

Reply to Referee #2

We appreciate the constructive comments and suggestions from Referee #2. The three main concerns by Referee #2 can be summarized as follows:

- 1) Lack of supporting data for stated conclusions;
- 2) Conceptual model scenarios that do not fully account for the observed data shown in the present study;
- 3) Inadequate consideration of nitrogen cycling processes in groundwater, and a generally weak literature review.

We have addressed the comments in our revised manuscript as described in the following.

Comments from Referee #2:

- 1) Lack of supporting data for stated conclusions:

In their conclusion, the authors state, “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.” Yet, the authors presented no nitrate data from either the soil water or the saturated groundwater from the wells in their present study of the springshed in Ireland which would enable them to quantify the availability of nitrate from those zones. Instead, the authors appear to rely on assumptions as to where the sources of nitrate occur in the springshed they studied, and proceed to apply those assumptions to their conceptual model, instead of testing the hypothesis with data. Clearly, as their review of the other studies from literature demonstrated, these end-members should be sampled in addition to the discharge at a spring in order to provide some measure of confidence in the sources of nitrate observed in the spring discharge, and hence to formulate and test hypotheses on nitrate mobilisation or dilution.

Response: The authors feel that the assumptions on the conceptual model are well qualified. In the present manuscript the high amount of nitrogen applied on the surface is well described in the Material and Methods section: ‘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.’

In addition, the study sites of the present study and a recent study of Huebsch et al. (2013) can be well compared with each other. Therefore, we have included the following sentence in the Material and Methods section:

‘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 kg ha⁻¹ 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.’

References:

European Community (EC): Council Directive 91/676/EEC of 21st May 1991 concerning the protection of waters against pollution by nitrates from agricultural sources, Off. J. Eur. Commun., 1-8, 1991.

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.

Jahangir, M. M. R., Johnston, P., Khalil, M. I., Hennessy, D., Humphreys, J., Fenton, O., and Richards, K. G.: Groundwater: A pathway for terrestrial c and n losses and indirect greenhouse gas emissions, *Agric., Ecosyst. and Environ.*, 159, 40-48, 2012a.

Landig, F.: Determination of nitrate fluxes in a fractured karst limestone aquifer below a dairy farm in Co. Cork, Ireland, University of Tübingen, 1-93, 2009.

Landig, F., Fenton, O., Bons, P., Hennessy, D., Richards, K., and Blum, P.: Estimation of nitrate discharge in a fractured limestone aquifer below a dairy farm in Ireland, *IAHS-AISH Publication*, 469-472, 2011.

2) Conceptual model scenarios that do not fully account for the observed data shown in the present study:

Another concluding statement is, “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.” True enough, but is this conclusion any different from the knowledge of the authors when they began their study? The studies from the literature that they have cited reveal that this same conclusion had been reached by other workers (e.g., Böhlke, 2002). Regarding the four nitrate response scenarios shown in Figure 5 and Figure 6, it is odd that the authors chose not to represent the very scenario that they have documented in their present study, i.e. that seasonal changes in nitrate responses are evident at this karst spring. Comparing events 1 and 4 in Figure 2, their data show clear seasonal differences among the nitrate response at the spring for discharge events of similar magnitude. The authors have generated a much higher resolution and longer duration dataset than any of those they chose to highlight from the literature. I do not understand why they have chosen not to highlight the clear seasonal differences, a finding that may in fact be the most important result of their study. A primary question to address would have been, what caused such a seasonal difference? Rather than addressing this question, the Discussion section is almost entirely devoted to summarizing the work of others, without coming to any truly useful conclusion. Contrary to the concluding statement, “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”, I find the presentation of the conceptual model scenarios and ensuing discussion to provide a source of confusion to those who would manage nitrate export from karst watersheds.

Response: The focus of the authors in the present manuscript is to describe ‘differences regarding predominance of dilution or mobilisation processes during different storm events’ and to explain why such differences can occur. Referee #2 asks if the answered objective is ‘any different from the knowledge of the authors when they began their study’. We believe ‘yes’. We agree that parts of the outcome have already been well described by other authors (e.g. Böhlke, 2002) (which are cited), but up to date no study proposes an explanation and description why nitrate can either be rapidly decreased or increased after high rainfall events in karst systems, and why such differences occur in karst environments in a global context. Our goal is ‘to get a more complete picture of the various environmental conditions’ (refers to comment of Referee #1). In addition, the authors have chosen not to focus on the question ‘what caused such a seasonal difference’ in nitrate responses in their present manuscript as this has been very well described by Bende-Michl et al. (2013) recently. Bende-Michel et al. (2013) illustrate in their studies the role of hydrologic conditions including low flow and high

flow conditions, source availability and the consequences for mobilised nutrient response. The findings of Bende-Michel et al. (2013) can be transferred to the dataset in the present manuscript. Therefore, the presented dataset would not support the groundwater community with new findings by focusing only on seasonal variations. By comparing the comments of Referee #1 and Referee #2 with each other, we agree that on the one hand the description of mobilisation/dilution processes and on the other hand the explanations on seasonal variations in the discussion section may cause confusion to the reader. (Referee #1 in contrast to Referee #2; Referee #1: ‘The models presented may be useful guides for regulators in determining the best actions to take in order to reduce nitrate concentrations.’ and ‘The models presented would be unnecessary for those familiar with nitrate contamination of karst springs. However, the models do provide a tool for regulators to quickly interpret nitrate patterns in spring water data. Such information would help guide them to making informed decisions in attempting to reduce nitrate levels in waterways.’; Referee #2: ‘I find the presentation of the conceptual model scenarios and ensuing discussion to provide a source of confusion to those who would manage nitrate export from karst watersheds.’) Thus, to increase the quality of the discussion section, we included the following sentence to ensure that the reader may not be confused with the difference between seasonal variations of nitrate responses and mobilisation/dilution processes: ‘In addition to mobilisation and dilution processes, seasonal variations need to be addressed.’ To provide clarity with respect to seasonal variations we have kept the following passage in the discussion section after the included aforementioned sentence and we have included more data to improve our conclusions:

‘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).‘

To utilize our high resolution data more effectively and to address the concerns of Referee #2 we have included additional data of effective drainage in addition to borehole data to back up assertions pertaining to nitrate concentrations at different times within the dataset. In section ‘3.1 Observations at the study site’ we added the following passage:

‘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.’

In relation to the aforementioned passage, we have extended the ‘seasonal variations’ passage in the discussion section:

‘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).

References:

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Stark, C. H., and Richards, K. G.: The continuing challenge of agricultural nitrogen loss to the environment in the context of global change and advancing research, *Dyn Soil Dyn Plant*, 2, 1-12, 2008.

3) Inadequate consideration of nitrogen cycling processes in groundwater, and a generally weak literature review:

The literature on nitrogen cycling in groundwater and agricultural watersheds is vast, even if the literature on nitrate cycling in karst systems may not be. I did not find the literature review conducted by the authors adequate enough to address topics such as potential atmospheric sources of nitrate, nitrogen cycling in unsaturated zones driven by denitrification and variable redox conditions, or distinguishing among nitrogen sources such as agricultural wastes and natural soil nitrate. This fact is demonstrated in the simplifications shown in Figure 4, where precipitation is shown as being a low N source (it can account for a large proportion of nitrogen exported from temperate watersheds; see Panno et al, 2001; Sebestyen et al., 2008), and groundwater is shown as having constant, average value of nitrate (redox zonation can dramatically affect nitrate concentrations in groundwater, e.g.

Liao et al., 2012). Without supporting data, treating nitrate as if it were a conservative tracer of hydrologic processes in karst settings is done at one's peril.

Response: The literature on nitrogen cycling in groundwater and agricultural watersheds is indeed vast. In order to keep the manuscript concise and focused, we do not give a comprehensive literature review on nitrogen cycling in groundwater and agricultural watersheds in general. However, we agree that addressing additional aspects, such as denitrification and variations in nitrogen derived from atmospheric sources, would improve the manuscript. Therefore, a comprehensive discussion of these aspects has been added to the revised version of the manuscript.

Denitrification potential/redox processes are discussed in the revised manuscript as follows:

‘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.’

Nitrogen derived from atmospheric sources is discussed in the revised manuscript as follows:

‘In the conceptual model (Fig. 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 $13.2 \text{ kg ha}^{-1} \text{ a}^{-1}$, 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 $170 \text{ kg ha}^{-1} \text{ a}^{-1}$ or $250 \text{ kg ha}^{-1} \text{ a}^{-1}$ on derogation farms.'

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