

Analysis of global surface ocean alkalinity to determine controlling processes



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

Article history:

Received 4 April 2014

Received in revised form 29 April 2015

Accepted 7 May 2015

Available online 13 May 2015

Keywords:

Alkalinity

Calcium carbonate

Biogeochemical cycles

Tracers

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 $\sim 110 \mu\text{mol kg}^{-1}$ and $\sim 85 \mu\text{mol kg}^{-1}$ 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 step-wise addition of hydrochloric acid to determine the equivalence points of the titration curve (Dickson, 1981, 2010; Gran, 1952). Total alkalinity can be written as:

$$\begin{aligned} Alk = & [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B}(\text{OH})_4^-] + [\text{OH}^-] + [\text{HPO}_4^{2-}] + 2[\text{PO}_4^{3-}] \\ & + [\text{H}_3\text{SiO}_4^-] + [\text{NH}_3] + [\text{HS}^-] - [\text{H}^+] - [\text{HSO}_4^-] - [\text{HF}] - [\text{H}_3\text{PO}_4] \\ & - [\text{HNO}_2]. \end{aligned} \quad (1)$$

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 CaCO₃ concentration lead to predictions of higher calcification rates at high latitudes than at low latitudes (Balch et al., 2005), fluxes of CaCO₃ into sediment traps (Berelson et al., 2007) and geochemical calculations (Sarmiento et al., 2002) point to most CaCO₃ 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 CaCO₃, and (b) alkalinity resupply through the upwards transport of CaCO₃ dissolution products from the ocean interior, hereafter jointly referred to as CaCO₃ 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 CaCO₃ cycle, and hence that the adjusted alkalinity can be used as a tracer of CaCO₃ cycling.

2. Methods

2.1. Seawater CO₂-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 (sea-floor 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:

$$M_{\text{NO}_3, \text{ATL}} = \frac{\left(\frac{1}{36} \sum_{i=1}^{i=36} \sigma(\text{NO}_{3i}^{\text{ATL}}) \right)}{\left(\max(\overline{\text{NO}_{3i}^{\text{ATL}}}) - \min(\overline{\text{NO}_{3i}^{\text{ATL}}}) \right)} \quad (2)$$

where $\overline{\text{NO}_{3i}^{\text{ATL}}}$ and $\sigma(\text{NO}_{3i}^{\text{ATL}})$ are the mean and standard deviation of the nitrate values, respectively, in the i 'th Atlantic bin.

After subtraction of all processes except the CaCO₃ cycle, the final surface distribution of alkalinity was assessed as a tracer of CaCO₃ 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.

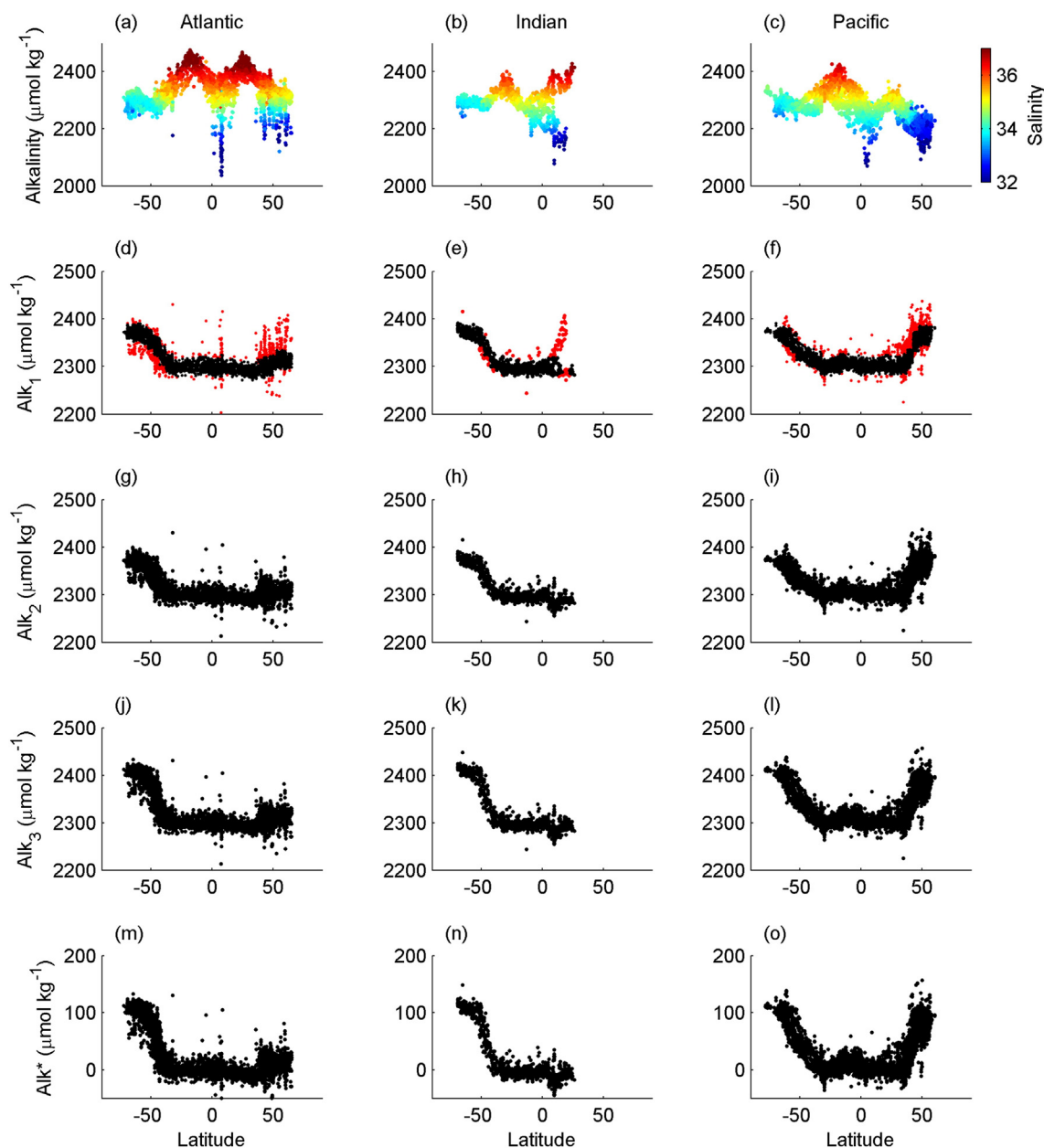


Fig. 1. The distribution of alkalinity ($\mu\text{mol kg}^{-1}$) and normalized alkalinity ($\mu\text{mol kg}^{-1}$) in each ocean basin. a, b, and c show the observed alkalinity with the colours indicating the salinity from 32 to 37. d, e, and f show salinity normalized alkalinity (Alk_1) with red points indicating values more than $20 \mu\text{mol kg}^{-1}$ from the 5° of latitude running mean. g, h and i are Alk_2 , where rivers are included for each basin. j, k, and l show Alk_3 , where the biological uptake of nutrients is also included, for each basin. m, n and o show Alk^* . Note the different y-axis scales on the first row of plots. (For interpretation of the references to colour in this figure, the reader is referred to the web version of this article.)

3.2. Riverine input

Although salinity normalization reduces the spatial variability in alkalinity in the subtropics, many features still remain (Fig. 1d, e and f).

For instance, in the north Indian Ocean there are two different regimes of alkalinity at a similar latitude: the Bay of Bengal is characterized by lower observed alkalinity and salinity, but by a higher normalized alkalinity than the Arabian Sea. There is also a significant high anomaly in

Table 1
Variability in alkalinity and nutrients^a.

	Alkalinity				Nutrients		
	Initial	After correction			Nitrate	Phosphate	Silicate
		Evaporation precipitation	Riverine input	Biological growth and remineralization			
Atlantic	0.17	0.14	0.13	0.095	0.064	0.077	0.067
Indian	0.11	0.095	0.080	0.071	0.066	0.086	0.060
Pacific	0.17	0.14	0.14	0.11	0.097	0.10	0.065

^a Calculated as the average of the standard deviations in the 5° latitude bins, divided by the range in the mean values of the 5° latitude bins. Calculations are made for each ocean basin after each cumulative stage has been taken into account, and for each macronutrient.

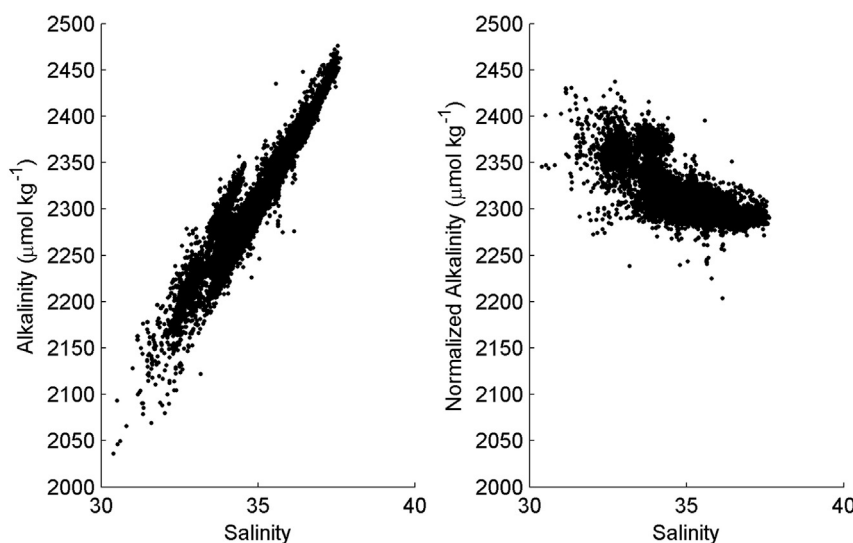


Fig. 2. Salinity versus (a) alkalinity ($\mu\text{mol kg}^{-1}$) and (b) normalized alkalinity (Alk_1 , $\mu\text{mol kg}^{-1}$) in the global surface ocean.

normalized alkalinity at 8°N in the Atlantic Ocean, and several high anomalous groups between 40°N and 60°N in the North Atlantic. In both oceans these areas also correspond to low observed salinity (compare Fig. 1a and Fig. 1d, and Fig. 1b and Fig. 1e; salinity-normalized alkalinity values that are more than $20 \mu\text{mol kg}^{-1}$ from the 5° latitude running mean are indicated in red).

Low salinity is not always produced by rainfall, but can also be produced by sea-ice melt or by inputs of river water. In non-polar waters, the obvious likely cause of the overcorrection from the salinity-normalization is therefore river input. Based on a global analysis of volume of river water received, the ocean areas most likely to be affected are the Arctic Ocean, the Bay of Bengal, the Labrador Sea, the Amazon River and Congo River plumes in the Atlantic, and the South China Sea (Kang et al., 2013).

Friis et al. (2003) found that misleading results are produced if Eq. (3) is used to normalize alkalinity to salinity in ocean regions receiving river outflows. Eq. (3) assumes that freshwater discharged by rivers (i.e., zero salinity) also has zero alkalinity, which is not the case since many rivers have substantial concentrations of alkalinity, in particular those draining limestone catchments (Cai et al., 2010). In marginal seas, the y-intercept of the relationship between alkalinity and salinity usually (although not always, see Jiang et al., 2014) corresponds to the alkalinity of the river end member, Alk_r , because, assuming conservative mixing, this is the value of alkalinity when the salinity is negligible (river water). Following Friis et al. (2003), we used Eq. (4) to account for river input:

$$Alk_2 = \frac{Alk_m - Alk_r}{S} \times 35 + Alk_r. \quad (4)$$

The peak at 8°N in the Atlantic basin is close to the South American continent; therefore, it is likely that these data have been influenced by the Amazon River, and examination of the geographical locations of the anomalous points confirms that they lie in the general area of the Amazon outflow plume. The water from the mouth of the Amazon River has an Alk_r value of around $300 \mu\text{mol kg}^{-1}$ (Cooley et al., 2007; Cooley and Yager, 2006). When the salinity normalization by Friis et al. (2003) (Eq. (4), with $Alk_r = 300 \mu\text{mol kg}^{-1}$) is applied for the region between the latitudes of 5 and 10°N and west of 45°W in the Atlantic basin, the anomalous peak at 8°N is eliminated (Fig. 1g versus Fig. 1d).

Fig. 3 shows that the anomalously high normalized alkalinity values in the region between 40°N and 60°N in Fig. 1a are geographically

situated close to the Labrador coast. Millero et al. (1998b) also found an anomalous area in salinity-normalized alkalinity in the vicinity of the Labrador Sea. Cai et al. (2010) suggested that the Labrador Current is the source of the anomalous alkalinity rather than local runoff. This implies that the intercept of the salinity-alkalinity relationship will not agree with the alkalinity for local continental runoff. The y-intercept of the Labrador Current, Alk_r , equals $1124 \mu\text{mol kg}^{-1}$, which is close to the composite of the runoff from the six largest Arctic rivers of approximately $1100 \mu\text{mol kg}^{-1}$ (Cooper et al., 2008). A revised alkalinity was calculated for the Atlantic Ocean (Fig. 1g) where an $Alk_r = 300 \mu\text{mol kg}^{-1}$ was used for the region between 5°N and 10°N and west of 45°W to correct for the Amazon River plume, and $Alk_r = 1100 \mu\text{mol kg}^{-1}$ in the Labrador Sea inflow area (defined as north of 40°N and west of 30°W). Comparing Fig. 1g to d, the Atlantic Ocean has fewer anomalously high points and a lower standard deviation (Table 1). However, some of the points in the Labrador Current are now lower than the mean and appear to have been overcorrected; this is most likely due to the presence of anomalous surface water in the area, of unknown origin, which has previously been found to have a much lower Alk_r of $273 \mu\text{mol kg}^{-1}$ (Cai et al., 2010).

Fig. 3 also shows that the high salinity normalized alkalinity values in Fig. 1e come from the Bay of Bengal. The mean measured alkalinity in the outflow of the Ganges-Brahmaputra is $1106 \mu\text{mol kg}^{-1}$ (Galy and France-Lanord, 1999). Using this as the value of Alk_r in the Bay of Bengal area (defined as the part of the Indian Ocean north of 5°N and between 80°E and 94°E) led to an overcorrection of the higher branch in the north Indian Ocean (Fig. 4). When river alkalinity based on modelling of annual river runoff and basin lithology and weathering ($Alk_r = 840 \mu\text{mol kg}^{-1}$; Amiotte Suchet et al., 2003) was used instead of direct measurements, the anomaly in the north Indian Ocean was successfully corrected (Fig. 1h). The Ganges-Brahmaputra alkalinity (Bates et al., 2006) and water (Kang et al., 2013) fluxes vary seasonally; the differences between modelled and observed Alk_r may therefore be down to seasonal differences.

After removing the salinity normalization error caused by large river inputs (summarized in Table 2), the remaining alkalinity distribution is as shown in Fig. 1g, h, i. The standard deviations of those basins where changes were made are improved (lower), as shown in Table 1.

3.3. Nutrient uptake and remineralization

Biological consumption and production of nitrate cause an equivalent change in alkalinity (Brewer and Goldman, 1976; Goldman and

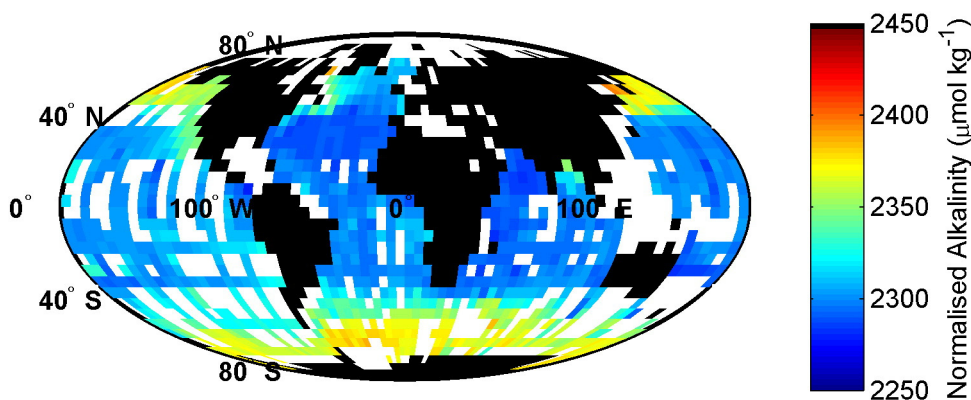


Fig. 3. Salinity-normalized alkalinity (Alk_1 , $\mu\text{mol kg}^{-1}$) gridded to 5° latitude and longitude in the surface ocean.

Brewer, 1980) despite the fact that nitrate does not appear in the formal definition of alkalinity (Eq. (1)). This is because nitrate consumption/production is stoichiometrically tied to the removal/addition of nitric acid, and the H^+ removed/added does affect alkalinity. A reduction in nitrate concentration has to be matched with an increase in alkalinity of the same magnitude in order to maintain the balance of charge in the water. Therefore, nitrate consumption and denitrification increase alkalinity, and nitrate generation (nitrification) following remineralization decreases alkalinity. Other species such as sulphate and phosphate have similar effects on alkalinity (Wolf-Gladrow et al., 2007).

The alkalinity changes arising from the biological cycling of nitrate are often accounted for in the concept of potential alkalinity, $pAlk$ (e.g. Brewer et al., 1975; Sarmiento et al., 2002), where the sum of the nitrate and alkalinity concentrations is normalized to a salinity of 35. Wolf-Gladrow et al. (2007) calculated changes in alkalinity from primary productivity, taking into account the proportional uptake of other ions such as phosphate and sulphate. They suggested that the impact of phytoplankton growth on alkalinity should be calculated by multiplying changes in the nitrate ion concentration, $[\text{NO}_3^-]$, by a factor of 1.36. Hence:

$$pAlk = \frac{Alk_m + 1.36 \times \text{NO}_3^-}{S} \times 35. \quad (5)$$

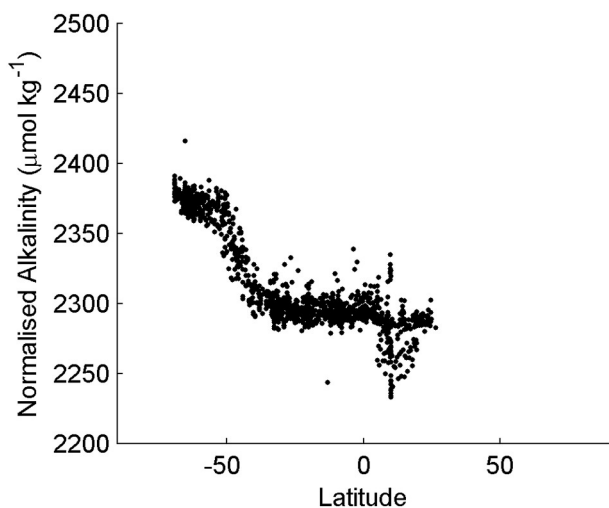


Fig. 4. Indian Ocean alkalinity ($\mu\text{mol kg}^{-1}$) as a function of latitude following salinity-normalization using Eq. (4) with $Alk_r = 1107 \mu\text{mol kg}^{-1}$ in the Bay of Bengal area (north of 5°N and between 80°E and 94°E).

Fig. 1j, k, and l show the resulting patterns in alkalinity, after variations in nutrient concentration have also been taken into account, using:

$$Alk_3 = \frac{Alk_m - Alk_r + 1.36 \times \text{NO}_3^-}{S} \times 35 + Alk_r. \quad (6)$$

Incorporation of the effects of creation and remineralization of biological matter increases the average offset between low latitudes and high latitudes from $\sim 75 \mu\text{mol kg}^{-1}$ to $\sim 100 \mu\text{mol kg}^{-1}$. This is because the Southern Ocean and subarctic North Pacific are both regions of the global ocean with high surface nitrate concentrations.

3.4. Pattern in the residual alkalinity

After excluding the effects of nutrients on alkalinity, there is a fairly uniform alkalinity of $\sim 2300 \mu\text{mol kg}^{-1}$ in the low-latitude surface oceans (30°N – 30°S). Table 1 shows that with every additional step the width of the data cloud relative to the overall range of the data has decreased. This suggests that the effects of processes causing variation have been successfully removed. The remaining variation is comparable to that of the major nutrients (Table 1). This would be expected if Alk_3 and the nutrients are mainly controlled by uptake to form new phytoplankton, and returned through exchange with deep water following export and remineralization.

To examine the remaining large-scale spatial pattern in the distribution of surface alkalinity, we define the new tracer Alk^* to have a low latitude concentration of $\sim 0 \mu\text{mol kg}^{-1}$ (i.e. $Alk^* = Alk_3 - 2300 \mu\text{mol kg}^{-1}$). Thus, the value of Alk^* corresponds to the “excess alkalinity” compared to the tropical and subtropical surface ocean. It can be seen (Fig. 1m, n and o) that Alk^* values in the high-latitude regions of the North Pacific and Southern Ocean are strongly elevated by $\sim 85 \mu\text{mol kg}^{-1}$ (north of 55°N) and $\sim 110 \mu\text{mol kg}^{-1}$ (south of 75°S), respectively. Interestingly, there is no correspondingly large elevation of Alk^* in the high-latitude North Atlantic: the average Alk^* value at 55°N in the Atlantic is only $24 \mu\text{mol kg}^{-1}$. Notably, the low-latitude to polar ocean increases in alkalinity are somewhat weaker when nutrient cycling effects are not included; the same overall geographic distribution is obtained but with smaller magnitude differences (e.g., compare Alk_2 in Fig. 1g, h, and i to Alk_3 in Fig. 1j, k, and l).

4. Discussion

4.1. Comparison to other approaches

In this paper we have derived a tracer for CaCO_3 cycling in the surface ocean based on observed alkalinity and removal of other influences, including: (1) freshwater evaporation and precipitation; (2) inputs of

Table 2
River alkalinity (Alk_r) corrections.

Area name	Ocean basin	Area boundaries	Alk_r ($\mu\text{mol kg}^{-1}$)
Amazon plume	Atlantic	$5^\circ\text{N} < \text{Latitude} < 10^\circ\text{N}$, $\text{Longitude} < -45^\circ\text{E}$	300
Labrador Sea	Atlantic	$\text{Latitude} > 40^\circ\text{N}$, $\text{Longitude} < -30^\circ\text{E}$	1100
Bay of Bengal	Indian	$\text{Latitude} > 5^\circ\text{N}$, $80^\circ\text{E} < \text{Longitude} < 94^\circ\text{E}$	840

river water containing alkalinity at negligible salinity; and (3) biological cycling of nutrients.

The procedure we employed is an extension of the potential alkalinity concept (Brewer et al., 1975; Rubin and Key, 2002; Sarmiento et al., 2002; Wolf-Gladrow et al., 2007); however, it also includes a correction for the influence of high-alkalinity rivers (Cai et al., 2010; Friis et al., 2003). Our analysis shows that high-alkalinity rivers can influence large ocean areas (e.g. Fig. 1g versus Fig. 1d). We show that the North Atlantic Ocean and the Bay of Bengal are strongly influenced by river derived alkalinity inputs. We expect that with incorporation of more marginal regions (Key et al., 2010), such as the South China Sea (Kang et al., 2013), and more seasonal data, river alkalinity will become an increasingly important part of alkalinity process analysis. Our Alk^* tracer for surface waters also bears some resemblance to that of 'excess' alkalinity (Feely et al., 2002, 2004; Sabine et al., 2002), which was developed to quantify CaCO_3 dissolution rates along isopycnal surfaces. We use Alk^* to constrain surface CaCO_3 cycling (as defined here) as a whole, as opposed to specifically targeting the dissolution of CaCO_3 at depth. This gives a tracer that is similar to nutrient tracers and can be used to investigate biological production in a similar way to that of nutrients.

In this paper we revisit some of the same issues as those of an earlier study (Millero et al., 1998b), which used salinity-normalized alkalinity. Some of the large-scale patterns we find were also noted previously by Millero et al. (1998b), but are now more clearly defined and can be accepted with greater confidence, based on the improved analysis techniques and larger quantity of data used in this study.

4.2. Accounting for the patterns in Alk^*

The surface field of Alk^* is distinct from the actual alkalinity observations (first and last rows of Fig. 1). Eliminating the effects of the hydrological cycle, rivers and nutrient cycling reveals coherent basin-scale patterns in Alk^* that are not apparent in Alk_m . We argue that these patterns directly reflect the imprint of the ocean's CaCO_3 cycle, or in other words that the patterns in Alk^* are maintained by the inorganic carbon pump acting against ocean overturning and mixing. As with dissolved nutrients, Alk^* is reduced when and where biological precipitation of CaCO_3 occurs. The CaCO_3 sinks from the mixed layer into the deep ocean, where CaCO_3 undersaturation causes it to dissolve and increase the deep Alk^* concentration. Large-scale ocean circulation brings the deep water back to the surface, producing higher Alk^* concentrations in the polar ocean surface of the Southern Ocean and the North Pacific.

4.3. High Alk^* in high-latitude oceans

In line with previous interpretations (Key et al., 2004; Lee et al., 2006; Millero et al., 1998b; Sabine et al., 2002), we identify the source of increased salinity-normalized alkalinity at high latitudes as supply of excess alkalinity from deep waters. High alkalinity at depth can be transferred to high-latitude surface waters either through upwelling, transfer along isopycnals outcropping at high latitudes, and/or entrainment of deep waters into the mixed layer during deep winter mixing. The individual contribution of these physical processes to high Alk^* in surface waters may vary among distinct regions, and subsurface waters are also expected to contain variable concentrations of excess alkalinity to be brought to the surface in different parts of the world's ocean (see explanation for low North Atlantic Alk^* below). In addition, the strength of these sources may vary seasonally; for example, deep winter mixing

may cause higher Alk^* in an area during winter with subsequent lower levels in summer.

We attribute the relatively low Alk^* values in the subarctic North Atlantic to the low Alk^* values at depth in this region. To illustrate the reason for this exception, we calculated Alk^* along a vertical ocean section from the North Atlantic, through the Southern Ocean and into the North Pacific (Fig. 5). From this interior ocean view of the alkalinity anomaly, it is clear that the high surface Alk^* values of the Southern Ocean and subarctic North Pacific directly correspond to elevated Alk^* in subsurface waters, whereas the low surface Alk^* values of the subarctic North Atlantic are above low Alk^* of the North Atlantic Deep Water (NADW). The difference between the regions can be attributed in part to differences in the ages of the deep waters underlying the various regions. The main source of NADW is surface water that was recently subducted following poleward transport from lower latitudes (e.g., Lozier, 2012). Therefore, the subpolar North Atlantic surface and NADW both inherit a low Alk^* from the Atlantic meridional overturning circulation passing through the low-latitude surface Atlantic, where Alk^* is also low. Because of the small vertical gradient, winter mixing in the high-latitude North Atlantic, although penetrating to considerable depths (hundreds of metres; de Boyer Montégut et al., 2004), produces little increase in surface Alk^* . Alkalinity distributions along similar sections to Fig. 5 have been explained (Pardo et al., 2011; Vázquez-Rodríguez et al., 2012) using the concept of pre-formed alkalinity, which is the alkalinity at the point subducting water loses contact with the atmosphere. As the high-latitude North Atlantic is a deep-water formation region, the low Alk^* determines the pre-formed value, with CaCO_3 dissolution increasing Alk^* as NADW travels southward through the Atlantic Ocean.

The subarctic North Atlantic contrasts with the subarctic North Pacific, where winter mixing, although not reaching to such great depths (up to about 150 m on the eastern side and 250 m on the western side; Ohno et al., 2009), does reach high Alk^* subsurface waters ($50\text{--}200 \mu\text{mol kg}^{-1}$) because of the strong vertical gradients (Fig. 5). In the Southern Ocean the situation is more complicated but there is no formation of deep water from low-latitude surface water, and deep water consequently has high Alk^* (Fig. 5). Furthermore, wind-driven upwelling introduces high Alk^* water to the surface from greater depths than in other parts of the world's ocean (Toggweiler and Samuels, 1995).

4.4. Low Alk^* in low-latitude oceans

To the degree that the global CaCO_3 cycle is near internal balance, the net upwards transport of dissolved Alk^* across the main thermocline must equal the global downwards CaCO_3 rain across the thermocline. Low Alk^* values in the tropical and subtropical surface oceans are therefore understood as resulting from CaCO_3 formation and export leading to removal of Alk^* from surface waters, together with an absence of significant replenishment from deep water. The data show surprisingly similar values in all basins at low latitudes (averages of 2297, 2294 and $2305 \mu\text{mol kg}^{-1}$ between 30°S and 30°N in the Atlantic, Indian and Pacific Oceans, respectively).

4.5. Similarity of residual alkalinity distribution to nutrients

Attributing the Alk^* patterns to CaCO_3 cycling is further supported by the partial resemblance between the latitudinal distributions of Alk^* and those of the nutrients: nitrate, phosphate and silicate (Fig. 6). Concentrations of all are depleted in the subtropical surface ocean due to

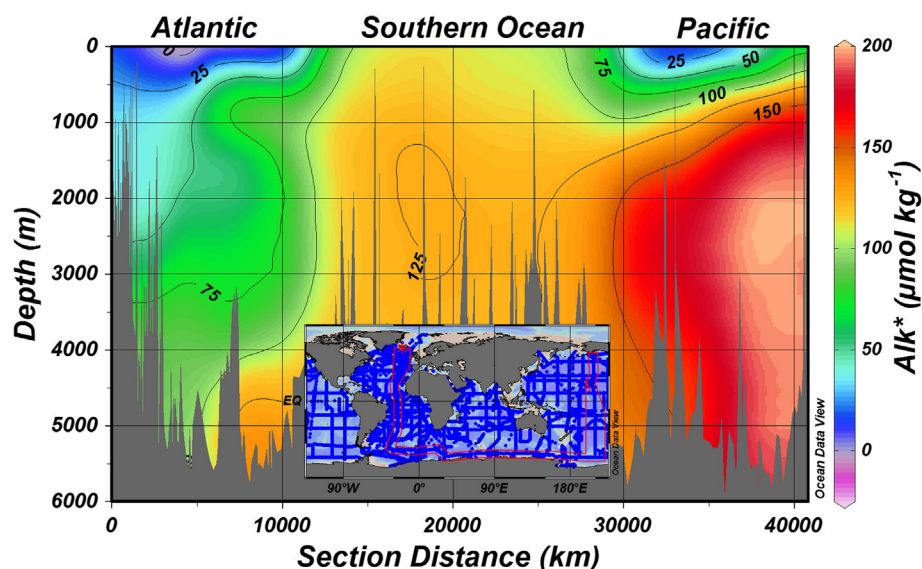


Fig. 5. Normalized alkalinity anomaly ($Alk^* = Alk_3 = 2300, \mu\text{mol kg}^{-1}$) along the GLODAP section illustrated in the insert.

biological use. All four exhibit maxima in concentrations at high latitudes in the Southern Ocean and North Pacific, but a more modest increase in the high-latitude North Atlantic.

There are however some differences. For example, in contrast to nitrate and phosphate, neither silicate nor alkalinity exhibit large increases in concentration in the north Indian Ocean or in the eastern Equatorial Pacific. This may reflect different remineralization depths (nitrate and phosphate are both returned to solution at much shallower depths than silicate from opal rain or alkalinity from CaCO_3 rain; Schlitzer, 2000) and the source of the water. Alternatively, it may be co-occurrence of upwelling and intensive CaCO_3 production, which would not be identified in our tracer. A previous study found salinity-normalized alkalinity to be $\sim 40 \mu\text{mol kg}^{-1}$ higher in upwelled water in the eastern Equatorial Pacific (Millero et al., 1998b).

A second difference is apparent when comparing the latitude at which all four variables decrease to negligible levels when moving northwards away from Antarctica. Concentrations of silicate have declined almost to zero by about 50°S , whereas Alk^* , nitrate, and phosphate are all still significantly elevated at this latitude and it is not until about 40°S that all three decline to near zero (Fig. 6). One explanation of this feature could be the greater competitive success of silicifiers in the Southern Ocean, with diatoms blooming and depleting silicate concentrations further south than other phytoplankton. Therefore, silicate is used up further south than nitrate, phosphate, and Alk^* (Sarmiento et al., 2004). Pronounced yearly blooms of coccolithophores are seen in satellite observations in the region of the subantarctic zone (about 50°S to 40°S) of the Southern Ocean (Iglesias-Rodríguez et al., 2002). This feature has been termed the “Great Calcite Belt” (Balch et al., 2011) and may be responsible for one third of global export of CaCO_3 (Jin et al., 2006). However, in order to identify more confidently where CaCO_3 production and export take place, the Alk^* tracer should ideally be used in conjunction with an ocean circulation model.

Overall, the nutrient-like distribution of Alk^* is consistent with the expected behaviour of a tracer of CaCO_3 production and dissolution.

4.6. Similarity of residual alkalinity to residual calcium

Results from a second and independent method of constraining CaCO_3 cycling can be compared to those from the Alk^* method. The concentration of calcium ions (measurable to a precision of about $\pm 3 \mu\text{mol kg}^{-1}$; Olson and Chen, 1982) is also directly affected by dilution and concentration, production and dissolution of CaCO_3 , and river input of CaCO_3 , but not biological cycling processes affecting alkalinity.

After salinity normalization, the surface ocean has a slightly lower concentration of calcium than at depth, due to the CaCO_3 pump (Milliman et al., 1999). The ratio of Ca^{2+} to salinity has previously been demonstrated as a tracer of CaCO_3 cycling in the South China Sea (Cao and Dai, 2011), and salinity-normalized calcium concentration (Nca) agrees well with salinity-normalized alkalinity as a tracer of CaCO_3 cycling in deep waters of the Sea of Okhotsk (Pavlova et al., 2008). Both Ca-based and Alk -based tracers of CaCO_3 cycling are made less effective in the deep ocean because low-temperature hydrothermal vents are an alternative source of calcium (Chen, 2002; de Villiers, 1998; de Villiers and Nelson, 1999).

If CaCO_3 cycling is the dominant influence over both Alk^* and Nca then we predict the following Nca patterns in surface waters: (1) it should be relatively invariant across low-latitude oceans; (2) it should differ by about $40 \mu\text{mol kg}^{-1}$ (ΔCa from CaCO_3 formation/dissolution = $0.5 * \Delta Alk^*$) between low and high latitudes in the North Pacific; (3) it should be about $55 \mu\text{mol kg}^{-1}$ higher in the high-latitude Southern Ocean than in low-latitude regions; and (4) it should not vary greatly between low and high latitudes in the North Atlantic.

Relatively few calcium data currently exist with which to test these predictions, and what does exist is only partly compatible with them. Chen (2002) reported calcium concentrations along 150°W in the North Pacific from 8 to 55°N : the highest Nca values along the transect were observed at the highest latitudes (north of 45°N); however, an unexpectedly high degree of low-latitude variability ($>20 \mu\text{mol kg}^{-1}$) is also apparent in the data. Nca values from the Weddell Sea are approximately $70 \mu\text{mol kg}^{-1}$ higher than values from the low-latitude Pacific Ocean (Chen, 2002). Tsunogai et al. (1973) found a poleward increase of the calcium to chlorinity ratio along 170°W .

4.7. Some uncertainties and how they might be reduced in future work

Here, we consider sources of uncertainty in Alk^* and, where applicable, how they might be minimized in future work. The geographical differences in Alk^* are large compared to the accuracy of alkalinity measurements ($\sim 3 \mu\text{mol kg}^{-1}$, Dickson et al., 2003), which can thus be ruled out as a cause. There is some bias in the collection of data, with surveys in high latitude regions occurring more frequently during summer months because of weather considerations (Key et al., 2004). Because alkalinity resupply to the surface by vertical mixing changes with season, including more wintertime data could increase high-latitude Alk^* values, thereby further increasing the contrast to the low-latitude surface that has no seasonal bias.

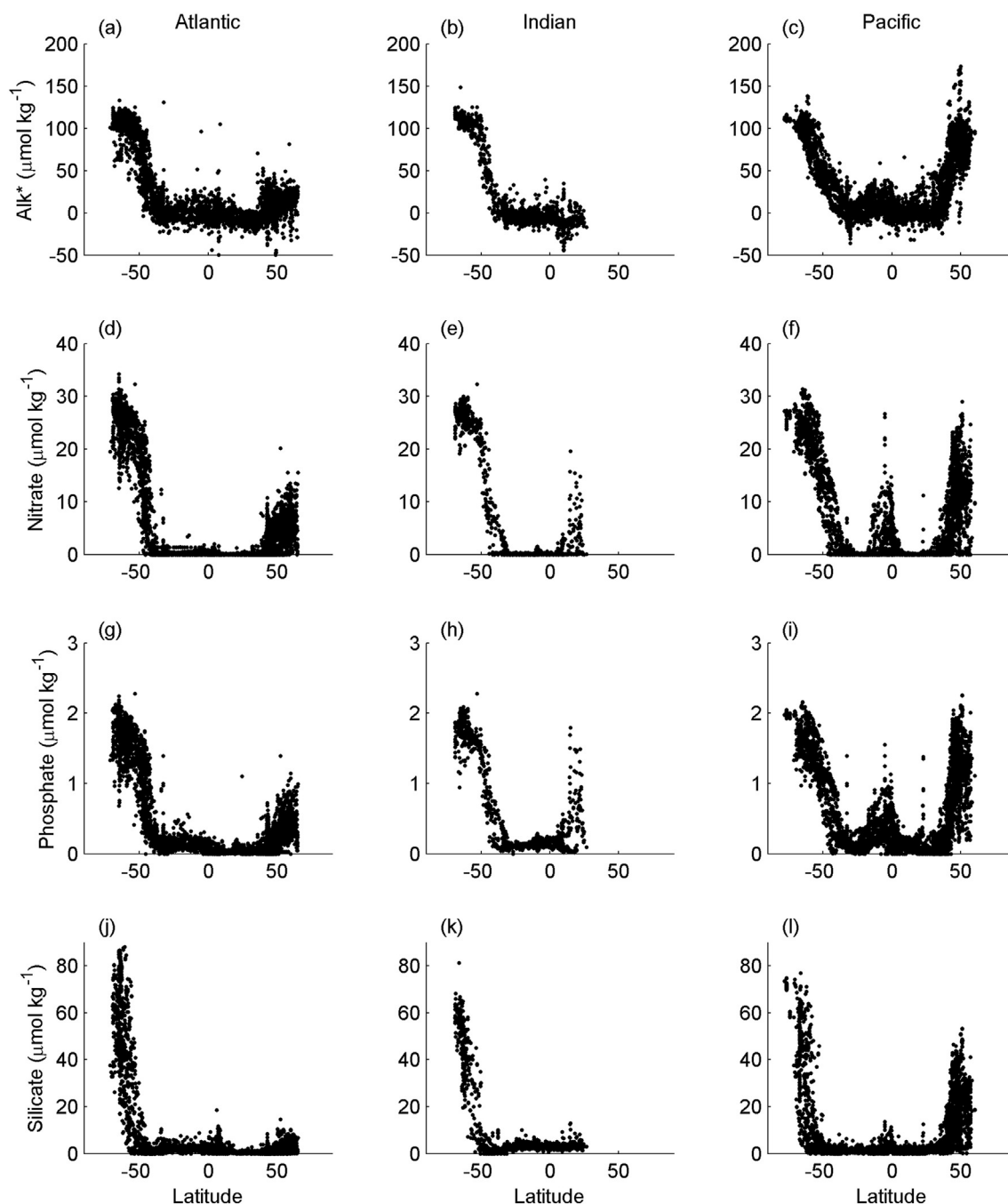


Fig. 6. Surface distribution of Alk^* $\mu\text{mol kg}^{-1}$ (a, b, c), nitrate $\mu\text{mol kg}^{-1}$ (d, e, f), phosphate $\mu\text{mol kg}^{-1}$ (g, h, i), silicate $\mu\text{mol kg}^{-1}$ (j, k, l) in each ocean basin from the GLODAP, CARINA and PACIFICA databases.

Some local river flows need to be considered when using open ocean data (Cai et al., 2010), as demonstrated here by the wide-scale influences of river derived alkalinity inputs to the Bay of Bengal and Atlantic Ocean. Kang et al. (2013) identified the South China Sea as another area affected by river inputs of alkalinity; however, we made no adjustment because of a lack of seawater data for the region. When using river alkalinity data to correct for river influences in offshore regions, it should be kept in mind that differences in riverine input alkalinity can be caused by non-conservative estuarine changes to fluxes such as from anaerobic processes occurring in the river delta (Hu and Cai, 2011), as has been recorded in river systems (Cai and Wang, 1998; Wong, 1979). Also, simply fitting a line to alkalinity–salinity data is not always a reliable method of determining the river end-member alkalinity (Jiang et al., 2014).

Further research is required on alkalinity in the outflows of major rivers and the penetration of their effects into the open ocean.

CaCO_3 cycling is the dominant influence on the residual alkalinity, but other processes will also have smaller effects. Some second-order or locally important processes for alkalinity have not been calculated and removed from Alk^* . These include anaerobic remineralization processes (denitrification and sulphate reduction could affect the surface waters in coastal regions), formation and destruction of sea-ice and ikaite (e.g. Rysgaard et al., 2012, 2013), organic alkalinity (Bradshaw and Brewer, 1988), and nitrogen-fixation (Wolf-Gladrow et al., 2007). Development of techniques for the removal of these influences would further improve Alk^* . Many of these processes, such as the impact of organic alkalinity, the formation and destruction of sea-ice, and anaerobic

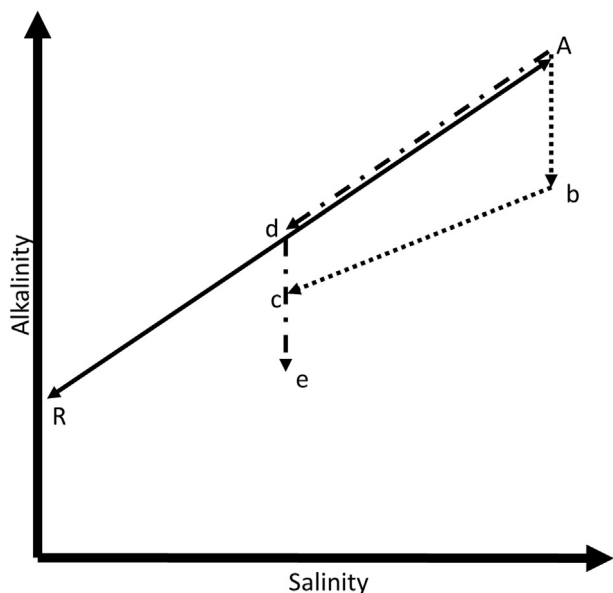


Fig. 7. The mixing relationship between salinity and alkalinity when calcification also takes place. When an ocean body (A) mixes with river water (R) and calcification occurs, the final alkalinity–salinity relationship will depend on whether the calcification occurred before (A to b to c) or after (A to d to e) mixing.

reminereralization are of greater importance in areas that are not included in this study, such as in coastal regions and the Arctic Ocean.

There is a limit to the accuracy with which the magnitude of calcification can be determined in river affected ocean from an alkalinity-based tracer. This is because the order in which calcification and mixing take place (which is not usually known) affects the resulting change in alkalinity (Jiang et al., 2014). This can be important when two bodies of water mix, for example when seawater mixes with river water. If calcification occurs (A to b in Fig. 7) before the mixing with river water (b towards R in Fig. 7), then the final alkalinity value (c in Fig. 7) differs from that when mixing occurs before calcification (A to d to e in Fig. 7). Eq. (6) for Alk^* assumes calcification occurs before mixing and so if they occur in the opposite order then the inferred amount of calcification would be inaccurate. But, from calculations on our dataset when we assumed a reversed order, the difference is within the current

measurement error of alkalinity ($<3 \mu\text{mol kg}^{-1}$). In addition, Alk^* is not completely conservative because of salinity-normalization. When two water bodies mix, the calculated Alk^* of the mixture is not exactly equal to the weighted average of the source Alk^* values, although the difference is usually small ($<5\%$).

We can quantify the propagated measurement uncertainty in Alk^* from the definition of Alk_3 (Eq. (6)), which in absolute terms has the same uncertainty as Alk^* , and from rules for propagating uncertainties through calculations (Taylor, 1982). The uncertainty in Alk^* values is calculated using Eq. (7) and measurement uncertainties of: alkalinity, ΔAlk_m , $3 \mu\text{mol kg}^{-1}$ (Dickson et al., 2003); salinity, ΔS , 0.0015 (Perkin and Lewis, 1980), and nitrate, ΔNO_3^- , $0.2 \mu\text{mol kg}^{-1}$ (Aminot and Kirkwood, 1995). Errors in river input measurements were not considered as most of the dataset is not affected by the adjustment. The estimated overall uncertainty of Alk^* , ΔAlk^* is $3.02 \mu\text{mol kg}^{-1}$. The uncertainties are thus small compared to the large latitudinal differences in Alk^* .

$$\Delta Alk^* = \frac{35 \times (Alk_m + 1.36 \times \text{NO}_3^-)}{S} \times \sqrt{\left(\frac{\Delta S}{S}\right)^2 + \frac{(\Delta Alk_m)^2 + (1.36 \times \Delta \text{NO}_3^-)^2}{(Alk_m + 1.36 \times \text{NO}_3^-)^2}} \quad (7)$$

4.8. Potential uses of Alk^*

This new tracer of surface CaCO_3 cycling is likely to be useful in a number of ways. The first example is in the calculation of CaCO_3 export fluxes.

Where horizontal and vertical water fluxes are known, they can be combined with Alk^* gradients to estimate the rate of loss of calcium carbonate (export flux) from the mixed layer. Fig. 8 shows the fluxes that affect Alk^* of the low-latitude surface water in the Atlantic. Supply of Alk^* through mixing across the thermocline and equatorial upwelling is assumed negligible as this process does not contribute to the observed surface ocean pattern. Average Alk_3 is $2299 \mu\text{mol kg}^{-1}$ at 30°S ($Alk^*_{S.Atl.} = -1$) and $2289 \mu\text{mol kg}^{-1}$ at 30°N ($Alk^*_{N.Atl.} = -11$) (Fig. 1j). If NADW formation (F_{NADW}) and the surface Ekman water flux from the Southern Ocean (F_{Ekman}) are equal at 18 ± 3 Sverdrups (Talley et al., 2003), then the rate of Alk^* vertical export, Q_{Atl} from the Atlantic Ocean can be calculated as a function of the water flux and

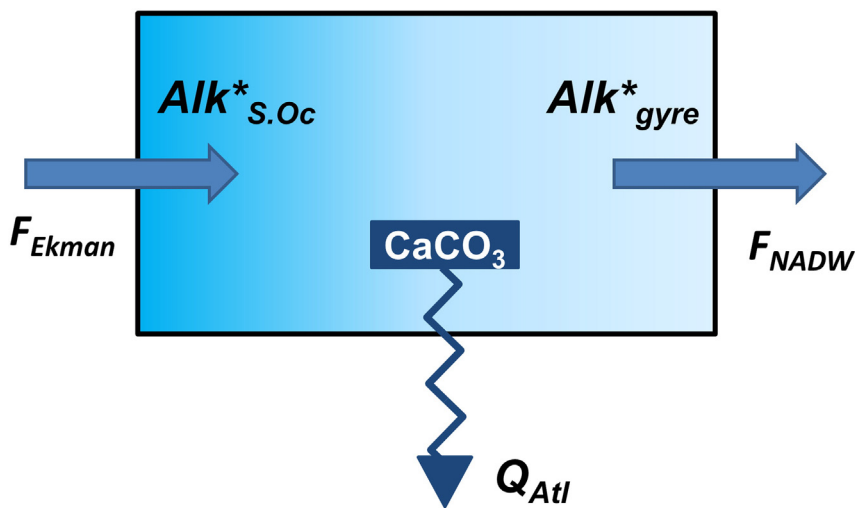


Fig. 8. Representation of Atlantic Basin circulation and fluxes. $Alk^*_{S.Oc}$ and Alk^*_{gyre} are the alkalinity anomalies of the Southern Ocean and Atlantic gyre, respectively. F_{Ekman} is the surface Ekman flux in the Southern Ocean, F_{NADW} the NADW flux and Q_{Atl} is the flux of alkalinity leaving the gyre through CaCO_3 precipitation. Equatorial upwelling and mixing across the thermocline are omitted as they do not contribute to the first order Alk^* pattern.

Table 3

Estimates of annual production of particulate inorganic carbon in the Atlantic Ocean basin.

	Pg PIC yr ⁻¹
Lee (2001)	0.43
Poulton et al. (2006)	0.69 ^a
Berelson et al. (2007)	0.11–0.35
Our estimate	0.03

^a Flux estimate from data collected during northern hemisphere spring (southern hemisphere autumn).

the decline in alkalinity in transit:

$$Q_{Atl} = F_{Ekman} \times Alk^*_{S.Atl} - F_{NADW} \times Alk^*_{N.Atl} \\ = F_{Ekman} \times (Alk^*_{S.Atl} - Alk^*_{N.Atl}). \quad (8)$$

This produces an estimated CaCO₃ export of ~0.03 Pg PIC yr⁻¹ with an uncertainty of ±0.01 based on the uncertainty in the Ekman flux. This value is significantly lower than previous estimates of Atlantic CaCO₃ production (0.11–0.69 Pg PIC yr⁻¹; see Table 3) and an Atlantic-wide estimate of CaCO₃ dissolution in deep water (0.13 Pg PIC yr⁻¹; Chung et al., 2003). Our value suggests that rather little calcification takes place in the upper mixed layer of the Atlantic. Our estimate is of export rather than production but dissolution is probably minor in the supersaturated surface ocean and so the two are probably similar. The discrepancy with other estimates could potentially be reconciled if calcification is primarily taking place in deeper parts of the euphotic zone, i.e. below the surface mixed layer (Poulton et al., 2006) or further south in the Atlantic sector of the Southern Ocean (Fig. 1j). Another explanation is that equatorial upwelling does supply Alk* and it is used too quickly to be seen in the surface concentrations. We suspect that the largest uncertainty in our calculation stems from the assumption that the only flows are NADW and associated net flow through the tropical Atlantic box, which is an oversimplification.

Alk* could also be used to analyze the spatial distribution of CaCO₃ export. Calculation of Alk* on different depth and/or density levels may help resolve the question about where in the oceans most CaCO₃

is produced and exported. In the surface layer at least, the steepest horizontal gradients in Alk* are at mid latitudes of 30°–40° (Fig. 1m, n and o). This concurs with satellite observations of the highest particulate inorganic carbon (PIC; coccoliths) concentrations in surface waters at high latitudes (Balch et al., 2005; Iglesias-Rodríguez et al., 2002; Moore et al., 2012). Likewise, Jin et al. (2006) found high CaCO₃ export at 40° latitude using global nutrient and alkalinity observations and a biogeochemical model; however, the authors also found an equally large peak in export at the equator. A peak in export at the equator would not show up in Alk* if the simultaneous impacts of upwelling and export cancelled each other out. Sediment trap compilations (Berelson et al., 2007) and theoretical calculations (Sarmiento et al., 2002), indicate the highest rain ratios (highest CaCO₃ export) towards the equator; however, there was no peak at mid latitudes.

Alk* could also be used to validate biogeochemical models and improve model quantifications of CaCO₃ fluxes. The broad patterns in Alk* should be reproduced in high-resolution global carbon cycle models if correctly formulated. The degree of agreement with Alk* can be used as a check of the representations of ocean physics and CaCO₃ formation and dissolution. It may also be possible to improve methods for deducing CaCO₃ particle fluxes from ocean alkalinity data, by basing the inversion method on this method for Alk*.

Finally, if ocean acidification leads to large reductions in calcification then an effect on ocean alkalinity may be detectable by 2040 (Ilyina et al., 2009). This may be more accurately determined using Alk* rather than measured alkalinity as the method corrects for changes in the water cycle (Huntington, 2006 and references therein) and productivity (e.g. Behrenfeld et al., 2006; Bopp et al., 2001; Gregg et al., 2003), which are also forecast to change. Time-series are often located close to the coast, because of ease of access, and consequently are frequently affected by river inputs. Alk* is less variable than potential alkalinity in river-affected areas. This is because the standard deviation is reduced by the river correction (Table 2), making long term trends easier to detect (higher signal-to-noise ratio). This is illustrated in a simplistic way (Fig. 9) in an example using data from the area of the Atlantic affected by the Amazon River outflow and an increase of 30 μmol kg⁻¹ by 2040 (Ilyina et al., 2009). Following Ilyina et al. (2009), the trend is

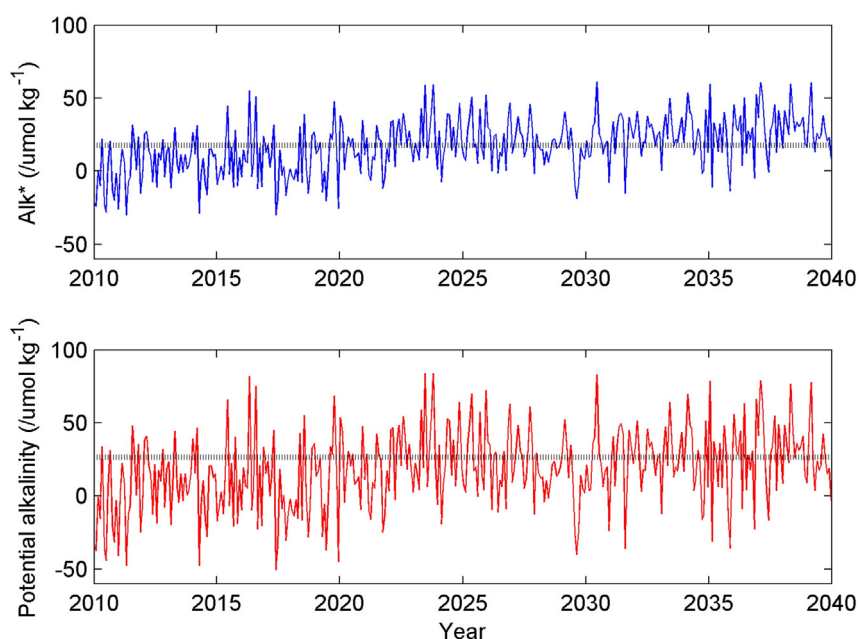


Fig. 9. Modelled Alk* in an area of the ocean affected intermittently by the Amazon River outflow. Alk* is shown both with river adjustment included (top) and without it (bottom). The simulated data was produced using a random number generator to produce random numbers from a normal distribution with a standard deviation (dashed line) of 16.5 μmol kg⁻¹ (top panel) and 25.6 μmol kg⁻¹ (bottom panel). These standard deviations are the standard deviations of the actual Alk* values in the region affected by the Amazon (Table 2), depending on whether adjusted to take account of Amazon alkalinity or not. An alkalinity increase over time of 30 μmol kg⁻¹ from 2010 until 2040 was added to the random numbers to produce the simulated data. Data sampling frequency of 30 days.

deemed to be detected when the magnitude of the change due to the trend exceeds the standard deviation of the data. According to this method (more sophisticated methods would be used in reality), the long-term trend is detectable by 2040 using Alk^* but not until 2060 using potential alkalinity.

5. Conclusions

In this study we derive a tracer for the ocean $CaCO_3$ cycle by subtracting the influences of other processes from the global surface alkalinity data, specifically (a) the hydrological cycle, (b) riverine discharge, and (c) the biological cycling of nutrients. On a regional scale, adjustment for the individual alkalinities of nearby large rivers was found to be particularly important in bringing anomalous values 'into line' in areas such as the tropical Atlantic Ocean, the Bay of Bengal and the Labrador Sea. The coherent geographic pattern revealed by our alkalinity tracer shows a constant value across the low latitudes of all major ocean basins, and well-defined, large magnitude increases of ~85 and ~110 $\mu\text{mol kg}^{-1}$ towards the North Pacific and Southern Ocean respectively. The surface subpolar North Atlantic and North Atlantic Deep Water inherit low residual alkalinity from their source waters in the Atlantic subtropical gyres. Comparisons to nutrient distributions and calcium data strongly suggest that these patterns in the residual alkalinity are caused by $CaCO_3$ cycling, i.e. upwelling mainly at high latitudes of deep water into which $CaCO_3$ has dissolved, and $CaCO_3$ export elsewhere that reduces Alk^* with increasing distance from the centres of upwelling. This residual alkalinity (Alk^*) therefore has considerable potential as a tracer of $CaCO_3$ cycling. This new tracer is likely to have many applications, including in quantification and localization of $CaCO_3$ export.

Acknowledgements

We thank all those who contributed to the collection, analysis, and synthesis of the GLODAP, CARINA, and PACIFICA databases. This study was financially supported by a NERC doctoral training grant to C. H. Fry (NE/K500926/1), and NERC IRF to M. P. Hain (NE/K00901X/1). We thank Dieter Wolf-Gladrow, Kitack Lee, Alex Poulton, Kevin Oliver and Mark Moore for their helpful discussions.

References

- Aminot, A., Kirkwood, D., 1995. Report on the results of the fifth ICES intercomparison exercise for nutrients in sea water. International Council for the Exploration of the Sea, Copenhagen, Denmark.
- Amiotte Suchet, P., Probst, J.-K., Ludwig, W., 2003. Worldwide distribution of continental rock lithology: implications for the atmospheric/soil CO_2 uptake by continental weathering and alkalinity river transport to the oceans. *Global Biogeochem. Cycles* 17 (2), 1038. <http://dx.doi.org/10.1029/2002GB001891>.
- Armstrong, R.A., Lee, C., Hedges, J.L., Honjo, S., Wakeham, S.G., 2002. A new, mechanistic model for organic carbon fluxes in the ocean based on the quantitative association of POC with ballast minerals. *Deep Sea Res. Part II* 49, 219–236. [http://dx.doi.org/10.1016/S0967-0645\(01\)00101-1](http://dx.doi.org/10.1016/S0967-0645(01)00101-1).
- Balch, W.M., Gordon, H.R., Bowler, B.C., Drapeau, D.T., Booth, E.S., 2005. Calcium carbonate measurements in the surface global ocean based on Moderate-Resolution Imaging Spectroradiometer data. *J. Geophys. Res.* 110, C07001. <http://dx.doi.org/10.1029/2004JC002560>.
- Balch, W.M., Drapeau, D.T., Bowler, B.C., Lyczskowski, E., Booth, E.S., Alley, D., 2011. The contribution of coccolithophores to the optical and inorganic carbon budgets during the Southern Ocean Gas Exchange Experiment: new evidence in support of the "Great Calcite Belt" hypothesis. *J. Geophys. Res.* 116, C00F06. <http://dx.doi.org/10.1029/2011JC006941>.
- Barker, S., Higgins, J.A., Elderfield, H., 2003. The future of the carbon cycle: review, calcification response, ballast and feedback on atmospheric CO_2 . *Philos. Trans. A Math. Phys. Eng. Sci.* 361 (1810), 1977–1999. <http://dx.doi.org/10.1098/rsta.2003.1238>.
- Bates, N.R., Pequignat, A.C., Sabine, C.L., 2006. Ocean carbon cycling in the Indian Ocean: 1. Spatiotemporal variability of inorganic carbon and air-sea CO_2 gas exchange. *Global Biogeochem. Cycles* 20 (3), 1–13. <http://dx.doi.org/10.1029/2005GB002491>.
- Behrenfeld, M.J., O'Malley, R.T., Siegel, D.A., McClain, C.R., Sarmiento, J.L., Feldman, G.C., Milligan, A.J., Falkowski, P.G., Letelier, R.M., Boss, E.S., 2006. Climate-driven trends in contemporary ocean productivity. *Nature* 444, 752–755. <http://dx.doi.org/10.1038/nature05317>.
- Berelson, W.M., Balch, W.M., Najjar, R., Feely, R.A., Sabine, C., Lee, K., 2007. Relating estimates of $CaCO_3$ production, export, and dissolution in the water column to measurements of $CaCO_3$ rain into sediment traps and dissolution on the sea floor: a revised global carbonate budget. *Global Biogeochem. Cycles* 21, GB1024. <http://dx.doi.org/10.1029/2006GB002803>.
- Bopp, L., Monfray, P., Aumont, O., Dufresne, J.L., Le Treut, H., Madec, G., Terray, L., Orr, J.C., 2001. Potential impact of climate change on marine export production. *Global Biogeochem. Cycles* 15 (1), 81–99. <http://dx.doi.org/10.1029/1999GB001256>.
- Bradshaw, A.L., Brewer, P.G., 1988. High precision measurements of alkalinity and total carbon dioxide in seawater by potentiometric titration. 2. Measurements on standard solutions. *Mar. Chem.* 24, 155–162. [http://dx.doi.org/10.1016/0304-4203\(88\)90046-1](http://dx.doi.org/10.1016/0304-4203(88)90046-1).
- Brewer, P.G., Goldman, J.C., 1976. Alkalinity changes generated by phytoplankton growth. *Limnol. Oceanogr.* 21 (1), 108–117.
- Brewer, P.G., Wong, G.T.F., Bacon, M.P., Spencer, D.W., 1975. An oceanic calcium problem? *Earth Planet. Sci. Lett.* 26, 81–87.
- Cai, W., Wang, Y., 1998. The chemistry, fluxes, and sources of carbon dioxide in estuarine waters of the Satilla and Altamaha Rivers, Georgia. *Limnol. Oceanogr.* 43 (4), 657–668.
- Cai, W.-J., Hu, X., Huang, W.-J., Jiang, L.-Q., Wang, Y., Peng, T.-H., Zhang, X., 2010. Alkalinity distribution in the western North Atlantic Ocean margins. *J. Geophys. Res.* 115, C08014. <http://dx.doi.org/10.1029/2009JC005482>.
- Cao, Z., Dai, M., 2011. Shallow-depth $CaCO_3$ dissolution: evidence from excess calcium in the South China Sea and its export to the Pacific Ocean. *Global Biogeochem. Cycles* 25, GB2019. <http://dx.doi.org/10.1029/2009GB003690>.
- Chen, C.T.A., 2002. Shelf- vs. dissolution-generated alkalinity above the chemical lysocline. *Deep Sea Res. Part II* 36, 5365–5375. [http://dx.doi.org/10.1016/S0967-0645\(02\)00196-0](http://dx.doi.org/10.1016/S0967-0645(02)00196-0).
- Chung, S.N., Lee, K., Feely, R.A., Sabine, C.L., Millero, F.J., Wanninkhof, R., Bullister, J.L., Key, R.M., Peng, T.-H., 2003. Calcium carbonate budget in the Atlantic Ocean based on water column inorganic carbon chemistry. *Global Biogeochem. Cycles* 17 (4), 1093. <http://dx.doi.org/10.1029/2002GB002001>.
- Cooley, S.R., Yager, P.L., 2006. Physical and biological contributions to the western tropical North Atlantic Ocean carbon sink formed by the Amazon River plume. *J. Geophys. Res.* 111, C08018. <http://dx.doi.org/10.1029/2005JC002954>.
- Cooley, S.R., Coles, V.J., Subramaniam, A., Yager, P.L., 2007. Seasonal variations in the Amazon plume-related atmospheric carbon sink. *Global Biogeochem. Cycles* 21, GB3014. <http://dx.doi.org/10.1029/2006GB002831>.
- Cooper, L.W., McClelland, J.W., Holmes, R.M., Raymond, P.A., Gibson, J.J., Guay, C.K., Peterson, B.J., 2008. Flow-weighted values of runoff tracers ($\delta^{18}O$, DOC, Ba, alkalinity) from the six largest Arctic rivers. *Geophys. Res. Lett.* 35, L18606. <http://dx.doi.org/10.1029/2008GL035007>.
- de Boyer Montégut, C., Madec, G., Fischer, A.S., Lazar, A., Iudicone, D., 2004. Mixed layer depth over the global ocean: an examination of profile data and a profile-based climatology. *J. Geophys. Res.* 109, C12003. <http://dx.doi.org/10.1029/2004JC002378>.
- de Villiers, S., 1998. Excess dissolved Ca in the deep ocean: a hydrothermal hypothesis. *Earth Planet. Sci. Lett.* 164, 627–741. [http://dx.doi.org/10.1016/S0012-821X\(98\)00232-5](http://dx.doi.org/10.1016/S0012-821X(98)00232-5).
- de Villiers, S., Nelson, B.K., 1999. Detection of low-temperature hydrothermal fluxes by seawater Mg and Ca anomalies. *Science* 285, 721–723. <http://dx.doi.org/10.1126/science.285.5428.721>.
- Dickson, A.G., 1981. An exact definition of total alkalinity and a procedure for the estimation of alkalinity and total inorganic carbon from titration data. *Deep. Res.* 28A (6), 609–623.
- Dickson, A.G., 2010. The carbon dioxide system in seawater: equilibrium chemistry and measurements. In: Riebesell, U., Fabry, V.J., Hansson, L., Gattuso, J.-P. (Eds.), *Guide to best practices for ocean acidification research and data reporting*. Publications Office of the European Union, Luxembourg.
- Dickson, A.G., Afghan, J.D., Anderson, G.C., 2003. Reference materials for oceanic CO_2 analysis: a method for the certification of total alkalinity. *Mar. Chem.* 80 (2), 185–197. [http://dx.doi.org/10.1016/S0304-4203\(02\)00133-0](http://dx.doi.org/10.1016/S0304-4203(02)00133-0).
- Dyrssen, D., Sillén, L.G., 1967. Alkalinity and total carbonate in sea water. A plea for p-T-independent data. *Tellus A* 19 (1), 113–121. <http://dx.doi.org/10.1111/j.2153-3490.1967.tb01464.x>.
- Feely, R.A., Sabine, C.L., Lee, K., Millero, F.J., Lamb, M.F., Greeley, D., Bullister, J.L., Key, R.M., Peng, T.-H., Kozyr, A., Ono, T., Wong, C.S., 2002. In situ calcium carbonate dissolution in the Pacific Ocean. *Global Biogeochem. Cycles* 16 (4), 1144. <http://dx.doi.org/10.1029/2002GB001866>.
- Feely, R.A., Sabine, C.L., Lee, K., Berelson, W., Kleypas, J., Fabry, V.J., Millero, F.J., 2004. Impact of anthropogenic CO_2 on the $CaCO_3$ system in the oceans. *Science* 305, 362–366. <http://dx.doi.org/10.1126/science.1097329>.
- Friis, K., Körtzinger, A., Wallace, D.W.R., 2003. The salinity normalization of marine inorganic carbon chemistry data. *Geophys. Res. Lett.* 30 (2), 1085. <http://dx.doi.org/10.1029/2002GL015898>.
- Galy, A., France-Lanord, C., 1999. Weathering processes in the Ganges-Brahmaputra basin and the riverine alkalinity budget. *Chem. Geol.* 159, 31–60. [http://dx.doi.org/10.1016/S0009-2541\(99\)00033-9](http://dx.doi.org/10.1016/S0009-2541(99)00033-9).
- Goldman, J.G., Brewer, P.G., 1980. Effect of nitrogen source and growth rate on phytoplankton mediated changes in alkalinity. *Limnol. Oceanogr.* 25 (2), 352–357.
- Gran, G., 1952. Determination of the equivalence point in potentiometric titrations — part II. *Analyst* 77, 661–671.
- Gregg, W.W., Conkright, M.E., Ginoux, P., O'Reilly, J.E., Casey, N.W., 2003. Ocean primary production and climate: global decadal changes. *Geophys. Res. Lett.* 30 (15), 1809. <http://dx.doi.org/10.1029/2003GL018889>.
- Hain, M.P., Sigman, D.M., Haug, G.H., 2010. Carbon dioxide effects of Antarctic stratification, North Atlantic Intermediate Water formation, and subantarctic nutrient drawdown

- during the last ice age: diagnosis and synthesis in a geochemical box model. *Global Biogeochem. Cycles* 24, GB4023. <http://dx.doi.org/10.1029/2010GB003790>.
- Holligan, P.M., Robertson, J.E., 1996. Significance of ocean carbonate budgets for the global carbon cycle. *Global Change Biol.* 2 (2), 85–95. <http://dx.doi.org/10.1111/j.1365-2486.1996.tb00053.x>.
- Hu, X., Cai, W.J., 2011. An assessment of ocean margin anaerobic processes on oceanic alkalinity budget. *Global Biogeochem. Cycles* 25, GB3003. <http://dx.doi.org/10.1029/2010GB003859>.
- Huntington, T.G., 2006. Evidence for intensification of the global water cycle: review and synthesis. *J. Hydrol.* 319, 83–95. <http://dx.doi.org/10.1016/j.jhydrol.2005.07.003>.
- Iglesias-Rodríguez, M.D., Brown, C.W., Doney, S.C., Kleypas, J., Kolber, D., Kolber, Z., Hayes, P.K., Falkowski, P.G., 2002. Representing key phytoplankton functional groups in ocean carbon cycle models: coccolithophorids. *Global Biogeochem. Cycles* 16 (4), 1100. <http://dx.doi.org/10.1029/2001GB001454>.
- Ilyina, T., Zeebe, R.E., Maier-Reimer, E., Heinze, C., 2009. Early detection of ocean acidification effects on marine calcification. *Global Biogeochem. Cycles* 23, GB1008. <http://dx.doi.org/10.1029/2008GB00327>.
- Jiang, Z.-P., Tyrrell, T., Hydes, D.J., Dai, M., Hartman, S., 2014. Variability of alkalinity and alkalinity–salinity relationship in the tropical and subtropical surface ocean. *Global Biogeochem. Cycles* 28 (7), 729–742. <http://dx.doi.org/10.1002/2013GB004678>.
- Jin, X., Gruber, N., Dunne, J.P., Sarmiento, J.L., Armstrong, R.A., 2006. Diagnosing the contribution of phytoplankton functional groups to the production and export of particulate organic carbon, CaCO₃, and opal from global nutrient and alkalinity distributions. *Global Biogeochem. Cycles* 20, GB2015. <http://dx.doi.org/10.1029/2005GB002532>.
- Kang, Y., Pan, D., Bai, Y., He, X., Chen, X., Chen, C.-T.A., Wang, D., 2013. Areas of the global major river plumes. *Acta Oceanol. Sin.* 32 (1), 79–88. <http://dx.doi.org/10.1007/s13131-013-0269-5>.
- Key, R., Kozyr, A., Sabine, C., Lee, K., Wanninkhof, R., Bullister, J.L., Feely, R.A., Millero, F.J., Mordy, C., Peng, T.-H., 2004. A global ocean carbon climatology: Results from Global Data Analysis Project (GLODAP). *Global Biogeochem. Cycles* 18, GB4031. <http://dx.doi.org/10.1029/2004GB002247>.
- Key, R.M., Tanhua, T., Olsen, A., Hoppema, M., Jutterström, S., Schirnack, C., van Heuven, S., Kozyr, A., Lin, X., Velo, A., Wallace, D.W.R., Mintrop, L., 2010. The CARINA data synthesis project: introduction and overview. *Earth Syst. Sci. Data* 2, 105–121. <http://dx.doi.org/10.5194/essd-2-105-2010>.
- Klaas, C., Archer, D.E., 2002. Association of sinking organic matter with various types of mineral ballast in the deep sea: Implication for the rain ratio. *Global Biogeochem. Cycles* 16 (4), 1116. <http://dx.doi.org/10.1029/2001GB001765>.
- Kwon, E.Y., Primeau, F., Sarmiento, J.L., 2009. The impact of remineralization depth on the air–sea carbon balance. *Nat. Geosci.* 2, 630–635. <http://dx.doi.org/10.1038/ngeo612>.
- Lee, K., 2001. Global net community production estimated from the annual cycle of surface water total dissolved inorganic carbon. *Limnol. Oceanogr.* 46 (6), 1287–1297. <http://dx.doi.org/10.4319/lo.2001.46.6.1287>.
- Lee, K., Tong, L.T., Millero, F.J., Sabine, C.L., Dickson, A.G., Goyet, C., Park, G.-H., Wanninkhof, R., Feely, R.A., Key, R.M., 2006. Global relationships of total alkalinity with salinity and temperature in surface waters of the world's oceans. *Geophys. Res. Lett.* 33, L19605. <http://dx.doi.org/10.1029/2006GL027207>.
- Lozier, M.S., 2012. Overturning in the North Atlantic. *Annu. Rev. Mar. Sci.* 4, 291–315. <http://dx.doi.org/10.1146/annurev-marine-120710-100740>.
- Millero, F.J., Dickson, A.G., Eiseid, G., Goyet, C., Guenther, P., Johnson, K.M., Key, R.M., Lee, K., Purkerson, D., Sabine, C.L., Schottle, R.G., Wallace, D.W.R., Lewis, E., Winn, C.D., 1998a. Assessment of the quality of the shipboard measurements of total alkalinity on the WOCE Hydrographic Program Indian Ocean CO₂ survey cruises 1994–1996. *Mar. Chem.* 63, 9–20. [http://dx.doi.org/10.1016/S0304-4203\(98\)00043-7](http://dx.doi.org/10.1016/S0304-4203(98)00043-7).
- Millero, F.J., Lee, K., Roche, M., 1998b. Distribution of alkalinity in the surface waters of the major oceans. *Mar. Chem.* 60, 111–130. [http://dx.doi.org/10.1016/S0304-4203\(97\)00084-4](http://dx.doi.org/10.1016/S0304-4203(97)00084-4).
- Milliman, J.D., Troy, P.J., Balch, W.M., Adams, A.K., Li, Y.-H., Mackenzie, F.T., 1999. Biologically mediated dissolution of calcium carbonate above the chemical lysocline? *Deep Sea Res. Part I* 46, 1653–1669. [http://dx.doi.org/10.1016/S0967-0637\(99\)00034-5](http://dx.doi.org/10.1016/S0967-0637(99)00034-5).
- Moore, T.S., Dowell, M.D., Franz, B.A., 2012. Detection of coccolithophore blooms in ocean color satellite imagery: a generalized approach for use with multiple sensors. *Remote Sens. Environ.* 117, 249–263. <http://dx.doi.org/10.1016/j.rse.2011.10.001>.
- Ohno, Y., Iwasaka, N., Kobashi, F., Sata, Y., 2009. Mixed layer depth climatology of the North Pacific based on Argo observations. *J. Oceanogr.* 65 (1), 1–16. <http://dx.doi.org/10.1007/s10872-009-0001-4>.
- Olson, E.J., Chen, C.T.A., 1982. Interference in the determination of calcium in seawater. *Limnol. Oceanogr.* 27 (2), 375–380.
- Pardo, P.C., Vázquez-Rodríguez, M., Pérez, F.F., Ríos, A.F., 2011. CO₂ air–sea disequilibrium and preformed alkalinity in the Pacific and Indian oceans calculated from subsurface layer data. *J. Mar. Syst.* 84, 67–77. <http://dx.doi.org/10.1016/j.jmarsys.2010.08.006>.
- Pavlova, G.Y., Tishchenko, P.Y., Nedashkovskii, A.P., 2008. Distribution of alkalinity and dissolved calcium in the Sea of Okhotsk. *Oceanology* 48 (1), 23–32. <http://dx.doi.org/10.1134/S0001437008010049>.
- Perkin, R.G., Lewis, E., 1980. The practical salinity scale 1978: fitting the data. 5 (1), 9–16. <http://dx.doi.org/10.1109/JOE.1980.1145441>.
- Postma, H., 1964. The exchange of oxygen and carbon dioxide between the ocean and the atmosphere. *Neth. J. Sea Res.* 2 (2), 258–283.
- Poulton, A.J., Sanders, R., Holligan, P.M., Stinchcombe, M.C., Adey, T.R., Brown, L., Chamberlain, K., 2006. Phytoplankton mineralization in the tropical and subtropical Atlantic Ocean. *Global Biogeochem. Cycles* 20, GB4002. <http://dx.doi.org/10.1029/2006GB002712>.
- Rubin, S.I., Key, R.M., 2002. Separating natural and bomb-produced radiocarbon in the ocean: the potential alkalinity method. *Global Biogeochem. Cycles* 16 (4), 1105. <http://dx.doi.org/10.1029/2001GB001432>.
- Rysgaard, S., Glud, R.N., Lennert, K., Cooper, M., Halden, N., Leakey, R.J.G., Hawthorne, F.C., Barber, D., 2012. Ikaite crystals in melting sea ice – implications for pCO₂ and pH levels in Arctic surface waters. *Cryosphere* 6, 1–8. <http://dx.doi.org/10.5194/tc-6-1-2012>.
- Rysgaard, S., Søgaard, D.H., Cooper, M., Pučko, M., Lennert, K., Papakyriakou, T.N., Wang, F., Geilfus, N.X., Glud, R.N., Ehn, J., McGinnis, D.F., Attard, K., Sievers, J., Deming, J.W., Barber, D., 2013. Ikaite crystal distribution in winter sea ice and implications for CO₂ system dynamics. *Cryosphere* 7, 707–718. <http://dx.doi.org/10.5194/tc-7-707-2013>.
- Sabine, C.L., Key, R.M., Feely, R.A., Greeley, D., 2002. Inorganic carbon in the Indian Ocean: distribution and dissolution processes. *Global Biogeochem. Cycles* 16 (4), 1067. <http://dx.doi.org/10.1029/2002GB001869>.
- Sarmiento, J.L., Dunne, J., Gnanadesikan, A., Key, R.M., Matsumoto, K., Slater, R., 2002. A new estimate of the CaCO₃ to organic carbon export ratio. *Global Biogeochem. Cycles* 16 (4), 1107. <http://dx.doi.org/10.1029/2002GB001919>.
- Sarmiento, J.L., Gruber, N., Brzezinski, M.A., Dunne, J.P., 2004. High-latitude controls of thermocline nutrients and low latitude biological productivity. *Nature* 427, 56–60. <http://dx.doi.org/10.1038/nature02204.1>.
- Schlitzer, R., 2000. Applying the adjoint method for biogeochemical modeling: export of particulate organic matter in the world ocean. In: Kasibhatla, P., Heimann, M., Rayner, P., Mahowald, N., Prinn, R.G., Hartley, D.E. (Eds.), *Inverse Methods in Global Biogeochemical Cycles*. AGU, Washington D.C., pp. 107–124.
- Talley, L.D., Reid, J.L., Robbins, P.E., 2003. Data-based meridional overturning streamfunctions for the global ocean. *J. Clim.* 16, 3213–3226. [http://dx.doi.org/10.1175/1520-0442\(2003\)016<3213:DMOSFT>2.0.CO;2](http://dx.doi.org/10.1175/1520-0442(2003)016<3213:DMOSFT>2.0.CO;2).
- Taylor, J.R., 1982. An introduction to error analysis: the study of uncertainties in physical measurements. University Science Books, Mill Valley, CA.
- Toggweiler, J.R., Samuels, B., 1995. Effect of Drake Passage on the global thermohaline circulation. *Deep Sea Res.* 42 (4), 477–500. [http://dx.doi.org/10.1016/0967-0637\(95\)00012-U](http://dx.doi.org/10.1016/0967-0637(95)00012-U).
- Tsunogai, S., Yamahata, H., Kudo, S., Saito, O., 1973. Calcium in the Pacific Ocean. *Deep Sea Res.* 20, 717–726.
- Vázquez-Rodríguez, M., Padin, X.A., Pardo, P.C., Ríos, A.F., Pérez, F.F., 2012. The subsurface layer reference to calculate preformed alkalinity and air–sea CO₂ disequilibrium in the Atlantic Ocean. *J. Mar. Syst.* 94, 52–63. <http://dx.doi.org/10.1016/j.jmarsys.2011.10.008>.
- Wolf-Gladrow, D.A., Zeebe, R.E., Klaas, C., Körtzinger, A., Dickson, A.G., 2007. Total alkalinity: the explicit conservative expression and its application to biogeochemical processes. *Mar. Chem.* 106 (1–2), 287–300. <http://dx.doi.org/10.1016/j.marchem.2007.01.006>.
- Wong, G.T.F., 1979. Alkalinity and pH in the southern Chesapeake Bay and the James River estuary. *Limnol. Oceanogr.* 24 (5), 970–977.