Interactive comment on “Tracing biogeochemical processes and pollution sources with stable isotopes in river systems: Kamniška Bistrica, North Slovenia” by T. Kanduč et al.

Anonymous Referee #2

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General comments:

Knowledge of the major chemical constituents and stable isotope composition of river waters as well as the characteristic seasonal variations of these constituents remain an essential key component in our understanding of the global cycles of carbon and nutrients, and their changes through anthropogenic impacts. In the present work, Kanduč and colleagues studied biogeochemical processes in the Kamniska Bistrica River catchment and within the stream. They precisely identified the various contributions of the different sources of river-borne solutes and particles using the stable isotopes C-13, N-15, O-18, and deuterium. Thermodynamic computations were used to evaluate the chemical speciation within the carbonate system. This study, which represents a systematic hydrogeochemical study of an Alpine River, is an interesting and timely piece of work and I think this material should be published after taking on board the points raised below.

Specific comments:

Conclusions, Line 4: “The majority of Kamniska Bistrica system was supersaturated or near equilibrium (in the upper reaches of the river) with respect to calcite/dolomite in all sampling seasons.”

True supersaturation of the river water with respect to both calcite and aragonite (or dolomite) should result in spontaneous nucleation and widespread abiotic precipitation of CaCO3 in the river system which is obviously not the case. In the scientific literature, there was a strong consensus that dissolved and colloidal organic carbon of terrestrial origin is more or less recalcitrant and contributes little to the support of aquatic metabolism. Only recently, it has been shown very clearly by Battin et al. (Nature Geoscience 1 (2), 2008, pp. 95-100) that large-scale biodegradation of terrestrial organic carbon in rivers is responsible for CO2 oversaturation with respect to the atmospheric CO2 partial pressure. This net heterotrophy in fluvial ecosystems is the main cause for enhanced calcite, aragonite and dolomite solubility in the river waters and the transport of huge amounts of dissolved Ca2+ and Mg2+ to the oceans. The results presented here are in perfect accordance with the work by Battin et al. (2008) and this should be mentioned by the authors. Moreover, the authors should mention that the Kamnska Bistrica River is in most cases not "truly" oversaturated with respect to calcium carbonate since the CO2 concentrations in the water column are very high, up to 25 times over atmospheric values as has been shown by the authors of the present study. Due to these high dissolved CO2 concentrations, the reaction CO32- + CO2 = 2 HCO3- is shifted towards right and the necessary conditions for CaCO3 precipitation are not fulfilled due to the resulting extremely low CO32- concentrations.