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Hydrology and Earth System Sciences Discussions

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 #1

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The manuscript "The chemical signature of a livestock farming catchment: synthesis from a high frequency multi-element long term monitoring" by Aubert et al. analyses and discusses long term data sets of several chemical components in stream flow and groundwater in a small, farmed catchment. The article is an interesting summary of long-term observations and culminates in a novel and potentially very useful classification / conceptualization of contrasting processes underlying the observed patterns of different individual chemical components. It is well structured and well written and the analysis methods used are sound. However, parts of the manuscript are a bit speculative and / or superficial and would benefit from a more in-depth analysis and discussion

which could ideally be brought into a wider context on what has already been published on the topic. Apart from that I would be happy to see this manuscript eventually published and I think it will be interesting to a wide part of the community. Please find below my detailed comments.

(1) title I feel that the title does not really tell the reader what to expect. It would be good if the different process types ("transport-" and "process-controlled") could be somehow incorporated or the classification scheme mentioned, while the emphasis on "livestock" could be reduced. This would make the article interesting to a wider community

(2) title and elsewhere in the manuscript Not sure if "element" is the best term here as strictly speaking you are talking about chemical compounds and not chemical elements.

(3) p.9716, l.3-4 Should read as something like: "Second, chemical elements have distinct short and long term mixing characteristics"

(4) p.9716, l.12 Instead of "present" maybe "exhibit"

(5) p.9716, l.13 Maybe better: "Nitrate and chloride are dominated by a seasonal flush,. . ."

(5) p.9716, l.14 Maybe better: "In contrast, sulphate, organic and inorganic carbon are dominated by storm flushes,. . ."

(6) p.9717, l.5 Maybe better: ". . .second because different chemical components can be characterized by different short and long term mixing dynamics."

(7) p.9717, l.7-20 Too long and not really necessary – can be considerably shortened

(8) p.9717, l.26-27 Please give references

(8) p.9717, l.28 Maybe better: ". . .impacted by other human activites. . ."

(9) p.9718, l.5 Please explain in a little sentence explaining why.

(10) p.9718, l.6 Sentence is incomplete and/or awkward. Please check.

(11) p.9718, l.13 Maybe add one of the Scottish long-term studies (e.g. Hrachowitz et al., 2010)

(12) p.9718, l.14 Maybe also add Scottish studies on seasonal variation (e.g. Dawson et al., 2008; 2011)

(13) p.9719, l.4 Maybe better: ". . .headwater catchment, drained by a 2nd order stream that can occasionally fall dry in summer."

(14) p.9719, l.5-6 Maybe better: "The catchment's observatory (ORE-AgrHys) belongs to the. . ."

(15) p.9719, l.8-12 Not really relevant information, can be considerably condensed

(16) p.9719, l.13-14 Maybe better: ". . .a layer of weathered material up to 30m thick."

(17) p.9719, l.15-16 A bit confusing. Are the soils silty loams or well-drained brown soils. Please clarify.

(18) p.9719, l.19 Maybe better: "The topography of the catchment is rather subdued, with a few slopes reaching a gradient of 5 %."

(19) p.9719, l.21 Maybe emphasize that it is a maritime climate.

(20) p.9720, l.2 Not sure, but I think not "cereals" but rather "crops" is the correct term here.

(21) p.9720, l.4 Please add a few words to explain N-efficiency here.

(22) p.9720, l.12-13 Please show approximate location of weather station in Figure 1

(23) p.9720, l.16 I suppose those were instantaneous grab samples, but please make this explicit

(24) p.9720, l.25-28 Too detailed, can be considerably shortened.

(25) p.9721, l.6 Title of section 2.3 a bit misleading. Make clear that this is the description of mathematical / statistical methods used in the analysis.

(26) p.9721, l.8-9 Sentence unclear – what do you mean by "monthly aggregation", what are "repetitions" and how do you come up with the number 300?

(27) p.9721, l.21-23 Sounds more like it belongs to the Methods section

(28) p.9722, l.23 – p.9722, l.4 Probably fits to the end of Discussion or into Conclusion section

(29) p.9722, l.2 Maybe better: ". . .on short term studies,. . ."

(30) p.9722, l.8 Maybe better: "Over the 10 year observation period,. . ."

(31) p.9723, l.3 The annual mean is rather meaningless due to the changing chloride concentrations in the rainfall. You need to compare it to the precipitation weighted mean value of chloride concentration.

(32) p.9723, l.10-27 Could be shortened

(33) p.9723, l.11 Maybe better: "..concentration was found to be 2.6. . .."

(34) p.9723, l.19 Maybe better: ". . .associated with comparably high. . ."

(35) p.9723, l.23 Not sure if Wytham is actually in Scotland – isn't it rather England?

(36) p.9723, l.26-27 Sentence unclear, please rephrase.

(37) p.9724, l.3-11 This reads rather speculative. Do you have further data or literature to support these statements? Or avoid terms such as "suspect", "seem", etc.

(38) p.9724, l.8 Should read as: ". . .processes in the soil."

(39) p.9724, l.9-11 Which biochemical processes? Please add some relevant examples and references here.

(40) p.9724, l.12-15 I suppose you refer to some kind of average (mean or median)

stream concentrations of nitrate and chloride here, but please make this explicit.

(41) p.9724, l.12-14 Please give some references for the suspected wetland denitrification. Do the observed values meet those reported in literature? Furthermore, please make clear for the chemical non-experts, why you do not expect denitrification in the shallow ground water.

(42) p.9724, l.14-15 Not sure that 4 % higher mean values of chloride in the stream are actually statistically significantly higher. Did you do a t-test or ANOVA? If not I would be careful with such statements as you have quite some variability around the mean. I would recommend treating stream and mid-slope groundwater as equal here unless otherwise tested. If a suitable statistical test suggested that the samples are significantly different from each other, what different options of additional source could you suggest here?

(43) p.9724, l.16 No, strictly speaking chloride is not a non-reactive element (Bastviken et al., 2007; Oda et al., 2009; Guan et al., 2010), but it is of treated as non-reactive. Please rephrase sentence.

(44) p.9724, l.16-18 I somehow disagree with this statement, as the accumulation of chloride does is not really affected by its (non-)reactivity but rather by the way water (and thus chloride) is routed through or stored in different parts of the catchment. In other words, I would rather suspect that wetlands show lower values as these are not directly fertilized and flow paths from the slopes might not be directly connected to the wetlands but rather connect directly to the streams, i.e. only allowing for limited accumulation of chloride in the wetlands.

(45) p.9724, l.18-19 Not sure what the authors want to say here. Please elaborate in a bit more detail.

(46) p.9724, l.21 The statement “no permanent DOC storage” is in my opinion much too strong and should be toned down accordingly. Although DOC is strongly influence

by catchment wetness, there is a certain base concentration present throughout the year.

(47) p.9724, l.26-27 Should go into Methods section

(48) p.9725, l.1-2 Maybe better something like: “Our results support the a priori conceptualization of annual nitrate patterns and allowed to extend the conceptualization by additional factors.”

(49) p.9725, l.2 Should read as: “On average, nitrate concentrations were lowest at the beginning. . .”

(50) p.9725, l.5 Please explain in a bit more detail what you mean exactly by “dilution effect”

(51) p.9725, l.5, Fig.2 This can not really be distinguished in Figure 2 – too small, too many symbols, not enough contrast between blue and green. Maybe include zoom-ins for a short example period for each chemical component.

(52) p.9725, l.9-11 Please also emphasize the potential importance of the activation of preferential flow paths

(53) p.9725, l.11-14 Please explain why upland groundwater contributes less in summer. I suppose because the catchment is drying and thus there only reduced nitrate transport capacity available, but please make this explicit and maybe also include some references.

(54) p.9725, l.14-16 “might” sounds very speculative. Do you have any evidence for that? What are these in-stream processes? Please clarify.

(55) p.9725, l.20-22 This sentence comes a bit surprising here. Please add an explanation of what is happening as a result of this water table rise (I suppose increased transport, but again, make this explicit)

(56) p.9725, l.23 What do you mean here? In my understanding one cannot propose a

pattern but only observe a pattern. Did you thus actually observe new, surprising patterns? Or did you rather propose a new explanation / conceptualization of the observed patterns? Please clarify.

(57) p.9725, l.24 Please make explicit here that at the beginning of the hydrological year, the catchment is wetting up fast, thus providing increased transport capacities.

(58) p.9725, l.26-28 What does this rainfall effect include? Only total rain volumes or also the seasonality in the chloride signal? In my opinion both need to be discussed here, even if the seasonality in the chloride signal is minor compared to the concentrations in the catchment here. It would be actually VERY interesting to see which contribution the well documented seasonality in the chloride signal (e.g. Neal et al., 1988; Dunn and Bacon, 2008; Shaw et al., 2008; Hrachowitz et al., 2009) has on the observed patterns in the study catchment.

(59) p.9725, l.28ff Again, although the storms did not influence annual means, the storms themselves have a seasonal variation in the chloride signal (see references above), that will, taking into account catchment travel times, reinforce exactly the signal you are observing. I think this needs to be discussed (with the above given references) in order to give a more complete picture of chloride patterns.

(60) p.9726, l.3 Should read as: "...observing similar annual chloride variations, we propose a new concept describing the seasonal patterns."

(61) p.9726, l.4-5 Maybe better as: "Few conceptualizations of seasonal chloride patterns in anthropogenically disturbed catchments have been described in the literature, partly due to the frequent assumption of chloride acting conservatively, meaning that the inputs closely reflect the outputs (Koirala et al., 2010)."

(62) p.9726, l.7-13 Please also note the potential importance of land-use changes in the frequently observed imbalances of the chloride budgets (e.g. Oda et al., 2009; Guan et al., 2010).

(63) p.9726, l.18-20 Please for completeness also mention the, albeit potentially low, impact of seasonality in the chloride signal here!

(64) p.9726, l.21-22 Again, I think it should rather be called "conceptualizations" rather than "pattern".

(65) p.9727, l.2-3 Two points concerning "unlimited stock": (a) it is a bit of an exaggeration, please tome it down a bit and (b) it seems to me that it directly contradicts your statement at p.9724, l.21, saying that there is no permanent DOC storage. Please clarify

(66) p.9727, l.2-3 Maybe better: "...carbon in shallow soil horizons of the wetland."

(65) p.9727, l.2-3 Why only in the wetland and not elsewhere in the catchment?

(67) p.9727, l.5-8 Add some references here, as these observations are similar to those made by others (e.g. Dawson et al., 2008; 2011)

(68) p.9727, l.12-14 Dawson et al. (2011) reported that both, catchment wetness (or Q) AND temperature are dominant controls on DOC export. I think it would be good to analyse this here as well and possibly incorporate it into the proposed conceptualizations.

(69) p.9727, l.16 Maybe better:"This intra-annual signature is evidence for the role of shallow groundwater connectivity in controlling..."

(70) p.9727, l.18-20 Not entirely clear what you want to say here. Please elaborate in a bit more detail.

(71) p.9727, l.25-26 Not only alternating dry and wet periods but also the hydrological connectivity during these periods.

(72) p.9728, l.2-3 Not only the variation in recharge but also differences in temperature (Dawson et al., 2011)! Please include this aspect as well!

(73) p.9728, l.7-8 Sentence is sort of awkward and I think “reinforced” is not the correct term here, maybe rather something like “support”.

(74) p.9728, l.10 Please avoid qualifications such as “perfectly”

(75) p.9728, l.13-14 Make sure to note that DOC is also subject to hydrological controls (catchment wetness, discharge) as you have pointed out above (e.g. p.9727, l.5ff or p.9728, l.2ff).

(76) p.9728, l.16-18 This is a bit confusing. Above (e.g. p.9727, l.5ff or p.9728, l.2ff) you stated that DOC is dependent on flow only, whereas here you mention the exclusive importance of temperature. Firstly, I think both are crucial controls on DOC (See comments and reference above), and secondly I think it would be beneficial if you made a clearer (and in the manuscript better structured) distinction between production and export/transport.

(77) p.9728, 20-21 Maybe better: “. . .dataset allowed a representative description of. . .”

(78) p.9728, l. 21-22 Should read as: “Its conceptualization lead to. . .”

(79) p.9728, l.20 – p.9729, l.7 I think it might be worth to go into a bit more detail here in particular for DOC. You could possibly better explain the DOC pattern as process driven by catchment wetness AND temperature (as detailed in the comments above).

(80) p.9729, l.12-13 This is wrong due to the seasonality in the chloride concentration in rain. Please change!

(81) p.9730, l.6 Maybe better: “. . .were present at similar concentration. . .”

(82) p.9730, l.9-11 Maybe better: “. . .DOC and DIC showed clear seasonal signals and were strongly correlated with temperature and ETo.”

(83) p.9730, l.9-11 Please also note the influence of flow on DOC and DIC, although it is less clear here than in other studies (but it can still be identified from fig.4 with the lower peaks in years with reduced discharge)

(84) Figure 2 As in comment (51), maybe add zoom-ins for some example periods to be better able to read the figure and also plot discharge in a separate panel above nitrate (for convenience show it as continuous record, i.e. as line without symbols)

(85) Figure 5 What are the thin blue lines? In the summary graphs?

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