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Interactive comment on "Continuous fluorescence-based monitoring of seawater pH in a temperate estuary" *by* John W. Runcie et al.

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Although I was interested to see the application of the Presens pH-sensitive spots to looking at seawater pH variability, I am not comfortable recommending this manuscript for publication in its present form.

The title, and the abstract, indicate that this paper is to be considered as an assessment of using this technique to monitor estuarine pH, and hence (when used in conjunction with salinity information) to provide information about the time-dependent variation of the seawater CO2 properties, and in particular the aragonite and calcite saturation states.

The authors however fail to make clear the likely overall uncertainty of their measure-

ments, a key parameter when assessing a measurement technique. Also, the data provided do not really cover a sufficient range of salinity to plausibly assess likely behavior in an estuary.

The calibration of the Presens sensor for use in seawater media seems odd, and is insufficiently described. In principle, a calibration curve was prepared documenting the instrument response as a function of the pH of a series of buffer solutions: phosphate buffers in a NaCl background (I = 0.7 M) . The pH values for the various buffer solutions -at a temperature of $\sim$22 °C - were themselves measured directly using a pH cell that had itself been calibrated against low ionic strength buffers ($\sim$0.1 M I suspect). The authors note that validation samples were collected and their pH measured spectrophotometrically (using m-cresol purple - though not purified), but the paper does not really show the direct comparison but simply comments that a "drift" in the fluorescence-based pH sensor was thus corrected for.

There is, I feel, so much wrong with this approach. First, it is not at all clear what really is being measured as pH (and this will cause a mismatch with the equilibrium constants used when the various saturation states are calculated), second I would have imagined that the response of the sensor dot would depend (at least to some extent) on temperature and salinity - this is not even mentioned.

Furthermore, the simple calibration of the conductivity sensor with a pure NaCl solution will likely affect the accuracy of estimated salinity values, and ultimately the accuracy of alkalinity values estimated from these.

Other notes (linked to line numbers)

103,4 The text refers to a commercial dye (Acros, and to the calibration for a purified dye. I would note that Acros was one of the worst commercial dyes, and that a recent paper in Marine Chemistry by Douglas & Byrne, suggests how to convert the behavior of the impure dye to approximate that of a pure dye.

123 It is stated that the conductivity probe was calibrated with a sodium chloride solution of known concentration. Surely one also needs a value for its conductivity, and a process for inferring seawater salinity from conductivity (rather than conductivity ratio - as implied by the definition of Practical Salinity).

133 Why "pCO2" here? It is not a measurement, nor is it discussed anywhere as a calculated value

133 The citation to "Dickson and Millero (1987) does not make clear which constants were chosen. The usual ones are those of Mehrbach, converted to the total hydrogen ion concentration pH scale, but a more explicit statement would be appropriate

136 The "precision" of the pH value is given as 0.022 - assuming this is some form of standard deviation, it is not clear how it was computed.

149 "psu" is not an appropriate unit abbreviation. The Practical Salinity Scale has the unit "1" I note in Figs. 4 and 5 that salinity is apparently in "ppt" - this may be a closer reflection of the calibration approach

155 two not "three" parameters?

156 The comment is made that the saturation state of aragonite has less "variability" than that of calcite. This is a necessary consequence of the definitions of saturation state whereby the ion product [Ca][CO3] is multiplied by 1/Ksp, and as the Ksp is different for aragonite and for calcite, so too is the multiplier with that for calcite being the larger.

182 The comment is made that temperature and salinity play an important role in seawater chemistry. This is, in part, because the various equilibrium constants are themselves function of T & S. But also, here alkalinity (the 2nd CO2 parameter required for calculations) is itself a function of salinity. - the m/s does not make this clear.

Figures I was surprised to see that the night/day cycle is identical in both April and December The time axis on the figures is hard to read (and needlessly varies from one

frame to another