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J. G. Jennings · P. D. Steinberg

In situ exudation of phlorotannins by the sublittoral kelp *Ecklonia radiata*

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Abstract Exudation of phlorotannins (polyphenolics) was measured in situ from the sublittoral kelp *Ecklonia radiata* at two locations near Sydney, New South Wales, Australia during 1992–1993. Minimally disruptive techniques were used in which individual plants were enclosed within clear plastic bags in order to concentrate exudates. Rates of exudation from *E. radiata* were low relative to most previous studies, with a mean rate (averaged across four seasons and two sites) of 5.5 μg g (dry wt)$^{-1}$ h^{-1}. Exudation was greatest in summer and least in winter at one site, but there were no seasonal differences at a second, more protected site. There was no measurable diurnal variation in exudation rates. Exudation after a period of heavy storms was not significantly different from exudation during calm weather, but severe physical damage to the kelp did increase exudation. Our results suggest that exudation of phlorotannins in temperate Australian waters may be less ecologically important than has been suggested for coastal systems in the Northern Hemisphere.

Introduction

Benthic marine macroalgae produce a wide diversity of so-called secondary metabolites (Hay and Fenical 1988). In the brown algae (division Phaeophyta), the most common of these metabolites are the phlorotannins which are polymers of phloroglucinol (1,3,5-trihydroxybenzene). Phlorotannins can comprise up to 15 to 20% of the thallus dry weight of brown algae (Steinberg 1985, 1989; Ragan and Glombitza 1986). The primary function of phlorotannins is thought to be as chemical defence against marine herbivores (Steinberg 1992), although it has been suggested that they function as deterrents or inhibitors of epiphytes (Sieburth and Conover 1965; Fletcher 1975; Langlois 1975; Davis et al 1989) or as inhibitors of microbial activity (Sieburth and Conover 1965).

Brown algae release phlorotannins (Ragan and Jensen 1979; Carlson and Carlson 1984) into the surrounding water either directly via exudation or indirectly (via erosion or shedding of macroscopic parts). Although exudation can occur from both healthy algae (Carlson and Carlson 1984) and following stress or injury (Craigie and McLachlan 1964), the amounts of phlorotannins exuded by healthy plants has been controversial. Exudation rates by healthy algae in a number of previous studies were quite high (Sieburth 1969; Sieburth and Jensen 1969; Zavodnik 1981; also see Table 19 in Ragan and Glombitza 1986), in the range of 100 s of microgrammes of phlorotannins exuded per gram algal dry mass per hour. Since brown algae – particularly kelps and fucoids – are often the dominant plants in temperate algal communties, these levels of exudation could have considerable consequences to the chemistry and ecology of coastal waters. Craigie and McLachlan (1964) and Sieburth and Jensen (1969) suggested that brown algal phenolics were a major component of detrital "Gelbstoff" in nearshore waters. High levels of phlorotannins in the water may also affect coastal water-absorbance characteristics (Carlson and Mayer 1983), contribute to surface slicks (Carlson 1982), and at the surface of an alga deter settlement of epiphytes (Sieburth and Conover 1965; Langlois 1975; Davis et al 1989).

Most studies of exudation of phlorotannins have been done on intertidal algae, or in the laboratory where the algae are likely to be stressed as a result of handling or changes in external conditions (Sieburth 1969; Moebus and Johnson 1974), which may have resulted in unnaturally high rates of exudation. When exudation has been measured in the field (Carlson and Carlson 1984), or in the laboratory where care was taken to avoid stress to the algae (Ragan and Jensen 1979), exudation rates were often an order of magnitude or more lower [e.g. 10 μg g (dry wt)$^{-1}$ h^{-1}] than those previously measured. Moreover, in intertidal brown algae, most exudation of phlorotannins probably

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J. G. Jennings · P. D. Steinberg (✉)
School of Biological Sciences, University of New South Wales, Sydney, New South Wales 2052, Australia

occurs immediately after plants are reimmersed following exposure to air at low tide (Carlson and Carlson 1984). Thus, exudation of phlorotannins by unstressed algae, and particularly sublittoral algae which are not subject to immersion/emersion cycles, may in particular be quite low.

In this paper we report for the first time in situ measurements of phlorotannin exudation from a sublittoral brown alga – the Australasian kelp *Ecklonia radiata* – carried out under natural, unstressed conditions. *E. radiata* is particularly relevant for such a study since it contains high levels of phlorotannins (Steinberg 1989) and is also one of the most abundant benthic alga in temperate Australia (Kirkman 1984). Diurnal, seasonal, and spatial variations in exudation rates were measured, as were the effects of stress and damage on exudation.

Materials and methods

Study sites

Experiments on exudation of phlorotannins from *Ecklonia radiata* were done in 1992–1993 at two locations near Sydney, New South Wales, Australia (34° 0′S, 151° 11′E); Cape Banks, a moderately exposed coastal site, and Nielsen Park, Vaucluse, a more protected site within Sydney Harbour.

Measurement of exudation

An initial pilot study indicated that phlorotannin levels in water within forests of *Ecklonia radiata* were below our detection limits of 30 μg l^{-1}. Thus in order to concentrate phlorotannins in the water, a technique was developed whereby we enclosed individual *E. radiata* thalli within plastic bags:

A clear 40-litre plastic bag was carefully placed over a mature *Ecklonia radiata* plant (e.g. one with well developed primary and secondary laminae as per Kirkman 1984). An empty 1-litre glass sample-bottle was placed in the bag with the plant, and the bag was sealed tightly around the stipe of the plant with a cable tie. Other bags containing sample bottles but not plants were sealed in the same way and attached to the substratum in the kelp bed with rope, to act as controls for any effect of the bags themselves on the enclosed water. Samples of the water column amongst the kelp bed were also taken at this time in order to monitor background levels of phlorotannins.

After a period of 6 h (see following subsection "Validation of technique"), the sample bottles were opened within the bag, allowed to fill with water, and resealed. The plants were then removed from the substratum and brought to the shore intact in the bags. The bottles were removed from the bags, and the volume of water in the bags (including the 1 litre in the bottle) was recorded. Wet and dry (24 h at 50 °C) mass of the plants was also recorded.

The plants, and the water samples from the bottles, were brought back to the University of New South Wales, where the water samples were concentrated to 200 ml in a rotary-evaporator and phlorotannin levels were analysed by the Folin-Denis technique (Ragan and Jensen 1977; Carlson and Carlson 1984), using phloroglucinol as a standard. This procedure enabled us to measure exudation as μg of phlorotannins exuded g^{-1} of *Ecklonia radiata* (dry wt) h^{-1}.

Validation of technique

We deemed that there were two likely potential sources of error using the technique described above. Firstly, compounds might somehow be lost from the bags or adsorb to their surfaces (although this latter possibility is unlikely given the polar nature of phlorotannins). These possibilities were examined by placing known quantities (1 mg l^{-1}) of extracted *Ecklonia radiata* phlorotannins (methods in Ragan and Glombitza 1986; Steinberg and van Altena 1992) into six bags, taking a water sample from the bag after 6 h as described above, and measuring the phenolic content of the water via the Folin–Denis technique.

Secondly, we needed to determine the appropriate amount of time to leave the bags on the plants. This represented a trade-off between the need to have measurable levels of phlorotannins in the bags and the possibility that exudation might artificially increase if the plants were left in the bags long enough to become stressed (Fankboner and De Burgh 1977). This was investigated in an experiment in which bags were left on the plants for 1, 3, 6, 8 and 12 h during the day and for 1, 3, 6 and 12 h during the night [N=3 for each time interval and for the controls (bags without plants) described above]. Dissolved O_2 and pH of the water were measured in the bags at the end of the experiments using a Yokal dissolved-oxygen meter and a standard benchtop pH meter, to see if water chemistry changed in a way which might be likely to stress the plants.

These experiments indicated that 6 h was the minimum time needed to consistently measure exudation (see "Results – Validation of technique"). This time interval was used in measurements of seasonal, spatial and diurnal variation in exudation, and to examine the effects of damage on exudation.

Seasonal and spatial variation

Exudation was measured during the day at Cape Banks and Nielsen Park for four seasons each during 1992–1993. At each location for each season, plants were bagged (N=3), with controls (N=3) run concurrently.

Diurnal variation

To examine diurnal variation in exudation rates, measurements were done during the day and at night at Cape Banks in summer and autumn. Daytime and night-time measurements were made in the same 24 h period. Daytime measurements were done after plants had been in the bags for 6 h as above (N=3 for each season). Preliminary night-time measurements indicated that there was a marked increase in exudation rates after 12 h (see "Results – Validation of technique"). In order to determine if this was due to (a) the experimental duration (12 h rather than 6 h), or (b) temporal variation in exudation rates during the course of the night, two sets of night-time measurements were done. These were: 6 h measurements during the first half of the night (18.00 to 24.00 hrs) and 6 h measurements during the second half of the night (24.00 to 06.00 hrs), with N=3 for each time interval and for each control. Dissolved oxygen and pH were measured in water from all bags at the end of each experiment. Background levels of polyphenolics, oxygen and pH were also monitored at the start of each experiment.

Exudation after periods of storms

To determine if exudation rates increase after periods of rougher conditions (presumably due to damage to the plants), 6 h daytime samples were collected during summer and autumn on the first diveable day after a week of very heavy seas at our more exposed location, Cape Banks. These were compared to samples collected during the same season during calm weather.

Exudation from damaged plants

To determine if damage to the plants had an effect on exudation of phlorotannins, we damaged six plants by tearing laminae and rubbing the plants against the substratum. Exudation from these plants was compared to that of six uninjured plants.

Statistical analyses

Variation in exudation among season, site, etc. was analysed by Student's *t*-tests or analyses of variance (ANOVA) followed by Tukey's multiple-comparison test. Most analyses were done using the statistical package Statview II for Macintosh computers.

Results

Validation of technique

In all experiments described here, the background levels of phenolics collected from the water column immediately above and amongst *Ecklonia radiata* beds were always below our detection limit of 30 μg l^{-1}, as were all control samples (bags enclosing bottles without plants).

The percent recovery of *Ecklonia radiata* phlorotannins added to bags at 1 mg l^{-1} and left in situ for 6 h was 97±2.3% (N=6), and we concluded that phlorotannins were not being lost from the bags, nor adsorbing on to the bags.

In order for phlorotannin concentrations in the bags to be above the measurable threshold of 30 μg l^{-1}, bags needed to be left in place for a minimum of 6 h (Fig. 1). Leaving *Ecklonia radiata* in the bags for longer than 6 h during the day did not result in increased exudation rates (Fig. 1A), suggesting that during the day the plants were not becoming stressed by the procedure (also see below). The 6 h time interval was used for all subsequent results reported below, unless otherwise noted.

Exudation rates from plants left in bags for 6 h at night were similar to daytime rates over 6 h (Fig. 1B). However, exudation rates measured over 12 h during the night were 40 to 50 times higher than in all other samples (Fig. 1B). We hypothesised that this effect was due to an artifact of the procedure, in which the plants were becoming stressed due to oxygen depletion. In support of this hypothesis, the dissolved oxygen levels in the bags during the night dropped significantly (ANOVA: $F_{2,6}$=118.015, P< 0.0001). Mean background levels of dissolved oxygen in the water were 5.2 mg l^{-1}(SE=0.03). After 6 h dissolved oxygen levels in the bags had dropped to 3.7 mg l^{-1}(SE=0.3), and after 12 h it was 1.8 mg l–1(SE=0.03) (N=3 for each time interval). In contrast, oxygen levels in the bags during the day significantly increased (ANOVA: $F_{2,6}$=55.43, P< 0.001) over time from background levels of 5.2 mg l^{-1} (SE=0.03) to 9.5 mg l–1 (SE=0.47) after 6 h and 10.65 mg l^{-1} (SE=0.45) after 12 h. The pH in the bags did not significantly change over time either during the day or night and there was no significant difference between daytime and night-time pH.

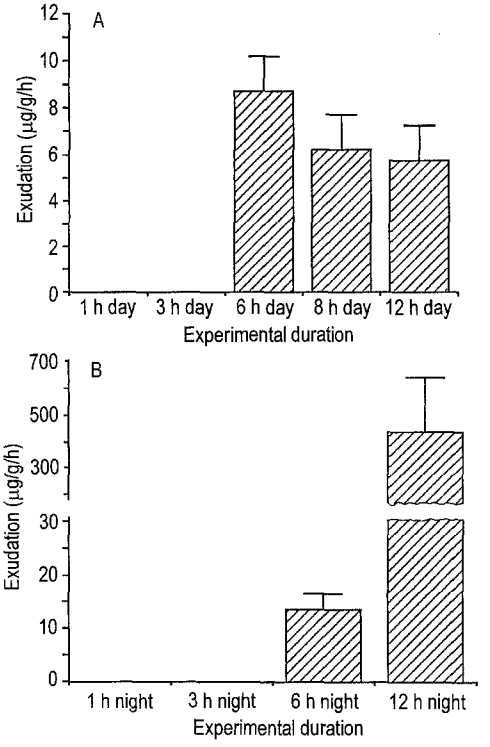

Fig. 1 *Ecklonia radiata*. Phlorotannin exudation after (**A**) 1, 3, 6, 8 and 12 daytime hours in bags at Cape Banks collected during autumn and summer 1992, and (**B**) 1, 3, 6 and 12 night-time hours in bags at Cape Banks (6 h data averaged over early- and late-night samples). Data are averages for summer 1992 and autumn 1992 and are means + SE, with N=6 for each time frame. Exudation is expressed as μg g (dry wt)$^{-1}$h^{-1}. Daytime exudation rates between 6, 8 and 12 h did not differ (one-way ANOVA, $F_{2,6}$=1.533, P>0.1, data for 1 and 3 h excluded). In **B**, note breaks in figure and ordinate for 12 h exudation at night

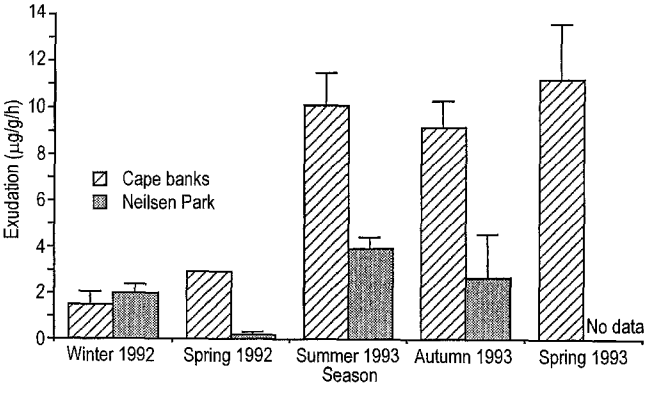

Fig. 2 *Ecklonia radiata*. Daytime phlorotannin exudation for four seasons at Cape Banks and Neilsen Park. Data are means +SE, with N=3 for each season at each location except for spring 1992 at Cape Banks (N =1). Exudation is expressed as μg g (dry wt)$^{-1}$ h^{-1}

Seasonal and spatial variation

Rates of daytime phlorotannin exudation at Cape Banks and Nielsen Park were generally low, only once exceeding a mean of 10 μg g (dry wt)$^{-1}$ h^{-1} for any season at any site (Fig. 2). However, there was significant variation in exudation among both season and sites (Table 1). At Cape Banks, exudation in the winter and spring was less than in summer and autumn (Tukey's test, α=0.05). However, at Nielsen Park, there was no significant seasonal variation. Rates of exudation in summer and autumn at Cape Banks were signficantly higher than at Nielsen Park. Winter and

Table 1 *Ecklonia radiata*. Two-factor analysis of variance for exudation of phlorotannins during day at Cape Banks and Neilsen Park

Factor	*df*	MS	*F*-test	*P*
Season	3	40.36	12.53	0.0003
Location	1	66.81	20.74	0.0005
Season × location	3	15.71	4.88	0.0159
Error	14	3.22		

Table 2 *Ecklonia radiata*. Two-factor analysis of variance for exudation of phlorotannins following calm weather and following storms at Cape Banks for two seasons – summer 1993 and autumn 1993

Factor	*df*	MS	*F*-test	*P*
Weather	1	106.28	2.422	0.1456
Season	1	38.009	0.866	0.3704
Weather × season	1	15.448	0.352	0.564
Error	12	43.889		

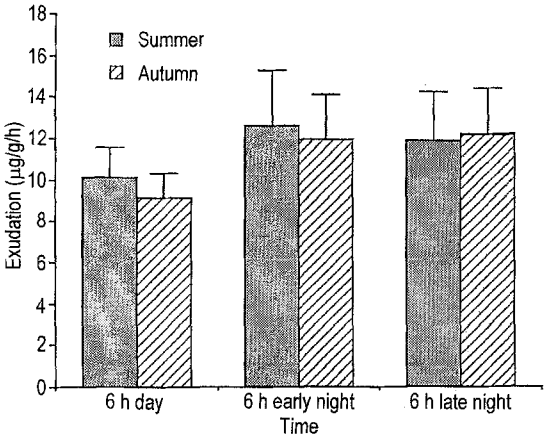

Fig. 3 *Ecklonia radiata*. Diurnal variation in phlorotannin exudation at Cape Banks during summer and autumn 1993. Samples are for a period of six daytime hours (6.00 to 24.00 hrs), six nightime hours early in night (18.00 to 24.00 hrs) and six night-time hours late in night (24.00 to 06.00 hrs). Data are means +SE (N=3 for each time period for each season)

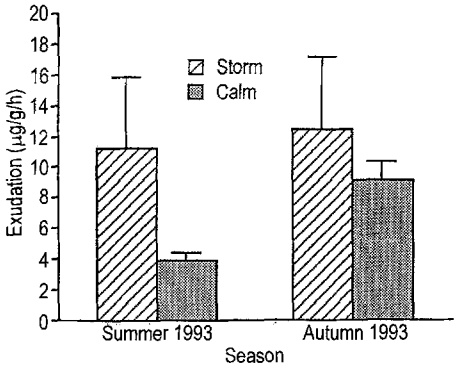

Fig. 4 *Ecklonia radiata*. Phlorotannin exudation following calm weather vs following storms at Cape Banks for summer and autumn 1993. Data are means +SE, with N=3 for each weather condition for each season

spring rates did not differ between the two sites (Fig. 2). A comparison of the data for spring 1992 and spring 1993 (not included in the analysis) suggests that exudation may also vary from year to year.

Diurnal variation

There were no significant differences in exudation rates between day and night at Cape Banks in either summer or autumn (Fig. 3; Two-factor ANOVA for season×time, P>0.05 for all F-ratios). Rates of exudation also did not vary as a function of the time of night the samples were taken, nor did they vary between seasons (Fig. 3).

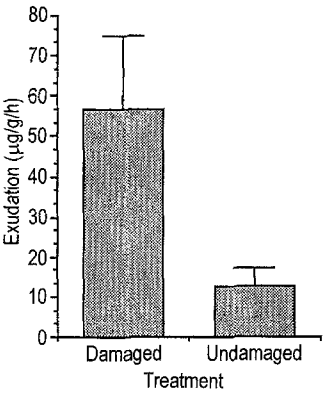

Fig. 5 *Ecklonia radiata*. Exudation of phlorotannins from both damaged and undamaged plants. Data collected during autumn 1993 at Cape Banks; means +SE, N=6 for each treatment

Exudation after periods of storms

Exudation from *Ecklonia radiata* at Cape Banks was not greater after storms than after periods of calm weather (Table 2, Fig. 4). Moreover, mean exudation rates for storm samples over the two seasons (11.9 µg g^{-1} h^{-1}) were comparable to previous seasonal samples at Cape Banks (Fig. 2).

Exudation from damaged plants

Exudation from damaged plants was significantly higher than exudation from undamaged plants (Fig. 5; Student's t-test; t=2.961, df=8, P< 0.05).

Discussion and conclusions

This study reports, for the first time, in situ measurements of phlorotannin exudation from a sublittoral brown alga. The overall mean rate of exudation from *Ecklonia radiata* (across seasons, sites, etc.) in this study was 5.5 µg g^{-1} h^{-1}.

This rate is considerably lower – often by 1 to 2 orders of magnitude – than exudation rates measured in most previous studies (reviewed in Ragan and Glombitza 1986), including those on sublittoral kelps (Sieburth 1969). The low rates of exudation observed in our study are particularly striking given the high concentration of phlorotannins typically found in *E. radiata* (often >15% by dry weight in some plants or parts of the thallus – Steinberg 1989).

A few previous studies have reported exudation rates comparable to those reported here. Ragan and Jensen (1979) found that exudation by *Ascophyllum nodosum* in the laboratory in unstressed conditions was 9.2±3.6 μg g (dry wt)$^{-1}$ h^{-1} during the day and barely measurable (1.4±1.6 μg g (dry wt)$^{-1}$ h^{-1}) at night. Carlson and Carlson (1984), who measured exudation of phlorotannins from intertidal *A. nodosum* in the field by placing fronds exposed at high tide into beakers of ambient sea water, found that exudation was very high – as much as 1.5 mg g (dry wt)$^{-1}$ h^{-1} – within the first few minutes of immersion of the thalli in the beakers [exudation rates calculated from Fig. 3 and the "Methods" section in Carlson and Carlson (1984) using a fresh weight to dry weight conversion factor of 0.2]. However, exudation rates dropped rapidly to 10 μg g^{-1}h^{-1} after thalli had been immersed for 1 h. Thus, in the three studies where exudation was either measured in the field (Carlson and Carlson 1984; and present study) or in carefully controlled laboratory situations (Ragan and Jensen 1979), rates of exudation of phlorotannins from brown algae were typically low (< 10 μg g^{-1} h^{-1}), except for brief periods during the emersion/immersion cycle. One difference between our work and these previous studies is that, unlike Ragan and Jensen, we did not observe diurnal variation in exudation.

Carlson and Carlson's (1984) finding that exudation was only high in recently reimmersed thalli has considerable relevance to the present study, and more generally to coastal Australian waters. Sublittoral species such as *Ecklonia radiata* are not subject to the same physiological changes as intertidal species, which must cope with daily changes in desiccation and reimmersion pressures. With the exception of a few species (e.g. *Hormosira banksii*), temperate rocky shores in coastal Australasia lack the extensive bands of high- and mid-intertidal fucoids so characteristic of Northern Hemisphere rocky shores. Thus, typical Australasian communities of brown algae should not experience the spike of exudation which apparently occurs in intertidal brown algae in the Northern Hemisphere when they are reimmersed following exposure to air.

As has been suggested by Ragan and Glombitza (1986), many of the high rates of phlorotannin exudation previously reported in the literature were probably the result of stress or physiological changes to the algae due to handling (Moebus and Johnson 1974), elevated light intensities (Ragan and Jensen 1979), reimmersion after exposure to air (Carlson and Carlson 1984), changes in pressure and temperature (Sieburth 1969) or other effects. In our study with *Ecklonia radiata*, the most obvious effect of stress was seen for plants which were bagged for >6 h during the night (Fig. 1B). This was probably due to a decrease in oxygen levels in the bags, e.g. an artifact of our methods. However, other factors may have played a role, such as the accumulation of other compounds (non-phlorotannins) in the bags which could have affected the physiological responses of the plants. Physical abrasion or damage also increased exudation, but only when essentially the whole thallus was actively torn or abraded. Such levels of damage probably require particularly heavy storms or attack by herbivores (Andrew and Jones 1990), and are likely to be of short duration. Exudation rates did not increase following storms, even though abrasion of kelps, and some sloughing of tissue, typically occurs at such times. Chronic exposure to heavy seas may have some affect on exudation rates, since exudation was higher at our exposed site (Cape Banks) than at the more protected site (Nielsen Park).

The generally low levels of exudation reported in this study, and our contention that such levels may more accurately reflect the natural field situation, particularly for sublittoral plants, have several consequences for coastal ecology.

Firstly, a number of authors have suggested that phlorotannins have important inhibitory or deterrent effects against epiphytes of brown algae (Sieburth and Conover 1965; Fletcher 1975; Langlois 1975; Hay and Fenical 1992; also see Davis et al. 1989 for a critique of this idea). In part, this is based on the assumption that the high rates of exudation frequently measured in laboratory experiments are representative of exudation in the field. We argue here that many previous measurements may in fact significantly overestimate natural exudation. Moreover, we are not aware of any studies in which both (a) exudation of phlorotannins has been measured in the field, and (b) the concentrations of phlorotannins thus determined have then been tested for their negative effects against epiphytes. Perhaps the likeliest scenario for a negative effect of phlorotannins against potential epiphytes is in tidepools during low tides (Conover and Sieburth 1966). Increased rates of exudation in such situations and the lack of flushing of the tide pools may result in concentrations of phlorotannins in a tidepool sufficient to kill settling propagules (Conover and Sieburth 1966). Such a scenario is not relevant for sublittoral species such as *Ecklonia radiata*. In general, the rate of exudation of phlorotannins from brown algae in the field and the resulting concentrations in the water column may often simply be too low to have a significant effect on epiphytes.

Secondly, it has been proposed that phlorotannins exuded into the water column play an important role in the detrital ecology of coastal systems via the formation of "Gelbstoff" (Sieburth and Jensen 1969; Carlson 1982; Carlson and Mayer 1983). Such a phenomenon may be less important in Australia where *Ecklonia radiata* is the dominant sublittoral alga (Kirkman 1984), than in the Northern Hemisphere systems previously studied (Sieburth and Jensen 1969; Ragan and Jensen 1979; Carlson and Carlson 1984). For phlorotannins to play an important role in detrital pathways in coastal waters, concentrations in the water presumably must be high. Since we never detected phlorotannins in our control samples, levels of phlorotannins in the water were always less than our measurement

threshold of 30 μg l^{-1}. In fact, concentrations of phlorotannins in local waters are almost certainly much less than this. For example if we assume an average density of 18 plants per m^2 of substratum (Andrew and Jones 1990), a dry weight of 100 g per plant (present study), a water depth of 10 m and a mean exudation rate at Cape Banks of 8 μg g^{-1} h^{-1}, the resulting concentration of phlorotannins from *E. radiata* (by far the most abundant brown alga in the system) in the water column above the kelp after 1 h would be 1.4 μg l^{-1}. Even this is likely to considerably overestimate the actual concentration in the water column, since our calculations do not take into account any dilution due to water movement. The actual concentration of phlorotannins in the water column in these Australian systems is probably on the order of hundreds of nanograms per litre or less, and thus phlorotannins probably play a reduced role in the detrital ecology of these systems relative to North American coastal waters [although locally high concentrations may sometimes occur in surface phenomena such as slicks (Carlson 1982)].

Finally, our results have relevance to marine plant/herbivore interactions, a field which has generated much of the interest on the ecological effects of phlorotannins (Ragan and Glombitza 1986; Steinberg 1992). One of the key assumptions of most theories for the evolution of plant chemical defenses against herbivores is that the defenses are "costly" (Hay and Steinberg 1992). That is, in order to be produced and maintained by the plant they require a substantial investment in terms of energy, enzymes, etc. The evidence for a cost of phlorotannins in brown algae is equivocal (Pfister 1992; Steinberg 1992; Yates and Peckol 1993). However, it has been suggested (Hay and Fenical 1992) that phlorotannins may not be costly because they and other carbon-based compounds were thought to be leaked so readily from the algae. Our results indicate that only a very small proportion of the phlorotannins in *Ecklonia radiata* are exuded from the plant and thereby lost. Hence, exudation of phlorotannins is not evidence that phlorotannins are not costly to these algae.

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