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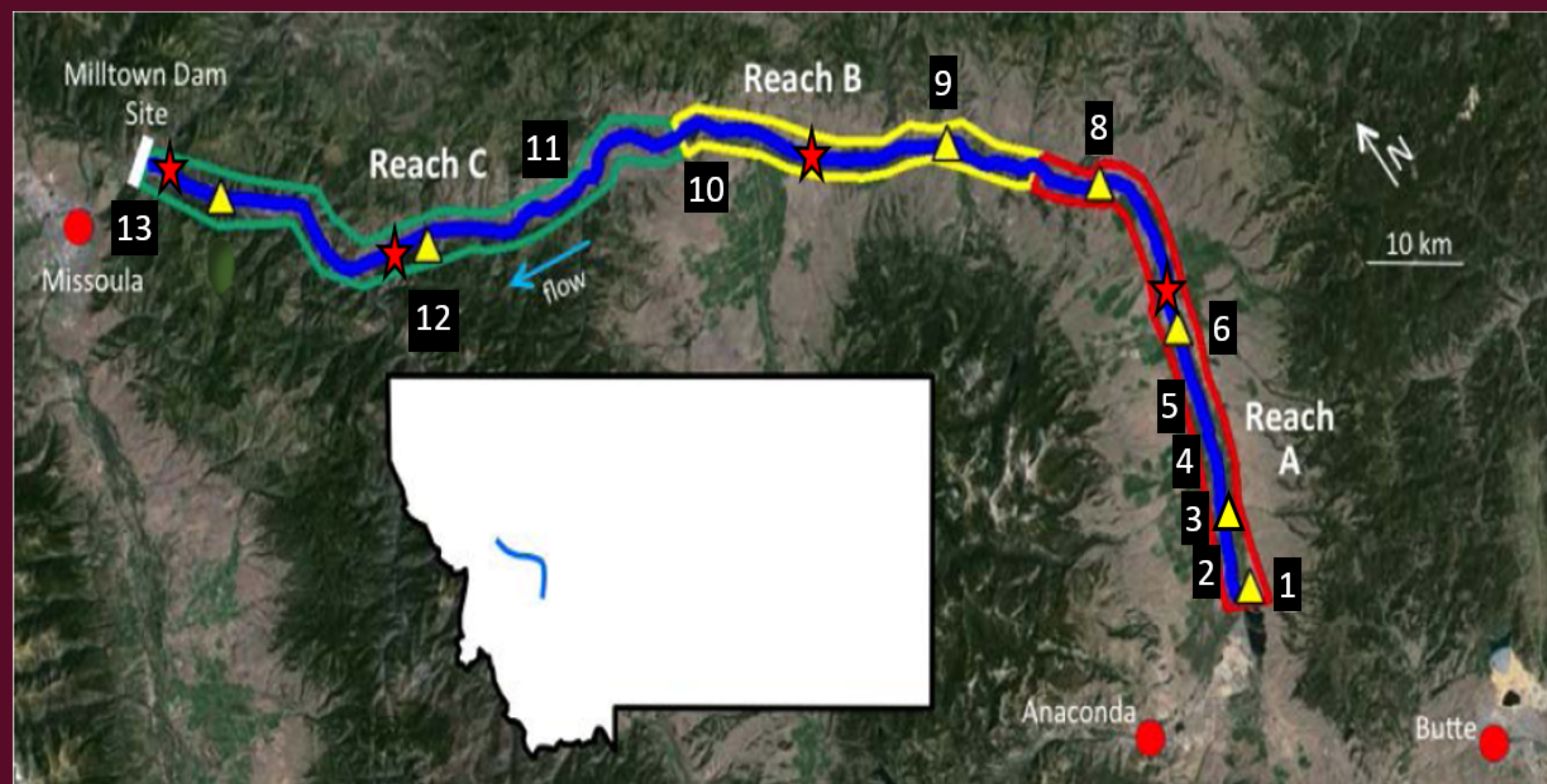
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# Comparison of Electrochemical and Spectrophotometric pH for Freshwater Analysis

Samantha C. King, Fischer L. Young and Michael D. DeGrandpre

## ABSTRACT

Electrochemical and spectrophotometric pH of the upper Clark Fork River were studied to assess the data quality of both methods. There have been very few comparisons between spectrophotometric pH and electrochemical pH. This comparison is important because pH electrodes remain the primary method for measuring freshwater pH but the data quality is always questionable. Using the spectrophotometric method for measuring pH could potentially improve pH data quality significantly. This is because spectrophotometric pH relies on absorbance measurements that are very reproducible whereas glass electrode measurements have various sources of inaccuracy that are difficult to quantify. Water samples were collected from August 30, 2017 to January 17, 2020 along the Clark Fork River near Anaconda down to Missoula. A total of 326 electrochemical and spectrophotometric samples have been analyzed. Our preliminary analysis shows that the electrochemical pH is higher than the spectrophotometric pH and that the spectrophotometric method is more precise. The standard deviation for the electrochemical method is  $\pm 0.18$  pH units and the standard deviation for the spectrophotometric method is  $\pm 0.11$  pH units. The next step in this study is to devise experiments to determine the sources of these offsets.



**Figure 1.** An aerial map of the UCFR with sampling locations outlined. Sampling sites begin at Warm Springs, MT and end at Missoula, MT. Red stars indicate major tributaries (Right to left: LBR, FC, RC, and BF) along the UCFR. Yellow triangles represent USGS gauge stations and black boxes with white numbers indicate sampling sites. This image was taken and modified from the NSF funded LTREB project focused on the UCFR (H.M. Valett, PI).

## METHODS

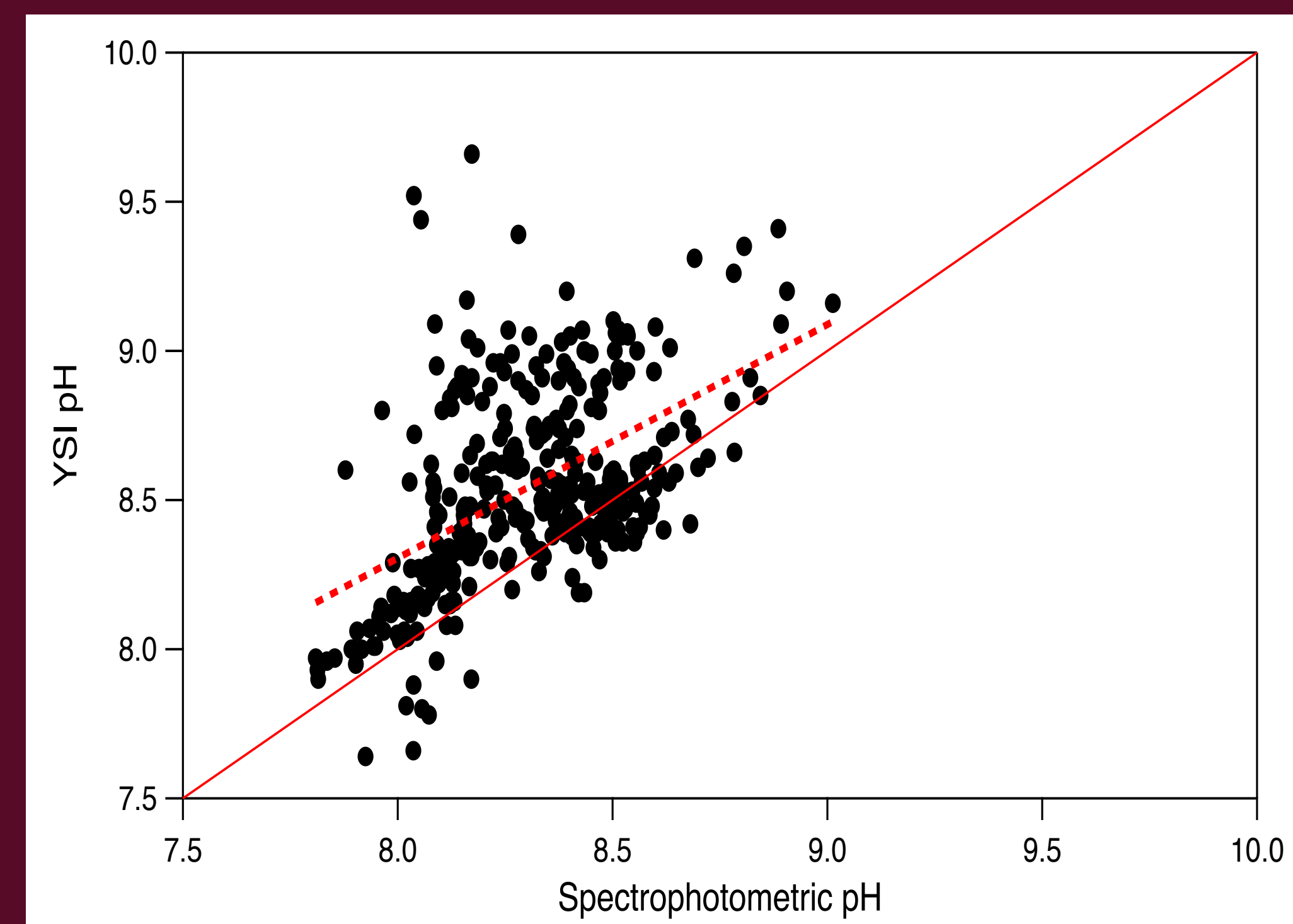
**Electrochemical:** Measurements were taken in the field at each sampling sight using a pH electrode (YSI 2030 multi-meter). Temperature was also measured using a temperature probe.

**Spectrophotometric:** Samples were brought back to the lab and measurements were carried out on a benchtop spectrophotometer (Cary 300, Varian) with a 10 cm path length, capped, glass cuvette. The solution temperature was controlled by a water-jacketed cell holder and the actual temperature of the solution was measured via a high accuracy temperature probe (Eutechnics, 15-060-381, Fischer Scientific).

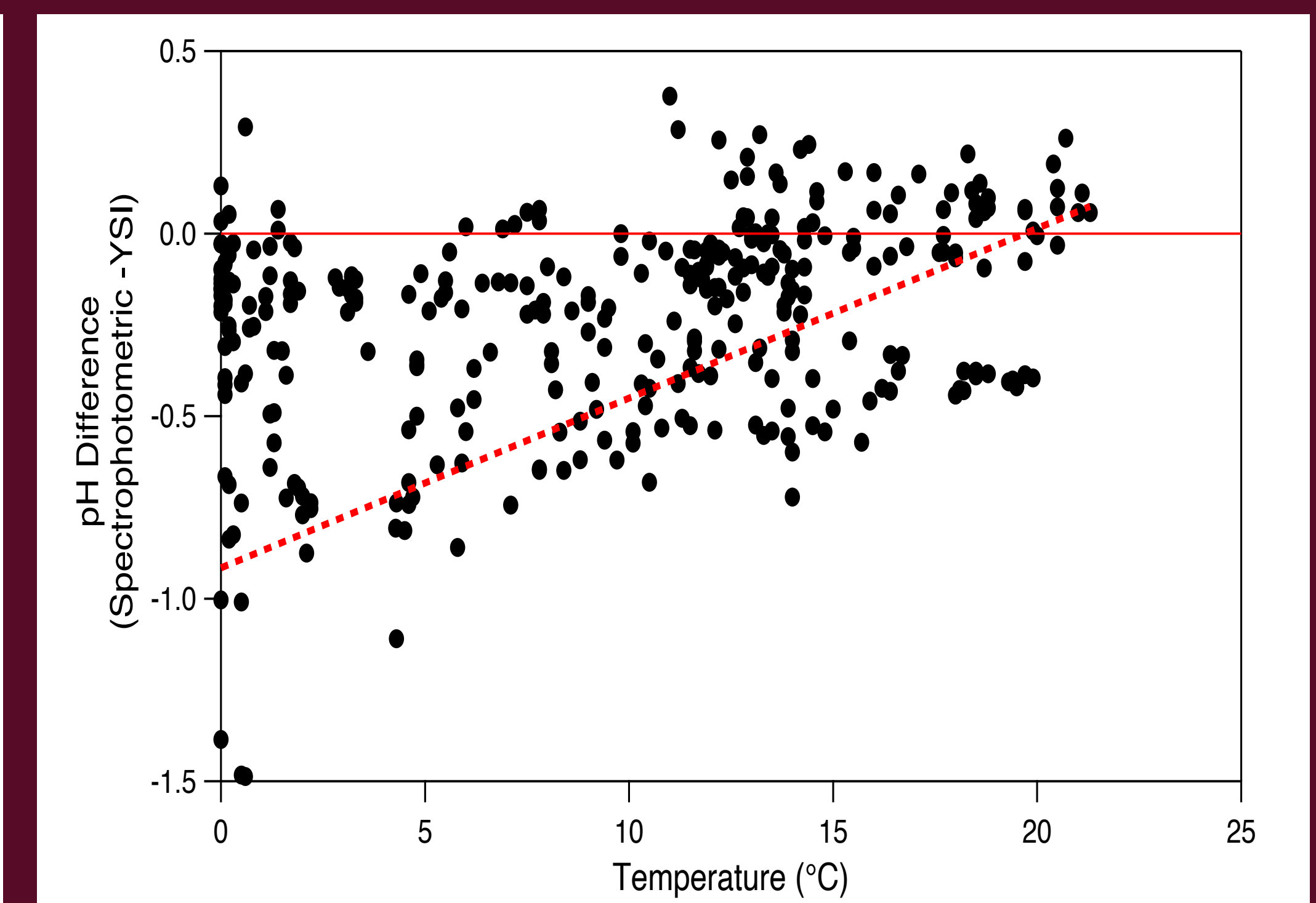
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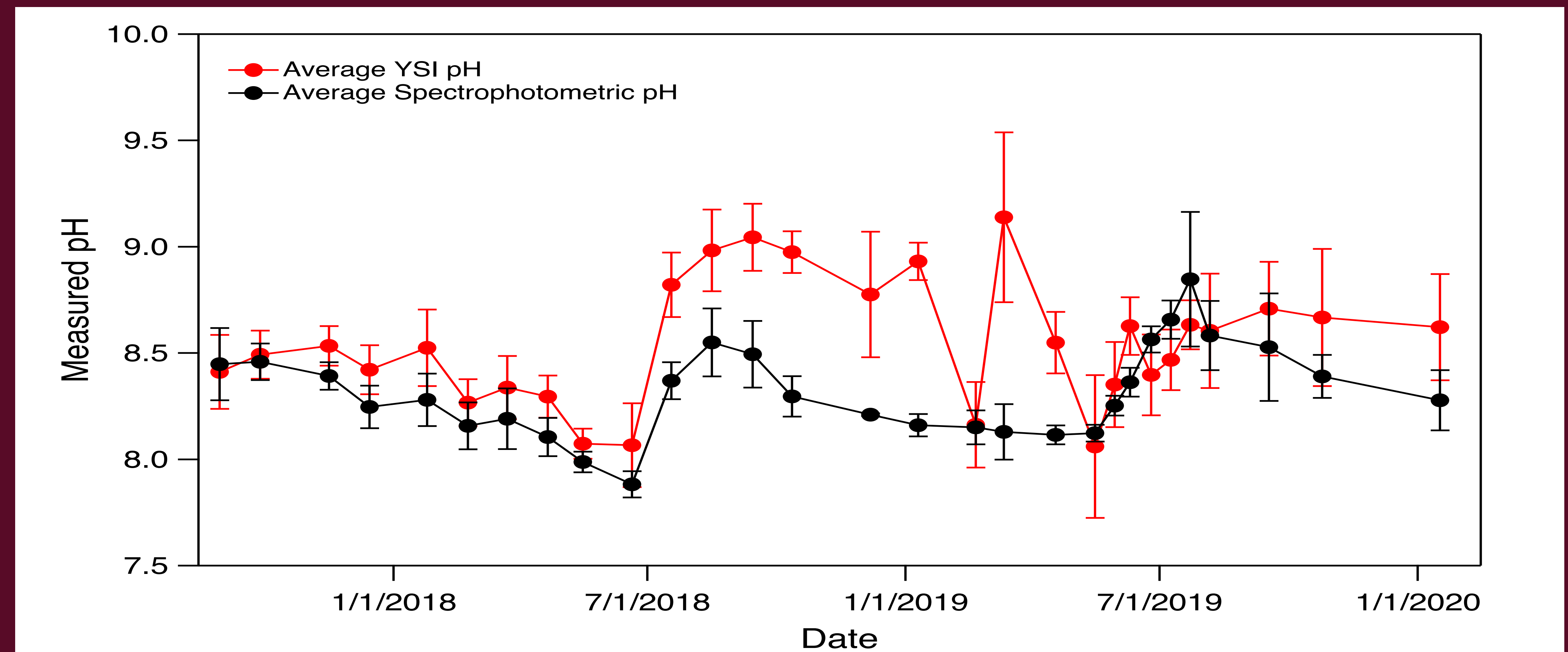
## RESULTS



**Figure 2.** The relationship between spectrophotometric pH and electrochemical pH. The 1:1 line (solid) and the line of best fit (dashed) are used to display the disparity between the two methods of measuring pH.



**Figure 3.** The difference (spectrophotometric minus YSI) between pH methods against measurement temperature. The line of best fit (black) helps to show the decrease in the pH difference with increasing temperature.



**Figure 4.** The average of the two pH methods over time. The red line represents electrochemical pH measurements and the red line represents spectrophotometric pH measurements. The error bars illustrate the variation among the 13 sampling locations during a given month.

## DISCUSSION

According to Figure 2 and Figure 4, the electrochemical method recorded a higher pH value than the spectrophotometric method for the same samples. Most of the data falls above the 1:1 line which shows the disparity in values between the two methods. Additionally, Figure 3 reveals that there is a larger range in differences at cooler temperatures than at warmer temperatures. This suggests variance and inaccuracies in the electrochemical method due to temperature since all spectrophotometric measurements are measured at the same temperature. YSI pH measurements are common measurements for field applications. However, this study highlights that this method may not always produce the highest quality pH measurement. This may be of interest for studies that use pH measurements for further calculations (i.e., calculating the partial pressure of  $\text{CO}_2$ ) to ensure that their calculations are as accurate and precise as possible (Abril et al. 2015; Butman and Raymond, 2011; and Hunt et al. 2011).

## Acknowledgements

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