The imprint of anthropogenic CO₂ emissions on Atlantic bluefin tuna otoliths

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Abstract

Otoliths of Atlantic bluefin tuna (Thunnus thynnus) collected from the Mediterranean Sea and North Atlantic Ocean were analyzed to evaluate changes in the seawater isotopic composition over time. We report an annual otolith δ13C record that documents the magnitude of the δ13C depletion in the Mediterranean Sea between 1989 and 2010. Atlantic bluefin tuna in our sample (n = 632) ranged from 1 to 22 years, and otolith material corresponding to the first year of life (back-calculated birth year) was used to reconstruct seawater isotopic composition. Otolith δ18O remained relatively stable between 1989 and 2010, whereas a statistically significant decrease in δ13C was detected across the time interval investigated, with a rate of decline of 0.05‰ yr⁻¹ (−0.94‰ depletion throughout the recorded period). The depletion in otolith δ13C over time was associated with the oceanic uptake of anthropogenically derived CO₂.

1. Introduction

The increase of anthropogenic emission of carbon dioxide (CO₂) and other greenhouse gases to the atmosphere since the industrial revolution is receiving growing attention in recent years (Pachauri and Meyer, 2014). The concentration of CO₂ in the atmosphere has increased almost 40% since preindustrial times in 1850 and continues to increase (Francey et al., 1999; Le Quéré et al., 2014). Carbon and oxygen stable isotope ratios δ13C and δ18O (expressed in parts per thousand in relation to Vienna Pee Dee Belemnite, hereafter represented by δ13C and δ18O respectively) in the atmosphere and ocean fluctuate temporally due to both natural and anthropogenic processes. Atmospheric δ13C has decreased by ~2‰, from −6.4‰ in 1850 (Suess, 1955; Friedli et al., 1986) to −8.4‰ in 2012 (Keeling et al., 2005 and http://scrippsco2.ucsd.edu/data/mlo.html). Global δ13C and CO₂ trends in the atmosphere are anticorrelated at both seasonal and annual scales (Keeling et al., 2011). Plants have less δ13C relative to the atmospheric δ13C due to fractionation during photosynthesis (Farquhar et al., 1989), and thus, the burning of most fossil fuels releases relatively light carbon isotopes. Hence, CO₂ released to the atmosphere by human activities is enriched in the lighter carbon isotope (¹²C), causing a noticeable depletion in atmospheric δ¹³C. Additionally, the lighter carbon isotope (¹²C) is preferably absorbed by plants to perform photosynthesis (O’Leary, 1981), and deforestation also contributes to the atmospheric depletion of δ¹³C. The combination of both elements leads to a depletion in atmospheric δ¹³C, which is commonly referred to as the “Suess effect” (Suess, 1955; Keeling, 1979; Verburg, 2007).

Atmospheric CO₂ partly dissolves into the ocean and the relative proportion of dissolved inorganic ¹³C in the oceans is steadily decreasing over time (Quay et al., 1992). Determining the rate of oceanic CO₂ uptake is of considerable importance in this context, and recent attention has focused on air–sea CO₂ exchange (e.g., Sarmiento et al., 2010; Raupach et al., 2014; Sitch et al., 2015). The air–sea gas exchange leads to the dissolution of atmospheric CO₂ into the ocean, and consequently the ¹³C-Suess effect is reflected in the marine environment (Suess, 1955; Broecker and Maier-Reimer, 1992; Lynch-Stieglitz et al., 1995; Bacastow et al., 1996). Additionally, biological processes, including carbon fixation by primary producers, soft part organic tissue degradation and hard-part CaCO₃ remineralization, may play an important role in controlling oceanic δ¹³C, which varies regionally and with
time and depth (Gruber et al., 1999; White, 2015). The marine $^{13}$C-Suess effect has attracted interest because it provides means for estimating the ocean’s uptake rate of anthropogenic CO$_2$ (Quay et al., 1992; Bacastow et al., 1996).

While surface ocean $^{13}$C changes are linked to complex interactions between biological, thermodynamic and kinetic processes, (Gruber et al., 1999; Tagliabue and Bopp, 2008), oxygen stable isotope ratios in seawater are related to water temperature and salinity, and seawater $^{18}$O varies with ice volume, precipitation, evaporation or continental runoff. Higher $^{18}$O values indicate lower temperatures and higher salinities, and thus, $^{18}$O values of seawater display seasonal, interannual and long-term variations related to hydrological cycle and climate changes (Craig and Gordon, 1965; Killingley and Berger, 1979).

Calculated structures such as shells or fish skeletons precipitate in equilibrium with seawater, recording seawater chemistry and other environmental conditions (Kerr and Campana, 2014). Carbon and oxygen stable isotopic differences associated with marine microfossils and corals are widely used in paleoceanography for climate reconstructions (e.g. Spero et al., 1997; Taricco et al., 2009; Felis and Rimbu, 2010). However, studies using structures from marine vertebrates like fish's balance, orientation, and sound detection (Campana and Neilson, 1985). Given that the chemical composition of otoliths is linked to ambient seawater conditions these calculated structures are a powerful tool to investigate environmental histories of fishes. Following this line, otoliths of the long lived species Atlantic bluefin tuna (Thunnus thynnus) have been previously used to reconstruct interdecadal variations in oceanic $^{13}$C and $^{18}$O (Schloesser et al., 2009).

Here we investigate temporal variation in the otolith $^{13}$C and $^{18}$O of Atlantic bluefin tuna during the age-0 period within the Mediterranean Sea as a proxy for examining changes in oceanic $^{13}$C (Suess effect) and $^{18}$O. During the first year, juvenile bluefin tuna can swim over vast geographic distances, but remain mainly in surface waters (Tudela et al., 2011; Galuardi and Lutcavage, 2012). Individuals produced in the Mediterranean Sea appear to stay within this basin (including the Strait of Gibraltar) during the first year of life (Rey, 1978), but as highly mobile predators, they may carry out local migrations to foraging areas throughout the Mediterranean Sea (Rooker et al., 2007). Therefore, otolith $^{13}$C and $^{18}$O accreted during the first year (hereafter referred to as otolith core) is likely reflective of seawater conditions within this basin. By analyzing stable isotopic composition of tuna otoliths we produced annual-resolution otolith $^{13}$C and $^{18}$O records for the Mediterranean Sea between 1989 and 2010, which was used to reconstruct seawater stable isotope composition shifts in this region. The time series of otolith $^{13}$C and $^{18}$O presented here contribute to our understanding of the oceanic carbon cycle, and enables to estimate the uptake rate of anthropogenic CO$_2$ by the Mediterranean Sea over the past two decades.

2. Material and methods

Bluefin tuna ($n = 632$) were captured between 2009 and 2011 from different locations in the Mediterranean Sea ($n = 150$), Strait of Gibraltar ($n = 174$) and the Bay of Biscay ($n = 308$) in the North Atlantic under an international biological sampling program by the International Commission for the Conservation of Atlantic Tunas (ICCAT, Fig. 1). Bluefin tuna from the foraging area in the Bay of Biscay were collected in the summer (June–September). Specimens from the Strait of Gibraltar were captured by Spanish traps in May, and by Portuguese traps mainly between late August and October. Sampling in the Mediterranean Sea included the eastern (Levantine Sea), central (region neighboring Malta in the Ionian Sea and waters around Sardinia in the Tyrrhenian Sea), and western (Balearic Sea) regions of the basin. Previous studies have demonstrated that the majority of bluefin tuna captured in these areas have originated in the Mediterranean Sea (> 95% in the Bay of Biscay and 100% in the Mediterranean Sea and Strait of Gibraltar based on Rooker et al., 2008, 2014; Fraile et al., 2015). Therefore, bluefin tuna used to characterize temporal shifts in otolith $^{13}$C and $^{18}$O were assumed to have resided within the Mediterranean Sea during their age-0 life period.

Fork length of each individual (FL, cm) was also recorded during the sample collection. Age–length relationship was used to estimate the age of individuals from length data by an inverse von Bertalanffy function (ICCAT, 2012, Cort, 1991). The sizes of individuals ranged from 52 to 282 cm FL with corresponding ages of 1 to 22 years, and birth year was back-calculated based on the estimated age and collection date (Table 1). The contribution of older individuals to the temporal patterns of otolith $^{13}$C and $^{18}$O was tested by selecting a subgroup of bluefin tuna <15 years and comparing these results with the complete
dataset. We used individuals of different age classes to investigate interannual variations over the last 22 years and represent the overall trend of isotopic values by capturing the different potential bluefin tuna subpopulations of the Mediterranean Sea.

After extraction, sagittal otoliths of bluefin the tuna were cleaned of tissues, soaked briefly in dilute nitric acid (1%), and then rinsed with deionized water. One otolith per fish was randomly selected and embedded in an Epoxy resin (Struers) to cut a transverse section of approximately 1.5 mm thick across the core using an IsoMet® low-speed saw. Sections were then glued in a sample plate with thermoplastic glue. The otolith zone corresponding to the first year of growth was isolated and powdered using a high-resolution New Wave Micromill System consisting of a microscope and imaging system, controlled by computer software. The drill path corresponding to the yearling period was the same as the one used in previous studies (Scholeser et al., 2009; Rooker et al., 2014). The aragonite powder samples were analyzed for carbon and oxygen stable isotopes on an automated carbonate preparation device (KIEL-III) coupled to a gas-ratio mass spectrometer (Finnigan MAT 252) from the Environmental Isotope Laboratory of the University of Arizona. All the measurements are reported in the standard δ notation. The isotopic ratio measurements were calibrated based on repeated measurements of National Bureau of Standards (NBS) NBS-19 and NBS-18, and the precision of isotope ratio measurements were ±0.10‰ for δ18O and ±0.08‰ for δ13C (1σ). Multiple isotopic measurements from a single otolith (0.03‰ for δ13C and 0.04‰ for δ18O) indicated relatively high analytical precision for otolith δ13C and δ18O.

For otoliths collected in the Bay of Biscay, quadratic discriminant function analysis (QDFA) was performed to identify potential western Atlantic migrants; only individuals from Mediterranean nursery origin were selected for this study (Fraile et al., 2015). No prior classification was performed in samples from the Strait of Gibraltar and Mediterranean Sea because previous studies have revealed that 100% of bluefin tuna from these areas are originated within the Mediterranean Sea (Rooker et al., 2014). Kendall’s tau test was used to identify temporal trends in otolith δ13C and δ18O values, and the statistical meaningfulness of the trend was further evaluated using the methodology developed by Brynh and Dimberg (2011). Values of R2 ≥ 0.65 and p < 0.05 were considered as statistically significant. Additionally, linear models (LM) were used to determine whether otolith δ13C and δ18O values varied significantly with birth year. When a significant relationship was identified, a linear regression was fitted to model the relationship between birth year and isotope values. Normal distribution assumption was tested with Shapiro–Wilk’s normality test applicable for isotope data to ensure that both δ13C and δ18O values were normally distributed (i.e., no prior transformation was needed). Further, the Breusch–Pagan test was used to check the assumption of homoscedasticity of the residuals from the linear regression, and no significant heteroscedasticity was detected (p-value > 0.05). To examine the effects of influential points on the linear regression, isotopic values corresponding to the oldest bluefin tuna from 1989 and 1990 were analyzed by computing Cook’s distance. Additionally, model fit was evaluated using standard diagnostic plots (residuals versus fitted values, standardized residuals against quantiles of the standard normal distribution), standardized residuals against fitted values and Cook’s distance plot), and the distribution of the residuals as well as the variance structure was found to be adequate to meet model assumptions.

Otolith δ13C values from 1989 to 2010 were then compared to environmental data (sea surface temperature (SST), sea surface salinity (SSS), surface chlorophyll-α concentration (chl-α) and CO2 emissions to the atmosphere) for the same time period in the Mediterranean Sea. Given the strong internal gradient in physico-chemical properties within the Mediterranean Sea, reference values from the Strait of Gibraltar (located at the western entrance to the Mediterranean Sea), Ionian Sea (central Mediterranean Sea) and Levantine Sea (eastern Mediterranean Sea) were used to represent the longitudinal range of environmental conditions within the basin. Night-time sea surface temperature (SST) data were derived from AVHRR Pathfinder Version 5.2 data, obtained from the US National Oceanographic Data Center and GHRSSS (http://pathfinder.nodc.noaa.gov; updated from Caseley et al., 2010). Statistical values averaged for 22.5° × 22.5° (latitude × longitude) grid were used, and mean August temperature was computed to represent summer SST variation. Eastern Mediterranean Sea SST corresponded to the average value East of 22.5° E, central Mediterranean SST represented the average temperature from 0 to 22.5° E, and the Strait of Gibraltar was considered the region west of 0°. Summer SSS of the Mediterranean Sea was derived from the Mediterranean Sea Physics Reanalysis (1987–2013) generated using Copericus Marine Environment Monitoring Service (CMEMS) products. Salinity estimates of three reference points have been selected to represent different Mediterranean regions: Levantine Sea representing eastern Mediterranean Sea (34°N 30°E), Ionian Sea representing the central Mediterranean Sea (34°N 15°E) and the Strait of Gibraltar representing the western limit of the age-0 tuna habitat (36°N 2°W). SeaWiFS monthly estimates of surface chl-α concentration in the Mediterranean Sea were used to describe summer chl-α variation between 1997 and 2010 (satellite launched in August 1997 by NASA’s Earth Observing System; Hooker and Esaias, 1993). Data from the Levantine Sea (34°N 30°E), Ionian Sea (34°N 15°E) and the Strait of Gibraltar (36°N 2°W) were used to represent eastern, central and western Mediterranean Sea regions (13 monthly dataset at a resolution of 9 km available from https://podaac.jpl.nasa.gov). The mean August chl-α value in the Strait of Gibraltar, central Mediterranean Sea and eastern Mediterranean Sea were used to represent summer chl-α concentration (mg m⁻³). Emissions of CO2 to the atmosphere from fossil-fuel combustion were estimated using the Carbon Dioxide Information Analysis Center (CDIAC), and emissions from countries surrounding the Mediterranean Sea were computed from 1989 to 2010 (Boden et al., 2013). Correlation analysis was used to examine the relationship between otolith δ13C and CO2 emissions.

3. Results and discussion

Otolith δ13C and δ18O values of bluefin tuna ranged from −10.24 to −6.96‰ and from −1.38 to 0.02‰, respectively. Kendall’s Tau test indicated a negative relation between otolith δ13C and birth year (p < 0.05) and the statistical meaningful of the trend was found to be significant (p < 0.05), with otolith δ13C becoming more depleted as the birth year approached 2010. Likewise, the LM analysis and showed a statistically significant (p < 0.05) depletion in δ13C values from 1989 to 2010. In contrast, temporal pattern in otolith δ18O was not significant based on Kendall’s Tau test, the statistical meaningfulness tests of Brynh and Dimberg (2011) and the LM analysis (Fig. 2). The isotopic values corresponding to otoliths of bluefin tuna born before 1993 were not influential on the overall trend, with Cook’s distance less than 1.

Otolith δ13C values decreased 0.94‰ from 1989 to 2010, which corresponds to annual depletion rate of 0.05‰. The marine Suess effect has been previously reported using otoliths from Atlantic bluefin tuna collected in the western Atlantic Ocean from 1947 to 2006, and the

Table 1

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<tr>
<th>FL (cm)</th>
<th>Age (year)</th>
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<tr>
<td>Range</td>
<td>Mean</td>
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<tr>
<td>52.5–182</td>
<td>103.5</td>
<td>1–8</td>
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<tr>
<td>161–278</td>
<td>209.6</td>
<td>6–21</td>
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<tr>
<td>112.7–282</td>
<td>206.1</td>
<td>3–22</td>
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depletion rate for otolith $\delta^{13}C$ reported in that study was 0.026‰ per year (Schloesser et al., 2009). The $\delta^{13}C$ depletion rate reported for the western Atlantic Ocean using bluefin tuna otolith was twice as low as that estimated for the Mediterranean Sea (Schloesser et al., 2009), which implies that the high depletion rate found in our tuna otolith is not a species specific characteristic, but may be due changes in seawater $\delta^{13}C$ in the Mediterranean Sea over the last two decades. Similarly, the Suess effect has been documented in other biogenic carbonates of the world’s oceans (e.g., corals [Pelejero et al., 2005; Swart et al., 2010; Dassié et al., 2013], mussel shells [Butler et al., 2009; Pfister et al., 2011] or planktonic foraminifera [Black et al., 2011; Beveridge and Shackleton, 1994; Bauch et al., 2000]), as well as in $\delta^{13}C$ reconstruction based on chlorofluorocarbons (CFCs) (Körtzinger and Quay, 2003). Although species specific carbonate fractionation or habitat use may influence the isotopic composition of their carbonates, $\delta^{13}C$ depletion rates estimated for the tropical North Atlantic Ocean using different marine organisms are of similar magnitude for a similar time frame ($-0.02\text{‰ yr}^{-1}$, $-0.027\text{‰ yr}^{-1}$ and $-0.03\text{‰ yr}^{-1}$ based on scleropleges, corals and planktonic foraminifera, respectively [Böhm et al., 1996; Swart et al., 2010; Black et al., 2011]). On the other hand, CFC-derived water ages have shown that the $\delta^{13}C$ depletion rates vary from region to region, with overall depletion rates being higher in tropical and subtropical oceans compared to polar regions (Sonnerup et al., 1999). Furthermore, an inter-ocean comparison based on $\delta^{13}C$ measurements in corals have revealed higher depletion rates in the Atlantic Ocean compared to Pacific Ocean and Indian Ocean (Swart et al., 2010). However, the magnitudes of depletion rates reported on these studies for the period 1960 – early 2000s were lower than the 0.05‰ yr$^{-1}$ recorded by fish otoliths in the Mediterranean Sea. The high depletion rates found in fish otoliths in the Mediterranean Sea may be due to the special characteristics of this semi-enclosed basin with narrow connection with the Atlantic Ocean making particularly sensitive to anthropogenic perturbations and climate change (Diffenbaugh and Giorgi, 2012). Due to the higher total alkalinity of the Mediterranean Sea compared to open ocean, it has a greater capacity to absorb anthropogenic CO$_2$ (Palmieri et al., 2015), leading to an amplification of the Suess effect. However, a recent study using mussels shells from the southern California estimated a $\delta^{13}C$ depletion rate of $-0.07\text{‰ yr}^{-1}$ from 1999 to 2009 (Pfister et al., 2011). The unusually high depletion rates found by Pfister et al. (2011) coupled with our observed rate of depletion may indicate an acceleration of the Suess effect over the last few decades.

An increase in sea surface temperature of the Mediterranean Sea, may also have contributed to the observed decline in otolith $\delta^{13}C$ values (Santoreli et al., 1995; Skliris et al., 2012). In order to quantify the effect of seawater temperature on otolith $\delta^{13}C$, summer sea surface temperatures (SST) from eastern Mediterranean Sea, central Mediterranean Sea and Strait of Gibraltar were derived from AVHRR Pathfinder Version 5.2 for the period 1989–2010 (Fig. 3). An increasing trend was visible for all localities, although this warming trend during the studied period was significant only in the eastern Mediterranean Sea (p-value < 0.05). The estimated increase of SST from the linear regression of satellite data was of 0.4 °C in the central Mediterranean Sea and Strait of Gibraltar and of 1.9 °C in the eastern Mediterranean Sea during the period studied. Using the thermodynamic relationship between $\delta^{13}C$ in otoliths and temperature from Thorrold et al. (1997) and assuming constant seawater $\delta^{13}C$ concentration, we estimated a depletion of 0.07‰ (in the Strait of Gibraltar and central Mediterranean) and 0.34‰ (in the eastern Mediterranean Sea) caused by the increase in temperature. The magnitude of the $\delta^{13}C$ depletion estimated in our study (0.94‰ over a 21 yr period) exceeds that expected from the temperature-$\delta^{13}C$ relationship presented by Thorrold et al. (1997), since an increase in surface temperature of approximately 5 °C would be needed to explain a depletion in otolith $\delta^{13}C$ of 0.94‰. Still, thermodynamic effect in carbonate fractionation may be important, especially in the eastern Mediterranean Sea where SST raise in the last decades has been more pronounced (Fig. 3). The depletion in otolith $\delta^{13}C$ after substracting thermodynamic effect on $\delta^{13}C$ fractionation was estimated to be between 0.6‰ and 0.87‰ over the studied period, which turns in a depletion rate of about 0.03‰–0.04‰ yr$^{-1}$. Alternatively, decreased primary production (reducing isotopically light carbon in seawater) could also contribute in decreasing otolith $\delta^{13}C$. However, chl-α concentration estimated from remote sensing data over the last 12 years for the three Mediterranean Sea regions indicated that the variation in summer phytoplankton production in these regions was not significant, suggesting that any effect on otolith $\delta^{13}C$ depletion is likely inconsequential (Fig. 3). An increase in summer surface salinity was detected from 1989 to 2010; although this temporal variation was significant only in the eastern Mediterranean Sea. Given that otolith $\delta^{13}C$ shows a positive relationship with salinity (Elsdon and Gillanders, 2002), the influence of salinity otolith $\delta^{13}C$ values of bluefin tuna was also assumed to be unimportant. Our findings suggest that seawater $\delta^{13}C$ variation is likely the main factor influencing the observed temporal pattern in otolith $\delta^{13}C$. The accelerated depletion of $\delta^{13}C$ observed in the otoliths of bluefin tuna may be linked to increased C0$_2$ emission rates observed in the last decade, and attributed primarily to increases in fossil fuel combustion and cement production (Le Quéré et al., 2014). Global atmospheric
CO₂ concentration and the uptake of CO₂ by ocean and terrestrial “CO₂ sinks” are still increasing with time, leading to declines in both atmospheric and oceanic δ₁³C (Le Quéré et al., 2014). Anthropogenic CO₂ emissions to the atmosphere from Mediterranean countries have increased significantly during the past few decades (Fig. 3). Between 1989 and 2010, CO₂ emissions and annual mean otolith δ₁³C values showed a strong negative correlation (correlation coefficient of −0.86), confirming the influence of anthropogenic CO₂ on otolith δ₁³C (Fig. 4).

Despite of the temporal decline in otolith δ₁³C values, the data exhibit much variability over the entire time period. This high variability can be explained by the differences in the migratory movements among individuals, meaning that individuals in our sample likely experienced different environmental conditions or water masses during the young

Fig. 3. A) Linear regression applied on AVHRR-derived SST data from 1989 to 2010 in the eastern Mediterranean Sea, central Mediterranean Sea and Strait of Gibraltar as indicated by nighttime satellite observations and corresponding δ₁³C depletion rate for the same period. Average August SST was used to represent summer temperature (Strait of Gibraltar and Ionian Sea: slope (b) = 0.02, standard error (SE) = 0.02, p-value > 0.05; Levantine Sea: b = 0.09, SE = 0.01, p-value 0.05; Ionian Sea: b = −0.002, SE = 0.001, p-value 0.05). C) Summer sea surface salinity from 1989 to 2010 in the eastern Mediterranean Sea, central Mediterranean Sea and Strait of Gibraltar (from Mediterranean Sea Physics Reanalysis [1987–2013] generated using CMEMS products) (Strait of Gibraltar: b = 0.001, SE = 0.005, p-value > 0.05; Ionian Sea: b = 0.01, SE = 0.008, p-value > 0.05; Levantine Sea: b = 0.01, SE = 0.004, p-value 2 emissions to the atmosphere between 1989 and 2010 around the Mediterranean countries (from Boden et al., 2013) (Strait of Gibraltar: b = 1.7·10³, SE = 85, p-value < 0.05; Ionian Sea: b = 1.4·10¹, SE = 69, p-value < 0.05; Levantine Sea: b = 2.3·10³, SE = 110, p-value < 0.05).

Fig. 4. Relationship between yearly mean otolith δ₁³C values between 1989 and 2010 measured on bluefin tuna (Thunnus thynnus) from the Mediterranean Sea and annual CO₂ emissions to the atmosphere around the Mediterranean countries (data from Boden et al., 2013).
of the year period. Movements of young individual bluefin tuna within the Mediterranean Sea are still not well resolved, but by the end of the age-0 period these fish are capable to swim long distances. When different schools of bluefin tuna occur at the same region, they tend to mix and regroup themselves into new school units (Hilborn, 1991). During these migrations, bluefin tuna feed on different types of prey and reside in water masses of distinct physico-chemical and biological properties, being exposed to conditions influencing δ13C incorporation into their otoliths. Thus, the high variability of carbon isotopes may be linked to differences among individuals in the diet, behavior and habitat types (with differing temperature and productivity regimes) during the first year of life. Additionally, seasonal and interannual variations in the comparatively fresher North Atlantic water mass entering through the Strait of Gibraltar may also introduce additional variability by influencing the isotopic signature of individuals that reside in the western part of the Mediterranean Sea (Macías et al., 2008). While individual δ13C values vary considerably, annual mean δ13C values reflect an integrated signal of the Mediterranean basin. Although individual movements result in the variability within a certain year, the observed decadal-scale trend in δ18O record that we observed in Atlantic bluefin tuna otoliths appears related to the carbon cycle in the Mediterranean Sea. Swart et al. (2010) suggested that δ13C in corals is an important tracer for oceanic uptake of anthropogenic CO2, as they reflect δ13C of the dissolved inorganic carbon of the surface ocean. Schloesser et al. (2009) found a strong correlation between δ18O in otoliths and atmospheric δ18O, and concluded that bluefin tuna otoliths effectively track changes in atmospheric δ18O. The progressive decline in otolith δ18O in the current study also could be ascribed to the Suess effect in the Mediterranean Sea. A recent study by Palmiéri et al. (2015) simulated Mediterranean Sea’s uptake of anthropogenic CO2 during the last two centuries, and found an steep increase in anthropogenic carbon since the industrial period. Likewise, an increase in dissolved inorganic carbon over the past few decades has been reported for the western and central Mediterranean Sea (Touratier and Goyet, 2009; Luchetta et al., 2010; Geri et al., 2014).

Results derived from the LM analysis indicated a lack of temporal pattern in otolith δ18O (Fig. 2). Seawater δ18O varies principally due to evaporation, precipitation and river input. The difference in otolith δ18O values of bluefin tuna measured by Schloesser et al. (2009) and the current work is likely due to salinity differences between the Mediterranean Sea and western North Atlantic Ocean (Fig. 2). The small but significant variation in otolith δ18O found by Schloesser et al. (2009) was associated to changes in salinity regimes around the Gulf Stream. In contrast, an increase in salinity between 1989 and 2010 was only significant in the eastern Mediterranean Sea (Fig. 3), with minor implications for the overall otolith δ18O trend. Moreover, previous studies have shown that δ18O fractionation in otoliths is also temperature dependent, with inverse relationship between otolith δ18O and water temperature (Thorrold et al., 1997). Assuming a SST increase between 0.4 and 1.9 °C (AVHRR Path), the increase of atmospheric δ18O over the time period investigated, likely due to the opposite effect of increasing SST and salinity in δ18O fractionation. Interdecadal changes recorded in the otoliths of bluefin tuna demonstrate the promise of the approach for tracking temporal changes in the seawater chemistry and past environmental conditions experienced by bluefin tuna.

4. Conclusions

We present an annual resolution δ13C and δ18O record from Atlantic bluefin tuna otoliths that reflects changes in oceanic δ13C of the Mediterranean Sea from 1989 to 2010. A year to year depletion in otolith δ13C was observed for the study period, which correlated with the increase of atmospheric CO2 emissions around the Mediterranean countries. As a result, otolith δ13C depletion could be attributed to the increase in anthropogenic CO2 emissions (Suess effect). A depletion of 0.94‰ was estimated over a 22 yr period, which translates in an annual depletion rate of 0.05‰. This depletion rate is higher than previously reported, and was interpreted as a consequence of combined thermodynamic effect on isotopic fractionation and the Suess effect. The increase of SST between 1989 and 2010 could explain part of the depletion observed in bluefin tuna otoliths. After subtracting thermodynamic effect, the net δ13C depletion between 0.6‰ and 0.87‰ was estimated to be due to the oceanic Suess effect, which turns in a depletion rate of about 0.03‰–0.04‰ yr⁻¹. This is still higher than most of the previously reported values in the tropical and temperate North Atlantic Ocean, suggesting that the Suess effect between 1989 and 2010 in the Mediterranean Sea may be magnified compared to open ocean regions. We also found little variation in otolith δ18O over the time period investigated, likely due to the opposite effect of increasing SST and salinity in δ18O fractionation.

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