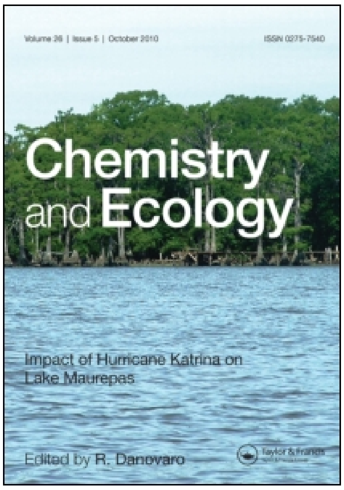

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New observations of CO_2-induced acidification in the northern Adriatic Sea over the last quarter century

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New observations of CO_2-induced acidification in the northern Adriatic Sea over the last quarter century

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Current global trends will lead to large-scale changes in climate patterns, ocean circulation and stratification; increased atmospheric CO_2 levels will cause acidification of the oceans, with significant impacts on marine biogeochemical cycles and calcareous organisms. In the Mediterranean area, the northern Adriatic Sea is one of the most suitable sites for studying the responses of marine pH to such occurrences because it is the northernmost basin affected by dense water formation during winter, and is also one of the most productive areas in the Mediterranean. The first comparison between two sets of data relating to the dense cold waters of the northern Adriatic, formed in the winters of 1982–1983 and 2007–2008, is presented here. pH values on the Nation Bureau Standard scale from the old dataset have been converted to the 'total hydrogen ion concentration scale' adopted for the new dataset, and are expressed as $\mu mol\,H^+ \cdot kg_{sw}^{-1}$. Results at 25 °C show acidification ($-0.063\,pH_T$ units) and a decrease in carbonate ion concentration ($-19.6\,\mu mol\,H^+ \cdot kg_{sw}^{-1}$) in the dense water mass between 1983 and 2008, whereas total alkalinity, carbonate alkalinity, dissolved inorganic carbon and CO_2 fugacity exhibit net increases of 74.4, 77.8 and 110.3 $\mu mol\,H^+ \cdot kg_{sw}^{-1}$, and 108.3 μatm, respectively, over the same period.

Keywords: ocean acidification; seawater pH; alkalinity; north Adriatic Sea; marine carbonate buffer system; atmospheric CO_2 dissolution; inorganic carbon chemistry; carbon dioxide

1. Introduction

The marine carbonate buffer system allows the oceans to take up carbon dioxide (CO_2) from the atmosphere far in excess of their potential uptake capacity based on gas solubility alone. In doing so, it controls the pH of the oceans. This control is achieved by a series of equilibrium reactions that transform carbon added as CO_2 into bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) ions. In particular, when atmospheric CO_2 is absorbed its partial pressure in seawater (pCO_2) increases, and this reduces both the pH and the concentration of carbonate ions in a process commonly referred to as 'ocean acidification'.

Over the past 250 years, the release of CO_2 from deforestation, industrial and other human activities has resulted in an increase in its atmospheric concentration from ∼280 to 387 μatm. The value is now higher than experienced on Earth for at least the last 800,000 years [1], but

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is expected to continue rising at a considerable rate in the coming decades. During this time, the ocean has absorbed about one-third of anthropogenic carbon emissions [2,3]. The uptake has benefited humankind by significantly reducing greenhouse gas levels in the atmosphere, thereby partly minimising global warming; however, the process is not benign because a reduction in the pH of the ocean surface waters of ∼0.1 units has already been observed [4], although with a degree of spatial and temporal variability [5,6]. The value is predicted to decrease by a further 0.3 pH units [7] if atmospheric CO_2 concentrations reach 800 μatm (the projected end-of-century concentration according to the IPCC business-as-usual emission scenario), implying that ocean acidity would increase by ∼150% relative to the beginning of the industrial revolution. Such a large decrease in pH has not been experienced by the oceans during the last 300,000 years.

Much of the concern about present-day acidification relates to the rate at which it is predicted to occur, which is at least one order of magnitude faster than has occurred for millions of years [8]. In view of this, it is easy to understand that seawater acidification, induced by atmospheric CO_2 dissolution (solubility pump), represents the other CO_2 problem [9–11] to have recently emerged as a serious concern because of its consequences for the buffering capacity of the ocean and for biogeochemistry, biota, marine ecosystems and marine food webs [12–15]. For example, acidification and the concomitant reduction in carbonate ion concentrations are expected to impact on biota and marine ecosystems [16–18]. The decrease in carbonate ion concentration is of particular concern with respect to many marine organisms: carbonate ions are actually a basic building block of skeletons and shells for a large number of marine organisms, including corals, shellfish and marine plankton [19–21]. Some of the smaller calcifying plankton are important food sources for higher trophic level marine organisms. Increased CO_2 with the changes in ocean chemistry may, therefore, alter the species composition and succession of primary producers and other microbes. This last, rapidly emerging, scientific issue has raised serious concerns across the scientific communities as to possible ecological and economic impacts.

Predictions of the further decrease in pH in the next decades are based on model simulations which, although reliable, include only physical processes in the control of pH and which are calibrated from a single year of data [7] rather than by using direct empirical measurements of ocean pH over time [6]. Empirical data documenting ocean pH over time are limited, although the gradual reduction in pH, from ∼8.21 to 8.10 [22], has long been recognised from hydrographic surveys and time-series data [7,19,23–26] on both large and local scales. However, such a reduction is not yet well documented in coastal oceans, nor in the eastern Mediterranean Sea in particular [27], which is reputed to be very sensitive and vulnerable to global climatic change. Experimental databases containing results of samples analysed according to standardised quality protocols are therefore welcome for comparing old and present-day data, to assess whether the decrease is affecting coastal environments and also to validate the predictions of models.

This article aims to contribute to this area of study by presenting the first comparison between two datasets from the northern Adriatic dense water (NAdDW) masses formed in winter in the northern part of the Adriatic basin, which represents the largest shelf area of the entire Mediterranean region [28]. There, carbon dioxide sequestration might be particularly efficient because of the Continental Shelf Pump mechanism [29], which requires both the solubility pump (cold, dense water formation) and the biological pump (biological activity) to work together. At the same time, the northern Adriatic Sea is subjected to high anthropogenic pressure, being surrounded by highly industrialised regions (giving rise to CO_2 emission into the atmosphere), and represents a key site for cold, dense water formation in the entire eastern Mediterranean region. It is actually the northernmost basin of the region, covers a shallow wide continental shelf area where dense water formation occurs in winter, and sustains a very intense primary productivity during spring through late summer.

The two datasets (containing pH, carbonate system properties, nutrients and dissolved oxygen) we compared concern samples collected in the dense, cold winter water mass (NAdDW) formed during the winter seasons of 1982–1983 and 2007–2008, over the same area.

2. Methods

2.1. *North Adriatic area and sampling scheme*

Data from two cruises (*ASCOP 2* and *VECSES 1*) were used; they were conducted in 1983 and 2008 over the reported area (Figure 1), which covers the whole north Adriatic Sea basin, defined as the area lying north of the 100 m isobath. It represents the largest shelf area of the entire Mediterranean Sea.

The *ASCOP 2* cruise (30 April to 8 May 1983) was carried out within the frame of the so-called Italy–Yugoslavia Project for the Monitoring of the Adriatic Sea. During the cruise, 21 hydrological stations were fully sampled. The *VECSES 1* cruise (15 to 19 February 2008) was carried out under the VECTOR Project of the Italian Ministry for University and Scientific Research, with a total of 27 hydrological stations sampled over the same area. This article compares the datasets collected during these two projects, which span 25 years.

Waters samples for pH, total alkalinity (TA), dissolved oxygen (DO) and dissolved inorganic nutrients were collected at the stations indicated in Figure 1. On both cruises, DO, pH and TA samples were the first to be drawn from Niskin bottles (10 L), which were fitted to a ‘rosette sampler’ system. They were treated with reagents (DO) and analysed on board during both cruises; pH samples were drawn, with no airspace, into 300 cm^3 BOD glass flasks (*ASCOP 2*) or directly into 10 cm path-length cells (*VECSES 1*) and analysed on board. TA samples were drawn into glass flasks with airspace, treated with saturated mercuric chloride and stored in the dark at room temperature until analysis.

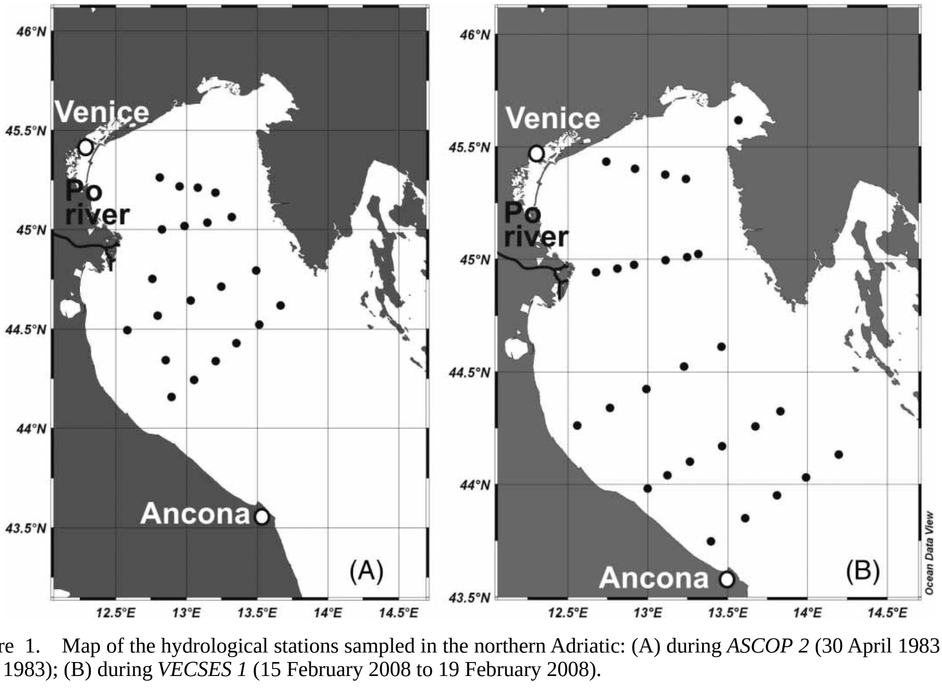

Figure 1. Map of the hydrological stations sampled in the northern Adriatic: (A) during *ASCOP 2* (30 April 1983 to 8 May 1983); (B) during *VECSES 1* (15 February 2008 to 19 February 2008).

2.2. *Hydrology*

In order to measure the hydrological characteristics, i.e. temperature (T) and salinity (S), of the water masses encountered, the CTD Neil Brown Mk 3 was employed in 1983 (*ASCOP 2*) and the CTD SBE 911-Plus was used in 2008 (*VECSES 1*). Both CTDs were fitted to a General Oceanics SA1-241 ‘rosette sampler’ system of 24 Niskin bottles, which was used to gather samples at several depths between the surface and bottom (maximum depths 52 and 75 m, respectively, in the two cruises). Temperature data are reported in °C and salinity in ‘psu’ according to the Practical Salinity Scale [30]. The density anomaly (σ_t) was then derived according to the sea water state equation [31], and the theoretical dissolved oxygen (DO′) values were computed according to Benson and Krause [32] from T and S data.

2.3. *Dissolved oxygen*

Samples were titrated directly on board, using the Winkler method [33], within a few hours after recovery of the rosette. In 1983, the titration end point was determined optically, whereas in 2008 it was determined potentiometrically on samples analysed by means of an automated titrator. In both cases, the results were expressed in $\mu\text{mol} \cdot \text{dm}^{-3}$ of O_2 and the same precision of $\pm 1\ \mu\text{mol} \cdot \text{dm}^{-3}$ was reached. Apparent oxygen utilisation (AOU; $\mu\text{mol} \cdot \text{dm}^{-3}$) was calculated as the difference between ‘theoretical’ and ‘measured’ DO, providing an approximation to the balance between biological processes of primary production and respiration/remineralisation occurring in the water mass.

2.4. *pH determination*

pH determination was performed on board immediately after sampling on both the *ASCOP 2* and *VECSES 1* cruises; however, in 1983 it was determined using a potentiometric method in an enclosed cell at 25 °C, as described by Grasshof [34] using NBS buffers at pH 7 and 9. The results were therefore expressed on the Nation Bureau Standard scale (pH_{NBS}) with $[\text{H}^+]$ in $\mu\text{molH}^+ \cdot \text{dm}^{-3}$ at 25 °C. Accuracy was presumed to be that of the NBS buffers (±0.02 pH units). In 2008, pH samples were determined using the more precise and accurate spectrophotometric method [35], recently recommended by the international standard quality protocols [36], and results were expressed on the ‘pH total hydrogen ion scale’ (pH_T) at 25 °C, in $\mu\text{mol H}^+ \cdot \text{kg}_{\text{sw}}^{-1}$, with a precision ±0.001 pH units.

In order to be able to compare the two datasets it was first necessary to convert the 1983 pH values expressed on the NBS scale and in $\mu\text{mol} \cdot \text{dm}^{-3}$ at 25 °C into the new pH_T scale, with H^+ concentrations expressed in $\mu\text{mol} \cdot \text{kg}_{\text{sw}}^{-1}$ at 25 °C. The lower precision of the original measurements, of course, remains with the converted values.

In the conversion procedure, the pH values from the *ASCOP 2* cruise on the NBS scale were assumed to correspond to the free proton scale (pH_F scale; defined as $\text{pH}_\text{F} = -\log m(\text{H}^+)$, where $m(\text{H}^+)$ is the molality of (H^+) at 25 °C); such an assumption has already been made by Byrne et al. [37] when comparing spectrophotometric and potentiometric pH measurements. Then values were converted into $\mu\text{mol H}^+ \cdot \text{kg}_{\text{sw}}^{-1}$ on the basis of sample salinities at 25 °C [38], according to Equation (1):

$$\text{pH}(\mu\text{mol H}^+ \cdot \text{kg}_{\text{sw}}^{-1}) = \text{pH}(\mu\text{mol H}^+ \cdot \text{kg}_{\text{H}_2\text{O}}^{-1}) - \log(1 - 0.00106^*\text{S}). \qquad (1)$$

Values were then converted into the pH_T scale (in $\mu\text{mol H}^+ \cdot \text{kg}_{\text{sw}}^{-1}$), using the relationship proposed by Millero [39], according to Equation (2):

$$\text{pH}_\text{T} = \text{pH}_\text{F} - \log(1 + [\text{SO}_4^{2-}]/\text{K}_{\text{H}_2\text{SO}_4}), \qquad (2)$$

where $K_{H_2SO_4}$ was according to the definition of Khoo [40] and the SO_4/chlorinity ratio of 0.13981 w/w defined for Adriatic seawater [41] was used to obtain the concentrations of total SO_4 from salinities.

2.5. *Total alkalinity*

In the *ASCOP 2* cruise, samples for TA were analysed on board within a few hours of sampling. Aliquots of 100 cm^3 were potentiometrically titrated with HCl, 0.02 $mol \cdot dm^{-3}$, in NaCl 35‰, in enclosed cells at 25 °C, according to Almgren et al. [42], and the results expressed as $\mu mol \cdot dm^{-3}$ with a reproducibility of $\pm 10\ \mu mol \cdot dm^{-3}$. Accuracy was determined from the standard acid (fixanal-hydrochloric acid; Riedel de Haën) used for titration and was $\pm 5\ \mu mol \cdot dm^{-3}$ of $[H^+]$. In order to compare these values with those of 2008, they were converted to $\mu mol \cdot kg^{-1}$ on the basis of their density at 25 °C.

In 2008 (*VECSES 1*), TA was analysed in the laboratory by potentiometric titration in open cells at 25 ± 0.05 °C of ~130 g precisely weighed (precision 0.002 g) with HCl 0.1 $mol \cdot kg^{-1}$ in NaCl 35‰. The acid was calibrated against seawater certified as reference material (CRM) for T_{CO_2} and TA (batch no. 83; supplied by Prof. A.G. Dickson, Scripps Institute of Oceanography, USA) and the equivalence point was determined with the derivative method described by Hernandez-Ayon et al. [43]. The accuracy was determined by titrating six replicates of another batch of CRM, with a different TA value (batch $n = 89$, TA $= 2214.06 \pm 0.24\ \mu mol \cdot kg^{-1}$): the measured mean value of TA was $2213.2 \pm 1.7\ \mu mol \cdot kg^{-1}$, within $1\ \mu mol \cdot kg^{-1}$ of the CRM value. Long-term precision was monitored daily by analysing CRM samples ($n = 33$, SD $= 2.9\ \mu mol \cdot kg^{-1}$).

Again, the two methods have different precisions, with resultant uncertainties.

2.6. *Computed seawater carbonate system properties*

The concentrations of other components of the carbonate system in seawater at 25 °C were derived from T, S, pH, TA, reactive silicate and phosphate experimental data, according to Lewis and Wallace [44]. In particular we took into consideration: the partial pressure of carbon dioxide (P_{CO_2}), its fugacity (fCO_2), carbonate alkalinity (CA), the concentrations of carbonic acid (H_2CO_3), bicarbonate ion (HCO_3^-), carbonate ion (CO_3^{2-}) and dissolved inorganic carbon (DIC), the calcium carbonate solubilities (calcite saturation, Ω_C, and aragonite saturation, Ω_A, respectively).

3. Results

3.1. *Hydrological structures in 1983 and 2008*

The hydrological structure and thermohaline circulation in the northern Adriatic Sea are well known [45]. The basin works as a dilution basin heavily influenced by freshwater inflow and is simultaneously a site of dense water formation. The dense water formed here, the NAdDW, is the densest water of the entire Mediterranean. The general circulation, driven by density differences and constrained by the shape of the coast, is cyclonic and results from being fed, on the one hand, by the northward flow of the Eastern Adriatic Current (EAC) along the eastern coast and, on the other hand, by the Western Adriatic Current (WAC) which flows southward along the Italian coast. The WAC, less saline because of several river inputs, is mostly confined to a narrow shallow area close to Italian shelf, especially in winter. Among river contributors, the River Po plume ($S < 35.0$) is the most significant, although reduced in winter, flowing directly southward

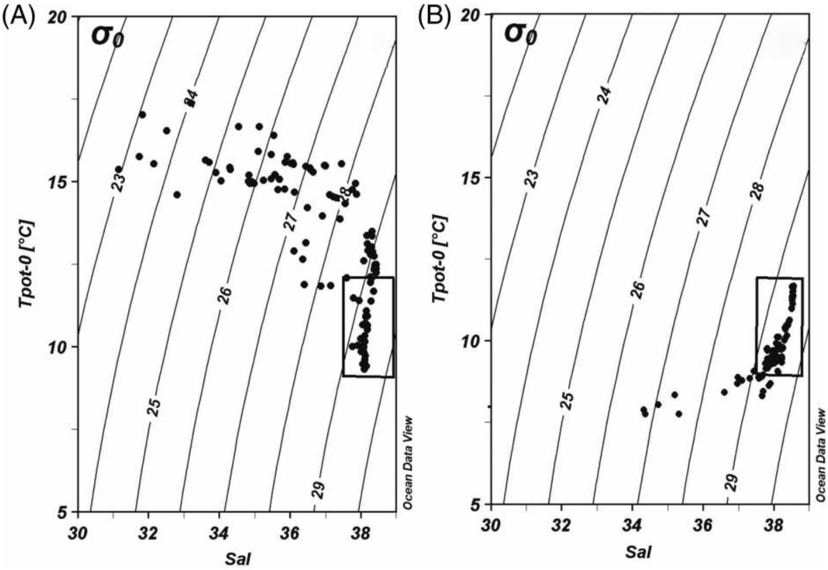

Figure 2. T/S diagram from the 1983 (A) and 2008 (B) datasets.

along the coast. On the other side of the basin, the EAC, more saline coming from the south (even from the Ionian Sea), closes the cyclonic circulation. During winter, the whole northern basin can be involved in the dense water formation process by outbreaks of cold and dry continental air associated with Bora wind events; the dense water then outflows southward, filling the Meso and Southern Adriatic Pits.

The T/S diagrams from the *ASCOP 2* (1983) and *VECSES 1* (2008) cruises (Figure 2) revealed the occurrence of the following different bodies of water:

(1) the fresh ($31.0 < S < 35.0$) surface water mass of the River Po plume, warm ($12.0 < T < 17.5\,°\mathrm{C}$) in 1983 and colder ($7.0 < T < 8.0\,°\mathrm{C}$) in 2008;
(2) the more saline ($35.0 < S < 37.5$) water mass probably advected by WAC, warmer ($12.0 < T < 17.0\,°\mathrm{C}$) in 1983 and cold ($8.0 < T < 9.0\,°\mathrm{C}$) in 2008; and
(3) the dense, more saline ($37.5 < S < 38.2$) and cold ($9.0 < T < 12.0\,°\mathrm{C}$) winter water mass.

In order to detect differences in pH values occurring between 1983 and 2008 caused by climatological changes it is appropriate to compare water bodies that are as similar as possible, not only for their hydrological properties, but also with regard to their origin. In Figure 2, the water body defined by $S > 37.5$ psu and T ranging between 9 and 12 °C (inside the black rectangle) occurred in both 1983 and 2008. The hydrological characteristics of this water body in both investigated periods are briefly summarised (Table 1). The mean density anomalies 29.302 (*ASCOP 2*) and 29.452 (*VECSES 1*) were very similar in 1983 and 2008, identifying these water bodies as the densest observed during those cruises. In addition, mean temperatures and salinities corresponded to NAdDW values [46]. This water type is formed under the combined effect of Bora wind and winter temperatures [47,48] in the northern part of the Adriatic Sea and it is usually characterised by $T = 11.35 \pm 1.40\,°\mathrm{C}$, $S = 38.30 \pm 0.28\,\mathrm{psu}$ and $\sigma_t > 29.2\,\mathrm{kg} \cdot \mathrm{m}^{-3}$, according to Artegiani et al. [46], although some variability can be observed on both interrannual and climatological time scales. Comparing characteristic NAdDW values with those reported in Table 1, we can infer that we are comparing the remnants of NAdDW formed during the winters of 1982–1983 and 2007–2008. However, during 2008 the water column was more homogeneous than in 1983: the dense water samples in 2008

Table 1. Physical properties of the water bodies chosen for comparison between 1983 and 2008.

	Parameter	Units	No. samples	Min.	Max.	Avg.	SD	Median value
ASCOP 2 (1983)	Depth	m	33	10	48	27.4	±8.6	30
	Salinity	psu	33	37.763	38.363	38.109	±0.121	38.114
	Temp.	°C	33	9.311	11.937	10.431	±0.752	10.322
	σ_t	$kg \cdot m^{-3}$	33	28.863	29.525	29.302	±0.140	29.329
VECSES 1 (2008)	Depth	m	63	1	72	19.5	±18.0	15.0
	Salinity	psu	63	37.734	38.550	38.301	±0.232	38.319
	Temp.	°C	63	9.087	11.689	10.426	±0.849	10.390
	σ_t	$kg \cdot m^{-3}$	63	29.221	29.579	29.452	±0.082	29.467

filled the whole water column (from the surface to -72 m), whereas in 1983 they filled only intermediate and deep layers (from -10 to -48 m). In addition, in May 1983 the thermohaline stratification had already started ($9.31 < T < 19.00\,°C$ and $31.00 < S < 38.36$), suggesting early spring season conditions, whereas in February 2008 the water column was still very cold ($9.087 < T < 11.942\,°C$) and mixed down to the bottom, conditions resembling the winter season.

3.2. *Dissolved oxygen and apparent oxygen utilisation variability in 1983 and 2008*

Analysis of AOU variabilities cannot be neglected because it provides valuable indications of biological processes such as primary production and bacterial respiration of organic matter, which contribute to the final pH of seawater by consuming or adding CO_2. In particular, under hypoxic conditions, the pH can decrease noticeably because of CO_2 produced by degradation processes. For the comparison performed, conditions with such high biological CO_2 emission or consumption should be avoided because they could obscure the effects of atmospheric CO_2 dissolution.

In 1983 and 2008, the NAdDW water bodies displayed the oxygenation state summarised in Table 2. During both the periods investigated the selected water bodies did not present low DO concentration values indicating hypoxic conditions. Water masses appeared only slightly undersaturated during the 1983 cruise (average AOU = 18.0 $\mu mol \cdot dm^{-3}$) and well oxygenated during 2008 (average AOU = -3.9 $\mu mol \cdot dm^{-3}$). The former positive value in May 1983 suggested a slight predominance of remineralisation over primary production, as often occurs in the early spring season; however, extensive processes of remineralisation, repeatedly observed in the northern Adriatic at the end of spring or in summer, were not affecting the water mass. The lower variability of AOU in 2008 ($-9.6 < AOU < 21.6\,\mu mol \cdot dm^{-3}$) than in 1983 ($-16.1 < AOU < 52.4\,\mu mol \cdot dm^{-3}$) confirms the seasonal conditions (winter and early spring, respectively) suggested by the T/S diagram analysis.

Table 2. Concentration of dissolved oxygen (DO) and apparent oxygen utilisation (AOU) of the water bodies of 1983 and 2008 chosen for comparison on the basis of thermohaline characterics.

	Parameter	Units	No. samples	Min.	Max.	Avg.	SD	Median value
ASCOP 2 (1983)	DO	$\mu mol \cdot dm^{-3}$	33	224.9	295.4	255.9	±17.2	253.4
	AOU	$\mu mol \cdot dm^{-3}$	33	−16.1	52.4	18.0	±19.9	21.1
VECSES 1 (2008)	DO	$\mu mol \cdot dm^{-3}$	63	256.9	289.0	277.6	±6.0	278.4
	AOU	$\mu mol \cdot dm^{-3}$	63	−9.6	21.9	−3.9	±4.6	−5.0

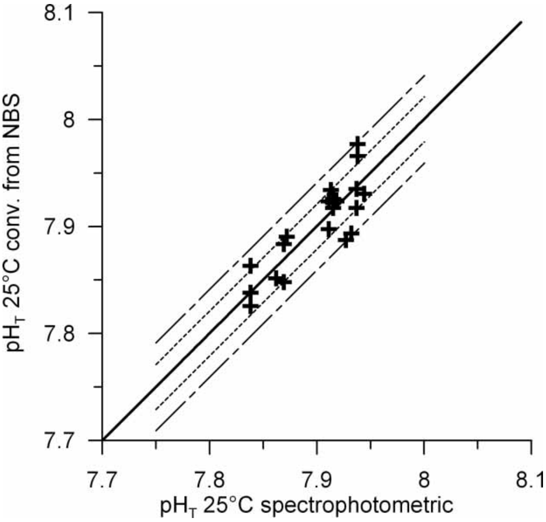

Figure 3. Plot of pH_T determined using the spectrophotometric method versus pH_T determined using the potentiometric method on the NBS scale and converted to the 'total scale' in μmol $H^+ \cdot kg_{sw}^{-1}$. The solid line is the theorical 1:1 conversion, dotted lines indicate 1SD (±0.0164) and dashed lines 2SD (±0.0329).

3.3. *Reliability of the conversion of pH from NBS to pH_T scales*

To test the reliability of the conversion procedure of pH values on the NBS scale into pH_T as proposed above, some samples of seawater ($n = 23$, salinity from 27.69 to 38.55) were analysed in parallel both with the potentiometric method on NBS scale, as done 1983, and with the colorimetric method on pH_T, as done in 2008.

The results on the NBS scale were converted to pH_T according to the procedure proposed here and matched with the pH_T values obtained using the spectrophotometric method (Figure 3). A similar comparison between results of the two methods was presented (on 46 samples) by Byrne et al. [37].

The mean difference between spectrophotometric pH_T and pH_T obtained from pH_{NBS} after the conversion ($X = -0.0016$) and its standard deviation ($SD \pm 0.0197$) agree well with the values (0.012 ± 0.010) obtained by Byrne [37]. For $t = 0.05$, a confidence interval of 95% resulted in $X \pm 0.00845$. Because this interval includes the value of 0 for null difference between the two methods, the conversion was not affected by any systematic error. The lower precision of the potentiometric method with respect the spectrophotometric contributes significantly to the scattering of the points around the line of theoretical correspondence ($1SD = \pm 0.0164$), affecting the confidence limits.

This basic result allows us to recover past datasets, in particular from the 1983 cruise, for further comparisons.

3.4. *Variability in pH and other carbonate system parameters in 1983 and 2008*

All of the measured and computed variables of the CO_2 system are briefly reported (Table 3). The ranges of variability within one cruise, with the average, SD and median values, are also reported. In general, the rather good correspondence between the average and the median value of each parameter indicates the Gaussian distribution of results.

All results are given at $T = 25\,°C$, the temperature of analysis, as recommended by protocols for quality control of results [36].

Table 3. pH and dissolved carbonate system, at 25 °C, in *ASCOP 2* and *VECSES 1* cruises.

	Parameter	Units	No. samples	Min	Max	Avg.	SD	Median value
ASCOP 2 (1983)	pH_T	$\mu mol\ H^+ \cdot kg_{sw}^{-1}$	33	7.914	8.099	8.010	±.046	8.005
	TA	$\mu mol \cdot kg^{-1}$	33	2564.1	2611.1	2584.5	±10.9	2584.8
	CA	$\mu mol \cdot kg^{-1}$	33	2452.4	2509.1	2481.7	±14.4	2483.0
	DIC	$\mu mol \cdot kg^{-1}$	33	2200.6	2323.7	2256.3	±32.1	2260.9
	fCO_2	μatm	33	375.2	629.8	485.1	±63.6	489.2
	pCO_2	μatm	33	376.4	631.9	486.7	±63.8	490.8
	H_2CO_3	$\mu mol \cdot kg^{-1}$	33	10.5	17.6	13.6	±1.8	13.7
	HCO_3^-	$\mu mol \cdot kg^{-1}$	33	1917.2	2103.5	2003.8	±49.0	2011.1
	$CO_3^=$	$\mu mol \cdot kg^{-1}$	33	200.1	278.9	239.0	±19.5	236.1
VECSES 1 (2008)	pH_T	$\mu mol\ H^+ \cdot kg_{sw}^{-1}$	56	7.917	7.973.	7.946	±0.012	7.947
	TA	$\mu mol \cdot kg^{-1}$	61	2622.9	2696.7	2658.9	±18.1	2658.1
	CA	$\mu mol \cdot kg^{-1}$	54	2528.7	2603.7	2569.5	±19.2	2572.4
	DIC	$\mu mol \cdot kg^{-1}$	54	2322.8	2413.2	2366.6	±21.6	2370.3
	fCO_2	μatm	54	547.3	650.4	593.4	±22.3	593.2
	pCO_2	μatm	54	549.0	652.5	595.3	±22.3	595.1
	H_2CO_3	$\mu mol \cdot kg^{-1}$	54	15.3	18.2	16.6	±0.6	16.6
	HCO_3^-	$\mu mol \cdot kg^{-1}$	54	2805.4	2186.3	2130.6	±23.9	2137.4
	CO_3^{2-}	$\mu mol \cdot kg^{-1}$	54	208.7	230.1	219.4	±4.9	219.5

3.4.1. *pH_T*

In 1983, values varied in the range 7.914–8.099 units ($\Delta_{pH} = 0.185$) with an average of 8.010 ± 0.046 pH_T units (on 33 samples). The winter 2008 range was 7.917–7.973 units ($\Delta_{pH} = 0.056$), average 7.946 ± 0.012 pH_T units (on 56 samples). Variability in 1983 was greater than in 2008, reflecting slightly different seasonal conditions which are discussed below.

In both 1983 and 2008 pH_T was highly correlated with fCO_2 ($r^2 = 0.991$ in 1983 and 0.709 in 2008; (Figure 4A), suggesting that the spatial variabilities in pH_T within the same dataset were mainly induced by fCO_2 variabilities.

The lack of correlation ($r^2 < 0.137$) between TA and fCO_2 in both winter seasons suggests that small TA changes within the datasets did not determine the observed pH_T variabilities.

3.4.2. *Total alkalinity*

In 1983, TA values for the related dataset varied between 2564.1 and 2611.1 $\mu mol \cdot kg^{-1}$ with an average value of 2584.5 ± 10.9 $\mu mol \cdot kg^{-1}$. In winter 2008 they varied between 2622.9 and 2696.7 $\mu mol \cdot kg^{-1}$, with an average value of 2658 ± 18.1 $\mu mol \cdot kg^{-1}$ (Table 3).

No correlation between TA and salinity was found in either year (Figure 4B) within the narrow salinity range selected. However, a general trend to higher TA values at lower salinity can be seen, demonstrating the significant role of the high-TA freshwater inputs into this sub-basin [49,50].

The lack of correlation between TA and fCO_2 ($r^2 < 0.001$ in 1983, $r^2 < 0.293$ in 2008) in both datasets indicates strong uncoupling between these two properties; this is not surprising because addition of carbon dioxide to ocean waters does not affect TA [39,51].

3.4.3. *Fugacity of CO_2*

In 1983, values varied between 375.2 and 629.8 μatm, with an average value of 485.1 ± 63.6 μatm.

In winter 2008, values ranged between 547.3 and 650.4 μatm, with an average value of 593.4 ± 22.3 μatm.

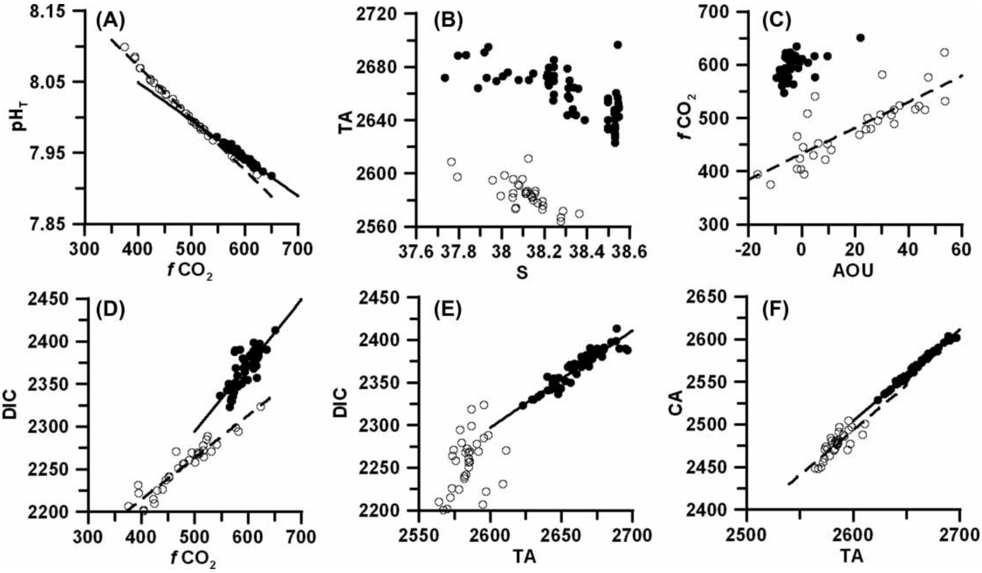

Figure 4. (A) pH_T versus fCO_2, at 25 °C, in 1983 (○) and 2008 (•); line represents the regression line. (B) TA versus salinity in 1983 (○) and 2008 (•). (C) fCO_2 versus AOU in 1983 (○) and 2008 (•); line represents the regression line. (D) DIC versus fCO_2, at 25 °C, in 1983 (○) and 2008 (•); the lines represent the regression line. (E) DIC versus TA, at 25 °C, in 1983 (○) and 2008 (•); the line represents the regression line. (F) CA versus TA, in 1983 (○) and 2008 (•).

The concentration of dissolved CO_2 in seawater is basically determined by the temperature, which drives atmospheric CO_2 absorption, and by biological processes. Temperature variability was very low ($\Delta T = 2.6\,°C$) in both datasets; this could explain the narrow fCO_2 variability in winter 2008, but not the broader spatial variability in 1983. The low but not negligible correlation ($r^2 = 0.669$) between fCO_2 and AOU in 1983 (Figure 4C) indicates that the remineralisation process was the major driver of the fCO_2 variability observed in early spring of that year. The narrower fCO_2 variability in winter 2008 agrees well with the occurrence of more wintry conditions when the biological demand on dissolved carbon was still very low.

3.4.4. *Dissolved inorganic carbon*

In 1983, DIC concentrations varied between 2200.6 and 2323.7 $\mu mol \cdot kg^{-1}$ ($\Delta_{DIC} = 123.1\,\mu mol \cdot kg^{-1}$) with an average value of $2256.3 \pm 32.1\,\mu mol \cdot kg^{-1}$. Both the very good correlations between fCO_2 and DIC (Figure 4D, $r^2 = 0.916$) and between DIC and pH ($r^2 = 0.896$), and the absence of any degree of correlation between TA and DIC ($r^2 = 0.137$; Figure 4E), suggest a strong dependence of DIC on dissolved CO_2 and pH_T, and a lack of coupling with TA values.

In winter 2008, DIC concentrations ranged between 2322.8 and 2413.2 $\mu mol \cdot kg^{-1}$ ($\Delta_{DIC} = 90.4\,\mu mol \cdot kg^{-1}$) with an average value of $2366.6 \pm 21.6\,\mu mol \cdot kg^{-1}$. The quite high degree of linearity between TA and DIC (Figure 4E; $r^2 = 0.846$) with much less correlation of fCO_2 with DIC ($r^2 = 0.637$) indicates that the DIC was strongly determined by the TA values and not coupled with CO_2.

The computed DIC concentration values are given by the sum of concentrations of all the inorganic carbon dissolved species: H_2CO_3 (or free dissolved CO_2), HCO_3^- and CO_3^{2-}. DIC therefore includes in its formulation chemical species that are directly influenced by CO_2 dissolution

(H_2CO_3) and chemical species (HCO_3^- and CO_3^{2-}) that are the major constituents of TA. For this reason, the DIC might exhibit some dissimilar behaviour depending on the prevalence of one chemical species over the others.

3.4.5. *Carbonate alkalinity*

In 1983, CA values for the corresponding dataset varied between 2452.4 and 2509.1 $\mu mol \cdot kg^{-1}$ with an average of $2481.7 \pm 14.4\,\mu mol \cdot kg^{-1}$. Because $TA = CA - \Sigma_{other\,bases}$ [39], the good correlation between TA and CA (Figure 4F) indicates that the contribution of other bases (in our case the dominant species of phosphoric and silicic acid at the pH of seawater) to TA was constant and much lower than that of CA. This is not obvious for water masses which can be influenced by considerable river input. The very low correlations with pH and fCO_2 ($r^2 = 0.412$ and 0.342, respectively) indicate that CA, too, was not influenced by atmospheric CO_2.

In 2008, CA values for the dataset varied between 2528.7 and 2603.7 $\mu mol \cdot kg^{-1}$ with an average of $2569.5 \pm 19.5\,\mu mol \cdot kg^{-1}$. During this winter also, TA and CA were well correlated (Figure 4F), indicating that the contribution of the other bases to TA was constant and much lower than the contribution of CA, as can be expected in a basin receiving highly calcareous river waters.

3.5. ***Decadal variability in pH and other carbonate system parameters between 1983 and 2008***

Relying on the general good correspondence between average and median values of each parameter within one dataset (Table 3), indicating the Gaussian distribution of results (as an example, see Figures 5 and 6), we compared the average values for the two different years. Statistical tests (ANOVA) were used to draw conclusions from the observed interannual (decadal) differences.

The decadal pH_T variability from the two datasets differs at the 95% confidence level on the basis of ANOVA (F ratio $= 129.3$, $p \ll 0.05$). The difference between the average values (ΔpH_T) gives a net decrease of 0.063 pH units. As can be seen from Figure 5, this value exceeds the potential errors becauser of: (1) the lower accuracy assumed for pH measured on the NBS scale (0.02 units); (2) the standard error of each method, which is smaller than ±0.020 units; and (3) the error deriving from conversion from the pH_{NBS} scale to the pH_T scale.

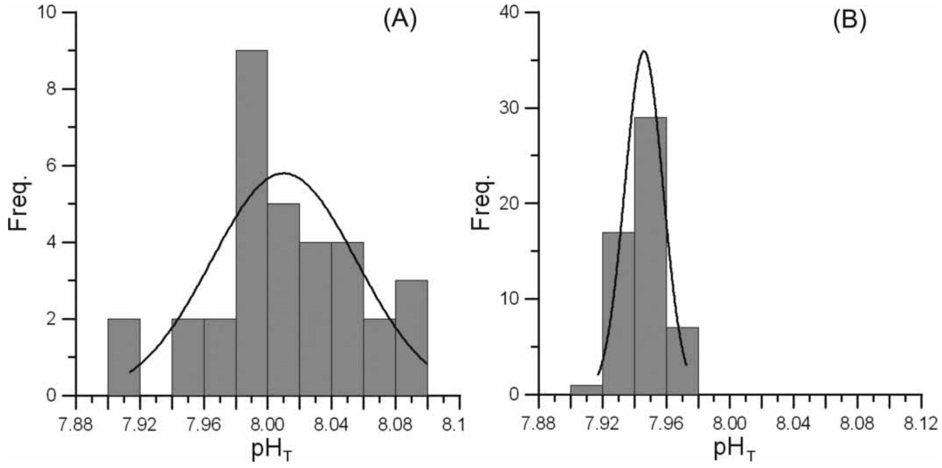

Figure 5. Distribution of pH_T values from the 1983 (A) and 2008 (B) datasets.

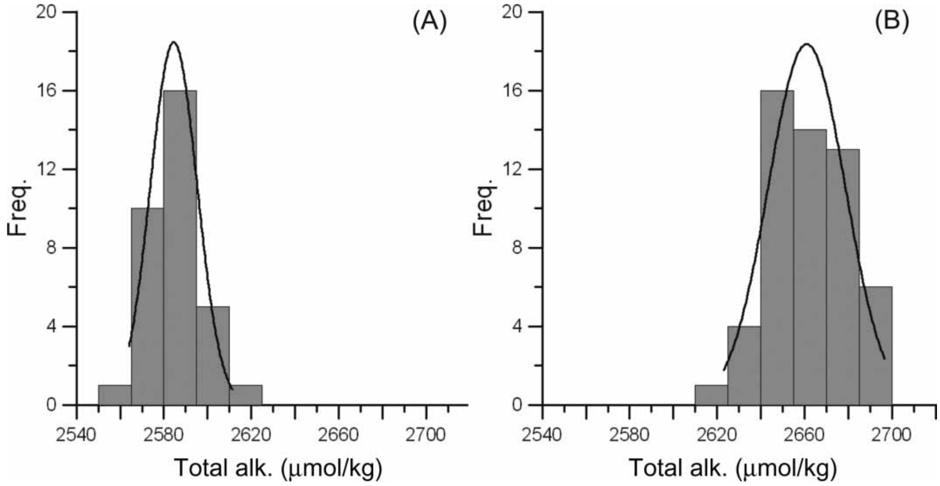

Figure 6. Distribution of TA values from the 1983 (A) and 2008 (B) datasets.

The TA decadal variabilies in the two datasets differ at the 95% confidence level (F ratio $=$ 498, $p \ll 0.05$). However, in contrast to what was observed concerning pH, the difference between average values (ΔTA) shows an increase in TA of 74.4 μmol $\cdot$ kg^{-1} (Figure 6). The increase greatly exceeds the potential error due to the accuracy of the two titration systems (± 6 μmol $\cdot$ kg^{-1}, 1983 data; ± 2 μmol $\cdot$ kg^{-1}, 2008 data).

The fCO_2 decadal variabilities differ at the 95% confidence interval (F ratio $= 131$, $p \ll 0.05$). The difference between the two average values (ΔfCO_2) gives a net mean increase of 108.3 μatm between 1983 and 2008. This result seems to suggest that the atmospheric CO_2 increase which occurred in the last two decades, up to values higher than 380 μatm, was the driving factor for the increase in dissolved CO_2 in seawater, as the T and S properties of the water mass remained similar ($\Delta T = 0.068\,^{\circ}$C, $\Delta S = 0.205$ psu) throughout the period under consideration.

All three statistically significant decadal changes will be discussed below in the context of the climatological influence on ocean acidification.

The difference between the average DIC concentration values (ΔDIC) gives a net increase of 110.3 μmol $\cdot$ kg^{-1}. The total increase (Table 3) appears to be due to an increase in both H_2CO_3 concentration, which is known to be caused by the fCO_2 increase, and bicarbonate (HCO_3^-) concentration, as a result of the conversion of carbonate ions (CO_3^{2-}) into bicarbonate (caused by acidification).

The net increase in CA (ΔCA $= 77.8$ μmol $\cdot$ kg^{-1}) is nearly coincident with the net increase in TA (74.4 μmol $\cdot$ kg^{-1}). Because the relationship between TA and CA is good and very similar in the two years (see linear regression in Figure 4F) we infer that the net increase in TA was determined by the net increase in CA, the contributions of the other bases being constant through the time span ($\mathrm{TA} = \mathrm{CA} - \Sigma_{\text{other bases}}$) [39]. This conclusion is unsurprising considering that rivers drain higly carbonatic basins.

4. Discussion

The interdecadal differences in fCO_2, TA and pH_T between 1983 and 2008 are statistically significant and merit consideration in a preliminary climatological discussion on the acidification of the northern Adriatic Sea.

In particular, the net pH decrease (−0.063 pH units) accompanied by the increase in fCO_2 (108.3 μatm) and TA (74.4 $\mu mol \cdot kg^{-1}$) over the same period is worthy of discussion in the context of ocean acidification. We wondered whether this change could be caused by the fCO_2 increment, through the solubility pump, induced by the CO_2 increase in the atmosphere. In order to answer this question we analysed the different forcing agents (drivers) impacting on the selected water masses during the two seasons and between the two winters (decadal comparison).

We start our discussion from fCO_2 and TA variabilities because they are independent of each other but both can affect the pH_T.

Starting from the observed changes in dissolved CO_2 and considering that the corresponding decadal variability in temperature ($\Delta T = 0.068\,°C$) was negligible, the following question arises: could the net increase in dissolved carbon dioxide ($\Delta fCO_2 = 108.3\,\mu atm$) be explained by the slightly different intensities of biological activity observed between the two seasons? In the early spring season of 1983 the biological activity was higher than during the 2008 more wintry season, as indicated by the average AOU values (18.0 and −3.9 $\mu mol \cdot dm^{-3}$, respectively). In 1983, the slight predominance of remineralisation processes added CO_2 to the water mass and hence contributed to the increase in fCO_2. If the average AOU had been $\sim 0\,\mu mol \cdot dm^{-3}$ (rather than 18.0 $\mu mol \cdot dm^{-3}$) the corresponding fCO_2 value would have been lower in 1983, so the resulting decadal variability would have been even higher than observed. Therefore, microbial activity (oxidation of organic matter) had the potential to make a contribution but it would have been in the opposite direction to that observed, eventually smoothing the change. This strongly suggests that the net fCO_2 increase was most probably due to the increase in pCO_2 in the atmosphere observed all over the world [4], including over the Adriatic region (390 μatm during winter cruise in 2008; Salvi and Schirone, pers. comm.).

We then asked whether the significant net increase in total alkalinity (74.4 $\mu mol \cdot kg^{-1}$) could have played a major role in determining the pH_T change.

The TA in the Adriatic Sea is heavily influenced by the riverine inputs containing high TA loads, as suggested by the negative TA/S trend (Figure 4B), which contrasts with the positive trend observed in the open Mediterranean [55]. Even though the riverine TA is mainly determined by the geological composition of drainage basins, it can significantly vary in relation to the river flows, loads and changes in the terrestrial carbon cycle. Hence the observed change in alkalinity could be due to a change in total alkalinity discharged by rivers [49,52] The observed change in alkalinity might also be explained by biogeochemical processes within shelf sediments, which have recently been indicated as playing an important role in providing a net TA source to shelf and marginal seas [53,54]. The extent to which these processes may be active in the northern Adriatic and the range of variability they exhibit has not yet been assessed, and future work is needed to understand their potential role in TA budgets. Also the dissolution of calcium carbonate ($CaCO_3$) from sediments due to the acidification of seawater might play a role in increasing TA, but this is difficult to support with our data as the investigated NAdDW appeared strongly supersaturated ($\Omega \gg 1$) with respect to both calcite ($\Omega_C = 5.60 \pm 0.46$ and 5.14 ± 0.11, in 1983 and 2008, respectively) and aragonite ($\Omega_A = 3.71 \pm 0.30$ and 3.40 ± 0.07, in 1983 and 2008, respectively), as already observed for the Mediterranean Sea [55]. Even if the cause of the TA increment cannot be assessed, it cannot account for the shift to lower pH_T values: TA is directly involved in the buffering capacity of the carbonate system and an increment would have produced an increase in pH_T instead of a decrease. We have calculated the pH_T increase corresponding to the TA increase of 74.4 $\mu m \cdot kg^{-1}$, under the same conditions as in 1983 for all other biogeochemical parameters required by the CO2SYS programme: the result was an increase of 0.012 pH_T units. Therefore the observed interdecadal pH_T decrease would have to have occurred against a total alkalinity increase.

Overall, our data strongly suggest that the long-term decrease in pH_T is due to fCO_2, from both (1) the good spatial correlation between fCO_2 and pH_T, which indicates that pH_T values were mainly determined by the amount of dissolved CO_2 in both years, and (2) the very similar regression lines, suggesting the chemistry of the carbonate system worked in the same way over the two years and the drivers were the same (the players of the game were the same). Still using the CO2SYS programme, we calculated the pH_T variation corresponding to the observed fCO_2 increase in 2008 but keeping constant values, as in 1983, of all the other biogeochemical parameters (TA, nutrients): the result is a decrease of ~0.100 pH_T units. Therefore the observed value of 0.063, being lower, seems absolutely reasonable taking into account the buffering action played by the increase in total alkalinity.

In conclusion, the observed decrease in pH_T in the NAdDW mass can be regarded as an acidification instance in the northern Adriatic Sea. It would correspond to an acidification rate of 0.0025 pH_T units $\cdot$ year^{-1}. Such a value would be slightly higher than the acidification rate of 0.0017 ± 0.0004 pH units $\cdot$ year^{-1} measured on a time series at the ESTOC station (1995–2004) in the open ocean (Atlantic, Canary Islands) reported by Santana-Casiano et al. [56] and almost double the acidification rate of 0.0012 ± 0.0004 pH units $\cdot$ year^{-1} from the time series at BATS, over the last 20 years, in the open ocean (Atlantic, Bermuda Islands) reported by Bates [57], but would be much lower than the acidification rate of 0.02 pH units $\cdot$ year^{-1} measured in the North Sea (Dutch WATERbase) over the period 1998–2004 [5].

The observed and computed acidification rates in the northern Adriatic Sea support that what Yilmaz et al. [58] reported for the supposed higher capacity to adsorb relatively more CO_2 in the Mediterranean Sea than in the Atlantic Ocean because of the higher total alkalinity of Mediterranean surface waters, and consequently the Mediterranean seawater would already present significant pH decreases.

Hence the northern Adriatic Sea can be proposed as very suitable site for observing the impact of acidification on marine biogeochemical cycles and marine ecosystems.

The increase in both TA and fCO_2 produced the observed DIC increase (110.3 μmol $\cdot$ kg^{-1}), which agrees with that forecast by ocean acidification theory and with that observed in other oceanic regions [22]; however, in the northern Adriatic Sea over the time span studied the increase in TA may also have impacted on the carbonate system variables.

The change in the slope of the DIC/fCO_2 linear regression shows the change in the CO_2 buffering capacity commonly referred to as the Revelle factor. The derived Revelle factor (R) was calculated for both datasets and showed lower average values in 1983 than in 2008 ($R = 9.773 \pm 0.469$ and 10.491 ± 0.168, respectively). As a smaller Revelle factor indicates higher buffering capacity [39], in our case, the reverse has occurred in the last 25 years, corresponding to a decrease in the buffering capacity of carbonate system.

These results indicate the need for careful checking, in the coming decades, of whether seawater acidification in the Adriatic Sea will continue, at significant rates, at the expense of a reduction in the overall buffering capacity of marine waters, because both processes can deeply affect marine biogeochemical cycles [13] and future ocean biogeochemistry [12]. In addition, it has recently been reported that the combined impacts of increased stratification, due to global warming, and changes in the ocean biology, caused by ocean acidification, cause a further decline in marine oxygen concentrations [59]. If this occurs in the northern Adriatic it might impact on the hypoxia and anoxia already occurring seasonally in the region [60], with the possible effect of exacerbating them.

5. Conclusions

The first comparison, concerning the northern Adriatic Sea, between old and recent datasets seems to us particularly interesting because it was performed on the cold winter water mass of NAdDW which, at our latitudes, can effectively dissolve much more CO_2 than warm water. If water masses are dense enough they can effectively sink to greater depths and retain CO_2 in marine water for a very long time. An ocean acidification process has been observed, accompanied by an increase in total alkalinity the origin of which we cannot state with confidence. Our results seems to confirm the general behaviour of the marine carbonate system already observed in other oceanic regions (Atlantic Ocean, ESTOC and BATS stations) and open sea regions (west Mediterranean, Dyfamed station) [61]. They therefore encourage us to continue the work, both by analysing additional old datasets in order to collect more robust evidence (based on larger quantities of data) for trends and by analysing data coming from the time series station very recently started in the Gulf of Trieste.

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