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Mapping and source identification of
groundwater pollution by nitrate
Theory and application to the Brusselian sand
groundwater body

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Décembre 2009

Thèse présentée en vue de l'obtention
du grade de Docteur en Sciences Agronomiques
et Ingénierie Biologique

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Remerciements

J'adresse mes profonds remerciements à mon promoteur de thèse, le professeur Marnik Vanclooster, pour la confiance qu'il m'a accordée depuis le début de ce projet, pour sa vision critique qui m'a permis de pousser mes recherches toujours plus loin, pour ses encouragements et pour les échanges constructifs que nous avons eus durant ces quatre années.

Merci aux membres de mon jury, les professeurs Patrick Bogaert, Serge Brouyère, Mathieu Sebilo et Philippe Sonnet pour leurs remarques expertes qui ont permis d'améliorer sensiblement la qualité de ce manuscrit.

Cette étude n'aurait pu être réalisée sans la contribution de Eric Chauveheid et de Jean-Pierre Zmikala (Vivaqua), de Gérard Peeters (Service hydrogéologique de l'UCL), de l'ISSeP, de l'IECBW et de la SWDE. Les semaines passées sur le terrain pour prélever les échantillons d'eau souterraine furent extrêmement instructives et enrichissantes.

J'exprime aussi ma gratitude à Francis Delloye, Cristina Popescu et Roland Masset du Service public de Wallonie pour la mise à disposition des milliers de données traitées dans cette thèse.

Une thèse, c'est le fruit d'une équipe. Merci à tous les collègues du GERU pour leur soutien, pour l'ambiance conviviale et la bonne humeur qui règnent dans nos bureaux et pour les échanges sur des sujets scientifiques... ou pas scientifiques du tout (!). Merci spécialement à Carine pour son écoute et son support administratif.

Je remercie le FRIA et le FNRS d'avoir financé ce projet, et toutes les personnes qui ont contribué à la réalisation de cette thèse.

Merci à ma p'tite famille de rendre nos vies si douces et agréables... on forme une sacrée équipe !

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Chapter 1

Introduction

1.1 Context

Nitrate contamination from agricultural and non-agricultural sources continue to exert a considerable pressure on subsurface groundwater bodies all over the world. In Europe for instance, 35% of the groundwater bodies are expected to be at risk of not reaching the European water framework directive objectives by 2015, one of which is to reduce nitrate concentrations in groundwater under the standard for drinking water of 50 mg NO₃/l, while 45% of the water bodies are insufficiently documented to be properly assessed (European Commission, 2007). In the overwhelming part of waterbodies at risk, nitrate remains one of the critical parameters.

Nitrate occurs naturally in soil and water and is essential for plant growth. In nature, nitrate derive mainly from the decomposition of plants, dead animals and their excreta and from atmospheric deposition. Other sources of nitrates are linked to human activities and are responsible for point and diffuse pollution. Anthropogenic nitrogen discharged into the environment originates mainly from domestic wastewater, industries and agricultural activities (Nitrawal, 2007). In agriculture, the trend towards intensification and higher productivity during much of the past fifty years was accompanied by a significant increase in fertilizer use and by a reduction of permanent grassland and of “buffer” areas (ditches and hedges, wetlands, etc.) which favors erosion, run-off and quicker drainage of nutrients to the aquatic ecosystems (Commission des Communautés Européennes, 2002). In urban areas, houses that are not connected to sewer system discharge their wastewater to septic tanks, streams or infiltrates into the soil.

The loss of excess nitrogen to the environment puts a pressure on the soil and water system, causing N enrichment and eutrophication (in association with phosphorus) of surface waters. It contributes also to acid rain damages on terrestrial flora and soils. Excessive nitrate in groundwater supplies can cause animal and human health problems (Cornblath and Hartmann, 1948; Knobeloch *et al.*, 2000; Mostaghimi *et al.*, 1997; Ridder *et al.*, 1974; Manassaram *et al.*, 2006; Weyer *et al.*, 2008). Nitrate per se is not toxic, but it is the precursor of nitrite which is produced through microbial reduction of nitrate in the intestine or in food preparations and which causes infant methaemoglobinemia (Terblanche, 1991).

Europe adopted Directives for reducing pressures of N on water resources: the European Council Directive concerning urban waste-water treatment for domestic and industrial sectors (91/271/EEC) and the Directive concerning the protection of waters against pollution caused by nitrates from agricultural sources (91/676/EEC). The transposition of this latter Directive requires each EU Member State to take a series of measures including the designation of land areas that contribute to water contamination (vulnerable zones), the establishment of monitoring and nitrate reduction action plans and the development of a code of good agricultural practices (Vandenberghe and Marcoen, 2004). The European Water Framework Directive (2000/60/EEC) commits European Union Member States to achieve good qualitative and quantitative status of all water bodies by 2015.

Despite all the nitrate reduction actions that were undertaken to meet EU directives, the nitrate concentrations in groundwater of the Walloon Region continue to increase (SPW, 2008). The Walloon Region has for instance been sentenced in 2005 by the European Court of Justice on the ground of lack of results concerning the reduction of groundwater pollution by nitrate.

1.2 Current challenges

Prerequisites for designing sustainable water management strategies e.g. when implementing the Water Framework Directive (2000/60/EC, 2000) include (i) to know where the pollution is (need for mapping), (ii) to know how the pollution will evolve (need for modelling taking into account the transfer time), (iii) to know where the pollution comes from and (iv) to know what processes affect the nitrate concentrations.

Groundwater quality is a spatially distributed attribute. It is generally accepted that knowledge of the spatial distribution of this attribute

allows the design of site specific protection and remediation measures. Therefore robust and validated techniques are needed to map the spatial distribution of groundwater quality within the groundwater body continuum.

Unfortunately, the locations where groundwater quality properties are measured are typically scarce and sparsely distributed over space. As a result, large uncertainties about the variable of interest arise in the mapping process, especially at prediction points located far away from monitoring stations. Given that the quality of the interpolation decreases rapidly with the distance to the monitoring station, the mapping of a variable of interest through classical geostatistical interpolation techniques will have limited practical utility in regions where a densely distributed monitoring network is not available. Unfortunately, this is rather the rule than the exception, and therefore alternative robust and validated methods are needed to provide more comprehensive and accurate information about the groundwater quality. Data fusion is such a method that can be used to combine optimally various sources of information about groundwater quality in a consistent and accurate model prediction.

Groundwater quality is however not only a space, but also a time variable attribute. While the temporal dynamics was considered by Christakos and Bogaert (1996) to generate a sequence of maps showing the evolution of the nitrate concentrations in the Dyle Basin in Belgium, it is not clear how to account for time variability in cases where the temporal component is much smaller than the spatial one (i.e. when only slight differences are observed in the sequence of maps of the variable of interest).

Furthermore, it is not clear to what extent the size of the sample population of the time series impacts on the mapping results. Indeed, nitrate concentration was measured hundreds of times at some monitoring stations, increasing the knowledge about the pollution at that location, while it was measured only once at some other places, leading to high uncertainty about the assessment of the pollution at those monitoring stations.

Knowing the travel time of water and nitrate in the vadose zone is a prerequisite for quantifying the recharge and load of groundwater bodies and hence, to evaluate the time needed to observe changes in groundwater quality in response to modification of anthropic activities (Orban, 2008). The vadose zone is a key component within terrestrial systems and plays an essential role in the hydrological cycle. Indeed, the vadose zone encompasses the unsaturated soil root zone and controls

thereby the fluxes of water, matter and energy between the atmosphere, land surface and subsurface water bodies.

Nitrate pollution can potentially originate from atmospheric dry and wet deposition, sewer leakage, septic tanks, nitrogen-based chemicals, fertilizers, urea used as a road de-icing agent, river or channel infiltration, ammonium as a by-product of many industrial processes, and nitrification of mineralized organic matter (Ford and Tellam, 1994; Wakida and Lerner, 2005). Knowledge of the contaminant release source is of primary importance to define an appropriate remediation strategy. Yet, the nitrate pollution sources identification remains a complicated task. Inversion approaches can be applied to give insight, but are limited by strong hypothesis which are hardly applied in practice (Atmadja and Bagtzoglou, 2001). As a consequence, empirical methods like statistical techniques and chemical fingerprinting are promising elements to identify the contamination source of observed water pollution.

1.3 Objectives

By the light of these current challenges, the overall aim of this thesis is to improve our understanding and assessment of groundwater nitrate pollution at the regional scale, using both the analysis of monitoring data and spatially distributed modelling.

This work has mainly been carried out with the data of a specific region, i.e. the Brusselian sand groundwater body (RWE051, defined in the context of the European Water Framework Directive) located in the center of Belgium. This study area of 965 km² is particularly vulnerable to nitrate pollution.

This thesis has two main objectives and several specific objectives. The first main objective is to make an inventory of the groundwater pollution by nitrate by mapping the nitrate concentrations in the aquifer. The specific objectives are as follows:

- to describe the spatial and temporal dynamics of nitrate concentrations at the scale of the Brusselian aquifer;
- to introduce the time variability of the measured nitrate concentrations into the mapping process;
- to take the sampling rate into account in the mapping process and
- to integrate potentially available secondary information sources in the mapping process.

The second main objective of the thesis is to identify sources of groundwater nitrate pollution in the study area. The specific objectives are as follows:

- to estimate the travel time of recharge water through the vadose zone;
- to assess the relative impact of land and land use properties on groundwater nitrate concentrations through multivariate statistical models and
- to identify nitrate contamination sources using the specific isotopic signatures of nitrate related to some well-known N sources.

1.4 Outline of the thesis

This thesis (except chapters 2 and 7) is based on articles published or submitted to international peer reviewed journals (cf. List of publications at the end of the document). This may in some cases lead to repetitions in the text, although in this way the different chapters of the thesis may be read independently. After having described the study area in chapter 2, chapters 3, 4, 5 and 6 deal with mapping and modelling of nitrate contamination at the regional scale and chapters 7 and 8 present how we used an isotopic approach to identify nitrate pollution sources in the study area.

Chapter 2 presents the main features of the Brusselian sand groundwater body, which is the study area of this thesis.

Chapter 3 deals with the estimation of travel time of recharge water through the vadose zone. In chapter 4, we apply multivariate statistical models to discriminate sources of groundwater nitrate pollution. Chapters 5 and 6 show how modern geostatistical methods can be applied to groundwater nitrate mapping. In chapter 5, we introduce time variability and sampling rate in the mapping process using BME. In chapter 6, Bayesian Data Fusion (BDF) is used to combine groundwater monitoring data with a statistical groundwater contamination model in the mapping process.

Chapter 7 gives an overview of the scientific literature on the use of natural abundance of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of nitrate to determine the sources of groundwater pollution by nitrate. In this chapter, emphasis will be put on processes affecting the isotopic composition of nitrate and on the isotopic signature of N sources. The results of a large space-time sampling campaign are presented in chapter 8. In particular, this chapter is

dedicated to the identification of the groundwater nitrate contamination sources using a dual-isotope approach.

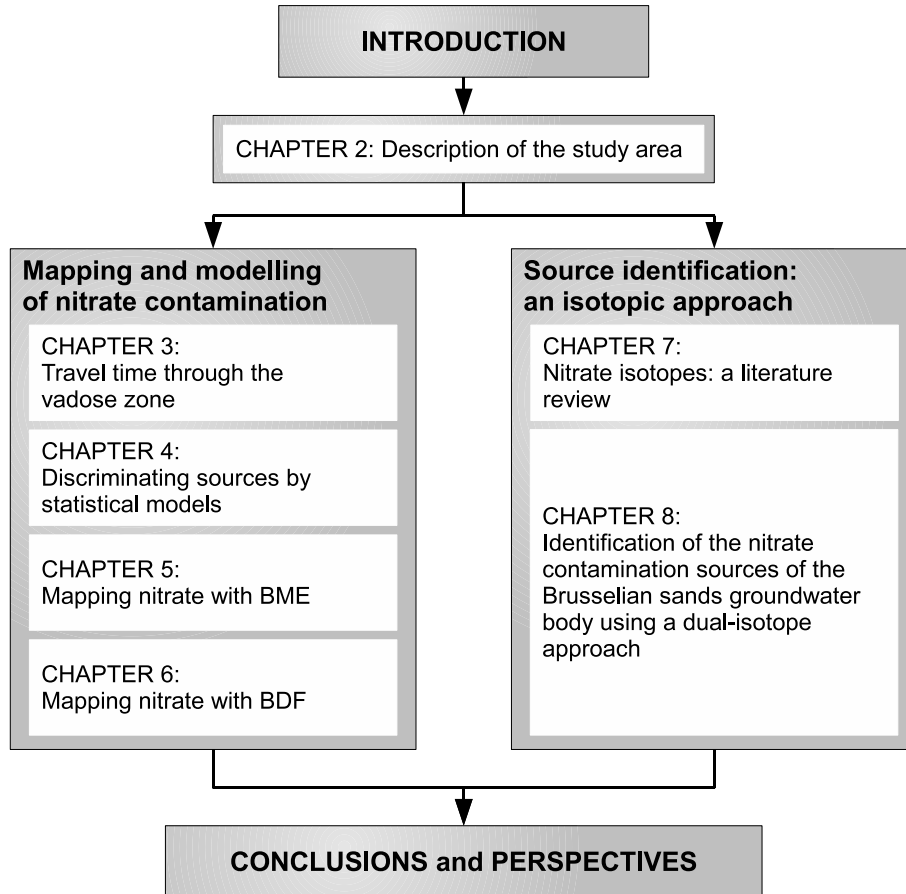


Figure 1.1: Outline of the thesis.

Chapter 2

Description of the study area

In order to avoid redundancy in the subsequent chapters, the study area is described in this chapter.

This study focuses on the unconfined Brusselian sands groundwater body (RWE051, defined in the context of the European Water Framework Directive) located in the center of Belgium (Fig. 2.1). This region of 965 km² encompasses aquifers which are of primary importance for drinking water supply. The study area is situated in a Nitrate Vulnerable Zone introduced in Europe to implement the EU nitrate directive.

2.1 Geomorphology

The main rivers in the study area are the Dyle, the Grande Gette and the Hain (Fig. 2.2). These streams and their tributaries deeply erode the sandy aquifer until reaching and exposing the underlying basement. They are natural drains of the groundwater body. The altitude of the study area varies between 25 and 180 m, with slopes varying from 0 to 21%. On Figure 2.3, we observe that silt loam is the dominant soil type on the plateaus while sandy soil develop in the valleys.

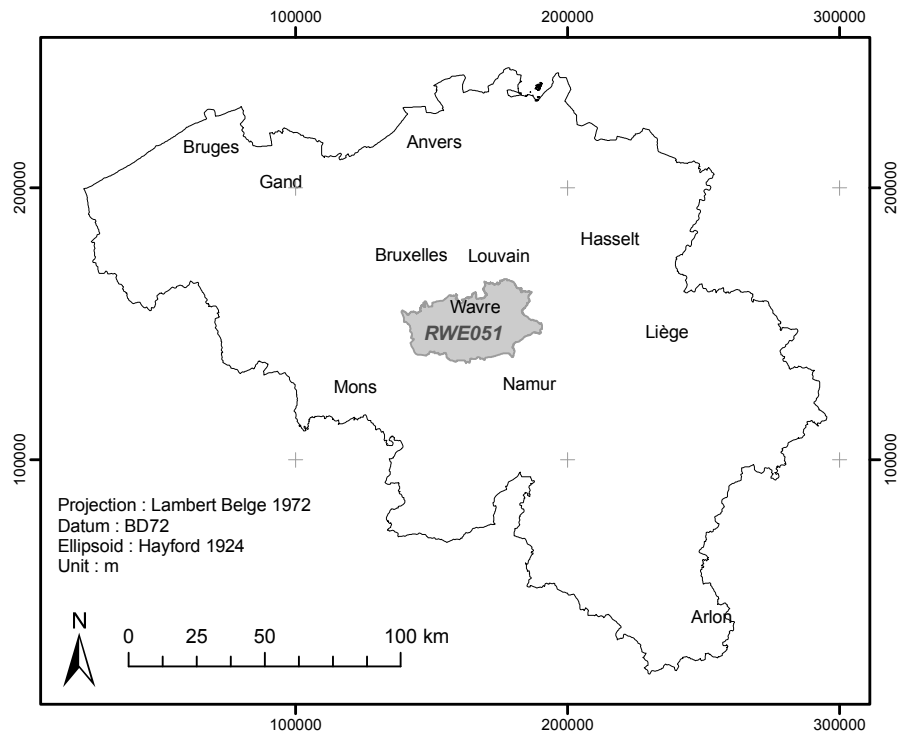


Figure 2.1: Location of the Brusselian sands groundwater body (RWE051) in Belgium.

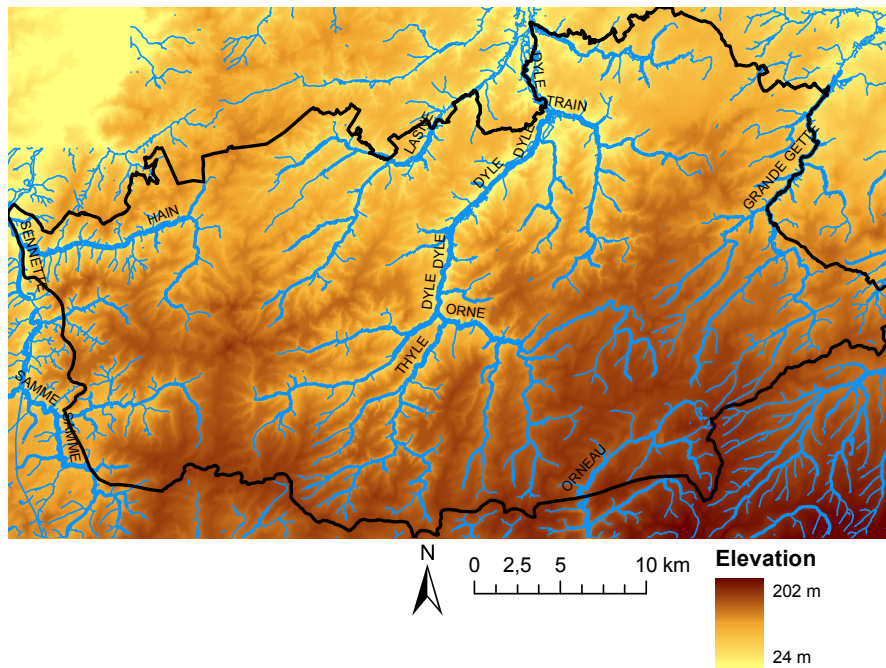


Figure 2.2: Hydrography and elevation of the study area.

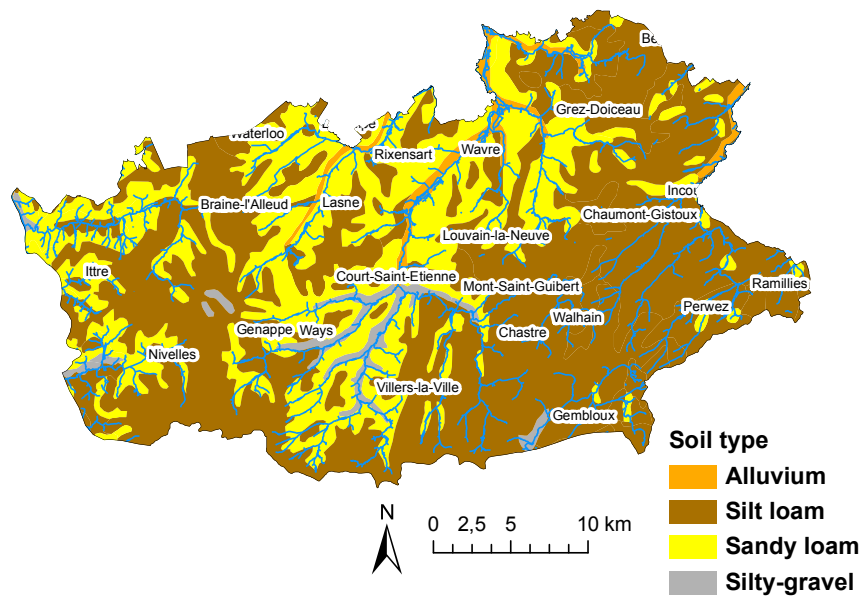


Figure 2.3: Soil types in the study area. Source: Tavernier and Maréchal (1958).

2.2 Geology

Geology of the study area is characterized by the presence of a Cambro-Ordovician-Silurian basement made of metamorphic rocks (phyllades, quartzo-phyllades and quartzites) referred to as the Brabant Massif. Eocene sands (including the Lutetian Brussels sands formation) overlies the Brabant Massif in the center of the study area, Cretaceous chinks in the north-eastern part of the study area and Devonian limestones in the south-west. The Brussels sands formation has a thickness that varies from a few meters to more than 70 m and is overlain by Pleistocene and Holocene eolian-deposited silt loams and alluvions of variable thickness (0 to 15 m) (Fig. 2.4 and 2.5) (DGRNE, 2002).

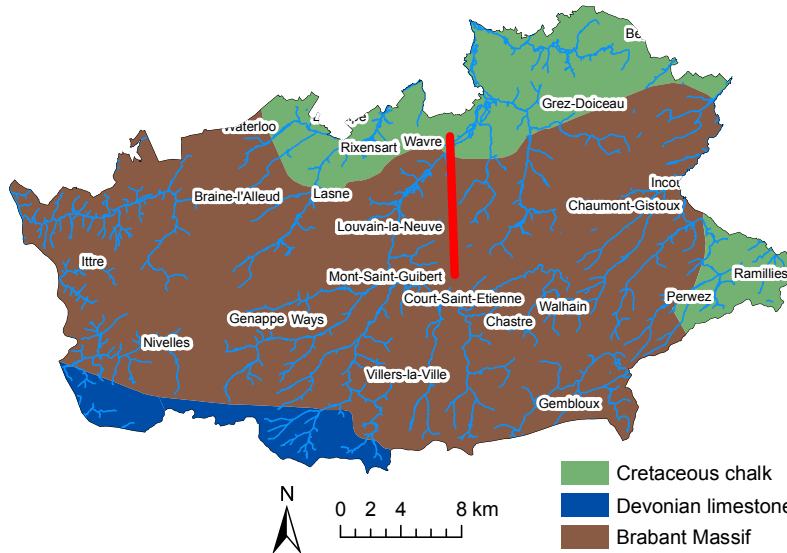


Figure 2.4: Geological formations underlying the Brussels sands formation in the study area.

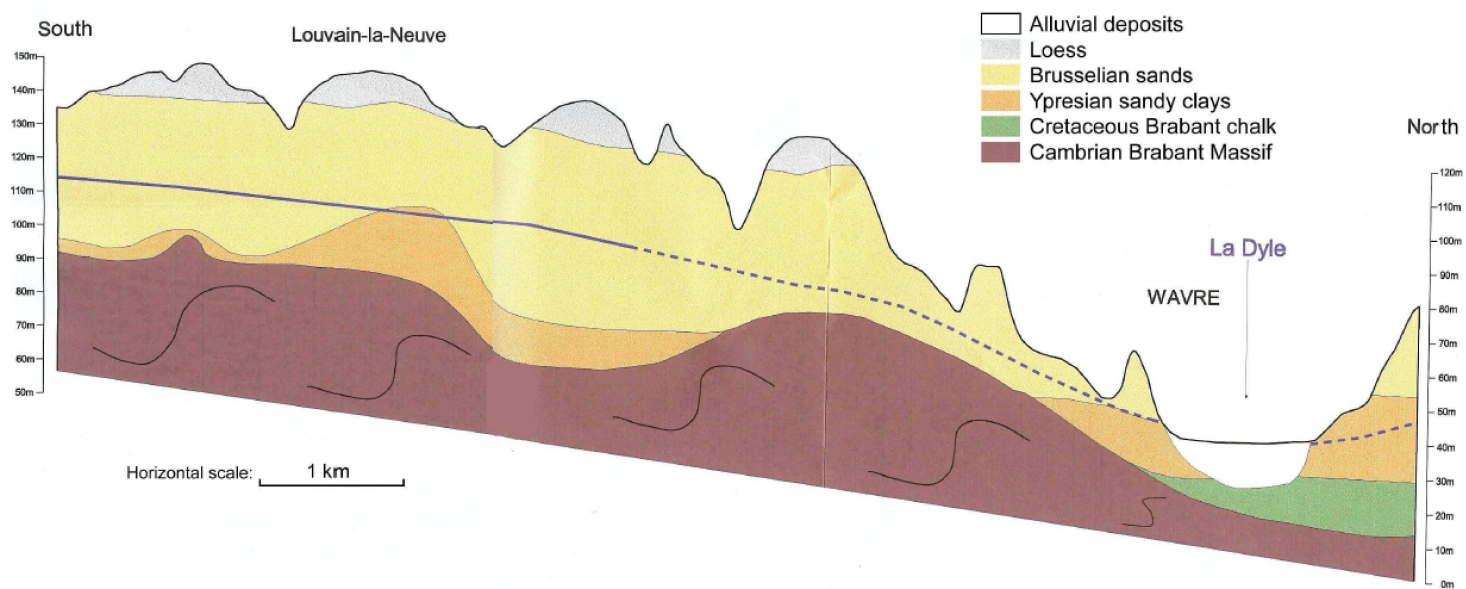
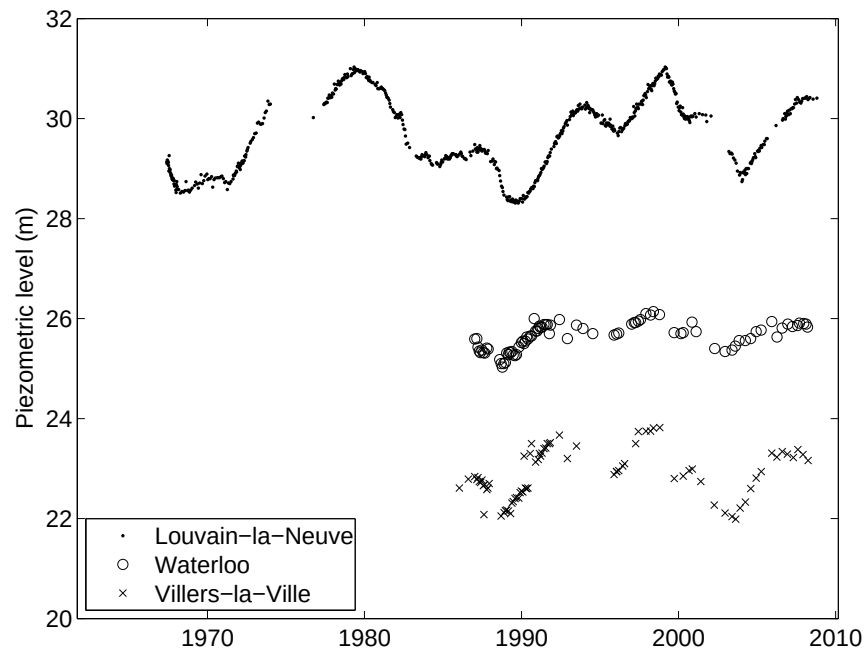


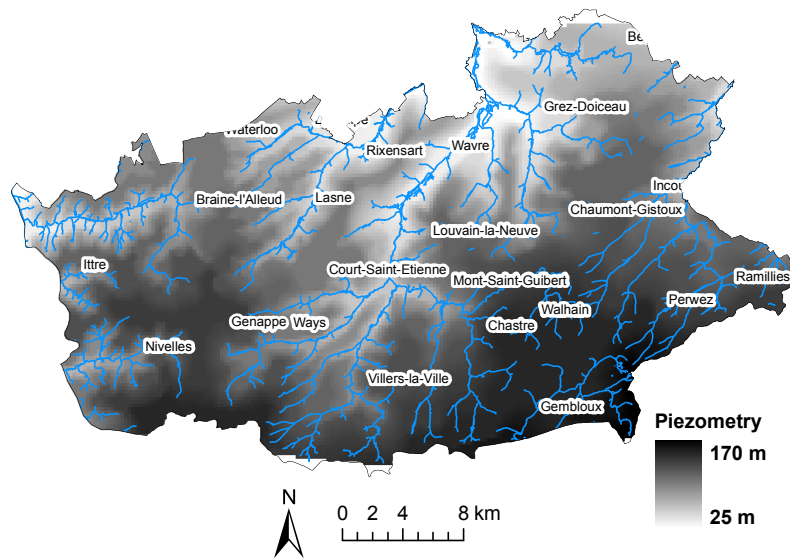
Figure 2.5: Hydrogeological section between Louvain-la-Neuve and Wavre, corresponding to the red line showed on Fig. 2.4. Source: DGRNE (2002).

2.3 Hydrogeology

Piezometric surveys are conducted regularly at more than 200 locations in the study area. Piezometric time series measured in the north (Waterloo), the center (Louvain-la-Neuve) and the south (Villers-la-Ville) of the study area are shown on Fig. 2.6a. The level of the groundwater table is relatively stable over time. The piezometric levels measured in the study area in 1984 were interpolated by D. Pinte (SCALDIT, 2006) using ordinary kriging manually constrained by the hydrographic network (i.e. a piezometric level equal to the DEM was attributed to the rivers before kriging) (Fig. 2.6b). Although the map was created with data from 25 years ago, the piezometric features are still valid and allow to illustrate some general characteristics of the groundwater table. The depth to the water table varies from 0 to more than 45 m with a mean value of about 10 m and is lower near the main draining rivers and higher on the plateaus in between (Mattern *et al.*, 2009). Mattern and Vanclooster (accepted article) estimated that the travel time of percolating water through this deep vadose zone shows a high spatial variability and varies between a few months to more than 15 years, depending also on the procedure for estimating the travel time. Transmissivity of the Brussels sands aquifer varies from 2.9×10^{-5} to 1.2×10^{-2} m²/s and its permeability varies from 1.4×10^{-6} to 6×10^{-3} m/s (IBW, 1987). The Brussels sands formation outcrop mainly in the valleys where sandy and sandy loam soils develop. In 2002, 25 079 406 m³ of water were extracted from the Brussels sands aquifer. The vast majority (96.5%) of which were collected for public water distribution.



(a)



(b)

Figure 2.6: (a) Time series of piezometry measured at 3 locations in the study area and (b) interpolated map of piezometric levels measured in 1984.

2.4 Hydrochemistry

The aquifer is monitored by the local administration and the water supply companies to comply with environmental legislation. These monitoring stations are wells (Fig. 2.7), galleries (Fig. 2.8a), springs (Fig. 2.8b) and drains. Galleries and drains are artificial tunnels (for galleries) and tubes (for drains) which collect water by gravity flow. Springs are any natural occurrence where water flows on to the surface of the earth from below the surface, and is thus where the aquifer surface meets the ground surface.

A sampling campaign conducted in January 2009 over a hundred monitoring stations in the study area showed that the Brusselian sands aquifer is dominated by calcium and bicarbonate, with sizable contributions of chloride, sulphate and nitrate (Fig. 2.9). Conductivity (at 25°C) varies generally between 400 and 900 $\mu\text{S}/\text{cm}$ and pH from 6.40 to 7.70 (see also Peeters *et al.* (2007)).

The groundwater nitrate concentration data are stored by the Walloon Region administration in a database (“CALYPSO”) which encompasses thousands of nitrate concentrations measured since early nineties on more than a hundred monitoring stations in the Brusselian sands groundwater body. The mean nitrate concentration in the Brusselian sands increased slightly since 1994 and varies around 44 mg/l (Fig. 2.10). Before 2001, less than 15% of the monitoring stations located in the study area had nitrate concentrations exceeding the standard for drinking water (50 mg- NO_3^-/l). From 2001 to 2006, this proportion of polluted monitoring stations reached 25% (DGRNE, 2007). The dynamics of nitrate concentrations is highly variable from one monitoring station to another. While the trend is often upward (Fig. 2.11a) or stable (Fig. 2.11b), a decrease is sometimes observed (Fig. 2.11c). In other cases, there is substantial variability over time (Fig. 2.11d). In some monitoring stations, sampling has been stopped after a few years (Fig. 2.11e), or a sample has been collected only once (Fig. 2.11f). Since different versions of the CALYPSO dataset were used in this thesis, a detailed description of the nitrate concentration data and the locations where they were collected will be presented in the “Material and methods” section of each chapter.



Figure 2.7: Three wells in the study area (top: “Puits 2 Waterloo”, middle: “Puits de Hazoi”, bottom: “Puits de Houtain 1”).



(a)



(b)

Figure 2.8: A gallery (“Galerie de Baulers”) (a) and a spring (“Source Ter-fosse”) (b) in the study area.

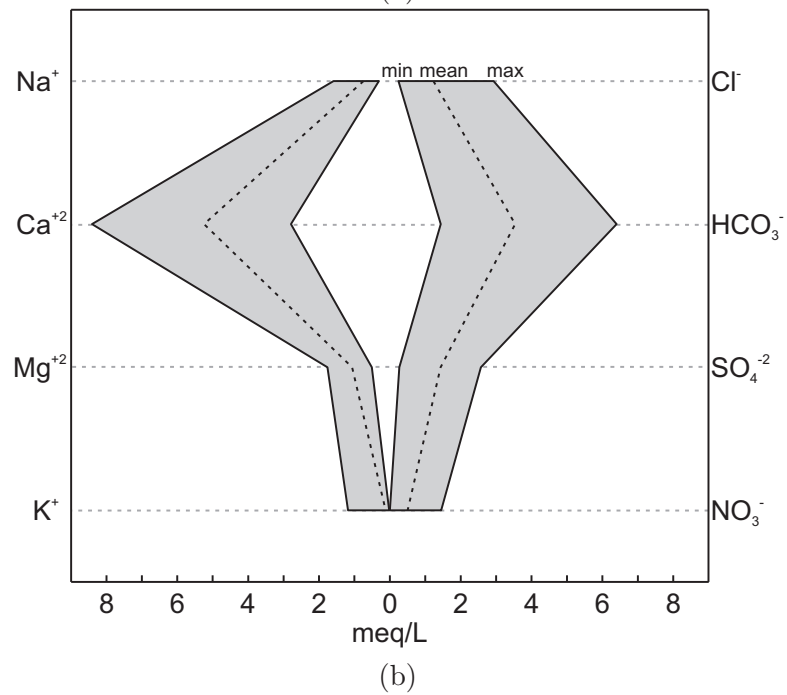
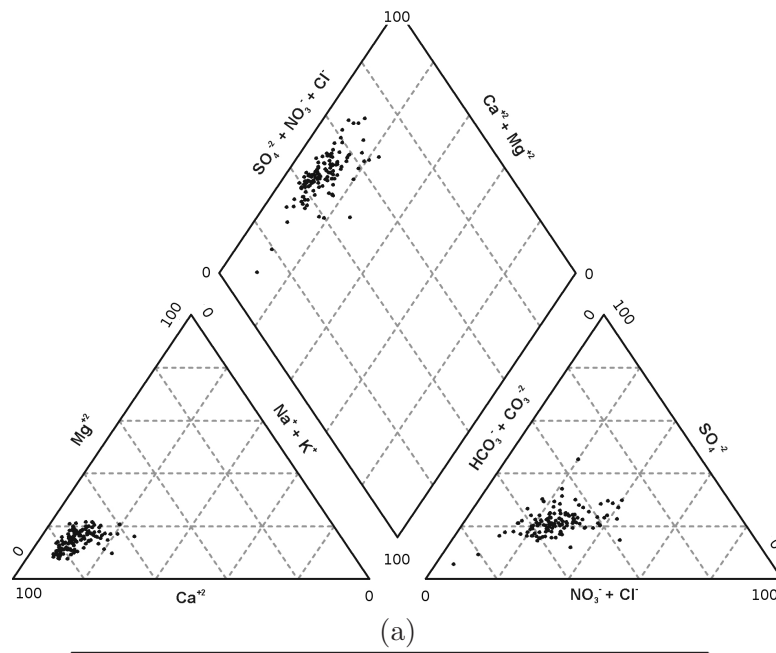


Figure 2.9: Piper plot (a) and Stiff plot (b) of groundwater data collected in the study area (January 2009).

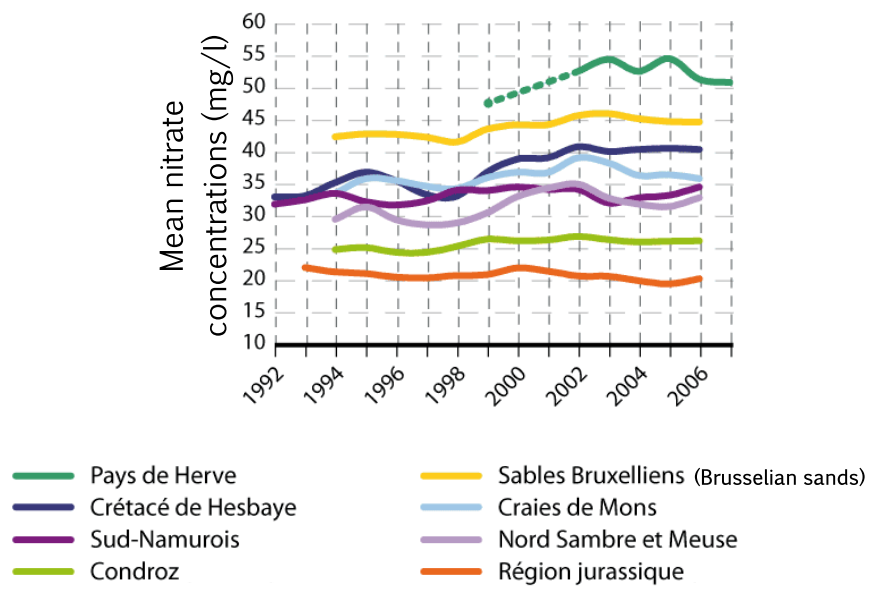


Figure 2.10: Nitrate concentration measured in various groundwater bodies of the Walloon Region. Source: SPW (2008).

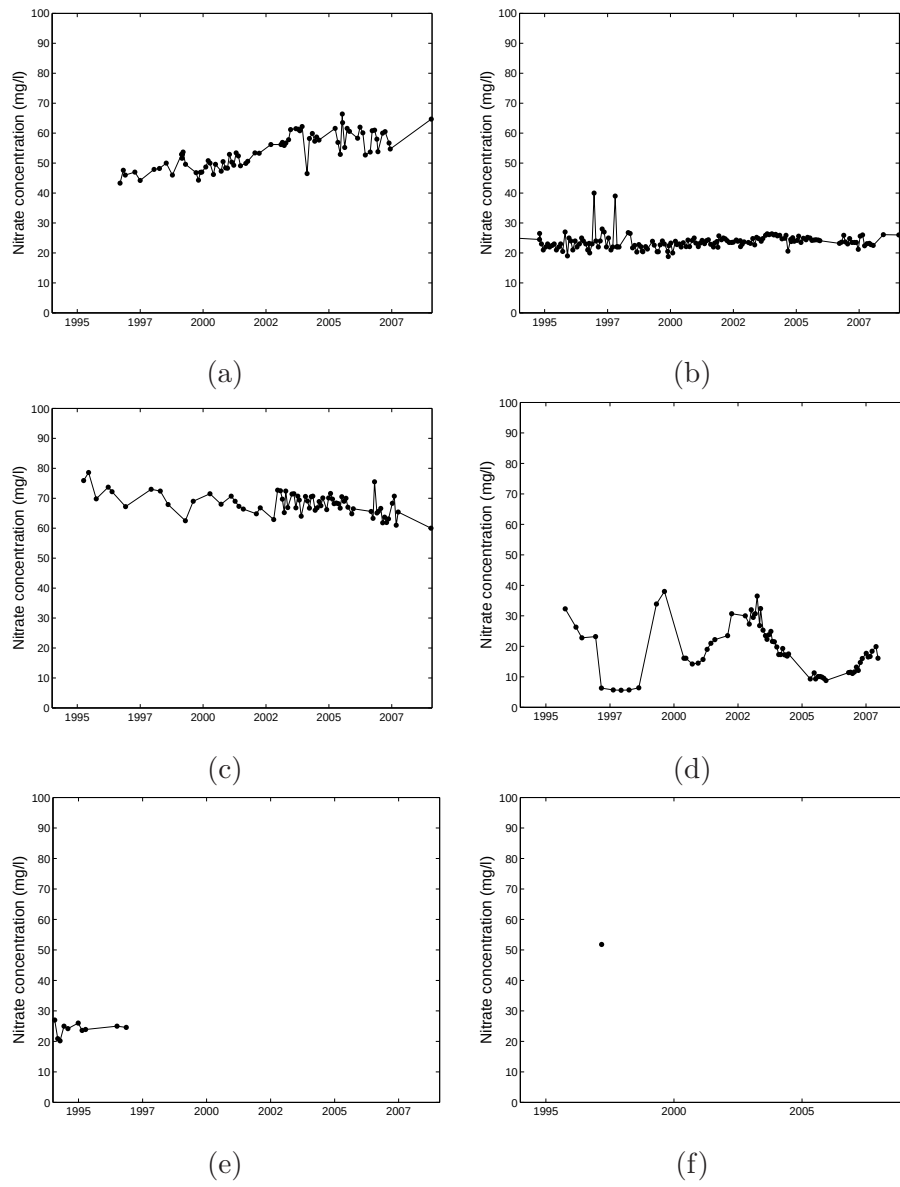


Figure 2.11: Time series of nitrate concentrations measured at six monitoring stations in the study area.

2.5 Climate

Climate is temperate maritime, with annual precipitation of 865 mm, mean annual temperature of 11.1 °C and annual potential evapotranspiration of 575 mm (Pameseb, 2000-2009, Louvain-la-Neuve). The mean groundwater recharge period, calculated from 1965 to 2007, extends from August to April, but recharge levels are highly variable from one year to another (Mattern and Vanclooster, accepted article).

2.6 Pressures on water quality

The basic information for assessing environmental pressures on groundwater is about land use. The study area is characterized by both the presence of intensive arable cropping and intense urban pressure (366 000 residents in 2006). In the study area, houses that are not connected to sewers discharge their wastewater to septic tanks, streams or infiltrates into the soil (personal communication, A. Battaglia, SPGE, 15-09-2009). The land use is highly fragmented. Typical land uses are arable land use, mainly wheat, sugar beet, maize and barley (found on loamy soils on the plateaus; about 51% of land use in the study area), urban (generally located in the valleys; about 17% of land use) and grassland and forests (found on valley slopes; about 13% and 10%, respectively). The 1 : 10 000 land use map with 65 land use classes of the Walloon Region was provided by the regional administration and reflects the situation of 2005 (PCNOSW, 2005) (Fig. 2.12). The vulnerability of the aquifer has been evaluated in the Scaldit project (SCALDIT, 2006) and was combined with information about the pressures on the aquifer, resulting in a map of contamination risk at the regional scale. The vast majority of the aquifer was identified as medium or high risk in terms of water quality.

2.7 Previous work on the study area

The Brusselian sands aquifer has been the subject of several studies, particularly in the area covered by the Dyle catchment. In its “monograph on the Dyle catchment”, Laurent (1977) made a detailed description of the Brusselian aquifer in the Dyle catchment. De Becker *et al.* (1985) tried to identify the nitrogen contamination sources in the Dyle catchment using a simplified mass balance, and concluded that nearly 84% of the groundwater nitrate occurs from agricultural soils and 16% from domestic activities. However, uncertainty associated with the different

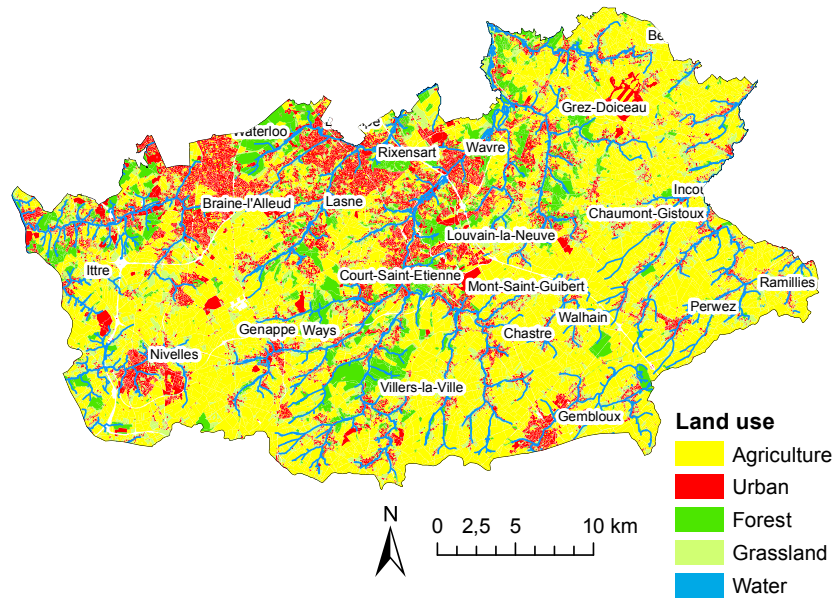


Figure 2.12: Land use in the study area. Source: PCNOSW (2005).

components of the balance and the unrealistic justification of some assumptions makes it difficult to interpret the results of this study. Bocken (1986) suggested that the lowest nitrate concentrations were measured under forest land use while the highest concentrations were measured in urban areas of the Dyle catchment. Wattecamps (1993) suggested that estimate of diffuse pollution by (De Becker *et al.*, 1985) was too high, highlighting the pressure of urban areas on the groundwater quality. Goovaerts *et al.* (1993) and Christakos and Bogaert (1996) used geostatistical methods to study the spring water composition in the Dyle catchment. Leterme *et al.* (2006) highlighted the impact of urban activities on the groundwater contamination by atrazine.

Chapter 3

Estimating travel time of recharge water through a deep vadose zone using a transfer function model

3.1 Outline

We estimate the travel time of percolating water through a deep vadose zone at the regional scale using a transfer function model and a physical based conceptual flow model (Hydrus-1D), thereby exploiting the time series of precipitation, actual evapotranspiration and groundwater piezometry and generic vadose zone data. With the transfer function model we observe a high variability of estimated travel time varying from 0.9 to 3.1 years, corresponding to estimated vertical water effective velocities varying from 6.6 to 28.0 m/year. These results were compared with the travel time estimated from the physical based conceptual model. With the flow model, estimated travel time varies between 4.7 and 15.5 years, corresponding to water effective velocities varying between 1.7 and 4.1 m/y. The estimated travel time calculated with the flow model were therefore about 5 times larger than those estimated with the transfer function model. This could be explained by the fact that the transfer function model considers heterogeneous recharge from the vadose zone as well as from the vicinity of the piezometer through the so-called piston flow effect. In addition, the flow model requires various hydrogeological and hydrodynamic parameters which were estimated using generic parametrisation approaches, that are largely affected by uncertainty and may not reflect the local conditions. In contrast, the transfer function

model only exploits available measurable time series and has the advantage of being site-specific.

3.2 Introduction

The vadose zone is a key component within terrestrial systems and plays an essential role in the hydrological cycle. The vadose zone encompasses the unsaturated soil root zone and controls thereby the fluxes of water, matter and energy between the atmosphere, land surface and subsurface water bodies. Knowing the travel time of water in the vadose zone is therefore a prerequisite for quantifying the recharge and load of groundwater bodies in terms of variable boundary conditions at the land surface interface (Feddes *et al.*, 2004).

Characterizing the travel time of water and associated matter in the vadose zone is complicated and this because of many reasons (Alvarez-Benedi and Munoz-Carpena, 2005). First, a wide set of physical, chemical and biological processes affect flow in the vadose zone. Second, the size and geometry of the vadose zone in natural conditions is often not well known. Third, the physical, chemical and biological properties of the vadose zone are variable in space and in time which makes the experimental assessment tedious. Fourth, as compared to technologies and tools available for characterizing surface hydrological and hydrogeological properties, much less technologies have been designed to characterize the partially saturated vadose zone. Fifth, water flow in the vadose zone is a highly non-linear process and depends very much on the saturation degree of water which on its turn is controlled by the variable water input at the land surface. Given this complexity, assessing travel time of water through the vadose zone has received far less attention as compared to travel time assessments in surface and groundwater bodies. The vadose zone is therefore still often a large gray box in our current hydrological knowledge.

Travel times of water through the vadose zone depend very much on the thickness of the vadose zone. In flat alluvial regions, where only a thin vadose zone is present, travel time may be small such that pressures exerted at the land surface will propagate fast to the groundwater body. In undulating landscapes, however, where the size of the vadose zone will generally be much larger, higher travel time is expected. In arid environments, for instance, the vadose zone can be hundreds of meters thick, and infiltration fluxes very low (Dyck *et al.*, 2005), resulting in the residence time of water ranging from several hundreds to thousands of years (Birdsell *et al.*, 2005). However, also in such a deep vadose zone,

flow can be extremely fast. For instance Levitt *et al.* (2005) showed that a surface applied tracer could reach a 78 m deep groundwater table in 8 to 14 days, proving the small travel time in such large formations.

Different methods exist to assess vadose zone travel times. Analysing at a given depth in the vadose zone the breakthrough of a land surface applied tracer allows determining the travel time from the moments of the time dependent breakthrough curve. Use have been made of single ionic inert tracers such as chloride (Allison *et al.*, 1985; Dettinger, 1989; Nativ *et al.*, 1995; O'Geen *et al.*, 2002; Javaux and Vanclooster, 2003a), stable and radiogenic isotopes (Barnes and Allison, 1988; Gee and Hillel, 1988), nitrate (Onsoy *et al.*, 2005), or a combination of different ionic tracers (Si and de Jong, 2007). Yet, given the complexity to carry out large scale tracer breakthrough experiments and the long time frames involved, an alternative approach relies on the inversion of conceptual flow and transport models. With such approaches use is made of some measured vadose zone property which is modelled using a transport model in which the travel time is considered, directly or indirectly, as the fitting model parameter. With the inverse approach, measured moisture content or resident tracer profiles have been used as fitting data by Wang *et al.* (2003); McElroy and Hubbell (2004); Hubbell *et al.* (2004); Flint and Ellett (2004) and Wu *et al.* (2004). Robinson *et al.* (2005) combines measurements of moisture content with the analysis of a tracer experiment. Constantz *et al.* (2003), proposes the logging of temperature profiles in combination with a coupled flow and heat transport model.

When using the inverse approach, physically based conceptual flow and transport models can be used that are based on the physical laws of mass, momentum and energy conservation and flow. The use of such flow and transport models is often prohibitive given the lack of data that are available for parametrising such models. Where nothing but only few time series of vadose zone properties are available, time series models are often preferred to the conceptual flow and transport models (Kim *et al.*, 2005). One of these, the transfer function model, was proposed by Jury (1982) to characterize field scale solute transport through an unsaturated soil. Using a transfer function model, it is considered that the internal transport mechanisms are unknown. Jury (1982) derived a simple theory for estimating the average and extreme behaviour of solutes moving through the vadose zone as a function of a simple field-measurable travel time probability density function (pdf). Inverting the transfer function for the parameters of the travel time pdf allows estimating the travel time through the vadose zone. This approach was applied for example by Vanderborght *et al.* (1996) and Javaux and Vanclooster (2003a) to determine the travel time through large undisturbed soil columns from

resident concentration data; by Gasser *et al.* (2003) to predict nitrate leaching under potato crops of an agricultural field; by Stewart and Loague (1999) to predict pesticide load of ground water at the regional scale; by van der Velde *et al.* (2006) to estimate the travel time through a volcanic soil on a small atoll in the Pacific Ocean.

Notwithstanding the availability of these methods, uncertainties in the estimation of the travel time through the vadose zone remain very high (Holt and Nicholl, 2004; Faust *et al.*, 2006). For instance, Cook *et al.* (1994) compared ionic tracer studies with radiogenic isotope tracer studies and concluded on the inconsistency between the estimates of the travel time with both methods. Given these uncertainties and inconsistencies, quite some scope exist to improve our knowledge on the travel time of water through the vadose zone.

The objective of this study is to evaluate the travel time of percolating water through a deep unsaturated zone using transfer function theory, thereby exploiting the measured time series of precipitation, actual evapotranspiration and groundwater piezometry. The underlying hypothesis is that the water flux wave at the soil surface will propagate through the vadose zone and, when it hits the ground water body, result in a ground water depth perturbation. Modeling this traveling wave by means of the transfer function model allows inferring the large scale travel time through the vadose zone. The results obtained by means of the transfer function model will further be compared with the travel time estimated by means of a physical based conceptual model (Hydrus-1D).

3.3 Material and methods

3.3.1 Data description

Daily precipitation measured at Uccle (Belgium) from 1961 to 2007 was provided by the European Climate Assessment & Dataset (Tank *et al.*, 2002), and was aggregated to monthly totals. A time series of monthly actual evapotranspiration was calculated by Oger (1991), using daily weather data collected at Gembloux (situated in the study region) from 1950 to 1989. In order to extrapolate these data to the period for which precipitation series were available (1961-2007), we calculated the mean actual evapotranspiration for each month and completed the time series of monthly evapotranspiration rates with the calculated mean per month. Completing the missing values as such is justified by the high reproducibility of the actual evapotranspiration cycle from one year to another. The time series of the piezometric height were provided by the regional administration (M.R.W.-D.G.R.N.E., 2008) and from the Hy-

drological Service of the Université catholique de Louvain. In the study area, ground water levels are measured on 241 piezometers. However, the vast majority of these piezometers cannot be used in the context of this study since either the length of the time series is insufficient, or the frequency with which the measurements are performed does not allow to capture the dynamics of the system. From the 241 available piezometers, only a subset of 18 piezometers were selected for which water levels are measured for a long period (1967 to 2007) and at a high measurement frequency (Fig. 3.1).

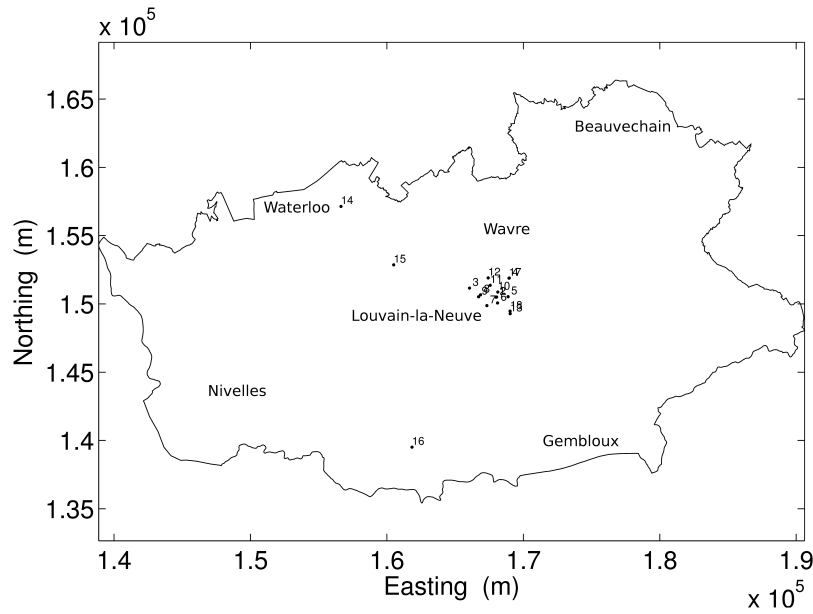


Figure 3.1: Location of the piezometers in the Brusselian sands ground water body.

3.3.2 The transfer function model

We use a transfer function model to describe water transport through the vadose zone. The underlying hypothesis is that a water flux wave and/or a pressure wave at the soil surface will propagate through the heterogeneous vadose zone and perturbate the water level when it hits the groundwater body. The vadose zone in this case study includes the biologically active soil root zone, a loamy substratum, and the unsaturated sandy substratum. The water flux wave at the soil surface is determined by infiltration of rain water in the soil, from which evapotranspiration rates are subtracted. The model further assumes that no

lateral run-off occurs and that no dispersion of percolating water takes place other than that which is implicitly represented by the travel time variations of the system (Jury, 1982). Water transport is assumed to be convective with a stochastic component expressing the variability of water travel time, due to heterogeneous pathways in the soil and subsoil (Gasser *et al.*, 2003). We consider only the vertical flux since the vertical travel time in the vadose zone is generally 1 to 3 orders of magnitude smaller than the horizontal one (Jury and Flühler, 1992).

The transfer function model uses a simple travel time probability density function (pdf) to relate an output time series to an input time series. The approach of Jury (1982) derives a distribution function based on the distribution of the travel time of solutes from the soil surface to a reference depth. Since the vadose zone between the surface and the aquifer smooth out the variations of water flux, a transfer function model can be used to describe the relation between the variation in rainfall and evapotranspiration and the variations of the level of the groundwater table. We use the transfer function model to describe the convolution of the variation in the rainfall minus the actual evapotranspiration with the transfer function to predict variation in the level of the ground water table:

$$P(t) - \mu_P = \alpha \int_0^T f(t)(I(t - \tau) - \mu_I)dt \quad (3.1)$$

where:

$I(t) = R(t) - E(t)$ is the input time series (percolating water, in mm/month);

$R(t)$ is the rainfall (mm/month);

$E(t)$ is the actual evapotranspiration (mm/month);

μ_I is the mean of I (mm/month);

$I(t) - \mu_I$ is the variation of input around μ_I (mm/month);

$f(t)$ is the transfer function equal to the travel time probability density function (pdf) (months⁻¹);

t is time (months);

τ is the time lag (months);

α is the scaling factor (-);

$P(t)$ is the piezometric level (mm/month);

μ_P is the mean of P (mm/month);

$P(t) - \mu_P$ is the variation of P around μ_P (mm/month).

The integral in equation 3.1 expresses the convolution between the variations around the mean percolating water ($I(t) - \mu_I$) with the travel time probability density function to predict the variations around the

mean of the piezometric level ($P(t) - \mu_P$). A log-normal probability density function was chosen for the transfer function $f(t; \mu, \sigma)$ to reflect the transport and mixing of the percolating water as it moves through a porous medium exhibiting a log-normal distribution of pore-water velocities (Ott, 1990). Hence:

$$f(t; \mu, \sigma) = \frac{1}{\sigma t \sqrt{2\pi}} \exp \left(-\frac{(\ln(t) - \mu)^2}{2\sigma^2} \right) \quad (3.2)$$

The model $f(t; \mu, \sigma)$ corresponds to a log-normal probability density function where μ and σ respectively correspond to the mean and standard deviation of the logarithm of the travel time through the vadose zone.

The transfer function was used to determine the modal transfer time, defined as the time where the probability density function reaches its maximum value, and the 5th and 95th percentiles, defined as the time needed by 5% and 95% percent of the percolating water to reach groundwater table. The parameters α , μ , and σ were obtained by minimizing the sum of squared errors for all observations within each piezometer (van der Velde *et al.*, 2006):

$$\Phi(\alpha, \mu, \sigma) = \frac{1}{n} \sum_{i=1}^n [(P - \mu_P)_{i, \text{simulated}} - (P - \mu_P)_{i, \text{observed}}]^2 \quad (3.3)$$

where:

- $\Phi(\alpha, \mu, \sigma)$ is the objective function to be minimized;
- $(P - \mu_P)_{i, \text{simulated}}$ is the simulated variation of P around μ_P (mm);
- $(P - \mu_P)_{i, \text{observed}}$ is the observed variation of P around μ_P (mm);
- n is the number of observations in each piezometer.

To avoid ill-posedness, an a-priori parameter domain was divided into a regular grid, covering a range from 0 to 5.5 for μ (Eq. 3.2) (corresponding to mean travel time from 1 month to 20 years), from 0 to 1 for σ (Eq. 3.2) and from 0 to 150 for the scaling factor α (Eq. 3.1). The objective function (Eq. 3.3) was calculated for each combination of the grid selected parameters. Afterward, the parameters minimizing the objective function were used as an input of the Nelder-Mead multidimensional unconstrained nonlinear minimization algorithm available in MatlabTM for a more accurate estimation of the optimal parameters.

We identified first the travel time pdf for each piezometer separately. Subsequently we identified an effective travel time by inverting all data simultaneously and compared these to the mean travel time pdf obtained from the local estimates. In case the traveling wave process through the

vadose zone is a linear process, than the local and effective travel time should converge.

3.3.3 The physical based conceptual flow model

We compared the estimated travel time by means of transfer function theory with predictions made by means of a physically based flow and transport model. We used the Hydrus-1D model (Simunek *et al.*, 2008) which solves numerically the 1-D governing flow model (Richards equation) for the vadose zone:

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial z} \left[K(h) \left(\frac{\partial h}{\partial z} + 1 \right) \right] - S \quad (3.4)$$

where z is the vertical coordinate (positive upwards), t is time (d), S is a sink term (d^{-1}), h is the pressure head (m), θ is the volumetric moisture content and K is the unsaturated hydraulic conductivity function (m/d); and the convection dispersion solute transport model:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial z^2} - \nu \frac{\partial C}{\partial z} \quad (3.5)$$

where C is the solute concentration (m^3m^{-3}), D is the dispersion coefficient (m^2d^{-1}) and ν is the water flux (md^{-1}). Hydrus-1D solves equations 3.4 and 3.5 for vertical heterogeneous porous media and transient boundary conditions by means of the Galerkin finite element method. The soil hydraulic functions used in Hydrus-1D are modelled according to the van Genuchten-Mualem model (Van Genuchten, 1980).

A variable flux condition was imposed on the soil surface, considering the same inputs $I(t)$ than those used in the transfer function model (Eq. 3.1). At the bottom of the flow domain a constant pressure head equal to zero was imposed, representing the position of the water table. The initial conditions were defined through a warming up procedure. In a first loop, the model was run from 1961 to 2007. The obtained moisture and pressure head profile at the end of this warming up loop was subsequently used as initial moisture and pressure head profile for the tracer simulation loop. In this second loop, a tracer pulse was applied on the top of the soil column during one time unit and followed through the profile allowing to infer convective solute travel time.

In contrast to the transfer function approach, we need information about the lithology of the sub-soil (i.e. a sandy layer overlain by a sandy loam layer) and the physical properties of each sub-soil layer to parametrise the formation profile in Hydrus-1D. The thickness of the different layers could be inferred from lithological logs that were collected

when installing the piezometers. However, these logs were only available for 12 out of the 18 piezometers. No data were available to parametrise the soil physical properties, and therefore use was made of three generic approaches to estimate these parameters (Tab. 3.1). The first set comes from the Hydrus catalog (Carsel and Parrish, 1988), the second one from Rosetta (Schaap *et al.*, 2001) and the third one from literature of measured hydraulic properties of media in the study area (Javaux and Vanclooster, 2004, 2006; Hupet *et al.*, 2004). Three typical different parameter sets describing the soil properties were used since we did not know the real soil properties at the location of the piezometers.

Except for the soil parameters, the generic parameters were used (e.g. single porosity, no hysteresis), because of the absence of data needed for a better parametrisation of the physically-based model.

Table 3.1: Soil properties used in the Hydrus-1D simulations

Source	Soil layer	Depth (m)	θ_r (-)	θ_s (-)	α (m ⁻¹)	n (-)	λ (-)	K_{sat} (m/y)	Dispersivity (m ⁻¹)
Hydrus catalog	Sandy loam	0 - 4	0.065	0.41	7.5	1.89	0.5	387.265	0.1
	Sand	4 - 14.3	0.045	0.43	14.5	2.68	0.5	2601.72	1
Rosetta	Sandy loam	0 - 4	0.0387	0.387	2.67	1.4484	0.5	139.612	0.1
	Sand	4 - 14.3	0.053	0.3747	3.53	3.1798	0.5	2346.88	1
Literature	Sandy loam	0 - 4	0	0.3894	0.4084	1.204	0.5	108.6	0.1
	Sand	4 - 14.3	0.0818	0.33	2.87	5.64	-0.555	189.8	1

3.4 Results

3.4.1 Input of the transfer function model

The monthly median of the monthly total percolating water flux at the soil-atmosphere interface, $I(t)$, calculated from 1965 to 2007, varies from nearly null from April to August, to 62 mm in December (Fig. 3.2a). The variability of the monthly total percolating water flux for each month is large. The input time series of the transfer function model was obtained by subtracting the average of the percolating water flux calculated for the complete time series from the monthly total percolating water flux time series $I(t)$ (Fig. 3.2b).

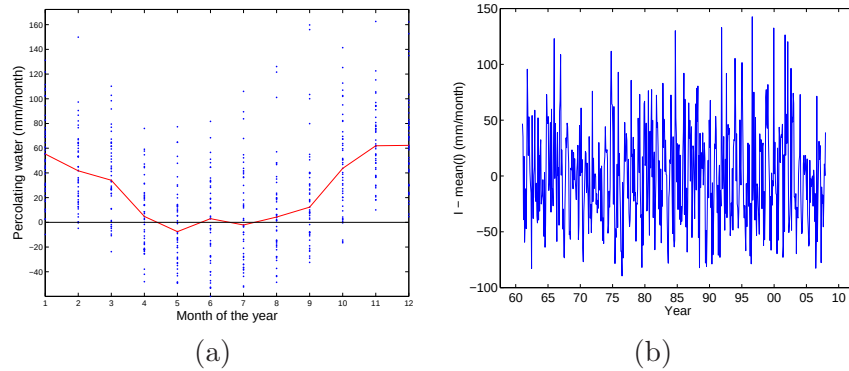


Figure 3.2: (a) Monthly total (dots) and monthly median of the monthly total (line) percolating water flux at the soil-atmosphere interface (mm/month), calculated from 1965 to 2007 and (b) variation of the monthly total percolation water flux around its mean value (mm/month) used as input time series of the transfer function model.

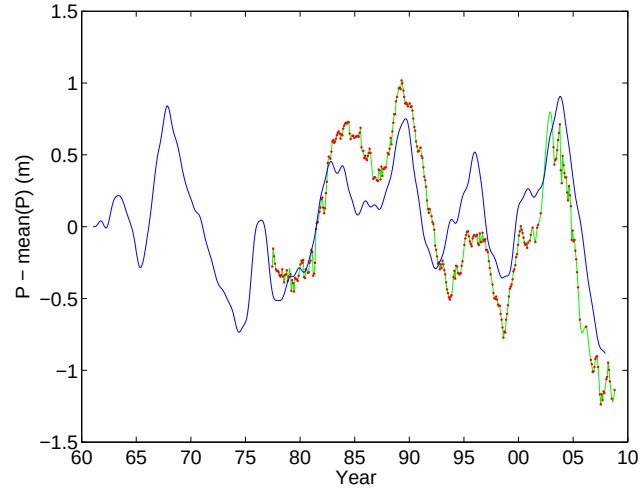
3.4.2 Travel time estimated from the transfer function model

Simulated versus measured variation of piezometry around the mean and the corresponding optimal log-normal transfer function are shown on Figures 3.3, 3.4, 3.5, 3.6, 3.7 for piezometers 4, 13, 14, 15 and 16, respectively. Piezometers 4 and 13 are located in Louvain-la-Neuve while piezometers 14, 15 and 16 correspond to the three piezometers located in the north and south parts of the study area (see Fig. 3.1). We observe that the transfer function model allows to describe the phase of the dynamic signal propagating through the deep vadose zone, but has more

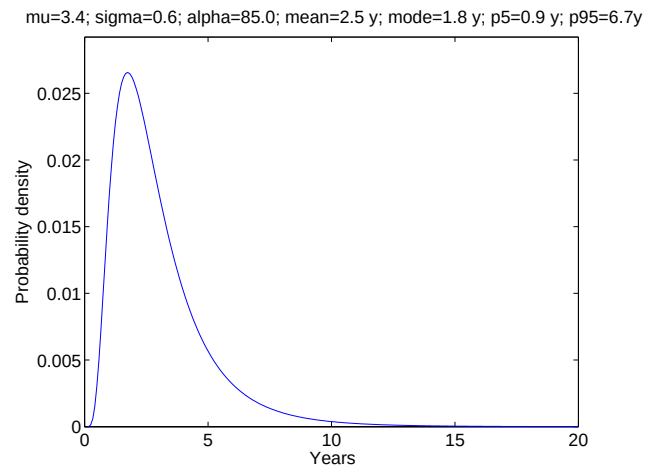
difficulty to predict correctly its amplitude. We also observe a systematic overestimation of the simulation between 1993 and 1998 which can be explained by the exploitation regime of ground water in this area, and which is not considered in the transfer function model. However, only the phase is important for estimating the travel time.

The modal value of the travel time of recharge water through the unsaturated zone, calculated from the transfer function model for 18 individual piezometers varies from 0.9 to 3.1 years (Tab. 3.2). The average of the modal transfer time of these 18 piezometers was 2.3 years, with a standard deviation of 0.6 years. Furthermore, the fifth percentile of the travel time for the 18 piezometers varies from 0.5 to 1.8 years and the 95th percentile from 5.2 to 15.1 years, which shows that, for a same location, the water wave propagates very quickly through the unsaturated zone while at other places wave propagations is much slower. The variability of the travel time between the piezometers can be explained by the differences in the thickness of the unsaturated zone, variability of hydrogeological properties, and flow phenomena that are not considered within the transfer function model. For instance, we observe that travel time increases with depth to the water table (Fig. 3.8a). By dividing the depth to the water table (Tab. 3.2) by the modal travel time (Tab. 3.2) for each piezometer, we can estimate that the water travel velocity through the vadose zone varies from 6.6 to 28.0 m/year (Tab. 3.2).

We also attempted to derive a regional transfer function model by fitting one log-normal transfer function to the mean of all the data of the 18 piezometers (Fig. 3.9a). Despite the differences characterizing the water fluxes through the vadose zone across the study area, the average function can give an approximate travel time representative for the whole area. This is supported by the fact that piezometric variations are similar across the study area as shown on Figure 3.9a. The resulting optimal log-normal pdf is characterized by a modal travel time of 2.8 years, which is close to the mean of the modal travel time of the 18 individual piezometers (2.3 years) (Fig 3.10). The 5th percentile of the travel time estimated on the mean of all piezometers was 1.5 year and the 95th was 10.5 years (Fig. 3.9b).

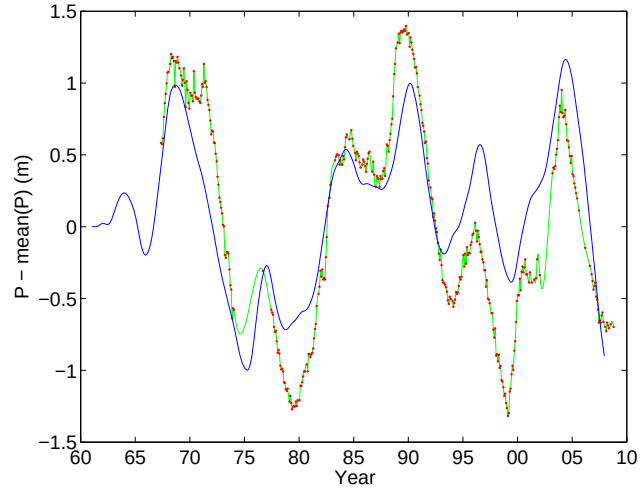


(a)

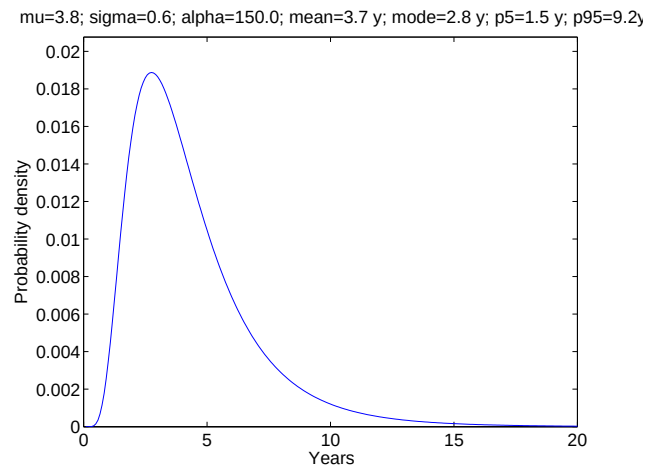


(b)

Figure 3.3: Measured (red dots) and simulated with the transfer function model (line) piezometric time series (a) and the corresponding optimal log-normal transfer functions (b) for piezometer 4.

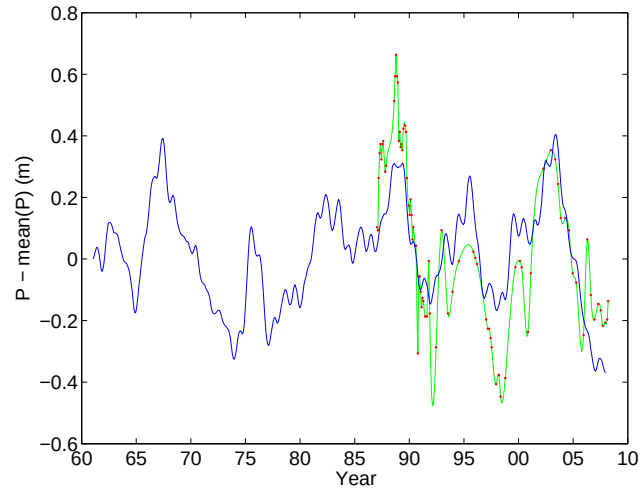


(a)



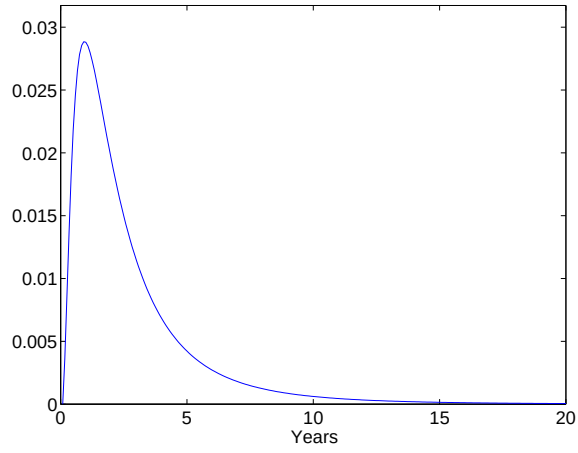
(b)

Figure 3.4: Measured (red dots) and simulated with the transfer function model (line) piezometric time series (a) and the corresponding optimal log-normal transfer functions (b) for piezometer 13.



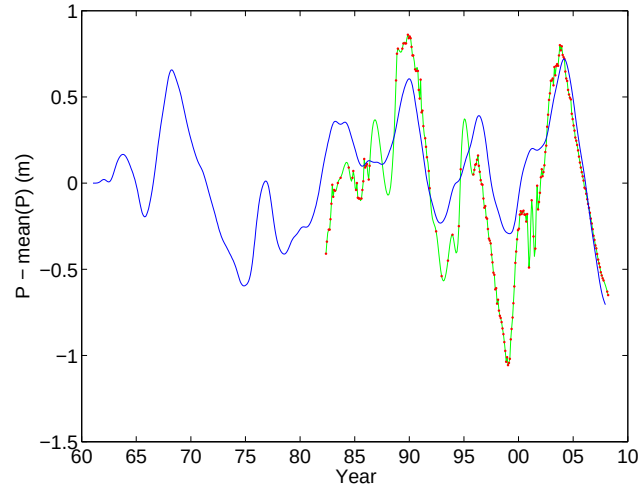
(a)

$\mu=3.1$; $\sigma=0.8$; $\alpha=35.0$; $\text{mean}=1.9 \text{ y}$; $\text{mode}=0.9 \text{ y}$; $p5=0.5 \text{ y}$; $p95=7.9 \text{ y}$



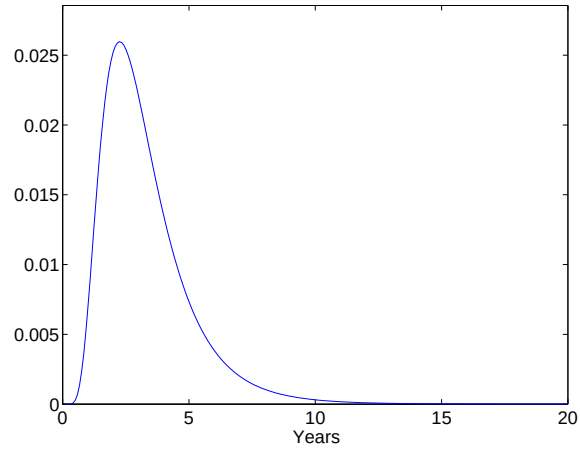
(b)

Figure 3.5: Measured (red dots) and simulated with the transfer function model (line) piezometric time series (a) and the corresponding optimal log-normal transfer functions (b) for piezometer 14.



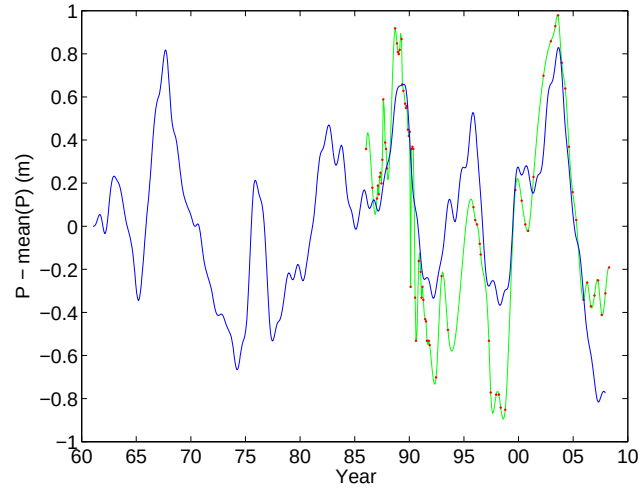
(a)

$\mu=3.5$; $\sigma=0.5$; $\alpha=70.0$; $\text{mean}=2.9$ y; $\text{mode}=2.2$ y; $p5=1.3$ y; $p95=6.6$ y



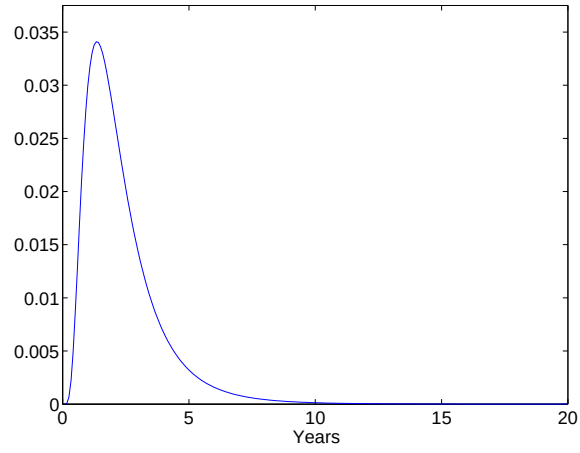
(b)

Figure 3.6: Measured (red dots) and simulated with the transfer function model (line) piezometric time series (a) and the corresponding optimal log-normal transfer functions (b) for piezometer 15.



(a)

$\mu=3.1$; $\sigma=0.6$; $\alpha=65.0$; $\text{mean}=1.9 \text{ y}$; $\text{mode}=1.3 \text{ y}$; $p5=0.7 \text{ y}$; $p95=5.2 \text{ y}$



(b)

Figure 3.7: Measured (red dots) and simulated with the transfer function model (line) piezometric time series (a) and the corresponding optimal log-normal transfer functions (b) for piezometer 16.

Table 3.2: Depth to the water table, travel time and water effective velocities calculated with the transfer function model and Hydrus-1D (with the three sets of soil properties) for the 18 piezometers

Piezometer	Depth (m)	Transfer function		Hydrus (Hydrus set)		Hydrus (Rosetta set)		Hydrus (Local literature set)	
		travel time (y)	velocity (m/y)	travel time (y)	velocity (m/y)	travel time (y)	velocity (m/y)	travel time (y)	velocity (m/y)
1	37.7	2.92	12.9	12.4	3.04	13.4	2.82	15.5	2.43
2	36.7	2.25	16.3	10.4	3.53	12.5	2.94	13.3	2.76
3	41.4	2.92	14.2	10.5	3.94	10.0	4.14	12.0	3.45
4	14.3	1.75	8.2	4.7	3.04	5.0	2.86	8.3	1.72
5	33.8	2.25	15.0	10.4	3.25	12.6	2.69	13.4	2.53
6	26.9	2.17	12.4	9.2	2.92	9.1	2.96	9.3	2.89
7	39.5	1.92	20.6	10.1	3.91	9.9	3.99	11.7	3.37
8	16.9	2.58	6.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
9	17.7	2.25	7.8	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
10	36.5	2.33	15.7	10.2	3.58	10.7	3.41	12.6	2.9
11	33.7	2.92	11.6	9.5	3.55	9.6	3.51	11.6	2.91
12	49.1	3.08	15.9	12.6	3.9	12.9	3.81	13.5	3.64
13	29.7	2.75	10.8	9.4	3.16	10.6	2.8	12.8	2.32
14	25.6	0.92	28.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
15	39.3	2.25	17.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
16	22.9	1.33	17.2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
17	14.5	2.17	6.7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
18	29.8	2.50	11.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

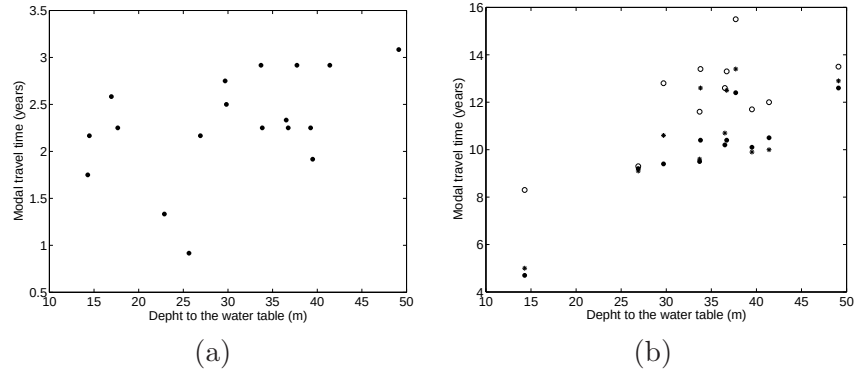


Figure 3.8: Relation between the depth to the water table and the modal travel time calculated with (a) the transfer function model and (b) Hydrus-1D (black circles, stars and white circles correspond to travel time calculated with the soil parameters of the Hydrus catalog, Rosetta and local literature, respectively).

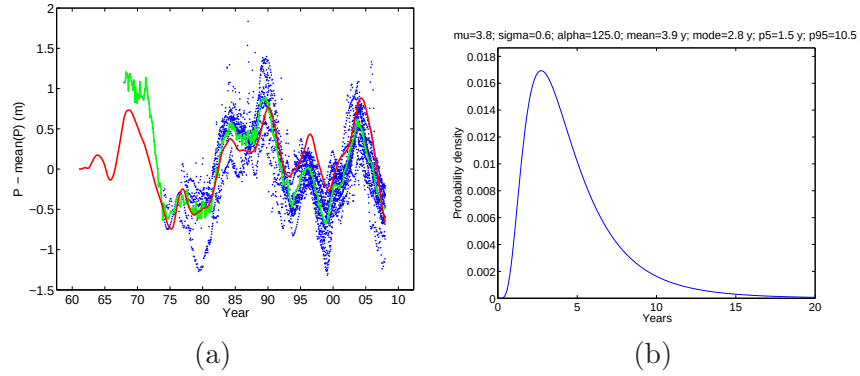


Figure 3.9: Measured data of all the piezometers (blue dots), their mean (green line) and the simulated piezometry (red line) (a) and corresponding optimal log-normal transfer function (b).

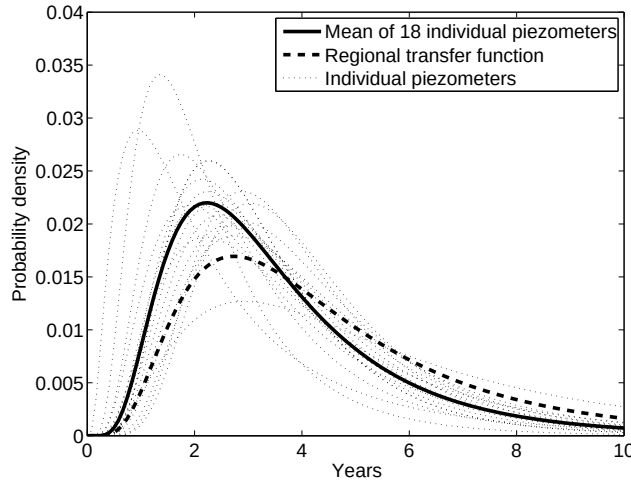
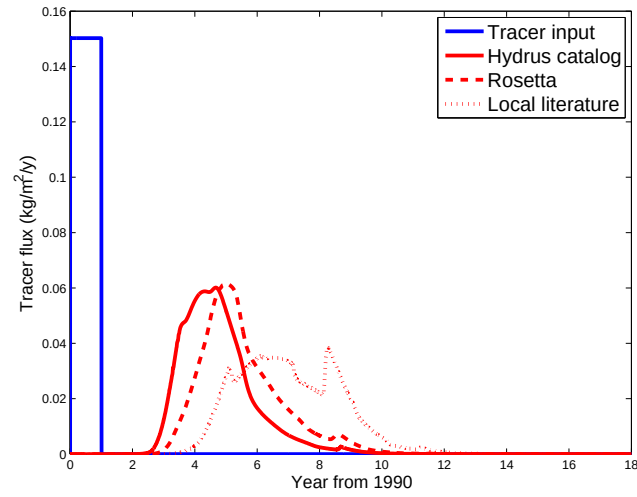


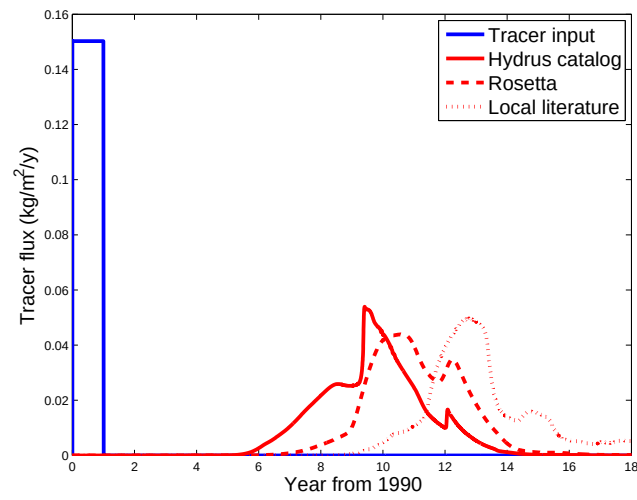
Figure 3.10: Transfer function models of the 18 individual piezometers (dotted lines), their mean (line) and regional transfer function model (broken line).

3.4.3 Travel time estimated from the conceptual flow and transport model

Travel time was also calculated from the breakthrough of a conservative tracer, simulated for 12 piezometers using the Hydrus-1D model. All 18 piezometers of the previous section could not be used since information about the thickness of the sandy and sandy loam layer was not available for 6 out of them. The breakthrough curve of the inert tracer at the bottom of the unsaturated zone column had a log-normal-like shape with a modal transfer time going from 4.7, 5.0 and 8.3 years to 12.6, 13.4 and 15.5 years for the first, second and third set of soil properties, respectively (Tab. 3.2). Figure 3.11 presents the simulated breakthrough curves for piezometers 4 and 13 located in Louvain-la-Neuve. Obviously, we observe also that travel time increases with depth to the water table (Fig. 3.8b).



(a)



(b)

Figure 3.11: Breakthrough curves calculate with Hydrus-1D for piezomter 4 (a) and 13 (b).

3.5 Discussion

The values of the travel time estimated with the physical based model are about 5 times larger than those estimated with the transfer function model. Differences can be explained by conceptual differences between both modelling approaches and the uncertainty associated with the parametrisation of the physically based conceptual flow and transport model.

Indeed, the travel time estimated from the simulated breakthrough curve of the inert tracer by means of the physical based conceptual model, considers 1D convective mass transport of an inert tracer with the moving water body through an unsaturated column on top of the piezometer. In this case, it has been hypothesized that the full water body within the vadose zone contributes to the conservative mass transport, and that the estimated travel time of the recharging water corresponds to the simulated travel time of the conservative tracer. In reality however, the measured piezometric position will not only be influenced by the local vertical recharge through the 1D vadose zone column on top of the piezometer, but also by the lateral recharge through the vadose zone and the groundwater body itself.

The transfer function model considers the geologic formation between the observation point (i.e. the local piezometer) and the surface input as a black box with no well defined geometry. With this modelling approach the flow domain does not necessarily pertain to a 1-D unsaturated soil column on top of the observation point, but may be equivalent to a geometrically irregular flow domain, encompassing stream tubes through the vadose zone and the groundwater body itself, where water is transported to the observation point in different directions. Hence, the transfer function model may conceptually encompass the recharge of the water coming from the vadose zone on top of the observation point as well as water that laterally feeds the observation point. The transfer function model will also consider the water that feeds the observation point through the so-called piston flow effect. Indeed, when pressure waves propagate through the vadose zone, resident water in the vicinity of the piezometer may be mobilized and contribute to piezometric variation. Pressure waves generally propagates through natural porous media at velocities which are much faster than mass transport waves (Bear, 1972), and piezometric variation does not necessarily reflect mass transport through the vadose zone. In case the lateral recharge is more important than the vertical recharge through the vadose zone, or in case the piston flow effect is significant, then travel time inferred from the transfer function modelling approach may easily be smaller than es-

estimated from a physically based 1D conceptual mass transport model through the vadose zone. This piston flow effect has a major impact on the estimated travel time and is probably the cause of the different results of the two models. Indeed, the piston flow effect is taken into account in the transfer function model but not in the physically based model, which only simulates mass transport

Further, vertical flow rate in the vadose zone may be faster than estimated from the conceptual mass transport model. Many experimental evidence show that only part of the available water in the vadose zone contributes to effective mass transport. Using small scale sandy columns collected from the same region as in the present case study, Vanclooster *et al.* (1993) showed that mass transport could much better be described with a two porosity flow model rather than a single porosity flow model, considering mobile water fractions ranging between 0.2 and 0.8 of total resident volumetric soil moisture. In case the mobile water fraction would indeed be 0.2, then effective velocities would be 5 times larger which is consistent with the estimates from the transfer function model in the present study. Based on detailed solute transport experiments at variable flow rates on an undisturbed 0.5 m³ size sandy soil monolith, collected from the sandy substratum of the Brusselian aquifer, Javaux and Vanclooster (2003b) showed that effective pore water velocity contributing to the mass transport of the inert tracer ranges between 0.8 and 1.6 times the theoretical pore water velocity. Also in the majority of the experiments of this last study, larger effective velocities than pore velocities estimated from a single region mass transfer model were obtained.

The unavailability of pore water to contribute to effective mass transport will further be exacerbated when heterogeneous flow develops in the flow domain feeding the piezometer. In-situ heterogeneous flow may first be induced by the local variability of the vadose zone transport parameters. The local scale variability of the vadose zone flow properties is indeed very large. Mallants *et al.* (1996), for instance, showed that the local scale saturated hydraulic conductivity of the loamy soil specific for the present study area could vary with 6 orders of magnitude, while saturated porosity could vary between 0.38 and 0.51. Together with the local scale variability of the unsaturated hydraulic properties, these induce variability of fluxes of a factor 12. Similar results were obtained when analyzing the local scale variability of the sandy substratum of the present case study area (Javaux and Vanclooster, 2006). Heterogeneous flow may further be promoted at the formation scale by the presence of distinguished structural features, such as clay lenses and discontinuous clay layers. Indeed, the sandy substratum of the study area is intersected

with different discontinuous clay layers which reflect the genesis of these natural formations. Flow across different textured layers will be unstable and induce heterogeneous flow. Within the unsaturated sandy soil core analyzed by Javaux *et al.* (2006), a distinguished structural feature was present which induced clearly heterogeneous flow at the macroscopic core scale. Similarly, when analyzing inert tracer transport through a 6 m deep observation well below an artificial lake, different clay layers were observed. The measured local flow velocity across the different layers varied between 2.5 and 13.1 m/y which is in the same order of magnitude of flow velocities that are calculated in the present study.

The difference in estimated travel time with both methods could also partially be explained by the uncertainty on the hydrogeological and hydrodynamic data feeding the 1D conceptual flow model. The 1D flow model requires a good knowledge of the lithology of the vadose zone and the unsaturated flow hydraulic properties. In case the hydraulic properties are not known, they can be estimated based on the knowledge of the granulometry and bulk density using so-called pedo-transfer functions. For the considered piezometers in this case study, the lithology of the vadose zone could rather correctly be reconstructed using the lithological logs that were collected when installing the piezometers. However, the hydraulic properties are far more uncertain. To consider the uncertainty in vadose zone hydraulic properties, three parametrisation strategies were considered in the present study. The different parametrisation schemes yield estimated travel time variations ranging between 4.7 to 15.5 years, corresponding to velocity variations from 1.7 to 4.1 m/year. Although largely significant, this suggests that uncertainty in hydraulic parametrisation only marginally explains the difference in estimated travel between both methods.

As a final remark, the important travel time through the vadose zone may have considerable consequences for water management in the study area. Indeed, the unconfined groundwater body of the Brusselian aquifer is exploited for drinking water purposes and is subjected to many pressures. Mattern *et al.* (2008) for instance describe the current pollution of the groundwater body by nitrates, while Leterme *et al.* (2006) discuss pollution by pesticides. Within the context of the implementation of the European Water Framework Directive and the European Nitrate Directive, the regional administration currently implements a set of land use management measures, envisaging to reduce emissions of pollutants from the land surface and the root active zone to the groundwater body. The important travel time through the vadose zone suggests that the impact of these measures on ground water quality can not be expected at the short term.

3.6 Conclusions

In this study, we used a transfer function model to estimate the travel time of percolating water through a deep vadose zone (Brusselian sands, Belgium) and we showed a high variability across the study area, with modal travel time varying from 0.9 to 3.1 years and transfer velocities varying from 6.6 to 28.0 m/year (in comparison, an estimation of 1 m/year across the unsaturated zone overlying the Hesbaye chalky aquifer in Belgium was cited by Brouyère *et al.* (2004)). These water effective velocities were compared with estimates made by means of a physically based conceptual flow model (Hydrus-1D). The transfer velocities calculated with the transfer function model were about five times higher than those simulated with the flow model. This could be explained by the fact that the flow model requires various hydrogeological inputs which are affected by considerable uncertainty and that it doesn't take the local soil characteristics and heterogeneities into account. In contrast, the transfer function only needs easily measurable time series and has the advantage to be site-specific. However, since the piston flow effect is intrinsically modeled with the transfer function model, the travel time estimated from the transfer function does not reflect real mass transport from the surface to the groundwater body. In contrast, the longer travel times simulated with Hydrus-1D are probably due to the fact that this model only models mass transport without piston flow effect. The importance of the piston flow effect could not be quantified with the present set-up. It is therefore suggested to complete this study with more advanced mass tracer experiments. In the context of nitrate transfer through the unsaturated zone, we therefore refer to the results obtained with Hydrus-1D, even if the implementation of this model is limited by the data availability about the hydrogeological context.

Chapter 4

Discriminating sources of nitrate pollution in an unconfined sandy aquifer

4.1 Outline

Correctly assessing the origin of groundwater pollution is an important prerequisite for efficient groundwater management. In this chapter, statistical modelling tools are applied to discriminate the sources of nitrate pollution in the unconfined deep sandy aquifer of the Brusselian sands (Belgium). Multiple regression and regression tree were compared to identify the factors affecting the nitrate concentration in this vulnerable groundwater body. The explanatory factors were related to land and land use properties in the capture zone. The tree model and the low fitting power of the multiple regression model showed the highly complex interaction pattern between explanatory variables. In the region, one explicative variable taken alone could not be considered responsible for the groundwater pollution by nitrate. However, both methods indicated the negative influence of residential land on the nitrate concentrations and a slight protective effect of low slope values. Furthermore, we showed the importance of delineating a proxy of capture zones on the basis of topography, the type of monitoring station and a simplified water mass balance, compared to circular capture zones centered on the monitoring stations.

4.2 Introduction

Nitrate emissions from agricultural and non-agricultural sources continue to exert a considerable pressure on subsurface groundwater bodies all over the world. Excessive nitrate in groundwater supplies can cause animal and human health problems (Cornblath and Hartmann, 1948; Knobeloch *et al.*, 2000; Mostaghimi *et al.*, 1997; Ridder *et al.*, 1974; Manassaram *et al.*, 2006). In Europe for instance, 35% of the groundwater bodies are expected to be at risk of not reaching the European water framework directive objectives by 2015, one of which is to reduce nitrate concentrations in groundwater under the standard of drinking water of 50 mg NO₃/l, while 45% of the water bodies are insufficiently documented to be properly assessed (European Commission, 2007). In the overwhelming part of waterbodies at risk, nitrate remains one of the critical parameters.

Nitrate pollution can potentially originate from atmospheric dry and wet deposition, sewer leakage, septic tanks, nitrogen-based chemicals, fertilizers, urea used as a road de-icing agent, river or channel infiltration, ammonium as a by-product of many industrial processes, and nitrification of mineralized organic matter (Ford and Tellam, 1994; Wakida and Lerner, 2005). Yet, the quantification of the contribution of all these different sources to the nitrate pollution problem remains a complicated task.

Previous studies have correlated land use and other environmental factors as proxies of pollution sources with water quality. Nolan and Stoner (2000) for instance, compared the nitrate concentration in shallow groundwater with land use in the United States and showed that the most polluted wells are beneath agricultural land, followed by those beneath urban land. Later on, Nolan and Hitt (2006) developed multivariate empirical models for nitrate in groundwater in the United States and showed that areas with high N application, high water input, well-drained soils, fractured rocks or those with high effective porosity, and lack of attenuation processes have the highest predicted nitrate concentration. Debernardi *et al.* (2007) used univariate statistics to try to correlate the nitrate concentration in the groundwater of the plain sector of Piemonte (Italy) with depth to the water table, land use and nitrogen input to the soil. They concluded that univariate statistics are not able to describe individually the complex phenomena affecting nitrate concentrations in soil, subsoil and groundwater in that region. Adopting a multivariate approach, Kaown *et al.* (2007) used Tobit regression to analyze the factors affecting the nitrate concentration in a shallow groundwater system in Yupori, Chuncheon (Korea) and concluded that

the agricultural activity in the vegetable fields and barns in a 100 m radius around each well were the major factors affecting the elevated nitrate concentration while the land slopes and elevations were negatively correlated with the nitrate concentration. Gardner and Vogel (2005) used maximum likelihood Tobit and logistic regression analyses of explanatory variables that characterize land use within a 300 m radius of each well to develop predictive equations for nitrate concentration at 69 wells on Nantucket Island, Massachusetts. They demonstrated that nitrate concentrations downgradient from agricultural land are significantly higher than nitrate concentrations elsewhere and that the number of septic tanks and the percentages of forest and high-density residential land are reliable predictors of nitrate concentration in groundwater. Rothwell *et al.* (2008) used classification and regression tree models to evaluate the key environmental drivers controlling dissolved inorganic nitrogen leaching from European forests. Spruill *et al.* (2002) applied a tree model to identify nitrate sources in ground water using predictor variables related to water chemistry. Few, if any, similar studies performed for groundwater in sandy unconfined aquifers of variable thickness have compared statistical methods applied on the same dataset and the effect of the delineation of the capture zones of the monitoring stations.

The main goal of this study is to determine the major factors controlling the nitrate pollution in a deep unconfined sandy aquifer of variable thickness. To achieve this goal, two multivariate statistical methods are used and compared considering land and land use attributes as explanatory variables. Multivariate methods are employed here because there was no clear bivariate relationship between groundwater nitrate concentration and any of the explanatory variables (not shown). The identification of the contributing factors is performed first by means of multiple regression analysis which model parameters are indicative of the sensitivity of the contributing factors to the nitrate pollution problem. The second approach is the use of regression trees to classify the explanatory variables and to investigate their interactions. Major advantages of regression tree models are that Gaussian distribution assumption of predictor variables do not need to be satisfied, that they can incorporate categorical data and that they allow the complex interactions between the predictor variables to be easily represented. Furthermore, while multiple linear regression identifies global relationships in the data set, regression trees are able to identify local relationships (Rothwell *et al.*, 2008). Furthermore, the impact of the delineation of the capture zones - the area around the monitoring wells where the explanatory variables

were measured - is tested by comparing circular and expert knowledge geometries.

The study is performed for the particular case of the groundwater body of the Brusselian aquifer in the center of Belgium. The groundwater pollution by nitrate in this aquifer is currently a major problem for the regional administration, which has to comply with the European Water Framework Directive (2000/60/EC, 2000) by 2015 and for the water supply companies, which are considering expensive denitrification treatments to avoid the closure of some polluted wells, at which nitrate concentrations up to 71.9 mg NO₃/l have been observed (personal communication). Despite the implementation of considerable nitrate reduction action plans, no improvement of the groundwater quality has been observed in this groundwater body during the last 15 years. The groundwater body is at variable deepness and the travel time in the unsaturated zone before surface loading of nitrate reaches the aquifer varies between a few months and more than 30 years (Vanclooster *et al.*, 2004).

4.3 Material and Methods

4.3.1 Data description

The depth to the water table was calculated by subtracting the kriged piezometry value from a 30 m resolution digital elevation model (DEM) which was provided by the regional administration. The piezometry map was calculated by interpolating the water table levels measured in 1984 using ordinary kriging. The slope at each monitoring station was calculated based on the DEM. The calculation of depth to the water table varies from 0 to more than 45 m with a mean value of 10.46 m (Fig. 4.1). The depth is lower near the main draining rivers and higher on the plateaus in between. The calculated slopes at the monitoring stations locations vary from 0 to 21% (not shown).

The aquifer is monitored by the local administration and the water supply companies to comply with environmental legislation. The groundwater nitrate concentration data set collected by the local administration was used (CALYPSO hydrochemical database of the Ministry for the Walloon Region, version 12/09/2006). The dataset encompasses 7 605 groundwater samples collected on 103 different monitoring stations between January 1994 and December 2005. These monitoring stations are wells, galleries, springs and drains (Fig. 4.2). Galleries and drains are artificial tunnels (for galleries) and tubes (for drains) which collect water by gravity flow. Springs are points where water flows out the ground.

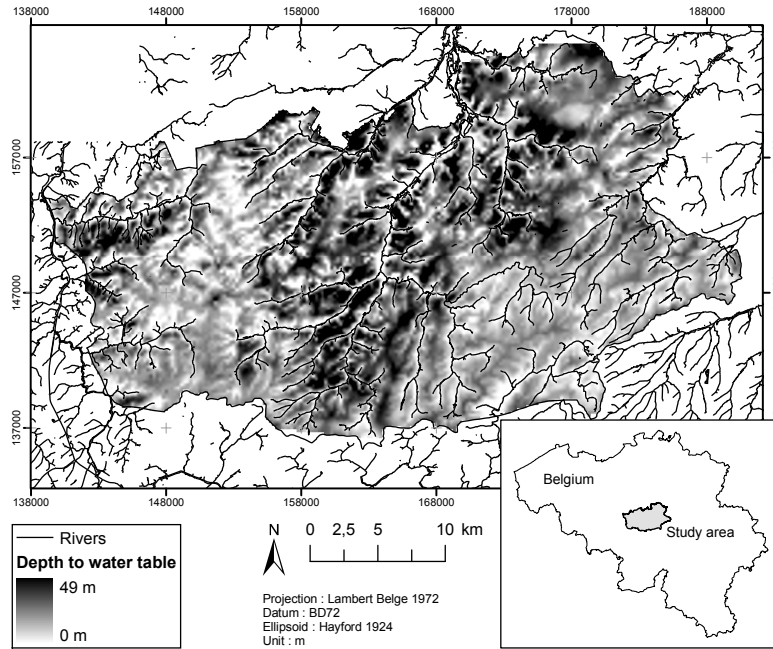


Figure 4.1: Depth to the water table.

A multiple comparison test was performed using the functions implemented in the Statistics ToolboxTM of MatlabTM. This test was unable to detect differences in mean nitrate concentrations of wells, galleries, sources and drains at a significance level of 0.01. All the analyses were conducted in ISO 17 025 registered laboratories. Annual nitrate concentrations statistics were calculated for each monitoring stations (Mattern *et al.*, 2008).

The nitrate concentrations show a wide spatial variability in the study area, with values going from 5.6 up to 93 mg/l (Tab. 4.1). The mean concentration seems to be generally slightly increasing over the 11 year period (from < 40 mg/l to 44.9 mg/l). From the 103 available monitoring stations, nitrate concentrations were measured on 43 of them in 1994 and on 82 in 2000 and 2001. The mean nitrate concentration of the two latter years was used in the subsequent analysis.

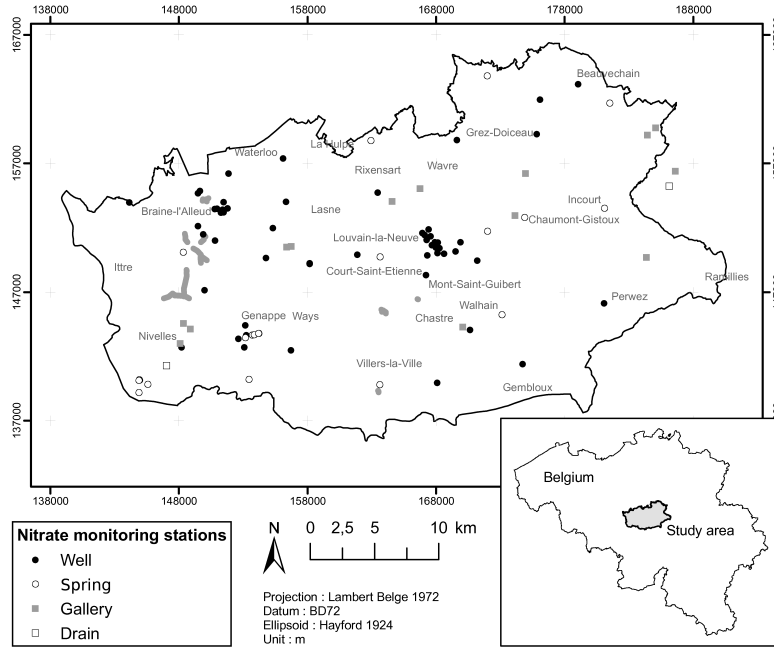


Figure 4.2: Location of the monitoring stations in the study area.

Table 4.1: Nitrate annual statistics.

Year	Nbr stations	Nbr samples	NO ₃ min (mg/l)	NO ₃ max (mg/l)	NO ₃ mean (mg/l)	NO ₃ stdv (mg/l)
1994	43	435	12.0	84.0	37.3	10.1
1995	58	559	8.3	80.0	38.9	11.4
1996	76	581	12.7	80.0	41.0	11.1
1997	75	534	5.6	77.0	40.9	10.9
1998	74	356	5.7	75.6	38.1	11.0
1999	78	464	10.4	75.8	42.2	11.7
2000	82	620	14.2	80.7	43.7	11.8
2001	82	784	15.7	82.9	43.1	11.4
2002	79	741	20.5	76.8	44.4	11.1
2003	75	989	18.8	81.7	45.0	11.4
2004	72	846	13.2	83.9	44.7	11.8
2005	81	696	7.2	93.0	44.9	13.2

4.3.2 Capture zones

The nitrate concentration was correlated with land and land use attributes into the capture zone of each monitoring station. A correct definition of the capture zone was therefore needed. Unfortunately, detailed hydrogeological modelling was not possible for all sampling wells. We therefore adopted a simplified approach to delineate a proxy of the capture zones of the sampling points, referred to as “expert knowledge delineated capture zones”. Our goal was to delineate an approximation of the area of influence around the monitoring station in a more realistic way than simply a circle. The so-called “capture zones” described in this chapter are therefore not supposed to correspond to the actual capture area of the monitoring station but to a rough approximation of the land surface that probably influences the measured groundwater quality. The delineation of capture zones by expert knowledge is based on the assumption that the flow paths of nitrates can be determined by the piezometric gradient. A direct delineation of the capture zone from the existing piezometric map was not appropriate since the existing piezometric map was obtained by interpolation of piezometric station data on a much coarser grid. The existing map is therefore subject to important prediction error at the scale of plausible capture zones. We therefore used DEM as a proxy of the piezometric height, which is measured at much higher spatial resolution as compared to raw piezometric heights. Hence, in the study area, the water table is supposed to be a smoothed replica of the ground surface elevation (Fasbender *et al.*, 2008a). In the second step, the type of monitoring station was taken into account by enlarging the catchment limits downgradient of the monitoring station in the case it is a pumping well since continuous pumping activities modifies the water flux direction as shown by the drawdown cone. Finally, the size of the capture zone was limited by a simplified water balance, taking into account the mean regional precipitation (780 mm/year), the mean regional potential evapotranspiration (510 mm/year) and the authorized extraction volume of each monitoring station (determined by the regional administration), imposing a steady state groundwater level. The use of these expert knowledge delineated capture zones in the statistical analysis was further compared with circular capture zones centered on the monitoring wells and which area was defined as the mean of the areas of all the expert knowledge delineated capture zones.

4.3.3 Multiple regression

Multiple regression (Pearson and Lee, 1908) assumes that a set of independent variables explains a proportion of the variance of a dependent variable. By comparing the slopes of the contributing factors in the regression equation, relative importance of the contributing factors can quantitatively be assessed. In this study, all independent variables are continuous variables which were standardized. The regression equation takes the form

$$\begin{bmatrix} \widehat{Y}_1 \\ \vdots \\ \widehat{Y}_n \end{bmatrix} = \begin{bmatrix} 1 & x_{11} & \cdots & x_{1k} & x_{11}x_{12} & \cdots & x_{1(k-1)}x_{1k} \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ 1 & x_{n1} & \cdots & x_{nk} & x_{n1}x_{n2} & \cdots & x_{n(k-1)}x_{nk} \end{bmatrix} \begin{bmatrix} \widehat{\beta}_1 \\ \vdots \\ \widehat{\beta}_p \end{bmatrix}$$

where the $\widehat{Y}$'s are the estimated dependents (i.e. the mean nitrate concentration at each of the n monitoring stations), the $\widehat{\beta}$'s are the p beta weights for the independent explanatory variables x_{nk} and $\widehat{\beta}_1$ is the constant or intercept. Interaction terms were added to the model to incorporate the joint effect of two variables. The explanatory variables x_{nk} used in this study are listed in Table 4.2. The expected value of the regression coefficients were calculated by inverting the system as follows:

$$\widehat{\beta} = (\mathbf{X}'\mathbf{X})^{-1}\mathbf{X}'\mathbf{Y}$$

After a first model run, the term with the highest resulting p-value (the probability for the $\widehat{\beta}$ parameter to be equal to zero) was removed of the system and the model was run again until the highest p-value was less than 0.10. Afterwards, the mild outliers were removed from the data set. These are defined as the values for which $(\widehat{Y} - Y)$ are lower (or higher) than $Q_1 - 1.5 \times IQR$ (or $Q_3 + 1.5 \times IQR$), where Q_1 and Q_3 are the first and third quartiles, respectively, and IQR is the interquartile range defined as $(Q_3 - Q_1)$. Finally, the model was run a last time without these outliers.

Table 4.2: Description of the variables used in the multiple regression method and in the regression tree method.

Variable description	Variable ID
Depth to the water table at the monitoring station (m)	Depth
Slope at the monitoring station (%)	Slope
Altitude at the monitoring station (m)	Altitude
Percentage of residential land in the capture zone around the monitoring station	LU11
Percentage of areas of economic activity, service and equipment in the capture zone around the monitoring station	LU12
Percentage of arable land in the capture zone around the monitoring station	LU21
Percentage of grassland in the capture zone around the monitoring station	LU23
Percentage of forests in the capture zone around the monitoring station	LU31
Percentage of shrub vegetation and/or herbaceous areas in the capture zone around the monitoring station	LU32

4.3.4 Regression tree

Regression tree modelling is an explanatory technique built through a process known as binary recursive partitioning. Regression trees became popular in environmental sciences in the early nineties (Baker *et al.*, 1993; Lees and Ritman, 1991). The algorithm works out which of the variables explains most of the variance in the response variable, then determines the threshold value of the explanatory variable that best partitions the variance in the response such that it minimizes the sum of the squared deviations from the mean in the separate parts. The process is repeated to each of the new branches until there is no residual explanatory power or according to the limitations imposed by the user. Regression trees do not have much in common with classical statistical regression as described in the former paragraph (Pachepsky and Schaap, 2005). The main difference with multiple regression is that interactions are clearly displayed and taken into account into the regression tree methods. In this study, the explanatory variables (Tab. 4.2) and the response (the mean nitrate concentration at each monitoring station) are the same as those used in the multiple regression method of the former paragraph. However, raw data were used for the regression tree since this method does not require a standardization step. The regression tree was computed by Matlab's "classregtree" function. Like in the multiple regression method, the mild outliers were removed from the data set.

4.4 Results

4.4.1 Capture zones

The expert knowledge delineated capture zones of the monitoring stations are shown on Figure 4.3. Their surface varies from 0.03 to 2.21 km² (mean 0.39 km²), which is compatible with studies realized in the same region by Leterme *et al.* (2006) who showed that atrazine concentrations in groundwater were best correlated with environmental variables located in a radius of 300 m around the monitoring wells. The size of the capture zones of the drains are in average three times smaller than those of the galleries (galleries are longer and deeper than drains), which are smaller than those of pumping wells. Springs have the largest capture zones. Based on the mean of the expert knowledge delineated capture zones' areas, the radius of the circular capture zones centered on the monitoring wells was set at 300 m.

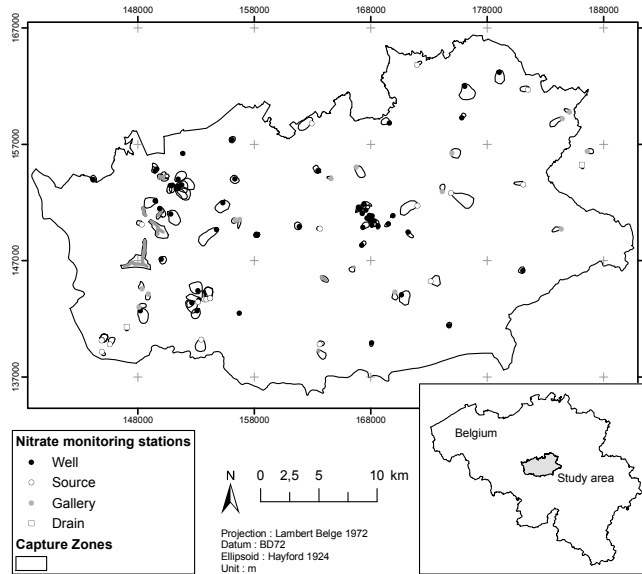


Figure 4.3: Expert knowledge capture zones around the nitrate monitoring stations.

4.4.2 Multiple regression

The analysis started with the nine variables listed in Table 4.2, which were combined in pairs to take their two-way interactions into account, yielding 46 parameters to estimate. The regression model was run and

the variable or joint variable with the highest p-value was removed. This removal process was run again until the highest p-value did not exceed 0.10. We had then only 14 and 8 parameters left for the expert knowledge delineated and circular capture zones respectively. Of the 82 monitoring stations, 5 were removed from the data set based on the outliers analysis for the expert knowledge delineated capture zones and only 1 for the circular capture zones. Most of these outliers were deep pumping wells for which the capture zones were difficult to estimate. The estimated nitrate concentrations are compared to the measured nitrate concentrations and multivariate regression quality indicators were calculated, resulting in an R^2 of 0.52 and an RMSE of 5.18 mg/l for the expert knowledge delineated capture zones (Figure 4.4a) and in an R^2 of 0.40 and an RMSE of 5.68 mg/l for the circular capture zones (Figure 4.4b). The resulting $\hat{\beta}$ coefficients estimates with their 95% confidence intervals for the expert knowledge delineated capture zones are shown on Figure 4.5. The main variables explaining nitrate concentrations in the multiple regression model when using circular capture zones are Altitude ($\hat{\beta} = 3.6$), $LU21 \times LU31$ ($\hat{\beta} = 0.6$), $LU12$ ($\hat{\beta} = -0.2$) and $LU11 \times LU14$ ($\hat{\beta} = 0.2$).

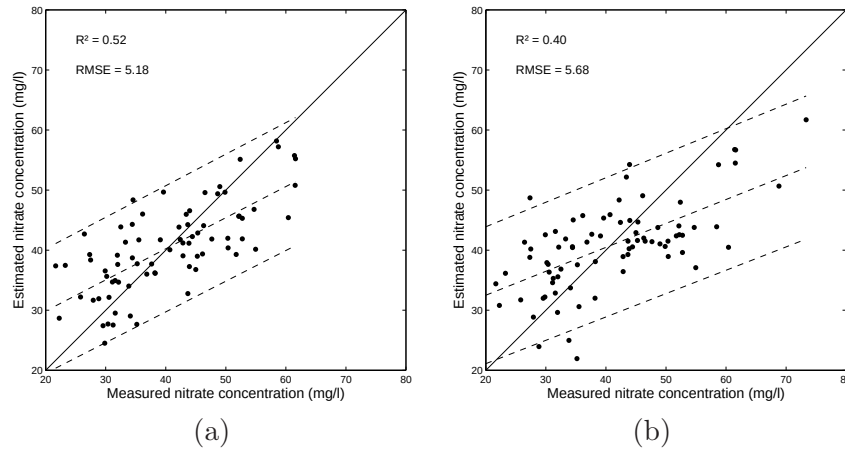


Figure 4.4: Comparison of the nitrate concentrations estimated by the multiple regression method to the measured nitrate concentrations for (a) expert knowledge delineated capture zones and (b) circular capture zones. The continuous line represents the 1:1 line, the dashed lines represents the first order polynomial fit with 95% confidence interval limits.

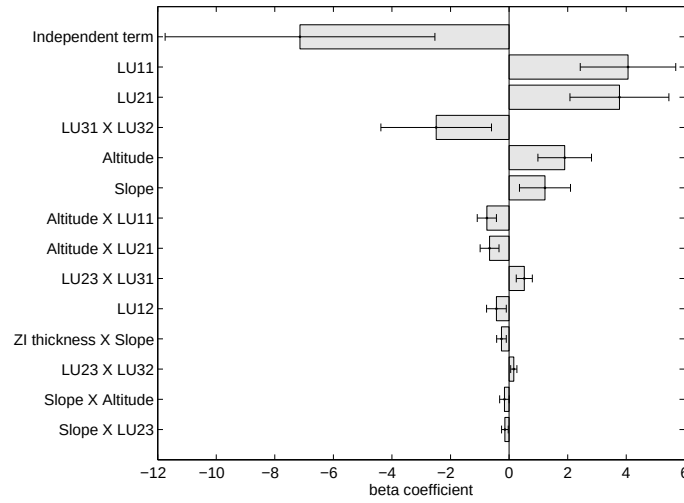


Figure 4.5: $\hat{\beta}$ coefficients estimates with their 95% confidence intervals resulting from the multiple regression method using expert knowledge delineated capture zones. For the legend, see Table 4.2.

4.4.3 Regression tree

The analysis used the nine variables listed in Table 4.2. From the 82 monitoring stations, eight were removed from the data set based on the outlier analysis for the expert knowledge delineated capture zones and six for the circular ones. The classification tree was applied to the dataset and the estimated nitrate concentrations were compared to the measured nitrate concentrations resulting in an R^2 of 0.85 and an RMSE of 4.00 mg/l for the expert knowledge delineated capture zones (Figure 4.6a) and in an R^2 of 0.76 and an RMSE of 4.78 mg/l for the circular capture zones (Figure 4.6b). As shown in Figure 4.7, representing the regression tree based on the expert knowledge delineated capture zones, the most important explanatory variable is the percentage of areas of economic activity, service and equipment in the capture zone around the monitoring station (LU12), and the threshold value separating low and high values of LU12 is 12.5%. For high values of LU12, the tree shows that the slope has a significant impact on groundwater pollution by nitrate. At high slope values ($> 5.6\%$) the mean level of groundwater pollution by nitrate was 44.5 mg/l while at low slope values, it is dependent also from the percentage of arable land in the capture zones around the monitoring stations (LU21) and altitude. For low values of LU12 ($< 12.5\%$), the percentage of residential land in the capture zone (LU11) is significant. High values of LU11 ($> 43.9\%$) have mean pollution levels

of 60.8 mg/l, while the depth to the water table has a significant impact on pollution for places where LU11 is low ($< 43.9\%$). When the water table is near to the surface (depth < 0.4 m), the pollution level was 71.7 mg/l while at higher depths the mean pollution level was lower and dependent from the other variables shown on the tree.

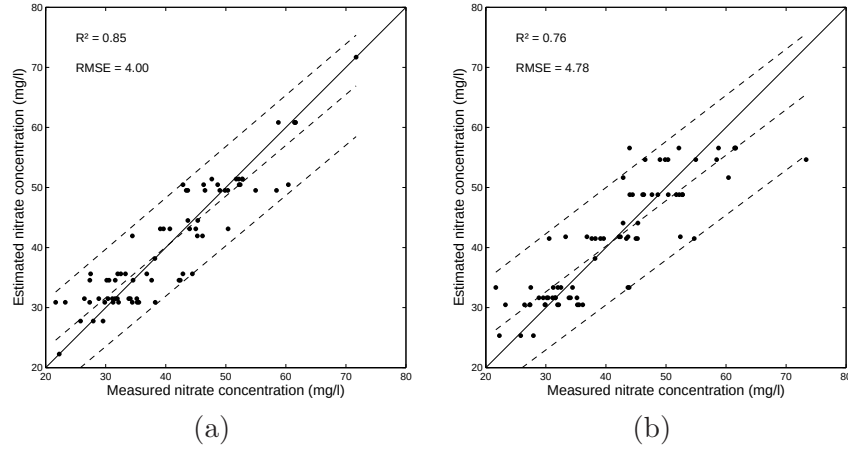


Figure 4.6: Comparison of the nitrate concentrations estimated by the regression tree method to the measured nitrate concentrations for (a) expert knowledge delineated capture zones and (b) circular capture zones. The continuous line represents the 1:1 line, the dashed lines represents the first order polynomial fit with 95% confidence interval limits.

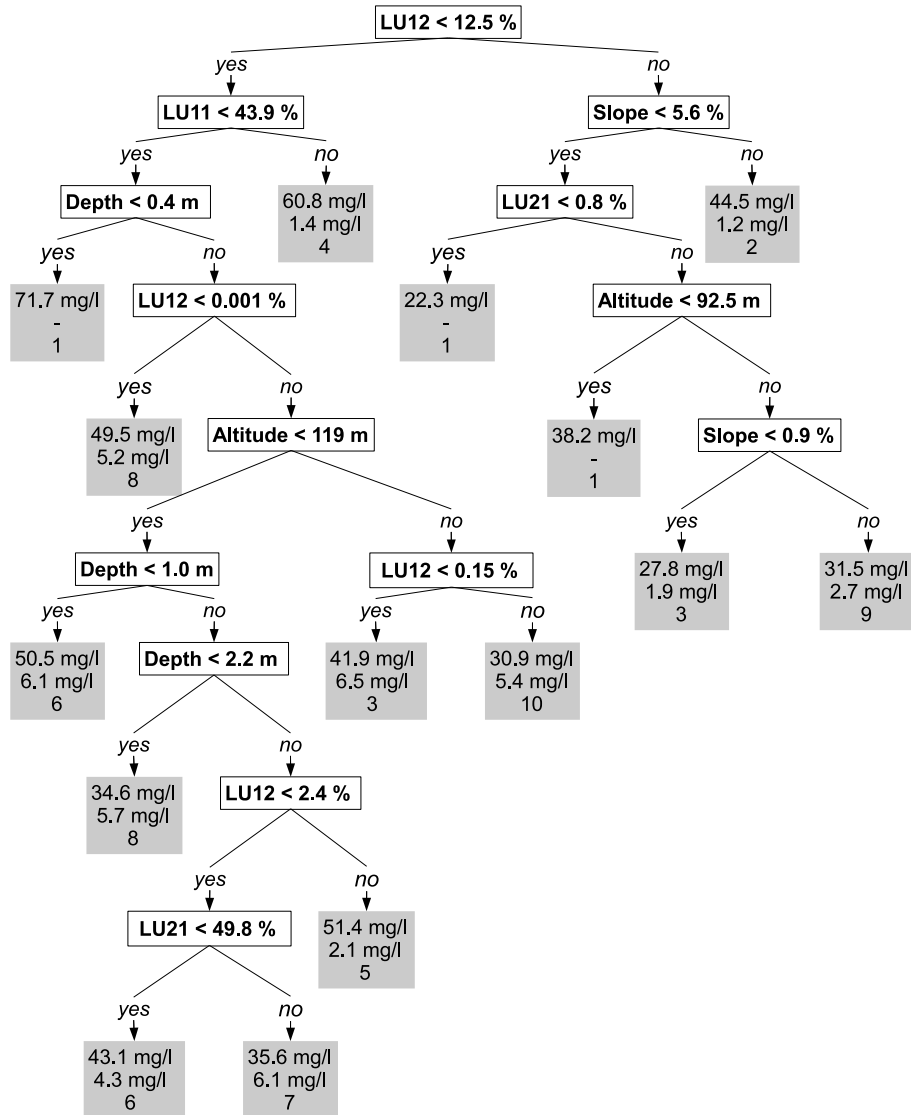


Figure 4.7: Regression tree for the dataset collected in the expert knowledge delineated capture zones. At the end of each branch, the first value is the mean nitrate concentration, the second is the standard deviation and the third the number of samples.

4.5 Discussion

The regression tree model showed a highly complex interaction pattern which was not captured by the multiple regression model that included only two-way interactions between all variables. This results in the fact that the regression tree method ($R^2 = 0.85$, $RMSE = 4.00$) used to identify and classify the main factors influencing the nitrate pollution levels in the unconfined Brusselian sandy aquifer had a better explicative power than the two-way interactions multiple regression model ($R^2 = 0.52$, $RMSE = 5.18$). Furthermore, the results of the multiple regression (Fig. 4.4) show an overprediction at low concentrations and an underprediction at high concentrations. This bias, which may indicate a key missing predictor, was present only in the results of the multiple regression method which considers single interactions between variables, and was not present in the results of the tree models where complex interactions are considered. It suggests that it is the complex combination of variables which is important to explain the pollution levels and that one explicative variable taken alone could not be considered responsible for the groundwater pollution by nitrate. Compared to multiple regression, tree models can capture complex interactions without making an *a priori* choice of interaction levels. Moreover, tree models can capture contextual effects or local phenomena by partitioning the dataset in more homogeneous clusters while the parameters resulting from multiple regression are fitted on the whole dataset and represent therefore global phenomena. However, while both methods uses continuous dependent variables, multiple regression has the advantage of having continuous outputs while those of regression trees are discrete.

Most of the used explanatory variables were measured in a given perimeter around the nitrate monitoring stations. We showed that using expert knowledge delineated capture zones instead of simple circular capture zones centered on the monitoring stations can significantly improve the prediction quality. For the multiple regression method, the R^2 is improved from 0.40 to 0.52 and the RMSE from 5.68 mg/l to 5.18 mg/l. For the regression tree method, the R^2 is improved from 0.76 to 0.85 and RMSE from 4.78 mg/l to 4.00 mg/l. These results are not surprising since the nitrate samples taken in the groundwater are generally not influenced by the land use downgradient of the monitoring station.

According to the regression tree, the most important explanatory variable is the percentage of areas of economic activity, service and equipment in the capture zone around the monitoring station. Since nitrate concentrations are generally higher for low levels of this variable,

its presence has a positive impact on the groundwater quality probably due to a better waste water management of these services, or to the fact that increased economic activity could be a surrogate for absence of agricultural land or residential land with septic systems, which could result in lower nitrate. Inversely, the absence of economic activity could be a surrogate for presence of agricultural land or residential land with septic systems, which could result in higher nitrate concentrations. This is for example the case for the node on the left of the tree with high nitrate concentrations (71.7 mg/l). This point is located in an area of low economic activity (3.6% of the surface of the capture zone), high agricultural activity (55.9% of the surface) and the presence of residential land which is not connected to a public sewage system (16.6% of the surface). The combination of low surfaces allocated to services and high residential densities has a negative impact on the nitrate levels, probably due to the fact that many houses are still not yet connected to the sewage. It appears from the regression tree that the depth to the water table has a protective effect, potentially due to dispersion and further degradation of the nitrate in the vadose zone. The negative impact of the slopes on the groundwater quality could be explained by a higher run-off rate conducting to an accumulation of the surface deposited nitrate or by a soil effect since in general more sandy slopes with less loam cover are found on the slopes, conducting to more vulnerable situations on the slopes. We can notice that the quasi total absence of arable land ($LU21 < 0.8 \%$) results in groundwater with low nitrate concentrations, but also that the effect of this variable has low explicative power (when $LU12 < 12.5 \%$).

The impact of the explanatory variables resulting from the multiple regression method must be interpreted carefully because of the low quality of the fit and for the reasons outlined above. However, as for the regression tree, we can notice the negative impact of residential land and slope (Figure 4.5). Similarly, Leterme *et al.* (2006) showed that residential land of the same region had a negative impact on the atrazine concentrations. Main differences with the regression tree are the clear negative impact of arable land and of interaction between forests and shrub vegetation and/or herbaceous areas on the groundwater quality.

4.6 Conclusion

This study envisaged to identify the origin of the groundwater pollution by nitrate of the Brusselian sands aquifer (Belgium) by modelling observed nitrate pollution in terms of land and land use attributes in

groundwater capture zones. For the modelling, a multiple regression method was compared with a regression tree method. Both methods linked the measured nitrate concentrations with the slope, the altitude and the depth to the water table at the monitoring station and with the land use in a proxy of the capture zone of the monitoring station. The analysis indicated that the choice of an appropriated statistical method could enhance the quality of the analysis. The tree model and the low fitting power of the two-way multiple regression model showed the highly complex interaction pattern between explanatory variables. In the region, one explicative variable taken alone could not be considered responsible for the groundwater pollution by nitrate.

Furthermore, the performance of expert knowledge delineated capture zones was compared to circular capture zones centered on the monitoring stations. We showed the importance to measure the explanatory variables in locations that have an impact on the monitoring station, by delineating correctly the capture zones. In this study, we illustrated the use of expert knowledge delineated capture zones which are defined on the basis of topography, the type of monitoring station and a simplified water mass balance.

It appears from this study that agricultural activity can not be regarded as major contributor to the pollution of groundwater by nitrate. This study also highlights the negative impact of residential land on groundwater quality. The results should however be nuanced by the limited sampling population size and the uncertainty on the data. In addition to the quantification of the factors controlling pollution in the groundwater body, the obtained regression model and the regression tree could be used, in future developments, to predict groundwater pollution at unsampled locations of the same groundwater body. The results of this study could further be compared with process based models, tracer experiments or natural indicators like nitrate isotopes in order to develop land management strategies to attempt to minimize future nitrate pollution in groundwater. Future work should also focus on further improving the delineation of the capture zones of the monitoring stations and on gaining insight concerning the nitrate transport throughout the soil and sub-soil compartments.

Chapter 5

Introducing time variability and sampling rate in the mapping of groundwater contamination by means of the Bayesian Maximum Entropy (BME) method

5.1 Outline

A Bayesian Maximum Entropy (BME) method is presented as a formal spatial modelling framework allowing an introduction of temporal variability of groundwater contamination and the sampling rate in a map for a case where the time variability of the process is much smaller than its spatial variability. The results of this approach are compared to results obtained by considering a pure spatial process. Only a small enhancement of the prediction was observed at the regional scale. Differences of 67% with the pure spatial process were observed in some parts of the study area where the sampling rate was low, and of 42% where the temporal variability was the highest. The method is illustrated for groundwater pollution by nitrate in a sandy aquifer located in central Belgium and subjected to different pressures from diffuse and point pollution sources.

5.2 Introduction

Assessing the quality of groundwater is a prerequisite for designing sustainable water management strategies e.g. when implementing the Water Framework Directive (2000/60/EC, 2000). Groundwater quality is, however, a spatially distributed attribute which allows the design of site specific measures that are believed to be effective and sustainable. Robust and validated techniques are needed to map the spatial distribution of groundwater quality within a groundwater body.

Groundwater quality can only be measured at the local scale. Mapping of groundwater quality within the groundwater body requires data interpolation, and the interpolation technique will have an impact on the final assessment. Geostatistics are often used to model groundwater quality. Hu *et al.* (2005) for example used kriging for mapping the spatial variability of nitrate concentrations in a shallow water body. Cinnirella *et al.* (2005) used Gaussian simulation techniques to introduce local uncertainty for mapping nitrate concentrations in groundwater in the Po Valley (Italy).

Groundwater quality also varies with time. To consider the temporal dynamics, Christakos and Bogaert (1996) integrated spatial and temporal components in a space/time continuum to generate maps of the evolution of nitrate concentrations in the Dyle Basin in Belgium. They later introduced the Bayesian Maximum Entropy (BME) method as composite space-time modelling, allowing the interpolation of 'hard' and 'soft' data (Christakos, 1990; Christakos and Bogaert, 1996; Christakos, 1998; Christakos and Li, 1998; Serre and Christakos, 1999; Christakos, 2000; Christakos *et al.*, 2002; Bogaert, 2002; Serre *et al.*, 2003; D'Or and Bogaert, 2003; Savelieva *et al.*, 2005; Law *et al.*, 2006). BME is a geostatistical technique that facilitates composite spatial-temporal analyses.

In a case study of river water pollution by tetrachloroethylene, Akita *et al.* (2007) demonstrated that a composite space-time analysis with the BME method leads to better results than a just spatial analysis. In their study however, the temporal variability was of the same order of magnitude as the spatial variability. In cases where the temporal component is much smaller than the spatial one, it is not clear whether composite modelling by means of BME will add much value. Furthermore, it is not clear to what extent the size of the sample population of the time series impacts on the mapping results.

This chapter analyses composite modelling of groundwater quality by means of BME for cases where the time variability is much smaller than the spatial variability. The time component in the spatial map for

groundwater quality is introduced by means of a Gaussian time distribution function in one approach, and the sampling rate at each monitoring station by a Student distribution function in another approach, taking the number of observations in the time series into account. The average of each time series will be interpolated by ordinary kriging (Approach 1). Also an approximation of each time series by a Gaussian (Approach 2) or Student (Approach 3) distribution is carried out and these distributions applied as an input of the BME interpolation model. To show the added value of the BME interpolation, the results of the composite modelling (Approaches 2 and 3) are compared with results obtained by the pure spatial process (Approach 1). The method is illustrated by a model of groundwater pollution by nitrate.

5.3 Material and Methods

5.3.1 Data

The groundwater nitrate concentration data set collected by the local administration was used (i.e. CALYPSO hydrochemical database of the Ministry for the Walloon Region, version 12/09/2006). This database contains all monitoring data collected by the different water production companies as a support information for licensing. The data base is complemented by data collected by the regional administration for background monitoring to comply with local legislation. The dataset encompasses 10 309 groundwater samples collected on 109 different monitoring stations between January 1995 and June 2006 in two groundwater bodies (RWE051 and RWM052) located in the Brusselian aquifer in the center of Belgium. These monitoring stations are wells, piezometers, galleries, springs and drains (Fig. 5.1). For each station, there is a time series describing the evolution of measured nitrate concentration. The sampling rate changes from one year to another and from station to station since a standardized and statistical designed monitoring protocol was not followed for establishing the data set. In addition, there are some missing data and erroneous measurements.

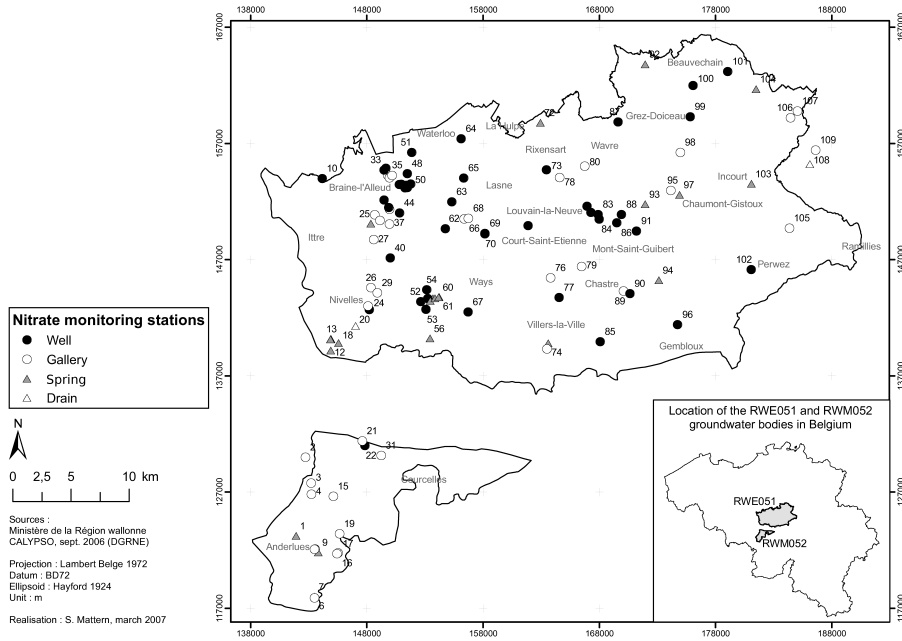


Figure 5.1: Location and classification of the monitoring stations in the Bruselian aquifers. Monitoring stations are labelled from 1 to 109.

5.3.2 Space versus Time variance

Since a statistical monitoring protocol was not followed, nitrate data were clustered in time classes to introduce the temporal component in the nitrate contamination map. Time intervals could be one month, one six-month period, one year, or even the whole study period yielding as such monthly, bi-annual, annual or time averaged nitrate contamination maps. To identify the optimal time interval, a comparison between the spatial and the temporal variability of the dataset was carried out. The spatial variability of the dataset was defined as the variance of the averages of the 109 concentrations measured in each station, calculated for the whole study period. The temporal variability is defined as the average of the 109 temporal variances of each time series.

5.3.3 Spatial mapping with temporal variability

It is beyond the scope of this thesis to present the whole underlying theory of BME. So only the most relevant information for our application will be presented hereafter. The interested reader may refer to Christakos *et al.* (2002) for a detailed description of the theory. The

BME mapping framework divides the prior information about the nitrate pollution, called total knowledge in the BME framework, into two main knowledge bases: the general knowledge base and the site specific knowledge base. This total knowledge is used to construct the posterior probability density function (pdf) of the variable of interest (nitrate concentration) at any mapping point.

The general knowledge base

The general knowledge base characterizes the spatial variability of the spatial random field. It could include physical laws, empirical relations, statistical moments of any order or scientific theories. In the groundwater pollution case considered in this work, the general knowledge includes only the mean trend (described by deterministic interpolation techniques, i.e. polynomial regressions of order 0, 1 and 2) of the spatial random field and its covariance which expresses the spatial correlation between any two sampling locations, as described in the semi-variogram analysis. The semi-variogram $\gamma(\mathbf{h})$ measures the difference between values Z at locations $\mathbf{s}$ separated by a distance $\mathbf{h}$. Two observations located one close to the other should, on average, resemble each other more than two distant observations (Tobler, 1970). The semi-variogram is given by

$$\gamma(\mathbf{h}) = \frac{1}{2} \text{Var}[Z(\mathbf{s}) - Z(\mathbf{s} + \mathbf{h})]. \quad (5.1)$$

If the field respects intrinsic and second order stationarity, the traditional estimator of $\gamma(\mathbf{h})$ is

$$\hat{\gamma}(\mathbf{h}) = \frac{1}{2} \frac{1}{N(\mathbf{h})} \sum_{N(\mathbf{h})} (Z(\mathbf{s}_i) - Z(\mathbf{s}_i + \mathbf{h}))^2 \quad (5.2)$$

where $N(\mathbf{h})$ is the number of pairs of points separated by a distance $\mathbf{h}$.

The estimated semi-variogram was modelled by an exponential model $Exp(\mathbf{h}; \sigma^2, a)$ (Eq. 5.3) with σ^2 the sill (in mg^2/l^2) and a the range of the variogram (in m).

$$\gamma(\mathbf{h}) = \sigma^2 (1 - \exp(-3 \frac{\mathbf{h}}{a})) \quad (5.3)$$

The site-specific knowledge base

The site-specific knowledge base includes real measurements, uncertain observations, and secondary information. It includes data measured with low error (high certainty) described as “hard (exact) data”, and

data measured with high error (low certainty) described as “soft data”. The soft data may be probabilistic data in the form of soft pdf which may take any arbitrary form. Three different kinds of site-specific knowledge base data have been developed:

- Approach 1: Hard data only: the algebraic average of the measured nitrate concentrations on the whole of the study period is applied at each monitoring station. This limiting case of BME corresponds to ordinary kriging.
- Approach 2: Soft Gaussian distributions: In this case, the data of the time series are approximated by a Gaussian distribution representing the Gaussian approximation of the distribution of all the measurements made at each monitoring station. However, it is not possible to construct Gaussian distributions when the variance of the time series is null, which is the case for the recently opened stations for which only one or two measurements are available. BME handles them as “hard” data (i.e. not probabilistic data). However, the weight associated to them during the interpolation process is higher than the weight associated to the “soft” data. This is contrary to the idea that the incorporation of a great number of measurements in the time series must increase the quality of the prediction. To solve this problem, a variance of $15.41 \text{ mg}^2/\text{l}^2$ was assigned, i.e. the mean of the temporal variances of all the monitoring stations, to those where the temporal variance is null.
- Approach 3: Soft Student distributions: When only a few samples have been taken at a given monitoring station, the problem arises of estimating the mean of this time series. The confidence intervals of such time series are broader than those where more data are available. Student distributions were used in order to incorporate the uncertainty associated to the size of the sample population of the time series into the mapping process. The shapes of the soft Student pdf were characterized at each monitoring station by means of three values: the mean, the variance and the number of measured concentrations composing the time series. In order to compute the Student distribution at every monitoring station, the number of observations was changed from 1 to 2 at the monitoring stations where only one sample has been taken.

The integration stage

At the integration (or posterior) stage, a Bayesian conditionalization rule is used to update the prior pdf generated in the prior stage with

site-specific data, generating a posterior pdf of the nitrate concentration at all estimation points (Christakos, 2000). This posterior pdf is not limited to the Gaussian form (since it is a function of the soft pdf which may take any arbitrary form), leading to a realistic stochastic description of the groundwater nitrate concentration in space.

In Approach 1, the site specific knowledge base was limited only to hard data. In this case, the BME posterior pdf is Gaussian, with the same mean and posterior variance as that of the ordinary kriging method. This limiting case illustrates the generalization power of the BME method, in that using only hard data leads to the well-known kriging estimates, while adding soft data leads to the more realistic and accurate non-Gaussian posterior pdf (Savelieva *et al.*, 2005).

Maps quantifying the uncertainty or error associated with contamination estimates are also generated at this stage using the variance of the BME posterior pdf.

BME predictions of the groundwater nitrate concentration were computed at the locations of the monitoring stations and at the nodes of a 500 by 500 m regular grid.

5.3.4 Comparison of methods

The mapping errors obtained with the mapping methods result from measurement errors (handling error when sampling, laboratory analysis error), encoding errors (encoding of the analysis, integration of the data in the Calypso regional database), errors due to the interpolation method and errors due to the type of information integrated into the model. To elucidate these last two errors and to illustrate the estimation accuracy, cross-validation was performed. The cross-validation measures used to compare the three approaches are the root mean squared error (RMSE), the mean absolute error (MAE) and the mean error (ME). They reflect the coherence between the average concentration measured in each station (variable to map) and the prediction of this variable by the interpolation methods. However, these quality indicators are valid only at the regional scale and they do not reflect local improvements of the mapping technique. All calculations were made in MatlabTM version R2006a, using the geostatistical BMElib package (Christakos *et al.*, 2002).

5.4 Results and discussion

5.4.1 Space versus Time variance

At a station scale, the nitrate concentration is temporarily stable or presents an upward trend at the majority of the stations. However, some have a decreasing level of pollution by nitrate. Some stations present a seasonal or multi annual cyclic variation. The contamination has a temporal variability more or less marked according to the station. At the regional scale, the calculated spatial variability of $217.0 \text{ mg}^2/\text{l}^2$ was nearly 14 times higher than the temporal one ($15.7 \text{ mg}^2/\text{l}^2$). This enables the average pollution for the whole of the period of study (1995-2006) to be mapped.

Figure 5.2 represents the evolution of the annual regional average of the nitrate concentration. This is relatively stable and oscillates around 44 mg/l . The standard deviations represented by vertical lines on Figure 5.2 reflect the spatial variability.

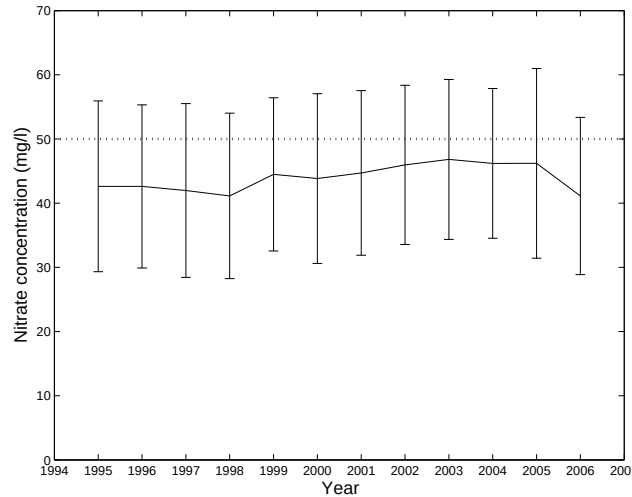


Figure 5.2: Evolution of the mean annual nitrate concentration (broken line) and its standard deviation (vertical bars). The horizontal dotted line represents the EU standard for drinking water.

Figure 5.3 was created by aggregating the data over the whole of the period of study, i.e., the arithmetic average of all values taken at one station from January 1995 until June 2006. The nitrate concentration monitoring data exhibit a high spatial variability, with higher concentrations observed mainly in the western parts of the region. Because of the relatively poor spatial resolution of the monitoring network, this

approach is not satisfactory to obtain a good view of the spatial patterns of the nitrate pollution on the whole of the study area. However, this map of the point averages of nitrate concentrations directly measured in groundwater at each monitoring station constitute the most direct indicator of pollution levels. Rather than applying various types of models or geostatistical methods which generate large uncertainties, the measured data directly reflect the quality of the groundwater with an uncertainty resulting only from the measurement and analytical errors.

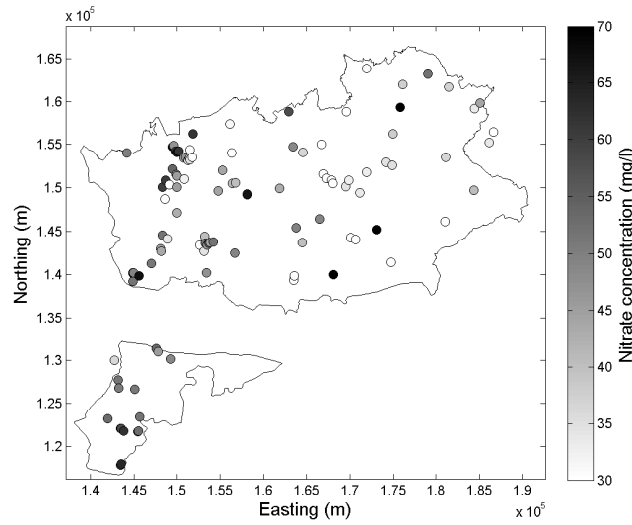


Figure 5.3: Averages of the nitrate concentrations measured at each monitoring station between 1995 and 2006.

Descriptive statistics calculated on the averages of the whole of the period of study are presented in Table 5.1. The average concentrations extend between 7.2 and 93 mg/l and the regional mean and standard deviation was 44.2 and 14.6 mg/l, respectively.

The histogram and the cumulative distribution function (cdf) of the averages of the concentrations calculated on the whole of the period of study were plotted (results not shown) and the spatial distribution of the data appears to be normal. However, three slight peaks at 30, 45 and 60 mg/l might represent the differences in origins of the pollution (Leterme *et al.*, 2006), the differences of laboratory analyses techniques or the absence of a “declustering” stage in the analysis.

Table 5.1: Descriptives statistics of the point averages of nitrate concentrations.

Amount of stations	109
Minimum concentration (mg/l)	7.2
Maximum concentration (mg/l)	93.0
Mean concentration (mg/l)	44.2
Variance (mg^2/l^2)	213.1
Standard deviation (mg/l)	14.6
Median (mg/l)	44.5
Kurtosis	0.4
Skewness	0.3
Maximum distance between 2 stations (m)	59044
Minimum distance between 2 stations (m)	32

5.4.2 Spatial mapping with temporal variability

The general knowledge base

The quality indicators resulting from the mean trend analysis are shown in Table 5.2. The results of these deterministic interpolation methods do not present differences justifying the choice of a regression of a high order. Thus, the mean trend was defined as a constant (regression of null order), equal to the average of the point data.

Table 5.2: Quality indicators of the regressions estimating the mean trend of the SRF.

Indicator	Regr. order 0	Regr. order 1	Regr. order 2
RMSE	14.53	13.52	13.23
MAE	11.54	9.51	9.20
ME	0.00	0.00	0.00

The experimental semi-variogram was calculated and fitted to an exponential model reaching $188 \text{ mg}^2/\text{l}^2$ at a range of 3 200 m (Figure 5.4). That means that monitoring stations separated by less than this distance are correlated. These correlated stations are linked on Figure 5.5.

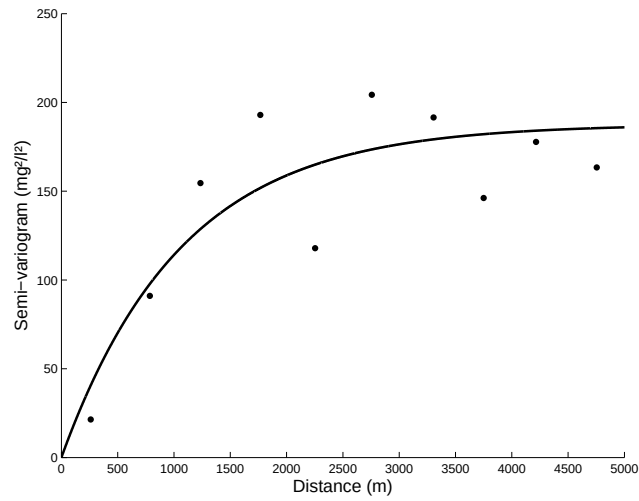


Figure 5.4: Semi-variogram of the averages of the nitrate concentrations in the Brussellian Sands calculated on the basis of the dataset over the whole period of study. The points represent the experimental semi-variogram, the line represents the fitted exponential semi-variogram.

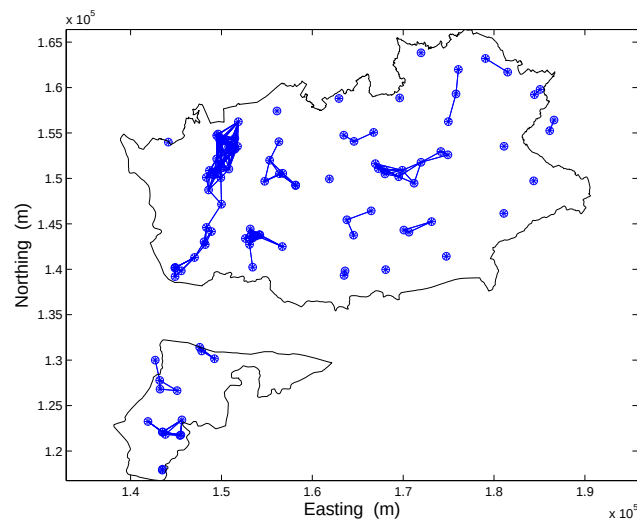


Figure 5.5: Stations separated by less than the correlation range of 3,200 m are shown with links.

The site-specific knowledge base

The performance of BME estimation using only hard data (Approach 1) was compared with the performance of BME using only soft data, which was a Gaussian (Approach 2) or a Student distribution (Approach 3).

An example of the measured concentrations and their distributions for three given monitoring stations is shown on Figure 5.6. In Figures 5.6b and d, the measured data distributions (histogram) were approximated by Gaussian distributions. Note that the assumption of normality of the inputs of the model is, for some monitoring stations, a rough approximation. The uncertainty associated with the mean of the time series is represented by the Student distributions. When many samples compose the time series, the uncertainty associated with the mean is low and the station is processed as a hard-like data point (Figure 5.6b). When only few samples have been taken at a given station, the uncertainty is high and the station is processed as a soft station. At monitoring station 10, only one sample has been taken, providing a nitrate concentration of 50 mg/l (Figure 5.6e). In order to plot a Gaussian and a Student distribution, it was assigned a variance of 15.41 and changed the number of observations from 1 to 2 at that monitoring station (Figure 5.6f).

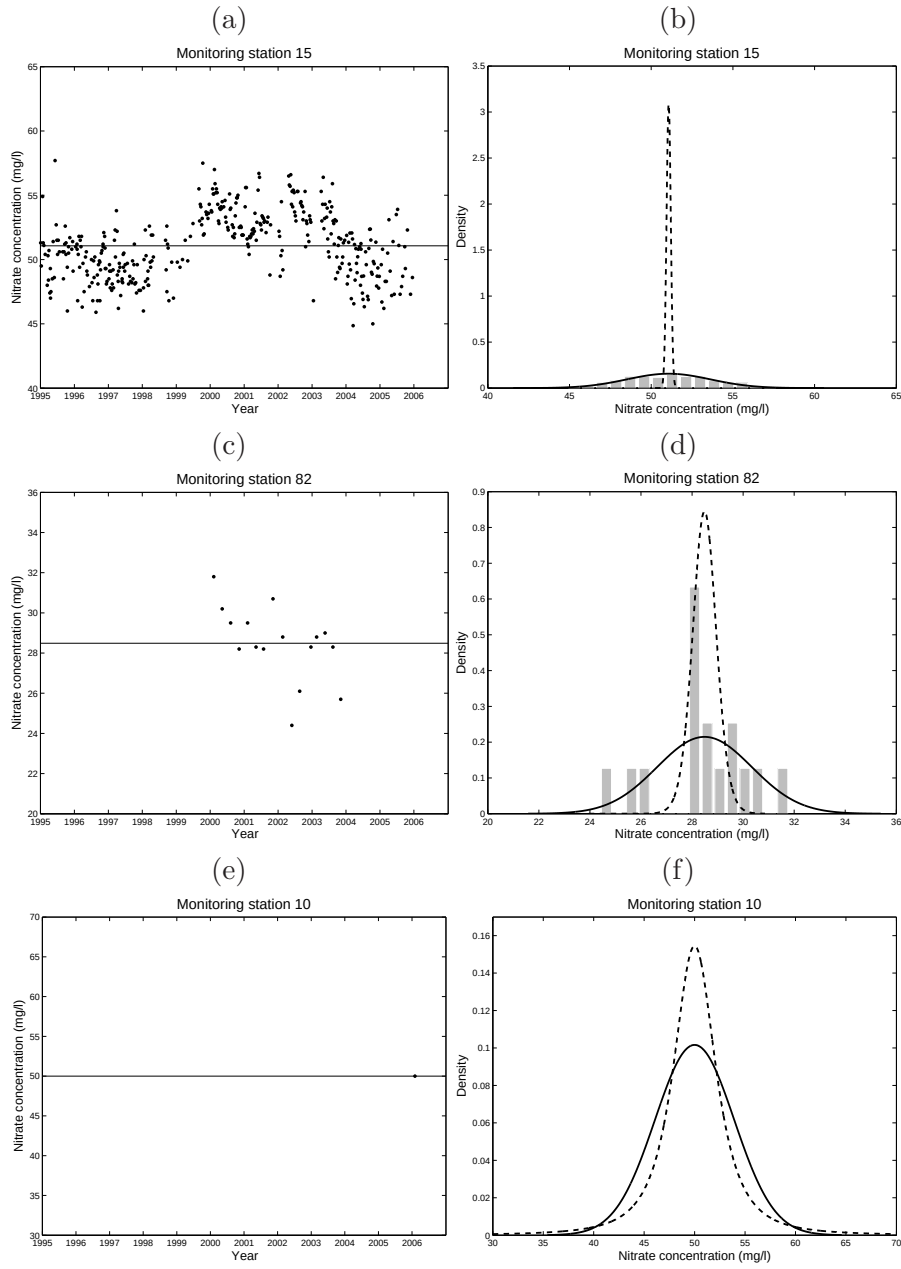


Figure 5.6: (a, c, e) Time series of the groundwater nitrate concentration measured at three given monitoring stations (horizontal line represents the mean value used in Approach 1) and (b, d, f) approximation of the histogram by Gaussian (full line) and Student distributions for the mean (dashed line).

The integration stage

The mean value of the posterior distribution functions resulting from BME estimation were plotted at each node of the grid, resulting in the maps using only hard data of Approach 1 (Figure 5.7a), soft Gaussian distributions of Approach 2 and Student distributions of Approach 3. For clarity reasons, the maps show only the absolute differences from Approaches 2 and 3 with Approach 1, expressed in percentages (Figure 5.7c and Figure 5.8c, respectively). The maps of Approaches 1 and 2 are similar, and it appears that the loss of information when mapping point data without taking the temporal variability into account is not relevant at the regional scale even if great differences (up to 42.44%) appear locally at monitoring stations where the temporal variability is high, as shown on Figure 5.7c. However, significant differences (up to 67.19%) appear between maps from Approach 1 and Approach 3 at monitoring stations where only few samples have been collected, showing the usefulness of integrating the number of samples into the mapping process.

The uncertainty maps are valuable tools in the analyses of environmental risk: they can highlight the limits of a monitoring network, help to identify the zones where complementary observations are needed, and help to optimize the conception of new monitoring networks (Christakos and Serre, 2000). The BME estimation error standard deviation map for Approach 1 is shown in figure 5.7b. The estimation error at the monitoring station is null since only hard data were used in this approach. The differences between the estimation error of Approach 2 and 3 and Approach 1 are mapped on Figure 5.7d and 5.8d, respectively. Figure 5.7d shows that the introduction of time variability by the Gaussian distribution of Approach 2 increases the estimation errors, especially at the monitoring stations where the time variability is high. When a Student distribution is applied, the estimation uncertainty increases (in comparison with Approach 1) where the number of samples of the time series is low and no differences are observed where this number is high (Figure 5.8d). The relative variation of the estimation errors varies up to 1174% and 610% for Approach 2 and 3, respectively, even if the scale ranges to 100% in the diagrams.

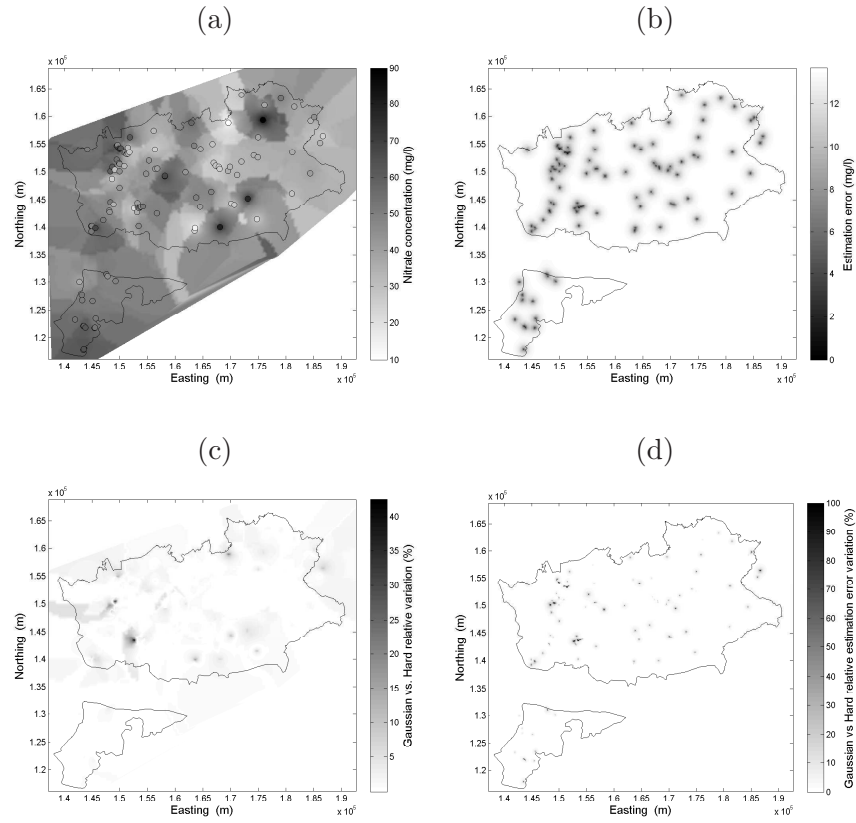


Figure 5.7: Spatial maps of (a) nitrate concentration and (b) corresponding spatial map of BME estimation error standard deviation for Approach 1; (c, d) maps of absolute variations (%) between Approach 1 and Approach 2 and variation of estimation of standard deviation between Approach 1 and Approach 2, respectively.

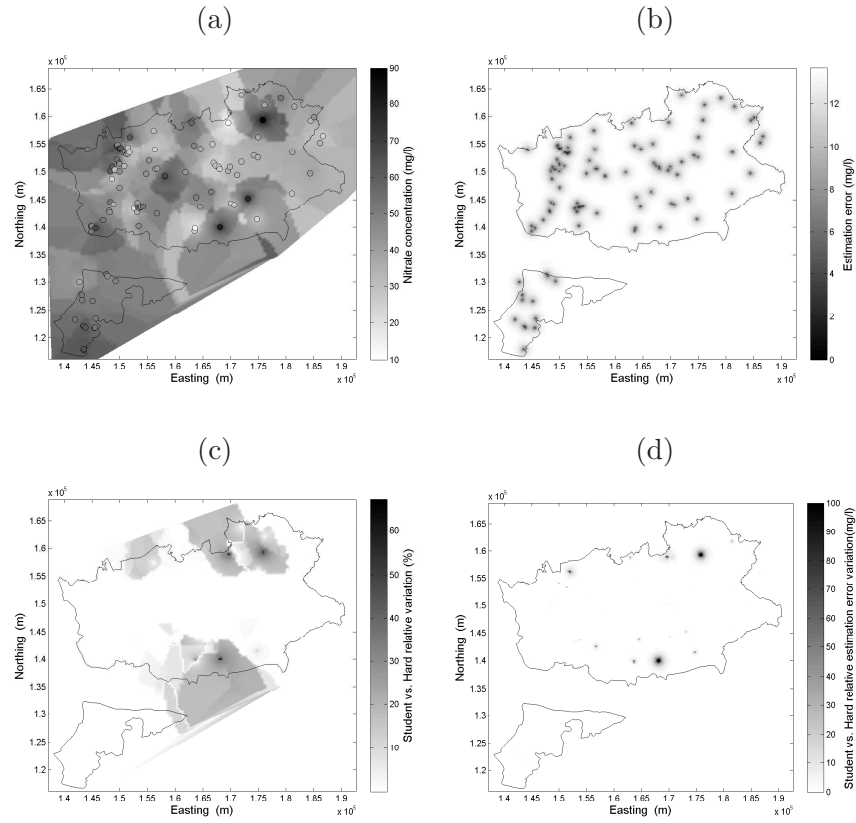


Figure 5.8: Spatial maps of (a) nitrate concentration and (b) corresponding spatial map of BME estimation error standard deviation for Approach 1; (c, d) maps of absolute variations (%) between Approach 1 and Approach 3 and variation of estimation of standard deviation between Approach 1 and Approach 3, respectively.

5.4.3 Comparison of methods

The results of the cross-validation presented in Table 5.3 show that the loss of prediction quality when omitting the temporal variability into the mapping process is negligible. This is explained by the small temporal variability of the measured nitrate concentrations compared to its spatial variability, as shown in Figure 5.9 presenting the Gaussian approximated distributions of the data for each monitoring station and the distribution of the mean data at each monitoring station which reflect the spatial variability of the nitrate concentrations accross the study area. However, these indicators only reflect the quality of the estimations at the regional scale. They do not show the enhancements obtained at local scale, as shown in Figure 5.7c and 5.8c. Furthermore, Approaches 2 and 3 permit locations where high uncertainty occurs to be detected due to the large temporal variability (Figure 5.7d) and low sampling rate (Figure 5.8d).

Table 5.3: Cross-validation results

BME method	RMSE	MAE	ME
Approach 1 (using hard data only)	13.81	9.10	0.33
Approach 2 (using Gaussian distributions only)	13.65	8.99	0.22
Approach 3 (using Student distributions only)	13.39	8.89	0.09

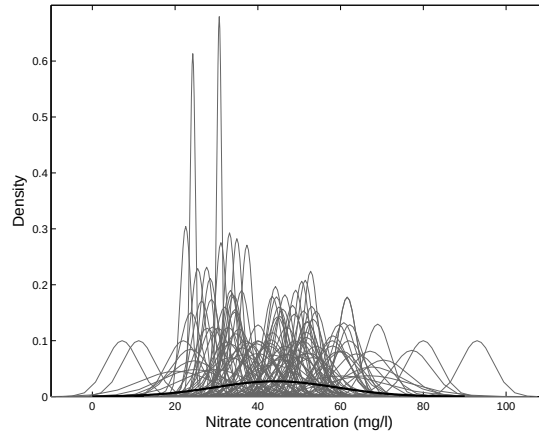


Figure 5.9: Soft prior distributions at each monitoring station, i.e. estimated from time series and modelled as Gaussian distributions (grey lines) and prior distribution of the hard data, i.e. the mean concentration at each monitoring station (black line).

5.5 Conclusions

The nitrate pollution of two groundwater bodies of the Brusselian sands have been mapped in order to gain a better view of the qualitative state of this natural resource. The study was based on 10 309 monitoring data collected between 1995 and 2006. The contamination process was sufficiently stable in time to work with the average values of pollution on the whole of the period of study. The mapped variable was the mean nitrate concentration on the whole of the period of study. Deterministic regression techniques highlighted that no major mean trend was identifiable on the study area. Three approaches were followed in order to interpolate the point data. Approach 1 consisted in interpolating the mean nitrate concentration at each monitoring station. Approach 2 aimed to introduce the temporal variability observed at every monitoring station by approximating their distributions of nitrate concentrations by a Gaussian distribution. Approach 3 aimed to introduce the uncertainty on the mean nitrate concentration at each monitoring station associated with the sampling rate, i.e. the number of samples composing the time series. The results showed that no relevant loss of estimation quality at the regional scale was observed when the temporal variability was not introduced into the spatial mapping process even if some local particularities were lost from high local temporal variability. The lack of information from small sampling rates impacts the mapping results.

The maps were created by interpolation of the measurements taken routinely by the water production companies and by regional administration in more than one hundred monitoring stations. They do not take account of the factors which can influence the spatial distribution of the contamination such as the hydrographic network, the anthropogenic pressures, the topography and the hydrogeology. They do not take into account the depths to which the water samples were taken, these data being unavailable at present. In addition, the monitoring station network was not conceived with the aim of carrying out environmental monitoring. The low sampling density in some places results in broad uncertainties for the estimate of the level of contamination in these zones.

The maps could be used to correlate the nitrate concentrations to the factors which cause the contamination, such as land use, topography, and depth of the water-table. The maps represent a tool which could be used by the regional administration and the water production companies to implement specific and local management and protection strategies, to improve the monitoring network or to have a better insight of the qualitative state of this natural resource.

Chapter 6

Bayesian Data Fusion (BDF) of monitoring data with a statistical groundwater contamination model to map groundwater quality at the regional scale

6.1 Outline

We mapped the nitrate groundwater contamination within an unconfined sandy aquifer using a Bayesian Data Fusion (BDF) framework. We therefore combined groundwater monitoring data with a statistical groundwater contamination model. Nitrate concentrations, measured at 99 monitoring stations irregularly distributed within the study area, were first spatialized using ordinary kriging. Secondly, a statistical regression tree model of nitrate contamination in groundwater was constructed using land use, depth to the water table, altitude and slope as predictor variables. This allowed the construction of a regression tree based contamination map. Subsequently, BDF was used to combine optimally the kriged nitrate contamination map with the regression tree based model into one single map, thereby weighing the kriged and regression tree based contamination map in terms of their estimation uncertainty. It is shown that BDF allows integrating different sources of information about contamination in a final map, allowing to quantify

the expected value and variance of the nitrate contamination estimation. It is also shown that the uncertainty in the final map is smaller than the uncertainty from the kriged or regression tree based contamination map.

6.2 Introduction

Assessing the quality of groundwater is a prerequisite for designing sustainable water management strategies e.g. when implementing the Water Framework Directive (2000/60/EC, 2000). Groundwater quality is, however, a spatially distributed attribute. It is generally accepted that knowledge of the spatial distribution of this attribute allows the design of site specific protection and remediation measures. Therefore robust and validated techniques are needed to map the spatial distribution of groundwater quality within the groundwater body continuum. Unfortunately, properties related to groundwater quality, such as nitrate concentration, can only directly be measured at the local scale. The mapping of groundwater quality within the water body continuum will therefore often build on data interpolation or prediction of properties related to groundwater quality through deterministic or stochastic models, and the adopted technique will impact the results of the final assessment.

Point data can be spatialized with traditional interpolation tools such as Voronoi tessellation, inverse distance weighting or kriging. Hu *et al.* (2005) and Fetouani *et al.* (2008) for instance used ordinary kriging for mapping the spatial variability of nitrate concentrations in a shallow water body. Cinnirella *et al.* (2005) used Gaussian simulation techniques to introduce local uncertainty for mapping nitrate concentrations within the groundwater bodies of the Po Valley (Italy). Among modern interpolation techniques, the Bayesian Maximum Entropy (BME) framework was developed recently by Christakos *et al.* (2002) as a generalization of classical techniques. Mattern *et al.* (2008) used BME as a formal spatial modelling framework allowing to introduce the temporal variability of groundwater contamination and the sampling rate in a spatial map.

Unfortunately, the locations where groundwater quality properties are measured are typically scarce and sparsely distributed over space. As a result, large uncertainties about the variable of interest arise in the mapping process, especially at prediction points located far away from monitoring stations. Given that the quality of the interpolation decreases rapidly with the distance to the monitoring station, the mapping of a variable of interest through classical geostatistical interpolation techniques will have limited practical utility in regions where a densely

distributed monitoring network is not available. Unfortunately, this is rather the rule than the exception, and therefore alternative robust and validated methods are needed to provide more comprehensive and accurate information about the groundwater quality. Data fusion is such a method that can be used to combine optimally various sources of information about groundwater quality in a consistent and accurate model prediction.

Data fusion techniques have already been used in various application fields, including for example biometrics verification systems (e.g., Duc *et al.*, 1997; Ross and Jain, 2003), surveillance systems (e.g., Jones *et al.*, 2003), robotics (e.g., Cremer *et al.*, 2001), medical imagery (e.g., Song *et al.*, 2002) or military/civil engineering (e.g., Gros *et al.*, 1999; Sohn and Lee, 2003). Data fusion also has important applications in classification of remote sensing images (e.g., Simone *et al.*, 2002) and in environmental modelling (Bogaert and Fasbender, 2007).

Among different data fusion techniques, a Bayesian Data Fusion (BDF) approach was recently proposed by Bogaert and Fasbender (2007). It was especially designed for spatial predictions problems and provides a consistent framework of fusing an arbitrary large number of information sources that are related to a same variable of interest in order to provide a unique spatial prediction. The main advantage of a Bayesian approach is to put the problem of data fusion into a clear probabilistic framework. BDF has already proved its relevance in various environmental sciences applications, such as fusion of remotely sensed images (Fasbender *et al.*, 2008b,c), water table estimation (Fasbender *et al.*, 2008a) and space-time prediction of air pollutants (Fasbender *et al.*, 2009). To the best of our knowledge, BDF has never been used for mapping groundwater pollution by nitrate.

In this chapter, the BDF approach is used as a formal framework to map groundwater contamination by nitrates. Groundwater contamination by nitrate remains a critical water quality issue for many groundwater bodies all over the world. We illustrate the approach for mapping groundwater contamination in the water body of the Brusselian sands located in an unconfined sandy aquifer in the centre of Belgium. This water body is one of the most affected by nitrate pollution.

Groundwater nitrate concentrations were measured at different monitoring stations irregularly distributed in the study area. These point data were interpolated on a grid covering the whole study area by classical (ordinary kriging) geostatistical techniques. With this interpolation method, the uncertainty on the prediction depends partly on the respective geometry of the monitoring station and the estimation point. As a consequence, the uncertainty on the predictions is larger in parts of

the study area where data are scarce, making these estimates useless at some points on the map. On the other hand, nitrate concentrations were predicted by a statistical model all over the study area. With this model, the prediction uncertainty depends on the uncertainty of underlying predictor variables such as depth to the water table, land use or altitude, along with the model uncertainty. Using BDF, nitrate concentrations estimated by the interpolation method will be combined with those obtained from the statistical model into a single prediction. The BDF prediction together with its estimated uncertainty will further be spatially mapped.

6.3 Material and methods

6.3.1 Data

The depth to the water table was calculated by subtracting the piezometry value from a 30 m resolution digital elevation model (DEM) which was furnished by the regional administration. The piezometry map was calculated by interpolating the water table levels measured in 1984 using ordinary kriging. The calculation of depth to the water table varies from 0 to more than 45 m with a mean value of 10.5 m.

The groundwater nitrate concentration data used in this study was recently collected over 99 monitoring stations in January and February 2009. These monitoring stations are wells, galleries, drains and springs. A one-way analysis of variance was performed for comparing the nitrate concentrations measured in the different types of monitoring stations and no significant differences were detected in the mean concentrations of the different groups at a significance level of 0.05. The nitrate concentrations show a wide spatial variability in the study area, with values going from 6.9 up to 93.4 mg NO₃/l. The regional mean and standard deviation are respectively equal to 45.6 and 17.2 mg NO₃/l (Table 6.1).

Table 6.1: Descriptive statistics of the measured nitrate concentrations.

Number of monitoring stations	99
Minimum (mg/l)	6.9
Maximum (mg/l)	93.4
Mean (mg/l)	45.6
Variance (mg ² /l ²)	297.0
Standard deviation (mg/l)	17.2
Median (mg/l)	43.3
Kurtosis	3.3
Skewness	0.4

6.3.2 Kriging

Kriging is a group of stochastic prediction techniques widely used in geostatistics to interpolate the value of a random field (e.g., the ground-water nitrate concentration here) at an unobserved location, based on a linear combination of observed values at nearby locations. Kriging incorporates the spatial dependence of the data in its estimation process through a variogram or a covariance function. The variogram function yields the average dissimilarity between locations separated by different intervals of distances. Kriging is known to provide a linear predictor that corresponds to the Best Linear Unbiased Predictor (BLUP) in the least squares sense. Additionally, it is the best possible predictor when random field is assumed to be multivariate Gaussian. Ordinary kriging is the most commonly used type of kriging. It assumes a constant but unknown mean and enough observations to reliably estimate the variogram. The measured nitrate concentrations are in reality representative of a volume of water in the aquifer around the monitoring station. This volume is however difficult to estimate and subject to large uncertainties. Kriging was therefore carried out assuming that the measured concentrations are point data.

6.3.3 Regression tree

Regression tree modelling is an explanatory technique relying on a process known as binary recursive partitioning. Regression trees became popular in environmental sciences in the early nineties (e.g., Baker *et al.*, 1993; Lees and Ritman, 1991; Vanlanen *et al.*, 1992). The algorithm identifies which of the variables explains most of the variance in the response variable, then determines the threshold value of the explanatory variable that best partitions the variance in the response such

that it minimizes the sum of the squared deviations from the mean in the two groups. The process is repeated for each new branch until there is no residual explanatory power, according to the limitations imposed by the user. Suppose that predictor variables $x_1, x_2, \dots, x_N$ and the response variable y are organized as columns in a table. The database table is sorted by the column of the first variable (x_1). Then the table is split into two parts (called left and right branch) until the number of samples in the branch to split is lower than a user defined threshold value M_{split} . For each possible split position, the two partitions are compared based on the reduction in non-homogeneity

$$\Delta D = D - D_L - D_R \quad (6.1)$$

that they provide. The non-homogeneity in a group of samples is measured by computing deviations and defined as

$$D = \sum_i (y_i - \bar{y})^2 \quad (6.2)$$

where $\bar{y}$ is the mean value across all observations y_i . Each partition generates left (D_L) and right (D_R) deviance values. This process is repeated for each of the N predictor variables. The partition that maximizes the change in deviance ΔD is the partition to choose. Each of the branches obtained after partitioning is partitioned again according to the limitations imposed by the M_{split} threshold.

Regression trees are often used to see whether complex interactions between explanatory variables exists and to identify which one of the predictors have the most important effect on the dependent variable (Crawley, 2005). Major advantages of regression tree models are that i) they are nonparametric, ii) Gaussian distribution assumption of predictor variables does not need to be satisfied, iii) they can incorporate categorical data, and iv) they allow possibly complex interactions between the predictor variables to be represented without assumptions of linearity. Furthermore, while multiple linear regression identifies global relationships in the data set, regression tree are able to identify local relationships (Rothwell *et al.*, 2008).

In this study, we created a regression tree for predicting nitrate concentrations as a function of the predictors listed in Table 6.2. The regression tree model was applied to the dataset to predict nitrate concentrations all over the study area at the nodes of a regular 50 m $\times$ 50 m grid.

Regression tree algorithms are implemented in various software packages such as MatlabTM, SASTM, RTM. The “classregtree” function implemented in the Matlab Statistical ToolboxTM was used in this study.

Table 6.2: Description of the variables used in the regression tree model.

Variable description	Variable ID
Depth to the water table at the prediction point (m)	Depth
Slope of the soil surface at the prediction point (%)	Slope
Altitude at the prediction point (m)	Altitude
Residential land ^a	LU11
Areas of economic activity, service and equipment ^a	LU12
Mining, landfills and abandoned areas ^a	LU13
Artificial non-agricultural green-spaces ^a	LU14
Arable land ^a	LU21
Permanent crops ^a	LU22
Grassland ^a	LU23
Forests ^a	LU31
Shrub vegetation and/or herbaceous areas ^a	LU32
Surface water ^a	LU51

^aexpressed as the percentage of the land use class in a 300 m radius around the prediction point.

6.3.4 BDF

It is beyond the scope of this thesis to present the whole underlying theory of BDF. So only theoretical results that are the most relevant for our application will be presented hereafter. The interested reader may refer to Bogaert and Fasbender (2007) for a detailed description of the theory. The general BDF equations can be simplified to simple analytical formulas when it is assumed that nitrate concentrations obtained by kriging and by the statistical model are Gaussian distributed (Fasbender *et al.*, 2008a). The final predicted mean nitrate concentration μ_P and its variance σ_P^2 are then given by

$$\begin{cases} \mu_P = \left(\frac{\mu_k}{\sigma_k^2} + \frac{\mu_m}{\sigma_m^2} - \frac{\mu_0}{\sigma_0^2} \right) \sigma_P^2 \\ \sigma_P^2 = \left(\frac{1}{\sigma_k^2} + \frac{1}{\sigma_m^2} - \frac{1}{\sigma_0^2} \right)^{-1} \end{cases} \quad (6.3)$$

where μ_k , μ_m and μ_0 are the means associated with the kriging prediction, the statistical model prediction and a “rough” estimation of the local mean obtained from the inverse distance method, respectively where σ_k^2 , σ_m^2 and σ_0^2 are the variance associated with the kriging prediction, the variance associated with the statistical model prediction and the sill of the semi-variogram, respectively.

6.3.5 Comparison of methods

The presented interpolation methods yield different cartographic results because of their inherent characteristics. Each map is subject to prediction errors. To elucidate those errors and to illustrate the estimation accuracy, a “leave-one-out” cross-validation approach was performed. The following indicators were chosen for accuracy assessment:

The root mean squared error (RMSE):

$$RMSE = \sqrt{\frac{1}{n} \sum_{i=1}^n (\hat{y}_i - y_i)^2} \quad (6.4)$$

The mean absolute error (MAE):

$$MAE = \frac{1}{n} \sum_{i=1}^n |\hat{y}_i - y_i| \quad (6.5)$$

The mean error (ME):

$$ME = \frac{1}{n} \sum_{i=1}^n (\hat{y}_i - y_i) \quad (6.6)$$

The coefficient of determination (R^2):

$$R^2 = 1 - \frac{\sum_i (y_i - \hat{y}_i)^2}{\sum_i (y_i - \bar{y})^2} \quad (6.7)$$

where n is the number of observations, $\bar{y}$ is the mean value across all observations y_i and where $\hat{y}_i$ are the predicted values.

It is worth noting that, these quality indicators only reflect the general regional accuracy of the predictions. Local improvements of the mapping process will therefore be observed on the maps of uncertainties.

All calculations were performed in Matlab R2008b, using the geo-statistical BMElib package (Christakos *et al.*, 2002). Data preparation was carried out in ArcGIS 9.3.

6.4 Results

6.4.1 Kriging

The first presented mapping method relies on the interpolation of the measured nitrate concentrations through ordinary kriging. An experimental semi-variogram was modelled as the sum of a nugget effect of

$67.2 \text{ mg}^2/\text{l}^2$ and an exponential model with total theoretical variance and range of $333 \text{ mg}^2/\text{l}^2$ and 12091 m , respectively (Fig. 6.1). The nugget effect is due to very local contamination in some wells conducting to high differences in nitrate concentrations measured in nearby monitoring station. About 67% of the study area has kriged nitrate concentrations lower than the standard of 50 mg/l , even if nitrate concentrations exceeding 80 mg/l are observed in some parts of the study area (Fig. 6.2a). The prediction errors (i.e. the square root of the variance of prediction error) of the kriged concentration is minimum at the location of the monitoring stations and raises up to 20 mg/l where the density of the monitoring stations is the lowest (Fig. 6.2b).

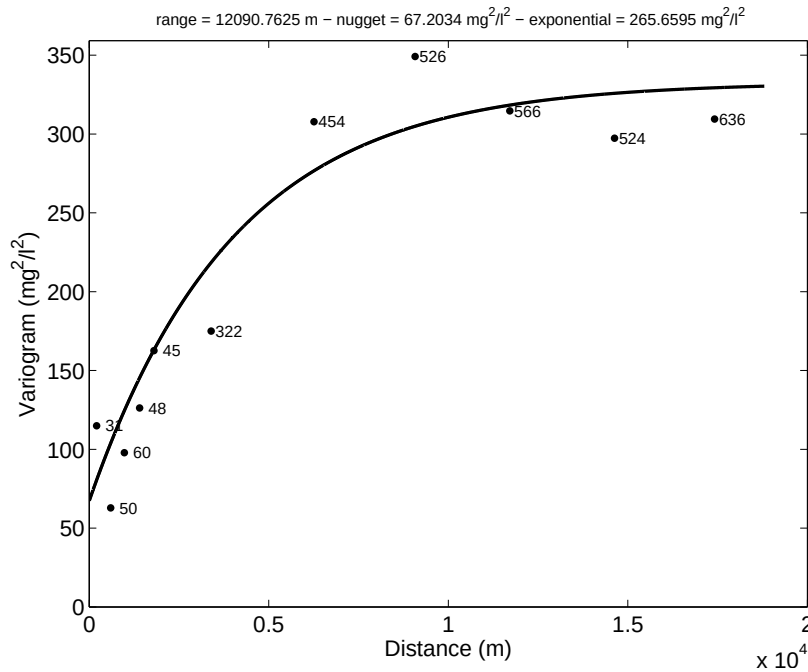


Figure 6.1: Semi-variogram of the nitrate concentrations in the Brusselian sands estimated on the basis of the dataset of January and February 2009. Dots represent the experimental semi-variogram, plain line represents the fitted semi-variogram.

Kriged nitrate concentrations were compared to measured nitrate concentrations by a “leave-one-out” cross validation (Fig. 6.3). While most of the data fall near the 1:1 line, showing that this interpolation method is able to unbiasedly predict nitrate concentrations in some parts of the area, other points are located further from the 1:1 line. This is not surprising since these particular sites are located in the regions where

the sampling network has a very low density. As a consequence, when the “leave-one-out” cross validation process removes these isolated point from the dataset, the prediction solely relies on data located far away from that point, thus resulting in an inaccurate prediction and a global poor coefficient of determination. Furthermore, the presence of a nugget effect of about 20% of the total variance can also be responsible for poor prediction results.

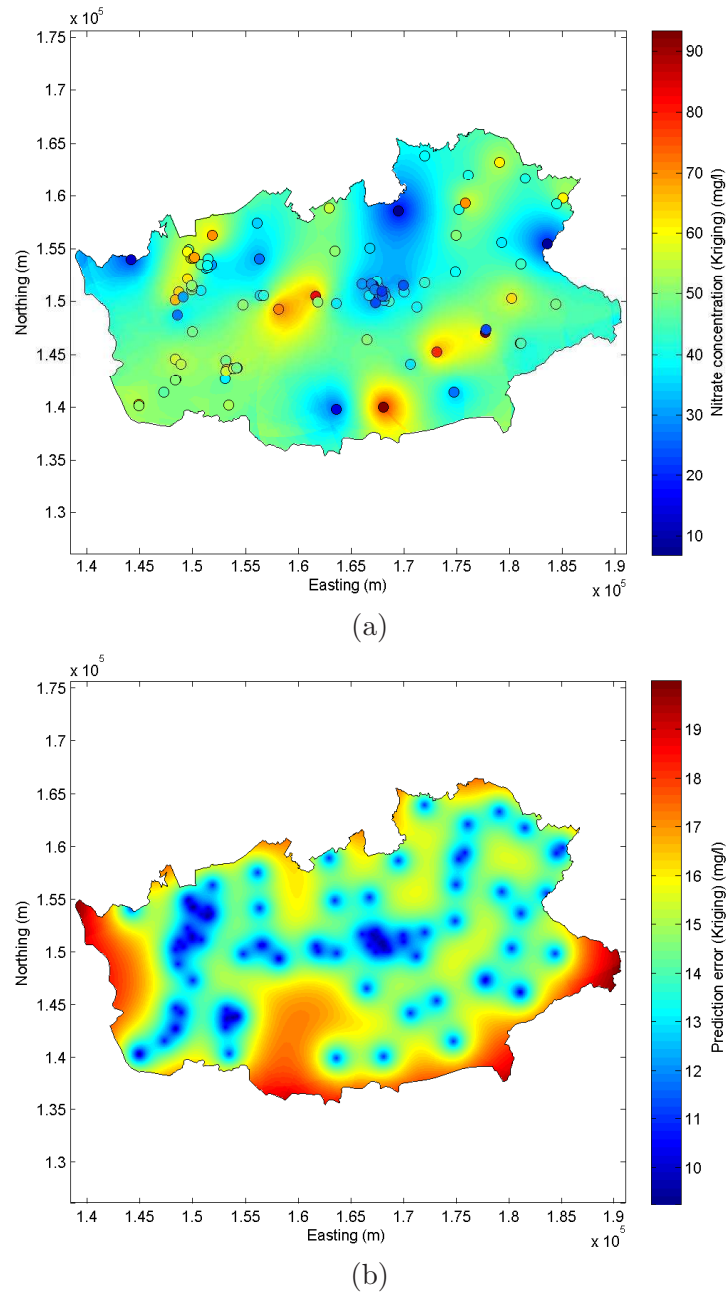


Figure 6.2: Map of kriged groundwater nitrate concentration (a) and associated prediction error (b). The monitoring stations are symbolized by circles on (a).

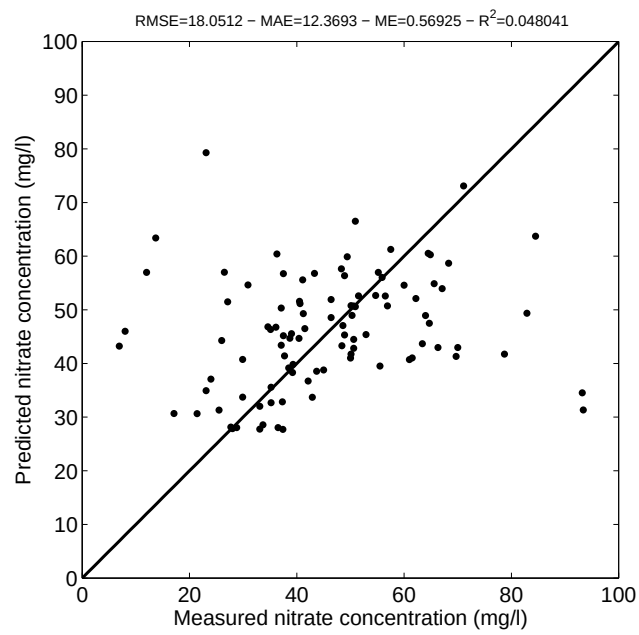


Figure 6.3: Comparison between kriged nitrate concentrations and measured nitrate concentrations. The plain line represents the 1:1 line.

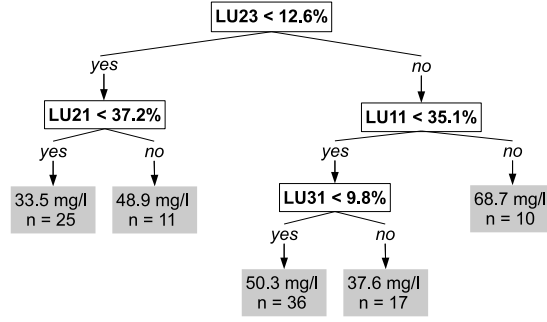
6.4.2 Regression tree

Development of the regression tree

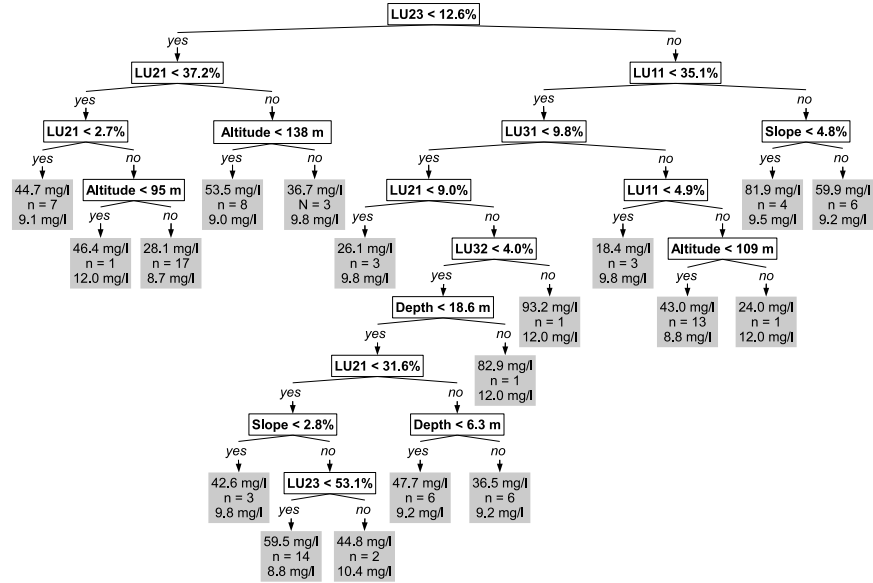
Nitrate concentrations measured at the 99 monitoring stations in January and February 2009 were related to the 13 variables listed in Table 6.2 through a regression tree model (Fig. 6.4b). As shown by Mattern *et al.* (2009) such models show highly complex interaction patterns, suggesting that a complex combination of variables explains observed pollution levels, rather than single explicative variables.

As shown on Fig. 6.4a, which represents a simplified version of the regression tree with only the upper part of the tree, the most important explanatory variable is the percentage of grassland in a 300 m radius around the prediction point (LU23) and the threshold value separating low and high values of LU23 is 12.6%. For low values of LU23, the tree shows that the percentage of arable land in a 300 m radius around the prediction point (LU21) has a significant impact on groundwater pollution by nitrate. Indeed, lower mean nitrate concentration (33.5 mg/l) are observed where less than about on third of the area around the prediction point is covered by arable land ($LU21 < 37.2\%$). For high values of LU23, the tree shows that the percentage of residential land in a 300 m radius around the prediction point (LU11) is significant. High values of LU11 ($> 35.1\%$) result in high mean nitrate concentration (68.7 mg/l), while for lower values of residential land ($LU11 < 35.1\%$) the mean nitrate concentration is lower and depends also on the percentage of forests in a 300 m radius around the prediction point.

The regression tree was applied to the dataset and the estimated nitrate concentrations were compared to the measured nitrate concentrations resulting in an R^2 of 0.80 and an RMSE of 7.66 mg/l (Fig. 6.5). All parameters of the model are significant at the 0.05 level.



(a)



(b)

Figure 6.4: Simplified (a) and complete (b) regression trees. At the end of each branch, the first value is the mean nitrate concentration; the second value is the number of samples and the third value is the prediction error. See Table 6.2 for legend.

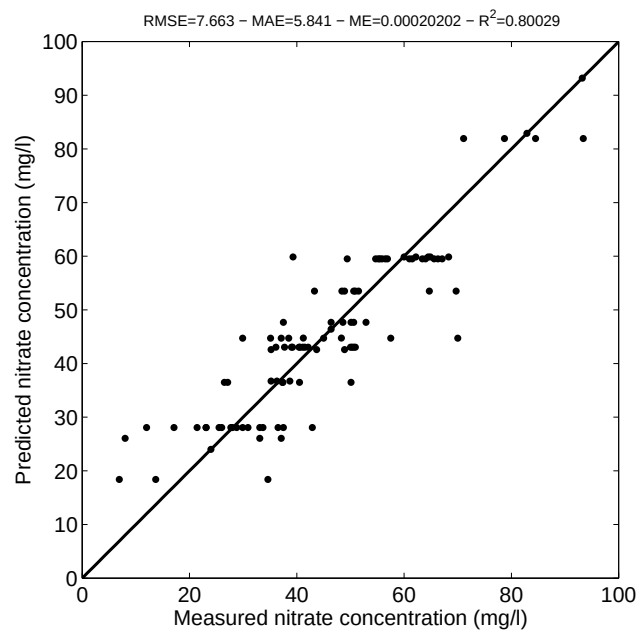


Figure 6.5: Comparison of the nitrate concentrations predicted with the regression tree model to the measured nitrate concentrations. The plain line represents the 1:1 line.

Prediction with the regression tree

The regression tree model was applied to the gridded dataset using variables listed in Table 6.2 to predict nitrate concentration at the nodes of the prediction grid. About 70.9% of the study area has predicted nitrate concentrations lower than 50 mg/l (Fig. 6.6a). As expected from the regression tree, the highest nitrate concentrations are observed in urban areas of the central and north-west parts of the study area, while lower concentrations are observed in the south-west and south-east. The prediction error of the regression tree model ranges from 9 to 12 mg/l (Fig. 6.6b).

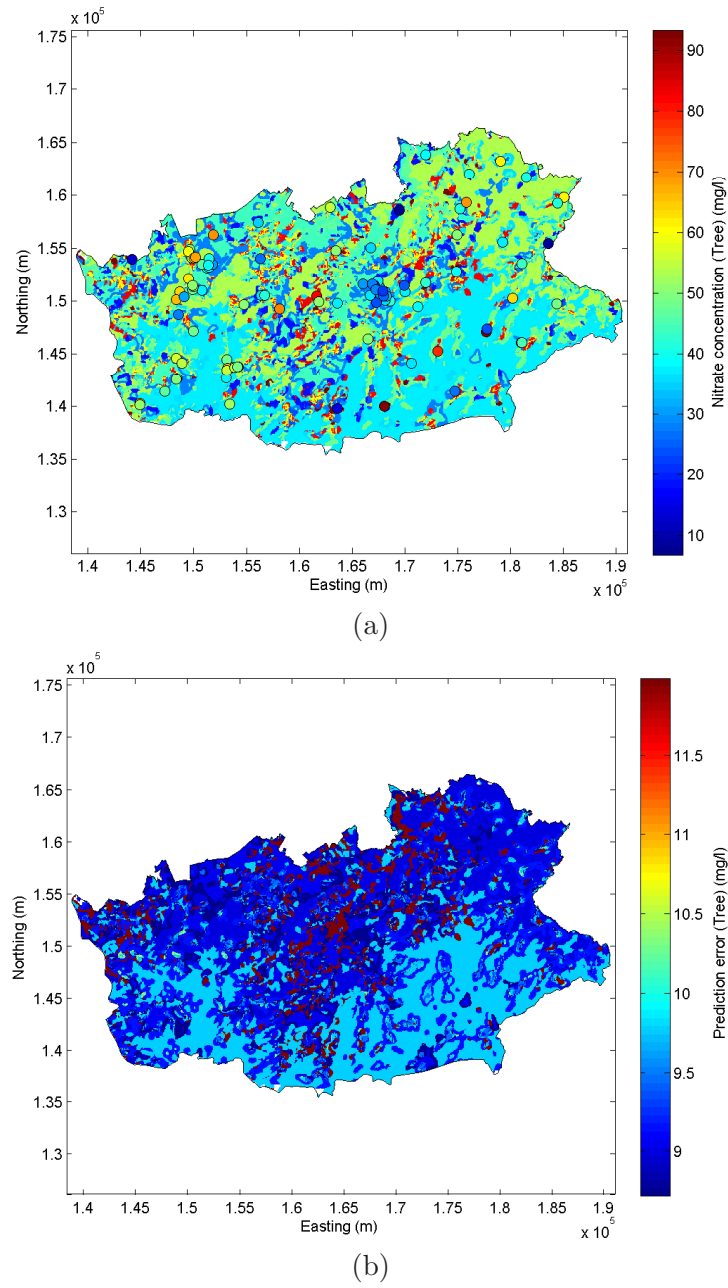
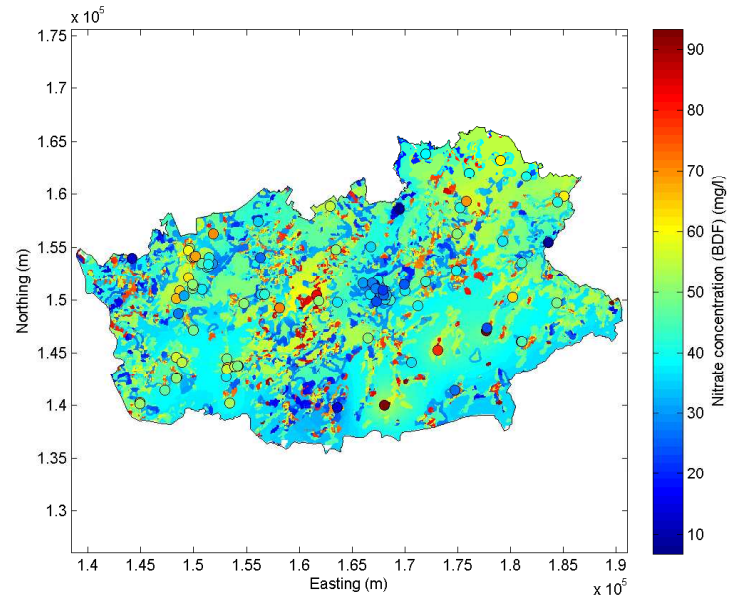


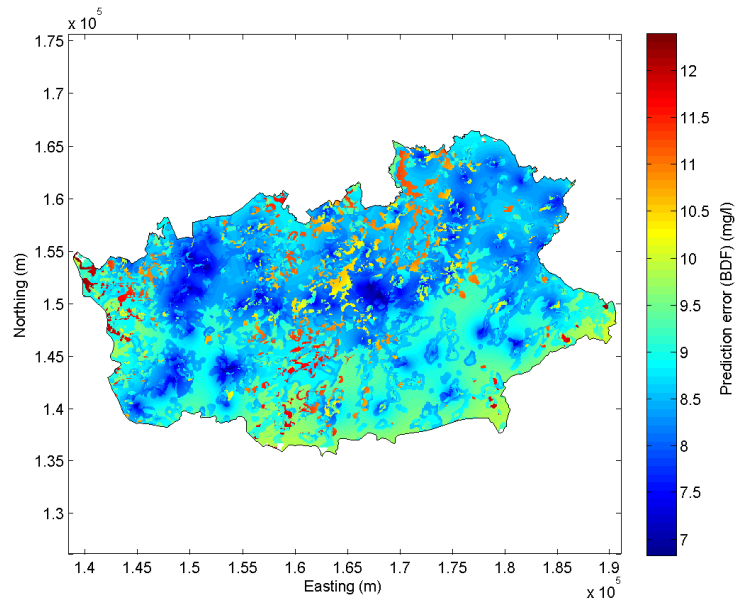
Figure 6.6: Map of groundwater nitrate concentration predicted by the regression tree model (a) and associated prediction error (b). The monitoring stations are symbolized by circles on (a).

6.4.3 BDF

The BDF method uses the results of the prediction map provided by the kriging interpolation model and the map resulting from the regression tree model for fusing these two information based on a weighing according their relative prediction errors. The nitrate concentration predicted by kriging will be preferred at places where the kriging prediction error is smaller than the prediction error of the regression tree, and reciprocally. Since the prediction error of the regression tree map is generally lower than for kriging, the BDF map is very close to the map made by the regression tree, except near the monitoring stations. In the map predicted by BDF, 64.6% of the study area has predicted nitrate concentrations lower than 50 mg/l (Fig. 6.7a) and the prediction error varies from less than 7 to about 12 mg/l (Fig. 6.7b). The nitrate concentrations estimated with BDF were compared to the measured nitrate concentrations resulting in an R^2 of 0.74 and an RMSE of 8.77 mg/l (Fig. 6.8).



(a)



(b)

Figure 6.7: Map of groundwater nitrate concentration predicted by BDF (a) and associated prediction error (b). The monitoring stations are symbolized by circles on (a).

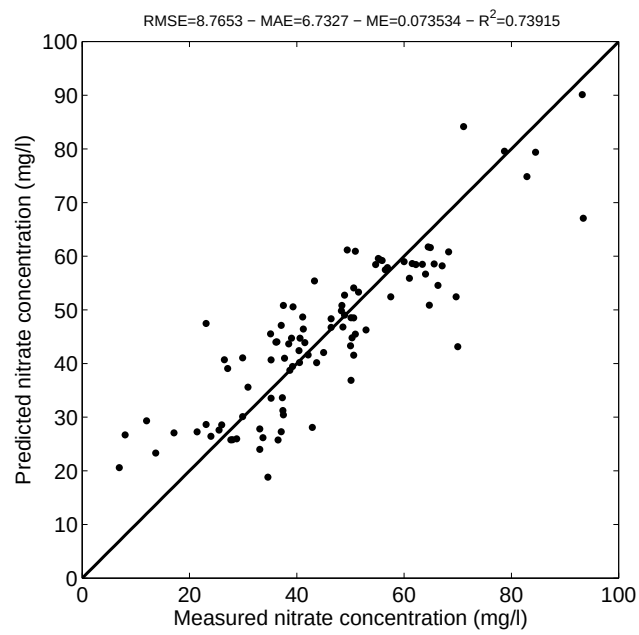


Figure 6.8: Comparison of the nitrate concentrations predicted by BDF to the measured nitrate concentrations. The plain line represents the 1:1 line.

6.5 Discussion

Nitrate concentrations measured at 99 monitoring stations irregularly distributed in the study area were spatialized on the whole region by ordinary kriging interpolation on the one hand and by a statistically based regression tree model on the other hand. The kriging predictions have the lowest uncertainties at proximity of the monitoring stations and huge uncertainties further away, while the predictions made by the regression tree have more homogeneous uncertainties throughout the study area. While kriging is an exact predictor, meaning that the concentration predicted at the locations of the measuring points is equal to the measured value, the regression tree model only predicts an expected value. As a consequence, the measured concentration do not honors the measurements on the map constructed from the regression tree and, hence, from BDF. Using Bayesian Data Fusion allows combining the nitrate concentrations estimated by the interpolation method with those estimated by the statistical model into a single final map and allows us to reduce the associated prediction uncertainty.

The quality of the map constructed from the kriging method is influenced by the density and geometry of the monitoring network. In low density sampling regions, a local pollution could be wrongly extrapolated to a big surrounding area. These singular points (with local extreme concentrations) are responsible for the global poor coefficient of determination resulting from the “leave-one-out” cross validation process. While they could be considered as outliers in a pure kriging process, and therefore removed from the analysis, these points make sense in a BDF framework since they will be weighted with the predictions made by the regression tree model.

The regression tree was able to estimate nitrate concentrations at the unsampled parts of the study area with a lower uncertainty than the kriging method. The fragmented aspect of the map constructed from the regression tree is due to the discontinuous land use which is the principle explanatory variable in the regression tree model. The regression tree model used to predict nitrate concentrations over the study area could further be enhanced by the incorporation of other variables related to, for example, soil properties, more detailed land use classes, or other environmental factors related to groundwater contamination. However, it must be kept in mind that the high mobility of nitrate ions and hence their wide propagation in the aquifer makes the identification of a causal relationship not trivial.

Nitrate concentrations predicted with BDF have a mean regional value of 44.4 mg/l. The highest concentrations are observed in the agri-

cultural regions of the center and east of the study area and in the north-west urban areas. It is worth noting that the quality indicators used to compare the enhancement of the results of the three models are valid only at the regional scale and they do not permit to emphasize the detailed improvements of the mapping technique at the local scale. For this reason, we mapped the differences between the results of the various models. It can be observed from Fig. 6.9a that large differences between kriged nitrate concentrations and concentrations predicted by BDF (from nearly -4 to 3 mg/l) appear between the two maps. Furthermore, we observe on Fig. 6.10a that BDF reduces the uncertainty up to 10 mg/l in the regions where the monitoring network is scarce. We observe on Fig. 6.9b that the differences between nitrate concentrations predicted by the regression tree model and concentrations predicted by BDF vary between -2.5 and 2 mg/l. These differences are located at proximity of the monitoring stations where the weight given to the kriged concentrations in the BDF process is higher than the weight of the concentration predicted by the regression tree model. We observe on Fig. 6.10b that BDF reduces the uncertainty up to nearly 4 mg/l in the regions where the monitoring network is scarce, compared to the regression tree. As a consequence, BDF has reduced prediction error compared both to kriging and the regression tree model and, in that sense, is an improvement for the mapping process. The method is especially useful when information to be combined have prediction errors of the same order of magnitude. If not, the BDF map will be very similar to the map with the lowest uncertainty. Since the BDF prediction errors are close to the regression tree ones except near the monitoring stations where the uncertainty associated with the kriging is minimal, the addition of new monitoring stations increases the quality of the prediction map here.

As shown in chapter 5, the temporal variability of nitrate concentrations measured in one monitoring station is smaller than the spatial variability at the regional scale. Furthermore, the goal of this chapter was to map nitrate concentrations at one given moment (January/February 2009) and temporal dynamics was therefore not integrated in the mapping process.

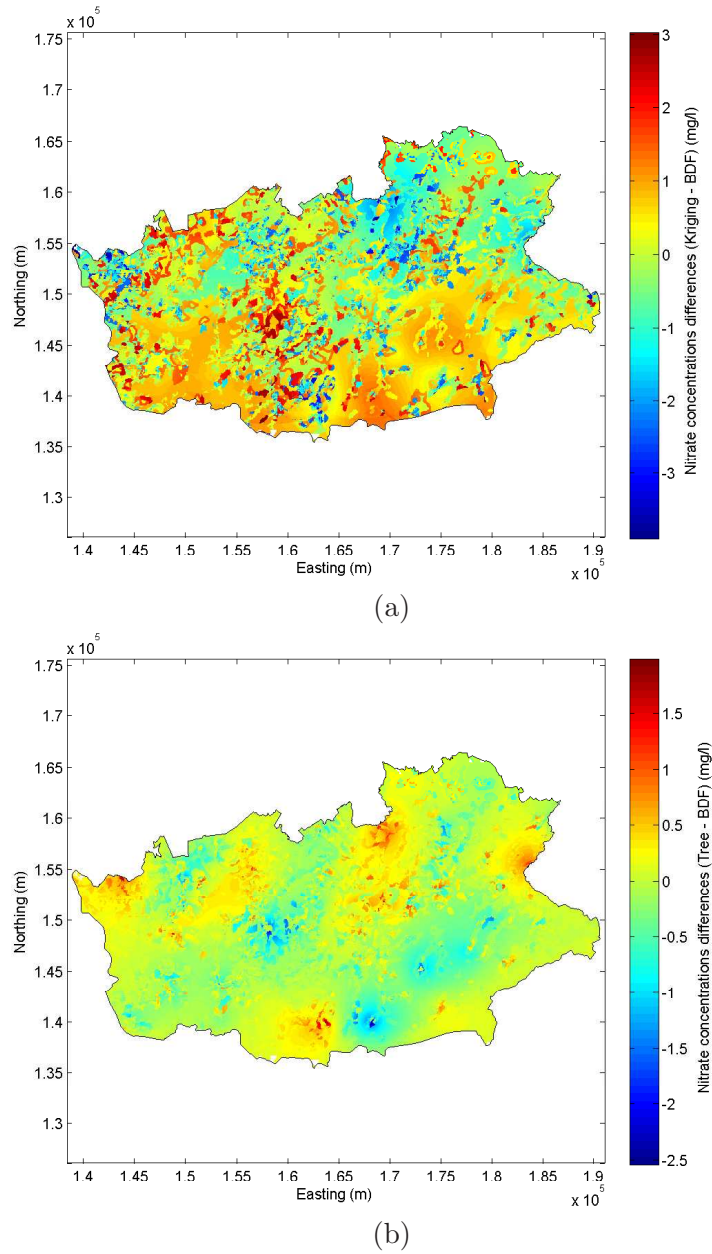
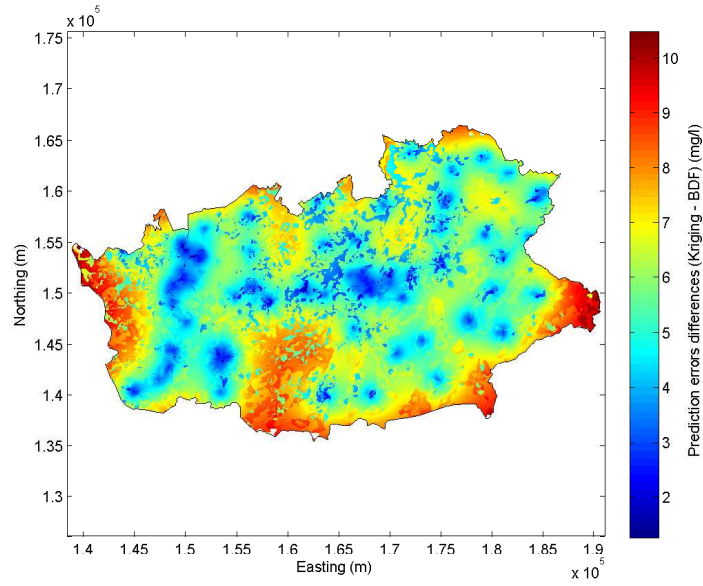
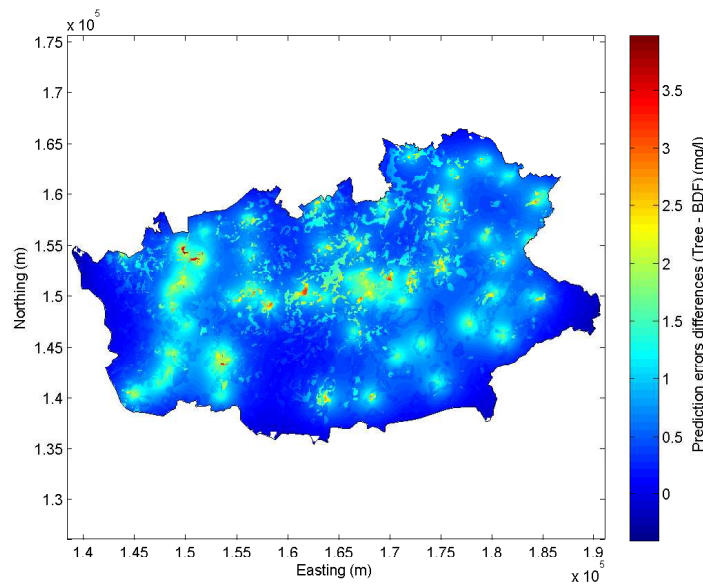


Figure 6.9: Differences between nitrate concentrations predicted by kriging and BDF (a) and between the regression tree model and BDF (b).



(a)



(b)

Figure 6.10: Differences between kriging prediction errors and BDF prediction errors (a) and between the regression tree prediction errors and BDF prediction errors (b).

6.6 Conclusions

In this chapter, we wanted to get a “picture” of groundwater nitrate concentrations of the Brusselian sands using a Bayesian Data Fusion framework, by combining groundwater monitoring data with a statistical groundwater contamination model. Nitrate concentrations measured in January and February 2009 were first spatialized over the whole study area using ordinary kriging. Since the monitoring stations are irregularly distributed in the study area, the kriging predictions have huge uncertainties where the density of monitoring stations is low. The monitoring network was not initially intended with environmental monitoring in mind. Its low density in some places explains these large uncertainties. Subsequently, nitrate contamination was estimated using a statistical regression tree model. The predictions made by the regression tree have more homogeneous uncertainties throughout the study area but the nitrate concentrations measured at the monitoring stations do not appear on the map. Bayesian Data Fusion allows combining the nitrate concentrations estimated by the interpolation method with those estimated by the statistical model into a single final map by weighting these estimates in terms of the associated uncertainty, thereby allocating a high weight to estimates which are very certain and a low weight to those that are very uncertain. It has been shown that the associated prediction uncertainty in the final map is smaller than those for the kriged map or the map predicted with the statistical model.

In this case study, only two sources of information were combined to assess the nitrate pollution of the groundwater body at a given moment in time. Yet, the formal Bayesian Data Fusion framework allows integrating easily other data and could therefore be used to update the estimated map when new monitoring and modelling data about the status of the groundwater body becomes available. Hence, Bayesian Data Fusion is considered to be appropriate to generate updated high quality maps of the groundwater contamination at the regional scale.

Such updated high quality maps of groundwater contamination represent a powerful tool which could be used by the regional administration and the water production companies to implement specific and local water management and protection strategies. However, increasing the density of the measurement network in the study area and using multilevel sampling tools would enhance the quality of the (geo)statistical analysis.

Chapter 7

On the use of natural abundance of ^{15}N - NO_3 and ^{18}O - NO_3 to determine the sources of groundwater pollution by nitrate: a literature review

7.1 Outline

This chapter gives an overview of the scientific literature on the use of natural abundance of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of nitrate to distinguish different sources of groundwater pollution by nitrate. In this chapter, emphasis will be put on processes affecting the isotopic abundance of nitrate and on the isotopic signature of N sources. An application of the use of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ will be presented afterwards, in chapter 8.

7.2 Introduction

7.2.1 Definitions and measurements of ^{15}N and ^{18}O in nitrate

Isotopes are any of the different types of atoms of the same chemical element, each having a different atomic mass (mass number). Isotopes of an element have nuclei with the same number of protons (the same

atomic number) but different numbers of neutrons. Therefore, isotopes have different mass numbers, which give the total number of nucleons, the number of protons plus neutrons. ^{14}N nuclei contain seven neutrons; ^{15}N nuclei, eight neutrons, both contain seven protons. Stable isotopes are chemical isotopes that are not radioactive (they have not been observed to decay, though a few of them may be theoretically unstable with exceedingly long half lives). There are 256 known stable isotopes of the 80 elements which have one or more stable isotopes. Unstable isotopes are radioactive and potentially hazardous to work with; stable isotopes are not radioactive.

Natural abundance refers to the abundance isotopes of a chemical element as naturally found on a planet (or the abundance of an isotope in samples to which no tracer has been added). The *isotope abundance* is the amount of an isotope, whether expressed on the atom-% or δ scale (see below).

The *isotope ratio* R is defined as the ratio of the number of heavy isotopes of an element to the number of light isotopes in a sample (Eq. 7.1) and is measured by mass spectrometry.

$$R = \frac{n_h}{n_l} \quad (7.1)$$

where, for e.g., n_h is the number of ^{15}N or ^{18}O atoms of N or O present in a sample, respectively, and n_l is the number of ^{14}N or ^{16}O atoms of N or O present in the sample, respectively.

The *atom percent abundance* A is defined as the percentage contribution of one isotope (e.g. ^{15}N) to the total number of atoms of that element in a sample (Eq. 7.2). Of the N atoms on earth, 99.6337% are ^{14}N ; the remaining 0.3663% are ^{15}N (Junk and Svec, 1958). The stable isotopes of oxygen (O) are ^{17}O (least abundant, 0.0375%), ^{18}O (next least abundant, 0.1995%) and ^{16}O (most abundant, 99.763%) (Cook and Lauer, 1968). Equation 7.2 is used when A exceeds ~ 0.5 atom-%, and therefore refers in practice to the studies in which ^{15}N is used as an enriched tracer.

$$A = 100 \cdot \frac{n_h}{n_h + n_l} = 100 \cdot \frac{R_{\text{sample}}}{R_{\text{sample}} + 1} \quad (7.2)$$

Because differences in isotopic abundance of an element from one substance to another are small, isotope ratios in all natural abundance studies are commonly reported as per mille (‰) deviation from an international standard using the so-called δ notation (Eq. 7.3), defined as

the difference in isotope ratio between the sample and a standard, normalized to the isotope ratio of the standard (expressed in units of parts per thousand, ‰).

$$\delta X (\text{‰}) = 1000 \cdot \frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} \quad (7.3)$$

where X is the isotope of interest (e.g., $\delta^{15}\text{N}$ or $\delta^{18}\text{O}$). The internationally accepted standard used for the calculation of $\delta^{15}\text{N}$ is atmospheric N_2 gas ($R = 0.0036765$, corresponding to $A = 0.3663$ atom-‰ ^{15}N), which has a uniform $\delta^{15}\text{N}$ from continent to continent (Junk and Svec, 1958; Mariotti, 1983). The standard of O is Vienna Standard Mean Ocean Water (VSMOW), which is an isotopic water standard defined in 1968 by the International Atomic Energy Agency, based on works of Craig (1961). The standards have defined $\delta^{15}\text{N}$ or $\delta^{18}\text{O}$ values of 0‰. The more ^{15}N -enriched a sample, the more positive (or less negative) its $\delta^{15}\text{N}$ (Robinson, 2001; Beller *et al.*, 2004; Clark and Fritz, 1997).

Three methods are available for analysing $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ in nitrate. The so called “ion-exchange” or “ AgNO_3 ” method has been developed by Chang *et al.* (1999) and Silva *et al.* (2000). Another technique is the so called “bacterial denitrification method” (Sigman *et al.*, 2001; Casciotti *et al.*, 2002; Rock and Ellert, 2007) and has been developed in recent years. The third technique is called “chemical denitrification method” (McIlvin and Altabet, 2005). The interested reader may refer to mentioned literature for more details about the analytical techniques.

7.2.2 Use of ^{15}N and ^{18}O in nitrate

Isotope methods are increasingly used in contaminant hydrogeology to differentiate between different sources of contamination and/or to identify contaminant transformation processes. These methods are based on the observation that different natural or anthropogenic sources of a compound often have a different isotopic signature and that transformation processes lead to a predictable change in the isotope ratio of a compound. The use of isotope data to trace transformation processes is motivated by the fact that chemical data often only provide limited information on transformation processes because concentrations are affected by a number of physical and reactive processes.

The earliest attempts to identify NO_3^- sources conducted using N natural isotopic abundances (Kohl *et al.*, 1971) were very controversial (e.g., Hauck *et al.*, 1972) due in large part to the oversimplification of the problem, and to a lack of recognition of potential fractionation

processes during transport (Kellman and Hillaire-Marcel, 1998). For almost four decades, analysis of the isotopic abundances of the NO_3^- ion has been used extensively and successfully to provide information on the origins and transformations of inorganic N in surface and ground waters (Létolle, 1980; Heaton, 1986; Mariotti *et al.*, 1988; Bottcher *et al.*, 1990; Wassenaar, 1995; Aravena and Robertson, 1998; Mengis *et al.*, 1999; Panno *et al.*, 2001). Nitrogen isotopes are now routinely used to monitor pollution of nitrate in groundwaters.

The isotopic fractionation of the natural isotopes of N and O in NO_3^- through biotic and abiotic processes results in different ranges for different N sources. Nitrogen isotopes in nitrate ions are useful for the identification of nitrate sources. Each nitrogen source has a typical range of isotopic values (Heaton, 1986; Kendall and McDonnell, 1998; Jun *et al.*, 2005). The isotope ratio of NO_3^- in natural environments is controlled by that of its source materials and by processes causing its subsequent biogeochemical alterations like production, consumption, or exchange (Ostrom *et al.*, 1998). In systems where the dominant sources of nitrate are isotopically distinctive, source contributions can - in theory - be determined despite significant fractionation. Many hydrogeological investigations report that distinctions between groundwater nitrate derived from human/animal waste, from atmospheric N depositions and from that derived from agricultural sources, such as inorganic fertilizers or mineralized soil organic nitrogen, can be made on the basis of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values in nitrate (Iqbal *et al.*, 1997) (Fig. 7.1).

The origin of NO_3^- must be linked to the entire N cycle, since values of $\delta^{15}\text{N}\text{-NO}_3^-$ can be biased due to mixing of distinct NO_3^- sources and kinetic isotopic fractionation (e.g. denitrification) (Kellman and Hillaire-Marcel, 1998). Hence, the $\delta^{15}\text{N}$ signature alone does not allow for conclusive identification of NO_3^- sources (Xue *et al.*, 2009). Therefore, the $\delta^{18}\text{O}$ of nitrate has been combined with $\delta^{15}\text{N}$ values in a dual isotope approach and has been used to provide more conclusive information for tracing sources of NO_3^- in water (Wassenaar, 1995; Amberger and Schmidt, 1987; Aravena *et al.*, 1993; Komor, 1997; Aravena and Robertson, 1998; Widory *et al.*, 2004; Seiler, 2005). This dual-isotope approach has two main potential benefits: (1) some nitrate sources that are usually indistinguishable with $\delta^{15}\text{N}$ alone (e.g., nitrate fertilizer vs. soil nitrate, or atmospheric vs. soil nitrate) may be identified only when the $\delta^{18}\text{O}$ is analyzed; (2) $\delta^{18}\text{O}$ values vary systematically with $\delta^{15}\text{N}$ during denitrification (Kendall *et al.*, 2007).

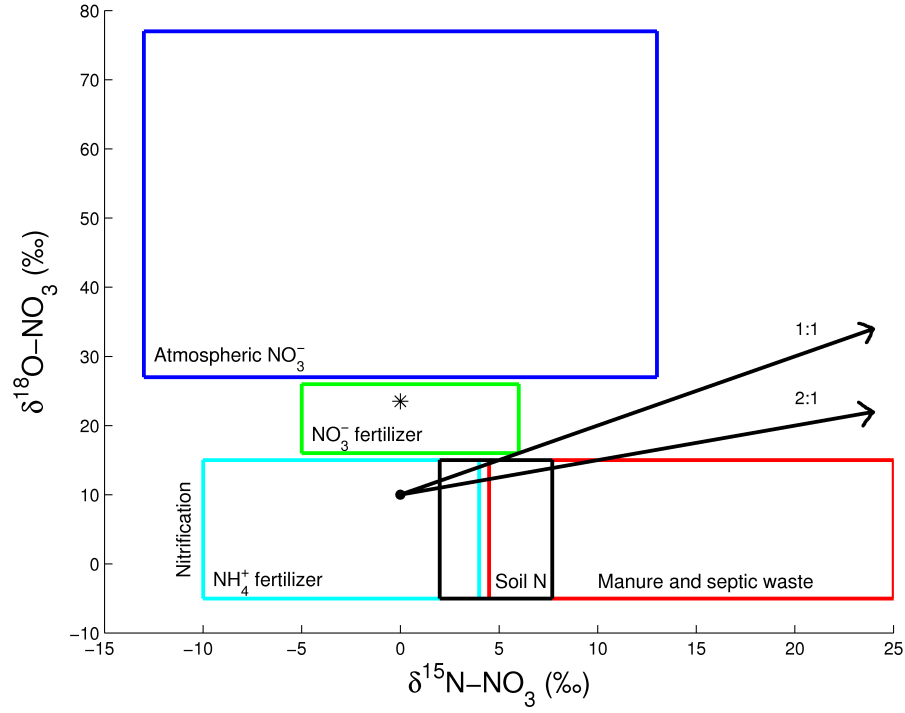


Figure 7.1: Typical values of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of nitrate derived or nitrified from various N sources. The two arrows indicate typical expected slopes (2:1 and 1:1, see text for explanation) for data resulting from denitrification of nitrate with initial $\delta^{15}\text{N}=0\text{‰}$ and $\delta^{18}\text{O}=+10\text{‰}$. The typical ranges of $\delta^{18}\text{O}-\text{NO}_3$ values produced by nitrification of ammonium and organic matter are denoted by “nitrification”. The star correspond to atmospheric N_2 and O_2 . Adapted from Kendall *et al.* (2007) and Xue *et al.* (2009).

7.3 Processes affecting the isotope ratio

Processes affecting the isotope ratio will be discussed in this section. After having introduced the isotopic fractionation (including the Rayleigh equation), we will present the impact of various processes of the N cycle on the isotopic signature of nitrate.

7.3.1 Isotopic fractionation

Isotope fractionation, also called “isotopic effect”, is the phenomenon which causes changes in the relative abundance of isotopes due to their differences in mass (Cole *et al.*, 1990). Because of the slight difference in atomic mass of the two isotopes, certain biological, chemical, and physical processes preferentially use one isotope, causing a relative depletion of that isotope in the product (referred to as depleted or light isotope) and a relative enrichment of the other isotope in the remaining reactants (referred to as enriched or heavy isotope) (Fogg *et al.*, 1998). This isotopic fractionation process causes NO_3^- from various N sources to show different N isotope ratios (Kreitler and Jones, 1975). Most, if not all, biotic processes (such as fixation, assimilation, mineralization, nitrification, and denitrification) show an isotope effect of variable intensity. Isotopic fractionation of ^{15}N also occurs during abiotic processes such as the diffusion of solutes, volatilization of NH_3 , and NH_4^+ exchange and fixation (Hübner, 1986; Bedard-Haughn *et al.*, 2003).

There are two categories of isotope fractionation effects: equilibrium and kinetic. An equilibrium effect will cause one isotope to concentrate in one component of a reversible system that is in equilibrium. In most circumstances the heavy isotope concentrates in the component in which the element is bound more strongly and thus equilibrium isotope effects usually reflect relative differences in the bond strengths of the isotopes in the various components of the system. For e.g., more energy is needed to break or form chemical bonds involving ^{15}N than ^{14}N . A kinetic isotope effect occurs when one isotope reacts more rapidly (e.g. with an enzyme) than the other in an irreversible system or a system in which the products are swept away from the reactants before they have an opportunity to come to equilibrium. Normally, the lighter isotope will react more rapidly than the heavy isotope and thus the product will be lighter than the reactant (Cole *et al.*, 1990). For biologically mediated processes, each step of a complete reaction sequence will have its own intrinsic kinetic isotope effect (Shearer and Kohl, 1986).

During a reaction occurring in a closed system, the $\delta^{15}\text{N}$ of residual substrate (δ_S) changes according to the following Rayleigh equation:

$$\delta_{S(t)} = \delta_{S(0)} + \epsilon \ln(S_t/S_0) \quad (7.4)$$

where ϵ is the enrichment factor, $\delta_{S(0)}$ and $\delta_{S(t)}$ represent the isotope abundances of the substrate at time 0 and t , and S_0 and S_t are the concentrations of the substrate at time 0 and t , respectively. If the supply of an N source is infinite relative to demand, the $\delta^{15}\text{N}$ of substrate N remains unaffected by fractionation. Isotope fractionation will only occur in systems in which there is both an isotope effect and a reaction that does not proceed to completion. Thus, even in the presence of an isotope effect, there will be no isotope fractionation if all the reactant goes to a single product because all the atoms have reacted and thus the ratio of the heavy to light isotope must be the same in the product as it was in the reactant (Cole *et al.*, 1990). In a multi-step reaction, most of the fractionation is caused by the rate-determining or limiting step. This step commonly involves a large pool of substrate where the amount reacting is small compared with the size of the reservoir. In contrast, a step that is not rate-determining generally involves a small pool of a compound that is rapidly converted from reactant to product. When the compound is converted to product as soon as it appears, there is little net fractionation at this step (Kendall *et al.*, 2007).

The *isotopic fractionation factor* α is defined as the ratio of the isotope ratio of a product R_{product} to that of the substrate $R_{\text{substrate}}$ in a given reaction (Eq. 7.5), which is equivalent as the ratio of the rate constants (k_{15}/k_{14}) (for N) or (k_{18}/k_{16}) (for O) of the reaction (Fry 1970). If the ratio is unity, there is no fractionation (Robinson, 2001).

$$\alpha = \frac{R_{\text{product}}}{R_{\text{substrate}}} \quad (7.5)$$

To allow α values to be expressed on the δ scale (Eq. 7.3), the *enrichment factor* ϵ is used (Eq. 7.6).

$$\epsilon (\text{‰}) = 1000(\alpha - 1) \quad (7.6)$$

For example, the median isotope fractionation factor reported for volatilization by Mariotti (1982) and Hermes *et al.* (1985) is $\alpha = 0.976$ (Bedard-Haughn *et al.*, 2003). So volatilization depletes the NH_3 by $\epsilon = 24\text{‰}$ and enriches the unreacted NH_4^+ with ^{15}N .

The overall extent of fractionation is often affected by environmental conditions, including the number and the specific mechanism of intermediate reaction steps, the sizes of reservoirs (pools) of various compounds

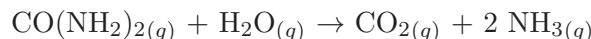
involved in the reactions, soil pH, temperature, species of the organism, water content of soils, etc. (Mariotti *et al.*, 1982; Kellman and Hillaire-Marcel, 1998; Kendall *et al.*, 2007; Shearer and Kohl, 1992).

Most nitrogen isotopic fractionation of nitrate occurs in the upper soil segment, and then nitrate is more conservative throughout the remaining vadose zone (Iqbal *et al.*, 1997).

7.3.2 Volatilization

Volatilization, the loss of ammonia gas (NH_3) to the atmosphere, is a highly fractionating process in which the lighter ^{14}N isotope is preferentially released in the gas. The volatilizing ammonia is enriched in lighter ^{14}N , which causes the residual nitrogen to become heavier with respect to $\delta^{15}\text{N}$ value.

Volatilization in farmlands results when ammonium-based fertilizers such as urea and manure are applied to fields, and occurs within piles of manure (Kendall *et al.*, 2007; Townsend *et al.*, 2003). Waste-N contains urea from urine that can be enzymatically hydrolyzed to ammonia and carbon dioxide and then nitrified to nitrate in soils (Iqbal *et al.*, 1997). The reaction is as follows:



The hydrolysis of urea (the main N form in animal waste) or NH_4^+ fertilizers causes a temporary increase in pH, which favors the NH_3 gas loss by volatilization (Xue *et al.*, 2009).

Volatilization involves equilibrium (reversible) reactions and kinetic (irreversible) reactions that can cause fractionation, including (i) the equilibrium fractionations between ammonium and ammonia in solution, and between aqueous and gaseous ammonia, and (ii) the kinetic fractionation caused by the diffusive loss of ^{15}N -depleted ammonia, which results in NH_4^+ enriched in ^{15}N (Kendall *et al.*, 2007).

Volatilization most frequently occurs when fertilizer or manure is applied to calcareous soils (Townsend *et al.*, 2003), where the soil pH is high ($\text{pH} > 8$). Ammonia volatilization is less pronounced if rain hydrolyzes the NH_3 shortly after preplant application than in times of drought. The overall process causes a fractionation of ca. 24‰ (Mariotti, 1982; Hermes *et al.*, 1985; Hübner, 1986; Kendall *et al.*, 2007). However, the actual fractionation depends on the pH, temperature, humidity and other factors, resulting in variable fractionation factors found in literature. Thus, a wide range in $\delta^{15}\text{N}$ values of NO_3^- could be produced from nitrification of animal waste sources.

For example, the initial isotopic abundance measured by Gormly and Spalding (1979) of recently deposited animal waste has $\delta^{15}\text{N}$ values ranging from $+2.9 \pm 0.9$ to $+4.8 \pm 1.4\text{‰}$. Fractionation occurs soon after deposition and is strongly influenced by ammonia volatilization. Kreitler (1975) observed final isotopic abundances of nitrates resulting from the decomposition of animal waste with $\delta^{15}\text{N}$ values ranging from $+10$ to $+22\text{‰}$.

In areas like the Abbotsford aquifer (British Columbia, Canada) where poultry manure is routinely used, Wassenaar (1995) measured fractionation due to volatilization up to $+8\text{‰}$. The $\delta^{15}\text{N}$ of solid poultry manure samples ranged between $+7.9$ and $+8.6\text{‰}$. Ammonia volatilization caused the $\delta^{15}\text{N}$ of groundwater NO_3^- produced from poultry manure N to range between $+8$ and $+16\text{‰}$. Other studies measured fractionation factors varying from $+8$ to $+16\text{‰}$ (Kreitler, 1979; Kreitler and Jones, 1975; Lindau and Spalding, 1984).

In a survey of fertilized soils in Texas, Kreitler (1975) attributed a $2\text{--}3\text{‰}$ increase in $\delta^{15}\text{N}\text{--NO}_3^-$ in underlying groundwater relative to the applied fertilizer to volatilization.

7.3.3 Nitrification

Introduction

Nitrification is the process of NH_4^+ oxidation to NO_3^- mediated by several different autotrophic bacteria or archaea for the purpose of deriving metabolic energy. Various byproducts or intermediates can also be produced during nitrification and released into the environment including aqueous compounds (e.g., NH_2OH and NO_2^-) as well as gaseous compounds (e.g., NO and N_2O) (Kendall *et al.*, 2007). There are generally three steps in nitrification: firstly, NH_4^+ is oxidized to NH_2OH catalyzed by ammonia monooxygenase, in which O from O_2 is incorporated; secondly, NH_2OH is oxidized to NO_2^- catalyzed by hydroxylamine oxidoreductase, in which O from H_2O is incorporated; and finally, NO_2^- is oxidized to NO_3^- catalyzed by nitrite oxidoreductase with incorporation of O from H_2O , in which O can exchange between H_2O and NO_2^- or NO_3^- as a result of reversibility of this step (Kool *et al.*, 2007; Xue *et al.*, 2009).

In the study area, nitrification rates are highest during the growing season; however, this is also a time of high nitrogen utilization by vegetation and microbes coupled with low groundwater recharge. A lack of water flux through the soil often prevents the leaching of nitrate below the rooting zone during the summer. Nitrification rates are lower

during the dormant season but a larger proportion of this nitrate may enter the groundwater because of lower rates of nitrate assimilation and higher recharge rates (Foster, 1989; Spoelstra *et al.*, 2001). Microbial processes such as immobilization and nitrification should proceed at very low rates during the winter in regions where low temperatures occur. On the basis of experiments with undisturbed soil cores, Esala and Leppanen (1998) concluded that microbial immobilization is likely to occur only at temperatures higher than 5 °C (Mengis *et al.*, 2001).

Mineralisation-nitrification are the main processes converting manure, ammonium-based fertilizers or organic nitrogen in soils, derived from decayed crop stubble and soil humus, to nitrate.

In contrast to the “coupled” nature of isotope effects for nitrate consuming processes such as assimilation and denitrification, nitrification can be considered “decoupled” because the sources of N and O atoms are unrelated. During nitrification, N atoms originate from NH_4^+ and/or NO_2^- molecules, while O atoms originate from O_2 and/or H_2O (Kendall *et al.*, 2007).

Effect of nitrification on $\delta^{15}\text{N}$

During nitrification, the conversion of NH_4^+ to NO_2^- and NO_3^- is accompanied by marked N isotope fractionation effects, resulting in NO_3^- depleted in ^{15}N relative to the initial NH_4^+ , while the residual NH_4^+ is characterized by progressively increasing $\delta^{15}\text{N}$ values (Delwiche and Steyn, 1970; Mariotti *et al.*, 1981; Macko and Ostrom, 1994; Xue *et al.*, 2009). The total fractionation associated with nitrification depends on which step is rate determining. Because the oxidation of NO_2^- to NO_3^- is generally rapid in natural systems, this is generally not the rate-determining step, and most of the N fractionation is caused by the slower oxidation of NH_4^+ to NO_2^- (Kendall *et al.*, 2007). This first step of nitrification has been well studied in cultures of ammonium oxidizing bacteria and has been shown to have a large N isotope effect, with enrichment factor ranging from -38 to -12‰ ($\delta^{15}\text{N}\text{-NO}_3 < \delta^{15}\text{N}\text{-NH}_4$) (Mariotti *et al.*, 1981; Casciotti *et al.*, 2003; Kendall and McDonnell, 1998).

In general, the extent of fractionation during nitrification is dependent on the fraction of the substrate pool (reservoir) that is consumed (see Eq. 7.4, “Rayleigh equation”). In N-limited systems, the fractionations are minimal. Hence, in soils where NH_4^+ is rapidly converted to NO_3^- or when NH_4^+ is not readily available, the $\delta^{15}\text{N}$ of soil NO_3^- is usually within a few permil of the $\delta^{15}\text{N}$ of total organic N in the soil (Kendall and McDonnell, 1998). For example, Ostrom *et al.* (1998) suggested that isotopic fractionation during nitrification was unlikely in his experiments

since the observation of NH_4^+ concentrations in leachate were near or at detection limits. In contrast, if there is a large amount of NH_4^+ available (e.g., artificial fertilizer recently applied), nitrification is stimulated, and the oxidation of fertilizer NH_4^+ becomes the rate-determining step; this would result in a large fractionation (Feigin *et al.*, 1974; Freyer and Aly, 1975; Heaton, 1986).

Effect of nitrification on $\delta^{18}\text{O}$

During nitrification, theoretically, about one third of the oxygen was derived from atmospheric O_2 and two thirds from soil water:

$$\delta^{18}\text{O-NO}_3^- = 2/3(\delta^{18}\text{O-H}_2\text{O}) + 1/3(\delta^{18}\text{O-O}_2)$$

where the $\delta^{18}\text{O-H}_2\text{O}$ is assumed to be that of ambient H_2O , and the $\delta^{18}\text{O-O}_2$ is assumed to be that of ambient O_2 .

The $\delta^{18}\text{O}$ of atmospheric O_2 is about +23.5‰ (Kroopnick and Craig, 1972) whereas the $\delta^{18}\text{O}$ of shallow soil water is commonly negative and expected to vary between -25 and +4‰ as the $\delta^{18}\text{O-H}_2\text{O}$ of precipitation changes during the year and because of spatial variability (Yoshinari and Wahlen, 1985; Spoelstra *et al.*, 2001; Panno *et al.*, 2001; Liu *et al.*, 2006; Anderson and Levine, 1986; Bohlke *et al.*, 1997; Durka *et al.*, 1994; Kendall and McDonnell, 1998; Wassenaar, 1995; Mayer *et al.*, 2001). This implies that during nitrification, the $\delta^{18}\text{O}$ of newly produced NO_3^- does not depend on the isotopic abundance of the N-source being mineralized, but depends on the $\delta^{18}\text{O}$ of H_2O and O_2 incorporation.

Nitrate derived from nitrification should theoretically have $\delta^{18}\text{O}$ values between -10‰ and +10‰. For example, in his study of the identification of the sources of pollution of the Abbotsford aquifer, Wassenaar (1995) measured that $\delta^{18}\text{O-H}_2\text{O}$ of groundwater varied slightly around -11‰. He therefore expected that NO_3^- produced from nitrification of manure or fertilizer NH_4^+ should have a relatively narrow $\delta^{18}\text{O-NO}_3$ range of $2/3 * (-11) + 1/3 * 23.5 = 0.5\text{‰}$ isotope values. However, all the $\delta^{18}\text{O-NO}_3^-$ values were slightly isotopically heavier, and mostly ranged between +2 and +5‰. He concluded that this apparent discrepancy suggested that the water involved in the soil nitrification process was not that which recharged the aquifer.

Many studies have used measurement of $\delta^{18}\text{O-NO}_3^-$ in freshwater systems for assessing sources and cycling. Often it has been found that the $\delta^{18}\text{O}$ of NO_3^- cycled by microbes during nitrification is up to 5‰ higher than expected theoretically if two of the oxygens in nitrate derive from H_2O and one derives from air as explained above. A variety of explanations have been offered for these high $\delta^{18}\text{O-NO}_3^-$ values including:

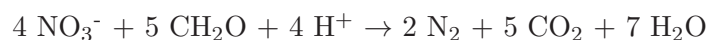
(1) the $\delta^{18}\text{O}$ value of H_2O is isotopically enriched as a result of evaporation (Bohlke *et al.*, 1997) or seasonal changes in rain $\delta^{18}\text{O}$ (Wassenaar, 1995); (2) the ratio of oxygen incorporation from H_2O and O_2 is not 2:1 (Aravena *et al.*, 1993); (3) nitrification using soil O_2 that has a higher $\delta^{18}\text{O}$ than that of atmospheric O_2 due to O isotope fractionation during respiration (Kendall and McDonnell, 1998); (4) a different bacterial process dominates the nitrification reaction and utilizes a greater amount of atmospheric O_2 in low pH environments (Aravena *et al.*, 1993; Wassenaar, 1995; Bohlke *et al.*, 1997; Kendall and McDonnell, 1998; Mayer *et al.*, 2001).

7.3.4 Denitrification

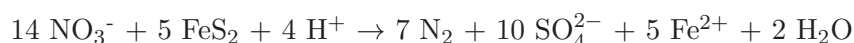
Introduction

Denitrification is a natural attenuation process referring to the microbial reduction of NO_3^- to gaseous products (N_2 , N_2O , or NO). Denitrification is driven by organic matter or by sulfides under anaerobic conditions.

Nitrate reduction by heterotrophic microbes (Kendall *et al.*, 2007) and the simultaneous respiration of CO_2 from the oxidation of organic matter is the generalized pathway of heterotrophic denitrification:



Most denitrifying heterotrophic microorganisms are actually facultatively anaerobic, switching from oxygen to nitrate respiration at O_2 levels of less than about 0.5 mg/L (Hübner, 1986). However, chemolithotrophic denitrification by bacteria such as *Thiobacillus denitrificans*, which oxidizes sulfur (Batchelor and Lawrence, 1978), can also be important in the presence of pyrite, which is probably not the case in our study area. The stoichiometry of the denitrification reaction mediated by *Thiobacillus denitrificans* is:



The observation that denitrification affects both N- and O-isotopes provides the basis to distinguish ^{15}N enrichment due to the presence of animal waste derived NO_3^- from ^{15}N enrichment due to denitrification (Hunkeler, 2004).

The “2:1 line”

It has been recognized that denitrification causes the $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ in the remaining pool of NO_3^- to increase in a relatively predictable pattern. As nitrate is denitrified, the residual nitrate becomes increasingly

enriched in ^{18}O and ^{15}N . It has been observed in several studies that the isotopic abundance of both nitrogen and oxygen increase during denitrification in a linear relation varying between 1:1 and 2:1 for ^{15}N relative to ^{18}O (Fig. 7.1). Thus, the enrichment factor ϵ of N in NO_3 is twice as large as the enrichment factor ϵ of O in NO_3 during denitrification if samples plot on the 2:1 line of Figure 7.1 (e.g., Bottcher *et al.*, 1990; Amberger and Schmidt, 1987; Aravena and Robertson, 1998; Mengis *et al.*, 1999; Fukada *et al.*, 2003; Clark and Fritz, 1997; Cey *et al.*, 1999; Panno *et al.*, 2006).

Bottcher *et al.* (1990) were among the first to measure both N and O isotopes to evaluate denitrification in an unconfined sandy aquifer. They observed a trend of increasing $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values with decreasing NO_3^- concentration and a strong correlation between $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values. Based on the field data they estimated isotopic enrichment factors of -15.9‰ for N and -8.0‰ for O. This isotopic pattern associated with denitrification was confirmed by a number of additional studies. Shifts of N and O isotope ratios have been used to demonstrate denitrification in a number of different environments such as river riparian zones (Mengis *et al.*, 1999; Devito *et al.*, 2000), urban aquifers (Fukada *et al.*, 2004) or river-bank infiltration (Fukada *et al.*, 2003).

Since oxygen and nitrogen isotopes fractionate at a relatively constant ratio to one another during denitrification, it generally has been accepted that using both isotopes in conjunction with each other helps determine the sources of NO_3^- and whether denitrification has occurred in the groundwater system. No clear mechanism was suggested for this phenomenon (Kendall *et al.*, 2007). The effects of denitrification on the dual isotopic ratio of NO_3^- are considered coupled since both the N and O atoms originate in the same molecule.

Typical fractionation due to denitrification

Denitrification is associated with substantial N- and O-isotope fractionation because the initial transformation of NO_3^- involves the splitting of an N-O bond.

Nitrogen isotope enrichment factors (ϵ) associated with denitrification are within -40‰ to -5‰ (Hübner, 1986; Aravena and Robertson, 1998; Smith *et al.*, 1991; Sebilo *et al.*, 2003), and oxygen isotopic enrichment factors are between -18‰ and -8‰ (Bottcher *et al.*, 1990; Mengis *et al.*, 1999; Fukada *et al.*, 2003; Lehmann *et al.*, 2003). So denitrification depletes the N_2O or N_2 with ^{15}N and enriches the residual NO_3^- by 5‰ to 40‰ with ^{15}N .

Using the laboratory incubation data of Delwiche and Steyn (1970) from a number of soils, the influence of denitrification on $\delta^{15}\text{N}$ values was estimated. If 10% of the original NO_3^- was denitrified, the $\delta^{15}\text{N}$ in the remaining NO_3^- would increase by approximately 2.7‰. If 50% of the original NO_3^- was denitrified, the $\delta^{15}\text{N}$ in the remaining NO_3^- would increase by approximately 11‰. These calculations gave results similar to the experimental data of Blackmer and Bremner (1977). Heaton (1984) showed that losses of NO_3^- due to denitrification as low as 20% can result in an increase in $\delta^{15}\text{N}$ by 8‰. Although these numbers are approximate, they indicate that if significant denitrification is occurring, NO_3^- concentrations will decrease along a flowpath, and the remaining NO_3^- will become increasingly enriched in ^{15}N and ^{18}O (Kellman and Hillaire-Marcel, 1998).

7.3.5 Fixation

The term N-fixation refers to processes that convert unreactive atmospheric N_2 into other forms of nitrogen. Bacterial fixation of atmospheric N_2 by the enzyme nitrogenase commonly produces organic materials with $\delta^{15}\text{N}$ values slightly less than 0‰ (Kendall *et al.*, 2007).

7.3.6 Assimilation

Assimilation refers to the transformation of inorganic N-bearing compounds into an organic form during biosynthesis by living organisms. Generally, oxidized forms of N are initially reduced to NH_4^+ and then assimilated into organic matter. Assimilation, like other biological reactions, discriminates between isotopes and generally favors the incorporation of the isotope with the lower mass (Kendall *et al.*, 2007). A large range of N fractionations (-30 to 0‰) has been measured in field studies (Cifuentes *et al.*, 1989; Montoya *et al.*, 1991), and in laboratory experiments (Pennock *et al.*, 1996; Waser *et al.*, 1998; Hoch *et al.*, 1992).

7.3.7 Mineralization

Mineralization is usually defined as the production of ammonium from organic matter ($\text{organic-N} \rightarrow \text{NH}_4^+$) and is also referred to as remineralization or ammonification. Mineralization is generally considered to favor incorporation of the light isotope in NH_4^+ (Nadelhoffer and Fry, 1994), resulting in a small fractionation (≈ 1 ‰) between soil organic matter and soil NH_4^+ (Kendall and McDonnell, 1998; Ostrom *et al.*, 1998).

7.3.8 Mixing

If nitrate in groundwater or surface water derives from the mixing of two different sources that are known to have distinctive δ_1 and δ_2 values, the resulting δ_{mix} is a mass-weighted mean of the δ of each pool:

$$\begin{cases} \delta_{mix} = \frac{\delta_1 f_1 + \delta_2 f_2}{f_1 + f_2} \\ f_1 + f_2 = 1 \end{cases} \quad (7.7)$$

where f is defined as the proportional mass contribution of the respective source. The relative contributions of each source can readily be calculated.

However, Moore and Semmens (2008) mentioned that this mixing model does not take into account the incorporation of several substantial sources of uncertainty. The first source of uncertainty is temporal and spatial variability in $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ in NO_3^- ; the second source of uncertainty is isotopic fractionation during denitrification; and the third is that too many NO_3^- sources contribute to the mixture so that the above equations cannot be solved exactly (Xue *et al.*, 2009).

A process that fractionates N isotopes can be distinguished from one involving the mixing of isotopically distinct pools. A fractionating process produces a linear relation between $\delta^{15}\text{N}$ of the source pool and $\ln(C)$, where C is the concentration of the source pool. A mixing process produces a linear relation between $\delta^{15}\text{N}$ and $1/C$ (Robinson, 2001; Mariotti *et al.*, 1988). Hence, a good test of whether $\delta^{15}\text{N}$ or $\delta^{18}\text{O}$ data can be explained by simple mixing is to plot the δ values vs. $1/\text{NO}_3^-$ (Kendall *et al.*, 2007).

Deutsch *et al.* (2006) successfully used the dual isotope approach and mixing models to determine the contribution of each of the three possible NO_3^- sources (water from artificially drained agricultural soils, groundwater and atmospheric deposition) to a river in Germany based on a mass-balance mixing model (Phillips and Koch, 2002). Results from the mixing model indicated that NO_3^- from the drainage water contributed 86% and the other two NO_3^- sources contributed 11% (groundwater) and 3% (atmospheric deposition) respectively.

Other authors applied mixing models with various degrees of success (e.g. Voss *et al.*, 2006).

7.4 Isotopic signature of N sources

Nitrate is the dominant nitrogen species in groundwater, which may be derived from soil organic nitrogen, synthetic fertilizer, livestock waste,

sewage effluent, and atmosphere precipitation. In many cases, these sources produce nitrate with distinguishable $^{15}\text{N}/^{14}\text{N}$ ratios (Liu *et al.*, 2006).

Nitrogen from fertilizers has $\delta^{15}\text{N}$ values around $0 \pm 4\text{‰}$ (Heaton, 1986; Gromley and Spalding, 1979). Nitrate from animal waste and septic systems generally has $\delta^{15}\text{N}$ values ranging from $+8\text{‰}$ to $+22\text{‰}$ (Heaton, 1986). Nitrate originating from natural organic matter buried in soils has $\delta^{15}\text{N}$ values typically between $+4\text{‰}$ and $+9\text{‰}$ (Heaton, 1986; Mariotti *et al.*, 1988). The $\delta^{18}\text{O}$ of NO_3^- may be quite different depending on whether the source of oxygen is completely atmospheric, such as with ammonium-nitrate fertilizer, or a combination of ground-water oxygen and atmospheric oxygen, which occurs during nitrification of ammonium (Panno *et al.*, 2001). These δ ranges, however, are not rigorously defined (Harrington *et al.*, 1998).

7.4.1 Fertilizers

Fertilizers can be organic (composed of organic matter), or inorganic (made of simple, inorganic chemicals or minerals). They can be naturally occurring compounds such as peat, guano or mineral deposits, or manufactured through natural processes (such as composting) or chemical processes (such as the Haber process), and microbial nitrate derived from ammonium fertilizers.

The $\delta^{15}\text{N}$ of fertilizers are in accordance with the compositions of the primary constituents used by the fertilizer industry. Fertilizer nitrogen compounds (synthetic ammonia, ammonium, nitrate, and urea) are manufactured by different industrial processes using, as nitrogen source, atmospheric nitrogen (0‰) (Mariotti, 1983) and, as nitrate oxygen source, atmospheric oxygen ($+23.5\text{‰}$) (Horibe *et al.*, 1973). Fertilizers inherit these isotopic signatures.

Inorganic fertilizers have $\delta^{15}\text{N}$ values that are uniformly low, as a result of small fractionation during subsequent processing of the fixed N (Flipse and Bonner, 1985), which are generally lower than other natural or anthropogenic nitrogen sources (Vitoria *et al.*, 2004), reflecting an origin from atmospheric N_2 , generally in the range of -4 to $+4\text{‰}$; however, some fertilizer samples have shown a total range of -8 to $+7\text{‰}$ (Hübner, 1986; Macko and Ostrom, 1994; Vitoria *et al.*, 2004; Kendall *et al.*, 2007). Nitrate fertilizers often have slightly higher $\delta^{15}\text{N}$ values than NH_4^+ fertilizers (Kendall *et al.*, 2007). Freyer and Aly (1975) explain the difference between the $\delta^{15}\text{N}\text{-NO}_3^-$ and the $\delta^{15}\text{N}\text{-NH}_4^+$ of about 2.5‰ by an isotopic exchange occurring after the oxidation of ammo-

nia in the nitric acid production involved in the fertilizer manufacture (Vitoria *et al.*, 2004).

The oxygen isotopic abundance of nitrate fertilizers ranges from +17.4 to +48.5‰ with a median value of +22.1‰ (Vitoria *et al.*, 2004). The range of values is apparently the result of fractionations during the manufacturing process (Silva *et al.*, 2002). Nitrate derived from nitrification of ammonium fertilizers has lower $\delta^{18}\text{O}$ values, usually in the range of -5 to +15‰. This range of $\delta^{18}\text{O}$ values reflects the normally observed range of $\delta^{18}\text{O}$ values for microbially produced nitrate in well-oxygenated soils, assuming a nitrification process.

This is the reason why Wassenaar (1995) suggested that $\delta^{18}\text{O}$ may be a good tracer of NO_3^- sources, because it can distinguish synthetic NO_3^- fertilizers from other NO_3^- sources. Inorganic nitrate fertilizers are significantly more positive in $\delta^{18}\text{O}$ (>15‰) as compared to nitrate from most other sources ($\delta^{18}\text{O}$ <10‰), except for atmospheric nitrate (Mengis *et al.*, 2001).

Another current, though less important, nitrate source for fertilizer manufacture are the Chilean nitrate deposits, with a $\delta^{15}\text{N}$ also close to 0‰ (from -5 to +5‰) and a $\delta^{18}\text{O}$ value between +35.6‰ and +50.4‰ (Bohlke *et al.*, 1997; Vitoria *et al.*, 2004).

7.4.2 Animal and human waste

Sewage (including animal waste) can often be distinguished from other nitrate sources on the basis of its relatively high $\delta^{15}\text{N}$ value. The widely accepted $\delta^{15}\text{N}$ ranges for human and animal waste nitrate vary between +8‰ and +20‰ (Iqbal *et al.*, 1997).

Animal waste products may be further enriched in ^{15}N because of volatilization of ^{15}N depleted ammonia, and subsequent oxidation of much of the residual waste material may result in nitrate with a high $\delta^{15}\text{N}$. By this process, when animal waste with a typical $\delta^{15}\text{N}$ value of about +5‰ is converted to nitrate, the $\delta^{15}\text{N}$ values are generally in the range of +8 to +20‰ (Kreitler and Jones, 1975; Kreitler, 1979). Nitrate derived from human and other animal waste becomes isotopically indistinguishable using $\delta^{15}\text{N}$.

As for nitrate originating from nitrification of soil organic nitrogen and ammonium from fertilizer, more depleted $\delta^{18}\text{O}$ values relative to synthetic fertilizer are expected for animal and human waste. Since this isotopic signature is mainly due to nitrification processes, they are discussed in section on nitrification.

7.4.3 Soil nitrate

Soluble dissolved inorganic nitrogen (DIN; mainly NO_3^-) constitutes about 1% of the N in soils, and represents a very small pool which can be much more sensitive to change than the larger organic pool (Kendall and McDonnell, 1998). The soil, considered as a source of nitrate, is often underestimated although many agricultural studies (Kreitler, 1979; Ostrom *et al.*, 1998) have shown its importance, especially in areas where vegetables or corn are grown. In those areas, the soils are regularly plowed, which stimulates the mineralization of soil organic nitrogen (Mengis *et al.*, 2001).

Nitrate produced from the soil source have $\delta^{15}\text{N}$ - NO_3^- values in the range of +3 to +5‰ and $\delta^{18}\text{O}$ values around 0‰ (Kendall and McDonnell, 1998; Mengis *et al.*, 2001). Soil nitrate, formed from the natural oxidation of organic nitrogen has, on average, a $\delta^{15}\text{N}$ value between that of synthetic fertilizer and sewage/animal waste but its range overlaps both (Silva *et al.*, 2002). The $\delta^{18}\text{O}$ value of naturally occurring soil nitrate may be indistinguishable from contaminant nitrate, such as produced by nitrification of ammonium fertilizer, if the contaminant was oxidized in the same environment as the soil nitrate (Silva *et al.*, 2002).

The $\delta^{15}\text{N}$ of the soil dissolved nitrate available for leaching depends on the rates of several soil processes including mineralization, nitrification, and assimilation of inorganic N that control the $\delta^{15}\text{N}$ of both the ammonium available to be nitrified and the resultant nitrate (Spoelstra *et al.*, 2001). Several soil studies have shown that nitrate from inorganic fertilizers can be rapidly immobilized as organic N by microbial incorporation (DeLuca and Keeney, 1995). This newly immobilized N is often referred to as “labile organic N” due to its high remineralization rates. Half-lives of immobilized nitrate depend on a number of factors such as the C/N ratio, soil moisture, or external factors such as soil tillage. Usually they are in the range of weeks to months. The proposed cycling of nitrate via immobilization as organic N, subsequent remineralization to ammonium, and finally nitrification back to nitrate is often referred to as “the mineralization-immobilization turnover” (MIT) concept (Jansson and Persson, 1982; Mengis *et al.*, 2001).

Since the rates of these processes vary spatially and temporally, it is expected that the $\delta^{15}\text{N}$ of nitrate produced by nitrification would also vary (Spoelstra *et al.*, 2001). The $\delta^{15}\text{N}$ of soil nitrate and organic matter is strongly affected by drainage, topographic position, vegetation, plant litter, land use, and rain amount (Amundson *et al.*, 2003). Depending on land use and proximity to possible atmospheric sources of anthropogenic contaminants, the soil nitrate $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ may reflect

“natural conditions” or the effects of various anthropogenic activities. Seasonal changes in soil temperature may also affect the $\delta^{15}\text{N}$ of nitrate, resulting in higher values in the summer in unfertilized fields (Ostrom *et al.*, 1998). In well-oxygenated vadose zones, there may be little or no change in the $\delta^{15}\text{N}$ of nitrate past the root zone, indicating little nitrogen cycling reactions during transport (Gormly and Spalding, 1979; Fogg *et al.*, 1998; Kendall and McDonnell, 1998).

7.4.4 Atmospheric N deposition

There is a huge variety of sources contributing to atmospheric nitrogen which can be distinguished by natural processes or human activities. Natural sources of atmospheric nitrogen include biogenic soil emissions (volatilization of ammonia from soils and animal waste, nitrification and denitrification in soils and surface waters), lightning (which generates NO_x from the thermal oxidation of atmospheric N_2) and biomass burning. Anthropogenic sources include fossil fuel combustion in coal-fired power plants or in vehicles, agricultural emissions, electricity generation, industrial processes.

The major sink for NO_x in the atmosphere is the oxidation to nitric acid (HNO_3), which readily dissociates to nitrate (NO_3^-) where it can be deposited as wet deposition. Dry deposition can contribute significant loads of atmospherically derived N to ecosystems as dry gases (HNO_3 vapor, NH_3 , NO_2 , HONO , NO , peroxyacetyl nitrate), dry aerosols (particulate NO_3^- , particulate NH_4^+), or in fogwater (Kendall *et al.*, 2007).

The mass of N-bearing compounds deposited from the atmosphere varies through space and time but are often only a minor source to water pollution by nitrate. The wet and dry atmospheric deposition measured by Mengis *et al.* (2001) in Zurich, Switzerland, was $<16 \text{ kg of N ha}^{-1}\text{yr}^{-1}$ (Zobrist *et al.*, 1993). In Ontario, Canada, Spoelstra *et al.* (2001) measured N-depositions of about $8.7 \text{ kg of N ha}^{-1}\text{yr}^{-1}$. In Louvain-la-Neuve, Belgium, the N-deposition are about $13.2 \text{ kg of N ha}^{-1}\text{yr}^{-1}$ (personal measurement, February 2009).

The stable isotopic ratios for nitrate in precipitation are controlled by complex atmospheric processes that are not well understood. These ratios show large spatial and temporal variability, even within a single storm event (Heaton, 1986). The typical $\delta^{15}\text{N}$ values for atmospheric N deposition are situated between -15‰ and $+15\text{‰}$ (Moore, 1977; Heaton, 1987; Garten, 1992; Paerl and Fogel, 1994; Ostrom *et al.*, 1998). Complex chemical reactions in the atmosphere result in a large range of $\delta^{15}\text{N}$ values of N-bearing gases and solutes depending on the compound involved, the season, meteorological conditions, ratio of NH_4^+ to NO_3^-

in the precipitation, types of anthropogenic inputs, proximity to pollution sources, distance from ocean, etc. (Hübner, 1986; Kendall and McDonnell, 1998). The $\delta^{18}\text{O}$ of atmospheric nitrate is enriched relative to atmospheric O_2 (+23.5‰), having a range of values that are generally between +25 and +75‰ (Durka *et al.*, 1994; Spoelstra *et al.*, 2001). The first published data on the $\delta^{18}\text{O}$ of nitrate in precipitation were from forests in Bavaria, Germany (Durka *et al.*, 1994), and showed a relatively tight cluster of $\delta^{18}\text{O}$ values in the range of +55 to +75‰. A much larger range of values (+18 to +70‰) was observed for some 110 rain, throughfall, snow, and snowmelt samples from three forested USGS research sites in the USA (Kendall and McDonnell, 1998). Possible explanations for the large range in $\delta^{18}\text{O}$ values include fractionations associated with nitrate formation in thunderstorms, incomplete combustion of fossil fuels in power plants and vehicle exhaust, and photochemical reactions in the atmosphere (Kendall and McDonnell, 1998). Even though atmospheric nitrate displays a wide range of $\delta^{18}\text{O}$ values there is a large isotopic separation between atmospheric and microbial nitrate.

Chapter 8

Identification of the nitrate contamination sources of the Brusselian sands groundwater body (Belgium) using a dual-isotope approach

8.1 Outline

Knowledge of the groundwater pollution source is of primary importance to define appropriate remediation strategies. Yet, the identification of the contamination sources remains a complicated task. A dual isotope approach (combination of ^{15}N and ^{18}O of nitrate) has been used to provide information for tracing sources of nitrate in water. In this study, we used the naturally occurring stable isotopic composition of groundwater nitrate (1) to evaluate the origin of nitrate in the Brussels sands aquifer (Belgium) and (2) to study the temporal dynamics of the isotope signature of groundwater nitrate in this region. Potential N sources sampled in the region, including e.g. ammonium and nitrate mineral fertilizers, sewage and rain, had isotopic signatures that fell within the corresponding typical ranges found in literature. Some of them however deviated from the isotopic ranges corresponding to typical N sources, illustrating the impact of processes affecting the isotopic signature of the nitrate sources. During a pluri-annual sampling campaign, groundwater sam-

ples were collected at 10 times between June 2007 and February of 2009 over 9 monitoring stations located in the western part of the study area. The isotopic data time series suggest that, most of the time, N applied on the soil has been cycled in the soil by micro-organisms before leaching to the groundwater, while the isotopic data and the high nitrate concentrations strongly suggests that nitrate of the groundwater sampled in January 2008 principally originates from mineral fertilizers. The isotopic data measured at some of the 114 monitoring stations across the study area strongly suggests that the sources of nitrate are mineral fertilizers used in agriculture and golf courses, manure leaching from unprotected stockpiles in farms, domestic gardening practices, septic tanks and probably cemeteries. Isotopic data are particularly helpful when associated with other information like historical data about monitoring stations, land use, chemical parameters of water or statistical and deterministic models and must therefore be considered as one of the many elements of pollution sources identification.

8.2 Introduction

Nitrate leaching from agricultural and non-agricultural sources continue to exert a considerable pressure on subsurface groundwater bodies all over the world. In Europe for instance, 35% of the groundwater bodies are expected to be at risk of not reaching the European water framework directive objectives by 2015, one of which is to reduce nitrate concentrations in groundwater under the standard of drinking water of 50 mg NO_3/l , while 45% of the water bodies are insufficiently documented to be properly assessed (European Commission, 2007). In the overwhelming part of waterbodies at risk, nitrate remains one of the critical parameters.

Nitrate pollution can potentially originate from atmospheric dry and wet deposition, sewer leakage, septic tanks, nitrogen-based chemicals, fertilizers, urea used as a road de-icing agent, river or channel infiltration, ammonium as a by-product of many industrial processes, and nitrification of mineralized organic matter (Ford and Tellam, 1994; Wakida and Lerner, 2005). Knowledge of the contaminant release source is of primary importance to define an appropriate remediation strategy. Yet, the identification of the groundwater nitrate pollution sources remains a complicated task since contaminant source identification is inherently ill posed and is sensitive to both data and model uncertainties.

Various methods of pollution source identification have been proposed in the last several decades, including optimization methods, in-

version methods, statistical modelling, GIS based methods and chemical fingerprint.

One of the early methods to backtrack the pollution source location was to run forward simulations and check the solutions with the measured spatial data observed. Due to the non-uniqueness of the solution and the infinite number of plausible combinations, Gorelick *et al.* (1983), Wagner (1992), Mahar and Datta (1997, 2000, 2001) used optimization methods to obtain the best-fitted solution.

Solving the advective dispersion equation backwards in time without relying on optimization approaches was only started in the 1990s (Atmadja and Bagtzoglou, 2001). Wilson and Liu (1994) solved the transport equation backwards in time, providing probability maps of the pollution source location. In the works of Bagtzoglou *et al.* (1992), probabilistic simulation approaches were used to identify solute sources in heterogeneous media. An inverse method based on analytical solutions of contaminant transport problems was presented by Sidauruk *et al.* (1998). This method needs only a set of measured concentrations and no other prior information, however it is applicable only to homogeneous aquifers with simple geometries and flow conditions. Birchwood (1999) used a Fourier-based inverse technique to recover the source location and release history of the groundwater contaminant plume from breakthrough curve data obtained from a single monitoring well, but the results were highly sensitive to the accuracy of the inferred source location.

Most of the above inversion approaches can be applied only if the processes controlling transport, advection, hydrodynamic dispersion, chemical, physical, and biological reactions that affect solute concentrations in the water are exactly known (Atmadja and Bagtzoglou, 2001). Since this is a seldom verified assumption in practice, empirical methods like statistical techniques and chemical fingerprinting have been major elements in environmental investigation to identify the contamination source in groundwater.

Statistical methods have been used by Terrado *et al.* (2006) who applied principal components analysis coupled to geographical information systems to identify contamination sources in the Ebro river basin (Spain). Spruill *et al.* (2002) successfully used classification-tree models to identify the important variables in the source-identification process. Masetti *et al.* (2008) presents an analysis of natural and anthropogenic factors influencing nitrate occurrence in groundwater using the weights of evidence modelling technique as a data exploratory tool which determines the relative impact of various categorical and numerical variables on nitrate occurrence in groundwater. A robust geostatistical ap-

proach to groundwater contaminant source identification was developed by Sun (2007) to account for model uncertainties in the identification process. Leterme *et al.* (2006) used non-parametric one-way analysis of variance to suggest that the vast majority of atrazine in the Brussels sands aquifer (Belgium) was from non-agricultural point sources. Mattern *et al.* (2009) used regression tree and multiple regression models to show that the groundwater nitrate pollution in this area is due to highly complex interactions between explanatory variables.

Stable isotope ratios of N ($^{15}\text{N}/^{14}\text{N}$) in NO_3^- have been frequently used since early 1970's to identify NO_3^- sources in surface- and groundwater (Kreitler and Jones, 1975; Gormly and Spalding, 1979; Kreitler, 1979; Flipse and Bonner, 1985; Kaplan and Magaritz, 1986; Wells and Krothe, 1989; Exner and Spalding, 1994; Fogg *et al.*, 1998; Kendall and McDonnell, 1998; Mayer *et al.*, 2002), because the isotopic abundance of N in NO_3^- is generally different among various NO_3^- sources such as atmospheric N_2 , soil, chemical fertilizers, and manure or sewage. However, the origin of NO_3^- must be linked to the entire N cycle, since values of $\delta^{15}\text{N}\text{-NO}_3^-$ can be biased due to mixing of distinct NO_3^- sources and kinetic isotopic fractionation (e.g. denitrification) (Kellman and Hillaire-Marcel, 1998). Hence, the $\delta^{15}\text{N}$ signature alone does not allow for conclusive identification of NO_3^- sources (Xue *et al.*, 2009). Therefore, a dual isotope approach (combination of ^{15}N and ^{18}O) has been widely used and provides more conclusive information for tracing sources of NO_3^- in water (Komor, 1997; Aravena and Robertson, 1998; Widory *et al.*, 2004; Seiler, 2005).

The high groundwater nitrate concentration levels are of big concern in the Brussels sands aquifer, which is of primary importance for drinking water supply in the region and which is at risk of not reaching the EU objectives of good quality for 2015. Previous work on this study area showed the difficulties to discriminate sources of nitrate pollution (and particularly point pollution) using statistical techniques and suggests the use of stable isotopes data to enhance the source identification.

The purpose of this study was to use the $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ stable isotopic abundance of groundwater nitrate (1) to evaluate the origin of nitrate in the Brussels sands aquifer (Belgium) and (2) to study the temporal dynamics of the isotope signature of groundwater nitrate in this region.

8.3 Material and methods

The aquifer is monitored by the regional administration and the water supply companies to comply with environmental legislation. These monitoring stations are wells, galleries, drains and springs. Three types of groundwater sampling campaigns were conducted (Fig. 8.1). The first campaign aimed to analyze the temporal dynamics of the groundwater quality and is called hereafter the “pluri-annual sampling campaign”. During this sampling campaign, groundwater samples were collected in June, July, August, September, October and November of 2007, in January, May and June of 2008 and in January/February of 2009 over 9 monitoring stations located in the western part of the study area. During the second type of sampling campaign (called hereafter the “spring sampling campaign”), carried out in late spring (May/June) of 2008, groundwater samples were collected over 25 monitoring stations spread over the whole study area. The third sampling campaign (the “winter sampling campaign”) aimed to collect groundwater samples at higher spatial resolution. We therefore sampled 114 monitoring stations during winter (January/February) of 2009.

When collecting groundwater, the sampling installations were purged prior to sampling in order to collect groundwater that is representative of the water bearing formation. The groundwater was sampled using high density polyethylene (HDPE) bottles. The samples were analyzed in the field for temperature, dissolved oxygen and pH. Field measurements for pH were made using an instrument that allow temperature compensation and that was calibrated with appropriate standards. All samples were kept frozen at approximately -4°C until analyses were completed in the laboratory.

All nitrate concentrations analyses of groundwater were conducted at the Laboratory of Applied Physical Chemistry (ISOFYS) of the Ghent University (Belgium), with a precision of 0.17 mg/l, except for samples collected in June, July, August and September of 2007 for which analyses were conducted at the ISO 17025 accredited laboratory of Vivaqua (Brussels, Belgium). To ensure that no differences can be observed between the results of these two laboratories, the 9 groundwater samples collected in October 2007 during the “pluri-annual sampling campaign” were analyzed in both laboratories. A one-way analysis of variance was performed using the “anova1” function implemented in the Statistics ToolboxTM of MatlabTM. This test was unable to detect differences among the nitrate concentrations measured in the two laboratories at a significance level of 0.01.

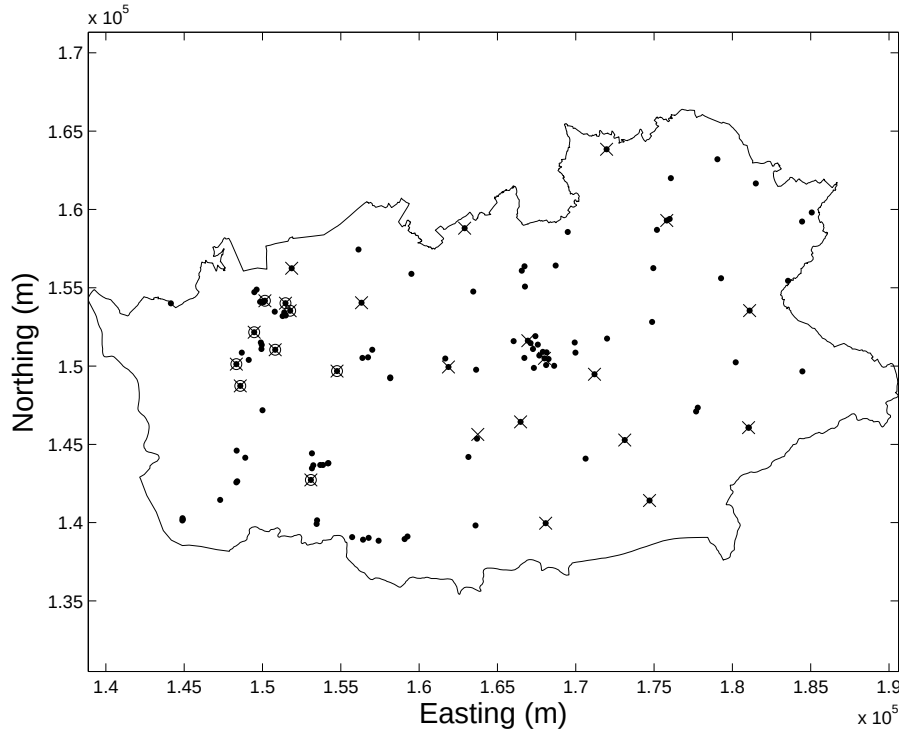


Figure 8.1: Location of the monitoring stations in the study area (Brusselian sands groundwater body, Belgium). Circles, crosses and dots represent monitoring stations sampled in the “pluri-annual sampling campaign”, the “spring sampling campaign” and the “winter sampling campaign”, respectively.

All measurements of isotope ratios of $^{15}\text{N}/^{14}\text{N}$ and $^{18}\text{O}/^{16}\text{O}$ in nitrate of the groundwater samples were conducted at ISOFYS, using the so-called “bacterial denitrification method” with a precision of 0.24‰ and 0.92‰ respectively (Sigman *et al.*, 2001; Casciotti *et al.*, 2002; Rock and Ellert, 2007), except for samples collected in June, July, August and September of 2007 for which analyses were conducted at the Environmental Isotope Laboratory (EIL) of the University of Waterloo (Canada), using the so-called “ AgNO_3 method” developed by Chang *et al.* (1999) and Silva *et al.* (2000). Xue *et al.* (Submitted), showed that the denitrification method used at ISOFYS gives identical isotope analyses of NO_3^- results to the AgNO_3 method. Stable isotope ratios are expressed using the delta per mil (‰) notation relative to an inter-

national reference standard:

$$\delta X (\text{‰}) = 1000 \cdot \frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} \quad (8.1)$$

where X is the isotope of interest (e.g., $\delta^{15}\text{N}$ or $\delta^{18}\text{O}$) and where R_{sample} and R_{standard} are the $^{15}\text{N}/^{14}\text{N}$ or $^{18}\text{O}/^{16}\text{O}$ ratios of the sample and international reference standard, respectively (Fukada *et al.*, 2004). The internationally accepted standard used for the calculation of $\delta^{15}\text{N}$ is atmospheric N_2 gas ($R = 0.0036765$), which has a uniform $\delta^{15}\text{N}$ from continent to continent (Junk and Svec, 1958; Mariotti, 1983). The standard of O is Vienna Standard Mean Ocean Water (VSMOW), which is an isotopic water standard defined in 1968 by the International Atomic Energy Agency, based on works of Craig (1961). The standards have defined $\delta^{15}\text{N}$ or $\delta^{18}\text{O}$ values of 0‰. Ranges for nitrate sources in the crossplots of $\delta^{18}\text{O}$ vs $\delta^{15}\text{N}$ are from Xue *et al.* (2009) and Kendall *et al.* (2007).

The specific conductance and K^+ , Na^+ and Cl^- concentrations of the groundwater samples collected during the winter 2009 campaign were measured at the Hydrochemistry Laboratory (Department of ARGENCo) of the University of Liège (Belgium). K^+ , Na^+ concentrations were determined by atomic absorption in an air-acetylene flame in the presence of an ionization buffer of cesium chloride. Cl^- concentration was determined by direct potentiometric titration of chloride in the sample by silver nitrate with detection of the term by an Ag electrode. The specific conductance (at 25°C) of the groundwater samples collected during the spring 2008 campaign were analyzed in the field using an instrument that allows temperature compensation and that was calibrated with appropriate standards.

In addition to groundwater analysis, we also sampled some potential sources of N pollution. The $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of eight synthetic fertilizers representative from the study area were analyzed. One sample of surface water running-off from a grassland field, and two rain samples were collected in February 2009 in the center of the study area. Sewage samples were collected at four locations in the sewerage system of Louvain-la-Neuve, a university campus located in the center of the study area. The sewage samples were taken downstream neutralization reservoirs where the sewage waters are buffered. All these samples, except for synthetic fertilizers which were in grains form, were collected in HDPE bottles and frozen at approximately -4°C until analyses were completed at ISOFYS.

All calculations were performed in MatlabTM R2008b. Data preparation was carried out in ArcGISTM 9.3.

8.4 Results

8.4.1 Potential N-sources

Potential N-sources were sampled in the study area in February 2009. Results are shown in Table 8.1 and in Figure 8.2. Mineral fertilizers show a $\delta^{15}\text{N}-\text{NO}_3^-$ between -1.04‰ and 4.68‰ with mean value of 1.32‰ and a $\delta^{18}\text{O}-\text{NO}_3^-$ between 17.20‰ and 27.48‰ with mean value of 22.41‰ , which is very close to the fertilizer isotopic published data compiled in a review by Vitoria *et al.* (2004). The urea-based mineral fertilizer sample ($\delta^{15}\text{N}=13.88\text{‰}$ and $\delta^{18}\text{O}=11.70\text{‰}$) falls in the $\delta^{15}\text{N}$ - $\delta^{18}\text{O}$ range corresponding to manure or septic N-source. The surface water sample collected at the bottom of a grassland slope had nitrate concentration of 9.0 mg/l and an isotopic signature corresponding to soil organic nitrogen source. The nitrate concentration in the rain samples was very low (mean=1.5 mg/l). The $\delta^{15}\text{N}$ (mean= 3.07‰) and $\delta^{18}\text{O}$ (mean= 75.67‰) of the rain samples fall in the range of values generally found in literature (Durka *et al.*, 1994). The samples collected in the sewerage network have similar $\delta^{18}\text{O}$ values (mean= 1.24‰), while samples “Sewage 1” and “Sewage 2” have higher $\delta^{15}\text{N}$ values (mean= 7.40‰) than samples “Sewage 3” and “Sewage 4” (mean= 1.38‰).

Table 8.1: Isotopic composition of 15 potential N-sources in the study area.

N source	$\delta^{15}\text{N}-\text{NO}_3^-$ (‰)	$\delta^{18}\text{O}-\text{NO}_3^-$ (‰)	NO_3^- (mg/l)
Fertilizer 1 (13.5% NO_3^- -N - 13.5% NH_4 -N - 4% MgO)	-0.06	27.48	-
Fertilizer 2 (5.4% NO_3^- -N - 9.6% NH_4 -N - 15% P_2O_5 - 15% K_2O)	2.79	22.08	-
Fertilizer 3 (7.5% NO_3^- -N - 18.5% NH_4 -N - 32.5% SO_3)	4.68	23.31	-
Fertilizer 4 (unknown composition)	0.08	23.14	-
Fertilizer 5 (unknown composition)	-0.79	21.59	-
Fertilizer 6 (unknown composition)	3.59	17.20	-
Fertilizer 7 (unknown composition)	-1.04	22.10	-
Urea-based fertilizer (3% urea-N 40g/l - 15% P_2O_5 - 4.7% Zn)	13.88	11.70	-
Surface water (grassland run-off on 18-02-2009)	7.52	4.79	9.0
Rain 1 (collected on 10-02-2009 at Louvain-la-Neuve)	1.55	77.53	1.7
Rain 2 (collected on 17-02-2009 at Louvain-la-Neuve)	4.58	73.80	1.3
Sewage 1 (collected on 19-02-2009 at Louvain-la-Neuve)	6.61	0.48	19.5
Sewage 2 (collected on 19-02-2009 at Louvain-la-Neuve)	8.19	0.69	9.2
Sewage 3 (collected on 19-02-2009 at Louvain-la-Neuve)	0.44	-0.42	7.6
Sewage 4 (collected on 19-02-2009 at Louvain-la-Neuve)	2.32	4.20	24.1

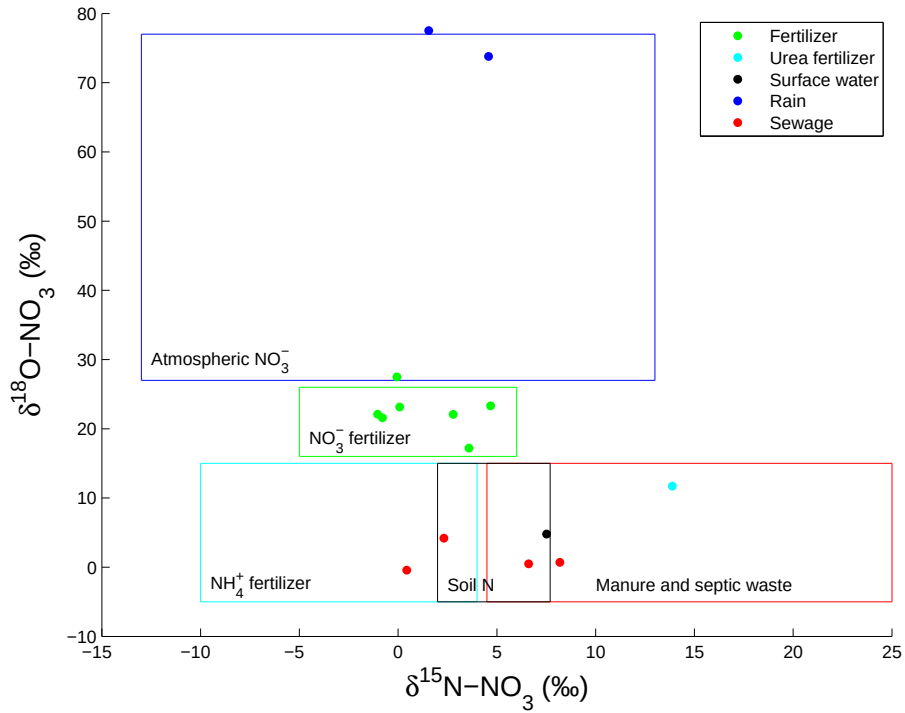


Figure 8.2: Cross-plot of the $\delta^{18}\text{O}-\text{NO}_3^-$ versus $\delta^{15}\text{N}-\text{NO}_3^-$ of 15 potential N-sources in the study area.

8.4.2 Pluri-annual sampling campaign

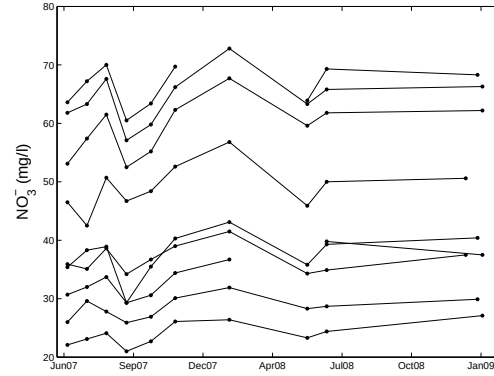
During the pluri-annual sampling campaign, 9 monitoring stations located in the western part of the study area were visited 10 times between June 2007 and January 2009, resulting in time series of groundwater nitrate concentration, $\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{18}\text{O}-\text{NO}_3^-$ (Fig. 8.3).

One-third of the monitoring stations had mean nitrate concentrations above the standard of 50 mg/l. The temporal dynamics of the nitrate concentrations was similar from one monitoring station to another (Fig. 8.3a), but time series differed mainly in average (ranging from 24.0 mg/l to 66.2 mg/l) and standard deviation (varying from 1.9 to 4.8 mg/l). Figure 8.4a suggests that the mean nitrate concentration decreases with the depth of the monitoring station. The outlier on this figure corresponds to a gallery of 6 km long, for which the depth at the sampling location is not representative of the depth along the gallery. The nitrate concentration at the lowest contaminated monitoring station (mean of 24.0 mg/l) was nearly stable during the studied period while variations of 15 mg/l were observed at the most polluted monitor-

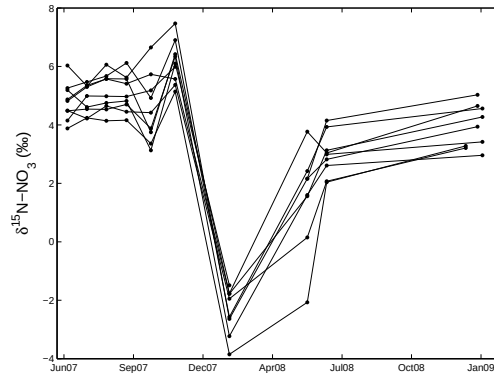
ing station during the same period (Fig. 8.3a). Figure 8.4b shows that the standard deviation of the nitrate concentration time series increases with the mean nitrate concentration. One monitoring station was removed from Figure 8.4b since its time series lacked one measure (the well was dry in January 2008), affecting the calculation of a standard deviation comparable to the other monitoring stations.

Figure 8.3b shows that the 9 monitoring stations present a similar $\delta^{15}\text{N-NO}_3^-$ pattern. The $\delta^{15}\text{N-NO}_3^-$ is quite stable from June to November 2007, varying around 5‰ which correspond to a soil nitrification source (Fig. 8.5). The $\delta^{15}\text{N-NO}_3^-$ decreases in January 2008 to values around -3‰ corresponding to nitrification of ammonium fertilizer source (Fig. 8.5). Higher variability was observed in May 2008, with $\delta^{15}\text{N-NO}_3^-$ values varying from -2.1‰ to 3.8‰.

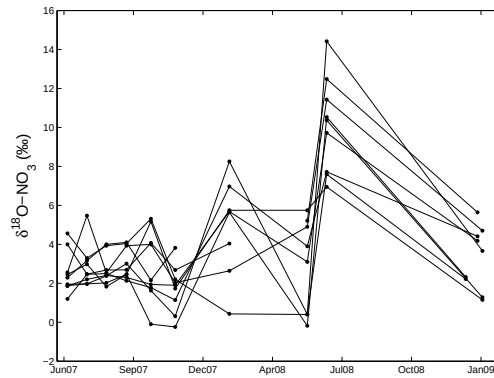
Excepted for January and June 2008, the $\delta^{18}\text{O-NO}_3^-$ measured in the 9 monitoring stations all vary between 0 and 6‰ (Fig. 8.3c and Fig. 8.5).



(a)



(b)



(c)

Figure 8.3: Time series of nitrate concentration (a), $\delta^{15}\text{N}$ (b) and $\delta^{18}\text{O}$ (c) at 9 monitoring stations sampled from June 2007 to January 2009.

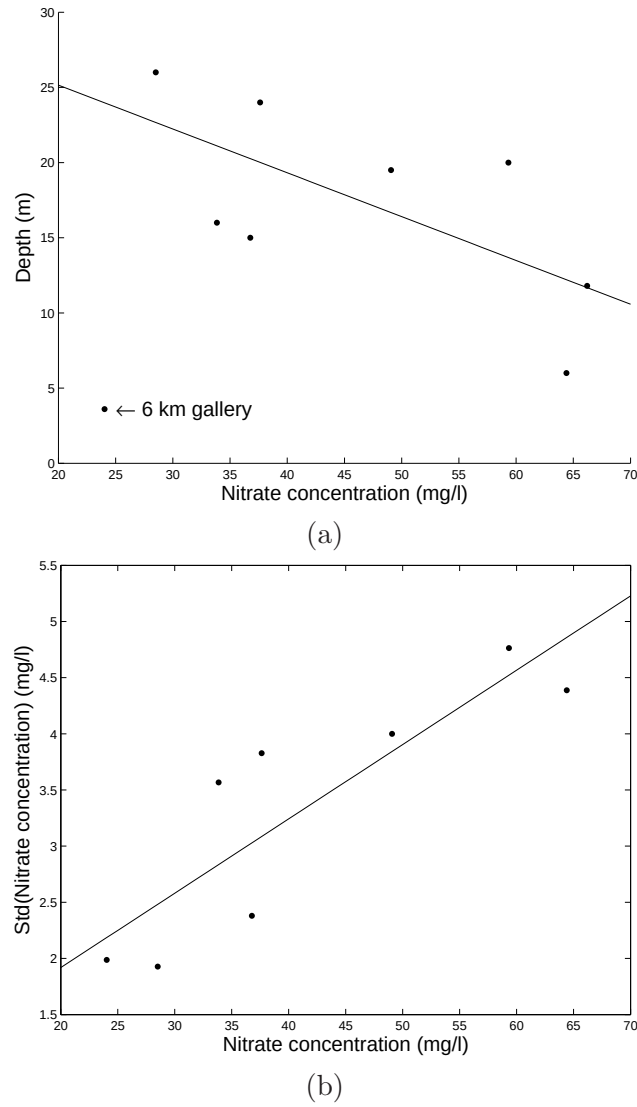


Figure 8.4: Depth of the monitoring station (a) and standard deviation of the nitrate concentration time series (b) versus the mean nitrate concentration at each monitoring station measured during the “pluri-annual sampling campaign”.

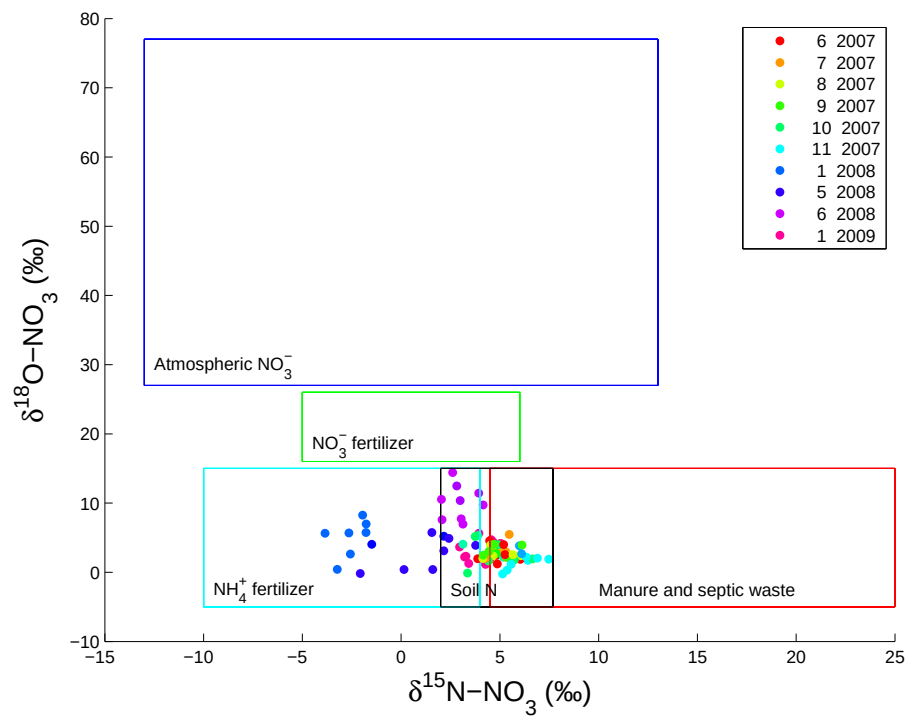


Figure 8.5: Crossplot of $\delta^{18}\text{O}$ versus $\delta^{15}\text{N}$ of the groundwater samples collected during the “pluri-annual sampling campaign”.

8.4.3 Campaigns of Spring 2008 and Winter 2009

The results of the spring 2008 and winter 2009 sampling campaigns are shown in Tables A.1 and A.2.

Nitrate concentrations show a wide spatial variability in the study area with nitrate concentrations that can vary considerably at very short distances (few tens of meters) (Fig. 8.6a). However, a general trend can be observed, with higher nitrate concentrations in the western part of the study area and lower in the center. During the Spring campaign, nitrate concentrations ranged from 24.4 to 97.3 mg NO_3^-/l ($n=25$, mean=47.2 mg/l), with 36% of the sampled monitoring stations having nitrate concentrations above the standard of 50 mg/l (Fig. 8.7a). During the winter campaign, nitrate concentrations ranged from 0.1 to 93.4 mg NO_3^-/l ($n=114$, mean=41.3 mg/l), with 33% of the monitoring stations having nitrate concentrations above 50 mg/l (Fig. 8.7b). Figure 8.8a shows that during the Spring 2008 campaign, the depth of the well versus nitrate concentration plots on a left-triangle. This relation can also be observed in Figure 8.8b, corresponding to the Winter campaign, with the exception of three particular points (samples Winter50, Winter53 and Winter55) having high nitrate concentrations (82.9, 84.5 and 71.1 mg/l, respectively) while being measured in deep wells (76, 60.5 and 62.7 m, respectively) and which will be raised in the “Discussion” section. Furthermore, a Kruskal-Wallis test was performed to compare the nitrate concentrations measured in the Brussels sands aquifer with the nitrate concentrations measured in underlying aquifers, resulting in significantly lower contamination levels in the deeper aquifers (at significance level of 0.01).

The $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ ranged respectively between 0.27 and 9.08‰ and -0.04 and 14.43‰ in the Spring campaign (Fig. 8.7a) and between -0.03 and 10.79‰ and -3.4 and 23.34‰ in the Winter campaign (Fig. 8.7b). Figure 8.6b shows that, in the center of the region, where the density of monitoring stations is high, we can observe a local south-east to north-west gradient of $\delta^{15}\text{N}$ values varying from less than 0‰ (corresponding to mineral fertilizer source) to more than 4‰ (corresponding to mineral fertilizer source or soil N source). Figure 8.9a shows that, for the Spring sampling campaign, 3 samples (Spring1, Spring20 and Spring23) fall in the “manure and sewage” range, 5 samples (Spring2, Spring3, Spring12, Spring17 and Spring18) fall in the “ammonium fertilizer” range and 13 fall in the range where it is impossible to distinguish between “ammonium fertilizer” and “soil N” sources. Figure 8.9b shows that, for the Winter campaign, 4 samples (Winter14, Winter93, Winter108 and Winter109) fall in the “manure and sewage” range, 2 samples (Winter78

and Winter104) fall in the “nitrate fertilizer” range, 5 samples (Winter1, Winter2, Winter3, Winter4 and Winter59) fall in the “ammonium fertilizer” range, 37 samples fall in the range where it is impossible to distinguish between “ammonium fertilizer” and “soil N” sources and 43 samples fall in the range where it is impossible to distinguish between “manure and sewage” and “soil N” sources.

From the 25 monitoring stations sampled during the Spring campaign, 24 were sampled again during the Winter campaign and the measured nitrate concentrations, $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values are compared on Figure 8.10. A Kruskal-Wallis test shows that, at significance level of 0.01, no significant differences can be observed between the nitrate concentrations of the two sampling campaigns, that the $\delta^{15}\text{N}$ values are significantly higher in winter 2009 than in spring 2008, and that the $\delta^{18}\text{O}$ values are significantly lower in winter 2009 than in spring 2008.

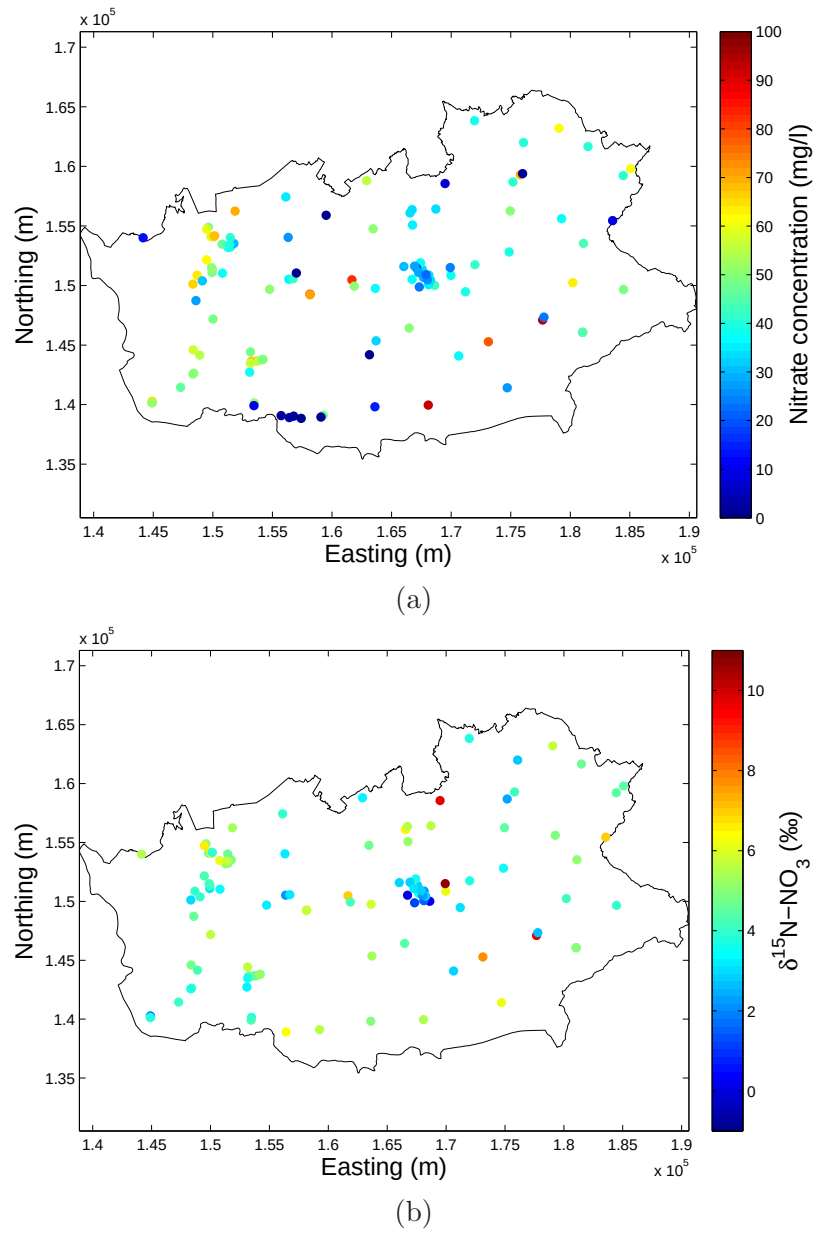


Figure 8.6: Nitrate concentrations (a) and $\delta^{15}\text{N-NO}_3^-$ (b) measured during the Winter 2009 sampling campaign in the study area.

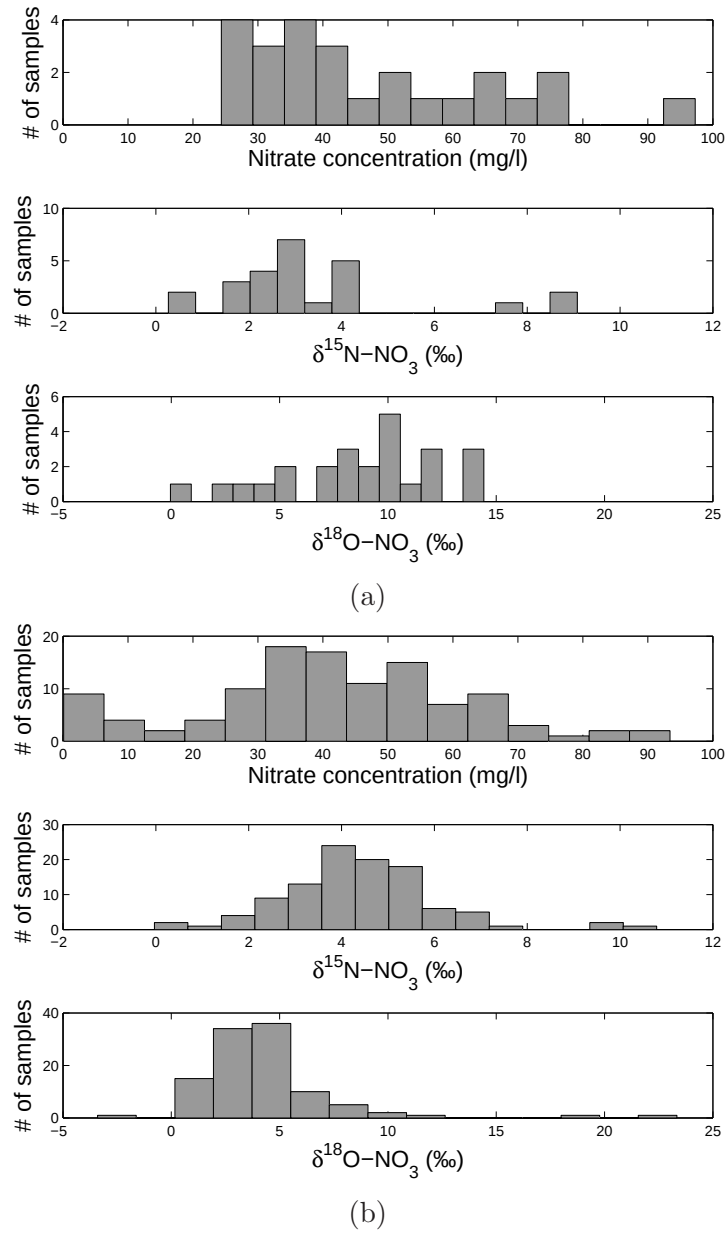


Figure 8.7: Histograms of nitrate concentration, $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of groundwater sampled during the Spring (a) and Winter (b) sampling campaigns.

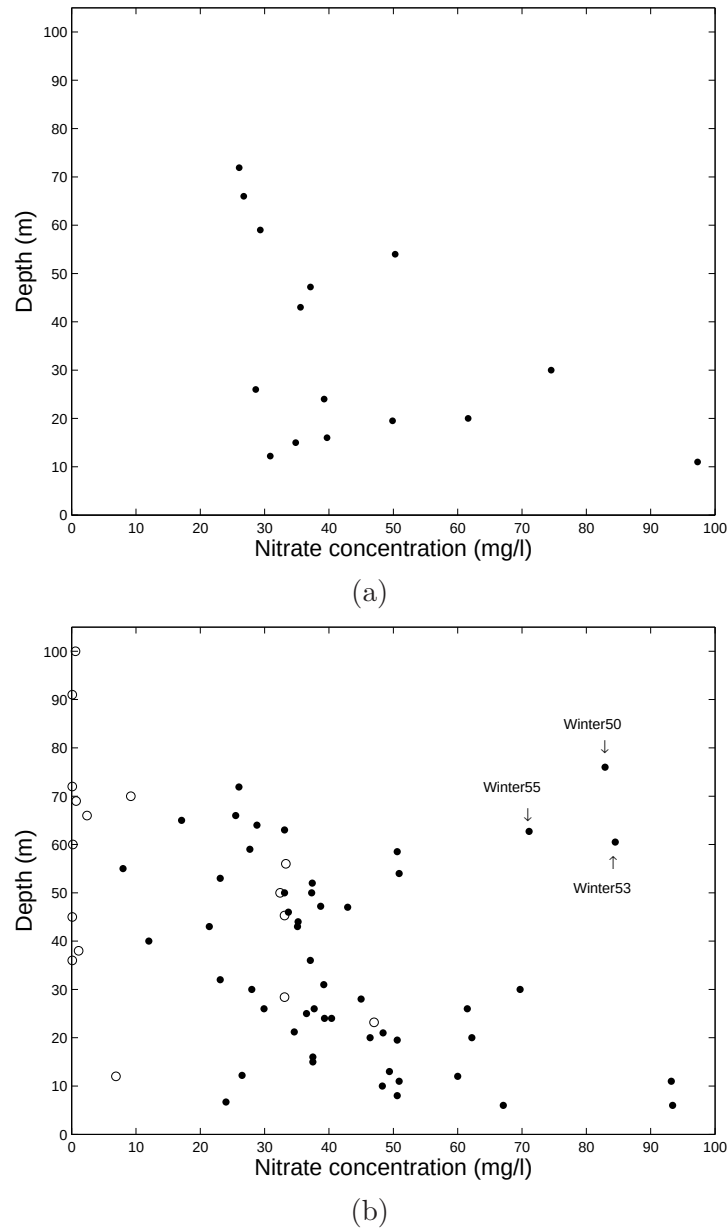
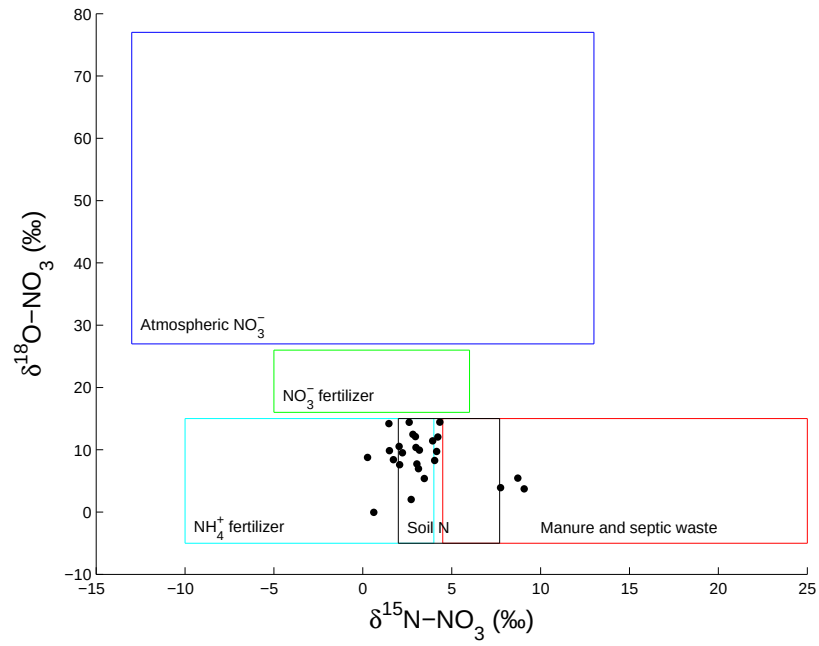
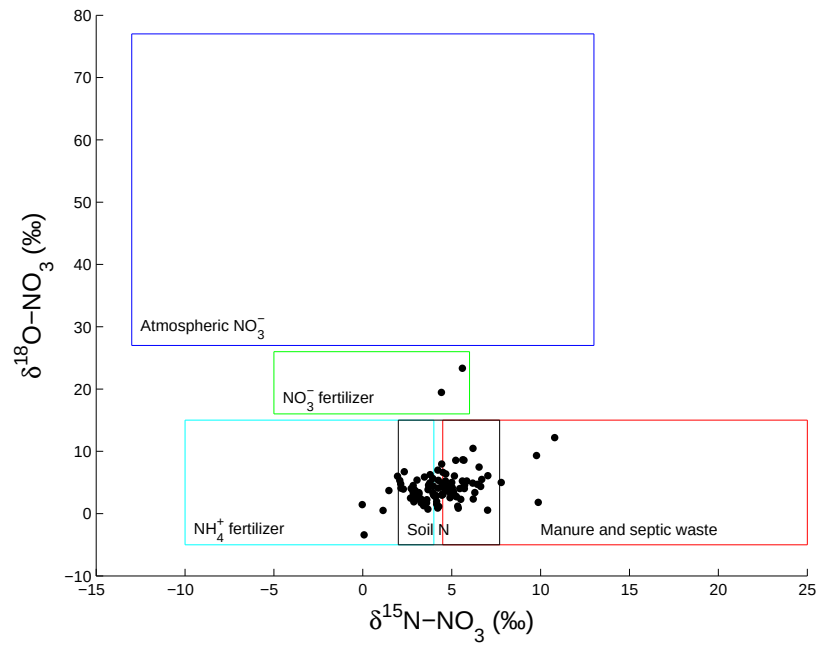


Figure 8.8: Depth of the wells versus the mean nitrate concentration measured during the Spring (a) and Winter (b) sampling campaigns. Black dots correspond to samples collected in the Brusselian sands aquifer, white rounds correspond to samples collected in underlying aquifers.



(a)



(b)

Figure 8.9: Crossplot of $\delta^{18}\text{O}$ versus $\delta^{15}\text{N}$ of the groundwater samples collected during the Spring (a) and Winter (b) sampling campaigns.

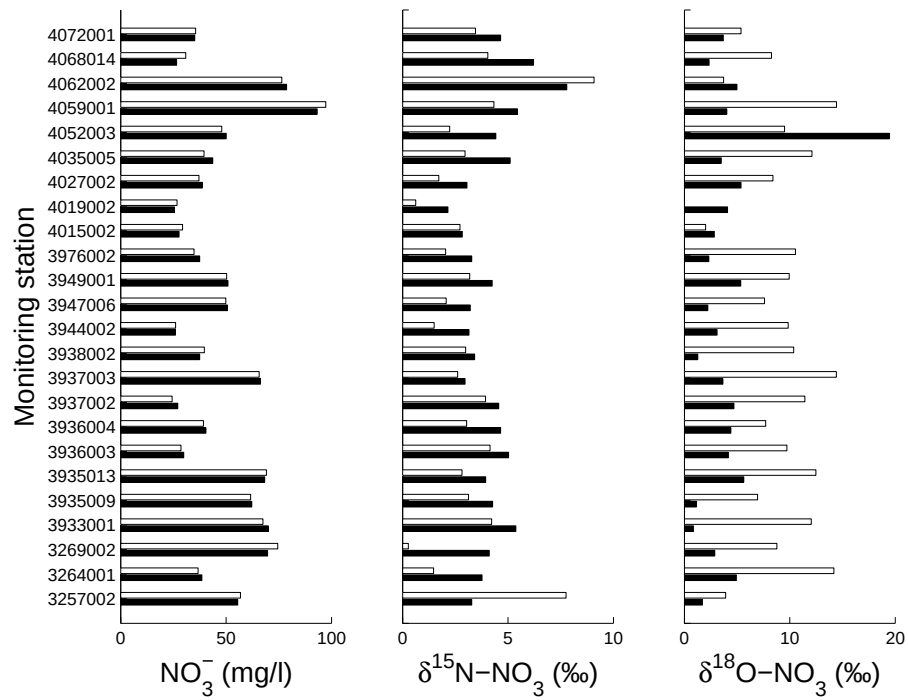


Figure 8.10: Comparison between nitrate concentrations, $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of the groundwater samples collected at the same monitoring stations during the Spring (white bars) and Winter (black bars) campaigns.

8.5 Discussion

8.5.1 Potential N-sources

The results of the isotopic analysis of the potential N-sources in the study area show that rain, surface water, synthetic fertilizers and two of the four sewage samples collected in the study area fall within the corresponding typical $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ ranges found in literature (Vitoria *et al.*, 2004; Durka *et al.*, 1994; Xue *et al.*, 2009; Kendall *et al.*, 2007).

Two of the four sewage samples (“Sewage 3” and “Sewage 4”) had lower $\delta^{15}\text{N}$ values than expected. This could easily be explained by the fact that these two samples were collected in the sewer network draining the waste water of two laboratories that extensively discharge huge amounts of water that is directly pumped in the underlying aquifer for operating heat exchange. This is confirmed by the fact that the isotopic signature of these two samples fall in the range of the isotopic signature of the groundwater of the underlying aquifer sampled in Louvain-la-Neuve (Fig. 8.11). The two other sewage samples (“Sewage 1” and “Sewage 2”), collected in other sewers, have higher $\delta^{15}\text{N}$ values (Fig. 8.11), suggesting an N source coming from e.g. toilet facilities. The presence of neutralization reservoirs avoids the dependence of the isotope signature with the sampling time.

Future studies on potential nitrogen sources in the study area could include septic tanks and manure. While the majority of the potential N-sources discussed in this study fall into the generally accepted ranges of water pollution sources, it also illustrates the impact of various processes affecting the isotopic signature and, hence, the difficulty for unequivocally discriminating groundwater pollution sources.

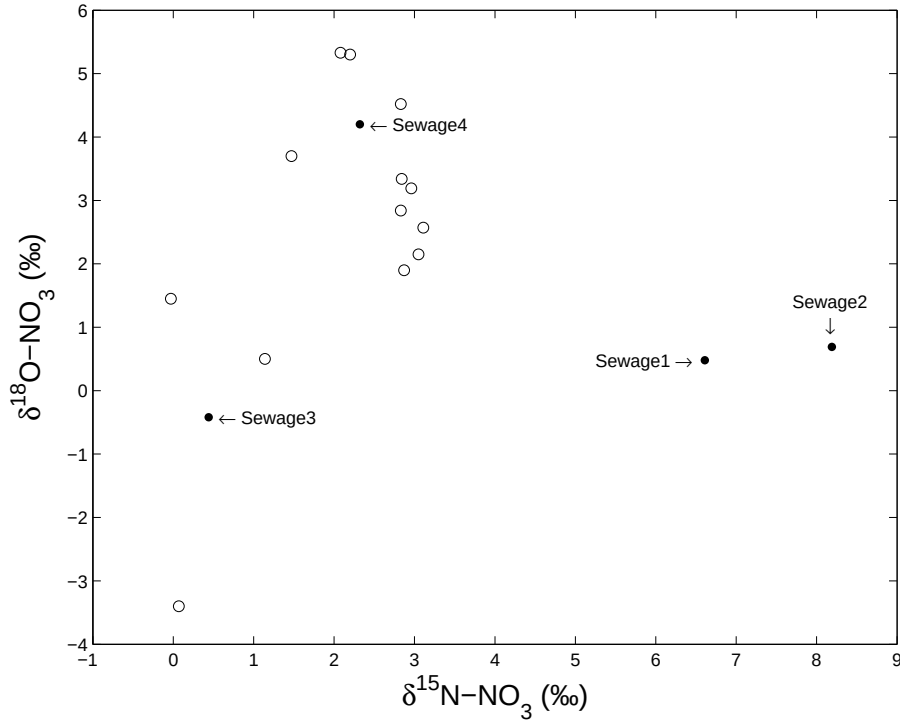


Figure 8.11: Cross-plot of the $\delta^{18}\text{O-NO}_3^-$ versus $\delta^{15}\text{N-NO}_3^-$ of sewage samples (black rounds) and groundwater samples (white rounds) collected in Louvain-la-Neuve.

8.5.2 Pluri-annual sampling campaign

During the “pluri-annual sampling campaign”, one-third of the monitoring stations had mean nitrate concentrations above the standard of 50 mg/l, suggesting anthropogenic pollution sources. This is further suggested by the isotopic signature and by the fact that the standard deviation of the nitrate concentration time series increases with the mean nitrate concentration, which is inversely correlated to depth of the well (Fig. 8.4). Nitrate concentration time series show a same time pattern, suggesting that a same process is responsible for the dynamics of the contamination in the 9 monitoring stations. Because of the large distances between the 9 monitoring stations and the fragmented land use, the temporal dynamics of nitrate concentrations could partially be explained by the dynamics of the net groundwater recharge (linked to rainfall and evapotranspiration) which is responsible for the transport of nitrate through the unsaturated zone. This is corroborated by the

relatively homogeneous temporal dynamic of the water table across the study area Mattern and Vanclooster (accepted article).

The $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ measured during the “pluri-annual sampling campaign” from June 2007 to November 2007 (Fig. 8.3) suggests that N applied on the soil has been cycled in the soil by micro-organisms before leaching to the groundwater. In January 2008 we observe a shift in the isotopic signature to values corresponding to nitrified mineral ammonium based fertilizers and a peak in the nitrate concentrations strongly suggesting that nitrate of the groundwater sampled in January 2008 principally originates from agricultural activity followed by rapid leaching of nitrate through the vadose zone without being cycled in the soil layer. We cannot estimate the application date of the fertilizers from the dataset. However, the shift observed in January 2008 suggests short travel times of nitrate between surface and the sampling location in the aquifer. Similarly, Iqbal *et al.* (1997) observed a shift in groundwater’s $\delta^{15}\text{N}$ values 9 months after application of N-fertilizers on the soil surface, indicating its delayed release into the system after substantial rainfall. The decrease in nitrate concentrations and the increasing $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values observed in May and June 2008 suggests denitrification processes. We can also notice that the isotopic signature time series has not an annual period, since the $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values observed in January 2008 and January 2009 are different. Again, this supports the fact that the dynamics of the nitrate contamination process is principally driven by recharge, more than by the N-inputs which, in case of fertilizer sources, are supposed to be cyclic.

The time series measured in the 9 monitoring stations samples during the “pluri-annual sampling campaign” show that, while the mean nitrate concentrations differ considerably from one monitoring station to another, the isotopic signatures are very similar among them (excepted for May 2008). As a consequence, the isotopes of only 1 of the 9 monitoring stations could be measured to catch the dynamics of the system in future monitoring campaigns.

8.5.3 Spring and winter sampling campaigns

Nitrate concentrations measured during the Winter 2009 campaign over 114 monitoring stations show a high variability through the study area, even at very short distances (few tens of meters). Part of this variability is due to the presence in the dataset of deep wells pumping water in aquifers underlying the Brussels sands aquifer and which have significantly lower nitrate concentrations. A consequence of the presence of these wells is that there are more low nitrate concentrations (<10 mg/l)

during the winter campaign than during the spring campaign during which we monitored only the Brussels sands aquifer. As a consequence, any interpolation attempt must focus on one given aquifer, which has been done in the same study area by Mattern *et al.* (2008). The high spatial variability of the nitrate concentrations across the study area is also a consequence of the different depths at which the samples were taken (even in a same aquifer), since no multi-level monitoring stations were available. Furthermore, high variability is introduced by the presence of local pollution sources, which is emphasized by the isotopic analyses as discussed below.

During the spring and winter campaigns, we observed an inverse relation between nitrate concentration and the depth of the wells (Fig. 8.8). This relation is clearly not unambiguous since low nitrate concentrations have been observed in shallow wells where low nitrate inputs occur as well as in deep wells where the nitrate concentrations were low because of nitrate reduction processes (mixing, dispersion, dilution, denitrification,...) through the unsaturated and saturated zones. In contrast, high nitrate concentrations have been measured only in shallow wells, excepted for three particular wells sampled during the winter 2009 campaign (samples “Winter50”, “Winter53” and “Winter55”) (Fig 8.8b). These deep wells are subject to point pollution highlighted by the isotopic analyses. Sample “Winter50” was collected in a 76 m deep well and had abnormally high nitrate concentration (82.9 mg/l). A first hypothesis of nitrate occurring from a nearby plant nursery using mineral fertilizers was rejected since the isotopic signature revealed a “manure/sewage” origin. Investigations suggested that the nitrate measured in that well originate from a septic tank located 30 m from it and that drains waste water and horses manure. Samples “Winter53” and “Winter55” were collected in two 60 m deep wells separated by a distance of 50 m and located in a residential area. Their high nitrate concentrations (>70 mg/l) and their isotopic signatures suggests the influence of a “manure/sewage” point source, which is compatible with the absence of a sewerage system until recently and the existence of septic tanks in the area.

It appears clearly (Fig. 8.9) that the groundwater nitrate isotopic signature of the majority of the monitoring stations falls in the range of “Soil N”, meaning that N-material applied on the soil is cycled by microorganisms before leaching to the groundwater. This is compatible with long travel time (from a few month to 15 years) for nitrate to reach the water table calculated in the study area by Mattern and Vanclooster (accepted article). This isotopic signature could however also be caused by mixing between mineral fertilizer sources and “manure/sewage” sources.

As a consequence, the source of nitrate in groundwater of these samples can not be revealed univocally by the isotopic results alone. Other groundwater samples had typical $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values helping in the identification of the nitrate origin.

One of the typical nitrate origins in the study area was “manure/sewage”. Three groundwater samples collected during the spring campaign (“Spring1”, “Spring20” and “Spring23”) had a “manure/sewage” signature. The impact of the land use is significant for these three monitoring stations since these sampling points are located near the soil surface (depth < 6 m). These three points have in common that they are close to a farm (<120 m) where manure is stored and leaches to the groundwater and close to cemeteries (<500 m) which are also known to contribute to nitrate groundwater pollution (EPA, 1993; Nas and Berk-tay, 2006; Laftouhi *et al.*, 2003). Sample “Winter108” was collected in the same monitoring station as “Spring23”. Its nitrate concentration, $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values did not vary significantly between spring 2008 and winter 2009. Four groundwater samples collected during the winter campaign had a “manure/sewage” signature. Sample “Winter93” was taken into a farm’s shallow well located 10 m from a manure pile and had elevated potassium concentrations (20 times more than average of winter 2009 samples). Sample “Winter109” had high nitrate concentration (93.4 mg/l) and was collected in a shallow well. This is an illustration of point pollution since nitrate concentrations measured in a well located 250 m further were only 23.1 mg/l. The local contamination origin of this well is supported by its $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values suggesting “manure/sewage” source and which is compatible with the fact that significant quantities of manure were applied in the vegetable garden located around the well for more than 30 years.

A second class of identified sources correspond to mineral fertilizers. Five samples (“Spring 2, 3, 12, 17 and 18”) collected during the spring 2008 campaign had typical ammonium fertilizer isotopic signatures. They all are located beneath agricultural areas and are surrounded by large fields, except for sample “Spring12” which is located beneath a golf course of about 100 hectares, both land uses are known sources of groundwater nitrate and are compatible with the mineral fertilizer origin of groundwater nitrate. Two samples collected during the winter 2009 campaign had typical nitrate fertilizer isotopic signature: “Winter104” was collected in intensive agricultural area while sample “Winter78” was sampled downstream of two golf courses surrounded by fields. From the five samples collected during the winter 2009 campaign having typical ammonium fertilizer isotopic signature, one (“Winter59”) was sampled in an intensive agricultural area while the four others were

sampled in the southern boundary of Louvain-la-Neuve, downstream of an intensive agricultural area. The impact of land use on nitrate isotopic signature is illustrated by the isotopic data measured in the dense monitoring network of Louvain-la-Neuve, in the center of the study area. As shown on Figure 8.6, the $\delta^{15}\text{N}$ signature varies from a “Mineral fertilizer” signal in the southern boundary of the city, located downstream of intensive arable land, to higher $\delta^{15}\text{N}$ values when crossing the city, following the south-north gradient of the groundwater flux.

The particular samples discussed above having specific isotopic signatures (synthetic fertilizers or manure/sewage) are all located in areas where land use can easily be linked to the isotopic data, while the samples having $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values falling in the “soil N” source range are collected from wells located in areas where the land use is mixed. This is supported by the inverse relation that can be observed in Figure 8.12a between $\delta^{15}\text{N}$ and percentage of agricultural land in the capture zone of the monitoring stations (the $\delta^{15}\text{N}$ fall generally in the “mineral fertilizer” range in intensive agricultural areas and have higher $\delta^{15}\text{N}$ values where there is no agriculture) and the positive relation that can be observed in Figure 8.12b between $\delta^{15}\text{N}$ and percentage of residential land in the capture zone of the monitoring stations. The tree outliers in this figure correspond to samples “Winter93”, “Winter108” and “Winter109” and are due to point contamination as discussed earlier. A first order polynomial was fitted to the data of Figure 8.12 showing significant relations between $\delta^{15}\text{N}$ and agriculture (slope of the polynomial = -0.01; p-val = 0.0402) and between $\delta^{15}\text{N}$ and residential land (slope of the polynomial = 0.04; p-val = 0.00064).

Isotopic analysis shows that the rain is not a significant source of groundwater nitrate in the study area (Fig. 8.9), which is compatible with the low nitrate concentrations measured in the rain samples (samples “Rain1” and “Rain2”).

Isotopic data helped to identify denitrification processes. Sample “Winter14” had low nitrate concentration, high $\delta^{15}\text{N}$, a low $\text{NO}_3^-/\text{Cl}^-$ ratio (0.2), low dissolved oxygen and was collected in a swampy area, strongly suggesting denitrification process in this part of the study area.

By comparing the results of the spring 2008 and winter 2009 campaigns, we observe a general shift from “mineral fertilizers” signature to a “soil N” signature, while no significant differences can be observed in the nitrate concentrations (Fig. 8.10). This shift is probably due to variation in N-inputs and rainfall in time.

The fact that groundwater nitrate coming from manure/sewage source is found only in shallow wells while fertilizers are also found in deep wells

suggests that nitrate derived from fertilizer are more conservative during transport in the vadose and saturated zones.

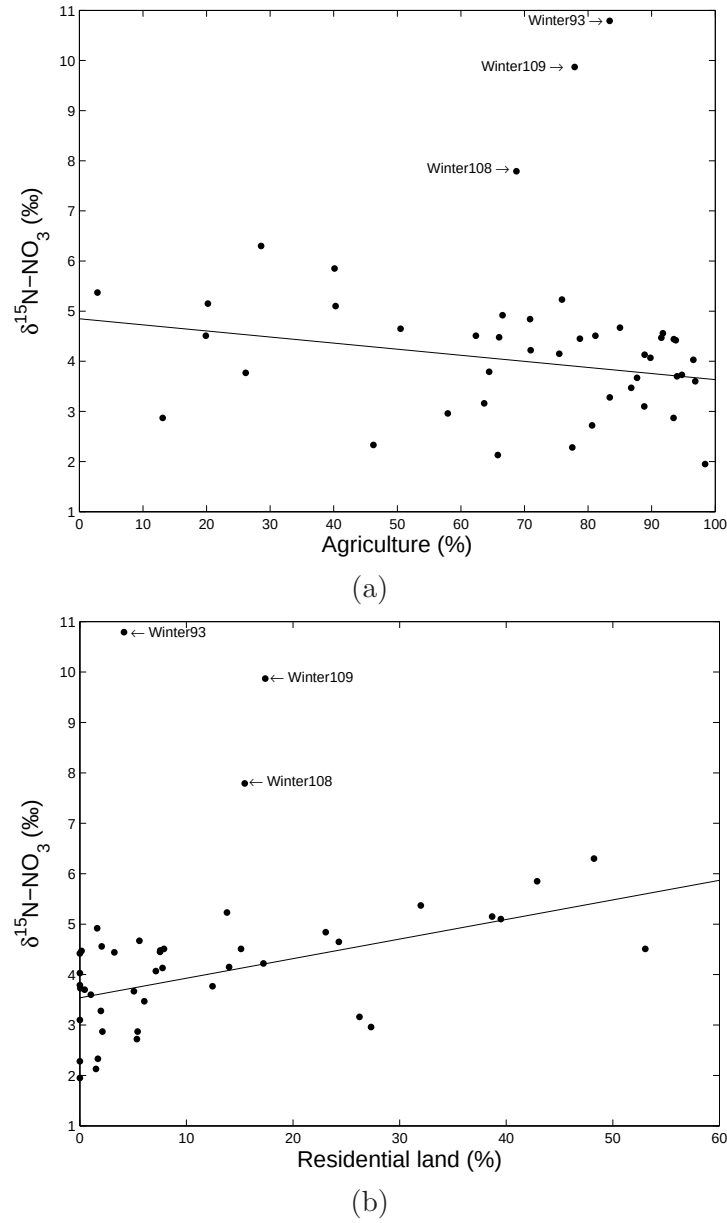


Figure 8.12: Cross-plots of $\delta^{15}\text{N}$ versus percentage of agricultural (a) and residential (b) land in the capture zone of the monitoring stations for samples collected in shallow monitoring stations (depth < 10 m) during the winter 2009 sampling campaign.

8.6 Conclusion

Large scale groundwater monitoring campaigns in the Brussels sands aquifer and underlying formations (Belgium) indicate that nitrate concentrations are well above the standard of 50 mg/l in 33% of the sampled monitoring stations. In general, higher nitrate levels were observed in the western part of the study area even if high spatial variability of concentrations was observed.

The $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ isotopic data successfully suggests that the sources of nitrate measured in some monitoring stations are mineral fertilizers occurring from intensive agriculture or from the presence of golf courses. Isotopic data associated with analysis of the land use revealed the source of the pollution due to manure leaching from unprotected stockpiles in farms. The data also suggested that nitrate occurs probably from cemeteries and domestic gardening practices. The $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$, associated with low nitrate concentrations helped in identifying denitrification processes in one part of the study area. Finally, the isotopic data clearly eliminated atmospheric deposition as a groundwater nitrate source in the study area. Relations between agriculture or residential land in the capture zones of the monitoring stations and the $\delta^{15}\text{N}$ was suggested, confirming anthropogenic impact on the groundwater nitrate pollution.

If the isotopic data successfully contributed to the pollution source identification of some particular monitoring stations, most of the $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values gave no clear indication on the nitrate source since nitrate has been cycled in the soil before leaching to the groundwater or since different nitrate sources mixed into the aquifer, which is compatible with the high fragmentation of the land use.

Monitoring the evolution of groundwater nitrate concentration and $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ data over time can highlight the dynamics of the nitrate sources. During a few months, we observed the passage of a nitrate plume that occurred from nitrification of ammonium based fertilizer applied on the soil surface.

Potential N-sources of the study area were analyzed. Most of them fall in the typical source ranges found in literature. The results highlight also the difficulties of unequivocally determine the nitrate sources from isotopic data due to the modifications of the isotopic signature during the N cycle.

Isotopic data are particularly helpful when associated with other information like historical data about monitoring stations, land use, chemical parameters of water or statistical and deterministic models and must

therefore be considered as one of the many elements of pollution sources identification.

The use of groundwater isotopic data can be valuable to delineate the capture zone of monitoring stations. Isotopes can also be used to define a patrimonial monitoring network by selecting only wells which are not affected by point pollution, which is, by definition, not representative of the general qualitative status of the groundwater body.

Isotopic data are potentially useful to identify groundwater pollution and, when available at high space and time resolution, they can be used to better understand the dynamic processes affecting the system.

Chapter 9

Conclusion and Perspectives

9.1 Summary

This thesis aimed to improve our understanding of groundwater pollution by nitrate at the regional scale of the Brusselian sand groundwater body (Belgium). Despite all the nitrate reduction actions that were undertaken to meet EU directives, this study area still presents one of the highest groundwater nitrate concentrations of the Walloon Region, with nitrate concentrations exceeding the standard of 50 mg/l in 33% of the monitoring stations sampled in January 2009. Further assessing the pollution levels of groundwater and identifying the contamination sources are therefore needed for designing sustainable water management strategies.

Our first main objective was to assess groundwater contamination at the regional scale by mapping the nitrate concentrations. The analysis was based on data collected since 1995 by the regional administration and by water supply companies and also on data collected in the context of this thesis.

In chapter 5, we showed that the mean nitrate concentration in the study area is relatively stable from 1995 to 2005 and oscillates around 44 mg/l. The calculated spatial variability of the nitrate concentrations in the study area was nearly 14 times higher than the temporal variability, allowing the average pollution for the whole of the period of study (1995-2005) to be mapped by using e.g. kriging interpolation. However, at the monitoring station scale, the nitrate concentration can sometimes vary considerably over time. In order to avoid this information about the temporal variability at the local scale to be lost in the mapping process,

we applied a Bayesian Maximum Entropy (BME) interpolation method and showed that great differences (up to 42.44%) in predicted nitrate concentrations appear locally at those monitoring stations where the temporal variability is high, when compared to kriging interpolation of averaged nitrate concentrations. Furthermore, some monitoring stations have long and abundant nitrate concentrations time series while nitrate concentrations have been measured only once at other monitoring stations. We used BME to introduce the sampling rate (i.e. the number of samples composing the time series) in the mapping process and showed that relevant differences (up to 66.19%) appear when compared to kriged nitrate concentration maps.

Unfortunately, the locations where groundwater quality properties were measured are scarce and sparsely distributed over space. As a result, large uncertainties about the groundwater nitrate concentrations arise in the mapping process, especially at prediction points located far away from monitoring stations. Given that the quality of the interpolation decreases rapidly with the distance to the monitoring station, the mapping of the variable of interest has limited practical utility. In chapter 6, we used a data fusion method in order to improve the mapping quality of groundwater nitrate concentrations in areas located far away from monitoring stations. We combined various sources of information that are in some way related to nitrate groundwater pollution in the mapping process. The first source of information was nitrate concentration predicted through kriging the nitrate concentrations measured during our sampling campaign of January/February 2009. The second source of information was nitrate concentration predicted all over the study area by a statistical regression tree model, which accounts for land and land use variables that have an impact on the groundwater pollution by nitrate. Bayesian Data Fusion (BDF) allows combining the nitrate concentrations estimated by the interpolation method with those estimated by the statistical model into a single final map by weighting these estimates in terms of the associated uncertainty, thereby allocating a high weight to estimates which are very certain and a low weight to those that are very uncertain. It has been shown that the associated prediction uncertainty in the final map is smaller than that for the kriged map, particularly in regions where the monitoring network is scarce.

Our second main objective was to identify sources of groundwater nitrate pollution in the study area. The transfer time of nitrate to the aquifer is one of the reasons that could explain the lack of improvement in water quality despite the implementation of directives related to anthropogenic release of nitrate. In order to have an idea about the time needed by anthropogenic activities to have an impact on groundwater

quality, we estimated the travel time of percolating water through the vadose zone in chapter 3. We observed a high variability of estimated travel time varying from a few months to more than 15 years. These percolating times correspond to vertical water effective velocities varying between 1.7 and 28 m/year and depend on the hydrogeological setting but also on the procedure for estimating the travel time. Water travel times through the vadose zone were considered as a proxy of the nitrate travel times since nitrate is very mobile in groundwater and tends not to adsorb or precipitate on aquifer solids (Hem, 1985).

In chapters 4 and 6, the nitrate concentration was correlated with land and land use attributes into the capture zone of each monitoring station. A correct definition of the capture zone was therefore needed. Unfortunately, detailed hydrogeological modelling was not possible for all sampling wells. We therefore adopted a simplified approach to delineate areas that probably have an impact on the groundwater quality measured in the monitoring stations. Two statistical methods (a multiple regression method and a regression tree method) were used to link the measured nitrate concentrations with the slope, the altitude and the depth to the water table at the monitoring station and with the land use in the capture zone of the monitoring station. We concluded that, in the region, one explicative variable taken alone could not be considered responsible for the groundwater pollution by nitrate because of the highly complex interaction pattern between explanatory variables. However, this study suggested that high nitrate concentrations are associated with residential and arable land use, while lower nitrate concentrations are associated with forest land use. These results must be viewed with caution because of the limited size of the dataset, the uncertainty on the data and the fact that statistical modelling highlights global trends at the regional scale but says very little about local contamination events (point pollution).

We have shown in chapter 8 that the isotopic signature of groundwater nitrate allowed to identify the source of point pollution observed in some monitoring stations, including manure leaching from unprotected stockpiles in farms, domestic gardening practices, septic tanks and probably cemeteries. Furthermore, nitrate isotopic data allowed to identify diffuse contamination sources like mineral fertilizers used in agriculture and golf courses. It is worth noting that the $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values helped in identifying denitrification processes in one part of the study area. If the isotopic data successfully contributed to the pollution source identification of some particular monitoring stations, most of the $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values gave no clear indication on the nitrate source since different nitrate sources mixed into the aquifer or since nitrate's isotopic signature

has been modified while cycling in the soil before leaching to the groundwater. Isotopic data are particularly helpful when associated with other information like statistical models, historical data about monitoring stations (e.g. time series of contaminant concentrations,...), land use or chemical parameters of water and must therefore be considered as one of the many elements of pollution sources identification.

9.2 Implications for science and policy

The current management of water resources in the European Union is influenced increasingly by the guidelines of the Water Framework Directive (2000/60/EC, 2000). The Member States have been translating the WFD regulatory aspects into their own legislations, and common environmental objectives (water quality, quantity...) are defined. For instance, one of the most cited quote of the WFD states that (ground)water resources have to reach a “good chemical status” by 2015. To achieve good groundwater chemical status, concentrations of pollutants should not exceed any of the quality standards (e.g. 50 mg/l for nitrate). However, this thesis has shown that the time lags necessary for the dilution of pollutants in groundwater may hamper the achievement of good chemical status within the period defined by the WFD. This should be taken into consideration when evaluating the efficiency of policies to reduce groundwater contamination. Huge uncertainty subsists about the correct estimation of travel time of nitrate through the unsaturated and saturated zones. While a deterministic mass-transfer model used in this thesis resulted in mean travel times through the vadose zone of more than one decade, the isotopic signature of nitrate dynamics suggested a faster response of the system. Further studies on this subject are needed.

The maps of nitrate concentrations represent a tool which could be used by the regional administration and the water production companies to implement specific and local management and protection strategies, or to have a better insight of the qualitative state of this natural resource. Such maps rely on the quality and density of the monitoring network. The spatial resolution of the monitoring network in the study area is clearly limiting for correctly assessing the large scale contamination levels. Efforts must be made in the coming years to increase the size of the monitoring network in order to refine the assessment of groundwater quality in the region. The maps of the associated prediction uncertainty could be used to identify areas where further investigation should be carried out. Furthermore, we showed that the use of information indi-

rectly related to the nitrate concentration can improve the quality of interpolation in a data fusion framework.

The statistical models developed in this thesis have shown that the unambiguous link between agricultural activity and pollution of groundwater by nitrates is not so obvious that one could imagine *a priori*. The results also highlight the negative impact of residential land on groundwater quality. However, these results do not take into account the processes that affect nitrate concentrations. The study on the natural abundance of isotopes of nitrate can provide valuable information about such processes. We therefore recommend to carry out routine measurements of nitrate's isotopic abundance with a high temporal frequency (of the order of six measurements per year). As shown in this thesis, these measurements will be useful for the identification of the origin of the pollution and the processes nitrate have undergone. Indirectly, these measurements may also be used, e.g., for delimiting capture zones of wells.

The main measures being taken by the regional administration (the Walloon region) to reduce organic pollution and nutrient enrichment of water are (i) wastewater treatment, (ii) implementation of a nitrogen sustainable management program (PGDA) and (iii) application of agri-environmental measures (MAE). These measures are too recent to have produced significant results. Indeed, the PGDA (of which some actions aimed at reducing the infiltration of nitrate in the aquifer) only started in 2002 and the agri-environmental measures are available to farmers in Wallonia only since 1995. In the study area, treatment of urban waste water was really significantly developed from 2000 (with the establishment of the Public Company of Water Management, Société Publique de la Gestion de l'Eau - SPGE). The coming years will be crucial for the study of the aquifer's contamination by nitrate. This thesis has shown the benefits of addressing this problem using various different tools. In the future, this multi-disciplinary approach should be further developed and tools further integrated.

9.3 Limitations and perspectives

In spite of the achievements described previously, this study has several limitations.

The monitoring network was not designed initially for environmental monitoring since it is composed mainly from wells used by water production companies. The network has further be complemented by "patrimonial" monitoring stations which are supposed to ensure the

representativeness of the measures in the groundwater body. However, the (geo)statistical analyses are restricted by the limited size (and density) of the monitoring network in the study area. Increasing frequency and density of routine sampling may provide important information for identifying contamination sources and processes affecting nitrate in the various compartments of soil and sub-soil.

Since no multi-level monitoring stations were available for this study, more data are also needed about the vertical distribution of nitrate concentrations in the saturated and unsaturated zones. The use of multi-level monitoring stations will bring valuable information by gaining insight on the three-dimensional distribution of the contamination.

The dynamics of the aquifer has been very little integrated into the study. The coupling of models describing the fluxes in the vadose zone with models describing the fluxes within the aquifer will open new avenues in understanding the dynamics of groundwater quality.

The definition of the monitoring station capture zones was approximated in this study by a simplified methodology. The delineation of capture zones based on detailed and specific modelling and tracer experiments will improve the quality of pollution source identification in the corresponding monitoring stations. We showed indeed in chapter 4 that the use of approximated capture zones already increases the statistical analysis when compared to simple circular capture zones around the monitoring stations.

While some monitoring stations have been monitored scarcely, nitrate concentrations have been measured on a weekly base since nearly fifteen years at some other monitoring stations, resulting in well furnished time series. In future works, this kind of information could be used in association with e.g. rainfall or piezometric time series to improve our knowledge about mechanisms that control nitrate fluxes. In fact, the major mechanism for mobilizing N from field soils is through the leaching during precipitation events (Tisdale *et al.*, 1993; Ostrom *et al.*, 1998).

Nitrate isotopic signature has proven its usefulness in identifying groundwater nitrate sources. However, long and dense time series of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ measured at high spatial resolution will give more information about processes and sources affecting nitrate concentrations.

The study of the isotopic signature of nitrate in the soil profile would increase our knowledge about the fate of nitrates in the environment.

This study could further be incorporated into a broader context to gain insight about processes affecting nitrate transport from its source to its release in the draining rivers, including a coupled detailed three-dimensional spatially distributed model of the vadose and saturated zones,

tracer experiments to validate travel times and pathways through the different soil and sub-soil compartments, particle tracking, or the use of various chemical groundwater quality indicators.

The next few years will be crucial to evaluate the impact of the nitrate reduction plans implemented since a decade in the study area to reduce domestic, agricultural and industrial nitrate loss to groundwater. The objectives defined by the EU Water Framework Directive should be perceived as stimulating challenges to improve groundwater quality. Development of an efficient groundwater monitoring network, associated with research on the subject will be an indispensable prerequisite to a really efficient and sustainable preservation strategy.

Appendices

Appendix A

Results of the Spring 2008 and Winter 2009 sampling campaigns

Table A.1: Data about the groundwater monitoring stations sampled during the Spring 2008 and Winter 2009 sampling campaigns.

Sample ID	Monitoring station	X ^a (m)	Y ^a (m)	Z (m)	Depth (m)	Type	Aquifer ^b
Winter1	58	168620	150011	148.0	47	Well	2
Winter2	59	168107	150065	140.0	44	Well	2
Winter3	60	167327	149879	141.0	53	Well	2
Winter4	62	166722	150520	107.6	25	Well	2
Winter5	63	168134	150874	140.0	46	Well	2
Winter6	64	167575	151364	124.0	50	Well	2
Winter7	65	167421	151905	130.0	52	Well	2
Winter8	67	168262	150450	144.0	63	Well	2
Winter9	68	167677	150675	140.0	64	Well	2
Winter10	70	167113	151461	125.0	65	Well	2
Winter11	555	147294	141450	123.0	1	Drain	2
Winter12	222222	166033	151590	77.7	0.1	Spring	2
Winter13	3257002	162907	158801	54.3	1	Spring	2
Winter14	3259002	169490	158558	39.2	12	Well	3
Winter15	3264001	171967	163835	41.7	1	Spring	1
Winter16	3266012	176073	161997	78.0	n.d.	Well	2
Winter17	3268029	175190	158690	59.0	n.d.	Spring	2
Winter18	3269002	175814	159293	106.5	30	Well	2
Winter19	3269003	175996	159388	106.4	100	Well	n.d.
Winter20	3274001	179050	163200	85.0	26	Well	2
Winter21	3275001	181495	161656	85.9	1	Spring	2
Winter22	3279001	185070	159800	61.0	n.d.	Gallery	2
Winter23	3279002	184450	159220	80.0	n.d.	Gallery	2
Winter24	3926002	144147	154000	114.0	40	Well	2
Winter25	3932002	149621	154884	90.0	13	Well	2
Winter26	3933001	151860	156240	124.0	n.d.	Well	2
Winter27	3935002	150071	154082	88.0	20.6	Gallery	2
Winter28	3935003	149844	154100	84.0	2.7	Gallery	2
Winter29	3935004	149474	154717	89.0	12	Well	2
Winter30	3935005	151280	153190	95.0	26	Well	2
Winter31	3935007	150015	154129	83.0	8.4	Gallery	2
Winter32	3935008	150783	153472	90.0	20	Well	2
Winter33	3935009	149471	152158	106.3	20	Well	2
Winter34	3935013	150150	154171	90.0	11.8	Gallery	2
Winter35	3936002	151481	153225	104.0	31	Well	2
Winter36	3936003	151768	153525	100.0	26	Well	2
Winter37	3936004	151462	154014	108.0	24	Well	2

Continued on Next Page...

Table A.1 – Continued

Sample ID	Monitoring station	X ^a (m)	Y ^a (m)	Z (m)	Depth (m)	Type	Aquifer ^b
Winter38	3936006	151388	153420	96.0	24	Well	2
Winter39	3937001	148677	150854	103.7	12.1	Gallery	2
Winter40	3937002	148582	148733	120.0	3.6	Gallery	2
Winter41	3937003	148324	150120	103.1	6	Spring	2
Winter42	3938001	149117	150394	113.0	32.6	Gallery	2
Winter43	3938002	150809	151034	109.6	16	Well	2
Winter44	3938003	149933	151084	99.7	5.9	Gallery	2
Winter45	3938004	149949	151346	100.0	17.1	Gallery	2
Winter46	3938005	149891	151498	93.0	11	Well	2
Winter47	3941002	156127	157434	63.1	21.2	Well	2
Winter48	3943016	159505	155888	58.9	45	Well	3
Winter49	3944002	156320	154040	123.5	71.9	Well	2
Winter50	3946001	161668	150476	139.1	76	Well	2
Winter51	3947003	156380	150520	83.2	2.5	Gallery	2
Winter52	3947006	154760	149680	96.0	19.5	Well	2
Winter53	3948001	158160	149270	147.5	60.5	Well	2
Winter54	3948002	156740	150560	80.0	2	Gallery	2
Winter55	3948003	158160	149220	147.2	62.7	Well	2
Winter56	3948004	157010	151040	75.9	60	Well	5
Winter57	3949001	161870	149940	131.7	54	Well	2
Winter58	3969001	144910	140194	125.1	1	Spring	2
Winter59	3969003	144893	140280	128.3	1	Gallery	2
Winter60	3969004	144882	140139	123.6	1	Spring	2
Winter61	3972001	150004	147181	133.5	21	Well	2
Winter62	3974001	148388	142642	122.5	8	Well	2
Winter63	3974008	148329	142575	123.0	1.1	Gallery	2
Winter64	3974010	148350	144600	114.0	n.d.	Gallery	2
Winter65	3975002	148900	144150	119.0	n.d.	Gallery	2
Winter66	3976002	153087	142728	130.0	15	Well	2
Winter67	3976004	153683	143679	116.0	2	Spring	2
Winter68	3976005	153155	144430	121.0	10	Well	2
Winter69	3976007	153244	143659	117.0	6	Well	2
Winter70	3976008	153151	143470	116.0	2	Spring	2
Winter71	3976009	153857	143685	110.0	2	Spring	2
Winter72	3979001	153483	140147	145.0	1	Spring	2
Winter73	3979002	153453	139913	146.7	70	Well	4
Winter74	3984003	154211	143800	108.0	2	Spring	2
Winter75	3984004	154175	143784	107.0	2	Spring	2
Winter76	3987001	155727	139075	151.0	69	Well	4
Winter77	3987002	156414	138917	139.0	66	Well	4
Winter78	3988004	159254	139114	130.0	23.2	Well	4
Winter79	3988005	156777	139030	137.0	38	Well	4
Winter80	3988007	157410	138846	131.8	72	Well	4
Winter81	3988008	159071	138957	124.2	91	Well	4
Winter82	4012002	166556	156089	52.2	28.4	Well	3
Winter83	4012004	166724	156366	61.0	45.3	Well	3
Winter84	4012005	166757	155074	48.0	8.3	Gallery	2
Winter85	4013005	168714	156418	58.7	56	Well	3
Winter86	4014005	163455	154758	114.0	58.5	Well	2
Winter87	4015002	166936	151619	124.9	59	Well	2
Winter88	4017004	163636	149760	66.0	1	Spring	2
Winter89	4018003	167269	151084	113.3	30	Well	2
Winter90	4019002	168003	150488	147.5	66	Well	2
Winter91	4019006	169984	150851	133.8	50	Well	2
Winter92	4019009	167894	150906	139.7	43	Well	2
Winter93	4019032	169931	151507	111.4	6.7	Well	2
Winter94	4022003	174958	156256	90.0	n.d.	Well	2
Winter95	4024001	171998	151748	100.0	1	Spring	2
Winter96	4025003	174876	152816	100.0	1	Spring	2
Winter97	4027002	171200	149470	144.5	47.2	Well	2
Winter98	4031005	179277	155609	136.0	36	Well	2
Winter99	4033098	183552	155445	90.9	55	Well	2
Winter100	4035005	181106	153538	102.3	1	Spring	2
Winter101	4037001	180217	150235	125.4	1	Spring	2
Winter102	4039001	184472	149654	119.1	n.d.	Gallery	2
Winter103	4051002	163700	145360	108.6	50	Well	5
Winter104	4052003	166480	146430	110.0	4	Gallery	2
Winter105	4054003	163150	144190	101.4	36	Well	5
Winter106	4057001	163600	139820	128.0	1	Spring	2
Winter107	4059001	168078	139967	147.0	11	Well	2
Winter108	4062002	173126	145276	147.0	1	Spring	2
Winter109	4063001	177682	147104	145.5	6	Well	2
Winter110	4063002	177788	147338	141.0	32	Well	2
Winter111	4064002	170631	144085	145.0	3	Drain	2
Winter112	4068014	174709	141413	158.4	12.2	Well	2
Winter113	4072001	181033	146068	160.7	43	Well	2

Continued on Next Page...

Table A.1 – Continued

Sample ID	Monitoring station	X ^a (m)	Y ^a (m)	Z (m)	Depth (m)	Type	Aquifer ^b
Winter114	4072003	181049	146071	160.7	28	Well	2
Spring1	3257002	162907	158801	54.3	1	Spring	2
Spring2	3264001	171967	163835	41.7	1	Spring	1
Spring3	3269002	175814	159293	106.5	30	Well	2
Spring4	3933001	151860	156240	124.0	n.d.	Well	2
Spring5	3935009	149471	152158	106.3	20	Well	2
Spring6	3935013	150150	154171	90.0	11.8	Gallery	2
Spring7	3936003	151768	153525	100.0	26	Well	2
Spring8	3936004	151462	154014	108.0	24	Well	2
Spring9	3937002	148582	148733	120.0	3.6	Gallery	2
Spring10	3937003	148324	150120	103.1	6	Spring	2
Spring11	3938002	150809	151034	109.6	16	Well	2
Spring12	3944002	156320	154040	123.5	71.9	Well	2
Spring13	3947006	154760	149680	96.0	19.5	Well	2
Spring14	3949001	161870	149940	131.7	54	Well	2
Spring15	3976002	153087	142728	130.0	15	Well	2
Spring16	4015002	166936	151619	124.9	59	Well	2
Spring17	4019002	168003	150488	147.5	66	Well	2
Spring18	4027002	171200	149470	144.5	47.2	Well	2
Spring19	4035005	181106	153538	102.3	1	Spring	2
Spring20	4051003	163744	145634	103.0	6	Well	2
Spring21	4052003	166480	146430	110.0	4	Well	2
Spring22	4059001	168078	139967	147.0	11	Well	2
Spring23	4062002	173126	145276	147.0	1	Spring	2
Spring24	4068014	174709	141413	158.4	12.2	Well	2
Spring25	4072001	181033	146068	160.7	43	Well	2

^a Belgian Lambert 72 coordinate system.^b 1=Not differentiated Holocene and Pleistocene, 2=Eocene and Paleocene sands, 3=Cretaceous chalks, 4=Devonian limestones, 5=Cambro-Ordovician-Silurian basement (Brabant Massif). n.d.=not determined.

Table A.2: Geochemical data collected during the Spring 2008 and Winter 2009 sampling campaigns.

Sample ID	Date	NO ₃ ⁻ (mg/l)	δ ¹⁵ N (‰)	δ ¹⁸ O (‰)	pH (-)	T (°C)	Diss. O ₂ (mg/l)	Cond. (μS/cm)	Na ⁺ (mg/l)	K ⁺ (mg/l)	Cl ⁻ (mg/l)
Winter1	19/01/2009	42.9	0.07	-3.40	6.82	11.7	9.2	732	14.62	0.70	77.78
Winter2	20/01/2009	35.2	1.47	3.70	7.09	11.2	9.1	810	14.61	0.76	101.46
Winter3	19/01/2009	23.1	1.14	0.50	7.06	9.8	6.9	511	8.78	1.05	32.88
Winter4	19/01/2009	36.5	-0.03	1.45	6.87	11.2	9.0	633	12.39	0.99	58.08
Winter5	20/01/2009	33.7	2.08	5.33	6.97	11.6	9.3	571	7.42	0.98	40.12
Winter6	21/01/2009	33.1	2.81	3.73	7.03	10.6	8.6	736	17.20	0.92	92.03
Winter7	21/01/2009	37.4	3.59	1.72	7.07	10.7	9.4	770	12.88	1.19	101.12
Winter8	20/01/2009	33.1	2.84	3.34	7.16	10.9	9.2	744	21.37	0.92	81.18
Winter9	20/01/2009	28.8	3.66	0.73	7.21	12.6	9.0	777	34.90	1.32	80.81
Winter10	21/01/2009	17.1	3.95	3.35	7.05	10.9	6.7	560	14.64	1.41	58.54
Winter11	26/01/2009	46.4	4.07	2.73	7.27	9.5	8.4	505	11.58	1.00	48.96
Winter12	15/01/2009	29.9	2.87	1.90	6.86	10.6	8.7	698	27.54	1.48	60.06
Winter13	13/01/2009	55.5	3.28	1.72	7.35	9.4	10.5	707	16.41	2.35	51.27
Winter14	13/01/2009	6.9	9.77	9.33	7.32	11.8	2.1	676	14.26	2.22	38.86
Winter15	13/01/2009	38.5	3.77	4.94	7.16	8.5	8.3	644	16.59	1.44	28.69
Winter16	21/01/2009	40.5	2.72	4.01	7.61	14.1	7.9	869	15.42	1.19	43.75
Winter17	28/01/2009	41.1	2.33	6.73	7.07	9.5	8.1	661	14.31	2.60	42.81
Winter18	13/01/2009	69.7	4.11	2.88	7.13	4.5	11.4	866	24.44	22.80	46.62
Winter19	13/01/2009	0.6	n.d.	n.d.	7.38	5.8	5.8	433	10.45	2.51	8.47
Winter20	21/01/2009	61.5	5.71	4.03	7.21	14.2	7.5	916	23.35	2.68	44.27
Winter21	06/02/2009	40.6	4.67	6.36	7.02	10.9	7.7	627	15.57	3.21	40.81
Winter22	21/01/2009	61.0	4.47	4.71	7.46	14.6	7.4	926	12.13	2.18	47.04
Winter23	21/01/2009	41.2	4.44	7.95	7.63	14.7	7.6	915	12.93	1.31	55.81
Winter24	14/01/2009	12.0	5.51	2.30	7.08	11.3	7.5	642	28.61	4.73	45.82
Winter25	22/01/2009	49.4	5.00	5.01	7.24	10.2	9.4	612	15.42	2.38	28.56
Winter26	14/01/2009	70.0	5.37	0.86	7.24	12.5	11.2	805	36.52	0.90	103.79
Winter27	22/01/2009	64.9	5.27	2.71	7.17	10.7	6.8	634	18.19	2.15	41.56
Winter28	22/01/2009	57.5	4.51	4.24	7.25	10.8	7.5	636	19.10	2.37	37.29
Winter29	22/01/2009	60.0	6.63	4.37	7.26	10.9	9.6	687	24.85	3.99	34.53
Winter30	22/01/2009	37.7	5.22	2.83	7.14	11.2	6.2	667	12.31	2.73	43.24
Winter31	22/01/2009	64.5	6.30	3.38	7.18	11.0	7.2	675	22.43	1.63	39.99
Winter32	22/01/2009	46.4	6.18	4.89	7.17	n.d.	7.2	700	17.54	1.29	44.41
Winter33	29/01/2009	62.2	4.27	1.15	7.35	10.7	8.1	720	14.21	1.40	48.89
Winter34	22/01/2009	68.3	3.94	5.64	7.38	10.0	7.4	754	12.75	1.33	37.19
Winter35	22/01/2009	39.2	4.86	3.73	7.22	10.8	6.1	647	10.07	1.58	39.46
Winter36	22/01/2009	29.9	5.03	4.18	7.16	10.1	6.3	677	12.54	1.46	45.21
Winter37	22/01/2009	40.4	4.65	4.41	7.23	n.d.	6.3	621	8.05	1.26	33.43
Winter38	22/01/2009	39.3	5.73	5.02	7.13	10.6	5.0	689	14.38	1.92	39.97
Winter39	29/01/2009	64.0	3.99	2.94	7.25	10.4	9.2	608	14.18	2.95	39.59
Winter40	29/01/2009	27.1	4.56	4.70	7.32	9.3	5.2	689	10.06	1.70	40.22
Winter41	29/01/2009	66.3	2.96	3.66	7.37	9.8	7.5	676	13.99	3.27	43.83

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Table A.2 – Continued

Sample ID	Date	NO ₃ ⁻ (mg/l)	δ ¹⁵ N (‰)	δ ¹⁸ O (‰)	pH (-)	T (°C)	Diss. O ₂ (mg/l)	Cond. (μS/cm)	Na ⁺ (mg/l)	K ⁺ (mg/l)	Cl ⁻ (mg/l)
Winter42	29/01/2009	30.9	3.97	4.41	7.31	10.2	4.6	650	11.41	2.07	42.02
Winter43	29/01/2009	37.5	3.42	1.28	7.29	10.6	7.3	580	11.01	1.18	36.80
Winter44	29/01/2009	48.6	3.10	3.35	7.39	10.2	6.8	563	11.42	1.05	38.50
Winter45	29/01/2009	50.3	4.21	0.89	7.41	10.3	6.9	694	15.26	2.09	42.66
Winter46	29/01/2009	50.9	4.15	1.94	7.31	10.4	6.6	640	11.81	1.47	33.68
Winter47	28/01/2009	34.6	3.96	3.17	6.98	11.1	6.9	575	13.69	2.06	31.64
Winter48	04/02/2009	0.1	n.d.	n.d.	7.41	10.8	7.5	478	10.70	2.08	23.83
Winter49	28/01/2009	26.0	3.15	3.11	7.14	10.4	8.5	498	9.02	1.12	26.92
Winter50	14/01/2009	82.9	7.03	6.09	7.08	8.4	10.1	731	23.07	1.90	60.53
Winter51	28/01/2009	36.1	2.13	4.77	7.12	10.0	8.3	497	9.85	2.45	28.17
Winter52	05/01/2009	50.6	3.21	2.22	7.39	9.9	7.8	696	10.95	1.91	40.58
Winter53	28/01/2009	84.5	6.69	5.50	6.85	10.8	10.1	632	24.44	2.49	46.95
Winter54	28/01/2009	41.5	3.16	3.36	7.09	10.0	8.1	511	11.81	2.05	36.07
Winter55	28/01/2009	71.1	5.73	4.60	7.05	10.9	10.0	658	27.59	3.50	56.05
Winter56	04/02/2009	0.2	n.d.	n.d.	7.21	11.1	6.0	577	12.30	1.44	35.55
Winter57	28/01/2009	50.9	4.25	5.35	6.95	10.4	9.7	597	19.59	1.53	52.67
Winter58	26/01/2009	43.3	2.28	3.93	7.17	10.3	8.3	619	17.75	0.97	47.52
Winter59	26/01/2009	64.7	1.95	6.01	7.27	9.6	11.2	509	11.04	0.69	39.02
Winter60	26/01/2009	51.5	3.79	6.26	7.20	10.3	8.5	612	14.97	1.48	59.09
Winter61	26/01/2009	48.4	5.66	5.05	7.22	9.5	5.3	544	10.05	0.86	25.61
Winter62	26/01/2009	50.6	4.48	3.15	7.22	10.1	6.4	614	10.70	1.04	38.01
Winter63	26/01/2009	50.1	3.67	3.86	7.35	9.9	7.0	620	12.66	1.04	44.20
Winter64	26/01/2009	56.9	4.84	4.39	7.24	10.0	8.1	664	13.28	1.47	49.66
Winter65	26/01/2009	54.7	4.22	6.97	7.22	10.1	8.0	541	13.58	1.48	50.45
Winter66	05/01/2009	37.5	3.28	2.32	7.49	9.6	8.8	654	13.48	1.12	35.81
Winter67	05/01/2009	65.6	4.45	2.96	7.34	9.0	7.6	655	11.94	1.77	42.29
Winter68	05/01/2009	48.3	5.69	8.57	7.50	10.3	3.8	724	16.39	5.40	33.35
Winter69	05/01/2009	67.1	4.51	3.10	7.33	10.1	6.0	738	14.82	2.34	40.36
Winter70	05/01/2009	55.9	3.60	2.23	7.48	9.6	7.0	653	17.07	1.52	45.74
Winter71	05/01/2009	55.2	4.65	5.24	7.46	8.2	6.8	658	10.99	1.72	45.50
Winter72	28/01/2009	52.9	3.70	4.57	7.27	10.3	9.5	602	12.16	0.93	41.14
Winter73	28/01/2009	9.2	4.24	4.08	7.32	11.4	5.3	462	9.00	3.94	27.14
Winter74	05/01/2009	56.5	4.15	1.50	7.27	9.6	7.3	680	13.62	2.44	38.92
Winter75	05/01/2009	48.9	5.23	8.55	7.29	10.0	6.7	734	13.43	1.80	44.34
Winter76	04/02/2009	0.7	n.d.	n.d.	7.22	10.7	6.1	497	7.08	2.39	26.88
Winter77	04/02/2009	2.4	6.44	4.71	7.15	10.4	5.3	659	10.58	2.15	50.64
Winter78	28/01/2009	47.0	5.60	23.34	6.77	10.3	n.d.	565	17.89	1.93	41.14
Winter79	04/02/2009	1.1	n.d.	n.d.	7.36	10.3	8.1	611	11.15	1.87	43.41
Winter80	04/02/2009	0.1	n.d.	n.d.	7.17	11.0	6.1	617	14.05	2.95	39.47
Winter81	04/02/2009	0.1	n.d.	n.d.	7.26	11.3	6.2	626	17.20	3.35	44.08
Winter82	28/01/2009	33.1	6.54	7.46	7.14	9.0	n.d.	585	18.95	3.39	40.89
Winter83	28/01/2009	33.1	5.62	8.64	7.22	11.4	n.d.	620	17.38	3.80	39.12
Winter84	28/01/2009	35.2	5.15	6.04	6.76	10.1	n.d.	569	17.81	1.97	51.92
Winter85	28/01/2009	33.3	5.60	5.24	7.35	8.3	n.d.	571	18.10	3.64	41.69

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Table A.2 – Continued

Sample ID	Date	NO ₃ ⁻ (mg/l)	δ ¹⁵ N (‰)	δ ¹⁸ O (‰)	pH (-)	T (°C)	Diss. O ₂ (mg/l)	Cond. (μS/cm)	Na ⁺ (mg/l)	K ⁺ (mg/l)	Cl ⁻ (mg/l)
Winter86	28/01/2009	50.6	4.73	3.97	7.23	10.6	n.d.	579	15.05	1.12	37.16
Winter87	15/01/2009	27.7	2.83	2.84	7.01	10.5	8.6	699	14.67	1.16	54.03
Winter88	14/01/2009	37.1	5.85	5.24	7.11	11.9	9.3	665	22.01	1.59	53.87
Winter89	15/01/2009	28.0	3.11	2.57	7.00	12.4	8.7	748	24.25	6.00	67.59
Winter90	15/01/2009	25.5	2.15	4.09	7.03	10.9	9.8	694	10.97	1.21	54.57
Winter91	05/02/2009	37.3	6.20	10.48	7.31	10.2	9.5	632	13.40	4.37	48.64
Winter92	15/01/2009	21.4	2.83	4.52	7.14	11.6	8.9	773	14.34	0.96	65.55
Winter93	15/01/2009	24.0	10.79	12.19	6.86	9.5	4.3	784	19.90	46.30	52.91
Winter94	28/01/2009	50.0	4.51	6.61	7.19	10.8	10.8	653	10.24	0.92	46.80
Winter95	21/01/2009	42.1	3.73	4.32	7.37	13.9	7.8	833	13.89	1.59	55.49
Winter96	21/01/2009	39.0	3.47	5.87	7.10	17.3	5.9	697	14.19	1.94	46.59
Winter97	28/01/2009	38.7	3.05	5.38	7.18	8.8	n.d.	609	12.12	1.31	41.88
Winter98	04/02/2009	37.1	4.91	2.56	7.05	14.9	8.8	760	14.96	1.64	57.48
Winter99	04/02/2009	8.0	7.02	0.54	7.29	9.1	8.1	464	10.59	4.25	15.47
Winter100	13/01/2009	43.7	5.10	3.50	7.07	11.1	7.0	745	20.41	3.49	64.08
Winter101	04/02/2009	63.4	4.13	2.88	6.98	9.3	8.4	755	17.13	1.95	53.95
Winter102	05/02/2009	48.9	4.03	2.95	7.15	10.7	7.7	728	22.03	1.27	56.86
Winter103	04/02/2009	32.4	5.34	1.19	6.62	8.3	8.7	533	15.11	1.78	29.70
Winter104	28/01/2009	50.1	4.42	19.46	6.57	9.2	n.d.	501	16.70	1.18	29.13
Winter105	04/02/2009	0.1	n.d.	n.d.	6.50	8.6	6.7	416	13.91	1.65	30.38
Winter106	12/01/2009	13.7	4.92	3.31	6.89	10.2	5.6	506	19.64	2.47	36.91
Winter107	12/01/2009	93.2	5.45	4.02	7.05	8.9	4.9	843	22.60	3.54	47.69
Winter108	27/01/2009	78.7	7.79	4.99	6.38	9.3	5.8	712	35.57	3.35	58.04
Winter109	04/02/2009	93.4	9.87	1.81	7.68	10.5	9.6	621	23.99	2.22	26.61
Winter110	04/02/2009	23.1	2.68	2.49	6.94	10.4	9.0	556	11.91	1.36	35.00
Winter111	12/01/2009	36.3	2.87	3.89	6.81	10.2	7.0	749	13.81	1.39	67.58
Winter112	12/01/2009	26.5	6.21	2.34	6.58	10.3	7.9	615	27.87	1.16	32.97
Winter113	30/01/2009	35.1	4.65	3.69	6.54	10.6	7.6	590	14.80	0.85	35.78
Winter114	30/01/2009	45.0	4.97	3.28	6.70	11.1	7.6	646	19.15	1.40	42.87
Spring1	28/05/2008	56.8	7.75	3.92	7.23	11.8	10.2	775	n.d.	n.d.	n.d.
Spring2	28/05/2008	36.7	1.47	14.19	7.21	11.4	8.2	632	n.d.	n.d.	n.d.
Spring3	26/05/2008	74.5	0.27	8.77	7.08	14.9	8.9	849	n.d.	n.d.	n.d.
Spring4	28/05/2008	67.5	4.22	12.04	7.15	13.2	10.0	887	n.d.	n.d.	n.d.
Spring5	19/06/2008	61.6	3.13	6.95	7.28	11.9	8.1	832	n.d.	n.d.	n.d.
Spring6	19/06/2008	69.1	2.82	12.48	7.26	12.2	7.0	885	n.d.	n.d.	n.d.
Spring7	19/06/2008	28.6	4.15	9.72	7.37	13.0	6.2	779	n.d.	n.d.	n.d.
Spring8	19/06/2008	39.3	3.04	7.72	7.54	10.9	6.3	723	n.d.	n.d.	n.d.
Spring9	19/06/2008	24.4	3.93	11.43	7.40	10.9	5.1	751	n.d.	n.d.	n.d.
Spring10	19/06/2008	65.7	2.61	14.42	7.38	11.9	8.1	769	n.d.	n.d.	n.d.
Spring11	19/06/2008	39.7	2.99	10.37	7.35	11.9	7.8	740	n.d.	n.d.	n.d.
Spring12	18/06/2008	26.1	1.50	9.85	6.90	n.d.	n.d.	600	n.d.	n.d.	n.d.
Spring13	19/06/2008	49.9	2.07	7.60	7.59	11.0	7.5	718	n.d.	n.d.	n.d.
Spring14	18/06/2008	50.3	3.18	9.95	6.70	n.d.	n.d.	562	n.d.	n.d.	n.d.
Spring15	19/06/2008	34.8	2.04	10.53	7.82	11.3	7.5	682	n.d.	n.d.	n.d.

Continued on Next Page...

Table A.2 – Continued											
Sample ID	Date	NO ₃ [−] (mg/l)	δ ¹⁵ N (‰)	δ ¹⁸ O (‰)	pH (-)	T (°C)	Diss. O ₂ (mg/l)	Cond. (μS/cm)	Na ⁺ (mg/l)	K ⁺ (mg/l)	Cl [−] (mg/l)
Spring16	12/06/2008	29.3	2.72	2.02	6.54	11.4	n.d.	728	n.d.	n.d.	n.d.
Spring17	12/06/2008	26.8	0.62	-0.04	6.70	11.3	n.d.	705	n.d.	n.d.	n.d.
Spring18	18/06/2008	37.1	1.72	8.40	6.50	n.d.	n.d.	735	n.d.	n.d.	n.d.
Spring19	26/05/2008	39.5	2.96	12.11	7.05	13.3	6.8	864	n.d.	n.d.	n.d.
Spring20	26/05/2008	33.0	8.72	5.44	6.68	12.5	8.4	551	n.d.	n.d.	n.d.
Spring21	18/06/2008	47.9	2.23	9.51	6.50	n.d.	n.d.	496	n.d.	n.d.	n.d.
Spring22	26/05/2008	97.3	4.33	14.43	7.10	13.7	5.0	860	n.d.	n.d.	n.d.
Spring23	26/05/2008	76.4	9.08	3.72	6.05	12.5	6.1	675	n.d.	n.d.	n.d.
Spring24	26/05/2008	30.9	4.04	8.27	6.52	14.5	7.0	587	n.d.	n.d.	n.d.
Spring25	16/06/2008	35.6	3.46	5.38	7.06	11.6	n.d.	633	n.d.	n.d.	n.d.

n.d.=not determined.

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- N°151, Fornelos Martins, Nadine, GIL01 and relatives, a new generation of tectiviruses infecting the *Bacillus cereus* group.

Département des sciences du milieu et de l'aménagement du territoire

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Pour plus d'informations, visitez <http://edoc.bib.ucl.ac.be/>

Publications and Conferences

Publications in international peer-reviewed journals or books

- Mattern, S., Bogaert, P. and Vanclooster, M., **Introducing time variability and sampling rate in the mapping of groundwater contamination by means of the Bayesian Maximum Entropy (BME) method**, in Candela, L.; Vadillo, I. and Elorza, F. J. (ed.), *Advances in Subsurface Pollution of Porous Media - Indicators, Processes and Modelling: IAH selected papers*, volume 14, Taylor and Francis, 2008.
- Mattern, S., Fasbender, D. and Vanclooster, M., **Discriminating sources of nitrate pollution in an unconfined sandy aquifer**, *Journal of Hydrology*, 2009, 376, 275-284.
- Mattern, S. and Vanclooster, M., **Estimating travel time of recharge water through a deep vadose zone using a transfer function model**, *Environmental Fluid Mechanics*, accepted article.
- Mattern, S., Raouafi, W., Bogaert, P., Fasbender, D., Bouhlila, R., Vanclooster, M., **Bayesian Data Fusion (BDF) of monitoring data with a statistical groundwater contamination model to map groundwater quality at the regional scale**, *Journal of Hydrology*, submitted article.
- **Identification of the nitrate contamination sources of the Brusselian sands groundwater body (Belgium) using a dual-isotope approach**. To be submitted.

Conferences and workshops

- Vanclooster, M., Leterme, B., Pinte, D., Sulmon, R., Pineros-Garcet, J., Mattern, S., **Valorisation de la carte pédologique dans la cartographie de la vulnérabilité des nappes souterraines**. Journée d'étude sur les appli-

cations et utilisations de la Carte numérique des sols de Wallonie, Gembloux, 18/10/2006.

- Mattern, S., Bogaert, P. and Vanclooster, M., **Introducing time variability in the mapping of groundwater contamination by means of the Bayesian Maximum Entropy (BME) method**, International Conference on Water Pollution in natural POrous media at different scales - Assessment of fate, impact and indicators. WAPO² Final Conference, COST Action 629, Barcelona, Spain, April 11-13, 2007.
- Mattern, S. and Vanclooster, M., **Factors affecting groundwater pollution by nitrate in a sandy aquifer**, EGU General Assembly 2008, Vienna, Austria, 14-18 April, 2008.
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- Mattern, S. and Vanclooster, M., **Facteurs influençant la pollution d'un aquifère sableux non confiné par les nitrates**, 33èmes journées du GFHN: Impact de l'usage du sol sur les ressources en eau souterraine, Avignon, France, 19 et 20 novembre 2008.
- Mattern, S. and Vanclooster, M., **Estimating travel times of recharge water through the unsaturated zone using a transfer function model**, EGU General Assembly 2009, Vienna, Austria, 20-24 April, 2009.

Posters

- Mattern, S., Bogaert, P., and Vanclooster, M., **Introducing time variability in the mapping of groundwater contamination by means of the Bayesian Maximum Entropy (BME) method**, Kick off event of the graduate school ENVITAM, Louvain-la-Neuve (Belgium), February 5, 2007.
- Mattern, S., Vanclooster, M., **Identification of the nitrate contamination sources of the Brusselian sands groundwater using a dual-isotope approach**, ISONITRATE Consortium, International workshop Towards new methods to manage nitrate pollution within the Water Framework Directive, December 10-11, 2009, UNESCO, Paris. Submitted poster.

Internal reports

- Mattern, S., Bogaert, P. and Vanclooster, M., **Cartographie de la pollution des masses d'eau souterraine des Sables bruxelliens par le nitrate**. Rapport interne, 84 p., Université catholique de Louvain, Unité de génie rural, 2007.

Summary

This thesis aimed to improve our understanding of groundwater pollution by nitrate at the regional scale of the Brusselian sand groundwater body (Belgium). Despite all the nitrate reduction actions that were undertaken to meet European directives, this study area still presents one of the highest groundwater nitrate concentrations of the Walloon Region. Further assessing the pollution levels of groundwater and identifying the contamination sources are therefore needed for designing sustainable water management strategies.

Our first main objective was to assess groundwater contamination at the regional scale by mapping the nitrate concentrations. The locations where groundwater quality properties were measured are scarce and sparsely distributed over space. We therefore used a data fusion method in order to improve the mapping quality of groundwater nitrate concentrations in areas located far away from monitoring stations.

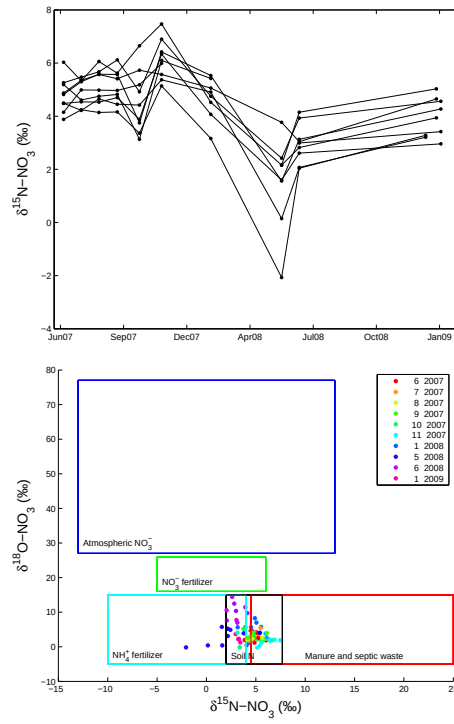
The transfer time of nitrate to the aquifer is one of the reasons that could explain the lack of improvement in water quality. We estimated the travel time of percolating water through the vadose zone.

Our second main objective was to identify sources of groundwater nitrate pollution in the study area. Two statistical methods were used to link the measured nitrate concentrations with land and land use attributes. The isotopic signature of groundwater nitrate allowed to identify the source of pollution observed in some monitoring stations, and gave insight about processes affecting the contamination.

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Erratum

In this thesis, efforts have been made to use high quality data. However, shortly after printing the final document, the laboratory where the groundwater samples collected in January 2008 were analyzed informed us that they made an error in the treatment of the data. Hence, they provided us with corrected data that are incorporated in the following figures. These figures replace Figures 8.3b and 8.5:



Although these corrections alter slightly the description and discussion of the results, they do not have a fundamental impact on the general discussion and conclusion.