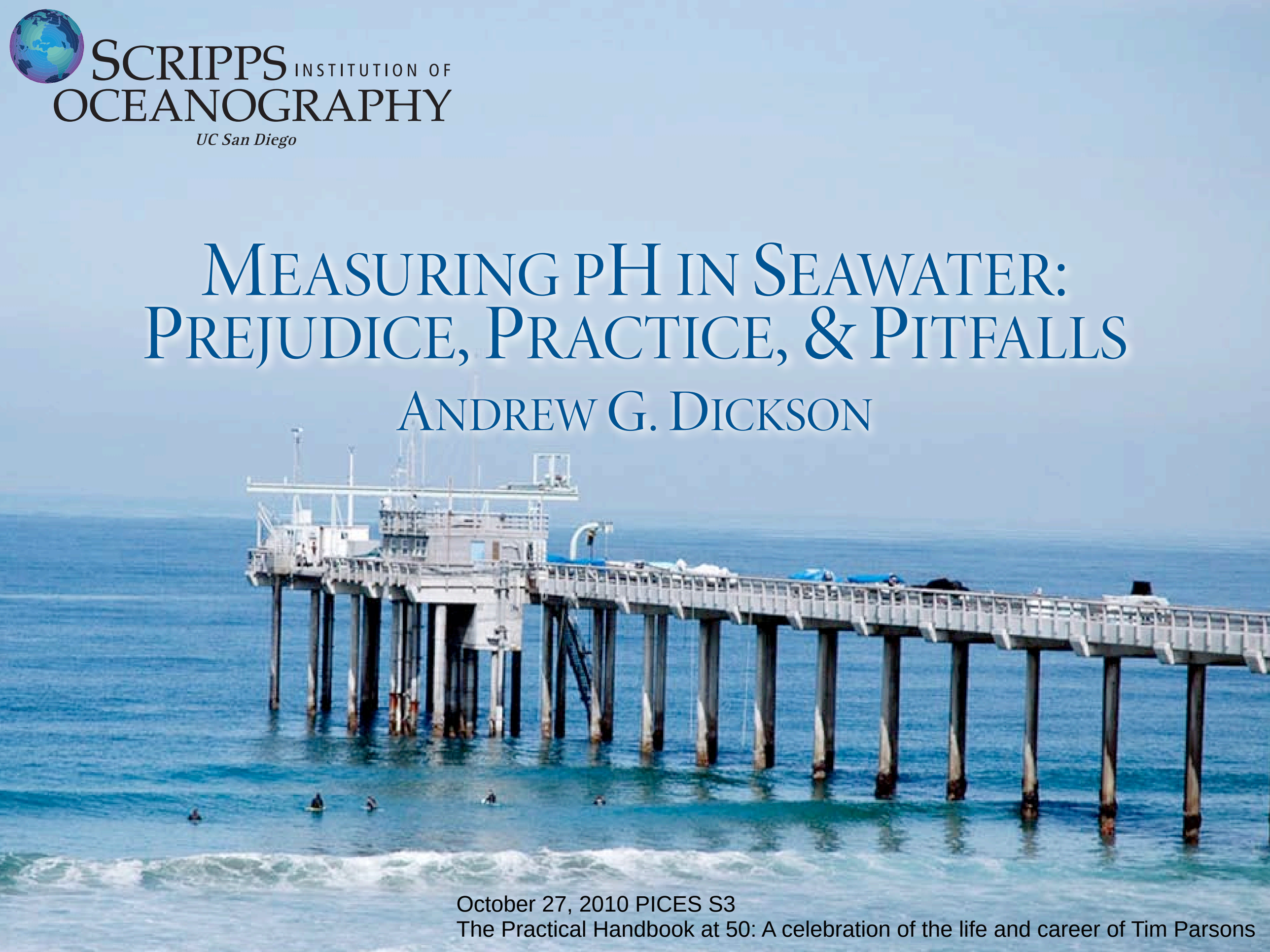
SCRIPPS INSTITUTION OF OCEANOGRAPHY
UC San Diego

Measuring pH in Seawater: Prejudice, Practice, & Pitfalls

Andrew G. Dickson



October 27, 2010 PICES S3
The Practical Handbook at 50: A celebration of the life and career of Tim Parsons

Carlsberg®

2009

100th Anniversary of the Development of the pH scale at the Carlsberg Laboratory, Copenhagen

50 years ago

A manual of sea water analysis (with special reference to the more common micronutrients and to particulate organic material)

J. D H. Strickland & T. R. Parsons

Bulletin (Fisheries Research Board of Canada), No. 125

So what do we mean by pH?

The **hydrogen ion concentration** of seawater is conventionally reported as a pH:

$$\mathrm{pH} = -\lg\left\{\frac{[\mathrm{H}^+]}{\mathrm{mol\ kg}^{-1}}\right\}$$

For seawater the hydrogen ion concentration in common use today is the so-called "total hydrogen ion concentration."

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decadic or Briggsian logarithm

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1. A potentiometric technique using an electrode sensitive to hydrogen ion in a “pH cell”;
2. A colorimetric technique in which an indicator dye is added to the solution and the pH inferred from the resulting absorbance spectrum.

pH measurement using a pH cell

Measuring hydrogen ion concentration using a pH cell

$$\text{reference electrode} \;\Big|\; \text{KCl solution } (c \geq 1\ \text{mol dm}^{-3}) \;\Big\|\; \text{test solution} \;\Big|\; \text{electrode reversible to } H^+(\text{aq})$$

$$\text{pH(X)} = \text{pH(S)} - \frac{E_\text{X} - E_\text{S}}{RT \ln 10 \,/\, F}$$

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This requires that measurements on the standard and on the sample are made at the same temperature (T)

The Nernst equation underlies this operational definition of pH:

$$E = E^{*}(S, T, p) - \left(\frac{RT\ln 10}{F}\right)\lg\left(\frac{[\mathrm{H}^{+}]}{\mathrm{mol\ kg}^{-1}}\right)$$

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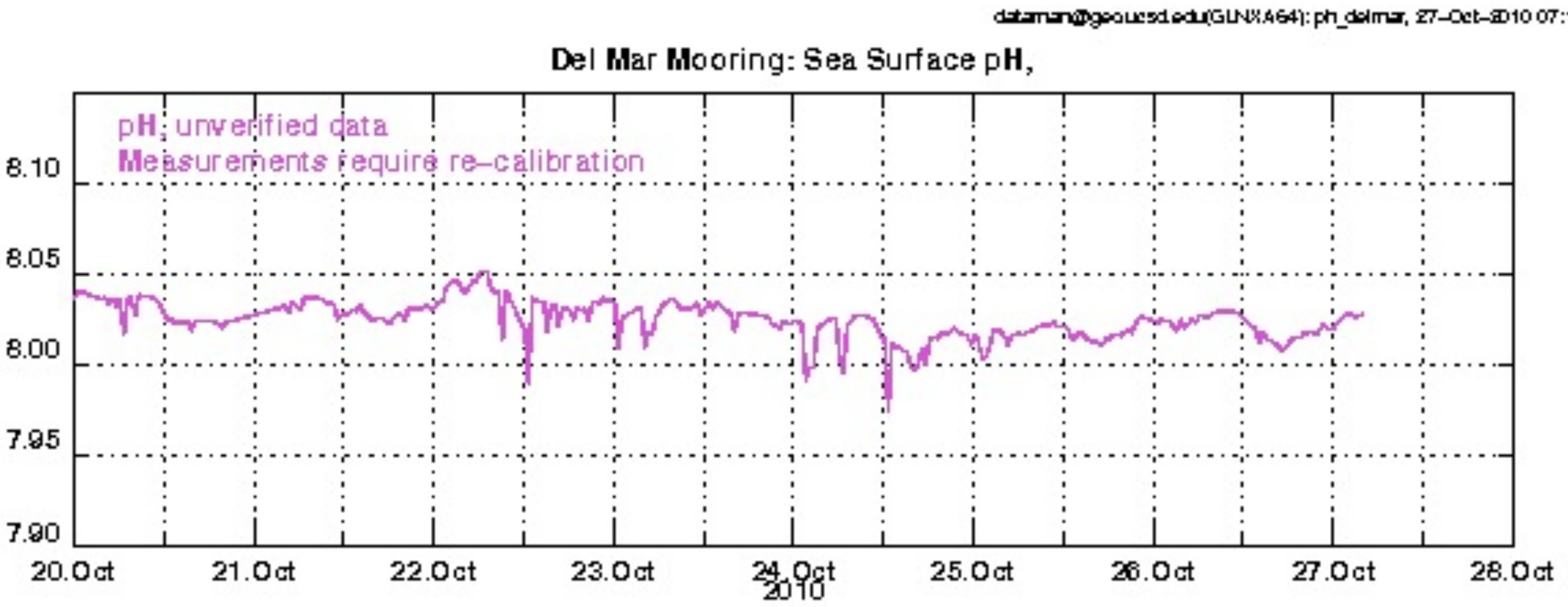
IT ISN'T!

Near real-time pH data from a mooring off Del Mar, CA Using Honeywell DuraFET® (Todd Martz)



http://mooring.ucsd.edu/

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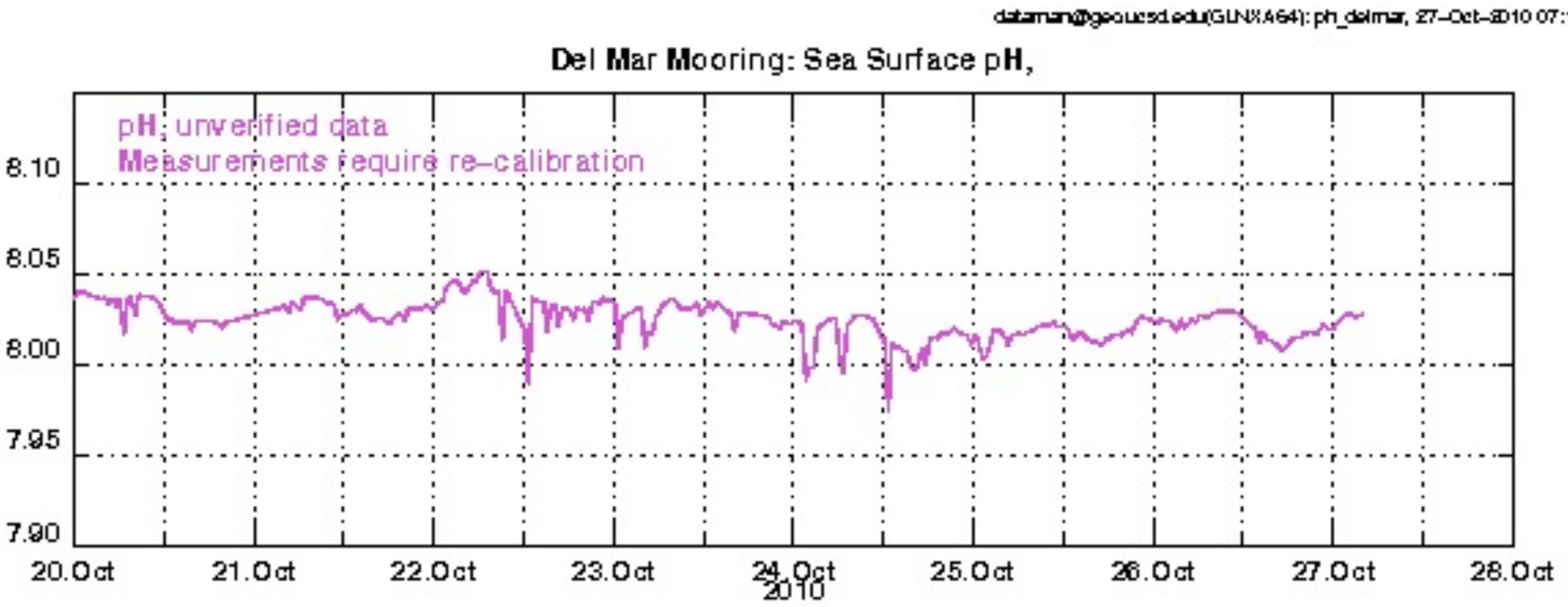

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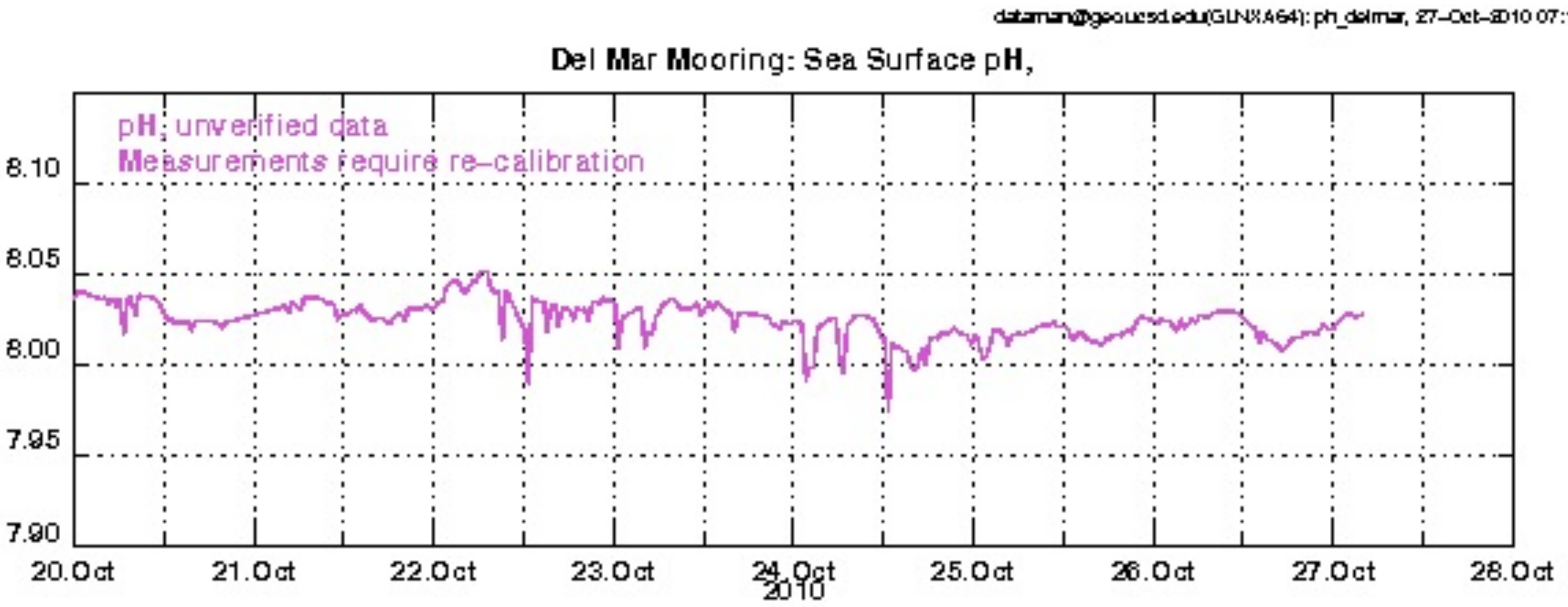

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Uncertain accuracy (0.01 – 0.02 in pH ?)

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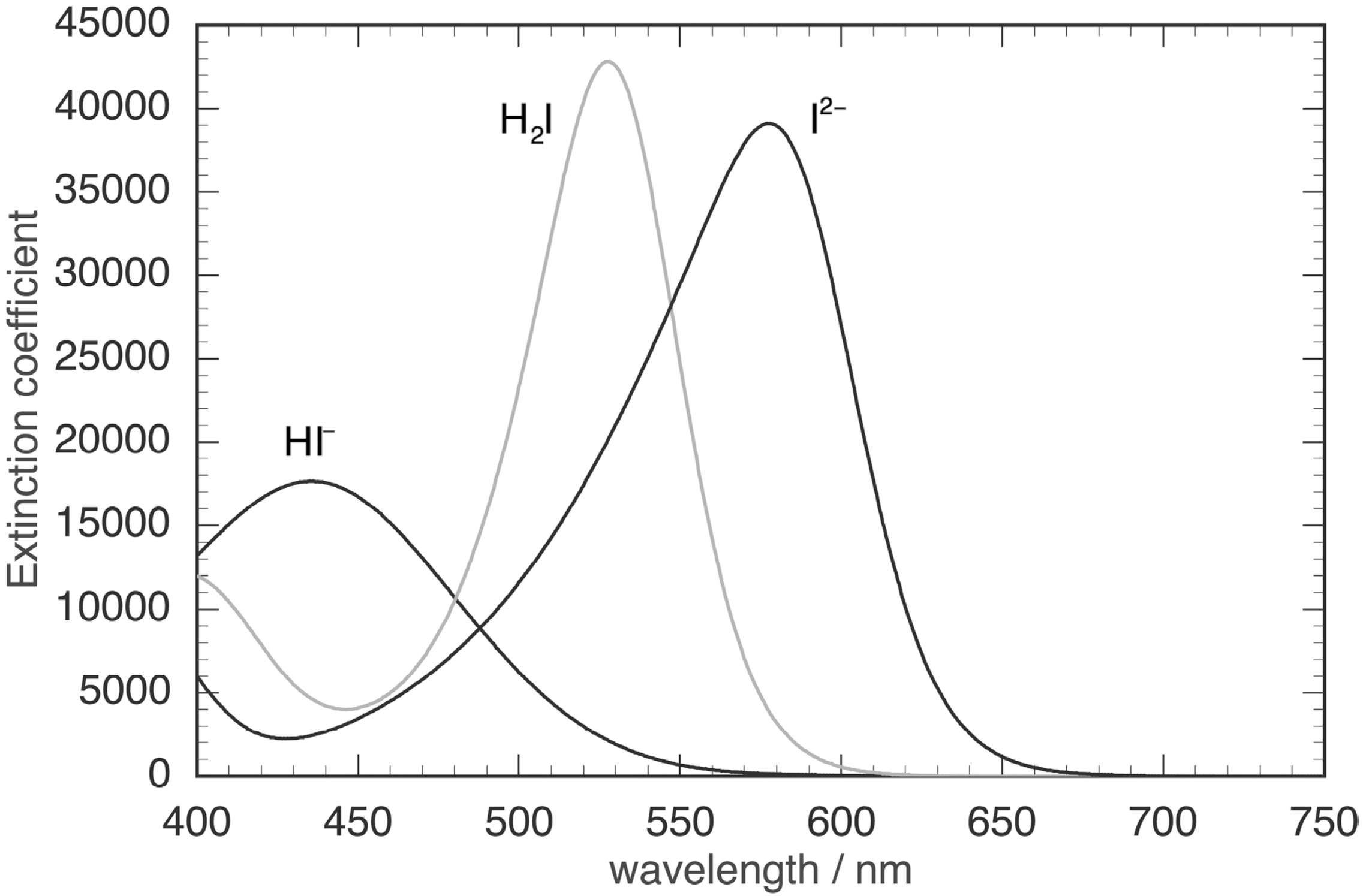
Colorimetric pH measurement

Extinction coefficients of *m*-cresol purple in 0.7 M NaCl



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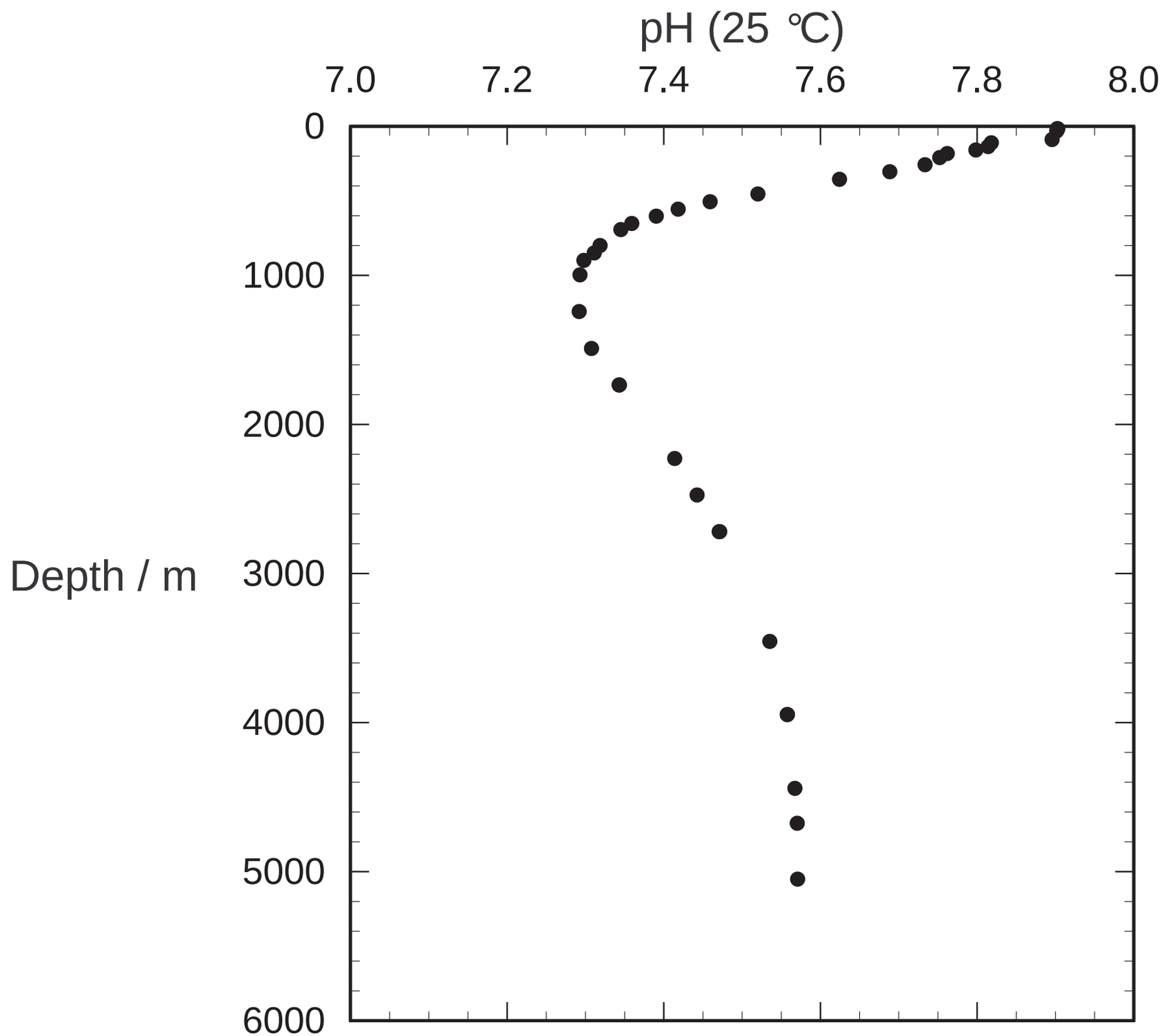
Need accurate calibration of dye properties
(and pure dye!)

Vertical profile of pH obtained spectrophotometrically using the indicator *m*-cresol purple (calibrated against "tris" buffers). From a NOAA cruise in 1991 at 41°59.6'N, 151°59.1'W (data provided by Tonya Clayton).



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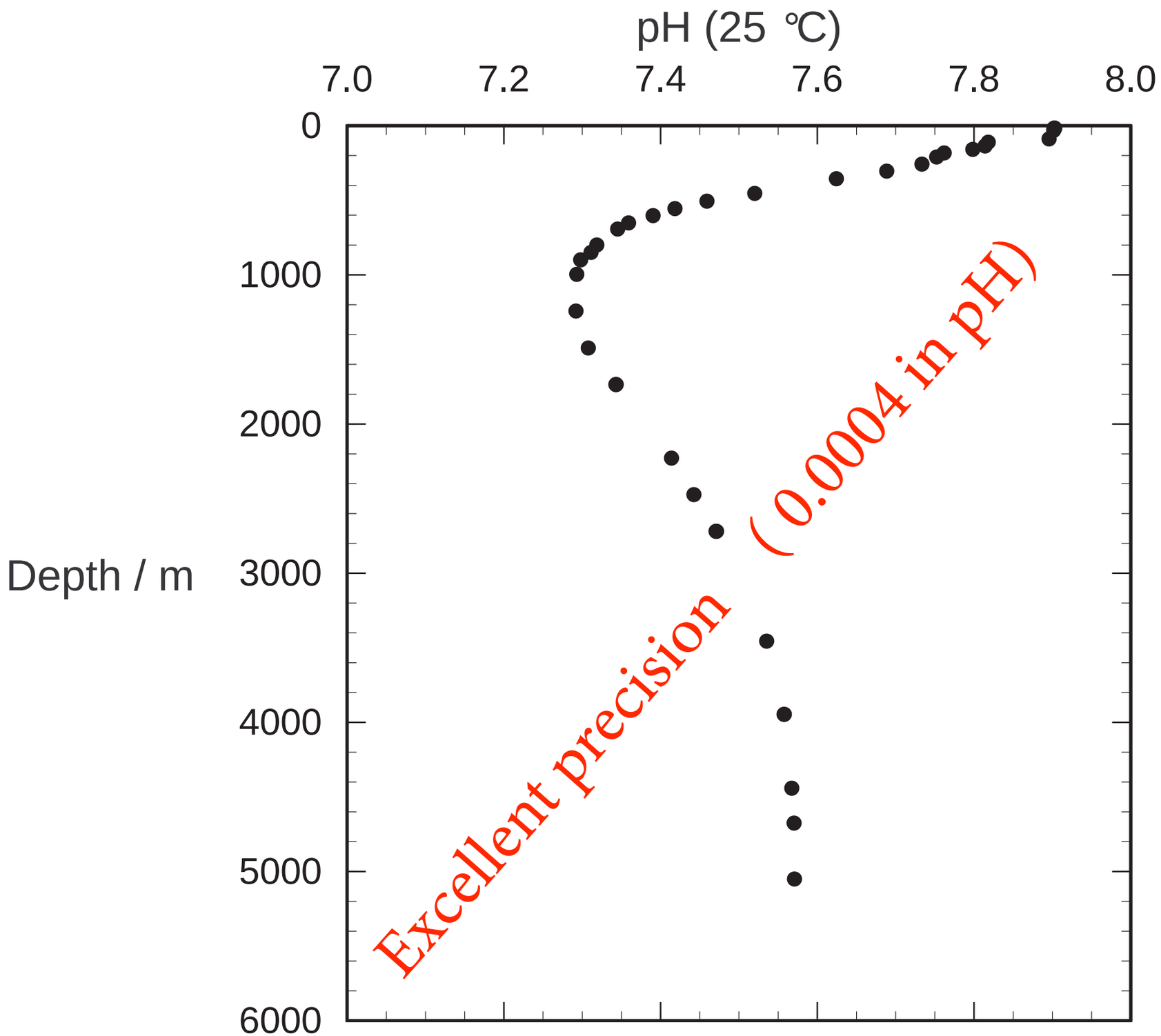
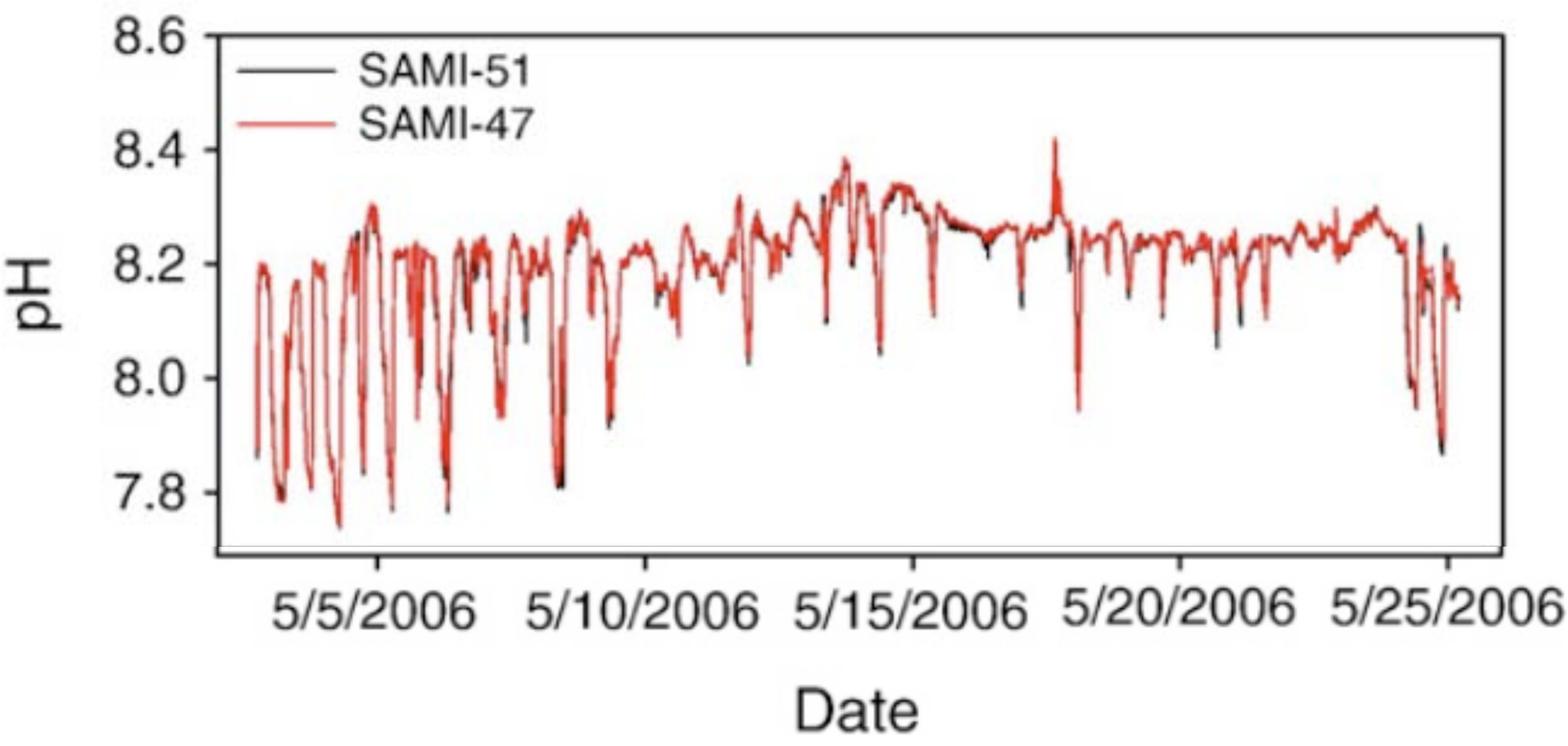


pH data from SAMI-pH instruments deployed off SIO pier



Seidel *et al.* (2008)

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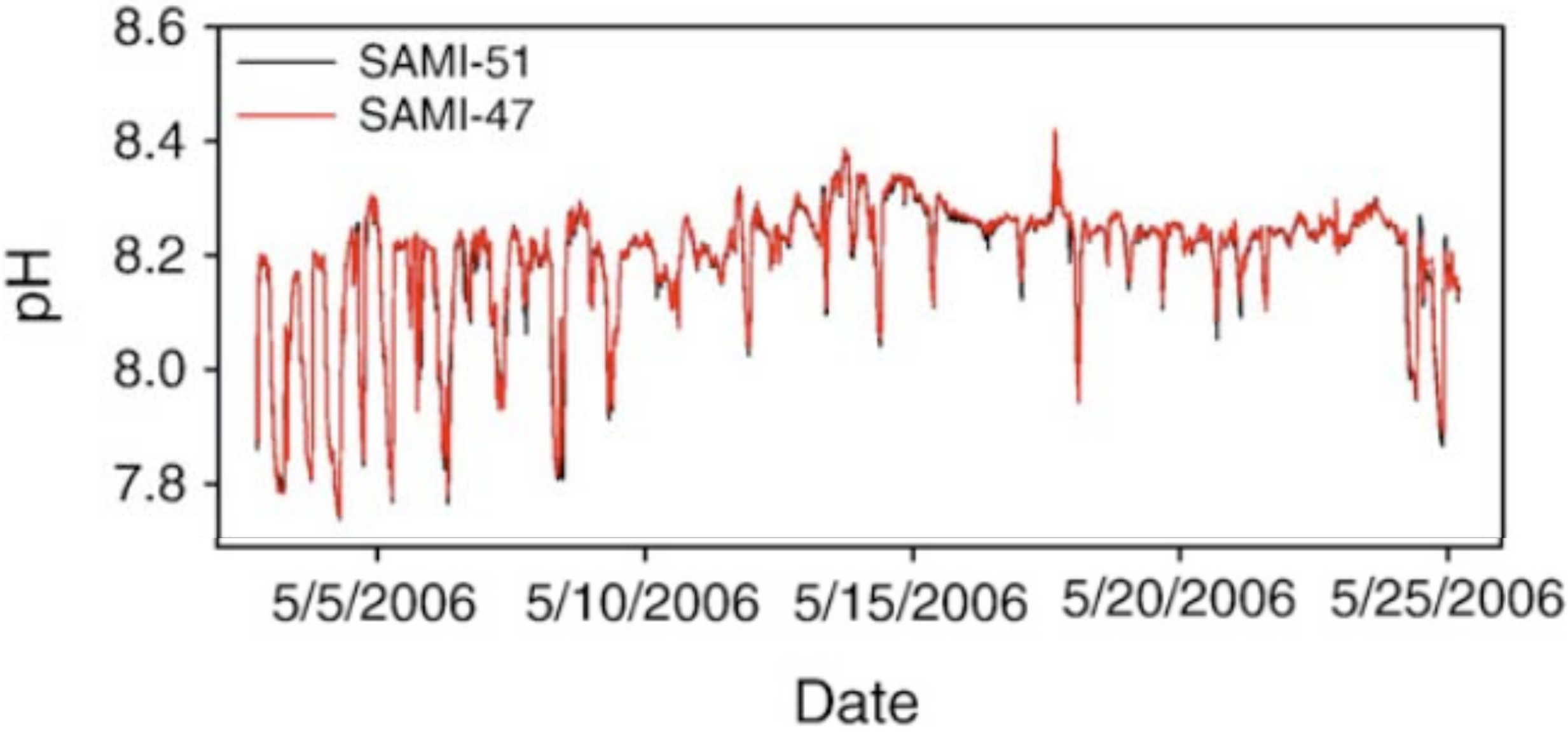

Excellent precision (0.0004 in pH)

Seidel *et al.* (2008)

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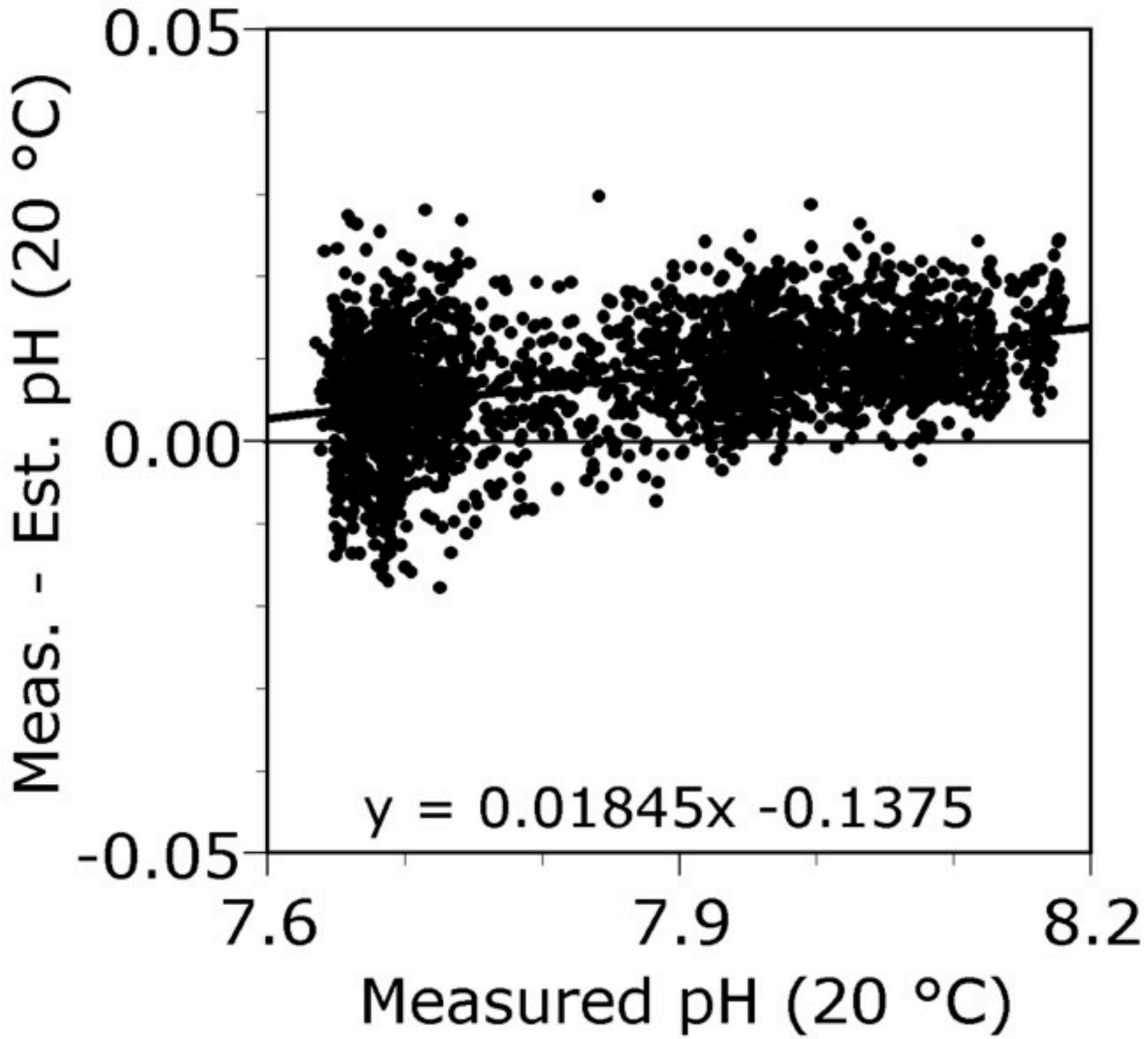

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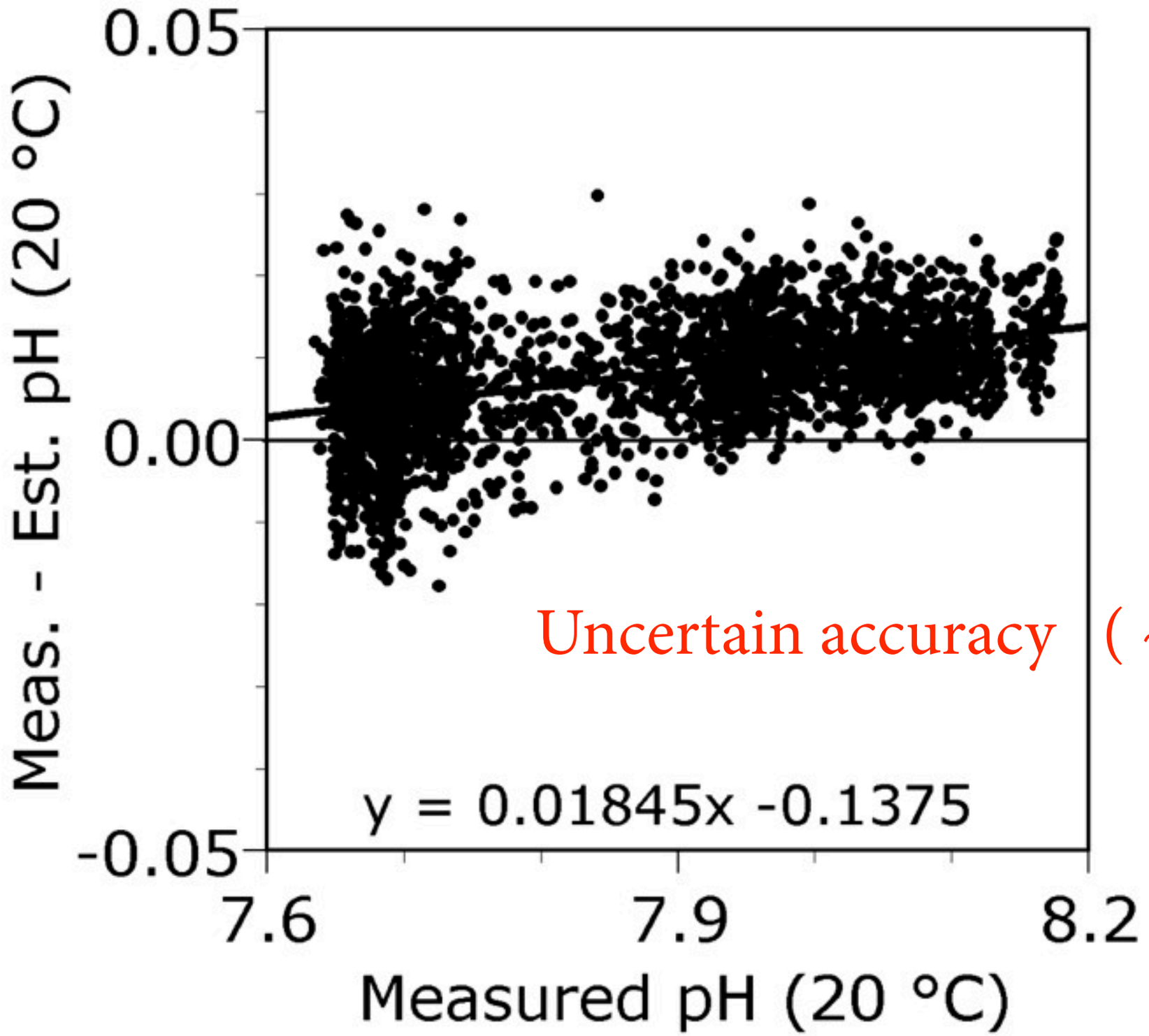

Uncertain accuracy (~0.01 in pH?)

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Marine Chemistry 107 (2007) 167–172
MARINE CHEMISTRY
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Impurities in indicators used for spectrophotometric seawater pH measurements: Assessment and remedies

Wensheng Yao, Xuewu Liu, Robert H. Byrne *

Differences in pH results obtained with various sources of *m*-cresol purple relative to that obtained with Kodak *m*CP: $\Delta pH = pH_{Vendor} - pH_{Kodak}$ (±0.001)

TCI-GR	Sigma-Aldrich	Alfar Aesar	Riedel-de-Haën	Acros Organics	J.T. Baker
0.008	0.005	0.003	0.002	−0.002	−0.002

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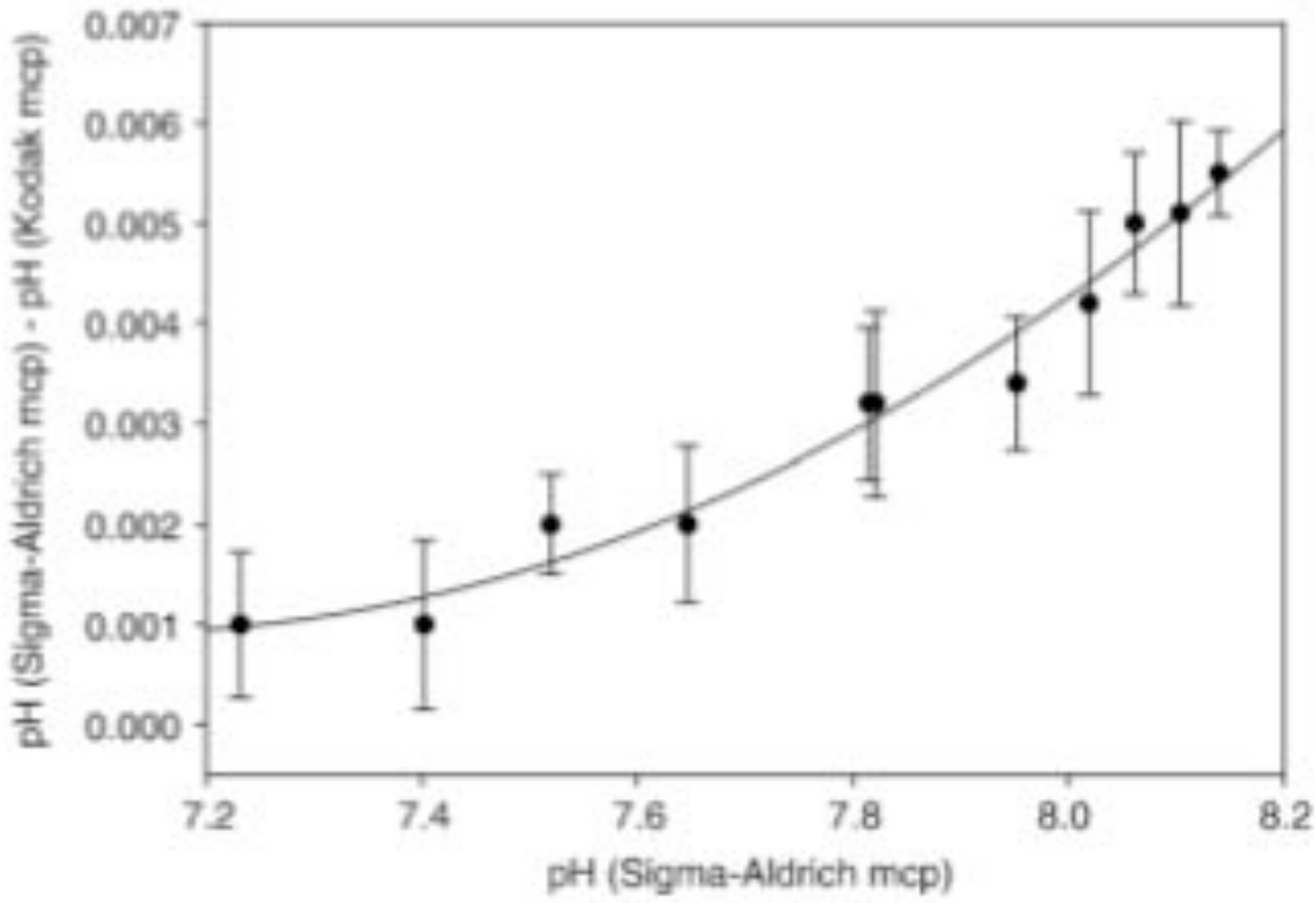
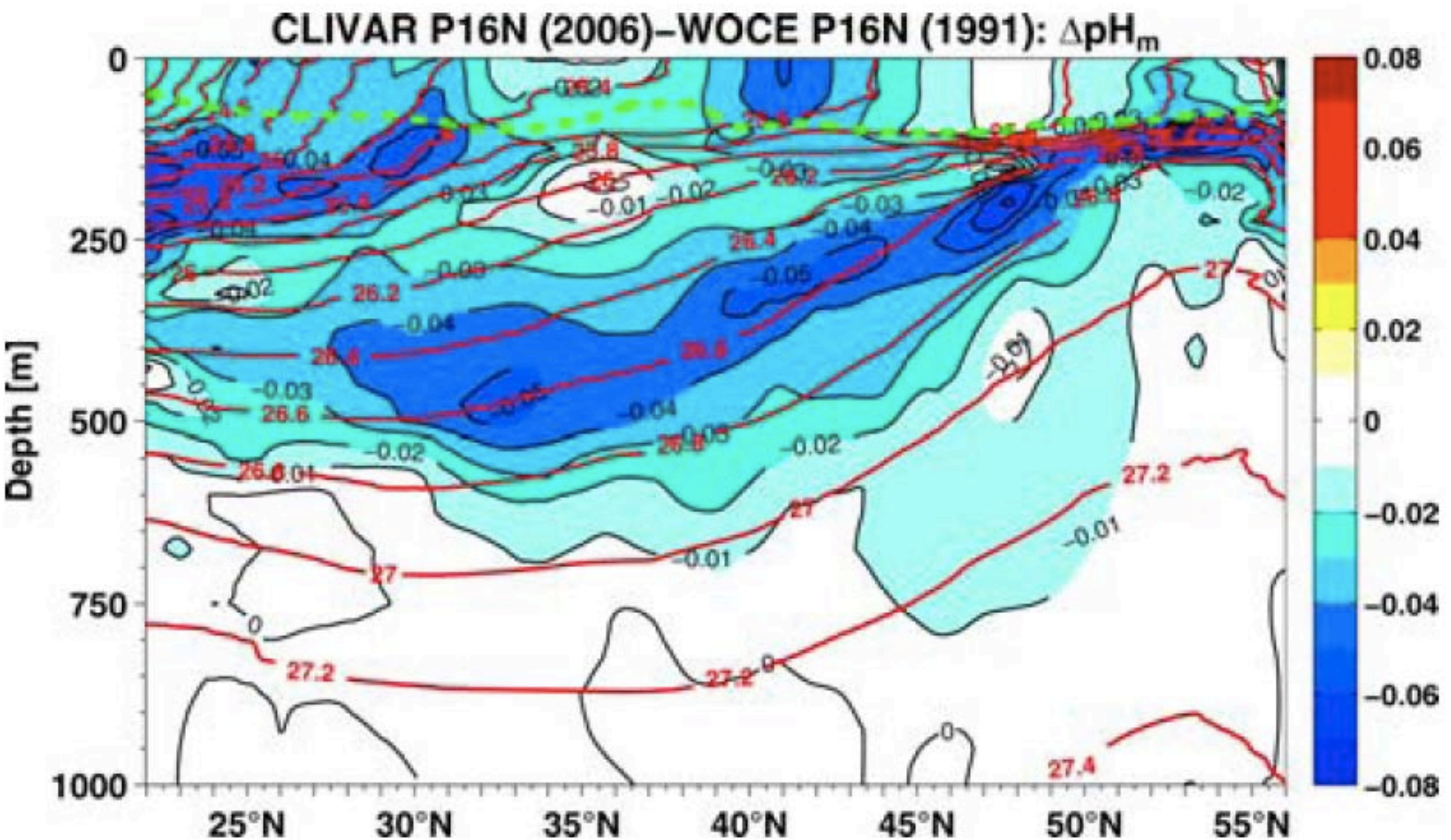


Fig. 2. Measured pH differences between Sigma-Aldrich and Kodak *m*CP as a function of sample pH.

Upper ocean pH change observed in North Pacific



Byrne *et al.*. (2010)

Conclusions

	Repeatability	Reproducibility	Accuracy
pH cell (glass electrode)	0.002	?	0.01 – 0.02 ?
pH cell (DuraFET®)	<0.001	?	0.01 – 0.02 ?
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Additional work needed to improve accuracy