Carbonate system variables at the POSEIDON-E1-M3A site (S. Aegean Sea, Eastern Mediterranean)

Krasakopoulou E.[1,2], Frangoulis C.[2], Psarra S.[2], Lagaria A.[2], Giannoudi L.[2], Petihakis G.[2]
[1]*Department of Marine Sciences, University of the Aegean, ekras@marine.aegean.gr*
[2]*Institute of Oceanography, Hellenic Centre for Marine Research, cfrangoulis@hcmr.gr, sparra@hcmr.gr, lagaria@hcmr.gr, lgiannoudi@hcmr.gr, pet@hcmr.gr*

Abstract

Sampling of the carbonate system parameters was included to the routine sampling at the POSEIDON-E1-M3A site for the period October 2011-December 2013, aiming to illustrate the present day conditions of carbonate chemistry and establish critical baselines necessary to track further acidification. The presented time-series data exhibited important seasonal variability depicting the ultra-oligotrophic character of the S. Aegean open waters. The minor impact of biological activity on C_T variability in the upper layer of the S. Aegean Sea was demonstrated. The scarceness and/or lack of relevant data in the parameterization process of the existing relationships in the literature led to inadequate retrieval of the measured A_T concentrations.

Keywords: Total dissolved inorganic carbon; total alkalinity; nutrients; Cretan Sea

1. Introduction

In 2000, a moored multi-sensor array was installed in the South Aegean Sea (Eastern Mediterranean), at the POSEIDON-E1-M3A site (35.7860 N, 24.9199 E; 1400m depth; ~20nm offshore). The aim of this observatory is the creation of long time-series of physical and biochemical parameters contributing thus to the international efforts in filling the gap in global ocean observatories in open-waters away from coastal anthropogenic pressures.

The location of the specific observatory in the open-waters of the South Aegean Sea provides an additional interest due to the special characteristics of the region. It is well recognised the role that Aegean plays in the thermohaline circulation of the Mediterranean. Being a place where dense waters with intermediate and deep characteristics are formed (e.g. Roether et al., 2007 and references therein) would have a major role in the anthropogenic CO_2 uptake and sequestration. Additionally, past research has highlighted the extremely oligotrophic character of its southern part (Psarra et al., 2000; Ignatiades et al., 2002).

Since 2010, water column sampling, including CTD casts and seawater/plankton sampling, is performed on a monthly frequency. During the period October 2011-December 2013, sampling for the determination of carbonate system parameters was also included aiming to provide a relatively more detailed mapping and better illustration of the present day conditions in terms of carbonate chemistry and establish critical baselines necessary to track further acidification.

2. Materials and methods

The POSEIDON-E1-M3A site was visited on a monthly basis, depending on the weather conditions, with an inflatable boat. Temperature and salinity were recorded with a Sea-Bird Electronics 25 CTD probe. Samples for the determination of bio-chemical parameters were collected from standard depths with Niskin bottles. Chlorophyll-a was determined using a TURNER DESIGNS TD 700 Fluorometer according to Yentsch & Menzel (1963). Nutrients were analysed on a HITACHI U-1800 spectrophotometer according to standard analytical protocols (NO_3+NO_2, NO_2, $Si(OH)_4$: Strickland & Parsons (1972); NH_4: Ivancic & Deggobis (1984), PO_4: Murphy & Riley (1962) for C>200nM and Rimmelin & Moutin (2005) for C<200nM). Total dissolved inorganic carbon (C_T) and total alkalinity (A_T) were measured by potentiometric acid titration using a closed cell (DOE, 1994).

3. Results & Discussion

3.1. Hydrography, nutrients and Chl-a

The presented time-series data, despite the gaps linked to very poor meteorological conditions that canceled the regular water sampling R/V visits, depict the importance of this type of pelagic monitoring work, revealing important seasonal variability at E1-M3A site. As shown by the temperature and salinity profiles (Fig. 1) the breaking of the thermal stratification in November 2011 leads to a perfect mixing of the surface layers down to 150 m depth in February-March 2012, to be followed in April by the onset and then the establishment of a pronounced thermal stratification period from May to October 2012. The interesting feature here, opposite to what was observed in winter 2011, is the mild winter 2012, prolonging the stratification period until the end of the year coupled to a slight uplifting of deeper cooler waters from beneath 150 m up to 100 m depth, directly reflected to all biochemical variables.

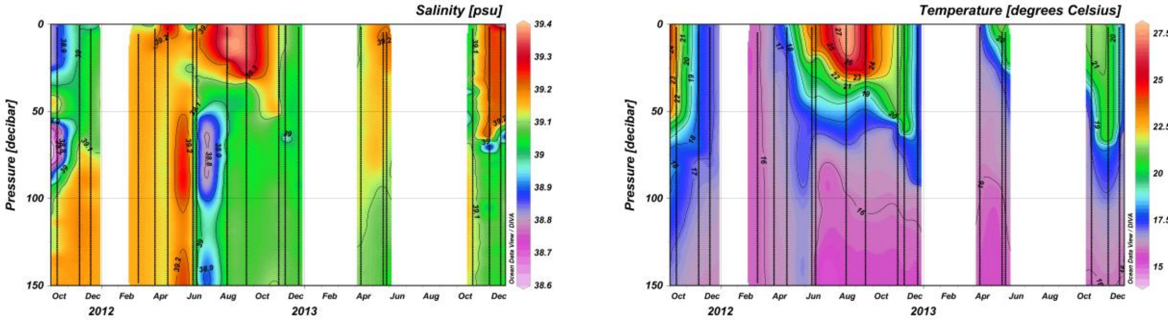

Fig. 1. Temporal variations of salinity and temperature, between 0 and 150 m depth in Poseidon E1-M3A site during the period October 2011 to December 2013.

Clearly, the fall-winter period displays fairly different characteristics between the different years of the current period of observations and the timing of the water column homogenization may vary 1-2 months from year to year.

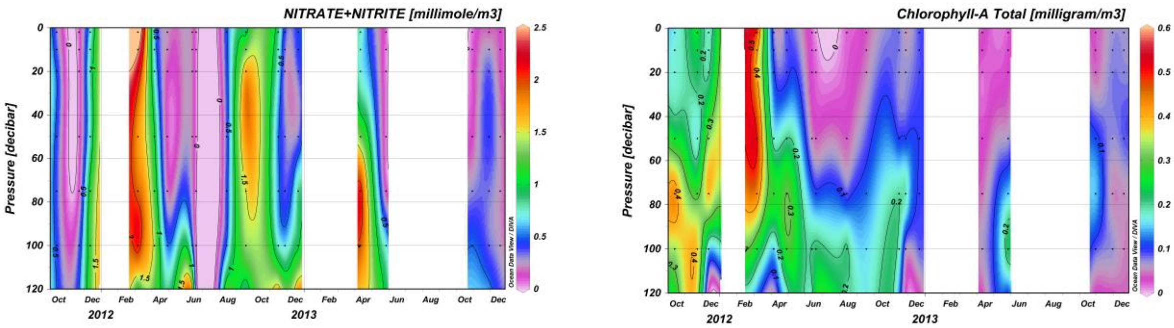

Fig. 2. Temporal variations of Nitrite+Nitrate and total Chlorophyll-a between 0 and 120 m depth in Poseidon E1-M3A site during the period October 2011 to December 2013.

The homogenization of the water column during February-April brings nutrients to the surface layers; nitrate/nitrite reach their maximum concentrations in February (Fig. 2), while the appearance of the maximum phosphate and silicate concentrations follows in March-April (not shown). Chlorophyll-a responded initially to the increase of nitrate presenting maxima in February-March in the 0-60 m surface layer, while the pronounced decrease of surface values during the stratified period (May to November 2012) due to the extinction of nutrients creates a mild Deep Chlorophyll Maximum between 75 and 100 m depth.

3.2 The carbonate system properties

During the same period, the C_T values varied between 2267 μmol kg^{-1} and 2338 μmol kg^{-1}, while the A_T values ranged from 2602 μmol kg^{-1} to 2672 μmol kg^{-1} in accordance with previous findings stating that the Eastern Mediterranean is clearly characterized by A_T>2600 μmol kg^{-1} (Schneider *et al*., 2007). C_T was strongly inversely correlated with both temperature and salinity, while surprisingly A_T didn't show any significant correlation with both hydrographic properties (Fig. 3). The dependency of C_T time-series data on the corresponding Chlorophyll-a concentrations exhibited very weak negative linear correlation (r^2= 0.137) implying that the biological activity has a slight effect but is not the driving force of the C_T variability in the upper layer of the Cretan Sea.

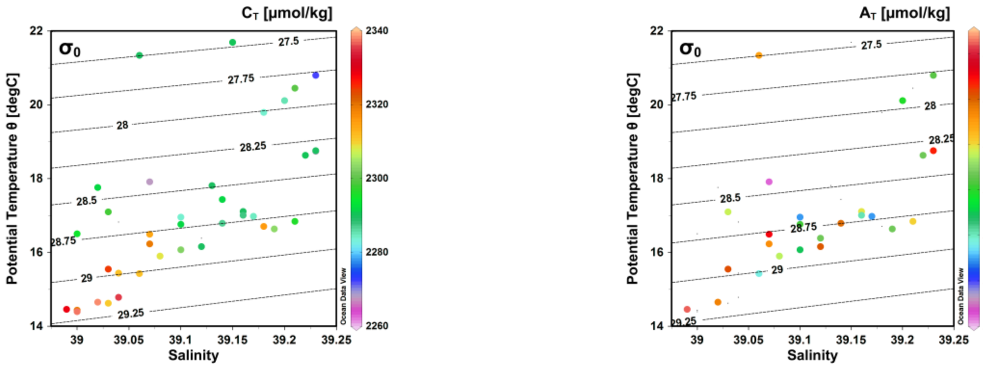

Fig. 3. C_T and A_T concentrations superimposed on θ/S diagrams in Poseidon E1-M3A site during the period October 2011 to December 2013.

Different relationships stated in the bibliography relevant for the Mediterranean waters were tested to reconstruct the A_T values measured in E1-M3A during the October 2011-December 2013 period. All of them provided poor results, underestimating in most cases the measured A_T. The RMSD that is a measure of the differences between predicted and actual values, was lower using the relationships of Touratier & Goyet (2011) and Rivaro et al. (2010) attaining however extremely high values (>22), while the standard deviation of the residuals is much higher than the usual precision of A_T measurements (>16.7 μmol kg^{-1}) implying that both relationships do not succeed to reproduce efficiently the A_T levels observed in the Cretan Sea.

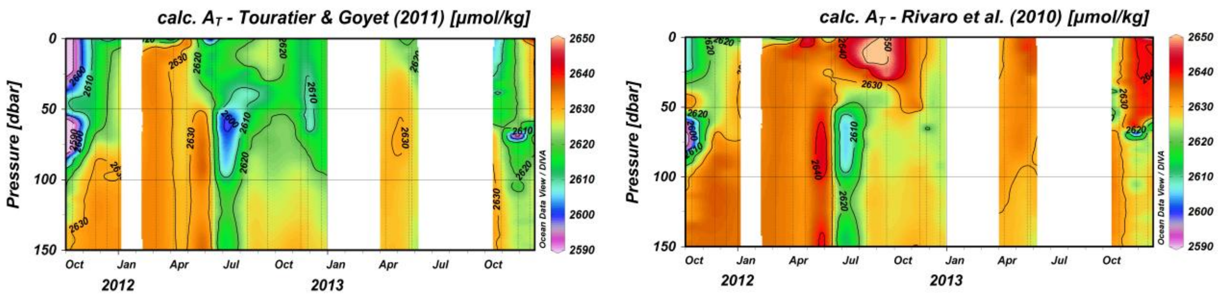

Fig. 4. Temporal variations of: A_T calculated using the relationships of Touratier & Goyet (2011) and Rivaro *et al*. (2010) between 0 and 150 m depth in Poseidon E1-M3A site during the period October 2011 to December 2013.

The A_T estimates obtained using the two relationships (Fig. 4) exhibit remarkable differences in the levels of calculated A_T. In the parameterization process of both relationships the carbonate system measurements from the Aegean Sea either are lacking (Rivaro et al., 2010) either are underrepresented (Touratier & Goyet, 2011) probably causing these deviations between the estimated values using these two selected relationships as well as between the measured and the calculated ones.

4. Conclusions

The presented time-series data from the E1-M3A site exhibited important seasonal variability depicting the importance of this type of pelagic monitoring work. The overall assessment of the above biochemical variables denotes the ultra-oligotrophic character of S. Aegean open waters. The very weak negative linear correlation between C_T and chlorophyll-a suggests that the biological activity has a slight effect but is not the driving force of the C_T variability in the upper layer of the S. Aegean Sea. The weakness of the existing relationships in the literature to reconstruct satisfactorily the measured A_T concentrations is indicative of the scarceness of relevant data and points out the necessity for carbonate chemistry measurements in the Aegean Sea.

5. Acknowledgements

This research has received funding from the EU 7th Framework Programme under grant agreements n° 265103 (MedSeA) and n° 287600 (Perseus). We would like to thank S. Diliberto, M. Ntoumas, M. Pettas, D. Podaras, M. Tsagaraki, M. Tsapakis for their help in sampling and S. Zivanovic, E. Dafnomili for the chemical analysis. Special thanks are due to Catherine Goyet for the C_T-A_T measurements.

6. References

Dickson, A.G. and Goyet, C. (eds). 1994. *Handbook of methods for the analysis of the various parameters of the carbon dioxide system in sea water*. DOE, Version 2, ORNL/CDIAC-74.

Ignatiades, L., Psarra, S., Zervakis, V., Pagou, K., Souvermezoglou, E. *et al*., 2002. Phytoplankton size-based dynamics in the Aegean Sea (Eastern Mediterranean). *Journal of Marine Systems*, 36, 11-28.

Ivancic, I. and Deggobis, D. 1984. An optimal manual procedure for ammonia analysis in natural waters by the indophenol blue method. *Water Research*, 18, 1143-1147.

Psarra, S., Tselepides, A. and Ignatiades, L. 2000. Primary productivity in the oligotrophic Cretan Sea (NE Mediterranean): seasonal and interannual variability. *Progress in Oceanography*, 46, (2-4), 187-204.

Rimmelin, P. and Moutin T. 2005. Re-examination of the MAGIC method to dermine low orthophosphate concentraion in seawater. *Analytical Chimical Acta*, 548, 174-182.

Rivaro, P., Massa, R., Massolo, S. and Frache, R. 2010. Distributions of carbonate properties along the water column in the Mediterranean Sea: spatial and temporal variations. *Marine Chemistry*, 121, 236–245.

Roether, W., Klein, B., Manca, B.B, Theocharis, A. and Kioroglou, S. 2007. Transient Eastern Mediterranean deep waters in response to the massive dense-water output of the Aegean Sea in the 1990s. *Progress in Oceanography*, 74, 540-571.

Schneider, A., Wallace, D.W.R. and Kortzinger, A., 2007. Alkalinity of the Mediterranean Sea. *Geophysical Research Letters*, 34, L15608, doi: 10,1029/2006GL028842.

Strickland, J.D. and Parsons, T.R. 1972. *A practical handbook of seawater analysis*. Bull Fisheries Research Board Canada, 167, 311 pp.

Touratier, F. and Goyet, C. 2011. Impact of the Eastern Mediterranean Transient on the distribution of anthropogenic CO_2 and first estimate of acidification for the Mediterranean Sea. *Deep-Sea Research I*, 58, 1-15.

Yentsch, C.S. and Menzel, D.W. 1963. A method for the determination of phytoplankton chlorophyll and phaeophytin by fluorescence. *Deep Sea Research*, 10, 221–231.