Hydrol. Earth Syst. Sci. Discuss.,
doi:10.5194/hess-2017-12-RC2, 2017

Hydrology and Earth System Sciences
Discussions

Interactive comment on "The Potamochemical symphony: new progresses in the high frequency acquisition of stream chemical data" *by* Paul Floury et al.

Anonymous Referee #2

Received and published: 25 February 2017

General comments

This manuscript presents first data from a field deployment of an instrument package ("River Lab" or "RL") for high-frequency analysis of natural streamwaters. The instrumentation includes dual-channel ion chromatography and various physical and electrochemical probes. Data are presented to illustrate the quality of the chemical time series that can be obtained.

This manuscript makes a useful contribution to the growing literature on field-based chemical analyses of natural waters. In particular, the data presented here show that on-line analyses can be much more precise than those based on conventional sampling with later analysis in the lab.

Printer-friendly version

Discussion paper

However, the manuscript's characterization of the River Lab as a "breakthrough" (three times!) is not appropriate. Many other studies have also deployed wet chemistry instruments in the field (see Rode et al. ES&T, 50, 10297, 2016, and similar reviews). For example, a Swiss research group has recently published (also in HESS) a field deployment of another on-line ion chromatography system. That system arguably goes beyond the one presented here (it also includes isotopic analysis, and analyzes both rainfall and streamwater, rather than just streamwater alone), but the Swiss group does not use self-congratulatory terms like "breakthrough" to describe their work.

Likewise the claim that "... the high frequency and high precision of the RL enabled unprecedented observations of the fine structure in hydrochemical time series" is exaggerated. Similarly detailed results have been obtained before for other analytes using other field instrumentation, as well as by the Swiss group for major ions using IC. The present manuscript does a good job of demonstrating the precision of the RL, and does so in greater detail than I have seen before. But the observations themselves (at least the ones that are actually shown here) do not merit superlative terms like "unprecedented".

Heroic claims like "Our study opens a new era of investigation into the fine structure of the hydrochemical signal in rivers" (line 478) will not create a favorable impression in the community of investigators who have already been working, in some cases for decades, on these questions. Similarly, claims like "Recording such fine stream hydrochemical variations is thus offering a new perspective on Critical Zone" (line 483) are unproven and should be removed, since no inferences about any catchment processes are derived in the present manuscript.

Several time series are shown to illustrate the results that can be obtained with the RL, and to illustrate the results that would be expected at lower sampling frequencies. This is fine as far as it goes, but given that the manuscript claims that the system has been measuring seven ions continuously for over a year, it seems strange that only a few days of data, for only two ions, are shown. Where is the rest of the data set, for

the rest of the ions? It is understandable that the authors want to defer the analysis of the longer-term data set for a later paper, but they should at least demonstrate its existence by showing it to the audience.

To quantify the effects of subsampling and sampling error, the manuscript calculates how they affect the first four moments (mean, standard deviation, skewness, and kurtosis) of the distribution of measured concentrations for two brief sampling periods. Despite the time and space devoted to this analysis (two entire figures and parts of four others), it is not well posed and adds little to the paper, for the following reasons:

1) The moments of concentration distributions are rarely subjects of interest, particularly over such short periods of time.

2) The distributions (particularly in Fig. 5) are sensitive to the interval of time that is considered. In particular, much comment is made about the "bimodal" distribution during the "flood event", but this is largely an artifact of the specific time interval that is chosen.

3) Skewness and kurtosis are mostly useful in characterizing uni-modal distributions, and their application to bimodal distributions is not very helpful.

4) Statistical moments calculated from only five data points (as in Fig. 5) really should not be taken seriously!

5) The error bars in Figures 7 and 10 are unrealistic estimates of the uncertainties in the data points, because they do not account for the rather strong autocorrelation in the time series.

6) Skewness and kurtosis are not ratio-scale variables (they do not have a natural zero), so calculating percentage changes in them makes no mathematical sense, for the same reason that a temperature increase from 1 to 21 degrees Celsius is not "an increase of 2,000 percent!"

7) The changes in distributions and statistical moments shown in Figures 8-10 are

unsurprising to anyone with even a modest background in statistics, given that we are mixing the distributions of the original data with an assumed error distribution that has a mean, skewness, and kurtosis of zero, plus a standard deviation that is substantial compared with that of the original data.

8) Statements like "the average is not sensitive to analytical precision" (line 429) are self-evident (of course it isn't, as long as the added noise has a mean of zero!).

The time series plots show the effects of subsampling and added noise very clearly. The statistical analysis does not help (and is often misleading), and should be omitted.

The manuscript is mostly well written, but in some places the grammar and word usage need improvement. To take just the two examples that arise in the title itself: "progresses" is not a noun in English, and "Potamochemical" is not a word in any language. While one can appreciate the authors' creativity here, the use of a made-up word like "Potamochemical" will seem pedantic to many readers. A few of us may still recall that "potamology" means "study of rivers", but the usage of this term has been declining steadily for about 50 years and there is no compelling reason to revive it. Readers should not need to reach for their dictionaries to look up obscure Greek roots of words, just to understand the title of a scientific paper.

Specific comments

The abstract claims that the RL was deployed "for over a year of continuous analyses" but the conclusion refers to measurements made "over several months". Which is it? Please provide plots showing "over a year of continuous analyses" of all ions, to substantiate the claim made in the abstract.

The abstract says that the daily oscillations observed during the summer drought were "unexpected". Why were these oscillations unexpected, given that they have been reported in many previous papers, including several that are cited here?

The characterization of sampling frequency in millihertz (i.e., 40-minute sampling is

described as 0.42 mHz) is unhelpful and will strike many readers as pedantry. If one wants to speak in terms of frequency, a more natural time base is 1 day (40-minute sampling is 36/day, 7-hour sampling is 3.42/day) or 1 week (40-minute sampling is 252/week, 7-hour sampling is 24/week).

The "flood event" represents an increase in flow of only about 50% or so, and even the highest flow in figure 5 (about 200 L/s) is 50 times smaller than the reported peak flow of over 10 m3/s (see line 105). In what sense is it appropriate to call this a "flood event"?

Figure 1 is artistic but less informative than it should be. Please provide a proper schematic of the instrumentation instead. Readers should be able to build a working version of the instrumentation (or at least understand the challenges involved in doing so) from the information provided.

Figure 3 focuses the reader's attention on the conductivity data (which is not the subject here), because it is darker than the Cl data. Plot the conductivity data in a light color and the Cl data in a dark color, and connect the Cl points. And don't show the artificial 0-to-100 scale; show the real concentrations and conductivities.

Figure 4 and associated text: why are cations shown for one date and anions shown for another date? Show all the ions for one date, so they can be compared. Also, the fonts in Figure 4 are inconsistent, and the placement of the panels is erratic. Didn't anyone notice this? And the two colors look the same in grayscale; again, didn't anyone check? Also, please show the real hour of the real day, not an artificial scale (I went crazy trying to figure out what was going on here, before I discovered that the scale was fake and the cations and anions have nothing to do with one another because they are on different days (but why does chloride stop before the other anions?).

The laboratory analyses were reportedly done on "IC devices similar to those installed in the RL", but what does "similar to" mean? Specify exactly what instruments those were, what columns were used, how old they were, and so on. This is important,

because the relatively poor performance of the laboratory analyses is attributed to the difference in sampling, rather than the difference in instrumentation. If the laboratory instruments are an earlier generation of IC, or are using older columns, or have not been maintained as well, or have not been operated as carefully, or, or, or... it is easy to see how the laboratory results could look poorer for many different reasons.

The obvious offset between the laboratory results and those from the RL are particularly concerning. What efforts have been undertaken to verify that these do not indicate an artifact in either the RL or the laboratory?

In Figure 8, add error to the whole time series, not just the arbitrarily defined "event" period.

Details (a partial list)

50: Rozemeijer, not Rozemeiler 51: Chapman et al is 1997, not 1996 (and it would be appropriate to cite Neal et al., Hydrological Processes 2531, 2013, here). 292: discretely, not discreetly many figures: probability, not "probality" (didn't anybody notice this?) 476: "the best orchestra available": clever phrase, but an unproven assertion and will be perceived as inappropriate bragging 477: "to play the potamological symphony": no, instruments *record* the symphony; nature plays it.

Interactive comment on Hydrol. Earth Syst. Sci. Discuss., doi:10.5194/hess-2017-12, 2017.