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Had Been Observing the Acidification of the Black Sea Upper Layer in XX Century?

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Abstract

The article's goal is to assess the rate of acidification of the Black sea upper layer in XX century using historical data since 1924. It is shown that statistically significant century-scale acidification cannot be extracted, while decadal-scale reduction of pH has been really observing in 1960's and between 1980 and 2000 in spite of high noise level and intense interannual pH variability. The rate of acidification for these periods reached 0.4 (0.2) pH units per decade at the surface (10 m depth). Such high level of acidification of the Black sea upper layer is mostly due not to the rise of carbon dioxide concentration in the atmosphere, but to natural quasi-periodical decadal-scale intensification of upward motions in the subsurface layer of the Black sea transporting the water with low-pH to the surface. Rough assessment of recent century-scale rate of acidification of the surface Black sea layer shows that its likely magnitude lies in the range -0.1 to -0.5 pH units per 100 years.

Keywords: pH variability, quasi-periodical decadal-scale intensification of vertical motion in the Black sea, space-time inhomogeneity of pH observations.

Introduction

One of the principal properties of the surface ocean/sea layer changing as a result of increased concentration of carbon dioxide in the troposphere is pH. In fact, its magnitude characterizes the acidity of sea waters. Increasing of acidity leads to pH decreasing. Ocean/sea acidification should be observed as a result of uptake of part of emitted carbon dioxide from the troposphere. Published results show that around 30% of total anthropogenically emitted CO_2 is sinking into the oceans and this leads to pH decreasing in the surface waters of the World Ocean (IPCC4 Assessment, 2007; Fierer *et al*., 2006). Ocean acidification in recent climatic epoch and expected pH decreasing in XXI century reach approximately -0.3 and -0.4 pH units per century, respectively. This is potentially dangerous for the marine biota (Caldeira and Wickett, 2003; Kerr, 2010). Acidification of different time scales can be also a result of sea water pollution. This kind of acidification primarily manifests itself in the upper sea layer of coastal regions.

At the same time there are regional natural interannual to millennium-scale fluctuations of pH which have not any relations with anthropogenic activity. For instance, El Niño events can cause dramatic changes of pH in the tropical regions (Normile, 2010). Other natural physical processes (such as intensified upwelling) can be also one of the reasons of pH reduction in the upper marine layer and, hence, lead to its acidification (IPCC Workshop, 2011). At the geological scales (T~ 10^3 to 10^4 years and more) quite fast (in comparison with the recent variations) changes of troposphere carbon dioxide concentration and associated pH decreasing in the upper layer of World Ocean occurred e.g., about 40 million years ago. In that time, the concentration of CO_2 in the low troposphere was at least half an order as larger as the recent concentration, temperature of the World Ocean was higher by about 5°C and pH was anomalously low. Enhanced volcanic activity in the Himalaya region was likely cause of additional emission of CO_2 and associated ocean acidification (Pearson, 2010). That is why the most recent definition accepted by IPCC WGII (IPCC Workshop, 2011) separates the ocean acidification and anthropogenic ocean acidification.

So, to specify the relative significance of anthropogenic and natural processes in marine acidification at the different time scales and for different regions is important task. Study of such kind for the Black sea has been recently begun by author (IPCC Workshop, 2011; Polonsky, 2012) Present article is continuing the analysis of recent acidification of the Black sea upper layer.

Data and Methodology

In the present study, the most comprehensive regional historical pH data from oceanographic database of Marine Hydrophysical Institute (Eremeev, 2004) for 1924-2000's have been used. Totally 44 635 samples of sea water at the standard levels from the surface to 2000 m are available for specified period. Space distribution of pH measurements is done at the insertion to Figure 1. In spite of numerous observations their quantity and quality are not enough for reliable assessment of century-scale trend. The most reliable data are available for the last decades of XX century (Polonsky, 2012; see also below).

To reduce the noise level which is due to random errors, poor sampling for resolution of relatively high-frequency (small/meso-scale) and seasonal fluctuations, the data have been at first averaged over entire basin for each year and standard level. As a result, the mean pH profile in the Black sea has been obtained. Then, the time pH series for upper levels (surface and 10 m) have been analyzed to extract the interannual to century-scale variability.

Vertical velocity in the upper layer was estimated using Ekman theory and wind fields from two (NCEP and ERA) re-analyses outputs [further details, see in (Polonsky and Shokurova, 2009)]. The quantitative impact of upward motion of subsurface low-pH water on the variability of pH in the upper layer is assessed by multiplication of vertical velocity and vertical pH gradient.

Results and Discussion

General Features of pH Distribution

The average vertical pH profile shows that pH is sharply decreasing between surface and core of cold intermediate layer. Reduction of pH within water column is approximately 0.55 pH units there (from more than 8.4 to approximately 7.9 pH units) (Figure 1). This is rather well-know peculiarity of vertical pH distribution in the Black sea (Simonov and Al'tman, 1991; Oguz, 2008). Such vertical structure leads to pH permanent decreasing in the subsurface layer of central part of Western and Eastern cyclonic gyres where the upward motion occurs (Krivosheya *et al*., 2000; Kostianoy and Kosarev, 2007). This reduction is about 0.5 pH units at the 100 m depth in

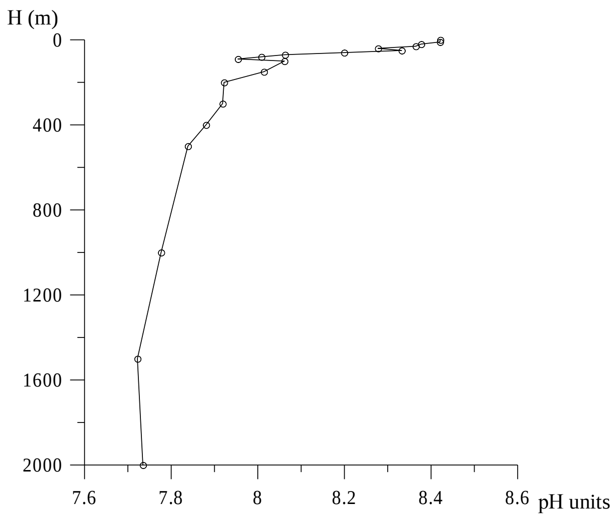
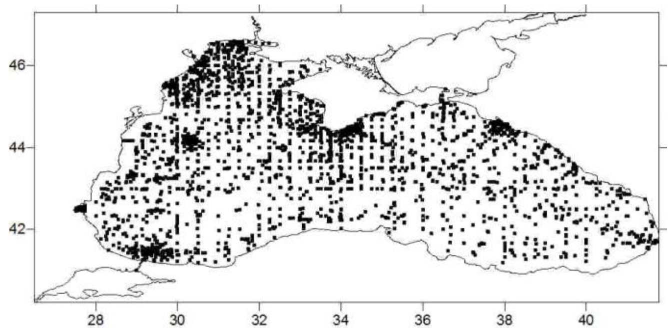


Figure 1. Mean profile of Black sea pH averaged at the standard levels using all data from 1924 to 2000. Insertion shows space distribution of pH observations for entire period (1924-2000's).



Insertion to Figure 1

comparison with the coastal periphery of Rim current (Polonsky, 2012).

At the surface, the gyre-related pH pattern cannot be extracted over the noise level (Figure 2). However, the average pH within the upper mixed layer is decreasing when subsurface upward velocity is increasing. For instance, difference of pH (averaged over entire basin) between seasonal extremes of climatic Black sea circulation is about 0.15 pH units (Polonsky, 2012).

There are also some peculiarities of space pH distribution at the surface in the vicinity of rivers' inflow, especially when the seasonal rivers' discharge is at a maximum (see, February-March pH distribution in the N-W part of the basin at Figure 2a). These peculiarities create the space pH inhomogeneities with typical magnitude reaching 0.5 pH units. As a result of that and space-time data coverage inhomogeneity, the noise level in low-frequency variability of the pH time series annually averaged over entire basin remains quite high even when small/meso-scale noise is effectively filtered. It is clear from Figure 3. However, a few important results concerning the low-frequency temporal pH variability can be established at the significant level. They will be done and discuss below.

Interannual to Decadal-Scale Variability of pH and Causes of Decadal pH Changes

In spite of high noise level discussed above, Figure 3 clear demonstrates three following remarkable points:

1. pH in the upper layer of the Black sea was decreasing in 1960's and between mid of 1980 and 2000, while between early 1970 and mid of 1980's it was in general high. As a result, significant parabolic pH trend occurred in 1970 – 2000's;
2. acidification of the surface waters in late 1980 to 2000 has been delayed in comparison with the acidification of subsurface waters by a few years;
3. decadal-scale pH decreasing at the surface during last 10-15 years of XX century exceeded the similar pH decreasing at 10 m. In fact, it reached about 0.4 pH units per decade at the surface, while at 10m depth it was about 0.2 pH units per decade.

The above first and second facts are consistent with the explanation of pH decadal variability which has been done early in the author's paper (Polonsky, 2012). The suggestion was that such variability is mostly induced by the changes of Ekman pumping intensity. In fact, the magnitude of quasi-periodical decadal changes of vertical velocity due to the variations of wind field circl (or rot$_z$ $\boldsymbol{\tau}$, where $\boldsymbol{\tau}$ is wind stress) of about 2 m per year is completely enough to explain the entire decadal-scale variations of pH at the 10 m depth. In fact, multiplying the basic vertical gradient of pH within the upper layer (which is about -0.01 pH units per meter, see Figure 1) by vertical velocity equaled to 2 m per year, one can receive the observed rate of acidification at 10 m depth (about 0.2 pH units per decade).

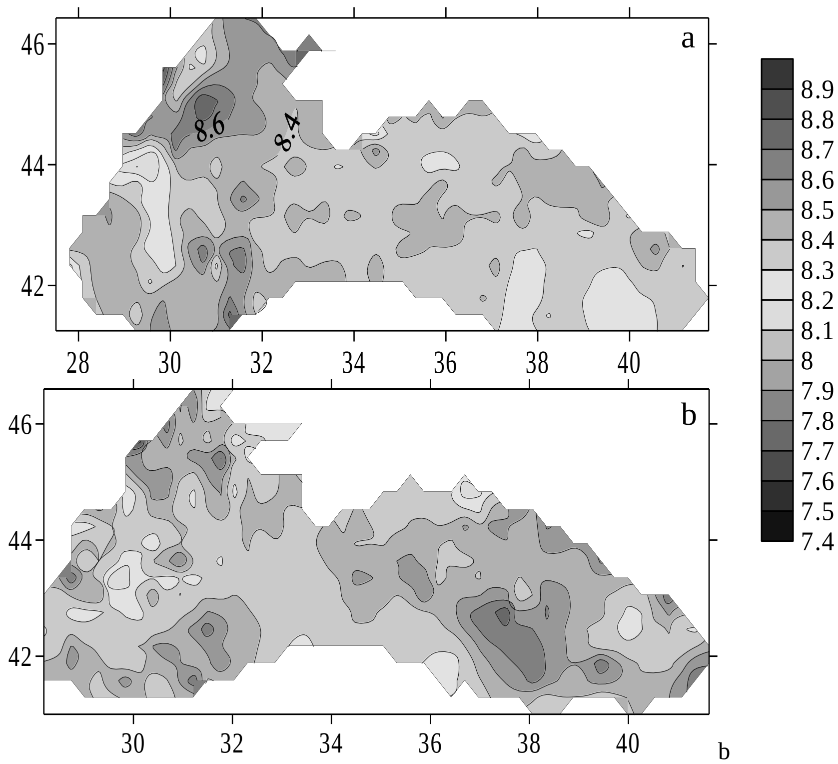


Figure 2. Space distribution of pH at the Black sea surface for February-March (FM) (a) and August-September (AS) (b). Contour interval is 0.1 pH units. pH mean=8.36 and 8.40 pH units for FM and AS, respectively.

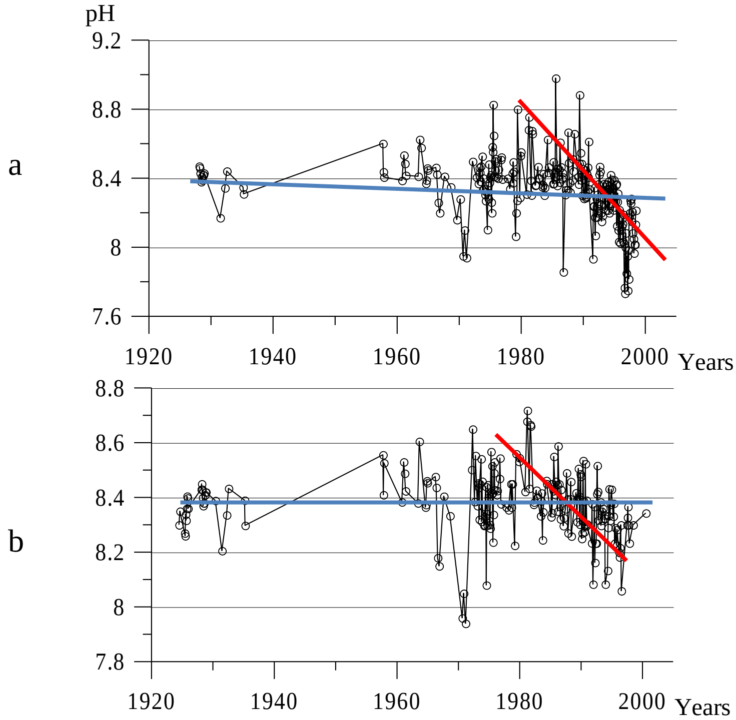


Figure 3. Interannual variability of mean annual pH averaged over the entire basin at the surface (a) and 10 m (b). Thick red lines specify the decadal-scale rate of acidification for the end of XX century, while thick black lines represents the (statistically insignificant) century-scale pH decreasing

Figure 4 confirms that associated (with the wind field variations) decadal-scale intensification of vertical velocity really occurred in 1960's and between mid of 1980's and mid of 1990's. Magnitude of assessed decadal variations of averaged (over entire basin) Ekman pumping using data from Figure 4 is a few times as smaller as 2 m per year. However, this assessment underestimates the actual magnitude of vertical motions and their changes because of coarse special resolution of the wind fields (~100 to 200 km) which were used for drawing of Figure 4. The utilization of higher-resolved wind field leads to more accurate assessment and necessary magnitude of the Ekman pumping (Polonsky and Garmashov, 2010).

The upward spread of analyzed signal (following from observed delay between surface and subsurface layers) confirms the reality of discussed mechanism. In fact, if the decadal-scale change of Ekman pumping intensity is about 2 m per year the associated delay between pH signal at the surface and 10 m depth is around 5 years. This is consistent with the time series at Figures 3a and 3b.

Possibility that discussed decadal-scale variability of surface pH is entirely artificial and it is due to space-time observational inhomogeneity is negligible. In fact, if one compares Figures 2 and 5, it is clear that decadal-scale variations of averaged over entire basin pH at the surface exceeding 0.2 pH units cannot be explained by such inhomogeneity taken into account quite large number of independent observations in different subregions of the Black sea. Certainly, the time differences which do not exceed 0.1 - 0.2 pH units within decade can be due to space-time data inhomogeneity. For instance, Figures 5c and 5d clear demonstrate that for the first part of 1990's the casts have been mostly carried out in the N-W part of the Black sea, while for the second part of this decade the observations have been mostly concentrated in the vicinity of the Crimea. Taken into consideration the space peculiarities of pH distribution (see discussion above and Figure 2), one can conclude that pH decreasing at the surface during 1990's of ~0.1-0.2 pH units (but not more!) can be explained just by space-time data inhomogeneity. So, this can be concluded that analyzed decadal-scale pH variations in the upper layer of the Black sea are mostly induced by changes of the Ekman pumping. Note that discussed variability of Ekman pumping intensity is due to regional consequences of decadal-scale processes in the coupled ocean-atmosphere system (Ozsoy and Mikaelyan, 1997; Polonsky and Garmashov, 2010).

Assessment of Century-Scale Marine Acidification

Further discussion concerns the assessment of possible recent rate of century-scale acidification of the upper layer in the Black sea. In contrast to decadal-scale pH reduction discussed above (which is mostly due to physical process), the century-scale acidification is mostly due to long-term uptake of human-emitted additional carbon dioxide from the

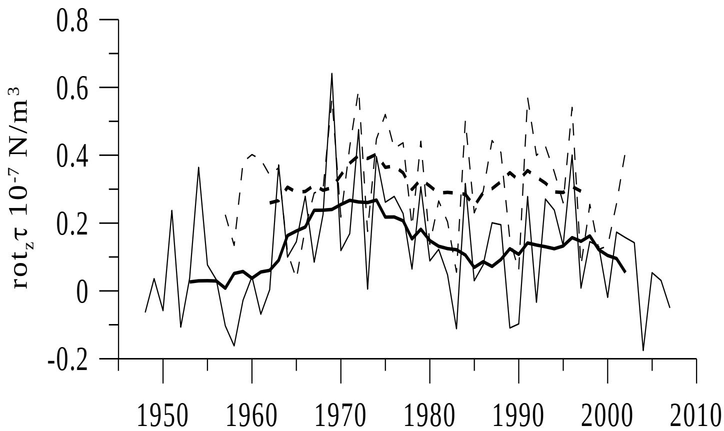


Figure 4. Time series of averaged over entire basin Ekman vertical velocity calculated using wind data of NCEP and ERA re-analyses (solid and dashed thin curves, respectively). Thick curves represent smoothed (by low-passed 11 yrs filter) time series. Positive values are due to upward motion.

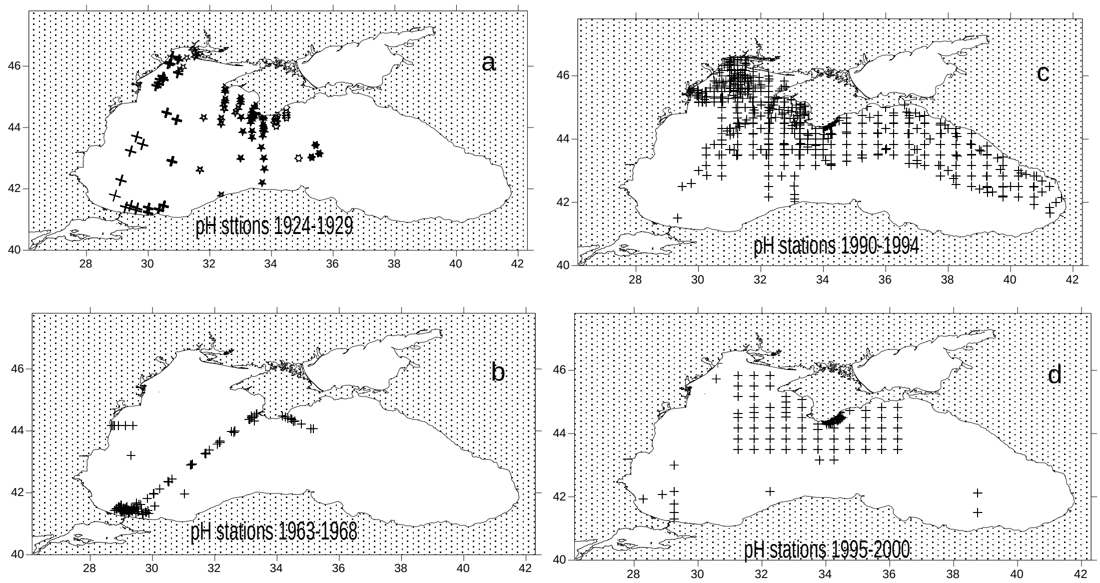


Figure 5. Space distribution of pH observations for different periods: 1924-1929 (a), 1963-1968 (b) 1990-1994 (c) and 1995-2000 (d)

troposphere.

Can we judge the rate of century-scale acidification of the surface marine layer in the Black sea from existed data? As a result of lack of data in some periods of XX century and high noise level, the century-scale linear pH trend is not significant either at the surface or 10 m depth (Figure 3). However, the rough assessment of the century-scale pH trend in the upper layer can be done using following considerations. First of all, the linear pH trend at the surface is negative (about -0.1 pH units per 75 years or -0.13 pH units per 100 years, see Figure 3,a) although it is not significant. Then, the third point mentioned above in the previous paragraph permits to give the upper assessment of recent rate of long-term acidification of the surface marine layer in the Black sea using more reliable data of two final decades of XX century. In fact, the positive difference of rates of acidification at the surface and 10 m depth between mid of 1980's and 2000 can be (at least partly) attributed to the result of human carbon dioxide emission. Of course, there is the other reason of such difference. This is fast decreasing of number of observations with the depth resulting in more numerous surface observations (in comparison with the observations at the 10 m depth) in the shallow coastal region of the N-W part of the Black sea in the early 1990's. This leads to enhanced artificial pH trend at the surface (in comparison with 10 m depth) which can reach 0.1 to 0.2 pH units per decade for 1990's (see above discussion). The absence of visible differences between pH drop at the surface and 10 m depth in 1960's (cf., Figures 3a and 3b) also confirms that because in 1960' the casts have not been concentrated in the N-W part of the Black sea (see, Figure 5b).

Using the assumption that difference of rates of acidification at the surface and 10 m depth in the end of XX century (remained after elimination of artificial trend) is due to human activity, one can assess the associated pH reduction in the surface marine layer in the Black sea as 0.05 pH units per decade. This is upper estimate for the most recent decades and it is close to the published maximal assessments of recent rate of acidification for the other regions of the World Ocean including the North Atlantic basin which is due to uptake of human-emitted carbon dioxide from the troposphere (Caldeira, 2003; IPCC Workshop, 2011; Kerr, 2010).

This should be emphasized once more that statistically significant century-scale acidification of the surface marine layer in XX century was not observed. It was insignificant and did not exceed -0.13 pH units per century. Thus, the likely rate of recent acidification of the surface marine layer in the Black sea can be roughly assessed between -0.1 and -0.5 pH units per 100 years. Certainly, enhanced rate of pH decreasing at the surface for the last decades of XX century should be confirmed by analysis of appropriate data for more extended period included XXI century.

Conclusions

Significant century scale acidification of the upper Black sea layer cannot be extracted from available historical data set for XX century because of lack of data for some periods, high level of the noise and intense interannual to decadal scale variability. Upper estimate of recent century-scale acidification is ~0.05 pH units per decade using the best observations of last two decades of XX century. Real century-scale rate of recent acidification of the surface Black sea layer can be roughly assessed in the range -0.1 to -0.5 pH units per 100 years. Decadal-scale acidification of the upper layer in the Black sea has been really observing in 1960's and between 1980 and 2000. The rate of acidification for these periods reached ~0.4 (0.2) pH units per decade at the surface (10 m depth). Such high level of acidification of the Black sea upper layer is mostly due not to the rise of carbon dioxide concentration in the atmosphere, but to natural quasi-periodical decadal-scale intensification of the upward motion in the subsurface layer of the Black sea transporting the low-pH water to the surface (say nothing about artificial trend due to space-time observational inhomogeneity).

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