# Analysis of global surface ocean alkalinity to determine controlling processes

CrossMark

Claudia H. Fry [a,*], Toby Tyrrell [a], Mathis P. Hain [a], Nicholas R. Bates [a,b], Eric P. Achterberg [a,c]

[a] University of Southampton, National Oceanography Centre Southampton, Southampton, UK
[b] Bermuda Institute of Ocean Sciences, Ferry Reach, Bermuda
[c] GEOMAR Helmholtz Centre for Ocean Research, 24148 Kiel, Germany

## ARTICLE INFO

## ABSTRACT

The export of calcium carbonate ($CaCO_3$) from the surface ocean is poorly constrained. A better understanding of the magnitude and spatial distribution of this flux would improve our knowledge of the ocean carbon cycle and marine biogeochemistry. Here, we investigate controls over the spatial distribution of total alkalinity in the surface global ocean and produce a tracer for $CaCO_3$ cycling. We took surface ocean bottle data for total alkalinity from global databases (GLODAP, CARINA, PACIFICA) and subtracted the effects of several processes: evaporation and precipitation, river discharge, and nutrient uptake and remineralization. The remaining variation in alkalinity exhibits a robust and coherent pattern including features of large amplitude and spatial extent. Most notably, the residual variation in alkalinity is more or less constant across low latitudes of the global ocean but shows a strong poleward increase. There are differences of ~110 $\mu$mol kg$^{-1}$ and ~85 $\mu$mol kg$^{-1}$ between low latitudes and the Southern Ocean and the subarctic North Pacific, respectively, but, in contrast, little increase in the high-latitude North Atlantic. This global pattern is most likely due to production and export of $CaCO_3$ and to physical resupply of alkalinity from deep waters. The use of river corrections highlights the large errors that are produced, particularly in the Bay of Bengal and the North Atlantic, if alkalinity normalization assumes all low salinities to be caused by rainfall. The residual alkalinity data can be used as a tracer to indicate where in the world's ocean most $CaCO_3$ export from the surface layer takes place, and of future changes in calcification, for instance due to ocean acidification.

© 2015 Published by Elsevier B.V.

## 1. Introduction

Total alkalinity, afterwards referred to as alkalinity (*Alk*), is a measure of the acid neutralization capacity of seawater, or, more technically, the excess of proton acceptors over proton donors compared to a zero level of protons at a pH of approximately 4.3. It is measured by the stepwise addition of hydrochloric acid to determine the equivalence points of the titration curve (Dickson, 1981, 2010; Gran, 1952). Total alkalinity can be written as:

$$Alk = \left[HCO_3^-\right] + 2\left[CO_3^{2-}\right] + \left[B(OH)_4^-\right] + \left[OH^-\right] + \left[HPO_4^{2-}\right] + 2\left[PO_4^{3-}\right] \\ + \left[H_3SiO_4^-\right] + \left[NH_3\right] + \left[HS^-\right] - \left[H^+\right] - \left[HSO_4^-\right] - \left[HF\right] - \left[H_3PO_4\right] \\ - \left[HNO_2\right].$$

(1)

Measurements of two of the seawater carbonate system variables (i.e., dissolved inorganic carbon (DIC), alkalinity, pH or the partial pressure of carbon dioxide ($pCO_2$)), in combination with observations of temperature, salinity, silicate and phosphate concentrations, are sufficient to determine the entirety of the carbonate system. The measurement of alkalinity is particularly useful because it is conservative with respect to water mass mixing. Alkalinity is also independent of changes in temperature and pressure, unlike $pCO_2$, pH, and concentrations of individual chemical species (e.g. carbonate and bicarbonate) of the seawater carbonate system (Dyrssen and Sillén, 1967; Wolf-Gladrow et al., 2007).

The sea surface distribution of alkalinity is affected by several processes. These include: (1) changes in seawater dilution caused by evaporation and precipitation (Millero et al., 1998b); (2) riverine inputs of alkalinity (Cai et al., 2010; Friis et al., 2003); (3) production and export of $CaCO_3$; (4) consumption or regeneration of nutrients from primary production or respiration, respectively (Brewer and Goldman, 1976; Millero et al., 1998b; Wolf-Gladrow et al., 2007), and; (5) ventilation and upwelling of subsurface waters with high alkalinity as a result of dissolution of calcium carbonate ($CaCO_3$) (Lee et al., 2006). The inorganic carbon pump is a fundamental component of the marine carbon cycle (e.g., Hain et al., 2010; Holligan and Robertson, 1996; Kwon et al., 2009), and may be important for sequestering organic carbon through ballasting organic matter to the deep ocean (Armstrong et al., 2002; Barker et al., 2003; Klaas and Archer, 2002). However, the magnitude of the ocean particulate $CaCO_3$ export flux is poorly known; it is

* Corresponding author.
 E-mail address: claudia.fry@noc.soton.ac.uk (C.H. Fry).

currently estimated only within a large range (0.4–1.8 Pg PIC yr$^{-1}$; Berelson et al., 2007) and its spatial distribution is also poorly constrained. For instance, whereas satellite-based determinations of surface $CaCO_3$ concentration lead to predictions of higher calcification rates at high latitudes than at low latitudes (Balch et al., 2005), fluxes of $CaCO_3$ into sediment traps (Berelson et al., 2007) and geochemical calculations (Sarmiento et al., 2002) point to most $CaCO_3$ export occurring at low latitudes.

In this study we combined potential alkalinity (Brewer et al., 1975; Sarmiento et al., 2002) with procedures for appropriately cancelling river impacts; we subtracted all of the major processes affecting alkalinity except for (a) alkalinity removal due to formation and export of $CaCO_3$, and (b) alkalinity resupply through the upwards transport of $CaCO_3$ dissolution products from the ocean interior, hereafter jointly referred to as $CaCO_3$ cycling. Our analyses showed the large impacts of rivers on alkalinity in specific ocean regions, particularly the Bay of Bengal and the North Atlantic Ocean. The surface alkalinity data, when adjusted to take this into account, reveal greatly elevated values in the Southern Ocean and North Pacific, with well-defined gradients separating these polar regions from the rest of the ocean, which is characterized by near constant values across low latitudes. We argue that this distinct spatial pattern is consistent with its being caused by the ocean's internal $CaCO_3$ cycle, and hence that the adjusted alkalinity can be used as a tracer of $CaCO_3$ cycling.

## 2. Methods

### 2.1. Seawater $CO_2$-carbonate chemistry data

Salinity, alkalinity, and nitrate data were downloaded from the GLODAP, CARINA and PACIFICA databases (http://cdiac.ornl.gov/oceans/glodap/, http://cdiac.ornl.gov/oceans/CARINA/, http://cdiac.ornl.gov/oceans/PACIFICA/). These databases were synthesized from data collected during various scientific programmes since the 1980s including: (1) the Geochemical Ocean Sections Study (GEOSECS); (2) the World Ocean Circulation Experiment (WOCE); (3) the Joint Global Ocean Flux Study (JGOFS), and; (4) the Ocean and Atmosphere Carbon Exchange Study (OACES). During synthesis of each database, the data were subjected to rigorous quality control procedures. First, data flags were used to indicate the quality of the individual measurements in the cruise. Then, the data from different cruises were compared using the assumption that deep values have low spatial and temporal variability, and therefore that adjacent data points from different cruises should have similar values. Data with a lower than acceptable quality were removed and small biases in cruises adjusted (Key et al., 2004, 2010; Millero et al., 1998a; http://cdiac.ornl.gov/oceans/PACIFICA/). For this study, we used only bottle data rather than any gridded products. The surface ocean was defined as shallower than 30 m at latitudes greater than 30°, and shallower than 20 m at latitudes less than 30°, as in previous studies (Lee et al., 2006). We included only open ocean data (seafloor depth > 200 m) in our analysis. Data from the Arctic and Mediterranean seas were excluded. Thus this study excluded shelf seas, shallow coastal seas, and enclosed seas.

### 2.2. Analysis of process contributions

Controls on surface alkalinity were analyzed using in-situ alkalinity data together with associated hydrographic properties. The impacts of various processes on the spatial distribution of alkalinity in the surface ocean were calculated from related variables. The effects of freshwater fluxes (evaporation, precipitation, river discharge) were quantified based on salinity, and biological fluxes of nutrients calculated using nitrate data.

Following the subtraction of each major process that affects alkalinity, the overall distribution of alkalinity was recalculated and reanalyzed to assess whether it had become more coherent (i.e., less scatter among

nearby observations). For each basin, the data were binned by 5° latitude, and the mean and standard deviation of each bin was calculated. To create a dimensionless statistical variable, the value of which could be compared to other hydrographic variables, the mean standard deviation for each basin was divided by the range of the bin means for that basin. The same statistical approach was undertaken for nitrate, phosphate, and silicate. As an example, for nitrate in the Atlantic, the metric for the average spread of the data cloud is calculated as:

$$M_{NO_3,ATL} = \frac{\left(\frac{1}{36}\sum_{i=1}^{i=36} \sigma\left(NO_{3i}^{ATL}\right)\right)}{\left(\max\left(NO_{3i}^{ATL}\right) - \min\left(NO_{3i}^{ATL}\right)\right)} \quad (2)$$

where $\overline{NO_{3i}^{ATL}}$ and $\sigma(NO_{3i}^{ATL})$ are the mean and standard deviation of the nitrate values, respectively, in the $i$'th Atlantic bin.

After subtraction of all processes except the $CaCO_3$ cycle, the final surface distribution of alkalinity was assessed as a tracer of $CaCO_3$ cycling.

## 3. Results

### 3.1. Evaporation and precipitation

Fig. 1a, b and c shows the measured surface ocean alkalinity distributions in the Atlantic, Indian and Pacific basins as a function of latitude, with colours indicating salinity. The relative mean standard deviations of the 5° bins are shown in Table 1. For all three basins, the most obvious features of the datasets are the local maxima of alkalinity around 30°N and 20°S, which correspond to the centres of the subtropical gyres. These peaks contrast with much lower values (up to 400 μmol kg$^{-1}$ lower) near the equator and in the polar ocean regions.

The consistent elevation of alkalinity in the subtropical gyres is caused principally by the hydrological cycle driving substantial excess evaporation over precipitation in these regions. Net evaporation concentrates substances dissolved in seawater, as freshwater is lost to the atmosphere and solutes are left behind. Conversely, net precipitation dilutes seawater, as relatively pure water is added. Because alkalinity is a weighted sum of different dissolved constituents (Eq. (1)), its concentration rises and falls proportionally with salinity.

Variations in salinity are used to calculate the balance between the effects of evaporation and those of precipitation. Fig. 2a shows alkalinity plotted against salinity in the global surface ocean. Pearson's correlation coefficients (r) were 0.94 in the Atlantic Ocean, 0.87 in the Indian Ocean, 0.92 in the Pacific Ocean, and 0.94 when data from all the oceans were combined. These strong correlations are consistent with evaporation and precipitation being responsible for most of the variation in alkalinity.

The effects of evaporation and precipitation can be removed from alkalinity by converting each alkalinity measurement, $Alk_m$, to its expected value at a salinity ($S$) of 35, i.e. by normalizing each value to a salinity of 35 (Postma, 1964; Millero et al., 1998b):

$$Alk_1 = \frac{Alk_m}{S} \times 35. \quad (3)$$

Fig. 2b shows that the major correlation between salinity and alkalinity, especially at high salinities, is removed using Eq. (3). Eq. (3) successfully negates the effect of the hydrological cycle, eliminating the elevated alkalinity of the subtropical gyres and the local minima of alkalinity along the equator, thereby resulting in fairly constant low-latitude surface $Alk_1$ (Fig. 1d, e and f). As can be seen in Table 1, the variability of alkalinity relative to its overall range is reduced in all three basins following removal of evaporation and precipitation effects.