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Short communication

Occurrence and accumulation of heavy metals in algal turf particulates and sediments on coral reefs

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ABSTRACT

Algal turfs form a critical interface on coral reefs that interacts with several key ecosystem processes. While we know these turfs have a remarkable propensity to accumulate sediments, which can have a range of ecosystem impacts, their role as sinks for heavy metals remains largely unexamined. Here we quantified the concentration of 15 metals in algal turf sediments from Lizard Island and Orpheus Island on the Great Barrier Reef, and specifically explored how the loads of arsenic, cobalt, iron and lead were related to turf length. Metal composition differed markedly between the two islands, with the composition at Orpheus Island suggesting closer links to terrestrial sediment sources. Furthermore, metal loads increased significantly with turf length, suggesting that longer turfs can accumulate these pollutants on reefs. Given that algal turfs are a crucial component of herbivorous/detritivorous trophic pathways, this could represent a key juncture at which these metals enter food chains.

1. Introduction

Algal turfs represent a critical ecological interface on coral reefs, with their cover on hard substratum often exceeding 50 % of the benthos (Smith et al., 2016; Koester et al., 2020). These turfs are, therefore, intimately connected to many fundamental reef processes, including herbivory (Choat and Clements, 1998; Kelly et al., 2017), primary productivity (Hatcher, 1988; Klumpp and McKinnon, 1992) and coral recruitment (Speare et al., 2019; Evans et al., 2020). A growing body of research has also revealed the key role that these turfs play in sediment dynamics on reefs, with a remarkable propensity to trap and accumulate sediments (Latrille et al., 2019; Heery et al., 2020; Pessarrodona et al., 2022). Such sediment trapping can lead to the formation of long sediment-laden algal turfs (Goatley et al., 2016; Tebbett et al., 2021), which can negatively impact the critical reef processes outlined above (Speare et al., 2019; Evans et al., 2020; Tebbett and Bellwood, 2020; Ng et al., 2021). However, along with sediments, algal turfs on coral reefs could also be acting as sinks for the accumulation of other contaminants, as they do in temperate systems (Ling et al., 2018; Denis-Roy et al., 2020).

Along with sediments and nutrients, other pollutants such as heavy metals can impact coral reefs (Takesue and Storlazzi, 2017; Jafarabadi et al., 2018; Kroon et al., 2020), with heavy metal contaminants coming from both natural and anthropogenic sources including mining, municipal wastewater, erosion, agriculture, traffic emissions, watercraft, and impervious surface runoff (Berry et al., 2013; Jafarabadi et al., 2017; Saha et al., 2019; Kroon et al., 2020). Once these metals enter coral reef systems (often in association with sediments and nutrients) they can be found suspended in the water column or in benthic sediments around coral reefs, with higher metal levels often found on reefs closer to anthropogenic development (Esslemont, 2000; Haynes and Johnson, 2000; Ali et al., 2011). While our knowledge remains limited, we do know that these metals can have a number of deleterious effects on reef organisms (van Dam et al., 2011; Wenger et al., 2017), and can bioaccumulate in fishes, corals and turtles (Ismail and Abu-Hilal, 2008; Berry et al., 2013; Gaus et al., 2019). However, the capacity for coral reef algal turfs to trap and accumulate sediment-associated heavy metals remains largely unexplored (but see Ling et al., 2018; Denis-Roy et al., 2020). Given the widespread cover of turfs on reefs, their links to multiple ecosystem processes, and their capacity to trap and retain particulates and sediments, they could represent an important sink for metals. The aim of this study, therefore, was to quantify the concentration of a range of metals in algal turf particulates/sediments and explore the capacity of turfs to accumulate sediment-associated metal loads. To do

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this, we examined metals in turf particulates/sediments at two markedly different reef locations to provide insights into how patterns may be shaped under different contexts.

2. Methods

2.1. Study sites

Sampling for this study was conducted at Lizard Island, in the remote Northern Great Barrier Reef (GBR) between March and April 2019, and Orpheus Island, in the Central GBR between April and May 2019 (Supporting information Fig. S1). At each island, sampling was conducted at two study sites. These sites were in relatively sheltered, leeward facing areas. All sampling was conducted on the shallow-water (0–5 m below chart datum) habitat stretching from the crest to the mid-flat. Lizard Island is located approximately 30 km from the mainland adjacent to Cape York Peninsula in an area with no major rivers and limited land area for runoff, while Orpheus Island is located approximately 15 km from the mainland adjacent to a notable river (the Herbert River) in an extensively farmed region of the mainland (Lewis et al., 2021). As a result, it is likely the two island's marine habitats are affected by terrestrial influences to differing extents.

2.2. Particulate/sediment sampling and processing

At each site, particulates/sediments within algal turfs were sampled from suitable algal turf-covered surfaces. These surfaces were smooth, flat, outside the territories of farming damselfishes, and free of sediment-retaining pits, macroalgae and encrusting organisms. Algal turf length was initially quantified for each sampling surface by measuring 10 haphazardly selected algal turf filaments using the depth probe of vernier callipers. We then sampled particulates trapped in the algal turfs, within a 58 cm^2 PVC ring, using a submersible electronic vacuum sampler. These methods for algal measurement and particulate sampling follow those described in Tebbett and Bellwood (2020). It is important to note that these methods collect both organic and inorganic particulate material, both of which metals associate with on reefs (Jafarabadi et al., 2020). A haphazardly selected subsample of 15–17 samples per site was utilised for detailed processing of metal composition.

Collected particulate samples were initially processed following Tebbett and Bellwood (2020), i.e. dried, weighed, bleached with American Chemical Society grade hydrogen peroxide (H_2O_2), re-dried and re-weighed to yield total inorganic sediment mass (full details of initial sample processing can be found in the supporting information Text S1). Following these initial processing procedures, the dried samples were then further processed to determine the concentration of metals. In brief, samples were quantified to micrograms of heavy metal contaminant per gram of sample ($\mu g\ g^{-1}$) through nitric acid digestion and inductively coupled plasma mass spectrometry (ICP-MS). These processing steps follow Whitall et al. (2014) and the full procedure is outlined in the supporting information (Text S2). Reliable readings were obtained for 15 of the 22 metals run (Table S1). Only samples with reliable readings for all 15 of these metals from both islands were retained for further analysis ($n = 14$–17 per site). For two Orpheus Island samples, cobalt readings were below detectable limits ($<0.01194\ \mu g\ g^{-1}$ of dry sediment). These samples were retained and a nominal value of 0.01 was used in analyses.

2.3. Statistical analyses

We initially explored how the composition of all 15 metals in sediment samples varied based on their concentration ($\mu g\ g^{-1}$ of dry sediment) between the two islands using a principal component analysis (PCA). This analysis was based on a Euclidean distance matrix of fourth-root transformed and range standardised data, due to the different magnitudes of variation among metals. The significance of island and site groupings was subsequently tested using a permutational multivariate analysis of variance (PERMANOVA), while between island and site variance in metal composition was examined using tests for permutational multivariance homogeneity of group dispersions (PERMDISP).

The nature of the relationships between the loads of arsenic, cobalt, iron, lead and algal turf length were then explored using generalised linear mixed effects models (GLMMs). The absolute load of each metal (in $\mu g\ cm^{-2}$) was calculated by standardising the concentration of the metal by the total inorganic sediment load for that sample. Note that herein the term 'load' refers to these absolute amounts. These four metals were selected for specific analyses based on their roles in driving separation between islands in the PCA, their potential ecological impacts, as well as the attention paid to these metals in past studies. For all GLMMs, the load of each metal was treated as the response variable, while island was treated as a categorical fixed effect, mean algal turf length (logged) was treated as a continuous fixed effect, and site was fitted as a random effect to account for any lack of spatial independence. All models utilised a Gamma distribution with a log link. Full models with an interaction term between the fixed effects were initially fitted, and the most parsimonious model was subsequently selected based on the corrected Akaike Information Criterion (AICc) (Table S2). Model assumptions and fit were examined using simulation residual model checking procedures. This indicated that model assumptions and fit were satisfactory. All statistical analyses were performed in the software R (R Core Team, 2020), using the *glmmTMB* (Brooks et al., 2017), and *vegan* (Oksanen et al., 2019) packages.

3. Results and discussion

The examination of metal composition in algal turf sediments was revealing, with a 10-fold difference in metal concentrations between islands in some cases (Table S1). Indeed, there was distinct separation along PC1 (which explained 76.62 % of total variation) between Lizard Island and Orpheus Island (Fig. 1; Table S1). A PERMANOVA suggested that these differences between islands were significant ($p < 0.001$; Table S3), with Orpheus Island also having a more variable metal composition than Lizard Island (PERMDISP: $p < 0.05$; Table S4). This separation between islands was clearly driven by several key metals. Specifically, Lizard Island sediments were typified by high concentrations of calcium and strontium (Fig. 1). This is relatively unsurprising given that sediments in this location are largely derived from on-reef sources, and both calcium and strontium are key components of the skeletons of calcifying organisms such as corals (Smith et al., 1979). By contrast, several elements that typified Orpheus Island sediments highlight stronger potential links to terrestrial sediment sources. For example, the concentrations of barium and vanadium, especially when compared to calcium, in coral skeletons is often taken to be indicative of terrestrial sediment runoff/flood plumes and associated land clearing (Saha et al., 2019). Likewise, high aluminium content in sediments has previously been used as an indicator of terrestrial sediment inputs (Takesue and Storlazzi, 2017). This supports prior evidence from Orpheus Island, which has demonstrated high levels of siliceous terrestrial-derived sediments in the algal turfs at this location (Goatley et al., 2016; Gordon et al., 2016).

Interestingly, the relative concentrations of many heavy metals (i.e. copper, lead, and zinc) were not particularly strong drivers of separation between Orpheus and Lizard Islands. This lack of difference for some metals could be due to the fact that while Orpheus Island is closer to the mainland, human development in this region is of a relatively low intensity and typified by rural cultivated crops and pasture, such as sugarcane farming and cattle grazing (Lewis et al., 2021), rather than highly developed areas. By contrast, high concentrations of metals such as lead and copper are often associated with more industrialised human activity (Esslemont, 2000; Haynes and Johnson, 2000; Jafarabadi et al., 2017). This may also explain why metals such as cadmium had very low

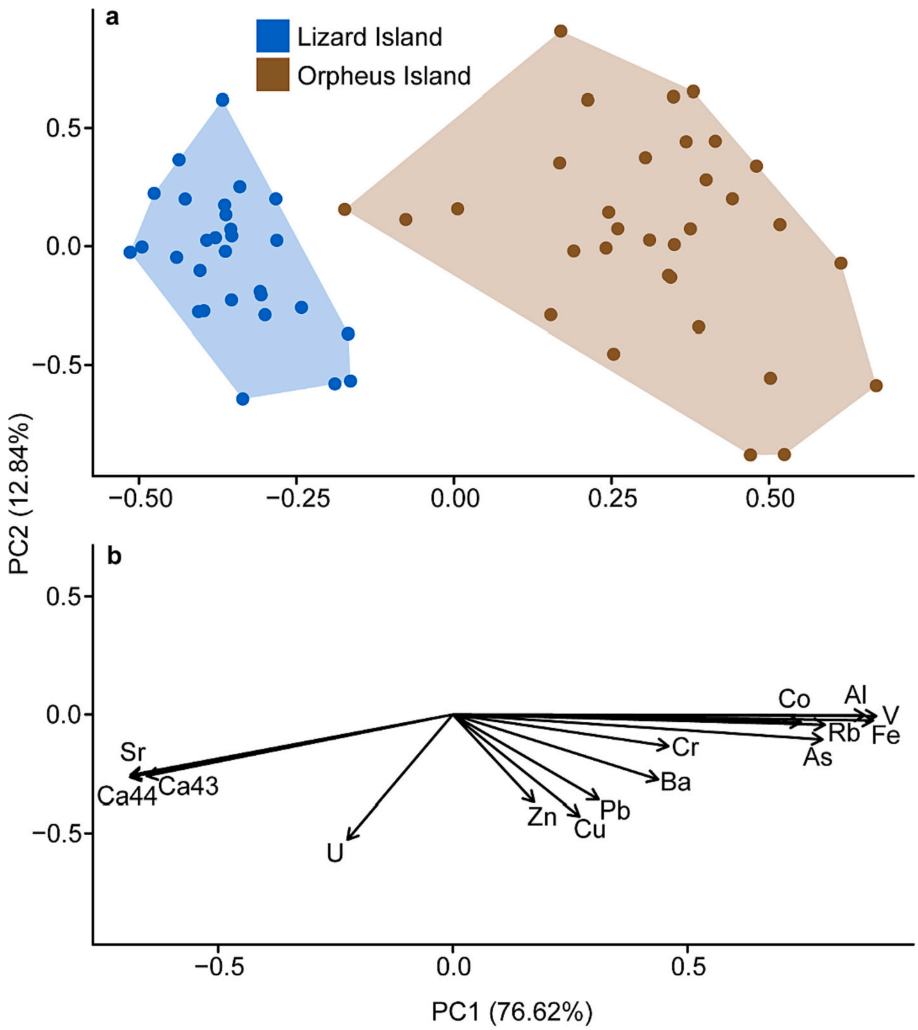

Fig. 1. a) Principal component analysis showing the composition of heavy metals in algal turf sediments at Lizard Island and Orpheus Island on the Australia's Great Barrier Reef. b) Vectors show the relationship among different heavy metals and how they influence the position of samples in the ordination.

concentrations and high relative standard deviation (which necessitated exclusion from analysis; Text S2) because elevated levels of such metals are often associated with human industrial activity or human population centres, such as on coral reefs in the Persian Gulf (Jafarabadi et al., 2017). Although, it should be noted that concentrations of arsenic, cobalt and iron were higher at Orpheus Island (Fig. 1) and while the exact sources of these metals are currently unclear, they could be related to human activities (Kroon et al., 2020). This between island comparison, however, was based on the relative concentration of metals, the capacity of turfs to trap and accumulate metals associated with particulates should also be considered.

When we examined the relationship between select key metals and algal turf length, a positive relationship was revealed in all cases (Fig. 2). Indeed, this relationship was significant across all four metals specifically examined ($p < 0.001$ in all cases; Table S5), with significantly higher levels of arsenic, iron and cobalt also documented at Orpheus Island compared to Lizard Island (Fig. 2; Table S5). Evidently, this suggests that longer algal turfs are related to higher loads of these sediment-associated metals even under markedly different contexts. Indeed, as there was no significant difference in the slope of this relationship between islands (Fig. 2) it suggests a similar physical mechanism of particulate/metal accumulation in turfs is operating at both islands. It is also important to note that algal turf length is positively related to the mass of both organic particulate material and inorganic sediments contained within the algal turf community (for details see Text S3; Tables S6, S7; Fig. S2). This suggests that as algal turfs get longer, they accumulate more organic/inorganic particulate material as well as the metals associated with this material (Figs. 2, S2). Given the marked capacity of algal turfs to retain organic particulates and inorganic sediments (Latrille et al., 2019), and the long-term stability of accumulated particulate/sediment loads (Gordon et al., 2016; Tebbett et al., 2021), algal turfs could, therefore, represent sinks for heavy metal accumulation on coral reefs.

Currently it is unclear how heavy metal accumulation in algal turf sediments could impact coral reef ecosystems, however, there is a range of possibilities. For example, some of the metals in these sediments could directly impact the algae (either via stimulatory or inhibitory affects). In this respect, as iron is a limiting nutrient in some locations, increased iron-rich sediments could facilitate algal growth (see Kelly et al., 2012). This enhanced growth would invariably lead to longer turfs and further sediment/metal trapping in a positive, if detrimental, feedback (Latrille et al., 2019). Furthermore, as sediments in algal turfs can directly impact herbivory/detritivory by fishes on reefs (Goatley et al., 2016; Ng et al., 2021; Akita et al., 2022), there is the potential that high loads of particular metals could interact with sediments to deter fish feeding behaviour. Finally, as most herbivory/detritivory on reefs involves interactions with algal turfs and at least some ingestion of associated sediments (Choat and Clements, 1998), this may represent a key conduit through which metals enter reef food chains. For example, a recent study from the GBR highlighted elevated levels of cobalt in turtles from inner-

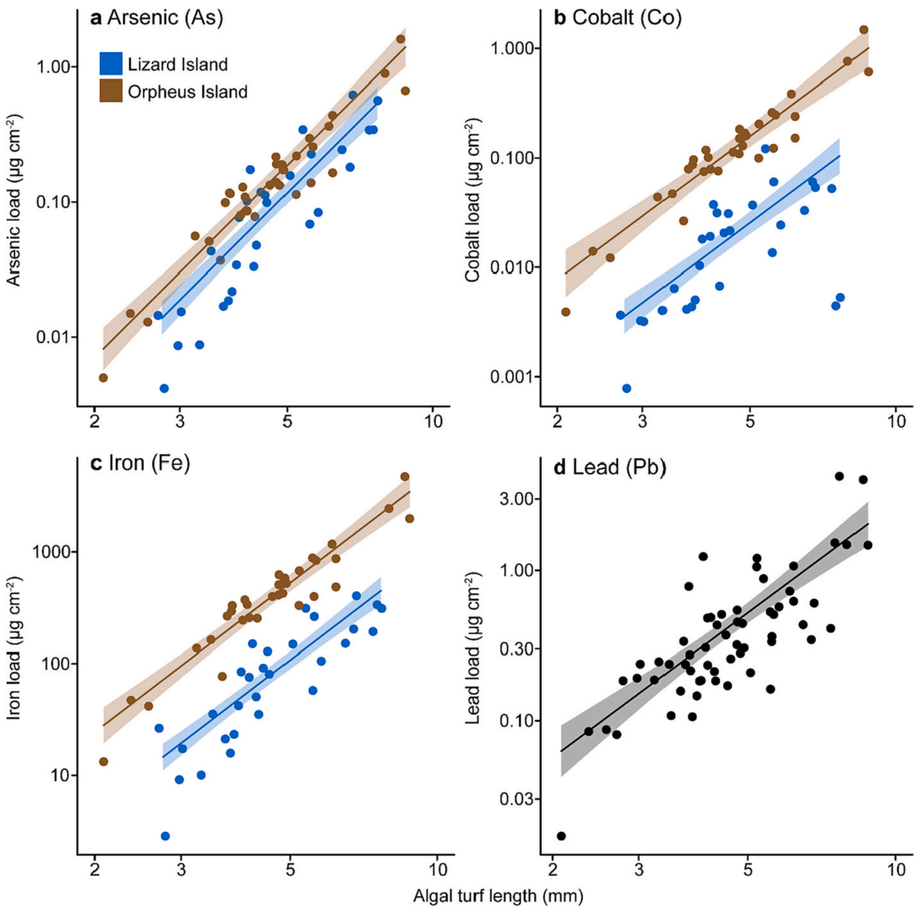

Fig. 2. The relationship between loads of a) arsenic, b) cobalt, c) iron, and d) lead in sediments and algal turf length at Lizard Island and Orpheus Island on Australia's Great Barrier Reef. Lines show the mean predicted fits of generalised linear mixed effects models, shaded ribbons are the upper and lower 95 % confidence intervals, and dots are the observed data points. Note the y-axis and x-axis are on the log10 scale in all cases. Also note that separate lines are not plotted for lead as no significant difference between islands was detected.

shelf areas (Gaus et al., 2019). As turtles are known to graze on algal turfs (Goatley et al., 2012), elevated cobalt loads in turf sediments may be readily ingested and accumulated. Similar accumulation could exist for herbivorous/detritivorous reef fishes, with the accumulation of metals in such fishes having been documented previously (Ismail and Abu-Hilal, 2008). Clearly there are a range of ways in which metals in algal turf sediments could impact coral reef ecosystems. Given the capacity for algal turfs to accumulate sediments and associated metals, this could represent a topical subject for future research.

Overall, this study revealed that particulates and sediments in algal turfs are associated with a variety of metals, although relative baseline concentrations and composition clearly differ markedly across coral reefs under varying contexts (Fig. 1). Moreover, the strong relationships between algal turf length and particulate/metal loads (Figs. 2; S2) suggests that if algal turf length increases on reefs (i.e. via reductions in herbivory [Goatley et al., 2016; Tebbett and Bellwood, 2020]), these longer turfs would have the capacity to accumulate more particulates and associated metals. It is important to note, however, that the current study only focused on the particulates/sediments bound within algal turf communities on coral reefs. Nevertheless, given the close association between metals, particulates/sediments, and the algae itself, in the future it may be interesting to examine the extent to which these metals bioaccumulate in the associated algae. This would be a particularly important research endeavour, as algal turf covered surfaces represent a critical nutritional interface on reefs (Choat and Clements, 1998; Kelly et al., 2017), potentially representing a key pathway for metals to enter food chains and biomagnify through higher trophic levels. Given these results, further research on, and monitoring of, the nature of algal turfs and the particulates they contain is warranted in ecological assessments of coral reefs.

CRediT authorship contribution statement

Sterling B. Tebbett: Conceptualization, Methodology, Formal analysis, Investigation, Visualization, Writing – original draft. **David R. Bellwood:** Conceptualization, Methodology, Funding acquisition, Writing – review & editing. **Erin R. Johnson:** Conceptualization, Methodology, Investigation, Writing – review & editing. **Tory J. Chase:** Conceptualization, Methodology, Investigation, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.marpolbul.2022.114113.

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