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Anthropogenic CO_2 fluxes in the Otranto Strait (E. Mediterranean) in February 1995

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ABSTRACT

This study presents the distribution and fluxes of dissolved inorganic carbon (C_T), total alkalinity (A_T) and anthropogenic carbon (C_{ant}) along the Otranto strait, during February 1995. Based on a limited number of properties (temperature, dissolved oxygen, total alkalinity and dissolved inorganic carbon), the composite tracer TrOCA was used to estimate the concentration of anthropogenic CO_2 in the Otranto strait.

Total alkalinity exhibits high values and weak variability throughout the water column of the strait, probably associated with the dense water formation processes in the Adriatic basin that induce a rapid transport of the coastal alkalinity to the deep waters. Elevated C_{ant} concentrations and high anthropogenic pH variations are observed in the bottom layer of the strait, associated with the presence of Adriatic Deep Water (ADW). The study shows that large amounts of C_{ant} have penetrated the highly alkaline Eastern Mediterranean waters, thereby causing a significant pH reduction since the pre-industrial era.

Estimates of the transports of C_T and C_{ant} through the strait indicate that during February 1995, the Adriatic Sea imports through the Otranto strait natural and anthropogenic carbon and acts as a net sink of carbon for the Ionian Sea. The anthropogenic carbon that is imported to the Adriatic Sea represents less than 1% of the net C_T inflow. The Levantine Intermediate Water (LIW) contributes to about one-third of the total C_T and C_{ant} inflow. Although the amounts of C_{ant} annually transported by LIW and ADW are almost equal, the contribution of C_{ant} to the C_T transported by each water mass is slightly higher in ADW (3.1%) than in LIW (2.6%), as a result of its higher mean C_{ant} concentration. The ADW, despite its weak contribution to the total outflow of C_{ant}, has a vital role for the sequestration and storage of the anthropogenic carbon, as this water mass is the main component of the Eastern Mediterranean Deep Waters and, thus, the anthropogenic CO_2 is transferred in the deep horizons of the Eastern Mediterranean, where it remains isolated for many years.

1. Introduction

The ocean is a key reservoir, which mitigates the accumulation of anthropogenic CO_2 in the atmosphere. It has been estimated that from ~1800 until 1994, the ocean removed about 118 ± 19 Pg C (~432 Pg CO_2) from the atmosphere, equivalent to about 50% of the CO_2 emitted from the burning of fossil fuels, or about 30% of the total anthropogenic CO_2 emissions, which additionally include emissions from land use change and cement production (Sabine et al., 2004). In the early 2000s the global ocean uptake flux of anthropogenic CO_2 was estimated at about 2.2 Pg C yr^{-1} (Gruber et al., 2009), giving a total inventory of anthropogenic carbon in the ocean of about 135 Pg C. Due to the rapid growth of global fossil fuel CO_2 emissions since 2000 (the emissions growth rate increased from 1.3% in 1990s to 3.3% per year in 2000–2006), the total cumulative emissions yield approximately 330 Pg C by 2006 (Canadell et al., 2007) revealing that the ocean storage of carbon has declined since the mid-1990s and accounts for only ~41% of the total fossil fuel emissions since the pre-industrial era. The weakening of the ocean sink of anthropogenic CO_2 compared to the increase of CO_2 emissions could be due to the response of ocean CO_2 sinks to climate variability and climate change (Le Quéré et al., 2009). If the land use change emissions, although highly uncertain, are included as part of this calculation, then the oceans are only absorbing about 25% of the current total anthropogenic emissions (Canadell et al., 2007), instead of about 30% that was previously estimated.

The addition of CO_2 to the ocean, either passively through the solubility and physical pumps, or actively through geo-engineering solutions, affects the ocean carbonate system, resulting in a decrease of both pH and carbonate-ion concentration, which have the potential

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to cause strong impacts on the marine biota (Caldeira and Wickett, 2005 and references therein; IPCC, 2007; Doney et al., 2009).

In order to quantify the ocean capacity to sequester anthropogenic CO_2 (C_{ant}) and the increase of acidification, the concentration of anthropogenic CO_2 should be accurately known. Since anthropogenic CO_2 cannot be measured directly, as it cannot be chemically discriminated from the bulk of dissolved inorganic carbon (C_T), several independent approaches for its indirect estimation, based on different concepts and assumptions, have been developed (Millero, 2007; Sabine and Tanhua, 2010). The different C_{ant} estimate approaches that are based on *in situ* observations (data-based methods) fall into three general categories (Sabine and Tanhua, 2010): back-calculation, tracer-based and scaled decadal change. The first attempts to estimate C_{ant} from oceanic measurements were based on the back-calculation method, proposed independently by Brewer (1978) and Chen and Millero (1979). Gruber et al. (1996), based on many of the principles outlined in the Chen method, proposed a different back-calculation technique based on the use of transient tracers. Several other methods, based upon completely different concepts, were also developed; one of them is based on water mass mixing (the MIX method; Goyet et al., 1999), another one on estimating Transit Time Distribution (TTD) or ages from transient tracers as CFCs, SF_6 or CCl_4 (TTD method; Waugh et al., 2004; Hall et al., 2004), one based on a composite tracer (TrOCA method; Touratier and Goyet, 2004a, 2004b; Touratier et al., 2007) and, finally, one using measurement of the decadal change of ocean carbon concentrations and the exponential nature of the atmospheric C_{ant} increase (scaled eMLR method; Tanhua et al., 2007). In addition, there are simulations from three-dimensional Ocean General Circulation Models (OGCM) (Orr et al., 2001). These different approaches to estimate C_{ant} have various advantages as well as weaknesses, and up until now, no clear conclusion can be drawn regarding the best method, even after several inter-comparison exercises (Vázquez-Rodríguez et al., 2009; Alvarez et al., 2009 and references therein).

The Tracer combining Oxygen, inorganic Carbon and total Alkalinity (TrOCA) approach is a carbon-based method and it has been chosen to calculate the anthropogenic carbon in the Otranto strait because (a) it is very easy to apply from only four known properties (θ, C_T, A_T and O_2), without the need for further knowledge regarding the water mass properties or water mass age tracers, (b) it has been extensively applied in the past, and has provided realistic estimates of the anthropogenic CO_2 throughout the whole Atlantic Ocean (Touratier and Goyet, 2004b), along a section of the Southern Ocean (Lo Monaco et al., 2005), in the tropical Atlantic Ocean (Touratier et al., 2005), in the Gulf of Cadiz (Aït-Ameur and Goyet, 2006), in the eastern South Pacific (Azouzi et al., 2009) and recently throughout the Mediterranean Sea (Touratier and Goyet, 2011), in the Bay of Biscay (Castaño-Carrera et al., accepted for publication) and in the Iberian basin (Fajar et al., accepted for publication). In general, in the upper 2000 m the results obtained by the TrOCA approach tend to be slightly higher than those estimated by other methods and thus probably provide an upper estimate (Alvarez et al., 2009; Gerber et al., 2009; Vázquez-Rodríguez et al., 2009; Huertas et al., 2009; Yool et al., 2010; Castaño-Carrera et al., accepted for publication; Fajar et al., accepted for publication). However the amplitude of the differences mainly depends upon kind of approach used. For instance the differences between results from 3-D modelling (Gerber et al., 2009; Yool et al., 2010) and results from the TrOCA approach are larger than those between CO_2-data-based methods (Alvarez et al., 2009; Vázquez-Rodríguez et al., 2009; Castaño-Carrera et al., accepted for publication; Fajar et al., accepted for publication). For example, the differences between the C_{ant} estimations from the φC_T^0 method (Vázquez-Rodríguez et al., 2009) and those from the TrOCA method are very small (0.7 ± 4.4 μmol kg^{-1}, $n=301$), while both C_{ant} estimates present the same spatial variations (Castaño-Carrera et al., accepted for publication). Similarly, the C_{ant} inventories in the Iberian basin indicate 93 ± 4 mol C m^{-2} using the TrOCA method and 89 ± 4 mol C m^{-2} using the φC_T^0 method (Fajar et al., accepted for publication). Thus, these recent comparisons further confirm that the TrOCA method provides similar spatial variations as other models and a reasonable upper limit of C_{ant} estimates (within the uncertainty of the results).

The Strait of Otranto forms a 75 km wide and up to 800 m deep connection between the Ionian Sea and the Adriatic Sea. The importance of the Strait in terms of circulation within the Mediterranean Sea is well-recognised, as it links the Eastern Mediterranean basin to one of the major sites of deep water formation in the Mediterranean. The Adriatic Sea receives significant freshwater inputs in its shallow northern basin, mainly due to high river runoff and it is prone to strong winter outbreaks of cold, dry northerly winds which induce extended heat losses and evaporation that drive deep-water formation events. As a consequence of the high heat losses in cases of low freshwater influence and of the shallow bathymetry, the vertical temperature and salinity profiles are almost uniform during winter, when the vertical mixing dominates over the horizontal baroclinic circulation, and the Northern Adriatic Dense Water (NAdDW), the densest water in the whole of the Mediterranean, is formed over the shallow northern shelf of the Adriatic (Vilibic, 2003 and references therein). In addition, its middle-southern basin constitutes a site where deep-convection type of dense water formation occurs (Vilibic and Orlic, 2002 and references therein). The Adriatic Deep Water (ADW) is produced during winter through open-ocean deep convection in the Southern Adriatic Pit, where a cyclonic gyre is nearly permanently present in the region (Ovchinnikov et al., 1985). The Strait of Otranto is recognised as an important region, in which different water masses, originating from the Adriatic Sea (Adriatic Deep Water, ADW, Adriatic Surface Water, ASW), Ionian Sea (Ionian Surface Water, ISW) and from the Eastern Mediterranean (Levantine Intermediate Water, LIW), are exchanged and, in turn, influence the thermohaline circulation of the adjacent basins. Recent results have shown that the volume of water imported from the Ionian depends on the amount of deep water produced in the Southern Adriatic (Samuel et al., 1999; Manca et al., 2002; Mantziafou and Lascaratos, 2004). The climatic, hydrological and meteorological conditions, in terms of air–sea interaction and fresh-water discharge over the Ionian and Adriatic basins on each side of the strait influence, to a large extent, variations both in the characteristics of the water masses and their dynamics.

Published works regarding the Otranto strait have dealt with hydrographic measurements (Ferentinos and Kastanos, 1988; Michelato and Kovacevic, 1991; Artegiani et al., 1993; Gacic et al., 1996; Kovacevic et al., 1999; Vilibic and Orlic, 2002), lateral and downward biogeochemical fluxes (Civitarese et al., 1998; De Lazzari et al., 1999) and the study of various components of the pelagic food web (Vilicic et al., 1995; Socal et al., 1999; La Ferla et al., 1999; Kršinic and Grbec, 2002).

The first distribution of the inorganic carbon system parameters in the Otranto strait (Eastern Mediterranean) is presented in this paper. Hydrochemical data collected in the strait, in February 1995, are used to investigate the anthropogenic carbon distribution using the TrOCA method. In addition, the transports of the inorganic and anthropogenic carbon through the Strait are estimated, in order to assess the potential role of the Adriatic Sea as source or sink of carbon for the Eastern Mediterranean Sea.

2. Dataset description and methodology

2.1. Data

For the estimation of anthropogenic CO_2 (C_{ant}, μmol/kg) using the TrOCA approach, potential temperature (θ, °C), oxygen (O_2,