Biogeosciences
Discussions

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Interactive comment on "Sources and transfer mechanisms of dissolved organic matter during storm and inter-storm conditions in a lowland headwater catchment: constraints from high-frequency molecular data" *by* L. Jeanneau et al.

Anonymous Referee #2

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Synopsis:

The authors use THM-GC-MS to characterize DOM from a headwater stream during 5 successive storm events and during inter-storm conditions, and compare to spectroscopic and isotopic measurements. Emphasis is placed on high-frequency sampling during storm events, leading to exciting and unique results. Additionally, the Kervidy-Naizin catchment is well studied, leading to a wealth of background information to aide

interpretation of this study's results.

Biomarker results are analyzed via carboxyC6/C5, C/V, and Ac/Al (V) ratios, and using a biomarker end-member mixing approach. The authors interpret changes in these metrics as representing three DOM export mechanisms: microbial biofilms, partitioning between particulate and dissolved phase, and erosion of macropore walls.

My main concerns are: lack of quantification in in biomarker detection procedure, selection of end-member values for EMMA, and highly specific hypotheses to explain observed trends (specifically periods 1 and 3 involving microbial biofilms and macropore walls). Simpler explanations should be considered to describe observed trends, for example: partitioning from particulate phase could continue in soils once turbidity has decreased without needing to invoke macropore wall erosion.

General comments:

- Grammar and syntax could be improved overall (i.e. confusion between singular and plural nouns, verb/noun agreement, pronoun usage, lengthy paragraphs)

- Much of section 2.1 and 2.2 should be moved to the results section, leaving only general statements about site description in the methods section (i.e. mean temperature, mean rainfall, bedrock lithology, etc.). Discussion on groundwater movement, hydrological periods, and previous results are better placed in the results section.

- Compound detection and quantification procedure is not quantitative. Compounds should be quantified in SIM mode for maximum sensitivity (e.g. http://www.shimadzu.com/an/sim-mode.html) and compared to an external standard calibration curve run at multiple dilutions for proper quantification. Internal standards or extraction of known mixtures should be used to quantify extraction recovery.

- Justification is needed for end-member definitions in the EMMA. Specifically, attributing FA <C19 to microbial (omitting C16:0 and C18:0) and >C19 to vascular plants is an oversimplification and will likely bias results. Heterotrophs and phytoplankton have

been shown to produce an array of FA with chain lengths longer than C19.

- Explanatory mechanisms for DOM trends during storm events seem speculative and highly specific. More evidence is necessary to justify these hypotheses.

Specific comments:

- Verbose title, should be shortened (e.g. to the shortened title listed in the side bar: "Transfer of DOM at the soil-stream interface in a lowland headwater catchment: Constraints from high-frequency molecular data")

- Abstract: Transfer of DOM is but one of many control mechanisms on these processes [page 3350, lines 1-3]. Abstract lists micropollutants and terrestrial v. marine C reservoirs as main motivation to study DOM [page 3350, lines 2-3, 24-25], while introduction lists UV light absorption and food source for bacteria as main motivation [page 3351, lines 2-3].

- Citation for statement that DOM is controlled by water flow paths? [page 3351, lnes 13-15]

- Why not cite original lignin export papers? e.g. Hedges and Mann, 1979; Hedges and Parker, 1976. Similarly original vascular plant fatty acid papers? e.g. Eglinton and Hamilton, 1967 [page 3353, line 8, 14].

- [page 3353, line 19-22] Is this a valid assumption? This assumption seems critical to the comparison between molecular and spectroscopic data, yet neither citation nor confirmation data are given. - Is 'soil solutions' a synonym for soil DOM? [page 3354, line 2] If so, this should be changed to 'soil DOM' throughout. If not, this should be defined.

- Concentrations should be listed in brackets, e.g. [DOC], [Cl-], etc. [page 3354, line 5]

- Soil molecular data [page 3356, line 3-19]: Why omit C6 in deoxyC6/C5 ratio, since C6 and deoxyC6 are listed as microbial? How is proportion of plant-derived markers

defined, specifically? It is unclear what the unit 'L mg-1m-1' is meant to represent. Is SUVA vs. deoxyC6/C5 regression for surface samples, deep, or both?

- More detail is needed on "removal of roots and gravels" – i.e. removed by eye? Sieved? If so, to what pore size? [page 3357, line 12]

- More detail needed on DOC sampling procedure [page 3357, line 21-23] – i.e. depth of sampling in water column, filtration pore size (if filtered?), sample volume, sample storage (bottle material), etc.

- [page 3358, line 4] 'soil or lyophilizate' implies that stream water samples were freeze-dried, yet this procedure was never discussed explicitly.

- Odd choice for transfer line temperature (321C) [page 3358, line 11]

- What is the justification for using full scan mode, rather than SIM mode, for peak detection and integration? Generally, quantitative measurements should be done in SIM mode, as sensitivity is higher, and compared to an external standard calibration curve [page 3358, line 17].

- [page 3359, line 4] 'C/V' and 'Ac/Al' have not been defined.

- 'R1 value' not defined [page 3359, line 17]

- [page 3359, line 18-20] This source separation is an oversimplification. Phytoplankton/bacteria have been shown to produce >C19 branched and unsaturated FA (see, e.g. Volkman et al., 1980).

- [page 3359, line 20-22] This mixing model description would be made much clearer with a simple equation.

- [page 3362, line 18-20] Is this statement statistically true? Looking at Figures 3 and 5, the fraction of plant-derived markers at the beginning of event 3 looks identical to inter-storm conditions.

- [page 3366, line 20-22] A citation for this claim should be provided.

- [Figure 2] 'PK1' is not defined.

- [Figure 3-4] These figures would be made much clearer with a legend for symbols. Additionally, measurements should maintain same symbol throughout figures (i.e. C/V data are black circles in Figure 3, but white triangles in Figure 4).