

Concentration of Heavy Metals in Three Distinct Algae Families from Humboldt County, California

Kodiak E. Miller
Cal Poly Humboldt


Caleb J. Strait
Cal Poly Humboldt

Jacob I. Begorre
Cal Poly Humboldt

Brittney L. Mitchell
Cal Poly Humboldt

Claire P. Till
Cal Poly Humboldt

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Kodiak E. Miller (Cal Poly Humboldt), Caleb J. Strait (Cal Poly Humboldt),
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Claire P. Till (Cal Poly Humboldt)

Abstract

Anthropogenic impacts on marine environments can impact metal fluxes and concentrations available to marine species. Monitoring these impacts is necessary to better understand the interactions between the biotic and abiotic components of these ecosystems and mitigate the risk posed by harmful toxins introduced by human activities. Biomonitors, like macroscopic algae, are useful indicators that illuminate the bioaccumulation of toxins commonly introduced from anthropogenic activity. With this in mind, the concentrations of heavy metals zinc (Zn), nickel (Ni), and copper (Cu) were analyzed via the assessment of algae (Representatives from *Ulva*, *Mastocarpus*, *Fucus*) in two sites in Humboldt County: Samoa (urbanized) and Petrolia (rural). Flame atomic absorption spectroscopy (FAAS) was used to quantify the concentration of metals in both algae and sedimental substrate, providing both algal metal content and a biota-sediment accumulation factor (BSAF). It was determined that the order of metal concentration followed $Zn > Ni \geq Cu$ within algae at both locations for all three algae families. This data is consistent with previous studies of algae species as bioindicators of heavy metal contamination (Kangas et al. 1984).

Keywords: Bioaccumulation, Heavy metals, Biogeochemical cycling, Macroalgae

Introduction

Anthropogenic activities have impacted the biogeochemical flux of elements through ecosystems. Heavy metals are elements of great concern that originate from various activities; from transportation to industrial operations or agriculture,

industrialization has intensified the rate and abundance of heavy metal introduction into the environment, which has adversely impacted aquatic ecosystems and organisms therein (Parmar and Thakur, 2013; Sardar et al., 2013). Copper (Cu), nickel (Ni), and zinc (Zn) are present in wastewater effluents that contain leachates from mining, pesticide applications,

fertilizer applications, paper production, battery manufacturing, electroplating, and other operations that make their way to aquatic ecosystems (Parmar and Thakur, 2013). Cu has been extensively used in biocidal management as an anti-fouling and anticorrosion agent present in ship hull sheathing (Davy, 1824) but also originates from paper and pulp production, petroleum refining, mining, wood preservation, electroplating, and fiber production (Parmar and Thakur, 2013). Ni has been used to refine precious metals like silver, is common in electroplating techniques, and is popular in battery operations and industry (Parmar and Thakur, 2013). Zn is used for battery operations, mining, galvanization, and smelting and is a common byproduct of industrial paints, polymer stabilizers, fossil fuel combustion, and fertilizer and pesticide applications (Parmar and Thakur, 2013).

Whether present in dilute or concentrated quantities, heavy metals like Cu, Ni, and Zn have mobile, recalcitrant, and persistent qualities that can accumulate within individual organisms and subsequently magnify up trophic levels, ultimately leading to sublethal and lethal concentrations that pose health risks to humans and nonhumans alike (Parmar and Thakur, 2013). Cu, Ni, and Zn are common carcinogens that have been found to cause brain and bone damage in humans, histological and morphological alterations in aquatic organism tissues, and impairment in physiological functions such as growth, development, motility, gas exchange, enzyme activity, behavior, and reproduction (Parmar and Thakur, 2013; Sardar et al., 2013). More specifically, Cu is toxic to organisms above thresholds necessary for its use as a micronutrient (Brand, 1986) and is reported to be highly toxic to kidney, liver, lung, and brain tissues (Parmar and Thakur, 2013). Ni is among the most toxic of metals and has been linked to the onset of asthma and dermatitis as well as lung, nose, and bone cancers (Parmar and Thakur, 2013). Zn exposure has been found to cause neurological stress (Parmar and Thakur, 2013) and impair growth and reproduction (Sardar et al., 2013).

Monitoring the flux and concentration of heavy metals throughout coastal regions is vital for the preservation and development of marine species and ecosystems (Bonanno et al., 2020). However, the flux of metals within a coastal, or more specifically, littoral environment, can be difficult to assess due to the mercurial and wide-ranging contribution of point and nonpoint elemental entrances and exits within the ecosystem.

Algae can be utilized as bioindicators of heavy metals and trace element contamination within a water body at a trophic level (Ho, 1990). A bioindicator is a living organism

(algae, animals, trees, microbes, etc.) that allows for assessing the overall quality and health of a specific ecosystem and the species within (Holt et al. 2010). Metal accumulation in algae primarily occurs via adsorption to the cell walls, in which the metals can ionically bind or form complexes with ligands on the cell wall.

As photosynthetic producers, algae inhabit a low trophic level, and elevated heavy metals within them create the risk of biomagnification of toxic metals in other biota that interact both directly and indirectly with algae. Algae are particularly valuable as a bioindicator due to their high absorption rate and high capacity of metals at nearly trace level concentrations (Bonanno, 2020). Furthermore, due to their ability to adapt to diverse environmental conditions, macroalgae can survive and act as an effective bioindicator in both non-polluted and contaminated water environments (Ho, 1990). Clarifying how strongly types of algae select for or against specific elements creates a powerful tool for analyzing biogeographic changes in an environment. An algae's elemental interactions can be determined by measuring metal concentrations using methods of spectroscopy such as flame atomic absorption spectroscopy (FAAS).

In order to study bioaccumulation capacity in algae, a comparison of the algae and its environment is necessary. Metal concentrations within seawater samples tend to be very diffuse and fall below FAAS detection limits, making analysis of marine environments difficult. Additionally, in FAAS of dilute analytes, extremely high sodium chloride concentrations can obscure analyte signals, making detection techniques with greater sensitivity necessary. FAAS is viable when measuring concentrations in sediment due to comparably higher metal concentrations and allows comparison of algae metal concentration with their immediate environment.

The biota-sediment accumulation factor (BSAF) acts as a standardized approach to calculating the bioaccumulation of metals within an aquatic species. BSAF is the ratio of metal concentration within an organism's tissue to the concentration within surrounding sediment. An organism with a high BSAF would be a concentrator, while an organism with BSAF <1 would be a deconcentrator. BSAF is specific to species/analyte relationship and its value and shouldn't change from one location to another.

BSAF provides insight into the abiotic to biotic pathways in an ecosystem. Knowing the primary consumers of high BSAF algae could illuminate species that are particularly vulnerable to contamination, possibly resulting in bioconcent-

tration. The concentration of a measured contaminant can be referenced with the known BSAF of an organism to allow an estimation of that contaminant's concentration within the corresponding species of that region.

For this study, three families of macroalgae were assessed for their suitability as bioindicators of heavy metal. The three genera studied included *Ulva*, green algae from the family Ulvaceae; *Fucus*, brown algae from the family Fucaceae; and *Mastocarpus*, red algae from the family Phyllophoraceae. *Ulva* has been utilized as a bioindicator for heavy metals in literature, in part due to the genus's ecological resilience and speed at which it develops across a wide variety of ecosystems (Gaudry et al., 2007). Metal uptake by Phaeophyta has been characterized in the literature as well (Tropin et al., 1997). The goal of this work was to conduct an initial characterization of algae as metal bioaccumulators across two sites in Humboldt County with distinct and varied anthropogenic stressors.

Materials and Methods

The methods are based on: *Distribution of Elements in Marine Algae of Karachi Coast* (Rizvi and Shameel, 2001) and *A Rapid Wet Digestion Method for Plant Analysis* (Pequereul et al., 2015), as described below.

Sample Collection

The algae samples were collected at two sites in Hum-

boldt County, California, in September 2019. Both sample sites were chosen based on the high availability of algae representing the three macroalgae groups selected for study, as well as the contrasting anthropogenic activities contemporarily and historically affecting the sites. The first site was located at the Samoa Boat Ramp (Latitude: 40.771 N, Longitude: -124.214 W) in the interior of the peninsula of Samoa, California (Google, n.d.), and the second sample site was located at the Devil's Gate Cape (Latitude: 40.408 N, Longitude: -124.391 W) within the Mattole watershed near Petrolia, California (Figure 1) (Google, n.d.). Algae were present in excess at both sites, allowing broad sampling. Both the Samoa and Petrolia sampling sites were sampled at low tides of -0.47 and 0.2 ft, respectively (NOAA 2020).

Algae were selected for their large populations present at sample sites. The benefits of a large population among the sample algae are twofold: a larger, more thoroughly dispersed population leads to a larger possible sample size and a more accurate measurement of the metal concentrations at the sample site.

Algae were collected at low tide above the water line but were within the tidal range. At the Samoa site, algae samples were collected from approximately 05:00-06:00 on September 17, 2020, in high humidity and heavy fog conditions at low tide. Petrolia algae samples were collected from 18:00-20:00 on September 19, 2021, in partially cloudy conditions at low tide. Samples were collected and stored in a freezer until processed within 24 hours of collection.



Figure 1. Sample site locations in: a. Samoa, CA and b. Petrolia, CA.

The full thallus (blades, stipe, holdfast) of the algae plant was collected as consistently as possible at both sample sites. Sample individuals were selected semi-randomly on location: efforts were made to spread out the sampling area for a particular algae family to better characterize the overall location. Given the widespread distribution of the algae, samples were selected to maximize the geographic range included in the data set. Algae that appeared unhealthy or colonized with significant epiphytes were omitted from the sampling to avoid metal concentration outliers from atypical algae.

Sample Processing

The algae and sediment samples were placed on ice and cleaned within 6 hours of collection. Prior to cleaning the algae and sediment samples, glassware was treated by acid washing with 10% nitric acid (HNO₃). Milli-Q water was used to wash the algal tissue and remove impurities such as sediment and epiphytes. The washed samples were then dried via oven at 65 for approximately 48 hours. (This is a difference from the established methods, which dried the plant matter in the shade.) Any algae samples that were not fully dry after the first 48 hours were placed back into the oven at 65°C to 100°C until they reached complete desiccation. After drying, algae were ground to a fine powder using a mortar and pestle, which was rinsed with 10% HNO₃ and dried with a paper towel between each sample. Samples were then stored in a polyethylene bottle in a cool, dry environment until later analysis.

Algae digestion was based on the method outlined in Jones (1984). All nitric acid and hydrochloric acid solutions were diluted to the proper concentration with Milli-Q water. The dried algae tissue was digested with a dry ashing method at high temperatures in a muffle furnace. Approximately one gram of each algae sample was weighed out within 0.1 mg and added to a porcelain crucible that had been acid washed with 10% nitric acid. The crucibles were placed in the furnace at 500°C for roughly 6 hours.

After cooling, 10 drops of deionized water and 4 mL of 1:1 diluted nitric acid was added to each crucible containing the ashed algae. The water and nitric acid were evaporated slowly on a hotplate before putting the crucibles back into the muffle furnace for another 2 hours at 500°C.

Following the previous drying step, 10 mL of 1:1 hydrochloric acid (HCl) was added, and the crucibles were returned to the hotplate to digest for 15 minutes. Following digestion, the remaining solution was vacuum filtered through a Whatman

1 filter paper (11 µm pore size). Once filtered, the solution was transferred into a clean 50 mL volumetric flask, and 5 mL of 1:1 HCl was pipetted into each flask. Each volumetric flask was then diluted to 50 mL with Milli-Q water for later analysis on the flame atomic absorption spectrophotometer.

Standards and Blanks

To prepare the standards, 1000 mg/L stock solutions of each metal were diluted to 50 to 5000 ppb Cu, 75 to 3000 ppb Ni, and 50 to 2000 ppb Zn, each of which was within the linear analytical range for each metal. 0.02 M HCl was added to each standard to keep the metals from adsorbing to the wall of the container. After the standard solutions, additional reagent blanks were created, undergoing the same processing as samples, resulting in solutions containing milliQ, HCl, and any metal ions resulting from lab contamination.

Analysis with Flame Atomic Absorption Spectrometry

Analyst flame atomic absorption spectrometer using an air-acetylene flame and WinLab software. In between each standard or sample, deionized (DI) was aspirated through the FAAS for at least 15 seconds to clear any residual solution or contaminants. Nickel, copper, and zinc absorbances were measured at wavelengths of 232.0, 324.8, and 213.9 nm, respectively.

Data Processing

The Bioconcentration Factor (BCF) compares the concentration of an element in biota to the concentration within the water itself. Metal concentration in plants and algae would be µg/g of moist mass, while metal concentration in water would be µg/mL. Bioconcentration is an indicator of a contaminant entering biota via aqueous routes. Bioconcentration factor was not determined in this study.

$$BCF = \frac{(\text{Metal Concentration (Plant Species)})}{(\text{Metal Concentration (Water)})} \quad (1)$$

The Bioaccumulation Sediment Accumulation Factor (BSAF) is a comparative ratio of the concentration of a contaminant within a biota versus the concentration within the sediment surrounding the biota, with the contaminant measured in µg/g. There are various methods for determining BSAF, which depend on the organism under investigation. Using a method similar to Krivokapic (2021), bioaccumulation factors of the three algae families were calculated as

a function the algae concentration divided by the ambient sediment concentration:

$$BSAF = \frac{\text{(Metal Concentration (Plant Species))}}{\text{(Metal Concentration (Sediment))}} \tag{2}$$

(2)

Results and Discussion

The zinc, nickel, and copper concentrations (mg kg⁻¹) within the three collected algae families are shown in Figure 2, along with ambient sediment concentrations. Some of the algae and sediment samples had absorbance values greater

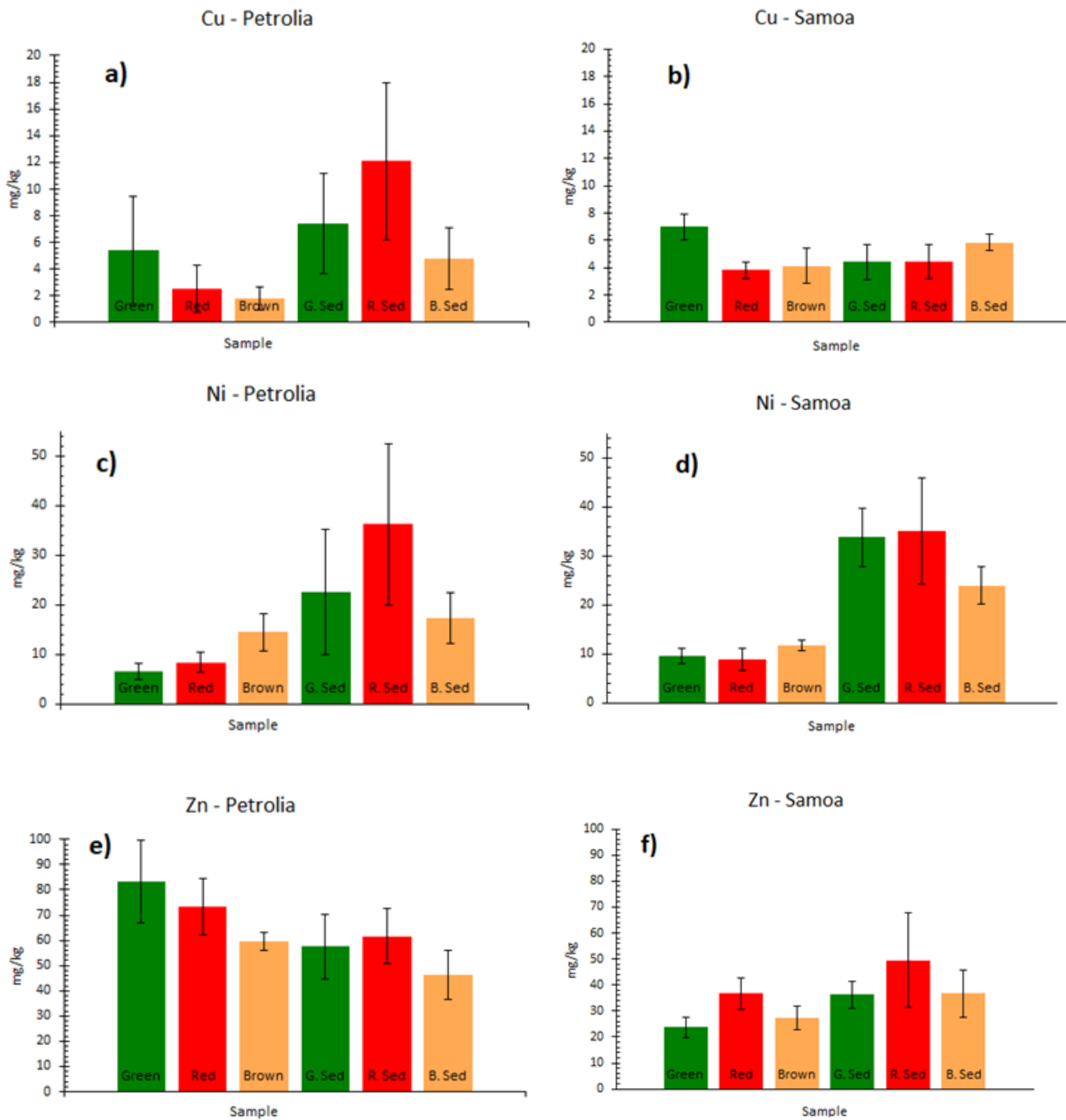


Figure 2. Cu (a, b), Ni (c, d), and Zn (e, f) concentrations in algae and sediment samples in Samoa (left panels) and Petrolia (right panels).

than the limit of linearity or outside the range of the standards; therefore, those concentrations will be underestimated in the final data.

Comparing Metals

The overall trend for the metal concentrations across all three algae families followed the order $Zn > Ni \geq Cu$ (Figure 2), which is the same trend found for *Ulva* in the Bonnanno et al. (2020) paper. According to Romera et al. (2007), the affinity of the metals to algae biomass is ordered $Cu > Ni > Zn$ (average of six algae species), indicating that copper is the most likely to adsorb to the surface of the algae. Furthermore, the maximum sorption of these three metals to biomass is ordered as $Cu > Ni > Zn$. Based on these absorption constants, it would be expected that copper has the greatest concentration within the algae families. However, this trend was not observed (Figure 2). It could be that Cu concentrations were relatively low in both sampling locations. This may suggest that anthropogenic sources of Cu are not significantly influencing the concentrations in Samoa and Petrolia, or there are system interactions that impact Cu uptake in algae. Alternatively, there could be nonpoint sources of Zn in both Samoa and Petrolia leading to relatively high Zn concentrations in those locations, which would explain the relatively high Zn concentrations in the algae. Assessment of Humboldt watersheds cites fertilizer and pesticide runoff as concerns (North Coast Regional Water Quality Control Board, 2005), both of which are plausible sources of Zn (Parmar and Thakur, 2013).

All three metals analyzed are utilized as micronutrients and are naturally present biotically and abiotically within the sampled environments. Environmental chemical processes at play are broad and difficult to isolate from one another and can obfuscate anthropogenic impacts on metal concentration within these systems; however, it can be broadly stated that sources that deliver metal ions into the observed system result in increased concentrations.

Comparing Algae Families

For the Petrolia samples, Cu and Zn concentrations follow the same pattern across algae: the highest metal concentrations were found in the green algae, followed by the red algae, and the lowest concentrations in the brown algae (Figure 2). However, nickel followed the opposite trend, with the highest concentrations in the brown algae, followed by the red algae, and then the green algae. This could indicate that the brown algae have a comparatively high nickel requirement than the green and red algae and are preferentially taking it up from the abiotic environment to a higher degree.

Comparing Sediment and Algae Concentrations

The biota-sediment accumulation factor (BSAF) was analyzed between algae and their sediments, and the calculated BSAF values (Equation 2) were averaged between sampling sites (Figure 3).

With regards to nickel, all three families took up less nickel than in their environment, with the brown algae taking

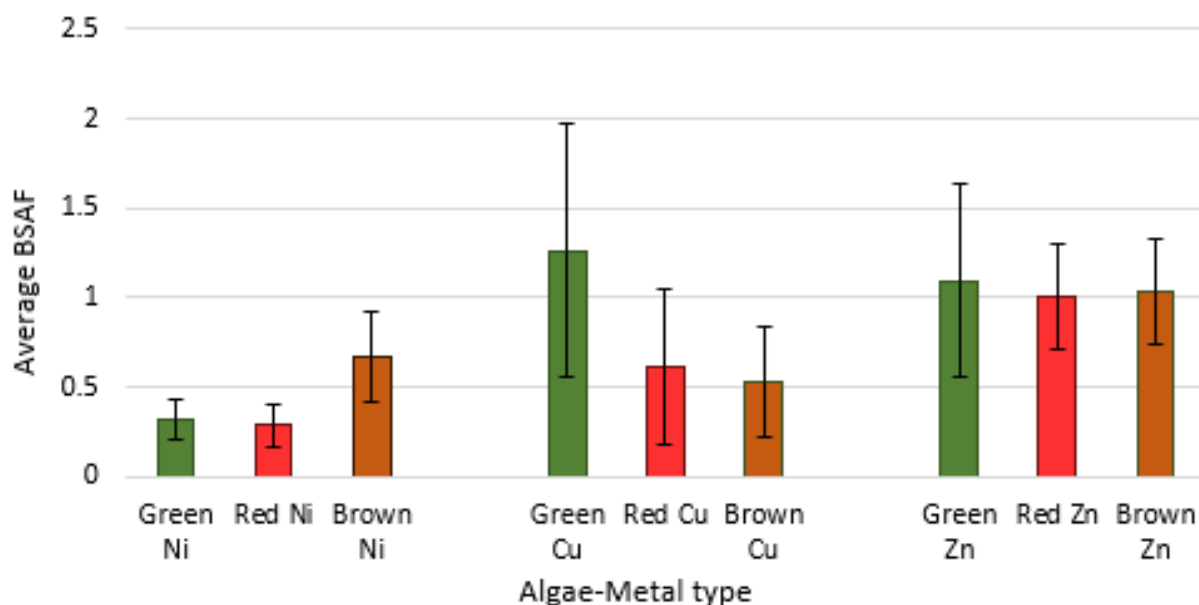


Figure 3. Calculated Petrolia & Samoa Average BSAF values (Zn, Cu, Ni) across algae.

up slightly more than green and red. Green algae acted as a concentrator of copper, while red and brown had a lower copper concentration compared to sediment background. Site-specific BSAF values shown below in figure 4 show a significant disparity in algae BSAF depending on the site. The difference in site BSAF values suggests either environmental factors that influence how a species selects for or against specific nutrients or an issue within the method disproportionately affecting one site over the other, as discussed below.

All three families in Petrolia showed a BSAF of 1 or greater for Zn, but all three families showed less than 1 in Samoa. At the Samoa sampling site, zinc concentrations were significantly lower in the algae samples when compared to Petrolia, leading to a greater BSAF value. Across both sample sites, nickel concentrations within sediment were noticeably greater than the concentrations in the algae samples (Figure 2), leading to relatively low BSAF values (Figure 3). This could be due to the algae having a lower biological need for nickel than the other metals and therefore taking it up less actively. Although published work for metal requirements in marine macroalgae is limited, Twining and Baner (2013) found that most marine phytoplankton required less nickel than zinc, supporting this hypothesis. However, most phytoplankton species required even less copper than nickel.

Comparing Sites

The Samoa and Petrolia sampling sites were chosen as a comparative pair due primarily to their respective urban and rural surroundings. The Samoa sampling site is located within

the Humboldt Bay watershed, where approximately 65,000 (59%) of the county population resides (Humboldt County Department of Health & Human Services, 2018). From this disproportionate population density, we expect a greater anthropogenic effect on the water ion composition within the sample site. Land use outside of the urban centers present includes timber production as well as agricultural grazing and dairies. The bay itself is a commercial, deep-water port and a site of significant commercial shellfish production. Due to commercial bay use and urban factors such as US Route 101 that bisects the watershed, greater metal contamination risk is expected. Reported water quality issues that would contribute to metal contamination include sedimentation from tributaries, automotive use, and shipping (North Coast Regional Water Quality Control Board, 2005). The Petrolia sample site located further south is contained within the Mattole watershed. The population within this watershed is much more diffuse, totaling approximately 2,000 people. Aside from 20th century timber harvest creating sedimentation issues via erosion, the Mattole watershed experiences comparatively less commercial and urban anthropogenic elemental agitation. There are no major roadways present within the watershed, and the sample site was exposed to the ocean, suggesting a more abstracted exposure to commercial shipping compared to the Samoa sample site within the bay (North Coast Regional Water Quality Control Board, 2005). The contrasts between sample sites suggest that the Samoa site would have greater anthropogenic disturbance contributing to more significant metal pollution; however, the data did not depict this.

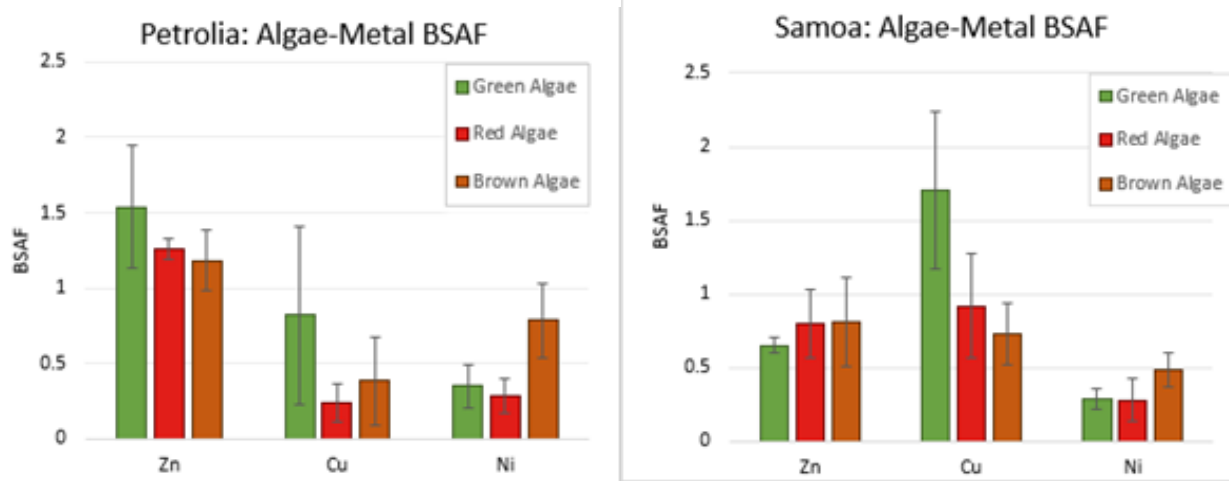


Figure 4. Calculated BSAF values (Zn, Cu, Ni) of the three algae families in Petrolia (left) and Samoa (right).

Comparing biotic and abiotic concentrations of the elements of interest regarding bioaccumulation yields several observable patterns. The sediment samples from Samoa were measured with lower Cu and Zn concentrations than Petrolia. All algae collected at the Samoa and Petrolia sites exhibited lower Ni concentrations than their surrounding sediment samples. Due to the algae exhibiting lower levels of Ni than ambient sediment, it is assumed that these algae do not concentrate Ni. Furthermore, this observation is indicative that sources of Ni are naturally occurring and that the algae is not contaminated with this metal.

Of the three metals measured, Cu had the lowest concentration in both algae and sediment samples at both sites.

Sources of Error

Samples that required additional drying in the initial oven treatment were likely subject to increased decomposition in the period between washing and drying of the samples. The desiccation time had the most significant disparity between families regardless of sample sites, with samples from *Fucus* generally requiring additional drying time compared to both *Ulva* and *Mastocarpus*.

At both sample sites, the full thallus (blades, stipe, holdfast) of the algae plant was collected as consistently as possible. However, the holdfast on several samples was not collect-

ed due to its strong retention to the sediment. Given that no particular family of algae was especially prone to this error, the impact on collected data is presumed to be marginal.

During the initial nitric acid evaporation step for Samoa samples, several sample crucibles experienced a loss of sample due to bumping from rapid heating. The effects this had on analyte concentration results cannot be reliably predicted. It was decided that while this is a source of error, it is unlikely that the observed metal uptake results were skewed enough to render them invalid for the purposes of this study.

Significant differences in sediment at both sample sites may have also impacted the mobilization of metals within the samples. Qualitatively, the substrate gathered at the Samoa site could be classified as sand, whereas the grain size for several samples at the Petrolia site was much larger and more pebble-like in quality. Given the discrepancy in surface area between sites, there was concern that the acid treatment would lead to a greater concentration of metals within the same mass of Samoa sediments. A rough assay can be conducted by averaging the metal concentration in Petrolia sediment samples that were noted as being larger in grain size compared to those with smaller-grain substrate. As visualized in figure 5, the results of this averaging show a greater average concentration in sediment samples with smaller grain sizes for all three metal ions analyzed.

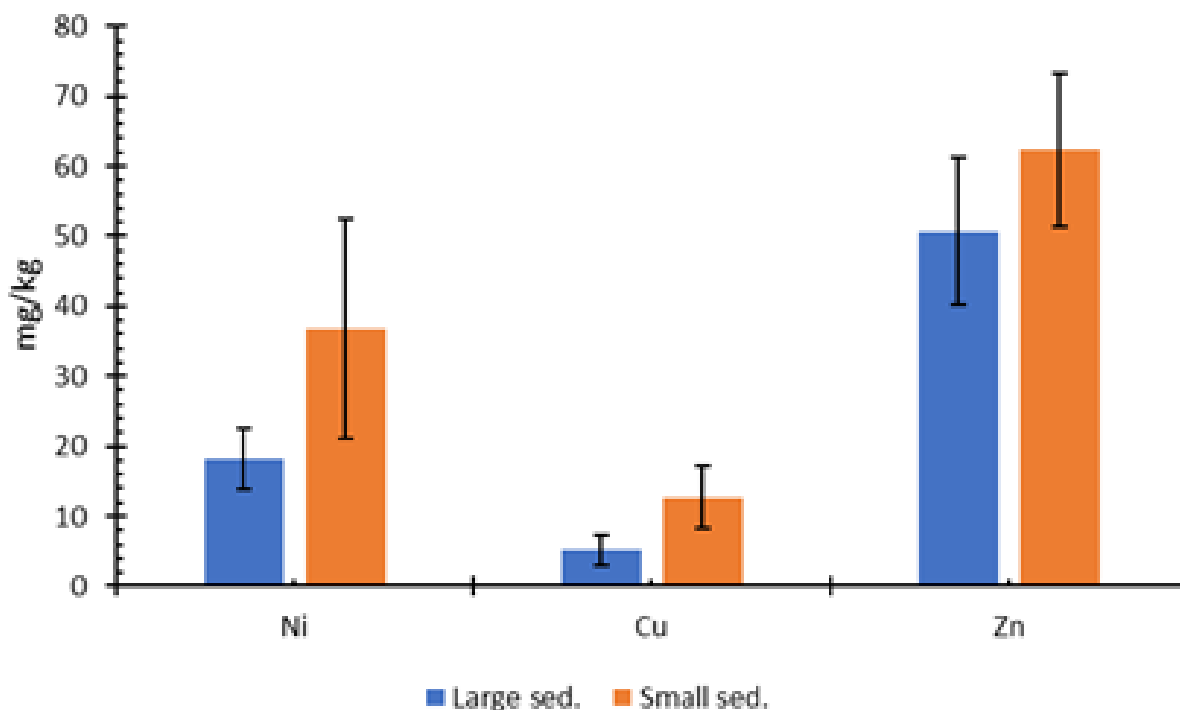


Figure 5. Metal concentration comparison between Petrolia sediment samples marked as being larger in size.

The effect on grain size in the measurement of sediment metal concentration has possible impacts on the resulting BSAF calculation. If larger grain size leads to a reduced quantity of metal during processing, the resulting BSAF of the algae at Petrolia would appear larger as a result of lower apparent metal concentration. Ni and Zn BSAF values are greater at the Petrolia site compared to Samoa; however, all algae had a lower Cu BSAF at Petrolia. If the larger sediment size at Petrolia artificially increased BSAF for all metals, then our conclusions based on the BSAF factor would need to be adjusted: there may be more pressure to select against copper at Petrolia or more pressure to select for copper at Samoa.

Conclusion

Anthropogenic activity has undoubtedly disrupted the concentration and flux of metals and other elements within environmental systems, and determination of species capable of acting as biomonitors is the first step to elucidating these changes. In this exploratory study, three algae genera (*Ulva*, *Mastocarpus*, *Fucus*) were compared for their suitability as bioindicators with regards to Cu, Ni, and Zn at urban and rural sites in Humboldt County using FAAS. Results suggest that all algae deconcentrate Ni, *Ulva* concentrates Cu, and all algae neither concentrate nor deconcentrate Zn.

The results of this study do suggest that certain algal families have predilections towards certain metals, but there is significant variability in these results, and more research is needed to have a conclusive understanding of these trends. Furthermore, this study was limited to two locations sampled once each, and a broader dataset would allow broader interpretations and conclusions. We propose the following future investigations to fill the gaps. Cross substrate analysis of water in addition to sediment metal concentrations would clarify how factors such as pH might affect measured concentrations in sediment as well as algae. Future work involving a comparison of sites would benefit from including a broader range of sites to reduce the likelihood of site to site processing differences (e.g., sediment surface area) disproportionately affecting the resulting BSAF of algae analyzed. Future studies could also assess whether there are metal concentration thresholds that a species will accept or reject from surrounding sediment and whether the BSAF of a given algae is static or dependent on its surroundings or its life stage.

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Supplementary Information

Table 1. Samoa samples

	Ni Avg. (mg/kg)	Ni Stdev	Cu Avg. (mg/kg)	Cu Stdev	Zn Avg. (mg/kg)	Zn Stdev
Green	9.57	1.53	6.99	0.95	23.76	3.86
Red	8.86	2.21	3.81	0.58	36.67	6.14
Brown	11.70	1.04	4.13	1.26	27.38	4.65
G. Sed.	33.86	5.95	4.41	1.29	36.24	5.28
R. Sed.	35.10	10.76	4.43	1.23	49.62	18.00
B. Sed.	24.00	3.73	5.85	0.63	36.67	9.24

Table 2. Petrolia sample data

	Ni Avg. (mg/kg)	Ni Stdev	Cu Avg. (mg/kg)	Cu Stdev	Zn Avg. (mg/kg)	Zn Stdev
Green	6.60	1.62	5.44	4.03	83.38	16.42
Red	8.42	2.03	2.53	1.75	73.37	11.24
Brown	14.48	3.78	1.79	0.88	59.62	3.47
G. Sed.	22.53	12.67	7.41	3.76	57.50	12.95
R. Sed.	36.25	16.28	12.08	5.89	61.65	10.87
B. Sed.	17.33	5.02	4.79	2.30	46.47	9.70

Table 3. Petrolia BSAF averages

	Zn	Cu	Ni
Green	1.536	0.820	0.352
Brown	1.184	0.386	0.787
Red	1.261	0.243	0.287

Table 4. Samoa BSAF averages

	Zn	Cu	Ni
Green	0.652	1.701	0.290
Brown	0.809	0.731	0.486
Red	0.798	0.918	0.280

Table 5. Large sediment comparison between Petrolia samples

	Ni	Stdev Ni	Cu	Stdev Cu	Zn	Stdev Zn
Large sed.	18.16	4.31	5.15	2.07	50.69	10.52
Small sed.	36.70	15.71	12.72	4.51	62.30	10.98

Table 6. Algae

	Ni	Cu	Zn
Green	0.320655 ± 0.110562	1.260489 ± 0.708	1.094144 ± 0.53787
Red	0.283493 ± 0.283	0.61117 ± 0.439	1.008847 ± 0.29521
Brown	0.666725 ± 0.249	0.524148 ± 0.306969	1.033881 ± 0.300