Response to referee (A. Dickson)

>The authors thank Professor Dickson for his comments. Please note responses are indented and follow the referee's comment.

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 measurements, 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 behaviour in an estuary.

>The intent of the work was to determine the utility of the Presens sensor for use in shallow inshore marine systems to detect variability in seawater carbonate chemistry over timescales of minutes to hours. While accuracy was an important factor, our intention, with proof-of-concept data, was to demonstrate that this technique is capable of showing clear patterns of variability.

>To avoid confusion, we propose changing the title to:
>"Continuous fluorescence-based monitoring of seawater pH *in situ*." This excludes the word estuary and will hopefully avoid any implication that the research is generally applicable to estuaries. While the study location can be said to be in the estuary, in reality it is close to the ocean and is primarily influenced by the ocean.

>The abstract is also modified to now include an estimate of uncertainty.
>Line 13: "…background variability. While the stated phase angle resolution of the lifetimes fluorometer translated into pH units was +/- 0.0028 pH units, the precision of calculated pH was +/- 0.022, indicating error associated with calibrating the device against known reference samples. Diel variability…"

>Further:
>Line 45: "…in the setting of an ocean-water dominated estuarine environment."
>Line 52: "… in surface waters. The study focussed on natural fluctuations in seawater pH and the capability of the fluorescence technique to address these fluctuations. Determining the accuracy of pH values obtaining from the fluorescence device was not an objective, as correct determinations would require considerable resources that were not available at the time of study."

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 _22 _C - were themselves measured directly using a pH cell that had itself been calibrated against low ionic strength buffers (_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.

> We now show a direct comparison of data obtained using the spectrophotometric technique and the fluorometric technique as indicated by the data points in Figures 4 and 5.

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),

> Our initial measurement of pH was conducted using the potentiometric technique, where we calibrated the glass electrode using standard buffers to ensure the electrode provided a reasonable estimate of pH, notwithstanding any effect of increased salinity on subsequent measurements. The phosphate buffers then enabled us to characterise the relationship across a range of pH values (with salinities similar to seawater) and various values of fluorescence lifetime. From this relationship we could then interpolate and use the fluorescence lifetime to indicate the "pH". However, only when the fluorescence sensor was directly compared with the spectrophotometric measurements of a collected sample were we able to apply corrections to the fluorescence-derived values for pH, and refer to them as "pH_T" in line with the spectrophotometric pH_T values.

> We also discuss the use of constants when calculating the seawater saturation state

 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.

> This will be mentioned in the introduction.
> L 44 "…changes in fluorescence intensity. As the fluorophores used in this study are sensitive to changes in temperature and salinity, careful measurement of these parameters remains essential.".

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.

> We agree that the use of NaCl to calibrate the salinity sensor is not ideal. However the aim of the exercise was to demonstrate the ability of the fluorescence-based technique to show diel variability in seawater carbonate chemistry.

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 behaviour of the impure dye to approximate that of a pure dye.

> In the introduction we now make it clear that our rationale was to demonstrate that the fluorescence method that can show natural variability of pH within an estuary over time scales of minutes to hours rather than provide highly accurate pH data.

> Line 52: "… in surface waters. The study has focussed on natural fluctuations in seawater pH and the capability of the fluorescence technique to address these fluctuations. Determining the accuracy of pH values obtained from the fluorescence device to the third decimal place was not an objective.

> While we did not correct for dye impurities - we agree that these new papers are important to cite.

> Line 104: "and calculations from Liu et al. (2011). No attempt was made to correct for dye impurities (Douglas and Byrne 2017a) nor variable salinity and temperature (Douglas and Byrne 2017b), where uncertainty attributable to these combined factors is within approximately ± 0.004 (Douglas and Byrne 2017b)."

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).

> A value for salinity in psu was sufficient to calculate seawater carbonate chemistry, and no attempt was made to infer conductivity from the sensor.

> Line 123: The sensor was calibrated directly against a pure NaCl solution across a range of concentrations (0 to 40 ppt) at temperatures similar to that expected of seawater at the sampling location (23°C).

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

> Alll reference to pCO2 has been removed from the text.

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

> Line 132: "Corrections were made to the raw data if required, and final pH, pCO2, temperature and alkalinity values were used (with equilibrium constants from

Mehrbach et al., 1973 refit by Dickson and Millero, 1987) to calculate Ω_{Ca} and Ω_{Ar} in CO2Sys (V2.1)."

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.

Suitable text describing the method for determining the precision of measurements has been added to the methods section:

Line 108: An additional series of continuous measurements were made in a static constant-temperature 20 L seawater system over an approximately three-hour period to determine the variability in measured pH. The resolution attributable to the lifetimes decay fluorometer (as stated by the manufacturer) can be matched with corresponding values of pH to provide resolution of pH measurement at the instrument level.

Line 136: "The precision of calculated pH_T (defined as the standard deviation of three hours of consecutive measurements of a static seawater solution) was ± 0.022 pH units. The phase angle resolution of the lifetimes fluorometer was stated by the manufacturer as 0.05 degrees, and this translated to an instrument resolution of 0.0028 pH units.

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

Line 149: "and ranged from 33.0 to 34.3 ppt…"

155 two not "three" parameters?

Line 155: "smoothed approximation of diel variation in these two parameters (Fig. 6).

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.

Thankyou for your insight
Line 156 "As a consequence of the definitions of saturation state, and form-specific values of K_{sp} for aragonite and calcite, Ω_{ara} was slightly less variable than Ω_{cal} (with values between 2.5 and 3.1, or 3.8 to 5.4 units respectively, Fig. 6).

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.

> Line 182: "These data show the important role that temperature and salinity play in determining seawater carbonate chemistry (Millero 1995). Further, as the saturation state in this study is in part derived from alkalinity which is in turn derived from salinity and temperature, the importance of obtaining accurate measurements of temperature and salinity is to be emphasised.

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

> Good spotting - we corrected this error in Figures 4 to 7 and the time axis is larger and now uniform across all figures.

> Additional references to add (Douglas and Byrne 2017a, and 2017b, Dickson 2010 [in Guide to best practises… edited by Riebesell et al])

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