Waikato Regional Council Technical Report 2020/16

A synthesis of New Zealand ocean acidification research, with relevance to the Hauraki Gulf

www.waikatoregion.govt.nz
ISSN 2230-4355 (Print)
ISSN 2230-4363 (Online)

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December 2020

Peer reviewed by:
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Approved for release by:
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Front Cover image:
Green lipped mussels on a dropper line (Louis Olsen, NIWA)

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NIWA CLIENT REPORT No: 2019165WN

Report date: May 2019
NIWA Project: WRC19302/1920

Quality Assurance Statement		
6/6/2019	Reviewed by:	Vonda Cummings
14/11/2019	Formatting checked by:	Patricia Rangel
14/6/2019	Approved for release by:	B. Hayden

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Executive summary

This document provides a synthesis of ocean acidification (OA) research findings of relevance to the Waikato region, obtained by the Coastal Acidification: Rate, Impacts & Management (CARIM) project and other New Zealand OA-related projects. The synthesis is focussed on the following specific areas, as requested by Waikato Regional Council:

- The problem of ocean acidification relevant to the Waikato Region (Firth of Thames):
  - *The chemistry, biological impacts and projected rates of OA are described, and the drivers of coastal acidification detailed.*
  - *Data from time-series moorings and synoptic spatial studies are used to determine the mean and temporal and spatial variability of pH and associated carbonate system parameters in the Firth of Thames, and the relationship with other biogeochemical variables. The data confirm that the minimum pH currently observed is equivalent to the pH projected for the global ocean by 2100 (under the RCP8.5 scenario).*
  - *pH projections for the Firth of Thames using the "business-as-usual" scenario (RCP8.5) indicate a reduction in pH to a value of 7.69-7.74 by 2100. This is derived from Earth System Model projections for the open ocean and does not take into account other factors that are likely to further influence pH in coastal waters.*
- The role of nutrient runoff in modifying pH and the effect that nutrient limit setting may have on future acidification:
  - *Data from time-series moorings and synoptic spatial studies are used to determine the mean and variability of nutrients and other biogeochemical variables in the Firth of Thames. The relationship between OA, warming, eutrophication and deoxygenation is examined, and the data incorporated into budgets to examine how different processes influence the regional pH and carbonate system.*
  - *The supply of dissolved inorganic nitrogen, the limiting nutrient, is primarily from the catchment. Further nutrient enrichment of the Firth should be avoided as it creates a positive feedback on eutrophication by suppressing denitrification. Mass balance budgets suggest that a decrease in denitrification may be responsible for an increase in nitrate availability for phytoplankton production, and this may indirectly fuel acidification via respiration of the enhanced biomass. Reduction in catchment nutrient loading may reduce organic loading in the Firth, although the timescale and magnitude of remediation are uncertain.*
  - *The results highlight that OA is one of a group of interrelated stressors that are influenced by local/regional scale (catchment run-off) and global-scale (climate change) processes.*
- The relationships between acidification and aquaculture, including finfish:
  - *The sensitivity of different life stages of green lipped mussels and pāua, and the larval stage of snapper, as determined in laboratory experiments, are described.*

  - *Growth and survival of mussels are relatively resilient to lower pH, although the embryo and late juvenile stages, show some degree of vulnerability. Some genetic variation in resilience to OA is suggested.*

  - *Pāua larvae are highly sensitive to lower pH, whereas snapper larvae are relatively resilient but show greater negative impacts at warmer temperature.*

- The broad objectives and findings of the CARIM project relevant to the Waikato Region:

  - The mean and variation of pH around New Zealand, as determined by CARIM and the national network (New Zealand Ocean Acidification Observing Network) are described, highlighting that the Firth of Thames experiences the lowest mean pH and the largest pH variability of all New Zealand sites monitored.

  - The development and application of regional coupled hydrodynamic - biogeochemistry models, and algorithms for the carbonate system are described.

  - Indirect effects of OA such as changes in phytoplankton community, food quality and biomass that were assessed in mesocosm experiments using natural plankton communities from Wellington Harbour are described. Results suggest that warming will have a greater effect than OA, and that future plankton communities may be less diverse with implications for coastal foodwebs and biogeochemistry.

  - Potential mitigation of OA at mussel farm scales has been examined as part of a Sustainable Seas Innovation Fund project. The placement of waste shell with mussels on dropper lines and its subsequent dissolution may not provide significant buffering against lower pH, whereas CO_2 stripping by aeration has some potential but requires both further testing and significant investment if implemented.

- Key information or data gaps:

  - *Results from a recent national OA synthesis are summarised, which identifies the major knowledge gaps in terms of the sensitivity of different biological classes to OA*

  - *The need for more research into the impacts on habitat-forming groups and higher trophic levels, interaction of multiple stressors and adaptation, are highlighted.*

- Suggestions for further work for Council or application of CARIM findings to the Firth of Thames relating to acidification or aquaculture management:

  - *Time-series observations of pH and the carbonate system are maintained in the Firth of Thames by optimising and rationalising existing NIWA /University of Auckland monitoring within a regional monitoring framework coordinated between the Regional Council and other stakeholders and partners.*

  - *Coordination with other stakeholders and partners of regional activities should be explored; for example, there are co-benefits of collaboration with aquaculture industry on monitoring and mitigation methods.*

- *Determination of the variability and controls of denitrification in the Firth is critical for establishing the potential of the natural ecosystem to accommodate nitrogen loading, and so a seasonal survey of denitrification rate and regional variability is recommended.*

- *Better insight and management could be achieved with improved coupled hydrodynamic – biogeochemistry models.*

- *Better coordination of data, science and policy on land-ocean interface between different organisations will increase the potential and opportunity for management and mitigation of coastal acidification.*

- *Monitoring and management need to consider the individual and combined effects of multiple stressors. A reduction in local stressors may reduce the impact of global stressors for which management is more challenging.*

- *An increased focus on strategies and tools to mitigate the impacts of OA on Taonga, key species and ecosystems in the Firth of Thames, as well as coastal economic assets such as mussel farms. For example, the potential for selective breeding of shellfish families that are more resilient to low pH could be further investigated.*

1 Introduction and Background to Ocean Acidification

This document provides a synthesis of our current understanding of the drivers, trends, impacts and projections for ocean acidification (OA), with a particular focus on the Firth of Thames (Hauraki Gulf) region. It has been produced in response to a request from Waikato Regional Council, and specifically addresses:

- The problem of ocean acidification relevant to the Waikato Region (Firth of Thames)
- The role of nutrient runoff in modifying pH and the effect that nutrient limit setting may have on future acidification
- The relationships between acidification and aquaculture, including finfish
- The broad objectives and findings of the CARIM project relevant to the Waikato Region
- Key information or data gaps
- Suggestions for further work for Council or application of CARIM findings to the Firth of Thames relating to acidification or aquaculture management

The report initially describes the global picture before focusing on New Zealand and the Firth of Thames. It primarily reports on the findings of the MBIE-funded *Coastal Acidification: Rate, Impacts & Management* (CARIM) Project which will terminate in March 2020, but also includes insights from other New Zealand OA research including the NZOA-ON (New Zealand Ocean Acidification Observing Network), a Sustainable Seas project examining potential OA mitigation options for the mussel aquaculture industry, and a number of OA projects funded by the Ministry for Primary Industries.

1.1 What is Ocean Acidification?

Ocean acidification (OA) is defined as the "*global-scale long-term decrease in seawater pH, that is currently primarily due to the human-driven increase in atmospheric* CO_2" (Secretariat of the Convention on Biological Diversity, 2014). Approximately 25-30% of all carbon dioxide (CO_2) emitted since the start of the industrial revolution has been taken up by the ocean (Ciais et al. 2013). Once considered beneficial, this CO_2 sink is now viewed with some concern as it is altering the chemistry of the ocean, with potential implications for marine biota and ecosystems (Orr et al. 2005; Fabry 2008).

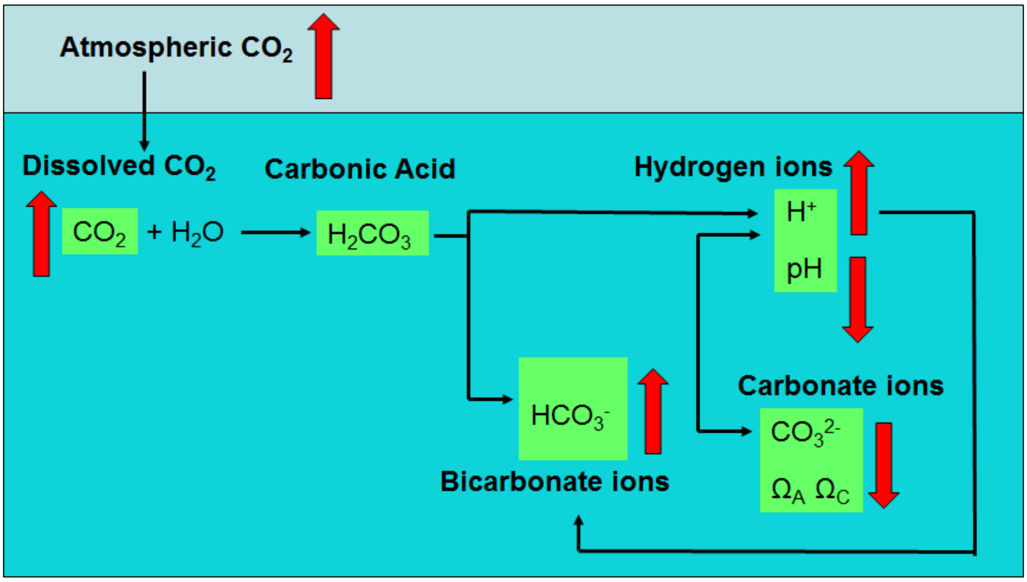


Figure 1-1 Diagram showing the reactions and chemical species of the marine carbonate system (black arrows). The direction of the red arrows indicates the net change associated with Ocean Acidification in response to increasing atmospheric CO_2 (from Law et al 2018).

OA encompasses not just a decline in seawater pH, but also changes in the concentration of different components of the marine carbonate system (Figure 1-1) The increase in CO_2 gas transferred from the atmosphere causes an increase in dissolved CO_2 (pCO_2), which reacts with seawater to form carbonic acid (H_2CO_3). This acid then dissociates to produce bicarbonate ions (HCO_3^-) and hydrogen ions (H^+), with the latter reacting with carbonate ions (CO_3^{2-}) to produce more HCO_3^-. Consequently, OA is characterised by an increase in pCO_2 and HCO_3^-, and corresponding decreases in pH (i.e. an increase in H^+) and CO_3^{2-} (Figure 1-1, Law et al. 2018). It also results in a decrease in the concentration of carbonate (saturation state, Ω). This Ω differs for the two main polymorphs of carbonate, calcite (Ω_C) and aragonite (Ω_A), due to their differing crystal structure and stability (Feeley et al, 2009).

1.2 Why the concern?

The fundamental shift in ocean chemistry may influence a variety of biotic, as well as abiotic, processes. International studies on the impacts of OA initially focussed on the decline in CO_3^{2-} availability and the potential detrimental effect on calcifying species that produce calcium carbonate shells (Orr et al. 2005; Langer et al. 2006). Ω is critical here, as when carbonate is supersaturated ($\Omega > 1$) it can precipitate in water. Conversely, when Ω is undersaturated ($\Omega < 1$) solid carbonate will dissolve. The value of 1 for Ω is primarily a thermodynamic threshold and solid carbonate can be generated below it, but this becomes energetically more demanding and has flow-on effects on other physiological processes. Carbonate shells can be produced by different pathways, primarily by using bicarbonate from seawater, or by the conversion of respiratory CO_2 (Roleda et al., 2012; Thomsen et al., 2015), but regardless, Ω has to be >1 at the site of calcification. This is achieved by active pumping of ions (McConnaughey and Gillikin, 2008), and consequently more energy is required if the external Ω is <1. Many carbonate-forming organisms have shown a negative response to low pH (Fabry, 2008). The decline in dissolved carbonate availability potentially threatens a wide variety of New Zealand organisms with carbonate shells or skeletons, including pāua, oysters, cockles, mussels and kina, which could be the main losers from ocean acidification.

Conversely, some groups may be winners from OA, with primary producers potentially benefitting from the increase in *p*CO_2 for photosynthesis. However, OA can affect the physiology of a broad range of marine organisms *via* alteration of their acid-base balance in response to changing [H^+] (Kroeker et al. 2013). The resulting additional metabolic cost in physiological compensation may then influence species survival (mortality, reproduction, fitness), and condition (growth, biomass, fecundity), with potential ramifications for foodwebs, ecosystem stability, services and economic value (Doney et al. 2009). In some cases, this change in acid-base balance may influence the neurosensory system and cause behavioural changes that may be detrimental to the survival of some species (Munday et al. 2010).

1.3 Global and regional trends in OA

Although OA is a global phenomenon, its impacts will vary regionally, dependent upon location and related factors such as depth, temperature, mixing regime and associated biogeochemistry. Over recent geological time the pH of the global ocean has been relatively stable at ~8.2, but since the late 1870s it has declined to 8.1 in response to anthropogenic CO_2 emissions (Raven et al. 2005). As pH is measured on a negative logarithmic scale, this decline of 0.1 is equivalent to an increase in hydrogen ion concentration (acidity) of ~30%. A similar rate of change has been observed in the New Zealand region; in a 13-year time series in Subantarctic waters, east of New Zealand, a mean pH of ~8.088 (range 8.04-8.13) was recorded, during which pH declined by 0.0013 per annum (Bates et al. 2014).

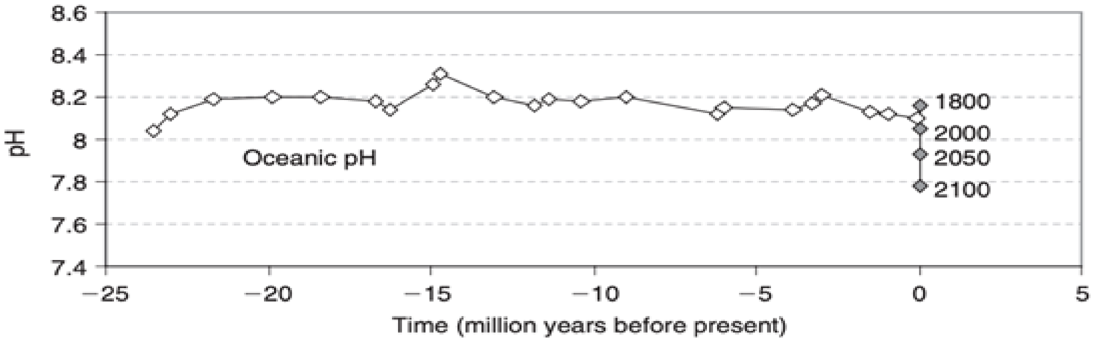


Figure 1-2 pH trend over the last 25 Million years (from Turley et al. 2006)

Critically, global projections indicate a significant decrease in pH, with a global ocean average of 7.7 by 2100 which is 100-125% more acidic (e.g. higher H^+ ion concentration) relative to the pre-industrial ocean. These projections indicate not just the lowest global pH value over long timescales but also the most rapid rate of pH change over the last 25M years (See Figure 1-2, Turley et al. 2006).

Projected changes in pH in the New Zealand region were estimated using Representative Concentration Pathways (RCPs), where the following number indicates the radiative forcing expected by the year 2100 (van Vuuren et al. 2011). These projections concur with those for the global ocean, with a projected decline of 0.33 by 2100 in New Zealand waters under RCP 8.5 (Law et al 2018b). Figure 1-3 illustrates how the projected surface ocean pH in the NZ region will vary with these future emission scenarios. The annual sinusoidal pattern, which reflects the seasonal variation in pH, results in an annual pH range of ~0.05, which initially obscures differences in the RCP projections. However, from 2035 pH deviates under the different RCPs, declining to 7.99 by 2050 and 7.95 by 2100 under RCP4.5, equivalent to respective increases of 32% and 42% in H^+ concentration relative to the present-day. The RCP8.5 projection has a steeper pH decline to 7.93 and 7.77 by 2050 and 2100, respectively, with the decline of 0.33 pH units by 2100, equivalent to an increase in H^+ concentration of 116%.

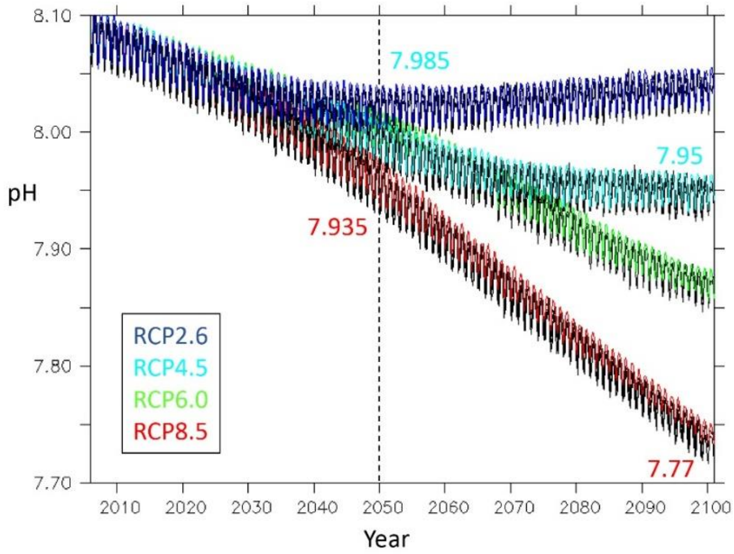


Figure 1-3 Projected surface pH for the NZ region under each Representative Concentration Pathway (RCP), with the Mid- and End-Century mean pH identified for RCP4.5 and 8.5. For each RCP, the black line indicates the mean of projections from six Earth System Models (ESMs) and the coloured line (Blue - RCP2.6, Cyan - RCP4.5, Green – RCP6.0, Red-RCP8.5) the projection generated using the GFDL-ESMG2 Earth System Model (reproduced from Law et al. 2018b).

2 Acidification of coastal waters with a focus on the Waikato Region (Firth of Thames)

2.1 Coastal processes

At the global scale, ocean acidification is proceeding in response to the injection of atmospheric CO_2 (Borges and Gypens 2010; Fennel et al. 2019) and, in some coastal areas, because of upwelling of historically acidified waters (Barton et al. 2012; Law et al. 2018). However, in many coastal zones, acidification related to coastal nutrient enrichment and consequent eutrophication is significantly outpacing atmospherically-driven acidification (Provoost et al. 2010; Duarte et al. 2013; Wallace et al. 2014; Law et al. 2018; Fennel et al. 2019). The mechanism driving this 'other eutrophication problem' is described by the intertwined cycles of carbon, nutrients and O_2 in the coastal system:

CO_2 + *inorganic nutrients* + *water* ↔ *organic matter* + O_2

This relationship describes, from left to right, the uptake of CO_2 and nutrients to produce organic matter and O_2 via photosynthesis (autotrophy), and from right to left, the respiration of organic matter, consuming O_2, reforming dissolved nutrients and CO_2 (heterotrophy). This balance of production and respiration defines the coastal system's Net Ecosystem Metabolism, or NEM (Gordon et al. 1996; Caffrey 2004; Zeldis and Swaney 2018). The relationship describes fluxes of dissolved inorganic carbon (DIC) and O_2, which control ecosystem stressors of decreased pH and deoxygenation (Kemp et al. 2005; Sunda and Cai 2012; Waldbusser and Salisbury 2014; Cai et al. 2017; Van Dam and Wang 2019). Oxygen and pH in the coastal system are thus strongly related by the underlying biogeochemistry of net ecosystem metabolism (NEM) and can also be consequences of eutrophication (excessive primary production driven by nutrients). These relationships are summarised in (Figure 2-1).

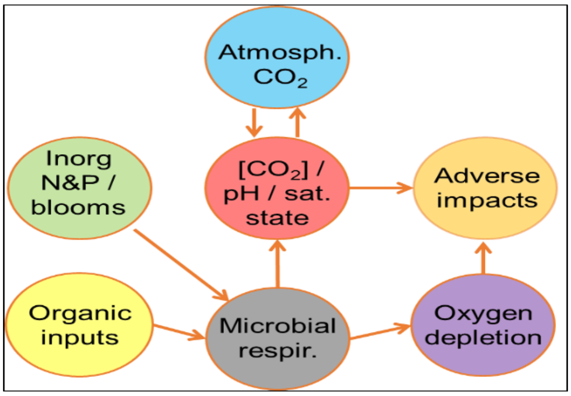


Figure 2-1 Mechanisms of oxic and pH-related hazards related to eutrophication. Organic inputs, and algal blooms stimulated by inorganic inputs, fuel microbial respiration, depleting O_2, generating CO_2 and lowering pH and carbonate saturation state. These cause adverse impacts through hypoxia and acidification, against the background of acidification caused by atmospheric CO_2 inputs. (Adapted from Sunda and Cai, 2012). Inorg. N&P: Inorganic Nitrogen and Phosphorus.

Respiration depletes O_2 in coastal waters, and when this exceeds the replenishment by photosynthesis, hydrodynamic and atmospheric exchange, O_2 concentrations become reduced, potentially leading to hypoxia (levels of O_2 that can no longer support living aquatic organisms) (Gray et al. 2002; Vaquer-Sunyer and Duarte 2008; Vaquer-Sunyer and Duarte 2011). In extreme cases, often in combination with physical processes such as water-column density stratification (Scully 2016), de-oxygenation can be catastrophic for biota and normal biogeochemical functioning of coastal ecosystems (Conley et al. 2009). Respiration of organic matter also generates CO_2, which enters the aqueous carbonate system and decreases pH (OA), and lowers the concentration of carbonate ions and Ω (Sunda and Cai 2012; Waldbusser and Salisbury 2014). From the perspective of an organism that requires calcium carbonate, the decrease in Ω is potentially deleterious as it requires more energy to be diverted to building shell at the expense of other key metabolic processes (Kroeker et al. 2010; Provoost et al. 2010; Gazeau et al. 2013; Capson and Guinotte 2014; Law et al. 2018).

2.2 Trends in the Firth of Thames

This section describes the manifestation of hypoxia and acidification in the Firth of Thames, as determined by NIWA and University of Auckland regional surveys. Water column profiles of dissolved O_2 (DO) were obtained in the outer Firth of Thames at the NIWA Firth of Thames monitoring site (orange circle in Figure 2-2), at 3-monthly intervals from 1998-2018 using a CTD-rosette instrument. This site was also used for nutrient and phytoplankton time-series studies (See Section 3). In addition, DO was surveyed from 2005-2014 using moored oxygen sensors at the outer Firth monitoring site, with DO sensors mounted in the upper (~10 m depth) and lower (~33 m depth) water column sampling every 15 minutes. Spatial surveys of multiple parameters including O_2 and carbonate were conducted across the Firth and Hauraki Gulf on several occasions, including at sites used for seasonal carbonate surveys and nutrient budget analyses (See Section 3).

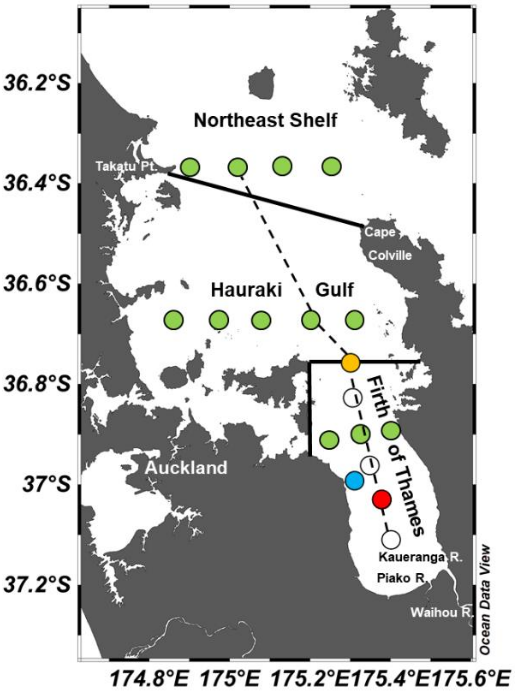


Figure 2-2 **Sampling locations in the Firth of Thames and Hauraki Gulf.** The orange circle marks the location of the long-term (1998–present) NIWA Firth monitoring site in the outer Firth of Thames, the red circle the more recent NIWA monitoring site in the inner Firth of Thames (2015-present) and the blue circle the University of Auckland monitoring site (2016-17). Green circles denote stations used in nutrient mass-balance analysis (Zeldis and Swaney 2018), separated by solid lines marking mass-balance compartment boundaries. The dashed line denotes

the transect stations used for water column property plots, including the open circles (See 3). Also labelled are the major rivers draining to the Firth.

The 3-monthly time series of DO profiles at the NIWA outer Firth monitoring site (Figure 2-3 (a and c)) show:

- The upper 20 m of the water column was generally well oxygenated in near equilibrium (>90% saturation) with the atmosphere, with about 7-9 mg O_2 L^{-1} (Figure 6a);
- However, in most summer and autumn surveys (when temperature was maximal: Figure 6b) there was usually DO depression in the lower 20 m of the water column;
- These low DO conditions were usually between 70% and 60% saturation, although extreme events of <40% were recorded, corresponding to DO about 5.7, 4.9 and 2.7 mg L^{-1}, respectively;
- The water column tended to be density-stratified during these low DO events (Figure 2-3 c).

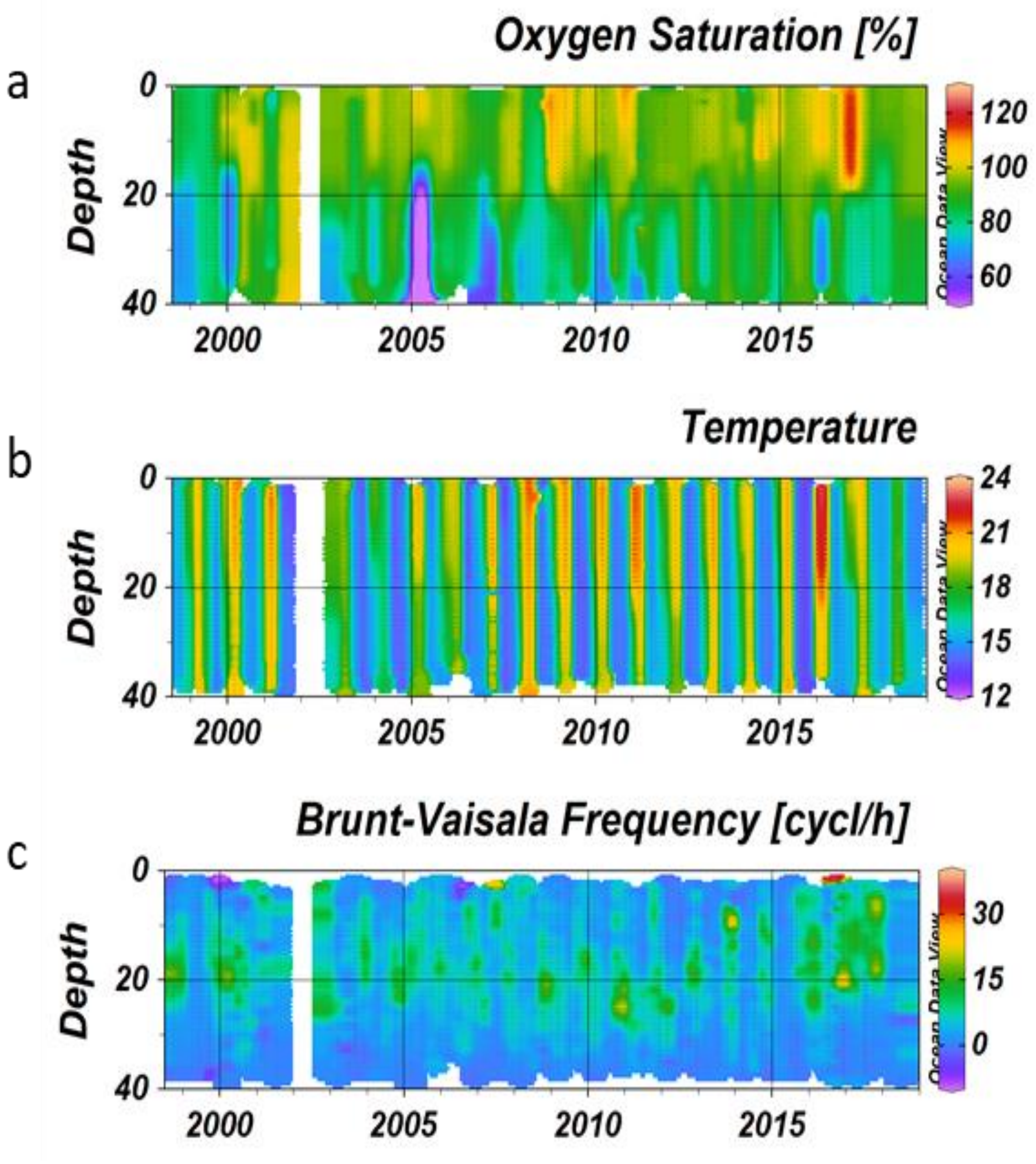


Figure 2-3 Depth contour plots of oxygen and physical properties from quarterly ship sampling at the NIWA outer Firth monitoring site, plotted by depth and time, from 1998 to 2018 (a) O_2 (% surface saturation), (b) temperature (°C) and (c) water column vertical stratification (Brunt-Väisälä frequency: higher values mean more strongly stratified). Vertical lines of dots show 1-m depth intervals and times of profiles. Ticks on x-axes are 1 January of each year.

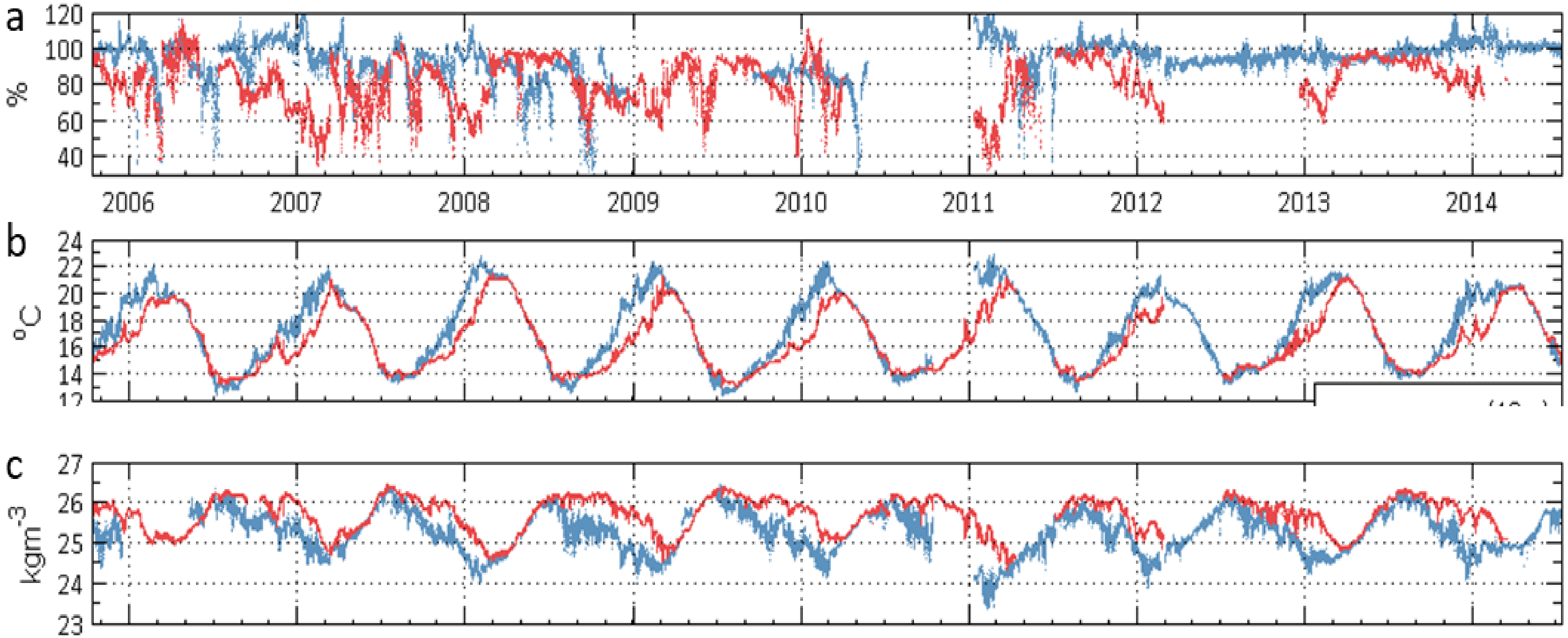


Figure 2-4 Water column properties at the NIWA outer Firth monitoring site, 2006-2014: (a) O_2 % saturation (b) temperature (°C), and (c) water column stratification (water densities (kg m^{-3}) at the upper (10m from surface, blue) and lower (33m from surface, red) depths.

The moored time series of DO at the NIWA outer Firth monitoring site Figure 2-4(a-c) shows:

- In the upper water column (10 m depth) oxygen was generally near saturation but events of lower oxygen (60% or 4.9 mg L^{-1}) occurred occasionally (Figure 7a);
- There were frequent DO depletion events (60% saturation) in the lower water column at 33 m, occasionally dropping as low as 40% or 2.7 mg L^{-1}. These low DO events were often missed by the temporally sparse 3-monthly CTD profiling (Figure 7a);
- The low DO periods generally corresponded to periods of warmer temperature and greater water column stratification Figure 2-4(b, c).

Temperature, salinity and pCO_2 were surveyed over the Firth and Hauraki Gulf on four seasonal surveys in 2012-13 (Figure 2-5). Underway mapping of the properties near surface (2m) was done while the ship steamed over the region. During these surveys the ship stopped at 17 sites distributed over the region (shown in Figure 5) to profile the water column for dissolved inorganic carbon (DIC) and total alkalinity, which were then used to calculate underway values of pH, DIC and alkalinity at all sample points (Figure 2-5) and compared with corresponding measurements in autumn 2010. Results of these surveys showed:

- In all five sampling occasions, there were increasing pCO_2 and DIC gradients from the Hauraki Gulf into the Firth and decreasing gradients of pH and alkalinity. These followed the decreasing gradient of salinity toward the head of the Firth, indicating an association with riverine input;
- pCO_2 in the Firth was highly seasonal, low in spring, reflecting spring bloom drawdown by actively growing phytoplankton, increasing through summer and highest in autumn (~500-550 µatm) during annual maximum temperatures and annual O_2 minima (respiratory maxima: Figure 2-5. The autumn 2010 survey had higher pCO_2 (~550-600 µatm) than the autumn 2012 survey;
- pH was highest in spring, reflecting CO_2 drawdown by growing phytoplankton, and lowest in autumn (~7.92), when respiration and CO_2 production maximised. It was near oceanic pH (~8.05-8.1) in all seasons in the outer Gulf. The minimum pH effects were stronger in autumn 2010 (<7.9) than autumn 2012;
- DIC often tracked pCO_2 (Figure 2-5) but diverged in winter when water column mixing was likely to have been strong and CO_2 was de-gassed from the water column to the atmosphere. Biological effects on pCO_2, pH and DIC will be discussed further in Section 3. Alkalinity tracked salinity closely with highest values in autumn when salinity was highest (and river flow lowest). This showed that the strong pH depression in autumn was not associated with loss of buffering capacity from high inputs of low alkalinity river water.

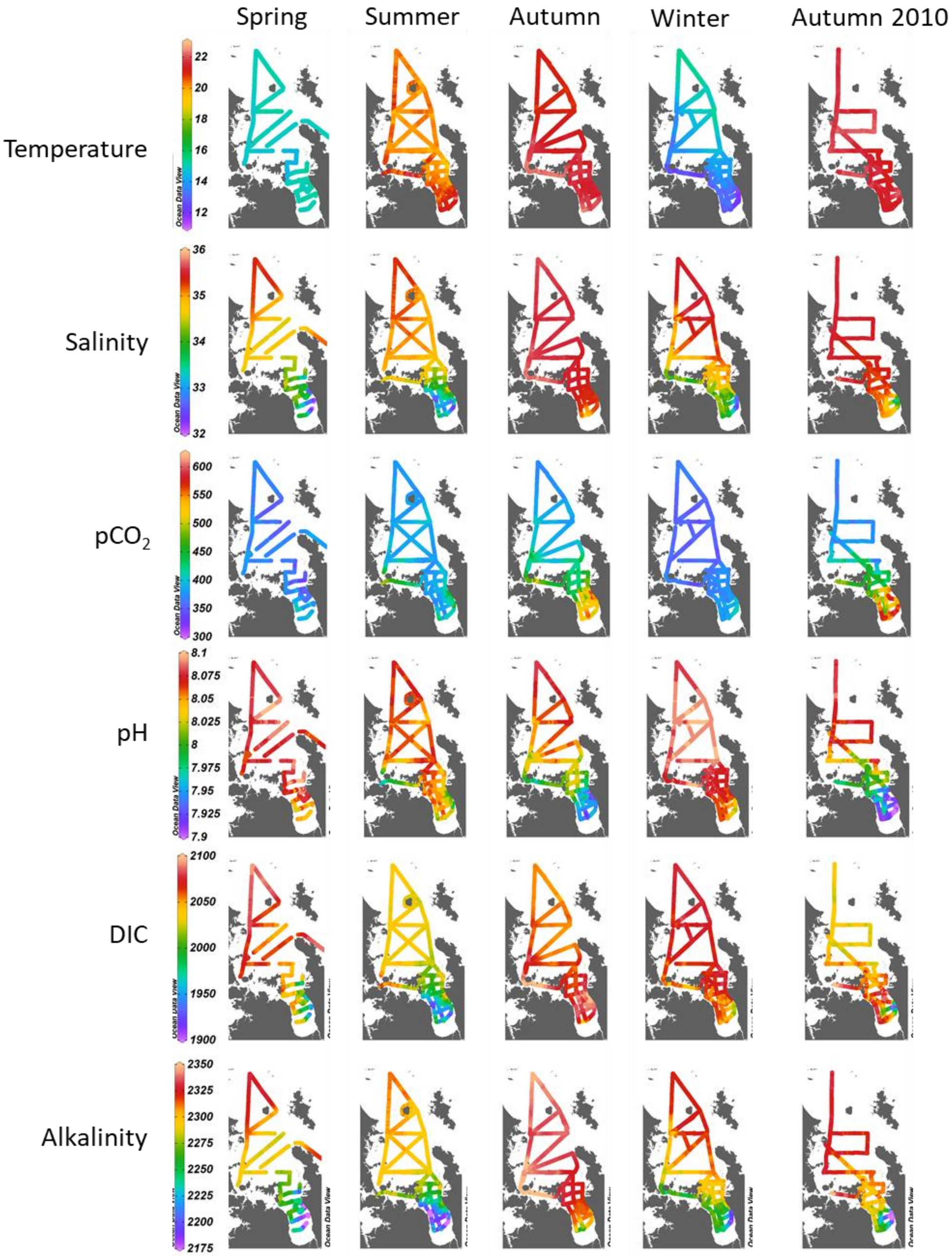


Figure 2-5 Seasonal and spatial gradients across Hauraki Gulf and Firth of Thames for near-surface temperature (°C), salinity, pCO_2 (µatm), DIC (µmol) and alkalinity (µmol) from four seasonal surveys in 2012-13, and in autumn 2010.

The discrete carbonate sampling (DIC and alkalinity) near-surface and near sea bed during the 4-season surveys at the 17 sites allowed calculation of carbonate parameters including *p*CO_2, pH and Ω_{Ar} (Omega$_{Ar}$), the saturation state of aragonite (Figure 9). Discrete *p*CO_2 was highest and pH lowest in autumn in the inner Firth. pH was lower near the sea bed than near the surface in spring and summer, but more equal in autumn and winter. These vertical contrasts were probably sustained by higher phytoplankton growth rates in spring and summer, which reduced *p*CO_2 (and increased pH) in the upper water column (see section 3). Productivity was lower in winter, and respiration was more evenly distributed in the water column (Figure 2-3and Section 3). There was a decreasing gradient in saturation state from offshore into the Firth. Values offshore were mainly Ω_{Ar} = 2.8-3.0 and in the Firth, were usually about Ω_{Ar} = 2.3-2.4. The Ω_{Ar} values sampled in autumn 2010 (not shown) were lower than in autumn 2013, reaching minimal values of ~1.8 and were typically ~ 2.2-2.3 in the Firth. Saturation state values are discussed further in Section 3

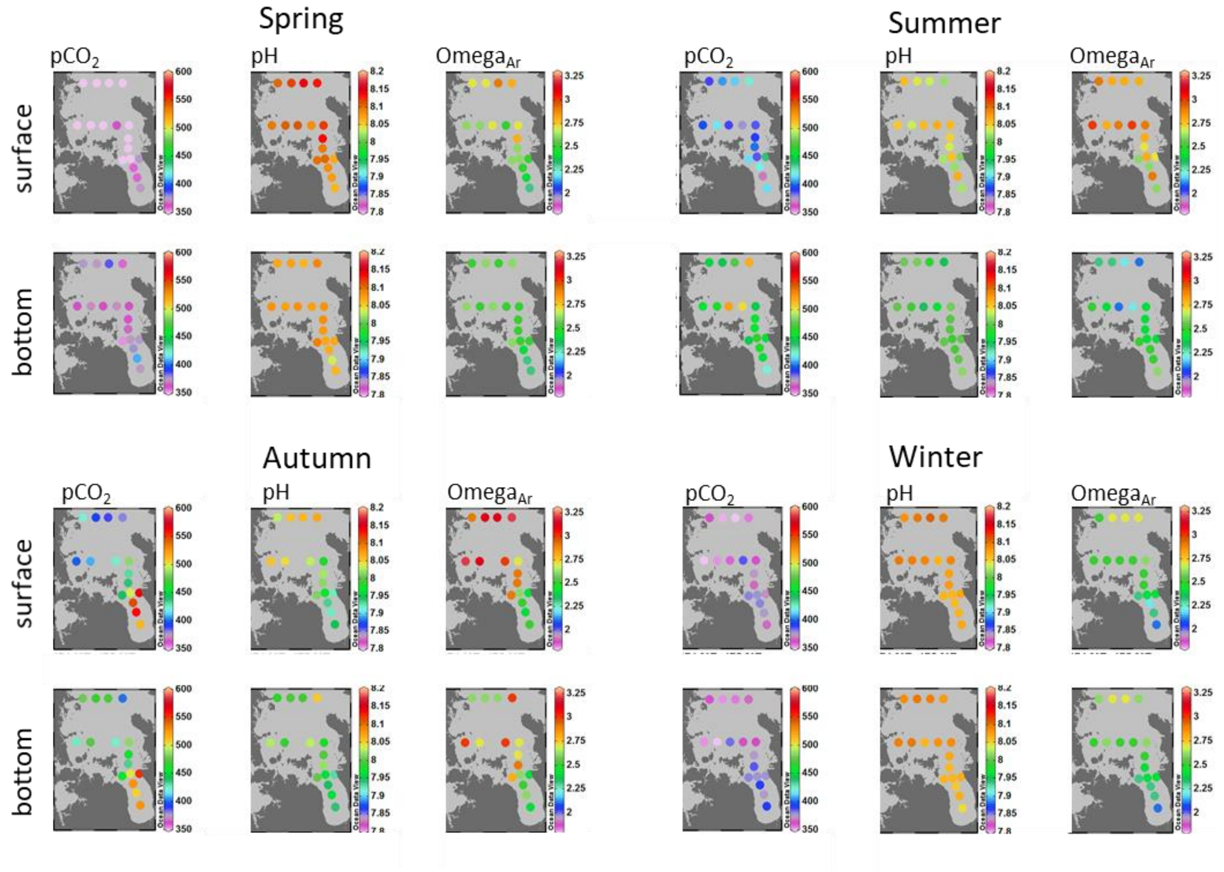


Figure 2-6 pCO_2 (µatm), pH and saturation state of aragonite (Omega$_{Ar}$) across Hauraki Gulf and Firth of Thames from four seasonal surveys in 2012-13. Data are shown for surface and near-seabed (bottom) discrete samples.

The results presented here are consistent with trends observed in enriched coastal systems overseas and confirm that coastal acidification related to catchment loading is proceeding considerably faster than atmospherically-driven acidification. The maximum pH reductions (relative to pre-industrial pH) observed in the Firth, of 0.2 units and up to 0.5, already rival the atmospherically-driven 0.4 reduction of pH projected for the open ocean by 2100 under some IPCC scenarios. The influence of the pH reductions on aquaculture species in the Firth will be considered in Section 4, with respect to their known tolerances to reduced pH and saturation state.

3 The role of nutrient runoff in modifying pH

The delivery of nutrients to New Zealand coastal waters has increased dramatically in post-colonial New Zealand (Snelder et al. 2017), driven by erosion, deforestation and land-use intensification. As described in Section 2 in the description of net ecosystem metabolism (NEM), this accelerated nutrient delivery can stimulate excessive primary production which is eventually respired, depleting oxygen, liberating CO_2 in the water, and leading to the hazards of hypoxia and acidification (Paerl 2006; Sutula 2011; Sunda and Cai 2012). It is important for resource managers to understand these relationships, to enable them to consider countermeasures through nutrient limits, land-use policy setting or point source remediation (Swaney and Giordani 2011; Wallace et al. 2014; Zeldis and Swaney 2018).

Nitrogen (N) is the key limiting nutrient in driving production and NEM in coastal waters (Howarth and Marino 2006), so understanding its supply, uptake and losses from the system is essential. Toward this, mass-balance nutrient budgeting was used by Zeldis and Swaney (2018) to understand NEM dynamics and N cycling in the Hauraki Gulf/Firth of Thames system, as detailed below. Mass-balance analyses are a way of obtaining 'whole system' viewpoints on coastal biogeochemical functions and their forcing, by balancing budgets of riverine, oceanic, atmospheric and biogeochemical sources and sinks of nutrients and carbon against budgets of water and salt (Figure 3-1)

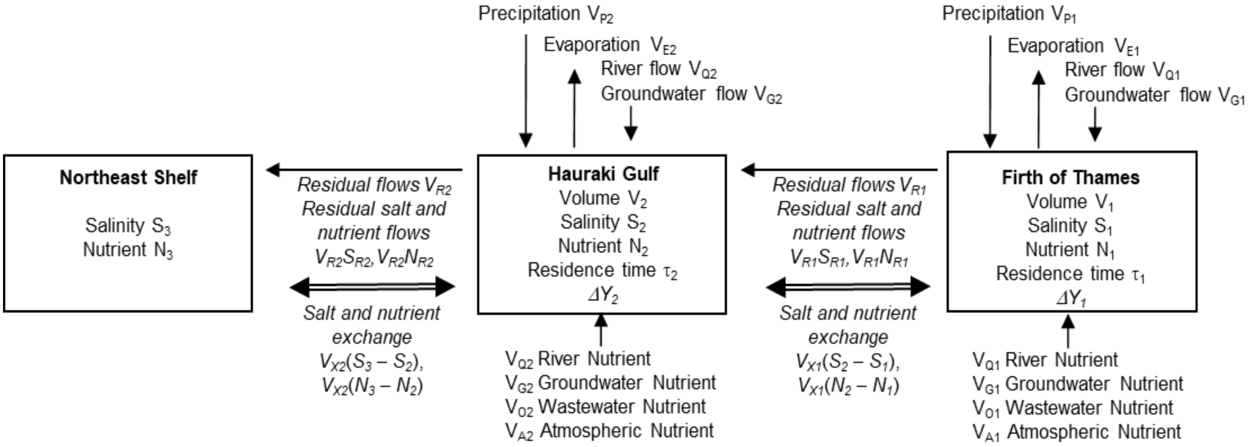


Figure 3-1 Schematic of system boxes used in the water-salt-nutrient mass balance budgets for Hauraki Gulf/Firth of Thames. Conservative and non-conservative fluxes of freshwater, salt and nutrients are shown with terms defined in Zeldis and Swaney (2018).The system boundaries and sampling stations used are shown in Figure 2-2.

Freshwater volumes and inorganic and organic N and phosphorus (P) inputs were balanced by salinity, N and P from the ocean surveys to determine conservative and non-conservative N and P fluxes. Other inputs included nutrient stoichiometry, DIC and nitrogen fluxes including denitrification. The study by Zeldis and Swaney (2018) included similar budgeting for Golden and Tasman Bays (Nelson Bays), which provided useful points of comparison with the Hauraki/Firth situation. In addition, because they budgeted the Hauraki Gulf/Firth of Thames system twice, in 2000–2001 and 2012–2013, they compared their functioning at two times separated by more than a decade (Zeldis and Swaney (2018).

Results of budgeting showed that dissolved inorganic nitrogen (DIN) supply to the Firth was much higher than to Nelson Bays and Hauraki Gulf (Figure 3-2). Furthermore, Firth organic N loads were about 25% of the inorganic loads and were high relative to organic loads to the Gulf and Nelson Bays.

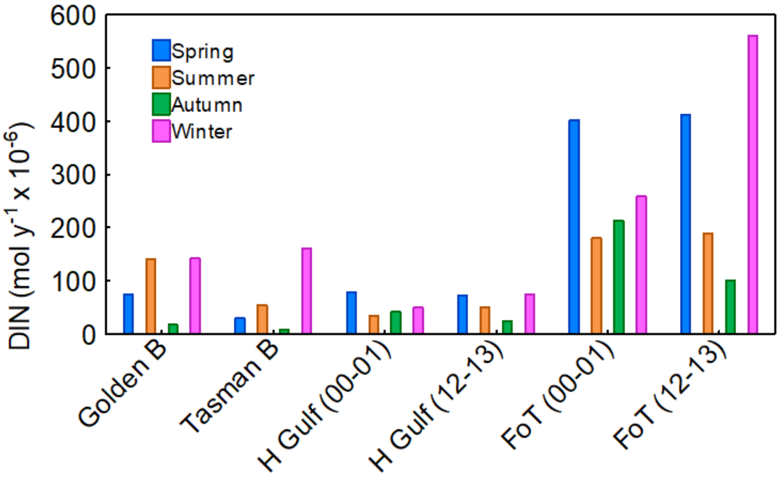


Figure 3-2 Seasonal freshwater dissolved inorganic nitrogen (DIN) loads (× 10^{-6} mol year^{-1}) to Golden Bay, Tasman Bay, Hauraki Gulf and Firth of Thames (FoT), with results for the latter shown for 2000–2001 and 2012–2013 budgets (Zeldis and Swaney 2018)

When the catchment DIN loads were compared with loads supplied by offshore waters, it was found that for Nelson Bays and Hauraki Gulf, exchange with adjacent shelf waters usually dominated DIN supply (80–85%) (Figure 3-3). In contrast, for the Firth of Thames, ~85% of DIN supply originated from its catchment.

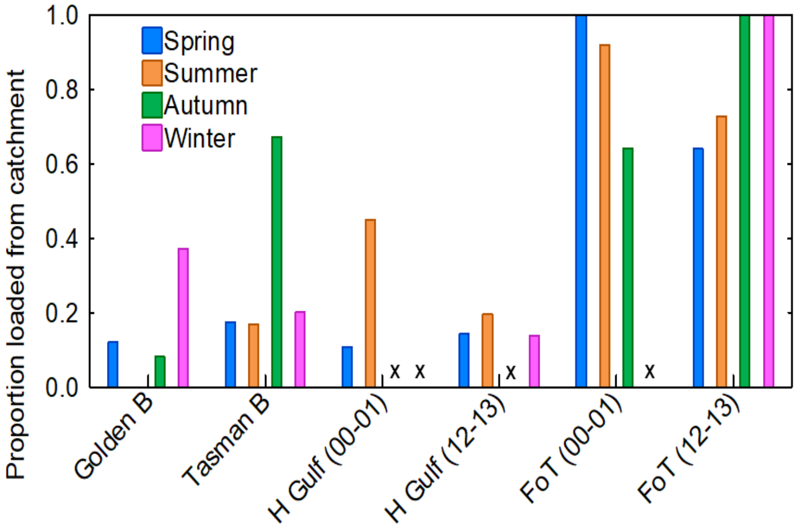


Figure 3-3 Proportions of DIN load from the catchments of the four systems for each season and year. Seasonal budgets for which valid proportions could not be calculated (Zeldis and Swaney 2018) denoted by ‘x’.

Sources of DIN for the Firth were thus primarily derived from runoff rather than offshore. N can also be supplied via atmospheric deposition (Da et al. 2018), and this was evaluated for the Firth and Hauraki Gulf (Zeldis and Swaney 2018). It was found that while atmospheric deposition was a significant proportion of the N supply to the Gulf, it was a relatively minor contributor to the Firth relative to river loading.

NEM (the balance of production and respiration; (Figure 3-4) of Nelson Bays and Hauraki Gulf was approximately balanced between autotrophy (net-productive) and heterotrophy (net-respiratory). In contrast, Firth NEM was highly seasonally variable, often exhibiting strong heterotrophy.

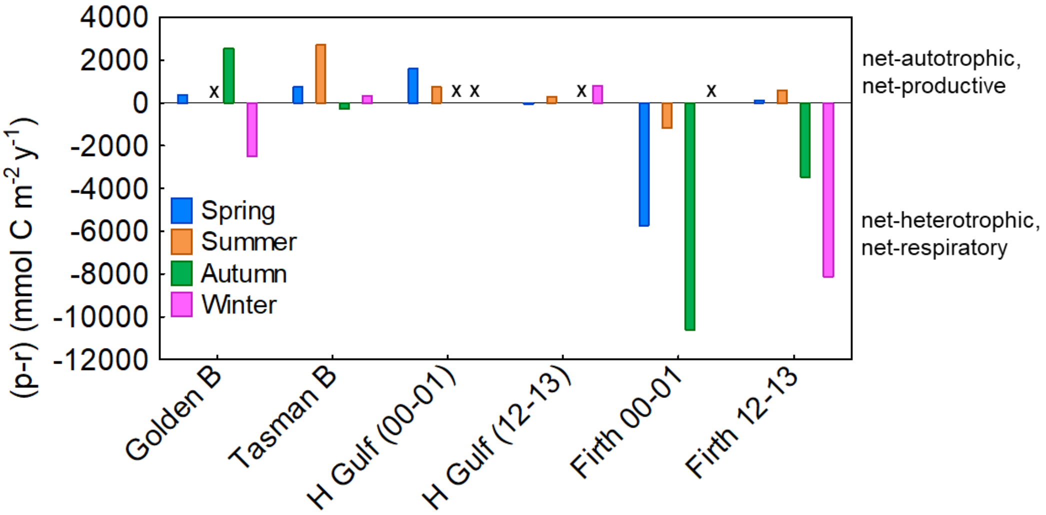


Figure 3-4 Seasonal difference of NEM (production minus respiration (p − r), mmol C m^{-2} $year^{-1}$) for the four systems for each season and year. Seasonal budgets for which valid fluxes could not be calculated (Zeldis and Swaney 2018) denoted by 'x'.

The samples for the mass-balance budget made in 2012-13 were collected at the 17 stations occupied during the underway carbonate surveys (Figure 2-2) The budgeting showed net-respiratory NEM in the Firth in Autumn 2013, consistent with the 2012-13 underway results which showed high pCO_2 (Figure 2-5), and with the low O_2 conditions seen in most autumns at the outer Firth (Figure 2-3 and Figure 2-4). However, the budgeting also showed net-respiratory conditions in winter 2013, which was not detected as high pCO_2/low pH in the winter underway data (Figure 8) or as low O_2 at the mooring/monitoring site (Figure 2-3)(Figure 2-4). This occurred when water column physical mixing was strong in winter (Figure 2-3)(Figure 2-4), which degassed CO_2 and O_2 from the water column to the atmosphere. Underway-measured DIC levels were high in winter (Figure 2-5) consistent with the net-respiratory prediction from the budgeting. Thus, although the inner Firth system was apparently net-respiratory in winter 2013, the physical mixing equilibrated CO_2 and O_2 with the atmosphere effectively 'protecting' it from low pH and O_2. Similar solubility/physical effects on concentrations of pCO_2 and O_2 have been described in large USA estuaries (Wallace et al. 2014; Ianson et al. 2016; Shen et al. 2019).

The mass-balance budgeting also yielded information on denitrification rates (loss of gaseous N to the atmosphere). Of special interest was that the budgets made 12 years apart for the Firth showed decreased denitrification efficiency (Figure 3-5). All seasonal budgets in common to the two surveys (spring, summer and autumn) showed lower values in 2012–2013 than in 2001–2002, with an average decrease of 51%.

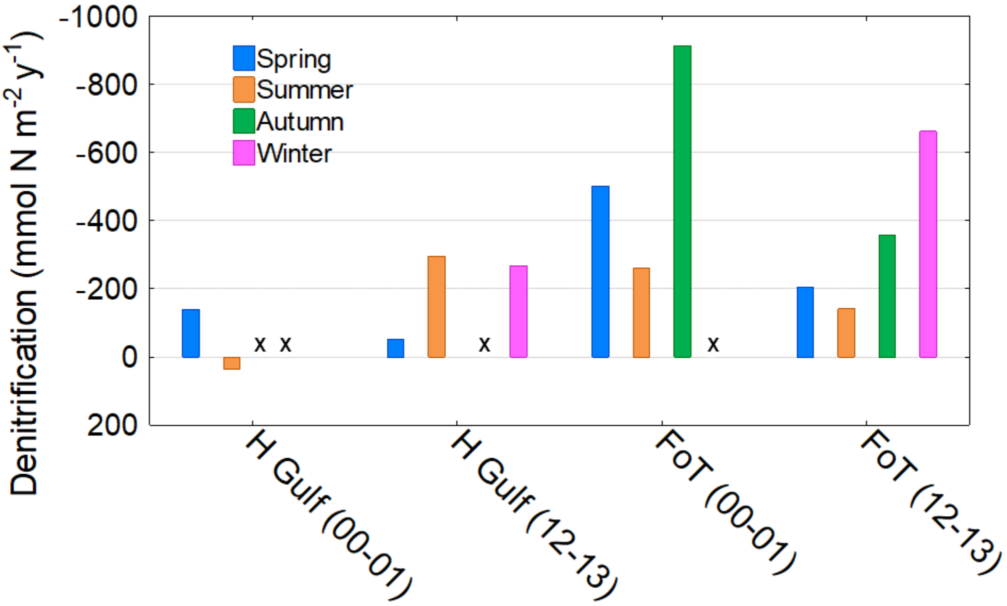


Figure 3-5 Seasonal denitrification rate (mmol N m−2 y−1) for Hauraki Gulf and Firth of Thames for 2000-01 and 2012-13 mass-balance budgets. Seasonal budgets for which valid fluxes could not be calculated (Zeldis and Swaney 2018) denoted by 'x'.

The decrease in denitrification rates coincided with a period of significant increases in N and phytoplankton concentrations (enrichment) in Firth waters (Figure 3-6). Sampling at the NIWA outer Firth monitoring site over the 15-year three-monthly time series showed a DIN increase of 5% per year ($p < 0.01$) from 1998 to 2013 (seasonal Kendall trend tests). Dissolved organic N (DON) increased by 2% per year ($p < 0.02$) and micro-phytoplankton cell numbers increased by 7% per year ($p < 0.00$). NIWA studies showing increased sediment O_2 consumption in 2003 and 2012 were consistent with this, and indicated enrichment in sediments of the Firth (reviewed in Zeldis and Swaney (2018)). Studies in USA and Australian coastal systems have shown that denitrification efficiency drops with degree of organic enrichment in sediments (Cook et al. 2004; Eyre and Ferguson 2009; Hale et al. 2016; Harris et al. 1996; Kemp et al. 2005; Kemp et al. 1990).

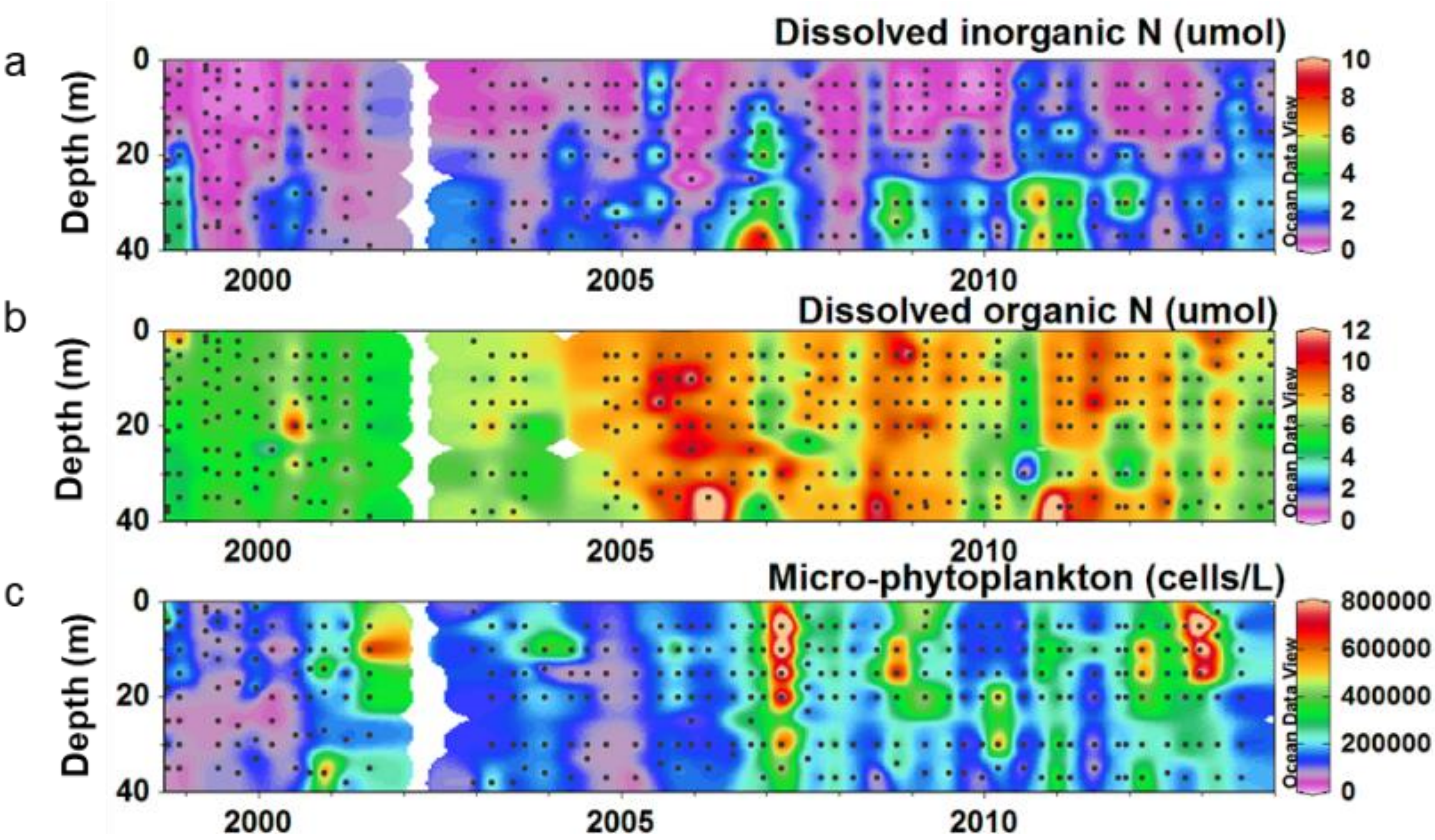


Figure 3-6 Nutrient and phytoplankton concentrations from water samples at the NIWA outer Firth of Thames monitoring site (orange circle, Figure 2-2), plotted by depth and time at three-monthly intervals from 1998 through 2013. Shown are (a) DIN (µmol), (b) DON (µmol) and (c) micro-phytoplankton (cells L^{-1}). Water samples depths are shown by black dots and ticks on the x-axes correspond to 1 January of each year.

The reduction in denitrification rate in the Firth could be significant for hypoxia and acidification, because of the retention of N in the system. The accelerated availability of nutrients to primary producers would be a positive feedback on eutrophication and organic enrichment. This appears to have occurred without any long-term change in N supply from offshore, seaward of the Firth (Zeldis and Swaney 2018), and without significant change in inflowing riverine water quantity or quality during 1993-2012 (Vant 2013). Although the trends of increasing nutrient and phytoplankton concentrations do not appear to be a consequence of contemporaneous increases in inflowing nutrients, it was hypothesised that they may be a consequence of cumulative effects of the high terrestrial nutrient loading the Firth has received over recent decades (Zeldis and Swaney 2018) arising from land-use intensification. It was concluded that the nutrient and phytoplankton enrichment for the Firth were consistent with the hypothesis that water quality in the Firth declined over 1998-2013 period because of reduced denitrification efficiency associated with the historic high nutrient loading.

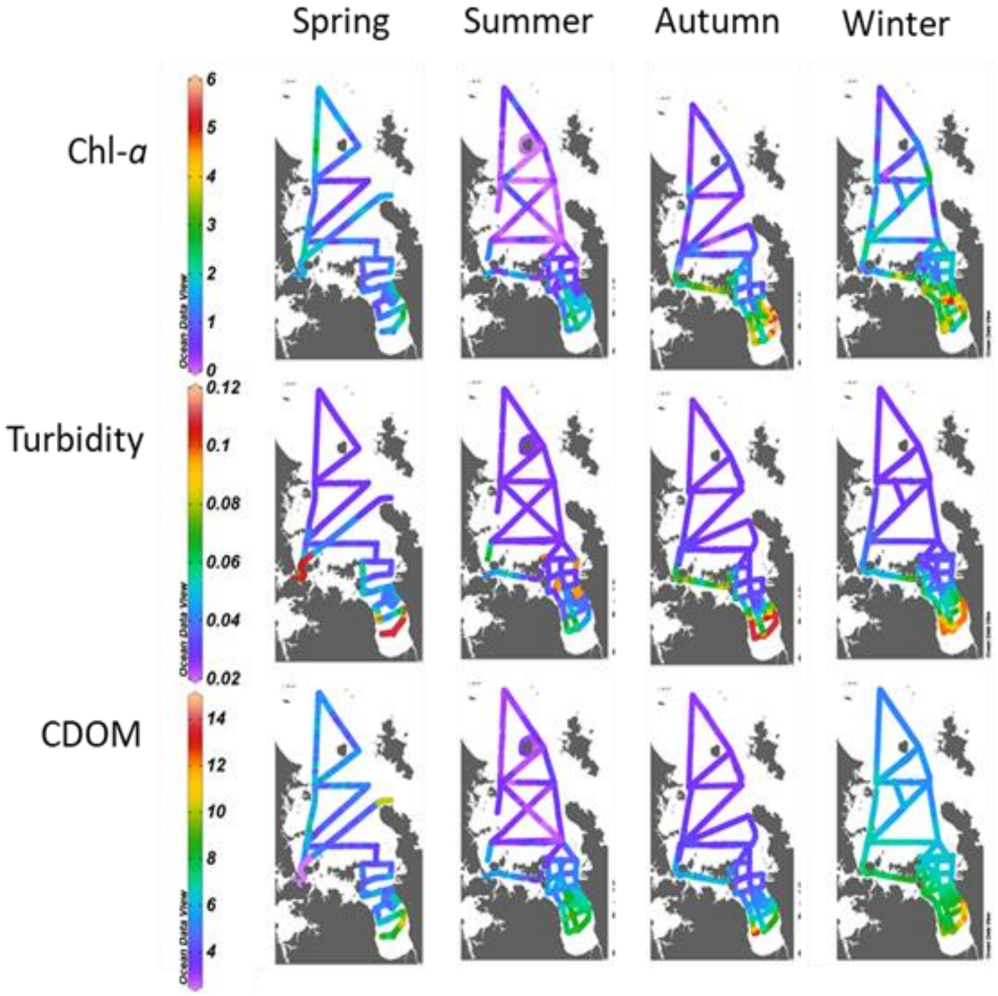


Figure 3-7 Seasonal and spatial gradients across Hauraki Gulf and Firth of Thames of chlorophyll-a (chl-a: mg m^{-3}), turbidity (backscatter: m^{-1} sr^{-1}) and coloured dissolved organic matter (CDOM: ppm) from underway surveys in 2012-13

These findings showed how nutrient budgets can inform coastal management, by considering inventories of nutrient inputs, balances of oceanic and terrestrial nutrient loading, and potential for risk associated with biogeochemical responses associated with NEM and denitrification. They provided evidence that the underlying causes of the expression of decreased O_2 and pH are rooted in the NEM dynamics of the Hauraki / Firth system.

The biogeochemical factors driving O_2 and carbonate states were informed by further sampling during the underway surveys in 2012-13, which included chlorophyll-*a*, turbidity and coloured dissolved organic matter (CDOM) across the region (Figure 3-7). These parameters indicate organic matter concentrations and all three increased shoreward, mirroring the decreasing shoreward gradients of salinity and pH (Figure 2-5) and showing close association of organic matter concentration with riverine input. This organic matter is both imported directly in river waters and generated *in situ* by primary production within the Firth.

As part of the CARIM project, another spatial survey of the Firth was conducted in April 2018; with mapping of near-surface (2 m) properties carried out while the vessel traversed the region (Figure 17). The results showed:

- Temperature was intermediate between autumn and winter temperatures of 2013 (compare Figure 2-5 and Figure 3-8);
- Salinity was quite low (Figure 3-8) in the inner Firth indicating high recent river inputs;
- pH was high (>8.1) over much of the Firth, especially in a zone in the eastern, inner Firth where pH as high as 8.4 was measured (Figure 3-8). The inner Firth pH values were uniformly greater than those measured in autumn or winter of 2013 (cf. Figure 2-5) Chlorophyll-*a* was high (>5 mg m^{-3}) over much of the inner Firth, especially in the zone of high pH in the eastern Firth where values up to 20 mg m^{-3} were measured (Figure 3-8), much greater than that of autumn or winter 2013 (cf. Figure 2-5).

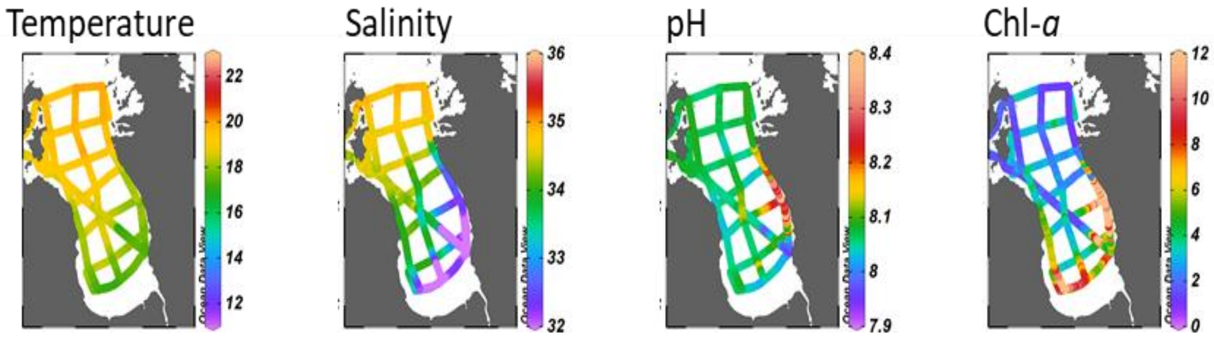


Figure 3-8 Spatial gradients across Firth of Thames of near-surface temperature (°C), salinity, pH and chlorophyll-a (mg m^{-3}) during the CARIM spatial survey of April 2018. Note the scale change for pH and chlorophyll-*a* relative to Figure 2-5.

As shown in (Figure 2-5**)**, pH levels are seasonally variable and tend to increase between autumn and winter. This is accompanied by seasonal breakdown of physical stratification, and temperature and salinity vertical profiles acquired during the April 2018 spatial survey showed this had occurred prior to this survey (not shown).

An additional feature of the April 2018 record was the very high pH seen in the inner, eastern Firth (~8.4), associated with very high chlorophyll-*a* (>20 mg m^{-3}). It is likely that this phytoplankton bloom had drawn pCO_2 down to low levels, increasing pH substantially. As will be shown below, pH in the inner Firth fluctuates at frequencies higher than seasonal, which could be driven by short-term blooms such as that sampled in the April 2018 survey.

Recent (2015-2017) NIWA mooring-acquired, coincident gross primary production (GPP), pH, O_2 and physical data recorded at high frequencies (Figure 18) at the inner and outer NIWA Firth monitoring sites (Figure 2-2) showed:

- Greater GPP in the inner Firth than the outer Firth, indicating its proximity to riverine and regenerated nutrient supply;
- Strong pH depression in autumn to early winter in the inner Firth (≤ 7.7), and more muted depression in the outer Firth. These patterns were consistent with the patterns in the four-season surveys (Figure 2-5) but, in the case of the inner Firth, exhibited more extreme pH values;
- Greater pH variability in the inner than outer Firth, including brief, low pH events in winter;
- More intense O_2 drawdown at the inner Firth than outer Firth, even though the water column was much shallower and less density-stratified. This indicated stronger respiratory activity (organic matter supply and microbial activity) at the inner relative to the outer site;
- A broad, seasonal-scale association of pH depression with DO depression at both sites, but with apparent de-coupling also, at higher frequencies. This is worthy of more in-depth examination in future work.

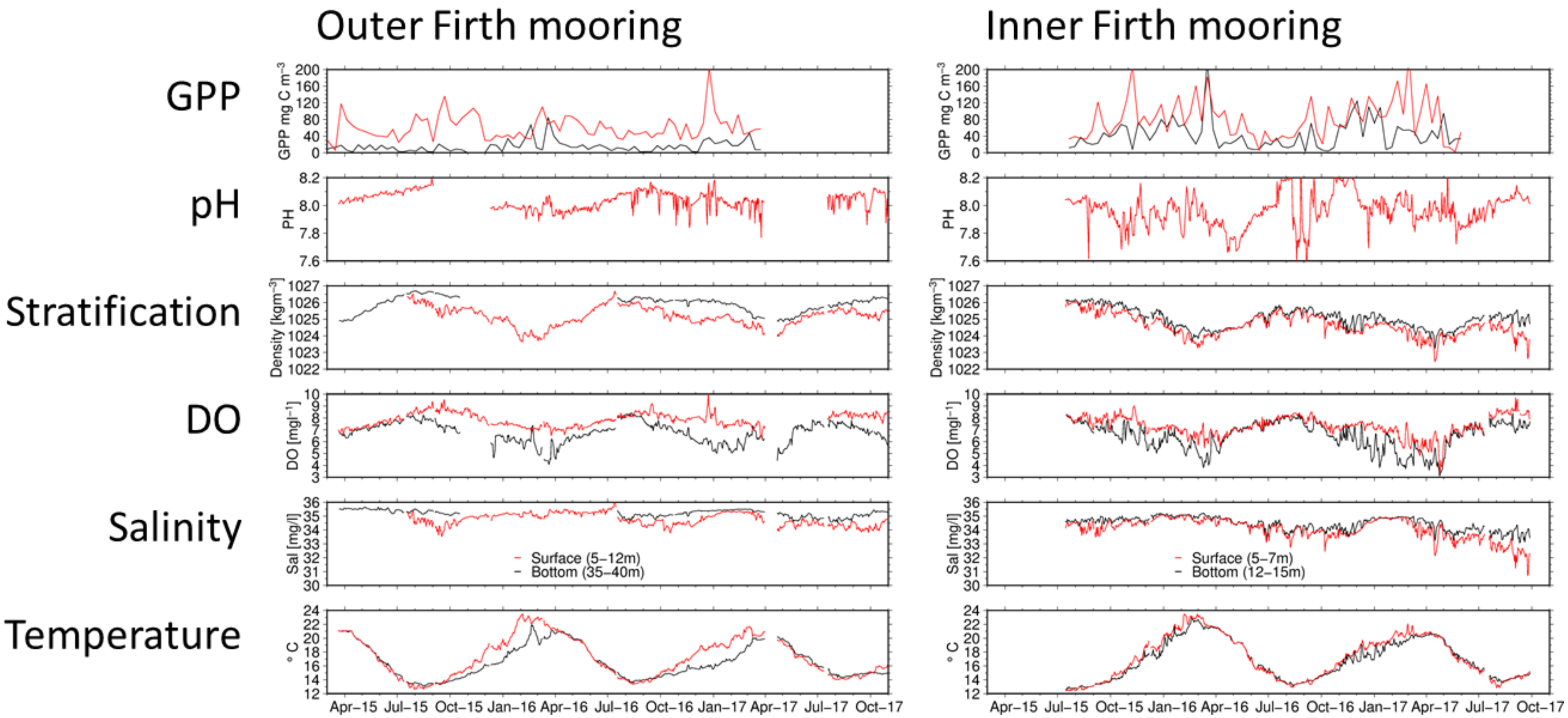


Figure 3-9 Biophysical mooring results from the NIWA Firth monitoring sites at Outer (40 m) and Inner (15 m) Firth locations (see Figure 2-2) from April 2015 to October 2017. The moorings supported Seabird microcat temperature/salinity/O_2 sensors at near-surface and near-bottom water column depths and SeaFET pH sensors at upper water column depth. GPP: gross primary production (mg C m^{-3} d^{-1}) from diel O_2 variation, Stratification: seawater density (kg m^{-3}) showing difference in density between upper and lower water column sensors, DO: dissolved O_2 (mg L^{-1}). SeaFET records were calibrated using DIC and alkalinity bottle samples collected at start and end of each 3-monthly deployment. Gaps in the microcat and SeaFET records were due to instrument failures.

As part of the CARIM project, the University of Auckland deployed a SeaFET instrument at 5m depth near an active mussel farm in the western Firth of Thames (blue circle, Figure 2-2) from June 2016 to March 2017, and also September 2017 to February 2018. Results, illustrated in Figure 3-10, showed:

- Substantial pH variation over seasons (range 8.16-7.74 in 2016-2017)
- Low pH in winter 2016 and summer 2017 and 2018, and elevated pH during spring. These patterns were similar to those at the NIWA inner Firth mooring (Figure 3-9) which was ~ 11 km to the ESE (Figure 2-2);
- Periods of variable pH during all seasons, again like the NIWA inner Firth mooring (Figure 3-9);
- Aragonite saturation state (Ω_{Ar}) approached 1.0 with a minimum of 0.74 briefly in the late summer of 2017 (Figure 3-10b). This is of direct relevance to the mussel industry (see section 4).
- Significant pH variability on diel timescales, with pH varying by > 0.1 over a 6-hour period during December 2016, but with lower variability (<0.025), during periods of elevated pH, as in November 2016 (Figure 3-11).

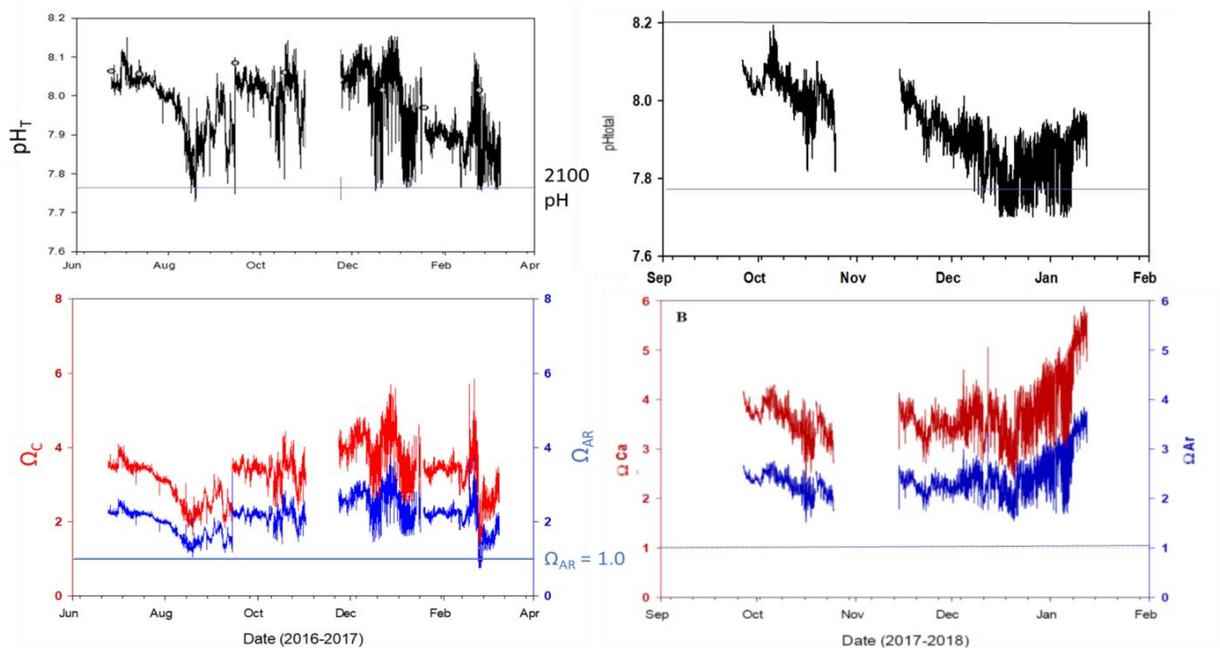


Figure 3-10 Mooring results from the University of Auckland pH monitoring site in the western Firth (Figure 2-2) during March-July 2016 (a,b) and September 2017- February 2018 (A,B), with pH_T data in (a) and (A) and saturation state for calcite (Ω_{Ca} red, left axis) and aragonite (Ω_{Ar} blue, right axis) in (b) and (B). Gaps in the pH record were due to biofouling (reproduced from Frost, 2019).

Low pH events in the University of Auckland data had a bimodal distribution with temperature (Figure 3-10; Frost, 2019), suggesting shifting influence of drivers of pH with season. At temperatures >16°C there was an evident diel cycle in pH (not shown), with lowest pH during night-time and elevated pH during day-time, indicating that biotic processes were driving pH change during the warmer months (higher pH during the day due to algal photosynthesis, and lower pH during the night due to respiration). These likely reflect background primary production/respiration augmented by respiration from the large mussel biomass on the farms. In winter, at temperatures < 16°C, low pH events occurred throughout the day suggesting less influence by primary production with respiration dominant. This was consistent with the marked decline in GPP in winter at the NIWA inner Firth site (Figure 3-10).

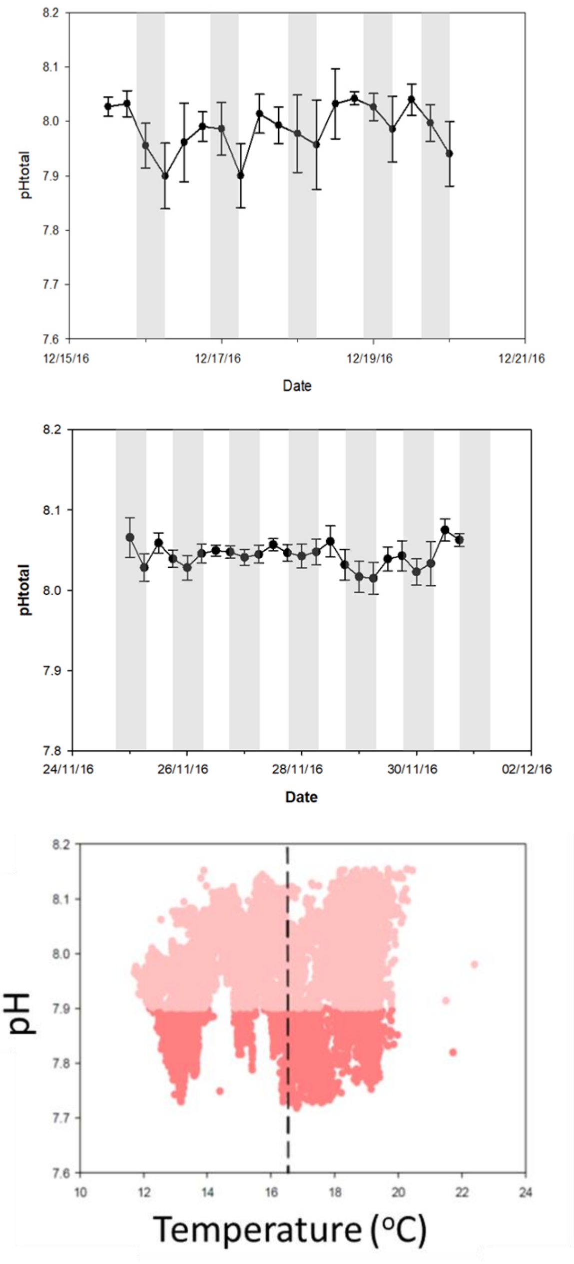


Figure 3-11. Diel variation in pH during a period of lower pH (December 2016, upper plot) and elevated pH (November 2016, middle plot), recorded by the University of Auckland SeaFET mooring on a mussel farm in the western Firth. The lower plot shows pH as a function of temperature from March-July 2016, with the darker points indicating low pH events (> 1 SD below mean pH) (Frost, 2019).

Other NIWA data showed the effects of interannual variation in physical and biological conditions, on O_2 and associated carbonate conditions. Depth-resolved data (Figure 3-12) collected on the transect from the inner Firth to the outer Hauraki Gulf (Figure 2-2) during the autumn surveys in 2010 and 2013 showed:

- DO depletion was variable between the two years with depletion in the lower water column greater in 2010 than 2013. This matched the 2010 and 2013 patterns seen in the moored DO record at the NIWA Firth monitoring site (Figure 2-3);
- The more intense DO depletion in 2010 was matched by the more intense carbonate features (high pCO_2, low pH) in 2010 relative to 2013 in the Firth (Figure 2-5);
- Density stratification was stronger in autumn 2010 than 2013, which corresponded with the more intense DO depletion in the lower water column and showed the influence of physical stratification on O_2 dynamics;
- The low DO feature of autumn 2010 occupied a large area of the Firth and inner Hauraki Gulf near-seabed environment;
- The more intense autumn DO minimum in 2010 than 2013 was also associated with a stronger deep phytoplankton (chlorophyll-*a*) maximum. The breakdown product of chlorophyll-*a*, phaeopigment, showed similar patterns, indicating greater respiration of organic matter derived from phytoplankton in 2010.

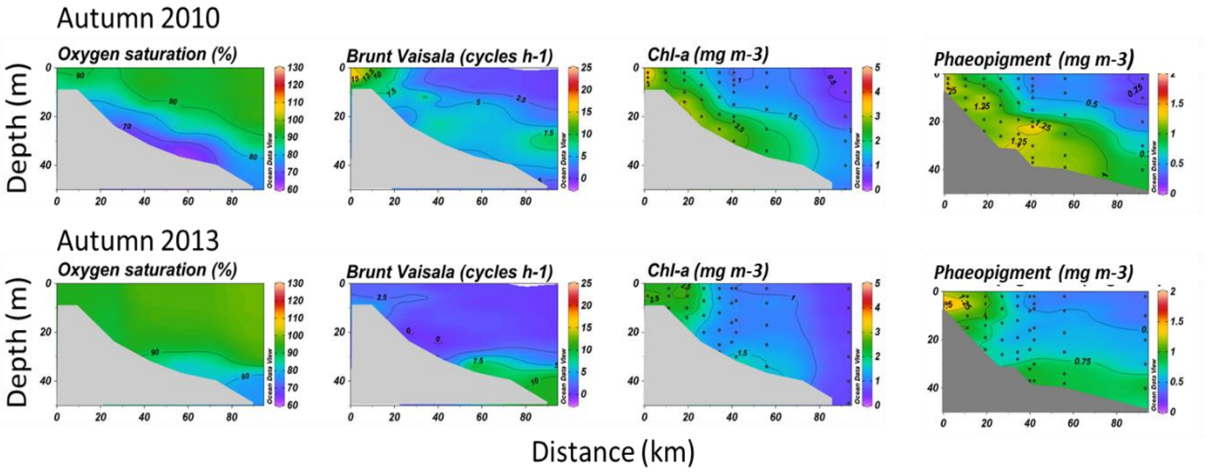


Figure 3-12 Oxygen, density stratification and phytoplankton conditions in Firth of Thames and Hauraki Gulf in autumn 2010 and 2013, at stations on the dashed line in Figure 2-2**.** Parameters shown from the left are O_2 (% surface saturation), water column vertical stratification (Brunt-Väisälä frequency: higher values mean more strongly stratified), chlorophyll-*a* (mg m^{-3}) and phaeopigment (chlorophyll-*a* breakdown product: mg m^{-3}).

3.1 Relationships between nutrients, production and acidification

The Firth underway carbonate surveys (Figure 2-5) and moored pH data (Figure 3-9) revealed strong temporal and spatial correlations of pCO_2 and pH with other indices including: proximity to riverine nutrient loading, higher concentrations of organic matter, accentuated primary production and O_2 consumption in the water column. The association of high nutrient loading to the Firth (Figure 3-2), the dominance of this loading with respect to oceanic supply (Figure 3-3), and the propensity of the

Firth to exhibit heterotrophic NEM (Figure 3-4) show that these features are pivotal in expression of hypoxia and acidification.

The mechanism by which this expression occurs was indicated by the seasonality of the primary production cycle in the Hauraki Gulf/Firth system (Figure 3-4). Gross primary production (GPP) measured at the NIWA inner and outer Firth monitoring sites increases in spring and is maximal in summer (Chang et al. 2003; Gall and Zeldis 2011; Zeldis and Willis 2014), but with onset of summer water column stratification (Figure 2-3) and (Figure 3-6) and decreased river loads (Figure 3-2), nutrients are reduced at rates faster than their re-supply. By autumn and early winter, nutrient and light limitation ensue, primary production slows, and senescence (respiration) of primary biomass increases, as reflected in the recurrent O_2 depletion seen in autumn (Figure 2-3, Figure 2-4, Figure 3-4). Thus, while production and respiration are continuous processes the year around, their seasonal balance changes, becoming increasingly heterotrophic later in the production season. The intensity of O_2 drawdown was correlated with physical density stratification and the concentrations of phaeopigment near the seabed (Figure 3-12), consistent with the interpretation that it is driven by respiration of senescent primary biomass and is metabolic in origin.

Higher CO_2 production and lower pH in the inner Firth than further seaward was consistent with benthic O_2 uptake measurements which showed the inner Firth sustains net-heterotrophy about twice that of the outer Firth (Zeldis et al. 2015). In all seasons, $p\mathrm{CO}_2$ was higher and pH and saturation state were lower toward the inner Firth than outer Firth and Hauraki Gulf, reflecting this spatial pattern of heterotrophy. Saturation state was also lower nearer the seabed with implications for benthic animals which, in addition to experiencing greater hypoxia, could also be exposed to more extreme pH effects (see Section 7).

In the outer Firth, ecosystem metabolism interacts with water column density stratification (Figure 3-9) to condition the expression of O_2 and carbonate effects, similar to controls of seasonal hypoxia and acidification in Chesapeake Bay (eastern USA; (Hagy et al. 2004; Scully 2016; Shen et al. 2019). Although O_2 depression and acidification are more severe in Chesapeake Bay than in the Firth, the two systems probably share this mechanism. Further seaward (outer Hauraki Gulf), the lower seasonal O_2 originates from a mixture of local O_2 consumption and upwelled low O_2 waters advected from offshore. This upwelled water appears in the outer Gulf in spring and early summer forming a reduced-O_2, near-bed layer (Zeldis 2004). Upwelling frequency declines markedly in the region after December, after which O_2 depletion is driven more by local remineralisation than by advection (Zeldis 2004). O_2 utilisation in the outer Firth at this time was approximately four times that of the outer Hauraki Gulf, indicating that the effects are local to the Firth. The formation of hypoxic, low pH water in the inner Firth occurs with only weak vertical stratification present (Figure 3-9), indicating the intense heterotrophic metabolism present there.

It is unlikely that Firth pH is currently strongly affected by anthropogenic CO_2 injected from the atmosphere (OA), as it is exhibiting greater pH depression than the open ocean, and its offshore waters (Hauraki shelf) currently have pH close to pre-industrial, oceanic levels (Figure 2-5). As noted previously, large alkalinity effects from freshwater runoff (Duarte et al. 2013) were also unlikely, as maximum depression of Firth pH occurred in autumn when river flows were at their annual minima. Atmospheric deposition of N can also influence eutrophication in some regions (Da et al. 2018) but calculations by Zeldis and Swaney (2018) indicate that atmospheric deposition of N to the Firth, while substantial, is nevertheless relatively minor compared to river inputs. These points favour the proposition that the drivers of the Firth carbonate system are derived predominately from inorganic riverine nutrient inputs and subsequent metabolic processing within the Firth primary production system, rather than by oceanographic inputs, freshwater alkalinity or atmospheric deposition effects.

The time series for carbonate sampling in the Hauraki / Firth region are relatively brief. However, the observation that the Firth's net-heterotrophy is driven strongly by nutrient loading, and that this loading has increased historically with land development (Snelder et al. 2017), leads to the conclusion that the 'carbonate climate' in the Firth has been altered over decades. This would apply also to the O_2 climate. For the developed catchments of the Firth (the Hauraki Plains), point and diffuse (agricultural) human sources now contribute about 8% and 70%, respectively, of total N load to its major rivers, with 'natural' sources the remainder (Vant 2013). Thus, while the Firth is now heavily catchment N-loaded, prior to land-use intensification ocean-side loading would likely have contributed a greater percentage to a much lower overall nutrient load. This is consistent with other studies showing dominant effects of agricultural intensification on nutrient export from New Zealand landscapes (Cooper and Thomsen 1988; Quinn and Stroud 2002; Snelder et al. 2017; Plew et al. 2018). Intensification has greatly increased nutrient leaching rates to the major Hauraki Plains rivers (Waihou and Piako Rivers), making them among the most heavily N-loaded rivers in NZ (Snelder et al. 2017).

The findings that *ca*. 78% of the loading from the Firth's catchment (Hauraki Plains) is anthropogenic, combined with the heavy catchment-side N loading shown by the budgeting of Zeldis and Swaney (2018), leads to the conclusion that land-use intensification has substantially increased the N loads to the Firth (estimated as 66% for DIN (ibid.). This estimate was consistent with the estimated anthropogenic increase estimated by Snelder et al. (2017) of 82% for total N of Waikato region rivers. A further conclusion to be drawn from the increased N loading is that prior to intensification the primary production rate in the Firth was probably substantially lower than in the present day. The findings of declining denitrification efficiency coincident with N and phytoplankton enrichment of the Firth over 2001 – 2014 (Figure 3-5, Figure 3-6) indicate that cumulative effects of the high terrestrial nutrient loading the Firth has received over recent decades may now be operating in the Firth. This is a concern for managers of Hauraki Gulf/Firth of Thames regional marine resources (Kelly et al. 2017). Nutrient addition enhances eutrophication both directly, via nitrogen supply for phytoplankton growth and indirectly by suppression of nitrogen loss via denitrification. Consequently, further enrichment of the Firth should be avoided, because of its positive effect on eutrophication and potential negative feedback on denitrification.

The trends over the last two decades of declining water quality in the Firth are probably adding to the 'shifted baseline' that has occurred in the Firth over decades, associated with the historical changes in nutrient loading rate and source. The responses are expressed in seasonal O_2 depletion and low pH. Such shifts to alternative states can occur in response to extreme events. Reactions to intense O_2 minimum events have been documented in Danish Straits and Chesapeake Bay (Kemp et al. (2005); Conley et al. (2009). Conceivably, this could have occurred in the Firth, with persistently lessened water quality (in terms of increased nutrients and phytoplankton) documented here, following large O_2 minimum events in autumn 2005 (<40% saturation), and 2007 (40-60% saturation) that lasted about 4 months Figure 2-3, Figure 2-4). Overseas examples (Chesapeake Bay, Danish Strait estuaries, Gulf of Mexico) show that relatively sudden events have led to systemic changes in oxygen conditions (Conley et al. 2009). In the case of Danish Straits, an identified change point occurred following a particularly strong hypoxic event. These are examples of non-linear responses to pressures that can resist return to the original state, upon remediation (hysteresis: Muradian (2001).

Catchment nutrient load reduction would be expected to reduce organic loading within the Firth system. However, it is not yet known what load reduction this would require. It is possible that changes to the internal N processing (denitrification efficiency) within the Firth is driving water quality change. If this is the case, remediation through load reduction may not be immediate. Understanding the cause of N enrichment over the last decade is important for assessing future risk, and capacity for remediation – does it represent a shift in the ecosystem's capacity to assimilate nitrogen? – and requires further research. To understand responses to nutrient load change, there is currently considerable effort underway by NIWA in developing dynamic biogeochemical Regional Ocean Modelling System (ROMS) models of the Firth (see Section 4 below). Examples of how ROMS-based dynamic models have been used for evaluating nutrient load reductions for control of hypoxia and acidification in Chesapeake Bay are those of Irby and Friedrichs (2019) and Shen et al. (2019). Shen et al. (2019) showed a decrease of 'acid water volume' in Chesapeake Bay of 25% with a modelled 50% load reduction. However, that study also showed that in the shallow area of Chesapeake Bay, pH increased with modelled load increase. The response of pH to high algal production seen in the CARIM spatial survey (Figure 17: high pH with high algal production) similarly indicates that pH responses may not decrease linearly with nutrient load reductions, possibly depending on season and stratification condition. Zhang et al. (2018) described trends in water quality in Chesapeake Bay and concluded that "… clear, significant linkages between [O_2 criteria] attainment status [and] management actions (e.g., reduction of nutrient loads), internal hydrodynamic characteristics, trophic interactions, and climatic and hydrological variability, remain elusive".

3.2 pH projections for the Firth of Thames

The 2015-2017 pH time series collected at the NIWA Outer Firth monitoring site (Figure 3-9) provided a present-day reference upon which to derive pH projections for the Firth of Thames (Figure 3-13), using the different RCPs (see Section 1.3). Comparison of these pH projections with those for NZ open ocean waters (Figure 1-3) shows:

- a lower initial present-day mean pH (8.05 vs ~8.09)
- greater interannual pH variability (-0.1 vs -0.05)
- later divergence between RCP projections (2050 vs 2035) for the Firth of Thames
- lower projected 2050 and 2100 pH under all RCPs for the Firth of Thames, with a projected pH range of 7.69-7.74 by 2100 under RCP8.5.

It should be noted that this projection only accounts for changes in atmospheric CO_2 and does not include changes in nutrient-driven productivity and respiration, which have been shown to be critical factors determining pH in the Firth of Thames in the above analysis. One observation here is that, regardless of any change in nutrients, the respiratory removal of oxygen and production of CO_2 will increase in response to warmer temperatures, and so the projections in Figure 22 represent an underestimate of future pH in the Firth of Thames.

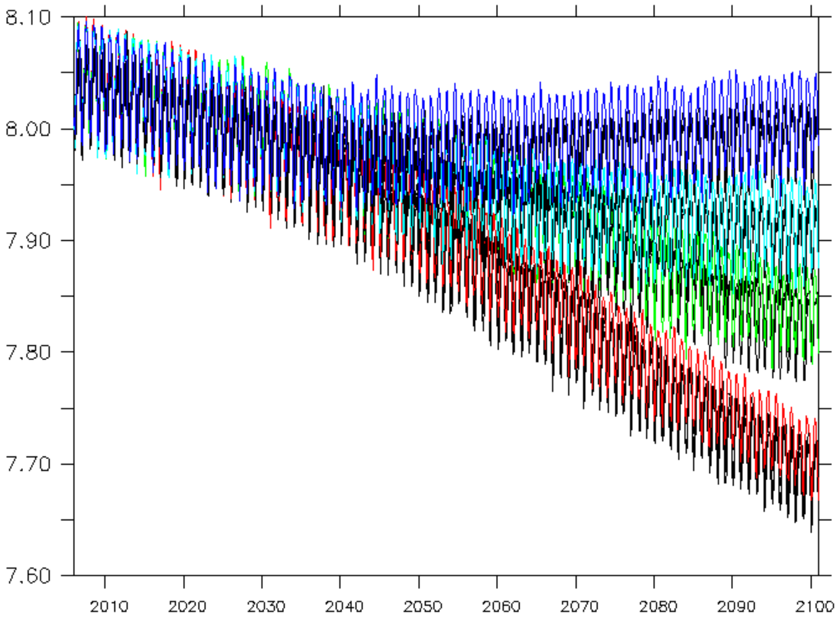


Figure 3-13 Projected surface pH for the Firth of Thames. For each RCP, the black line indicates the mean of six ESMs and the coloured line (Blue-RCP2.6, Cyan-RCP4.5, Green-RCP6.0, Red-RCP8.5) the projection generated using the GFDL-ESMG2 Earth System Model. (See Law et al, 2018b).

4 The relationships between acidification and aquaculture

The CARIM programme has taken an integrated life-cycle approach to understand the potential vulnerability of NZ green lipped mussels (*Perna canaliculus*) and pāua (*Haliotis iris*) to increasing ocean acidification as part of Research Aim 4 (hereafter 'RA'; See Section 5). The same project is also investigating vulnerability of larval snapper (*Chrysophrys auratus*).

Green lipped mussels and pāua were targeted in CARIM due to their considerable economic, ecological and cultural value to New Zealanders, and their potential vulnerability to OA. Green lipped mussel is NZ's most valuable aquaculture species, where they are marketed as Greenshell^{TM} Mussels. Existing mussel farms in the Firth of Thames are potentially at risk when carbonate saturation becomes affected, as outlined above in Section 2 or 3. Pāua are a predominantly wild-caught fishery, although hatchery facilities exist. Pāua in the WRC region are managed as part of the Northland/Auckland NZ quota management area, PAU1, under New Zealand's quota management system.

Both green lipped mussels and pāua are important sentinel species which may signal environmental change, given their reliance upon phytoplankton or macroalgae, respectively, for food. Shells of green lipped mussels are constructed from aragonite, the form of calcium carbonate that is most vulnerable to acidification, while pāua shells have a combination of aragonite and the less soluble calcite.

OA is progressing at a rate far faster than the usual pace of evolution. A key component of the ongoing success of mussel and pāua may therefore be due to the presence of more resilient strains within the current gene pool (RA 5.1). The identification of different genetic strains with differing levels of OA resilience, also provides an exceptional opportunity to characterise the biological mechanisms supporting resilience (RA 5.2), including differences in the way food energy is used. This information can, in turn, be used to construct models predicting population-level changes that could be expected in the coming decades (RA 6.1).

4.1 Green lipped mussels

The implications of OA were explored in targeted laboratory trials, where mussels were exposed to near-future predicted seawater chemistry, based upon CARIM field measurements and model projections. All trials contrasted performance under present day (400 µatm CO_2, pH ~8) and projected end-of-century conditions (1100 µatm CO_2, pH 7.65); the effects of long-term exposure of adults was also examined under the additional scenario of projected mid-century conditions (850 µatm CO_2, pH 7.74). These controlled trials allowed a systematic examination of all life stages to identify potential bottlenecks (CARIM RA 4.1). The importance of OA across generations was examined, with a working hypothesis that parents exposed to increased acidification would correspondingly produce offspring with increased resilience (RA 4.2).

The following sections outline some key findings, based on preliminary data analysis. The interpretations should be regarded as provisional, subject to formal statistical analysis.

4.1.1 Methods

Most mussel trials were conducted at the Cawthron Aquaculture Park, Nelson, using aquaculture principles and animals supplied by SpatNZ and Sanford. Dissolved CO_2 (pCO_2) levels were controlled to achieve the designed water chemistry (pCO_2 and pH), while all other parameters were maintained at constant optimal levels (seawater temperatures of 16 - 18°C depending on life stage, and an abundant supply of microalgal food).

Adult mussels were sourced from a number of farm sites in the Pelorus Sound (Marlborough) and either used immediately for breeding (genetic studies) or suspended in conditioning tanks for up to 14 months (Figures 4-1), where they received either ambient (400 µatm pCO_2) or elevated pCO_2 seawater (OA, 850 or 1100 µatm). These adults were induced to spawn after 4 months acclimation to their pCO_2 environment. *In vitro* fertilization of the eggs and subsequent incubation of the embryo stages was then carried out at both 400 and 1100 µatm pCO_2 to establish whether the prior experience of the parents influenced the subsequent resilience of the young offspring. The embryo trials were conducted in 4mL tissue culture dish wells held in insulated incubators (Figure 4-1) receiving flowing CO_2-enriched air. The embryos were raised for 2 days to establish the proportion successfully developing to feeding 'D shaped' veliger larvae.

Fully pedigreed adult mussels from the Cawthron/SpatNZ selective breeding programme provided access to a broad range of genetically differentiated broodstock. A reciprocal breeding design was used to create 96 new full-sibling offspring families, which were again assessed through the vulnerable first 48 hours of life under both present day and end-of-century CO_2 conditions. Ten of the most differentiated (most resilient and most vulnerable) families were re-created 4 months later, using the same parents. These new families were raised through the feeding larval stages to settling juveniles, with growth and survival monitored over 9 months.

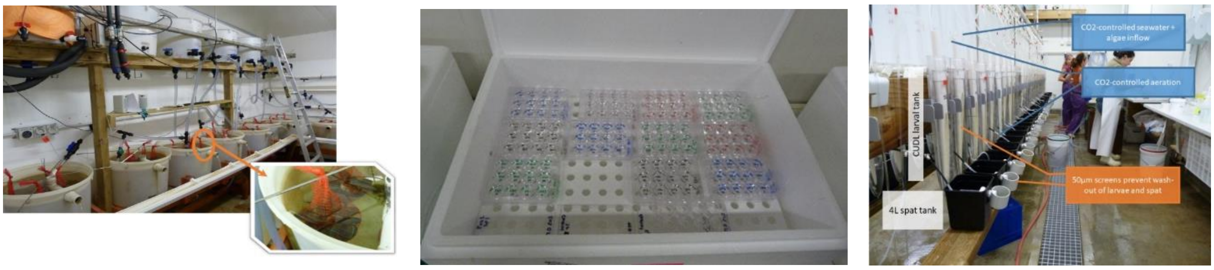


Figure 4-1 (a) Seawater system used for chronic acclimation of breeding adult mussels; (b) Tissue Culture Dish assay for assessment of embryo development to 48h post-fertilization; (c) array of combined larvae and juvenile (spat) rearing tanks operating in series.

4.1.2 Key findings (preliminary analysis)

As trials effectively examined all life stages and consistently exposed mussels to standardised present day (400 µatm pCO_2) or year 2100 conditions (1100 µatm pCO_2), it is possible to summarise their relative sensitivities to OA. Survival and shell growth under 1100 µatm pCO_2 is expressed as a percentage of corresponding performance under current ('control') conditions, in Figure 4-2. By considering the variability between replicate tanks (typically 6) we can define a 95% confidence band (bounded by dotted lines on Figure 4-2). If the 95% band includes 100% of the control, we conclude that there is no difference between performance under present day and elevated pCO_2 conditions. Using this simple approach, **growth and survival do not appear to diminish significantly under end of century pCO_2 conditions for most life stages**. As expected, however, the average growth and survival of the embryo stages is generally reduced under higher pCO_2, as was the average growth of older juveniles (4 – 6 months old; 6 of 8 assessed families showed significantly arrested growth, (Figure 4-2)(a). This is surprising as late juvenile mussels are generally regarded as representing a particularly resilient life stage; however, this stage has been recently implicated as vulnerable to 'Summer Mortality' and therefore warrants more focused attention. Importantly, the variability in response increased dramatically as the exposure period was extended, emphasising that the sensitivity of individual animals, families and tanks to chronic high pCO_2 is highly variable.

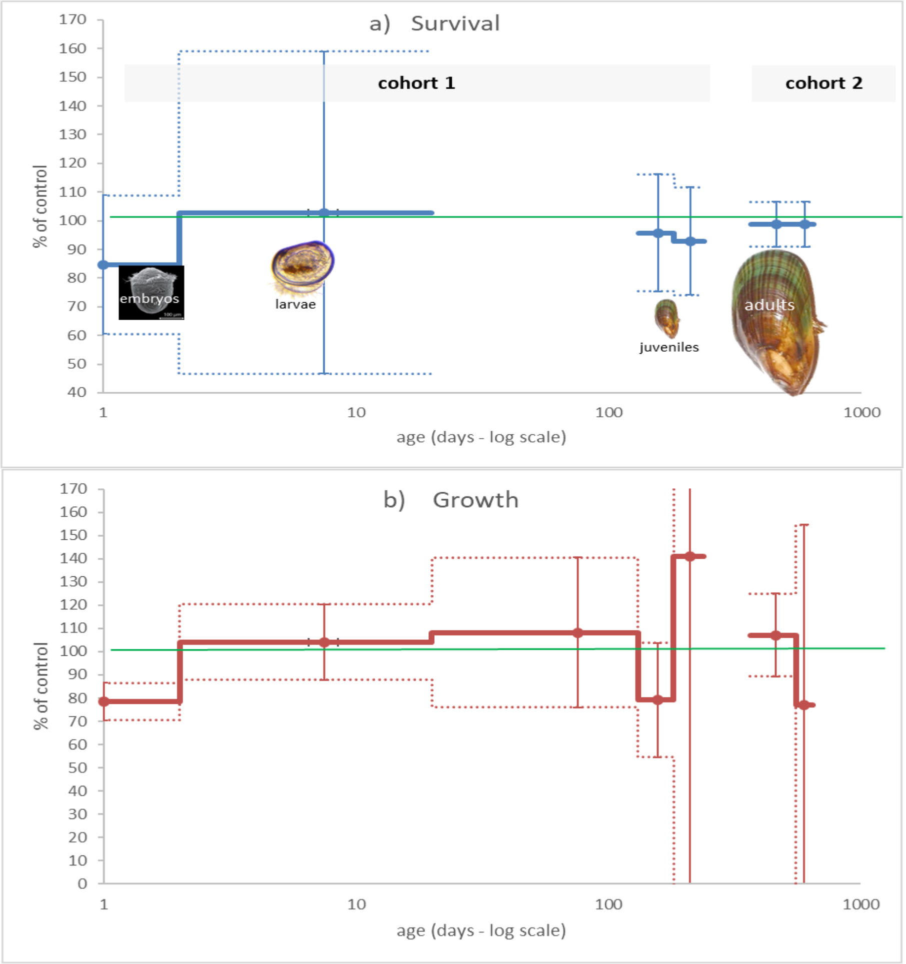


Figure 4-2 (a) **S**urvival and (b) growth of mussels reared in projected year 2100 seawater (1100 µatm pCO$_2$, pH 7.65) expressed as a % of mussels reared in present day "control" seawater (400 µatm pCO$_2$, pH ~8)

Two cohorts were tracked to capture the entire life cycle: Cohort 1 represents 10 separate families spawned in captivity and fertilised and grown at the target pH to late juvenile stage. Cohort 2 represents naïve adults introduced to their target pH at ~1-year old. Average performance for each life stage is represented as the heavy line and the 95% confidence region is bounded by a dotted line. Where variability between the 6 replicate tanks becomes substantial, the 95% confidence intervals may fall beyond the axis limits. The green 100% line represents the control animal's performance; this line remains within the 95% confidence region for all life stages, suggesting the absence of a significant impact upon growth or survival. Note that this graphic representation is only designed to provide a general indication of life stage vulnerability, in lieu of formal statistical analyses which will also consider the effects of breeding family.

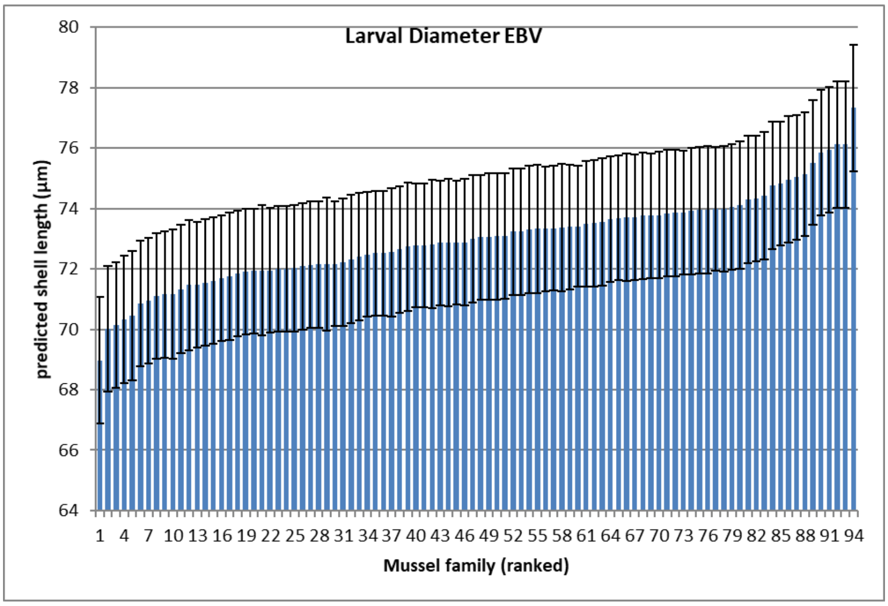
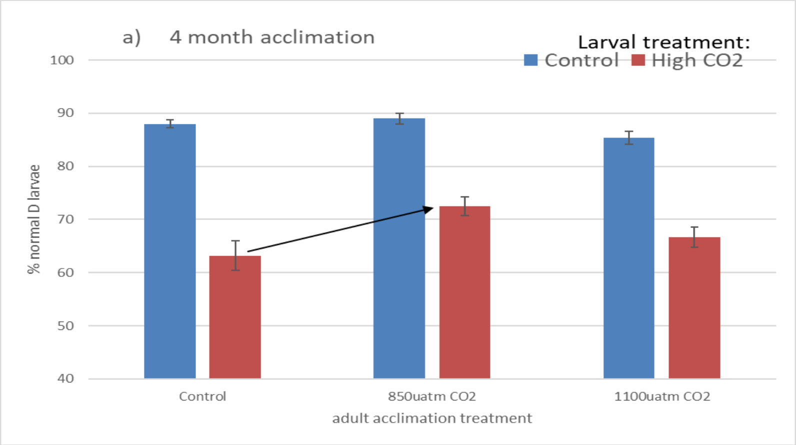


Figure 4-3 Net embryo performance determined by size of first shell formed 2 days after fertilization. Shell lengths for 96 full sibling families are shown, assessed in two separate trials exposing embryos to year 2100 *p*CO₂ levels (1100 µatm *p*CO₂, pH 7.65). Values represent mean estimated family performance (Estimated Breeding Values ± standard error) based on BLUP (best linear unbiased predictor) estimates.

Two key responses of 96 genetically diverse family embryos were analysed (ASReml™ software): net survival to 2 days old and the size of the first larval shell. Shell size of newly formed larvae is considered to be a key predictor of subsequent larval performance and recruitment to the juvenile population. Shell size varied significantly between families (Figure 4-3) and was found to be under significant genetic control, with a predicted heritability (h^2) of 0.33 (i.e. 1/3 of size variability is explained by genetics). While net survival during the first 2 days of life was not influenced by genetics (h^2 ~0), a strong maternal effect of 0.32 was detected. As these very early life stages are non-feeding, individuals are entirely dependent upon energy reserves from the egg. Mothers who produce well-resourced eggs may, therefore, significantly improve the chance of their offspring's initial survival; and parents with favourable genetics may potentially enhance the size and longer-term performance of their offspring under OA conditions.



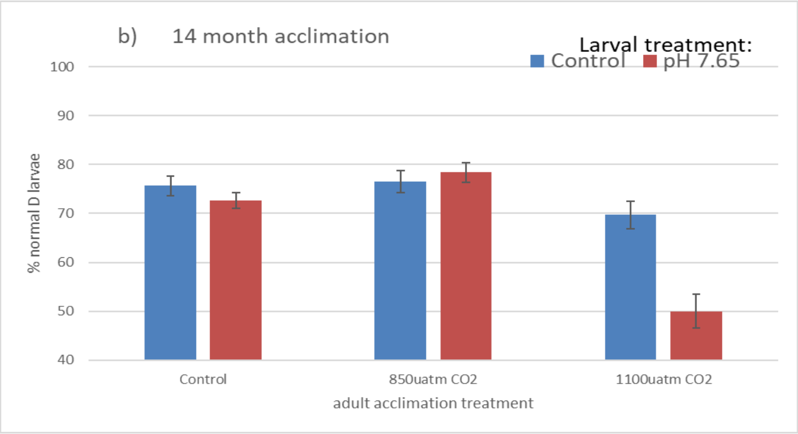


Figure 4-4 Performance of young offspring measured as the % of fertilized eggs successfully forming a 'D' veliger shell and transforming into a feeding larva (0-2 days old). Parents were exposed to present-day (400 µatm pCO2, pH ~8) mid-century (850 µatm pCO_2, pH 7.74) or year 2100-predicted seawater (1100 µatm pCO_2, pH 7.65) (x-axis), and the effects on their offspring assessed under present day and year 2100 conditions (coloured bars). This transgenerational assessment was repeated after 4 and 14 months of adult acclimation (a and b, respectively).

If the embryos of adults acclimated to present day CO_2 conditions subsequently experience elevated pCO_2 (1100 µatm), the normally high tank-based survival to the 2-day old larval D shell larval stage is reduced by about 1/3 (Figure 4-4 a) Control). However, if the adults have been acclimated to mid-century pCO_2 for 4 months (850 µatm), the impact of subsequent 1100 µatm CO_2 water upon the embryos is approximately halved (black arrow, Figure 4-4a). Most of the apparent benefit of pre-exposure of the parents is lost if they are also exposed to 1100 µatm pCO_2 before breeding (Figure 4-4 a) 1100 µatm). If the adult acclimation period is extended to 14 months, a different pattern emerges: the embryo offspring of adults exposed to present day or mid-century conditions do less well under 400 µatm incubation conditions but remain unaffected when exposed to elevated pCO_2 (Figure 4-4 b) 1100 µatm); conversely, in embryos of adults exposed to end of century conditions for 14 months, survival is compromised under 400 µatm and particularly under 1100 µatm pCO_2 (Figure 4-4 b) 1100 µatm). It is suspected that epigenetic mechanisms allow some conferral of resilience to offspring, but this effect may be overwhelmed by the high energetic maintenance costs associated with prolonged parent exposure to high pCO_2 conditions. Egg quality analyses are currently underway to corroborate this hypothesis.

4.1.3 Work in progress

The data interpretations described above are preliminary. Formal statistical analysis is currently being completed. A major contribution of the CARIM programme will be the exploration of the molecular responses of these mussels that enhance resilience to acidification. An integrated molecular description of the 10 highly differentiated families is underway and will be presented in the final CARIM report. The role of maternal investment in embryo performance is being characterised by assessment of egg composition.

4.1.4 Conclusions

Green lipped mussels show surprising resilience when exposed to elevated pCO_2 levels projected for the end of 2100. The survival, growth, feeding and metabolism of the 'average' individual do not appear to be significantly impacted. However, as with other bivalve species, the pre-shelled embryo stages represent the most vulnerable life stages. The vulnerability or resilience of individual embryos is influenced by genetic heritage and the experiences of the parents. It therefore seems likely that populations with genetically-advantaged embryos or those inhabiting food-rich regions (supporting greater maternal egg investment), will be favoured under rising pCO_2 conditions. It is also important to remember that the trials reported here deliberately isolated the effects of elevated CO_2. The interacting influences of other environmental factors, including rising temperatures and suspended solids, require specific further investigation.

The findings suggest that aquaculture managers should consider exploring both selective breeding and broodstock husbandry 'hardening' options to create seed stock predisposed to increased resilience to OA. The potential for OA to specifically impact upon growth performance of late stage juveniles (Figure 4-2b) may hint at an unexpected increased vulnerability, ; interestingly, recent anecdotal observations of increased summer mortality have also been made in this life stage, suggesting further investigation is warranted to establish if there are intrinsic physiological vulnerabilities associated with this life stage.

4.1.5 Priorities for future work

Prolonged exposure (>6 months) to elevated pCO_2 seawater appeared to dramatically increase the variability of individual responses. To fully appreciate the ecological implications of OA for whole populations, it would therefore be valuable to conduct extended, multi-generational exposure trials. Mussel farmers regularly express concerns regarding 'drop-off' of adult animals as they approach harvest size. Declining pH has been shown to influence byssal thread attachment of other mussel species by reducing adhesion strength and thread flexibility (O'Donnell et al, 2013; Zhao et al, 2017). It would therefore be valuable to consider the role of OA in exacerbating drop-off in *P. canaliculus*.

The green lipped mussel seems resilient to the effects of OA in isolation. Future work will need to consider the effects of OA in combination with other changing factors. Importantly the studies described here used aquaculture best practices, including stable, optimum temperature and, perhaps most importantly, excess food availability. Inevitably declining pH exerts a metabolic burden upon the mussel, which must increasingly divert energetic resources to maintain acid-base status and shell growth. Vulnerability to OA is therefore likely to be closely correlated with food availability. New Zealand is now experiencing marine heatwaves and increases in other anthropogenic stressors, which also need to be considered in combination with OA. If elevated temperatures decrease food availability or intake, then there could be deleterious effects: *P. canaliculus* meat yield has been shown to decrease in tandem with decreased environmental food supply in Pelorus Sound (Zeldis et al. 2008; Zeldis et al. 2013).

4.1.6 The influence of oxygen and pH on green lipped mussel and other calcifying organisms

This section considers the influence of both O_2 and pH-related stressors for green lipped mussel (*Perna canaliculus*) culture in the Firth, because the two are linked by their underlying biogeochemistry, as described in Sections 2 and 3. For O_2, meta-analyses have outlined a taxonomic progression of decreasing sensitivities to DO stress, progressing from fish → crustaceans→ annelids → bivalves (Gray et al. 2002; Vaquer-Sunyer and Duarte 2008). Fish and crustaceans had the highest (i.e. were most susceptible) lethal concentration thresholds, followed by bivalves. Sublethal thresholds, associated with factors such as reduced growth and reproduction, increased physiological stress, forced migration, reduction of suitable habitat, increased vulnerability to predation, and disruption of life-cycles were found to be highest for fish and crustacea, followed by molluscs (Figure 4-5)(b). Lethal times (after exposure to acute hypoxia) were shortest for crustacea and fish (order of few hours to a few days) while times for molluscs were order of a few hundred hours (Figure 4-5) (c).

A level of 4.6 mg L^{-1} (~50% saturation) was recommended by (Vaquer-Sunyer and Duarte 2008) as 'a precautionary limit to avoid catastrophic mortality events, except for the most sensitive (e.g. crab) species, and effectively preserve biodiversity'. Within New Zealand and based on this information it was recommended in the Horizon's Regional Council 'One Plan' that DO saturation standards proposed for its estuary management subzone should be 70% DO saturation (Zeldis 2009). A level of 80% saturation is recommended in Waikato Regional Council standards to avoid unsatisfactory conditions. As shown here, these standards for minimum O_2 levels are often breached, both at the outer Firth site in the lower water column and especially the inner Firth site.

The meta-analyses (Figure 4-5) (a) suggests that bivalve molluscs are among the more resilient invertebrates to low O_2. This is relevant to the observations of low O_2 near the Wilson Bay Areas A and B Marine Farm Zones. From the limited data available to date, O_2 conditions appear to be sufficient for bivalve farming, but there is no information on O_2 tolerances of cultured *P. canaliculus* adults. For larvae, data for *P. canaliculus* showed large negative effects on survival and settlement at 6 mg O_2 L^{-1} (~65% saturation), but spat survival or settlement were not affected (Alfaro 2005). Values as low as 4.2 mg L^{-1} (~45% saturation) have been measured at the inner Firth site at 15 m depth south of Area B and near the seabed at the outer Firth site to the north (Figure 3-9 and Figure 3-12), but near-surface values are higher (minimum values ~60% saturation). Also, given that settled spat, rather than larvae, are used in farming operations these results may indicate a reduced risk to operations, although effects on farmed spat should be further investigated.

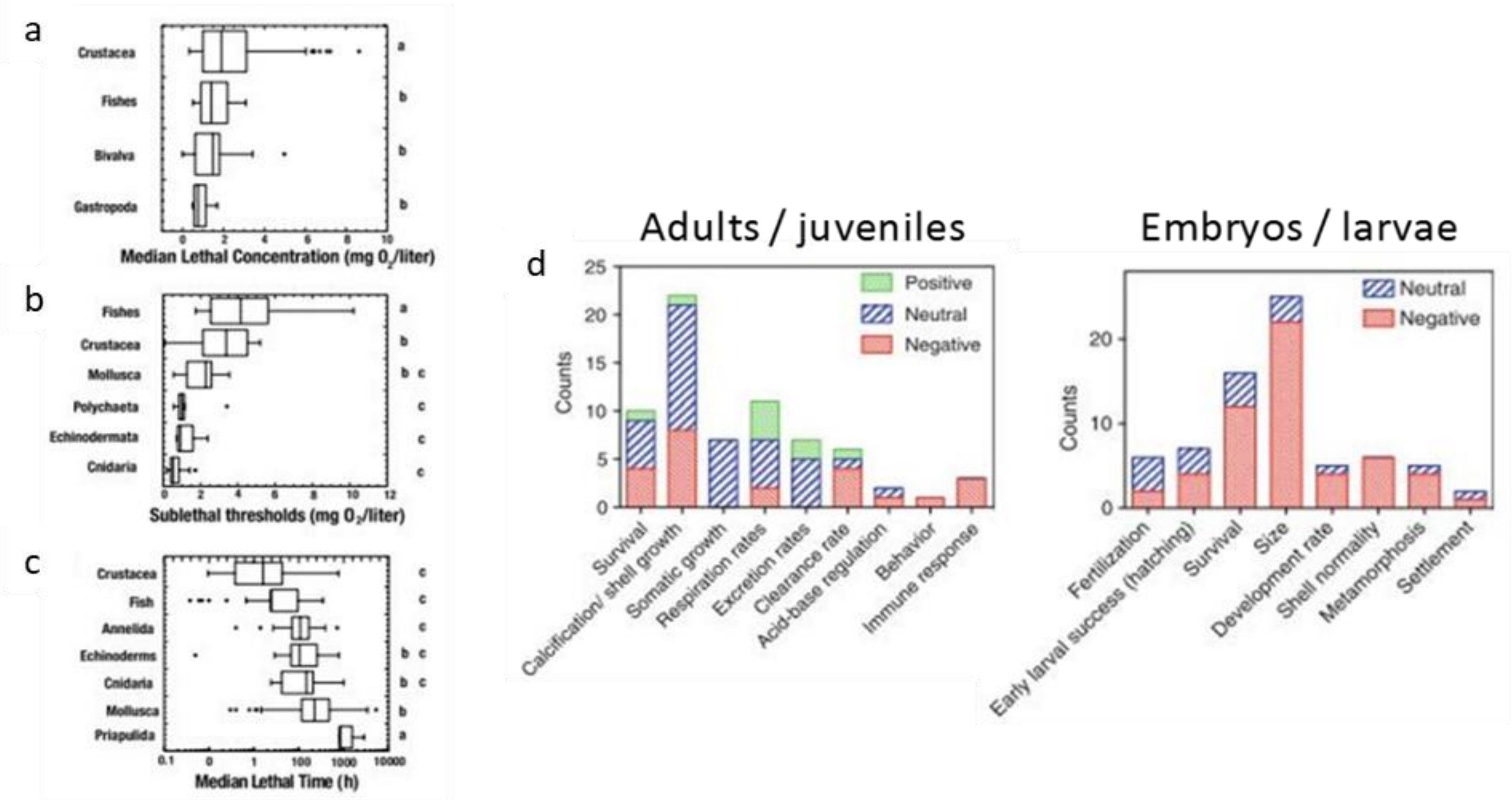


Figure 4-5 Box plots showing the distributions of oxygen thresholds among higher order taxa groups. (a) median lethal concentration (mg O_2 L^{-1}), (b) median sublethal concentration (mg O_2 L^{-1}), (c) median lethal time under acute hypoxia (2 mg O_2 L-1), adapted from Vaquer-Sunyer and Duarte (2008), (d) summary of the literature describing impacts of OA on marine-shelled molluscs for studies considering a pH decrease of up to 0.4. Results are given separately for adults and juveniles, and embryos and larvae. Adapted from Gazeau et al. (2013).

Published meta-analyses (Kroeker et al. 2010; Gazeau et al. 2013; Law et al. 2018) have found biological effects of acidification to be large and negative but with important variation across taxa, and also that larvae are generally more sensitive than adults (as confirmed above in Section 4.1.2). Work in New Zealand on molluscan responses to acidification have been reported at a shellfish-focussed workshop (Capson and Guinotte 2014) and by Law et al. (2018). *P. canaliculus* larvae underwent significant (nearly 50%) reductions in growth rate in pH = 7.7 vs 8.0 treatments (Erikson, 2010; (Law et al. 2018). Large effects on shell thickness were also demonstrated, though pH ranges were not detailed. Testing on adult (5-14-month-old) cockles (reburial), abalone (respiration), and flat oyster (survival), showed impairment at pH declines of 0.3–0.4 pH units and Ω_{Ar} states above 1. A relevant example to the Firth of Thames is oyster larval production in US Pacific Northwest hatcheries, which declined at Ω_{Ar} values below 2.0 (Capson and Guinotte 2014). For comparison with the Firth of Thames the latter exhibited minimal values during the seasonal surveys of 1.8 with a mean of 2.2-2 (Figure 2-5), and the University of Auckland deployments in the western Firth detected values approaching, and occasionally dropping below, 1.0 (Figure 3-11).

To summarise, the information regarding O_2 and carbonate-related stressor thresholds for cultured *P. canaliculus*, it is not known if these stressors have reached levels deleterious to aquaculture operations in the Firth, although, it is likely that such levels are being ‘approached’.

4.2 Pāua

4.2.1 Experimental investigations: influences of OA on different pāua life stages

Pāua responses to OA were investigated experimentally as part of the CARIM project investigations on iconic NZ fisheries species. The extent to which prolonged exposure of adult pāua broodstock to reduced pH would confer resilience to their offspring was examined in a 16-month long experiment conducted at NIWA’s Marine Environmental Manipulation Facility (MEMF, Figure 4-6a). Pāua were maintained in seawater pH/$p\text{CO}_2$ treatments with conditions representative of ambient conditions in Wellington Harbour (pH ~8.00/$p\text{CO}_2$ 400 μatm), and their responses compared to pāua from projected mid- and end-of century conditions (pH 7.85/$p\text{CO}_2$ 850 μatm, and pH 7.65/$p\text{CO}_2$ 1100 μatm, respectively). Temperature was allowed to vary naturally over this 16-month period, as per the conditions within Wellington Harbour source water, and ranged from ~10-19°C.

Broodstock were spawned after 3 and 16 months, and fertilisation success and subsequent larval development were evaluated. At each time point the larvae produced from the different broodstock treatments were reared in ambient, mid-century and end-century seawater. The aim was to determine the relative importance of parental history and seawater conditions during development, on larval survival, development and characteristics. Additionally, the responses of the adult broodstock themselves were evaluated after 16 months.

Figure 4-6 Juvenile pāua in experimental facility holding tanks (left) and NIWA's Marine Environmental Manipulation Facility (right). Images courtesy D. Allen, NIWA.

Results indicate that exposure of the broodstock to lower pH negatively affects spawning success, but after 16 months there was no significant effect on the pāua themselves. Survival, growth and condition were not significantly affected, nor were a number of proximate variables that could be important for taste and mouth feel (including total fat, carbohydrate, moisture, protein, energy content) of the flesh (V. Cummings (NIWA) unpublished data).

In contrast, fertilisation and early larval development of offspring produced by this broodstock was reduced after both 3 and 16 months, suggesting that preconditioning may not confer resilience – at least over the time frame tested. Strikingly, larval survival in pH 7.65 seawater was minimal, regardless of their parent history. For the 16-month spawning, we also evaluated subsequent settlement by competent larvae on encrusting coralline algae. Settlement by healthy larvae, originating from ambient pH parents and reared in ambient pH seawater, exhibited higher settlement than those with the same parental history but reared in reduced pH seawater (Espinel-Velasco et al., 2020).

A separate 4-month long experiment on juvenile pāua (24 mm average shell length) showed significant erosion (dissolution) and thinning of the outer shell surface under end of century pH levels (pH 7.66/pCO_2 1000 μatm), with potential implications to predator resistance (Cummings et al., 2019). Juvenile pāua were able to biomineralise aragonite and calcite shell layers under end-of-century pH conditions, and carbonate composition was not affected. There was some thickening of the nacre layer in the newly deposited shell with reduced pH. Most obvious was post-depositional alteration of the shell under lowered pH: the prismatic calcite layer was thinner, and there was greater etching of the external shell surface. While no effects on physiological condition, metabolism or growth were apparent in this experiment, a previous experiment in which seawater carbonate saturation states were lower, found significant negative effects on slightly smaller and slightly larger sized pāua (Cunningham et al. 2016), these different results may be attributable to the differences in carbonate saturation states experienced in the different studies (Cummings et al., 2019).

4.2.2 Pāua OA responses and broader evaluations of climate change impacts

Pāua is one of 32 NZ fisheries species being broadly assessed for their vulnerability to projected environmental change (resulting from climate change and ocean acidification). An MPI-funded synthesis has identified that ocean acidification, sedimentation and warming are all likely to affect various stages of the pāua life cycle and has identified and evaluated a number of management options for addressing and overcoming these threats in future. A final report on this work will be available in 2020 (Cummings et al. 2020).

4.3 Finfish

Finfish are generally considered to be resistant to OA because they do not have a carbonate shell, are good acid–base regulators, and mortality generally only occurs at very high pCO_2 levels. However, early fish life stages (eggs and larvae) have a higher surface area to volume ratio and may not have fully developed their regulatory mechanisms. The resulting burden that acid–base regulation imposes on energy consumption can therefore lead to negative effects for fish during these early life stages. Some studies focussing on early fish life stages have observed that end of century levels of OA can result in negative effects on growth and survival (Baumann et al. 2011, Miller et al. 2012). The most consistent direct impact of OA on fish, however, is on the behaviour and sensory systems of larvae. One of the first such studies observed that under elevated pCO_2 conditions clownfish reversed their normal olfactory response to predator odour, and actually demonstrated a preference for the odour of a common predator (Dixson et al. 2010). Since then a large amount of research has been conducted on behavioural and sensory system responses to elevated pCO_2, with recent results even showing olfactory impairment of adult European sea bass in response to elevated CO_2 (Porteus et al. 2018). Apart from olfaction, other behavioural and sensory systems that are influence by OA include vision, aggression, anxiety, cognition, swimming ability, auditory ability and escape response, which can potentially lead to reduced recruitment success (see Munday et al. 2012). It is important to note, however, that results are highly dependent on the particular species being investigated.

Very little is known about the effect of OA on New Zealand finfish, with the exception of kingfish and snapper. Both species are abundant and highly valued culturally and commercially within the Waikato Region, with kingfish being a species that also has aquaculture potential. Of particular relevance to the Waikato Region, the Firth of Thames (which already has seasonally elevated pCO_2 levels) is one of the main spawning areas for New Zealand's largest snapper population and was likely a historically important nursery area for juvenile fish (Zeldis and Francis 1998; Zeldis et al. 2005; Parsons et al. 2014).

For both kingfish and snapper, tank experiments were conducted to replicate the effect of end of century temperature and CO_2 levels on their larval stages (see Figure 5-1). Kingfish demonstrated a stronger response to temperature, with survival reduced and growth increased (Watson et al. 2018); conversely, elevated pCO_2 had little effect on survival and growth, but did have negative effects on swimming performance. For snapper, results are only preliminary, but similar tank experiments suggested that elevated CO_2 has little effect on survival, and elevated temperature has a positive effect on growth (P. Munday, James Cook University, unpublished data). Trials were also conducted on the fish reared in these tank experiments to assess oxygen physiology and critical swimming speed. Elevated CO_2 had a negative effect on both metabolic rate and swimming speed (S. McMahon, James Cook University, unpublished data). Results are now being prepared for publication.

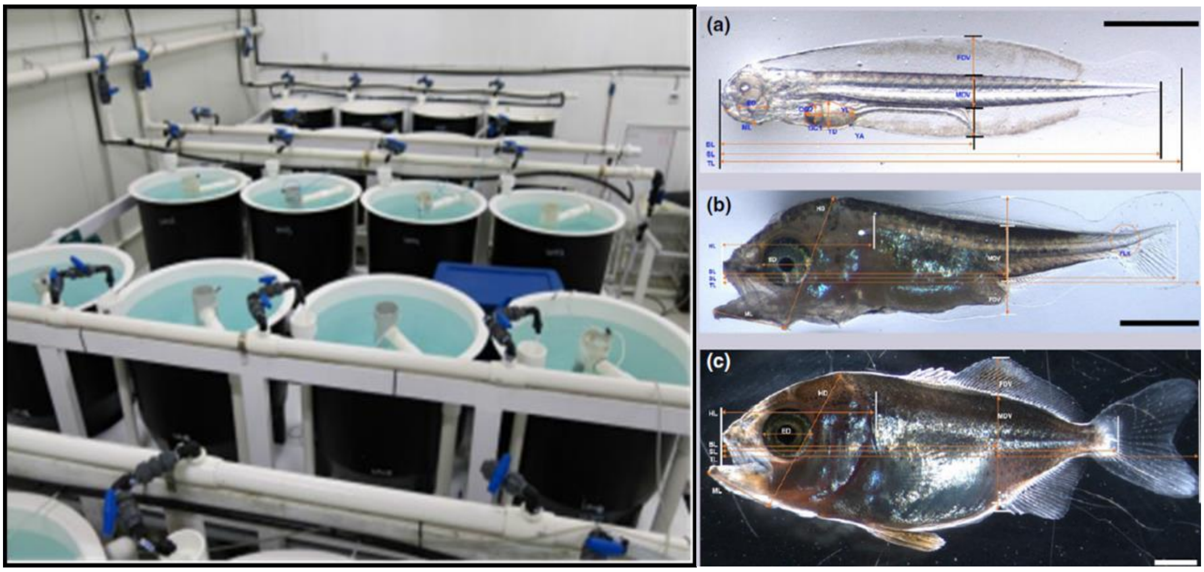


Figure 4-7 Yellowtail kingfish and snapper larvae testing tanks at NIWA Bream Bay (left hand image), images of larval yellowtail kingfish indicating the morphometric measurements used in impact assessments (right hand panel, a-c).

While the direct effects described above suggest that snapper and kingfish may be relatively tolerant to OA, they do not assess the indirect effects of OA. For example, reduced swimming performance and aerobic capacity may lead to higher rates of predation on larvae. Furthermore, these results do not provide any insight about the flow–on impact of OA on other ecosystem components (e.g. prey, nursery habitat structure) that fish are dependent on. Impacts of OA on the species composition and productivity of plankton communities, the base of productivity in marine ecosystems, are likely to be of particular importance (especially for fish larvae which feed directly on zooplankton).

Oxygen minima of varying intensities form in the lower 20 m of the water column at the outer Firth monitoring site, as the water column stratifies in summer and autumn each year (Figure 3-9). The minima are largely confined to the deeper water but, on occasion, penetrate the upper water column. This is relevant because of the proximity of the monitoring site to the zone designated for fish farming off Coromandel (~ 2 km to the ESE of the monitoring site) signifying that O_2 depletion events could affect the farm. Another relevant issue is that O_2 levels below fish pens near the seabed can become hypoxic because of organic matter deposition from the pens. The likelihood of this is highly dependent on the rate of supply of O_2, which, in turn, determines the rate of mineralisation of waste. This rate will be determined by the local deposition, and by the ambient field of O_2 in the wider environment. The frequent occurrence of O_2 minima below 6 mg L^{-1} in the lower 20 m of the water column at the Firth monitoring site (Figure 3-9) and the propensity for this condition to penetrate to shallower depths (Figure 3-9 and Figure 3-12) are of concern for management of prospective fish farming in the Firth and require further investigation. The O_2 minima extend well into the Firth, including waters adjacent to the large mussel farms at Wilson Bay Areas A and B, and into the inner Hauraki Gulf, largely congruent with the seaward extent of high phytoplankton densities.

5 The CARIM project

5.1 Project Structure

The MBIE-funded CARIM project is a four-year research programme (March 2016-February 2020), led by NIWA that aims to establish the rate and impacts of acidification, and inform measures to manage New Zealand coastal ecosystems. The project consists of a series of interconnected and nested Research Aims (RAs) between which information is exchanged to direct and maximise the research direction, outputs and outcomes (see Figure 5-2). Although CARIM is a national project it has three regional focal sites - the Firth of Thames, Nelson Bays (top of the South), and the East Otago Taiapure at Karitane. At each focal site, the variation in pH and associated parameters is established by regular monitoring (RA1), which subsequently informs long-term projections and experimental conditions in the other RAs. The three focal sites not only provide national coverage and represent different coastal morphotypes (a muddy embayment that experiences anthropogenic multiple pressures, a well-flushed inlet, and a relatively pristine rocky shore) but each site is a significant location for one or more of the three key NZ species studied by CARIM (RA4). The Firth of Thames is the prime CARIM focal site due to the existence of historical data, the ongoing maintenance of multisensor monitoring platforms and the recognition that this region is characterised by lower pH (see Sections 2 & 3 above). Consequently, additional activities for this region have focussed on the development of budgets and models to assist management (RA2).

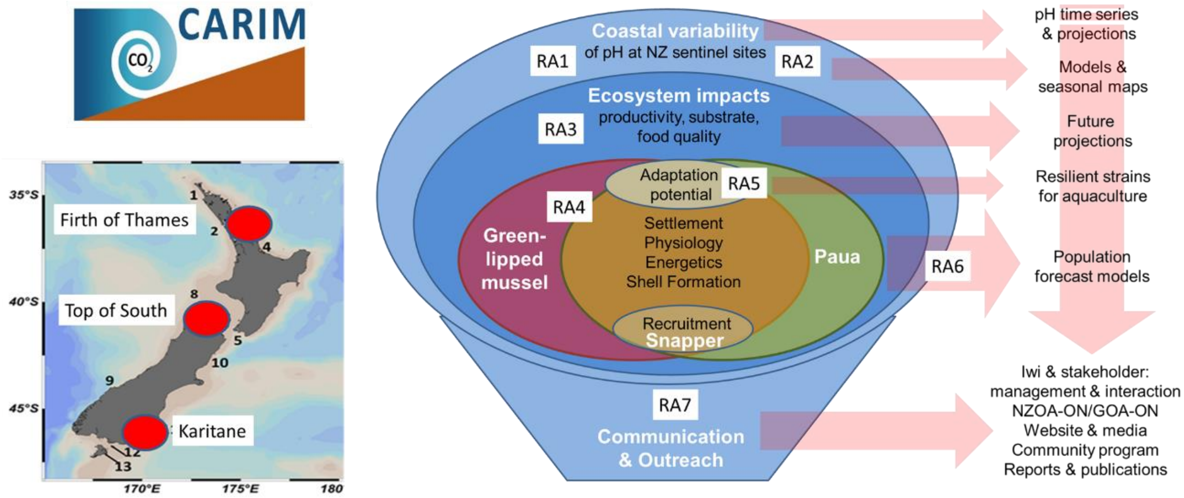


Figure 5-1 The CARIM project, showing logo on upper left, three focal locations on the left, the nested project structure in the centre and the outputs on the right.

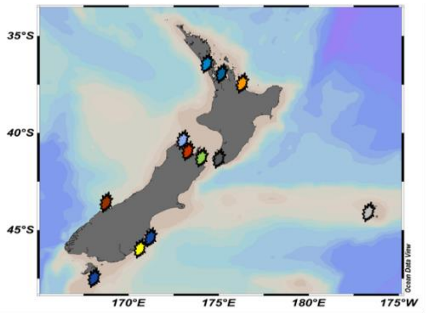
The direct effect of low pH on the sensitivity of three iconic New Zealand species – green-lipped mussels, pāua and snapper – has been determined across the life cycle for the two shellfish species, and on the larval stage of snapper (RA4). Potential indirect impacts of OA on these species have also been examined (RA3), including the sensitivity of coastal foodwebs (plankton biomass and diversity), and habitat availability (calcifying coralline algae). This information will then be applied in different models to determine the influence of OA on future population success (RA6). The adaptive potential of the shellfish species is determined in RA5 by exposing different pāua and mussel families to high CO_2 and between-family responses of the larvae. CARIM also includes an outreach component (RA7) which engages with stakeholders and iwi for co-design of sampling and implementation of outcomes. The following section provides further brief details of each RA, noting that some of the results and outputs of certain RAs have already been discussed in previous sections of this report.

5.2 RA1: variation in coastal pH

This RA maintains time-series measurement of pH and carbonate system parameters at the three focal sites using two approaches: a continuous record of pH and temperature obtained by a SeaFeT pH sensor (which records at 10-minute intervals), augmented by a periodic bottle sampling programme with samples collected and sent to the Dept Chemistry, University of Otago for analysis. pH and ancillary variables in the Firth of Thames are presented in Section 2 above. The pH trends recorded by bottle and SeaFET sampling in the Firth can be compared with those from other sites around New Zealand as part of the NZ Ocean Acidification Observing Network (NZOA-ON).

5.2.1 The New Zealand Ocean Acidification Observing Network (NZOA-ON)

The NZOA-ON was established in 2015 and is supported primarily by NIWA Strategic Investment Funding as part of the Climate Atmosphere and Hazards Centre. It provides a coherent monitoring approach to provide insights into the spatial and temporal variability of pH in coastal locations around New Zealand, with water samples collected fortnightly at 14 sites around the country by different sampling partners. Several of the sites also have SeaFET pH sensors deployed (Figure 5-2). Data collection methods follow protocols set up by the Global Ocean Acidification Observing Network (GOA-ON), and the data are publicly accessible and can be located at https://marinedata.niwa.co.nz/nzoa-on/



NZOA-ON
New Zealand Ocean Acidification Observing Network

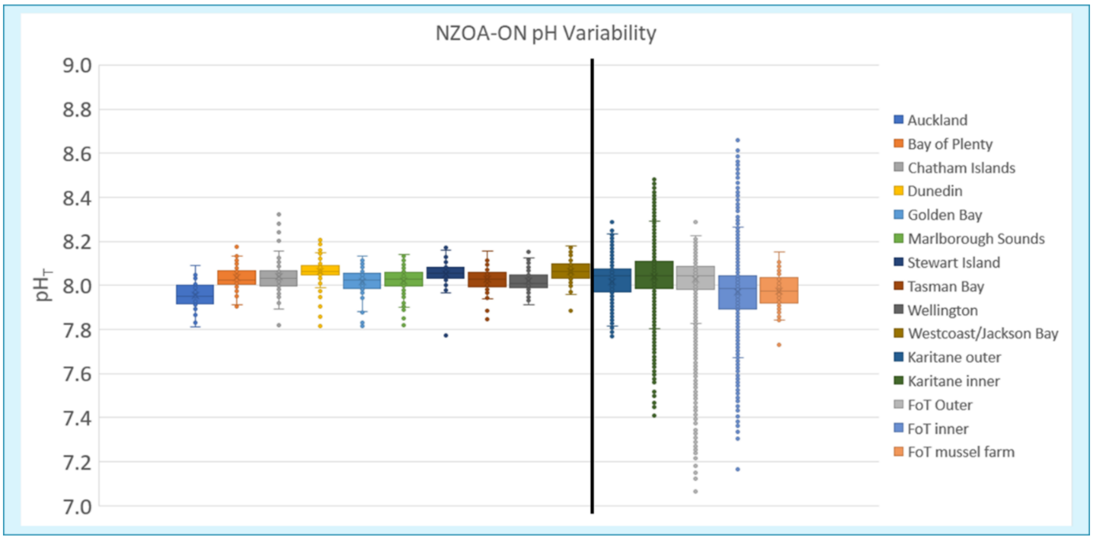


Figure 5-2 Location of the NZOA-ON sampling sites around NZ (upper left), and the mean, standard deviation and range of the pH at each sampling site (lower figure). For the five sites on the right-hand side of the black vertical line, the data are from both SeaFETs sensors and bottle samples, while those on the left are from fortnightly-bottle sampling only.

The mean of the fortnightly sampling values measured during 2015 – 2018 ranges from 7.95 at the Auckland site to 8.06 at Dunedin and West Coast sites (Figure 5-3). The pH range within any site (maximum – minimum) is greatest at the Chatham Island and Firth of Thames sites (~0.5 pH units) and lowest at the Wellington site (0.24 pH units). The mean pH measured by SeaFETS sensor at 5 sites is similar to that of the respective bottle sampling, however the range is greater, as diel and tidal signals are resolved (Table 5-1). The three Firth of Thames sites (inner and outer mooring, and mussel farm; shaded rows in Table 5-1) show some of the lowest pH values (mean and minimum), *and these data will be further augmented by bottle sample data from the mussel farm site.*

Table 5-1 Summary of pH data from the NZOAN stations, with Firth of Thames sites highlighted in the shaded rows

Site	**mean pH_T**	**Standard deviation**	**min**	**max**	**data period**	
Fortnightly bottle sampling						
Auckland	7.954	0.058	7.813	8.089	Apr-15	Aug-18
Bay of Plenty	8.036	0.048	7.905	8.174	Feb-15	Sep-18
Chatham Islands	8.038	0.076	7.819	8.324	Jan-15	Jul-18
Dunedin	8.062	0.057	7.814	8.208	Feb-15	Jul-18
Golden Bay	8.018	0.060	7.815	8.132	Feb-15	Sep-18
Marlborough Sounds	8.020	0.063	7.820	8.142	Jul-15	Oct-18
Stewart Island	8.052	0.068	7.774	8.170	Jun-15	Oct-18
Tasman Bay	8.026	0.051	7.846	8.157	Mar-15	Oct-18
Wellington	8.020	0.046	7.912	8.151	Feb-15	Sep-18
Jackson Bay	8.064	0.049	7.886	8.181	Jan-15	Nov-18
SeaFET pH sensor						
Karitane outer	8.057	0.048	7.770	8.286	Dec-15	Sep-17
Karitane inner	8.041	0.122	7.410	8.491	Dec-15	Mar-18
FoT outer	8.028	0.087	7.065	8.296	Apr-15	Nov-17
FoT inner	7.970	0.122	7.167	8.657	Jul-15	Sep-17
FoT mussel farm	7.974	0.081	7.729	8.153	Jun-16	Apr-17

5.3 RA2 Models and tools for the Firth of Thames

This RA focuses upon the development of approaches for constraining the spatial and temporal variation and primary drivers and controls of pH and the carbonate system in the Firth of Thames. The ultimate aim of this RA is to provide tools for management of OA in coastal waters by informing on how different processes and source contribute to observed pH. The application and results of the first component of RA2, the creation of biogeochemical budgets for the Firth of Thames, has been discussed in Section 3 above, and the other two components are described below.

5.3.1 Carbonate algorithms

The carbonate parameters pH, pCO_2, alkalinity, and DIC have only been measured in the Firth since 2009, with several comprehensive surveys during 2012-2013 and ongoing seasonal measurements at the 2 mooring locations. In order to provide better temporal and spatial coverage we used a multiple linear regression (MLR) approach, which has previously been used in the open ocean around New Zealand (Bostock et al. 2013) and has recently been applied in other coastal systems to estimate carbonate parameters (Signorini et al. 2013; Salisbury and Jonsson, 2018). The MLR, determined using R, uses the measured carbonate data (alkalinity and DIC) and the hydrographic data (temperature, salinity, oxygen, depth) to determine a relationship. For the Firth ~300 coupled alkalinity and DIC data points from 2009-2016, with their associated hydrographic data, were initially used to develop an MLR. These initial relationships were used to identify significant outliers, which were then removed (<10 data points, most previously identified as bad measurements of DIC or alkalinity), and the MLR was then re-run to produce a MLR relationship for alkalinity and DIC.

Alkalinity = Constant + $\alpha T + \beta S$

Where T = temperature (°C), S = Salinity, Constant = 342.437, $\alpha = -1.711$, $\beta = 56.794$

$R^2=0.83$ and the Root Mean Square Error (RMSE) = 14.76 µmol/kg

DIC = Constant + $\alpha T + \beta S + \gamma O + \delta D$

Where T = temperature (°C), S = salinity, O = oxygen (µmol/kg), D = depth, Constant = 1314.767, $\alpha = -5.348$, $\beta = 28.357$, $\gamma = -0.699$, $\delta = 0.266$

$R^2=0.75$ and the Root Mean Square Error (RMSE) = 18.51 µmol/kg

The high R^2 values indicate a good correlation between the measured and estimated alkalinity and DIC using the MLR algorithms. Alkalinity is strongly controlled by salinity, while the DIC is strongly controlled by salinity and oxygen. The other carbonate parameters (pH, $p\mathrm{CO}_2$ and Ω_{Ar}) were calculated using the program CO2sys.

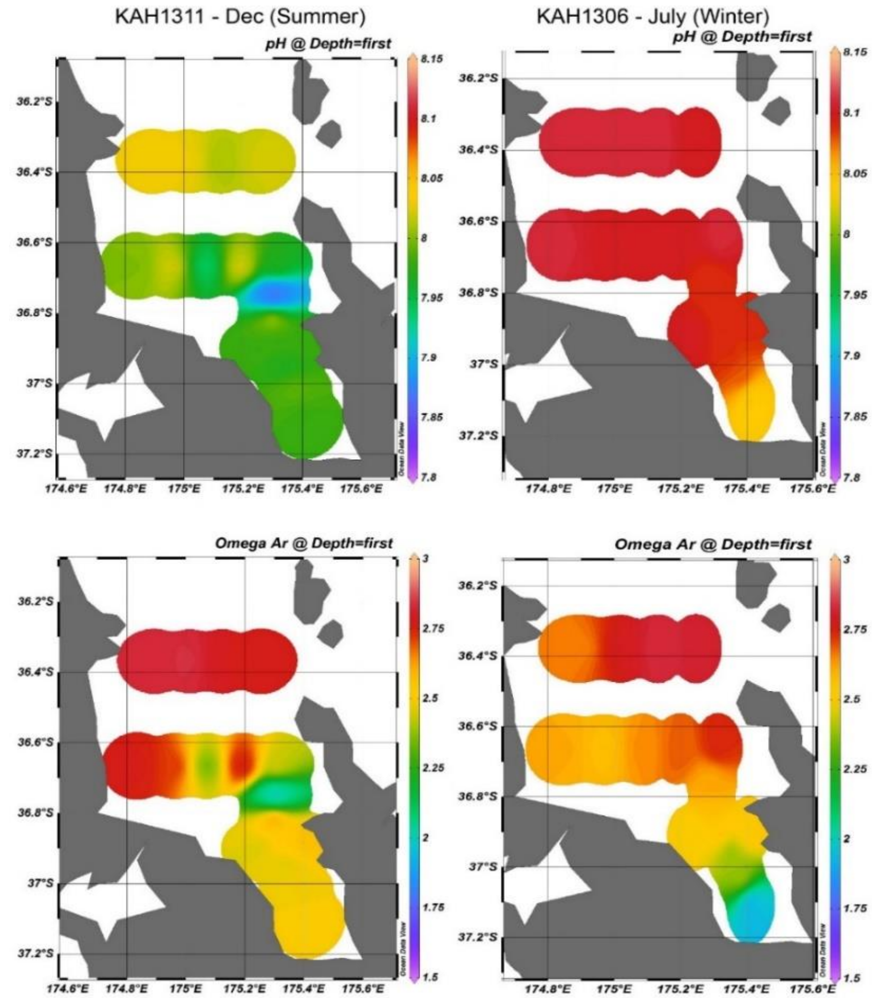


Figure 5-3 Estimated surface pH (top) and aragonite saturation states (Omega Ar : ΩAr; bottom) for summer and winter 2013.

Using the hydrographic data to estimate pH and the aragonite saturation state we can map the spatial variability in the surface waters of the Firth (see Figure 5-3). Two different seasons are shown; summer (voyage KAH1311, December 2012?) in which pH was slightly depressed, and winter (voyage KAH1306, July 2013 ?) in which pH was highest and more similar to offshore open ocean values. In both cases Ω_{Ar} is similar, with lower values inshore and elevated values in the outer Hauraki Gulf. pH was then estimated from the MLR algorithms for the 2012 and 2013 seasonal surveys and compared with measured pH from the underway system to further test the algorithms applicability to the natural system. It is evident that the estimated pH is too low during summer and too high in the inner Firth during autumn (compare Figure 2-5 and Figure 5-3), indicating the influence of a physical or biological process that is not accounted for by the MLR approach.

Using the MLR algorithms, we also hindcast the carbonate parameters from temperature, salinity and oxygen data collected at the outer Firth mooring (Figure 2-4) during 1998-2018 (Figure 5-4). The algorithm allowed us to estimate how the carbonate parameters varied seasonally over 20 years, for which no data was previously available. The results show strong seasonal variability where DIC is strongly influenced by O_2 concentrations and as a result displays a strong seasonal cycle with surface waters showing low DIC in the winter, while deep waters (>15m) display high DIC in the summer and autumn. $p\mathrm{CO}_2$ shows a similar trend to DIC, while pH shows the opposite trend (Figure 5-4). Alkalinity is strongly associated with the salinity (freshwater) influx, which can occur at any time of the year.

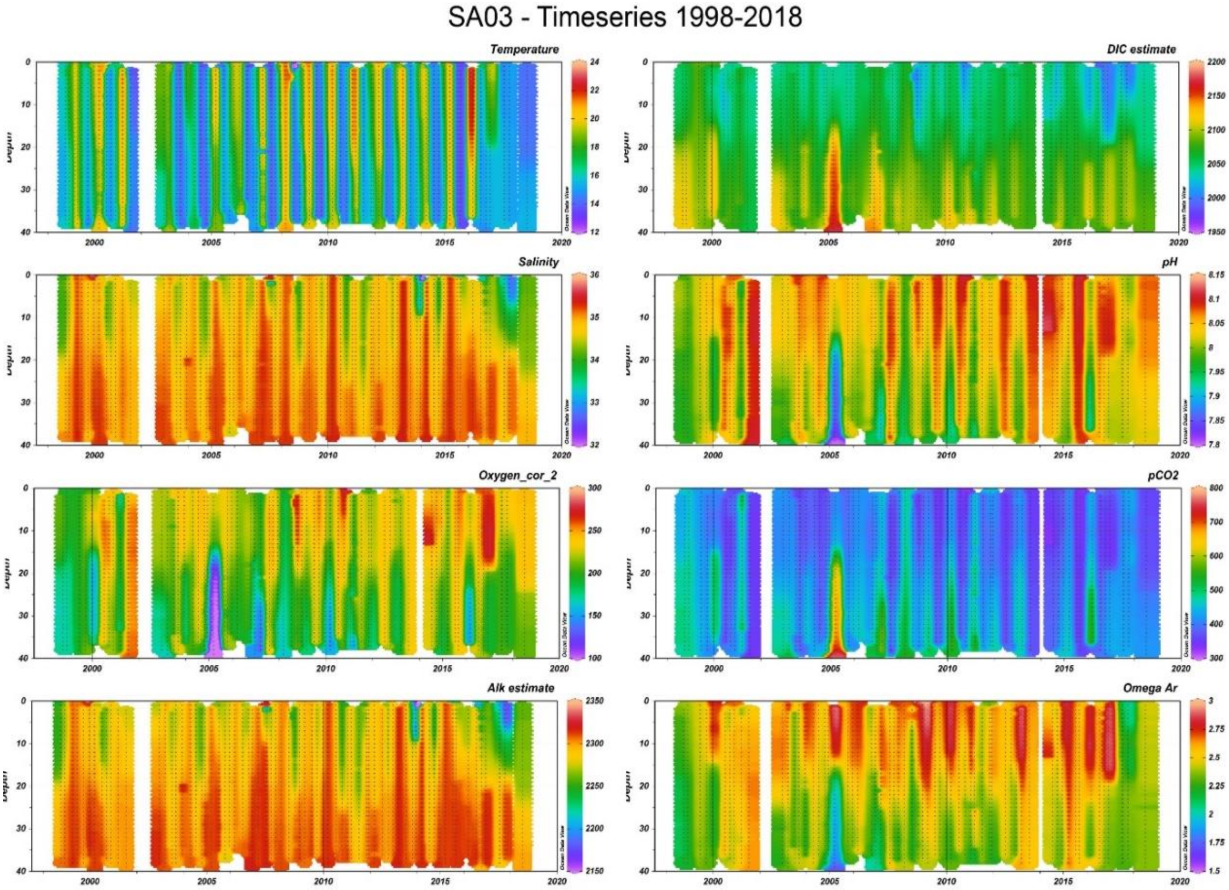


Figure 5-4 Seasonal maps of measured temperature, salinity and O_2, and estimated carbonate parameters (alkalinity, DIC, pH, pCO_2 and aragonite saturation state (ΩAr)) for the outer Firth for 1998-2018.

It is likely that these hindcast estimates are an overestimate of pH, Alkalinity and DIC, as the changing atmospheric CO_2, and consequently the surface ocean waters, was not included. Nevertheless, this provides insight as to how the system changes seasonally, and also the critical times and depths for undersaturation. The algorithms can also be used to look at the spatial and seasonal variability in the system, by estimating the carbonate parameters for the other sites within the FoT/HG, and compared with the SeaFet pH data.

Overall, the MLR algorithm shows considerable promise for application in the Firth of Thames, and consequently to other coastal regions if comparable datasets are available. Development and refinement of the MLR algorithm would benefit from targeted measurements in the inner Firth in summer and autumn, and further spatial mapping. The seasonal maps generated are a valuable source of information for planning and management which, together with ROMS models (see Section 5.3.2), can provide insight into more favourable locations for shellfish aquaculture and identify potentially more vulnerable or resilient regions for natural shellfish beds.

5.3.2 Coupled physical biogeochemical models

The third component of RA2 was the development of a coupled physical biogeochemical model for the Firth of Thames, to provide time-evolving estimates of ocean variables (in a similar manner to models used for weather predictions). For the model setup, the variables estimated are: sea surface height, velocity, barotropic velocity, temperature, salinity, nitrate, ammonium, chlorophyll-*a*, phytoplankton, zooplankton, detritus, total inorganic carbon, total alkalinity, and O_2. These variables can also be used to calculate other aspects of the carbonate system, such as pH. These models can investigate multiple processes and the effect of multiple stressors in the ocean, including changes in offshore ocean conditions (e.g. marine heatwaves, OA), changes in riverine inputs of nutrients, changes in nutrient inputs due to aquaculture, and many more.

Model set up requires an understanding of the non-linear interactions between biological (e.g. food availability, predator-prey dynamics), biochemical (nutrient and carbon cycling) and physical (e.g. temperature, currents) processes. To model these interactions, we set up the Rutgers physical model, ROMS (Shchepetkin and McWilliams 2003; Shchepetkin and McWilliams 2005), and the Fennel biogeochemical model (Fennel et al. 2006). The models are set up for two different domains with resolutions of approximately 2km and 750m respectively (see 5.5), and so the variables estimated by the model are given on grids of resolution 2km and 750m respectively.

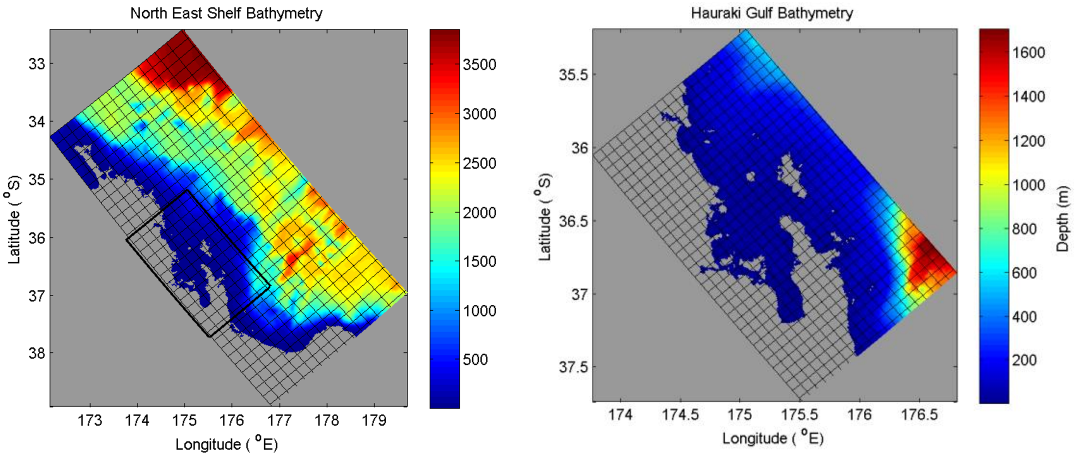


Figure 5-5 Bathymetry for the North East Shelf simulation (left). Every 10th grid cell is shown, and the position of the Hauraki Gulf grid is indicated as a black rectangle. Bathymetry for the Hauraki Gulf simulation, with every 10th grid cell shown.

To represent the system, information on the properties of variables entering the model domain (from the atmosphere, land runoff and the offshore ocean) are required. Atmospheric data is sourced from an atmospheric model, NCEP (Kalnay et al. 1996) and atmospheric CO_2 levels set to 370 µatm (representing a pre-industrial state). The initial and open boundary conditions are set using output from NIWA's larger-scale Biogeochemical model, PISCES. Riverine input is sourced using a combination of climatological data and a relationship between measured upstream river properties and river mouth properties (Broekhuizen, 2017; NIWA Internal report).

Figure 5-6 shows average surface nitrates and chlorophyll-*a* for the Hauraki Gulf/Firth of Thames. At the inner Hauraki Gulf region near the Firth of Thames, the riverine input dominates the system. Towards the outer Hauraki Gulf, inputs from offshore oceanic waters begin to dominate. These plots show how the model is successfully predicting the depletion of the riverine nitrate in the Firth by its high primary production, as indexed by chlorophyll.

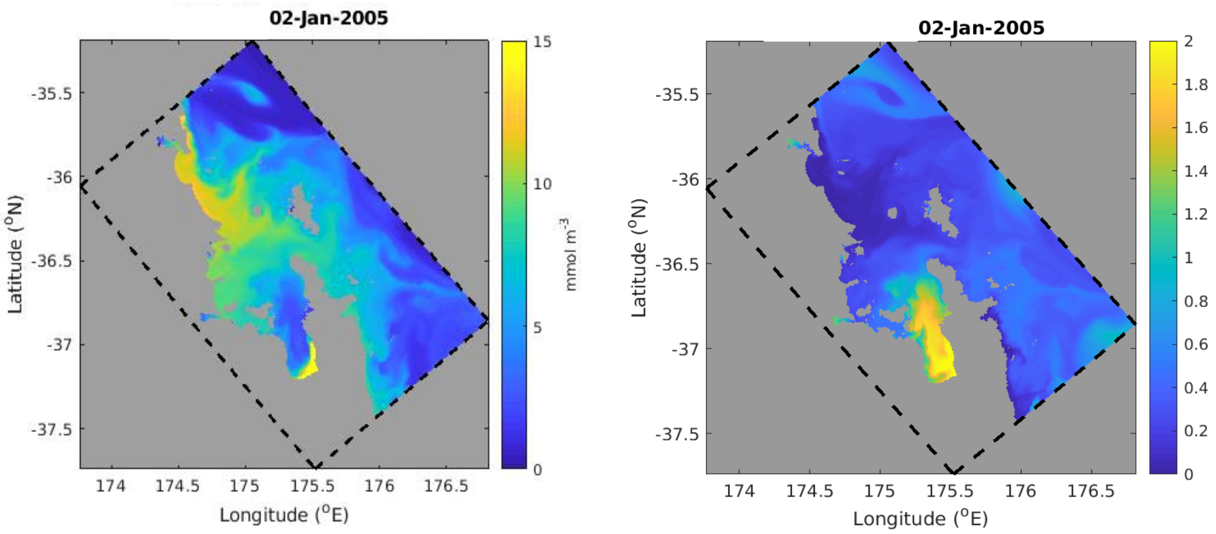


Figure 5-6 Output examples from the coupled physical-biogeochemical model of the Hauraki Gulf/Firth region showing surface nutrient concentration (left) and chlorophyll-a (right) on the 2nd Jun 2005. Yellow indicates a high concentration and blue indicates a low concentration.

A model needs to capture processes important to the problem under investigation, yet not all processes can be represented at once and so the model setup here is a generic "base model" that can be tweaked to address more specific problems. Currently we are working on better representation of carbon inputs from rivers and a tuning of parameters to improve the representation of the biological system to accurately model spatial and temporal variation in pH and the carbonate system. *This development of the model will provide insight into the controls of OA in the Firth of Thames and the effect that nutrient limit setting may have on future acidification.* We are working on adding representation of aquaculture farms to the base model which would enable changes in aquaculture use to be assessed

5.4 RA3: Indirect effects of ocean acidification in coastal waters

Ocean acidification may impact species directly via effects on their physiology, growth and behaviour, and also indirectly at the environmental level by altering their food and/or habitat availability. As key determinants of productivity and biogeochemistry, the response of phytoplankton to OA is of considerable relevance to the future status of coastal ecosystems. RA3 examined the effect of projected decreases in pH and increases in temperature on coastal phytoplankton communities. The response of a variety of parameters was determined to lower pH, and also lower pH combined with warmer temperature, in four experiments using natural plankton communities from Evans Bay, Wellington Harbour, under different nutrient and bloom states. The experimental treatments, representing present day and future projected pH and temperature were maintained in triplicate 4000-litre containers for periods of 18-22 days in a mesocosm facility (see Figure 5-7). In one experiment (Mesocosm 3) two different future timepoints were tested with pH &

temperature altered to projected conditions for New Zealand open ocean waters of +2.5°C/-0.33 (Year 2100) and +4.5°C/-0.5 (Year 2150).

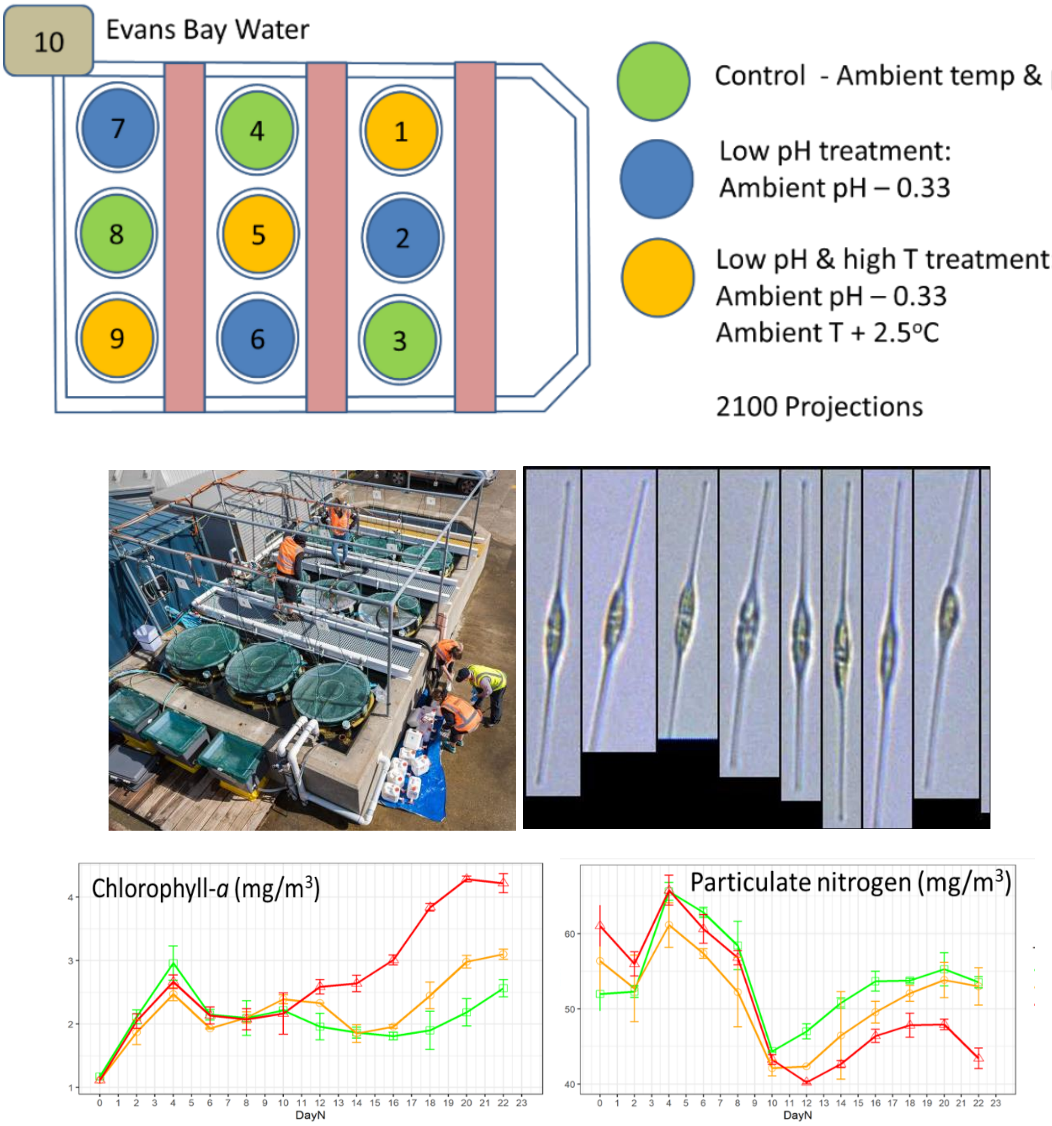


Figure 5-7 Mesocosm phytoplankton experiments, showing a schematic of the experimental layout of triplicate treatments and controls (upper figure); CARIM Mesocosm test facility (left middle image; D. Allen, NIWA); images of the dominant pennate diatom *Cylindrocatheca closterium* (right middle image)*;* and responses of chlorophyll-*a* (lower left graph) and particulate nitrogen (lower right graph) over 22 days during the Mesocosm 3 experiment (Control: green lines; 2100 pH/temperature: orange lines; 2150 pH/temperature: red lines).

The preliminary results of the CARIM mesocosm experiments indicate no significant effect of a lower pH (-0.33) on phytoplankton biomass (chlorophyll-*a*). However, there were significant effects in treatments of combined elevated temperature (+2.5C) and lower pH (-0.33), with higher chlorophyll-*a* biomass relative to the control when nutrients were not limiting. As warming and acidification will be mutually inclusive, this suggests an increase in phytoplankton biomass is likely to occur in future coastal waters. Furthermore, both treatment conditions for 2100 (+2.5°C/-0.33) and 2150 (+4.5°C, pH-0.5) showed higher chlorophyll-*a*, with increases of 29% and 86% in biomass, respectively, relative to the control (see Figure 5-7d). A higher biomass provisionally indicates greater energy and carbon availability at the base of coastal foodwebs, but also potentially greater eutrophication and associated problems, in the future. There was some indication of an effect of lower pH on and phytoplankton community composition with an increase in diatoms in both low pH only and combined treatments. This increase generally occurred as an increase in pennate diatoms which may have implications for future coastal food webs with a potential shift in consumers.

Particulate carbon did not show significant differences between the treatments and control for pH alone or in combination with elevated temperature, indicating insignificant change in carbon availability in future coastal waters. Conversely, particulate nitrogen decreased in the combined high temperature/low pH treatments relative to the control, with an 8% and 16% reduction in 2100 and 2150, respectively, (see Fig. 35), suggesting a future decline in the quality of particulate matter and reduction in nitrogen supply in coastal foodwebs.

The particle size spectrum altered in the combined low pH and higher temperature, with a decrease in the 0.2-5 µm size fraction (picoplankton) and increase in the 5-20 µm size fraction (nanoplankton). This was accompanied by changes in phytoplankton community composition in the combined low pH/high temperature treatments relative to the controls, including a decrease at 4-6 µm, potentially reflecting loss of coccolithophores and small flagellates, and an increase in the 10-15 µm fraction. The latter reflected dominance by the pennate diatom species *Cylindrocatheca closterium* (see Figure 5-7), and to a lesser an increase in dinoflagellate abundance, under future conditions. Overall, there was an evolution from a diverse community of phytoplankton of broader cell size range to fewer taxa with the community dominated by pennate diatoms of narrower size range in the 10-15 µm fraction.

The implications of these future changes for coastal foodwebs and biogeochemistry are still being assessed, but additional experiments in Mesocosm 3 identified a decrease in zooplankton (copepod) grazing rate, measured as carbon ingestion, in the future treatments. There was also an increase in particulate monounsaturated, saturated, and total fatty acids under lower pH/higher temperature, but not in the Polyunsaturated Fatty Acids (PUFAs). Fatty Acids are bioessential compounds, particularly the PUFAs which cannot be synthesised by grazers and so are required in their diet. A proportional decrease in particulate PUFAs observed in Mesocosm 3 indicates a decline in availability of these essential compounds. These observed changes in the particulate Fatty Acids in Mesocosm 3 were replicated in subsequent incubations of the pennate diatom *C. clostridium* (see Figure 5-7c), confirming that the response of this diatom species was responsible for the change in particulate Fatty Acids. Despite the observed enhancement of phytoplankton biomass under future conditions, there was no observed effect on zooplankton community composition or abundance, which may be due to the limited experimental duration of 18-22 days which is shorter than the generation time (one month) of copepods.

Overall, the results suggest that in future coastal waters may have higher chlorophyll-*a* biomass in response to warmer temperatures and lower pH, but a less diverse phytoplankton community potentially with a lower food quality due to a reduction in particulate nitrogen and essential fatty acids. However, it should be noted that these results are for Wellington coastal waters, and may not be applicable to the Firth of Thames due to differences in phytoplankton biomass and community composition.

5.5 RA4: Sensitivity of key species to lower pH

The aim of RA4 was to determine the acclimation potential of key NZ species (green lipped mussels, pāua, snapper) to future coastal acidification. The focus for the two shellfish species was to establish their acclimation potential across their life history and identify potential life stage bottlenecks. Part of this involved long term experiments to determine whether exposure of their respective broodstock to lower pH conditions would affect reproductive success, and/or confer resilience to their offspring under these conditions (carryover effects; Parker et al. 2012). The susceptibility of these three focal species are described above in Sections 4.1, 4.2 and 4.3, respectively.

5.6 RA5: Adaptive capacity of shellfish

This RA builds upon information gained on pāua and green lipped mussel resilience to OA in RA4, by exploring their genetic capacity for adaptation. For both species, a range of families were investigated to determine larval responses under projected 2100 pH/$p\mathrm{CO}_2$ levels. The experiments and results on the adaptive capacity of mussels are detailed in Section 4.2. Pāua adaptive capacity, survival and development for the first 48 h of life were determined for larvae from a range of families currently available at Moana NZ pāua farm (Ruakaka, Northland).

5.7 RA6: Modelling population success in lower pH waters

This RA synthesises the relevant information on physiological responses of pāua, mussels and snapper, along with natural variation in pH and other environmental variables generated in the other RAs in a modelling framework. Models most appropriate for each species will assess the population-level impacts of future coastal acidification and enable comment on potential implications for coastal ecosystems, wild harvest, aquaculture. An energetics model is in development for green lipped mussels (e.g. Ren et al. 2019). In the coming months, a Bayesian Belief Network modelling approach will be applied for pāua and the existing stock assessment model for snapper will be adapted to incorporate OA effects at the larval stage.

6 Other OA projects relevant to the Waikato Region

6.1 Sustainable Seas Innovation Fund project on mitigation of ocean acidification on mussel farms

This two-year project was initiated in response to the increasing awareness of the potential impacts of OA on shellfish aquaculture, particularly following the decimation of the oyster industry on the Pacific NW US coast over the last decade (Barton et al. 2012*)*. Subsequent research prior to and within CARIM has identified potential susceptibility of certain life stages of green lipped mussels (see Section 4.1; Erikson 2010; Law et al. 2018), highlighting a potential future issue for the New Zealand shellfish aquaculture industry. The aim of this project was to determine the potential of techniques that could be deployed at the scale of a mussel farm to alleviate the effects of OA by providing some buffering capacity during periods of low pH and carbonate. Cost effectiveness and practicality for the industry were also important considerations.

Coastal waters can exhibit significant variation in pH and carbonate saturation over seasonal and diel timescales, as shown in Figures 3-9 and 3-10. Seasonal trends reflect temperature cycles and associated changes in productivity, respiration, ventilation and freshwater input (see discussion in Section 3). However, diel changes can also be significant with a daily pH variation of 0.5 in some coastal environments (Cornwall et al. 2013), that results from the interplay between daytime photosynthesis and respiratory production of CO_2 at night. This diel cycle may be exacerbated on a mussel farm by the additional a large biomass of mussels and associated biofouling causing significant CO_2 production at night. Application of OA mitigation techniques may then alleviate acidification stress during both diel and seasonal periods of low pH.

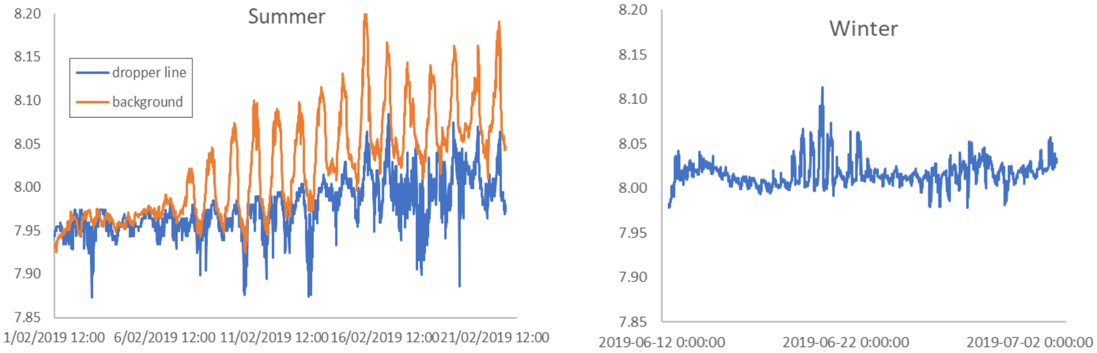


Figure 6-1 pH time series a) inside mussel and associated biomass on a dropper line (blue line), and in background water 12 cm from the mussels on the dropper line (orange line), over a 3-week period in February 2019, and b) inside mussel and associated biomass on the dropper line (blue line) over a 3-week period during June-July 2019 at Sanford EcoFarm, Marlborough Sounds.

Time series measurements of pH and carbonate system parameters on a Sanford mussel farm in the Marlborough Sounds identified higher pH during winter and a diel pH trend that was more pronounced in summer (see Figure 6-1a). During summer pH in the mussel (and associated) biomass on the dropper line was generally lower than in the surrounding water, by 0.1-0.15, with the diel trend reflecting respiratory production of CO_2 at night and removal of CO_2 during photosynthesis during the day. Minima of 7.87 were recorded during night-time on a number of occasions during February 2019, equivalent to the pH projected for region by 2050 under the RCP8.5 scenario (see Figure 3-13). Mussels on the dropper lines already experience future projected pH values for a portion of each diel cycle; consequently, they will be exposed to even lower pH in the future and alleviation of pH stress may be required maintain condition and survival of mussels.

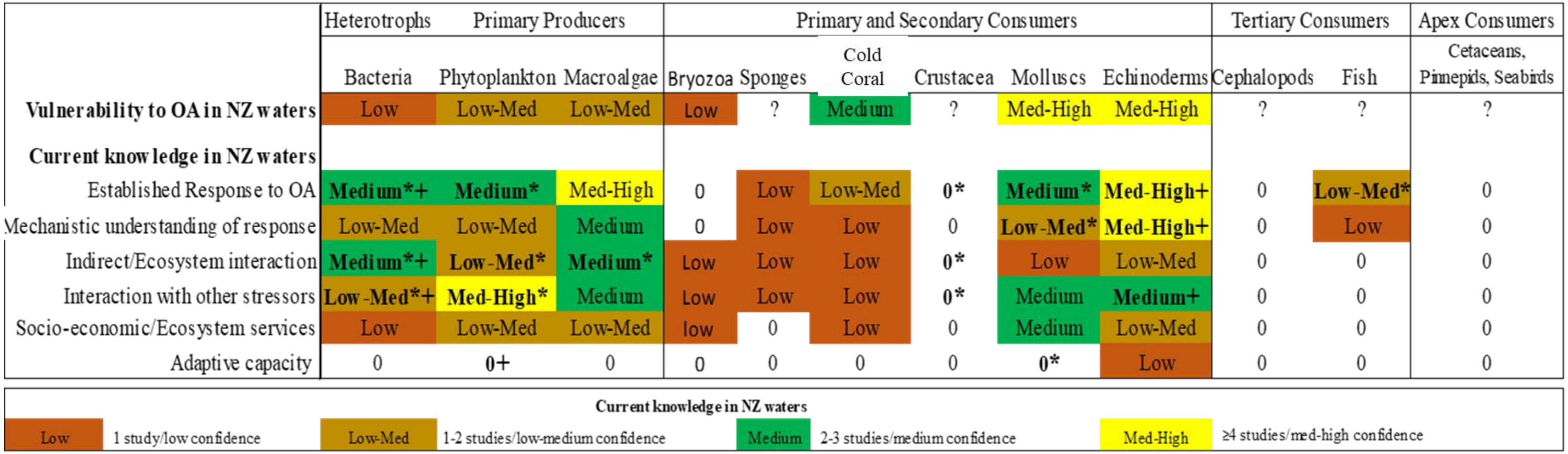
Strategic aeration by bubbling with air was assessed as a mitigation option by stripping CO_2 at night. The CO_2 gradient is positive (e.g. pCO_2 > atmospheric CO_2), thereby raising pH and carbonate saturation. This approach has potential co-benefits of increasing DO concentrations, and the technology is already available and used in freshwater waterways, lakes and by the finfish aquaculture industry. However, CO_2 does not behave as other gases such as O_2, in that there is not a simple exchange between the dissolved and gaseous phase. Instead, most of the CO_2 in seawater is in the form of bicarbonate and carbonate (see Figure 1), and consequently stripping CO_2 by bubbling takes considerably longer. A series of tests in a saltwater pond at NIWA Wellington, using different aeration tubing, flow rates and depths tested the potential of raising pH by CO_2 removal. Application of the observed stripping rates indicates that aeration would only be moderately effective (e.g. aragonite saturation raised by 5%) if aeration was carried out over >50% of a mussel farm, in part due to dilution by currents. In addition to cost and delivery mechanism the additional logistical challenges of aeration (such as the requirement for infrastructure and power supply which are lacking on mussel farms), suggests this technique has limited potential for mitigating OA.

The second mitigation approach assessed was alkalinisation, using the waste mussel shell generated as a by-product by the industry. This represents a potential source of carbonate that could potentially raise pH and carbonate availability at the scale of a mussel farm. The industry is currently unable to return the waste shell back into coastal waters, and so it is added to soils or accumulates in shell mounds at sites around the country. The challenge with this method is to dissolve the shell; pre-treatment of shell to convert it to lime requires high temperatures, and so high energy input and expense. Screening tests confirmed that simple treatments that can be implemented at low cost to increase the dissolution rate of the shells; however, the challenge is to find *in situ* conditions where waste shell will dissolve. NZOA-ON time series data from the surface waters of the Marlborough Sounds (see Section 5.2) shows a current Ω_{Ar} range of 1.4-2.7, which is above the Ω_{Ar} at which aragonite shell dissolution will occur. The surface sediment represents a potential site, as Ω_{Ar} is lower here; however, any dissolved carbonate in the surface sediment would not benefit mussels on the overlying dropper lines in a mussel farm, due to high dilution and advection in the water column before the dissolved carbonate reached the dropper lines. A more practical approach of incorporating waste shell on the dropper line with live mussels during spat and seed setting was considered but was unable to be tested due to spat shortages. Measurement of waste shell dissolution in the laboratory and in bags suspended on dropper lines identified low rates of shell mass loss; however dilution would minimise any benefit any indicating low level shell dissolution.

7 Key Information or data gaps

The current status of New Zealand Ocean Acidification research was detailed in Law et al. (2018). New Zealand is relatively well-informed on the rate and variability of pH in its coastal and oceanic waters compared to other nations, due to investment in the Munida transect, the NZOA-ON, the CARIM project and the NIWA Coasts and Oceans Programme; however, there are major gaps in our understanding of the potential impacts of OA, as summarised in Table 7-1.

Table 7-1 Qualitative assessment of a) the vulnerability, and b) the current state of knowledge on different aspects of OA research, for the major biotic groups in New Zealand waters based upon publications cited in Law et al (2018). "?" indicates where vulnerability is currently unknown, and "0"where no studies have been carried out. Current and ongoing studies on New Zealand species and locations are indicated in bold font and by "+", with studies within the CARIM project indicated by "*" (reproduced from Law et al, 2018).



	Heterotrophs	Primary Producers		Primary and Secondary Consumers						Tertiary Consumers		Apex Consumers
	Bacteria	Phytoplankton	Macroalgae	Bryozoa	Sponges	Cold Coral	Crustacea	Molluscs	Echinoderms	Cephalopods	Fish	Cetaceans, Pinnepids, Seabirds
Vulnerability to OA in NZ waters	Low	Low-Med	Low-Med	Low	?	Medium	?	Med-High	Med-High	?	?	?
Current knowledge in NZ waters												
Established Response to OA	**Medium*+**	**Medium***	Med-High	0	Low	Low-Med	**0***	**Medium***	**Med-High+**	0	**Low-Med***	0
Mechanistic understanding of response	Low-Med	Low-Med	Medium	0	Low	Low	0	**Low-Med***	**Med-High+**	0	Low	0
Indirect/Ecosystem interaction	**Medium*+**	**Low-Med***	**Medium***	Low	Low	Low	**0***	Low	Low-Med	0	0	0
Interaction with other stressors	**Low-Med*+**	**Med-High***	Medium	Low	Low	Low	**0***	Medium	**Medium+**	0	0	0
Socio-economic/Ecosystem services	Low	Low-Med	Low-Med	low	0	Low	0	Medium	Low-Med	0	0	0
Adaptive capacity	0	**0+**	0	0	0	0	0	**0***	Low	0	0	0

Current knowledge in NZ waters

Low	1 study/low confidence	Low-Med	1-2 studies/low-medium confidence	Medium	2-3 studies/medium confidence	Med-High	≥4 studies/med-high confidence

Not surprisingly there is greater insight into the potential impacts in the lower food web, but less on higher trophic levels as the latter are harder to maintain in experimental conditions and constrain in the natural environment. Groups such as the Bryozoa, cold water corals and sponges are poorly studied yet these provide important habitat for other biotic groups and their loss, in the case of the first two groups and/or increase in the latter, may have ramifications for their other biotic groups that dependent upon them. There have been very few studies on the effect of OA on New Zealand crustacea, which is surprising given their significance in coastal and oceanic foodwebs, the economic and recreational value of certain species such as crayfish and lobsters, and potential OA impacts identified in international studies (Miller et al. 2016). Similarly, there is a lack of information on the impacts on cephalopods and apex predators including seabirds, pinnipeds and cetaceans. It is important to note that the indirect impacts of OA, via changes in diet, food quality and availability, may be more significant than the direct effects for these groups.

A major knowledge gap is the interaction of OA with other stressors, a critical consideration bearing in mind that the major interaction of two or more stressors is often synergistic, and so greater than the sum of the individual stressor effects (Gunderson et al. 2016). Multiple stressor research is perhaps more tractable in the open ocean where other stressors are largely associated with climate change and can be projected and clustered to determine future effects (Boyd et al. 2016). Conversely in coastal regions, there are a multitude of additional stressors, including sedimentation, nutrient enrichment/eutrophication, deoxygenation, toxins and pollutants, each of which varies on different spatial and temporal scales, which makes it difficult to derive robust experimental frameworks. Whereas some research within CARIM has looked at the net effects of warming and OA combined (see Section 5.3) there is clearly a need to consider the effects of multiple stressors in coastal regions such as the Firth of Thames (see Section 3.1). Indeed, the inter-relationships between OA, deoxygenation, warming and nutrients, described in Section 2.1, provides a potential framework for considering and determining the net effects of multiple stressors.

Studies of organism adaptation capacity have been limited to date and, although there is preliminary evidence of adaptation potential in phytoplankton (Lohbeck et al. 2012), this has only been determined in coccolithophores in New Zealand (Armstrong et al, unpubl.). Although long-term adaptation studies present considerable logistical challenges, particularly for more advance biotic groups, information on adaptation is essential to determining future success under prolonged exposure to OA. Adaptive capacity may be related to life-history or environmental niches that increase short-term exposure to extreme conditions, and the preliminary studies of CARIM on transgenerational benefits from parental exposure to low pH (see Sections 4.1 and 4.2 could be further developed for other key coastal species.

8 Areas of further work and application of CARIM findings in the Firth of Thames relating to acidification or aquaculture management.

- The value of time-series monitoring has been identified for establishing the mean state and variation in the biogeochemistry of the Firth of Thames, and the inter-relationships between stressors. In addition, the time series data illustrates how these stressors are influenced by external drivers, such as land use and climate change, and also provides valuable information for validating biogeochemical models. It is recommended that time-series observations are maintained in the Firth of Thames by optimising and rationalising existing monitoring within a regional monitoring framework coordinated between the Regional Council and other stakeholders and partners. This does not have to be high-resolution and high-cost; for example, the NZOA-ON has demonstrated that fortnightly bottle sampling can be carried out by local stakeholders (although there are currently technical challenges of use of poisons in samples that need to be overcome).

- There are opportunities for co-development and implementation of both monitoring and mitigation studies of coastal acidification between the Aquaculture industry and Regional Councils. For example, the resource consent requirements for mussel and finfish aquaculture provide an opportunity to incorporate monitoring of OA and other stressors, that would benefit both parties. Recent interactions in the Sustainable Seas OA Futureproofing project with Sanford have highlighted the co-benefits of collaboration on OA monitoring and impacts.

- Nutrient budgets for the Firth of Thames indicate that declining denitrification in combination with an increase in dissolved inorganic nitrogen loading may exacerbate eutrophication, leading to an increase in respiratory CO_2 production and acidification (although this needs to be confirmed). Determination of the variability and controls of denitrification in the Firth is critical to establishing the potential of the natural ecosystem to accommodate nitrogen loading, and so a seasonal survey of denitrification rate and its regional variability is recommended.

- Greater insight and management could be achieved with improved coupled hydrodynamic – biogeochemistry models. For example, the addition of a sediment component in the model would provide insight into the influence of processes such as denitrification or the carbonate system of the Firth. A more advanced model would also enable testing of past and future scenarios; for example, examining the state of the carbonate system, and so acidification, of the Firth under different freshwater and atmospheric loadings.

- Better coordination between organisations of data, science and policy across the land-ocean interface will increase the potential and opportunity for management and mitigation of coastal acidification, particularly in the Firth of Thames, for example, by addressing freshwater nutrient and organic loading.

- An increased focus on strategies and tools to mitigate the impacts of OA on Taonga, key species and ecosystems in the Firth of Thames, as well as coastal economic assets such as mussel farms. For example, targeted mitigation strategies could reduce OA exposure and stress on the vulnerable embryo and juvenile life stages of organisms with carbonate shells, such as green-lipped mussel and pāua. Enhancing resilience to OA and other stressors via selective breeding and/or "hardening" represent other potential pathways for maintaining healthy, functioning species and ecosystems.
- Monitoring and management need to consider the individual and combined effects of multiple stressors. Organisms and ecosystems in the Firth of Thames are under pressure from a range of different stressors, yet there is a dearth of information on the impact of multiple stressors and whether their overall impact is synergistic, additive or negative. Extrapolation of available experimental data to *in situ* conditions is hampered by the current limitations of one or two stressors in experimental studies. Recently developed frameworks for multiple stressor experimentation have made this more tractable. Furthermore, establishing the relationships between the major stressors (OA, warming, eutrophication, deoxygenation; see Section 3) in the Firth of Thames by time-series monitoring will provide a framework for more realistic experimentation to determine multiple stressor impacts, and identify approaches and efficiencies in addressing the sources of these stressors.
- As different stressors in coastal waters often have common sources (freshwater input: nutrients, organics, pollutants) consideration of multiple stressor impacts provides additional benefits of management. A reduction in local stressors that are amenable to control may reduce the impact of global stressors for which management is more challenging.

9 Acknowledgements

We acknowledge funding and support for research presented in this report provided by MBIE (C01X1510: Coastal Acidification: Rate, Impacts and Management (CARIM)), Sustainable Seas National Science Challenge (Innovation Fund project IF2.2.2.1: A feasibility study of coastal acidification mitigation strategies for the mussel industry), NZ Fisheries (Project ZBD201607: Multiple Stressors on Coastal Ecosystems – In Situ Experiments), and for SSIF Funding and facilities provided by NIWA and the Cawthron Institute; support for PhD students from the University of Otago and infrastructure and operational support from NIWA.

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