Response to referees comments on "Characterization of deep aquifer dynamics using principle component analysis of sequential multilevel data" by Kurtzman et al., submitted for publication in HESS

We thank both referees for their useful comments which will help to improve the presentation. In the following, referees comments are written in *italic* and responses in plain text.

Anonymous Referee #1

General comments

The study deals with results of sequential multilevel profiles obtained in a well penetrating a contaminated aquifer. Chemical results analyzed by PCA, together with monitoring of the electrical conductivity of water, allowed to interpret the origin of the observed changes in the hydrochemical profile of the aquifer. The paper presents an original analysis for a contaminated aquifer case-study, strictly applying methods and tools well-known in literature. The contribution to scientific progress within the scope of HESS consists in the demonstration that sequential multilevel profiles, when correlated to the aquifer hydrodynamics, represent an efficient method for evaluating the contamination propagation in the aquifers. The overall quality of the discussion paper can be considered good. Some suggestions concerning mainly the presentation of the results and the structure of the paper are given in the next sections.

We appreciate the referee's positive view of our study's contribution, and thank him/her for the detailed comments which will help us improve the clarity of the revised manuscript.

Specific comments

1. In Section 2.1 (Site and observation well), a concise description of the geological and hydrogeological context of the well location can better introduce the reader to the following matter of the paper, such as that reported at lines 22-24 pag. 9493 concerning the presence of discontinuous clayey lens in the aquifer.

In the revised version, a concise description of the geological and hydrological context of the well will be included. Moreover, a discussion of the continuity of the clay lenses will be introduced in the "Site and Observation Well" section.

2. I think that a better structure of the manuscript can facilitate the reading of the paper. I suggest a division of results from discussion, rearranging the contents of the sections 3.1, 3.2, 3.3 and 3.4.

We thank the referee for this comment. This issue was extensively debated between the co-authors before submission, and the rationale behind the current arrangement was the linkage between the MLS profiles (section 3.1) and their PCA (section 3.2). Therefore, these sections were placed one after the other in a united Results and Discussion section. However, we concur that the referee's suggestion to clearly distinguish between Results and Discussion may very well facilitate the reading of the paper. Accordingly, the structure will be changed in the revised manuscript.

3. Please indicate the reference of the equation 1 employed for the estimation of specific discharge; also the mathematical presentation of the equation and its solution could be improved.

We appreciate this comment. In the revised manuscript, more details, improved presentation and references will be added as well as further explanation of the derivation of specific discharge. See revised text as follows (underline indicates revised text):

"Change in concentrations in the packed-off section during this passage is caused by water from the interval with concentration C leaving the interval and new water with lower concentration C2 entering the interval (Eq. 1, Fig. 6).

$$\frac{dC}{dt} = -\frac{Q}{V}(C - C2) \qquad (1)$$

where t is time (T), Q is flow-rate through the interval ($L^3\ T^{-1}$) and V is the volume of the packed-off section (minus the probe volume) (L^3). Equation 1 is similar to mass balance equations used for interpretation of dilution tests (e.g. Brouye`re et al., 2005; Kurtzman et al., 2005). The solution of Eq. 1 for our case is:

$$\ln\left(\frac{C - C2}{C1 - C2}\right) = -\frac{Q}{V}(t - t1) \qquad (2)$$

where C1 and t1 are the time and concentration at the beginning of the concentration change (Fig. 6). Plotting the left hand side of Eq. 2 against t-t1, enables calculation of –Q/V (the slope). Since V is known, Q can be determined. Groundwater specific discharge, q ($L\ T^{-1}$), is derived by Eq. 3.

$$q = \frac{Q}{L_s D_s \alpha} \qquad (3)$$

where L_s and D_s are the section's length and diameter, respectively (L) and α (-) is a factor correcting for the convergence of the natural aquifer flow towards the well (α = 2 is widely accepted and used here; e.g. Pitrak et al., 2007)."

4. Line 10 pag. 9492: Please check "v _ 150 m yr-1" (or 160 m yr-1 ?).

While it is true that the exact calculation would give a value of 160 m yr^{-1}, we round this value to velocity of ~150 m yr^{-1}. The reasons for using a rounded value rather than the exact numerical result are: 1) This velocity is calculated for a specific depth at a specific time, therefore its significance in the context of the paper is that it is an example of the order of magnitude of horizontal velocities that exist in the aquifer; and 2) The propagation of the error through the measurements, assumptions and calculations leads to a relative standard error that exceeds 10%.

5. The contents of the section 3.3 could be replaced in the section "Results" before the presentation of the results of PCA. The contents of the section 3.3 cannot be considered "Supplemental information" but they constitute an important part of the hydraulic characterization of the overlapped aquifers.
We agree with this comment. After reorganization of the manuscript (general comment # 2), this section will be in the Results chapter and it will not be considered as supplemental information.

6. The final version of the paper requests a better revision and editing, as regarding to the language, symbols and figures (see next section).
Thank you for this comment; a thorough editing will be performed on the revised paper.

Technical corrections
Some of the aforementioned technical and typographical corrections requested are the following:

1. Line 20 pag. 9482: Please replace "data. (b) The fact" by "data; (b) the fact".
This will be corrected.

2. Line 28 pag. 9488 and lines 1, 3, 5, 13, 15 pag. 9489: Please use homogeneous symbols for the type profile (types (a), (b): : : in section 3.1 and types a, b: : :in section 3.1).
Thank you for the suggestion. All profile type symbols will be changed to within parenthesis i.e. (a), (b) ….

3. Line 14 pag. 9490: Please replace "bodies: Depths" by "bodies: depths".
This will be corrected, thank you.

4. Line 22 pag. 9491 : "packed-of" or "packed-off"?
Thank you, this will be corrected to packed-off.

5. Line 6 pag. 9492: Please check the symbol "L" and unit "L".
The second L is not a unit but a sign for the length dimension of the unit. For clarity, the L in Eq. 3 and the corresponding symbol in the revised text will be changed to L_s - length of the packed-off section.

6. Line 13 pag. 9494: Please explain the symbol "P".
We assume the reviewer is referring to page 9492, where "p" will be changed to P value. P value is defined as a measure of significance, or of evidence against the null hypothesis (e.g., that there is no correlation between two variables). Small P values imply that the correlation (and regression model) is significant.

7. Fig. 1: Please use a more appropriate lithological term for "loam" (silt?).
This will be changed to silt.

8. Fig. 2: Please explain in the caption the symbols "wt", and horizontal stripes and dash lines. Please check "red 3 cells" (red-3 cells ?).
The wt symbol will be changed to the conventional inverted triangle symbol for water table. Also, the text in the caption will be changed as suggested.

9. Fig. 3: What does "LOQ – limit of quantification" refer to?
LOQ – limit of quantification in the caption refers to panel f, and will be specified accordingly in the revised manuscript.

10. Fig. 4: Several labels are placed one upon another. Please improve this figure. I suggest a general language revision to make the reading of the paper more fluent.
Tabs will be added for the variable labels that overlap (Fig. 4a and 4b) and for some case-labels (Fig. 4c and 4d). The revised manuscript will undergo thorough editing to improve its arrangement, clarity, and language fluency.

Anonymous Referee #2

In this paper, two sequential multilevel profiles for a contaminated aquifer were analyzed using principle component analysis of data on major ions and trace elements. Additionally, electric conductivity in a packed off section of the observation well and hydraulic heads for two sub aquifers divided by clay lenses were measured during the multilevel sampling campaign. The authors infer from their data analysis that distinct water bodies of 10-100m vertical and horizontal dimensions laterally flow under this contaminated site.

General comment:

11) This well written paper uses innovative methods to analyze an interesting and practically relevant data set. However, implications of their findings for monitoring and remediation remain unclear. What do exactly mean their findings for monitoring and remediation?

We appreciate the referee's positive view of the paper, and thank him for his constructive suggestion to add some discussion of the implications for monitoring and remediation. We agree that this would be valuable, and will do so in the revised manuscript. Perhaps one of the most novel outcomes of this work is the idea that by sampling a single monitoring well via multilevel sampler a few times, it is possible to arrive at a certain understanding of the spatial character of the subsurface contamination. This is because ambient water flows pass through the monitoring well and can be characterized. This information can then be used to develop a site-specific monitoring network and remediation plan. For example, at the study site, a distinct difference between contamination extents in the upper and lower parts of the aquifer is apparent. In the upper part of the aquifer, the presence of distinct water bodies having limited horizontal and vertical extents suggest that the spacing between monitoring wells should be small (on the order of 10s of meters). In the lower part of the aquifer, contamination levels are much lower, such that the density of monitoring wells there can be significantly lower. Differences in contamination characteristics between the water packets and their large degree of mobility could also impact both the selection of remediation technologies and the progression of the cleanup. At the study site, for instance, this would mean that remediation methods would need to be able to handle contaminants whose concentrations vary greatly both spatially and temporally due to the movement of distinct water bodies. Apparent remedial progress may not be linear in such a system, not because the method does not work, but because background concentrations change due to movement of distinct water packets.

Specific comments:

12). P9486, L17: MLS1 had 17 cases but 23 variables were used for PCA. Number of variables cannot be greater than number of cases.

Thank you for this comment. Many rules of thumb can be found for how many cases or cases-to-variables-ratio are appropriate for PCA and Factor Analysis, and there is no single rule that holds for all types of analysis and confidence that one can have in the results. In this work, the number of cases (depths) is limited, thus the question of whether to reduce the number of variables included in the PCA could be justified in order to improve confidence. For example, using only major ions (8 variables, 17 cases, MLS1; see Figure A below), we would have obtained higher loadings (and communalities) for the first two principle components (i.e., all variables are close to the perimeter of the unit circle drawn on the PC1-PC2 plane), yet our ability to interpret PC2 would have been very limited, because all the variables have negative and relatively low loadings for this PC (see Figure A below). When including the trace elements in the analysis, we indeed can explain less of the total variability (some variables have weak loadings (e.g., Ni and Al, Fig. 4a), but we gain the ability to assess the nature of PC2 due to variables like Co, Mn, and As (Fig. 4a)). Therefore, if the purpose of the PCA is data exploration (or descriptive statistics) rather than building a predictive model, the cases-to-variables ratio criterion may be more relaxed. In this work, keeping more variables in the PCA was fruitful because it enabled interpreting the nature of the second PC.

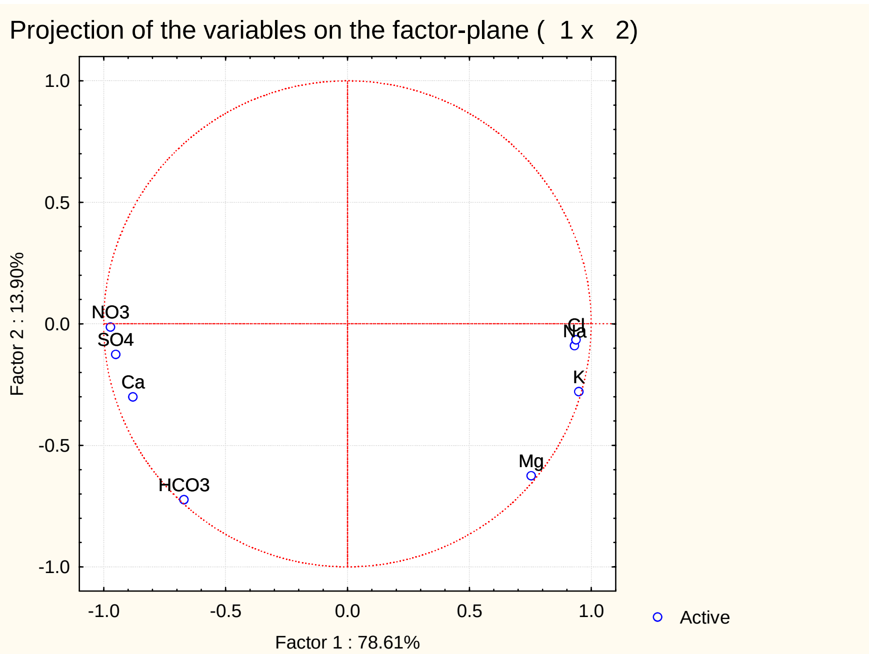

Figure A. Major ions (8 variables, 17 cases) projected on PC1-PC2 plain, as an alternative for the 23 variables used for the PCA of MLS1 in the paper.

In groundwater hydrology, the number of samples (cases) is often limited, such that using a PCA with a large number of variables can serve to compliment PCAs with a smaller number of variables (e.g., Stezenbach et al. (1999) analyzed 45 trace elements from only 18 locations). In other fields where observations are also limited, the use of small number of cases with many variables may be useful in factor analysis, especially if communalities are high and the number of factors is small (Preacher and MacCallum, 2002, Behavior Genetics, Vol. 32, No. 2.). This is generally the case in our analysis.

13) P9486, L25: Why was no rotation used for PCA? Better interpretation may be achieved through rotation of components.

Rotation is usually performed to obtain a simple structure in which variables load most strongly on one factor (PC), and much more weakly on the other factors. In our multilevel data, the nature of the PCs is reflected by the variables profile, and we are interested in preserving the association of the variables with more than one PC, if appropriate. For example, in our analysis, Mg^{2+} has high loadings with PC1 because it generally increases with depth, yet it also has high loading with PC2 because it shows a counter-trend decrease in concentration at the deepest cases. Therefore, to maintain the ability to roughly sketch the variable's profile from its location on the PC1-PC2 plane, rotation is not favorable. Varimax rotation within a factor analysis of the data was tried and interpretation of the factors with respect to the variables depth profiles (like the one demonstrated for the un-rotated PC's in the paper) was not possible.

14) P9486, L25: Did variables depart significantly from normal distribution. If yes, Box-Cox transformation may be used. Non-normality can significantly influence correlation matrix and thus results of PCA.

With the exception of Cr, which has some very high concentrations in the upper sub-aquifer, and Mn with high concentrations in the bottom of the aquifer (MLS1), changes in the other variables used in the PCA were relatively smooth and pass the Kolmogorov-Smirnov test for normal distribution with high probabilities. Therefore, the un-transformed correlation matrix is useful, and transformations like Box-Cox are an un-necessary sophistication that will not improve the analysis.

15) P9490, L9: How did 3 water bodies vary in terms of VOCs?

We thank the reviewer for this remark. VOCs concentrations differ significantly between the top and intermediate water bodies. The change in location of the boundary between these two water bodies from the 70-84 m interval in MLS1 to the 59-67 m interval in MLS2 is clearly reflected in the VOCs' profiles similarly to variables that were included in the PCA (e.g. Mg^{2+}, SO_4^{2-} and Co; Fig 3 a,b,f,g,h). The bottom and intermediate water bodies do not differ significantly with respect to VOCs. For clarification, two sentences dealing with this issue will be added to the discussion in the revised manuscript.

16) Black vertical lines (observation well) are inconsistent for Figures 7 (a) and (b).

We thank the referee for this comment. Figure 7a (the vertical flow hypothesis) demonstrates that the configuration of the water-bodies in MLS2 is a result of the configuration in MLS1 and the assumed vertical flow that existed at the time between MLS1 and MLS2. Figure 7b demonstrates that the configuration of the water bodies in MLS2 is a result of different water bodies flowing through the observation well at the time of sampling. We apologize, the time arrow added to the base of Fig. 7b was confusing, and will be removed in the revised manuscript. The horizontal axis of this plot is spatial (in the opposite direction of flow). Therefore, the observation well should be located only in one location on the panel (not like in Figure 7a). We have chosen a place which represents the situation before the sampling date of MLS 1 to enhance the perception of water bodies that flowed through the sampling well and sampled at the two sampling dates. The figure was and clarification was added to the figure's caption in the revised manuscript. See revised Figure 7 and caption here (underline indicates new text).

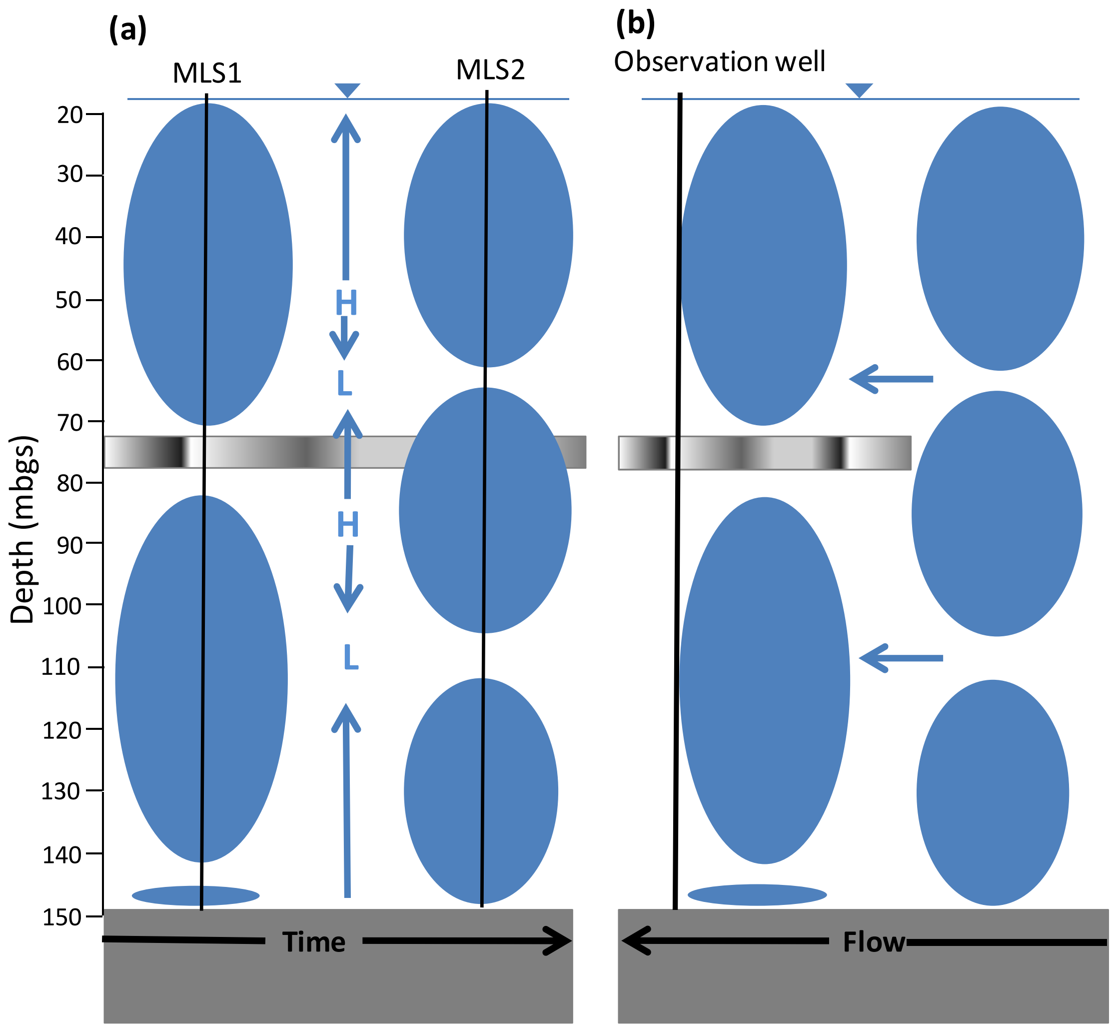

Figure 7. Considering possible flow regimes in the vicinity of the observation well. Blue ellipses resemble the water bodies inferred in the PCA of MLS1 (left) and MLS2 (right). (a) Vertical-dominant flow regime at the time between samplings that may support the differences in the vertical distribution of the water bodies observed in the two campaigns. L and H are relative low and high hydraulic heads. (b) Lateral flow of water bodies passing through the observation well as an alternative explanation of the differences. An arbitrary snapshot before the sampling date of MLS1 is presented. Note the assumed origin of the MLS2-water bodies from an area where the clayey bed at 73-79 mbgs is absent.