

***Interactive comment on* “The chemical signature of a livestock farming catchment: synthesis from a high-frequency multi-element long term monitoring” by A. H. Aubert et al.**

Anonymous Referee #2

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General Comments

This paper is a study of a small, intensively farmed catchment comprising 10 years of daily chemical measurements for nitrate, sulphate, chloride, DOC and DIC in streamwater, supplemented by occasional groundwater analysis. Though intensive agriculture is a common and important land use, small catchment studies of runoff from this land use type are much less common, and datasets of this length and sampling frequency are even rarer. This paper thus reports on an important dataset which the scientific community should be aware of. The subject of the paper is within the

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Discussion Paper

scope of HESS, and some novel insights and ideas are presented. Some parts of the paper are rather hard to follow, however, and I do not agree with all the interpretations.

Specific Comments

Title: I agree with Referee 1 that this needs modification. With 20% cereal and 30% maize as well as livestock, I would describe this as a mixed farming catchment (or even just a farming catchment). Something like “The chemical signature of a mixed farming catchment: a synthesis from high frequency, long-term monitoring of several determinands” would be better.

The hydrochemical and hydrological interpretations of the catchment responses are generally insightful, and the statistical techniques are skilfully applied, as it is a formidable problem to generalize from such a large and variable dataset. However, the data seem to me to show one thing very clearly which the authors do not comment on – the composition of the wetland groundwater is so different from that of the upland groundwater that it is unlikely that the main source of supply of the wetland water is from the upland catchment. The low nitrate concentration is ascribed to denitrification, but it would require a very productive wetland producing large amounts of decomposable organic matter to reduce concentrations from 20 mg L⁻¹ to 0.2 mg L⁻¹ – it would be interesting to see whether there is any precedent in the literature for this. But even if there was, it is hard to see why sulphate-S would increase from 1.7 to 5.2 mg L⁻¹ when you would expect a decrease due to sulphate reduction, or chloride decrease from 33 to 16 mg L⁻¹. Unusually also, the wetland is not supplying the baseflow concentrations to the stream – at least if the measurements are representative of the catchment wetlands in general – that point ought to be discussed somewhere. Instead the wetland contributes during high flow conditions, explaining the reductions of nitrate and chloride, and the increases in sulphate and DOC at high flows. A reduction in nitrate concentrations in storm events implies that the upland, high nitrate, shallow groundwater is not the dominant contributor at high flows. This is a less usual situation - more often there is an increase in nitrate with flow as excess fertiliser is washed out (see e.g.

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Rozemeijer, JC et al. Environ. Sci. Technol., 2010, 44 (16), 6305–6312).

If the wetland connected first with the stream after a dry summer, as one would expect and as stated on p. 9727 l.27, you would expect the stream composition to be close to wetland groundwater. This is true for nitrate (relatively low concentrations) but not for chloride (high instead of low), perhaps true for sulphate (concentrations in streamwater somewhat higher than wetland groundwater), but not for DOC (groundwater concentrations much lower than stream) or DIC (groundwater concentrations much higher – that is, however to be expected). There may be reasons for this (e.g. general wetland groundwater samples are not representative of groundwater at the time of re-wetting), but I would like to see the authors consider them in the discussion. To summarize, it is not possible from the authors' account in this paper to get a picture of how the hydrology of this catchment works. What are the water flowpaths during low flows? – clearly not via the measured wetlands. I would like to see the authors address these issues in a revised version of the paper. Therefore I do not think the authors can claim that the responses they have observed are typical of a livestock (or mixed) farming catchment, not without further evidence. They appear instead to be driven by some rather unusual hydrological characteristics. However, the approach used in the paper and the data are valuable contributions, so I would encourage the authors to revise the paper to meet the referees' criticisms.

Technical Comments and Typographic Errors

The English is good and generally comprehensible, but not quite idiomatic in places. Here I suggest some corrections and improvements. Where I agree with Referee #1 (which is most of the time) I do not mention it here, unless to reinforce or extend Referee 1's comments.

p9716 (Abstract)

p9716 l.8 "...from the Kervidy..."

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p9716 I.10 “every four months. . .”

p9716 I.12 “nitrate and chloride present a seasonal flush. . .”. I don’t think that the data as presented in Figs. 2 and 3 or as discussed in the text justify this statement. Chloride shows a re-wetting flush at the start of the hydrological year; nitrate does not flush at all, but increases fairly smoothly to a maximum at times when the catchment is wettest, for reasons discussed in the text.

p9716 I15-16 “typical of a livestock farming catchment. . .”. I do not think this has been established (see above).

p9717 I.6 Better “Such signatures can be identified thanks to the establishment of long-term data observatories” (It is a recent trend to call these networks “observatories” – best to make it clear what is being discussed).

p9717 I.7-20. Not sure I agree with Referee#1 that this is not necessary – I at least found it useful.

p9718 I.3 “. . .as was recently done with the Plynlimon. . .”

p9718 I.6 Better “The conclusions that can be drawn are influenced by time series length and sampling frequency. . .”

p9718 I. 14 “intermediate” for “intermediary”

p9718 I.25 “signatures”.

p9719 I.16 I’ve never heard of Alocrisols – not in the WRB Classification. =Acrisols? – possible, though more characteristic of the tropics.

p9720 I.2 “cereals” is correct (if what is meant is such things as wheat, barley etc.).

p9720 I.11 “operated” for “operating”

p9729 I.14 More experimental detail needed here. What amount of time elapsed between sampling and analysis? Were the sample bottles kept closed with minimum

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airspace? Some of these waters have high DIC concentrations and loss of DIC by degassing of CO₂ could be a significant problem unless precautions were taken.

p9720 I.23 should be K-phthalate

p9721 I.4 what is GNWP?

p9721 I. 6 Agree with Referee1 that this heading should be “Statistical Analysis” or similar

p9721 I.16 1.5 mm seems a rather low rainfall to justify a “stormflow” classification – even if there is no evapotranspiration and it all runs off on the same day, it equates only to about 84 L s⁻¹ (compared to the mean flow of about 53 L s⁻¹).

p9721 I.21 “Concentrations” is better than “Concentration levels”. Thus we can have “Based on concentrations of the different. . .” and in p9721 I. 24 “analysing (i) concentrations and spatial sources of water components, considered as. . .”

p.9722 I.1-4 Agree this should go into Discussion or Conclusions. Also need a reference for “previously proposed patterns” and it should be “Both aspects of the signature lead. . .”

p.9722 I.8 “in the stream”

p9722 I.23 When comparing chloride concentrations, note the 3 catchments cited are in very different physio-geographical situations to Kervidy. Catchments on the east side of the USA such as Hubbard Brook and Oak Ridge have very little marine influence, hence low chloride. Plynlimon has a large marine influence, but also a much higher rainfall (c. 2600 mm yr⁻¹) which dilutes the chloride. A more comparable non-agricultural catchment might be the Tillingbourne in Surrey, UK (e.g. Hill et al., 2002, The Science of the Total Environment 282-3, 81-97) which has lower Cl⁻ concentrations in bulk precipitation than Kervidy (about 3 mg L⁻¹) but still has stream Cl⁻ concentrations of about 13 mg L⁻¹. The difference is due to dry deposition of seasalt aerosol to the (forested) catchment, as well as the concentrating effect of evapotran-

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spiration. As Kervidy is only about 40 km from the Atlantic coast, these effects cannot be neglected there, but I agree the stream concentrations seem too high at Kervidy for the chloride to be sourced from natural processes, and that agricultural inputs must be significant.

p9722 I.25 Better “High chloride concentrations were described in a catchment with the same. . .”

p9723 I.23 Wytham is definitely in England.

p9723 I.25 “. . .same range in mid-slope groundwater. . .”

p9724 I.10 I agree with Referee 1 here – which biogeochemical processes? As the wetland is apparently very effective at denitrification, you would also expect some sulphate reduction, leading to lower sulphate concentrations. This will be true even though sulphate reduction needs a lower redox potential than nitrate reduction (any information on the redox potential?).

p9724 I.16 “shorter residence time may explain why chloride concentrations are lower.” I do not follow this argument at all. If chloride is unreactive, the only mechanism I can think of in which residence time might affect the concentration is that longer residence times would give more scope for evaporative concentration. But this is the opposite of what is observed. And is there any evidence that the residence time is in fact shorter?

p9725 I.16 “increased rate of decrease”?? = “marked decrease”? There does not seem any need to cite in-stream processes to explain this decrease, but note that the cited paper (Mulholland and Hill, 1997) used end-member mixing analysis to distinguish in-stream from catchment-controlled processes. Is there any prospect of doing this at Kervidy? If not, I would suggest this explanation is unnecessarily speculative.

p9727 I.1 “Morel’s”. “The seasonal pattern. . .”

p9727 I.2 stock of C may be large but it is not unlimited. In this paragraph the authors need to distinguish organic C (i.e. the solid phase) from DOC. It is the stock of DOC

which is being depleted – organic C may or may not be, but there are no measurements of this.

p9727 I.16-20. This is all too vague. Which inter-annual signature? Why discuss here when the next section is about inter-annual signatures? What did the cited authors show (in the Kervidy catchment, presumably), and how do the results presented here extend what they showed? Which studies are the last two sentences discussing?

p9728 I.7 “enables” for “enable”

p9728 I.8 Figure 4 is a nice illustration of the different responses of the variables. Is “variogram” the correct description? Most variograms I have seen are estimates of spatial autocorrelation, and Fig. 4 would be called a periodogram. However, I am far from expert here. Whichever it is, the authors need to justify the use of 30 days for the lag.

p9728 I.21 “leads” is correct if the authors want present tense. Past tense would be “led”.

p9729 I.10 “allows”

p9729 I.20 “. . .interaction with the upper. . .”

Figures – These need to be reproduced sufficiently large – the “printer-friendly” versions are too small to assess.

Figure 5 is a good summary of the responses of the different determinands. The blue lines are presumably typical storm events – but it should say so in the legend.

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