Shifts in species composition in kelp forest communities: implications of differences in total phenolic composition among species

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ABSTRACT: The purpose of our study was to measure total phenolic concentrations (TPC) of 14 species in the Phaeophyceae comprising kelp beds in the Otago Harbour Region (New Zealand). Our survey included 9 fucoids (order Fucales), 4 'true kelps' (order Laminariales), and 1 species in the order Desmarestiales over 4 seasons from multiple sheltered and wave-exposed sites. TPC observed among species varied by 2 orders of magnitude from the most concentrated in *Carpophyllum flexuosum* (estimated marginal mean [emmean] 212.6 ± 24.77 µmol per gram dry tissue weight [g DTW^{-1}]) to the least concentrated in *Lessonia variegata* (emmean 10.88 ± 2.84 µmol g DTW^{-1}). Within the sheltered kelp bed communities of the Otago Harbour, TPC was higher in the warmer months and lower in the cooler months within species. In the wave-exposed communities, TPC was on average higher in the spring compared to the summer within the observed community. Lastly, within one species across both inner and outer Harbour communities, a Vargha and Delaney's *A* measure suggests a specimen collected from the sheltered inner harbour sites would have a higher probability of being more concentrated in TPC than a specimen from the wave-exposed sites in the spring and summer (*A*-estimates 0.90 and 0.76, respectively) and a high probability of being more concentrated in the winter (*A*-estimate 0.70). Overall, variation in TPC among species within macroalgal communities suggests shifts toward more opportunistic species may impact community-wide TPC. Changes in species composition have important implications for the palatability of organic matter produced from macroalgal communities and the pathways for macroalgal-derived organic matter into coastal food webs.

KEY WORDS: Macroalgae assemblages · Chemical defence · Phlorotannin · Species composition · Grazer deterrent

1. INTRODUCTION

Macroalgae in the class Phaeophyceae form critical 3-dimensional habitat in and provide basal organic matter to the rocky nearshore ecosystems of the world's temperate and subpolar oceans (Mann 1973, Schiel & Foster 2015). In the Pacific, the most common canopy-forming species in macroalgal forests is the giant kelp *Macrocystis pyrifera*, which can grow to a terminal height of 45 m (Abbott & Hollenberg 1992) and provides annual net production of organic matter of up to 537 g C m^{-2} yr^{-1} to the surrounding ecosystem (Jackson 1987, Krumhansl & Scheibling 2012, Udy et al. 2019a). *M. pyrifera* provides a dense canopy in macroalgal communities of southern New Zealand and several of the subAntarctic islands, where it

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shelters stipitate species of true kelps such as *Ecklonia radiata* and shallow subtidal fucoids that together form multi-layered macroalgal forests comprising some of the largest biogenic structures in marine systems (Dayton 1985, Schiel & Foster 2015). In addition to immense macroalgal biomass, macroalgal forests act as ecosystem engineers, responsible for providing a scaffolding on which an immense diversity of marine life is supported. The relationship between macroalgae and faunal biomass collectively make macroalgal forests one of the most diverse and productive ecosystems (Mann 1973). Unfortunately, the future of this highly productive system is under threat both globally and in New Zealand, where natural disturbances, anthropogenically induced stressors, and the introduction of non-native species can result in both a contraction of the range and reduction in species composition of macroalgal forests (Krumhansl et al. 2016, Wernberg et al. 2019, Blain et al. 2021).

Consideration of the consequences of shifting kelp forest community structure is essential for understanding ecosystem function in the nearshore, as primary productivity from large brown algae provides a significant source of organic matter for coastal marine ecosystems (Mann 1973). Although only about 10% of living macroalgal material may be actively consumed by grazing herbivores within healthy forests (Wing 2009, Wing & Wing 2015), organic matter derived from macroalgae also enters the food web as 'drift kelp' (i.e. macroalgae severed from the living forest) and as detrital particulate organic material (Duggins et al. 1989). Drift kelp from common species such as *M. pyrifera* can be readily consumed in the benthic coastal environment by detritivores (Dayton 1985, Paine 2002, Wing et al. 2008, Jack & Wing 2011, Wing & Wing 2015, Udy et al. 2019b), fish communities (Udy et al. 2019a,b, Sabadel et al. 2020, Wing et al. 2022), suspension feeders (Wing & Jack 2012, Schlieman et al. 2022), on sandy beaches (Dugan et al. 2003), and in deep-sea communities (Harrold et al. 1998, Ramirez-Llodra et al. 2021). Nevertheless, minimal consideration has been given to how shifts in the community structure of the world's macroalgae forests could potentially influence the quality and accessibility of macroalgal-derived organic matter for coastal food webs.

Shifting community structures will change the occurrence and quantity of phytochemicals distributed within macroalgal communities. In particular, the changes to phenolic compounds, broadly characterized as 'phlorotannins', have gained attention recently due to the numerous biologic and economic impacts these secondary metabolites can cause. Phlo-

rotannins are long chain polymers of phloroglucinol (1,3,5- trihydroxybenzene) which are found exclusively in the class Phaeophyceae (Ragan & Glombitza 1986). As the name suggests, phlorotannins share similar chemical properties with vascular plant tannins (Arnold & Targett 2002) and play central roles in cell wall construction (Schoenwaelder 2002), storage capabilities (Ragan & Glombitza 1986), and reproduction (Schoenwaelder & Clayton 1998, Vreeland et al. 1998). In addition, phlorotannins can aid in secondary roles including antiherbivore deterrence by echinoderms and finfishes (Van Alstyne 1988, Steinberg & van Altena 1992, Peckol et al. 1996, Pavia & Toth 2000, Lüder & Clayton 2004, Hemmi et al. 2005) and protection from UV radiation (Pavia & Brock 2000, Swanson & Druehl 2002).

It has been well documented that phlorotannin concentrations vary immensely within the anatomy of a single specimen (Steinberg 1984, Tuomi et al. 1989, Van Alstyne et al. 1999, Pavia & Toth 2000, Pavia et al. 2003), between individuals of the same species within a population (Pavia et al. 2003), between populations (Van Alstyne et al. 1999, Pavia & Toth 2000, Pavia et al. 2003), and between different species of brown macroalgae (Steinberg 1989, Van Alstyne et al. 1999, Fairhead et al. 2005, Kamiya et al. 2010). The observed variation in phlorotannin concentrations has been demonstrated to differ based on factors including irradiance (Cronin & Hay 1996, Cronin & Lodge 2003), nutrient concentrations (Yates & Peckol 1993, Cronin & Hay 1996, Cronin & Lodge 2003, Jormalainen et al. 2003, Pavia et al. 2003, Hemmi et al. 2004), and grazing pressure (Van Alstyne 1988, Pavia & Toth 2000, Jormalainen et al. 2003, Pavia et al. 2003). The magnitude of variability among species has been shown to have an effect on the palatability of macroalgal material for a range of grazer species, where Phaeophyceae with high concentrations of phlorotannins are generally less palatable than species with lower phlorotannin concentrations (Steinberg 1989, Van Alstyne & Paul 1990, Steinberg & van Altena 1992).

Currently, our understanding of the natural distributions of phlorotannin concentrations is limited to individual species from a small number of locations. Further, our consideration of community wide variability in phlorotannin concentrations among diverse macroalgal communities is understudied, particularly in New Zealand. However, due to the implications phenolic compounds have on palatability and pathways for uptake of macroalgal-derived organic matter in marine food webs, consideration should be given to the role that variability in phlorotannin concentra-

tions within and among species could play in the eco-system function of temperate macroalgal communities. As the chemical structure of phlorotannins shares similar chemical properties with terrestrial tannins (Arnold & Targett 2002), it is possible they may act in a way similar to tannins, which are increasingly reported to impact microbial degradation rates in sediments and nitrogen cycling in systems. In particular, tannins have showed the potential to alter the availability and retention of nitrogen within estuarine red mangrove *Rhizophora mangle* (Maie et al. 2008), spruce *Picea abies* stands (Adamczyk et al. 2011), and poplar *Populus* spp. forests (Schweitzer et al. 2008).

To address these current gaps in knowledge, we sampled 5 macroalgal communities distributed between the inner regions of the Otago Harbour and the adjacent wave-exposed outer coastline over a calendar year. In doing so, we investigated how phlorotannin concentration (measured as total phenolic concentration, TPC) in mature blade material varied among species within a community, among seasons, among sites within a harbour zone, and between inner harbour wave-protected and outer coast wave-exposed zones. In addition, we compared how successional replacement of weedy species or non-native species could alter the relative TPC of living macroalgal material within the observed gradient in composition of macroalgal communities.

2. MATERIALS AND METHODS

2.1. Site location and sample collection

We collected samples of macroalgae from multiple sites along a gradient within and outside of the Otago Harbour. Our inner-harbour sites consisted of the Portobello Marine Laboratory (PML), Te Umukuri (Weller's Rock), and Harington Point, while our outer-harbour sites were Purakaunui Bay/Mapoutahi Pa (collections possible under an East Otago Taiāpure special collection permit) and Whareakeake (Murdering Bay) Beach (Fig. 1). Collections occurred seasonally in October/November 2021 (spring), February/March 2022 (summer), May/June 2022 (autumn), and August 2022 (winter). All macroalgal specimens were collected by divers (both SCUBA and free divers). Unfortunately, due to complications caused by the COVID-19 pandemic, autumn collections were not possible at Whareakeake Beach. Following initial collections, additional sampling efforts took place to collect the New Zealand 'common kelp' *Ecklonia radiata*, which was not found within our original sample lo-
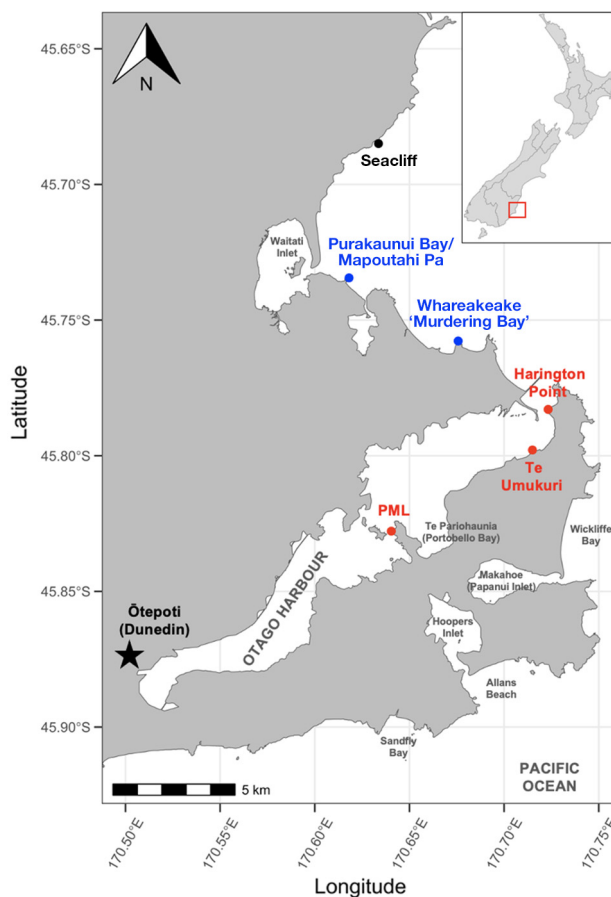

Fig. 1. Field sites used in this study. Sites in red (Harington Point, Portobello Marine Lab [PML], and Te Umukuri [Weller's Rock]) were within the Otago Harbour; sites in blue (Purakaunui Bay/Mapoutahi Pa, and Whareakeake [Murdering Bay] Beach) were outside the Otago Harbour. The site in black (Seacliff) was visited to collect *Ecklonia radiata*, which was not observed in the southern sampling locations

cations. We examined *E. radiata* specimens collected from Seacliff in September 2023 under an East Otago Taiāpure special collection permit to allow us to compare TPC in *E. radiata* to other species sampled within the spring season. The diversity of large brown algae collected were the following: *Carpophyllum flexuosum, Cystophora retroflexa, Cystophora torulosa, Desmarestia ligulata, Durvillaea* spp., *Ecklonia radiata, Hormosira banksia, Lessonia variegata, Macrocystis pyrifera, Marginariella boryana, Marginariella urvilliana, Sargassum sinclairii, Undaria pinnatifida,* and *Xiphophora gladiata.* During each sampling event, mature blade samples were taken from 5 different individuals if they were present in each community. When present, *Ulva* spp. was also sampled. *Ulva* spp. was selected over other non-Phaeophyceae specimens as it has a high biomass within the Otago Harbour particularly in

summer. In addition, *Ulva* spp. provided a macroalgal standard for a baseline zero concentration for phlorotannin abundance.

Following collection, blade samples were contained in mesh bags to keep specimens separated by site during transit. The mesh bags were kept inside a cooler full of seawater with ice packs to limit degradation while specimens were transported back to the PML for further processing. Care was taken to reduce the amount of time between the harvest of macroalgal blades and freezing of samples to be under 2 h.

2.2. Sample preparation

Following collection, individual specimens were washed thoroughly with distilled water and care was taken to select for blades with no biofouling or epiphyte coverage. For Phaeophyceae with large blades (i.e. *Durvillaea* spp., *E. radiata*, *L. variegata*, *M. pyrifera*, *M. boryana*, *M. urvilliana*, *U. pinnatifida*, and *X. gladiata)*, individual blades were cut down a vertical midline with a ceramic knife into left and right halves by individual for separate sample processing. For Phaeophyceae with small blades (i.e. *C. flexuosum*, *C. retroflexa*, *C. torulosa*, *D. ligulata*, *H. banksia*, and *S. sinclairii)*, separate blades from the sample individual were portioned for the separate analyzes. When collected, *Ulva* spp. was processed following the protocol for the large-bladed Phaeophyceae species.

For phlorotannin sample preparation, blades were placed into 50 ml, acid-washed, falcon tubes, and stored frozen (−80°C) until processing. Tissue samples were then freeze-dried to a constant mass and ground into a homogenous powder using a stainless-steel electric spice grinder.

2.3. Phlorotannin concentration analysis

We used a solid liquid extraction (SLE) procedure to measure the TPC in a known mass of homogenous macroalgal tissue. Blade material was extracted in 60% aqueous acetone over 1 h in the dark under constant agitation in 15 ml of acetone. Following extraction, the algal material was separated from the supernatant by centrifugation (5300 rpm [3140 × g] for 10 min), and the acetone was removed from the supernatant via evaporation until only the ~40% aqueous fraction remained. The sample was then diluted with distilled water back up to extraction volume, filtered (Thermo Scientific 30 mm Nylon, 0.45 μm pore size) to remove precipitated lipophilic compounds (Pavia & Toth

2000) and analyzed by photometry using a variation of the Folin-Ciocalteu method with gallic acid (Gallic acid monohydrate, ACS reagent, ⩾98.0%, Sigma-Aldrich 398225) as a standard (Ainsworth & Gillespie 2007). TPC was extrapolated based on the linear relationship between gallic acid concentrations and absorbency from standard curves for 6 concentrations (all $r^2 \geqslant 0.95$). All standard curves had 6 known concentrations in addition to a MilliQ water blank. The resulting TPC was scaled by dry macroalgal tissue mass and reported as μmol per gram dry tissue weight (g DTW^{-1}).

2.4. Statistical analysis

All statistical analyses were conducted using R statistical software (version 4.2.3). To explore differences in TPC across all observed (1) species, and (2) seasons within the inner harbour, we used a parametric approach and created general linear mixed models (GLMMs) using the *glmmTMB* package (Brooks et al. 2017). Both models included a zero-inflated gamma family with a log link which avoided the requirement for transformation usually required to achieve normality and equality of variance assumptions associated with conventional ANOVA analysis. The model assumptions and fit to the recorded data were tested and validated using the *DHARMa* package (Hartig & Lohse 2022).

In the first model, 'Species' was the only fixed effect in the model. In the second model, 4 species (*C. retroflexa*, *M. pyrifera*, *Ulva* spp. and *U. pinnatifida*) were included in the analysis as they were present across all seasons (spring, summer, autumn, and winter) at all 3 inner harbour sites (Harington Point, PML, and Te Umukuri [Weller's Rock]). The 2-way interactions between the fixed effects, 'Species', 'Site', and 'Season' were utilized in our second model. For all models, we then compare if TPC was significantly different using pairwise least-square mean tests via the *emmeans* package (Lenth 2024).

To explore differences in TPC across (3) season within the outer harbour, we used a non-parametric approach to compare medians using the *mood.medtest* function from the *RVAideMemoire* package to compare medians (Herve 2023). If at least one median was revealed to be statistically significantly different to another, we performed a post-hoc comparison using the *pairwiseMedianTest* function from the *rcompanion* package to explore if median TPC was statistically different across observed species (Mangiafico 2016). To explore TPC within species across the observed

outer harbor community, we began by sub-setting the data into summer and spring seasons as the post-hoc could only explore the interactions of 2 levels. To investigate the season effect across all observed species in the outer harbour, we used the *mood.medtest* function to explore the interaction between TPC and season. In addition, we utilized the Vargha and Delaney's *A* measure to explore the effect size of the probability of a sample taken from the spring community having a higher TPC value than a sample taken from the summer community (Vargha & Delaney 2000). The Vargha and Delaney's *A* measure considers the effect size to be small when *A* = 0.56−0.64, medium when *A* = 0.65−0.70, and large when *A* ⩾ 0.71 (Vargha & Delaney 2000).

Finally, to explore the effect of (4) season and harbour zone within a singular species (*U. pinnatifida*), we also utilized the *mood.medtest* function to explore how TPC varied within a season (spring, summer, and winter) between the 2 harbour zones (inner and outer). In addition, we utilized the Vargha and Delaney's *A* measure to explore the probability of a *U. pinnatifida* collected from the greater inner harbour population (i.e. the combined populations from Harington Point, PML, and Te Umukuri [Weller's Rock]) having a higher TPC value than a *U. pinnatifida* from the outer harbour population (i.e. the population from Purakaunui Bay/Mapoutahi Pa) in the spring, summer, and winter months (Vargha & Delaney 2000).

3. RESULTS

3.1. Statistical summaries

Summary outputs from the GLMMs used to address TPC across all observed (1) species, and (2) species present across all seasons within inner harbour communities can be found in Tables S1 to S4 in the Supplement; www.int-res.com/articles/suppl/m744p017_supp.pdf. In addition, the summary outputs for the post-hoc comparison exploring (3) TPC across species present during 3 seasons within the outer harbour community at Purakaunui Bay/Mapoutahi Pa can be found in Tables S5 & S6.

3.2. Diversity of collected species

A summary of the bulk phenol concentrations and the presence and absence of 15 macroalgal species across seasons, sites, and harbour zones can be found in Table 1. Due to observed differences in composition of macroalgal forests among sites, some species were found exclusively within the inner harbour sites (Harington Point, PML, and Te Umukuri [Weller's Rock,]) or outer harbour sites (Purakaunui Bay/Mapoutahi Pa, Seacliff, and Whareakeake [Murdering Bay] Beach). In addition, the presence of annual species changed over the sampling period, resulting in some species only occurring in selective seasons.

3.3. Bulk phlorotannin concentration in blade tissue across species

When species was held as a fixed effect, TPC was significantly different among species (chi^2 = 1025.8, p < 0.01, Fig. 2) and spanned a range of concentrations from 0 µmol g DTW^{-1} to a maximum concentration of 327.32 µmol g DTW^{-1} analyzed in a *Carpophyllum flexuosum* blade.

On average, *C. flexuosum*, *Cystophora retroflexa*, *Ecklonia radiata*, and *Xiphophora gladiata* had the highest TPC observed among species, but they were statistically comparable to each other (212.60 ± 95% CI = 169.20 to 267.13 µmol g DTW^{-1}, 166.74 ± 95% CI = 138.97 to 200.05 µmol g DTW^{-1}, 164.40 ± 95% CI = 107.25 to 252.01 µmol g DTW^{-1}, and 72.68 ± 95% CI = 56.79 to 93.00 µmol g DTW^{-1}, respectively; from here, all results reported as emmean ± 95% lower asymptomatic confidence interval, upper asymptomatic confidence interval) (Fig. 2, Table S1).

C. flexuosum and *C. retroflexa* displayed concentrations many times higher than the species that regularly reported concentrations above ~10 µmol g DTW^{-1} such as *Sargassum sinclairii*, *Cystophora torulosa*, *Marginariella boryana*, *Marginariella urvilliana*, *Hormosira banksia*, and *Macrocystis pyrifera* (Fig. 2, Table S2). However, among this group of mildly potent species, except for *M. pyrifera*, TPC was on average statistically similar in TPC to the lowest of the highly potent macroalgal species, *X. gladiata* (Fig. 2, Table S2). Among the mild species, *M. pyrifera* had the lowest average TPC (20.21 ± 95% CI = 17.14 to 23.84 µmol g DTW^{-1}) and was statistical similar in concentration with *M. urvilliana* (38.41 ± 95% CI = 27.10 to 54.43 µmol g DTW^{-1}) and *H. banksia* (29.84 ± 95% CI = 19.47 to 45.75 µmol g DTW^{-1}) but significantly lower in TPC than *S. sinclairii* (72.68 ± 95% CI = 56.79 to 93.00 µmol g DTW^{-1}), *C. torulosa* (67.54 ± 95% CI = 47.65 to 95.72 µmol g DTW^{-1}), and *M. boryana* (62.76 ± 95% CI = 49.95 to 78.86 µmol g DTW^{-1}) (Fig. 2, Table S2).

Desmarestia ligulata, *Durvillaea* spp., *Lessonia variegata*, and *Undaria pinnatifida* on average had

Table 1. Blades (n = 5 per sampling event) collected from 15 macroalgal species across season (n = 4), harbour zones (n = 2), sites (n = 6), and average seasonal total phenolic concentration (TPC, μmol g DTW^{-1}). Sites: Harington Point (HP), Portobello Marine Lab (PML), Purakaunui Bay/Mapoutahi Pa (P), Te Umukuri (Weller's Rock) (WR), Whareakeake (Murdering Bay) Beach (W), and Seacliff (SC). All values are mean ± SE

Species	Seasons	Harbour zones	Sites	TPC (μmol g DTW^{-1})
Carpophyllum flexuosum	Spring	Inner	WR	294.68 ± 8.86
	Summer	Inner	HP, WR	233.00 ± 15.30
	Autumn	Inner	HP, WR	173.16 ± 19.70
	Winter	Inner	HP, WR	190.61 ± 15.62
Cystophora retroflexa	Spring	Inner	PML, WR	156.96 ± 7.68
	Summer	Inner	PML, WR	252.63 ± 5.71
	Autumn	Inner	HP, PML, WR	176.82 ± 16.15
	Winter	Inner & Outer	HP, PML, P, WR	121.12 ± 5.43
Cystophora torulosa	Summer	Inner	PML	127.05 ± 6.29
	Autumn	Inner	PML	28.40 ± 3.66
	Winter	Inner	PML	47.16 ± 7.88
Desmarestia ligulata	Spring	Outer	W, P	16.26 ± 5.69
	Summer	Outer	W, P	1.50 ± 1.39
Durvillaea spp.	Spring	Outer	P	41.50 ± 3.29
	Summer	Outer	W, P	5.33 ± 2.25
	Winter	Outer	W, P	0.00 ± 0.00
Ecklonia radiata	Spring	Outer	SC	164.40 ± 9.52
Hormosira banksia	Autumn	Inner	PML	24.56 ± 3.00
	Winter	Inner	PML	35.12 ± 4.48
Lessonia variegata	Spring	Outer	W	12.52 ± 5.61
	Summer	Outer	W	2.72 ± 2.21
Macrocystis pyrifera	Spring	Inner & Outer	HP, P, PML, WR	27.67 ± 4.53
	Summer	Inner & Outer	HP, P, PML, WR	22.59 ± 2.39
	Autumn	Inner	HP, PML, WR	11.38 ± 1.91
	Winter	Inner	HP, PML, WR	11.87 ± 2.48
Marginariella boryana	Spring	Inner	HP	98.57 ± 11.62
	Summer	Inner	HP, WR	40.10 ± 4.80
	Autumn	Inner	HP, WR	60.99 ± 10.22
	Winter	Inner	HP, WR	69.29 ± 10.42
Marginariella urvilliana	Spring	Outer	P	47.29 ± 5.80
	Summer	Outer	P	28.44 ± 16.61
	Winter	Outer	P	39.48 ± 17.14
Sargassum sinclairii	Spring	Inner	HP	140.77 ± 20.82
	Summer	Inner	HP, WR	128.86 ± 28.52
	Autumn	Inner	HP, WR	32.74 ± 4.42
	Winter	Inner	HP, WR	50.47 ± 11.62
Undaria pinnatifida	Spring	Inner & Outer	HP, P, PML, WR	6.21 ± 1.80
	Summer	Inner & Outer	HP, P, PML, WR	15.36 ± 2.10
	Autumn	Inner	HP, PML, WR	3.36 ± 1.23
	Winter	Inner & Outer	HP, P, PML, WR	1.53 ± 0.64
Xiphophora gladiata	Winter	Outer	W	79.46 ± 12.24
Ulva spp.	Spring	Inner	HP, PML, WR	3.01 ± 0.68
	Summer	Inner	HP, PML, WR	1.43 ± 0.51
	Autumn	Inner	HP, WR	10.35 ± 2.52
	Winter	Inner	HP, PML, WR	5.06 ± 1.90

annual TPC that were statistically like the Chlorophyta *Ulva* spp. (Fig. 2, Table S2) as concentrations were regularly recorded in the range of ~0−0 μmol g DTW^{-1} within these species. However, as we were measuring TPC, it is possible trace amounts of phenolic compounds that are not phlorotannins were sometimes present in *Ulva* spp., suggesting that our array's precision for reliably detecting low concentrations of phlorotannins in the 'low-level' species has limited accuracy under ~10 μmol g DTW^{-1}.
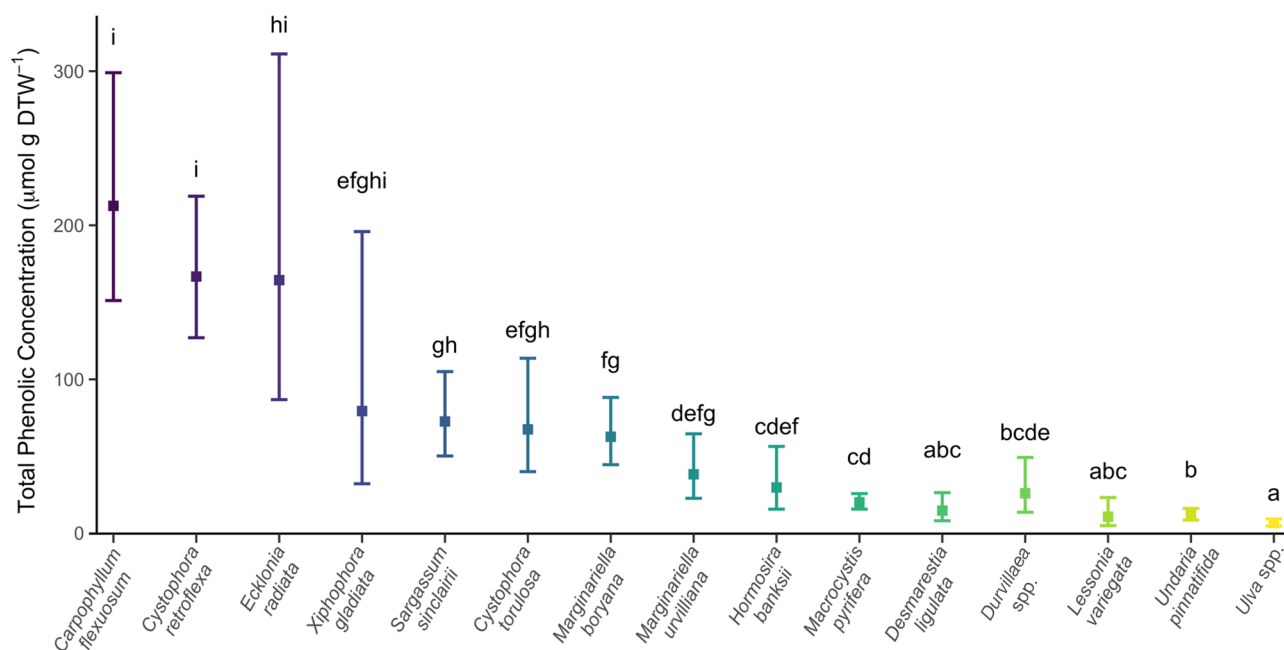
Fig. 2. Total phenolic concentration (TPC, µmol g DTW^{-1}) of 14 species of Phaeophyceae and *Ulva* spp. from the Otago Harbour Region. Boxes: annual marginal estimated mean (emmean) of TPC for each species. Error bars: 95% asymptomatic confidence intervals of the emmean. Emmeans sharing a letter are not significantly different in TPC (Šidák-adjusted comparisons)

3.4. Influence of seasonality on TPC within inner harbour species

Within the inner harbour, *C. retroflexa*, *M. pyrifera*, *U. pinnatifida* and the Chlorophyta *Ulva* spp. were regularly collected across all seasons and sites (Table 1). TPC was significantly different across these 4 species (post-hoc comparison of estimated marginal means, p < 0.01, Fig. 3a) and was significantly influenced by the main effects of 'Species' and 'Season', but not 'Site' (Table 2). All 2-way interactions among effects were found to significantly explain variation in TPC within the inner harbour communities (Table 2).

Across all sites and seasons, *C. retroflexa* was always a magnitude more concentrated in TPC than the 2 Laminariales and *Ulva* spp. (Fig. 3, Table S3). TPC observed within *M. pyrifera* and *U. pinnatifida* was more complicated to explore. When results were averaged over the fixed effect season, *M. pyrifera* was more concentrated in TPC than *U. pinnatifida* at Harington Point and Te Umukuri (Weller's Rock), but statistical similar in concentration at PML (Fig. 3a). In addition, TPC in both *M. pyrifera* and *U. pinnatifida* could not be distinguished from the TPC recorded in the Chlorophyte *Ulva* spp. at the PML site, nor between *U. pinnatifida* and *Ulva* spp. at the Weller's Rock site (Fig. 3a).

When results were averaged over the fixed effect site, *M. pyrifera* was more concentrated in TPC than *U. pinnatifida* only in the winter months but was statistically similar in TPC during the spring, summer, and autumn months (Fig. 3b). In addition, *U. pinnatifida* could not be distinguished from *Ulva* spp. during the winter months, and *M. pyrifera* was statistically similar in TPC with *Ulva* spp. in the autumn months (Fig. 3b).

3.5. Influence of seasonality on TPC within outer harbour species

In the outer harbour, *D. ligulata*, *Durvillaea* spp., *M. pyrifera*, *M. urvilliana*, and *U. pinnatifida* were collected for at least 2 seasons from Purakaunui Bay/ Mapoutahi Pa (Table 1). In general, TPC observed across *D. ligulata*, *Durvillaea* spp., *M. pyrifera*, and *M. urvilliana* was higher in the spring months than the summer months when concentrations were more regularly reported under ~10 µmol g DTW^{-1} (Fig. 4). Within the spring sampling event, median TPC was statistically different between *M. pyrifera* and *D. ligulata* (post-hoc comparison of medians, adjusted p-value 0.014) and *M. pyrifera* and *Durvillaea* spp., (adjusted p-value 0.014) but statistically similar between all other species (Fig. 4, Table S5). In addition,
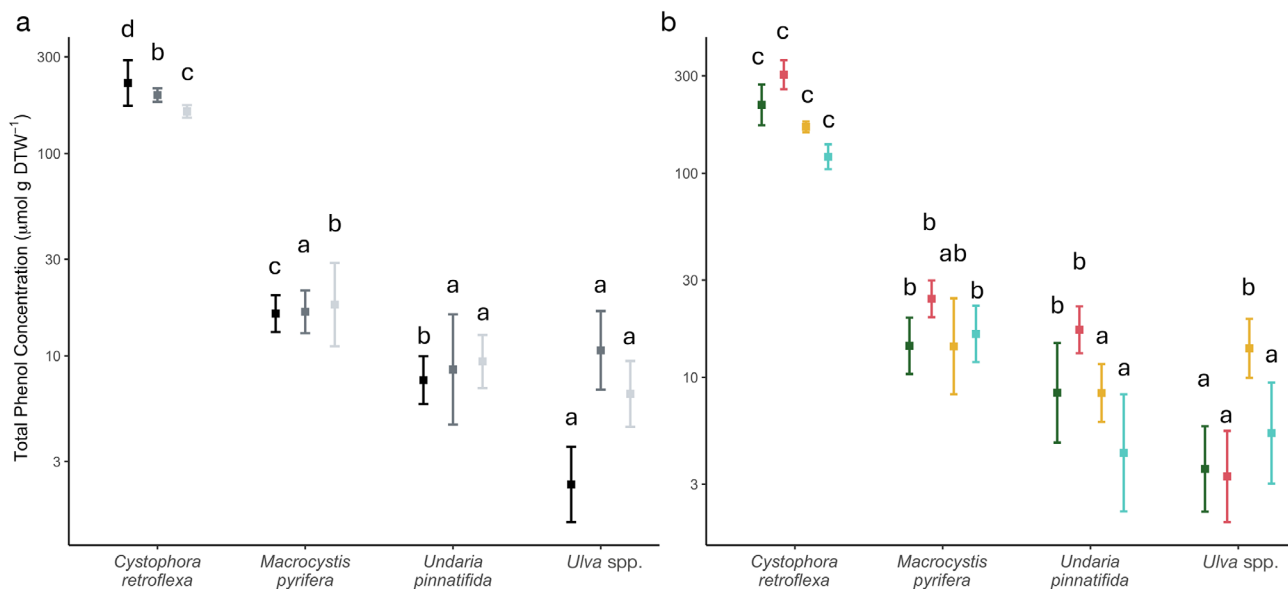
Fig. 3. Total phenolic concentration (TPC, µmol g DTW^{-1}) of 3 Phaeophyceae species and *Ulva* spp. observed from (a) 3 sites (black: Harington Point; slate-grey: Portobello Marine Laboratory; light-grey: Te Umukuri [Weller's Rock]), across (b) 4 seasons (spring: green; summer: red: yellow: autumn; blue: winter) inside the Otago Harbour. Boxes indicate the marginal estimated mean (emmean) of TPC for each species at (a) the observed site when results were averaged over the fixed effect season and (b) within each season when results were averaged over the fixed effect site. Error bars: 95% asymptomatic confidence intervals of the emmean. Emmeans sharing a letter are not significantly different in TPC (Šidák-adjusted comparisons) (a) within site or (b) within season

Table 2. Analysis of deviance (Type III Wald chi^2 tests) of a generalized linear mixed model using template model builder analyzing the total phenolic concentration (TPC, µmol g DTW^{-1}) in 4 species of macroalgae from 3 sites in the Inner Otago Harbour (Harington Point, Portobello Marine Lab, and Te Umukuri [Weller's Rock]) present in the community across all 4 seasons cover (n = 224)

Variables	Chi^2	Chi df	p (>chi^2)
Species	1054.1	3	p < 0.001
Site	108.41	2	p < 0.001
Season	62.379	3	p < 0.001
Species:Site	64.149	6	p < 0.001
Species:Season	87.877	9	p < 0.001
Site:Season	125.62	6	p < 0.001

TPC observed in *U. pinnatifida* was nearly statistically different than all other observed species (adjusted p-value = 0.067, Fig. 4, Table S5). However, *U. pinnatifida* sample size was low (n = 3), and all concentrations reported as 0 µmol g DTW^{-1} during the spring sampling event, which could not be compared within the pairwise comparison, resulting in a 'non-significant' result. TPC concentrations in the summer sampling period were generally lower in all species than TPC observed in the spring. Within the summer period, TPC was statistically lower in *D. ligu-*

lata than the observed concentrations in *M. pyrifera*, and *M. urvilliana* (adjusted p-value = 0.014 and 0.014, respectively) but statistically similar between all other species (Fig. 4, Table S6).

3.6. Influence of harbour zone on phlorotannin concentrations

U. pinnatifida was the only species observed across communities both within the sheltered inner harbour sites (Harington Point, PML, and Te Umukuri (Weller's Rock), and the wave-exposed outer harbour site Purakaunui Bay/Mapoutahi Pa in the spring, summer, and winter months. When comparing TPC measured within the inner and outer harbour populations of *U. pinnatifida*, the Mood's median test did not suggest a significant different in TPC between populations observed in the spring (chi^2 = 1.60, p-value = 0.21), summer (chi^2 = 1.07, p-value = 0.30), or winter (chi^2 = 1.27, p-value = 0.26) (Fig. 5). However, post-hoc comparisons in the summer and winter populations were not possible due to the high occurrence of TPC in the outer harbour populations regularly reporting as 0 µmol g DTW^{-1} (Fig. 5). Despite this, Vargha and Delaney's *A* measures do suggest that the probability of TPC

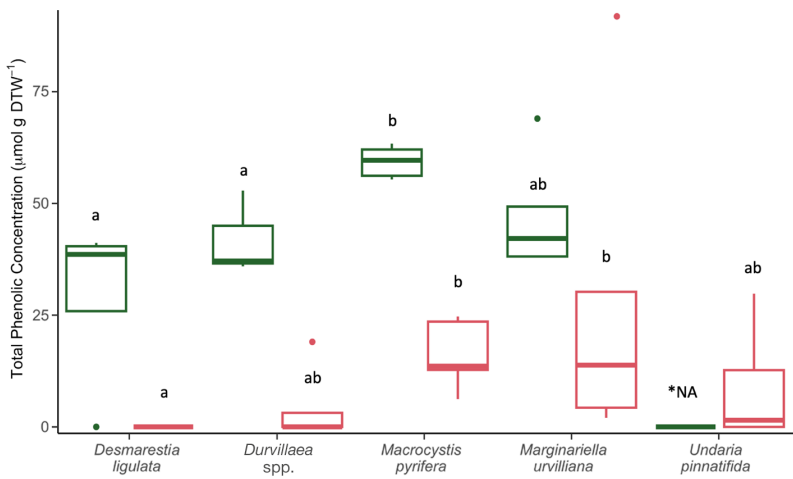Fig. 4. Total phenolic concentration (TPC, µmol g DTW^{-1}) of 5 Phaeophyceae species observed from 1 wave-exposed site outside the Otago Harbour Region (Purakaunui Bay/Mapoutahi Pa). TPC was compared between the 5 species within the spring (green) and summer (red) seasons. Medians sharing a letter are not significantly different in TPC (pairwise-adjusted comparisons) from other species within the observed community during the seasonal sampling event. Boxes: interquartile range between the first (lower, 25th percentile) and third (upper, 75th percentile) around the median (line within the box). Whiskers: minimum and maximum scores of the data; outliers: dots. *NA: result of the inability for the pairwise comparison to compare spring *Undaria pinnatifida* with concurrent species due to low sample size (n = 3); all concentrations reported to be 0 µmol g DTW^{-1}

4. DISCUSSION

4.1. Overview

The observed variation in TPC of the 14 species of large brown macroalgae among sites and seasons could be largely explained by a variation among species which was observed to range across 2 orders of magnitude. The most potent species recorded was *Carpophyllum flexuosum*, with a maximum observed TPC of 327.32 µmol g DTW^{-1} from an individual specimen sampled in the spring and an annual average concentration of 212.60 ± 95% CI = 169.20 to 267.13 µmol g DTW^{-1}. Our most dilute species included *Durvillaea* spp., *Desmarestia ligulata*, *Lessonia variegata*, and *Undaria pinnatifida*, which had annual concentrations so low that they could not be differentiated from our green algal control *Ulva* spp.

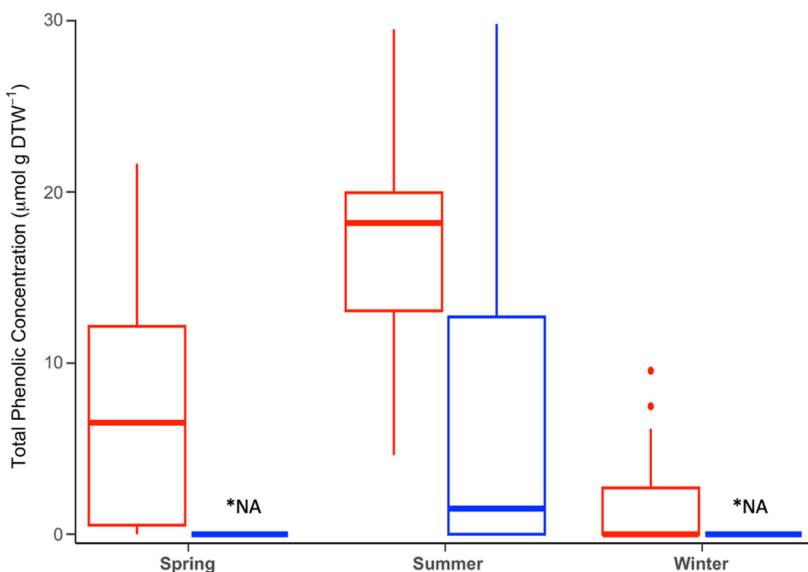In New Zealand, macroalgal community composition is changing as a response to persistent stressors and disturbances. Forests that historically were dominated by large canopy forming species such as *Macrocystis pyrifera* and *Durvillaea* spp. are of particular concern as continued oceanic warming, more frequent extreme heat wave events, and increasing coastal sedimentation loading are reported to be the primary causes of range shifts and losses within

being higher within a specimen collected from the inner harbour *U. pinnatifida* population in comparison to an individual from the outer harbour population is high in the spring and summer months (*A*-measures of 0.90 and 0.76, respectively) and probable in the winter months (*A*-measure of 0.70).

Fig. 5. Total phenolic concentration (TPC, µmol g DTW^{-1}) from populations of *Undaria pinnatifida* observed from inner (red) and outer (blue) harbour populations in the Otago Harbour Region. TPC was compared across harbour zones within the seasons using the Mood's median test and was found to be statistically similar across all sites within a season. Boxes: interquartile range between the first (lower, 25th percentile) and third (upper, 75th percentile) around the median (line within the box). Whiskers: minimum and maximum scores of the data; outliers: dots. Vargha and Delaney's *A* measures suggest a specimen collected from an inner harbour location would have a high probability of being more concentrated than a specimen outside the harbour in the spring and summer months (*A*-estimates 0.90 and 0.76, respectively) and a reasonable probability in the winter (*A*-estimate 0.70). *NA: result of the inability for the pairwise comparison to compare TPC due to a high occurrence of reported 0 µmol g DTW^{-1} concentrations in the spring and winter outer harbour population

these species (Johnson et al. 2011, Vergés et al. 2014, Thomsen et al. 2019, Butler et al. 2020, Tait et al. 2021). Both *M. pyrifera* and *Durvillaea* spp. are long-lived, large-bodied, perennial species that act as foundation species in the subtidal and intertidal zones. Their presence provides community structure, ultimately setting the scaffolding for habitat stability and providing organic matter for the food webs supporting culturally and economically impactful species, including reef fishes (e.g. blue cod *Parapercis colias*, green bone *Odax pullus*), kōura (the red rock lobster *Jasus edwardsii,*), kina (endemic urchin *Evechinus chloroticus*), kūtai (the green-lipped mussel *Perna canaliculus*), and pāua (*Haliotis iris, H. australis,* and *H. virginea*) (Schiel et al. 1995, 2018, Jack & Wing 2010, 2011, Wing & Jack 2012, Hinojosa et al. 2015, Wing & Wing 2015, Udy et al. 2019b, Schlieman et al. 2022).

The TPCs of mature blade material measured from *M. pyrifera* and *Durvillaea* spp. were among the most dilute of the observed species. However, it remains largely unknown to what extent the loss of canopy-forming species and the replacement by taxa capable of living in degraded states, with TPC magnitudes more concentrated, may lead to ecosystem-wide changes in the quality and palatability of organic material produced from macroalgal communities. Here, we will apply the TPC measured across a range of macroalgal species in the present study to reported observations of shifts in forest community composition in New Zealand and consider how variations in phenolic content may impact the phenolic composition of macroalgal-derived organic matter.

4.2. Implications of shifting community composition: *C. flexuosum*

C. flexuosum was on average the most potent species for phlorotannin concentrations observed in our analysis (Fig. 2). *C. flexuosum* is reported among some of the most resilient of the fucoid species, capable of surviving in the heavily degraded Marlborough Sounds region, which has experienced widespread loss of *M. pyrifera* since the 1960s, and it is now the dominant species on many reefs, including within Queen Charlotte Sound (QCS) (Neil et al. 2018, Anderson et al. 2020, Tait et al. 2021). The expanded occurrence of *C. flexuosum* despite ongoing loss of historic biodiverse *M. pyrifera* forests may help to explain the relatively low utilization of macroalgal-derived organic matter in marine food webs within the Marlborough Sounds (Udy et al. 2019b).

Unfortunately, our understanding of the degradation rates of phenolic compounds in macroalgal detritus entering marine systems is largely unquantified, limiting our understanding of how TPC within living tissues could have wider impacts on the palatability of detrital material produced from macroalgal communities. However, it is possible that phlorotannins may act like terrestrial tannins , particularly in their ability to alter the bioavailability of nitrogen within systems and which also have wider ecologic implications for community structure in terrestrial communities (Peter Constabel et al. 2014).

In addition to degradation rates, it is unclear if the classes of phlorotannins present within macroalgal species may influence overall bioavailability of detrital material produced from more potent or labile species. Our assay measured TPC, but it is important to consider the different classes of phlorotannins reported within our observed species, especially among the more potent species. Phlorotannins can be isolated into groups according to the molecular structure of the phloroglucinol monomeric unit combinations which build the resulting oligomers. Based on these linkages and the number of additional hydroxyl groups, phlorotannins can be identified within 6 groups: phlorethols, fucols, fuhalols, fucophlorethols, isofuhalols, and eckols (Arbenz & Averous 2015). In *C. flexuosum,* the majority of phlorotannins fall into the fuhalol group (Zhang et al. 2018), while in *C. retroflexa* the majority of phlorotannins are phlorethols and fucophlorethols (Sailler & Glombitza 1999).

In addition to the 6 classes of phlorotannins, phlorotannins can be halogenated, mostly in brominated, chlorinated, and iodinated forms. Halogenated organic compounds, particularly brominated or chlorinated secondary metabolites, are relatively uncommon in the brown algae where less than 1% contain such compounds. In comparison, 90% of the secondary metabolites in Rhodophytes (the red alga) and 7% in the Chlorophytes (the green alga) contain brominated and chlorinated forms (La Barre et al. 2010). Among brown macroalgae, Fucales have the most common incidence of halogenated phlorotannins in addition to other halogenated phenolic compounds (La Barre et al. 2010). It has been suggested that both the intracellular stockpiling and external oxidative burst release of these volatile halogenated organic compounds, which include halogenated phlorotannins and other halogenated phenolic compounds, could be a defensive strategy against pathogenic, biofouling, and grazing threats due to their increased relative toxicity (Fairhead et al. 2005).

In *C. retroflexa,* 17 halogenated phlorotannins (brominated, chlorinated, and iodinated) have been identified in addition to 30 non-halogenated forms (Sailler & Glombitza 1999) while at least 4 halogenated metabolites have been isolated in *Carpophyllum angustifolium* (Glombitza & Schmidt 1999). To date, no study has explored what effect the different compositions of phlorotannin classes or presence of halogenated phlorotannins among macroalgae may have on grazing preference. All studies have only focused on bulk phlorotannin composition, and future studies should consider if the intrinsic differences in phlorotannin class could be an important factor for grazing deterrence among Phaeophyceae.

4.3. Implications of *U. pinnatifida* for macroalgal organic material availability

From our observations, *U. pinnatifida* has on average one of the lowest annual phlorotannin concentrations among Phaeophyceae species. Although concentrations were comparable to *Durvillaea* spp., the physiological and life history differences between these species have important consequences for the temporal patterns in production of organic matter supplied by the 2 species. *D. antarctica* is a highly productive species with projected daily spring net primary productivity (NPP) rates around 10 g C m^{-2} d^{-1}. *U. pinnatifida* displays daily spring NPP rates around 8 g C m^{-2} d^{-1}, which are similar to other sub-canopy species such as *Cystophora torulosa* (7 g C m^{-2} d^{-1}) (Tait et al. 2015). From this high NPP, low phlorotannin content, and the annual life history of *U. pinnatifida*, it has been suggested that the expansion of the non-native kelp could have the potential to increase carbon export to surrounding ecosystems when compared to similar perennial native fucoid species. Therefore, it is suggested *U. pinnatifida* may have a positive effect on fluxes of macroalgal-derived organic matter into rocky reef ecosystems (Tait et al. 2015).

It is less clear how expansion of *U. pinnatifida* into *M. pyrifera*-dominated forests may shift organic matter loading to local marine food webs. To date, there is little evidence that these 2 Laminarians display interspecific competition (Raffo et al. 2009), and instead the arrival of the palatable annual *U. pinnatifida* may increase overall productivity within the forest. Both species have been observed to be important sources of organic matter for marine food webs (Suárez-Jiménez et al. 2017, Udy et al. 2019a, Lozada et al. 2023), and with relatively low phlorotannin concentrations, we would expect these species would provide labile material for both direct consumption by grazers and particulate detrital consumption by suspension feeders from a biochemical perspective.

4.4. Scenarios of shifting community composition: a biomass estimate approach

From our average annual concentrations, we will compare the general change in phlorotannins across several shifting forest communities. As observed in the QCS, the fucoid *C. flexuosum* can settle in areas once dominated by *M. pyrifera.* If we assume a standing biomass of 100 g DTW m^{-2} for both species, a replacement of an equal *C. flexuosum* biomass would cause TPC to increase more than 10-fold in living macroalgal tissue (annual estimated marginal mean TPC from $20.21 \pm 95\%$ CI $= 17.14$ to 23.84 µmol g DTW^{-1} in *M. pyrifera* to $212.60 \pm 95\%$ CI $= 169.20$ to 267.13 µmol g DTW^{-1} in *C. flexuosum*). However, on the other end of the spectrum, if a 100 g DTW m^{-2} *U. pinnatifida* biomass was to replace a similar *M. pyrifera* biomass, average phlorotannin concentrations would decrease by nearly half (annual emmean TPC from $20.21 \pm 95\%$ CI $= 17.14$ to 23.84 µmol g DTW^{-1} in *M. pyrifera* to $11.90 \pm 95\%$ CI $= 9.66$ to 14.66 µmol g DTW^{-1} in *U. pinnatifida*). If we instead apply our observed concentrations to the trends observed in recruitment of *U. pinnatifida* following the clearance of *Durvillaea* spp. canopy assemblages, the change to average phlorotannin concentration would be undistinguishable as these species were statistically similar in phlorotannin concentration (Fig. 2). However, the difference in life history could have important implications for the patterns in annual organic matter loading provided by these alternative species. Whereas *Durvillaea* as a perennial species stores large amounts of biomass and produces detrital organic matter relatively consistently throughout the year. *Undaria* supplies a large pulse of organic matter as the mature blades senesce seasonally. The difference in temporal supply of organic matter between these 2 species could be important for the efficient uptake of organic matter into food webs where a saturating type II functional response will result in reduced uptake during pulsed supply events (Wing et al. 2012).

4.5. Limitations of the Folin-Ciocalteu reaction for phlorotannin measurements

The extraction of pure samples of phlorotannins is difficult regardless of the assay used. Polyphenolic

compounds are sensitive to oxidation, and in combination with the tendancy for polyphenolics to precipitate proteins, underestimates of concentration are likely unless these factors are controlled (Ragan & Glombitza 1986). We used a modified version of the Folin-Ciocalteu assay to measure TPC within 14 Phaeophyceae species and 1 Chlorophyta, *Ulva* spp. The Folin-Ciocalteu (F-C) reaction is a well-known reaction that is an improvement to the Folin-Denis (F-D) assay, which is the most widely utilized assay to measure TPC (Amsler & Fairhead 2006). By utilizing the modified F-C reagent, the amount of precipitates is reduced (Van Alstyne 1995) and smaller sample sizes can be used (Stern et al. 1996). However, in both the F-C and F-D assays the reagent is also reactive with other compounds in addition to phenolics, but this represents only a small fraction of the overall measurement (Van Alstyne 1995). The reactive nature of the F-C reagent, however, might explain why we recorded trace amounts of 'phlorotannins' in our green macroalgal control which have not been reported to contain phlorotannins. If we wished to correct for the additional reactive compounds within the *Ulva* spp. to standardize our samples, we would require additional analysis utilizing microwave assisted extraction (MAE) and high precision liquid chromatography coupled to mass spectrometry (HPLC-MS) to identified individual compounds. Instead, we can conclude the utilization of the F-C assay has limitations in accurately measuring phlorotannin concentrations less than ~10 µmol g DTW^{-1}.

5. CONCLUSIONS AND FUTURE RESEARCH

The current study highlights important consequences of shifts in the community structure of macroalgal forests for the chemical composition of macroalgal-derived organic matter and possible influences on function of coastal rocky reef ecosystems. From our observations, we found that phlorotannin concentrations can vary across 2 orders of magnitude among individuals and species, indicating that changes in community composition will change the overall phenolic composition of macroalgal-derived organic matter produced by these communities. Currently, it is unclear how the shifts in phlorotannin concentrations within the resulting pool of organic matter could affect ecosystem function. To fully understand how shifts in macroalgal community structure may impact the palatability of organic matter supplied by macroalgal detritus, research is required to understand the fine-scale degradation

rates of phlorotannins in macroalgal-derived detrital material as well as the sources and fates of particle movements surrounding macroalgal forest communities. These data highlight important consequences of shifts in both the abundance and species composition of forest macroalgal communities for the chemical composition of macroalgal-derived organic matter and show how multiple stressors on macroalgal forests could potentially alter food webs and productivity of the coastal ecosystem.

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