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Assessment of pH variability at a coastal CO_2 vent for ocean acidification studies

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A B S T R A C T

Marine environments with naturally high CO_2 concentrations have become important research sites for studying the impacts of future ocean acidification on biological processes. We conducted high temporal resolution pH and temperature measurements in and around a shallow (2.5–3 m) CO_2 vent site off Ischia, Italy in May and June 2008. Loggers were deployed at five stations to monitor water at both the surface and benthos. Our reference station, 500 m from the CO_2 vent, had no noticeable vent influence. It had a naturally high and stable benthic pH (mean 8.16, inter-quartile range (IQ): 8.14–8.18) fluctuating with diel periodicity, presumably driven by community photosynthesis and respiration. A principal component analysis (PCA) revealed that the pH of this station was well constrained by meteorological parameters. In contrast, a station positioned within the vent zone, had a low and very variable benthic mean pH of 7.11 (IQ: 6.91–7.62) with large pH fluctuations not well constrained by a PCA. Any stations positioned within 20 m of the main vent zone had lowered pH, but suffered from abnormally large pH fluctuations making them unsuitable representatives to predict future changes to a shallow coastal environment. Between these extremes, we identified a benthic area with a lower pH of 7.84 (IQ: 7.83–7.88) that retained many of the characteristics of the reference station such as a natural diel pH periodicity and low variability. Our results indicate that a range of pH environments maybe commonplace near CO_2 vents due to their characteristic acidification of benthic water over a wide area. Such environments could become invaluable natural laboratories for ocean acidification research, closely mimicking future CO_2 conditions in a natural setting.

1. Introduction

1.1. Ocean acidification

The release of anthropogenic carbon dioxide (aCO_2) from the burning of fossil fuels, cement manufacture and land-use change is increasing the partial pressure of carbon dioxide (pCO_2) in the atmosphere (Forster et al., 2007). To reach equilibrium with the ocean, a portion of the aCO_2 dissolves into the surface waters forming carbonic acid (Zeebe and Wolf-Gladrow, 2001). Ocean time-series data indicate that the surface ocean pCO_2 increase is similar to the rate expected from oceanic uptake (Bates, 2007) and maybe even greater in coastal areas (Wootton et al., 2008). This process, known as ocean acidification (Raven et al., 2005), is due to the uptake of ca. 50% of the aCO_2 emissions between 1800 and 1994 (Sabine et al., 2004) and has increased the acidity of the ocean by 30% resulting in a decrease of the average surface ocean pH by more than 0.1 units since the start of the industrial revolution (Haugan and Drange, 1996). Increasing aCO_2 release will result in continued surface ocean acidification over this century and it is predicted that the average ocean pH may decrease by a further 0.4 units by 2100 (Turley, 2008).

1.2. pH variability in seawater

The major driver of surface ocean pH change is the addition or removal of CO_2 by physical or biological activity (Schmalz and Swanson, 1969; Dickson, 2010). Photoautotrophic CO_2 depletion can cause significant diel pH oscillation (Frankignoulle and Disteche, 1987; Middelboe and Hansen, 2007; Yates et al., 2007) with the lowest pH occurring during the night when CO_2 is released by respiration, while the highest values occur during the afternoon when photosynthesis removes CO_2 (Schmalz and Swanson, 1969; Bensoussan and Gattuso, 2007). This diurnal oscillation is superimposed upon seasonal variations in pH, with lowest mean pH occurring in winter and highest in summer, due to changes in water temperature and the gross photosynthesis and respiration of the

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community (Frankignoulle and Bouquegneau, 1987, 1990; Borges and Frankignoulle, 1999; Takahashi et al., 2002; Wootton et al., 2008).

The surface waters of the open ocean vary between pH 7.9 and 8.3 (Bindoff et al., 2007), with differences in mean and variability generally dictated by the geographic region, and seasonal variations of up to 60% above and below the equilibrium of 385 µatm (Takahashi et al., 2002). In contrast, coastal waters routinely vary between mean pH 7.5 and 8.5 dependent on the habitat (Hinga, 2002) and show much larger seasonal and diel fluctuations (Middelboe and Hansen, 2007; Wootton et al., 2008). Hence, deviations from atmospheric CO_2 equilibrium in surface waters are common, particularly in coastal areas of high productivity especially where surface water circulation is restricted such as in semi-enclosed water bodies (Hansen, 2002; Middelboe and Hansen, 2007; Semesi et al., 2009; Gagliano et al., 2010).

1.3. Volcanic CO_2 vents

Areas with naturally high CO_2 may serve as useful sites to predict the impacts of ocean acidification on coastal environments (Barry et al., 2010). Hall-Spencer et al. (2008) reported on the benthic ecosystem changes associated with a natural pH gradient at a coastal Mediterranean cold CO_2 vent off Ischia, Italy. Here, the benthic floral and faunal communities are greatly affected by the lower pH water close to the vents (Hall-Spencer et al., 2008; Martin et al., 2008; Cigliano et al., 2010; Dias et al., 2010). The authors used point measurements of pH to establish zones relating to mean pH of 8.14, 7.76 and 6.47 and found large pH variability close to the main vent zone. This variability casts some doubt over the value of these specific zones for assessing the effect of ocean acidification, since future ocean acidification will not be characterised by such large variability in pH (Riebesell, 2008). It has been proposed that high temporal resolution monitoring of pH at natural CO_2 vents is essential to improve their use as natural laboratories (Barry et al., 2010), but to date this has not been carried out.

1.4. Aim

Here we report data on pH monitoring at five stations in and around a CO_2 vent off Ischia, Italy. The aim was to use measurements conducted at high temporal resolution to assess the pH characteristics around the site. The main hypothesis was that large pH fluctuations will render stations close to areas of CO_2 venting unsuitable for ocean acidification research. It follows that areas will exist with increasing distance from the main venting that are characterised by decreased pH and low pH fluctuations. These latter locations could best serve as natural laboratories for the prediction of biotic responses to ocean acidification.

2. Materials and methods

2.1. Site characterisation

Fieldwork was conducted from 9 May to 18 June 2008 off Ischia, Italy where cold CO_2 vents release 1500 m^3 of gas per day due to geological activity (Hall-Spencer et al., 2008). The CO_2 vents create a natural pH gradient from a pH of 8.1 in the background to as low as 5.6 within the embayment created by the Castello Aragonese, its causeway and the mainland (Fig. 1a; Table 1). The vent gas has a composition of: 90.1% CO_2, 6.6% N_2, 2.5% O_2 + Ar and 0.8% CH_4 with no detectable sulphur throughout (Hall-Spencer et al., 2008). The venting is diffuse over 3000 m^2 (usually with >5 vents m^{-2}) with no detectable seasonal, tidal or diel variation within the main vent zone.

According to previous reports (Hall-Spencer et al., 2008; Martin et al., 2008), the bay has a salinity of 38 (practical salinity scale) and a total alkalinity of 2.5 mequiv l^{-1}. These salinity and total alkalinity values were confirmed from filtered, preserved water samples analysed at the University of Essex in July 2008 using a DIGIT 032 ATC refractometer (Medline, Oxfordshire, UK) and alkalinity titration using a Ross series electrode (Thermo Electron Corporation, Beverly, MA, USA) in a temperature controlled open cell. Alkalinity

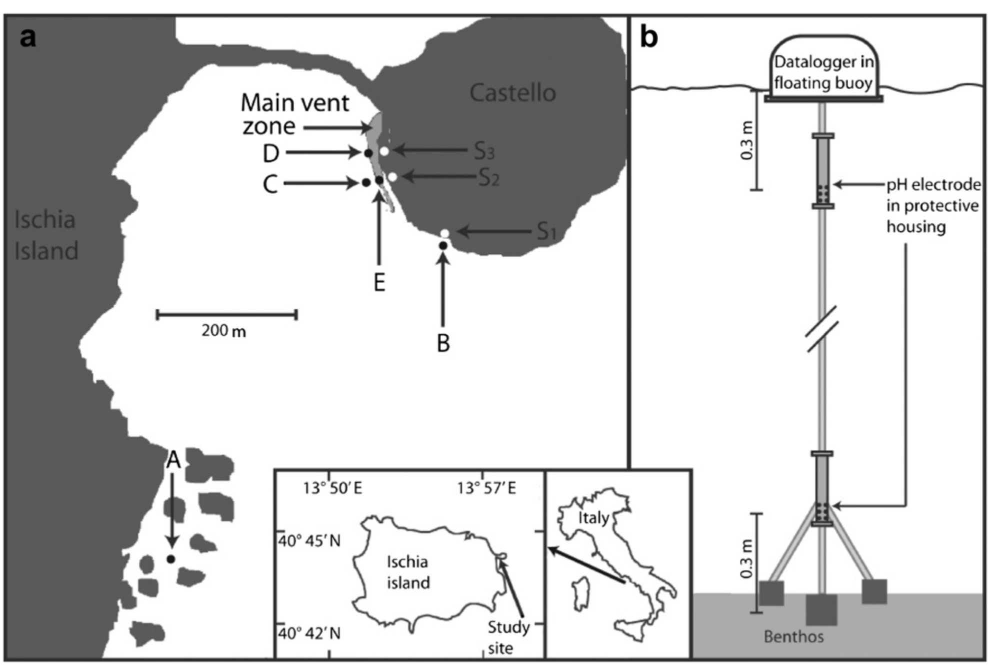

Fig. 1. (a) Investigated stations A–E within the embayment created by the Castello Aragonese, its causeway and the Ischian mainland, Bay of Cartaromana, Ischia, Italy. The light grey area represents a region of cold CO_2 venting, while S_1, S_2 and S_3 identify the approximate location of intertidal zones representing distinct pH environments described along the south transect in Hall-Spencer et al. (2008). (b) Diagram of the temperature and pH loggers used in this study.

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Table 1
Location of stations A–E off Ischia, Italy, relative to site description of the south transect in Hall-Spencer et al. (2008). Locations are illustrated in Fig. 1.

Station	Location (lat/long)	Description
A	40.7266 N 13.9603 E	>500 m from venting zone described in Hall-Spencer et al., 2008
B	40.7297 N 13.9647 E	0 m along south transect, adjacent to zone S_1, 2–3 m from rockface
C	40.7304 N 13.9630 E	200 m along south transect, adjacent to zone S_2, 39 m from rockface
D	40.7307 N 13.9631 E	220 m along south transect, adjacent to zone S_3, 16 m from rockface
E	40.7304 N 13.9633 E	200 m along south transect, adjacent to zone S_2, 20 m from rockface

data were analysed with the Alkalinity Calculator software (Rounds, 2009) using a Gran function (Gran, 1950, 1952), which determines the carbonate and bicarbonate endpoint by titrating over the pH range 4.2 and 3.0. We conducted preliminary 24 h pH measurements before selecting five stations for constant monitoring of pH over 3–10 days. Three stations were selected close to stations S_1, S_2 and S_3 as described in Hall-Spencer et al. (2008) (stations B, E and D in Fig. 1a and Table 1). Two additional stations (A and C in Fig. 1a and Table 1) were selected to further characterize variation in pH within the bay. To verify the validity of temporally separated pH measurements, one-day cross-comparisons were made to confirm that the pH characteristics for all sites were similar in both May and June (data not shown).

2.2. pH and temperature logging

pH was logged using a modification of the datalogging systems used by Davison et al. (1994) and Maberly (1996). Dataloggers (HOBO U12-008, Onset Computer Corporation, Pocasset, MA, USA) were sealed in airtight buoys floating on the surface, anchored to the seabed (Fig. 1b). Two pH probes (AmpHel HI-2911B/5, Hanna Instruments Ltd, Bedfordshire, UK) were waterproofed and connected to each logger through a gland in the buoy. Each probe was enclosed for protection within a plastic tube housing (200 mm length, 45 mm diameter) with numerous 5 mm holes to allow free exchange of water (Fig. 1b). Temperature dataloggers (HOBO Pendant, UA-001-64, Onset Computer Corporation, Pocasset, MA, USA) were attached to the underside of each probe housing. The synchronised pH and temperature loggers recorded data every minute for up to 10 days at each station. Two datalogging systems were available, so that two stations could be monitored simultaneously. At each station, water depth was between 2.5 and 3 m and probes were positioned 0.3 m from both the surface and benthos (Fig. 1b). These two positions are referred to as surface and benthic/benthos throughout this study.

Calibration and probe cleaning were performed before, after and every 3–4 days during the deployment at a recorded temperature. The millivolt signal recorded by the logger was converted to a pH signal by calibration against a range of known free scale pH standards (National Institute of Standards and Technology, U.S.A.). Linear regressions between voltage and pH resulted in r^2 values >0.99. pH was then converted to the seawater scale and corrected for temperature and salinity using the SEACARB package (Lavigne et al., 2008). The pH was recorded with an accuracy of 0.012 units. The drift in buffer readings between calibrations was found to be less than 0.05 units. Laboratory testing in artificial seawater, at a constant temperature and pH, confirmed that the millivolt drift from the pH loggers was within the standard tolerance of a 'well-behaved pH cell' (Dickson et al., 2007). The loggers had a lower pH detection threshold of ca. 6.75 that was instrument- and calibration-dependent. Carbonate chemistry at each station was calculated for each datum independently based on the simultaneous pH and temperature measurements and the measured salinity and total alkalinity using SEACARB (Lavigne et al., 2008).

2.3. Analysis of pH data

For the analyses, pH data were converted to hydrogen ion concentrations. Significance testing employed the Minitab statistical package (Minitab Inc, release 13.20). The data satisfied the Anderson–Darling test for normality (Anderson and Darling, 1952; Sokal and Rohlf, 1995). *t-Tests* and one-way analysis of variance (ANOVA) in combination with a *post-hoc* Fisher least significant differences test (LSD) were used to compare pH and temperature between stations and the two depths. Means and inter-quartile ranges (25–75%) were calculated from hydrogen ion concentrations and then re-converted to pH. Data are displayed as means and the distance from this point to the upper and lower quartile (e.g. $8.38 \pm 0.05/0.04$).

At each station the variability in pH between each consecutive 1 min sample was calculated and then grouped at 0.01 unit intervals (for example 0.00, 0.01. 0.02 units change etc.) to determine the frequency distribution of these pH changes. pH data at the detection threshold were excluded from this analysis.

For each station the variables listed below were entered into a principal components analysis (PCA), to explain variation in pH, using MVSP v.3.11c software (Kovach Computing Services, 2009) on natural log transformed data with an accuracy of 10^{-8}. Data for half-hourly meteorological measurements (air temperature, barometric pressure, humidity, cloud cover, rain, visibility, wind speed and direction) from nearby Naples (28 km) were retrieved from Eurometeo (Ciraci, 2008). Sunrise, solar noon and sunset times were also collected. Tidal heights and the rate of tidal height change were calculated from high and low tide times for Ischia Porto, 2.5 km from the study site, provided by Easytide (http://easytide.ukho.gov.uk). pH and temperature measurements were averaged over the 30 min in synchrony with the available meteorological data. Wind data were reduced from 16 to 8 directions and entered into the analysis as the strength of the directional wind on the Beaufort scale and using a measure of wind direction consistency based on the wind history immediately prior to sampling. pH data at the detection threshold were excluded from this analysis.

3. Results

3.1. Water temperature

Water temperature did not show any major differences between each station, moving in very close synchrony whenever two stations were logged simultaneously. Temperature data followed a typical daily pattern: lowest (*t*-test, $p < 0.001$) and very stable overnight increasing by ca. 2 °C after sunrise to a maximum 1–2 h after solar noon. It then decreased over the rest of the day and night until the following sunrise (Fig. 2). When averaged, temperature was significantly higher at the surface than the benthos by 0.16–0.31 °C depending on the site (*t*-test, $p < 0.001$).

Over the study period the night-time temperature increased by 2.5 °C. Cross-comparisons between stations confirmed that this temperature increase was uniform throughout the site. Therefore it must be noted that the difference in average temperature of stations A, B and C (June) in comparison to stations D and E (May) is an artefact due to the timing of these measurements (Table 2).

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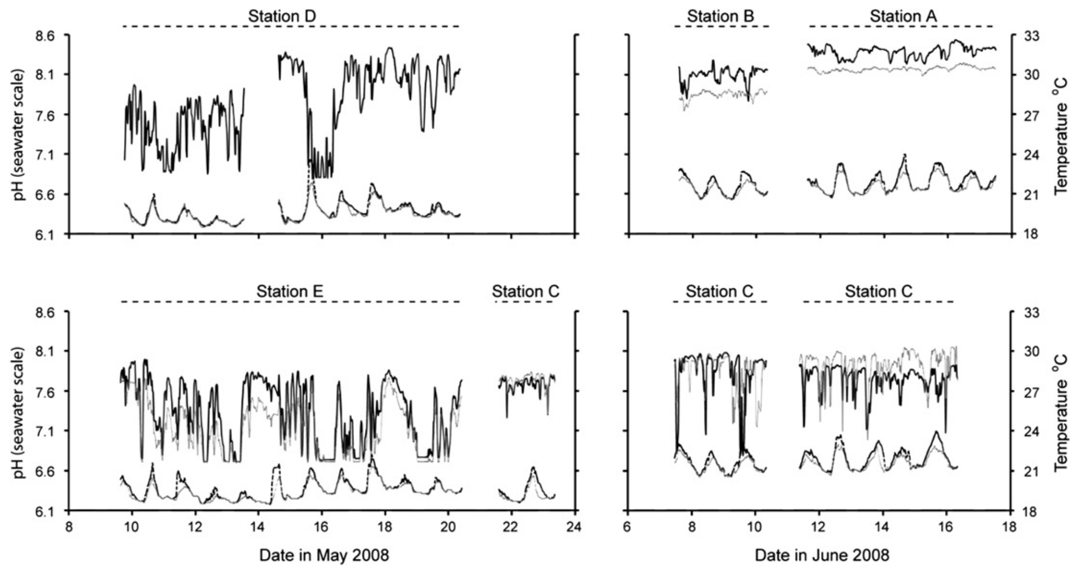

Fig. 2. Half-hourly averages of pH and temperature data collected at five stations (A–E) off Ischia, Italy using two dataloggers in May and June 2008. Black and grey lines represent surface and benthic pH measurements, while dashed black and grey lines show surface and benthic temperature data, respectively.

3.2. Overview of pH distribution

pH was significantly different between all stations investigated (ANOVA, $p < 0.001$, *post-hoc* Fisher LSD test, all significant, $p < 0.05$), and varied from pH ca. 8.6 to below the lower detection threshold at a pH of ca. 6.75 (Fig. 2). Station A had the highest and most stable pH with the pH decreasing towards stations D and E (Fig. 3) where the pH was most variable and frequently underwent substantial pH fluctuations within 1 h (Fig. 2). The decrease in mean pH from stations A to E was accompanied by an increase in the pH variability, represented by the inter-quartile range in Fig. 3. These differences produced a distinct carbonate chemistry at each station and a substantial decrease in the calcite and aragonite saturation states from stations A to E (Table 2). The range of pH values recorded also increased closer to the vents, with the maximum range found at the surface of station D. The surface and benthic pH were closely coupled with the benthic between 0.04 and 0.24 units lower and more stable (Table 2). An exception to this pattern is station C where the mean pH at the benthos was higher and more variable than at the surface (Fig. 2).

Table 2
Carbonate chemistry at five stations (A–E) off Ischia, Italy. Total alkalinity (TA) and water temperature (Temp.) are shown as mean ± standard deviation, while all other parameters are shown as the mean ± inter-quartile range (i.e. distance to 25% and 75% quartile). The salinity of all stations was constant at 38.

Depth	Station	TA (μmol kg^{-1})	Temp. (°C)	pH_{SWS}	HCO_3^- (μM)	CO_3^{2-} (μM)	CO_2 (μM)	fCO_2 (μatm)	pCO_2 (μatm)	$\Omega_{calcite}$	Ω_{arag}
Surface	A	2519 ± 4	21.85 ± 0.73	8.38	1556	392	4.6	153	154	9.16	6.00
				+0.05	−80	+32	−0.7	−22	−22	+0.76	+0.50
				−0.04	+54	−22	+0.6	+22	+22	−0.52	−0.34
	B	2519 ± 5	21.58 ± 0.69	8.08	1931	240	11.6	381	382	5.61	3.67
				+0.08	−80	+34	−2.2	−78	−78	+0.79	+0.52
				−0.02	+26	−10	+0.9	+25	+25	−0.23	−0.15
	C	2514 ± 7	21.39 ± 1.23	7.68	2243	111	33.9	1105	1109	2.59	1.69
				+0.22	−156	+66	−15.2	−491	−492	+1.54	+1.01
				+0.01	−9.2	+2	+0.5	−15	−15	+0.04	+0.03
	D	2525 ± 4	19.64 ± 0.82	7.48	2359	68	59.5	1847	1954	1.59	1.03
				+0.69	−488	+199	−49.9	−1548	−1554	+4.64	+3.03
				−0.05	+18	−7	+8.2	+222	+223	−0.17	−0.11
	E	2518 ± 6	19.57 ± 0.74	7.15	2438	33	131.6	4078	4092	0.77	0.50
				+0.55	−186	+76	−97.6	−3027	−3037	+1.77	+1.15
				−0.20	+29	−12	+80.1	+2523	+2532	−0.28	−0.18
Benthic	A	2512 ± 6	21.67 ± 0.57	8.16	1833	277	9.1	299	300	6.47	4.24
				+0.02	−34	+14	−0.7	−18	−18	+0.34	+0.23
				−0.02	+16	−6	+0.4	+11	+11	−0.14	−0.10
	B	2512 ± 5	21.33 ± 0.51	7.84	2140	152	22.5	731	734	3.55	2.32
				+0.04	−30	+12	−2.3	−77	−77	+0.28	+0.18
				−0.01	+12	−5	+0.8	+29	+29	−0.11	−0.08
	C	2514 ± 3	21.08 ± 1.09	7.80	2174	139	25.2	815	818	3.25	2.13
				+0.21	−166	+68	−11.6	−355	−356	+1.58	+1.03
				−0.04	+21	−8	+2.5	+78	+78	−0.20	−0.13
	D	2514 ± 6	19.48 ± 0.65	No data							
	E	2517 ± 5	19.40 ± 0.61	7.01	2458	24	181.3	5593	5612	0.56	0.37
				+0.36	−73	+30	−105.2	−3236	−3247	+0.70	+0.45
				−0.21	+22	−9	+110.2	+3440	+3451	−0.21	−0.13

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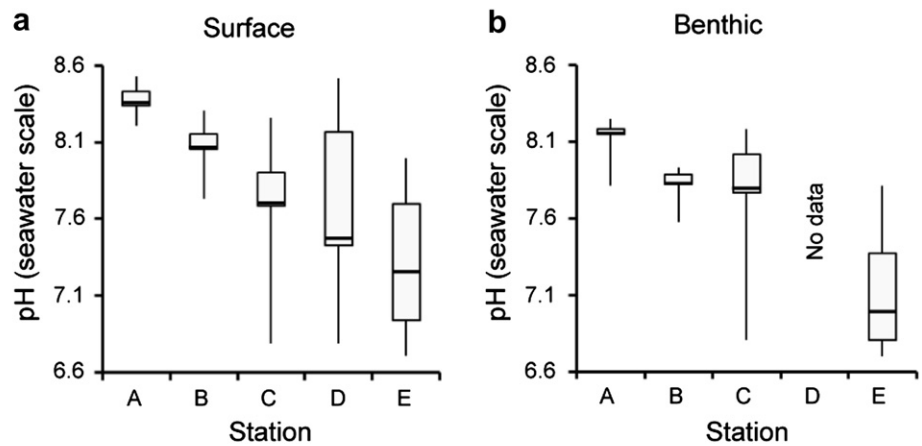

Fig. 3. pH variation at five stations (A–E) off Ischia, Italy. Data are separated into (a) measurements ca. 0.3 m below the surface and (b) 0.3 m above the benthos. Water depth ranged from 2.5 to 3 m. The boxes show inter-quartile range and the whiskers represent the range of data. The black horizontal bar within each box indicates the mean.

At stations C, D and E, pH decreased to below the lower detection threshold (approximately pH 6.75) for 0.01%, 16.9% and 20.9% of the collected data, respectively. Therefore data for these stations overestimate the mean pH and underestimate the pH range, particularly at stations D and E where pH was below this threshold for long periods (Fig. 2). pH has been recorded to decrease to low values around the site (pH 6.3 in Hall-Spencer et al., 2008; pH 5.3 in Hopkins, 2010), in agreement with pH measurements at other vent sites (Aliani et al., 2010).

3.3. Variability and diel periodicity in pH

The surface of station A is characterized by a relatively high and stable pH (8.38 ± 0.05/0.04; Table 2) undergoing a significant and regular diel pH oscillation of about 0.08 units (*t*-test, $p < 0.001$). Maximum pH occurred in the mid-morning and maximum stability in pH was around noon (Fig. 4a and b). This pattern was the same at the benthos (pH 8.16 ± 0.02/0.02). In comparison to station A, pH was lower at station B (8.08 ± 0.08/0.02) with greater overall variation (*t*-test, $p < 0.001$), but still showed a significant diel pH change (*t*-test, $p < 0.001$) (Fig. 4c and d).

Within 18 m of the main vent zone at station C, the pH was variable with a low mean (7.68 + 0.22/+0.01). Maximum pH was around sunrise and sunset each day, remaining steady and high overnight and decreasing to a daily low around noon (Fig. 4e and f). Maximum pH variability occurred in the early afternoon, while pH was most stable at sunrise and sunset. pH at the benthos underwent a significant diel pH change (*t*-test, $p < 0.001$), whereas the surface pH did not ($p > 0.05$).

Within 20 m of the main venting at station D, the pH was more variable with a low mean (7.48 ± 0.69/0.05). Maximum pH occurred in the late afternoon at the time of the daily stability maximum while pH is lowest and least stable around sunrise (Fig. 4g). There was no significant diel pH change ($p > 0.05$).

Directly within the main vent zone, station E had a low and highly variable pH (7.15 ± 0.55/0.20). The daily pH shows a mid-afternoon maximum and an early morning minimum with an amplitude of 0.5 pH units (Fig. 4h and i). This diel change was significant (*t*-test, $p < 0.001$). In the early morning, the lower quartile is at, or very close to, the detection threshold of the data-logger, indicating that ca. 25% of the recorded data at this time was below this detection threshold. Hence the calculated mean pH is overestimated at this time of day. Surface and benthic pH were not significantly different ($p > 0.05$).

3.4. Minute-to-minute pH variation

Changes in pH on small temporal scales (1 min) were evident at all stations. At benthic station A, 82.1% of consecutive samples showed no change in pH units and most of the remaining showed a 0.01 unit change. Only 1% of the data showed a change of ≥0.03 units (Table 3). With increasing proximity to the vents, greater pH change was more common. At stations B and C the modal group was still 0.00 unit but the frequency decreased to 60.8 and 42.8%, respectively, due the influence of the vents. At D and E the modal group was 0.01 units, while 0.00 unit change became much less frequent with only 11.8% at benthic station E. At this station, 1% of the data had fluctuations ≥0.27 units, illustrating sudden pH changes in the main venting zone.

3.5. Principal component analysis (PCA)

The physical variables entered into the PCA were more highly related to changes in pH at stations far from the CO_2 vents. At the reference station 79% of the variation in pH was explained, which was reduced to 69%, 76%, 67% and 63% at stations B–E, respectively (Table S1). At all stations the PCA revealed physical variables which were consistently important components and appeared to correlate with variations in pH. These included: cloud cover, wind speed and consistency and wind blowing from the west to south. Other variables, such as the time of day and the tidal height, were important at station A but became less so nearer to the vents. In addition to the variables above, close to the vents at stations D and E the major variables were the time of day, individual day, northerly and north-easterly winds. However, in all cases using individual variables in simple correlations with pH did not reveal any consistent patterns.

4. Discussion

4.1. Overview of pH gradient and stations

The main CO_2 venting at station E resulted in the localized acidification of seawater and large fluctuations in pH around the vent zone, as previously reported for this site and another vent in the Aeolian Islands (Hall-Spencer et al., 2008; Aliani et al., 2010). These fluctuations are far greater than typically found in the ocean (Takahashi et al., 2002; Bindoff et al., 2007). To evaluate the pH environment across the site, it is necessary to first establish the character and suitability of our reference station.

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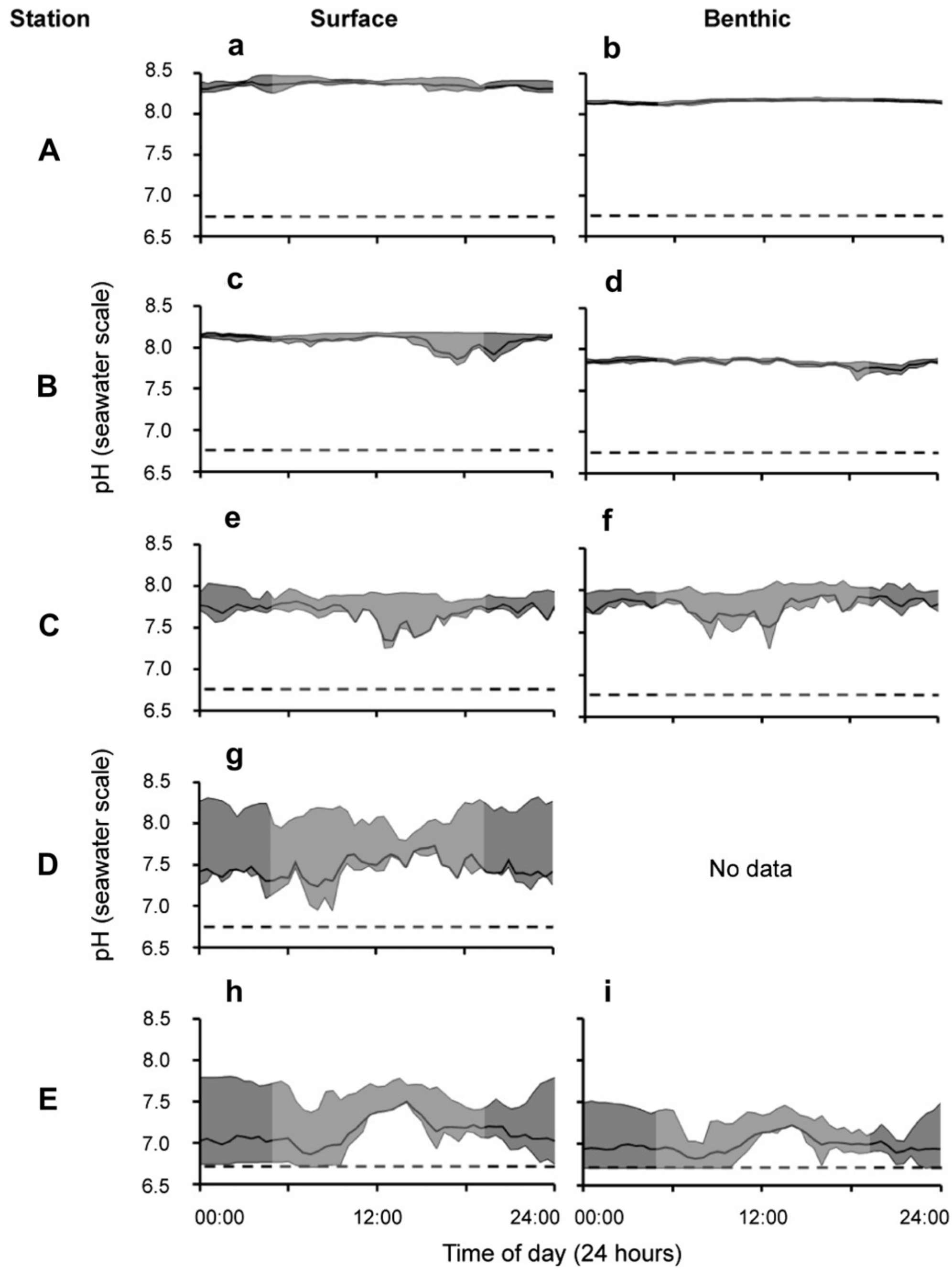

Fig. 4. pH data from five stations (A–E) off Ischia, Italy. Shown are 30 min bin averages (black lines) and inter-quartile ranges (25–75%; shaded areas that also indicate the day–night transitions) over several 24 h cycles. The horizontal dashed lines show the detection thresholds of the dataloggers. Surface data (ca. 0.3 m below the surface) are presented on the left panel and benthic data (ca. 0.3 m above the benthos) on the right panel. Panels (a) and (b): station A (data for 5 d); panels (c) and (d): station B (2.9 d); panels (e) and (f): station C (8 d); panel (g): station D (8 d); panels (h) and (i): station E (10 d).

The pH environment of the reference station A was typical of a natural sublittoral environment, with a stable pH displaying regular diel periodicity (Schmalz and Swanson, 1969; Bensoussan and Gattuso, 2007; Yates et al., 2007). Minute-to-minute variation in pH was very low and pH variations over time were well described by a PCA incorporating many common environmental parameters.

Both the surface and benthos of station A had a stable pH, depleted relative to the 2008 average atmospheric CO_2 concentration of 385 μatm (Forster et al., 2007; Table 2). Such disequilibrium with the atmosphere is unsurprising in a highly productive coastal zone in early summer (Hansen, 2002; Middelboe and Hansen, 2007), with a similar summer pH reported in nearby coastal Corsica (Frankignoulle and Bouquegneau, 1987) and higher pH reported elsewhere in the Mediterranean (Atkan, 2011). In such areas, CO_2 depletion, due to net photosynthetic production, exceeds its replenishment from atmospheric infiltration, respiration or from other sources (Semesi et al., 2009). It should be noted however, that sources of CO_2, e.g. calcification, can cause oversaturation of surface waters, even in the presence of high photosynthetic production such as reported on some coral reefs (Kawahata et al., 1997; Suzuki et al., 2001).

The lower pH water near the benthos is likely to be due to benthic CO_2 sources such as respiration and calcification, combined with its separation from surface waters by minor temperature

Table 3
Minute-to-minute pH change at five stations (A–E) off Ischia, Italy. Shown are the frequency (%) of groups with 0.00 and 0.01 pH units of change (modal values in italics) and the pH unit change measured at the 95th and 99th percentile.

Depth	Station	Percentage of data where pH change is either 0.00 or 0.01 units		pH change observed at 95th and 99th percentile	
		0.00	0.01	95th	99th
Surface	A	*75.8*	22.8	0.01	0.03
	B	*56.7*	32.8	0.02	0.06
	C	*43.9*	29.5	0.07	0.16
	D	17.8	*25.6*	0.13	0.23
	E	11.8	*18.5*	0.16	0.27
Benthic	A	*82.1*	17.5	0.01	0.01
	B	*60.8*	34.7	0.01	0.03
	C	*42.8*	35.1	0.06	0.11
	D	No data		No data	
	E	11.8	*24.2*	0.16	0.27

stratification. Notwithstanding this, the lower benthic pH may also be an indication of some vent influence at this station either through long-range lateral transfer of acidified benthic water, or direct CO_2 dissolution into the water without visible bubbling. These are possible explanations; however, they do not affect the suitability of this site as a reference for comparison with the other stations since the pH at station A was within the natural range, very stable and displayed a smooth diel cycle. Therefore the benthos of station A represents a reference pH.

Our stations C–E were strongly influenced by the CO_2 vent with a decreased mean pH and large pH variability, when compared to the reference station A. Much larger minute-to-minute pH variability was measured near the venting and is likely typical of all CO_2 vent sites. The pH of station C was usually stable, but displayed sudden decreases in pH due to the influx of low pH water from the vent zone.

The natural diel periodicity observed at the reference station was not present at stations C–E. Station E had an exaggerated diel periodicity, with much larger amplitude than could be a result of photosynthesis-dependent depletion of CO_2. This pattern was probably driven by diel changes in CO_2 dissolution rate and water refreshment, both of which could result in higher pH during the day and lower pH at night. During the day, the elevated water temperature reduces the dissolution rate of bubbling CO_2, while wind-driven mixing causes water replacement within the vent zone. During the night, colder water temperature results in greater dissolution of CO_2, while night-time decrease in near-shore wind speed (this study: data not shown; Barthelmie et al., 1996) slow the water replenishment to the site resulting in the lower night-time pH.

At station C the diel periodicity was reversed, with the lowest pH experienced at around midday. It appears likely that this is a consequence of the daytime increase in lateral movement of low pH water from the vent zone as just described. The increased daytime mixing advects low pH water from the main vent zone to this station, resulting in a decrease in pH around midday. Station D appears to be intermediate between stations C and E, and so is without significant diel periodicity. The data for mean pH around midday are similar for stations C–E (Fig. 4) and further support the hypothesis that increased mixing during the day controls the diel periodicity in pH at these stations.

As far as we are aware, the full biological implications of this change in CO_2 periodicity are unknown. However, diel periodicity in pH depletion around seagrass leaves has been shown to enhance calcification of neighbouring organisms (Semesi et al., 2009). This loss of periodicity may have also contributed to the reduced calcification observed near the CO_2 vents (Hall-Spencer et al., 2008; Cigliano et al., 2010; Dias et al., 2010).

The pH environment of stations C, D and E is not predicted to occur due to future ocean acidification (Riebesell, 2008). However, they do present an excellent opportunity to assess the functioning of CO_2 tolerant species and communities as well as the possible consequences of a shallow geological CO_2 storage leak (Caldeira et al., 2005).

Station B provided an intermediate between the unperturbed waters and the acidified, variable waters closer to the vent. This benthic location is characterised by a stable pH 0.32 units below the reference station A with a calculated pCO_2 of 734 μatm (IQ: ± 29/77 μatm) (Table 2). This value falls within the uncertainty range that many IPCC scenarios predict the CO_2 concentration to reach by 2100 (Baede, 2001). A minor influence of the venting was evident in the minute-to-minute pH variation, but this was small when compared to the other stations. To sum-up, station B has a lower than average pH due to the venting, but only a slight change in its pH variability and maintains natural diel CO_2 periodicity. Therefore, it may be considered as a suitable representative of the Mediterranean coastal benthic environment in 2100.

4.2. The lateral spread of low benthic pH from CO_2 vent sites

The spread of low pH water around this site is in agreement with depth profile data collected over the same study period (Hopkins, 2010) and pH data from the vent site in the Aeolian Islands (Aliani et al., 2010). Surface waters near the vent (e.g. station C) may have a lower pH than the benthos due to lateral movement of acidified surface water from the plume. However, further from the main venting, at station B, the benthos had a lower pH than the surface. For the vent site in the Aeolian Islands, Aliani et al. (2010) suggested that a similar observation was due to the sinking of acidic ion-dense vent fluids. At Ischia, there is no intrusion of ion-rich vent fluid within the site, confirmed by the constant salinity and total alkalinity measurements. It is likely that at Ischia this phenomenon is due to the diffuse bubbling present outside the main vent zone over a wider area. Many of these smaller CO_2 bubbles dissolve before breaking the surface (Philip Kerrison, personal observation), acidifying mainly the colder bottom water. Independent of the source of low pH at the benthos, the pH comparison of stations A and B suggest that these stations are highly suitable for ocean acidification experimentation. Given the regional spread of the acidified benthic water (this study; Aliani et al., 2010; Hopkins, 2010), similar suitable locations may be commonplace near many CO_2 vent sites.

Coastal sites generally show higher variability in biological, physical and chemical parameters in comparison to the open ocean; pH is no exception to this and so all investigations at natural experimentation sites should be carefully replicated and accompanied by a complete description of *in situ* pH throughout the experiment (Barry et al., 2010). By careful examination of the benthic pH around similar CO_2 vent sites, many stable, independent, stations of increased pCO_2 may be found, possibly covering a variety of habitats. These could act as invaluable natural laboratories, closely mimicking future conditions while retaining natural characteristics such as diel pH periodicity and low minute-to-minute pH variation.

4.3. PCA conclusion

The PCA revealed that environmental factors could explain much of the pH variation at the reference station A but little of the variation within the main vent zone. However, it was not possible

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to identify how individual environmental factors influenced the pH around the site. This could be due to poor replication of some conditions (e.g. rainfall and certain directional winds) and the distance between the site and the meteorological station (28 km). As discussed above, it is likely that changes in advection around the site strongly influenced the local station pH, a parameter not represented in our PCA.

4.4. Comparison with findings in Hall-Spencer et al. (2008)

Hall-Spencer et al. (2008) designated three zones (S_1, S_2 and S_3) in the rockface community. Of these, S_1 had a mean pH of 8.14 (IQ: $\pm$0.01/0.01) and was used as the reference station, while S_2 had a mean pH of 7.76 (IQ: $\pm$0.30/0.07). It is important to note that these values have been recalculated to correct for an error of pH averaging (see Section 4.5 below). Our stations B and E were positioned as close as possible to S_1 and S_2 and, in contrast with their results, found each station to have a significantly lower and less stable pH than their adjacent zones by 0.06 and 0.61 pH units respectively (*t*-test, $p < 0.001$). Station D was considered to be too distant from zone S_3 for a direct comparison to be made.

The most likely explanation for these differences is that the Hall-Spencer et al. (2008) characterisation was based on a low number of point pH measurements (S_1: $n = 7$, S_2: $n = 19$) which were insufficient to fully characterize the pH environment in each zone; therefore some of the results of Hall-Spencer et al. (2008) should be interpreted with caution. As such, our data highlight the need for adequate pH monitoring of stations before and during research at this and similar natural laboratories.

Other important factors may have contributed to the discrepancies in pH data. These include: year-to-year variability in biological processes and physical conditions (Wootton et al., 2008), the exact geographical location of stations and zones in the two studies, and/or changes in vent position or venting rate (Aliani et al., 2010). With regards to the latter, the venting rate at Ischia is described as stable over tides, different seasons and years (Pecoraino et al., 2005; Hall-Spencer et al., 2008). However, changes in the venting rate have been recorded at the Aeolian Islands vent (Aliani et al., 2010) and so it is possible that they could occur at Ischia over longer time-scales.

4.5. pH measurements and analysis

pH should be measured on the appropriate scale or necessary corrections should be conducted (Zeebe and Wolf-Gladrow, 2001; Dickson, 2010). Correct pH averaging is imperative: analysis of pH data should be performed after the initial transformation to hydrogen ion concentration. Once data analysis and statistical testing has concluded, output values can then be re-converted to units on the logarithmic pH scale. Incorrectly averaged data can significantly overestimate the mean and underestimate the variability of the data, particularly in environments with large pH variability where the error produced is amplified. Since this procedure produces a skewed and non-representative deviation around the mean, we decided that using the inter-quartile range was more suitable than other more common statistical parameters for our highly variable pH dataset. We suggest that this procedure should be followed for the analysis of pH data from similar environments.

Most commercially available dataloggers can record both positive and negative voltages. However, the dataloggers used for this study were unable to record negative voltages and hence our set-up was restricted to record measurements above a pH of ca. 6.75. pH this low is unusual for coastal waters and will only occur in particular situations such as described here. Unfortunately, this limitation prevented the full characterization of pH fluctuations close to the vents, particularly at stations D and E. Despite this drawback, we believe that this study still represents the best characterization of pH at a CO_2 vent site to date, revealing the stochastic nature of pH fluctuations near the venting.

4.6. Conclusions

The five stations chosen for this study provided a gradient from a stable background pH to the highly variable low pH, within a CO_2 vent zone. At our reference station A, pH was within the normal range expected from a shallow coastal site, exhibited diel periodicity and pH variations that were well explained by environmental factors and biological activity. The near pure CO_2 release within the vent zone produced a highly variable pH environment which masked the subtle signature of biological activity, and also exhibited characteristically large minute-to-minute pH variations that could not be explained by our ancillary data.

Stations B and C on the other hand, may be more representative for ocean acidification research as their benthic pCO_2 is predicted for the end of this century. Station B has a less stable pH than that of station A, but retains the natural diel pH periodicity and therefore would be an excellent candidate for ocean acidification experimentation. Station C is less suitable as it has greater pH variability and is characterized by irregular sudden pH reductions. For these reasons it does not provide a suitable representation of the coastal habitat expected in the future but may still offer valuable insights into community shifts and species resilience.

Surveying of pH at CO_2 vent sites is an important and essential step as we begin to use such sites as natural laboratories for the prediction of biotic responses to ocean acidification. Careful examination of the pH gradient should reveal many stable pH environments within the range similar to our findings for stations A and B and thus should serve as excellent study sites.

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Appendix. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.ecss.2011.05.025.

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