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Hydrology and Earth System Sciences
Discussions

Interactive comment on "Mobilisation or dilution? Nitrate response of karst springs to high rainfall events" *by* M. Huebsch et al.

Anonymous Referee #2

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Review of:

Mobilisation or dilution? Nitrate response of karst springs to high rainfall events By: M. Huebsch, O. Fenton, B. Horan, D. Hennessy, K. G. Richards, P. Jordan, N. Goldscheider, C. Butscher, and P. Blum

This paper presents the results of a study of a karst spring and nearby wells in southern Ireland, and relates the changes in spring discharge and ground water levels to the variation in nitrate concentrations observed at the spring. The authors employed a state-of-the-art photometric sensor for obtaining continuous, high temporal resolution (15 min) nitrate concentration data at the spring, and compared the nitrate response to water level and discharge fluctuations at the same time scale. The data presented

appear to be of high quality, and the results obtained should be of use for testing hypotheses about the local conditions that influence nitrate export within that particular springshed.

The authors proceed to extend their results to formulate conceptual models of nitrate export from karst systems in general. To do so, they compare several published datasets, and pose the question, "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?" Unfortunately, this is where the paper falls far short of its goal. Although the authors demonstrate from their literature review that, yes, nitrate occasionally increases at karst springs during storm events, and occasionally decreases, they have presented little in terms of identifying the "key factors" through this comparison, or from the data obtained in their present study.

The primary shortcomings of the paper 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.

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 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.

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.

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.

In conclusion, the present study certainly has value in providing a novel dataset of high-resolution nitrate response to rainfall events in a targeted karst springshed within an agricultural catchment. Unfortunately, the remainder of the paper is an attempt to make broad, unsupported generalizations while missing the opportunity to provide some advancement in scientific understanding through the focused analysis of the rich dataset that had been acquired.

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