

1 **Supporting Information for**

2 **Decoupling of estuarine hypoxia and acidification as revealed by historical**
3 **water quality data**

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13 **Content of this file**

14 Text S1, Table S1, Figure S1-S3

15 **Introduction**

16 This supporting information provides additional text, table and figures for the main article.

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21 **Text S1: Modeling of total alkalinity and dissolved inorganic carbon**

22 DIC and TA are two key state variables for carbonate chemistry and are particularly useful for
23 process modeling because they are conservative with respect to changes in temperature, salinity, and
24 pressure (unlike pH and Ω_{ar}). However, while pH has been consistently measured at a bay-wide scale
25 since 1985, DIC has been rarely measured in Chesapeake Bay until very recently and TA has been
26 measured only at a limited number of stations and times. Therefore, we used a modeling approach to
27 estimate TA and DIC from available long-term water quality observations.

28 Prior field measurements in the Bay and its tributaries have revealed a variety of patterns of TA
29 along the salinity gradient,^{1,2} and several studies have demonstrated a relatively linear relationship
30 between TA and salinity.^{3,4,5} In this study, we adapted an empirical model of TA in the mainstem Bay
31 from Herrmann et al.⁶ Specifically, TA is modeled as a function of measured estuarine salinity and
32 temporally varying riverine TA, assuming conservative mixing of two main sources of water for the
33 mainstem Bay: Atlantic Ocean shelf (high-salinity source) and the Susquehanna River (USGS gage
34 number 01578310, zero-salinity source). Because the model configuration reported in Herrmann et al.⁶
35 was fit to surface salinity observations only, for this study we refit the model to include salinity
36 observations from all available depths. The uncertainty in the mixing model was assessed using high-
37 quality measurements of TA during 2016–2018 cruises. Specifically, water samples during the cruises
38 were collected in 250ml borosilicate bottles, and were fixed using a saturated solution of mercuric
39 chloride (HgCl₂) immediately after collection, then stored in the dark. Concentrations of TA were
40 measured using an open-cell potentiometric titrator in laboratories.^{4,7} The model captures the substantial
41 effects of the seasonality and long-term increase in Susquehanna River TA on TA in the mainstem Bay.
42 The refit empirical model was used to generate vertical profiles of TA at the 21 stations used in the
43 present study.

44 A 200-member Monte Carlo ensemble of DIC was computed from observed CBP pH, temperature,
45 salinity, and modeled TA corrected for organic alkalinity, by propagating the measurement uncertainty in

46 pH (0.2 standard pH units, NBS), the uncertainty in modeled TA, and the uncertainty in the assumed
47 organic alkalinity contribution ($20 \pm 30 \mu\text{M}$) as described in Herrmann et al.⁶ Ω_{ar} was also computed to
48 contextualize some of the results. Computations were done at each station at the native time and depth
49 resolution using CO2SYS.⁸ We used the carbonic acid equilibrium constants of Cai and Wang,⁹ the
50 equilibrium constant for bisulfate ion of Dickson,¹⁰ and the ratio of total boron to salinity of Uppström.¹¹
51 The phosphate and silicate concentrations were assumed to be zero, as we found the pH variations were
52 extremely small (i.e., < 0.014 unit) despite the high phosphate and silicate levels according to our
53 calculations using CO2SYS. Meanwhile, silicate data were not available in the latter 1-2 decades of the
54 monitoring program. we also assumed that the zero-salinity end member has a zero calcium ion
55 concentration, an assumption that leads to a minimal bias in calculated Ω_{ar} along the salinity gradient of
56 the mainstem.

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60 Table S1. USGS gauge stations used for freshwater inputs (Q_f) and CBP water quality stations used for
 61 computing tributary salinity (S_t) in the box model.

Major tributary	USGS ID	CBP Stations	Box Model Segment
Susquehanna River	01578310	CB1.1	1
Patuxent River	01594440	TF1.5, TF1.6, TF1.7, RET1.1, LE1.1, LE1.2, LE1.3, LE1.4,	5
Potomac River	01646500	TF4.2, TF2.0, TF2.1, TF2.2, TF2.3, TF2.4, RET2.2, RET2.4, LE2.2, LE2.3	6
Rappahannock River	01668000	TF3.2, TF3.3, RET3.1, RET3.2, LE3.1, LE3.2, LE3.4, LE3.6	7
York River	01674500/ 0167300	TF4.2, RET4.1, RET4.3, LE4.1, LE4.2, LE4.3, WE4.2	8
James River	02037500/ 02040892	TF5.6, RET5.2, LE5.1, LE5.2, LE5.3, LE5.4, LE5.5	9

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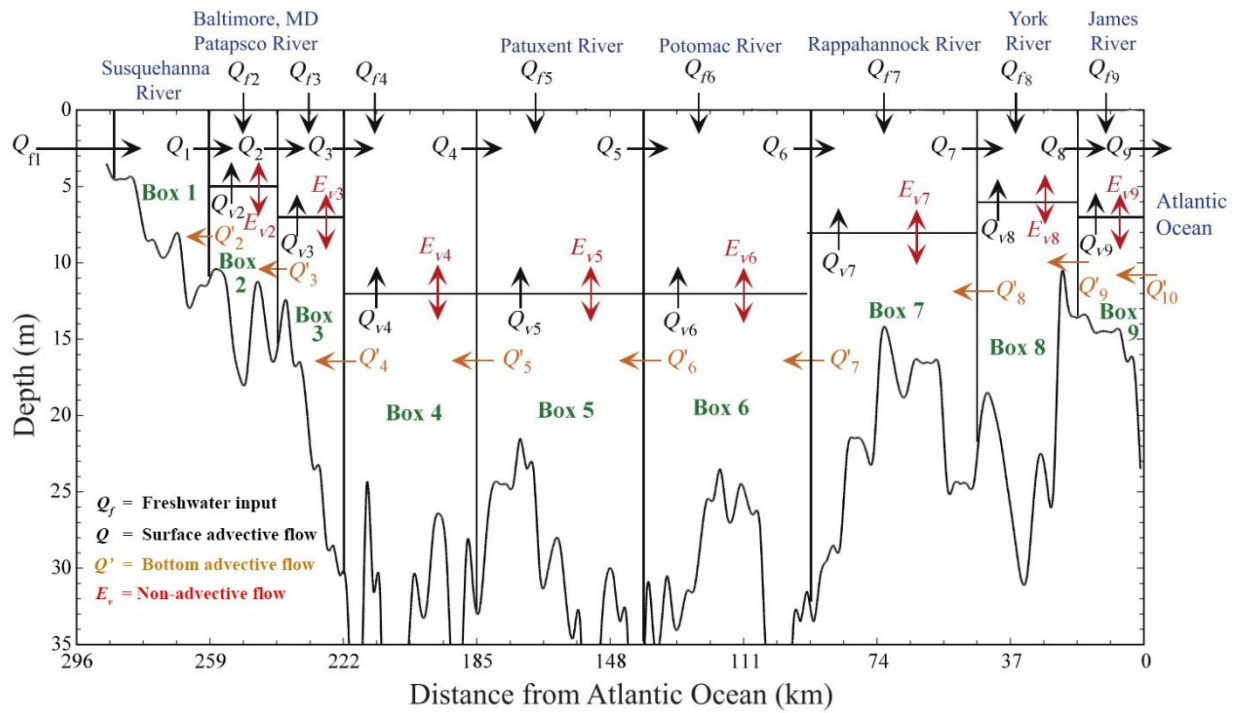


Fig. S1. Diagram of box model for Chesapeake Bay, including relevant freshwater inputs and transport fluxes. Diagram is adapted from Testa et al. (2018). An aerial view of this model is included in Fig. 1.

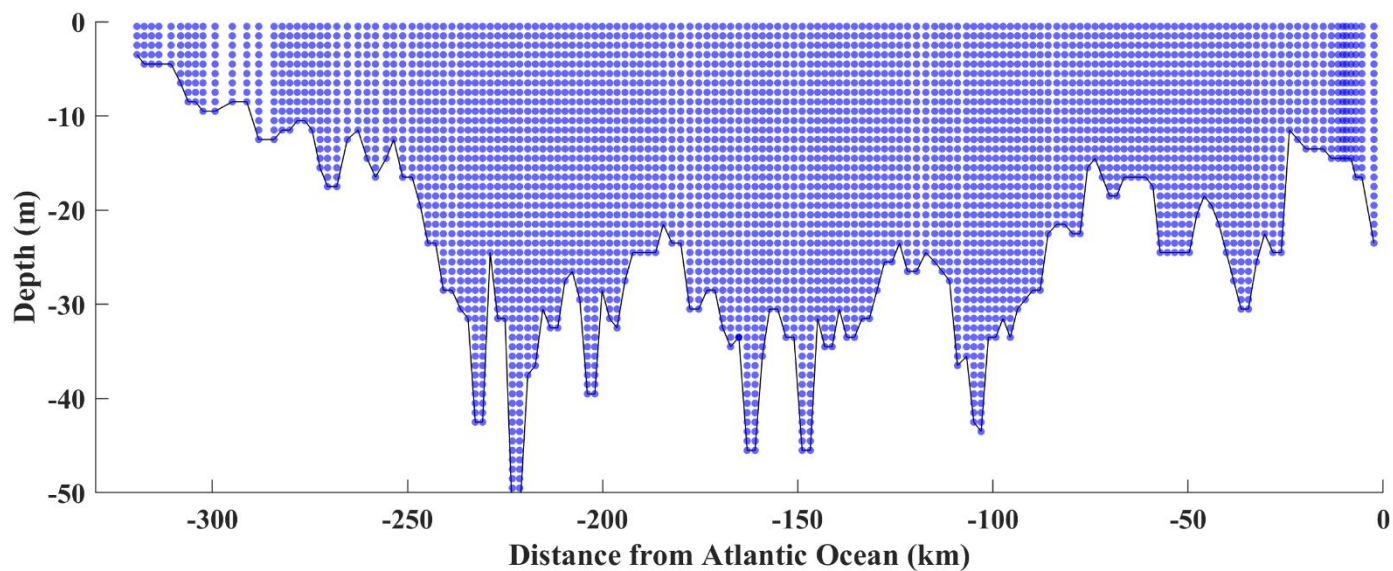


Fig. S2. Two-dimensional depth-length grid along the mainstem Bay used for interpolation.

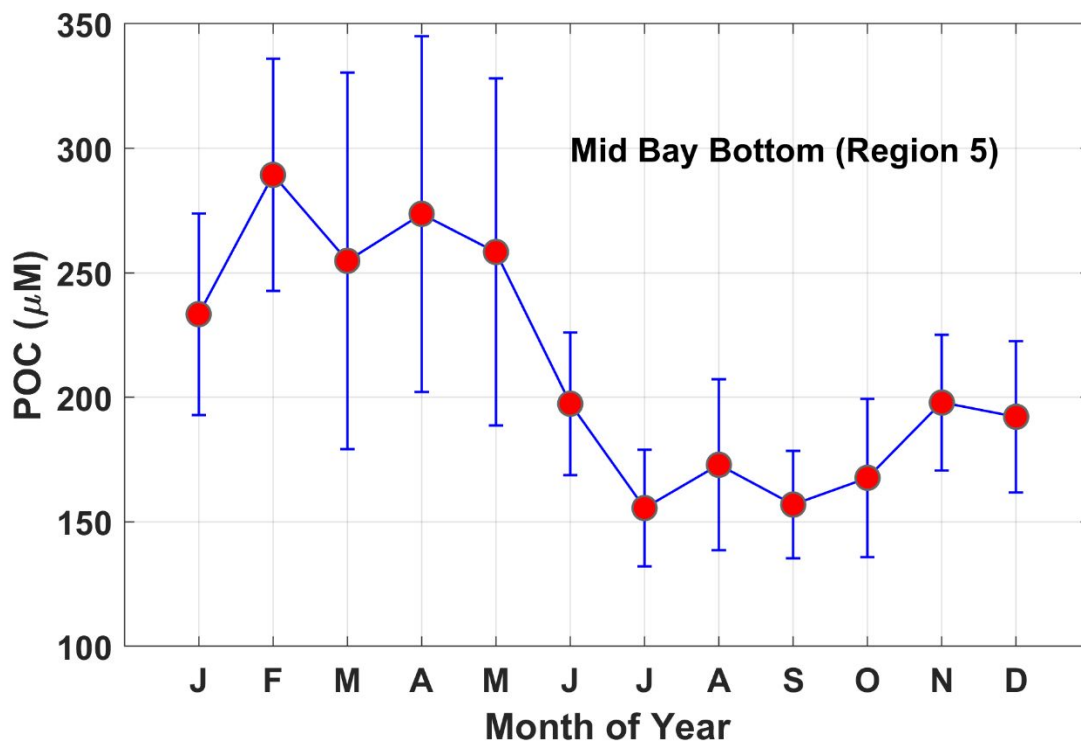


Fig. S3. Long-term (1986-2018) monthly average particulate organic carbon (POC) concentration measured in bottom waters at mid-bay region (Region 5). The bars represent one standard deviation.

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