ISSN: 2148-9173 Vol: 8 Issue:4 December 2021

International Journal of Environment and Geoinformatics (IJEGEO) is an international, multidisciplinary, peer reviewed, open access journal.

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Abstracting and Indexing: TR DIZIN, DOAJ, Index Copernicus, OAJI, Scientific Indexing Services, International Scientific Indexing, Journal Factor, Google Scholar, Ulrich's Periodicals Directory, WorldCat, DRJI, ResearchBib, SOBIAD

IJEGEO

International Journal of Environment and Geoinformatics 8(4):467-474 (2021)

Research Article

Analysis of Black Sea Ocean Acidification

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Received 11.01.2021
Accepted 22.08.2021

How to cite: Elge (2021). Acidification Analysis of Black Sea. *International Journal of Environment and Geoinformatics (IJEGEO)*, 8(4): 467- 474. doi. 10.30897/ijegeo. 857893

Abstract

Increasing anthropogenic CO2 concentration in the troposphere causes more uptake by oceans and results in ocean acidification. Albeit, food web in the ocean, marine animals and calcifying bioata are affected negatively. Some marine species might have the possibility of extinction and some may have evolved eventually due to ocean acidification. In this study, the acidification of Black Sea is analyzed based on the pH observations made between 1990 and 2014. Sea surface pH value is found to be decreased by 0,07 and increased by 0,104 between 1990-2004 and 2005-2014 respectively. The pH annual variations also compared analytically to the annual averages of air temperature and CO2 emissions of Turkey. Both the air temperature and CO2 emission is increasing either in 1990-2004 or 2005-2014, while the rate of increase in 2005-2014 is greater than in 1990-2004. The decreasing pH (which means acidification) in 1990-2004 is found to be the reason of this difference, because some CO2 is considered to be absorbed by Black Sea. In terms of climate change, it shows that this acidification is a little bit slowing down the temperature increase over the Black Sea region while CO2 and air temperature increasing rate is less between 1990-2004 (where surface pH of Black Sea decreases) than 2005-2014.

Keywords: Black Sea, Acidification, Anthropogenic CO2, Air Temperature, Climate Change

Introduction

One of the consequences of global climate change is the increase of acid rates in the oceans and seas which is called as ocean acidification. CO2 amount in the troposphere has been increasing artificially by the anthropogenic activities. The great portion of this CO2 is absorbed by the oceans and seas. Fierer et al (2006) described that 30% of the human induced CO2 is penetrating into oceans and seas by absorption. This process decreases the alkalinity and pH of the oceans, and results in acidification (Gazioğlu et al., 2015; Gazioğlu and Okutan, 2016). Since the beginning of industrial period, the pH of the oceans and seas decreased 0,1 unit on average which means that 26% acidification (IPCC5 2014; Ülker et al., 2018; Mersin et al., 2020; Ahmetoğlu and Tanık 2020). This acidification usually happens in the surface layer of oceans and seas where air-sea interaction mostly occurs.

As a result of this acidification, the calcium of the sea water decreases which causes an unhealthy condition for skeleton and bones of marine animals and calcifying bioata (Buckingham, 2005). Additionally, some species might have the possibility of extinction or some may have evolution eventually. Because of this process, marine life ecosystem may be affected and food chain may have some tremendous changes. Recently, more scientific research has been concentrated on the chemical and biological effects of acidification affecting marine life. Villalobos et. al (2020) studied the combined effects of ocean acidification and warming on Pacific herring (Clupea pallasi) early life history stages. Rölfer et al. (2021) explored the combined effect of temperature increase and ocean acidification on the competition between the coral Porites lobata and on the Great Barrier Reef abundant macroalga Cholorodesmis fastigiata, while they indicated that information on the impacts of global and climate change on ecological interactions are still underrepresented in the literature.

However, absorption of CO2 in the troposphere by oceans decreases the amount of greenhouse gases in the lower atmosphere which is in turn a positive contribution to diminish the temperature increases due to the greenhouse gases. Albeit, acidification of the oceans is a negative effect on climate change.

There are other factors beside the CO2 absorption which causes acidification in the oceans and seas, such as increase of fresh water, decrease of sea water temperature, upwelling, transportation of industrial remnants by river run off.

IPCC5 2014 states that fresh and cold water can absorb more CO2 from the atmosphere which will enable acidification in this kind water masses. Black Sea surface water temperature is about 17-19 ℃ at average (where around 14 ℃ during winter and 25 ℃ during summer) and salinity is about 17-18 psu at average (Oguz et al 1993). Beside low temperature and fresh water at the surface, there is a Cold Intemediate Water Layer (CIL) within the 100 m sub surface of the Black Sea (most of its pcynocline), and characterized by 8 ℃

temperature which is the lowest for the Black Sea (Miladinova et al 2018, Flippov 1968, Oguz et al 1993, Oguz and Besiktepe 1999, Ovchinnikov and Popov 1987). The basin's oceanography is strongly influenced by fresh water inputs by rivers, active atmospheric forcing, and thermohaline driving factors (Rim current and shelf eddies), fluxes through straits and sharp changes in topography (Özsoy and Ünlüata 1997).

Since it has colder and fresher surface waters than the Mediterranean and Agean Sea surrounding Turkey, Black Sea is potentially the most absorber of CO2 amongst these seas. As a result of this, there might be an acidification in Black Sea as well. However, there is not enough research on pH variations to scientifically understand the acidification occurs in Black Sea or not except Polonsky 2012. Orr (2012) explained the details of ocean acidification where estimated how 21st century acidification of Baltic, Mediterranean and Black Sea may differ from that of the global ocean by using thermodynamics constants and assuming equilibrium between atmospheric and oceanic CO2 at the chemical and hydrographic conditions typical of each sea.
In this study, pH variations between 1990 and 2014 of surface water of Black Sea were analyzed with the aim of presence of acidification. Additionally, these pH variations relations with anthropogenic CO2 emissions and air temperature were statically calculated.

Materials and Methods

The pH data used for analysis between 1990 and 2014 in Black Sea were mainly obtained from European Union Sea Data Net-2 Project data portal (URL 1 2015) and few data from Office of Navigation, Hydrography and Oceanography. Most of the data were available in SeaDataNet2 data portal which were provided by SeaDataNet project partners (URL1 2015) and Upgrade Black Sea Scene Project partners (URL 2 2015) from Black Sea Nations for scientific research. Data policy indicated by SeaDataNet2 project (URL 3 2015) was applied in this study. The spatial and temporal distribution along with the number of stations in each year of analyzed pH data is shown in Figure 1. The data intensity of northern part of Black Sea is more than the southern part.

pH data were analyzed at the surface and the bottom layers separately. Since Özsoy and Ünlüata 1997 indicated that surface mixing depth is within the 30m and halocline and pycnocline are at typically 100-200 m, data within the 30 m were considered as surface layer whereas data at deeper layer than 100 m were considered as bottom layer. Ocean Data View software (Schlitzer. R., 2015) was used to data analysis. First, data was quality controlled to get rid of insignificant spikes, and then averaged over entire basin at surface and bottom layers separately. pH decrease and increase tendency were analyzed for whole period and the years 1990-2004 and 2005-2014 individually by considering the annual average sea surface temperature anomalies and the amount of fresh water inputs. The resulting tendencies were compared statistically to air temperature and anthropogenic CO_2 emissions. Air temperature was obtained from Turkish Meteorological Office, anthropogenic CO_2 emissions were from the 2013 Climate Change Report of Turkish Meteorological Office was sourced from Turkish Statistical Institute (TUIK). The annual average sea surface temperature anomalies were directly retrieved from European Environment Agency (URL 4 2020).

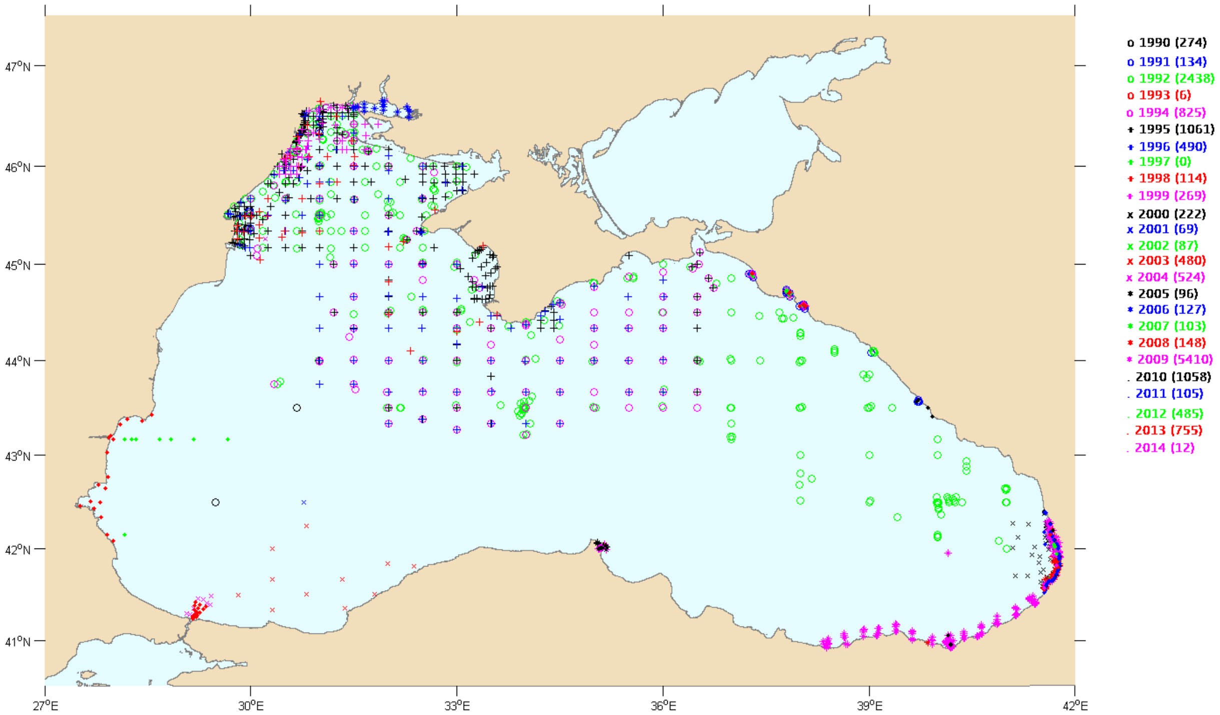


Fig. 1: Analyzed pH data observation stations in Black Sea between 1990 and 2014.

Results

Surface layer (0-30 m) pH variations for 1990-2014 period is presented in Figure 2. The maximum and minimum pH are about 8,7 and 7,4 respectively. Bottom layer pH values (Figure 3) are less than surface layer as expected. Since there is lack of data for 10 years at the bottom layer, this may not represent the real tendency of pH. The general tendency of pH is a little increasing for the whole period. But there is very distinct increase after 2004 while little decrease before it. On the other hand, very significant decrease from 2003 to 2004 (about 0,8 unit) occurred and after 2004, pH increased in a periodic manner till 2014. Since the surface layer pH variations are mostly affect the acidification, the analysis in this study were mainly focused on the surface layer (0-30m). IPCC5 2014 states that fresh and cold water can absorb more CO_2 from the atmosphere which will enable acidification in this kind water masses. Therefore, sea surface temperature and salinity were analyzed for the same period. Albeit, the annual average sea surface temperature anomaly between 1990-2014 is represented in Figure 4 by using the data retrieved from European Environment Agency (URL 4 2020). It is clear that SST anomaly between 1990-2004 is less than (mostly below zero) between 2005-2014 which shows cold SST within this period. This is consisted with decreasing pH within 1990-2004 period since it is assumed that cold surface waters absorbed more CO_2 from the atmosphere. On the other hand, higher SST values between 2005-2014 (average anomalies mostly above zero) made the surface waters of Black Sea less absorber of CO_2 from the atmosphere and this is consisted with increasing pH within this period as well.

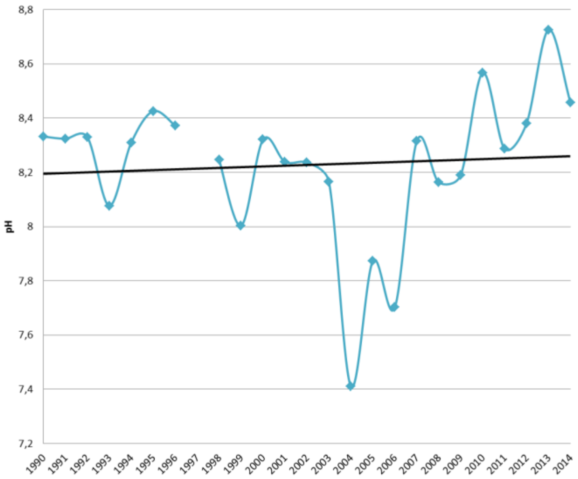


Fig. 2: Annual average pH variations at the surface layer (0-30m) of Black Sea for the period of 1990-2014.

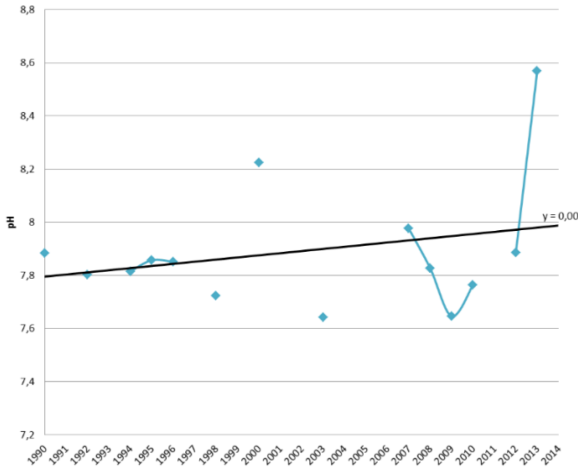


Fig. 3: Annual average pH variations at the bottom layer (100m and deeper) of Black Sea for the period of 1990-2014.

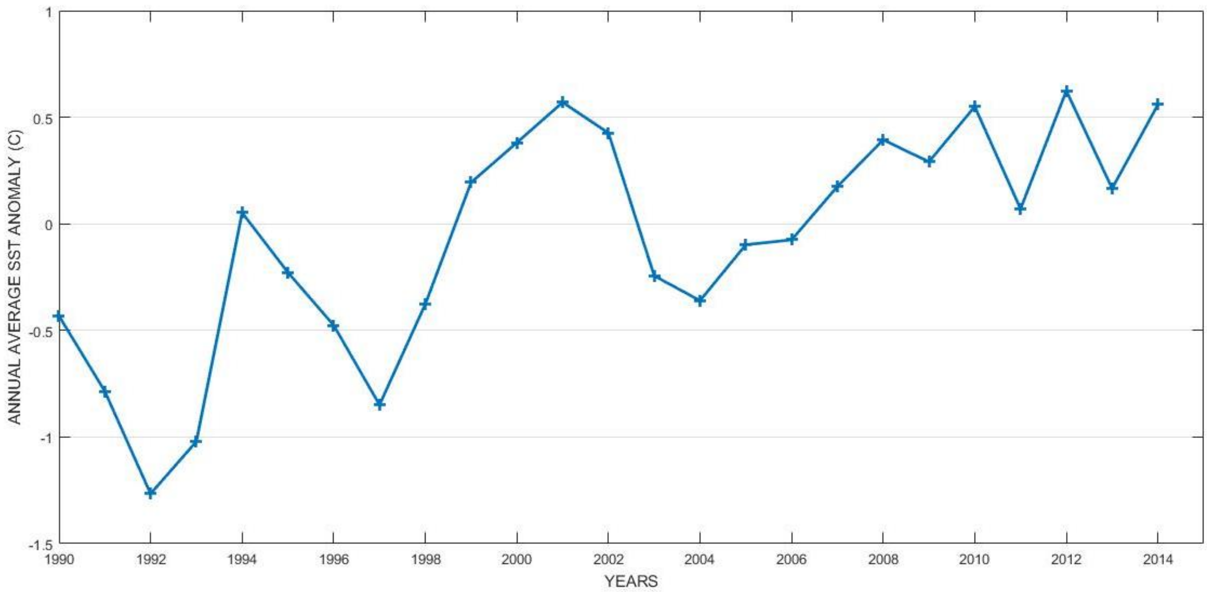


Fig. 4: Annual average SST anomaly of Black Sea between 1990-2014.

Besides the SST, the fresh water input is also important for the salinity feature and acidification. There are 211 river runoff in the Black Sea and great amount of atmospheric precipitation (BSC 2019) which creates a lot of fresh water input to the Black Sea and increase the possibility of CO_2 absorption. BSC 2019 presented annual average river discharge, atmospheric precipitation and total fresh water balance as shown in Figure 5, Figure 6 and Figure 7 respectively.

It can be absolutely discerned from these figures that between 1990 and 2004, the river discharges, atmospheric precipitation and total fresh water balance has increasing tendency and between 2005 and 2014 these features have a tremendous decrease, especially the precipitation and total fresh water balance. This means that fresh water input between 1990-2004 supports the pH decrease while less fresh water between 2005 and 2014 supports the pH increase.

According to these results, it is expected that Black Sea is more likely to absorb CO_2 within the period of 1990-2004 which causes a small acidification with a -0.07 pH decrease and less likely to absorb CO_2 within the period of 2005-2014 which diminish the acidification with a 0.104 pH increase. These total values of increase and decrease were calculated by summing up the differences between consecutive years for each period.

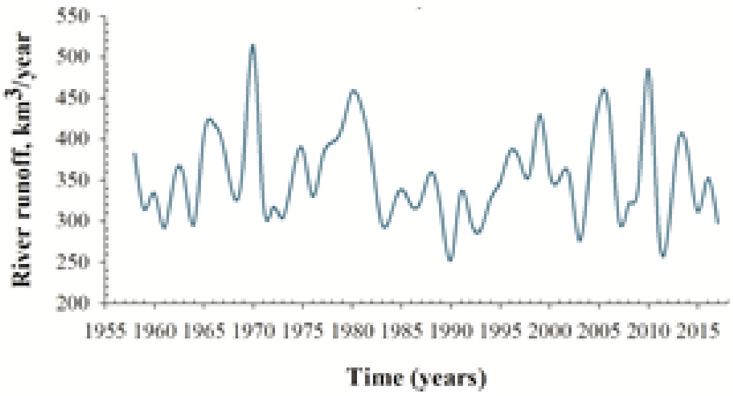


Fig. 5: Annual average river runoff in the Black Sea between 1955-2016. (figure from BSC 2019, page 30)

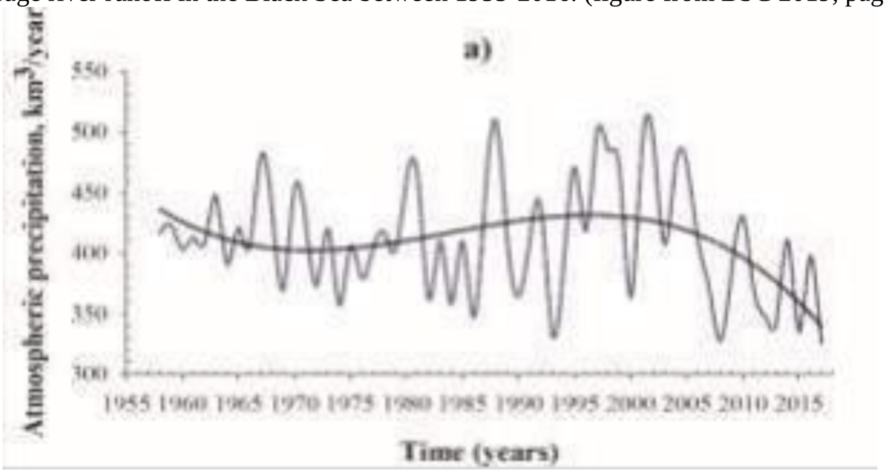


Fig. 6: Annual average atmospheric precipitation in the Black Sea between 1955-2016. (figure from BSC 2019, page 33)

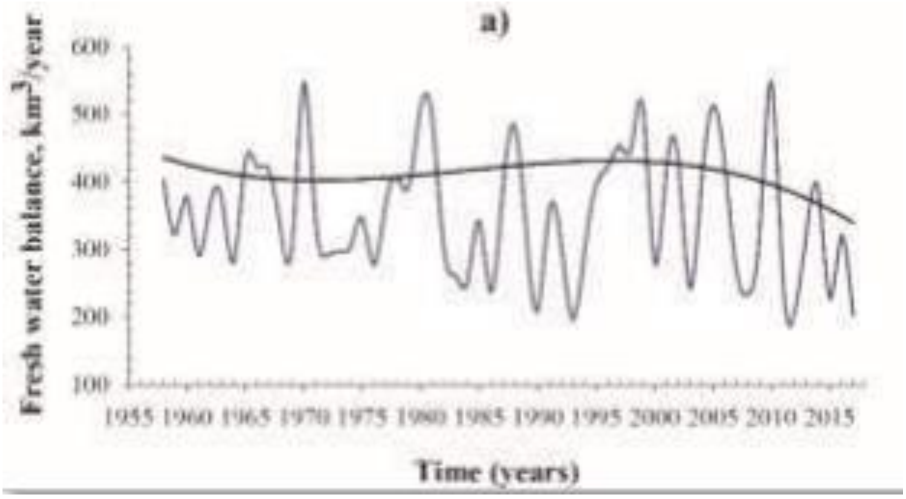


Fig. 7: Annual average fresh water balance in the Black Sea between 1955-2016. (figure from BSC 2019, page 35)

Furthermore, CO_2 emissions, atmospheric temperature and pH variations were statically analyzed to understand if there is a correlation amongst them. Annual Average CO_2 emissions, annual average atmospheric temperature of Turkey and pH time series of Black Sea are presented with their linear equation to understand increasing and decreasing tendency in Figure 8 and Figure 9 for the periods of 1990-2004 and 2005-2014 respectively.

For the period of 1990-2004, air temperature (varies between 11,5-14C) increased linearly with a 0.08 slope, anthropogenic CO_2 emission (from 200-400 million ton) increased linearly with a 8.6 slope where the pH decreased 0.07 unit with a small linear slope of -0.03. This is consistent with the SST anomaly below zero and more fresh water input within the same period (i.e. cold and fresh water, more CO2 absorption and less pH?)

For the period of 2005-2014, air temperature (vary between 13-15℃) increased linearly with a 0.102 slope, anthropogenic CO_2 emission (from 350-450 million ton) increased linearly with a 14.23 slope where the pH increased 0.104 units with a small linear slope of 0.082. Which is consistent with the SST anomaly above zero and less fresh water input within the same period (i.e. warmer and more saline water, less CO_2 absorption and more pH)?

Within the period of 2005-2014, the increasing rate of CO_2 amount in the lower atmosphere is about 1.5 times more than the increasing rate for 1990-2004. By considering that other factors may contribute to this increasing pattern of CO_2, increasing pH is probably the main factor for less Black Sea CO_2 absorption from the atmosphere in the period of 2005-2014 than in the period of 1990-2004 where pH of Black Sea surface waters decreased.

On the other hand, as result of less absorption of CO_2 from the atmosphere, increasing amount of greenhouse gases resulted in more air temperature increase in the period of 2005-2014 than the period of 1990-2004. Since SST is mostly effected by the lower atmosphere through interaction, the colder air temperature supported the colder SST as well as more fresh water discharge in 1990-2004 period. But after 2004, less fresh water discharge (i.e, warmer SST and salinification) and more anthropogenic CO_2 emissions prevented Black Sea surface waters to absorb as much CO_2 as before 2005, and resulted in increase of pH and air temperature.

Polonsky 2012, only unique research on acidification of Black Sea, analyzed the pH observations taken between 1924-2000 to extract interannual to century scale pH variations at surface and 10 m depth layers. He reported that decrease of pH in 1960's and between mid of 1980 and 2000 while between early 1970 and mid of 1980 it was generally high. He also indicated that decadal-scale pH decrease within the last 10-15 years of 20^{th} century at the surface exceeded similar pH decrease at 10 m depth since the decrease reached 0.4 units at the surface while reached 0.2 units at 10 m depth.

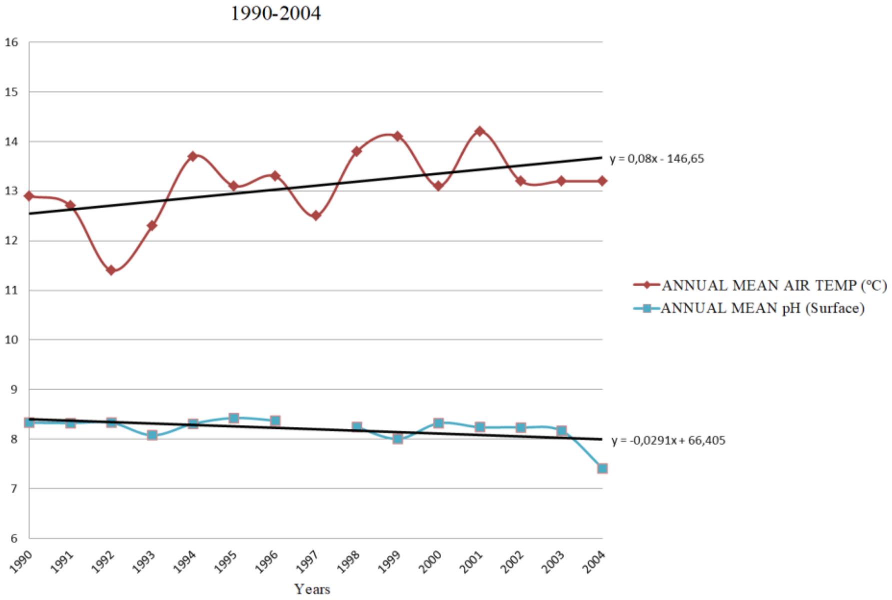
Physical processes of uplifting due to Ekman pumping were explained as the main reason for the decrease of pH at a decadal-scale by Polonsky 2012. Although the decreasing pattern of pH described by Polonsky 2012 is in consistent with decreasing trend of pH for the 1990-2004 period at the surface layer in this study, the magnitude of each pattern is different because of the data temporal and spatial distribution, and the calculation methods (i.e. in this study it is calculated within the first 30 m while in Polonsky 2012, it was calculated at surface thin layer and at 10 m and he used the pH basic vertical gradient multiplied by 2 m per year vertical velocities) are different used in both study.

In Polonsky 2012, it was also discussed surface century scale acidification (which was explained as acidification due to long term uptake of human emitted CO_2 from the troposphere) by considering the 0.2 units of pH decreasing rate difference between surface and 10 m depth between 1980 and 2000. He calculated 0.05 units of century scale pH decrease at the surface. This result is also in consistent with 0.07 units decrease proposed in this study at the surface layer. The question is the increasing trend after 2004 till 2014. According to the theory, proposed by Polonsky 2012, of physical processes of Ekman pumping is the main source of pH increase at decadal scale, one can expect pH decrease in this period as well. But, warming of surface temperature and salinification due to lack of fresh water input after 2004 discussed above not only weakened the physical processes (Ekman transport due to wind stress, thermohaline circulations, Rim current) but also support less human induced CO_2 uptake from the troposphere.

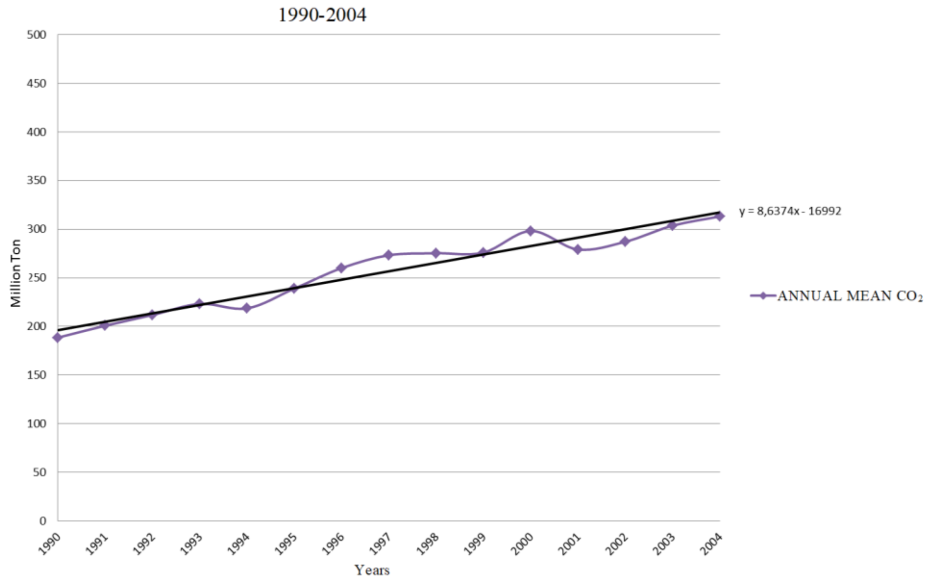
One of the most recent studies of climate change effects on Black Sea, Stanev 2019 indicated that warming and salinification of the surface waters and Cold Intermediate Waters of Black Sea affect the water masses in the region, and emphasized that this evolution is due to the warmer winter over the last 14 years. So, the climate change effect on Black Sea leads to change of physical processes of the region as well as the absorption of CO_2 from the atmosphere.

Discussion and Conclusion

According to the results, the pH of Black Sea surface waters decreased 0.07 units between 1990 2004, and increased 0.104 units between 2005-2014. Small magnitude of acidification between 1990-2004 is considered to be due to not only in Ekman transport but also CO_2 absorption from the troposphere. Since anthropogenic CO_2 increase rate in the atmosphere between 1990-2004 is less than the increase rate between 2005-2014. This conclusion is being supported by the sea surface temperature increase and fresh water input decrease (warming and salinification) which make the surface waters less absorber for the CO_2 between 2005 and 2014. In addition to that, atmospheric temperature increase between 1990 and 2004 is also less than between 2005 and 2014 which shows more greenhouse gases accumulation in the atmosphere in the latter period.

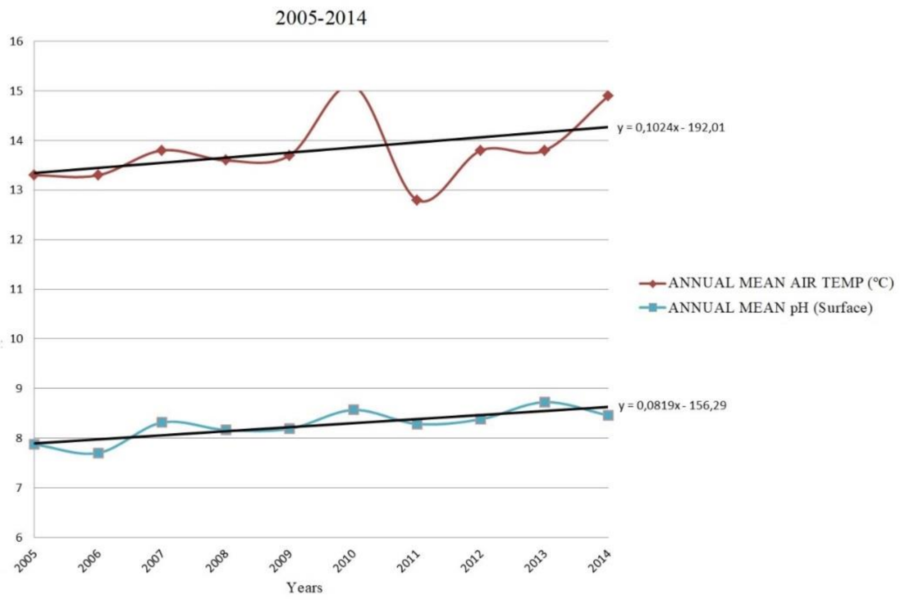


(a)

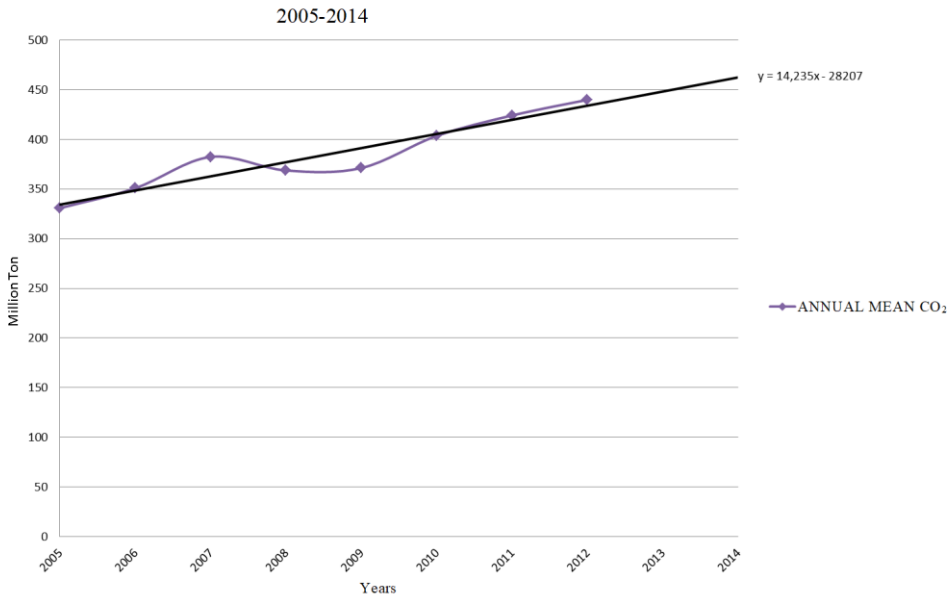


(b)

Fig. 8: 1990-2004 (a) surface layer pH and annual average air temperature of Turkey (b) annual average anthropogenic CO_2 emission of Turkey.



(a)



(b)

Fig. 9: 2005-2014 (a) Surface layer pH and annual average air temperature of Turkey (b) Average Anthropogenic CO_2 emission of Turkey.

Table 1. Linear regression coefficient between surface waters pH and CO_2; and air temperature for 1990-2004 and 2005-2014 periods.

	R	
Parameter	1990-2004	2005-2014
pH-CO_2	-0.5	0.77
pH-Air Temperature	-0.12	0.56

Additionally, the warmer winters in the years between 2005 and 2014 also supported the SST increase and salinification. The result of this warming and salinification might decrease the horizontal temperature and salinity gradient over entire region which changes the physical processes of Black Sea. Linear regression coefficient between surface waters pH and CO_2; and air temperature are shown in Table 1 for the two different periods.

There is a partially high regression between pH-CO_2, but negative between 1990-2004 which means a slowing down CO_2 increase in this period by being uptaken by surface water which results in pH decrease i.e acidification. On the other hand, both pH and CO_2 are increasing with more regression (0.77) between 2005 and 2014, which supports the theory of less absorption of CO_2 by Black Sea which cause pH increase.

Finally, data analyzed in this study is inhomogeneous spatially and temporally. pH measurements are very crucial to analyze the acidification and climate change effects in Black Sea, so there is a need of sustainable and cooperative longer time observations at stations homogeneously distributed over the entire region.

As proposed by Polonsky 2012, decadal and century scale analysis of acidification will be more significant with such data set.

Acknowledgements

The Author specially acknowledge SeaDataNet project partners for their data make open for scientific research purposes, Turkey Office of Navigation, Hyrdography and Oceanography. And special thanks to Mr. S. Mutlu from TUBİTAK MAM for his contribution to plot some figures.

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