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Interactive comment on “Controls on pH in surface waters of northwestern European shelf seas” by V. M. C. Rérolle et al.

Anonymous Referee #2

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Controls on pH in surface waters of northwestern European shelf seas

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Anonymous referee #

General comments

Biogeochemical processes in the surface of ocean shelf waters are complex and many of them have influence on sea water pH. In this work the authors analyze underway data collected by state of the art instruments during a summer cruise which lasted 33 days. The parameters measured were pH, CT, AT, pCO₂, T, S and Chl. Measurements were recorded every 6 minutes. The instruments have thus provided much data. The

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goal here is to investigate which processes control the sea water pH and to evaluate their relative importance for explaining the observed pH variance.

In the introduction section of the paper a discussion is provided on the inorganic parameters which come into the carbonate system equilibria and influence the pH. Namely, temperature, salinity (discharges of river water), CT and AT. However, there is no assessment of the relative importance of these parameters in relation to their ranges in the data to be analyzed. Speculations are abundant on the complexities that might arise from processes such as primary production and input of river water nutrients.

The voluminous data provide opportunities, but in the opinion of this reviewer, analysis of it demands a strategy carefully based on the controls of the sea water carbonate system and on an understanding of regional and seasonal processes.

The general state of the waters investigated in relation to seasonal variability is not described. The summary data on nutrients and chlorophyll presented in Table 1 do, however, tell a lot about it.

The approach taken here is to use statistics, stepwise multi-linear regression to relate pH variations to environmental parameters. Prior to the statistical analyses all data are log-transformed. This means e.g. that the hydrogen ion concentration is twice log-transformed.

Without much reasoning, the data are divided into 11 regions based on geography and water masses. Is there any real oceanographic ground for introducing 11 water masses? Why is there not attempted a wholistic view of the study area?

The overview of the mean properties observed in the 11 regions and listed in Table 1 clearly shows that apart from region 9, the standard deviations of both mean temperatures and mean salinities in each region are quite small. This means that the temperature and salinity ranges are small in each region. Looking secondly on T and S in all 11 regions, the overall variability observed with respect to possible influences

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on pH lies in essence in the temperature data, again with region 9 excepted.

Table 2 lists the statistical evaluation results of the influences salinity, temperature and chlorophyll have on the pH, by region. The lower part of the table reveals that the equation coefficients for temperature and salinity are for some regions +ive and in other cases –ive. Is this consistent with carbonate chemistry? No! How can this help us understand carbonate chemistry and pH variations? The explanations offered in lines 20-25 on page 956 do not hold for this data. The Eppley, 1972, paper referred to is on maximum expected specific growth rates of phytoplankton in the temperature range 2-40°C. The within regions temperature ranges are very narrow in this study.

The futility of using only statistics to unravel the main processes controlling the carbonate chemistry dynamics is clear from Tables 2 and 3. For Region 1 in Table 2, temperature explains 45.62% of the pH variance, chlorophyll 48.47%. In Table 3, the temperature effect in Region 1 has vanished and the pH variance is explained by chlorophyll and silicate, two correlated parameters!

The statistics by region approach is abandoned for two regions, numbers 4 and 11, where mixing was active. The influences of mixing are in general poorly and only qualitatively described. The reader would ask about the concentrations of the main end-members that mix, deep upwelling water, oceanic water masses and the river fresh water. Low alkalinity and high DOC of the fresh water is suggested in the text but no concentrations are mentioned nor concentration variability.

This reviewer cannot recommend publication of this manuscript. The reasons are strong doubts about the methods used for data evaluation and interpretation. Also, the results presented have a pronounced qualitative character and a wholistic view as missing. The results do not add much to earlier studies.

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