Hindawi Publishing Corporation
Journal of Computational Environmental Sciences
Volume 2014, Article ID 201819, 7 pages
http://dx.doi.org/10.1155/2014/201819

Research Article

Forecast of Sea Surface Acidification in the Northwestern Mediterranean Sea

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Received 18 November 2013; Revised 22 March 2014; Accepted 25 March 2014; Published 17 April 2014

Academic Editor: Wen-Cheng Liu

Observation data from DYFAMED site, in northwestern Mediterranean Sea between 1995 and 2011, are used to study mathematical forecasts of sea water surface pH evolution over the next century. In a preliminary study, daily and monthly data have been used to compute total inorganic carbon (C_T) and total alkalinity (A_T) concentrations. Due to the arbitrary number of missing monthly observations from 1995 to 2011, mean pH values have been calculated from the available data in order to obtain a convenient monthly time series. Based on these results, we used in this paper a cubic spline method for interpolation within the range of known time series and then tested two extrapolation methods: linear and exponential smoothing. A 100-year simulated period is performed in order to have information beyond seasonal variations and observations. The mean seasonal variation allows us to draw forecast evolutions from 0.3 to 0.4 pH units decrease in the water surface at the end of the century. Although these simple forecasts do not pretend to present realistic predictions, these obtained theoretical results provide limits on pH variations in the northwestern Mediterranean Sea similar to those in the open ocean.

1. Introduction

Since the beginning of the 19th century, the industrial era has produced an increasing amount of CO_2. The evolution of CO_2 concentration in the atmosphere during the last decades has been extremely important and several studies show and underline its effects on climate change (see [1–5]).

The increasing trend of global atmospheric CO_2 concentrations roughly follows that of the global anthropogenic injection into the atmosphere. Nowadays, we know that the world ocean (covering 71% of the Earth's surface) acts as the biggest buffer for the atmospheric CO_2 concentration by absorbing an important part of it.

Studies show that the ocean absorbs about 2 $\text{Ptg}\cdot\text{yr}^{-1}$ (see [6, 7]). Ocean pH is decreasing, as shown in several models and studies (see [1, 4, 7, 8]), due to CO_2 absorption across air-sea interface.

Predictions for the end of the century suggest a mean decrease of about 0.3 pH units to 0.5 pH units (see [3, 7]).

The absorbed CO_2 affects the ocean through several factors. Partial pressure of CO_2 in the atmosphere rises with anthropogenic evolution, while in water partial pressure is affected by surface absorption and biogeochemical processes. Those modifications of properties directly affect sea surface CO_2 absorption. The variations in total inorganic carbon (C_T) due to physical and biological processes will modify the carbonate system. Therefore acidification of sea waters may affect marine organisms and biological balance. Increase of CO_2 could be a factor of a rise of the biological activity of some plankton species. However acidification could cause several problems for calcium carbonate skeletons of marine species [9].

The Mediterranean Sea which represents 0.8% of the world ocean is a quasienclosed sea which has been extensively studied over the last decades. It is a specific place, with its own properties and evolution. Its temperature, salinity, total alkalinity, and total CO_2 properties are significantly higher than in the open ocean.

Around the Mediterranean Sea, human population and activity have substantially increased since 1950. Consequently partial anthropogenic CO_2 pressure reaches higher levels [5].

This is probably one of the most important factors for water surface pH decrease.

The aim of this paper is to estimate the long-term trend of sea surface water pH in the Mediterranean Sea using the measurements performed at DYFAMED for the temperature, salinity, total alkalinity, pressure, and total dissolved carbon from 1995 to 2011. Due to the missing data (measurements from years 1995 to 1997 and other unavailable monthly data) required for computing pH values, the monthly time series has been obtained by considering the mean values of the pH between 1995 and 2011. The used cubic spline polynomial interpolation will provide a time series which moves in a smooth way during the period for known data. This also will serve us to make forecast of the mean pH evolution. In this paper, two standard extrapolations scenarios are presented as the limits on the level of pH values evolution: a linear evolution of the pH annual mean values, and an exponential one.

The first one is quite simple and is used as a reference for the observations and comparisons. The exponential evolution is considered for a more realistic behavior of the observed evolution in ocean's water. Evolution of mean pH values is studied with these two extreme scenarios where a random term based on observed monthly variations was also added in order to take into account the stochastic nature of pH fluctuations. The observed decrease of mean pH values for both scenarios remains bounded and the obtained behaviour in the form of cyclic oscillations agrees with the existing temporal variabilities of seawater pH.

Moreover, all these evolutions lead to the conclusion that the forecast could not exceed 50 years. The observed differences during simulations are too high to fit to something realistic. The importance of the predicted pH decrease also depends on the considered scenario and its own decrease speed. The impact of this decrease on environment and biology will also depend on which scenario is considered as well as on how they will adapt to the pH changes. Most studies present the effect of the acidification but without conclusion on the gravity of the acceleration of this modification of sea water pH (see [1, 9, 10]).

The approach used in this paper assumes that the mean pH values estimated from the measured data move in a smooth and continuous way to make a reasonable estimate about its future evolution. It is known that the used cubic spline method of interpolation as well as other methods of seasonal adjustment and trend estimation is relatively weak at the end of series where volatility of the spline function may be observed. Indeed, at the end of the series only the past information is available, not the future. This was easily overcome in this study by extending the original monthly series using a vector made of 13 points including the last pH value of the previous year and the twelve newly calculated by the considered linear and exponential forecasting methods.

2. Data and Method

2.1. Data. Estimations of the annual pH values for the referenced time series are based on measurements made on the DYFAMED (DYnamique des Flux Atmosphériques en MEDiterranée) site (http://www.obs-vlfr.fr/sodyf/img/Map2014.png), located in the Ligurian Sea at 43.42 N, 7.87 E, in the northwestern of the Mediterranean Sea.

Measurements of salinity (S), temperature (T), pressure (P), total alkalinity (A_T), and total dissolved carbon (C_T) have been used for pH calculations. DYFAMED database (http://www.obs-vlfr.fr/dyfBase/) and all details on the collections methods are presented on the sodyfamed program homepage (http://www.obs-vlfr.fr/sodyf/). In addition, from 1995 to 1997, CARIOCA buoys provided surface data. Available measurements for S, A_T, and C_T were provided by sodyfamed monthly observations.

The missing data (T, S, A_T, and C_T) within the two sampled periods (1995–2000 and 2004–2011) had to be estimated in order to compute surface pH values at 10 meter-depth [2].

2.1.1. Water Surface Temperature and Salinity. Temperature and salinity data were fitted with hydrological data from DYFAMED measurements. The TABLE CURVE 3Dv4.0 software was used to test thousands of equation to determine an appropriate function to fit to the S, T data. The estimated error (i.e., observed standard deviations) for temperature and salinity calculations with this method is 0.0020°C and 0.0040, respectively.

2.1.2. Water Surfaces A_T and C_T. Between 1995 and 1997, A_T and C_T were not available beyond measured properties. The CO_2 fugacity (fCO_2) was the only data on this period ([2]). The surface alkalinity was estimated from S and T from empirical relationships in (1) (see [11]):

$$A_T = 1\left(\left(-6.57 * 10^{-5} + 1.77^{-2}\right)/S - \left(5.93 * 10^{-4} * \ln(\theta)\right)/\theta^2\right)^{-1}, \quad (1)$$

with θ the potential temperature.

C_T was computed from estimated A_T and measured fCO_2, T, and S data using the CO2SYS software.

2.1.3. Calculation of Surface Water pH. The time series of surface water pH at 10 meter-depth were computed using the CO2SYS software [12] from the time series data for S, T, P, A_T, and C_T. The apparent dissociation constant of Goyet and Poisson [13] was used to take into account the high salinity of the Mediterranean Sea. The pH measurements from 1998 to 2011 and computed data showed a strong covariance ($r = 0.99$), validating the calculated pH (see [2]).

2.2. Method. We used a polynomial interpolation method, the cubic spline, which is a powerful tool for data analysis. This method is used first to fill in the gaps of missing data points within a monthly time series of mean pH values and allows to draw smooth curves through a number of points. Using this process, series of unique cubic polynomials are fitted between each of the data points. These polynomials will have the same slope and curvature at the points where they join. At the end point of the data set on which we fit the function with spline curves there are no joining polynomials. This will provoke uncertainties which will be overcome using a forecasting method to extend the original series.

For each year the cubic spline polynomial interpolation method is used with an extended input time series consisting of a vector made of 13 points instead of the 12 original monthly data. This will include the last pH value of the previous year. The new twelve points will be calculated using two extrapolation procedures which are described below. Starting from the initial monthly time series, the interpolation will be applied on values that evolve year over year without discontinuities.

For each extrapolation, we will present results for a simple, deterministic forecast, as well as results for a forecast including a random term. Seasonal mean from 1995 to 2011 pH data [2] provides 12 pH values, one for each month. Utilisation of mean values for initializing the extrapolation procedure in this study can put some irregularities for the trends on several years. In order to avoid this problem, simulations used adapted data based on the obtained pH values. The adaptations, shown in Figure 1, offset a significant difference between January and December for the initial mean of pH data from 1995 to 2011. The adaptation has also been used in order to represent the continuous evolution of the pH year over year by smoothing this difference ($\Delta_{\text{data}} = 0.0107$, $\Delta_{\text{modified}} = 0.0016$).

The seasonal mean pH values of the first year are used to initialize the forecasts. The evolution year over year is then computed by the next two steps: evolution of the monthly values by extrapolation and interpolation of the pH.

(1) Evolution by Extrapolation. From the initial pH values used for the first year (Figure 1), we use an iterative method to compute the forecast pH values. With the seasonal mean pH values of year i, we calculate pH for the next year $i+1$ as follows:

$$\text{pH}\left(\text{yr}_{i+1}\left(\text{month}\right)\right) = \text{pH}\left(\text{yr}_{i}\left(\text{month}\right)\right) + X, \quad (2)$$

where X is the evolution applied to data and "i" indexing the current year, from 1 to 99.

(2) Interpolation. The precision of the Spline method depends on the number of points used as values for the interpolation. One year is represented by 12 monthly values. The vector used in this study is made of 13 points including the last value of the end of the previous year and the twelve newly calculated monthly values. For the first year, we considered two times the first January value to obtain an input series of 13 points. It is clear that the best performance for the used spline method could be obtained with more inputs of the spline method.

For the curve displayed in Figure 1, 60 points have been used for plotting the function from the spline cubic procedure. The known X values represent the values of x-axis corresponding to months and the known Y values represent the values of y-axis corresponding to the mean pH values.

In this paper, we consider two extrapolation methods for a forecast over a century. Those extrapolations will be used

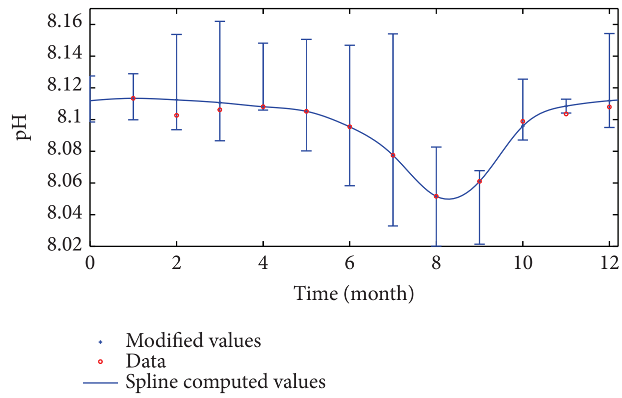

Figure 1: Data and interpolated pH on the 12 months of the reference year. The error bars represent the range between minimum and maximum observed pH from 1995 to 2011.

to provide insight into the limits of pH variability at the sea surface based on DYFAMED site data.

(i) The first one is based on the relative short term observation (over 11 years) of a linear decrease of 0.003 unit of pH per year [2]. This observation concurs with results from the Intergovernmental Panel on Climate Change (IPCC) that reports an average decrease of 0.3 pH units in the sea water over the end of the century. In this case, we have

$$X = -0.003\left(\text{pH units per year}\right), \quad (3)$$

where X represents the pH variation in (2) and t the current time step for a decrease of 0.3 pH units per century.

(ii) The second one is taken from forecasts applied on IPCC results [14], with an exponential acceleration of the lowering of the sea water pH [15]. This evolution may seem to be more realistic with a similar average decrease of pH over a century. In this case, X follows an exponential function:

$$X = -\tau_1 * \left(\exp\left(\tau_2 * \text{yr}_i\right)\right) \ \left(\text{pH units per year}\right), \quad (4)$$

with $\tau_1 = 0.0038$ and $\tau_2 = 0.022$.

For both extrapolations/forecasts, we will add a random term based on observed monthly standard variations [2]. The random coefficient is calculated by random MATLAB function (randn). It computes a pseudorandom term from a normal distribution with mean zero and standard deviation one. We compute an average of 500 runs for a result with the random evolution forecasts. The number of 500 runs was chosen to have enough information from the average of the runs. Additional runs (from 100 to 1500 runs) were performed but did not provide more information. The minimum and maximum pH computed for each year are represented in Figures 3 and 5. They indicate the amplitude of the pH variations.

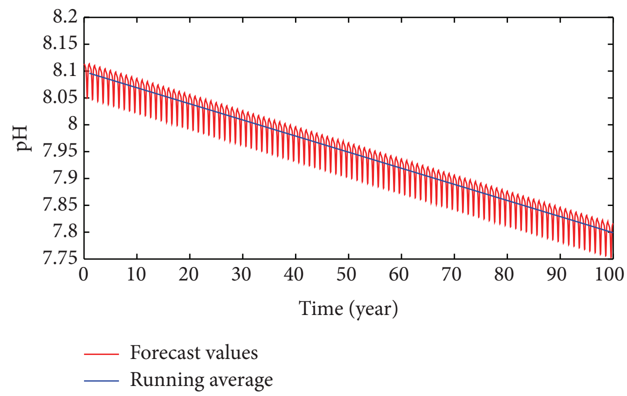

Figure 2: Forecast of pH sea surface water with a constant decrease of 0.003 yr^{-1} pH units.

3. Results

3.1. Constant Decrease for the Next Century

3.1.1. Simple Linear Evolution. Figure 2 shows the simulation results using the simple linear evolution (see evolution in (3)) starting from the initial pH (see Table 1).

We can observe that after a century the mean pH will decrease from 8.0825 ± 0.0309 to 7.7855 ± 0.0309 pH units. Running averages for the 1st, the 50th, and the 100th years are 8.0960, 7.9490, and 7.7990 pH units, respectively. These values will be compared with the random coupled forecast results which will be given in the following section.

The acidification evolution is more complex than a simple linear evolution over a century. Anthropogenic CO_2 in the atmosphere will evolve depending on human action in the world and so partial pressure on the sea surface water too. The absorbed CO_2, the temperature, the salinity (with sea level, e.g.), and biological activity will modify these evolutions. Ocean could absorb a big amount of CO_2, but it is assumed that there is a limit in the quantities that could be absorbed as shown in previous studies on north Atlantic ocean [16].

3.1.2. Random Evolution Coupled to the Slow Linear Decrease. In order to obtain a more realistic forecast we applied a random variation to the constant decrease. Results from two (out of 30) representative averages of the 500 runs of random variation around the mean are presented in Figure 3.

The time period of 100 years chosen for the forecasts is relatively long. Noncoherent values could rise over the years. After 50 years of simulation, amplitude variations of most forecasts simulations become higher than 0.3 pH units. These results indicate that such forecast is highly variable after 50 years and thus probably unreliable after this period. The two simulation forecast results (Figure 3) provide values (Table 2) for the running average. A comparison with the simple linear evolution is presented in Table 2 where Δ_{ra} is the difference between the running average shown in Figure 2 and the running average shown in Figure 3 (either Figure 3(a) or Figure 3(b)).

On the performed simulations, maximum observed variations are from +0.0049 to −0.0149. The highest difference between min and max pH values is 0.3191 pH units (minimum = 7.679, maximum = 7.998) for the 72nd year and 0.1702 for the 96th year (Figures 3(a) and 3(b), resp.). During the first 50-year period, the highest difference is 0.1657 pH units (minimum = 7.856, maximum = 8.022) for the 46th year and 0.1431 for the 48th year (Figures 3(b) and 3(a), resp.).

3.2. Exponential Evolution

3.2. Exponential Evolution. Based on IPCC observations and predictions we can assume that atmospheric CO_2 will dramatically increase before the end of the century. An exponential growth of anthropogenic CO_2 is observed at the beginning of the industrial era. The modifications of the ocean acidity by absorption of the anthropogenic gases may follow a kind of exponential growing as presented in [15], based on IPCC scenarios [14].

3.2.1. Simple Exponential Evolution. Based on [15] that shows an exponential evolution forecast from 1900 to 2100, we build the exponential scenario for the century (2000–2100). The exponential equation (4) is proposed to match this study result.

The decrease of 0.3 units on the 100 years corresponding to the 21st century is still represented in this scenario. We have a soft decrease at the beginning of the forecast and a slow acceleration over the years. The evolution may be different with such modifications of sea water pH. However, with both constant decrease and the following exponential evolution we have a loss of 0.3 units on a 100-year period.

Here, the first, 50th, and 100th years running average values are 8.0648, 7.9968, and 7.7903 pH units, respectively (see Figure 4).

3.2.2. Random Evolution Coupled to the Exponential Decrease. In order to have a better comparison between linear and exponential evolution, we add a random factor based on monthly standard variation values.

As presented for the linear evolution, forecasts longer than 50 years show large differences and variations on a year period to be considered consistent. For example, the variations on a year period could reach more than ±0.3 pH units (Figure 5(b)).

The running average values for two (out of 30) representative simulation results (Figure 5) are given in Table 3 with the variations from the simple exponential evolutions running average values.

The annual mean variations present more differences with this evolution than with the linear decrease. The main parameters of these variations are the average variation values used as coefficients for the random evolution. Some results have shown high increase in the amplitude variation (more than 300% of the initial yearly pH variation around the 40th year) or strong modifications over the time period.

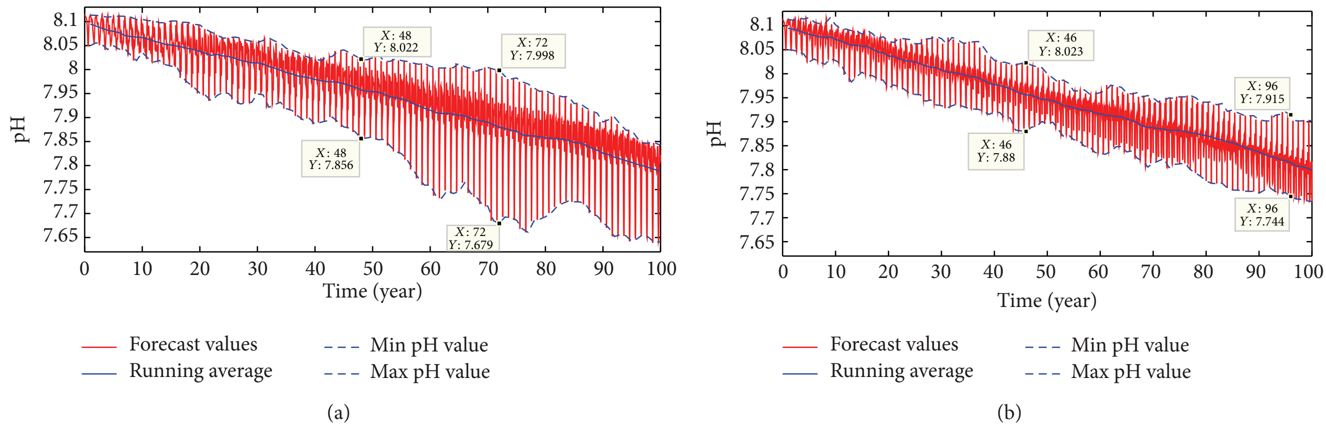

Figure 3: Two (out of 30) representative evolution forecasts with random evolution around the linear variation.

Table 1: Initial pH data, interpolated pH, ΔpH, Δ_{range}, and minimum and maximum observed pH, from 1995 to 2011. The difference between data and adapted values for interpolation is given by $\Delta pH = pH_{data} - pH_{interpolated}$. Consider that Δ_{range} = maximun − minimum show monthly pH range observed from 1995 to 2011.

Month	Mean measured pH data	Modified pH	ΔpH	Δ_{range}	Observed pH from 1995 to 2011	
					Minimum	Maximum
January	8.1027	8.1124	+0.0097	0.0581	8.0756	8.1337
February	8.1062	8.1107	+0.0045	0.1202	8.0686	8.1888
March	8.1081	8.1081	0.00	0.1506	8.0599	8.2106
April	8.1052	8.1052	0.00	0.0760	8.1094	8.1854
May	8.0954	8.0954	0.00	0.1406	8.0455	8.1861
June	8.0775	8.0775	0.00	0.1772	8.0033	8.1805
July	8.0516	8.0516	0.00	0.2423	7.9624	8.2047
August	8.0610	8.0610	0.00	0.1250	7.9981	8.1231
September	8.0989	8.0959	−0.003	0.0928	8.0197	8.1125
October	8.1035	8.1085	+0.005	0.0767	8.0859	8.1627
November	8.1079	8.1119	+0.004	0.0000	8.1166	8.1166
December	8.1134	8.1134	0.00	0.1185	8.0796	8.1982

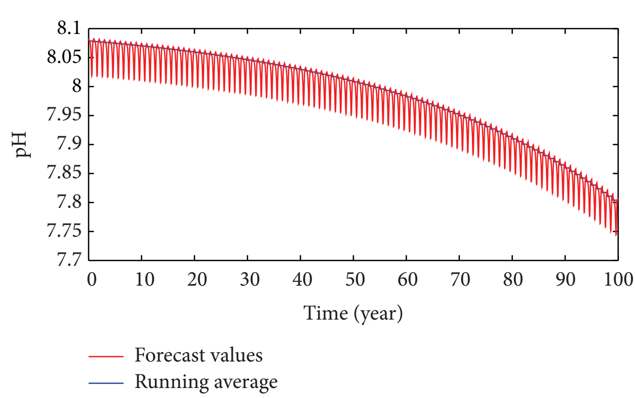

Figure 4: Exponential profile for an evolution forecast over the next 100-year period.

We consider that those results are not representative of realistic forecasts to be used in comparisons. The biggest variation amplitude observed among eligible results is presented in (Figure 5(b)). The highest difference between minimum (7.723) and maximum (8.034) is 0.3114 pH units for the 67th year. According to the observations made on the linear approach results, we consider the 1 to 50-year period. The highest difference is for the 38th year with an amplitude of 0.1890 pH units.

4. Discussion

The evolution of carbon chemistry and acidification in the Mediterranean Sea seems to be higher than those observed in other oceans. Previous studies ([2]) have shown high variations in the observed pH over the seasons. The variations are mainly caused by the anthropogenic CO_2 absorbed by the sea water surface. The long-term evolution is under interest in order to clarify hypothesis over water chemistry, biological evolutions, and potential evolutions of marine species.

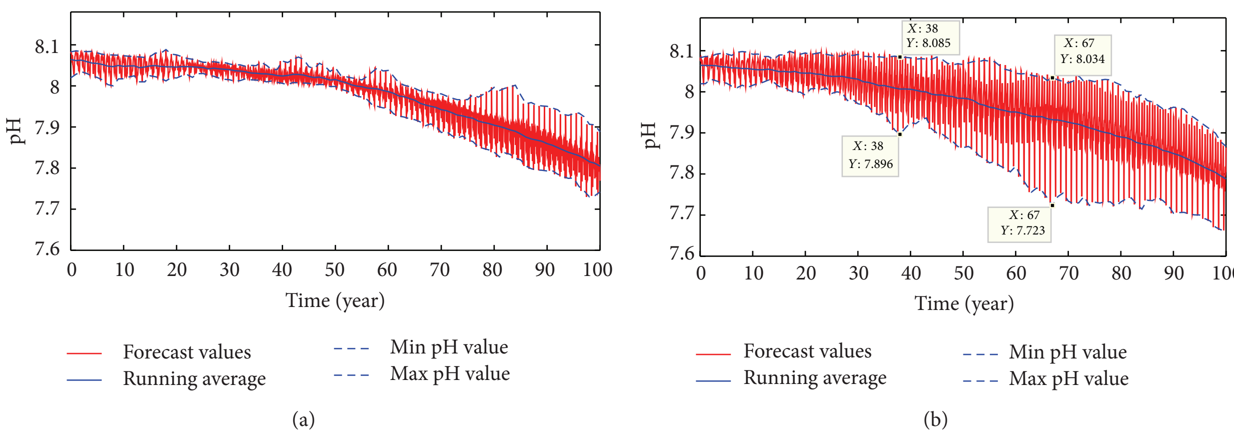

Figure 5: Two (out of 30) representative simulation results with random variation around exponential pH extrapolations.

Table 2: Running average values for linear decrease with random factor and differences with the simple linear evolution.

	First year	50th year	100th year
Running average Figure 3(a)	8.0947	7.9539	(7.7880)
Δ_{ra} (Figure 2-Figure 3(a))	−0.0013	+0.0049	(−0.0110)
Running average Figure 3(b)	8.0960	7.9489	(7.7990)
Δ_{ra} (Figure 2-Figure 3(b))	0.00	−0.0001	(0.00)

Table 3: Running average values for exponential decrease with random factor and differences with the simple exponential evolution.

	1st year	50th year	100th year
Running average for Figure 5(a)	8.0616	8.0111	(7.8048)
Δ_{ra} (Figure 4-Figure 5(a))	−0.0052	+0.0143	(−0.0145)
Running average for Figure 5(b)	8.0641	7.9842	(7.7881)
Δ_{ra} (Figure 4-Figure 5(b))	−0.0007	−0.0126	(+0.0022)

We notice that the limit of the reliable values for these forecasts is around 50 years. The amplification of pH variations considered as erratic became too high around year 50. Therefore we have considered forecasts reliable up to 50 years, not beyond. The performed simulations have shown that extrapolation methods should be chosen carefully in order to avoid the creation of aberrant values on a long enough time period.

The accuracy of the data and the modifications done for this study are under the observed variation of pH over the 11 years used as reference. The extrapolations and the values used for the initial year of each test are the main point of this study.

The number of 500 runs for each average results presented in this paper is an arbitrary decision. Yet a higher number of runs for the calculation of an average result would be useless. This value is voluntarily high in order to obtain usable results and additional runs would not provide further information at this level of detail.

Some results could seem usable over the full 100-year period (see Figure 3(b) or Figure 5(a)). The amplitude evolution could be very slow and for several simulation forecasts there is only a slight increase. In (Figure 5(a)) the amplitude shows small variations until the last 20 years, from 0.0618 pH units for the 1st year to 1.806 for the 97th year. Two representative results have been shown for both linear and exponential extrapolations. The linear approach comes as a simplification used in the literature to compare contemporary revisions to historical observations. The exponential one is based on forecasts about the evolution of CO_2 in the atmosphere from contemporary observations. We assumed that both approaches reach the same sea water pH reduction for the end of the century, but the evolution of the environments and the marine species would be affected differently.

The linear approach provides a base for the comparisons. The two main points that are underlined in the results are the observed decrease variations and the annual mean amplitudes. Running average values provide meaningful information about the variations which lead to useful curves drawing the amplitude modifications. With a random variation, the resulting deviation of the average profile is quite large only after 50 years. Consequently, we have opted for running average values from 1 to 50 years of extrapolations.

Simple linear approach forecasts a pH of 7.9490 for the 50th year. With the addition of the random factor, we observe a variation from a minimum of −0.015 to a maximum of +0.005 pH units. The stronger trend for negative variation is due to higher values of standard variation in summer than in winter [2]. Surface water pH is low in the summer, compared to the annual average value. These variations are under the amplitude of the annual mean initialization data (0.0618 pH units). Similarly, a simple exponential approach running average value for the 50th year is 7.9968. The variations observed with random variations are from −0.017 to +0.014 pH units.

Linear and exponential extrapolations give, respectively, running average values of 7.9490 ± 0.005 and 7.9490 ± 0.014 pH units at 50th year with a decrease of 0.1290 ± 0.0179 and 0.0680 ± 0.0247 pH units between the 1st and the 50th year.

At first glance this simple study indicates that the exponential evolution is a more realistic mathematical method to fit to the natural evolution. The running average pH values obtained up to 50 years are slightly higher (+0.048) with the exponential evolution method than with the linear one due to the slow evolution on the first period followed by the acceleration of the decrease until the end of the period.

In summary according to the exponential extrapolation over 50 years (which represent around year 2060), pH in surface water at DYFAMED would be 7.9968 ± 0.013 which represents a decrease of 0.068 pH units (which mean a decrease of 0.00136 pH units per year).

In any case, pH in surface water of the Mediterranean Sea is decreasing at a rate of 0.002 ± 0.001 units per year. The absorption of anthropogenic CO_2 affects seawater pH and may have significant impact on our environment. The positive and negative effects remain to be unraveled.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

The research leading to these results has received funding from the European Community's Seventh Framework Programme under Grant agreement 265103 (Project MedSeA). Authors acknowledge the Dyfamed/Moose observation system, Dr. Koffi Marcellin Yao, and Dr. Olivier Marcou for useful information and work.

References

[1] Secrétariat de la Convention sur la Diversité Biologique, "Synthèse scientifique des impacts de l'acidification des océans sur la biodiversité marine: Montréal," Tech. Rep., Secrétariat de la Convention sur la Diversité Biologique, 2010.

[2] Y. Koffi Marcelin, O. Marcou, C. Goyet, V. Guglielmi, F. Touratier, and J.-P. Savy, "Distribution and temporal evolution of the acidification of the mediterranean sea anthropogenic CO_2 over the past two decades," in *The Ocean in a High-CO2 World Conference*, Monterey, Calif, USA, 2012.

[3] C. L. Sabine, R. A. Feely, N. Gruber et al., "The oceanic sink for anthropogenic CO_2," *Science*, vol. 305, no. 5682, pp. 367–371, 2004.

[4] T. Midorikawa, H. Y. Inoue, M. Ishii et al., "Decreasing pH trend estimated from 35-year time series of carbonate parameters in the Pacific sector of the Southern Ocean in summer," *Deep-Sea Research I*, vol. 61, pp. 131–139, 2012.

[5] F. Touratier and C. Goyet, "Decadal evolution of anthropogenic CO_2 in the northwestern Mediterranean Sea from the mid-1990s to the mid-2000s," *Deep-Sea Research I*, vol. 56, no. 10, pp. 1708–1716, 2009.

[6] R. Cicerone, J. Orr, P. Brewer et al., "Meeting report," Tech. Rep., The Ocean in a High-CO_2 World—SCOR/IOC Symposium Planning Committee, 2004.

[7] J. Raven, K. Caldeira, H. Elderfield et al., Ocean acidification due to increasing atmospheric carbon dioxide, The Royal Society, 2005, http://royalsociety.org/document.asp?id=3249.

[8] U. Schuster, A. J. Watson, N. R. Bates et al., "Trends in North Atlantic sea-surface fCO_2 from 1990 to 2006," *Deep-Sea Research II: Topical Studies in Oceanography*, vol. 56, no. 8–10, pp. 620–629, 2009.

[9] S. C. Talmage and C. J. Gobler, "Effects of past, present, and future ocean carbon dioxide concentrations on the growth and survival of larval shellfish," *Proceedings of the National Academy of Sciences of the United States of America*, vol. 107, no. 40, pp. 17246–17251, 2010.

[10] R. M. Key, A. Kozyr, C. L. Sabine et al., "A global ocean carbon climatology: results from Global Data Analysis Project (GLODAP)," *Global Biogeochemical Cycles*, vol. 18, no. 4, pp. 1–23, 2004.

[11] F. Touratier and C. Goyet, "Impact of the Eastern Mediterranean Transient on the distribution of anthropogenic CO_2 and first estimate of acidification for the Mediterranean Sea," *Deep-Sea Research I*, vol. 58, no. 1, pp. 1–15, 2011.

[12] E. Lewis and D. W. R. Wallace, "Program developed for CO_2 system calculations," Oak Ridge, Tenn, USA, ORNL/CDIAC-1105, Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.US. Department of Energy, 1998, http://cdiac.ornl.gov/oceans/co2rprt.html.

[13] C. Goyet and A. Poisson, "New determination of carbonic acid dissociation constants in seawater as a function of temperature and salinity," *Deep Sea Research A*, vol. 36, no. 11, pp. 1635–1654, 1989.

[14] N. Nakicenvoic and R. Swart, "Special report on emissions scenarios," Tech. Rep., Working Group III of the Intergovernmental Panel on Climate Change, 2000.

[15] C. Pelejero, E. Calvo, and O. Hoegh-Guldberg, "Paleo-perspectives on ocean acidification," *Trends in Ecology and Evolution*, vol. 25, no. 6, pp. 332–344, 2010.

[16] G. A. McKinley, A. R. Fay, T. Takahashi, and N. Metzl, "Convergence of atmospheric and North Atlantic carbon dioxide trends on multidecadal timescales," *Nature Geoscience*, vol. 4, no. 9, pp. 606–610, 2011.