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Biogeosciences Discussions

Interactive comment on "Daily CO_2 partial pressure and CO_2 outgassing in the upper Yangtze River basin: a case study of Longchuanjiang, China" *by* S. Y. Li et al.

Anonymous Referee #1

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This paper reports a pH/total alkalinity (TA) dataset during more than one year at one station in a small tributary of the Yangtze River. Sampling frequency is one day, which make the study promising for describing temporal patterns. In the context of Cole's plumbed carbon cycle, the interest of publishing pCO2 and CO2 degassing from freshwaters becomes higher and higher, as these data will fuel the databases necessary for a better integration of spatial and temporal heterogeneity at the global scale. However, unlike in the ocean, there is no consensual definition of the adequate methodology to measure or calculate pCO2 in freshwaters and, in the case of pCO2 calculated from pH and TA, many methodological problems and interferences with chemical species other than carbonates may lead to large errors in the calculated pCO2 (generally over-

estimates, see for instance Contribution of non-carbonate anions to total alkalinity and overestimation of pCO2 in New England and New Brunswick rivers C. W. Hunt, J. E. Salisbury, and D. Vandemark Biogeosciences, 8, 3069-3076, 2011). As pH and TA are easy and cheap to measure, the temptation of submitting calculated pCO2 is high. Here calculated pCO2 reaches 63 000 ppmv (pH 6.3 and TA > 3mmol.kg-1), a value never reached in other world rivers, and most importantly, a value never measured directly (e.g. by IR detection) in surface waters. Only groundwaters have such high pCO2 and 90% of this CO2 is lost in the few 100m downstream of spring emergence points (see for instance Johnson et al. 2008 GRL) So, when a "world record" in a river, like this value of 63 000 ppmv, is obtained, we must be sure of its validity and we must know on its biogeochemical origin before publication. What are the processes potentially driving such huge pCO2 (6 times higher than the highest value in the Amazon River)? In the Li et al. MS, methods are quite opaque and no satisfactory explanation on the origin of this CO2 is given. I suspect strong and unrepresentative pollution of these samples by sewage. Reference to literature is also incomplete, inadequate and superficial. English is poor.

Methodology – TA titration is made with very diluted HCl (0.0226 mol/L), so the volume of the sample where pH is measured increase a lot during the titration. Generally 0.1N HCl is used and this leads to an increase of less than 3% of the volume titrated. Here the increase in the volume will be 15%, so the pH is progressively measured in a mixture of sample and diluted acid. How do the author deal with that dilution? Do they make any pH correction? In addition is it a 2 points or a Gran titration? Vials are acid washed, did the authors take care to neutralize the vials walls before sampling otherwise it would affect the TA?

A standard method is briefly given for pH. However, when looking carefully at the data in Figure 3, In November, at the beginning of the exceptional pH falling (and pCO2 rising) event, pH decreases from $\sim$8.2 to 6.2 in ONE DAY. Then the day after it goes back to 8.1 and then the next day again to 6.3. What can create such huge and rapid

pH variation in a river? As the authors write P10650 -Chuxiong County, adjacent to the sampling location, greatly contributes to riverine solutes-, and as sampling was performed -0.5m below the surface water from the central part of the river-, I suspect low pH and high TA data are from a sewage plume (larger during flooding of the urban area) whereas high pH values are from outside of the plume. If true, the extremely high pCO2 values come from the sewage, and are not representative of riverine processes. Sewage load consistently occur after flooding. Sampling point is probably not appropriate, as the sewage and the river are not mixed. Sampling should have been done either upstream and would not account for sewage contribution, or well downstream, after mixing, and would account for sewage contribution. So all the interpretation of the data should be re-thought and the comparison with other large river as presented in the paper is inappropriate.

Others

P10651- –HCO3- is considered equaling to alkalinity (i.e. accounting for more than 99% of the total alkalinity) because of the pH values ranging from 6.31-8.51 in the Longchuajiang (Yao et al. 2007)– If pH, alkalinity and T are known, all DIC species can be calculated. There is no need for such approximation. It would more correct to calculate the pCO2 by solving the entire carbonate system. At high pH, carbonate ions account for much more than 1% of DIC, and may contribute up to 10% of alkalinity.

pCO2 versus pH correlation (Figure 6 and section 4.3) is a truism, as one is calculated from the other as in equation 8. When considering pCO2 drivers, pH is not an “environmental” variable, but rather a “thermodynamic” variable. Environmental variables would be watershed occupation, hydrology, organic matter or nutrient levels, and in the case here, sewage load, but not pH, as pH is controlled by the CO2 itself (carbonic acid). None of these ancillary variables are discussed in the paper. It would be important to know on the behaviour of Ca2+, DOC, POC particularly during the flooding and low pH. For sure a careful analysis of these parameters would demonstrate the predominance of sewage water when pCO2 is high.

Interactive comment on Biogeosciences Discuss., 8, 10645, 2011.