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Interactive comment on "Factors governing the pH in a heterotrophic, turbid, tidal estuary" *by* A. F. Hofmann et al.

Anonymous Referee #3

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This is a generally well written paper that uses a modeling approach to analyses factors influencing pH variations, primarily of the inter-annual variation in the Scheldt estuary. They find that "nitrification is the main process governing the pH profile of this estuary, while CO_2 degassing and advective-dispersive transport 'buffer' the effect of nitrification". They also suggest that "CO_2 degassing accounts for the largest proton turnover per year in the whole estuary". The authors argue that are the first to quantify the influences of kinetic processes on the pH for an entire estuarine ecosystem like the Scheldt estuary. Such a conclusion is not entirely new. For example, based on field observations, Frankignoulle (1996) stated that "in the highly polluted Scheldt estuary, both respiration of organic matter and nitrification acidify the system, but the release of CO_2 to the atmosphere strongly reduces the decrease of pH". In addition, Abril

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and Frankignoulle (2001) have shown, semi-quantitatively that nitrogen transformation strongly influence the acid-base properties of the Scheldt basin water. However, I judged that the present study is novel by applying time variable acid-base dissociation constants, and I also welcome the quantitative way to elucidate the factors that modulate pH, which is indeed the way that biogeochemistry should go towards. Having said so, I still have major concerns of this study. The authors primarily used yearly averages to validate and analyze their model outputs. I am not that familiar with the system of Scheldt estuary, but wonder how dynamic the system is. I bet that like every estuary, the Scheldt should be subject to high variability in time (e.g., seasonal and diurnal) and space. If this is the case, then I would argue how meaningful the pH-distance plot presented in Fig 3 (the only validation this study presents) is? This concern also holds when looking at the shorter time scale. If the seasonal variation is substantial, how would the authors resolve for the inter-annual time scale? I did not check back the previous modeling efforts by the authors in 2008a and b, but the present study should be self-completed. This means that I would like to see the authors perform similar validation and model analysis at least at the seasonal time scale in order to convince the readers that their modeling approach is in order and their quantitative analysis of individual process stands.

Specific comments: 1) Clearly state in the title that this study is a modeling work and in the Scheldt estuary. 2) Is it significant to use different pH scales in the Schedlt estuary, and how it differs along the salinity spectrum? I noticed the current study uses NBS, as Fig. 3 the only validation of this study. 3) Two major much relevant studies by Frankignoulle (1996) and Abril and Frankignoulle (2001) should be cited and fully discussed, and state upfront the novelty of this study as compared to the previous modeling work by the authors.

References:

Abril, G., Frankignoulle, M., 2001. Nitrogen-alkalinity interactions in the highly polluted Scheldt Basin (Belgium). Wat. Res. 35, 844-850.

Frankignoulle, M., 1996. Atmospheric CO_2 fluxes in a highly polluted estuary (the Scheldt). Limnol. Oceanogr. 41, 365-369.

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