

Biogeosciences Discuss., referee comment RC1
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Comment on bg-2022-19

Peter Herzprung (Referee)

Referee comment on "Organic matter transformations are disconnected between surface water and the hyporheic zone" by James C. Stegen et al., Biogeosciences Discuss., <https://doi.org/10.5194/bg-2022-19-RC1>, 2022

General comments

From an FTICR-MS formula data set of sediment and surface water samples biogeochemical transformations were derived and compared. Mass shifts in the mass spectra of the samples and a known list of metabolic relevant mass differences were used. The main outcome was that surface water DOM transformations are driven by upstream catchment processes and hyporheic zone transformations local to the sample volume.

DOM cycling is of biogeochemical importance. The data evaluation and the hypotheses made are plausible. The study is so far well structured and understandable. Recent and appropriate literature was used for discussion. This indicates that the present study is appropriate to Biogeosciences.

Detail comments

Lines 32 – 34: Why is it surprising that DOM transformation processes are different from

those in sediment or sediment pore-water? One can suggest that redox conditions and many other parameters are highly different as such nutrient (N, P) availability. In addition one can expect that processes must be different. In sediments and hyporheic zone adsorption / desorption processes (with participation of iron and other minerals) may play a role. In surface water photochemical transformations are possible whereas in sediment are of minor importance. In addition in surface water and sediment pore water different DOM species may be dominant driving other processes.

Lines 68 – 74: Here it is convincingly argued that photoproducts (which can be available) produced at the water surface can via hydrologic mixing enhance microbial turnover in the hyporheic zone.

Line 114: How many mL of filtrated supernatant sediment water extract were passed through which PPL cartridges (50 mg, 100 mg, 500 mg...)?

Line 117 – 123: Please provide at least the elements allowed to the mass calculator (how many N, S, P) and give basic information about formula assignment or cite software use, for example: Fu, Q. L.; Fujii, M.; Riedel, T., Development and comparison of formula assignment algorithms for ultrahigh-resolution mass spectra of natural organic matter. *Anal. Chim. Acta* 2020, 1125, 247-257.

Line 137 – 138: list of common biochemical transformations, the associated data package, please refer to Table S3 there. The readership should have the opportunity to immediately find it.

Please provide a list of all abbreviations used in Tables S1 – S5 (may be in an additional

table there)

Line 140: this is an interesting idea to regard mass shifts between components as transformation. From my viewpoint one can support the hypothesis that such transformation must have occurred. However there is no reference system to be sure at what time or at what place this transformation did occur. It might have occurred randomly in the past anywhere in the soil or catchment area.

In any case the limitations of the mass shifts assumptions as transformation should be discussed.

Line 150: the composition of transformations, is biotic and abiotic meant, and the list in Table S3? Is it possible to mark in an additional column which fragment is suggested biotic and which abiotic?

Question: Only the mass shifts were evaluated, not the mass peak intensities? Is this the reason why the intensities were not provided in Table S2?

Line 184 – 185: As a limitation of this statement, only the number of mass shifts was evaluated. There is no information if Y shifts came from leaching the sediment and X additional shifts came from further reactions in the pore-water. Biogeochemically active means this location where the sample was taken from, not the place from where the sample composition was generated and afterwards transported to the location under consideration.

Line 188 – 192: to mention this limitation, “not the rate of transformation”, is very important here. I applaud all the limitations mentioned here.

Line 197: the accumulation of transformations (larger diversity) is a convincing hypothesis.

Line 269 – 271: as abiotic transformations, adsorption / desorption should be taken into account besides redox reactions