Spatial and temporal nitrate distribution in carbonate aquifers under dairy farms in Ireland

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Abstract

High nitrate (NO_3^-) concentrations in groundwater contribute significantly to eutrophication of water and can have serious consequences for human health. High nitrate occurrence in groundwater often correlates with intensive agriculture due to high nitrogen (N) applications on the surface. Because denitrification potential and response times in such systems are typically low, nitrate can discharge often to surface waters unabated. Shortest vertical travel times from source to groundwater occur if thin free draining soils and karstified limestones are present. Such short time lags allow an assessment of how management change and high rainfall may affect nitrate distribution in groundwater. For the present PhD thesis two commercial dairy farms in South Ireland were studied, each underlain by carbonate aquifers.

The first study of the cumulative PhD study elucidates the consequences of agronomic practices on groundwater quality whilst also considering time lags from source to groundwater. Detailed agronomic loadings of nitrogen, (hydro-)geological site characteristics and local weather conditions are evaluated in connection with groundwater nitrate occurrence during a 11 year study period (2002 – 2011). ArcGIS and SAS were used as spatial analysis and statistical modelling (multiple linear regression) tools. Four scenarios were created to compare paddock specific changes to groundwater wells while using topographic and hydrogeological assumptions of a tracer test and a geoelectric survey. In addition, a time lag from source to groundwater of up to 3 years was considered. Statistical results showed that a combination of improved agronomic practices and site specific characteristics such as thicknesses of the soil and unsaturated zone together with hydrogeological connections of wells and local weather conditions such as rainfall, sunshine and soil moisture deficit were important explanatory variables for nitrate concentrations. In particular, results suggest that agronomic practices became more important after a time lag of 1 to 2 years and agronomic practices such as: reductions in inorganic fertilizer application, changes of timing of slurry application, the relocation of a dairy soiled water irrigator to a less karstified area and the implementation of minimum cultivation reseeding instead of ploughing, led to reduced nitrate occurrence in the aquifer.

The second publication focuses on nitrate patterns observed in karst springs as a response to high rainfall events. In response to high rainfall events, nitrate concentrations can alter significantly, i.e., rapidly decreasing or increasing concentrations. The aim of the study is to elucidate the controlling key factors that lead to mobilisation and/or dilution of nitrate concentrations due to high rainfall events. To determine typical nitrate pattern in karst aquifers, firstly, high-resolution data of nitrate and discharge in a specific karst spring in Southern Ireland together with on-farm borehole groundwater fluctuation data are evaluated. Secondly, a scientific hypothesis of possible scenarios of different nitrate responses to storm events is formulated. Additional case studies from the literature are used to verify this hypothesis. The controlling key factors for mobilisation/dilution processes were hydrological condition and in particular, nutrient source and the pathway taken in relation to land use and karstification, respectively.

The third part of the study deals with the technical aspect and the comparison of two different spectrophotometric sensors, i.e. a double wavelength spectrophotometer (DWS) and a multiple wavelength spectrophotometer (MWS) that are used for high resolution monitoring of nitrate. The DWS was deployed at a field site in Ireland, whereas the MWS was installed at a field site in Jordan. The technique gives the opportunity to observe trends and rapid changes of nitrate-nitrogen (NO_3-N) concentrations whilst using a solid-state methodology without reagents. For comparison of the sensors the following issues are addressed: Hardware options, ease of calibration, accuracy, influence of additional substances, positive and negative aspects of the two sensors, troubleshooting and trade-offs. Both sensors proofed to be sufficient for monitoring highly time resolved nitrate concentrations in groundwater. However, the accuracy of the sensors can be affected if the content of additional substances such as turbidity, organic matter, nitrite or hydrogen carbonate significantly varies after the sensors have been calibrated to a particular water matrix. In addition, the chosen path length of the sensors influences the sensitivity and the range of detectable nitrate. It is reasonable to conclude that high-resolution monitoring will greatly contribute to a better understanding of groundwater processes in the future.

The PhD study improves the understanding of nitrate distributions in relation to agronomic and hydrological drivers and (hydro-)geological site characteristics in karst areas and provides practical experience regarding two spectrophotometer used for determining highly time resolved nitrate concentrations. The results of the study can be used to guide and provide practical advice for environmental modellers, scientists, consultants, policy makers and drinking water managers. In particular, the study supports the assessment of the impact of present and future legislation implementation especially in vulnerable areas with respect to the current regulations of the European Union Water Framework Directive.

Kurzfassung

Hohe Nitratkonzentrationen (NO_3^-) im Grundwasser tragen signifikant zur Eutrophierung von Gewässern bei und können schwerwiegende Auswirkungen auf die menschliche Gesundheit haben. Hohe Nitratvorkommen im Grundwasser sind oft durch einen hohen Stickstoffauftrag an der Oberfläche aufgrund intensiver Agrarlandnutzung zu erklären. Bei geklüfteten und verkarsteten Grundwasserleitern mit geringer Bodenmächtigkeit wirken sich anthropogene Einflüsse auf die Grundwasserqualität besonders stark aus. Das meist geringe Denitrifizierungspotential in Karstgebieten trägt dazu bei, dass sich Nitrat oft bis zu den Oberflächengewässern unvermindert ausbreiten kann. Zusätzlich sind kurze Transitzeiten zwischen landwirtschaftlichem Auftrag an der Oberfläche und Grundwasser typisch. Durch diese sind ideale Bedingungen gegeben, um Veränderungen von Nitratkonzentrationen im Grundwasser und deren Einflussfaktoren zu untersuchen. Von besonderem Interesse ist hierbei z.B. der Einfluss des Agrarmanagements. Jedoch spielen auch weitere Einflüsse wie beispielsweise Starkregenereignisse eine wichtige Rolle. Für die Doktorarbeit wurden zwei kommerziell genutzte Milchviehbetriebe im Süden von Irland untersucht, welche beide in einem Karstgebiet liegen.

Im ersten Teil der Doktorarbeit werden die Auswirkungen landwirtschaftlicher Praktiken auf die Grundwasserqualität unter Berücksichtigung von vertikalen Wegzeiten vom Auftrag zum Grundwasser untersucht. Dabei wird der Einfluss von (hydro-)geologischen Standorteigenschaften, lokalen Wetterbedingungen und Veränderungen der Menge und Anwendungsverfahren vom landwirtschaftlichen Stickstoffauftrag eines Milchviehbetriebes auf Nitratkonzentrationen eines irischen Karstgrundwasserleiters ausgewertet. Für die Studie wurden innerhalb von 11 Jahren (2002-2011) monatliche Nitratkonzentrationen in 11 Grundwassermessstellen gemessen als auch die verschiedenen Stickstoffauftrags-arten und Mengen jeder Weidekoppel. Zur räumlichen Analyse wurde ArcGIS verwendet und als statistisches Verfahren multiple lineare Regression angewendet. Ein Markierungsversuch und geoelektrische Messungen dienen als Grundlage von 4 Szenarien, welche die gemessenen Nitratkonzentrationen der einzelnen Grundwassermessstellen in Bezug zu unterschiedlichen Clustern einzelner Weidekoppeln setzen. Zusätzlich wurde eine zeitliche Verzögerung vom Stickstoffauftrag an der Oberfläche zur gemessenen Nitratkonzentration im Grundwasser von 1 bis 3 Jahren berücksichtigt. Die Ergebnisse der statistischen Analyse weisen darauf hin, dass sowohl spezifische Standorteigenschaften wie Mächtigkeit des Bodens und der ungesättigten Zone, also auch lokale Wetterbedingungen wie Niederschlag und Sonnenscheindauer wichtige Einflussfaktoren darstellen. Des Weiteren deuten die Ergebnisse an, dass landwirtschaftliche Veränderungen der Bewirtschaftung nach einer Dauer von 1 bis 2 Jahren zu einer Reduktion der Nitratkonzentrationen im Grundwasser geführt haben. Dabei spielten die Veränderung der Auftragszeit der Gülle im jeweiligen Kalenderjahr, als auch die Reduktion von anorganischem Dünger eine große Rolle. Zudem ist davon auszugehen, dass der Standortwechsel eines Schmutzwasserverteilers in eine weniger verkarstete Region und die Einführung von minimaler Bodenbearbeitung mit anschließender

Aussaat anstatt von Pflügen zu einer Verbesserung der Grundwasserqualität beigetragen haben.

Im zweiten Teil der Doktorarbeit werden typische Nitratmuster in Karstquellen aufgrund von Starkregenereignissen untersucht. Nitratkonzentrationen in Karstquellen können stark ansteigen oder abfallen aufgrund von Starkregenereignissen. Innerhalb der Studie werden dazu mögliche Haupteinflussfaktoren von Mobilisierungs- und Verdünnungsprozessen diskutiert und erläutert. Dafür werden zeitlich hochaufgelöste Nitratkonzentrationsdaten und der Durchfluss einer irischen Karstquelle zusammen mit aufgenommen Grundwasser-schwankungen von vier Grundwassermessstellen in der Nähe der Quelle untersucht. Des Weiteren werden mögliche Szenarien von verschiedenen Nitratcharakteristika aufgrund von Starkregenereignissen formuliert. Diese beinhalten entweder abrupt erhöhte oder gesenkte Nitratkonzentrationen oder eine Kombination aus beiden, welche während dem gleichen Event oder auf darauffolgenden Events in der gleichen Karstquelle auftreten können. Um diese These verifizieren zu können, werden zusätzliche wissenschaftliche Fallstudien hinzugezogen. Als Haupteinflussfaktoren konnten hydrologische Bedingungen, Verkarstung und Landnutzung identifiziert werden. Des Weiteren deutet die Studie darauf hin, dass verschiedene Nitratcharakteristika in Karstaquiferen stark vom Kontaminationsherd und dem zurückgelegten Transportweg abhängen.

Der dritte Teil der Doktorarbeit befasst sich mit dem technischen Aspekt von zwei unterschiedlichen UV/VIS-Spektralphotometern, welche für die Messung von zeitlich hochaufgelösten Nitratkonzentrationen im Grundwasser vor Ort stationär eingesetzt werden können. Dabei handelt es sich um einen Zweistrahl-Spektralphotometer und einen Mehrfach-Spektralphotometer. Der Zweistrahl-Spektralphotometer wurde für Feldstudien in Irland benutzt, der Mehrfach-Spektralphotometer für Feldstudien in Jordanien. Die Methode hat den Vorteil, dass Trends und starke Schwankungen von Nitratstickstoff photometrisch und damit physikalisch und ohne Reagenzien gemessen werden können. Zum Vergleich der beiden Spektralphotometer wurden folgende Aspekte beleuchtet: Hardwareoptionen, Bedienungsfreundlichkeit der Kalibrierung, Genauigkeit, Einfluss von zusätzlichen Substanzen, positive und negative Aspekte, Störungen und deren Behebung. Beide Spektralphotometer erwiesen sich als ausreichend um zeitlich hochaufgelöste Nitratkonzentrationen zu messen. Die Genauigkeit der Spektralphotometer kann beeinträchtigt werden, wenn sich Trübung oder zusätzliche Stoffe wie organische Stoffe, Nitrit oder Hydrogenkarbonat stark verändern, nachdem die Sensoren anhand einer typischen Wasserzusammensetzung kalibriert wurden. Zusätzlich hat die gewählte Pfadlänge Einfluss auf die Sensitivität und die Spanne der messbaren Nitratkonzentrationen. Man kann erwarten, dass hochaufgelöstes UV/VIS Monitoring zukünftig eine wichtige Rolle einnehmen wird für ein besseres Verständnis von Grundwasserprozessen.

Die Untersuchungen der Doktorarbeit verbessern das Verständnis von Nitratkontamination in Karstgrundwasserleitern in Bezug auf beeinflussende Faktoren wie landwirtschaftlicher Auftrag, hydrologische Bedingungen und (hydro-)geologische Standortcharakteristika. Weiterhin stellt die Studie eine praktische Hilfe bezüglich der Messung hochaufgelöster

Nitratkonzentrationen durch zwei Spektralphotometer dar. Die Studie kann Modellierern, Wissenschaftlern, Fachberatern, politischen Entscheidungsträgern und Trinkwassermanagern praktische Hilfestellung und Anleitung sein. Weiterhin können gegenwärtige und zukünftige Gesetzesbestimmung zur Erreichung eines „guten“ Zustands der Gewässer durch die Studie besser eingeschätzt und verbessert werden. Dies gilt besonders in vulnerablen Gebieten unter Berücksichtigung der derzeitigen Bestimmungen der Europäischen Wasserrahmenrichtlinie.

Contents

Abbreviations

AOD	above ordnance datum
COD	chemical oxygen demand
DSW	dairy soiled water
DWS	double wavelength spectrophotometer
ED	effective drainage
EM	element for measuring
ER	element for reference
EU	European Union
FTU	Formazin Turbidity Unit
ISE	ion sensitive electrode
MAC	maximum allowable concentration
MWS	multiple wavelength spectrophotometer
N	nitrogen
N_2	nitrogen gas
N_2O	nitrous oxide
NO_2^-	nitrite
NO_2-N	nitrite-nitrogen
NO_3^-	nitrate
NO_3-N	nitrate-nitrogen
NO_x-N	total oxidized nitrogen
NH_4^+	ammonium
P	phosphorus
POM	programmes of measures
RMSE	root mean square error
SMD	soil moisture deficit
TON	total oxidized nitrogen
UV/VIS	ultraviolet/visible (light)
WFD	Water Framework Directive

1 Introduction

1.1 Nitrate pollution as environmental risk factor

Agriculture is known as a main contributor of nitrogen (N) occurrence in groundwater, mainly because of inorganic and organic fertilisation (Stigter et al., 2011). High nitrate (NO_3^-) concentrations in groundwater are deemed to be harmful to humans and the environment. Consequences are e.g. eutrophication of surface water bodies (Thieu et al., 2010), toxicity in livestock as well as abortion to cattle (Di and Cameron, 2002) and methemoglobinemia in infants which result into life-threatening organic or lifetime chronic disorders of the organism (WHO, 2007; Knobeloch et al., 2000).

As NO_3^- concentrations rose gradually in many countries due to intensive agriculture after the 1950s (Cao et al., 2013) and as exceeding limits (50 mg NO_3^- L^{-1}) of drinking water for NO_3^- in groundwater were common (Heathwaite et al., 1996), in Europe the protection of groundwater obtained a new focus by the implementation of the European Union (EU) Water Framework Directive (WFD; OJEC, 2000) to achieve at least good water quality status by 2015. Thus, programmes of measures (POM) were implemented by 2012. A maximum admissible concentration of 50 mg NO_3^- L^{-1} for groundwater is imposed. No such standard exists for surface water but instead, in countries such as the Republic of Ireland, a lower MAC of 11.5 mg NO_3^- L^{-1} exists for estuaries (Statutory Instruments S.I. No. 272 of 2009). Recent assessments have found that 16% of Irish groundwater bodies were 'at risk' of poor status due to the potential deterioration of associated estuarine and coastal water quality by NO_3^- from groundwater (Tedd et al., 2014). In the EU, the Nitrates Directive (EC, 1991) is a major contributor to the decrease of the soil nitrogen balance (N surplus), particularly in Belgium, Denmark, Ireland, the Netherlands and the United Kingdom. Since 2000, this is accompanied by a modest decrease of NO_3^- concentrations in fresh surface waters in most EU countries (Van Grinsven et al., 2012).

1.2 Rural economy in Ireland

In Ireland, dairy and beef cattle production from managed grassland is the dominant agricultural land use (CSO, 2011). Milk quotas have limited the Irish dairy production and the EU has decided to remove those quotas to contribute to a more efficient European dairy industry. The abolition of EU milk quota in 2015 is anticipated to result in a 50% increase in milk production in Ireland during the next decade (DAFF, 2010). The environmental consequences of increased stocking rates, slurry from the dairy herd and artificial fertiliser due to an increased need for effective grass grow on the farm to ensure supplementary feed needs to be assessed. While the growth of the dairy sector has the potential to contribute to the Irish economy, it is imperative that any increases in productivity are achieved in an environmentally sustainable manner and are matched by the highest standards of nutrient management practice on Irish dairy farms to protect the natural environment and to ensure at least good water quality status in the future as stipulated by the Nitrates Directive. However, it can be assumed that climate change will play an important role to the hydrological cycle in the future with changes to recharge, groundwater levels and flow processes including subsequent changes to groundwater quality (Brouyère et al., 2004). Local weather changes can result in reduced agronomic response to fertiliser application resulting in lower yields and greater N surpluses on farms (Derby et al., 2005). This can exacerbate the environmental impact due to agricultural activity in the future and makes it more difficult to achieve the targets of the agri-food sector.

At farm level, leaching of applied N to groundwater can occur from point sources such as farmyard storage or from diffuse chronic sources from soil or through incidental losses during or after application of fertilisers especially when this coincides with an episodic rainfall event (Basu et al., 2011; Brennan et al., 2012). However, not only the total amount of N application is relevant. Anthropogenic N occurs in many forms in groundwater such as NO_3^-, nitrite (NO_2^-), ammonium (NH_4^+) and organic N through leaching (Di and Cameron, 2002; Murphy et al., 2000). Different agronomic practices and the type of applied N have an impact of the likelihood and amount of leached N (Liu et al., 2013; Oenema et al., 2012). For example, inorganic N fertilisers are on the one hand immediately available for the plant, but on the other hand highly susceptible to leaching, whereas organic N fertiliser provide a more constant source of nitrate for the plant on a long term basis due to mineralisation processes (Di and Cameron, 2002; Thorburn et al., 2003; Whitehead, 1995). Di et al. (1998) emphasised that the application rate for organic and inorganic N fertiliser should be regulated differently according to their effects on NO_3^- leaching. In addition, best nutrient management practices can contribute to increased N use efficiency at farm level which directly implies reduced nitrate loss from surface to groundwater (Buckley and Carney, 2013; Oenema et al., 2005).

Up to date, in Ireland all potential N inputs at farm level are restricted by the Nitrates Directive (EC, 1991), which is Ireland's agricultural POM: organic and inorganic fertilizer rates of use, the time of spreading and their storage, cattle stocking rates (170 kg N per hectare or 250 kg N per hectare on derogation farms). The application time of inorganic fertilizers is limited to February until August, whereas the spreading times of organic fertilizers are restricted from February to September for slurry and from February to October for farmyard manure. The spreading of dirty water is allowed during times when there is no rain forecast within 48 hr of application and application rates must not exceed 50 m^3 ha^{-1}.

1.3 Nitrate distribution in karst areas

The impact of anthropogenic contamination to groundwater quality is complicated by the time lag of nutrient transport from source to receptor via hydrological and hydrogeological pathways (Fenton et al., 2011) and depends highly on the heterogeneity of the unsaturated and saturated zone and thickness of the overburden (Levison and Novakowski, 2009). Especially karst areas are known for their high heterogeneity, high vulnerability and fast groundwater flows (Bakalowicz, 2005). In addition, karst aquifers represent an important water resource as approx. 20-25% of the world´s population rely on drinking water obtained from karst aquifers (Ford and William, 2007). Compared to other hydrological areas, the interest and discussion about contaminant transport in karst aquifers is a relatively new development. Freeze and Cherry were the first pioneers of contaminant transport in the late 70s (Freeze and Cherry, 1979). Since then the understanding and knowledge increased, but open questions are remaining. In the 2000s, White (2002) stated that in karst aquifers processes and mechanisms for contaminant transport still needs to be specified.

Carboniferous limestones make up to 50% of the bedrock of the Irish Republic (GSI, 2000). These highly heterogeneous karst aquifers are the greatest water resources in Ireland and are influenced by intensive agriculture (Drew and Hötzl, 1999). Due to their high heterogeneity, rapid transport of NO_3^- in a time range of hours to days is likely in many karst systems during high rainfall events (Yang et al., 2013). This is especially worrying if groundwater of those systems is used as drinking water during times of high contamination. Karst specific infiltration possibilities (e.g. swallow holes) contribute to rapid contamination distribution (Ryan and Meiman, 1996).

NO_3^- is much more affected to sudden changes such as less mobile ions, e.g. phosphorus (P), due to its high solubility and mobility (Hem, 1992). To understand the processes, which are leading to sudden increases and decreases of NO_3^- concentrations in karst aquifers after a high rainfall event, high resolution monitoring is essential. Often, the methods used for high-resolution monitoring such as ion sensitive electrode (ISE) sensors are time consuming due to high calibration intervals and/or cost intensive on a long term basis (Bende-Michl and Hairsine, 2010). For the recent study, a spectrophotometric UV (ultraviolet) sensor has been installed at a karst spring to detect rapid changes of NO_3^- concentrations in 15 min intervals. This technology has been first applied in waste water treatment plants (Drolc and Vrtovšek, 2010; Langergraber et al., 2004) and recently in the field to assess NO_3^- concentrations at freshwater ecosystems such as rivers or karst springs discharging to surface water (Storey et al., 2011; Pu et al., 2011). UV/VIS (ultraviolet/visible) spectrophotometry gives the opportunity to observe trends and rapid changes of NO_3^- whilst using a methodology without reagents that requires less frequent calibration and maintenance than other common in-situ methods.

In addition to sudden changes of NO_3^- concentrations in heterogeneous environments, seasonal variations need to be considered. In Fig. 1-1 seasonal variations and the role of hydrologic conditions including low flow and high flow conditions, source availability and the consequences for mobilised NO_3^- response is illustrated. Bende-Michl et al. (2013) linked riverine NO_3^- responses with agricultural source availability throughout the year (e.g. time of inorganic and organic N fertilisation; NO_3^- build-up from organic matter in summer after organic N fertiliser application such as manure) and with hydrologic mobilisation due to high flow conditions in the Duck river catchment in north western Tasmania, Australia. Those processes can be transferred to other agricultural influenced catchments in temperate zones as well. Typically, during spring time inorganic N fertiliser and organic N fertiliser is applied on agricultural land for promoting better plant growth. In relation to organic N fertilisers, inorganic N fertilisers are much more affected to leaching directly after application (Di and Cameron, 2002). In combination with high flow conditions and rainfall events, that are typical for spring time, an increase of NO_3^- can occur in the catchment. During summer, low flow conditions are expected. In combination with higher temperatures that are increasing the mineralisation process of organic N fertilisers, i.e. manure, a build-up of NO_3^- source availability on the surface occurs. Animal manure is known to have a greater potential for leaching of N on a longterm basis in comparison to inorganic N fertilisers (Bergström and Kirchmann, 1999). Typically in autumn, the amount of rainfall increases, crop uptake decreased and a change from low to high flow conditions can be expected. Due to build-up of NO_3^- source availability, rapid mobilisation and delivery to the catchment as response to rainfall events takes place. After flushing of NO_3^- to the groundwater and a high NO_3^- response in the catchment, supply gets limited and NO_3^- response starts to decrease. If new source areas are connected due to expansion of the area during high flow conditions in winter, an increase in NO_3^- response is possible as well. To sum up, throughout the year higher peaks of NO_3^- concentration response should occur (1) during spring after inorganic fertiliser application, (2) during autumn because of increased mineralisation and nitrification processes of organic matter in summer and eventually (3) during winter due to possible expansion of the source area during high flow conditions.

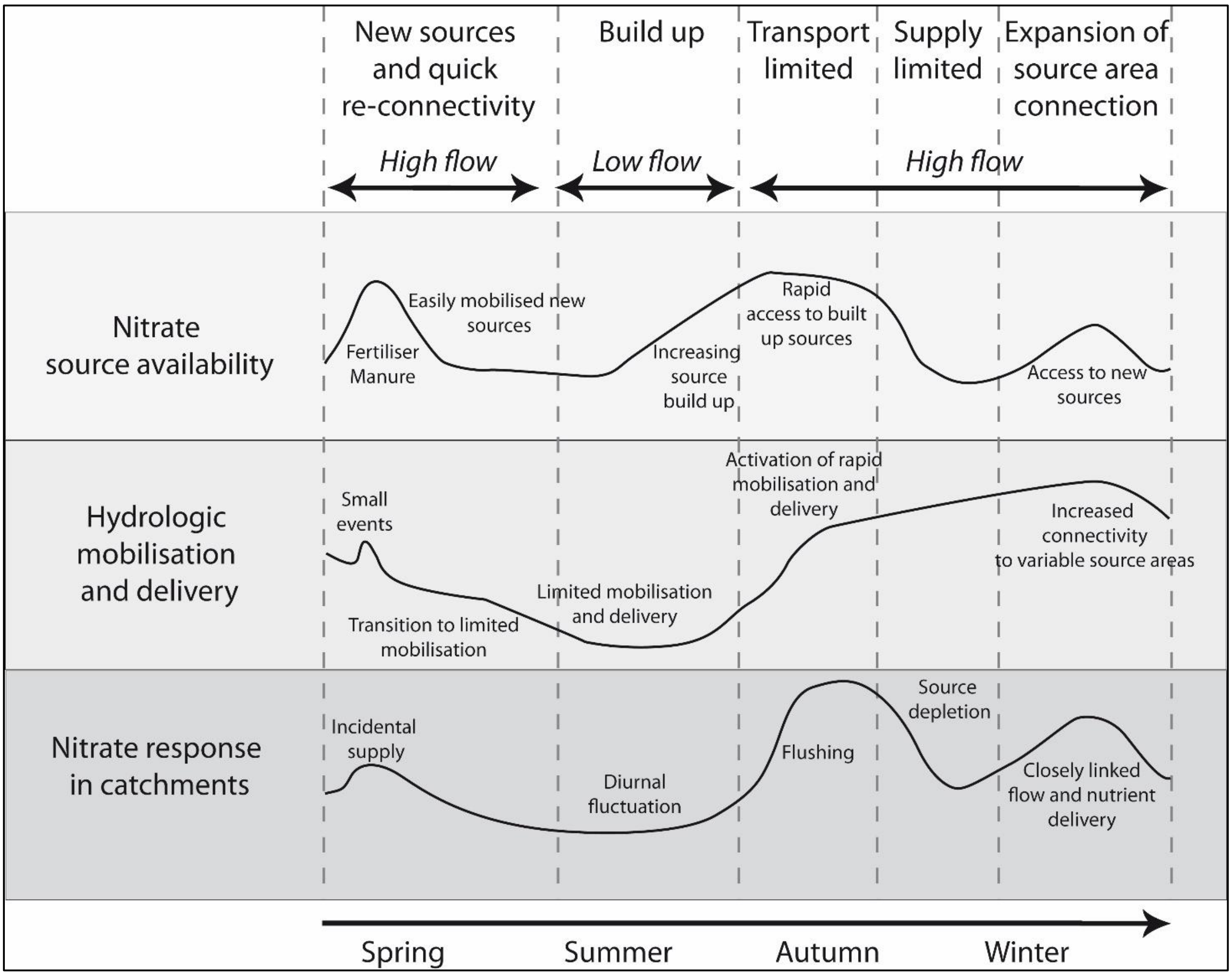

Fig. 1-1: Influences of high and low flow conditions and nitrate (NO_3^-) source availability on NO_3^- responses in catchments in temperate zones throughout the year (adapted from Bende-Michel et al. (2013))

1.4 Study sites

The PhD study focuses on two intensive dairy farms approximately 35 km north of Cork close to Fermoy, Co. Cork, Ireland (cf. Fig. 3-1 and Fig. 4-1, 8°15'W, 52°10'N). Locally these farms are known as Curtins farm and Dairygold farm. Curtins farm is 48.1 ha large. Dairygold farm has an average size of 110 ha with an agricultural farmed area of 97 ha. Both dairy farms are owned and used for research by Teagasc – The Agriculture and Food Development Authority. Teagasc focuses on research for innovations in the agricultural, agricultural derived food and environmental sector. On Curtins farm all agricultural activities are documented for each paddock together with monthly measured on-farm NO_3^- data in groundwater from 11 available boreholes. On Dairygold farm, on the one hand, N inputs are much less documented, but on the other hand, the occurrence of intermittent and permanent karst springs in combination with 6 on-site wells offer better conditions for hydrogeological monitoring of NO_3^- in groundwater.

The soil at Curtins farm (cf. chapter 3) consists of freely drained acid brown earth, derived from mixed sandstone-limestone glacial till, and has a thickness of up to 4.5 m (Kramers et al., 2009). On Dairygold farm (cf. chapter 4) the soil is composed of a relatively free draining till of loamy texture which thickness ranges from 4 to 12 m (Landig et al., 2011). Two different carboniferous limestone types occur at the study sites: the Ballysteen Formation and the Waulsortian Limestone, which both developed during the Variscan Orogeny (GSI, 2000). The Ballysteen Formations consists of a sequence of medium to dark grey, argillaceous, bioclastic limestones (Shearley, 1989). The Waulsortian Limestone overlays the Ballysteen Formation, has a light to dark grey colour and covers 1.7% of the land area of Ireland (Ryan et al., 2006). It is in general less bedded and more karstified than the Ballysteen Formation due to the occurrence of coalescenced massive calcareous mud-mounds and the much lower content of shale components **(**GSI, 2000**)**. A surface conductivity and resistivity geophysical survey, which has been previously carried out at Curtins farm (cf. Fig. 3-2), leads to the interpretation that conduits and/or larger cavities are expected on site. Similarly, at Dairygold farm, a cave with a diameter of around 2 m can be observed which acts as an intermittent spring. In total, 17 boreholes are in the two study areas. Tracer tests were used in the study to verify the connections between boreholes and one permanent spring. Bartley (2002) performed a tracer test with bromide (BH 7) and proofed connectivity between some boreholes on Curtins farm (BH 4, BH 5, BH 9 and BH 10, respectively; cf. Fig 3-1). During the current PhD study, a tracer test with uranine and two tracer tests with optical brightener were performed. To test the hydraulic connectivity to the aquifer, slug tests have been conducted on Dairgold farm. The analysis after Bouwer and Rice (1976) showed hydraulic conductivity (k_f) values ranging from 1x 10^{-6} to 2.5 x 10^{-7} m s^{-1}.

Short vertical travel times from N application to NO_3^- enrichment in groundwater are expected at the sites (Fenton et al., 2009a). In the past, NO_3^- concentrations close to and above the maximum allowable concentration of 50 mg L^{-1} determined by the Nitrates Directive were common in this area (Bartley, 2002; Landig, 2009). The two study sites in Southern Ireland represent an ideal test site for the assessment of NO_3^- distributions to high rainfall events because of the combination of intensive agronomic N loading on the surface, an underlying karst aquifer, that implies short vertical travel times, and hydrometeorological conditions that ensure rainfall events throughout the year.

1.5 Objectives

An interdisciplinary approach is needed to improve our knowledge of NO_3^- distributions as response to agronomic and hydrological drivers.

Specifically, one objectives of the PhD study is to relate changes in detailed agronomic N-loading, local weather conditions, hydrogeological and geological site characteristics with groundwater N occurrence over an 11 year period on an intensive dairy farm with free draining soils and a vulnerable limestone aquifer, whilst also considering time lag.

Secondly, one issue of this PhD study is to understand the key drivers controlling NO_3^- distributions in karst areas from soil surface to groundwater. To assess the key drivers that are leading to mobilisation and/or dilution processes. A conceptual model of possible scenarios of NO_3^- responses during storm events is formulated and for verification of this hypothesis other examples from the literature together with data from a study site monitored during the PhD period are used.

Thirdly, an investigation was made to assess and compare two different spectrophotometric sensors, i.e. a double wavelength spectrophotometer (DWS) and a multiple wavelength spectrophotometer (MWS) used at field sites in Ireland and Jordan, respectively. It is reasonable to conclude that high-resolution UV/VIS monitoring will greatly contribute to a better understanding of groundwater processes in the future and one achievement of this study is to provide a more detailed insight and practical support for the user. For comparison of the sensors the following issues are addressed: Hardware options, ease of calibration, accuracy, influence of additional substances, positive and negative aspects of the two sensors, troubleshooting and trade-offs.

In general, the results of the study can be used to guide and provide practical advice for environmental modellers, scientists, consultants, policy makers and drinking water managers. The results can contribute to an improved understanding of when and under what conditions NO_3^- is released to groundwater and fresh surface waters. In particular, as the Nitrates Directive is fully implemented on both study sites, the PhD study allows the assessment of the effect of present and future legislation implementation for critical NO_3^- occurrence in groundwater due to agronomic activity especially in vulnerable areas with respect to the current regulations.

2 Thesis structure

The actual thesis contains three individual studies that were conducted during the PhD period. All studies were submitted to ISI-listed journals. The studies are listed chronologically in this thesis. The first and second studies are already published. The last study is currently under review. The first study is published in Agriculture, Ecosystems and Environment (Impact Factor 2.859; 5-Year Impact Factor 3.673) and additional aspects are presented in the book 'Water Pollution XII' (ISBN 978-1-84564-776-6). The second study is published in Hydrology and Earth System Sciences (Impact Factor 3.587; 5-Year Impact Factor 3.984). The third study was submitted to special issue called ‘High resolution monitoring strategies for nutrients in groundwater and surface waters: big data jump in the future to assist EU Directives’ in Hydrology and Earth System Sciences (Impact Factor 3.587; 5-Year Impact Factor 3.984).

Study one (chapter 3) focuses on the impact of agronomic practices of a dairy farm on N concentrations in a karst aquifer. The study was conducted on Curtins farm in South Ireland. The study aims to relate changes in farm management, local weather conditions, hydrogeological and geological site characteristics with groundwater quality over an 11 year period on an intensive dairy farm with free draining soils and a vulnerable limestone aquifer, while also considering time lag from source to receptor.

In the second publication (chapter 4) mobilisation and/or dilution processes on NO_3^- concentrations in karst aquifer due to high rainfall events and their controlling key factors are discussed. This study was performed on Dairygold Farm in South Ireland. Collected high resolution field data (discharge, groundwater level variations in the boreholes and NO_3^- measurements) were used to determine typical NO_3^- pattern in karst spring during high rainfall events. In addition, a scientific hypothesis of possible scenarios in relation to NO_3^- responses due to high rainfall events was formulated and additional case studies from the literature were used to verify this hypothesis.

In the third study (chapter 5) two different in-situ spectrophotometers are compared that were used in the field to determine nitrate-nitrogen (NO_3-N) concentrations at two distinct spring discharge sites. One sensor is a double wavelength spectrophotometer (DWS) that was used for monitoring NO_3^- pattern at Dairygold Farm in South Ireland for the second publication. In this study, the DWS is compared with a multiple wavelength spectrophotometer (MWS) that was installed in a flowing spring emergence in Jordan. The objective of the study was to review the hardware options, determine ease of calibration, accuracy, influence of additional substances and to assess positive and negative aspects of the two sensors as well as troubleshooting and trade-offs.

3 Impact of agronomic practices on nitrogen concentrations in a karst aquifer

Reproduced from:

a) *Huebsch, M., Horan, B., Blum, P., Richards, K. G., Grant, J., and Fenton, O.: Impact of agronomic practices of an intensive dairy farm on nitrogen concentrations in a karst aquifer in Ireland, Agric. Ecosyst. Environ., 179, 187-199, http://dx.doi.org/10.1016/j.agee.2013.08.021, 2013.*

b) *Huebsch, M., Horan, B., Blum, P., Richards, K.G., Grant, J., and Fenton, O: Statistical analysis correlating changing agronomic practices with nitrate concentrations in a karst aquifer in Ireland, In: Water Pollution XII, Wessex Institute of Technology, UK, vol. 182, 1- 412, ISBN 978-1-84564-776-6, 2014.*

Abstract

Exploring the relationship between agricultural nitrogen loading on a dairy farm and groundwater reactive nitrogen concentration such as nitrate is particularly challenging in areas underlain by thin soils and karstified limestone aquifers. The objective of this study is to relate changes in detailed agronomic N-loading, local weather conditions, hydrogeological and geological site characteristics with groundwater N occurrence over an 11 year period on an intensive dairy farm with free draining soils and a vulnerable limestone aquifer. In addition, the concept of vertical time lag from source to receptor is considered. Statistical analysis used regression with automatic variable selection. Four scenarios were proposed to describe the relationships between paddock and groundwater wells using topographic and hydrogeological assumptions. Monitored nitrate concentrations in the studied limestone aquifer showed a general decrease in the observed time period (2002 – 2011). Statistical results showed that a combination of improved agronomic practices and site specific characteristics such as thicknesses of the soil and unsaturated zone together with hydrogeological connections of wells and local weather conditions such as rainfall, sunshine and soil moisture deficit were important explanatory variables for nitrate concentrations. Statistical results suggested that the following agronomic changes improved groundwater quality over the 11 year period: reductions in inorganic fertiliser usage, improvements in timing of slurry application, the movement of a dairy soiled water irrigator to less karstified areas of the farm and the usage of minimum cultivation reseeding on the farm. In many cases the explanatory variables of farm management practices tended to become more important after a 1 or 2 year time lag. Results indicated that the present approach can be used to elucidate the effect of farm management changes to groundwater quality and therefore the assessment of present and future legislation implementations.

3.1 Introduction

Global population growth is predicted to increase the demand for food by up to 100% by 2050 (Godfray et al., 2010). To meet the growing worldwide need for food, environmentally sustainable, economically viable and productive farming systems are required (Tilman et al., 2002). In Ireland, agriculture is dominated by dairy and beef cattle production from managed grassland (CSO, 2011). The European Union (EU) milk policy is due to change radically in 2015 with the abolition of farm level milk quotas and the ambitious target of a 50% increase in milk production by 2020 has been set in Ireland under the Food Harvest report (DAFF, 2010). Such targets for the agri-food sector must be achieved within current EU environmental legislation and will be further exacerbated by climate change such as an increase in precipitation during the winter time (Brouyère et al., 2004). The EU Water Framework Directive (WFD; OJEC, 2000) is a multi-part and multi-stage piece of legislation that aims, *inter alia*, to achieve at least “good” water quality status in all water bodies by 2015 with programmes of measures (POM) to achieve such a status implemented by 2012. In Ireland, the Nitrates Directive (EC, 2001) implemented since 2007 is Ireland’s agricultural POM. This Directive places restrictions on all potential N inputs into a farming system including: cattle stocking rates with a default of 170 kg N per ha^{-1} or 250 kg N per ha^{-1} on derogation farms (present study site), organic and inorganic fertiliser rates of use, the time of spreading and their storage. Closed periods are in place for spreading of inorganic fertiliser (September to January) and some organic slurry (October to January) and farmyard manure (November to January). Application of dairy soiled water (DSW) may occur provided there is no rain forecast within 48 hours of application and application rates must not exceed 50 m^3 ha^{-1}. In general, 59% of Ireland’s rivers, over 47% of the lakes, 64% of the estuaries and 85% of the groundwater are already at “good” to “high” ecological status (EPA, 2010). For areas where the targets of the WFD will not be achieved by 2015 further legislative steps may be taken in areas of non-compliance and this could reduce farm productivity or at least add to production costs in some circumstances (Dillon and Delaby, 2009).

Leaching of nitrogen (N) fluxes from an agricultural system to groundwater occur from point sources such as farmyard storage or from diffuse chronic sources from soil or through incidental losses during or after application of fertilisers especially when this coincides with an episodic rainfall event (Basu et al., 2011; Brennan et al., 2012). Once anthropogenic reactive N (N_r) is lost it cascades through the environment (Galloway and Cowling, 2002) and occurs in many forms in groundwater such as nitrate (NO_3^-), nitrite (NO_2^-) ammonium (NH_4^+) and organic N through leaching (Murphy et al., 2000). Stuart et al. (2011) indicate that leached losses could increase in future decades due to predicted changes in agricultural land use and precipitation as well as an increase in temperature and evapotranspiration in the UK. The assessment of the effect of weather variation such as rainfall intensity on NO_3^- leaching is complicated by the requirement for long term datasets of groundwater chemistry, farm management practices and meteorology (Randall and Vetsch, 2005). Local weather changes can result in reduced agronomic response to fertiliser application resulting in lower yields and greater nitrogen surpluses on farms (Derby et al., 2005). In addition, it can be assumed that climate change will play an important role to the hydrological cycle with changes to recharge, groundwater levels and flow processes including subsequent changes to groundwater quality (Brouyère et al., 2004).

Karst aquifers are an important water resource, which cover about 20% of the earth's dry ice-free surface and provide potable water for approximately 20-25% of the world's population (Ford and Williams, 2007). Although karst aquifers are very vulnerable in terms of water quality, the exploration, understanding and interpretation of karst aquifers is still rather challenging mainly due to fast groundwater flow velocities in the conduit systems (Goldscheider et al., 2007). Classical hydrogeological site investigations such as pumping test analysis and/or determination of groundwater isolines have a high potential for failure as the results often only reflect the specific (i.e. local) area that has been monitored and do not show the flow behavior of the entire study area (Bakalowicz, 2005). The characterisation of conduit systems has many complications such as spatial distribution of the conduits and temporally variable discharge (Goldscheider et al., 2008). To elucidate the shape and connections of shallow conduits, 2D and 3D geoelectric resistivity surveying (Hamdan et al., 2012) has been used as well as microgravity surveying in karst systems (Hickey, 2010).

Exploratory data analysis applied to groundwater NO_3^- data is an affective means of explaining spatial and temporal trends of NO_3^- in shallow groundwater (< 30 m) (Nas, 2009). Maximum likelihood Tobit regression analyses (sets a censored NO_3^- concentration e.g. background level and builds a model based on the significance of explanatory variables) has been used by many to investigate elevated NO_3^- concentrations in aquifer systems (Fenton et al., 2009b; Yen et al., 1996). Explanatory variables across these studies include but are not limited to: landuse around individual monitoring wells, distance of the monitoring well from potential point sources, saturated hydraulic conductivity (k_s) of screen intervals, screen interval depth, depth to top of aquifer, denitrification potential determined by groundwater di-nitrogen (N_2)/argon (Ar) ratios, redox potential, dissolved oxygen concentration and N_2. Other techniques such as logistic regression can predict the likelihood that a certain groundwater threshold concentration will be breached (Menció et al., 2011). This can also be used to find significant explanatory variables that explain spatial and temporal patterns of groundwater NO_3^- concentrations (e.g. well depth, geology and presence of a fracture network, nitrogen fertiliser loading, soil drainage class percentages, seasonality of water table position) (Nolan, 2001). Furthermore, Oenema et al. (2010) used multiple linear regression to evaluate the significance of different agricultural practices on NO_3^- groundwater occurrences in the Netherlands.

Many studies have been undertaken to help to define, develop and improve best management practices to achieve better groundwater quality worldwide (Zhang et al., 1996;Thorburn et al., 2003;Jalali, 2005). However, exploring relationships between farm management practices and groundwater water quality is further complicated due to time lags from source to receptor via hydrological and hydrogeological pathways (Wang et al., 2012). For Ireland, it is now clear that the achievement of WFD targets by 2015 may not be possible where time lags are too long (Fenton et al., 2011a). Such time lags depend on socio-economic factors such as the delay in implementing measures due to the costs and perception of farmers, soil/subsoil type, bedrock geology/hydrogeology and climatic factors such as rainfall (Stark and Richards, 2008) and should be estimated when attempting to relate agricultural management and groundwater quality (Meals et al., 2010). Farms present in areas of moderate to high recharge, with shallow free draining soils of low effective porosity (n_e), underlain by extremely vulnerable limestone aquifers typically have: 1) optimal conditions for grass growth which is needed for intensive dairy farming and 2) the shortest vertical travel times to groundwater (1-2 years on the current study site e.g. Fenton et al., 2009a). Therefore, such farms have the capacity to affect groundwater quality quickly through management change, but it is difficult to provide a tool for the prediction of time lag that has to be simple on the one hand and be reflective of a highly complex environment on the other.

To date there has been limited work relating long term farm management and local weather variation with NO_3^- concentrations in groundwater at farm scale, especially in highly vulnerable areas. The objective of this study is to relate changes in detailed agronomic N-loading, local weather conditions, hydrogeological and geological site characteristics with groundwater N occurrence over an 11 year period on an intensive dairy farm with free draining soils and a vulnerable limestone aquifer, whilst also considering time lag.

3.2 Materials and methods

3.2.1 Site description and characterisation

The intensive dairy farm study site (48.1 ha) at the Teagasc Dairy Production Centre, Fermoy, Co. Cork (8°15’W, 52°10’N) is located in a lowland limestone area in southern Ireland. The site is up-gradient of the Funshion River, close to a public water supply well and down-gradient of the large River Blackwater (Fig. 3-1). The perennial grassland farm is located on a limestone plateau with flat topography and negligible runoff. Two inferred groundwater divides are presented in Fig. 3-1, emanating from the juncture of the two rivers and intersecting the southern boundary of the site (Kelly and Motherway, 2000; Preston and Mills, 2002). The study site consists of 11 boreholes (BH 1-12, note BH 6 collapsed shortly after installation and was not suitable for this study) drilled at different stages since 2001 and are distributed across the entire farm (Fig. 3-1). Three wells (BH 4, BH 11, BH 12) are 150 mm diameter open boreholes and the remainder consist of a 50 mm diameter piezometer casing. Average drilling depth on site is 40.8 m (minimum depth of 22.0 m at BH 5 and maximum depth of 59.5 m at BH 3).

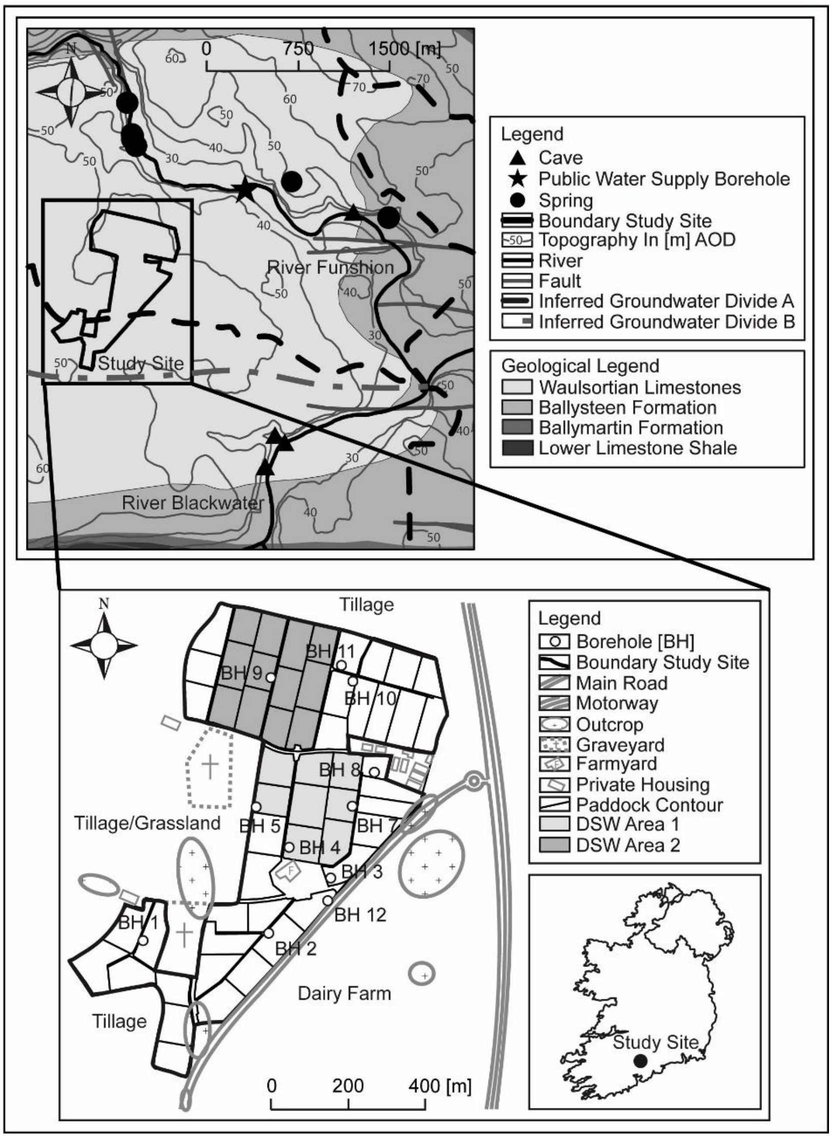

Fig. 3-1: Location and characteristics of the study site.

3.2.2 Soil and geology

The soil consists of a freely drained acid brown earth (Haplic cambisol), derived from mixed sandstone-limestone glacial till (Kramers et al., 2009). Soil thickness ranges from 0 to 4.5 m (Bartley and Johnston, 2006), which is underlain by a karstified Waulsortian limestone bedrock commonly occurring at an average of 2.5 m depth (Bartley, 2003). The A horizon of the soil consists of 53% sand, 31% silt, 16% clay with a dry bulk density of 1.1 g cm^{-3} and a total porosity of 52% (Kramers et al., 2009). This is confounded by limited preferential flow in the A-B soil horizons (Kramers et al., 2009). The Waulsortian Limestone covers 1.7% of the land area of Ireland (Ryan et al., 2006a) and is generally more karstified and less bedded than other limestone types (GSI, 2000) such as the Ballysteen Formation (Fig. 3-1). A land survey was carried out to determine the borehole surface elevation for comparing gathered water table depth of different boreholes with each other in metre above ordinance datum (AOD). Soil thickness, thickness of the epikarst, depth of unsaturated zone, k_s and connectivity between the borehole (open or piezometer casing) were gathered for each borehole based on drilling logs and data collected from Bartley (2003).

3.2.3 Hydrogeology and groundwater quality

On the study site a bromide tracer test was performed on the surface around BH 7 by Bartley (2003), which indicated a hydrogeological pathway from BH 7 to BH 5, BH 9, and BH 10 (Fig. 3-2). Depth from surface to groundwater was measured regularly (in total 72 times) between July 2001 and September 2003, sporadically between 2004 and 2011 and more intensively in May 2011 for a shorter time period. All well elevations were surveyed and depth to groundwater converted to hydraulic heads in metre AOD. Drilling logs, failed boreholes and resistivity profiles indicate the abundance of dry locations in the farm subsurface up to a depth of 50 m (Fig. 3-2). This indicates the possibility that the observed heads do not represent a true water table, but rather heads in discrete conduits and fractures. Thus, a conduit flow hypothesis is supported, in which the conduits dominate the flow with the existence of a perched water table at discrete locations. To determine nitrogen concentrations in groundwater on the study site, a farm-scale hydrogeological investigation was established in 2001, which also included monthly NO_3^- measurements in groundwater starting in 2002. Briefly, after purging the previous day, a Grundfoss pump was used to collect 100 ml of groundwater. The samples were filtered immediately, using a 0.45 µm micropore membrane filter, transferred to polyethylene screw top bottles, and frozen prior to chemical analysis. Analysis of groundwater quality followed the standard procedures such as described of Jahangir et al. (2012a). For the present study NO_3^-, NO_2^-, NH_4^+ and total oxidized nitrogen (TON) were taken into account.

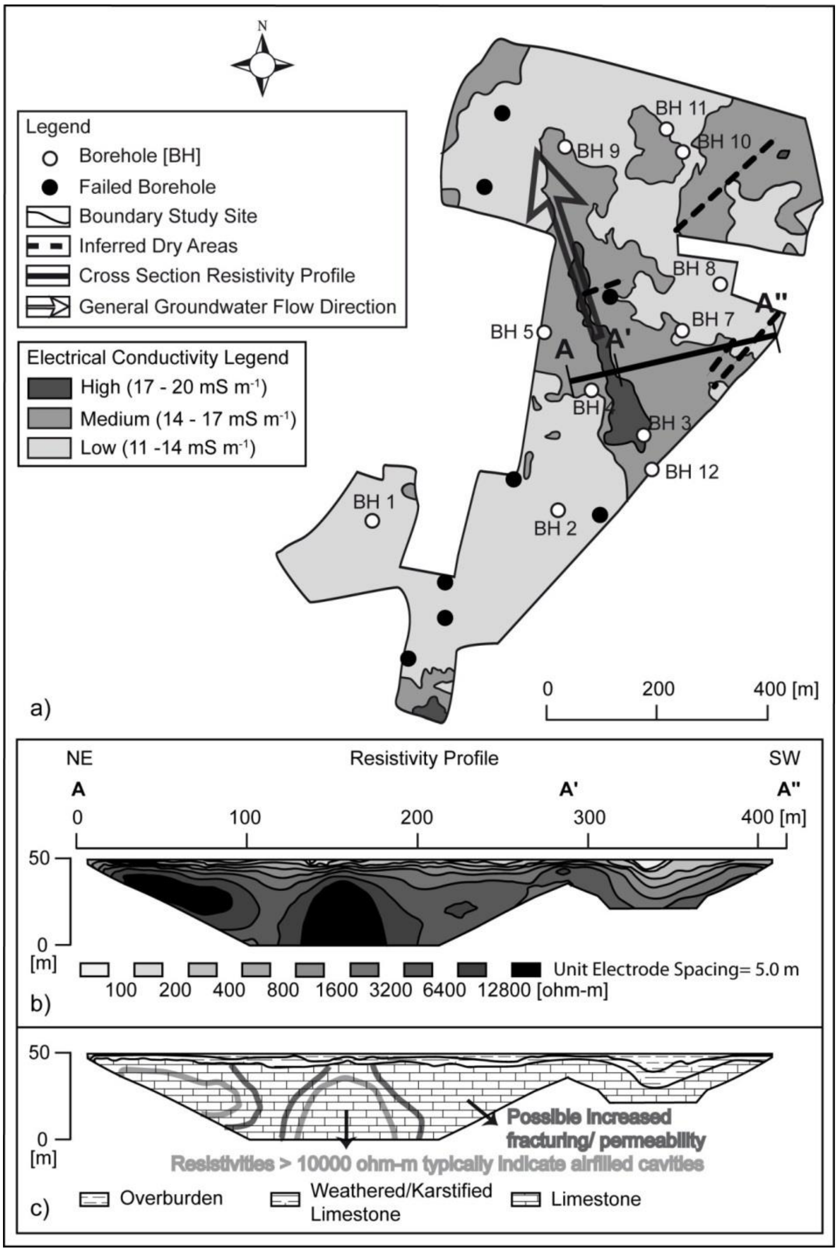

Fig. 3-2: Surface conductivity map on the study site including resistivity profile, groundwater flow direction trend and dry areas. A) Electrical conductivity on the study site with information of dry areas and general groundwater flow direction. B) Resistivity profile. C) Geological interpretation of resistivity profile.

3.2.4 Geophysical survey

Surface conductivity (to 6 m depth) and resistivity (to 50 m depth) geophysical surveys (Apex Geoservices) of the farm were carried out to ascertain lateral and vertical variations in overburden material, depth to bedrock and bedrock lithology (Fig. 3-2).Three electrical conductivity (EC) intervals from low (11-14 mS m^{-1}) to high (17-20 mS m^{-1}) were observed at the site (Fig. 3-2). High EC interpret collapse structures that are filled with finer materials such as silt or clay due to the karstified underground (Fig. 3-2). Using this information an elongated conduit system trending north-west to south-east is inferred in the middle of the farm. Furthermore, a resistivity profile (A-B, Fig. 3-2) shows that bedrock is affected by karst features such as conduits, air-filled cavities and increased fracturing in the middle of the farm and general groundwater flow direction is also influenced by this conduit system (Fig. 3-2).

3.2.5 Local weather conditions

The studied local weather data consists of daily measurements of average, minimum and maximum air temperature, total solar radiation and daily rainfall, which were recorded at the experimental site during the entire study period. Daily meteorological input parameters (rainfall, air temperature and sunshine hours) were inputted into the hybrid model for Irish grasslands of Schulte et al. (2005) to elucidate daily soil moisture deficit (SMD), actual evapotranspiration and effective drainage (ED).

3.2.6 N loss

Nitrogen (N) loss (kg ha^{-1}) was determined annually by multiplying the average NO_3-N concentrations (mg L^{-1}) with ED (mm) as used in previous studies (e.g. Hooker et al., 2008).

3.2.7 Agronomy

A total of 48.1 ha of permanent grassland containing greater than 80% of perennial ryegrass (*Lolium perenne*) and grazed exclusively by dairy cattle were used for this study. The experimental site was used to compare diverse animal genotypes and nutritional treatments during the 10 year evaluation period (Coleman et al., 2008; Horan et al., 2004; McCarthy et al., 2012). In all experiments, a rotational grazing management system was practiced usually commencing in early February and concluding in late November each year. The frequency and intensity of grazing was recorded as the number of grazing days per hectare per month for each paddock. In the winter months between late November and early February, all animals were housed and all animal slurry was collected and stored. During periods of excessive rainfall during the grazing season, animals were occasionally housed and on-off grazing (Kennedy et al., 2009) was used as a management tool to facilitate grazing and to avoid soil structural damage. The N surplus at the paddock level can be calculated as proposed by Farrugia et al. (1997). The N surplus takes account of the total N inputs on the field (i.e. fertiliser, concentrates, symbiotic fixation, atmospheric decomposition) and total output (i.e. mild, harvested forage and slurry). The internal N flows are not taken into account in the calculation of N surplus at the paddock level. The overall N efficiency at the paddock level is largely driven by N inputs (mainly chemical fertiliser and concentrate input) and only moderately affected by the efficiency of feed utilisation by the herd. Best nutrient management practices have been applied on the farm in recent years with an increased focus since 2008 due to the implementation of the Nitrates Directive in 2007 to increase slurry use efficiency and reduce fertiliser N application to the levels stipulated under Statutory Instruments. All animal slurry generated from dairy cattle on site during winter was reapplied to the land area during the following grazing season. The total N inputs at the paddock level (weighted on the basis of paddock size) in the form of both inorganic and organic fertilisers and slurry were monthly recorded during the study, while off-takes of harvested grass for silage conservation were deducted. The volumes of slurry and DSW applied to each paddock were recorded and the N content of slurry (3350 mg N L^{-1}) and DSW (578 mg N L^{-1}) was reported previously by Ryan et al. (2006b) from the same site. A centre pivot DSW irrigation system was operated on site to reapply dairy yard washings. In 2006 the area used for DSW irrigation was changed from the highly vulnerable middle area (10 ha) to the north-western area (22 ha) of the farm (Fig. 3-1). The total N irrigated as DSW is known for the years 2002, 2003 and 2004, because of N leaching studies of Ryan et al. (2006b) during that time where total N in DSW ranged from 20.0 to 823.0 mg L^{-1} and the amount of N applied ranged from 0.5 to 84.7 kg ha^{-1}. The amount of DSW ranged from 0.3 m^3 ha^{-1} to 241.3 m^3 ha^{-1}. Approximately, 15% of the total farm area was reseeded annually from 2006 to 2011. In 2006 and 2007, seedbed preparation for reseeding was achieved by inversion ploughing. However, this practice was discontinued and replaced by minimum tilling cultivation techniques from 2008 onwards.

3.2.8 Conceptual site model

By combining the aforementioned collected data, a conceptual site model was developed and is illustrated in Fig. 3-3. The most vulnerable part of the site is north of the groundwater divide in the central paddocks of the farm (Fig. 3-2). Short unsaturated zone travel times to groundwater are driven by high ED and thin soil. Soil NO_3^- resulting from inorganic/organic fertilisation, grazing animal urine/dung returns, soil mineralisation and atmospheric N deposition can rapidly migrate along a well-connected conduit system to down gradient receptors. Large cavities in the karstified rock are known, but connectivity to the larger conduit system can be low, which is known because of the long recovery duration of the aquifer after pumping at BH 4.

3.2.9 GIS applications

A spatial analysis of the farm was carried out by using GIS applications. Total agronomic N inputs on the surface were compared on paddock level with NO_3^- occurrences in all wells on a yearly basis as well as for the whole period.

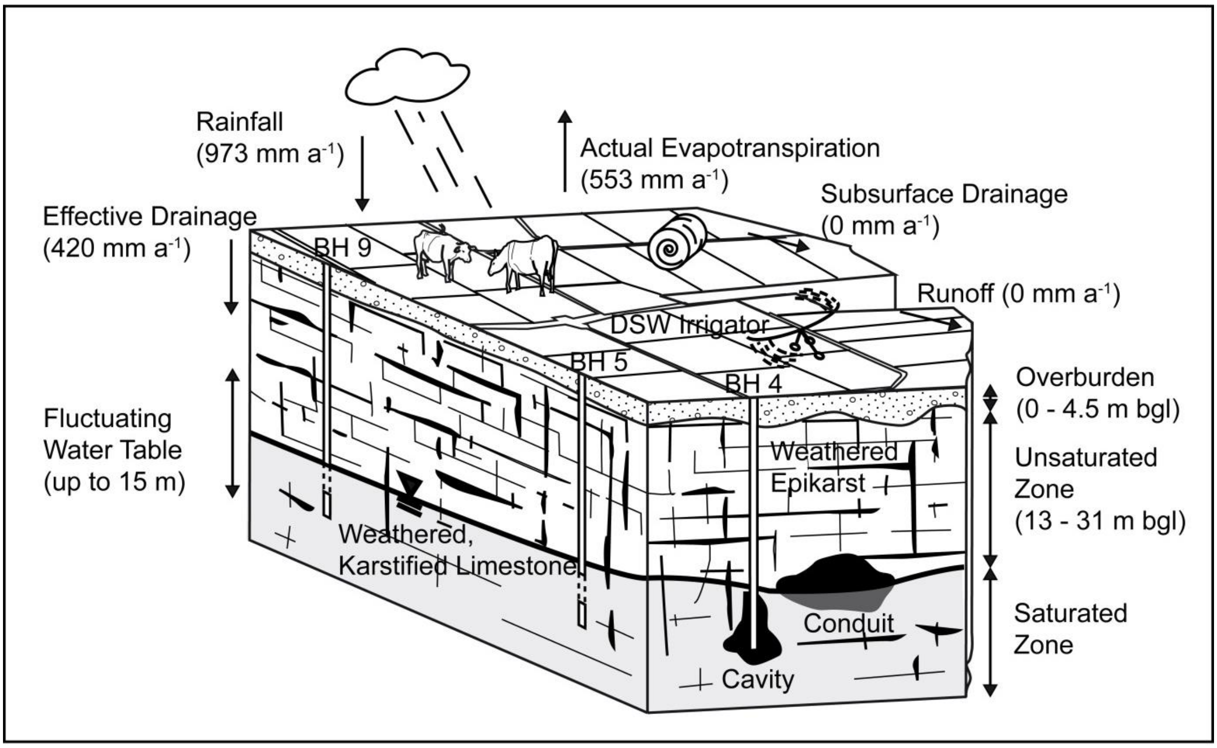

Fig. 3-3: Conceptual site model using data from 2005 as an example.

3.2.10 Statistical analysis

3.2.10.1 Descriptive analysis

Mixed models (Proc Mixed, SAS Institute, 2006) of repeated measures as used by Philibert et al. (2012) were carried out to determine the effect of month and year on climatic and groundwater quality data with month included as a repeated effect within borehole. A compound symmetry covariance structure among records within borehole provided the best fit to the data and Tukey's test was used to determine differences between treatment means.

3.2.10.2 Regression analysis

Relationships between groundwater quality data such as NO_3^-, TON, NO_2^- and NH_4^+ (Table 3-1) as response variables and the possible explanatory variables in the overall dataset (Table 3-2), which are related to previous sections, were explored by regression using automatic variable selection. As the agronomic inputs (e.g. slurry application in kg N ha^{-1}) and outputs (e.g. silage harvest in kg N ha^{-1}) for the paddocks were available on an annual basis, the monthly measurements and records were summarised for the analysis. The variables were modelled using Normal distribution based multiple linear regression except for the response variables NO_2^- and NH_4^+ (Table 3-1) as NO_2^- and NH_4^+ observations were heavily censored below the detection limit. Therefore, for NO_2^- and NH_4^+ a count of detections was used in a logistic regression based on the proportion of detections observed. To assess evidence of time lag, the explanatory variables (Table 3-2) were lagged from 0 to 3 years (based on the proposed time lag of 1 to 2 years for this site by Fenton et al., 2009a) and the effect on variable selection was explored. The size of F and Wald statistics was used for the interpretation of relative importance in explanatory variables (Table 3-2) influencing groundwater quality (Table 3-1).

For NO_3^-, TON and NH_4^+ (Table 3-1) two approaches were taken: 1) Differentiation between years and 2) Bulk period assumption (Fig. 3-4). The first approach included fitting year as a factor in the statistical analysis, effectively examining processes within year. This allowed a broad assessment of the extent to which the measured explanatory variables in the data set (Table 3-2) were sufficient to describe the overall processes. The second approach provided an approximation to the best description of the constant processes such as water table deviations or surface conductivity that was possible with the information available. Without year as a factor all changes over the period of investigation have to be 'explained' explicitly by the statistical outcome including the first approach (differentiation between years). As a consequence of numerical difficulties with the data for NO_2^- only the first approach without year as a factor was reliable and therefore used for evaluation. Goodness of fit statistics (R^2) was calculated using the reduction in residual variance between a model with intercept only and the full fitted model.

Four scenarios were proposed for the statistical analysis (Fig. 3-4). Each scenario defined sets of paddocks for each borehole that were likely to contribute to the observed responses. The different scenarios were based on topographic assumptions (e.g. concentric distribution of paddocks around the borehole; Fig. 3-1) and the hydrogeological assumptions on groundwater pathways from an on-site tracer experiment (Bartley, 2003). The difference between the four scenarios is illustrated in Figure 3-5 taking BH 9 as an example. In general, for scenario 2 a smaller catchment area with 25 paddocks was taken into account compared to scenario 4 where the greater catchment area included 34 paddocks. In addition to the proposed scenarios, a possible time lag of 0 to 3 years was considered (Fig. 3-4). Thus, 84 cases were evaluated for the statistical analysis.

Tab. 3-1: Total number of samples, standard deviation, mean, median, minimum and maximum groundwater nitrogen concentrations (mg L^{-1}) including the detection limit of the laboratory method used during the study period (2002 to 2011).

N species concentration (mg L^{-1})	Total No. of Samples	Standard Deviation	Mean	Median	Minimum	Maximum	Detection limit§
NO_3-N	694	6.1	11.6	11.2	≤ 0.02	59.0	0.02
NO_2-N	694	0.1	0.1	≤ 0.002	≤ 0.002	1.9	0.002
NH_4-N	656	0.9	0.3	≤ 0.02	≤ 0.02	11.0	0.02

§ Laboratory method detection limits for the varying nitrogen species quantified.

Tab. 3-2: Explanatory variables used for regression analysis at farm scale.

Topic	Explanatory variable	Explanation	Range
Local weather conditions	rainfall	Monthly rainfall in [mm]	3.5 – 259.5
	EFFrainfrd	Effective drainage calculated after Schulte et al. (2005) for free drained soil in [mm month^{-1}]	0.0 – 233.2
	temp	Monthly mean temperature in [°C]	0.6 – 17.4
	sunshine	Monthly cumulative sunshine hours in [hr]	23.7 – 243.4
	SMDfrdTOT	Monthly cumulative soil moisture deficit in [mm]	1.5 – 2251.2
	SMDfrdAVER	Monthly average soil moisture deficit in [mm]	0.0 – 72.6
	SMDfrdMAX	Monthly maximum soil moisture deficit in [mm]	0.5 – 82.3
Agriculture	reseeded	Reseeding status during the study period (no reseeding = 0; ploughing and reseeding = 1; minimum-tillage reseeding = 2)	0 – 2
	fertiliser	Yearly fertiliser application in [kg N ha^{-1}] per paddock	0 – 420
	slurry	Yearly slurry application in [kg N ha^{-1}] per paddock	0 – 282
	DSW	Yearly mean irrigation of dairy soiled water in [kg N ha^{-1}] estimated from observations of Ryan et al. (2006b) per paddock (no irrigation = 0; irrigation = 67)	0 – 67
	silageNremov	Amount of N removed because of silage harvest on the paddock in [kg N ha^{-1}]	0 – 210
	totN	Total N application (fertiliser, slurry and dairy soiled water less silage harvest) in [kg N ha^{-1}]	0 – 459
	grazingd	Yearly grazing days per [ha]	5.8 – 32.4
(Hydro-)geology	zAOD	End of well in [m] above ordinance datum (AOD)	-5.9 – 21.5
	zbgl	Total depth of each well below ground level in [m]	33.0 – 59.5
	grelevAOD	Ground elevation on the surface at each well in [m] AOD	52.2 – 56.0
	toprockAOD	First rock appearance in well in [m] AOD	49.6 – 54.0
	soilthick	Soil thickness at each well in [m]	2.0 – 4.0
	epikthick	Thickness of epikarst at each well in [m]	30.5 – 57.0
	soilrockthickWT	Thickness of soil and epikarst to the water table at each well in [m]	20.6 – 28.5
	screentopelev	Top of screen in well with piezometer casing in [m] AOD	22.2 – 27.5
	screenbottomelev	Bottom of screen in well with piezometer casing in [m] AOD	18.2 – 24.5
	piezoropen	Open well or well with piezometer casing (p = piezometer; o = open well)	
	maxwtableAOD	Maximum water table above ordinance datum in [m] taken from 72 measurements between 2001 and 2003 after Bartley (2003)	25.1 – 26.1
	minwtableAOD	Minimum water table rise above ordinance datum in [m] taken from 72 measurements between 2001 and 2003 after Bartley (2003)	29.5 – 41.1
	wtablerange	Range of water table deviation in [m]	4.0 – 15.0
	kf	Hydraulic conductivity in [m day^{-1}] after Bartley (2003)	0.004 – 27.0
	kfrange	Defined zones with low, medium, high hydraulic conductivity (K_f) (K_f low = 1; K_f medium = 2; K_f high = 3)	1 – 3
	geophysmSm	Surface conductivity at each well in [mS m^{-1}]	11.5 – 16.0
	geopysKAT	Defined zones with low, medium, high surface conductivity at each well (low conductivity = 1; medium conductivity = 2; high conductivity = 3)	1 – 3

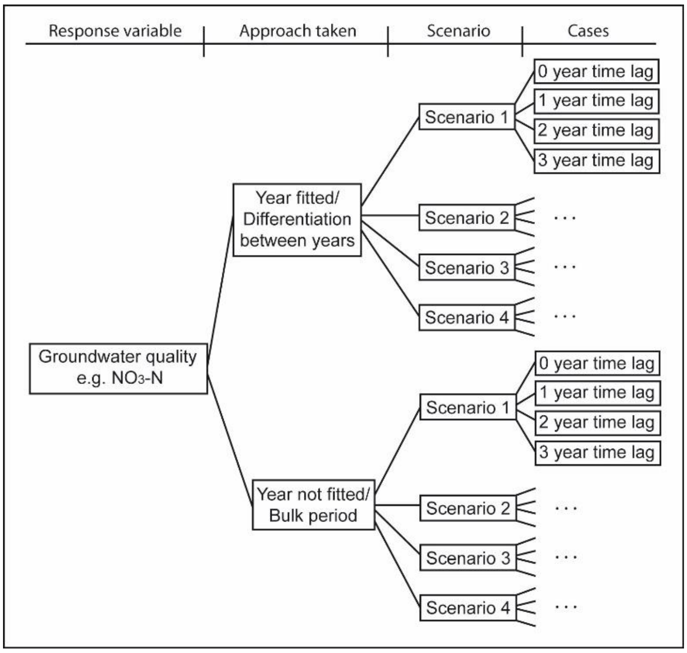

Fig. 3-4: Organisational chart of the regression analysis.

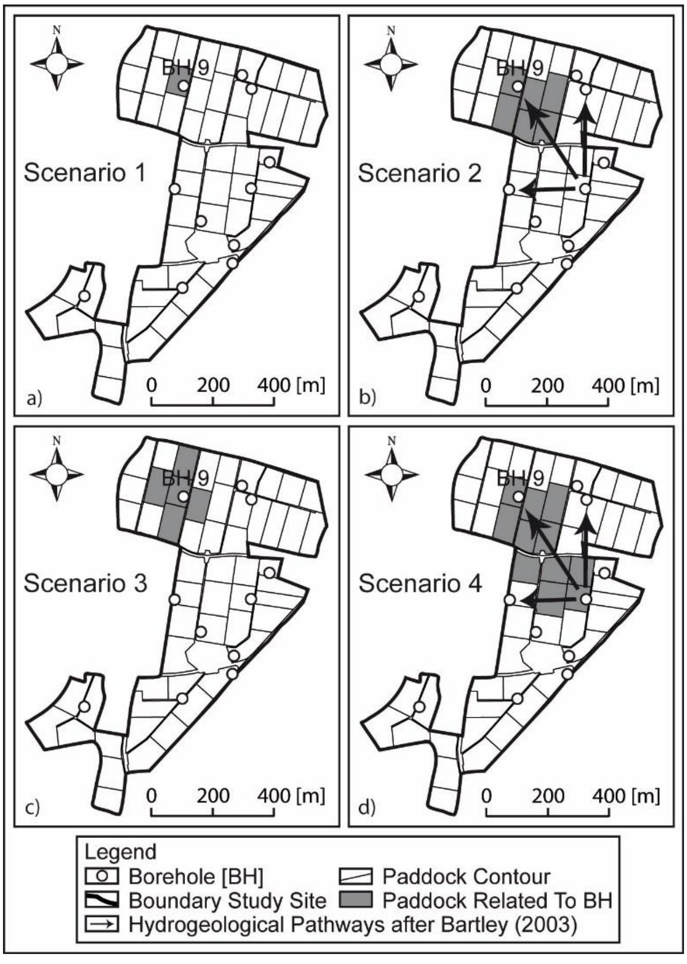

Fig. 3-5: Paddock to borehole relationship of scenario 1 to 4 as used in the regression analysis taking BH 9 as an example. a) One paddock associated with a borehole within this paddock. B) The assumption of paddock to borehole relationship was made using a small catchment area (25 paddocks for all boreholes) by reverting to the known hydrogeological pathways from a tracer experiment (Bartley, 2003) and the general groundwater flow direction towards northeast c)

Topographic assumption using concentric relationships. D) Same assumptions were taken as in b) but with a greater catchment area (34 paddocks for all boreholes).

3.3 Results

3.3.1 Local weather conditions

Mean monthly rainfall and ED data for 11 years (2001-2011) and the 30 year average (1982-2011) are presented in Table 3-3. Weather conditions varied considerably between years during the study period. Rainfall averaged 996 mm over the 11 year period, whereas the 30 year average was 1022 mm. Over the 11 year period, the highest monthly rainfall and ED was recorded in November (115 and 89 mm, respectively) while February (61 and 38 mm, respectively) and April (61 and 18 mm, respectively) had the lowest monthly rainfall and ED. From the 30 year average data, rainfall was highest in October (112 mm) including 70 mm ED and lowest in July (64 mm) including 9 mm ED. Mean monthly ED was 39.9 mm during the study and was highest in 2002 and 2009 (63.9 and 57.0 mm, respectively) and lowest during 2010 and 2011 (27.9 and 26.6 mm, respectively).

Tab. 3-3: Mean monthly rainfall and effective drainage for the study site during the study period (2001 to 2011) compared to the 30 year average.

	Rainfall (mm)		Effective drainage (mm)	
Month	30 year average	2001 – 2011	30 year average	2001 – 2011
January	111	109	90	89
February	79	61	57	38
March	83	79	48	39
April	67	61	27	18
May	65	78	15	19
June	71	75	13	10
July	65	86	9	19
August	86	69	27	23
September	75	74	26	13
October	113	108	72	62
November	105	115	80	89
December	101	81	80	59
Total Annual	1,021	996	544	478

3.3.2 Agronomy (2001 – 2011)

A broad characterisation of farming practices derived from farm inputs and outputs at the experimental site during the study period is outlined in Table 3-4. A Code of Good Agricultural Practice to Protect Waters from Pollution by Nitrates gave guidance and advice to farmers up to 2007 (Anon, 1996). This changed in 2007 when the Nitrates Directive was implemented in Ireland, which was subsequently taken as Ireland's agricultural POM under the EU WFD. Proposing a time lag effect of 1 year on the present site, management changes coupled with ED in subsequent years changed the overall NO_3^- trends on the farm (Fig. 3-6). During the 11 year study period, the overall dairy herd size increased from 108 to 138 dairy cows (equivalent to a stocking rate increase of 28%). Grazing season length was increased from 231 days in 2001 to highs of 295 and 306 days in 2005 and 2007, respectively. From 2002 this figure was always greater than 272 days and is presently maintained at greater than 280 since 2009. Fertiliser N was reduced to comply with the nitrates regulations introduced in Ireland in 2007, while feed N input was also reduced based upon experimental requirements. The overall reduction in fertiliser and feed N use and increased overall farm stocking rate was achieved by increasing organic fertiliser application during spring to replace inorganic N application and by increasing grazed grass utilisation at the experimental site. As a consequence of the overall increase in herd size, both milk and milk fat plus protein production increased during the study. Table 3-4 also shows the farm gate surplus and N use efficiency during the study period. The N surplus and N use efficiency at the paddock level was least favourable in 2001 (260 kg and 22.4%) and 2005 (275 kg and 25.4%) and most favourable in 2008 (174 kg and 34.8%) and 2011 (174 kg and 36.0%). The N surplus per ton of fat plus protein produced per hectare consequently declined from 279 kg N in 2001 to 136 kg N in 2011.

Tab. 3-4: Farm system characteristics at the study site (2001 to 2011).

Year	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011
Experimental cow (No.)	108	117	117	117	126	126	128	140	138	138	138
Stocking rate (cows ha^{-1})	2.25	2.44	2.44	2.44	2.63	2.63	2.67	2.92	2.88	2.88	2.88
Grazing season (days)	231	272	293	291	295	273	306	301	287	282	285
N inputs (kg ha^{-1})											
Fertiliser	294	294	289	296	331	259	313	244	248	252	249
Feed	41	41	39	35	37	40	20	23	29	36	25
Total	335	335	328	331	368	299	333	267	277	288	274
N exports (kg ha^{-1})											
Total	75	88	92	93	93	91	89	93	92	96	98
N balance											
Surplus (kg ha^{-1})	260	247	236	238	275	208	244	174	180	180	174
N-use efficiency (%)	22.4	26.2	28.0	28.1	25.4	30.5	26.7	34.8	33.9	34.9	36.0
N-use efficiency per ton fat plus protein produced per ha (%)	279	222	204	198	227	175	216	148	153	142	136
Milk production											
Milk volume ('000 L ha^{-1})	12.4	14.6	15.6	15.5	15.5	15.5	14.6	14.6	14.4	15.5	15.3
Fat plus protein (tons ha^{-1})	0.93	1.11	1.16	1.20	1.21	1.19	1.13	1.18	1.18	1.27	1.28

3.3.3 Groundwater quality trends

From 2002-2011, the combined application of DSW, slurry and chemical fertiliser was relatively consistent including reductions after the implementation of the Nitrates Directive in 2007 (Fig. 3-6). Concentrations of NO_3^- in groundwater were highly variable throughout the study, but were typically greatest during autumn and early winter. In addition, some very high NO_3^- concentrations (up to 59 mg NO_3-N L^{-1}) occurred close to two boreholes (BH 7 and

BH 8) in the middle of the farm in 2002 when the DSW irrigator was placed in this highly vulnerable area (Fig. 3-1, Fig. 3-2). In the present study, on average, groundwater NO_3-N concentrations across the farm declined over the study from 16.0 mg L^{-1} in 2002 to 7.3 mg L^{-1} during 2010 with a low of 6.6 mg L^{-1} in 2011 (Fig. 3-6). The overall mean concentration of NO_3-N were similar or exceeded the maximum allowable concentration (MAC) in groundwater defined by the WFD in Ireland (11.3 mg NO_3-N L^{-1}) during the first 7 years of the study and declined below the MAC for the last 3 years of the study period (2009, 2010 and 2011).

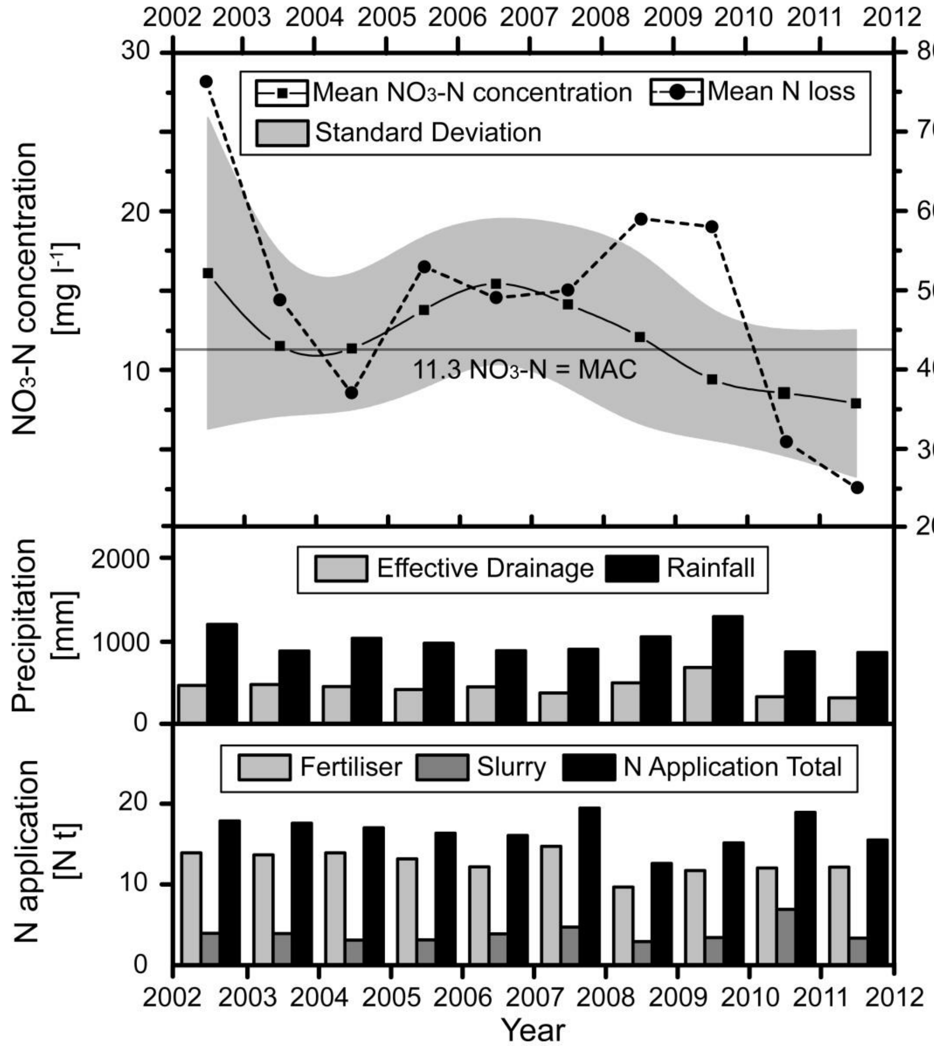

Fig. 3-6: Mean NO_3-N concentrations determined from all boreholes, mean N-loss derived from NO_3-N concentrations and effective drainage, precipitation and total N application per year during the study period. The data concerning NO_3-N concentrations refers to the left y-axis whereas the data for N loss is related to the right y-axis in the first part of the diagram. In 2010 additional slurry application was to replace DSW applications due to a dysfunctional DSW irrigator system.

3.3.4 N loss

The estimated N loss decreased in the study period in total with the maximum value of 76 kg ha^{-1} in 2002 and the minimum value of 25 kg ha^{-1} in 2011 including a deviation between

2005 and 2009, when mean N loss ranged from 49 to 58 kg ha^{-1} (Fig. 3-6). In 2002 high N losses were related to high NO_3-N concentrations in groundwater in addition to high ED. After the decrease of N losses in 2004 and 2005, N losses increased from 2005 to 2009. The increased N losses between 2005 and 2006 referred to high NO_3-N concentrations and medium ED. In 2007 N losses were related to high NO_3-N concentrations and the lowest ED of the study period, whereas in the following two years N losses referred to medium (in 2008) and high (in 2009) ED coupled with already decreasing NO_3-N concentrations. From 2010 to 2011 ED was low and NO_3-N concentrations were under MAC ensuring lower N losses than previous years.

3.3.5 Spatial analysis

The spatial analysis of the farm by using GIS applications brought no obvious relationships between N application per paddock, soil concentration and NO_3-N concentration. Fig. 4 illustrates the different N distributions for 2004. Areas with medium to high N input e.g. on the south western corner had NO_3-N concentrations below MAC during that year. Whereas in the middle of the farm lower N inputs were applied and NO_3-N concentrations were above MAC.

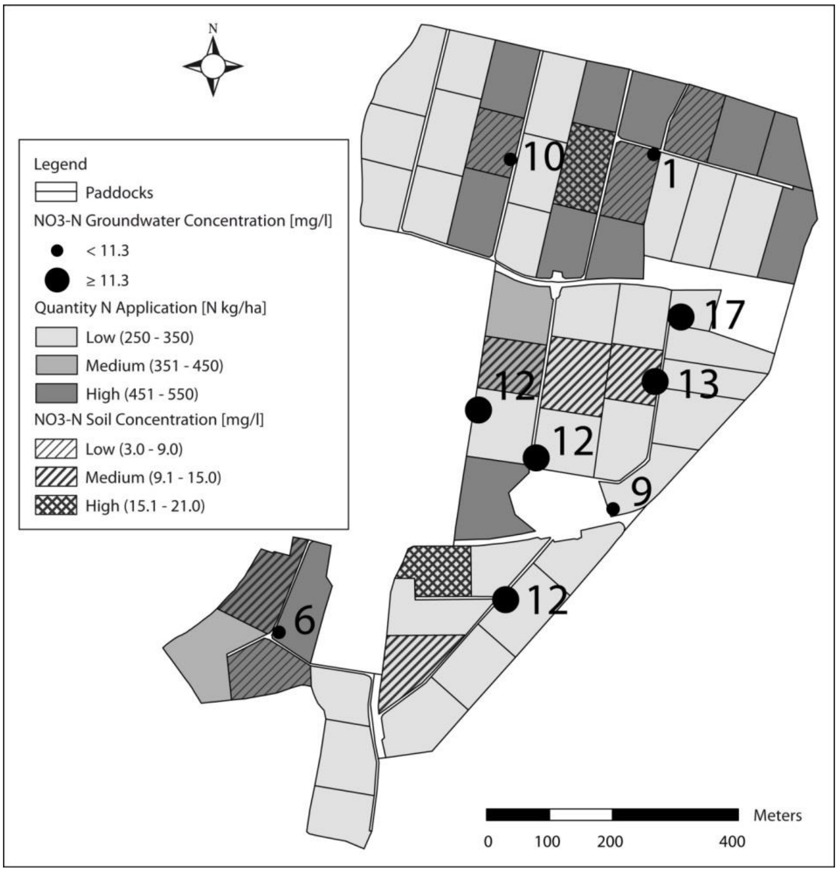

Fig. 3-7: Example of GIS analysis for 2004 taken total N input on paddock level, NO_3-N concentration in soil observed by Ryan et al. (2006b) and mean monthly NO_3-N concentrations in the boreholes into account.

3.3.6 Statistical analysis

The scenarios created for NO_3^- and TON using Normal-based regression with automatic selection had a range of R^2 from 0.43 to 0.79. Best results were achieved for NO_3^- from scenario 1 (Fig. 3-5). In this case the R^2 ranged from 0.68 to 0.75 including a slightly better result with year fitted as a factor than for selections with year not fitted (Fig. 3-4). For NO_2^- and NH_4^+ the model selections for the logistic regressions were likely to be liberal as there were technical difficulties in fitting a repeated measures structure to the limited, year-averaged dataset.

Comparing scenarios 1 to 4 (Fig. 3-5) for NO_3^- with each other, scenario 1 seems to give the most interesting results from a climatic, geological and agronomic perspective. The F statistic indicates that the main factors influencing NO_3^- concentrations in groundwater were soil and rock thickness in the unsaturated zone to the top of the water table and the connections of the boreholes especially those already known by the tracer test of Bartley (2003) (BH 7, BH 8, BH 9 and BH 10). Other factors showing an effect on NO_3^- concentrations in groundwater were borehole type (closed piezometer casing or open borehole), SMD, sunshine, year, the different intensity of karst features on the study site indicated by the geophysical survey, fertiliser, grazing days, silage and slurry.

For TON, the R^2 values are slightly lower than in the NO_3^- scenarios ranging from 0.43 to 0.75 for the year fitted cases and from 0.40 to 0.74 for the year not fitted cases (Fig. 3-4). The results with the highest R^2 values were achieved for the year fitted cases for scenario 1, 3 and 4. Scenario 2 seemed to have less predictive potential compared to the other scenarios (Fig. 3-5). The statistical outcomes for TON data were similar to the NO_3^- outcome as well. The explanatory variables for local weather conditions (Table 3-2) such as sunshine and SMD showed a significant influence together with geological settings such as thickness of soil and epikarst in the unsaturated zone to the water table. Farm management practices appeared to be associated with a 1 and 2 year time lag. These practices included fertiliser application and grazing days if year was included, silage if not and slurry for year and year not fitted.

For NO_2^- and NH_4^+ no single variable was most descriptive as the relative importance of the variables was similar, as indicated by the Wald statistic. In addition, the R^2 values reached only 0.49 as the maximum value. In addition to the factors that were already observed in the aforementioned cases, reseeding, ED and DSW appeared to be the first time. DSW appeared only for NH_4^+ and showed one of the highest influences on the NH_4^+ concentrations.

Overall the statistical results showed that geological settings such as soil and rock thickness in the unsaturated zone to the top of the water table and local weather conditions such as rainfall, sunshine and SMD consistently were important. In many cases the explanatory variables of farm management practices tended to become more important after 1 or 2 years of time lag, which concurs with those estimated by Fenton et al. (2011a).

3.4 Discussion

3.4.1 The approach taken

To comply with the Irish obligations pursuant to the EU Nitrate Directive derogation request (EC, 1991), the current study was undertaken to study the impact of local weather conditions, site specific conditions and agronomic management to groundwater quality beneath an intensive dairy production system. Several studies on grassland sites with less complex geology concur with some of the findings of this study (Levison and Novakowski, 2009). However, this study is unique as the statistical approach used herein, albeit with a high resolution 11 year dataset, allowed such an assessment to work on a more complex terrain. Such complex terrains are often avoided as they are deemed too expensive and complex to monitor. Also shorter term datasets on such terrains could result in inaccurate management decisions. It is also important to point out that such an approach is appropriate where nutrient concentrations and not fluxes are deemed to be important such as under the present restrictions of the EU WFD in which concentration thresholds and MAC are important and not fluxes. This negates the need for hydrogeological data collection such as hydraulic and physio-chemical spring responses e.g. by using environmental tracers or such as defining volume and storage capacity of the conduit system (Einsiedl, 2005).

3.4.2 Local weather conditions

Statistical results of the present study indicate that local weather conditions are always a factor to consider while studying groundwater quality. Given the temporal variability in weather conditions and NO_3^- concentrations over the period of this study, it was only possible to explore indicative relationships between NO_3^- concentrations in groundwater and climate, (hydro-)geological factors and surface level nutrient management (see also Fenton et al., 2011b; Fraters et al., 2005). As shown in previous hydrogeological studies in karst environments, high rainfall events coincide with major mobilisation of NO_3^- in quick pulses through the unsaturated zone, rather than slow uniform recharge (Drew and Hötzl, 1999). This is augmented for NO_3^- originating from inorganic sources (Wells and Krothe, 1989). To gain a better impression of the impact of local weather conditions especially in karstified regions and to improve future management decisions, the current statistical approach would benefit from a higher resolution monitoring system such as high resolution sensors at a spring outlet or at least the collection of in-situ borehole mean nutrient concentrations over time via passive diffusion samplers.

3.4.3 Agronomy (2001 – 2011)

Nitrogen fertiliser is well known as an important contributor to agricultural production (Whitehead, 1995), but the efficiency of N use within animal-based systems is often poor (Watson and Atkinson, 1999). The evaluation of the impact of grazing systems to the impact on water quality is complicated by the nature of water movement in soils, the possibility of external influences on groundwater quality and the time lag between the surface and groundwater (Baily et al., 2012; Fenton et al., 2011a).

In the current study, statistical analysis suggested that slurry and fertiliser application are closely related to NO_3^- leaching. Organic and inorganic fertilisers can vary significantly due to their different properties and compositions. Organic waste has often less mineral N immediately available for plant uptake than inorganic fertilisers (Whitehead, 1995). Therefore, on a total N application basis, inorganic fertilisers are often more likely to be affected by immediate leaching than organic wastes (Di et al., 1998; Thorburn et al., 2003). Di et al. (1998) emphasised that the application rate for organic wastes and inorganic fertiliser should be regulated differently according to their effects on NO_3^- leaching. In addition, N use efficiency of organic wastes can be improved by choosing application times carefully (Smith and Chambers, 1993). Lalor et al. (2011) observed that N use efficiency can be optimized by switching application of slurry from summer to spring (April instead of June because of cooler and wet weather conditions combined with strong grass growth) or changing the application method (e.g. use of the trailing shoe application method instead of the splashplate). The method of slurry application (e.g. trailing shoe) can lead to reduced ammonia (NH_3) emissions to the environment as well (Smith et al., 2000; Lalor and Schulte, 2008), although study observations vary from enhanced to unchanged nitrous oxide (N_2O) emissions due to different application methods (Velthof and Mosquera, 2011). On the present study site, improvements in slurry utilisation in relation to NO_3^- losses to groundwater were achieved by choosing application times more specifically in spring and autumn, thereby reducing the requirement for inorganic fertiliser application from 2008 onwards. For example in 2001 the application of slurry was in May, whereas in 2008 the application was performed in January, February, March and April. In 2009 the application of slurry was performed only in February and March. The reduction in farm-gate fertiliser N use coupled with the increased overall stocking rate (and consequently milk production from the site) was indicative of increased N use efficiency on the research farm contributing to increased N retention within the farm system.

An earlier study on the present site by Bartley (2003) showed that groundwater NO_3^- concentrations were highest in the areas of highest organic N loading. Similarly, Strebel et al. (1989) and Oenema et al. (2010) demonstrated that grazing is one of the most important factors that affects NO_3^- leaching at farm scale. In the present study the statistical results also indicate that grazing is an important factor that can have a significant effect on groundwater quality. This was notable especially after a 1 year time lag for NO_3^- and TON within scenario 1 (Fig. 3-5). The results of this analysis suggest that, although grazing intensity increased at the site over the study period and while nutrient management practices improved and NO_3^- concentrations decreased, increased grazing intensity should be strategically positioned on less vulnerable areas within the site (similar to DSW irrigation) to reduce risk to groundwater resources.

Division of a farm into high and low risk leaching areas could be an effective management approach for the positioning of a DSW irrigation system. Consistent with the current study, data from an EPA (2005) study point to the avoidance of DSW irrigation on vulnerable areas within the site as an effective strategy to improve groundwater quality. By combining the DSW irrigation dataset of Ryan et al. (2006a) who monitored leaching observations taken in ceramic cups at a depth of 1 meter between 2001 and 2004 and the water quality information for BH 7 from 2002 and 2004, a relationship with increasing NO_3^- can be concluded. In 2006 the DSW irrigator was moved from the smaller high risk DWS area 1 zone to the larger lower risk zone of DSW area 2 (Fig. 3-1). It is noteworthy that this change coincided with a general decrease of NO_3^- concentrations on the farm including BH 7 and the boreholes affected by the DSW area 1 for which the connection is known from a bromide tracer experiment (Bartley, 2003). The statistical outcomes of this analysis indicate a relationship between DSW spreading and NH_4^+ in groundwater. However, the statistical approach adopted in this study did not find a relationship between DSW application and NO_3^- in groundwater, which could also indicate that other factors were more important for the overall NO_3^- concentration changes. In addition, assuming a time lag on a yearly basis could under predict DSW vertical travel times. This can be seen in context within the study of Gibbons et al. (2006) who observed that the duration of topsoil saturation following the application of large amounts of dairy wastewater at the same site can be very short during rainfall events.

Ploughing is well known as a contributor to soil organic N releases (Whitmore et al., 1992). Strebel et al. (1989) noted that ploughing results in a significant decrease of soil organic N content coupled with intensive NO_3^- leaching for a short time period until a new steady-state condition is achieved with less organic N content in the soil. The statistical results did not show a strong relationship between NO_3^- concentrations in groundwater and changes in management regarding the gradual transition of the start of the adoption of minimum till cultivation reseeding in 2006 and the stopping of ploughing in 2008 although the change of this management practice coincided with a general decrease in NO_3^- concentrations. It may be the case that such a change was not a significant factor in the statistical results due to the 2 year transitional period involved or perhaps due to other factors such as a reduction in fertiliser inputs or improvement in slurry application techniques also introduced at this time. While acknowledging the difficulty of fitting a suitable correlation structure to the comparably smaller NH_4^+ concentration dataset, the statistical outcomes suggest that the used reseeding method can have an influence on NH_4^+ concentrations in groundwater.

3.4.4 Groundwater quality trends

On this site, statistical results indicated that the connectivity with the entire aquifer as opposed to screened intervals was a better predictor of N concentrations in the aquifer. Open boreholes are in contact with nutrients as they migrate vertically through the subsoil, through the weathered epikarst (the thickness of which was highly significant) and therefore represent a composite nutrient concentration where cross contamination from surface input to groundwater can occur. However, where fluxes are important (perhaps in the future of the EU WFD) discrete fractures or conduits may be more important (Haag and Kaupenjohann, 2001; Landig et al. 2011) and therefore discrete screens or packers in conjunction with open boreholes may be needed. Wells with integrated piezometers are drilled to a certain depth and the water strike may or may not have good connectivity with the aquifer. On the one hand wells with piezometer casing can give a more reliable measurement if the connectivity to the aquifer is good because the water samples that were taken are always from the same aquifer level. But on the other hand the same type of well could give less reliable groundwater quality measurements if the connectivity is bad. In general, it needs to be taken into account if a water sample was taken from an open borehole or a borehole with piezometer especially if water samples are compared with each other.

The analysis of NO_3^- occurrence data from 2002 to 2011 showed overall a decreasing trend of mean NO_3^- concentrations on the farm (Fig. 3-6). The statistical results indicate that the implementation of the Nitrates Directive helped in some parts to improve the water quality on the study site. Van Grinsven et al. (2012) stated that a general, convincing decrease of NO_3^- in groundwater could not be observed in north-western countries of Europe since 2000 despite major improvements to soil N balance. As increased NO_3^- concentrations due to agriculture coupled with karst environments is not a concern for most of the north-western European countries, these countries also have to deal with longer time lags. In some areas in the UK time lags are even estimated up to several decades (Wang et al., 2012). This leads to the conclusion that the implementation of the Nitrates Directive could effectively lead to better water quality, but it may be the case that in most of the areas the improvement cannot be recognised quickly.

3.4.5 Statistical analysis

The statistical approach that incorporates a time lag effect can be used to predict future changes in water quality. It is also important to note that for a highly complex terrain such as in the present site the easiest statistical scenario (Scenario 1, Fig. 3-5) proved most effective. This prevents the immediate deployment of expensive hydrogeological equipment and also should encourage researchers to attempt further investigations of equally complicated sites over a similar timeframe. Because of significant changes in farm management (i.e. appropriate slurry and fertiliser application rate and strategy including a significant reduction in fertiliser rate since 2008; avoiding ploughing; careful management of high risk zones within the farm) and the already declining NO_3^- concentrations in groundwater, it is expected that this site will be able to comply with desired water quality standards as stipulated by WFD into the future.

3.5 Conclusions

The statistical approach used herein is an effective method for exploring the relationships between farm management, local weather conditions and groundwater nutrient concentrations both spatially and temporally. Results can guide the expectations of farm managers and policy makers with respect to the achievement of water quality targets within certain time frames. It is especially useful for farming areas within the remit of the EU WFD as it is a nutrient concentration driven approach and not concerned with nutrient fluxes. It therefore allows the practitioner to explore complex terrains such as free draining soils underlain with karst limestone aquifers without the need for a high end hydrogeological investigation. Over the 11 year monitoring period, the results of this study indicate that a combination of site characteristics (i.e. depth of the unsaturated zone, soil/subsoil and rock thickness), local weather conditions (such as rainfall, sunshine and SMD) and agronomic practices (i.e. reduced fertiliser rate, appropriate slurry and DSW application strategy, minimum cultivation and strategic management of high risk zones) were important factors influencing NO_3^- concentrations in groundwater. Furthermore, these results indicate that improved nutrient management practices on a highly vulnerable site with free draining soil can have relatively fast impacts ($\leq$ 2 years) on groundwater quality and can lead to an achievement of the water quality targets set by for example the WFD.

4 Mobilisation or dilution? Nitrate response of karst springs to high rainfall events

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Abstract

Nitrate (NO_3^-) contamination of groundwater associated with agronomic activity is of major concern in many countries. Where agriculture, thin free draining soils and karst aquifers coincide, groundwater is highly vulnerable to nitrate contamination. As residence times and denitrification potential in such systems are typically low, nitrate can discharge to surface waters unabated. However, such systems also react quickest to agricultural management changes that aim to improve water quality. In response to storm events, nitrate concentrations can alter significantly, i.e., rapidly decreasing or increasing concentrations. The current study examines the response of a specific karst spring situated on a grassland farm in south Ireland to rainfall events utilising high-resolution nitrate and discharge data together with on-farm borehole groundwater fluctuation data. Specifically, the objectives of the study are to formulate a scientific hypothesis of possible scenarios relating to nitrate responses during storm events, and to verify this hypothesis using additional case studies from the literature. This elucidates the controlling key factors that lead to mobilisation and/or dilution of nitrate concentrations during storm events. These were land use, hydrological condition and karstification, which in combination can lead to differential responses of mobilised and/or diluted nitrate concentrations. Furthermore, the results indicate that nitrate response in karst is strongly dependent on nutrient source, whether mobilisation and/or dilution occur and the pathway taken. This will have consequences for the delivery of nitrate to a surface water receptor. The current study improves our understanding of nitrate responses in karst systems and therefore can guide environmental modellers, policy makers and drinking water managers with respect to the regulations of the European Union (EU) Water Framework Directive (WFD). In future, more research should focus on high resolution monitoring of karst aquifers to capture the high variability of hydrochemical processes, which occur at time intervals of hours to days.

4.1 Introduction

The consequences of groundwater contamination by reactive nitrogen (N_r, e.g. nitrate NO_3^-), derived from agricultural sources, is of major concern in many countries (Galloway and Cowling, 2002; Spalding and Exner, 1993; L'hirondel, 2002). As groundwater response times affect the physical and economic viability of different mitigation measures, there is a realisation that such responses must be incorporated into environmental policy. However, such processes are poorly understood (Sophocleous, 2012), particularly where nitrate discharges unabated from high N input agricultural systems underlain by thin free draining soils and karst aquifers (Huebsch et al., 2013). Denitrification potential and response times in such systems are low (Jahangir et al., 2012) and at karst springs processes such as mobilisation and/or dilution during rainfall events inevitably control nitrate concentrations. In the European Union (EU) the Water Framework Directive (WFD; OJEC, 2000) aims to achieve at least good water quality status in all water bodies by 2015 and for groundwater a maximum admissible concentration (MAC) of 50 mg NO_3^- L^{-1} is in place. In karst regions, characterising nitrate dynamics in aquifers can help to predict when concentrations are likely to breach this MAC or not. No such standard exists for surface water but instead, in countries such as the Republic of Ireland, a much lower MAC of 11.5 mg NO_3^- L^{-1} exists for estuaries (Statutory Instruments S.I. No. 272 of 2009). Recent assessments have found that 16% of Irish groundwater bodies were ‘at risk’ of poor status due to the potential deterioration of associated estuarine and coastal water quality by nitrate from groundwater (Tedd et al., 2014). Improving our conceptual model of nitrate mobilisation and/or dilution in karst systems will therefore allow us to better manage agricultural systems in the future.

Karst areas exhibit a challenge for the protection of groundwater resources, because high heterogeneity, high vulnerability and fast groundwater flow result in low natural attenuation of contamination (Bakalowicz, 2005). Karst systems can vary significantly in the vadose zone from direct to slow infiltration and in the phreatic zone due to the complexity of conduit systems, fracture development and matrix porosity (Bakalowicz and Mangion, 2003). Episodic rainfall events can lead to rapid recharge, which has strong impact on discharge at and contaminant transport to karst springs, particularly if the conduit system is well developed (Butscher et al., 2011; Goldscheider et al., 2010). In addition, karst specific surface features (e.g. swallow holes) can contribute to a rapid contamination of the underlying aquifer (Ryan and Meiman, 1996). As a result of all these specific characteristics, karst aquifers overlain by thin free draining soils respond quickest to changes in N loading on the surface (Huebsch et al., 2013).

Leaching of organic and inorganic N can vary significantly. Organic N that has been applied on the surface provides mineral N to the plant on a longer basis due to mineralisation processes, whereas inorganic N is immediately available for the plant and hence, highly susceptible to leaching, especially in the first hours to days after application (Di et al., 1998). Due to its high solubility and mobility, nitrate responds much quicker and stronger to changes in hydrologic conditions and land use than less mobile ions such as phosphorus (P) (Hem, 1992). Because of this, in karst aquifers, low-resolution monitoring of nitrate (e.g., time intervals on a weekly basis) is unlikely to adequately characterise the system. This is especially true during rainfall events (Pu et al., 2011). As the dynamics of the system can change not only within, but also across events, it is important to have high resolution monitoring over long time periods. Long-term high-resolution monitoring can reveal rapid dilution of nitrate concentrations (Mahler et al., 2008), rapid mobilisation of nitrate concentrations (Baran et al., 2008; Plagnes and Bakalowicz, 2002; Pu et al., 2011; Yang et al., 2013) or a combination of mobilisation and dilution of nitrate concentrations during one or several rainfall events (Stueber and Criss, 2005; Rowden et al., 2001; Peterson et al., 2002).

In recent years, high-resolution monitoring in karst catchments over extended periods of time received greater attention (Mellander et al., 2013; Schwientek et al., 2013). Also, spectrophotometrical ultraviolet/visible (UV/VIS) light monitoring, which has originally been developed for monitoring waste water treatment plants (Drolc and Vrtovšek, 2010), has been applied to karst springs in recent years to continuously monitor nitrate concentrations (Grimmeisen et al., 2012; Pu et al., 2011). Such techniques offer the opportunity to observe both long-term trends, sudden changes of nitrate concentrations (Storey et al., 2011) and to increase the understanding of nitrate transport dynamics.

In this study, high-resolution UV monitoring, discharge and groundwater level fluctuation measurements were performed to observe nitrate concentration patterns and their relation to karst spring discharge and groundwater level fluctuations in response to storm events. The study site in Southern Ireland represents an ideal test site for nitrate responses in karst springs to storm events because of the combination of intensive agronomic N loading on the surface, an underlying karst aquifer and hydrometeorological conditions that ensure storm events throughout the year.

By looking at different nitrate characteristics during storm events, we aim to answer the following questions: What are the key factors controlling increased (i.e. mobilised) or decreased (i.e. diluted) nitrate concentrations in karst springs as response to storm events? Does it depend on the karst system alone, the hydrological situation or land use and/or of a combination of all these components together? Specifically, the objectives of the present study are to formulate a conceptual model of possible scenarios of nitrate responses during storm events, and to verify this hypothesis using other examples from the literature together with data from our study site. The results of this study can contribute to an improved understanding of when and under what conditions nitrate is released to fresh surface waters and, therefore, can guide environmental modellers, drinking water suppliers and environmental policy makers with respect to the regulations of the EU Water Framework Directive.

4.2 Materials and methods

4.2.1 Site description

The study site of 1.1 km^2 is located approximately 35 km north of Cork city in the Republic of Ireland and adjacent to the Teagasc, Animal and Grassland Research and Innovation Centre, Moorepark, in Fermoy (8°15'W, 52°10'N). About 0.97 km^2 (~ 90 %) of the area is farmed. To the east, the study site is bounded by the River Funshion (Fig. 4-1). A public water supply well is located approximately 50 m up-gradient from the most westerly part of the study site at the River Funshion. Due to the topography, the study site can be sectioned into three parts. The upper part is intensively used as grassland for dairy farming, whereas the lower part is only periodically utilized as grassland, as it can be flooded for large periods of the year due to the proximity to the River Funshion and a shallow groundwater table. A steep slope between these two parts, which is the third part of the study site, has been forested to prevent erosion. The farm yard is located centrally on the study site. It includes the housing for the dairy herd and an intensively operated piggery.

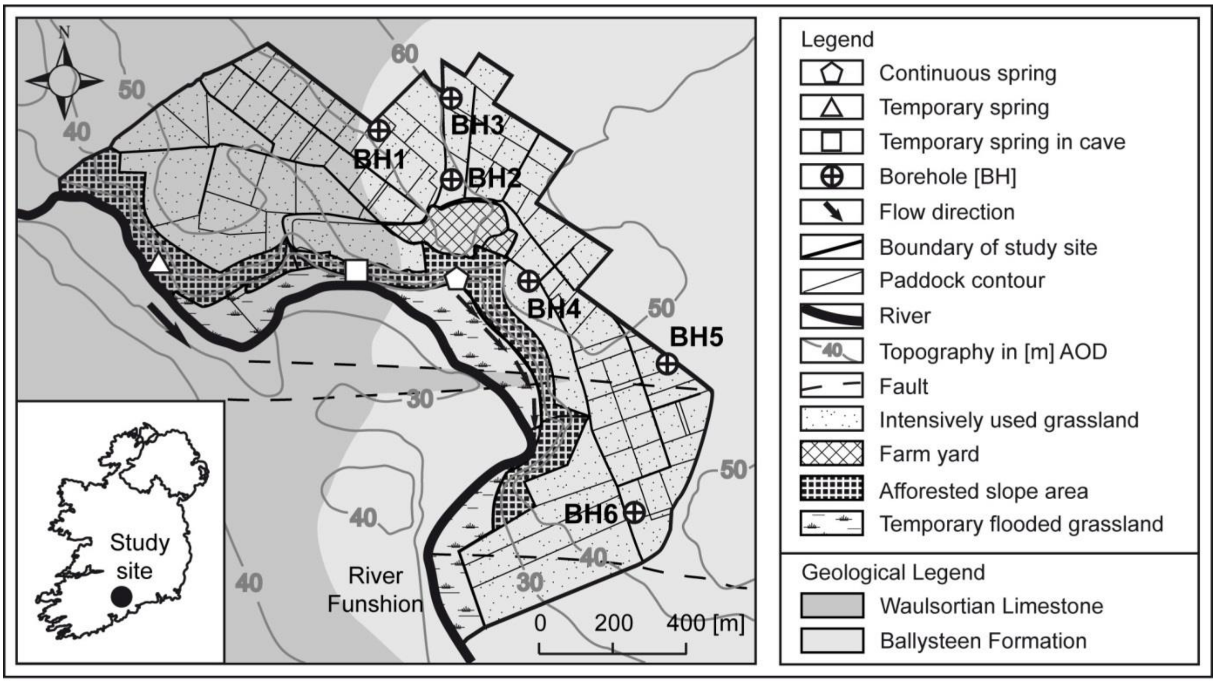

Fig. 4-1: Site map for the study area in the Republic of Ireland. The smaller arrows indicate the water flow direction of the continuous spring in a ditch to the river.

The study site has been a research farm (dairy) with a commercially farmed, intensive pig farm in the farm yard since 2006. Prior to 2006, the farm was an intensive commercial dairy and pig farm with high fertiliser and feed inputs. All nutrients (slurry, cattle and pig manures) generated on the farm were applied to the farm land. No historic nutrient records are available. Since 2006, the dairy farm has been operating as a research farm and nitrogen fertiliser application rates are maintained within the Nitrates Directive (EC, 1991) which was implemented in Ireland in 2007. Jahangir et al. (2012a) calculated the annual N surplus for the research farm between 2009 and 2010 at 263 kg N ha^{-1} by subtracting the annual N output (35 kg N ha^{-1}) from input (298 kg N ha^{-1}). Furthermore, they estimated the possible amount of N leached at 148 kg N ha^{-1} for the same years by taking N losses via volatilization and denitrification in soil surface into account. All slurry and manure generated from the dairy enterprise is applied to the grassland on the farm. The piggery is privately operated and all associated nutrients (slurry and manure) are exported off the farm. The present study site is comparable with a dairy farm approx. 2 km apart in terms of agronomic N-loading, local weather conditions, hydrogeological and geological site characteristics. The neighboring dairy farm has been described in detail by Huebsch et al. (2013). In this study agricultural practices were analyzed and the applied nitrogen input on the surface was related to recorded nitrate occurrence in groundwater over an 11-year period whilst also considering a time lag from source to groundwater. N-inputs at this study site were 335 to 274 kg ha^{-1} between 2001 and 2011 whereas the calculated N surplus (N inputs – N exports) at farm level was 260 to 174 kg ha^{-1}. Those findings can also be compared to the study of Landig et al. (2011) who calculated N-inputs at the present study site for 2008. N inputs were 337 kg ha^{-1} while 209 kg ha^{-1} were derived from organic N sources and 128 from inorganic N sources (Landig et al., 2009). In addition, on the present study site the availability of N on the land surface during autumn has increased as the farm has extended grazing during that period.

The top soil (0 – 0.5 m) of the study site consists of sandy loam, whereas the subsoil (0.5 – 10.0 m) is composed of sand and gravel (Jahangir et al., 2012b). Two different types of Carboniferous limestone occur at the study site: the Waulsortian Limestone and the Ballysteen Formation (Fig. 4-1) (GSI, 2000). The Waulsortian Limestone is in general less bedded and more karstified than the Ballysteen Formation due to the occurrence of massive calcareous mud-mounds and a lower content of shale components **(**GSI, 2000**)**. In Fig. 4-1 the boundary of the two limestone types is adapted from mapping by the Geological Survey of Ireland (GSI), which was conducted at a larger scale. Therefore, and because of the lack of bedrock cores of the wells that have been drilled, the exact boundary on the local scale is uncertain.

Six boreholes (BH1 to BH6) with diameters of 150 mm were drilled in 2005 (Fig. 4-1). Five wells (BH1 and BH3 to BH6) consist of a 50 mm diameter piezometer casing. A multilevel piezometer was installed in BH1 with 6 m screen sections beginning at 25.18 m AOD and 43.18 m AOD. BH3 to BH6 each consist of a single piezometer with a 6 m screen section beginning at 19.85, 24.68, 20.38 and 17.57 m AOD, respectively. BH2 is an open borehole with 150 mm diameter. It was found to be dry to a drilling depth of 62.9 m and subsequently filled with water already the day after drilling. The average drilling depth on site is 45.9 m with a minimum depth of 31.2 m at BH6 and a maximum depth of 62.9 m at BH2.

A perennial spring is located at the foot of the slope area (Fig. 4-1). The spring discharge is captured in a reservoir of about 23 m^2 and used as water supply for the dairy farm and the piggery. Water that is not needed for the farm flows over a weir via a channel towards the river.

4.2.2 Spring, water level and meteorological data

High-resolution monitoring of nitrate-nitrogen (NO_3-N) in spring water was performed photometrically between the 11th of July 2011 and the 20th of April 2013 at 15 min intervals with a two-beam UV sensor (NITRATAX plus sc, Hach Lange GmbH, Germany) using a 5 mm measuring path. The sensor reports NO_3-N by measuring total oxidised N (TON), and assuming negligible nitrite (NO_2-N). To verify the UV sensor measurements, 12 water samples (50 ml) were taken at the sensor location in July 2011, 4 water samples in October 2012 and 12 water samples in May 2013. Half of the samples were filtered immediately using a 0.45-µm micropore membrane, the other half were kept unfiltered to determine the influence of organic substances, as the accuracy of the sensor can be affected by those. All samples were transferred to 50 ml polyethylene screw top bottles, which were kept frozen prior to chemical analysis. TON and NO_2-N content were determined in the laboratory (Aquakem 600A, Thermo Scientific, Finland), from which the nitrate concentration was calculated. For TON and NO_2-N determination the hydrazine reduction method was used (Kamphake et al., 1967). The analysis of the unfiltered and filtered samples showed that UV sensor measurements were reliable and not affected by organic substances. NO_2-N was negligible and the measured TON was reported as NO_3-N.

To determine spring discharge, a trapezoidal weir was installed at the outlet of the spring capture reservoir (e.g. Walkowiak, 2006). The water level in the reservoir was measured with an electronic pressure transducer (Mini-Diver, Eijelkamp, Netherlands) in a stilling well at 15 min intervals. As the reservoir is used to provide water to the farm, a flow metre with data logger was also installed in the water supply pipe to measure pumped outflow. Changes in groundwater levels were continuously monitored at 15 min intervals in BH1, BH3, BH4 and BH6 using electronic pressure transducers (Mini-Diver, Eijelkamp, Netherlands).

Rainfall was recorded every hour at a Met Èireann weather station of approximately 500 m from the study site. Effective Drainage (ED) was calculated as precipitation minus actual evapotranspiration, which was calculated from daily recordings of maximum and minimum temperature, precipitation, wind speed and solar radiation at the Met Èireann weather station after Schulte et al. (2005). In 2011 the annual rainfall was 855 mm and ED 364 mm, whereas in 2012 the annual rainfall was 1097 and ED 578 mm.

4.3 Results

4.3.1 Observations at the study site

Two periods were evaluated: (1) from 13th November 2011 to 20th January 2012 including high-resolution observations of NO_3-N concentrations in spring water, precipitation and discharge (Fig. 4-2) and (2) from 1st February to 1st October 2012 including high-resolution observations of NO_3-N concentrations in spring water, precipitation and groundwater level fluctuations in BH1, BH3, BH4 and BH6 (Fig. 4-3).

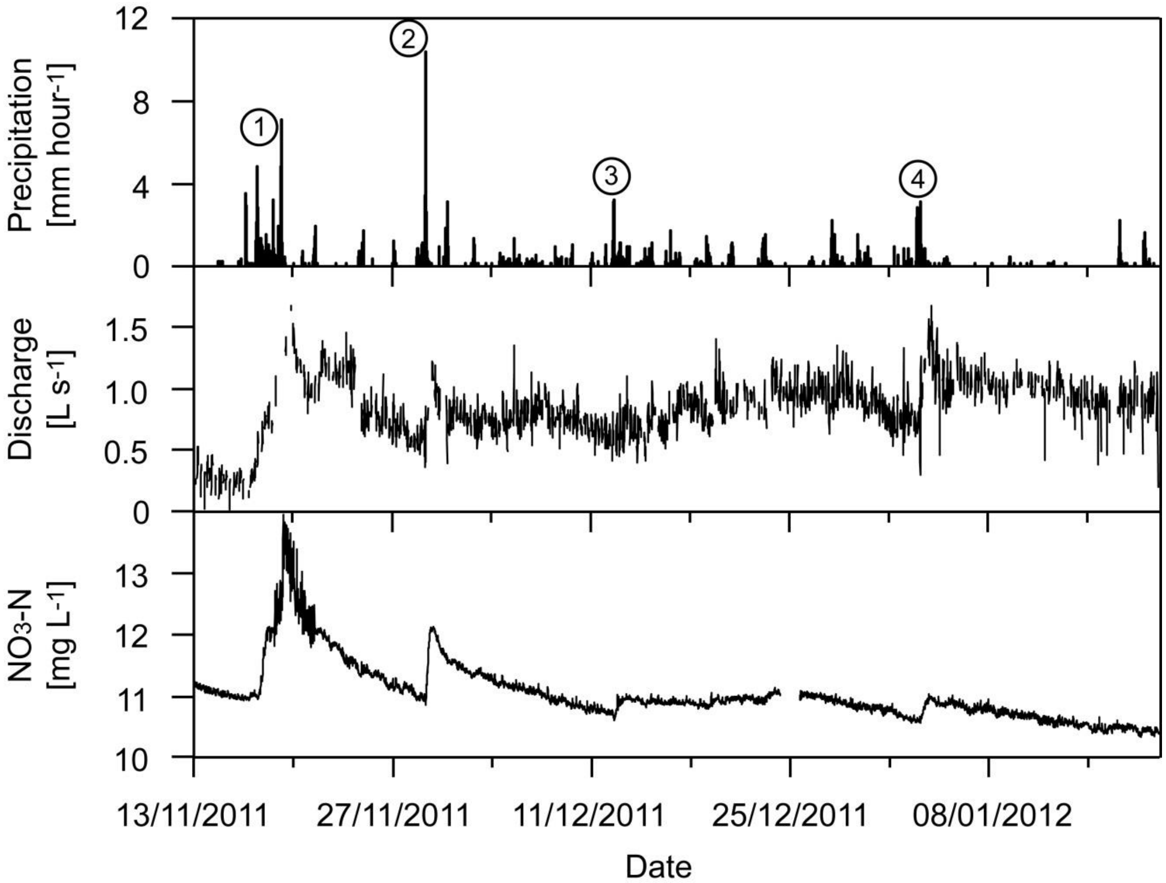

Fig. 4-2: Observations at the study site in period (1) between the 13th of November 2011 and the 20th of January 2012. The symbols 1 to 4 indicate different storm events, which had a visible influence on the discharge and nitrate pattern at the spring.

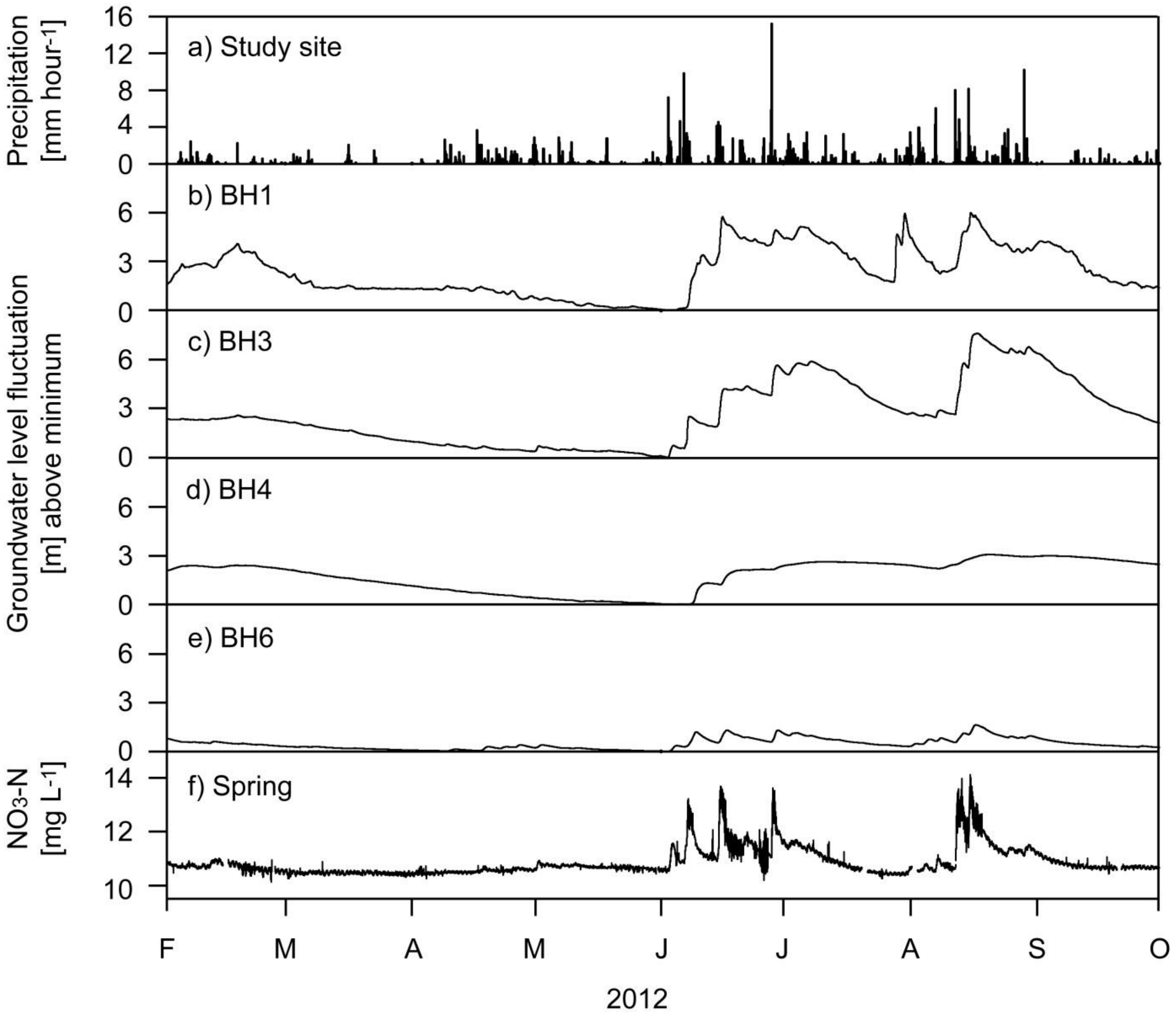

Fig. 4-3: Observations at the study site in period (2) between the 1st of February and the 1st of October 2012: a) precipitation; b) to e) groundwater fluctuation at BH1, BH3, BH4 and BH6 in [m] above minimum; f) NO_3-N pattern at the spring.

Fig. 4-2 illustrates the impact of four storm events on discharge and nitrate patterns at the spring for period (1). Storm events were separated from each other if precipitation was less than 0.2 mm h^{-1} for at least 24 hours in accordance to Kurz et al. (2005). Only storm events with a total amount of minimum 10 mm precipitation were taken into account.

The first storm event started on the 16th of November 2011 at 4 pm and ended on the 19th of November at 10 am. A total of 60.3 mm precipitation was recorded during this time. Discharge started to rise on the 16th at 11.30 pm at 0.2 L s^{-1} and reached its maximum of 1.7 L s^{-1} on the 19th of November at 8:30 pm. After the maximum was reached, discharge decreased at first, and then showed a second increase, probably due a recurrence of intensified rainfall. NO_3-N concentrations increased around 18.5 hours later than discharge on the 17th of November at 5 pm and rose to 13.8 mg L^{-1} until the 19th of November at 10:45 am. Hence, the NO_3-N increase started later than the discharge increase but reached its maximum 9.75 hours earlier. After the maximum was reached, NO_3-N exponentially decreased to 11.0 mg L^{-} until the 29th of November at 9 am.

The second storm event started on the 28th of November 2011 at 5 pm. Rainfall intensified and reached a total of 33.5 mm by the 30th of November at 10 pm. Discharge started to increase at 0.5 L s^{-1} on the 28th of November at 10:45 pm, and the first maximum discharge of 1.2 L s^{-1} was measured on the 29th of November at 7:30 pm. However, the maximum discharge could have been higher and earlier. Intensive pumping at the reservoir between 12:15 and 7 pm led to a lack of stationary discharge values during that time. The increased discharge value of 1.0 L s^{-1} or more was maintained until the 30th of November 2:30 am and decreased afterwards. The NO_3-N concentrations started to increase at the 29th of November at 9 am at 11.0 mg L^{-1} and reached its maximum of 12.1 mg L^{-1}on the 29th of November at 5:45 pm. The NO_3-N peak was observed about 1.45 hours earlier than the discharge peak.

During the third and fourth storm event, the same characteristics as described in the aforementioned storm events were observed at the spring. The total amount of precipitation was 28.8 mm for the third event and 18.7 mm for the fourth event. After rainfall intensified, discharge rose followed by increased NO_3-N concentrations a few hours later. Again, the maximum NO_3-N concentrations were reached earlier than the discharge peak. Specifically, during the third storm event discharge started to rise at 0.4 L s^{-1} on the 12th of December 2011 at 11:45 am, while NO_3-N started to increase at 10.6 mg L^{-1} on the 12th of December 2011 at 3:15 pm. Highest discharge values were observed at 1.1 L s^{-1} on the 13th of December 2011 at 12:30 pm. The NO_3-N peak was reached at 11.0 mg L^{-1} at 11:15 am on the same day and was therefore 1.15 hours earlier than the discharge peak. During the fourth storm event discharge started to increase at 0.3 L s^{-1} on the 3rd of January 2012 at 4:30 am and NO_3-N started to rise at 10.6 mg L^{-1} on the same day at 5:00 am. The maximum discharge was reached at 1.5 L s^{-1} on the 4th of January 2012 at 00:15 am and the maximum NO_3-N concentration at 11.0 mg L^{-1} on the 3rd of January 2012 at 7 pm. Thus, the discharge maximum was reached 5.25 hours later than the NO_3-N maximum.

In addition, groundwater level fluctuations at BH1 and BH3 to BH6 were observed and can be related to precipitation and NO_3-N concentrations at the spring (Fig. 4-3). During the 1st of February 2012 and the 1st of October 2012 groundwater level fluctuations in the boreholes accounted for up to 7.60 m. BH1 and BH3 had maximum water level fluctuations of 5.98 m on the 15th of August 2012 and 7.60 m on the 17th of August 2012, respectively. In the eastern part of the study site (Fig. 4-1), maximum water level fluctuations were lower. At BH4 and BH6 maximum values of 3.06 m on the 20th of August 2012 and 1.62 m on the 17th of August 2012, respectively, were observed. In all wells, the lowest groundwater level was observed at the beginning of June 2012 after a longer period of sparse precipitation. BH1 and BH3 in particular showed similar groundwater level fluctuation patterns as the response of NO_3-N concentrations at the spring. Groundwater level fluctuations are reflecting ED. Between 11th of February 2012 and the 25th of April 2012 no ED occurred. Little ED was observed between 26th of April 2012 and 10th of June 2012 with a maximum peak of 13.3 mm and 27.3 mm in total. Between 11th of June 2012 and the 2nd of July 2012 no ED occurred. During those periods groundwater levels dropped and no significant change in nitrate concentrations was observed at the spring. In the following period ED increased and three higher ED events > 20 mm were observed on the 7th of June 2012 (23.7 mm), the 15th of June 2012 (21.4 mm) and the 28th of June 2012 (27.4 mm). In August 2012 on the 12th and on the 15th high ED > 20 mm of 25.4 mm and 25.1 mm, respectively, was observed. In Fig. 3 the high amounts of ED match with significantly increased nitrate concentrations at the spring. The maximum nitrate concentrations during the 5 events were 13.2 mg L^{-1} on the 7th of June 2012 at 5.30 pm, 13.7 mg L^{-1}on the 15th of June 2012 at 6.30 pm, on the 28th of June 2012 13.6 mg L^{-1}at 9.00 am, 13.6 mg L^{-1}on the 12th of August 2012 at 7 pm and 14.1 mg L^{-1} on the 15th of August 2012 at 6 pm.

4.3.2 Conceptual model of nitrate responses in karst systems

A conceptual model of nitrate responses in karst groundwater systems was developed to elucidate the relationship between nitrate responses in karst springs and proposed driving factors such as hydrological conditions, N availability through land use and karst features (Fig. 4-4).

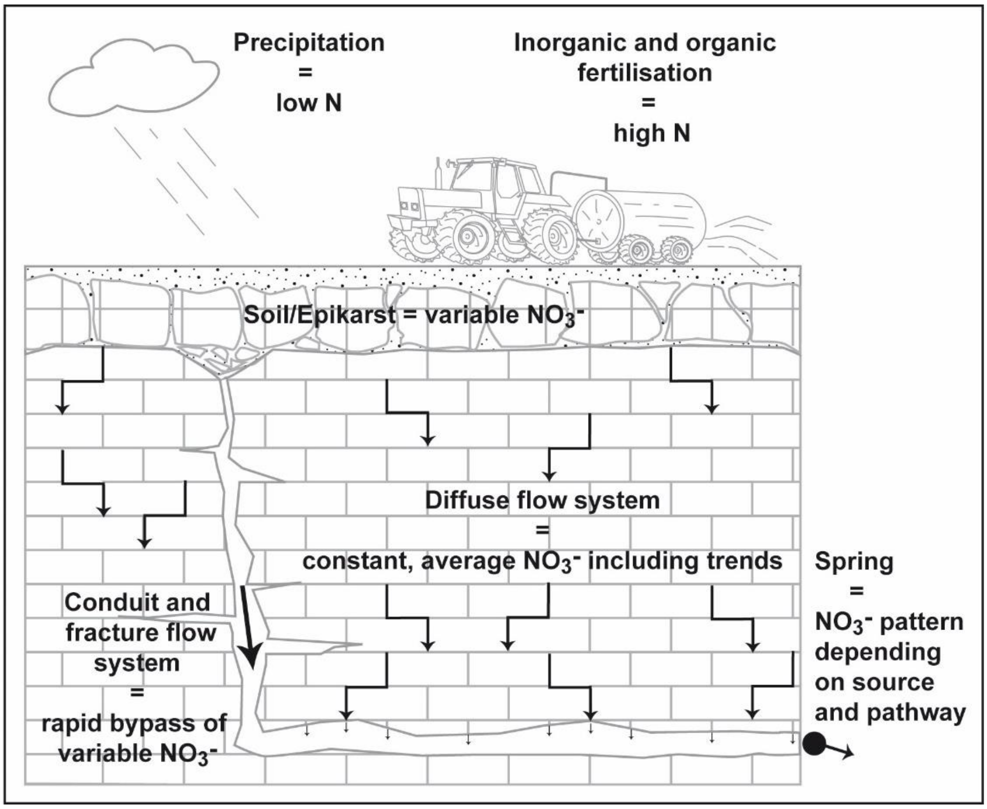

Fig. 4-4: Conceptual model of nitrate response in karst systems.

Agriculture is known to be a main contributor of nitrate in groundwater, mainly because of inorganic and organic N fertilisation (Stigter et al., 2011). Current and past N applications, storage capacity and hydrological conditions can result in nitrate accumulation in the soil and epikarst (Fig. 4-4), while rainwater itself is typically low in nitrate concentration (about 0.3 mg L^{-1}, (Gächter et al., 2004)).

Groundwater flow in karst aquifer aquifers can be conceptualized by a dual flow system: water flows in pipe-like conduits and open cave stream channels (conduit flow system) as well as flow through fractures and pores (diffuse flow system). This dual flow concept is described in the literature and widely used in karst studies (e.g., Shuster and White, 1971; Atkinson, 1977; White, 1988; Kiraly, 1998; Ford and Williams, 2007). Other researchers use a triple porosity concept for the description of karst aquifers, where groundwater flow is attributed to conduits, pores of the rock matrix and an intermediate flow system representing fissures and joints (e.g., Worthington et al., 2000; Baedke and Krothe, 2001). In the conceptual model of the present study, the simpler dual porosity concept is used, which is well suited to describe the nitrate characteristics of the observed karst springs. Nitrate that recharges into the diffuse flow system during a storm event can hardly change nitrate concentrations within this large groundwater storage (Peterson et al., 2002). Hence, groundwater in the diffuse flow system is characterised by relatively stable nitrate concentrations that reflect average nitrate values of groundwater recharge and long-term trends. At the spring, stable nitrate concentrations representing water from the diffuse flow systems can be observed during base flow conditions.

During a storm event, water recharges also into the conduit flow system and bypasses the diffuse flow system. Nitrate concentrations of this recharge water strongly depend on hydrological conditions and land use. If nitrate concentrations in the soil and epikarst are high prior to a storm event, for example after N fertilisation, nitrate becomes mobilised and water with high nitrate concentration enters the conduit flow system. At the spring, a fast increase of nitrate concentrations can be observed as a storm response, which reflects nitrate mobilisation in the soil and epikarst by storm water. If nitrate concentrations in the soil and epikarst are low prior to a storm event, rainwater with low nitrate concentration enters the conduit flow system without a marked increase in nitrate concentration. At the spring, a fast decrease of nitrate concentrations can be observed as a storm response, which reflects the dilution of spring water by storm water.

Our conceptual model of karst spring responses to storm events can be summarized in four possible scenarios (Fig. 4-5). Scenario 1 (Fig. 4-5a) shows mobilisation of nitrate in the soil/epikarst during storm events and fast increasing nitrate concentrations as response at the spring, corresponding to observations of period (1) and (2) in the present study. Scenario 2 (Fig. 4-5b) shows dilution of spring water after storm events with fast decreasing nitrate concentrations. In Scenario 3 (Fig. 4-5c), nitrate in the soil/epikarst becomes mobilized during storm events, resulting in an initial increase in nitrate concentrations in spring water, followed by dilution of spring water with low nitrate storm water when groundwater recharge continues after mobilised nitrate has been flushed through the system. Scenario 4 (Fig. 4-5d) shows different responses to storm events depending on the availability of nitrate in the soil/epikarst. During the first event, little nitrate was available and dilution can be observed at the spring. Before the second event, high nitrate concentrations accumulated in the soil/epikarst. Nitrate then becomes mobilised during the second storm event and a sharp nitrate peak can be observed as response at the spring.

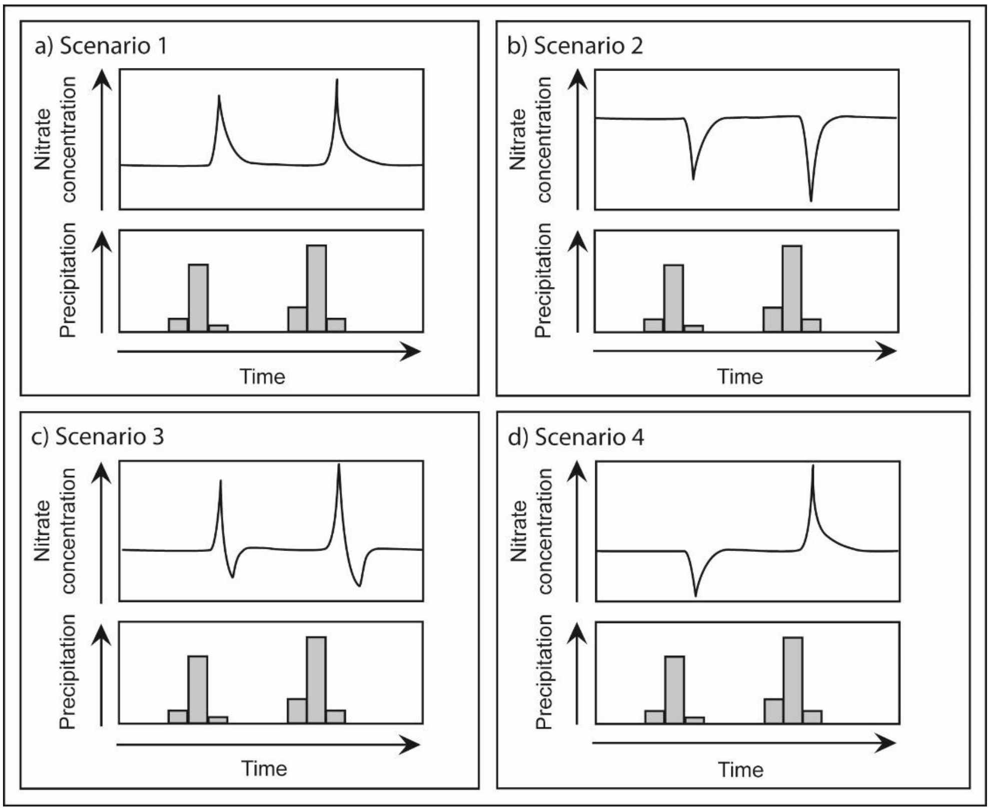

Fig. 4-5: Hypothesis of nitrate response scenarios: Predominance of a) nitrate mobilisation; b) nitrate dilution; c) mobilisation and dilution during one event; d) mobilisation and dilution during multiple rainfall events.

The fast increase in nitrate concentrations after storm events indicates that mobilisation is the main process influencing nitrate patterns at the spring (Figs. 4-2 and 4-3). At the site, intensive agriculture is the dominant land use including application of inorganic and organic N fertiliser. During dry weather, soil moisture deficit leads to an accumulation of nitrate and minor to zero leaching in the soil. This can be recognised at the spring during base flow conditions when nitrate concentrations remain fairly constant (for example between March and May 2012, Fig. 4-3). During storm events (for example in June 2012), residual nitrate that was not consumed by plants gets mobilised in the soil (Fig. 4-5a). At the spring, the rapid increase of nitrate concentrations, only a few hours after the start of a storm event, indicates that recharging water rapidly bypasses the diffuse flow systems in the rock matrix in activated conduit systems.

4.3.3 Comparison with other studies

To further test our conceptual model, documented nitrate responses to storm events were reanalysed with respect to the proposed processes (Fig. 4-4) and related to the various possible scenarios (Fig. 4-5). Four representative studies were selected that correspond to Scenarios 1 – 4 (Fig. 4-6).

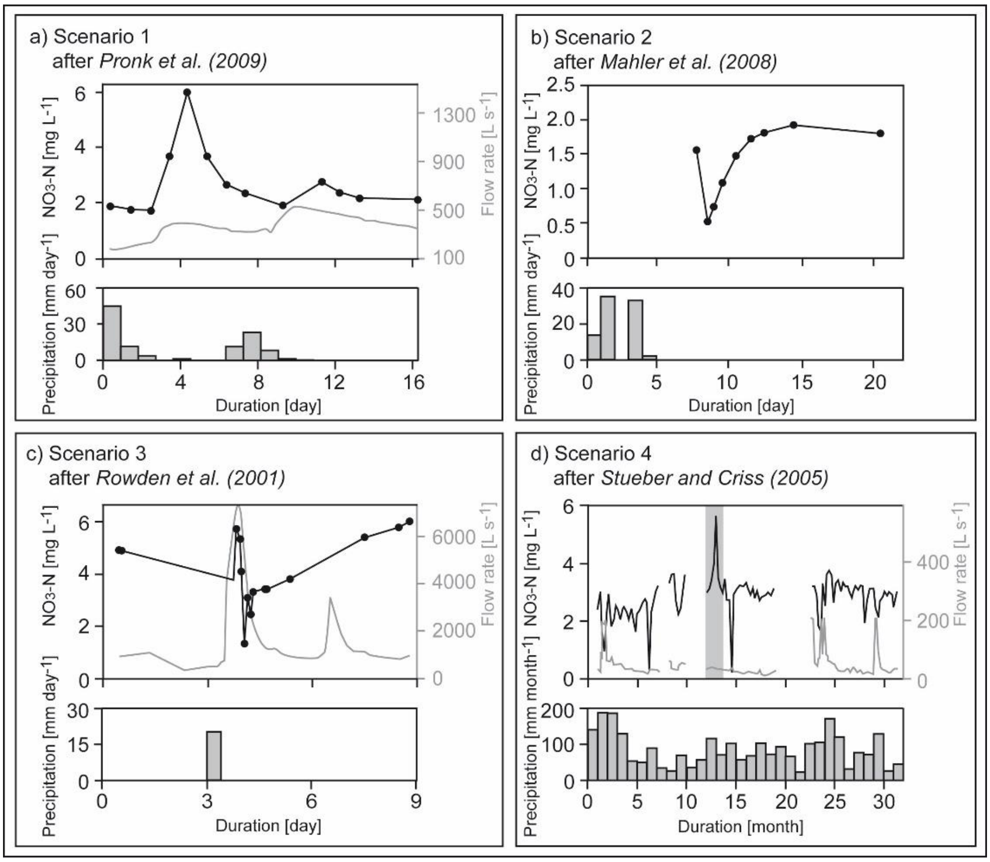

Fig. 4-6: Four illustrating case studies: Predominance of a) nitrate mobilisation; b) nitrate dilution; c) mobilisation and dilution during one single event; d) mobilisation and dilution during multiple rainfall events (the grey bar in the upper diagram indicates the event with nitrate mobilisation).

Study 1 – Yverdon karst aquifer system, Switzerland (Pronk et al., 2009)

In this study, a similar response of discharge and nitrate concentrations after a storm event as in the present study was observed (Fig. 4-6a). During the whole study period, a nitrate range of 1.0 to 7.0 mg NO_3-N L^{-1} and a discharge range of 21 to 539 L s^{-1} was monitored. After the storm event, discharge increased at the spring, followed by a steep nitrate increase with a slower drop down after the maximum was reached. According to our conceptual model, this pattern corresponds to mobilisation (Scenario 1, Fig. 4-5a). Pronk et al. (2007) observed that a stream draining into a swallow hole in an agricultural dominated area contributes significantly to nitrate variations at the spring during storm events. Their interpretation is in line with the conceptual model of the present study, where mobilisation in the soil/epikarst and subsequent transport of nitrate via the conduit flow system occur, i.e. rapidly by-passing the diffuse flow system of the rock matrix.

Study 2 – Chalk aquifer in Normandy, France, and Edwards aquifer, Texas, U.S.A. (Mahler et al., 2008)

In the second study, the observed predominant process after storm events (Fig. 4-6b) corresponds to dilution according to our conceptual model (Scenario 2, Fig. 4-5b). The observed NO_3-N concentrations in the aquifer range between 2.2 and 9.0 mg L^{-1}. Three days after the storm event, nitrate concentration decreased rapidly and rose gradually afterwards. The authors state that (recharging) surface runoff was rapidly transported through the conduit system, leading to dilution effects during the storm event. When the event water became increasingly replaced after the event by groundwater stored in the rock matrix, nitrate concentrations started to rise again.

Study 3 – Big Spring basin, Iowa, U.S.A. (Rowden et al., 2001)

In the third study, a storm event of 20 mm in total caused first predominance of mobilisation, directly followed by dilution during one event (Fig. 4-6c). This nitrate pattern corresponds well to Scenario 3 in our conceptual model (Fig. 4-5c). Rising nitrate concentrations during the event can be explained by first mobilisation of nitrate by infiltrating recharge, followed by dilution after mobilised nitrate is already flushed through the system and storm water continues to recharge into the conduit flow system. During the study period, discharge ranged from 300 to 7300 L s^{-1} and NO_3-N from 1.3 to 6.0 mg L^{-1}.

Study 4 – Karst watershed, Illinois, U.S.A. (Stueber and Criss, 2005)

In this study, predominance of mobilisation during one and dilution during other events were observed (Fig. 4-6d), corresponding to Scenario 4 (Fig. 4-5d) of our conceptual model. Between May 2000 and December 2002, the authors frequently observed dilution during storm events. However, during one storm event, nitrate concentrations showed a different response – the concentrations increased rapidly (Fig. 4-5d, grey bar). The cause of the sharp nitrate increase was detected as heavy N fertilisation in the catchment during this time. A relatively constant NO_3-N trend was monitored at 3.5 mg L^{-1}, whereas during storm events concentrations decreased to 0.2 mg L^{-1} and increased up to 5.6 mg L^{-1}.

4.4 Discussion

In this chapter, the role of different key drivers in resulting nitrate responses at karst springs is discussed, including the hydrogeological setting of the karst system, mixing of water from different sources, hydrological conditions and land use practises. In addition, adequate sampling strategies for studying nitrate characteristics of karst systems are briefly discussed.

Transport of nitrate can occur quickly within conduits and fissures or be strongly retarded in less mobile water within the rock matrix (Baran et al., 2008). Hence, the development of the karst system itself plays an important role. But what karst features are most relevant for dilution and mobilisation processes?

In the study of Pronk et al. (2009), a sinking stream strongly impacts nitrate concentrations (and faecal bacteria) in spring water after storm events. The sinking stream points at the presence of a well-developed conduit system in the karst aquifer. The spring investigated in their study shows the same nitrate characteristics as the spring investigated in the present study. Also at the present study site, the existence of a well-developed conduit network is likely. For example, a cave exists at the study site (Fig. 1). However, the exact hydraulic properties of the karst system are uncertain.

In the study by Mahler et al. (2008) two karst systems that differ significantly in matrix porosity, thickness of soil and epikarst and land use were compared. In both karst systems, dilution was the observed predominant process after storm events. One karst system of this study is illustrated as an example in Fig. 4-6b. In contrast, the study of Baran et al. (2008), which focuses on a chalk aquifer in northern France comparable to one of the karst systems described in the aforementioned study of Mahler et al. (2008), shows predominance of nitrate mobilisation and not dilution, just as in the present study. Both chalk aquifers are characterised by a total matrix porosity between 30 and 40 %, low hydraulic conductivity of about 10^{-9} – 10^{-8} m s^{-1} and the presence of a conduit system with an observed hydraulic conductivity of 10^{-3} m s^{-1} (Mahler et al., 2008) and 10^{-5} to 10^{-3} m s^{-1} (Baran et al., 2008). Nevertheless, a dual flow system will react differently to an isolated conduit system. A lower magnitude of the varying concentration is expected and the time lag between rise in spring discharge and response in concentration should be higher (Birk et al., 2006).

Similarly, Rowden et al. (2001) observed that the combination of infiltration and runoff recharge can have a significant influence on nitrate patterns at springs. The proportion of runoff recharge can vary significantly and changed in the study by Ribolzi et al. (2000) between 12 % for low intensity rain fall events and 82 % for high intensity rainfall events. In the study by Peterson et al. (2002) a step multiple regression analysis technique was used. The authors state that base flow conditions had an influence of 74 % of the nitrate concentrations at the karst spring and storm events made up to 26 %. Even if higher nitrate concentrations in soil cores can be directly related to fertilisation, during storm events surface runoff is dominating in well-developed karst systems. Thus, recharging water contains mainly surface derived nitrate and the impact of soil nitrate is only minor (Peterson et al., 2002). Zhijun et al. (2010) related a higher increase in nitrate concentrations in groundwater to rapid transportation after storm events combined with previous intensive N fertilisation in the catchment.

Ribolzi et al. (2000) monitored nitrate concentrations in a spring in a Mediterranean catchment and observed the predominance of either dilution or mobilisation during different rainfall events. Their results are similar to the results of the study by Stueber and

Criss (2005) which were reanalysed in this study (Fig. 4-6d). They observed that mobilisation of nitrate concentrations occurred only after heavy N fertilisation coinciding with increased rainfall intensity of 107 mm during a four-week period. From this it follows that the different nitrate behaviour at the spring depends on source combination of land use and hydrological conditions. Similarly, Ribolzi et al. (2000) stated that dilution during one event was to the result of mixing of rainwater containing low nitrate concentrations and groundwater, whereas mobilisation during another event occurred due to mixing of two different groundwater types while water levels increased. This is similar to the interpretations of Toran and White (2005), who suggest that nitrate changes can depend on changing recharge pathways in karst environments.

Denitrification potential can vary in space and time in karst aquifers (Heffernan et al., 2011). Musgrove et al. (2014), for example, studied two hydrogeologically differing karst aquifers regarding their denitrification potential: the oxic Edward aquifer and the anoxic Upper Floridan aquifer in Florida (US). They concluded that, despite the differences in hydrogeology and in oxic/anoxic conditions, nitrate concentrations of spring water were strongly influenced by fast conduit-driven flow. These observations are in line with the conceptual model of the present study, where nitrate responses to storm events at karst springs are mainly influenced by rapid flow in the conduit system, and denitrification in the diffuse flow system (rock matrix) may influence nitrate characteristics of the spring (only) during base flow conditions significantly. Also Panno et al. (2001) observed a significant degree of denitrification in karst springs on the western margin of the Illinois Basin (Illinois, US). These authors reported a high density of sinkholes which caused rapid influx of agrichemicals to the springs, accounting for highest nitrate concentrations (Panno, 1996). These observations also justify the conceptual model of the present study, which is based on the assumption that the diffuse flow system transfers average nitrate concentrations and may account for long-term trends, while rapid bypass of lower or higher nitrate concentrations after storm events via karst conduits accounts for (mobilized or diluted) peak concentrations at the spring. Nevertheless, water that flows through the karst matrix with longer travel time is likely to be affected by denitrification and redox processes (Einsiedl et al., 2005; Liao et al., 2012; White, 2002). One should therefore bear in mind that such processes can also contribute to variable nitrate concentrations at karst springs.

In the conceptual model (Fig. 4-4), precipitation is conceptualized as a low N source. However, precipitation can also be enriched with atmospheric derived nitrate (Einsiedl and Mayer, 2006). Sebestyen et al. (2008) showed for a catchment in an upland forest in northeast Vermont, USA, that atmospheric derived nitrate can account for more than 50% of nitrate concentrations in groundwater, especially during snowmelt. In the same catchment, Campbell et al. (2004) estimated the average total N input from atmospheric derived nitrate to be 13.2 kg ha^{-1} a^{-1}, which can be significant in such a catchment where atmospheric nitrogen is the most influencing nitrate source. However, this N-input is relatively low compared to an intensively operated agricultural area. In Ireland, for example, the Nitrates

Directive (EC, 1991) allows cattle stocking rates with a nitrate input of 170 kg ha^{-1} a^{-1} or 250 kg ha^{-1} a^{-1} on derogation farms.

Several authors discussed the link between land use practices, hydrological conditions and N availability (Andrade and Stigter, 2009; Badruzzaman et al., 2012; Kaçaroğlu, 1999). Although nitrate is often not the major form of N application to agricultural land, it is usually the major form observed in recharge (Böhlke, 2002). In addition, in agricultural dominated areas not only the total amount of N application is relevant. Also different agronomic practices of N application have a consequence on the likelihood and amount of N leaching (Liu et al., 2013; Oenema et al., 2012). For example, the type of N applied has an influence on the leaching behaviour throughout the year. Inorganic N fertilisers are on the one hand immediately available for the plant, but on the other hand highly susceptible to leaching, whereas organic N fertiliser provide a more constant source of nitrate for the plant on a long term basis due to mineralisation processes (Whitehead, 1995). Best nutrient management practices are contributing to an increased N use efficiency which directly implies reduced nitrate loss from surface to groundwater (Rahman et al., 2011; Buckley and Carney, 2013; Oenema et al., 2005). Huebsch et al. (2013) used multiple linear regression to explore the impact of agronomic practices on nitrate concentrations in karst groundwater on a similar site and concluded that improvements in management, such as timing of slurry application, reductions in inorganic fertiliser usage or the change from ploughing to minimum cultivation reseeding, contributed to reduced nitrate concentrations in groundwater.

In addition to mobilisation and dilution processes, seasonal variations need to be addressed. Mineralisation of organic N can also lead to a different leaching behaviour throughout the year. For example, Mudarra et al. (2012) linked increased mobilisation of nitrate at the Sierra del Rey-Los Tajos carbonate aquifer in autumn with increased soil microbial activities, which are directly related to decreased evaporation and increased soil moisture. In contrast, Panno and Kelly (2004) recorded a seasonal trend with greatest nitrate concentrations during late spring and summer and lowest during late fall and winter. Interestingly, Arheimer and Lidén (2000) monitored riverine inorganic and organic N concentrations from agricultural catchments and showed that inorganic N concentrations were lower during summer and higher during autumn, whereas organic N was higher in summer than during the rest of the year.

Similarly, Bende-Michel et al. (2013) linked riverine nitrate response with agricultural source availability throughout the year (e.g. time of inorganic and organic N fertilisation; nitrate build-up from organic matter in summer after organic N fertiliser application) and with hydrologic mobilisation due to a change from low to high flow conditions. They assumed that higher peaks of nutrient concentration response should occur (1) during spring after inorganic fertiliser application, (2) during autumn because of increased mineralisation and nitrification processes of organic matter in summer and eventually (3) during winter due to possible expansion of the source area during high flow conditions. In addition, Rowden

(2001) showed that larger losses of applied N occurred during wetter years (concentrations and loads). Rainfall intensity and duration is influencing soil moisture. Wet conditions coupled with high nitrate availability in soil due to accumulation intensify leaching from the soil and in the unsaturated zone (Di and Cameron, 2002; Stark and Richards, 2008). In the present study site, the highest peaks of mobilised nitrate concentrations occurred in November 2011 and between June and September of 2012. Seasonal variations are driven by recharge and N availability at the surface. During the summer period, on the one hand, intensive recharge may transport lower nitrate concentrations if there is a lot of plant growth but on the other hand, it also may increase transport if there is inorganic N in the soil after fertilisation application. During autumn reduced crop uptake and increased recharge due to longer and more intensified rainfall events typically increases leaching of residual N in soil (Patil et al., 2010).

Because of rapidly changing concentrations of nitrate and other chemical or microbial contaminants in karst systems, traditional sampling strategies with sampling intervals of weeks to months are inadequate to assess water quality in such systems. This is especially of interest in context of the EU Water Framework Directive, which requires improving the quality of critical water bodies affected by high nitrate from groundwater, such as estuaries and coastal waters. In addition, high-resolution monitoring offers the possibility to detect predominance of mobilisation that can lead to sudden nitrate peaks above the MAC. Hence, if karst groundwater is used as drinking water this technique can help to prevent serious threat to humans and animals such as toxicity in livestock (Di and Cameron, 2002) or methemoglobinemia in infants also known as the ´blue baby syndrome´ which can progress rapidly to cause coma and death (Knobeloch et al., 2000). An intensification of high-resolution monitoring in the future is therefore essential to assure good water quality of karst groundwater and water bodies highly affected by karst groundwater.

4.5 Conclusions

The proposed conceptual model of nitrate response in karst systems is able to explain various nitrate response scenarios, the nitrate patterns at the spring of the current study and the findings from other studies. In the current study, four possible nitrate response scenarios in karst aquifers to storm events were hypothesized. Scenario 1 relates to mobilised nitrate concentrations, Scenario 2 diluted nitrate concentrations, Scenario 3 a combination of mobilised and diluted nitrate concentrations during one event and Scenario 4 mobilised and diluted nitrate concentrations during multiple events. The proposed conceptual model of nitrate in karst systems elucidates the relation of nitrate responses at karst springs with driving factors such as hydrological conditions, N availability through land use and karst features. Predominance of mobilisation or dilution and therefore rapid rise or decline of nitrate concentrations during storm events depend highly on the availability of nitrate accumulated in soil and unsaturated zone. A well-developed karst system as well as wet conditions are crucial for rapid transport and have an influence on the intensity and time lag of nitrate concentration changes. Differences regarding predominance of dilution or mobilisation processes during different storm events on the same study site occur if 1) the source of N at the surface changes over time and/or 2) the activation of different flow paths causes mixing of water sources containing more or less nitrate than the average nitrate concentration in groundwater at the study site. The presented conceptual model of nitrate responses in karst systems contributes to a more comprehensive understanding of nitrate occurrences in the environment and therefore also facilitates an improved implementation of the EU Water Framework Directive in environmental activities, planning and policy. Finally, the study also highlighted the important role of continuous and long-term nitrate monitoring in karst systems.

5 Field experiences using UV/VIS Sensors for high-resolution monitoring of nitrate

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Abstract

Two different in-situ spectrophotometers are compared that were used in the field to determine nitrate-nitrogen (NO_3-N) concentrations at two distinct spring discharge sites. One sensor was a double wavelength spectrophotometer (DWS) and the other a multiple wavelength spectrophotometer (MWS). The objective of the study was to review the hardware options, determine ease of calibration, accuracy, influence of additional substances and to assess positive and negative aspects of the two sensors as well as troubleshooting and trade-offs. Both sensors are sufficient to monitor highly time-resolved NO_3-N concentrations in emergent groundwater. However, the chosen path length of the sensors had a significant influence on the sensitivity and the range of detectable NO_3-N. The accuracy of the calculated NO_3-N concentrations of the sensors can be affected, if the content of additional substances such as turbidity, organic matter, nitrite or hydrogen carbonate significantly varies after the sensors have been calibrated to a particular water matrix. The MWS offers more possibilities for calibration and error detection, but requires more expertise compared with the DWS.

5.1 Introduction

Present and predicted future shortage of drinking water is a worldwide problem and global population growth increases the demand for high-quality potable water (Schiermeier, 2014). Thus, the importance of the protection of drinking water quality is acknowledged worldwide by the implementation of international programs such as the European Union (EU) Water Framework Directive (OJEC, 2000) and daughter directives, the US National Water Quality Assessment Program (NAWQA) and Maximum Daily Load Program (TMDL) (Elshorbagy et al., 2005) or the Australian National Water Quality Management Strategy (ANZECC, 2000). Built into these regulations is a fundamental need to monitor the quality of drinking water supplies. However, especially in karst and/or fractured aquifers, water quality can change rapidly in a time frame from hours to days (Huebsch et al., 2014; Mahler et al., 2008; Pronk et al., 2009). Nitrate (NO_3^-) is particularly noted as being a risk to human health when in high concentrations in source drinking water (L'hirondel, 2002) and also contributes significantly to eutrophication of water (Stark and Richards, 2008).

High resolution flow and nitrate-nitrogen (NO_3-N) concentration data from short residence time aquifers enable an improved understanding of the mobilisation/dilution dynamics in karst aquifers (Huebsch et al., 2014) and to prevent negative consequences from NO_3-N concentrations breaching the maximum allowable concentration (MAC). In the EU for example, the MAC is 11.3 mg NO_3-N L^{-1}, to prevent health concerns (Knobeloch et al., 2000), abortion to cattle or toxicity in livestock (Di and Cameron, 2002).

Photometrical ultraviolet/visible light (UV/VIS) sensors have been first employed at municipal wastewater treatment plants to control NO_3-N effluent concentrations (Langergraber et al., 2003; Rieger et al., 2004). In addition, UV/VIS sensors have been recently used in groundwater and surface water applications to assess highly resolved NO_3-N concentrations (Pu et al., 2011; Wade et al., 2012). The technique gives the opportunity to observe trends and rapid changes of NO_3-N whilst using a solid-state methodology without reagents. Thus, less frequent calibration and maintenance than other common in-situ methods such as ion sensitive electrode applications is required (Bende-Michl and Hairsine, 2010).

The technical note provides an assessment of two different spectrophotometric sensors, i.e. a double wavelength spectrophotometer (DWS) and a multiple wavelength spectrophotometer (MWS) used at field sites in Ireland and Jordan, respectively. The following issues are addressed in the present study: Hardware options, ease of calibration, accuracy, influence of additional substances, positive and negative aspects of the two sensors, troubleshooting and trade-offs.

5.2 Materials and methods

NO_3-N dissolved in water absorbs light below 250 nm (Armstrong, 1963) although the specification for NO_3-N determination due to absorbance varies in the literature. Karlsson et al. (1995) and Drolc and Vrtovšek (2010) describe specific parameter determination of NO_3-N at 205 nm, Thomas et al. (1990) at 205 to 210 nm, Ferree and Shannon (2001) at ~224 nm and Armstrong (1963) at 227 nm. The relationship between absorbance, i.e. extinction of light (E) at a specific wavelength, and NO_3-N concentration is linear and follows the Lambert Beer´s Law (Eq. 1):

$$E = log\frac{I_0}{I}, \tag{1}$$

where I_0 is the light intensity emitted by the sensor lamp and I is the light intensity after the light has passed the water matrix. Hence, physically increased light absorption of NO_3-N dissolved in water correlates to increased NO_3-N concentrations. However, in natural water, additional substances other than NO_3-N occur. Turbidity has a major influence on light absorbance as the presence of suspended material such as organic particles can lead to scattering effects on the recorded absorption values of NO_3-N (Chýlek, 1977; Rieger et al., 2008; Vaillant et al., 2002). In addition, substances that absorb in the investigated spectral range such as nitrite-nitrogen (NO_2-N) or humic acids can lead to superposition of absorbance (Kröckel et al., 2011). The consequences are that multivariate data analysis approaches are needed to determine NO_3-N, such as principal component analysis or partial least square regression (Dahlén et al., 2000; Gallot and Thomas, 1993a; Karlsson et al., 1995; Macintosh et al., 2011).

In this study, a DWS (NITRATAX plus sc, Hach Lange GmbH, Germany) and a MWS (s::can sprectro::lyser^{TM}, s::can Messtechnik GmbH, Austria) were used (Fig. 5-1). The DWS was installed in a flowing spring emergence (Spring A) in south-west Ireland and the MWS in a flowing spring emergence (Spring B) in Jordan. The study sites are described in more detail in a previous study of Huebsch et al. (2014) and Grimmeisen et al. (2014), respectively. Both springs discharge karst aquifers; however, Spring A is located in an agricultural catchment and Spring B in an urban catchment.

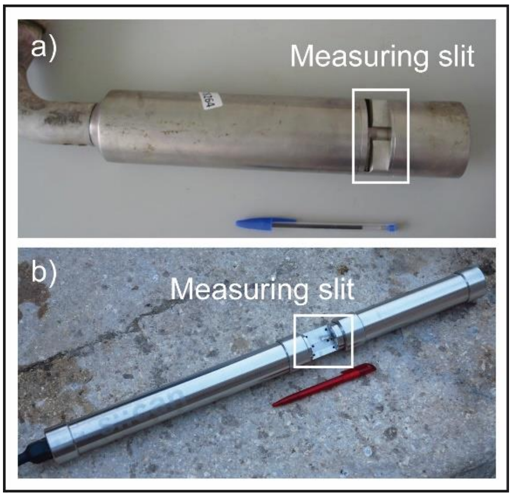

Fig. 5-1: UV/VIS sensors: a) Double wavelength spectrophotometer (DWS) with measuring path of 5 mm; b) Multiple wavelength spectrophotometer (MWS) with measuring path of 35 mm.

The DWS measures UV absorbance at a wavelength of 218 nm at a measuring receiver (EM – element for measuring) and at 228 nm at a reference receiver (ER – element for reference). The recorded measurements at two different wavelengths at EM and ER are designed to compensate interference of organic and/or suspended matter (Thomas et al., 1990) by interpreting the difference between the absorbance values at EM and ER which is expressed by ΔE. In comparison, a UV sensor using only one single wavelength is not able to compensate additional interferences (van den Broeke et al., 2006). The MWS measures absorbance at 256 different wavelengths between 200 nm and 750 nm within 15 sec (Rieger et al., 2004). Both sensors feature the possibility to export the monitored absorbance values and the calculated concentrations. As a result of the different measuring methods, the DWS makes no difference between NO_3-N and NO_2-N and therefore, reports the NO_x-N concentration (or total oxidised nitrogen, TON) instead of NO_3-N (Drolc and Vrtovšek, 2010) and assumes negligible NO_2-N. Due to the range of measurements in the scan, the MWS is able to provide the specific NO_3-N concentration. NO_3-N/NO_x-N concentrations observed with the DWS and MWS were compared with NO_3-N/NO_x-N concentrations determined in the laboratory. Water samples used for determination of NO_3-N/NO_x-N concentrations were measured in the water in situ with the sensors. For comparison, water samples were also filtered using a 0.45 -µm micropore membrane to determine NO_3-N/NO_x-N concentrations in the laboratory. For determination Aquakem 600A (Thermo Scientific, Finland) and Dionex ICS-2100 (Thermo Scientific, Finland) was used, respectively. The DWS was installed in July 2011 in spring A. NO_x-N concentrations were fluctuating approx. between 10 mg L^{-1} and 14 mg L^{-1} until September 2014. The MWS was installed in spring B in May 2011 and observed approx. minimum and maximum concentrations of 12 mg NO_3-N L^{-1} and 15 mg NO_3-N L^{-1} until September 2014, respectively.

There are several sensor options available for the DWS and the MWS from the manufacturers. The DWS is available with three different path-lengths of 1, 2 and 5 mm, which cover a NO_x^-N detection range of 0.1 to 100.0 mg L^{-1}, 0.1 to 50.0 mg L^{-1} and 0.1 to 25.0

mg L^{-1}, respectively. The range of NO_x^--N detection increases with a shorter path length. However, a shorter path length implies also a lowered overall sensitivity of the measurement (Thomas et al., 1990). In this study, a DWS with a path length of 5 mm was used.

There are also several options for the MWS for possible measuring paths and applications. For natural waters, it is advisable to choose a measuring path of 5, 15 or 35 mm. A measuring path of 5 mm covers a NO_3-N detection range of 0.02 to 70.0 mg L^{-1}, a measuring path of 15 mm a detection range of 0.02 to 40.0 mg L^{-1} and a measuring path of 35 mm a detection range of 0.02 to 10.0 mg L^{-1}. Thus, the advised measuring paths for both sensors differ by the manufacturers due to the divergent measuring methods. The studied MWS had a measuring path of 35 mm and the software capability to measure turbidity, NO_3-N, total organic carbon (TOC) and dissolved organic carbon (DOC). The manufacturer advises to use a path length of 35 mm in natural water, even if this might not be the optimal path length for the monitored NO_3-N concentrations in the field (optimal at ≤10 mg L^{-1}). If additional measuring options are included such as turbidity, TOC and DOC, the path length has to be suitable for the combined options. Those may occur at different ranges and the best compromise has to be selected.

For calibration, the applied DWS has the option for a two-point calibration, in addition to a four-point manufacturer´s calibration with standard solutions at 0, 25, 50 and 100 mg L^{-1}. The MWS offers two main options for calibration, off-site and on-site calibration, which are also in addition to the manufacturer pre-adjustment. The off-site calibration is based on wavelength-concentration datasets previously analysed by the manufacturer (Langergraber et al., 2004c), whereas the on-site calibration offers the possibility for an improved adaption to the matrix of the monitored water (Rieger et al., 2006). This is also possible with the DWS. On-site calibration can be performed with a linear (local 1) or a polynomial (local 2) function.

5.3 Results and discussion

5.3.1 Hardware options

Table 5-1 provides an overview of the available hardware and software options, output format, maintenance, warranty and costs of the DWS and MWS. Important differences between both sensors despite the measuring method are: 1) the cleaning device for the MWS is offered as an additional hardware option, (but highly necessary in natural waters,), whereas the DWS is already equipped with a wiper for cleaning; 2) the purchase price for the DWS is lower than the MWS (~16.000 € and 20.000 € excluding VAT in 2014, respectively). Both sensors report the raw dataset of the absorbance measurements, which is based on the two different measuring methods (DWS: two wavelengths; MWS: full absorbance spectrum). The investment costs for both sensors are based on the advanced and comparable version of both manufacturers, which means that first, turbidity can be compensated, second, the raw dataset is included and third, error detection for both sensors is possible afterwards. The costs are based on elementary equipment: sensor, cable and basic handling device. Additional upgrades such as remote control, advanced handling device and flow-through unit, which ensures sufficient flow through the measuring slit, are also available which lead to an increase in pricing.

Tab. 5-1: Description of the double wavelength spectrophotometer (DWS) and the multiple wavelength spectrophotometer (MWS).

Components	DWS	MWS
Hardware	• Sensor incl. wiper for cleaning, cable, handling device (station terminal) • Internal memory included	• Sensor, cable, handling device (station terminal) • Internal memory included
Hardware options	• Flow through-unit • GSM modem • Mobile display for on-site operations • Additional analogue outputs for up to 8 sensors	• Cleaning device necessary in natural waters • GSM modem • Additional analogue outputs (terminal) • Interfaces for 1 MWS and 3 other sensors
Software options	• WINXP-based • Remote control • Alarm option • Display on-site: concentrations and daily or weekly trend line over time • Password for protection of display possible	• WINXP-based • Remote control • Calibration menu for on-site calibration • Alarm option • Display on-site: switching between nitrate concentrations over time and spectra • Automated light source check
Output	• Absorption values at EM and ER • Calculated NO_x-N concentrations • Output via memory card and/or remote control	• Absorption spectra • Calculated NO_3-N concentrations • Output via memory card and/or remote control
Maintenance	• Low • Manufacturers calibration of sensor needs to be refreshed after 1 – 2 years	• Low • After 2 years check of light source at the manufacturer necessary (cost intensive ~ 1.000 € excl. VAT)
Warranty	• 5 years on light source	• 3 years
Costs	• Low maintenance and labour costs • Purchase price: ~ 16.000 € excl. VAT	• Low maintenance and labour costs • Purchase price: ~ 20.000 € excl. VAT

5.3.2 Ease of calibration and accuracy after calibration

Fig. 5-2 shows the accuracy of the two sensors immediately after calibration using the available calibration methods. The DWS was calibrated with standard solutions, which provided a good result for the monitored water in the area (spring water A; Fig 5-3a). The root mean square error (RMSE) to the ideal straight line of y = x (measured sensor concentrations vs. concentrations measured in the laboratory) was 0.42. For the MWS, higher accuracy was reached by using water samples from adjacent springs, which had a higher affinity to the water matrix of the monitored spring than standard solutions (spring water B; Fig. 5-3b). These water samples were also used to test the accuracy of the sensor. The best results were obtained with the on-site calibration using a second order polynomial function (local 2; Fig 5-2d) including a RMSE of 0.36. For off-site calibration (Fig 5-2b) and on-site calibration with a linear function (local 1; Fig. 5-2c) RMSE was 2.11 and 0.82, respectively. In addition, Fig. 5-2 shows that the accuracy of the sensor decreases with higher NO_3-N concentrations, especially for the two point calibration of the DWS sensor and the off-site calibration of the MWS. In general, the precision of the sensor readings are dependent on the sensor path length (Kröckel et al., 2011). The MWS with 35 mm path length becomes less accurate with higher concentrations, as the optimal measurement range for 35 mm path length is 0.02 to 10 mg L^{-1} NO_3-N. However, the manufacturer claims the NO_3-N concentration range between 10 to 15 mg L^{-1} to be sufficient and applicable for monitoring. The path length of 35 mm was recommended for including additional measuring options such as turbidity, TOC and DOC. The accuracy of both sensors is dependent on a) the selected path length for measuring the concentrations, b) a comparable and similar water matrix to the standard solution used for calibration and/or c) the option to use local water having minimum and maximum NO_3-N concentrations characteristic for the NO_3-N measured with similar matrix structure for calibration. As the last two points are rather challenging in the field, we suggest calibrating the sensors with water from the field site. If necessary a number of those waters can be used that are diluted or concentrated with standard solution to get approximate representative minimum and maximum values for calibration. However, after calibration changes of the water matrix in a natural environment due to e.g. mixing of different groundwater can lead to less qualitative results. Complex changes of the water matrix can affect the “trueness” and precision of the sensor readings, because the sensor is calibrated to a specific water composition (Langergraber et al., 2004b; Maribas et al., 2008; Stumwöhrer et al., 2003).

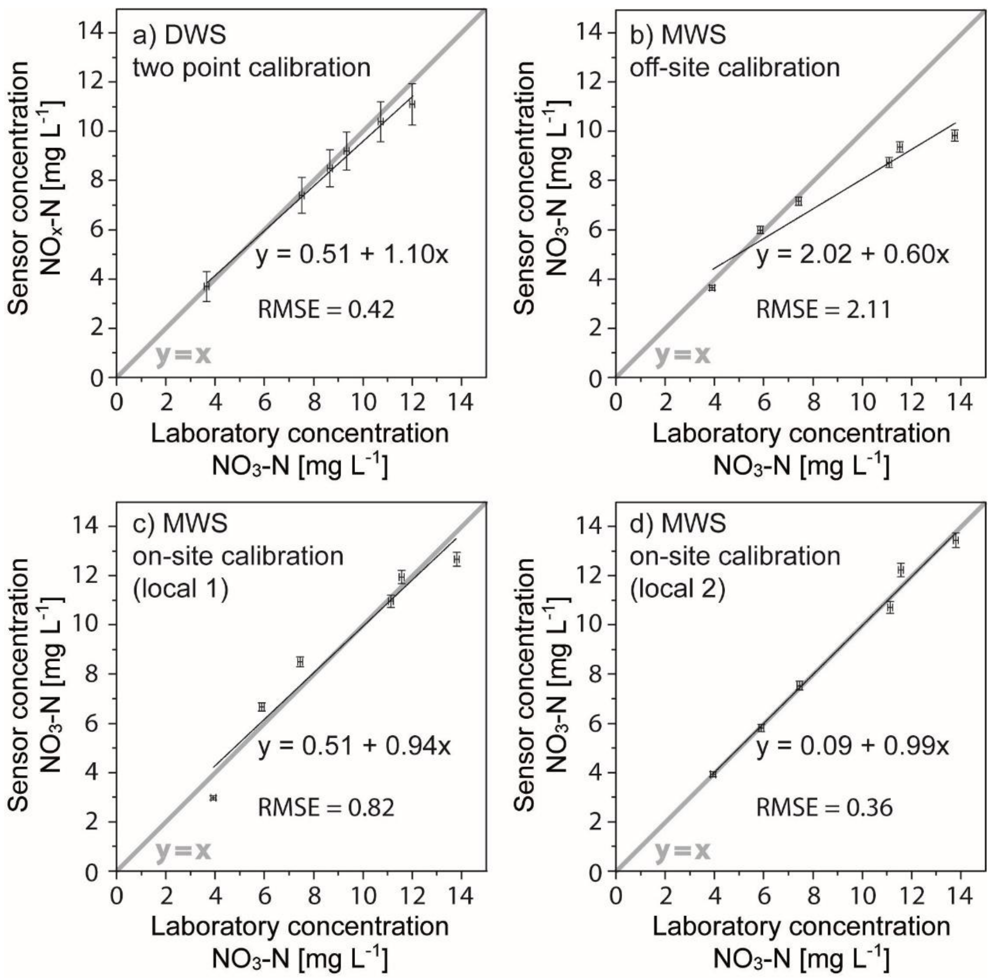

Fig. 5-2: Accuracy of double wavelength spectrophotometer (DWS) and multiple wavelength spectrophotometer (MWS) immediately after calibration. To test the accuracy of the DWS, while considering the matrix compostion of the studied water, spring water (highest concentration), water from a close-by river (lowest concentration) and a mix of river and spring water was used. For the MWS, spring water and water from other close springs were used. Error bars were calculated after the manufacturers specifications. Recorded sensor measurements are compared with measured concentrations analysed in the laboratory. The root mean square error (RMSE) was calculated by relating the measured sensor concentrations with the optimum calibration (ideal straight line y = x).The DWS has one option for calibration, whereas the MWS offers three options for calibration. All calibration options are in addition to the factory calibration provided by the manufacturer.

5.3.3 Influence of additional substances

In natural waters, the absorption spectra can vary significantly due to, for example, different contents of natural organic matter (Thomas and Burgess, 2007) and so interference effects of substances that are absorbing light in a similar wavelength range to NO_3-N are possible (Macintosh et al., 2011). Fig. 5-3 shows absorbance spectra and first derivative of four different water samples, which were determined with the MWS. Spring waters A and B were constantly monitored during the research period for the DWS and MWS, respectively. Spring water A was sampled in a karst spring in an agricultural dominated area in South Ireland, whereas spring water B occurs in an urbanized catchment and is continuously contaminated by faecal matter from sewer seepage of Salt, a city in Jordan. For Fig. 5-3, the spring water samples used have a similar NO_3-N concentration of 11.4 mg L^{-1} and 11.1 mg L^{-1}, respectively. For comparison, two other samples with similar NO_3-N concentrations of 3.9

and 4.1 mg L^{-1}, respectively, were plotted: a sample of mains water of the Jordanian city, a water mix of spring, river and pond water sampled and mixed at the area in South Ireland mentioned above. The mains water is a mix of treated spring and river water, whereas the spring-river-pond water is a mix of water from spring water A, a nearby river and water from a pond. In Fig. 5-3a, the high absorbance values below 250 nm specify the presence of NO_3-N in the water. Isobestic points are an indicator for different matrix compositions of the samples (Gallot and Thomas, 1993b; Vaillant et al., 2002). Other substances such as NO_2-N, HCO_3^- or dissolved organic matter in water can result in a superposition of the absorbance values (Kröckel et al., 2011; Langergraber et al., 2004a; van den Broeke et al., 2006), even if the maximum absorbance values of those substances occur at different wavelengths than NO_3-N absorbance. In Fig. 5-3, the water mix of spring, river and pond water has higher absorbance values than the other samples, although the NO_3-N content is low in relation to spring waters A and B. This can be explained by the influence of interfering substances other than NO_3-N, which are leading to superposition of the absorbance values and are clearly indicated by increased absorbance values above 250 nm. The first derivative allows a more detailed interpretation of the NO_3-N concentration: Samples with similar NO_3-N concentration follow a much more similar curve progression (Fig. 5-3b) than the absorbance spectra (Fig. 5-3a). In addition, positive values in the majority of the first derivative between 220 and 240 nm indicate that the light or energy source is damaged and needs to be replaced. The MWS uses derivative methods, amongst others, for calculating the NO_3-N concentrations, whereas the DWS records the absorbance values at two wavelengths (218 and 228 nm) and defines the NO_x-N concentration by using the difference between those wavelengths. This means that the DWS sensor takes the slope into account as well as the interval of the absorbance difference at the two wavelengths, which implies that superposition by additional substances are considered. Nevertheless, this and other studies indicate problems due to superposition of substances (Maribas et al., 2008).

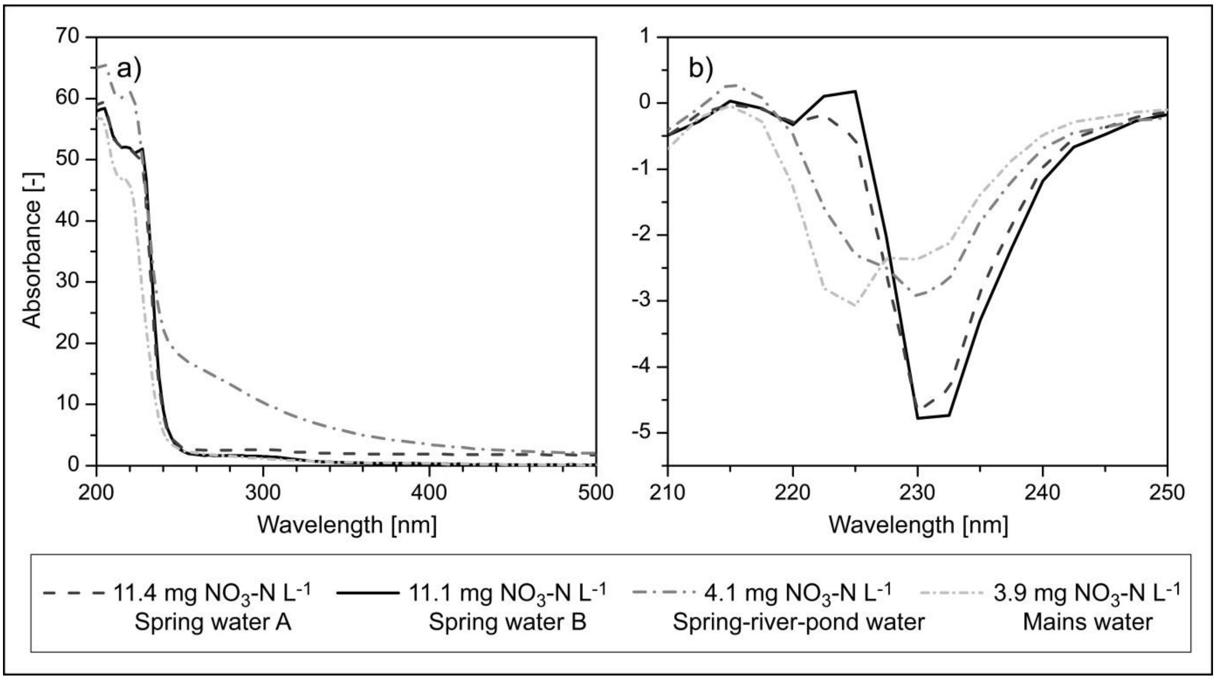

Fig. 5-3: Absorbance vs. wavelength of 4 different samples measured with the multiple wavelength spectrophotometer (MWS). Spring water A was constantly monitored by the double wavelength spectrophotometer (DWS), whereas spring water B was the monitored by MWS. a) The isobestic points indicate different matrix compositions of the samples. Nitrate and nitrite are strongly absorbed below 250 nm. Other substances such as COD, trace organics, humic substances or turbidity in water can increase the absorbance value below 250 nm. The maximum influence of those substances can be recognised at higher wavelengths, for example at the obvious differences of the samples between 250 and 400 nm. b) The first derivative of samples allows a finer interpretation of the nitrate content in the water. The samples with similar nitrate concentration show more similar curve progression than in a).

5.3.4 Positive and negative aspects of the two sensors

Table 5-2 gives an overview of positive and negative aspects of the two sensors regarding installation, requirements, calibration and error detection. Installation of both sensors is straightforward. The manufacturer of the DWS supplies L-brackets for installation of the instrument in the correct position. For both sensors, a mains power source is required for operation, which may be a problem for field applications. A power supply of 230vAC is sufficient. Positive aspects of both sensors are that the calibration intervals can be performed on a long term basis which is an asset compared to other NO_3-N detection methods (Beaupré, 2010). Calibration can be simple, if the water matrix is similar to standard solutions provided by the manufacturer, but more complicated if the water matrix differs significantly from standard solutions or if collection of water samples representing a broad range of NO_3-N concentrations of the monitored water is difficult. The MWS offers more options for calibration than the DWS, which can lead to higher precicion (Fig. 5-2). In contrast, the on-site calibration methods require more expertise and, therefore, can be time consuming. Even if calibration intervals are on a long-term basis, it is advisable to perform regular controls such as regular conventional measurements of NO_3-N concentrations to ensure the reliability of the data provided by the sensor. In addition, the manufacturer of the DWS advises to return the sensor to the manufacturer on an annual basis to refresh the four-point calibration, replace seals and check the sensor. Error detection is possible with both sensors, but costs more compared to similar sensor types provided by the manufacturers with no error detection. The manufacturer gives advice to check the light source every two years as this has to be renewed. Because the MWS measures the full absorption range, more detailed information of possible disturbances can be utilised.

Tab. 5-2: Evaluation of appliance of the double wavelength spectrophotometer (DWS) and the multiple wavelength spectrophotometer (MWS): positive (+), negative (–) and neutral (o) aspects

Positive, negative and neutral aspects		**DWS**	**MWS**
Installation	+	• Easy • A L-bracket provided by the manufacturer makes it simple to install the instrument in the correct position	• Easy
	–		• Must be aware that the measuring path needs to be orientated in a horizontal position with the measuring path down especially if used without cleaning device
Requirements	–	• Power source needed for operation	• Power source needed for operation
Calibration	+	• Easy if water matrix is similar to standard solutions provided by the manufacturer	• Off-site calibration provided by the manufacturer and site specific on-site calibration possible offering higher precision • Recalibration of the raw dataset possible
	–	• Only 2 point calibration possible for the user • On-site calibration complicated if water matrix differs significantly from standard solutions provide by the manufacturer or if collection of water samples representing the monitored NO_3-N range remains difficult	• Achievement of a sufficient level of expertise is necessary if off-site calibration is not useful • On-site calibration complicated if water matrix differs significantly from standard solutions provide by the manufacturer or if collection of water samples representing the monitored NO_3-N range remains difficult
Error detection	+	• Relationship Delta E to calculated concentration gives possibility for detection	• First derivative of spectra gives more detailed information, e.g. if values between 220 and 240 nm are positive, light or energy source is damaged
	–	• Dependence on manufacturer for provision of additional information	• Dependent on help of the manufacturer

5.3.5 Troubleshooting and trade-offs

During operation of both sensors, two difficulties occurred that affected the reliability of the recorded NO_x-N concentrations (Fig. 5-4, Fig. 5-5). Fig. 5-4 illustrates discrepancies between wavelength measurements and calculated NO_x-N concentrations above 12.12 mg L^{-1} of the DWS. In Fig. 5-4a, the raw dataset of the difference between absorbance values at 218 and 228 nm, ΔE, is shown. In Fig 5-4b, the reported NO_x-N concentrations are illustrated, which were calculated from the raw dataset and followed an inverse trend if NO_x-N concentrations were above 12.12 mg L^{-1}, contrary to Lambert Beer's Law. The manufacturer assumed a software problem and the probe had a complete control check after the detection of the error. The manufacturer's background calibration was therefore refreshed and the software and light source were replaced. However, because the raw absorption dataset was recorded, it was possible to eliminate the error retrospectively and quantitatively by using a regression line, which was extrapolated from the correct calculated values (Fig. 5-4c).

During operation of the MWS, suspicious readings were recorded, which occurred immediately after installation due to a technical mistake (Fig. 5-5). The sensor was first installed in a vertical position without a cleaning device. This led to an accumulation of suspended material at the measuring slit. Consequently, the recorded values for turbidity increased. If the turbidity signal reaches values at or above 20 FTU (Formazin Turbidity Units), determined NO_3-N values are not reliable. For turbidity ≥ 20 FTU the recorded NO_3-N values showed a decreasing trend. At turbidity ≥ 80 FTU no NO_3-N concentrations were reported. The sensor was cleaned on a weekly basis, which explains the periodic, weekly pattern of turbidity and NO_3-N values. After error detection, the sensor was reinstalled in a horizontal position with a downwards orientated measuring path. However, it was necessary to purchase a cleaning device from the manufacturer as fouling of the measuring slit still disturbed the readings. The manufacturer offers the sensor with the purchase of an air pressure cleaning device as an option (Tab. 5-1). In contrast, the DWS uses a wiper for cleaning, which is already included in the standard probe. Hence, we strongly recommend purchasing the cleaning device together with the MWS sensor, if the system is operated in natural waters.

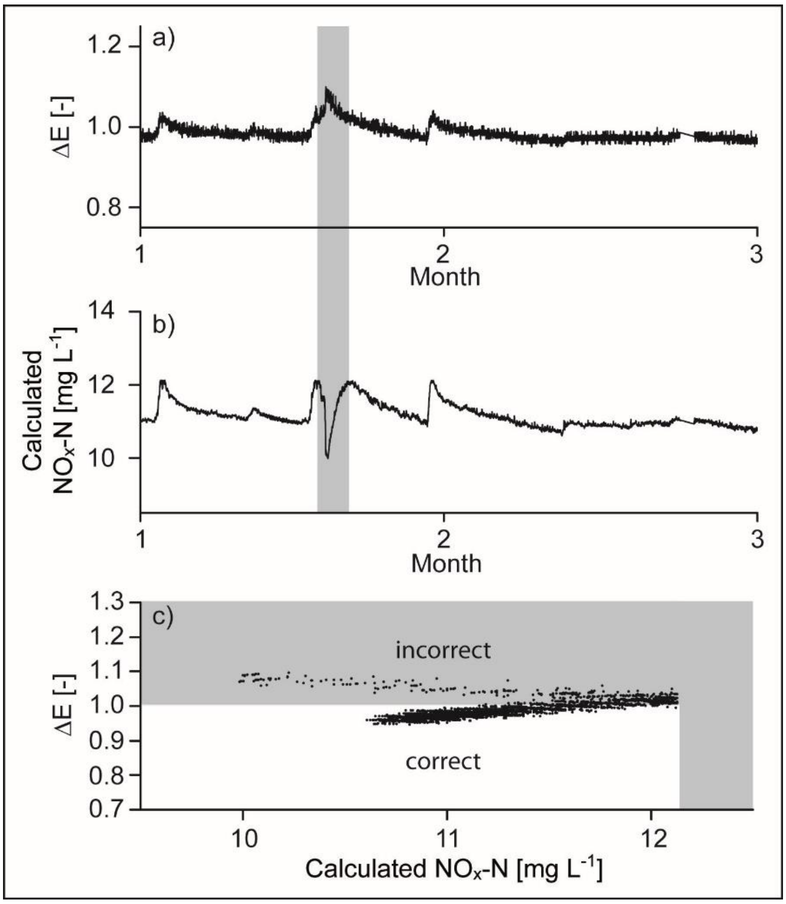

Fig. 5-4: Example of discrepancies between wavelength and calculated NO_x-N concentrations as displayed by the double wavelength spectrophotometer (DWS). The shaded grey area highlights the dataset of incorrect NO_x-N calculated values. a) Raw dataset of recorded wavelength values during 2 months. ΔE is the difference between light extinction at 218 and 228 nm. b) Calculated NO_x-N concentrations from the raw dataset as reported by the DWS. c) Values of the raw dataset (ΔE) and the reported NO_x-N concentrations of the DWS. Once NO_x-N values reached 12.12 mg L^{-1}, values were incorrectly calculated in an opposite trend.

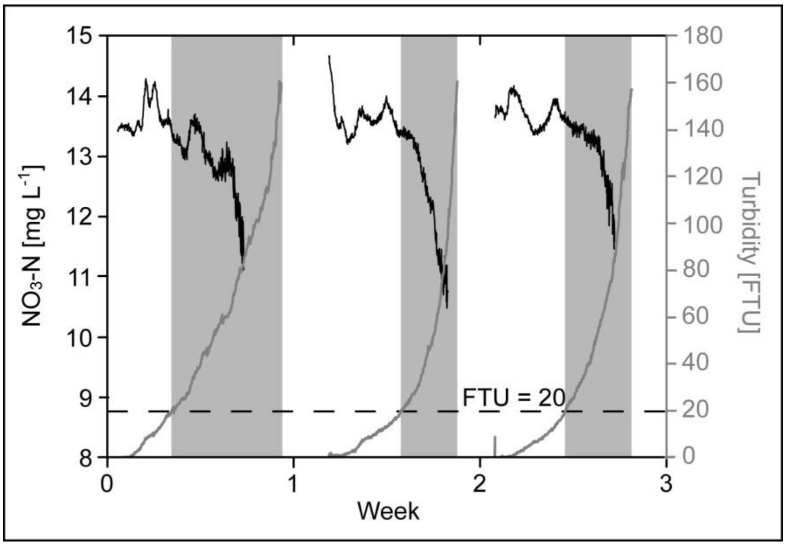

Fig. 5-5: Interference of deposition of suspended matter at the measuring path of the multiple wavelength spectrophotometer (MWS) due to vertical installation of the sensor. The grey areas indicate the time range when the FTU signal is ≥ 20 and thus the reported NO_3-N concentrations are not reliable during that time. Reporting of NO_3-N concentrations breaks down at 80 FTU.

During operation of the DWS the computer system was unstable and shut down several times causing data gaps of several hours, until the system started recording again. Maribas et al. (2008) also describes disturbances of the MWS measurements caused by air bubbles in the water. They state that where bubbles exist in the water, the measuring path needs to be orientated to allow the bubbles to pass. Kröckel et al. (2011) advises to use a filter such as a flow through-unit to prevent inaccurate measurements due to air bubbles (Tab. 5-1) although these can be unreliable in highly turbid waters. One should also notice that reliable measurements of both sensors cannot be determined, if the sensor measurements are affected by saline water. If the measured water is influenced by water with salt content, for example due to flooding and close installation to the coast or in deeper wells, the determination of NO_3-N by the UV sensors would be affected as salt has a strong UV absorption in the NO_3-N absorption range (Kröckel et al., 2011). In addition, in highly heterogeneous environments, such as karst aquifers, rapid groundwater fluctuations and temporary activated conduit inlets might result in mixing of waters with different water quality and therefore matrix. This can have an effect on the accuracy of the NO_3-N concentration dataset. Even though the MWS measures over the full absorption spectra, detections remain difficult in that case and might result in less accurate concentrations. This could be a problem especially if absolute values instead of general water quality trends are necessary in a rapidly changing environment. However, both sensors offer a reliable detection of highly resolved NO_x-N concentration trends with low maintenance effort, which is an asset in the field compared to other common in-situ methods such as ion sensitive electrode applications (Bende-Michl and Hairsine, 2010).

5.4 Conclusions

Both sensors were efficient for continuously monitoring highly time-resolved NO_3-N in groundwater emergences (i.e. flowing water) in this study and deemed fit for purpose. Although, the calibration procedure for the DWS is easier than for the MWS, the wavelength spectra of the latter provides a more detailed insight of the absorption and consequently improved NO_3-N calculations. If NO_2-N is a major concern in the studied water, the MWS should be chosen for monitoring, as the DWS does not distinguish between NO_3-N and NO_2-N. For ease of use and with an emphasis on measuring TON (where NO_2-N is known to be negligible), the DWS could be also considered. In addition, the path length of the two sensors should be carefully chosen. The chosen path length is significant for the accuracy of the sensor measurements at a specific measurement range. It is reasonable to conclude that high-resolution UV/VIS monitoring will greatly contribute to a better understanding of groundwater processes in the future.

6 Conclusions and outlook

The current study contains three main focuses which are partitioned into chapter 3 to 5.

In the study presented in chapter 3 a statistical approach was used to explore the relationships between farm management, local weather variations and groundwater nutrient concentrations spatially and temporally in a highly complex free draining soil and karst aquifer environment over an 11 year monitoring period. The approach proofed to be an effective method and can be used to predict future changes in water quality especially if nutrient concentration thresholds and not fluxes are important as currently stipulated by the EU WFD. In addition, complex terrains such as free draining soils underlain with karst limestone aquifers can be explored without the urgent need for expensive, high end hydrogeological investigations. The results indicate that travel times from N application at the surface to nitrate contamination in groundwater can be quick (≤ 2 years). Furthermore, it can be concluded that a combination of site characteristics (depth of the unsaturated zone, soil/subsoil and rock thickness), climatic factors (such as rainfall, sunshine and SMD) and agronomic practices (reduced fertiliser rate, appropriate slurry and DSW application strategy, minimum cultivation and strategic management of high risk zones) were important factors influencing NO_3^- loss to groundwater.

The study in chapter 4 involves a proposed conceptual model of NO_3^- responses due to high rainfall events. The conceptual model elucidates the relationship of NO_3^- responses in karst systems while considering important factors such as N availability through land use, karst features and hydrological conditions. Furthermore, the conceptual model is able to explain several NO_3^- response scenarios in relation to observed NO_3^- pattern at a permanent spring at Dairygold farm and other case studies from the literature. Abrupt increased or decreased NO_3^- concentrations due to intensive rainfall events are reflecting predominance of mobilisation or dilution processes and are highly depending on the availability of NO_3^- accumulated in soil and unsaturated zone. Rapid transportation is enabled by a well-developed karst system in combination with wet conditions which both are crucially influencing the intensity of NO_3^- concentration changes and travel time from source to receptor. In addition, 4 scenarios of NO_3^- responses in karst aquifers to high rainfall events were hypothesized. Scenario 1 relates to mobilised NO_3^- concentrations, Scenario 2 diluted NO_3^- concentrations, Scenario 3 a combination of mobilised and diluted NO_3^- concentrations during one event and Scenario 4 mobilised and diluted NO_3^- concentrations during multiple events. Those scenarios are driven by 1) different source availability of N over time e.g. due to different intensity of agricultural N applications and/or 2) the activation of different flow paths that causes mixing of different water sources containing more or less NO_3^- than the average NO_3^- concentration in the aquifer.

In chapter 5 two different in-situ spectrophotometers are compared that were used in the field to determine NO_3-N concentrations at two distinct spring discharge sites: A double wavelength spectrophotometer and a multiple wavelength spectrophotometer. The objective of the study is to review the hardware options, determine ease of calibration, accuracy, influence of additional substances and to assess positive and negative aspects of the two sensors as well as troubleshooting and trade-offs. The study shows that both sensors were efficient for continuously monitoring highly time-resolved NO_3-N in groundwater emergences (i.e. flowing water) in this study and deemed fit for purpose. It is reasonable to conclude that high-resolution UV/VIS monitoring will greatly contribute to a better understanding of groundwater processes in the future.

In general, the results can contribute to an improved understanding of when and under what conditions NO_3^- is released to groundwater and fresh surface waters. As the Nitrates Directive is fully implemented on both study sites, all three studies can be used to guide and provide practical advice for environmental modellers, scientists, consultants, policy makers and drinking water managers. The present study can support an improvement of present and future implementations of the EU WFD in environmental activities, planning and policy especially in vulnerable areas.

Traditional sampling strategies with sampling intervals of weeks to months often fail to characterize the intensity of NO_3^- occurrence in karst aquifers because of rapidly changing concentrations (Stigter et al., 2011). These sampling strategies can miss critical NO_3^- concentrations above the maximum admissible concentration of 50 mg NO_3^- L^{-1} e.g. because of predominance of mobilisation processes due to high rainfall events leading to sudden NO_3^- peaks. This is especially worrying if the affected karst groundwater is used as drinking water as high NO_3^- concentrations can lead to live-threatening disorders especially for infants and animals (Di and Cameron, 2002; Knobeloch et al., 2000). As approximately one quarter of the world´s population relies on karst groundwater resources (Ford and Williams, 2007) and the need for groundwater resources is predicted to increase due to global population growth (Godfray et al, 2010), high-resolution monitoring needs to be intensified to assure good drinking water quality in the future. In addition, the statistical approach, which is used in the first study, would benefit from a higher resolution monitoring system such as high resolution sensors at a spring outlet or at least the collection of in-situ borehole mean nutrient concentrations over time via passive diffusion samplers. It seems to be advisable to adapt the present POM for karst areas and to implement high-resolution monitoring or at least passive diffusion samplers in the present legislations.

More extreme weather conditions such as heavy precipitation, heat waves, cold spells etc. are expected in the future due to climate change (Vajda et al., 2014). During these conditions, i.e. especially during heavy, intensified rainfall events, rapid mobilisation and dilution processes of NO_3^- can play a more important role in karst aquifers in the future. Hence, it seems to be essential that more work should be invested in the characterisation of

NO_3^- dynamics in karst aquifers to improve the predictions when NO_3^- concentrations are likely to breach the maximum allowable concentration or not. The recent PhD study focusses on a qualitative description of NO_3^- responses to high rainfall events. So far, the quantitative content of the individual key drivers to the observed NO_3^- concentrations remain unknown. Hence, a quantitative characterisation of NO_3^- pattern in karst systems is planned as follow-up project, i.e. a PhD study, and could be achieved by using numerical groundwater models. Up to date, several modelling approaches exist to quantify the transport of dissolved substances in karst aquifers (Göppert and Goldscheider, 2008; Field and Nash, 1997; Birk et al., 2006). Butscher and Huggenberger (2008) proposed a method to quantitatively estimate the quality of karst groundwater using global numerical models (Reichert, 1994). Butscher et al. (2011) also presented a study that validated this approach for bacterial contamination by field experiments. They used linear storage models, i.e. rainfall discharge models (Sauter et al., 2006), which rely on an input output relationship between hydraulic responses of a karst system to recharge pattern caused by several rainfall events. Similarly, Hartmann et al. (2013) show that process-based karst modelling can be used to relate hydrodynamic and hydrochemical characteristics of karst springs to karst system properties. Such numerical models combined with long-term high resolution data can be used to quantify the key drivers that control NO_3^- pattern at karst springs. Therefore, a numerical model could help especially drinking water suppliers and users in the future for the quantitative estimation of karst groundwater quality.

The PhD study showed that different agronomic practices are having consequences on the intensity of NO_3^- loss to groundwater. The following question is remaining: Are these techniques having also positive or even adverse effects on other critical substances occurring in groundwater such as N emissions to air or P? For example, improved slurry application methods such as trailing shoe instead of splashplate are known for reduced NH_4^+ emissions to air (Lalor and Schulte, 2008), but study observations vary from enhanced to unchanged nitrous oxide (N_2O) emissions (Velthof and Mosquera, 2011). To get a more holistic view of the environmental consequences, more investments should be made of studying the impact of the observed agronomic, NO_3^- reducing techniques to other critical substances. In addition, due to increased fertiliser prices in the last years and hence, an increased, evolved imbalance between input and output prices for farmers, dairy farmers are taken changes in traditional management practices into consideration (Powell et al., 2010). The study in chapter 3 deals with agronomic practices on a pure perennial ryegrass sward that are known to be highly profitable, but also rely on a high amount of frequent applied N fertiliser (Whitehead, 1995; Cunningham, 1994). Other studies show that including clover in the sward instead of using a pure fertilised perennial ryegrass sward can increase N use efficiency on the farm (Eriksen et al., 2004; Owens et al., 1994). On the one hand, white clover can derive on average 100 kg ha^{-1} N per annum from nitrogen gas (N_2) fixation from the air, are cost efficient and therefore a profitable alternative to fertiliser N-based dairy farms (Andrews et al., 2007). On the other hand, clover can be inhibited by taken up N from the atmosphere and as consequence in its growth, if additional fertiliser is applied (Enriquez-

Hidalgo et al., 2014). Although it has been observed that leaching losses can be reduced by cultivating additional white clover to the sward (Hooda et al., 1998), the impact of the combination with the observed, improved management techniques of this PhD study on NO_3^- losses at these dairy systems needs to be assessed. In future, the usage of the applied statistical method at similar dairy systems on vulnerable sites farming on perennial ryegrass/white clover pasture instead of pure perennial ryegrass could support the goal to achieve efficient, increased profitable dairy farms that are economically and environmentally sound.

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8 Declaration of authorship

First study

Citation

Huebsch, M., Horan, B., Blum, P., Richards, K. G., Grant, J., and Fenton, O.: Impact of agronomic practices of an intensive dairy farm on nitrogen concentrations in a karst aquifer in Ireland, Agric. Ecosyst. Environ., 179, 187-199, 10.1016/j.agee.2013.08.021, 2013.

Huebsch, M., Horan, B., Blum, P., Richards, K.G., Grant, J., and Fenton, O.: Statistical analysis correlating changing agronomic practices with nitrate concentrations in a karst aquifer in Ireland, In: Water Pollution XII, Wessex Institute of Technology, UK, vol. 182, 1- 412, ISBN 978-1-84564-776-6, 2014.

Declaration of authorship

Manuela Hübsch took water level measurements in all wells on Curtins farm for 3 weeks in May 2011, conducted a land survey and converted depth to groundwater to hydraulic heads in metre AOD. She also prepared and structured a 11 year dataset of agronomic N loadings of an intensive dairy farm, NO_3^- concentrations in groundwater, precipitation and (hydro-) geological features primarily with Microsoft Access. During this process Brendan Horan guided Manuela Hübsch and provided data of detailed agronomic N-loading and NO_3^- concentrations in groundwater over the 11 year period. In addition to preparing the dataset, Manuela Hübsch analysed the dataset with ArcGis spacially. As common procedure at Teagasc, the Microsoft access dataset was given to the Teagasc statistician, Jim Grant, who analysed the dataset with SAS. Manuela Hübsch evaluated the results. The results were discussed between Manuela Hübsch and the Irish team of Brendan Horan, Karl G. Richards, Owen Fenton and Jim Grant. Manuela Hübsch wrote the manuscript. Owen Fenton was the major contact person during this process, gave guidance regarding scientific writing, discussed the structure of the manuscript with Manuela Hübsch and reviewed the manuscript during the writing process. The final manuscript was reviewed by all authors.

Second study

Citation

Huebsch, M., Fenton, O., Horan, B., Hennesy, D., Richards, K.G., Jordan, P., Goldscheider, N., Butscher, C., Blum, P.: Mobilisation or dilution? Nitrate responses in karst springs to high rainfall events. Hydrol. Earth Syst. Sci. Disc., 11, 4131-4161, doi:10.5194/hessd-11-4131-2014, 2014. (accepted)

Declaration of authorship

Manuela Hübsch installed a UV sensor (double wavelength spectrophotometer), a weir and a flow meter for a pumping system at a karst spring to observe continuous discharge and NO_3^- measurements. Furthermore, she installed a hollow pole made of steel with slots for installation of a Mini-Diver for determining discharge measurements. Phil Jordan borrowed the UV sensor. Technical staff at Moorepark, Fermoy, and in particular Owen Fenton helped during the installation process at the spring. In addition, Mini-Divers were placed at the wells for observing water level fluctuations close to the spring by Manuela Hübsch. She downloaded the data of the Mini-Divers at the wells regularly, conducted a land survey, two optical brightener tests and one tracer test with uranine. She guided Christoph Walter, Florian Schwarzbauer and Elisabeth Bieri who took water samples together with her during day and night. In addition, Manuela Hübsch took water samples at the spring to compare NO_3^- values from the sensor with laboratory measurements. During the time Manuela Hübsch was absent (e.g. 4 month research stay in Canada or her stays in between in Germany), Tristan Ibrahim and Owen Fenton helped by taking water samples and downloading data at the spring. The manuscript was written by Manuela Hübsch. Christoph Butscher was the major contact person during the writing process. Christoph Butscher, Manuela Hübsch and Philipp Blum had meetings before and during the writing process to discuss the structure and parts of the manuscript. The final manuscript was reviewed by all authors.

Third study

Citation

Huebsch, M., Grimmeisen, F., Zemann, M., Fenton, O., Richards, K.G., Jordan, P., Sawarieh, Al, Blum, P., Goldscheider, N.: Field experiences using UV/VIS Sensors for high-resolution monitoring of nitrate in groundwater. In: High resolution monitoring strategies for nutrients in groundwater and surface waters: big data jump in the future to assist EU Directives, Hydrol. Earth Syst. Sci. Disc. (submitted)

Declaration of authorship

Manuela Hübsch installed a UV sensor (double wavelength spectrophotometer) at Dairygold Farm, downloaded data of the sensor and took water samples at the spring to compare NO_3^- values determined by the sensor with laboratory measurements. Phil Jordan borrowed the double wavelength spectrophotometer. Tristan Ibrahim and Owen Fenton helped by downloading data at the spring and taking water samples during times of absence of Manuela Hübsch. Philipp Blum initiated the collaboration between Manuela Hübsch and Felix Grimmeisen regarding the preparation of the technical note. Felix Grimmeisen contributed with data and experience of an additional UV/VIS sensor (multiple wavelength spectrophotometer) used in Jordan. Manuela Hübsch prepared and structured the collected data from Ireland for the third study. She combined her dataset with the dataset provided by Felix Grimmeisen while discussing the structure in between in particular with Felix Grimmeisen, prepared the tables and diagrams and wrote the manuscript. Felix Grimmeisen shared his experience and expertise regarding the multiple wavelength spectrophotometer with her during this process. The diagrams and tables were discussed in between by all authors and more particular between Manuela Hübsch, Nico Goldscheider, Felix Grimmeisen and Philipp Blum. The final manuscript was reviewed by all authors as well.

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