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Title: Quantifying nutrient fluxes in Hyporheic Zones with a new Passive Flux Meter (HPFM)
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Content

The article describes a very interesting passive approach to determine and couple interstitial water flow and nutrient transport in the hyporheic zone, the hyporheic passive flux meter (HPFM). The method is based on alcohol dilution from activated carbon and ion exchange resins. They firstly tested the ion exchange resins to obtain the most appropriate one. Secondly tested the HPFM in the field and compared the results with a most commonly used method such as pore water sampling. The presented approach is very interesting since it reduces temporal variability and the sampling effort, and it is very relevant because couples nutrients and water flow, to obtain hyporheic fluxes.

General comments

While interesting and novel, I have five major concerns as summarized herein. First, I have concerns about the approach in the field test. The number and distribution of the HPFMs in the field seems to be done assuming a very homogeneous hyporheic zone, however this hardly ever happens. As a consequence the high spatial variability arises among all the measurements. There is not enough replication for basic statistical tests, and therefore, the comparison with the reference method, the pore water sampling (MLS), is very difficult to interpret. At least the analysis of the data should be done using those layers that have been measured as replicated presenting means and standard deviations/errors. And when possible perform statistical tests that proof or not the differences.

Second, the data from the HPFM should be explored with more detail and use the information provided by the coupled information to obtain more accurate information. In its present form the usage of the data is slightly superficial. A part of showing whether the HPFMs worked or not, the manuscript should also show which information can be obtained with them.

Third, the growth of biofilm appears to be very significant in the HPFMs both in the laboratory columns and in the field. This could have strongly influenced the results and should be taken into account by the future or potential users of the HPFMs compared with other methods based on diffusion; however no data on this aspect are shown.

Fourth, while the abstract is quite direct, the introduction is too detailed what makes the reading confusing and lacks of a clear and direct objective. The methods section provides numerous and useful details as should be in a methodological manuscript, however they could be arranged in another way more intuitive that eases the reading. In general terms, the manuscript would be more convincing if it were presented as a comparison with MLS.

Fifth, the text is well written in general however a revision of expressions and grammatical mistakes is needed.

Specific comments

Page 1 Lines 25-27: In the manuscript, the HPFMs was placed in the streambed for a week and once recovered provided information on the total flux of nutrients and water during the study period however did not provide any information on temporal variability. In fact, pore water sampling could account for much more temporal variability than the presented approach.

Page 1 Lines 9-33: The abstract or the keywords should provide some more detailed information about the method; more specifically include the use of resins and activated carbon.

Page 1 Line 15: it is not clear the meaning of the term load, does it refer to nutrient concentration?

Page 2 Lines 13-14: The definition of hyporheic zone excluded groundwater, however in line 20 (page 2) there is a reference to the significance of groundwater for nitrogen cycling in the hyporheic zone. I suggest expanding the definition, seeing for example Boulton, A. J.; Findlay, S.; Marmonier, P.; Stanley, E. H.; Valett, H. M., The functional significance of the hyporheic zone in streams and rivers. Annual Review of Ecology and Systematics 1998, 29, 59-81.

Page 2 Line 29: In the discussion, the term hotspot has been used, I suggest keeping the term uniform and use it here as well.

Page 2 Line 35: Does “exchange rates” correspond to water, nutrients or both?

Page 4 Line 32: In the present study biofouling is also not clearly regarded since no control or no data are shown.

Page 5 Lines 2-13: Please include information about the resin and AC such as pore size, specific surface, porosity... Please include also an estimation of the maximum potential adsorption, how much mass of the studied nutrient can be measured? Which is the detection limit of the HPFMs for nutrient and which is the minimum Darcy velocity that can be detected?
Please indicate in this section as well that resin and AC aimed to inform about two different parameters/processes.

Page 5 Lines 11-12: Why was this mesh size selected? Taking into account the characteristics of the streambed sediment, of the resin and/or AC, or both? Very fine streambed sediment could clog the mesh, or even enter the resin and AC and clog it. On the other hand, in a very permeable streambed the HPFM would probably act as an impermeable layer and limit the exchange of tracer and nutrients to diffusion. See Ward, A. S., et al. (2011). "How can subsurface modifications to hydraulic conductivity be designed as stream restoration structures? Analysis of Vaux’s conceptual models to enhance hyporheic exchange." Water Resources Research 47: W08512.

Page 5 Line 4: Please indicate that the tracer loaded carrier is the activated carbon (AC).

Page 5 Lines 34-35, Page 6 lines 1-6: Were the HPFMs stored dry? When placing the HPFMs in the streambed there was a first wash of the resin and AC, could it be estimated how much is this first contact with stream water influencing the final result? How much of the maximum potential adsorption/dilution (%) is lost in this first step?

Page 6 Line 14: The heading of this section is confusing since it is commonly placed at the end of the methods section; however this is a methodological manuscript. This section would be better merged with the correspondent method, Section 2.2.1 included right after the description of the AC, and section 2.2.2. merged with the description of the resins.

Page 7 Lines 4-6: Is "J_N" time-averaged advective horizontal nutrient flux? Please indicate it together with the correspondent units.

Page 7 Line 10: The heading of section 2.3. is a bit confusing, does not reflect the aim of the section, to ease the reading, it might be better to swift this section to right after section 2.1.1.
Page 7 Line 11: If as indicated experiments described in that paragraph were accomplished on triplicate; please present the data as means +/- standard error, or standard deviation.

Page 7 Lines 16-29: Please, provide more details on the experimental setup, for instance were the columns pump bottom-top or top-bottom direction, where the columns placed vertically or horizontally, for how long were the tests run. Please provide the brand of the pump.

Page 7 Line 19: I wonder whether at the same nutrient flux into the HPFMs (high concentrations and low flow, or low concentrations at high flow) the differences in interstitial velocity (i.e. Darcy velocity) would influence the adsorption/dilution due to turbulent flow and finer diffusive boundary layer.

Page 7 Lines 30-32: Please provide these results.

Page 8 Lines 1-2: The lower or higher concentrations of N and P respectively contained after the incubation were used to correct the obtained data in the field experiment?

Page 8 Line 17: Does "stones" refer to Boulders or cobbles? Please specify. If possible, please provide information on the granulometry of the streambed.

Page 8 Line 33 Which is the reasoning for doing such combination of resin and AC? Would the results be more accurate in this way? If the aim is to test simultaneously both approaches, this arrangement does not seem appropriate since each layer is considered independent from the other one, and it is not clearly assumed that the streambed will have uniform nutrient concentrations or interstitial flows.

Page 9 Lines 5-7: Are the presented results corrected with this control?

Page 9 Lines 19-20: it is not clear why the oxygen loggers had to be placed four weeks in advance for re-equilibration, while the HPFMs where placed without re-requilibration period. Would it be wise for future measurements to leave for example a perforated metal case in the streambed for certain period before placing the HPFMs? In this way, would the hyporheic zone be re-equilibrated after hammering the metal case in the streambed?

Page 9 Lines 21-37 and Page 10 Lines 1-3: The manuscript aims to compare the HPFMs with the pore water sampler (MLS), therefore this has to be clearly stated and well explained in the methods.

Page 9 Line 23 and figure 2: Why is the MLS A located so far (>2m) from the rest of the measurement points?

Page 10 Lines 1-3: Are the N and P data from June presented in the manuscript? Or for June just information on SO_3 and B are provided? And data from N and P just correspond to October?

Page 10 Lines 4-13: The measurements presented here should have an appropriate heading as the MLS, oxygen profiles… or do these methods belong to the MLS?

Page 10 Line 7: Within the context of the manuscript it is also interesting to provide the detection limit.

Page 10 Lines 10-13: Most of the parameters measured with the YSI probes are not provided in the results or tables. Please include them in a table, with mean and standard error or deviation for the incubation period.

Page 10 Lines 12-13: Which is the relevance of Chlorophyll-a for the aim of the manuscript?

Page 10 Lines 17-19: Indicate clearer, if correct, the abbreviations of all terms: "the proportion of surface water (Q_{SW}, $m^3\ s^{-1}$) infiltrating…"

Page 10 Lines 17-19: Considering the interesting information about Darcy velocities in the hyporheic zone provided by the HPFM, it would be more accurate to calculate the proportion of infiltrated surface water from the cumulative Q_{HZ} for each layer, so the ratio will be $\Delta Q_{HZ}/Q_{SW.}$
Since one of the advantages of the HPFM is that it can measure nutrients and Darcy velocities simultaneously and at different depths, the results will be more complete using an approach that includes that information.

Page 10 Line 18: I am not sure if the measured velocity in the HPFMs can be described as horizontal it could have also been diagonal. Of course according to the calculation it is horizontal but it confuses the reading especially when the results from the temperature show that there was a very strong vertical downwelling. Another term such as interstitial velocity may be more appropriate.

Page 10 Lines 20-21: Due to the lag between the water entering the hyporheic zone from the surface and the measurements in deeper layers, it is no easy to calculate the removal of any nutrient in the hyporheic zone. The N removal activity of the hyporheic zone, as calculated, seems to underestimate the capacity of the hyporheic zone. Considering the interesting information from each layer provided by the HPFMs, it would be interesting to take advantage of it and calculate the removal as something like what follows:
Since there is a quite strong vertical flow, we can assume that the concentration in one layer depends on the previous one. In this way, it can be calculated that the uptake at each layer results from the difference in fluxes ($layer_y$ – $layer_{y+1}$). Of course, as indicated in the introduction, one has to take into account both flow and concentration, that is why it seems better to use the fluxes and not the concentrations. The combined uptake of all layers will provide the total uptake rate in the studied section of the hyporheic zone that can be then compared with the N flux from the surface water.
Additionally, it could be calculated the amount of N removed in the hyporheic zone to the flux of N in the stream to have larger scale information. This would answer the question of how much does the hyporheic zone removes from what is in the stream/ecosystem?

Page 10 Line 31: How could this influence the results? Please include some data.

Page 11 Lines 33-34: See comment on page 5 lines 11-12, could this observation explain, at least partially, the measured darcy velocities (figure 3) in the deeper layers?

Page 12 Lines 4-7: The high variability between both measurements (A and B), the lack of replicates and hence the lack of statistical tests, makes it difficult to draw such conclusions out of the presented data. The presented values represent very high spatial variability in the hyporheic zone, either due to heterogeneous flow or the presence of hotspot/moments during the day. A more cautious sentence should be used, and in the discussion refer to data from the literature.

Page 12 Lines 8-9: Are these values means or just punctual measurements, standard deviations should be then provided. If enough data are available, a simple statistical test should be applied, for instance, one-way analysis of variance (ANOVA).

Page 12 Lines 13-14: The temperature profiles provided information on vertical downwelling from the surface water. However, the darcy velocity obtained from the HPFMs was named as horizontal, however it is not possible to know which the actual direction of the water was. To avoid confusion with the fact that the flow was strongly vertical it might be better to name the flux obtained in the HPFMs as interstitial velocity and assume the sediment was isotropic.

Page 12 Lines 19-23: Considering the high variability shown with two HPFMs in the manuscript, at least three per parameter should be placed in the streambed (flow or nutrients). Even in channelized rivers, small scale variability and heterogeneous residence time distribution occurs (see for example data from vertical water flux Mendoza-Lera, C. and M. Mutz (2013). "Microbial activity and sediment disturbance modulate the vertical water flux in sandy sediments." Freshwater Science 32(1): 26-35.). Additionally, even if low variability is assumed, such approach would be statistically more consistent.

Page 12 Lines 30-31: Data on substantial biofilm growth are not provided, please include.

Page 12 Lines 31-34: Not only biofouling could influence the results, what about uptake/release of nutrients by the biofilm? Right after placing the device in the streambed in was a sterile substrate, which informed about the nutrient concentration in the water flowing through it, and therefore about the surrounding conditions in the hyporheic zone. However, after certain time the HPFMs become an actual physical substrate where the microbial community developed, and therefore the HPFMs became part of the hyporheic zone. Therefore, the information provided by the HPFMs after the incubation also refers to the community inhabiting it.

Page 13 Lines 4-6: Please provide example of the intrusive measurements of hyporheic flow. As occurs when placing piezometers of smaller diameter than the HPFMs+metal case disturbance is created and likely after removing the metal casing fine sediment was sucked into the HPFMs as happens when placing piezometers. When the HPFMs were removed from the streambed and the measurements perform, was there evidence of fine sediment intrusion? Was there any evidence of clogging in the mesh?

Page 13 Lines 11-17: It would be interesting to know which is the time scale detected by the method. If oscillation occurs within 12 hours or less, could the method be further adapted? For example placing the HPFMs for few hours?

Page 13 Lines 30-32: I am not sure whether such assertions can be done in the light of the limited replication and statistical tests. Since the difference in P concentration has not been proofed (no

statistics) it is no possible to link the dynamics of phosphorous with oxygen. However, it could be interesting to take advantage of the oxygen profiles and determine if the dynamics observed in N and P in the HPFM and/or MLS correlate with the mean oxygen concentration.

Page 13 Lines 36-37: The HPFMs provide information of a flowpath, the length, velocity and residence time of the water before reaching the HPFMs is not known (further tracer tests could be implemented in combination with the HPFMs). Then it is difficult to determine whether there are hot spots for denitrification or hot moments, or both (see Abbott, B. W., et al. (2016). "Using multi-tracer inference to move beyond single-catchment ecohydrology." Earth-Science Reviews). Additionally, downwelling into the hyporheic zone does not occur as a front but rather as semicircular flowpaths, see for instance:

Thibodeaux, L. J. and J. D. Boyle (1987). "Bedform-Generated Convective-Transport in Bottom Sediment." Nature 325(6102): 341-343.

Salehin, M., et al. (2004). "Hyporheic exchange with heterogeneous streambeds: laboratory experiments and modeling." Water Resource Research 40: W11504.

Rehg, K. J., et al. (2005). "Effects of suspended sediment characteristics and bed sediment transport on streambed clogging." Hydrological Processes 19(2): 413-427.\

Page 14 Line 10: I suggest including in this section an summary in the form of a table of the factors that should be taken into account for applying the HPFMs in different contexts, for example pH should be taken into account in an acidic stream in a mining area, or permeability is to be taken into account to approximate the permeability of the studied reach (for instance the following method could be used to define the appropriate permeability in the HPFMs Datry, T., et al. (2014). "Estimation of sediment hydraulic conductivity in river reaches and its potential use to evaluate streambed clogging." River Research and Applications 31(7): 880–891).

Page 14 Lines 2-5: I agree, the hyporheic zone is probably deeper than the scale of the HPFMs, however it is as well very heterogeneous in residence time distribution and therefore increasing the number of measurements and/or the scale will be a very interesting. This, together with the high variability of the provided data, indicates that future applications of HPFMs should have enough replicates.

Page 15 Line 20: When more than one author it is uncommon to acknowledge in first person.

Table 2: Please include either ranges or means +/- standard deviation.

Table 3: Please include either ranges or means +/- standard deviation.

Figure 1: Please indicate to which approach corresponds the picture resin or AC, or alternating segments.

Figure 2: For a non-german reader this map won't be very informative, especially because the aim of the manuscript is not to study that stream. I encourage presenting other information instead such as the temperature profiles.

Figure 3: It might be more appropriate to express the fluxes per volume of sediment, in this way confusion with the denitrification rate units would be avoided. Additionally, in table 2, mass fluxes for nutrients are expressed with other units.

Figure 5: I am not familiar with the symbol for diameter to indicate mean concentrations, and it is a bit confusing. I suggest to simply adding surface water.
Considering the variability of the values measured in the hyporheic zone, it would be interesting to include the range of concentrations, or mean +/- standard error or deviation, of the surface water during the deployment time, as understood from the method the nutrient concentrations were measured every 15 mins.

Technical corrections

Page 2 Line 18: Correct phosphate, per phosphorous, or P per PO_4^-

Page 3 Line 20: Correct technics, per techniques.

Page 4 Line 34: Space missing in "…Pin…"

Page 7 Line 35: Correct KCL per KCl

Page 8 Line 13: Correct figure 2 instead of figure 3

Page 10 Line 2: Correct sun rise, per sunrise

Page 10 Line 20: Correct NO_3^-, per NO_3^--N

Page 12 Line 4: Correct SRP, per SRP-P

Page 12 Line 14: For which sentence stands the citation (Layton, 2015)?

Page 14 Line 20: Correct hot spot, per hotspot