An Update for Locally Interpolated Alkalinity Regression: More Data, Better Fits, Better Uncertainty Estimates, and Estimates of pH and Nitrate

Carter, B. R.1,2, Williams, N. L.3, Feely, R. A.2 others?

1Joint Institute for the Study of the Atmosphere and Ocean, University of Washington, 3737 Brooklyn Avenue, Seattle, WA, USA, 98105

2Pacific Marine Environmental Laboratory, National Oceanic and Atmospheric Administration, 7600 Sand Point Way NE, Seattle, WA, USA, 98115

3College of Earth, Ocean, and Atmospheric Sciences, Oregon State University, Corvallis, Oregon, USA, 97331

**Abstract**

We have taken advantage of the release of version 2 of the Global Data Analysis Project (GLODAPv2) data product (Olsen et al. 2016) to refine the Locally Interpolated Alkalinity Regression (LIAR) code for global total titration alkalinity of seawater (*A*T) estimation, and to extend the method to pH and nitrate (*N*) estimates. The updated MATLAB software and method are distributed as supplementary materials to this paper and referred to as LIAR version 2 (LIARv2), Locally Interpolated Nitrate Regression (LINR), and Locally Interpolated pH Regression (LIPHR). Collectively they are referred to as Locally Interpolated Regressions (LIRs). Relative to LIARv1, LIARv2 has a 1/5th to 1/3rd lower *A*T estimate RMSE, more accurate error estimates, and fewer regions in which the method has little or no available training data. LIARv2, LINR, and LIPHR produce estimates globally with comparable or better skill than regional alternatives produce in the regions they were developed for. Current software versions can be found as supplementary materials for this article. These versions and future updates can be found at: <http://tinyurl.com/gtyjgpd>.

**Introduction**

The LIAR method and software was developed to estimate *A*T globally from other measurable seawater parameters (Carter et al. 2016b). Applications for the method include providing *A*T estimates as a second carbonate constraint for the emerging network of biogeochemical floats that measure pH (Wanninkhof et al. 2016). Also, they may prove useful for studies or models interested in estimating a baseline or climatological *A*T value (Carter et al. 2016a). The approach follows numerous earlier studies estimating regional regression fits for *A*T. These regressions often have excellent skill, but typically only apply regionally. The LIAR method takes the step of estimating many such regionally-appropriate regression coefficient sets and interpolating between them to arbitrary locations at which regression estimates are desired.

The LINR and LIPHR methods and software are developed primarily to provide cross-comparisons for nitrate (*N*) and pH sensor measurements as tools for assessing potential sensor errors or measurement drift. Profiling biogeochemical floats cannot typically be retrieved for sensor recalibration, so it is important to have independent means to assess such problems that may arise during or after float deployment. A common approach is to use known atmospheric, surface, or climatological (Bushinsky et al. 2016; Takeshita et al. 2015; Pfister et al. 2014; Plant et al. 2016; Takeshita et al. 2013) concentrations to recalibrate sensors, but such known values are not always available for *N* and pH. LINR and LIPHR are designed to provide an alternative using well-estimated values in the stable intermediate ocean to cross compare. LINR and LIPHR have secondary scientific applications anytime biogeochemical estimates are desirable and measurements are unavailable. Like LIAR(v1 and v2), they have the limitation that they are unable to capture long term changes in the relationships between *N* and pH and the properties used as predictors. An example of such an unresolved change is the influence of ocean acidification (OA), or the effect of continued ocean storage of anthropogenic carbon dioxide (CO2) on seawater pH. Unlike LINR and LIARv2, LIPHR contains an optional adjustment to counteract the effects of OA on pH, but we expect OA to lead to LIPHR estimates becoming less skillful over time regardless because the provided adjustment is simplistic. These methods are therefore most useful at depths where the effects of OA and other climate changes are slower than at the surface, or for estimates made close in time to the dates of the measurements in the training data product.

Regressions for estimating pH, *N*, and *A*T have been reported numerous times in literature. *A*T regressions are the most common variant (e.g. McNeil and Sasse 2016; Lee et al. 2006; Alin et al. 2012; Velo et al. 2013; Bostock et al. 2013; Millero et al. 1998; Sasse et al. 2013) with regressions for pH being less frequently reported (e.g. Alin et al. 2012; Williams et al. 2016) and nitrate regressions being even less frequently reported (e.g. Williams et al. 2016, supplementary information). The LIRs here make improvements over these earlier versions with respect to global applicability, ease of use, and attention to estimate uncertainty. Critically, they also produce estimates that are as accurate as or more accurate than earlier versions. The bulk of the improvement is owed to the larger quantity and span of data available through the GLODAPv2 data product (Olsen et al. 2016) than was available to train earlier methods.

In the remainder of this paper we describe version 2 of the LIAR software (LIARv2) in the context of the improvements relative to version 1 (LIARv1: Carter et al. 2016b), and extend the approach to nitrate and total scale seawater pH estimates with LINR and LIPHR.

**2 Methods**

*2.1 Summary of LIR methods*

As with LIARv1, all LIR methods use regression coefficients that are determined at each location on a 5° latitude and longitude grid with 33 depth surfaces (44,957 total locations). Each set of regression coefficients is determined using a robust multiple linear regression of the subset of measurements from the global training dataset that are found within latitude, longitude, and depth/density windows of the grid coordinates. The LIAR software then interpolates between these locations to arbitrary locations where the user desires regression estimates. LIARv2 and LIPHR work with 16 different combinations of the predictor variables: salinity *S*, potential temperature *θ*, nitrate *N*, apparent oxygen utilization AOU, and silicate *Si*. LINR uses the same combinations with phosphate *P* in place of *N* in the 8 regressions with *N*. A full description of the LIARv1 method is provided by Carter et al. (2016b).

*2.2 Data products used to train and test LIRs*

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| **Figure 1.** Maps of the data used for the training (left) and test (right) data sets for LIAR (top, a. and b.), LIPHR (middle, c. and d.), and LINR (bottom, e. and f.) regression coefficients. |

The primary improvement in LIARv2 relative to LIARv1 is that regression coefficients have been re-estimated using the Global Data Analysis Project version 2 data product (GLODAPv2: Olsen et al. 2016). All measured and calculated values in GLODAPv2 were used except those from 161 cruises (40,303 measurements) that had *A*T quality control (QC) adjustments of ±10 or greater, were flagged as poor data, or were not quality controlled for *A*T. The new training data set is comprised of 236,852 viable *A*T measurements and calculations, 211,704 of which had the property measurements required for training all 16 regressions (Figure 1). GLODAPv2 has the advantage over the merged data product used to train LIARv1 that all cruise datasets were QC’d identically upon assimilation into the GLODAPv2 product.

LINR regression coefficients were estimated using 684,475 *N* measurements, 569,761 of which had associated property measurements required for training all 16 regressions. This training dataset is all GLODAPv2 dataproduct *N* measurements excepting those from 187 cruises that had multiplicative adjustments greater than 10%, that were not QC’d, or that were flagged as having poor quality measurements. In keeping with GLODAPv2 QC protocols, unphysical negative LINR nitrate estimates are changed to 0 μmol kg˗1.

LIPHR estimates pH on the total scale at *in situ* conditions. LIPHR regression coefficients were estimated using 201,939 calculations and measurements, 189,402 of which had associated property measurements required for training all 16 regressions. These totals exclude measurements and calculations from 22 cruises (1704 measurements) with offset adjustments estimated to be larger than ±0.015 pH units, that were calculated from cruises with total dissolved inorganic carbon (*C*T) or total seawater titration alkalinity (*A*T) adjustments greater than ±10 μmol kg˗1, or that had adjustments flagged by the GLODAPv2 team with QC code “-777: poor data, no adjustment suggested.” We also omitted data from 7 cruises (expocodes: 49K619990523, 49HG19950414, 49HG19940413, 49HG19930807, 49HG19930413, 33RR19971202, 318M19940327) because they came from series of cruises with large and variable adjustments or because the calculated and measured pH values did not agree to within ±0.03 pH units. Total scale pH is calculated from *A*T and *C*T using carbonate constants from Lueker et al. (2000), borate dissociation coefficients from Dickson (1990), and total borate from Uppström (1974). Including calculated pH in our training data set marginally improves the accuracy of LIPHR reconstructions of our test data set, which includes only the 105,570 direct measurements of pH (and excludes calculated pH values).

*2.3 An ocean acidification adjustment for pH estimates*

LIPHR includes an optional adjustment to reflect the expected effects of OA on future seawater pH. The rate of pH change () is estimated for this adjustment from the robust regression:



 (1)

This is a regression between the reconstruction error () and the difference between the mean decimal years of the training measurements used to estimate the regression coefficients () and the decimal years of the test data (). This regression has been performed for the 8 subsets of the GLODAPv2 data product used separated by every 12.5th percentile of potential density (σ*θ*) (Figure 2). If the adjustment is used, is linearly interpolated by σ*θ* to the σ*θ* estimated for the query data location and the adjusted LIPHR estimate () is supplied as:



 (2)

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| Figure 2. The “per year” rate of ocean acidification (OA)-related impacts on LIPHR estimate errors () calculated for every 12.5th percentile of potential density (σ*θ*) in the GLODAPv2 data product. If the optional LIPHR OA adjustment is used, the routine subtracts the product of —interpolated between black dots to the measurement density—and the difference between the year of the measurement and the mean year of measurement of the training data used for the regression from the final pH estimate. The green envelope indicates 95% confidence intervals of the fits. The blue envelope shows the larger confidence intervals obtained if only one degree of freedom is assumed for each cruise rather than each measurement. |

These simplistic OA adjustments may be poor estimates of the impacts of OA on seawater pH generally both because they treat all water of a given density identically (despite strong regional differences in the degree of water mass ventilation and Canth storage) and because they are biased by an unknown amount of LIPHR pH estimate change from long term changes in regression parameters. Nevertheless, we believe the optional adjustment is appropriate for LIPHR pH estimates made in the coming decades, and note that including the adjustment decreases mean estimate RMSE by 10%. Limited experimentation suggested more cruises would be needed to adequately constrain regional differences in this adjustment. The assessment values we report include this adjustment.

*2.4 Update to uncertainty estimation*

As with LIARv1, uncertainty estimates () are quantified as:



(3)



for all LIRs. represents *A*T, *N*, and pH measurement uncertainties in our data product, and is assumed to be a constant 3 µmol kg−1 *A*T, 0.3 µmol kg−1 N, and 0.004 pH units for this calculation. *U* are the *n* input uncertainties provided by the user or default uncertainties specific to the regression properties if no *U* values are provided. The default uncertainties are now 0.003 0.003 °C and 1% of *N*, *P*, AOU, and *Si*. Theterms are the *n* regression coefficients used in the estimate. The *E*MLR term represents the component of the overall uncertainty inherent to regression based estimates. *E*MLR is estimated by interpolating *E*MLR estimates against *S* (for *A*T) or depth (for *N* and pH) ranges to the *S* or depth of the input properties. Relative to LIARv1, the LIARv2 update changes that the salinity values used for the *E*MLR interpolation are every 5th percentile of the measured salinity in the GLODAPv2 data product instead of every 1 salinity unit. This change was made because a fixed 1 salinity unit resolution of *E*MLR both poorly resolves *E*MLR in the narrow salinity range most ocean measurements fall within and provides excessive resolution to the outlier salinity ranges with few measurements. This inadequacy was leading to an uncertainty over-estimation when interpolating *E*MLR against salinity, and was poorly constraining *E*MLR for high and low salinity values. LINR and LIPHR errors also scale with salinity, but not as strongly as LIAR errors do because of the smaller impact of freshwater cycling on *N* and pH than on *A*T. Rather, LINR and LIPHR uncertainties both decrease strongly with depth due to a decreased impact of seasonality and episodic biogeochemical cycling and gas exchange events at depth. For LINR and LIPHR, *E*MLR is quantified for every 10th percentile of depth in the GLODAPv2 data product and interpolated between these estimates to the query depth.



*2.5 Minimum uncertainty estimates*

One difficulty with LIRs is choosing between up to 16 possible estimates. We have added (optional) functionality to the LIR routines that automatically picks the estimate with the smallest uncertainty from among the estimates it is possible to generate using the input data provided. This feature was considered for LIARv1, but scrapped because it occasionally led to decreased performance relative to using the estimate with the most regression parameters. With improvements to the uncertainty estimates (section 3.4) this option now decreases estimate RMSE by 0 to 1%. This improvement is minimal, but allows for a simplified outputs for a range of use cases without harming estimate accuracy. Also, the improvement becomes more marked with (known) larger input uncertainties such as those that will be common with sensor measurements. For example, the RMSE for estimates made after applying simulated errors to AOU (normally distributed offsets with a mean of 0 and a standard deviation of 5 μmol kg˗1 O2) is 5% smaller than the RMSE for estimates with the same inputs from regression 1 or 3.

**3 Assessment**

RMS errors are calculated identically to the error estimates provided by Carter et al. (2016) save that they are calculated using the larger subsets of the GLODAPv2 data product specified in section 2.2. An important feature of the RMS error estimation method we use is that a separate set of regression coefficients is estimated for each data point in the GLODAPv2 data product, and is estimated without using any data from the cruise that produced that datum. Data from the same cruise is omitted is to avoid under-estimating error by including numerous measurements in the training dataset found proximally in time and space to the test measurement. Such measurements will not have been part of the training datasets for regression estimates made with these methods in the future, so it is inappropriate to include them in the training data set used to train the method we use for our test data set.

*3.1 LIARv2*

The updates to LIAR decreased the overall reconstruction errors () for all 16 regressions relative to by 7% to 26% (average 18%, this is calculated using an identical test dataset). The largest improvements are for the regressions with the fewest predictors. We attribute the majority of the improvements to the increased size and quality of the subset of the GLODAPv2 data product we used relative to the merged data product we used for LIARv1 (Figure 3).



LIARv1 compared favorably to regional *A*T regressions in literature (many are compared in Carter et al., 2016) and Table 1 shows LIARv2 does have somewhat better still. Interestingly, regression 3 (*S*, *θ*, AOU, and *Si*) outperforms regression 1 (*S*, *θ*, *N*, AOU, and *Si*) on average, suggesting that regression 1 is over-fitting *A*T in places (this is not true if we include the test data in the training data). The newly added minimum-uncertainty functionality (section 2.5) is designed to avoid such errors from overfitting, since overfitting tends to generate larger regression coefficients ( terms in equation 3) and hence larger uncertainty estimates.

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| **Figure 3.** A 2-dimensional histogram of measured *A*T (x-axis) against estimated *A*T (y-axis). Darker colors along the thin blue 1:1 line indicate orders of magnitude more measurements fall on the line than in the light colored histogram bins off the line. |

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| **Table 1.** Error estimates for the subset of our data product found within the open-ocean salinity range of 33 to 38. is error estimated to be inherent to the use of a MLR approach, is error arising from uncertainties in the input data,is the overall estimate uncertainty for LIARv2, andis the same term for LIARv1. GLODAPv2 data product is used as test data for all estimates. Errors are expressed as standard errors in μmol *A*T kg‒1. | | | | |
| Reg. # | Parameters used |  |  |  |
| 1 | *S*, *θ*, *N,* AOU, *Si* | 3.6 | 0.8 | 5.0 |
| 2 | *S*, *θ*, *N, Si* | 3.7 | 0.7 | 5.0 |
| 3 | *S*, *θ*, AOU, *Si* | 3.6 | 0.7 | 4.9 |
| 4 | *S*, *θ*, *Si* | 3.7 | 0.6 | 5.0 |
| 5 | *S*, *θ*, *N,* AOU | 3.8 | 0.9 | 5.1 |
| 6 | *S*, *θ*, *N* | 4.0 | 0.9 | 5.3 |
| 7 | *S*, *θ*, AOU | 3.8 | 0.7 | 5.1 |
| 8 | *S*, *θ* | 4.3 | 0.5 | 5.5 |
| 9 | *S*, *N,* AOU, *Si* | 3.6 | 0.8 | 5.0 |
| 10 | *S*, *N, Si* | 3.7 | 0.7 | 5.0 |
| 11 | *S*, AOU, *Si* | 3.6 | 0.6 | 5.0 |
| 12 | *S*, *Si* | 3.7 | 0.6 | 5.0 |
| 13 | *S*, *N,* AOU | 4.6 | 1.2 | 5.8 |
| 14 | *S*, *N* | 4.4 | 1.0 | 5.6 |
| 15 | *S*, AOU | 4.6 | 0.8 | 5.7 |
| 16 | *S* | 5.1 | 0.4 | 6.1 |

*3.2 LIPHR*

LIPHR pH estimates reconstruct the pH test data set well (Table 2, Figure 4). We separately estimate error between 1500 and 2500 m as these estimates are more appropriate for the estimates that would be used to compare with float data.

LIPHR estimates also do well relative to the few published pH regression estimates. Williams et al. (2016) designed regression estimates for south of 45°S between 2006 and 2017 and between 0 and 2100 m depth. For the subset of our data product within these bounds these regressions have a RMSE of 0.029 and 0.037, while LIPHR (regression 7, with *θ*, *S*, and AOU) has a 0.017 RMSE. They also report a regression for estimates in the same region but between 1000 and 2100 m depth that has a RMSE of 0.015. LIPHR has the same RMSE for this depth range. LIPHR (also regression 7) estimates have a RMSE of 0.009 in the California Current Ecosystem specific window of 114°N to 124°W, 27°N to 36°N and 15 to 500 m depth after 1994 where the algorithm from Alin et al. (2012) uses temperature and O2 measurements to generate estimates with a RMSE of 0.043. Juranek et al. (2011) provide a pair of pH estimation algorithms specific to the Subartic Pacific between 40 and 55°N between 30 and 500 m depth. These algorithms have RMSEs of 0.042 and 0.037 for this region, where LIPHR has a RMSE of 0.22.

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| **Figure 4.** A 2 dimensional histogram of measured or calculated pH (x-axis) against OA-adjusted estimated pH (y-axis). Darker colors along the thin blue 1:1 line indicate orders of magnitude more measurements fall on the line than in light colored histogram bins off the line. |

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| **Table 2.** LIPHR error estimates for the subset of our data product found within the open-ocean salinity range of 33 to 38. is error estimate to inherent to the use of a MLR approach, is error arising from uncertainties in the input data, and is the overall estimate uncertainty. Errors are expressed as standard errors in pH units. is the uncertainty estimate for pH measurements between 1500 and 2500 m, or the approximate depth range at which biogeochemical floats will require pH estimates to cross-compare with. | | | | | |
| Reg. # | Parameters used |  |  |  |  |
| 1 | *S*, *θ*, *N,* AOU, *Si* | 0.009 | 0.010 | 0.015 | 0.012 |
| 2 | *S*, *θ*, *N, Si* | 0.008 | 0.010 | 0.015 | 0.011 |
| 3 | *S*, *θ*, AOU, *Si* | 0.011 | 0.009 | 0.015 | 0.012 |
| 4 | *S*, *θ*, *Si* | 0.017 | 0.008 | 0.020 | 0.012 |
| 5 | *S*, *θ*, *N,* AOU | 0.009 | 0.010 | 0.015 | 0.012 |
| 6 | *S*, *θ*, *N* | 0.012 | 0.010 | 0.017 | 0.012 |
| 7 | *S*, *θ*, AOU | 0.012 | 0.008 | 0.015 | 0.012 |
| 8 | *S*, *θ* | 0.027 | 0.008 | 0.029 | 0.014 |
| 9 | *S*, *N,* AOU, *Si* | 0.010 | 0.010 | 0.015 | 0.011 |
| 10 | *S*, *N, Si* | 0.012 | 0.010 | 0.017 | 0.011 |
| 11 | *S*, AOU, *Si* | 0.011 | 0.008 | 0.015 | 0.012 |
| 12 | *S*, *Si* | 0.021 | 0.008 | 0.023 | 0.012 |
| 13 | *S*, *N,* AOU | 0.012 | 0.009 | 0.016 | 0.011 |
| 14 | *S*, *N* | 0.017 | 0.010 | 0.021 | 0.012 |
| 15 | *S*, AOU | 0.014 | 0.008 | 0.017 | 0.011 |
| 16 | *S* | 0.037 | 0.007 | 0.038 | 0.014 |

3.3 LINR

LINR estimates also reproduce the test data product well (Table 3, Figure 5). Williams et al. (2016) provide a *N* estimation algorithm specific to the Pacific sector of the Southern Ocean south of 45°S between 1000 and 2100 m. This algorithm has a 1.37 μmol kg˗1 RMSE for the portion of our data product in the target region for this regression. LINR (Regression 7) has a RMSE of 0.45 μmol kg˗1 for this same subset. Need to double check Nancy’s Calc.

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| **Figure 5.** A 2 dimensional histogram of measured *N* (x-axis) against estimated *N* (y-axis). Darker colors along the thin blue 1:1 line indicate orders of magnitude more measurements fall on the line than in the light colored histogram bins off the line. |

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| **Table 3.** LINR error estimates for the subset of our data product found within the open-ocean salinity range of 33 to 38. is error estimate to be inherent to the use of a MLR approach, is error arising from uncertainties in the input data, and is the overall estimate uncertainty. Errors are expressed as standard errors in μmol kg‒1. is the uncertainty estimate for pH measurements between 1500 and 2500 m, or the approximate depth range at which biogeochemical floats will require pH estimates to cross-compare with. | | | | | |
| Reg. # | Parameters used |  |  |  |  |
| 1 | *S*, *θ*, *P,* AOU, *Si* | 0.51 | 0.12 | 0.61 | 0.41 |
| 2 | *S*, *θ*, *P, Si* | 0.55 | 0.14 | 0.64 | 0.43 |
| 3 | *S*, *θ*, AOU, *Si* | 0.76 | 0.10 | 0.82 | 0.78 |
| 4 | *S*, *θ*, *Si* | 0.95 | 0.09 | 1.00 | 0.82 |
| 5 | *S*, *θ*, *P,* AOU | 0.52 | 0.13 | 0.61 | 0.42 |
| 6 | *S*, *θ*, *P* | 0.56 | 0.16 | 0.65 | 0.46 |
| 7 | *S*, *θ*, AOU | 0.73 | 0.11 | 0.79 | 0.44 |
| 8 | *S*, *θ* | 1.14 | 0.07 | 1.19 | 0.52 |
| 9 | *S*, *P,* AOU, *Si* | 0.54 | 0.13 | 0.63 | 0.42 |
| 10 | *S*, *P, Si* | 0.57 | 0.15 | 0.66 | 0.44 |
| 11 | *S*, AOU, *Si* | 0.81 | 0.11 | 0.87 | 0.74 |
| 12 | *S*, *Si* | 0.99 | 0.10 | 1.04 | 0.72 |
| 13 | *S*, *P,* AOU | 0.58 | 0.14 | 0.66 | 0.43 |
| 14 | *S*, *P* | 0.61 | 0.18 | 0.70 | 0.47 |
| 15 | *S*, AOU | 0.89 | 0.11 | 0.94 | 0.44 |
| 16 | *S* | 1.60 | 0.07 | 1.63 | 0.56 |

*3.4 Uncertainty estimation skill*

With the changes to the error estimation strategy noted in Section 2.4, the overall standard error estimates provided by the software are now greater than or equal to the test data set reconstruction error for 73% of the data product for LIARv2, for 69% for LIPHR, and for 70% for LINR. For perfectly-estimated normally-distributed RMS errors, this number would be 68%. This was true for 87% of the data product with LIARv1. We therefore conclude the LIARv2 error estimates are better estimates of error than the LIARv1 error estimates.

**Future Directions**

Climatological distributions of carbonate parameters from LIAR *A*T and LIPHR pH—or calculated from this pair of properties—may be of interest and would be simply calculated for the measurement-dense World Ocean Atlas climatology (Locarnini et al. 2013; Zweng et al. 2013; Baranova 2015) or similar products. Such a regression based climatology, like the *A*T climatologies created by Lee et al. (2006) and used by Takahashi et al. (2014), would be one step further removed from the measurements than gridded climatologies like those provided by Lauvset et al. (2016) and Key et al. (2004). However, it would have the advantage that it could be based on property measurements (such as O2, *S*, and temperature) that are more multitudinous, more broadly spatially and temporally distributed, and less seasonally biased than the carbonate measurements.

The OA adjustment (Equation 2) provides means to incorporate a large amount of measurements that are disparate in space and time. This framework could be applied to examine the scientific questions of whether long term trends are occurring in *A*T (c.f. Carter et al. 2016a) or *N* relative to other measured parameters. A discussion of the trends found is beyond the scope of this paper, but figures equivalent to Figure 2 are included for *A*T and *N* in the supplementary materials.

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