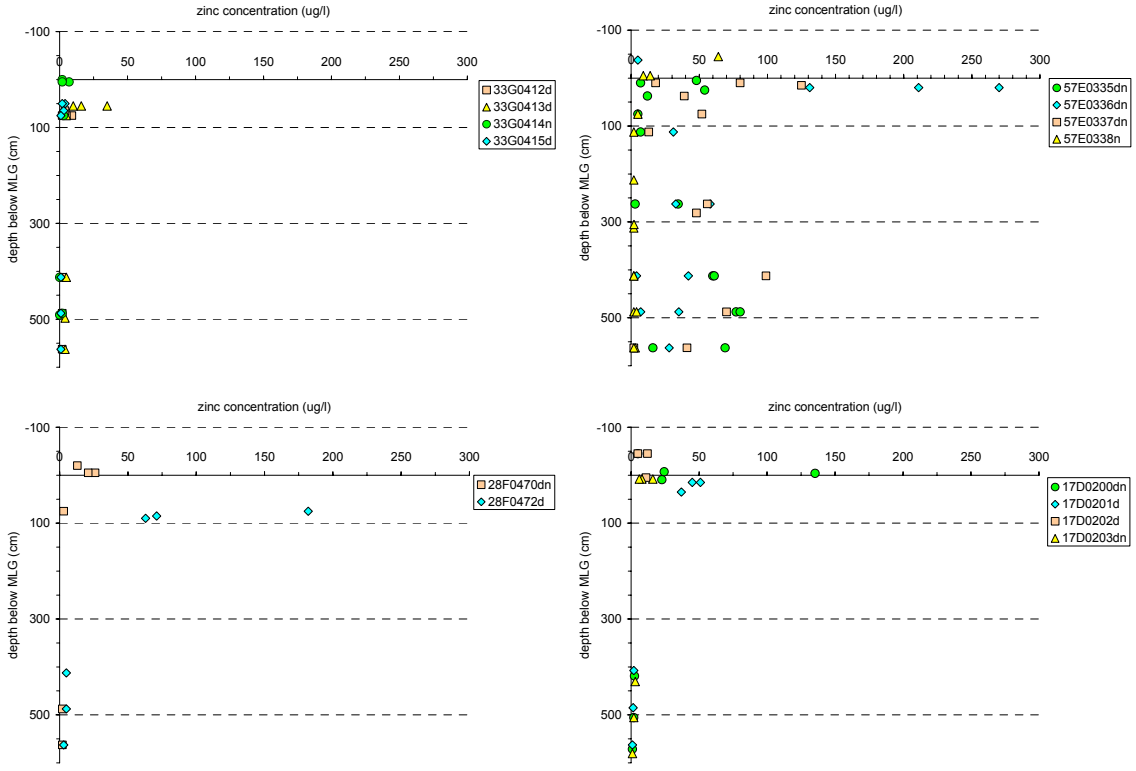

Figure B7.6 Zinc concentrations. For an explanation see the text for Figure B7.5.

Appendix 8: Results of potential denitrification and analyses of $CaCl_2$ extract

DNP = potential denitrification; pH = acidity; SON = soluble organic nitrogen
SOC = soluble organic carbon (for explanation see section 5.2).
Depth in centimetres below surface level.

Nieuweroord

Profile No.	Stratum, cm (below surface level)	DNP	pH	NO_3-N	NH4-N	SON	SOC
		µg N/kg/day		mg/l	mg/l	mg/l	mg/l
17D0201	206-228	0	4.2	n/a	28	n/a	416
17D0201	310-331	0	4.3	n/a	13	n/a	272
17D0201	354-332	0	4.3	n/a	18	n/a	231
17D0201	379-400	0	4.4	n/a	22	n/a	154
17D0201	483-505	0	4.4	8	46	n/a	111
17D0201	528-548	76	5.0	9	86	n/a	76
17D0201	548-565	0	4.4	7	136	n/a	77
17D0201	583-605	0	4.3	n/a	415	n/a	69
17D0201	679-701	0	4.0	n/a	251	n/a	78
17D0201	708-730	1	4.0	n/a	247	n/a	79
17D0201	779-801	0	4.1	n/a	239	n/a	117
17D0202	158-180	0	4.2	10	24	n/a	171
17D0202	232-254	0	4.1	n/a	312	n/a	70
17D0202	258-278	0	4.0	n/a	311	n/a	60
17D0202	283-305	0	5.2	n/a	253	n/a	60
17D0202	384-405	0	3.9	n/a	274	n/a	69
17D0202	437-459	0	4.0	n/a	258	n/a	62
17D0202	487-509	0	4.0	n/a	231	n/a	72
17D0202	549-571	0	4.3	n/a	174	n/a	80
17D0202	675-697	0	4.4	n/a	157	n/a	56
17D0200	281-303	0	4.2	n/a	562	n/a	90
17D0200	337-359	0	4.1	n/a	454	n/a	60
17D0200	401-423	0	4.1	n/a	440	n/a	156
17D0200	444-466	0	4.1	n/a	370	n/a	61
17D0200	495-517	15	4.2	9	356	n/a	185
17D0200	636-658	0	4.2	n/a	324	n/a	128
17D0200	764-786	0	4.4	n/a	251	n/a	163
17D0200	909-931	0	5.0	n/a	88	n/a	38
17D0203	113-135	0	4.1	42	357	n/a	83
17D0203	137-159	0	4.2	12	432	n/a	56
17D0203	251-273	0	4.1	n/a	380	n/a	72
17D0203	382-404	0	4.2	n/a	375	n/a	68
17D0203	442-464	0	4.2	n/a	269	n/a	67
17D0203	581-603	0	4.2	n/a	163	n/a	56
17D0203	655-677	0	5.7	n/a	51	n/a	35
17D0203	692-714	0	4.4	n/a	196	n/a	99
17D0203	763-785	0	4.5	n/a	180	n/a	192

Spankeren

Profile No.	Stratum, cm below surface level	DNP	pH	NO_3-N	NH4-N	SON	SOC
		µg N/kg/day		mg/l	mg/l	mg/l	mg/l
33G0415	235-257	5	7.0	33	n/a	n/a	76
33G0415	293-315	118	7.9	9	5	n/a	63
33G0415	317-339	2	7.9	24	4	n/a	59
33G0415	334-356	80	8.0	31	12	n/a	137
33G0415	372-394	9	8.0	13	n/a	n/a	31
33G0415	476-498	117	7.7	n/a	12	n/a	118
33G0415	689-711	1	7.4	43	5	n/a	57
33G0415	747-769	0	7.9	47	6	n/a	47
33G0415	794-816	2	6.5	45	7	n/a	35
33G0412	242-264	0	7.5	30	6	n/a	97
33G0412	265-287	0	7.8	25	4	n/a	79
33G0412	331-353	0	7.9	17	n/a	n/a	41
33G0412	377-399	1	8.1	46	n/a	n/a	38
33G0412	470-492	562	8.1	20	n/a	n/a	41
33G0412	580-602	0	8.0	19	n/a	n/a	32
33G0412	669-691	0	7.9	16	6	n/a	44
33G0412	727-749	0	7.3	25	8	n/a	39
33G0412	756-778	0	8.0	42	n/a	n/a	39
33G0413	292-314	0	8.0	51	7	n/a	65
33G0413	371-393	3	8.0	30	7	n/a	78
33G0413	413-435	0	8.1	28	6	n/a	52
33G0413	452-474	0	8.0	29	5	n/a	32
33G0413	533-555	15	8.0	27	8	n/a	70
33G0413	566-588	852	7.8	99	19	n/a	214
33G0413	592-614	32	8.0	26	8	n/a	69
33G0413	691-713	12	8.2	25	10	n/a	79
33G0413	757-779	0	8.2	34	7	n/a	49
33G0413	792-814	36	7.9	24	6	n/a	115
33G0414	69-91	14	7.8	5	n/a	n/a	154
33G0414	109-131	16	8.0	n/a	10	n/a	108
33G0414	141-163	0	8.1	n/a	14	n/a	125
33G0414	148-170	0	8.1	n/a	10	n/a	114
33G0414	227-249	621	7.7	n/a	45	10	229
33G0414	328-350	1425	7.7	n/a	37	n/a	193
33G0414	386-408	0	7.6	n/a	32	n/a	165
33G0414	440-462	120	8.0	n/a	12	n/a	107
33G0414	515-537	331	8.1	n/a	13	n/a	77
33G0414	550-572	4013	6.5	n/a	7	7	165

Nutter

Profile No.	Stratum, cm below surface level	DNP	pH	NO_3-N	NH4-N	SON	SOC
		µg N/kg/day		mg/l	mg/l	mg/l	mg/l
28F0470	168-190	0	5.4	6	5	n/a	93
28F0470	221-243	0	5.4	7	5	n/a	69
28F0470	248-270	0	5.4	8	6	n/a	67
28F0470	305-327	0	5.7	10	6	n/a	70
28F0470	347-369	18	5.7	7	4	n/a	61
28F0470	383-405	0	5.4	7	n/a	n/a	52
28F0470	513-535	0	5.5	9	n/a	n/a	53
28F0470	604-626	2	5.6	6	3	n/a	42
28F0470	715-737	67	5.8	6	n/a	n/a	31
28F0473	272-294	0	3.8	35	10	8	87
28F0473	329-351	0	3.8	24	5	n/a	48
28F0473	351-373	3	3.8	30	11	n/a	68
28F0473	429-451	0	4.0	24	n/a	n/a	40
28F0473	473-495	0	3.9	19	6	n/a	44
28F0473	539-561	0	4.0	22	9	n/a	38
28F0473	626-648	20	3.9	33	5	n/a	45
28F0473	739-761	0	6.0	n/a	9	n/a	61
28F0472	472-494	0	3.9	21	6	n/a	47
28F0472	654-676	0	4.3	10	6	n/a	32
28F0472	716-738	0	5.1	11	n/a	n/a	22
28F0472	754-776	0	4.9	14	n/a	n/a	24
28F0472	935-957	0	4.5	9	5	n/a	28
28F0471	366-388	0	4.1	19	17	n/a	84
28F0471	386-408	0	4.0	19	5	n/a	40
28F0471	414-436	0	4.0	12	n/a	n/a	40
28F0471	483-505	2	4.4	10	12	n/a	55
28F0471	534-556	0	4.5	29	n/a	n/a	31
28F0471	562-584	0	4.4	30	4	n/a	27
28F0471	796-818	0	4.2	16	4	n/a	33
28F0471	845-867	0	4.1	16	8	n/a	42

Maarheeze

Profile No.	Stratum, cm below surface level	DNP	pH	NO_3-N	NH4-N	SON	SOC
		µg N/kg/day		mg/l	mg/l	mg/l	mg/l
57E0335	110-132	6	5.2	n/a	n/a	27	761
57E0335	137-159	0	4.9	n/a	10	27	670
57E0335	160-182	0	4.5	n/a	7	18	452
57E0335	237-259	0	4.7	n/a	8	14	266
57E0335	297-319	45	4.6	n/a	9	9	176
57E0335	346-368	0	4.4	n/a	10	n/a	98
57E0335	445-467	0	4.7	n/a	7	n/a	59
57E0335	533-555	0	5.2	n/a	n/a	n/a	44
57E0335	604-626	0	4.6	9	6	n/a	44
57E0337	74-96	0	5.6	23	9	18	277
57E0337	171-193	0	5.9	28	11	n/a	167
57E0337	230-252	1	5.5	n/a	12	n/a	158
57E0337	334-356	0	4.2	n/a	25	n/a	66
57E0337	376-398	0	4.5	n/a	11	n/a	68
57E0337	478-500	0	4.8	n/a	10	n/a	75
57E0337	524-546	0	4.2	n/a	17	n/a	50
57E0337	591-613	1	4.5	7	10	n/a	41
57E0337	680-702	0	5.0	17	11	n/a	47
57E0336	177-199	0	4.9	51	10	14	256
57E0336	304-326	0	4.8	22	n/a	n/a	122
57E0336	363-385	0	4.6	6	n/a	n/a	94
57E0336	414-436	0	4.6	18	n/a	n/a	71
57E0336	474-496	0	4.7	20	10	n/a	81
57E0336	547-569	0	5.6	20	13	n/a	104
57E0336	657-679	0	5.0	12	14	n/a	56
57E0336	698-720	0	4.7	12	22	n/a	60
57E0336	733-755	0	4.8	9	20	n/a	64
57E0338	148-170	113	5.0	n/a	10	6	94
57E0338	198-220	284	5.1	n/a	7	n/a	94
57E0338	277-299	88	4.9	n/a	n/a	n/a	87
57E0338	373-395	51	6.0	n/a	n/a	n/a	69
57E0338	452-474	1	5.6	n/a	n/a	n/a	46
57E0338	551-573	0	5.9	n/a	7	n/a	47
57E0338	646-668	1	5.6	n/a	7	n/a	81
57E0338	744-766	0	5.7	n/a	n/a	n/a	47

Appendix 9: Results of physical and chemical analyses

Lutum = clay content (particles smaller than 8 µm); M50 = median particle size of sand fraction (fraction between 63 µm and 2000 µm); TOC = total organic matter after decalcification (for explanation see section 6.2).
Depth in centimetres below surface level.

Nieuweroord

Profile No.	Depth cm below surface level	Lutum % <8 µm	M50 Sand	Carbonate (%)	TOC (%)	Reactive Fe (%)	Pyrite FeS_2 (%)
17D0200	229	7	174	-1.4	0.2	-0.3	0.0
17D0200	285	8	196	-1.9	0.1	7.6	0.0
17D0200	349	10	183	-1.3	0.1	0.1	0.0
17D0200	392	9	195	-1.4	0.1	0.0	0.0
17D0200	443	10	200	-1.2	0.1	0.1	0.0
17D0200	584	9	180	-2.5	0.2	0.1	0.0
17D0200	712	12	115	-4.6	0.6	0.2	0.0
17D0200	857	2	137	3.6	0.1	-0.1	0.3
17D0201	221	3	213	-0.8	0.1	-0.2	0.0
17D0201	323	14	178	-0.3	0.0	-0.2	0.0
17D0201	388	15	153	-1.7	0.1	-0.1	0.0
17D0201	498	13	168	-0.8	0.0	-0.1	0.0
17D0201	531	12	189	-1.2	0.1	-0.1	0.0
17D0201	557	12	177	-1.2	0.1	-0.1	0.0
17D0201	598	11	194	-1.1	0.0	-0.1	0.0
17D0201	694	14	173	-0.8	0.3	-0.1	0.0
17D0201	723	12	170	-1.3	0.3	-0.1	0.0
17D0201	794	9	156	-1.1	0.2	-0.1	0.0
17D0202	169	9	203	-1.5	0.1	-0.2	0.0
17D0202	243	17	131	-1.5	0.1	-0.2	0.0
17D0202	257	11	166	-1.5	0.1	0.1	0.0
17D0202	294	9	195	-1.3	0.1	0.2	0.0
17D0202	401	12	172	-1.6	0.0	0.2	0.0
17D0202	448	12	176	-1.8	0.1	0.1	0.0
17D0202	498	11	173	-1.6	0.3	0.1	0.0
17D0202	560	15	169	-0.9	0.4	0.2	0.2
17D0202	686	16	140	-1.2	0.4	0.1	0.0
17D0203	124	10	171	-2.3	0.1	0.0	0.0
17D0203	148	11	168	-1.0	0.1	0.0	0.0
17D0203	262	8	204	-1.4	0.1	0.1	0.0
17D0203	393	13	158	-1.4	0.1	0.2	0.0
17D0203	453	9	183	-1.5	0.1	0.1	0.0
17D0203	592	12	161	-1.0	0.3	0.1	0.0
17D0203	666	1	367	-1.3	0.1	-0.2	0.0
17D0203	703	12	120	-1.7	0.4	0.0	0.0
17D0203	774	15	103	-2.1	0.6	0.1	0.0

Spankeren

Profile No.	Depth cm below surface level	Lutum % <8 µm	M50 Sand	Carbonate (%)	TOC (%)	Reactive Fe (%)	Pyrite FeS_2 (%)
33G0412	276	5	158	16.8	0.1	0.5	0.0
33G0412	342	13	68	26.9	0.1	1.2	0.0
33G0412	388	0	432	3.1	0.0	0.0	0.0
33G0412	481	8	79	20.2	0.2	0.6	0.0
33G0412	591	0	343	2.6	0.0	-0.1	0.0
33G0412	680	1	357	3.0	0.0	-0.1	0.0
33G0412	738	0	732	0.8	0.0	-0.1	0.0
33G0412	767	46	9	9.5	0.3	1.6	0.0
33G0413	353	20	54	25.4	0.2	0.7	0.0
33G0413	432	64	6	39.1	0.3	2.4	0.0
33G0413	474	8	113	22.5	0.1	0.4	0.0
33G0413	513	0	307	5.3	0.0	0.0	0.0
33G0413	594	6	146	18.3	0.7	0.4	0.0
33G0413	627	3	128	17.3	0.1	0.3	0.0
33G0413	653	8	97	19.3	0.4	0.5	0.0
33G0413	752	1	246	9.9	0.1	0.0	0.0
33G0413	818	1	293	6.1	0.2	0.0	0.0
33G0413	853	24	57	15.6	0.6	1.1	0.0
33G0414	121	13	75	0.3	0.0	1.5	0.0
33G0414	161	3	122	2.2	0.0	-0.1	0.0
33G0414	193	0	472	-0.3	0.1	0.0	0.0
33G0414	200	1	199	4.7	0.0	0.0	0.0
33G0414	259	42	11	27.5	0.6	2.2	0.1
33G0414	360	30	18	30.9	0.0	1.4	0.0
33G0414	418	4	282	4.2	0.0	0.2	0.0
33G0414	472	45	9	29.1	0.3	2.0	0.1
33G0414	547	0	749	0.4	0.0	0.0	0.0
33G0414	582	2	99	4.3	40.1	2.6	2.6
33G0415	256	5	132	-1.0	0.1	0.4	0.0
33G0415	314	9	69	19.9	0.5	1.2	0.0
33G0415	338	21	28	19.2	0.9	1.7	0.0
33G0415	355	3	638	-0.6	0.1	0.2	0.0
33G0415	393	0	406	-1.8	0.1	-0.1	0.0
33G0415	497	10	90	18.0	0.3	1.0	0.4
33G0415	546	24	30	35.8	2.5	2.8	0.6
33G0415	557	19	36	29.8	0.4	-0.1	0.1
33G0415	578	9	89	28.1	3.4	1.9	0.3
33G0415	584	4	126	24.8	2.5	2.1	0.2
33G0415	595	10	107	26.7	11.0	1.6	0.9
33G0415	605	14	72	40.5	9.8	2.2	0.9
33G0415	610	1	240	4.2	0.0	0.1	0.1
33G0415	620	23	30	26.2	3.5	2.7	0.4
33G0415	622	20	30	22.5	1.1	1.8	0.2
33G0415	668	1	435	-0.4	0.3	0.0	0.0
33G0415	715	0	468	-1.6	0.1	-0.1	0.0

Nutter

Profile No.	Depth cm below surface level	Lutum % <8 µm	M50 Sand	Carbonate (%)	TOC (%)	Reactive Fe (%)	Pyrite FeS_2 (%)
28F0470	149	3	92	0.8	0.0	1.0	0.0
28F0470	186	4	91	0.8	0.0	1.0	0.0
28F0470	202	11	83	1.1	0.0	1.1	0.0
28F0470	229	18	59	1.1	0.1	1.7	0.0
28F0470	328	22	71	1.0	0.2	1.9	0.0
28F0470	364	6	86	1.4	0.0	3.5	0.0
28F0470	494	3	91	1.2	-0.1	1.0	0.0
28F0470	585	23	65	0.1	0.4	1.5	0.0
28F0470	696	5	83	1.0	-0.1	0.9	0.0
28F0471	562	7	89	1.2	-0.1	0.8	0.0
28F0471	582	1	106	1.9	-0.2	1.1	0.0
28F0471	610	3	86	2.3	-0.2	1.2	0.0
28F0471	679	10	81	1.7	-0.1	1.1	0.0
28F0471	730	2	87	1.0	-0.1	1.6	0.0
28F0471	758	10	77	0.9	0.0	2.4	0.0
28F0471	992	6	80	1.4	-0.1	1.3	0.0
28F0471	1041	12	81	1.1	-0.1	1.7	0.0
28F0472	486	4	87	0.4	0.0	1.5	0.0
28F0472	668	22	22	0.8	0.0	2.9	0.0
28F0472	730	2	94	0.4	0.0	1.1	0.0
28F0472	768	10	76	1.2	0.0	2.0	0.0
28F0472	949	1	93	0.8	-0.1	1.0	0.0
28F0473	192	10	80	1.0	0.0	2.1	0.0
28F0473	249	29	29	3.4	-0.3	2.4	0.0
28F0473	249	2	95	0.9	0.1	3.9	0.0
28F0473	261	5	97	0.7	-0.1	2.1	0.0
28F0473	271	16	76	0.7	0.0	1.9	0.0
28F0473	393	9	87	1.0	0.0	1.6	0.0
28F0473	459	12	103	0.9	0.0	1.8	0.0
28F0473	546	4	91	1.5	-0.1	1.7	0.5
28F0473	659	18	69	1.0	0.1	2.1	1.0

Maarheeze

Profile No.	Depth cm below surface level	Lutum % <8 µm	M50 Sand	Carbonate (%)	TOC (%)	Reactive Fe (%)	Pyrite FeS_2 (%)
57E0335	129	3	142	0.5	0.2	-0.1	0.0
57E0335	156	2	213	1.4	0.0	-0.1	0.0
57E0335	179	5	193	1.5	0.3	0.0	0.0
57E0335	256	0	208	1.3	0.0	-0.1	0.0
57E0335	316	4	162	-1.6	8.0	-0.1	0.3
57E0335	365	1	194	1.3	0.0	-0.1	0.0
57E0335	464	1	315	*	-0.1	*	*
57E0335	552	0	296	0.8	-0.1	-0.1	0.0
57E0335	623	0	264	1.6	-0.1	-0.1	0.0
57E0336	188	0	272	1.1	-0.1	-0.1	0.0
57E0336	315	0	305	1.2	-0.1	0.0	0.0
57E0336	374	0	271	1.2	-0.1	-0.1	0.0
57E0336	425	0	363	1.2	-0.1	0.0	0.0
57E0336	485	1	276	1.1	0.0	-0.1	0.0
57E0336	558	9	182	1.1	0.4	0.1	0.0
57E0336	668	2	257	1.0	-0.1	-0.1	0.0
57E0336	709	12	142	0.7	0.0	0.0	0.0
57E0336	744	14	74	1.0	0.1	0.0	0.0
57E0337	106	14	79	0.6	0.0	-0.1	0.0
57E0337	203	1	188	0.5	0.0	-0.1	0.0
57E0337	262	0	346	1.1	0.2	-0.1	0.0
57E0337	366	1	261	0.9	0.0	0.0	0.0
57E0337	408	2	216	0.7	0.0	-0.1	0.0
57E0337	510	5	202	0.9	0.0	-0.1	0.0
57E0337	556	10	159	0.7	0.0	0.0	0.0
57E0337	623	1	233	0.9	-0.1	-0.1	0.0
57E0337	712	1	227	1.0	-0.1	-0.1	0.1
57E0338	189	4	177	-0.1	3.4	0.8	0.6
57E0338	239	2	199	1.0	2.6	0.2	0.2
57E0338	318	0	592	0.7	0.2	0.1	0.1
57E0338	414	1	188	2.2	0.6	-0.1	0.0
57E0338	493	0	263	1.1	0.0	-0.1	0.0
57E0338	592	1	243	0.7	0.0	-0.1	0.0
57E0338	687	1	194	0.6	0.1	-0.1	0.0
57E0338	785	1	181	0.8	0.0	-0.1	0.0

Appendix 10: Displacement effects: comparison of LMM and LMG data

Method and materials

An impression of the displacement effects can be gained by checking in each region whether there is an increase in cations (Ca, Mg, K, Na), sulphate and heavy metals (As, Cd, Cu, Ni, Pb, and Zn) between the observation depth of the National Programme for Monitoring the Effectiveness of Minerals Policy (LMM) and that of the National Groundwater Quality Monitoring Network (LMG). The LMM samples the first metre of groundwater in the sand region. Sampling in the LMG takes place at 8-10 m below surface level, which averages out at 6.5-8.5 m below the groundwater table in the sand region. As we expect denitrification to take place mainly in the root zone at high groundwater levels, in addition to a regional average the drainage classes 'wet', 'neutral' and 'dry' are examined on a regional basis (see section 1.1.3). In the case of the LMG wells it is easy to distinguish between wet, neutral and dry soils, but this is not possible with the LMM data, as it relates to mixed samples at farm level. The distribution of groundwater table classes over the farm area is known, however, hence the distribution among the drainage classes. For each region and farm statistical interpolation was used to find values for the concentrations of cations, sulphate and heavy metals in the first metre of groundwater in 100% wet, neutral and dry soils. The estimate was not reported if the ratio of the standard error to the estimated value was less than 3:1.

Results

The tables below show the statistically interpolated difference between the concentrations in the first metre of groundwater (LMM) and 13-15 metres below surface level (LMG) in the drainage classes 'wet', 'neutral' and 'dry'.

Nitrate

There is a decrease in nitrate concentration with depth in every region except the central sandy region (39% increase: see Table B10.1). No general pattern can be deduced from the differences between the drainage classes.

Table B10.1 Percentage decrease in nitrate concentration between the first metre of groundwater (LMM) and the first screen in the LMG by area.

	Drainage class		
AREAS	Wet	Neutral	Dry
Stream valley	100	100	
Sand central	14		
High moorland	99	95	100
Peelhorst + terrace	10	-1	30
Boulder clay	26	53	82
Sand east	100	20	56
Graben	89	38	61
Valley	83	99	16
Sand southwest		-10	86

Hardness
The hardness of the water (Ca + Mg) increases with depth in three of the nine regions and decreases in the others. There are no clear differences in increase or decrease between the drainage classes.

Table B10.2 Percentage increase in water hardness between the first metre of groundwater and the first screen in the LMG by area.

	Drainage class		
AREAS	Wet	Neutral	Dry
Stream valley			
Sand central			
High moorland	8		
Peelhorst + terrace		7	-33
Boulder clay	-7	-31	
Sand east		55	39
Graben	16	1	
Valley		22	
Sand southwest		8	

Sulphate
The sulphate concentration increases in the same three regions where water hardness increases. The other regions show a decrease in sulphate concentration with depth. Statistically significant differences were found between the calculated sulphate concentrations in the LMM and LMG by drainage class only in the case of soils in the ‘neutral’ class.

Table B10.3 Percentage increase in sulphate concentration between the first metre of groundwater and the first screen in the LMG by area.

	Drainage class		
AREAS	Wet	Neutral	Dry
Stream valley			
Sand central			
High moorland			
Peelhorst + terrace		11	
Boulder clay		-15	
Sand east			
Graben		-7	
Valley			
Sand southwest		-15	

Heavy metals
The total heavy metal concentration (As, Cd, Cu, Ni, Pb, and Zn) decreases with depth in every region except ‘Peelhorst and terrace’. Nothing can be said about differences between drainage classes, as no significant differences in metal concentrations between the LMM and LMG depths were calculated in most of the regions.

Table B10.4 Percentage increase in total heavy metal concentration between the first metre of groundwater and the first screen in the LMG by area.

	Drainage class		
AREAS	Wet	Neutral	Dry
Stream valley			
Sand central			
High moorland			
Peelhorst + terrace		19	-7
Boulder clay		-50	
Sand east	-84	-69	
Graben		-72	
Valley			
Sand southwest		-22	

Conclusions

Comparison of the data collected with the LMM and LMG clearly shows that the nitrate concentrations were lower at a depth of 6.8-8.0 m below the groundwater table than in the first metre. No differences were found between drainage classes. The data however do not show any increase in water hardness, sulphate or heavy metals with depth.

Appendix 11: Agency studies

Introduction

Three agency studies were carried out to answer the various sub-questions, in addition, of course, to a general survey of the available literature on the problem of compliance checking levels and on specific topics to answer the research questions. The studies involved (a) a reanalysis of the data collected in the RIVM study of ten dairy farms at the end of the 1980s; (b) comparing data on the top level of groundwater from the National Programme for Monitoring the Effectiveness of Minerals Policy (LMM) with data on deeper groundwater from the National Groundwater Quality Monitoring Network (LMG); and (c) analysing recent data on nitrate concentrations in groundwater, drainage water and surface water on farms in the wetter areas of the sand region.

Reanalysis of data from dairy farms study

Intensive research into the variations in nitrate concentrations in space and time was carried out at ten dairy farms in the sand region at the end of the 1980s (Boumans, 1990; Boumans et al., 1989).

Suitable locations for sampling the groundwater down to six metres below surface level at these farms were identified on the basis of geophysical investigation. The expectation was that the groundwater at these locations would come from rainwater infiltrated on the farm. An average of nine wells were sunk on each farm at the beginning of 1986. Each well was fitted with a number of screens. The first three screens were 20 cm long and spaced out at 30 cm intervals, the next four were 50 cm long and spaced out at 50 cm intervals. The screens were placed at an average depth below ground level of approximately 110, 160, 210, 275, 375, 475 and 575 cm. The top two screens were usually between mean highest groundwater level (MHG) and mean lowest groundwater level (MLG). The screens were flushed out immediately after insertion. The wells were flushed out again in the second half of 1986 and some were also sampled. A total of 90 multi-screen wells were sunk and 83 sampled in both 1987 and 1988; some of these had also been sampled in 1986.

The farms were also mapped to show soil types and groundwater table classes. Of the wells sampled in 1986-88, data are available on the groundwater table classes for 46 wells in 1986, 85 in 1987 and 80 in 1988.

The concentration in the first metre was calculated by averaging the results from the top two screens; the concentration in the fifth metre was taken to be equal to that in the bottom screen. To calculate the average in the first five metres the results from all the screens were used.

Map B11.1 Location of the ten dairy farms on sandy soil in the study by Boumans (1990)

Comparison of LMM and LMG data on the sand region

For this part of the study the data from the LMM programme in the sand region for the 1992-95 period were used (Fraters et al., 1997, Boumans et al., 1997) and from the LMG for 2002-2003 period (for a recent overview see Reijnders et al., 2004). The LMM data cover approximately 100 farms sampled three or four times during the 1992-95 period. The LMG data cover approximately 100 wells sampled in both 2002 and 2003 that relate to agriculture.

For the purpose of comparison the relationship between nitrate concentration and groundwater table class was examined in the case of both the LMM and LMG data. The study distinguished between nitrate vulnerable soils (Gt VI and above) and other sandy soils. In the case of the LMM data allowance had to be made for the fact that soil types other than sand can occur on the farms in question. In the case of the LMG data the actual age of the water had to be taken into account: this was determined from tritium measurements carried out in 1984. In both cases land use was also taken into account, as we know that leaching can be different under grassland than under farmland.

For results see Appendices 3 and 10.

Study of the relationship between groundwater and surface water

For this part of the study data were used from four studies carried out on farms in the sand region, namely 24 farms participating in the winter programme in the sand region, two farms

participating in the 'Koeien en Kansen' (sustainable dairy farming) project, two farms in the study discussed at section B10.2 on ten dairy farms on sandy soils and three arable farms participating in the study at the end of the 1980s.

Sand region winter programme

The sand region winter programme began in October 2004. The aim was to ascertain the effects of farming on surface water quality and changes in this over time in relation to changes in farming practice. The programme began with 24 LMM farms where the top level of groundwater had been sampled one or more times in the summer period using the open borehole method. All the farms had to have at least 25% of their area drained with drainage pipes. In the winter period (October-April) the groundwater was sampled once (from open boreholes) and the drainage and ditch water one to four times. The groundwater was sampled in the same way as in the summer (16 boreholes spread over each farm). On each farm 16 drains were selected and eight locations for sampling ditch water. For details see Fraters and Boumans (2005).

‘Koeien en Kansen’ (Cows and Opportunities)

The farms in question have been participating in this project since 1999. The farm in Eibergen is situated in the eastern sandy region and the one in IJsselsteyn in the southern sandy region. On the Eibergen farm the first metre of groundwater was sampled at the end of 1999 and the beginning of 2000 at some 10 locations using the open borehole method. It was not possible to do this at more locations because of the soil conditions, so from 2001 it was decided to sample the soil water at approximately 1-3 m below surface level at 16 locations every autumn. In addition, the drainage water was sampled during the winter period at 16 locations starting in 1999.

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