

Effect of filtration on the total alkalinity of open-ocean seawater

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Abstract

Total alkalinity (TA) of filtered and unfiltered samples was measured during the P16N 2006 cruise in the Pacific Ocean and the I9N 2007 cruise in the Indian Ocean. Although filtering coastal water samples may be important to remove the contributions of phytoplankton and bacteria on the measured TA, it is not the case for open ocean samples. In this study, our results show that the at-sea measured total alkalinity of filtered and unfiltered samples were not statistically different. Measurements of 180 samples of surface, oxygen minimum, and deep waters in the Pacific and Indian oceans for unfiltered and filtered agreed to $\pm 2 \mu\text{mol kg}^{-1}$. Therefore, the findings of this article show that it is not necessary to filter seawater samples when measuring total alkalinity in the open ocean.

Total alkalinity (TA) is a parameter that is often measured along with pH, total inorganic CO_2 (TCO_2), and partial pressure of CO_2 (pCO_2) for the understanding of the oceanic CO_2 system. Measuring two of these four parameters allows one to calculate the other two. The total alkalinity of seawater is the amount of acid that needs to be added (per kilogram of seawater) to react with all the bases in seawater (Dickson 1981). The major bases in seawater are HCO_3^- , CO_3^{2-} and B(OH)_4^- and make major contributions to alkalinity. In deep waters, the TA increases due to the dissolution of CaCO_3 (Chen 1978). In surface seawater, the change in salinity and temperature manifested by evaporation or fresh water input contribute to TA variations (Lee et al. 2000; Millero et al. 1998). Changes in alkalinity also can be affected by the growth of phytoplankton (Brewer and Goldman 1976). The assimilation of nitrate or ammonia by phytoplankton generates a strong base or strong acid respectively and therefore increases or decreases TA. More

recently, Kim et al. (2006) reported that phytoplankton and bacterial cells can affect the measured alkalinity of unfiltered seawater samples collected in Young-II Bay, Korea. Kim et al. (2006) particularly suggested that the alkalinity measurements made at sea should be made on filtered seawater. Although this may be true for coastal waters, this article provides measurements that show that there is no need to filter seawater samples collected in the open ocean. The results are based on samples analyzed at sea during the CLiVAR/CO₂ repeat hydrography on P16N and I9N cruises in the Pacific and Indian oceans.

Materials and procedures

The cruises were part of the Repeat Hydrography CLiVAR/CO₂ program. The P16N cruise was divided in a leg from Tahiti to Hawaii (13 February 2006–3 March 2006) and a leg from Hawaii to Kodiak, Alaska (10 March 2006–30 March 2006). The I9N cruise started in Fremantle, Australia on 22 March 2006 and ended in Phuket, Thailand on 1 May 2006. Both cruise tracks are illustrated in Fig. 1. Filtered samples were taken at different depths and stations. Unfiltered samples also were collected at the same stations and depths for comparison. A Welch vacuum pump model 2546B-01 was used, and the samples were filtered through 0.45 μm membrane filters right after collecting them from the Niskin bottles. After filtration, total alkalinity was determined according to the method described elsewhere (Millero et al. 1993). The maximum salinity change due to filtration was 0.008, which is equivalent to a maximum change in TA of 0.5 $\mu\text{mol kg}^{-1}$.

Two titration systems were used at sea and were checked for accuracy using several batches of Certified Reference Material (CRM). The mean TA difference between the measured values

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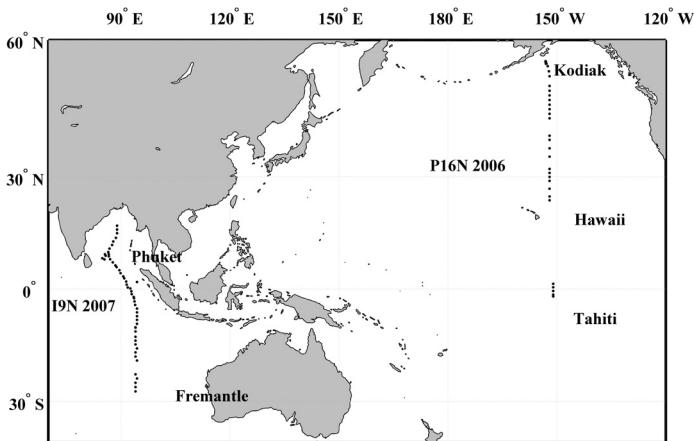


Fig. 1. The P16N 2006 and I9N 2007 cruise tracks in the Pacific Ocean from 13 February 2006–30 March 2006 and in the Indian Ocean from 22 March 2007–1 May 2007. Each dot represents a station where total alkalinity was measured on both unfiltered and filtered seawater samples.

and the certified values was $-1.2 \pm 4.3 \mu\text{mol kg}^{-1}$ ($n = 125$) in the Pacific Ocean and $0.8 \pm 3.3 \mu\text{mol kg}^{-1}$ ($n = 168$) in the Indian Ocean. The precision was checked by making duplicate measurements of the same Niskin bottles on the same system A or B or by using the two systems A and B. The true standard deviation from a set of duplicate measurements was calculated as described in SOP 23 §3.2 in Dickson and Goyet (DOE 1994). All the filtered and unfiltered samples were measured on the same titration system.

Assessment and discussion

The differences in alkalinity between unfiltered and filtered samples are shown in Fig. 2 and Fig. 3 as a function of latitude (left panels) and depth (right panels) and yield a mean value of $-0.10 \pm 1.1 \mu\text{mol kg}^{-1}$ in the Pacific and $0.13 \pm 1.25 \mu\text{mol kg}^{-1}$ in the Indian Ocean. The results indicate that, statistically, there is no difference in the measured TA at sea between the unfiltered and filtered seawater samples. This also proves that there was no need to check if water depth or latitude were factors that contribute to any measured TA changes.

Kim et al. (2006) showed that the difference between the unfiltered and filtered TA is greater than $5 \mu\text{mol kg}^{-1}$ and increase when the particulate organic carbon (POC) values are greater than $200 \mu\text{mol L}^{-1}$. Since oceanic POC values are typically around $5 \mu\text{mol L}^{-1}$ (Bacon et al. 1996; Gardner et al. 2003), the change in TA due to POC concentration is insignificant in the open ocean. Moreover, all the TA measurements made during the iron enrichment experiments inside and outside the patch agree to a maximum of $5 \mu\text{mol kg}^{-1}$ (Coale et al. 2004; Hiscock and Millero 2005). Hiscock and Millero (2005) reported TA changes observed during earlier iron enrichment experiments (IronEx) and compared them with those observed during Southern Ocean Iron Experiment (SOFeX). TA changed by $-2 \pm 2 \mu\text{mol kg}^{-1}$ during IronEx I, $-1 \pm 3 \mu\text{mol kg}^{-1}$ during

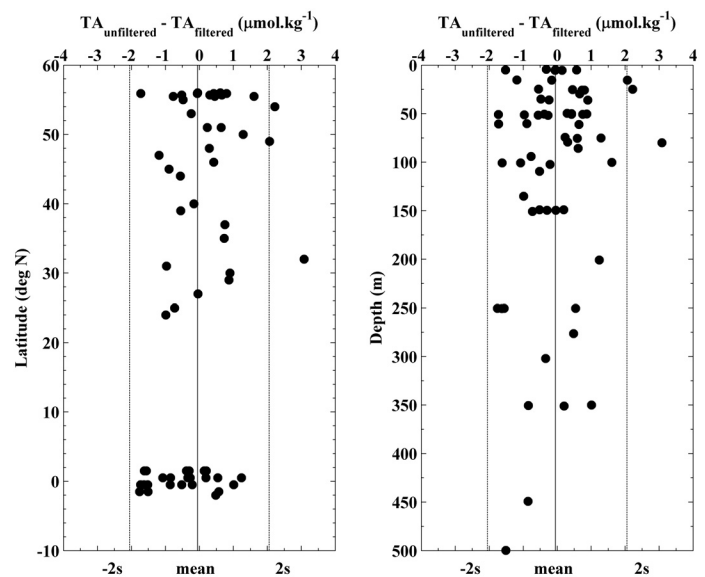


Fig. 2. The differences in the unfiltered and filtered samples of seawater ($n = 60$) collected in the North Pacific during the P16N 2006 cruise as a function of latitude (left) and depth (right). The vertical solid line represents the mean difference (mean = $-0.10 \mu\text{mol.kg}^{-1}$) and the vertical dashed lines represent 2 standard deviation from the mean ($1 s = 0.95 \mu\text{mol.kg}^{-1}$).

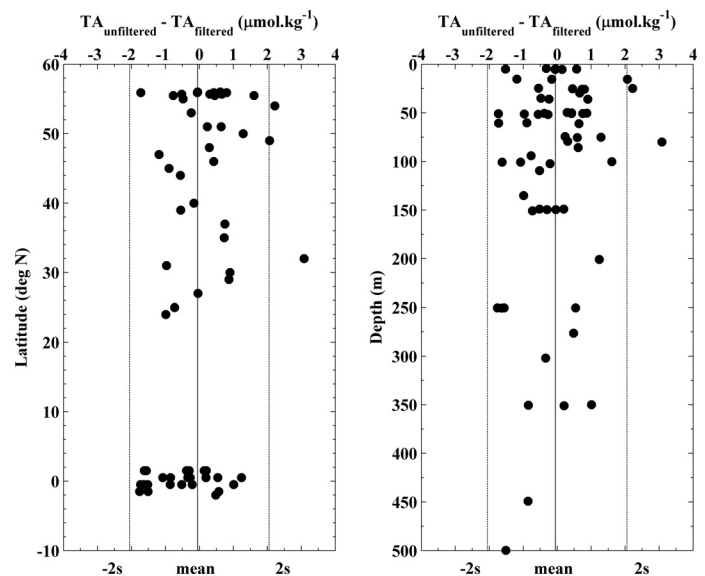


Fig. 3. The differences in the unfiltered and filtered samples of seawater ($n = 120$) collected in the Indian Ocean during the I9N 2007 cruise as a function of latitude (left) and depth (right). The vertical solid line represents the mean difference (mean = $-0.13 \mu\text{mol.kg}^{-1}$) and the vertical dashed lines represent 2 standard deviation from the mean ($1 s = 1.25 \mu\text{mol.kg}^{-1}$).

IronEx II, and $0 \pm 5 \mu\text{mol kg}^{-1}$ in the North and South patch during SOFeX. The SOFeX TA changes occurred with increasing POC of 8 ± 0.8 and $11 \pm 3 \mu\text{mol L}^{-1}$ in the North and South patch respectively. The maximum POC values recorded were around $15 \mu\text{mol L}^{-1}$ (Coale et al. 2004). These results demon-

strate that the reported TA values were within experimental errors and did not change during the iron experiments. Therefore, even in high nutrient low chlorophyll areas such as the Southern Ocean, filtering seawater samples for alkalinity measurements would not be necessary.

The findings of this paper demonstrate that filtration of open-ocean seawater is not necessary when measuring TA. This means that one does not have to take the time to filter samples before measuring the TA and more importantly that the unfiltered measurements made on seawater over the last 20 yr are not affected by not filtering the samples.

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