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Is Ocean Acidification an Open-Ocean Syndrome? Understanding Anthropogenic Impacts on Seawater pH

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Abstract Ocean acidification due to anthropogenic CO_2 emissions is a dominant driver of long-term changes in pH in the open ocean, raising concern for the future of calcifying organisms, many of which are present in coastal habitats. However, changes in pH in coastal ecosystems result from a multitude of drivers, including impacts from watershed processes, nutrient inputs, and changes in ecosystem structure and metabolism. Interaction between ocean acidification due to anthropogenic CO_2 emissions and the dynamic regional to local drivers of coastal ecosystems have resulted in complex regulation of pH in coastal waters. Changes in the watershed can, for example, lead to changes in alkalinity and CO_2 fluxes that, together with metabolic processes and oceanic dynamics, yield high-magnitude decadal changes of up to 0.5 units in coastal pH. Metabolism results in strong diel to seasonal fluctuations in pH, with characteristic ranges of 0.3 pH units, with metabolically intense habitats exceeding this range on a daily basis. The intense variability and multiple, complex controls on pH implies that the concept of ocean acidification due to anthropogenic CO_2 emissions cannot be transposed to coastal ecosystems directly. Furthermore, in coastal ecosystems, the detection of trends towards acidification is not trivial and the attribution of these changes to anthropogenic CO_2 emissions is even more problematic. Coastal ecosystems may show acidification or basification, depending on the balance between the invasion of coastal waters by anthropogenic CO_2, watershed export of alkalinity, organic matter and CO_2, and changes in the balance between primary production, respiration and calcification rates in response to changes in nutrient inputs and losses of ecosystem components. Hence, we contend that ocean acidification from anthropogenic CO_2 is largely an open-ocean syndrome and that a concept of anthropogenic impacts on marine pH, which is applicable across the entire ocean, from coastal to open-ocean environments, provides a superior framework to consider the multiple components of the anthropogenic perturbation of marine pH trajectories. The concept of anthropogenic impacts on seawater pH acknowledges that a regional focus is necessary to predict future trajectories in the pH of coastal waters and points at opportunities to manage these trajectories locally to conserve coastal organisms vulnerable to ocean acidification.

Keywords pH · Ocean acidification · Watershed changes · Eutrophication · Alkalinity · Anthropogenic impacts

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Introduction

Ocean uptake of anthropogenic CO_2 is leading to a decline in the pH of the world's surface oceans (Caldeira and Wickett 2003, 2005; Orr et al. 2005; Raven et al. 2005). This process, driven by rapidly increasing anthropogenic CO_2, is commonly referred to as "ocean acidification" (OA) is resulting in a decline in CO_3^{2-} concentrations and, hence, the saturation state (Ω) of $CaCO_3$ minerals in seawater, which is described by the equation

$$\Omega = \left[Ca^{2+}\right]\left[{CO_3}^{2-}\right]/K_{spx} \qquad (1)$$

where $[Ca^{2+}]$ and $[CO_3^{2-}]$ are the concentrations of dissolved calcium and carbonate ions in seawater and K_{spx} is the solubility constant for either aragonite or calcite, the forms of calcium carbonate commonly formed by some shell-forming organisms. The realized and projected decline in seawater, Ω, has caused concern for the future of calcifying organisms (Caldeira and Wickett 2003, 2005; Orr et al. 2005; Raven et al. 2005, Doney et al. 2009). Marine life vulnerable to OA include open-ocean species, such as coccolithophores, pelagic mollusks and foraminifera, among others, but the greatest concern is with coastal calcifying organisms, including bivalves, shallow-water calcareous algae and particularly corals (Doney 2006, Doney et al. 2009).

The potential impact of OA on coastal organisms has been inferred largely from experiments where the performance of organisms under the pCO_2 and pH conditions predicted for the open ocean in year 2100 (Doney et al. 2009; Ries et al. 2009; Hendriks et al. 2010a; Kroeker et al. 2010) have been determined and compared to the observed responses of coastal calcifying organisms to present (e.g. Waldbusser et al. 2011, Barton et al. 2012) and past situations of low pH (e.g. Pelejero et al. 2010; Hönisch et al. 2012). However, the conditions predicted for the open ocean may not reflect the future conditions in the coastal zone, where many of these organisms live (Hendriks et al. 2010a, b; Hofmann et al. 2011; Kelly and Hofmann 2012), and results derived from changes in pH in coastal ecosystems often include processes other than OA, such as emissions from volcanic vents, eutrophication, upwelling and long-term changes in the geological cycle of CO_2, which commonly involve simultaneous changes in other key factors affecting the performance of calcifiers, thereby confounding the response expected from OA by anthropogenic CO_2 alone.

Coastal ecosystems are complex as coastal biogeochemical dynamics are governed by interactions between processes on land, in the open ocean and the atmosphere (Aufdenkampe et al. 2011), many of them affected by anthropogenic processes. Unlike pelagic ecosystems, coastal ecosystems are often dominated by benthic ecosystems, including engineering species (e.g. corals, seagrass, macroalgae, salt marshes, mangroves, sponges, oyster reefs) with the capacity to modulate the chemical and physical conditions of their environment (Gutiérrez et al. 2011). These factors interact in the coastal ocean, so the coastal zone carbon system is more dynamic and complex than that of the open ocean (Borges and Gypens 2010; Cai 2011).

In particular, anthropogenic CO_2 inputs may play a smaller role relative to other sources of pH variability, natural and anthropogenic, in the coastal ocean as compared to the open ocean (e.g. Borges and Gypens 2010; Provoost et al. 2010; Cai et al. 2011; Hofmann et al. 2011). Hence, how the pH of coastal ecosystems in year 2100 will differ from current ones is difficult to predict due to lack of understanding of the average values and their variability in current environments and of the future trajectories of the multiple factors affecting coastal pH compared to the open ocean. Furthermore, understanding the dynamics of coastal pH and the carbon system is important to assess the conditions under which vulnerable coastal organisms evolved (Hendriks et al. 2010a, b; Hofmann et al. 2011; Kelly and Hofmann 2012). Thus, our awareness of the variability and complexity of pH regulation in the coastal ocean is currently disconnected from OA projections, which are based on general circulation models (GCMs) focused on anthropogenic CO_2 as the main driver, with little capacity to resolve the coastal ocean.

Here, we formulate an alternative, more holistic concept of anthropogenic impacts on seawater pH. Although the concept of OA by anthropogenic CO_2 has played a key role in alerting us of the challenges facing calcifying organisms resulting from declines in pH, we believe that this concept fails to provide a realistic framework addressing anthropogenic forcing of pH in coastal waters. In particular, we formulate the thesis that the current concept of OA by anthropogenic CO_2 should be subsumed within a broader, more encompassing paradigm of anthropogenic impacts on marine pH.

This new concept of anthropogenic impacts on seawater pH formulated here accommodates the broad range of mechanisms involved in the anthropogenic forcing of pH in coastal ecosystems, including changes in land use, nutrient inputs, ecosystem structure and net metabolism, and emissions of gases to the atmosphere affecting the carbon system and associated pH. The new paradigm is applicable across marine systems, from open-ocean and ocean-dominated coastal systems, where OA by anthropogenic CO_2 is the dominant mechanism of anthropogenic impacts on marine pH, to coastal ecosystems where a range of natural and anthropogenic processes may operate to affect pH.

Drawing a parallel with progress in understanding human perturbations to the carbon cycle, our approach in assessing anthropogenic impacts on seawater pH is to separate the regulation of pH in ocean surface waters into two modes—regulation in the pre-disturbance Holocene ocean and anthropogenic processes regulating pH—with the interplay between both components acting to regulate seawater pH in the Anthropocene.

Regulation of Seawater pH in the Pre-disturbed Holocene Ocean

Proxy reconstructions indicate that oceanic pH has remained relatively uniform over the past 20 Myr (Pearson and Palmer 2000; Pagani et al. 2005) compared to present and projected changes. Marine pH in the pre-disturbed Holocene, referring to the centuries preceding the industrial revolution, was regulated by a complex array of factors acting upon marine acid/base chemistry and the associated carbonate buffering system, mostly through variabilities in CO_2, DIC and Ca^{2+} fluxes (Table 1). Long-term geological processes, particularly those involving silicate weathering, are relevant at scales of hundreds of thousands of years and need not, therefore, be considered here. At the global scale, major processes include global metabolic processes, ocean ventilation and volcanic emissions, affecting the atmospheric concentration of CO_2 and hence the equilibrium concentration in ocean waters, and carbonate weathering on land and the associated discharge, through rivers and groundwater, of Ca^{2+}, carbonate alkalinity, and inorganic and organic carbon to the ocean (Aufdenkampe et al. 2011; Table 1).

The pH in surface open-ocean waters was regulated largely by changes in CO_2 because the carbonate ion concentration (CO_3^-) concentration is relatively uniform over the timescales of interest and ocean waters are mostly saturated in Ca^{2+} (Caldeira and Berner 1999). However, large changes occurred over longer (100 Myr) timescales (Tyrrell and Zeebe 2004). CO_2 concentrations, in turn, were regulated by metabolic processes and CO_2 exchanges with the atmosphere and deeper waters (Falkowski et al. 2000).

In contrast, the regulation of pH in surface coastal waters is far more complex as it depends on the processes affecting pH in the open ocean as well as watershed inputs of Ca^{2+}, carbonate alkalinity, inorganic and organic carbon and nutrients, and ecosystem metabolism as well as hydrological processes that dictate the mixing between open ocean and coastal waters (Table 1). Watershed effects depend, in turn, on the climatic, hydrological and geological regimes as well as the dynamics of the ecosystems in the watershed (Aufdenkampe et al. 2011). Seepage of groundwater can lead to areas of high pCO_2 and low pH in coastal ecosystems (Basterretxea et al. 2010). Groundwater with a low carbonate saturation state ($\Omega \approx 0.5$) and reduced pH (6.70–7.30) seeps through the seafloor, creating localized low seawater pH in the natural submarine groundwater springs at Puerto Morales, Mexico (Crook et al. 2012). Submarine volcanic vents or groundwater seeps can also lead to high CO_2 and low pH in surface coastal waters. Volcanic CO_2 vents produce shallow-water gradients of pH across tens of meters, reaching values as low as 6.6–6.8 in the Mediterranean, for example around the most active vents in Ischia and Vulcano Islands, Italy (Hall-Spencer et al. 2008; Johnson et al. 2013) and pH values <7.7 (as low as 7.21) in volcanic seeps in Papua New Guinea (Fabricius et al. 2011). Natural gradients in pH exists across a distance of <100 m from these volcanic CO_2 vents, where the pH increases to normal seawater values of 7.97–8.14 (Hall-Spencer et al. 2008; Johnson et al. 2013; Fabricius et al. 2011). Volcanic eruptions may lead to extreme pH, such as the 6.2 values recorded in coastal waters following an underwater eruption giving rise to a novel shallow submarine volcano south of the island of El Hierro, Canary Islands, Spain (Fraile-Nuñez et al. 2012).

Metabolic effects, represented by net community production and calcification rates, tend to be order of magnitude greater in coastal than in open-ocean ecosystems (Duarte and Cerbrian 1996; Gattuso et al. 1998) and play a major role in the pH control of coastal and estuarine ecosystems (Anthony et al. 2011; Table 2). Observations of pH in a variety of coastal habitats indicate characteristic site-specific diel, semi-diurnal and stochastic patterns of varying amplitudes

Table 1 Summary of processes driving changes in surface water pH in marine ecosystems

Driver	Pre-disturbance	Anthropogenic disturbance
Air–sea exchange	Air–sea CO_2 exchange	Ocean uptake of anthroporgenic CO_2
		Deposition of anthropogenic acids and bases
Watershed processes	Weathering	Mining
	Volcanic activity	Acid sulphate soil disturbance
	Ecosystem processes	Changes in land use
	Climatic variability	Agricultural practices
		Melting and thermokarst processes
		Hydrological perturbations
		Anthropogenic climate change
Ecosystem processes	Community metabolism	Eutrophication
	Mixing and water residence time	Habitat loss
		Anthropogenic climate change

Table 2 Summary of diel changes in pH in coastal ecosystems

System		Location	Variability	pH range	pH (min–max)	Depth	Reference
Open ocean		CCE-1, USA	30-d	0.024	8.059–8.082	2	Hofmann et al. (2011)
Polar		Mc Murdo Sound, Antarctica	20-d	0.06	7.99–8.05		Kelly and Hofmann (2012)^{c}
Polar	Benthic	Cape Evans, Antarctica^{a}	Diel, min and max 20-d	0.043	8.002–8.050	15	Matson et al. (2011)
Polar	Benthic	Cindercones, Antarctica^{a}	Diel, min and max 16-d	0.092	8.039–8.134	15	Matson et al. (2011)
Polar	Benthic	Cindercones, Antarctica	15-d	0.096	8.039–8.134	15	Hofmann et al. (2011)
Polar	Benthic	Cape Evans, Antarctica	15-d	0.047	8.002–8.050	15	Hofmann et al. (2011)
Polar	Pelagic	Erebus Basin, Antarctica	Diel, min and max 14-d	0.114	8.019–8.134	15	Matson et al. (2011)
Upwelling		MBARI M1 Mooring	Diurnal	0.4	7.7–8.1		Booth et al. (2012)
Upwelling	–	MBARI MO buoy	Stochastic	0.35	8.35–8.0		Cullison-Gray et al. (2011)
Upwelling		Pt. Conception (CCE2), USA	30-d	0.397	7.869–8.266	2	Hofmann et al. (2011)
Upwelling		Pt. Ano Nuevo, USA	30-d	0.467	7.685–8.152	2	Hofmann et al. (2011)
Coastal	Pelagic	Monterey Bay (M1), USA	30-d	0.499	7.857–8.356	1	Hofmann et al. (2011)
Coastal		Santa Barbara Channel, USA	25-d	0.54	7.70–8.24		Kelly and Hofmann (2012)^{c}
Estuary		Elkhorn Slough (L1), USA	30-d	0.992	7.435–8.427	1	Hofmann et al. (2011)
Estuary		Netarts Bay, USA	64-d				Barton et al. (2012)^{c}
Estuary		Netarts Bay, USA	Diurnal^{b}		7.69–8.15		Barton et al. (2012)^{c}
Estuary		Temperate	Diurnal	0.4–0.6			Park et al. (1958); Nixon et al. (1976)
Coral reef		Media Luna reef, Puerto Rico	Seasonal, summer	0.079		4	Cullison-Gray et al. (2012)
Coral reef		Media Luna reef, Puerto Rico	Seasonal, winter	0.067		4	Cullison-Gray et al. (2012)
Coral reef		Media Luna reef, Puerto Rico	Seasonal, fall	0.93		4	Cullison-Gray et al. (2012)
Coral reef		Red Sea	Monthly	0.1	8.2–8.3	1.5–1.8	Silverman et al. (2007)
Coral reef	Pacific	Gulf of Panama	Seasonal, dry season, day	0.13	7.95–8.08		Manzello (2010)
Coral reef	Pacific	Gulf of Panama	Seasonal, wet season, day	0.28	7.95–8.23		Manzello (2010)
Coral reef	Pacific	Gulf of Panama	Seasonal, wet season, night	0.04	7.96–8.00		Manzello (2010)
Coral reef	Pacific	Gulf of Chiriquí	Seasonal, dry season, day	0.57	7.63–8.20		Manzello (2010)
Coral reef	Pacific	Gulf of Chiriquí	Seasonal, wet season, day	0.32	7.94–8.26		Manzello (2010)
Coral reef	Pacific	Gulf of Chiriquí	Seasonal, dry season, night	0.2	7.84–8.04		Manzello (2010)
Coral reef	Pacific	Gulf of Chiriquí	Seasonal, wet season, night	0.15	7.86–8.01		Manzello (2010)
Coral reef		Moorea, French Polynesia	50-d	0.12	8.04–8.16		Kelly et al. (2012)^{c}
Coral reef		Kingman Reef	30-d	0.025	8.009–8.034	10	Hofmann et al. (2011)
Coral reef	Fore reef	Palmyra	30-d	0.121	7.915–8.035	10	Hofmann et al. (2011)
Coral reef	Reef terrace	Palmyra,	30-d	0.253	7.851–8.104	5	Hofmann et al. (2011)
Coral reef	Fringing reef	Moorea, French Polynesia	30-d	0.101	8.017–8.118	10	Hofmann et al. (2011)
Coral reef			Diurnal	0.5			Odhe and Woesik (1999)
Coral reef	–	Ecuador	Diurnal	0.28	7.824–8.104		Price et al. (2012)
Coral reef	–	Japan	Diurnal	0.5	8.4–7.9		Kayanne et al. (2005)
Coral reef	–	China	Diurnal	0.3–0.6			Wei et al. (2011)

Table 2 (continued)

System		Location	Variability	pH range	pH (min–max)	Depth	Reference
Coral reef	–		Diurnal	0.2–04			Yates and Halley (2006)
Coral reef	–	GBR, Australia	Diurnal	0.61	8.30–7.69		Santos et al. (2011)
Coral reef	Water column	Heron Island GBR	Diel	0.4	7.96–8.36		Cyronak et al. (2013)[c]
Coral reef	Pacific	Galápagos	Day, cool	0.34	7.65–7.99		Manzello (2010)
Coral reef	Pacific	Galápagos	Day, warm	0.37	7.70–8.07		Manzello (2010)
Coral reef	Pacific	Majuro Atoll	day	0.14	8.04–8.18		Suzuki et al. (1997)[d]
Coral reef	Pacific	GBR Lagoon	Day and night	0.06	8.03–8.09		Suzuki et al. (2001)[d]
Coral reef	Pacific	Moorea	Day and night	0.29	7.90–8.19		Gattuso et al. (1997)[d]
Coral reef	Pacific	Palau		0.1	7.96–8.06		Watanabe et al. (2006)[d]
Coral reef	Pacific	Hawaii	Day	0.51	7.80–8.31		Yates and Halley (2006)[d]
Coral reef	Pacific	Hawaii	Night	0.41	7.70–8.12		Yates and Halley (2006)[d]
Coral reef	Japan	Okinawa	Day	0.54	8.12–8.58		Ohde and van Woesik (1999)[d]
Coral reef	Japan	Okinawa	Night	0.35	7.70–8.05		Ohde and van Woesik (1999)[d]
Coral reef	Japan	Shiraho Reef	Day	0.46	7.80–8.26		Nakamura and Nakamori (2009)[d]
Coral reef	Japan	Shiraho Reef	Night	0.35	7.71–8.06		Nakamura and Nakamori (2009)[d]
Macroalgae	Kelp	La Jolla, USA	30-d	0.259	7.970–8.229	7	Hofmann et al. (2011)
Macroalgae	Macroalgal mats		Diurnal	0.7	8.3–9.0		Menéndez et al. (2001)
Macroalgae	Fucus-dominated communities		Diurnal	0.4		0.2 m	Middelboe and Hansen, (2007)
Macroalgae	–		Diurnal	0.5		0.4 m	Middelboe and Hansen, (2007)
Macroalgae	–		Diurnal	0.3		0.6 m	Middelboe and Hansen, (2007)
Macroalgae	Kelp	*Macrocystis pyrifera*	Diurnal	1.04	8.07–9.11		Delille et al. (2000)
Macroalgae	Kelp	SBC Mohawk Reef		0.544	7.700–8.244	8	Hofmann et al. (2011)
Seagrass	Posidonia	Mediterranean	Diurnal	0.3	8.15–8.45	1 m	Invers et al. (1997)
Seagrass	–	Mediterranean	Diurnal	0.17	8.34–8.17	4 m	Invers et al. (1997)
Seagrass	–	Mediterranean	Diurnal	0.24	7.91–8.15	5–12 m	I. Hendriks, unpublished
Seagrass	Cymodocea	Mediterranean	Diurnal	0.48	8.11–8.59		Invers et al. (1997)
Seagrass	*Thalassia testudinum*	Bermuda	Diurnal	0.29	8.06–8.35		Schmalz and Swanson (1969)
Seagrass	Tropical	Chwaka Bay, Tanzania	Diurnal	1			Semesi et al. (2009)
Salt marsh	Rhizosphere		Diurnal	2			Wolaver et al. (1986)
Salt marsh		Florida	Diurnal	0.9	8.2–9.1		Stevens (2002)
Submarine spring		Puerto Morelos , Mexico	30-d	0.905	7.143–8.048	5	Hofmann et al. (2011)
Submarine vulcano	5-M after eruption	El Hierro, Spain	Stochastic	0.3-0.4		Surface waters	Fraile-Nuñez et al. (2012)
CO_2 vent		Ischia (South zone), Italy	30-d	1.43	6.699–8.129	1	Hofmann et al. (2011)
CO_2 vent	Seagrass	Posidonia, P1	21-d	0.03	8.15–8.18		Hall-Spencer et al. (2008) (S1)
CO_2 vent	Seagrass	Posidonia, P2	21-d	0.07	8.13–8.20		Hall-Spencer et al. (2008) (S1)
CO_2 vent	Seagrass	Posidonia, P3	21-d	0.49	7.67–8.16		Hall-Spencer et al. (2008) (S1)
CO_2 vent	Seagrass	Posidonia, P4	21-d	1.16	6.98–8.14		Hall-Spencer et al. (2008) (S1)

Table 2 (continued)

System		Location	Variability	pH range	pH (min–max)	Depth	Reference
CO_2 vent		S1	21-d	0.04	8.13–8.17		Hall-Spencer et al. (2008) (S1)
CO_2 vent		S2	21-d	0.81	7.35–8.16		Hall-Spencer et al. (2008) (S1)
CO_2 vent		S3	21-d	1.3	6.07–7.37		Hall-Spencer et al. (2008) (S1)
CO_2 vent		N1	21-d	0.23	7.96–8.19		Hall-Spencer et al. (2008) (S1)
CO_2 vent		N2	21-d	0.63	7.54–8.17		Hall-Spencer et al. (2008) (S1)
CO_2 vent		N3	21-d	1.59	6.31–7.9		Hall-Spencer et al. (2008) (S1)
CO_2 vent	Posidonia	Ischia, IT	Diurnal	1.0–1.6			Y. Olsen, unpublished

pH variability in coastal ecosystems. We refer as stochastic to short-lived events, like upwelling, storms, etc., diurnal 24-h cycle. Depth is deployment depth

[a] Measuring period partially overlapping with Hofmann et al. (2011)

[b] Average range, 7-day period

[c] Data extracted from graph with Graphclick 3.0

[d] As (re)calculated by Manzello 2010

(Hofmann et al. 2011; Table 2). Metabolic-intense ecosystems, such as seagrass meadows, mangroves, salt marshes, coral reefs and macroalgal beds, can support diel changes in pH as high as 1.0 unit (Table 2). Coastal phytoplankton blooms can also modify water column pH significantly, with pH increasing to 8.6–9.0 during phytoplankton blooms (Brussaard et al. 1996; Spilling 2007; Dai et al. 2008). Conversely, the collapse and subsequent remineralization of phytoplankton blooms can lead to substantial drops in pH, such as a seasonal decline in pH of 0.3–0.4 units reported in bottom waters at Seto Inland Sea, Japan (Taguchi and Fujiwara 2010), and Bohai Sea, China (Zhai et al. 2012).

Benthic microbial processes can also modify alkalinity and pH through sediment–water fluxes in coastal ecosystems (Cyronak et al. 2013). The primary process affecting alkalinity in anoxic sediments is bacterial sulfate reduction, which may supersaturate pore waters with $CaCO_3$ (Berner et al. 1970; Hines et al. 1989). Net alkalinity gain is, however, only achieved during anaerobic processes that involve a permanent loss of remineralization products, e.g. through denitrification or pyrite burial (Hu and Cai 2003). Vegetation modifies sediment biogeochemical processes and, thus, affects the pH and alkalinity of pore waters. Rapid changes in subsurface biogeochemical processes measured in a New England salt marsh coincided with temporal variations in the physiology of *Spartina alterniflora* (Hines et al. 1989). Sulfate reduction rates increased fivefold during phases of active plant growth, probably fueled by dissolved organic matter released from the plant roots.

In summary, surface water pH in open ocean locations is relatively stable, with a narrow range of variability, typically at <0.1 pH units inter-annually (e.g. Doney et al. 2009), compared to high variability, of as much as 1 pH unit, in coastal ecosystems at scales ranging from diel (e.g. Hofmann et al. 2011; Table 2), driven by the metabolic signal to seasonal and decadal oscillations with amplitudes >0.3 pH units (e.g. Borges and Gypens 2010; Provoost et al. 2010; Barton et al. 2012; Cai et al. 2011; Hofmann et al. 2011; Mercado and Gordillo 2011; Waldbusser et al. 2011; Melzner et al. 2013; Fig. 1). In addition, as most rivers are acidic, and have saturation states for aragonite (Ω) lower than receiving ocean waters, dynamic gradients in pH and Ω exist along salinity gradients in coastal waters, which sometimes show conservative behaviour, dominated by mixing processes (e.g. Salisbury et al. 2008), but can be affected by in situ metabolic processes, deviating from conservative behaviour, in others (e.g. Cai et al. 2011).

Hence, the regulation of pH and Ω can be modelled by considering a three end-member system: open-ocean and freshwater end-members and ecosystem metabolism, the later not being properly an end-member but a process causing deviation from the open ocean to freshwater conservative mixing line (e.g. Guo et al. 2012). Ocean-dominated systems, such as the open-ocean and coastal ecosystems

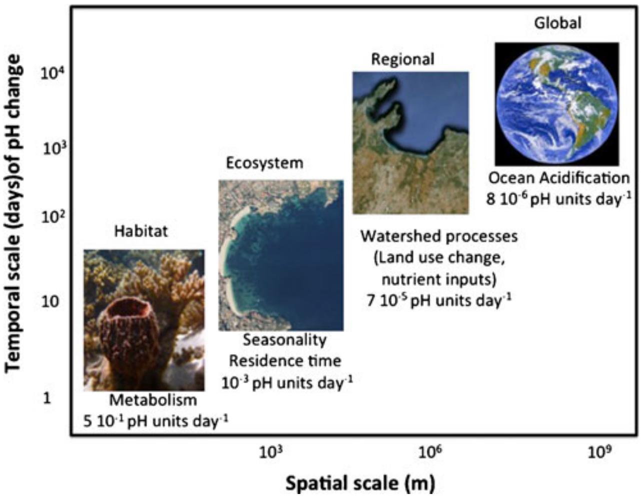

Fig. 1 Conceptual diagram showing the multiple processes contributing to variability in pH in coastal ecosystems across domains with scales spanning from patch to global and day to century. The rate values correspond to the characteristic rate of change in pH for the various domains

adjacent to arid land (e.g. those in Antarctica and adjacent to arid regions, such as NW Australia; Falter et al. 2013) and very small watersheds, such as those in atolls and small islands, will likely reflect the open-ocean pH and Ω dynamics (Falter et al. 2013). River-dominated systems will reflect the dynamics of the freshwater end-member, and the deviation of coastal ecosystems supporting intense metabolism from the conservative mixing lines delineated by the open-ocean and freshwater end-members will depend on water residence time and mixing processes (Anthony et al. 2011; Falter et al. 2013). Hence, use of coastal typologies, which consider the elements above, has led to an improved capacity to represent and integrate ocean biogeochemistry and CO_2 fluxes (Laruelle et al. 2010) and may help identify contrasting modes of pH and Ω regulation in coastal waters.

Regulation of Open-Ocean and Coastal pH in the Anthropocene

The rapid increase in the capacity of humans to impact the key processes regulating the functioning of the biosphere into the Anthropocene (Steffen et al. 2007) has extended to a capacity to impact marine pH (Table 1). Human activities can act on marine pH through impacts propagated through the atmosphere, freshwater discharges and direct impacts on ecosystem components (Table 1). Accordingly, there are three main vectors of anthropogenic impacts on marine pH: (1) emissions of CO_2, and other gases affecting marine pH, to the atmosphere; (2) perturbation of watershed processes affecting the inputs of nutrients, organic and inorganic carbon, acids and carbonate alkalinity to the ocean; and (3) impacts on ecosystem structure (Table 1). These drivers add to the processes operating prior to the human perturbation to regulate marine pH in the Anthropocene.

Impacts of Anthropogenic CO_2 Emissions on Seawater pH

The impacts on marine pH derived from anthropogenic CO_2 emissions have received the greatest attention and have led to a growing spectrum of research programs focused around the paradigm of OA by anthropogenic CO_2 (Caldeira and Wickett 2003; Raven et al. 2005; Doney et al. 2009). CO_2 emissions from the burning of fossil fuels and land use change since the industrial revolution have caused an increase in atmospheric CO_2 concentrations from 280 to 390 ppm (globally averaged mean surface value for 2011; Thomas Conway and Pieter Tans, NOAA/ESRL, www.esrl.noaa.gov/gmd/ccgg/trends/). The global oceans have absorbed about 40 % of the anthropogenic carbon emissions (Sabine and Tanhua 2010), leading to a decline in pH evident in surface open-ocean time series (Caldeira and Wickett 2003; Raven et al. 2005; Doney et al. 2009). In addition to impacting surface water pH, accumulation of anthropogenic carbon in deeper waters is leading to shoaling of the horizon for aragonite saturation (Feely et al. 2010). Accordingly, upwelling of waters acidified by anthropogenic CO_2 has led to a further decrease in surface pH, as reported in the eastern Pacific Ocean along the west coast of North America, from central Canada to northern Mexico, where shoaling of the layer of seawater undersaturated with aragonite increased the frequency and magnitude of coastal acidification associated with upwelling events (Feely et al. 2008, 2010).

Human emissions of reactive sulfur and nitrogen, derived from fossil fuel combustion and agriculture, have led to increased deposition of strong acids (HNO_3 and H_2SO_4) and bases (NH_3) to the ocean, hence affecting seawater pH (Doney et al. 2007). Whereas these effects on open-ocean pH are calculated to be minor, they can be higher, at rates of $0.02–0.12 \times 10^{-3}$ pH units per year (<10 % of OA by anthropogenic CO_2), in coastal ecosystems (Doney et al. 2007), where atmospheric deposition is intense and the waters can be more weakly buffered.

Impacts of Anthropogenic Watershed Perturbations on Seawater pH

Changes in land use over the past centuries have affected the biogeochemical cycles of carbon and nutrients in the coastal zone strongly (Nixon 1995; Doney 2010; Hooke and Martín-Duque 2012). In particular, human activity has altered the watershed export of organic and inorganic carbon, carbonate alkalinity, acids and nutrients to the ocean, affecting pH (Aufdenkampe et al. 2011). However, these impacts are largely restricted to the coastal ocean, where these inputs are received.

Deforestation, agricultural (Oh and Raymond 2006), mining (Brake et al. 2001; Raymond and Oh 2009) and urban/suburban practices (Barnes and Raymond 2009) were linked to direct changes in the delivery of buffering capacity to streams and rivers. These changes have the potential to alter the concentrations of inorganic C species expected through the mixing of freshwater and seawater in estuaries, thereby affecting pH in coastal water (Aufdenkampe et al. 2011). Mining activities typically yield an increase in acid export, leading to a decline in pH in the receiving coastal waters (Brake et al. 2001; Raymond and Oh 2009). In an extreme example, a pH of <3 was reported in the estuarine reaches of the Río Tinto estuary, SW Spain (Elbaz-Poulichet et al. 1999). Alteration of tropical acid sulphate soils also releases large amounts of acids (Wilson et al. 1999; Johnston et al. 2009), affecting coastal waters containing vulnerable organisms, such as corals in the inner Great Barrier Reef ecosystem (Powell and Martens 2005).

Watershed processes, including export of alkalinity, derived from the weathering of carbonate rock and the use of lime in agriculture to reduce soil acidity (West and McBride 2005) can affect the magnitude of the alkalinity buffer in coastal waters. Changes in land use and increasing precipitation and/or runoff can also enhance alkalinity export from land to coastal ecosystems through chemical weathering (Raymond et al. 2008). These changes may counteract the tendency for pH to decline from OA due to anthropogenic CO_2 or increase in heterotrophy from eutrophication (sensu Nixon 1995). For example, the alkalinity export from the Mississippi River to the Gulf of Mexico has increased by almost 50 % over the last 50–100 years due to increasing areas of cropland and increasing precipitation over the watershed (Raymond and Cole 2003; Raymond et al. 2008). Although freshwater discharge accounts for a large part of enhanced alkalinity export, concentrations of alkalinity in rivers have increased over time (Fig. 2a). Long-term records of river alkalinity from other areas (Fig. 2b, c) suggest a common global trend of increasing alkalinity exported from land to coastal ecosystems, which can lead to changes in pH on the order of 0.02–0.04 pH units, sufficient to offset more than a decade of OA.

Inputs of organic matter, nitrogen and phosphorus to coastal ecosystems have increased greatly (Nixon 1995; Howarth et al. 1996; Conley 2000; Stedmon et al. 2006; Sharp 2010). Although eutrophication is the major concern related to these inputs, the pH of coastal waters is also influenced through the enhanced CO_2 uptake from primary production and CO_2 release from respiration associated with increased nutrient inputs. When in balance, primary production and respiration processes result in large diel variability (Table 2), but are essentially CO_2-neutral; however, over longer timescales, spatial and/or temporal decoupling of these processes can change pH drastically (Borges and Gypens 2010; Provoost et al. 2010; Cai et al. 2011). The effects of eutrophication on carbonate chemistry can exceed that of OA from anthropogenic CO_2 by either increasing pH, when enhanced CO_2 uptake by primary producers prevails (Borges and Gypens 2010), or by decreasing pH, where enhanced respiratory CO_2 release prevails (Cai et al. 2011), a condition often associated with coastal hypoxia (Feely et al. 2010).

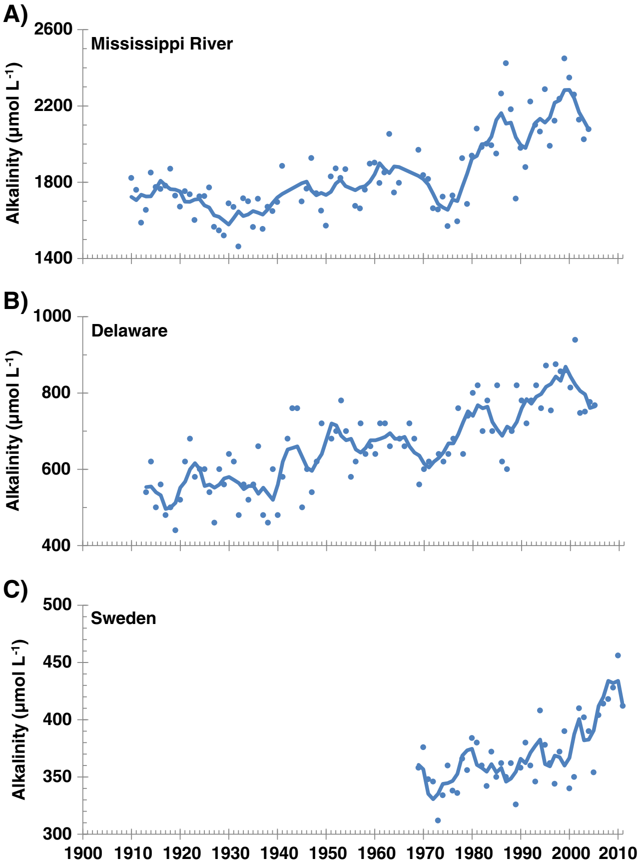

Fig. 2 Time series of alkalinity concentration in rivers from Mississippi River (**a**) (data from Raymond et al. 2008), Delaware River (**b**) (data from Sharp 2010) and Swedish rivers (**c**) (data from www.slu.se). *Solid lines* represent a 5-year moving average of the annual mean concentrations

Impacts on pH by Anthropogenic Changes in Coastal Habitats

Coastal ecosystems contain multiple habitats that play an engineering role, affecting the physical and chemical properties of the ecosystem (Gutiérrez et al. 2011). These ecosystems include vegetated coastal habitats (seagrass meadows, macroalgal beds, salt marshes and mangroves) and coral and oyster reefs, among others (Gutiérrez et al. 2011). All coastal engineering communities support intense metabolic processes, including high primary production, respiration and calcification rates, thereby affecting CO_2, CO_3^{-}, and alkalinity concentrations and surface water pH.

However, many metabolically intense coastal habitats are experiencing global declines in their abundance at rates in excess of 1 % per year (Duarte et al. 2008; Ermgassen et al. 2013). These shifts in coastal habitats have major, although largely unreported, consequences for coastal pH, affecting both their mean values and variability. Likewise, the restoration and redistribution of these habitats may affect pH in coastal ecosystems significantly. For instance, Arctic warming may allow the poleward spread of macroalgae and seagrasses, which could affect the pH of the coastal waters of these highly vulnerable regions seasonally.

Current Trends in Open-Ocean and Coastal pH

Open-ocean time series show that surface ocean pH has decreased on average by 0.1 pH units since the industrial revolution (Caldeira and Wickett 2005; Orr et al. 2005; Doney et al. 2009), with open-ocean pH decreasing steadily over the last few decades at a rate of 0.0019 per year (Doney 2010). These trends match the expectations for OA driven by increasing levels of atmospheric CO_2, confirming that this vector dominates the anthropogenic perturbation of pH in the open ocean. Model calculations (Orr et al. 2005) indicate that a decrease in carbonate mineral saturation states is occurring throughout the global open ocean and will impact the polar oceans first (Orr et al. 2005). During the summer of 2008, the Canada Basin of the Arctic Ocean was undersaturated with respect to aragonite (Yamamoto-Kawai et al. 2009).

However, observations of reported trends in surface water pH in coastal ecosystems reveal a variety of patterns, including periods of both increasing and decreasing pH (Fig. 3), in response to human alterations of the biogeochemical cycles in coastal ecosystems and their watersheds. A caveat in the interpretation of long-term trends in pH in coastal systems is that the measurement scale for pH is often not reported and that conventional measurement with glass electrodes along salinity gradients may introduce uncertainties (Provoost et al. 2010). Changes in salinity of 10 units can contribute an error in these pH determinations of about 0.03 units (Easley and Byrne, 2012), and the associated uncertainty in pH measured with an electrode calibrated at a single pH is ±0.3 units over a 3-unit change in pH (Easley and Byrne 2012; Waters 2012), indicative of ±0.03 units over the 0.3-unit range typically observed in coastal systems. Collectively, these factors may introduce a random error of ±0.1, generally much less than the inter-annual range of changes observed in coastal ecosystems (typically>0.3). As the patterns in coastal pH are based on averages over hundreds to thousands of measurements, the trends are nevertheless robust despite these uncertainties (Provoost et al. 2010).

Contrary to the reported trends in open-ocean pH, none of the available records of long-term pH change in coastal ecosystems, that we are aware of, show the decline expected from OA alone (Provoost et al. 2010; Fig. 3). Long-term changes in coastal pH display patterns driven by a much more complex suite of anthropogenic impacts than those in the open ocean. In Chesapeake Bay, for example, pH in surface waters has not displayed a clear trend over the last 60 years, although it showed high variability before 1980 (Fig. 3a). This behaviour is presumably a combination of pH increases in the mesohaline mainstem and decreases in the polyhaline mainstem of the bay (Waldbusser et al. 2011). In

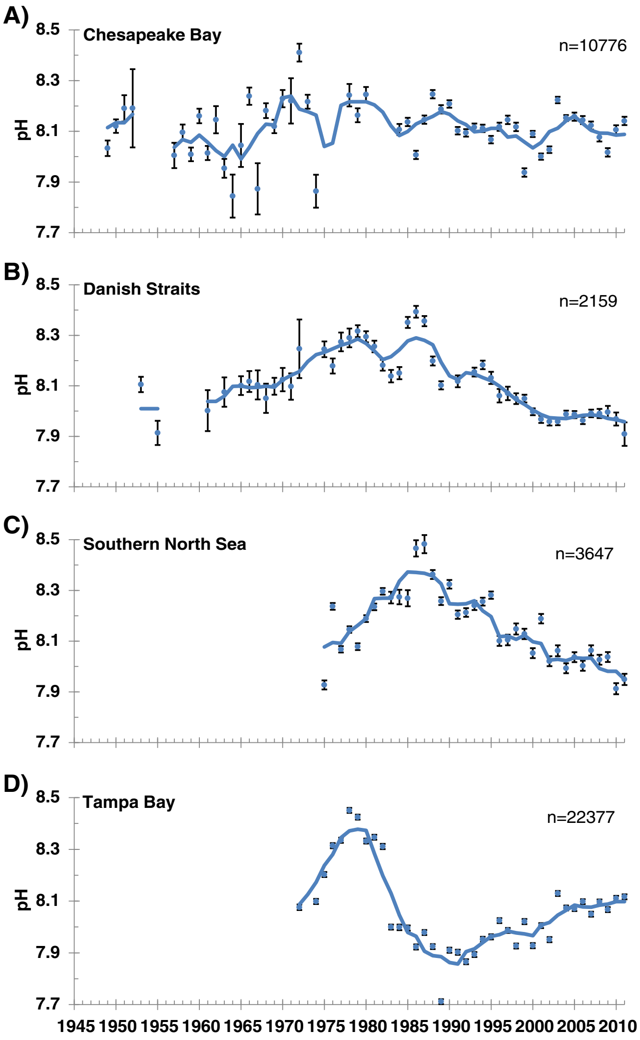

Fig. 3 Long-term trends in pH for selected coastal ecosystems: **a** Chesapeake Bay (mesohaline and polyhaline mainstem). **b** Danish Straits. **c** Southern North Sea. **d** Tampa Bay. Chesapeake Bay mainstem and Danish Straits are permanently stratified and trends were calculated for the surface layer (0–10 m), whereas trends in Southern North Sea and Tampa Bay represent the entire water column. Trends were calculated applying a statistical decomposition method (see Carstensen et al. 2006) to data downloaded from public databases (www.chesapeakebay.net (**a**), mads.dmu.dk (**b**), www.waterbase.nl (**c**) and www.tbep.org (**d**)). *Symbols* are annual means, with *error bars* showing the standard error of the means. *Solid lines* show the 5-year moving average of the annual means

the Susquehanna catchment, which delivers more than half of the freshwater input to Chesapeake Bay (Schubel and Pritchard 1986), reduced coal mining activity during the last century has led to increased river pH by 0.8 units (Raymond and Oh 2009), which, together with eutrophication, has partially counteracted processes that would reduce pH in the surface layer, such as OA and increased respiration.

The pH in the Danish Straits has also increased up to the mid-1980s (Fig. 3b), but then decreased by about 0.3 units in the surface layer over the last two and a half decades. This decrease is much steeper than can be explained by OA. Nutrient reduction plans, implemented since 1987, have reduced nitrogen inputs by 50 % (Carstensen et al. 2006), but primary production remains high (Carstensen et al. 2011). The increase in surface pH before ca. 1985 is consistent with the trend in nitrogen inputs (Conley et al. 2009), whereas the subsequent decrease can be explained by enhanced ecosystem respiration.

Similar trends were observed in the southern North Sea. The pH values peaked around 1985, but declined thereafter by almost 0.4 units (Fig. 3c). This decline is far greater than can be explained by OA from anthropogenic CO_2 alone, but oligotrophication was suggested as a potential reason (Provoost et al. 2010). Nutrient inputs to the area were reduced significantly and have reached levels similar to those in the early 1970s, but phytoplankton biomass and, hence, primary production have not responded accordingly (Duarte et al. 2009; Carstensen et al. 2011). Thus, the large decline in pH could be due to a combination of OA, oligotrophication and enhanced respiration.

Conversely, pH in Tampa Bay displayed a somewhat different pattern, with strong increases up to 1980 followed by an almost instantaneous drop in pH and then a general increasing trend (Fig. 3d). Population growth in the Tampa Bay watershed has been high during this period, and nutrient removal from wastewater was not initiated until 1980 (Greening and Janicki 2006). A drop in primary production following this removal could explain the large decline in pH shortly thereafter throughout the bay. Seagrasses have expanded and water quality improved after implementation of the nutrient management plan, which should lead to enhanced CO_2 uptake and pH increase.

Remarkably, these multi-decadal trends in coastal pH involve fluctuations of about 0.5 pH units, much larger than the 0.1-unit decline of pH attributable to OA alone. Hence, we conclude that OA from anthropogenic CO_2 is, to date, a relatively minor component of pH fluctuations in many coastal ecosystems, where enhanced primary production or respiration is often the primary driver. Moreover, changes could have been even larger, but competing watershed processes have buffered many of these changes.

Future Trajectories of Open-Ocean and Coastal pH

Scenarios of OA by anthropogenic CO_2, driven by CGMs, predict a decline of pH by 0.3 units and a shoaling of the horizon for dissolution of carbonate minerals, particularly aragonite, by the end of the century as a result of increased anthropogenic CO_2 in the ocean (Caldeira and Wickett 2003, 2005; Orr et al. 2005; Raven et al. 2005; Meehl et al. 2007). Model projections (McNeil and Matear 2008) predict that winters in the Southern Ocean will be characterized by undersaturated waters with respect to aragonite by around 2040. This projection is consistent with the models (Orr et al. 2005) which predict that the Southern Ocean surface waters will be undersaturated in aragonite throughout the year by 2050.

Upwelling waters are corrosive naturally, but their pH may decline further over time due to OA. Accordingly, the pH of coastal waters affected by coastal upwelling is expected to decline in the future. A modelled simulation of the California Current upwelling region (Gruber et al. 2012) forecasts that summer-long undersaturation will occur in the top 60 m of the water column by year 2040 and that by 2050 aragonite saturation states greater than 1.5 will have disappeared, driving more than one half of the water column to undersaturation year-round. Additionally, the seafloor will be undersaturated year-round within the next 20–30 years.

However, global model projections have coarse resolution, with grid cell sizes of 200×200 km or more, reflecting limitations of the ocean GCM component of global coupled climate and ocean circulation–biogeochemical models. Although models of improved resolution for ocean circulation are being developed, they do not yet incorporate biogeochemical properties. Consequently, models offering projections of future ocean pH and the saturation state of carbonate minerals only resolve adequately the open ocean and thus are incapable of resolving even the largest coastal ecosystems. Hence, the pH dynamics of coastal ecosystems are not captured adequately by current models projecting changes through the twenty-first century.

Attempts to extend current global models to coastal ecosystems may yield spurious results, unless these models capture other relevant processes, such as regional watershed processes and changes in landscapes at the ecosystem level, which are not tractable at the global scale. The difficulties in modelling pH changes in coastal ecosystems result not only from the resolution of global models but also from the greater complexity of pH regulation and the multiple vectors of anthropogenic impacts in pH operating in coastal ecosystems (Borges and Gypens 2010; Provoost et al. 2010; Barton et al. 2012; Cai et al. 2011; Hofmann et al. 2011; Mercado and Gordillo 2011; Waldbusser et al. 2011). Thus, predictions of future trajectories of pH in coastal ecosystems are still highly uncertain even though model predictions can provide reliable predictions for the future trajectories of open-ocean pH and, thereby, the open-ocean end-member affecting coastal pH. Moreover, we argue that even the expectation that the component of coastal pH change associated with OA from anthropogenic CO_2 will follow the same pattern as that in the open ocean is not necessarily supported. The reason for this conclusion is that, unlike the open ocean, pCO_2 in coastal ecosystems is not necessarily in equilibrium with the atmosphere at even annual timescales and many coastal ecosystems emit CO_2 into the atmosphere (Laruelle et al. 2010; Cai 2011). Calculations to resolve the anthropogenic component of CO_2 are remarkably difficult for the coastal ocean, where the assumptions of the various methods (Sabine and Tanhua 2010) are not met, thereby precluding a direct calculation of the effect of anthropogenic CO_2 on observed trends in coastal pH. Calculations based on mixing between an open-ocean end-member displaying the trajectories predicted from OA and the freshwater end-member are also unreliable because pH and the carbon system do not necessarily behave conservatively within the coastal zone and because the freshwater end-member may also shift into the future.

Hence, paradoxically, we lack guidance on the future trajectories of pH in coastal ecosystems where some of the most vulnerable taxa to OA live (e.g. Doney et al. 2010; Hendriks et al. 2010a; Kroeker et al. 2010). Producing these forecasts requires the coupling of scenarios of global CO_2 emissions with regional scenarios of likely changes in the inputs of inorganic and organic carbon, nutrients, acid and carbonate alkalinity from watersheds, and trajectories of habitat changes, thereby encompassing all relevant anthropogenic drivers of marine pH change. Coupling ocean and riverine biogeochemistry models is a first, necessary step, if a challenging one (Aufdenkampe et al. 2011). Nested models may help generate future scenarios for pH in coastal ecosystems at the regional level. These models would be composed of regional oceanographic modelling systems, forced both by GCMs, capturing the transport of anthropogenic CO_2 to the coastal ocean and watershed processes. Integrating all changes that may occur on a watershed with the potential to impact coastal pH downstream (e.g. changes in land use, nutrient export, changes in runoff, changes in industrial and urban exports of alkalinity, mining activities) over a century timescale is challenging.

Depending on the balance between the anthropogenic drivers impacting marine pH, the trajectories of future pH of some coastal ecosystems will range from steep acidification, several-fold faster than expected from anthropogenic CO_2 emissions alone, to basification. Coastal ecosystems with attenuated or low-level watershed influences, such as Antarctic ecosystems and those adjacent to arid regions, are expected to show patterns consistent with OA by anthropogenic CO_2 as they typically show little pH variability comparable to open-ocean waters (Hofmann et al. 2011; Matson et al. 2011; Falter et al. 2013). In general, increasing nutrient inputs, as expected throughout much of the developing world (Nixon 2009), may lead to increased pH, whereas oligotrophication (Nixon 2009) may lead to acidification, adding to the same trend imposed by anthropogenic CO_2 emission. Loss of vegetated coastal habitats should lead to a decline in pH, whilst loss in the cover of corals and oyster reefs and regime shifts towards a great dominance of macroalgae may lead to increased pH (Anthony et al. 2011). The intensification of the hydrological cycle, with increased freshwater discharge, may also lead to decreased pH, although this effect may be partially compensated by increased alkalinity export, depending on land use changes. This change is likely to be most dramatic in Arctic coastal waters, which are rapidly freshening due to the melting of ice on glaciers and permafrost (McPhee et al. 2009), accelerating OA and $\Omega_{aragonite}$ decline relative to the rates expected from anthropogenic CO_2 alone (Tank et al. 2012). Freshening of the Arctic is so intense (McPhee et al. 2009) that the Arctic Ocean, progressively transformed into the Arctic Ocean Estuary (McClelland et al. 2012), is possibly the only ocean basin where OA by anthropogenic CO_2 may not suffice to account for the observed and predicted pH and $\Omega_{aragonite}$ trends.

Towards a Canonical Paradigm on Anthropogenic Impacts on Seawater pH

The concept of OA by anthropogenic CO_2 suffices to accommodate the changes observed in the open ocean, where other perturbations such as atmospheric deposition of reactive sulfur and nitrogen play a minor role and where, perhaps with the exception of the Arctic Ocean, watershed perturbations are minimal. However, as concluded above, pH trajectories based on OA by anthropogenic CO_2 cannot be extrapolated directly to most coastal ecosystems or much of the Arctic Ocean, except for ocean-dominated coastal ecosystems. We propose that OA due to anthropogenic CO_2 emissions is largely an open-ocean syndrome and concur with the statement that “the role ocean acidification will play in estuaries may be different from the open ocean” (Feeley et al. 2010).

We propose here a new paradigm of anthropogenic impacts on seawater pH. This new paradigm provides a canonical approach towards integrating the multiple components of anthropogenic forcing that lead to changes in coastal pH. We believe that this paradigm, whilst accommodating that of OA by anthropogenic CO_2, avoids the limitations the current OA paradigm faces to account for the dynamics of coastal ecosystems, where some ecosystems are not showing any acidification or basification trend whilst others show a much steeper acidification than expected for reasons entirely different from anthropogenic CO_2 emissions.

Human activities impacting watershed processes predate anthropogenic increases in atmospheric CO_2 levels (Valiela 2006). Anthropogenic impacts on coastal pH driven by activities within the watershed may have been in operation over centuries to millennia (Valiela 2006; Hooke and Martín-Duque 2012), depending on the extent and intensity of human occupation. Hence, the current narrative of OA as an anthropogenic process driven by increased CO_2 emissions to the atmosphere and subsequent dissolution in the ocean is only applicable partially to the coastal ocean where anthropogenic impacts on pH have multiple sources and vary in intensity and direction.

In contrast, the revised paradigm of anthropogenic impacts on seawater pH accommodates the full range of realized and future trends in pH of both open-ocean and coastal ecosystems and provides an improved framework to understand and model the dynamic pH environment of coastal ecosystems, with observed daily fluctuations often exceeding the range of mean pH values estimated for the open ocean as a consequence of OA during the twenty-first century by GCMs (Price et al. 2012; Tables 1 and 2).

Concern about the impacts that OA may pose to calcifying organisms has made a major contribution to an improved understanding of the drivers of changes in pH, including those derived from natural processes as well as by the full range of anthropogenic drivers, including anthropogenic CO_2 emissions. The new paradigm proposed here can accommodate the progress made through observations, modelling, and experimental and mechanistic research. Importantly, it provides a superior framework to assess the vulnerability of marine biota to changes in pH. This approach allows the experimental and modelling frameworks that take account of the full suite of effects rather than just the scenarios derived from OA by anthropogenic CO_2 alone, which may not adequately portray the range of possible future scenarios (Hendriks et al. 2010a, b; Hofmann et al. 2011), to be proposed. This paradigm may also guide major improvements in the detection and attribution of OA by anthropogenic CO_2 as a component of climate change by identifying and apportioning components of pH trajectories attributable to factors other than anthropogenic CO_2. Whereas detection of OA by anthropogenic CO_2 has been achieved in open-ocean time series, we contend that it has not yet been achieved reliably in coastal ecosystems and that attribution of observed changes in vulnerable organisms to OA has been confounded in the past by failure to acknowledge the different components of anthropogenic impacts on pH possibly involved.

The paradigm of anthropogenic impacts on seawater pH can also help differentiate between primary drivers and symptoms. For instance, nutrient inputs and not pH are the force driving changes in pH in estuarine and coastal ecosystems derived from enhanced or suppressed net community production associated with eutrophication and oligotrophication processes. Hence, the master driver that needs to be managed is nutrient input, not pH. Similarly, the enhanced photosynthetic activity of marine primary producers under elevated CO_2 is often reported as an impact of OA, but the primary response is to CO_2, not pH. Indeed, enhanced photosynthetic activity with increased CO_2 has been referred to for three decades as the CO_2 fertilization effect (e.g. Tans et al. 1990). Referring to the CO_2 fertilization effect when it happens in the ocean as OA generates confusion and misguides the proper understanding of the drivers.

A canonical paradigm of anthropogenic impacts on seawater pH can more effectively be used to formulate policies to conserve vulnerable calcifying organisms by acknowledging the various anthropogenic drivers of change in pH, identifying regional and even local actions that may help vulnerable coastal organisms adapt to the impacts of OA by anthropogenic CO_2 (Kelly et al. 2011) in parallel to global mitigation efforts. The strong controls that ecosystem metabolism and watershed processes exert on the pH in coastal ecosystems suggest that strategies based on the management of ecosystem components and watershed processes may help buffer the impacts of OA by anthropogenic CO_2 locally, an option not available for the open ocean.

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