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Proxy-based reconstruction of surface water acidification and carbonate saturation of the Levant Sea during the Anthropocene

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ABSTRACT

Ocean Acidification (OA) in marginal seas and shelf environments is a multifaceted phenomenon, most notably due to watershed export in the form of riverine influx. In this study, we examined the effect of decadal changes in alkalinity driven by fresh water influx from the Nile River before and after its damming, as well as the effect of this change on OA of the South-East Mediterranean (SE-Med) shelf. Two independent data sets were used to calculate the change in pH and aragonite saturation (Ω_{ar}) from 1948 to 2002: observational salinity data from which total alkalinity (A_T) was calculated and a $\delta^{13}C$ record of the endemic *Dendropoma* reefs from which dissolved inorganic carbon (DIC) was estimated. Our calculations indicate the development of a localized low pH/low Ω_{ar} zone along the SE-Med shelf, associated to the Nile plumes. Following the damming of the Nile, a distinct acidification trend is observed. We infer an acidification rate of $-0.0022 \pm 0.0002\ yr^{-1}$ in the SE-Med following the damming; this rate exceeds those of the open-oceans but is comparable to other marginal seas. This trend is significantly correlated with the increase in atmospheric CO_2 since the 1960s, supporting the notion of a more substantial atmospheric impact from that period onward. However, despite evident acidification, the modern level of high alkalinity helped to buffer the system and maintained high levels of pH and aragonite saturation all year long.

1. Introduction

Nearly a third of the anthropogenic CO_2 (C_{ant}) added to the atmosphere is sequestered by the ocean's surface (Sabine and Feely, 2007; Sabine et al., 2004). As result, CO_2 dissolution-derived acidification has decreased surface ocean pH by ~0.1 units relative to preindustrial levels. This reduction in pH since the industrial revolution is commonly referred to as ocean acidification (OA; Caldeira and Wickett, 2003; Caldeira and Berner, 1999; Doney et al., 2009). Another 0.3–0.4 pH unit decrease is expected by 2100, considering the exponentially increasing atmospheric CO_2 (Caldeira and Wickett, 2003; Feely et al., 2008; Orr et al., 2005).

Anthropogenic acidification induced by CO_2 accumulation alters carbon speciation and consequently affects the calcium carbonate saturation state (Zeebe and Wolf-Gladrow, 2001). This process had been corroborated by models, hydrographic surveys and time series data (Caldeira and Wickett, 2003; Feely et al., 2008, 2004; Orr et al., 2005; Solomon, 2007). The change in the marine carbon chemistry has multiple effects on marine ecosystems (Beman et al., 2011; Hönisch et al., 2012). The decline in carbonate ion solubility may impose the greatest threat on shell-forming organisms, as aragonite under-saturation may become a reality for future oceans (Doney et al., 2009; Hall-Spencer et al., 2008; Hoegh-Guldberg et al., 2007).

The uptake of CO_2 by the ocean's surface is not globally uniform, and the variability is particularly strong in marginal seas and coastal waters (Dai et al., 2013; Duarte et al., 2013). These environments are highly sensitive to nutrient and fresh water fluxes, which affect their physical and chemical state. At the same time, coastal waters and marginal seas host a substantial amount of carbonate burial (e.g., Sabine et al., 2004). Therefore, it is necessary to understand the effect of temporal changes in

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freshwater influx and temperature in these environments in order to evaluate their OA fully.

Coastal and marginal marine primary productivity, respiration and calcification rates are strongly affected by watershed export of alkalinity, organic matter and nutrient inputs, as well as the invasion of anthropogenic CO_2 (Aufdenkampe et al., 2011; Waldbusser and Salisbury, 2014). Watershed export, mainly in the form of riverine influx, is one of the major factors for the development of localized zones of low seawater alkalinity and increased metabolic processes, yielding high-magnitude variability and reaching 1.4 units in coastal pH (Duarte et al., 2013; Hofmann et al., 2011). The thermal component is also important because warming coastal waters may impose a major impact over OA through both CO_2 solubility and oceanic dynamics, such as increasing stratification and decreasing mixing and ventilation.

The coasts of the world form a narrow interface zone between marine and terrestrial areas that is highly influenced by human activity. River-mouth systems including deltas and estuaries were recently identified as highly sensitive ecosystem to human-induced stresses by the Land–Ocean Interactions in the Coastal Zone (LOICZ) project (Ramesh et al., 2015 and Ref. therein). Damming of rivers is extremely important ecologically and economically, affecting a wide variety of ecosystem and services such as fisheries, ecological habitats, agricultural land and storm protection (Ramesh et al., 2015 and Ref. therein). Intense land-ocean interactions were documented in oligotrophic ecosystems, where primary production is highly dependent on soil erosion and nutrient enrichment via runoff (Dalton et al., 2014).

Among these ecosystems, the intertidal vermetid reef formations of the oligotrophic Mediterranean, Levantine basin is highly sensitive to environmental changes and already suffers from a great loss of habitat (Galil, 2013). Vermetids reefs are highly important bio- constructions that colonize the abrasion platform rims along rocky shorelines (Safriel, 1975a; Laborel and Laborel-Deguen, 1996; Antonioli et al., 1999). These reefs protect coasts from erosion, regulate sediment transport and accumulation, serve as carbon sinks and provide habitat for other species. Similar to other reef formations, the vermetid reef builder, *Dendropoma petraeum* is at high risk to OA and affects the aragonite saturation in seawater. The significant shell dissolution of *D. petraeum* due to long-term exposure to acidified conditions predicted for the year 2100 and beyond was recently verified by Milazzo et al. (2014) based on field experiments.

The Mediterranean Sea is considered a region that is capable of absorbing a significant amount of anthropogenic CO_2 per unit area. Its high total alkalinity (Copin-Montégut, 1993; Cossarini et al., 2015; Schneider et al., 2007) gives it greater chemical capacity to take up C_{ant} (Álvarez et al., 2014). Furthermore, this sea's deep waters are ventilated on relatively short time scales (ca. 100 years, Schneider et al., 2014; Stöven and Tanhua, 2014), allowing penetration of C_{ant} into deep water layers (Palmiéri et al., 2015; Schneider et al., 2010; Touratier and Goyet, 2011).

Anthropogenic CO_2, however, cannot be measured directly because the anthropogenic component cannot be distinguished from the much larger natural background (Palmiéri et al., 2015). Instead, this CO_2 has been estimated indirectly from observable physical and biogeochemical quantities (Schneider et al., 2010; Touratier and Goyet, 2011). Recent studies have reported that carbon with anthropogenic origins with a total of 1.0–1.7 Pg C entered the Mediterranean water column, where 52% are from the air–sea flux and 48% are from the Atlantic water inflow (Palmiéri et al., 2015; Schneider et al., 2010). Simulations based on the TrOCA approach showed that all water masses in the Mediterranean Sea are already acidified between −0.14 and −0.05 (El Rahman Hassoun et al., 2015; Touratier and Goyet, 2011), indicating an amplified acidification relative to the global average surface ocean. An acidification similar to the global-ocean average was simulated by Palmiéri et al. (2015) based on a thermodynamic model. Nevertheless, such model simulations lack OA predictions for the marginal marine environment, where significant changes in salinity/alkalinity may have occurred, due to decadal changes in freshwater influx.

The general salinity/alkalinity relationship of the Mediterranean results from high rates of evaporation along the eastward circulation pattern of the Atlantic water that occupies the upper 25–100 m, as well as the secondary effect of high alkalinity freshwater influx from marginal seas, the Black Sea, the Adriatic and the Aegean (Copin-Montégut, 1993; Cossarini et al., 2015; Rivaro et al., 2010; Schneider et al., 2007). On a regional scale, a complex spatial pattern appears: in regions of freshwater influence, the two quantities are negatively correlated due to riverine high alkalinity input (higher than that of the Mediterranean), whereas they are positively correlated in open sea areas of the Mediterranean Sea (Cossarini et al., 2015). Positively correlated salinity-alkalinity is most prominent in the southern margin of the Mediterranean, in the Ionian and Levantine Seas, where evaporation rate exceeds riverine input (Cossarini et al., 2015; Sisma-Ventura et al., 2016).

In order to obtain the carbonate properties in sea water, two of six parameters must be known: A_T, C_T, $[CO_3{}^{2-}]$, $[HCO_3{}^{-}]$, pH and pCO_2. With these, it is possible to calculate the entire carbonate properties in sea water, including the $CaCO_3$ saturation (Dickson et al., 2007). Obtaining historical carbonate data is, however, relatively difficult, as it relies on reliable physical and chemical observations, which are scarce for most oceanic basins. Fortunately, for the southeastern Levantine Sea (SE-Med, Fig. 1a), such data sets can be constructed for the second half of the 20th century.

This study focuses on the effect of decadal changes in watershed export of alkalinity over the OA of the South-East Mediterranean (SE-Med). This region has undergone significant changes in its freshwater balance since the final Nile damming (Gertman and Hecht, 2002; Skliris and Lascaratos, 2004), notably with respect to salinity and alkalinity. We use a combination of historical oceanographic data and proxy records from this region to estimate the effect of decadal changes in the carbonate system over OA of SE-Med coastal water while attempting to evaluate the effect of the diminished Nile influx following the construction of the Aswan dam.

2. Background, data sets and calculations

2.1. Study area

This study integrates cruise data and a proxy record of *Dendropoma* reefs (Fig. 1b) to evaluate OA in the SE-Med. The observational data of salinity and temperature were obtained from cruise data covering the SE-Med shelf (Depth < 120 m) and are supplemented by off-shelf data when gaps were found (Fig. 1a).

The SE-Med region was historically highly affected by the Nile summer floods (Bethoux, 1993). During the pre-Aswan damming period (prior to 1964), the salinity in this region was controlled by a balance between high rates of evaporation and the Nile seasonal flooding, where decreasing salinity on the Levant shelf maintained for multiple weeks during floods. During this period, an annual plume, stemming from the Nile, would extend during flood season. Typically a low salinity tongue, this plume would propagate northward on the SE continental shelf of the Levant basin from the Nile delta and along the Israeli coast (Hecht, 1964, 1992). However, following the construction of the Aswan high dam in 1964, the Nile discharge has been reduced from approximately 40 km^3 per year to approximately 4 km^3 per year (Hecht, 1992), resulting in an

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