Chemical Contaminants in Corals (*Pocillopora damicornis*) in Tinian, CNMI

NOAA NOS National Centers for Coastal Ocean Science
Center for Coastal Monitoring and Assessment
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About this Document

This document presents results and interpretation from a recent analysis of contaminants in coral tissues offshore from Tinian in the Commonwealth of Northern Mariana Islands, in and around the Tinian Marine Reserve.

The report details: (1) contaminant (e.g. PAHs, PCBs, pesticides, heavy metals) magnitudes and distributions in coral tissues (*Pocillopora damicornis*) and (2) a one time "snapshot" of surface water nutrient concentrations in the study area.

The efforts discussed here were led by the National Centers for Coastal Ocean Science (NCCOS), with significant participation from partners, including NOAA's Coral Reef Conservation Program and the Commonwealth of the Northern Mariana Island's (CNMI) Division of Environmental Quality. NCCOS has been proactive in collaborating with other NOAA line offices as well as federal, state and nongovernmental organization partners to maximize cost-sharing efforts and reach its goals. Their efforts and extramural funding has made it possible to complete assessments that would have otherwise been unobtainable through federal funding alone.

Live hyperlinks to related products (indicated by blue text) are embedded throughout this report and are accessible when viewing this document as a PDF. For more information about this report and others like it, please visit the NCCOS web site, http://coastalscience.noaa.gov/, or direct comments to:

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EXECUTIVE SUMMARY

Tinian is an island in the Commonwealth of Northern Mariana Islands. It is a raised limestone island with a tropical climate. The southwest corner of the island is home to the Tinian Marine Reserve. Significant coral reef ecosystems are present in and around the Reserve. These valuable habitats may be impacted by the transport of pollutants from the land to the marine ecosystem, via runoff and/or groundwater fluxes. The National Oceanic and Atmospheric Administration's (NOAA) Coral Reef Conservation Program (CRCP) and National Centers for Coastal Ocean Science (NCCOS), in consultation with local and regional experts, quantified coral tissue contaminant and water column nutrient magnitudes, and distribution patterns along the southwest shore of Tinian. This work was conducted using many of the same protocols as ongoing NOAA monitoring work underway elsewhere in the U.S. coral jurisdictions and has enabled comparisons among coral reef ecosystems between this study and other locations in the United States.

This characterization of Tinian marine ecosystems establishes benchmark conditions that can be used for comparative documentation of future change, including possible negative outcomes due to future land use change, or improvement in environmental conditions arising from management actions.

The main findings of this study are as follows:

- Concentrations of most analytes in coral tissues are similar to or lower than what has been reported in other U.S. coral jurisdictions. An exception to this was tin (Sn), which was higher in Tinian. The source of this tin is unknown, although differences in metals uptake between species must be considered when comparing datasets.

- While there are no statistically significant spatial patterns in contaminant concentrations, some contaminants (e.g. PAHs, Cu, Ni, Pb, Zn) are qualitatively highest in the area around the harbor, which is likely related to modern day and historical boat traffic.

- There were no clear spatial patterns in water column nutrient concentrations, nor were there significant differences between surface and bottom concentrations.

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Introduction

Purpose and Objective
This document presents environmental data collected in August 2013 consisting of coral tissue (*Pocillopora damicornis*) contaminants and surface water nutrients offshore from Tinian in the Commonwealth of Northern Mariana Islands (CNMI). The study area is in and around the Tinian Marine Reserve on the southwest corner of the island. Despite being a marine protected area, there is very little information on pollution stressors to this protected ecosystem. These new data provide a survey of the system, including the magnitude and spatial extent of pollution in coral tissues. These data also provide an important starting point against which to measure future change.

Figure 1: Location of study site (yellow boundary) offshore of Tinian, CNMI. Red shows location of Tinian Marine Reserve. Inset shows location of Tinian (blue star) in the Pacific Ocean. The town of San Jose is located at 14.97°N, 145.63°E.

Background
The Tinian Marine Reserve was established by the Commonwealth government in 2007 in order to preserve the natural resources of this area of Tinian's marine environment. The legislation regulates the fishing and harvesting of marine life by establishing it as a "no-take" reserve. It is the only marine protected area located on Tinian.

The reserve is bounded by the Tinian Recreational Boat Harbor to the north and Puntas Carolinas to the south, from the high-tide mark on shore to one-half mile from shore.

Tinian Marine Reserve regulations prohibit fishing, taking any marine animals or plants, feeding fish, damaging habitat, interfering with World War Two historical sites, or collecting shells/sand/coral. There are exceptions for certain species of seasonal fish which may be harvested only during their respective seasons (CNMI DFW 2016).

Image 1: Beach at resort/casino.

Geographic Context
The island of Tinian, with a land area of 39 square miles, is the second largest island in CNMI. The study area was on the southwest shore of Tinian, extending from Punta Diablo in the north to Punta Carolinas in the south (Figure 1), including the Tinian Marine Reserve.

Geology
Tinian is a raised limestone island with a shoreline typified by cliffs of varying heights, many of which have been undercut by wave action (Eldredge 1983). The only well defined beach in the study area is in Tinian Harbor.

Climate
The climate of Tinian is uniformly warm (average annual temperature of 27℃) with consistently high humidity (Eldredge 1983). Precipitation varies seasonally between a dry season from January to May and a wet season from July to November (Eldredge 1983). The island has historically been impacted by tropical cyclones (Eldredge 1983).

Image 2: Landscaping at resort/casino on Tinian.

Marine Environment
The major sea surface currents affecting the island are the Northern Equatorial Current, which flows westward and the Subtropical Countercurrent flowing east (Eldredge 1983). The average sea surface temperature has been reported as 28 ℃ (Eldredge 1983).
There is a limited coastal shelf around the island with depths dropping off to hundreds of meters within very close distances (~100 m) from shore. The nearshore benthic habitat is a mix of reefs, seagrasses and unconsolidated sediments. Of the mapped habitat, 41% of the benthic habitat of Tinian is hardbottom, including coral reefs (NOAA, 2004). Tinian has been identified as supporting important sea turtle habitat (Kolinski 2001).

Land Use, Population and Economy
The U.S. government occupies all but 13 square miles of the island, which is home to about 3,000 people (US Census 2010). There is some agricultural production, including a recent increase in animal agriculture (primarily cattle), limited retail shops (focused in the village of San Jose) and a casino/resort which attracts tourism from off island (Image 1). The heavily landscaped grounds of the resort (Image 2) represent a potential for agrochemicals (fertilizers/pesticides) to reach the study area.

There is a small diesel fuel power plant to the north of the harbor (Image 3) which consists of four 2.5 megawatt generators and two 5 megawatt generators (US DoN 2010) In 2010, it used approximately 200,000 gallons of fuel per month (Marianas Variety, 2011). There are two emissions stacks which are potential sources of airborne pollutants to the marine ecosystem.There is no centralized sewage treatment system for the island. The resort operates a small 0.17 million gallons per day plant with tertiary treatment; its effluent is discharged to a leach field on the resort property. The rest of the residents rely on household septic systems with leach fields or cesspools (US DoN 2010). The extent to which human waste contributes to the nutrient budget of the near coastal waters is unclear, but improperly functioning septic systems or leach fields have the potential to adversely affect marine biogeochemistry.

Solid waste disposal on the island consists of an unlined open dump operated by the CNMI Department of Public Works. This facility is located approximately 0.8 kilometer north of the town of San Jose. Open burn-

Image 3: Power plant stack on southwest shore of Tinian.

ing routinely occurs at this site and was observed by field crews during the sampling mission. Current practice also includes the disposal of pumped materials from septic tanks, cesspools, or portable sanitation devices to be discharged at this open dumpsite (US DoN 2010).   This site represents a potential source of a variety of pollutants (metals, pesticides, pharmaceuticals, nutrients) which could potentially reach the marine ecosystem through groundwater leaching, surface runoff or atmospheric deposition.

There has been significant historical boat use in the harbor, and field crews observed a number of small boat operators in the area during the field mission, including a vessel that was actively leaking oil (Image 4). In addition to PAHs, boating activities also have the potential to introduce other contaminants (TBTs, Cu, Sn, Zn) to the system.

Military History and Proposed Military Uses
Tinian was an important strategic site during World War II. The United States captured Tinian from the Japanese in the summer of 1944. The relatively flat geography of Tinian made it useful for military air base operations. Today a portion of Tinian is a National Historical Site, based on its historical military significance.
As the U.S. military presence has increased on Guam, plans have been proposed to use Tinian for the training of ground troops (USDoD, 2015) including live fire exercises. A decision on this plan is expected in 2016.

Rationale for Collection of Contaminant Data in *Pocillopora damicornis* Tissues
Land based sources of pollution (LBSP) in coral reef ecosystems have been identified as a research/management priority for the Commonwealth (CNMI and NOAA, 2010). However, little, if any, data on pollution stressors exist for the marine environment of Tinian. In order to assess the potential for adverse ecosystem effects of LBSP, and to track potential changes over time, environmental quantification of pollution is required. Coral tissues were selected as a matrix for contaminant analyses for multiple reasons. First, biological samples tend to act as integrators of water quality over time and are far less temporally variable than water column grab samples. Sessile organisms, such as corals, are preferable to highly motile species (e.g. fish) they reflect contaminant exposure at the site of collection, rather than integrating over an unknown spatial area.

Finally, incorporation of toxic materials into the tissues of environmentally important species (corals) can be an important metric of ecosystem impact. Pocillopora damicornis was selected as the target species because they are commonly occurring in the study area.

Figure 4. Oil slick near harbor.

Pocillopora damicornis is a hard coral with colonies that are usually less than 30 cm tall with a branched structure. *P. damicornis* exhibits greater branching than other similar species. It appears pink to green, or shades of brown in color. It is particularly abundant between 5 to 20 m with a depth range from the surface to more than 40 m. It is common in both lagoons and reef slopes (Veron 2000). P. damicornis has a wide geographic distribution and might be considered the most abundant coral species (Sheppard, 1998).

Methods

Sampling Design
Because subterranean groundwater discharge (SGD), also called groundwater seeps, can be a common feature of many islands in the Pacific, gridded salinity measurements were made across the study area, with the intent to stratify sampling around the seeps. However, both surface and bottom water salinity was nearly constant across the study region (with all value falling between 34 and 35 psu), suggesting that groundwater inputs via offshore seeps are small. As such, a stratified random sampling design purely based on geography, benthic habitat and depth, with very deep waters being excluded due to the limits of SCUBA. The sampling allows for an assessment of the overall contaminant condition of the ecosystem, and to be able to make geographically explicit conclusions about how pollutants vary spatially. In this method, all hard bottom areas within a stratum had an equal chance of being selected as a sampling site. The final sampling design yielded three strata (North, Central and South) with four sampling sites per strata, as well as pre-defined alternate sites.

If a site could not be sampled (e.g. if the site was too deep, or if the target species was not present) a pre-selected randomly determined alternate site from within that stratum was sampled.   Twelve coral sites were

sampled in August of 2013. Grab samples of surface and bottom water were collected from study sites concurrently for nutrient analysis. All relevant permits for sample collection and export were obtained through CNMI's Division of Fish and Wildlife.

Figure 2. Salinity grid, plus coral and nutrient sampling sites offshore from Tinian.

Field and Analytical Methods
Coral samples were collected using standard NOAA National Status and Trends (NS&T) Program protocols (Apeti et al, 2012). Briefly, samples were collected by SCUBA divers using steel clippers. This method resulted in the sample containing both tissue and skeletal material. Field personnel wore nitrile gloves to avoid contamination.

Corals were collected into a certified clean (IChem®) 250 ml labeled jar, capped and then placed on ice in a cooler. After returning from the field each day, coral samples were frozen (-15°C) at the CNMI DEP or the CNMI Division of Fish and Wildlife labs in Saipan. Nutrient samples were collected in pre-cleaned HDPE bottles and frozen until analysis. Samples were hand carried on ice via commercial air from Saipan to Hawai'i, where they were re-frozen prior to overnight shipment to the contract laboratories in Texas (contaminants) and Guam (nutrients). The analyte lists are shown in Tables 2a and 2b.

Laboratory analyses were conducted following the protocols of the National Status and Trends Program (Kimbrough et al. 2006, Kimbrough and Lauenstein et al. 2006) using a NOAA contract lab (TDI Brooks International). Briefly, polycyclic aromatic hydrocarbons (PAHs) were analyzed in the laboratory using gas chromatography/mass spectrometry in the selected ion monitoring (SIM) mode. Selected chlorinated organics, such as polychlorinated biphenyls (PCBs) and pesticides, were analyzed using gas chromatography/electron capture detection. Butyltins were analyzed using gas chromatography/flame photometric detection.

Silver, cadmium, copper, lead, antimony, and tin were analyzed using inductively coupled plasma - mass spectrometry. Aluminum, arsenic, chromium, iron, manganese, nickel, silicon and zinc were analyzed using inductively coupled plasma - optical emission spectrometry. Mercury was analyzed using cold vapor - atomic absorption spectrometry. Selenium was analyzed using atomic fluorescence spectrometry. For each element, total elemental concentration (i.e. sum of all oxidation states) was measured.

Water samples were analyzed for a standard suite of nutrient analytes: nitrate (NO_3^-), nitrite (NO_2^-), orthophosphate ($HPO_4^=$), ammonium (NH_4^+), urea (($NH_2)_2CO$), total nitrogen and total phosphorus. All nutrient analyses were conducted under contract at the Water and Environmental Research Institute (WERI) at the University of Guam using a four channel, automated, flow injection ion analyzer (Lachet, Australia) using the manufactures recommended QuickChem® methods. Total N and P were determined following persulfate oxidation.

Statistical Analysis
All contaminant data were analyzed using JMP® statistical software. The data were first tested for normality using the Shapiro-Wilk test. The data were not normally distributed. A non-parametric multiple comparisons test (Wilcoxon with post-hoc Dunn Method for Joint Ranking, α=0.05) was used to evaluate differences among strata. Spearman Rank correlations (**α**=0.05) were examined to evaluate the relationships between contaminant variables. All data is presented on a dry weight basis. In addition, organic concentrations were normalized based on tissue lipid content, but this did not affect any of the statistical interpretation of these data.

Providing Context for Results
In addition to comparing contamination results between strata, concentrations observed in Tinian can be compared to other studies of coral tissue contaminants. Denton et al (1999) quantified PAHs, PCBs and some metals in corals, including *P. damicornis* in nearby Guam. Because Denton et al. (1999) did not quantify all contaminants measured in this current study, findings from Tinian were also compared to NOAA's National Status and Trends Program coral tissue contaminant data which exists at multiple sites in the U.S. Caribbean (Pait et al. 2009, Whitall et al. 2011, Apeti et al. 2014, Whitall et al. 2013) using *Porites astreoides* as the target species. While differences in species prevent a direct statistical comparison, these are the most comprehensive (in terms of number of analytes) coral tissue data available, and will be used here for comparison.

Care should be taken when interpreting comparisons based on potential differences in sampling and analytical methodologies. Specifically, multiple researchers (McConchie and Harriott, 1993; Esselmont 2000; Reichelt-Brushett and McOrist, 2003) have shown that different analytes accumulate at different rates between zooxanthellae, tissue and skeleton. Data presented in this paper represent concentrations from a combination of tissue and skeleton because the skeleton could not be removed (i.e. via acidification) without also destroying organic compounds of interest (e.g. PAHs, pesticides). Other NOAA studies (cited above) used the same methodology and are thus directly comparable. It is not clear how Denton et al. (1999) treated their hard corals, although no mention is made of removing skeletal tissue, so comparison with data from the current study is likely valid.

Table 1: Site descriptions. Depths are approximate.

Site Name	Longitude (deg)	Latitude (deg)	Strata	Depth (m)	Date Collected
N02P	145.60107	14.99107	North	7.5	8/30/2013
N14A	145.60395	14.99104	North	1.5	8/30/2013
N15A	145.59953	14.99061	North	3.5	8/27/2013
C08A	145.61487	14.96922	North	2.5	8/27/2013
C17A	145.61654	14.96779	Central	3	8/30/2013
C11A	145.62463	14.96394	Central	5.5	8/28/2013
C09A	145.61972	14.96112	Central	3.5	8/28/2013
C16A	145.62937	14.95695	Central	1.5	8/30/2013
C13A	145.62973	14.95442	South	2.5	8/28/2013
C20A	145.63106	14.95163	South	3.5	8/30/2013
C05A	145.62871	14.94922	South	7.5	8/27/2013
S02P	145.62801	14.94379	South	6.5	8/27/2013

Table 2a: List of contaminants quantified in coral tissues.

PAHs - Low Molecular Weight	PAHs - High Molecular Weight	PCBs	Organochlorine Pesticides
Naphthalene*	Fluoranthene*	PCB8/5	Aldrin
1-Methylnaphthalene*	Pyrene*	PCB18	Dieldrin
2-Methylnaphthalene*	C1-Fluoranthenes/Pyrenes	PCB28	Endrin
2,6-Dimethylnaphthalene*	C2-Fluoranthenes/Pyrenes	PCB29	Heptachlor
1,6,7-Trimethylnaphtha-lene*	C3-Fluoranthenes/Pyrenes	PCB31	Heptachlor-Epoxide
C1-Naphthalenes	Naphthobenzothiophene	PCB44	Oxychlordane
C2-Naphthalenes	C1-Naphthobenzothiophenes	PCB45	Alpha-Chlordane
C3-Naphthalenes	C2-Naphthobenzothiophenes	PCB49	Gamma-Chlordane
C4-Naphthalenes	C3-Naphthobenzothiophenes	PCB52	Trans-Nonachlor
Benzothiophene	Benz(a)anthracene*	PCB56/60	Cis-Nonachlor
C1-Benzothiophenes	Chrysene*	PCB66	Alpha-HCH
C2-Benzothiophenes	C1-Chrysenes	PCB70	Beta-HCH
C3-Benzothiophenes	C2-Chrysenes	PCB74/61	Delta-HCH
Biphenyl*	C3-Chrysenes	PCB87/115	Gamma-HCH
Acenaphthylene*	C4-Chrysenes	PCB95	2,4'-DDT
Acenaphthene*	Benzo(b)fluoranthene*	PCB99	4,4'-DDT
Dibenzofuran	Benzo(k)fluoranthene*	PCB101/90	2,4'-DDD
Fluorene*	Benzo(e)pyrene*	PCB105	4,4'-DDD
C1-Fluorenes	Benzo(a)pyrene*	PCB110/77	2,4'-DDE
C2-Fluorenes	Perylene*	PCB118	4,4'-DDE
C3-Fluorenes	Indeno(1,2,3-c,d)pyrene*	PCB128	DDMU
Anthracene*	Dibenzo(a,h)anthracene*	PCB138/160	1,2,3,4-Tetrachlorobenzene

Table 2a: List of contaminants quantified in coral tissues contd.

Phenanthrene*	C1-Dibenzo(a,h)anthracenes	PCB146	1,2,4,5-Tetrachlorobenzene
1-Methylphenanthrene*	C2-Dibenzo(a,h)anthracenes	PCB149/123	Hexachlorobenzene
C1-Phenanthrene/Anthracenes	C3-Dibenzo(a,h)anthracenes	PCB151	Pentachloroanisole
C2-Phenanthrene/Anthracenes	Benzo(g,h,i)perylene*	PCB153/132	Pentachlorobenzene
C3-			
Phenanthrene/Anthracenes		PCB156/171/202	
C4-Phenanthrene/Anthracenes	Trace Elements	PCB158	Mirex
Dibenzothiophene	Aluminum	PCB170/190	Chlorpyrifos
C1-Dibenzothiophenes	Arsenic	PCB174	
C2-Dibenzothiophenes	Cadmium	PCB180	Butyltins
C3-Dibenzothiophenes	Chromium	PCB183	Monobutyltin
	Copper	PCB187	Dibutyltin
	Iron	PCB194	Tributyltin
	Lead	PCB195/208	Tetrabutyltin
	Manganese	PCB199	
	Mercury	PCB201/157/173	
	Nickel	PCB206	
	Selenium	PCB209	
	Silver		
	Tin		
	Zinc		

*Compounds used in the calculation of total PAHs
PAHs = polycyclic aromatic hydrocarbons; PCBs = polychlorinated biphenyls

Table 2b: Nutrient species analyzed in this study
Ammonium (NH_4^+)
Nitrate (NO_3^-)
Total Nitrogen (TN)
Orthophosphate (PO_4^{3-})
Total Phosphorus (TP)

Results and Discussion
Summary statistics for the chemical constituents quantified in this study are shown in Tables 3 and 4. Each analyte, including background information on sources/uses, environmental impacts, and analysis of spatial patterns, is discussed by pollutant group (e.g. PCBs) or by individual analyte (e.g. metals). For data maps, blue dots always represent zero values and other data bins (colors) are based on statistical quartiles.

Table 3: Summary statistics for organics and metals in coral tissues for Tinian. All values are expressed on a dry weight basis. Metals are total concentrations.

Analyte	Units	Min	Max	Mean	Stdev
Chlordane (total)	ng/g	0.000	0.219	0.049	0.073
DDT (total)	ng/g	0.000	0.062	0.005	0.018
HCH (total)	ng/g	0.000	0.000	0.000	0.000
PAHs (sum)	ng/g	4.20	127.95	21.76	35.12
PCBs (sum)	ng/g	0.027	1.162	0.445	0.328
TBT (total)	ng/g	0.00	0.00	0.00	0.00
Aluminum	µg/g	0.00	14.60	7.11	5.13
Arsenic	µg/g	0.21	0.60	0.44	0.10
Cadmium	µg/g	0.00	0.00	0.00	0.00
Chromium	µg/g	0.00	0.19	0.08	0.08
Copper	µg/g	0.00	0.26	0.02	0.08
Iron	µg/g	1.60	10.30	5.52	2.22
Lead	µg/g	0.00	0.13	0.01	0.04
Manganese	µg/g	0.21	0.46	0.35	0.08
Mercury	µg/g	0.00	0.00	0.00	0.00
Nickel	µg/g	0.55	2.29	1.05	0.49
Selenium	µg/g	0.00	0.00	0.00	0.00
Silver	µg/g	0.00	0.00	0.00	0.00
Tin	µg/g	0.00	16.30	2.99	5.03
Zinc	µg/g	1.60	4.85	2.48	1.03

Table 4. Comparison of data from this study with coral tissue data from the Guam (Denton et al. 1999) and U.S. Caribbean (Pait et al. 2009, Whitall et al. 2011, Apeti et al. 2014b, Whitall et al. 2013).

	Mean Tinian	Mean Guam	Mean Guanica	Mean SW PR	Mean Jobos Bay	Mean Vieques	Mean STEER	Max Tinian	Max Guam	Max Guanica	Max SW PR	Max Jobos Bay	Max Vieques	Max STEER
DDT	0.005	NA	0.055	0.081	0.038	0.130	0.010	0.062	NA	0.285	0.620	0.600	2.259	0.080
PAHs	21.76	0.047	4.35	41.91	4.58	15.00	22.04	127.95	0.117	8.70	154.00	6.40	21.50	80.40
PCBs	0.445	1056	0.464	1.016	0.120	0.229	0.000	1.162	4103	3.518	5.390	0.623	1.711	0.000
HCH	0.000	NA	0.094	0.000	0.000	0.002	0.000	0.000	NA	1.283	0.000	0.000	0.050	0.000
Chlordane	0.049	NA	0.038	0.000	0.000	0.119	0.010	0.219	NA	0.518	0.000	0.000	0.812	0.050
Ag	0.00	0.073	0.00	0.00	0.00	0.01	0.01	0.00	0.26	0.06	0.09	0.00	0.03	0.02
Al	7.11	NA	68.51	37.80	177.69	30.75	22.33	14.60	NA	140.00	82.20	333.00	103.00	201.00
As	0.44	11.392	1.42	0.00	1.68	0.24	1.26	0.60	67.10	2.37	0.00	2.44	3.42	1.76
Cd	0.00	0.067	0.27	0.00	0.25	0.19	0.01	0.00	0.24	0.33	0.00	0.31	0.29	0.05
Cr	0.08	0.078	0.00	0.00	0.00	0.18	0.39	0.19	0.33	0.00	0.00	0.00	0.29	1.52
Cu	0.02	0.083	22.47	2.06	50.30	0.76	2.69	0.26	0.24	76.90	3.54	97.20	6.51	4.07
Fe	5.52	NA	101	91	212	51	72	10	NA	480	353	480	526	275
Hg	0.00	0.003	0.00	0.00	0.00	0.00	0.00	0.00	0.006	0.00	0.00	0.00	0.00	0.00
Mn	0.35	NA	10.48	3.01	13.33	2.66	10.10	0.46	NA	21.20	5.36	24.60	8.24	19.60
Ni	1.05	0.123	4.66	1.32	3.13	0.90	2.18	2.29	0.29	11.60	2.70	6.84	8.09	8.33
Pb	0.01	0.000	0.13	0.00	1.43	0.07	0.16	0.13	0.00	0.32	0.07	12.50	0.17	0.42
Se	0.00	NA	0.19	0.05	0.18	0.10	0.01	0.00	NA	0.25	0.37	0.26	0.34	0.12
Sn	2.99	0.193	0.07	0.02	0.01	0.25	0.00	16.30	0.63	0.27	0.14	0.10	0.40	0.04
Zn	2.48	5.025	9.42	6.09	8.59	3.43	5.98	4.85	7.66	25.20	18.30	16.90	15.20	14.80

Chemical Contaminants in Corals (*Pocillopora damicornis*) in Tinian, CNM

Legend

Coral Tissue Contaminants

Total_Chlordane (ng/g)

- 0.000
- 0.001 - 0.018
- 0.019 - 0.021
- 0.022 - 0.083
- 0.084 - 0.219
- Sampling Strata

Chlordanes

Background: Chlordane, and its various forms, are man-made organic chemicals which were used historically as organochlorine pesticides. In this study we present total chlordane, which is the sum of heptachlor, heptachlor-epoxide, oxychlordane, alpha-chlordane, gamma-chlordane, trans-nonachlor and cis-nonachlor.

Uses: Prior to 1978, chlordane was widely used as an insecticide in agriculture, lawns and gardens, but was banned for these uses in the United States in 1978. In 1983, chlordane was approved for termite control use in the United States, and was used in this capacity until 1988 when it was banned for all uses due to toxicity concerns (EPA 2000). Like many other chlorinated compounds, it is relatively persistent in the environment.

Environmental effects: Chlordane primarily acts on biota as a neurotoxin. Chlordanes are also toxic to aquatic life including crayfish, shrimp and fish (EPA 2000). Chlordane has been shown to negatively affect coral, through depression of photosynthesis and respiration, decreased algal densities and mortality (Firman 1995), and other studies have demonstrated that chlordane does accumulate in coral tissues (Whitall et al. 2014).

Figure 3. Total chlordane concentrations in coral.

Concentration in Tinian Corals: Concentrations of chlordane in coral in Tinian ranged from below limits of detection to 0.5 ng/g, with a mean of 0.22 ng/g.

Spatial Patterns: There were no statistically significant differences between the strata (Dunn's test, **α**=0.05)

Discussion: Chlordane levels measured here were within the range of values reported elsewhere for chlordane in coral tissue (Table 4; Pait et al. 2009; Whitall et al. 2014; Apeti et al. 2014). While there are no clear sources of chlordane on modern Tinian (chlordane was banned in the U.S. in 1988), historical insecticide use, especially for termite control may have contributed to the observed chlordane levels. More research is needed to establish body burden threshold above which corals are adversely affected by chlordane and other pollutants.
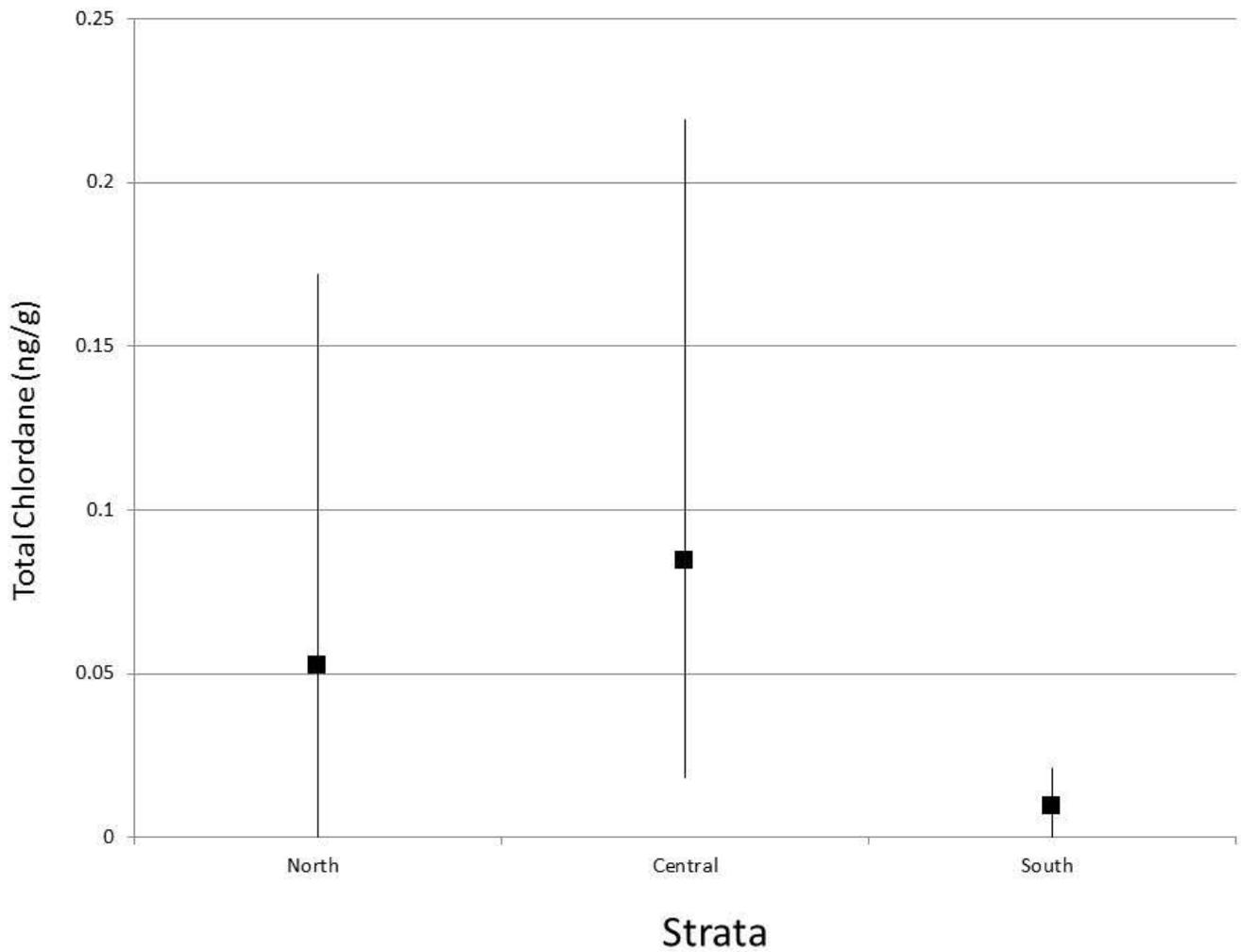
Figure 4: Coral chlordane concentrations by strata. Squares are mean values; lines show maximum and minimum values. There were no statistically significant differences between strata (Dunn's test, α=0.05)

Figure 5: Total DDT concentrations in corals.

DDT

Background: Dichlorodiphenyltrichloroethane (DDT) is a hydrophobic, man-made organic chemical which was used historically as an organochlorine pesticide. In this study we present total DDT, which is the sum of DDT and its degradation products (DDMU, DDE and DDD).

Uses: DDT was widely used as an insecticide, both in agriculture and for mosquito control, until it was banned in the United States in 1972 due to environmental concerns.

Environmental effects: DDT is of concern due to its environmental persistence, potential to bioaccumulate, and toxicity to non-target organisms. These concerns led to its ban in the United States, but because of its persistence and heavy use in the past, residues of DDT are commonly found in the environment, including biota. DDT is still used in some parts of the world, especially for malaria control. Like chlordane, DDTs act on biota as a neurotoxin and have been shown to be an endocrine disruptor. DDT and its metabolite DDE have been specifically linked to eggshell thinning in birds, particularly raptors. DDT is also toxic to aquatic life including crayfish, shrimp and some species of fish (EPA 2009).

Concentration in Tinian Corals: Coral concentrations of total DDT in Tinian ranged from below limits of detection to 0.06 ng/g, with a mean of 0.01 ng/g. Only one site, located in the south stratum, had detectable total DDT.

Spatial Patterns: Statistically, there were no statistically significant differences (Dunn's test, **α**=0.05, p=0.027) between the strata.

Discussion: DDT levels measured here were lower than the range of values reported elsewhere for DDT in coral tissue (Table 4; Pait et al. 2009; Whitall et al. 2010; Whitall et al. 2014; Apeti et al. 2014). Because DDT was widely used as an insecticide and is chemically persistent in the environment, it is not surprising to find DDT in animal tissues in the marine environment. Lower values in Tinian may reflect less historical DDT use when compared to other areas, or may reflect differences in species uptake. More research is needed to establish body burden threshold above which corals are adversely affected by DDT and other pollutants.

Figure 6: Coral DDT concentrations by strata. Squares are mean values; lines show maximum and minimum values. There are no statistically significant differences between strata (Dunn's test α=0.05).
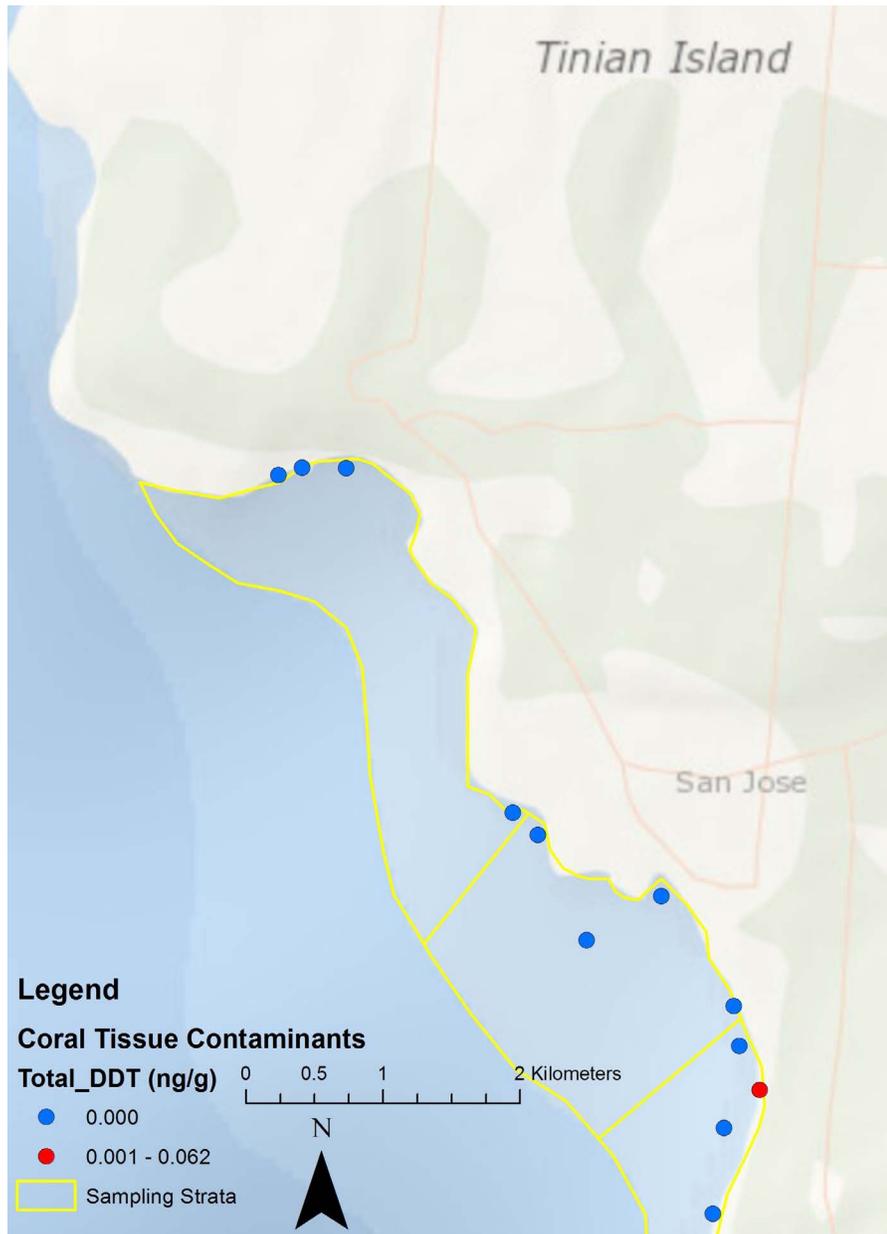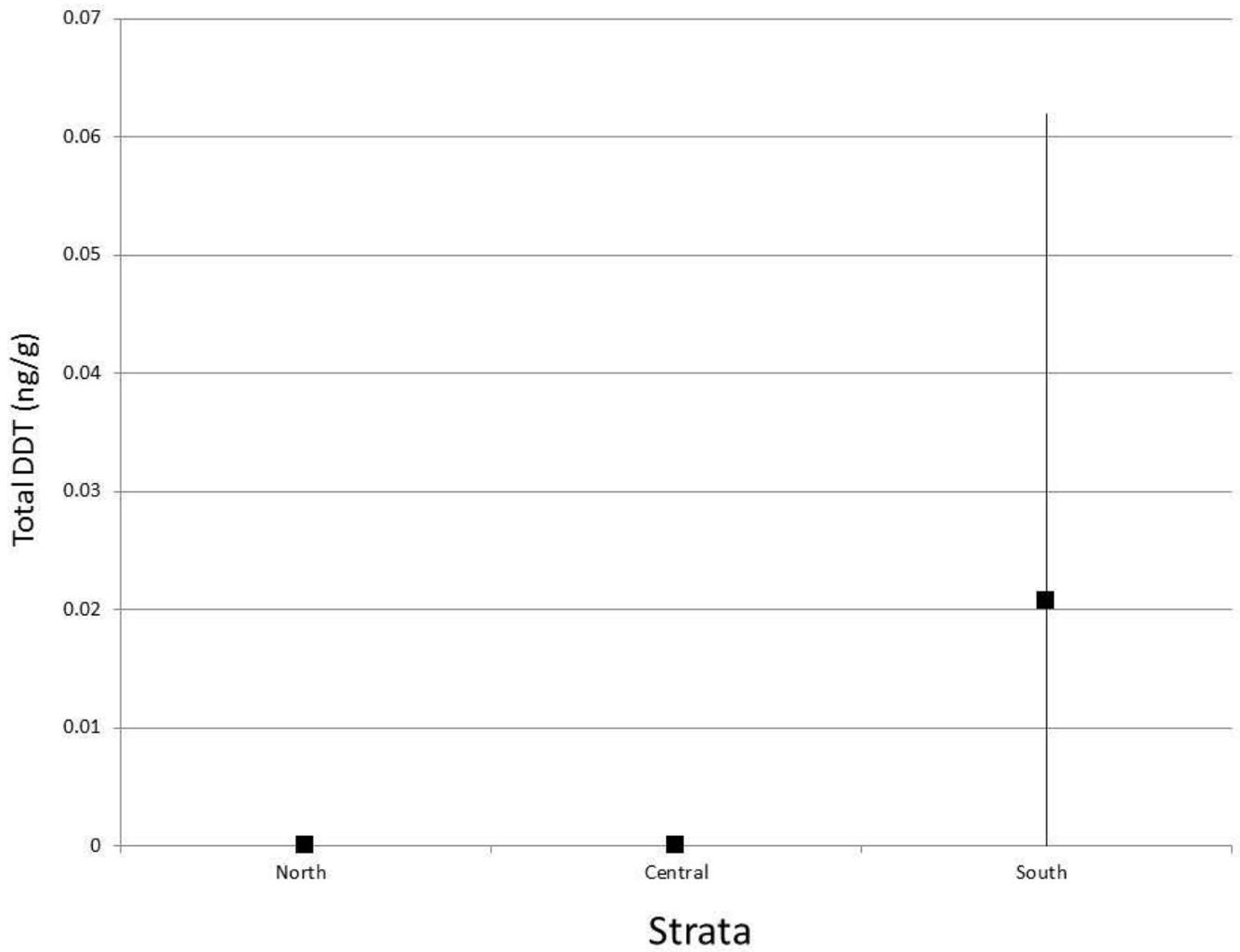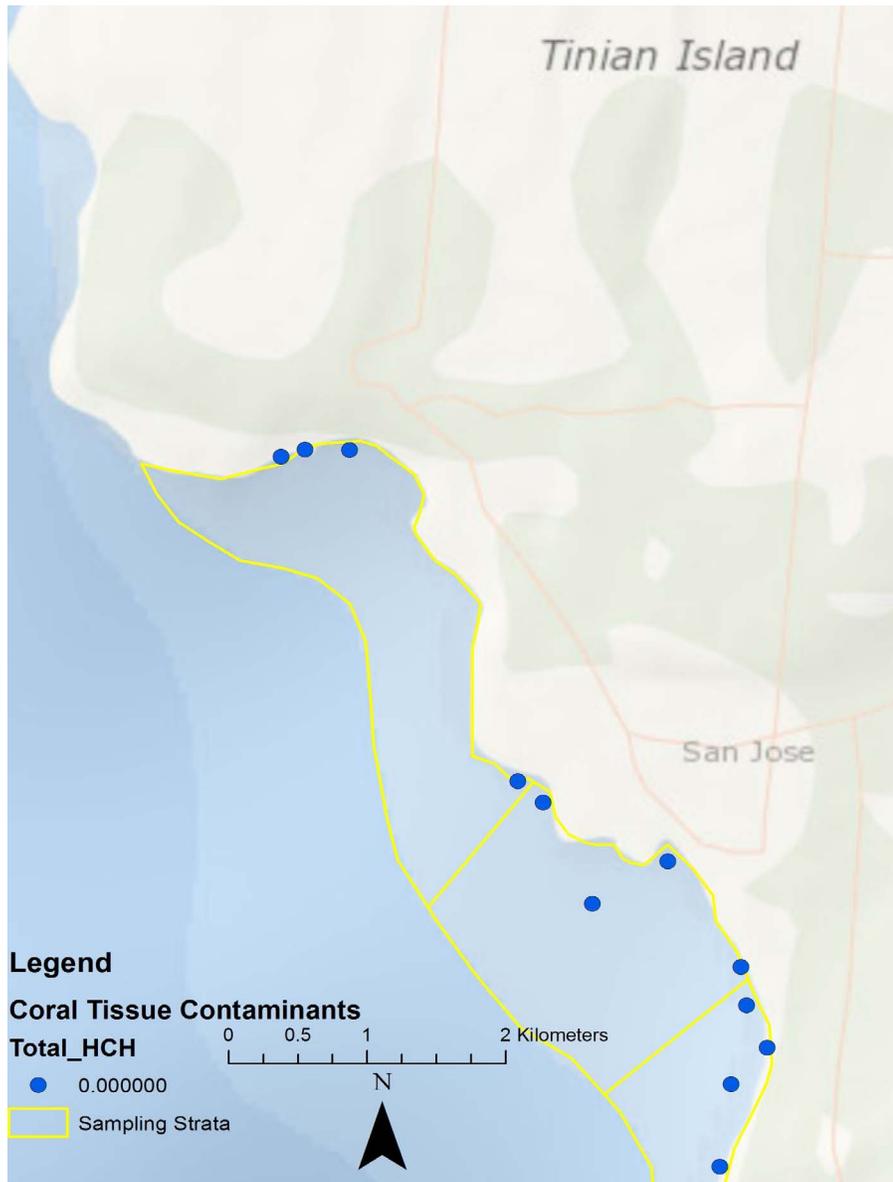
Figure 7. Total HCH concentrations in corals.

HCHs

Background: Isomers of hexachlo-rocyclohexane (HCH) include alpha, beta, delta and gamma HCH. These are man-made chemicals that were used as organochlorine pesticides. The most common of these was gamma HCH, also known as lindane.

Uses: Historically, HCH has been used for veterinary and pharmaceutical purposes. Agricultural uses were phased out in the United State in 2007 (EPA 2006), but pharmaceutical uses (e.g. for lice) are still permitted.

Environmental effects: Like other organochlorine pesticides, HCH primarily acts on biota as a neurotoxin. HCH is also toxic to aquatic life including crayfish, shrimp and some species of fish. HCH is environmentally persistent and is transported readily through the environment (EPA 2006). HCH's effect on corals has not been well documented, but other studies have demonstrated that HCH does accumulate in coral tissues (Whitall et al. 2014).

Concentration in Tinian Corals: HCH was not detected in coral tissue samples in Tinian.

Discussion: HCH has been detected in other coral species in other locations (Table 4; Pait et al. 2009; Whitall et al. 2014) but was not found in this study. This could be due to differences in species uptake (Porites astreoides vs P. damicornis) or a lack of HCH use in Tinian.

Other Pesticides

Background: A variety of other less common synthetic pesticides have been historically used for pest control in the United States. This study quantified concentrations of a variety of other pesticides and their degradation products, including: aldrin, dieldrin, endrin, 1,2,3,4-tetrachlorobenzene, 1,2,4,5-tetrachlorobenzene, hexachlorobenzene, pentachloroanisole, pentachlorobenzene, mirex and chlorpyrifos.

Environmental effects: Like DDT and chlordane, these pesticides primarily act on biota as neurotoxins and endocrine disruptors, and may bioaccumulate. Markey et al. (2007) showed decreases in settlement and metamorphosis in the coral Acropora millepora when exposed to low water column concentrations (0.3 to 1 ug/L) of chlorpyrifos. A number of organochlorine pesticides are toxic to fish and other aquatic organisms. These pesticides include legacy fungicides and insecticides, which persist in the environment despite being phased out (USEPA 2015).

Concentration in Tinian Corals: Of the other pesticides quantified, only hexachlorobenzene and pentachloroanisole were detected. Hexachlorobenzene was detected at all sites (Figure 8), and pentachloroanisole

Figure 8. Hexachlorobenzene concentrations in coral.

(Figure 9) was detected at all but 2 sites. Summary statistics are show in Table 5.

Spatial Patterns: There are no statistically significant differences between strata (Dunn's Test, **α**=0.05) for any of these analytes.

Discussion: Levels of detected pesticides are relatively low and likely represent low level historical use in the near coastal areas.

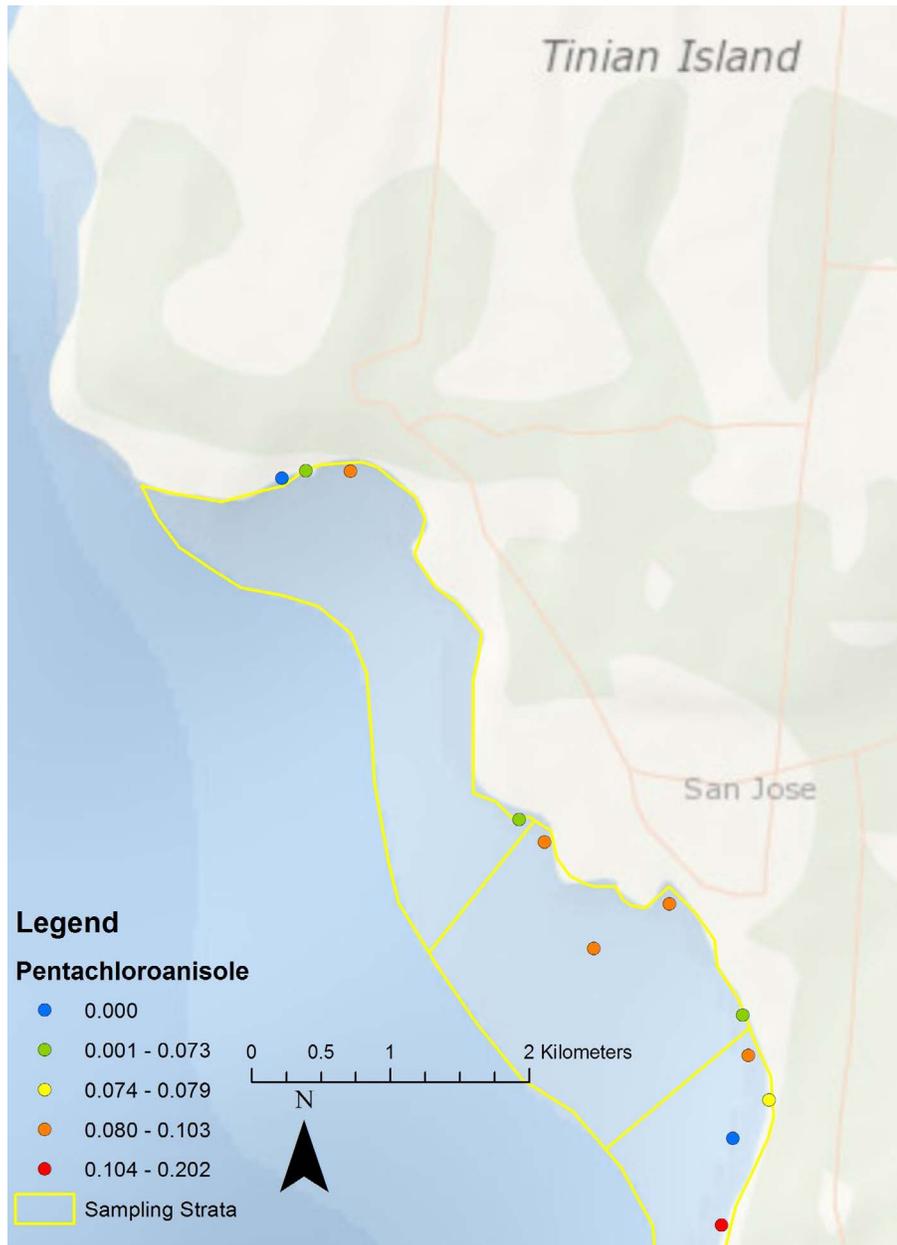**Table 5: Detected pesticides in Tinian corals (ng/g)**

	Min	Max	Mean	Stdev
Hexachlorobenzene	0.04	0.12	0.07	0.02
Pentachloroanisole	0.00	0.20	0.08	0.05

Figure 9. Pentachloroanisole concentrations in corals.

Figure 10. Total BT concentrations in corals.

Organotins

Background: Tributyltin (TBT) refers to man-made organotin compounds containing the compound $(C_4H_9)_3Sn$. In the aquatic environment, TBT is broken down by bacteria and photodegradation (Bennett, 1996). The breakdown process involves sequential debutylization resulting in dibutyltin, monobutyltin, and finally inorganic tin (Batley, 1996). TBT and its breakdown products (dibutyltin and monobutyltin), as well as tetrabutyltin (a manufacturing by-product), were quantified here. For simplicity, total butyltins (sum of all forms) are presented.

Uses: TBT was widely used antifouling agent in boat paint but was gradually phased out due to toxicity concerns.

Environmental effects: TBT is of environmental concern due to its environmental persistence and toxicity to aquatic organisms. TBT poses a significant ecological risk because it is specifically designed to prevent settlement and growth of algae and-invertebrates. In addition, its method of action on non-target organisms, including bivalves and gastropod molluscs, is through endocrine disruption (EPA 2004). TBT has also show to adversely affect the symbiotic zooxanthellae in sea anemones (Mercier et al. 1997).

Concentration in Tinian Corals: Neither TBT, nor its organic breakdown products, were detected in coral tissue samples in Tinian.

Discussion: TBT has been detected in other coral species in other locations (Pait et al. 2009) but was not found in this study. This could be due to differences in species uptake (Porites astreoides vs P. damicornis) or a lack of TBT use in Tinian. Based on the history of large ships in the harbor the latter seems, unlikely. Furthermore, relatively high concentrations of tin (the ultimate breakdown product of TBT) were quantified in corals in Tinian. It is also possible that TBT was present in the environment but has broken down to its elemental form.

Figure 11: PCB concentrations in corals.

Legend

Coral Tissue Contaminants

Total_PCBs (ng/g)
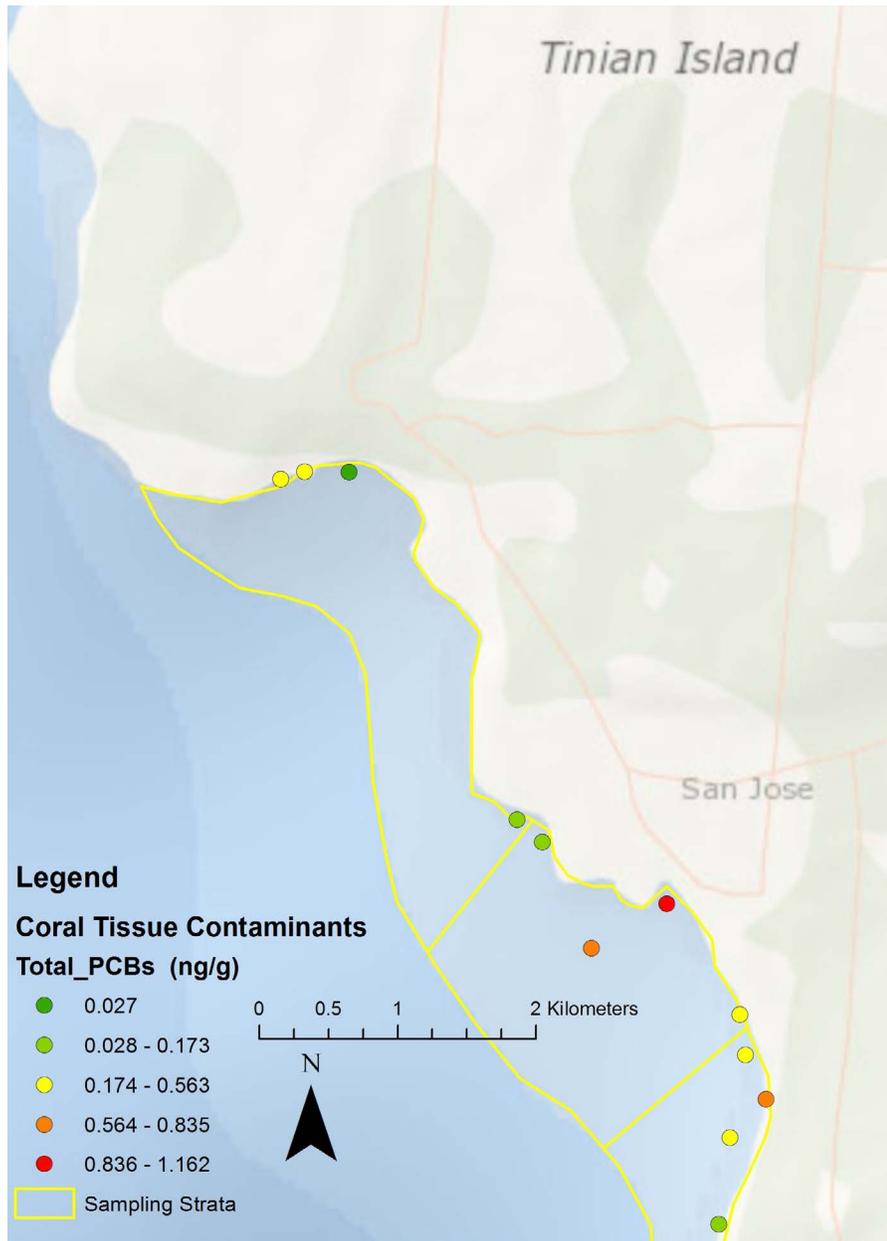- 0.027
- 0.028 - 0.173
- 0.174 - 0.563
- 0.564 - 0.835
- 0.836 - 1.162
- Sampling Strata

PCBs

Background: Polychlorinated biphenyls (PCBs) are environmentally persistent, man-made organic compounds. The structure of PCBs includes a biphenyl ring structure (two benzene rings with a carbon to carbon bond) and chlorine atoms, the latter of which varies in both number and location on the rings. There are 209 possible PCB congeners.

Uses: PCBs have a wide range of uses including: electrical transformers and capacitors, hydraulic and heat transfer fluids, pesticides and paints. Manufacture of PCBs has been banned in the United States, but in some cases, use of equipment containing PCBs (e.g. railroad locomotive transformers) is still permitted (CFR 1998).

Environmental effects: Exposure to PCBs has been linked to reduced growth, reproductive impairment and vertebral abnormalities in fish (EPA 1997). Solbakken et al. (1984) quantified the bioconcentration of radiolabeled hexaPCB (2,4,5,2',4',5'-hexachlorobiphenyl) in coral. The PCB was rapidly accumulated in Diploria strigosa and Madracis decatis; however, depuration proceeded at a slow rate. After 275 days nearly 33 percent of the original radioactivity from the PCB remained in the coral, suggesting that PCBs are quite persistent in coral tissues.

Concentration in Tinian Corals: Total PCBs are reported as the sum of all measured PCB congeners. Coral concentrations of PCBs in Tinian ranged from 0.027 ng/g to 1.162 ng/g, with a mean of 0.44 ng/g.

Spatial Patterns: Statistically, there were no statistically significant differences between the strata (Dunn's test, α=0.05)

Discussion: PCB levels measured here were within the range of values reported elsewhere for PCBs in hard coral tissue (Table 4; Pait et al. 2009; Whitall et al. 2014; Apeti et al. 2014), although lower than what was reported in Guam for soft corals (3.72 to 4,103 ng/g; Denton et al. 1999). While there are no clear sources of PCBs on modern Tinian (PCB production was banned in the U.S. in 1979), the environmental persistence of PCBs makes them fairly common in the environment. More research is needed to establish body burden threshold above which corals are adversely affected by PCBs and other pollutants.
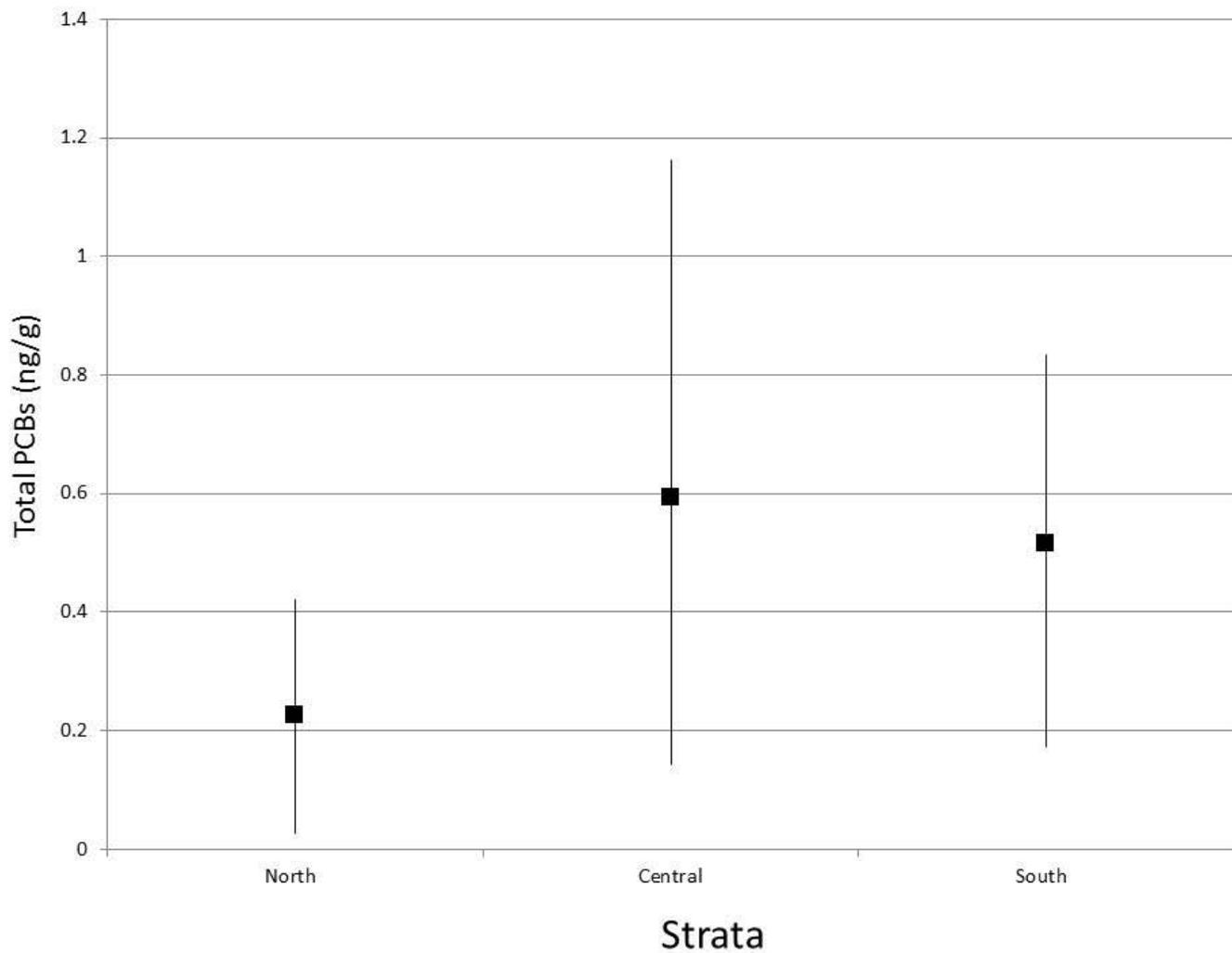
Figure 12. : Coral PCBs concentrations by strata. Squares are mean values; lines show maximum and minimum values. There were no statistically significant differences between strata (Dunn's test, α=0.05)

Legend

Coral Tissue Contaminants

Total_PAHs (ng/g)

- 4.198 - 5.145
- 5.146 - 9.886
- 9.887 - 27.801
- 27.802 - 37.958
- 37.959 - 127.948
- ☐ Sampling Strata

0   0.5   1   2 Kilometers

N

Figure 13. Total PAH concentrations in coral.

Polcyclic Aromatic Hydrocarbons (PAHs)

Background: Polycyclic aromatic hydrocarbons (PAHs) are multiple ringed organic compounds consisting of carbon and hydrogen. They can occur naturally or result from human activities, such as fossil fuel combustion. In this study, we present total PAHs as the sum of the PAHs analyzed (see Table 2a).

Uses: PAHs are associated with the use and combustion of fossil fuels and other organic materials (e.g., wood). Natural sources of PAHs include forest fires and volcanoes. In addition to fossil fuels, PAHs are used in industrial processes and are found in cigarette smoke.

Environmental effects: Because of their hydrophobic nature, PAHs tend to accumulate in marine organisms through direct exposure (e.g body surface, gills) or through the food chain (Neff 1985). Exposure to PAHs has been associated with oxidative stress, immune system and endocrine system problems, and developmental abnormalities in marine organisms (Peachy and Crosby 1996, Hylland 2006). Toxicity may be related to light exposure (Peachy and Crosby, 1995). Furthermore, a number of individual PAHs have been previously identified as likely carcinogens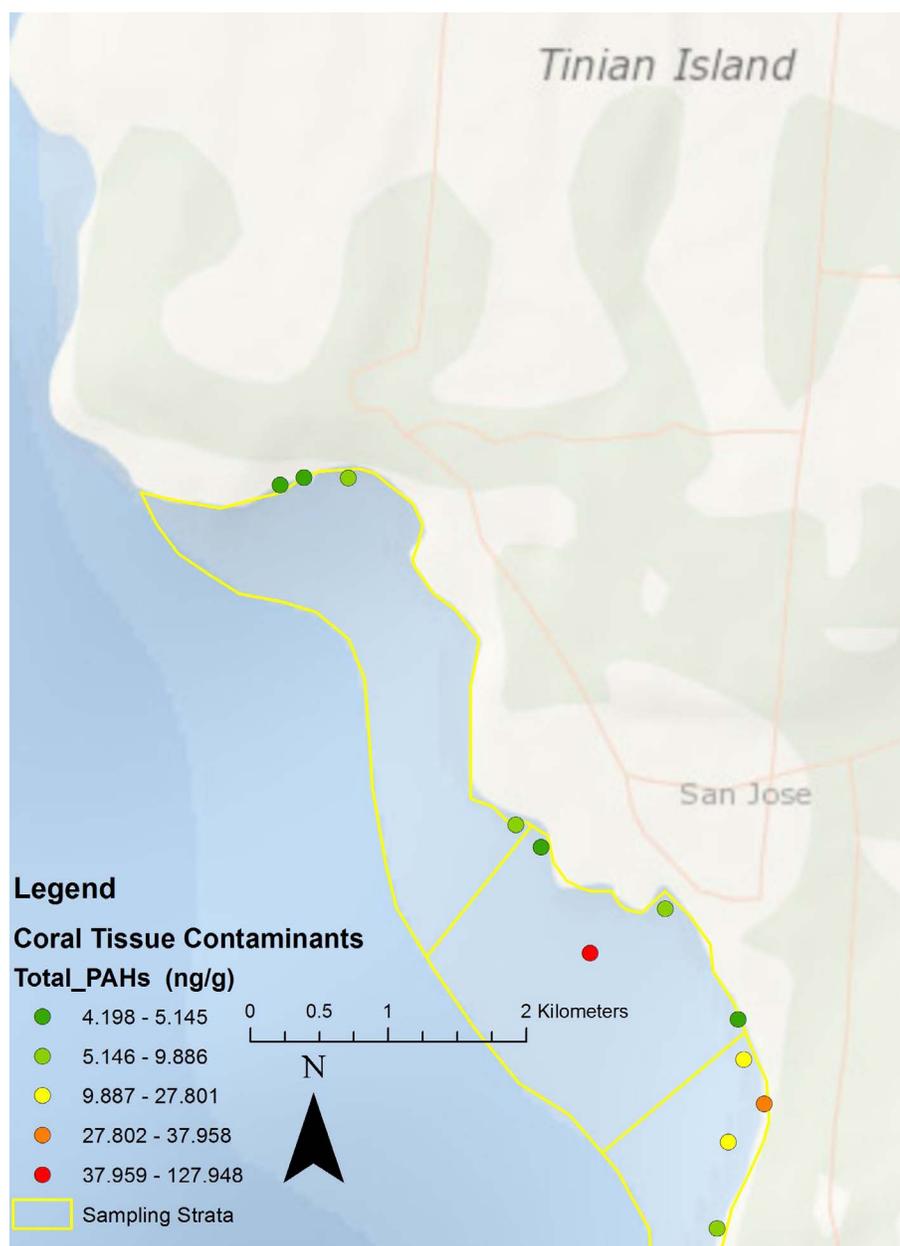 (USDHHS 1995). The carcinogenic nature of PAHs in marine organisms is associated with their metabolic breakdown which generates reactive epoxides which can affect cellular components such as DNA (Hylland 2006; Neff 1985). In corals, PAHs can affect the zooxanthellae. Bioaccumulation in corals has been documented (Ko et al. 2014) and appears to be related to the lipid content of both the coral and the algae (Kennedy et al. 1992). Adverse effects of fuel oil have been documented in Pocillopora damicornis (Rougée et al. 2006).

Concentration in Tinian Corals: Coral concentrations of PAHs in Tinian ranged from 4.20 ng/g to 127.95 ng/g, with a mean of 21.76 ng/g.

Spatial Patterns: There were no statistically significant differences between the strata (Dunn's test, **α**=0.05), although qualitatively concentrations were higher in the central stratum where the harbor is located.

Discussion: PAH levels measured here were within the range of values reported elsewhere for PAHs in hard coral tissue (Table 4; Pait et al. 2009; Whitall et al. 2014; Apeti et al. 2014), although the values in Tinian are towards the higher end of reported values, especially in term of maximum values. Values for soft coral tissues

Figure 14: Coral PAHs concentrations by strata. Squares are mean values; lines show maximum and minimum values. No statistically significantly differences between strata (Dunn's test, α=0.05)

in Guam (Denton et al. 1999) were lower with most samples being below limits of detection for Sinularia sp. Boat traffic, both historical and current, especially in the harbor area, likely explains the observed PAHs levels. More research is needed to establish body burden threshold above which corals are adversely affected by PAHs and other pollutants.

Figure 15: Aluminum concentrations in coral.

Aluminum

Background: Aluminum (Al) is the most common metallic element in the Earth's crust.

Uses: Aluminum has a wide range of uses due to its malleability, lightweight nature and resistance to corrosion. Common uses include cans, foils, kitchen utensils, window frames, beer kegs and airplane parts. It is also used in alloys with copper, manganese, magnesium and silicon (RSC 2016a).

Environmental effects: Aluminum is generally not considered to be toxic in the environment, but ratios of aluminum to other elements can provide information about sources (see Additional Analysis section).

Concentration in Tinian Corals: Coral concentrations of aluminum in Tinian ranged from below limits of detection to 14.6 µg/g, with a mean of 7.1 µg/g.

Spatial Patterns: Statistically, there were no significant differences (Dunn's test, α=0.05) between the strata.

Discussion: Aluminum levels measured here were lower than the range of values reported elsewhere for Al in coral tissue (Table 4; Pait et al. 2009; Whitall et al. 2010; Whitall et al. 2014; Apeti et al. 2014). Aluminum is the most common metal in the Earth's crust and is generally not considered to be a pollutant in the environment. Relatively low aluminum concentration may be a reflection of local geology, the lack of strong riverine inputs to the southwest shore of Tinian, or species differences between this study and previously published data.
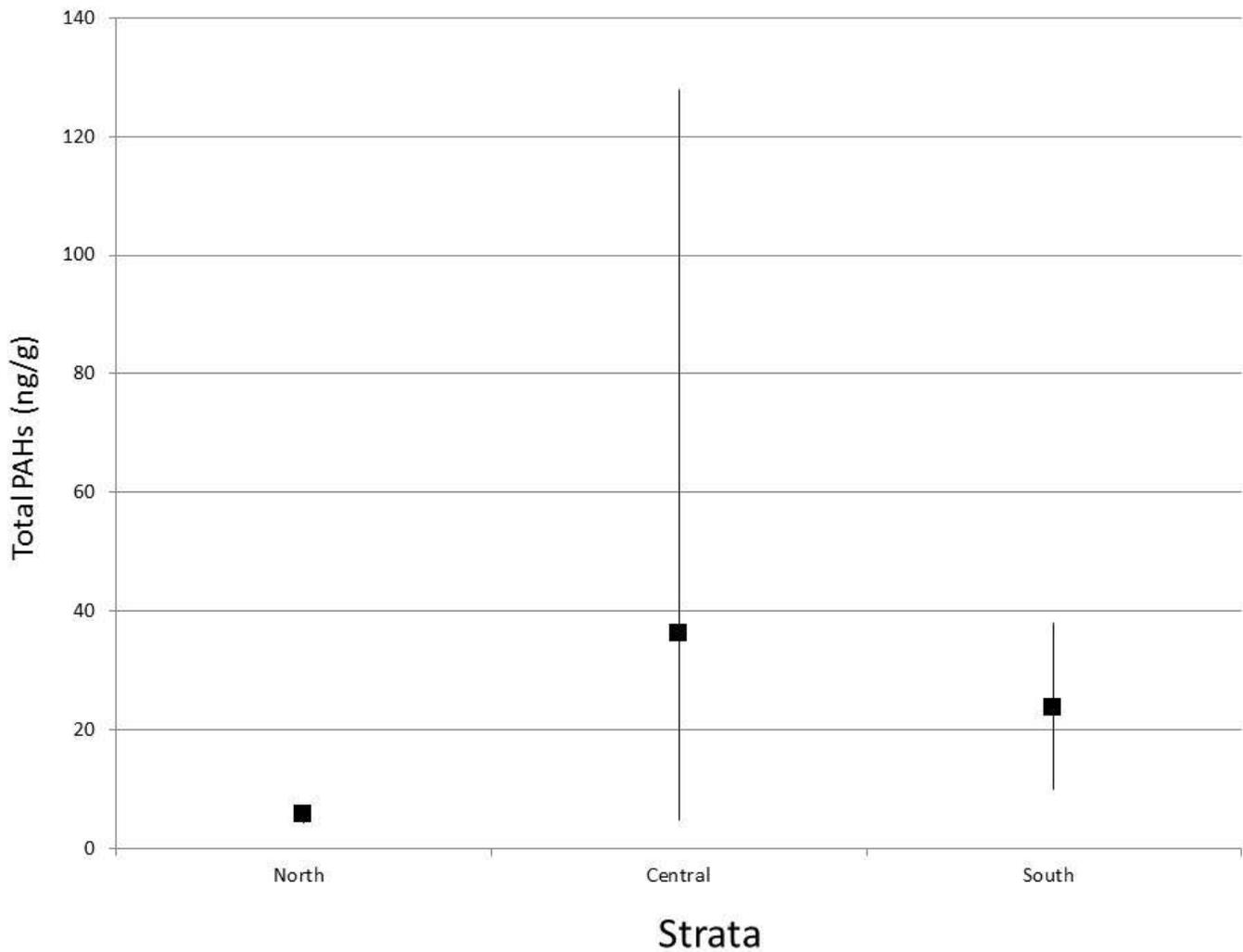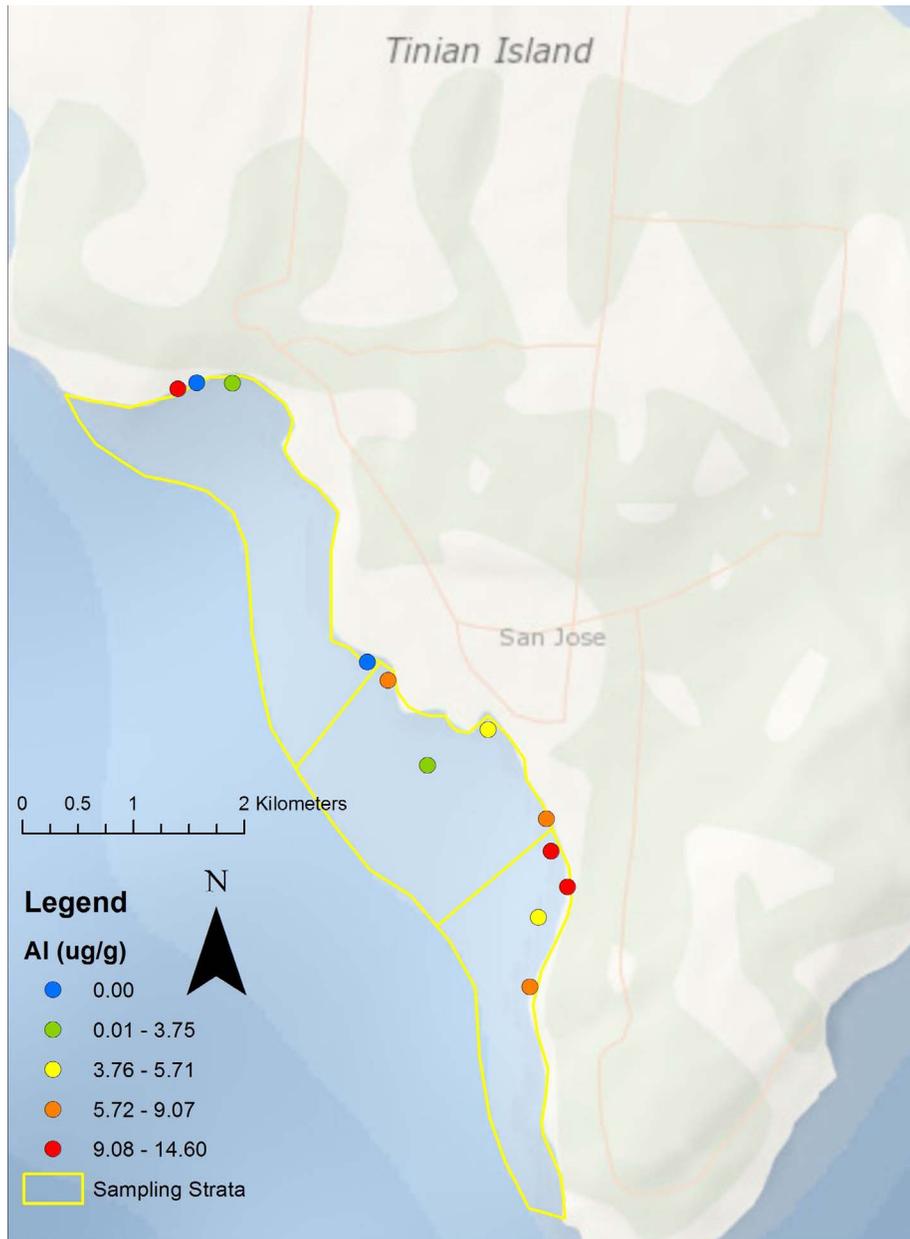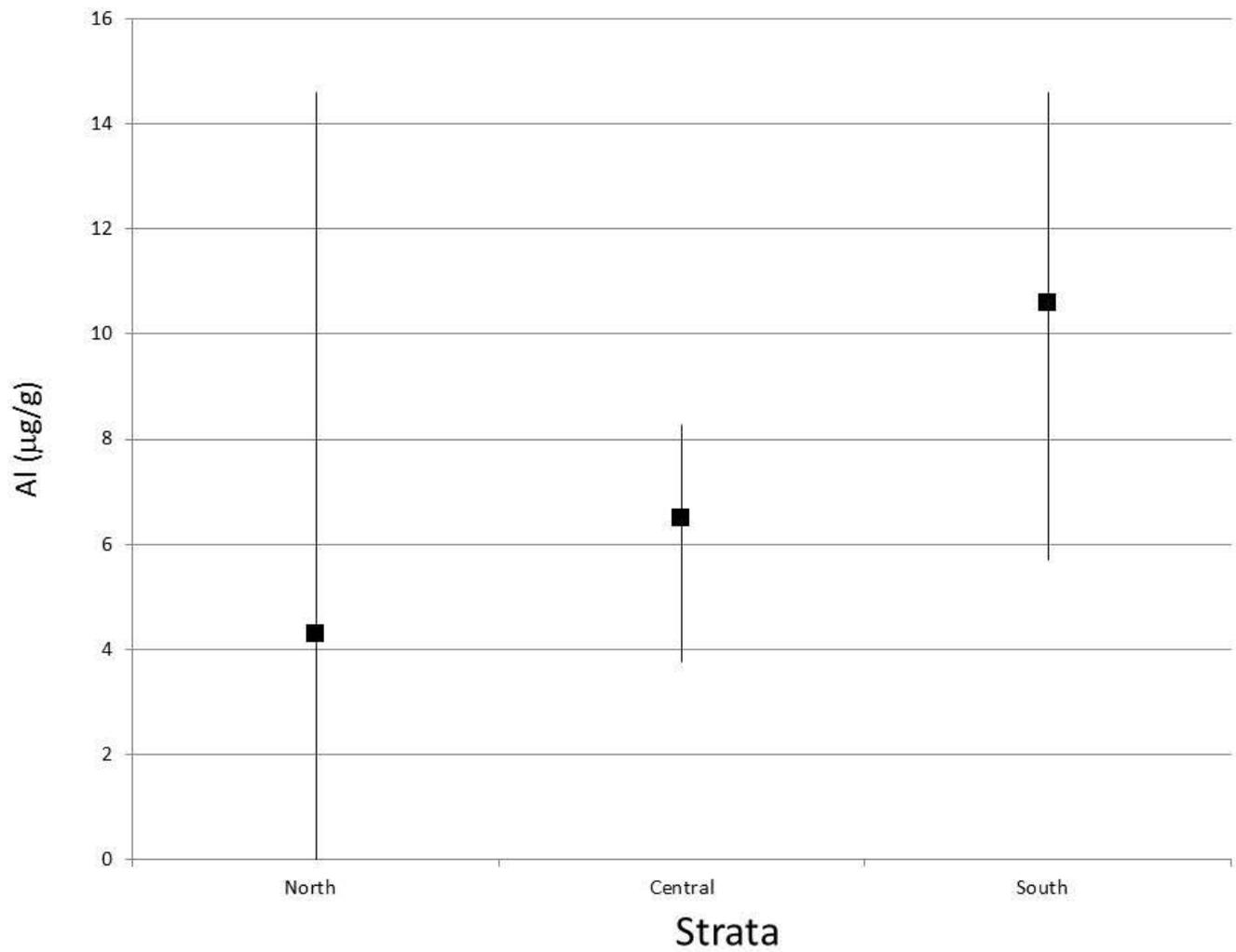
Figure 16: Coral aluminum concentrations by strata. Squares are mean values; lines show maximum and minimum values. There were no statistically significant differences between strata (Dunn's test, α=0.05).
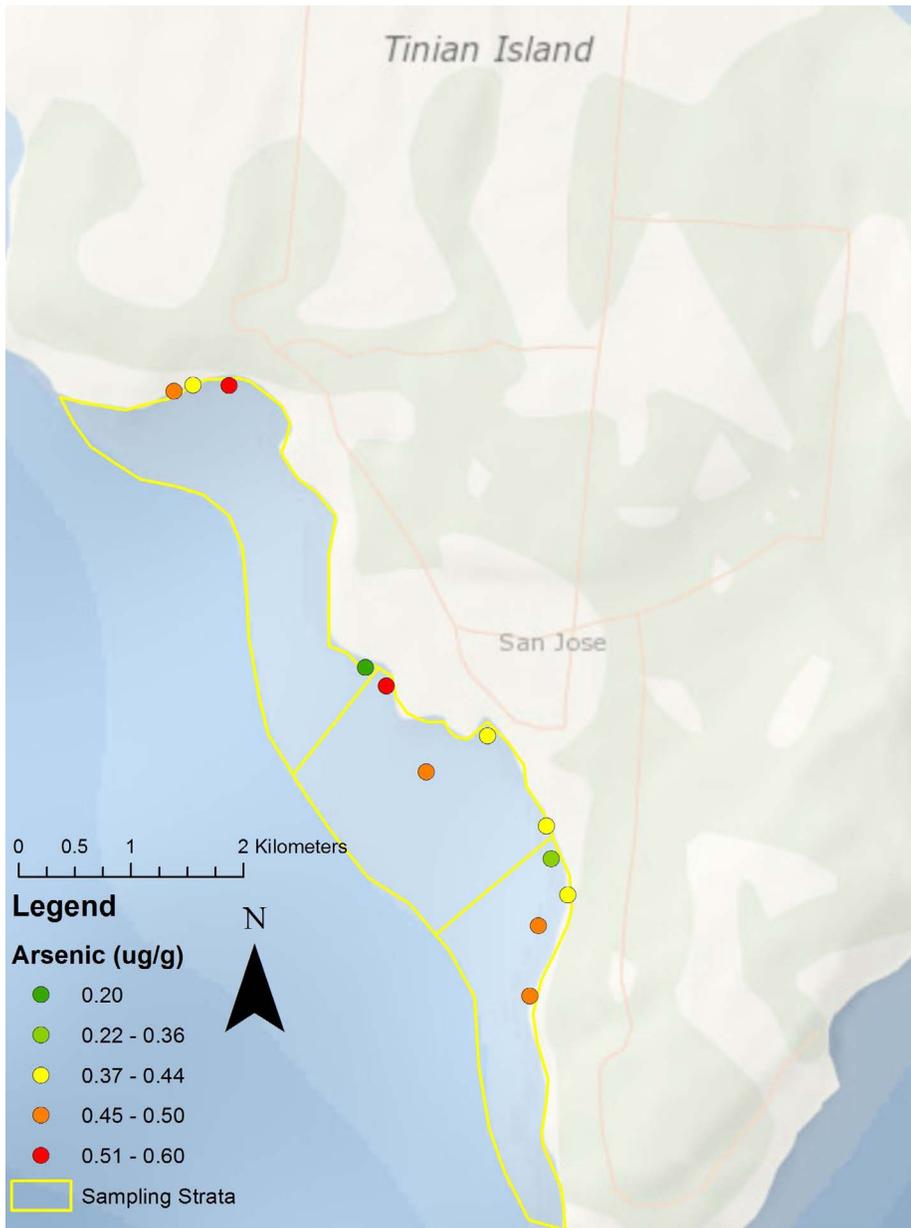
Figure 17. Arsenic concentrations in corals.

Arsenic

Background: Arsenic (As) is a metalloid element that naturally occurs in the Earth's crust. It can exist as either an inorganic or organic compound. Mining and use of arsenic has increased the amount of arsenic present in the environment.

Uses: Arsenic has been widely used for centuries in applications ranging from pharmaceuticals to agriculture. Although arsenic use has declined in recently years due to concerns over toxicity, the most common uses of arsenic are pesticides, herbicides, desiccants, wood treatments and growth stimulants for agricultural crops and livestock (Eisler 1988). Arsenic can also be released into the environment through smelting. Inorganic forms of arsenic are generally much more toxic than organic forms.

Environmental effects: Arsenic is a known carcinogen, mutagen and teratogen. Its adverse effects have been quantified in humans, various mammalian species and fish, as well as in plants and invertebrates (Eisler 1988, Novellini et al. 2003). Arsenic's effect on corals has not been well documented.

Concentration in Tinian Corals: Coral concentrations of arsenic in Tinian ranged from 0.20 µg/g to 0.6 µg/g, with a mean of 0.44 µg/g.

Spatial Patterns: Statistically, there were no statistically significant differences between the strata (Dunn's test, α=0.05).

Discussion: Arsenic levels measured here were an order of magnitude lower than maximum reported values for P. damicornis in Guam (Table 4; Denton et al. 1999), suggesting that arsenic concentrations in Tinian are low. Like all metals, arsenic has both natural and anthropogenic uses. While there are no clear sources of arsenic on modern Tinian, historical land use, including military activities, may have contributed to the observed As levels. More research is needed to establish body burden threshold above which corals are adversely affected by As and other pollutants.
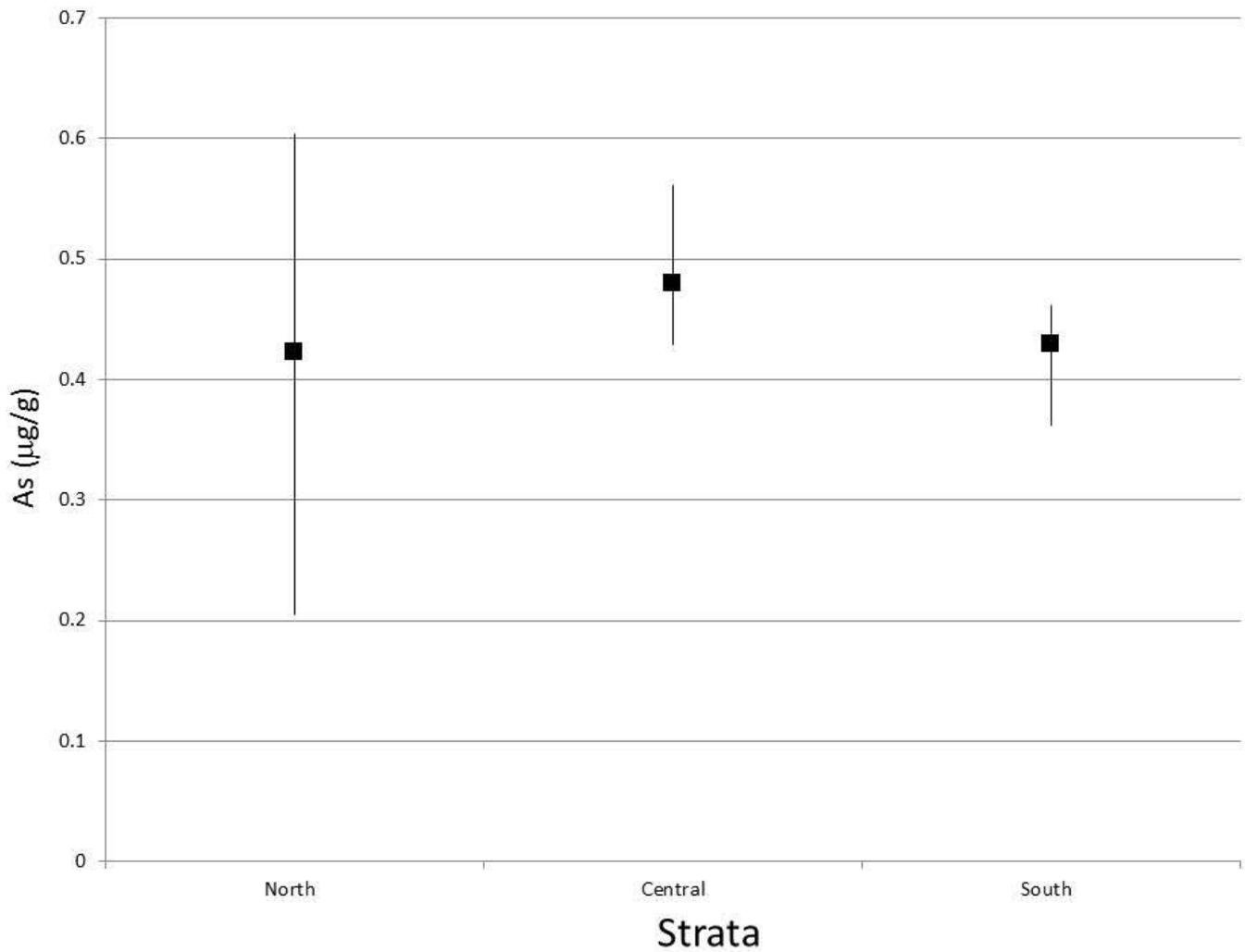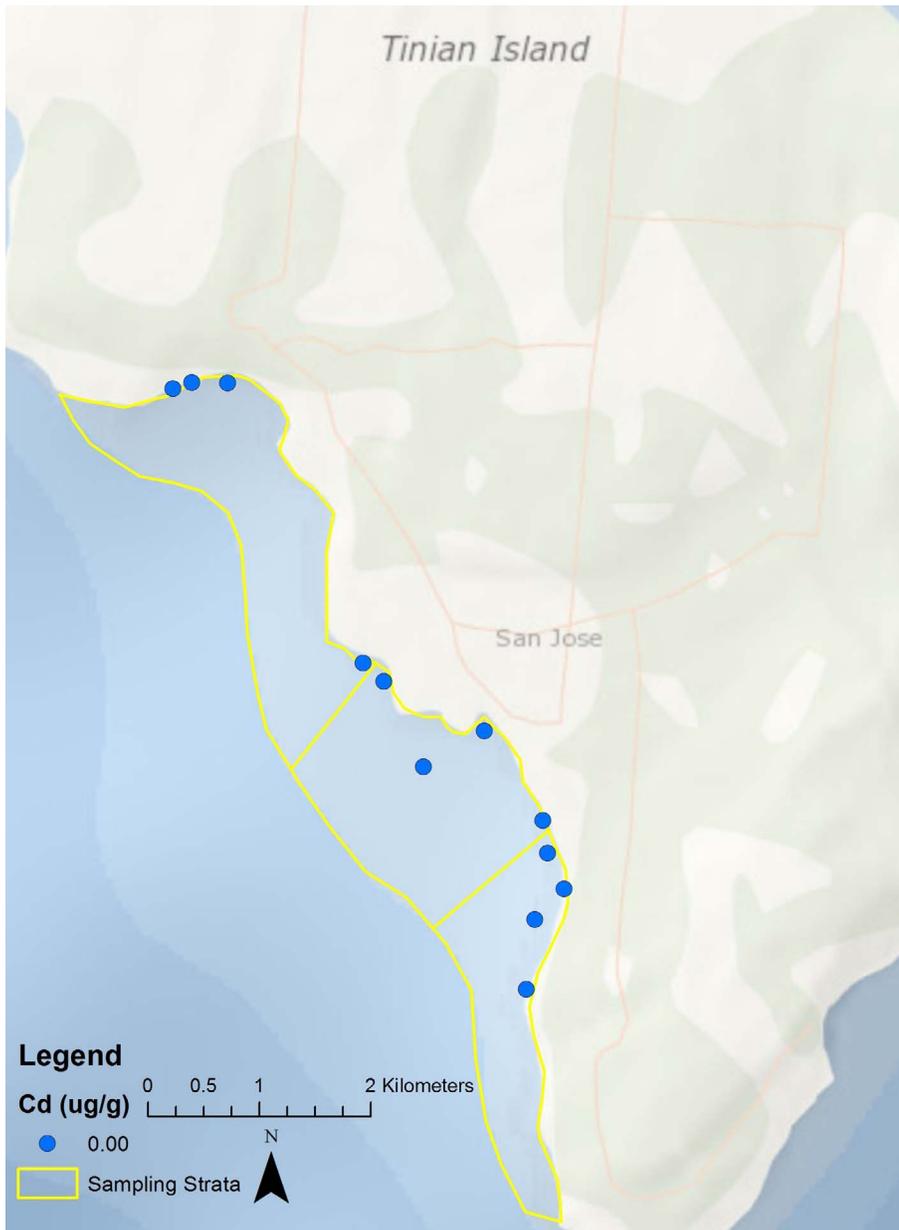
Figure 18: Coral arsenic concentrations by strata. Squares are mean values; lines show maximum and minimum values. There are no statistically significant differences between strata (Dunn's test α=0.05)

Figure 19. Cadmium concentrations in coral.

Cadmium

Background: Cadmium (Cd) is a metallic element that naturally occurs in the Earth's crust. Mining and use of cadmium has increased the amount of cadmium present in the environment.

Uses: Cadmium has historically been widely used in batteries, pigments and in electroplating. Cadmium use is being reduced due to concerns over toxicity (RSC 2016b).

Environmental effects: Although cadmium is a minor nutrient for plant growth, it is relatively toxic to aquatic organisms. Toxicity to sea urchins (Edullantes and Galapate, 2014, Dermeche et al. 2012), bivalves, crustaceans, coral invertebrates and fish has been reported (EPA 2001), including effects on development and reproduction in several invertebrate species, and the potential to impede osmoregulation in herring larvae (US-DHHS 1999; Eisler 1985). Previous studies (e.g. Mitchelmore et al. 2007, Whitall et al. 2014) have shown that cadmium is taken up by corals, and that cadmium is primarily accumulated in tissues rather than skeletons (Metian et al. 2014). Cadmium inhibits fertilization in scleractinian coral at relatively high concentrations (5,000 µg/L, Reichelt-Brushett and Harrison, 2005).

Concentration in Tinian Corals: Cadmium was not detected in coral tissue samples in Tinian.

Discussion: Cadmium has been detected in other coral species in other locations (Table 4; Pait et al. 2009; Whitall et al. 2010; Whitall et al. 2014; Apeti et al. 2014), and was detected in three of six samples in P. damicornis in Guam (Denton et al. 1999). but was not found in this study. This could be due to a lack of anthropogenic cadmium use in Tinian or the geologic makeup of the island.
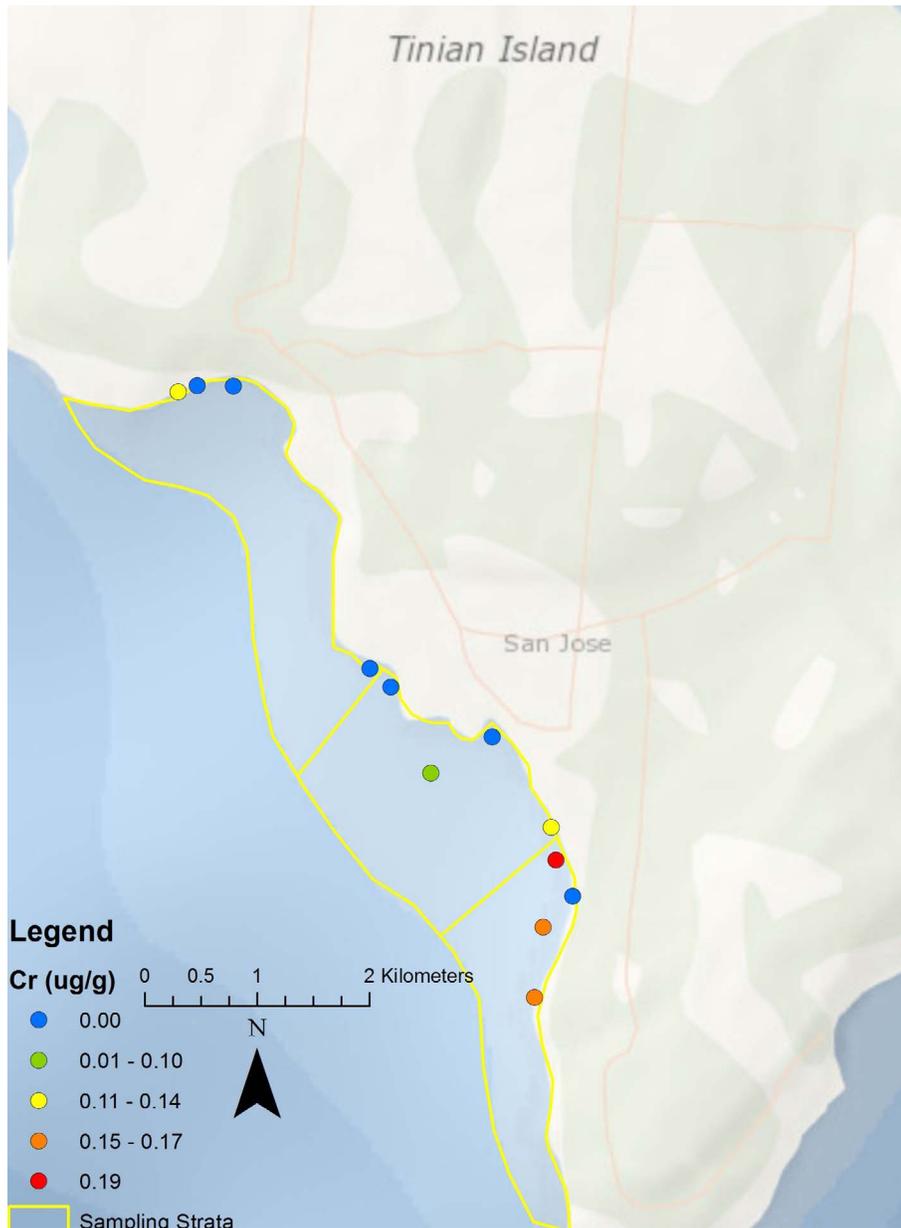
Chromium

Background: Chromium (Cr) is a metallic element that naturally occurs in the Earth's crust. Mining and use of chromium has increased the amount of chromium present in the environment.

Uses: Chromium has a variety of uses including leather tanning, stainless steel, metallic plating and in industrial catalysts (RSC 2016c). Chromium is an essential nutrient for plants and animals but can be toxic in excessive concentrations.

Environmental effects: Chromium has been shown to reduce survival and fecundity in the cladoceran Daphnia magna, decreased reproductive success in the sea urchin Paracentrotus lividus (Novellini et al. 2003) and reduced growth in fingerling chinook salmon (Oncorhynchus tshawytscha) (Eisler 1986). Chromium's effect on corals has not been well documented.

Concentration in Tinian Corals: Coral concentrations of chromium in Tinian ranged from below limits of detection to 0.19 µg/g, with a mean of 0.08 µg/g.

Spatial Patterns: There were no statistically significant differences between the strata (Dunn's test, **α**=0.05).

Figure 20. Chromium concentrations in coral.

Discussion: Cr levels measured here were similar to values reported for P. damicornis in Guam (Table 4; Denton et al. 1999). Like all metals, chromium has both natural and anthropogenic uses. While there are no clear sources of chromium on modern Tinian, historical land use, including military activities, may have contributed to the observed Cr levels. More research is needed to establish body burden threshold above which corals are adversely affected by Cr and other pollutants.
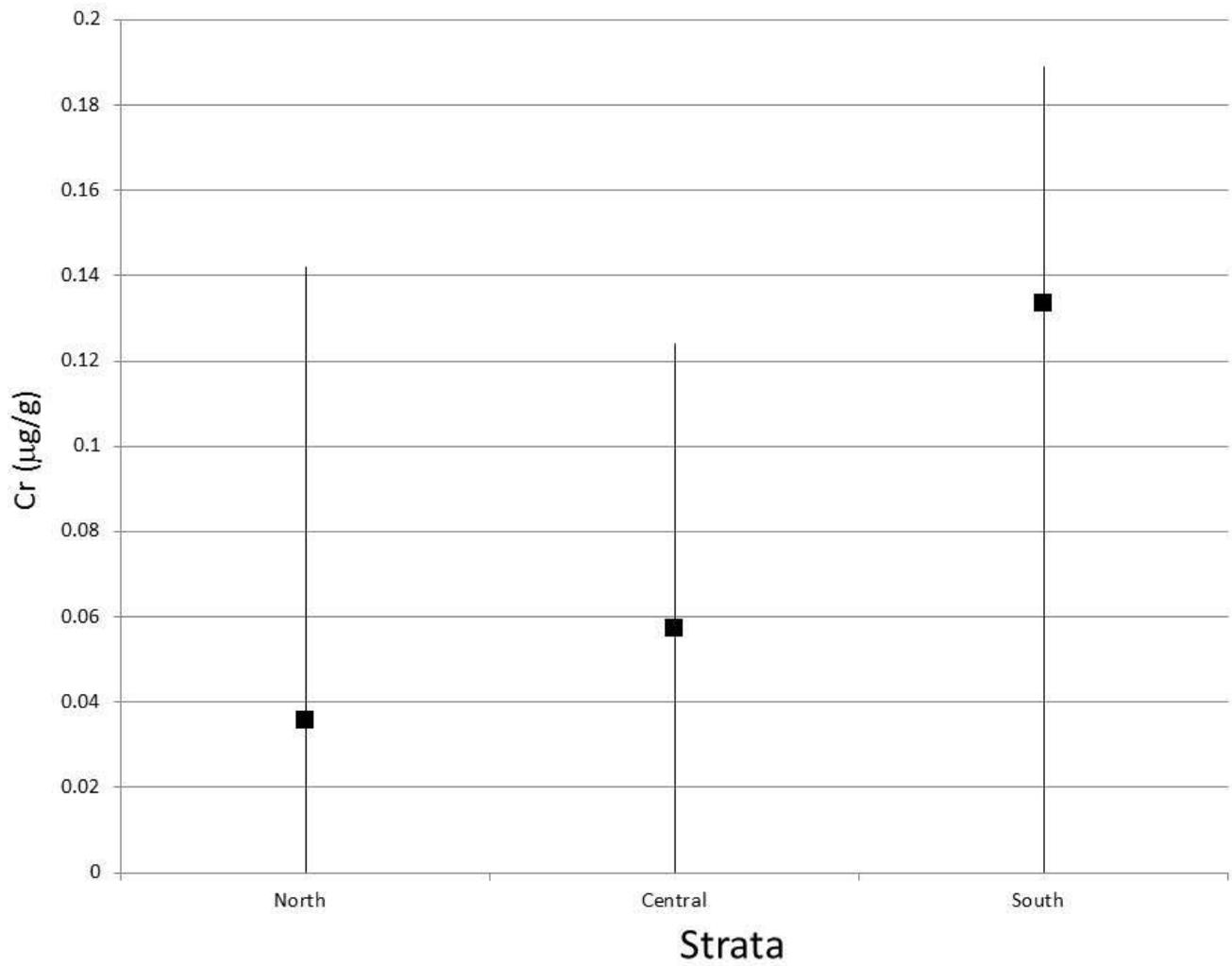
Figure 21: Coral chromium concentrations by strata. Squares are mean values; lines show maximum and minimum values. There were no statistically significant differences (Dunn's test, α=0.05) between strata.

Figure 22. Chromium concentrations in coral.

Legend

Cu (ug/g)
- 0.00
- 0.01 - 0.26
- Sampling Strata

Copper

Background: Copper (Cu) is a metallic element with excellent conductivity that naturally occurs in the Earth's crust. Mining and use of copper has increased the amount of copper present in the environment.

Uses: Copper has a wide array of uses ranging from coins to wires to pipes to pesticides to industrial materials (e.g. heat exchangers) to anti-fouling paints to alloys. Copper is an essential micronutrient for plants and animals but can have adverse effects at high concentrations.

Environmental effects: In aquatic environments, copper can have deleterious effects on reproduction and development in mysid shrimp (Eisler 1998), and sea urchins (Edullantes and Galpate, 2014; Dermeche et al. 2012; Novellini et al. 2003). In corals, copper concentrations of 20 µg/L have been shown to significantly reduce fertilization success in brain coral Goniastrea aspera (Reichelt-Brushett and Harrison, 2005). At copper concentrations at or above 75 µg/L, fertilization success was reduced to one percent or less. Fertilization success was also significantly reduced in the coral Acropora longicyathus at 24 µg/L, a similar concentration level at which effects were observed in G. aspera. In Galaxea fascicularis, short term exposures to copper at relatively low concentrations (0.1 mg/L) have been shown to cause tissue bleaching and death (Sabdono 2009). Copper has been shown to accumulate in Pocillopora damicornis during sub-lethal exposures (Mitchelmore et al. 2007) and in field studies (Esselmont 2000).

Concentration in Tinian Corals: Concentrations of copper in coral in Tinian ranged from below limits of detection to 0.26 µg/g, with a mean of 0.02 µg/g. Copper was only detected at one site, located in the central stratum.

Spatial Patterns: Statistically, there were no statistically significant differences (Dunn's test, α=0.05, p=0.027) between the strata.

Discussion: Copper levels measured here were very similar to what was reported for P. damicornis in Guam (Table 4; Denton et al. 1999). Copper has a variety of uses (see above) but the use most relevant to Tinian is its use in anti-fouling boat paint. Somewhat surprisingly, copper was only detected at one site in the central

stratum, although this is the area of highest boat traffic. Copper concentrations reported here may be lower than reported elsewhere due to a smaller magnitude of anthropogenic sources and/or less geologic input. Although copper is an essential micronutrient, more research is needed to establish body burden threshold above which corals are adversely affected by Cu and other pollutants.
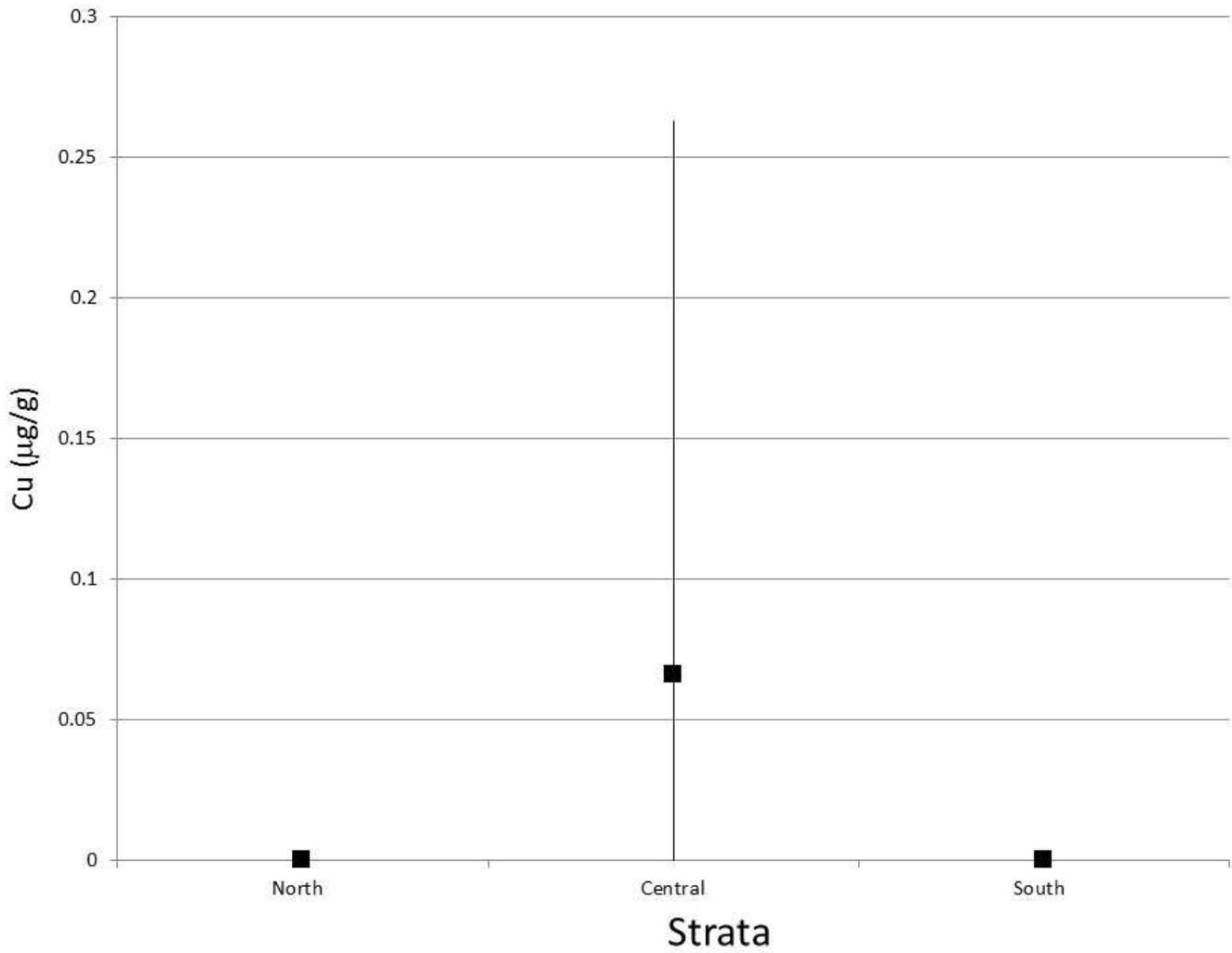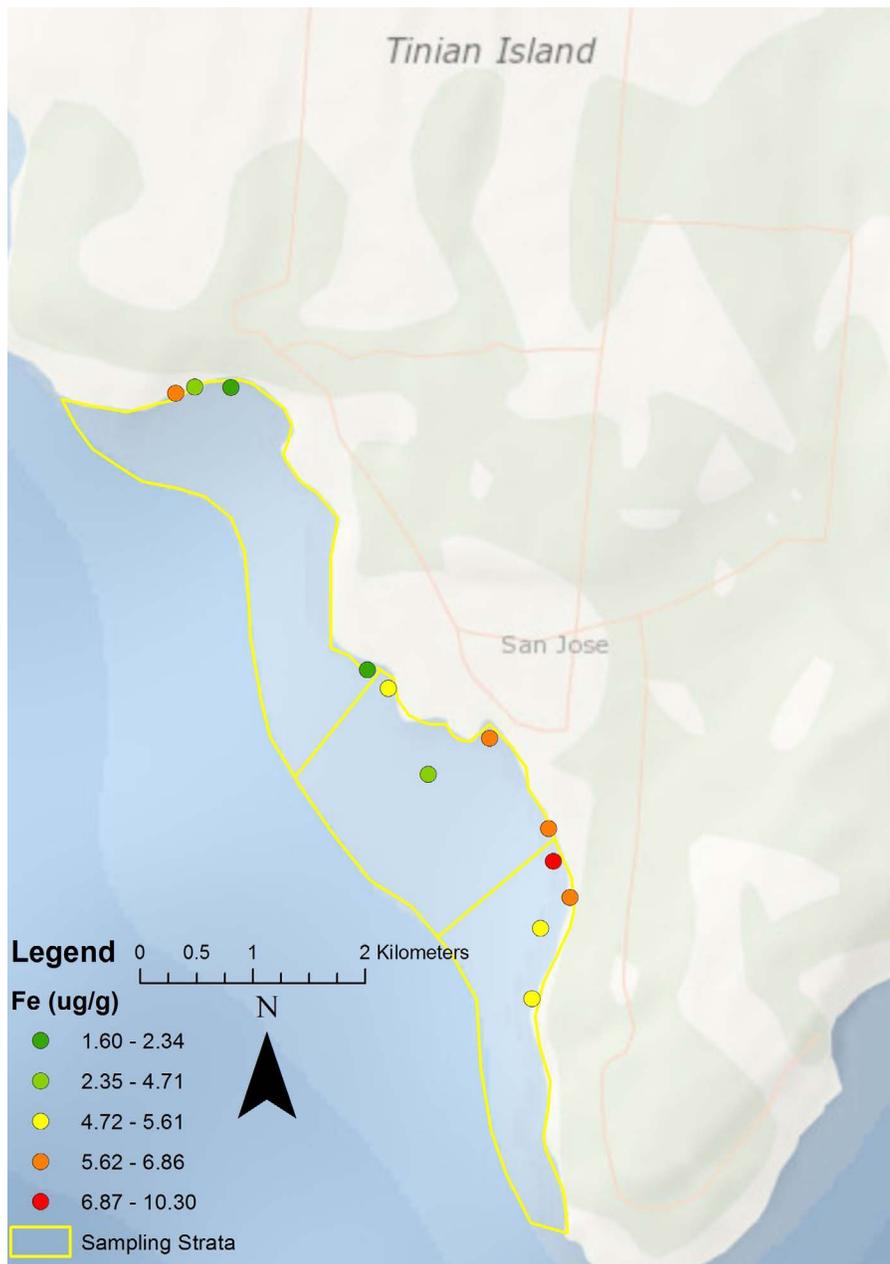

Figure 23: Coral copper concentrations by strata. Squares are mean values; lines show maximum and minimum values. There are no statistically significant differences between strata (Dunn's test, α=0.05)

Figure 24. Iron concentrations in coral.

Iron

Background: Iron (Fe) is a metallic element that by mass is the most abundant element in the Earth's crust. Mining and use of iron has increased the amount of iron present in the environment.

Uses: Iron is used in many materials for construction and manufacturing including steel, stainless steel and cast iron. Iron is an essential nutrient for both plants and animals.

Environmental effects: Iron is generally not considered to be toxic in the environment (RSC 2016d), but is an essential nutrient that can increase primary productivity.

Concentration in Tinian Corals: Coral concentrations of iron in Tinian ranged from 1.60 µg/g to 10.3 µg/g, with a mean of 5.52 µg/g.

Spatial Patterns: Statistically, there were no significant differences (Dunn's test, α=0.05, p=0.027) between the strata.

Discussion: Iron levels measured here were lower than the range of values reported elsewhere for Fe in coral tissue (Table 4; Pait et al. 2009; Whitall et al. 2010; Whitall et al. 2014; Apeti et al. 2014). In addition to a variety of anthropogenic uses (e.g. steel), iron is a very common metal in the Earth's crust and is generally not considered to be a pollutant in the environment. Relatively low iron concentration may be a reflection of local geology, the lack of strong riverine inputs to the southwest shore of Tinian or species differences between this study and previously published data.
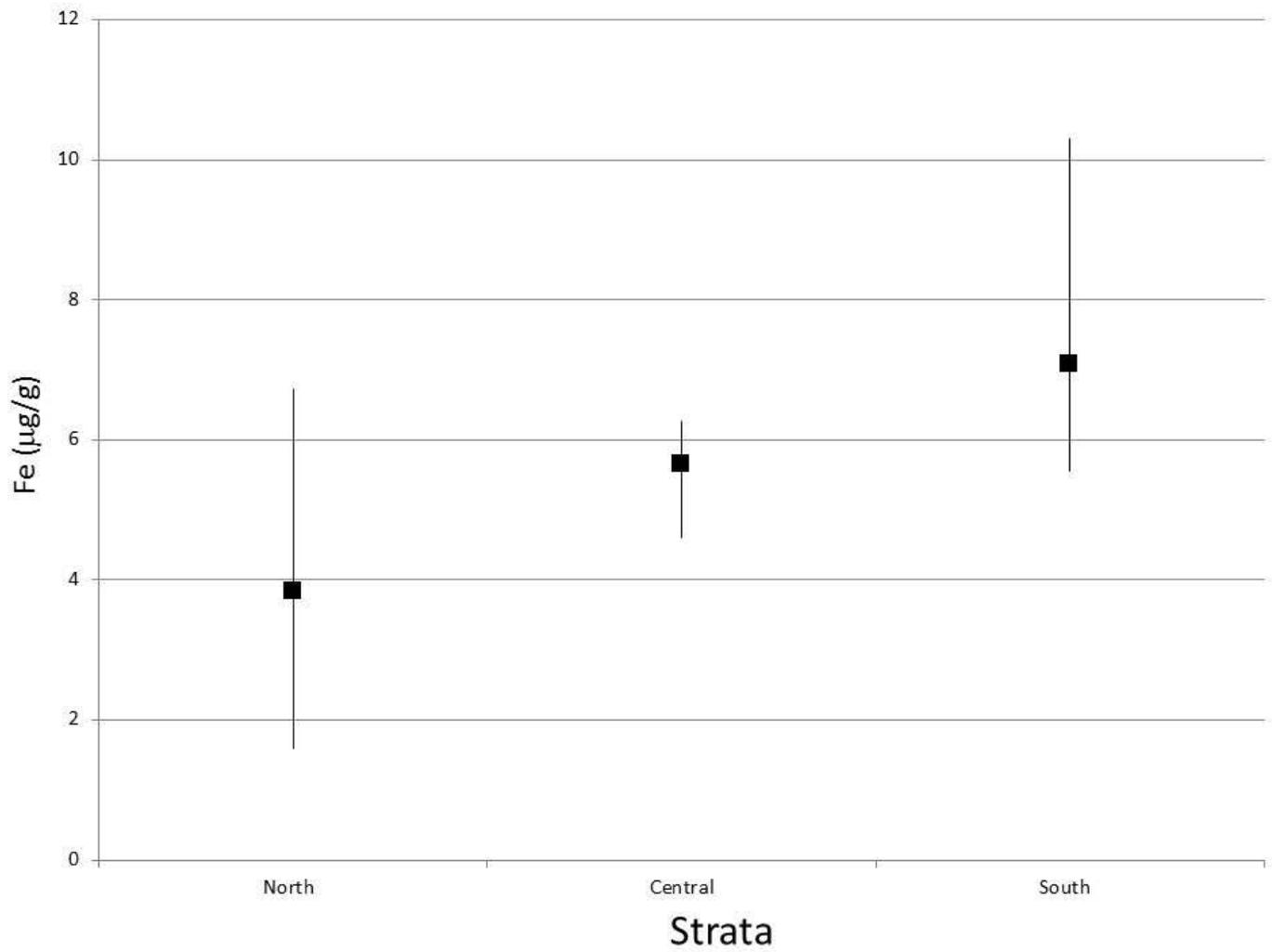
Figure 25: Coral iron concentrations by strata. Squares are mean values; lines show maximum and minimum values. There are no statistically significant differences between strata (Dunn's test, α=0.05)
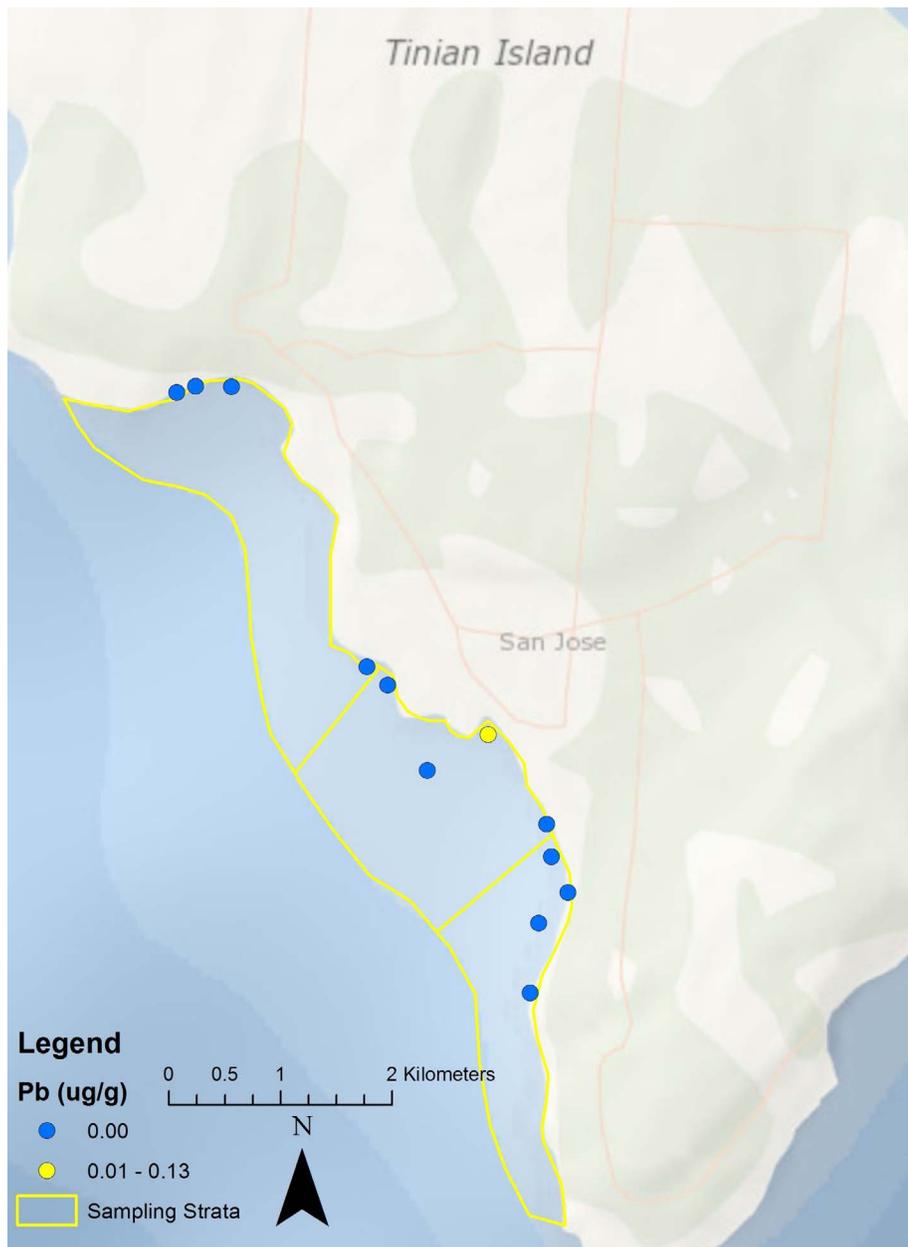
Lead

Background: Lead (Pb) is a malleable, corrosion resistant metallic element that naturally occurs in the Earth's crust. Mining and use of lead has increased the amount of lead present in the environment.

Uses: Lead has been widely used for centuries in pipes, pewter, paints, pottery glazes, insecticides, hair dyes and gasoline additives. These uses have been greatly reduced due to concerns over lead toxicity. Lead is still widely used in car batteries, ammunition, weights (e.g. barbells and dive belts), crystal glass, solder and radiation protection (RSC 2016e).

Environmental effects: Lead has no known nutritional role in plant or animal health. It can be acutely toxic as well as a carcinogen and teratogen (RSC 2016g). Reproductive effects on sea urchins have been previously documented (Novellini et al. 2003, Dermeche et al. 2012). Reichelt-Brushett and Harrison (2005) showed that relatively high lead concentrations resulted in lower fertilization success in multiple coral species.

Concentration in Tinian Corals: Coral concentrations of lead in Tinian ranged from below limits of detection to 0.13 µg/g, with a mean of 0.01 µg/g. Lead was only detected at one site, located in the central stratum.

Figure 26 Lead concentrations in coral.

Spatial Patterns: Statistically, there were no significant differences between the strata (Dunn's test, **α**=0.05). Discussion: Lead was only detected at one site, which is very similar to what was reported for P. damicornis in Guam (Denton et al. 1999; all non-detects). Lead sequestration has been shown for other species in the U.S. Caribbean (Table 4; Pait et al. 2009; Whitall et al. 2010; Whitall et al. 2014; Apeti et al. 2014), so it is unclear if this is a species effect or differences between environmental lead levels among the studies areas. Like all metals, lead has both natural and anthropogenic sources. While there are no clear sources of lead on modern Tinian, historical land use, including military activities, may have contributed to the observed lead levels. More research is needed to establish body burden threshold above which corals are adversely affected by lead and other pollutants.

Discussion: Lead was only detected at one site, which is very similar to what was reported for *P. damicornis* in Guam (Denton et al. 1999; all non-detects). Lead sequestration has been shown for other species in the U.S. Caribbean (Table 4; Pait et al. 2009; Whitall et al. 2010; Whitall et al. 2014; Apeti et al. 2014), so it is unclear if this is a species effect or differences between environmental lead levels among the studies areas. Like all

metals, lead has both natural and anthropogenic sources. While there are no clear sources of lead on modern Tinian, historical land use, including military activities, may have contributed to the observed lead levels. More research is needed to establish body burden threshold above which corals are adversely affected by lead and other pollutants.
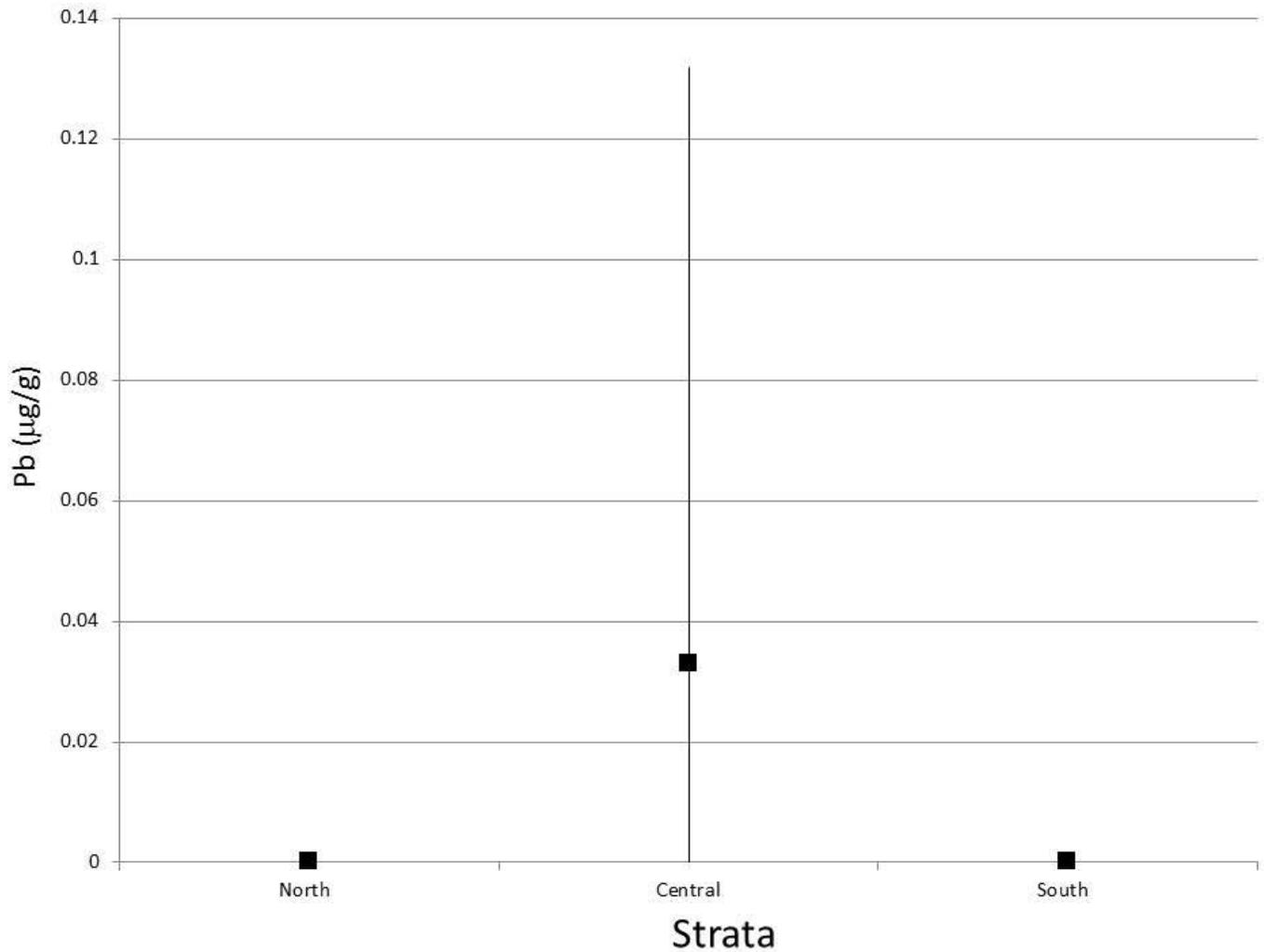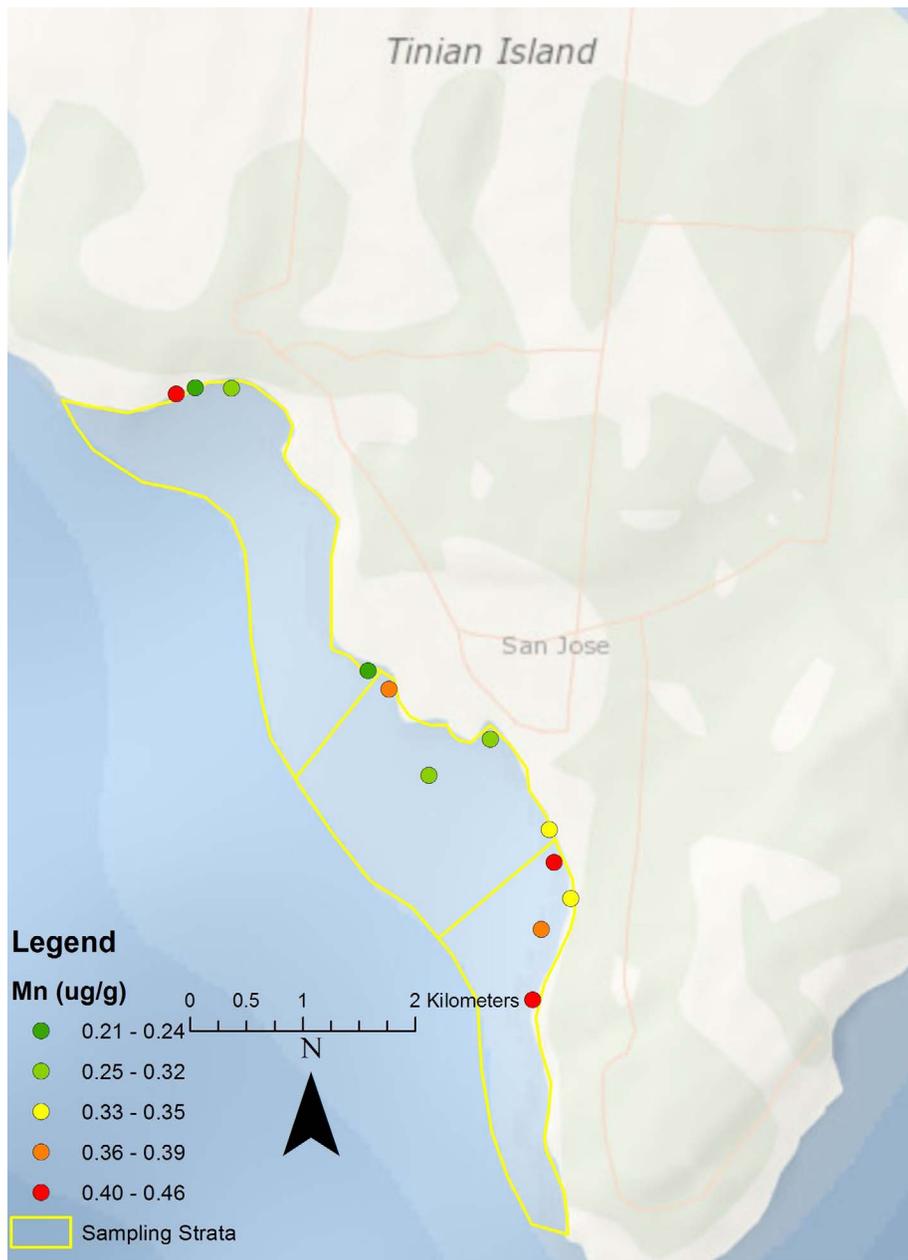

Figure 27: Coral lead concentrations by strata. Squares are mean values; lines show maximum and minimum values. There were no statistically significant differences between strata (Dunn's test, α=0.05).

Figure 28. Manganese concentrations in coral.

Manganese

Background: Manganese (Mn) is a brittle metallic element that naturally occurs in the Earth's crust. Mining and use of manganese has increased the amount of manganese present in the environment.

Uses: Because of its brittle nature, manganese is primarily used in alloys with steel and aluminum, as well as a catalyst, rubber additive, in fertilizers and in pesticides (RSC 2016f).

Environmental effects: Manganese is an essential element for plants and animals although it can be toxic to aquatic invertebrates at chronic high doses (Norwood et al. 2007). Studies have demonstrated that manganese, like other major and trace elements, does accumulate in coral tissues (Whitall et al. 2014) and is primarily sequestered in the tissues, rather than the skeleton (Metian et al. 2014). Like aluminum and iron, ratios of manganese with other metals can shed light on likely sources (e.g. crustal erosion vs. anthropogenic sources, see Additional Analysis section).

Concentration in Tinian Corals: Concentrations of manganese in coral in Tinian ranged from 0.21 µg/g to 0.46 µg/g, with a mean of 0.35 µg/g.

Spatial Patterns: Statistically, there were no significant differences (Dunn's test, **α**=0.05) between the strata.

Discussion: Manganese levels measured here were lower than the range of values reported elsewhere for Mn in coral tissue (Table 4; Pait et al. 2009; Whitall et al. 2010; Whitall et al. 2014; Apeti et al. 2014). In addition to a variety of anthropogenic uses, Mn is a very common metal in the Earth's crust and is generally not considered to be a pollutant in the environment. Relatively low Mn concentration may be a reflection of local geology, the lack of strong riverine inputs to the southwest shore of Tinian, or species differences between this study and previously published data.
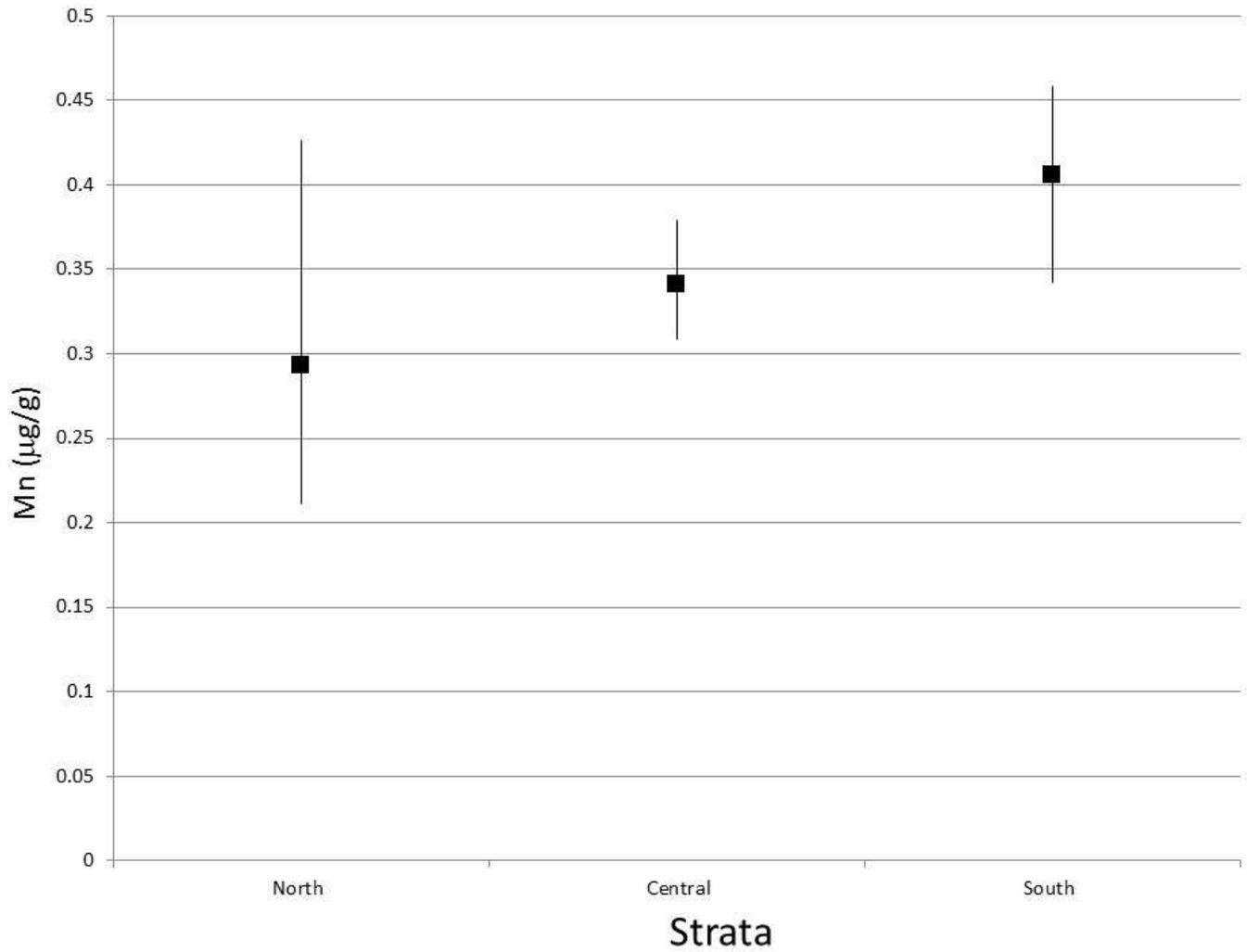
Figure 29: Coral manganese concentrations by strata. Squares are mean values; lines show maximum and minimum values. There were no statistically significant differences between strata (Dunn's test, α=0.05)

Figure 30. Mercury concentrations in coral.

Mercury

Background: Mercury (Hg) is a naturally occurring heavy metal that is liquid at room temperature in its elemental form. It exists in natural geologic formations as a solid in various compounds. Mining and use of mercury has increased the amount of mercury present in the environment.

Uses: Historically, mercury was used in manufacturing, batteries, fluorescent lights, dental fillings, felt production and thermometers, but these uses have been gradually phased out due to mercury toxicity. It is currently used in the chemical industry as a catalyst, and in some electrical switches.

Environmental effects: Methyl mercury (CH_3Hg) is the most toxic form of mercury. Mercury can be toxic to birds and invertebrates, and bioaccumulates in fish, which can have human health implications for fisheries species (USGS 2000). Mercury has been shown to be more toxic to sea urchins than other metals (Novellini et al. 2003). Although toxic effects of mercury on corals are not well understood, mercury uptake by corals has been previously demonstrated (e.g. Whitall et al. 2014; Guzman and Garcia, 2002), and mercury accumulates more in coral tissues than in the skeleton (Bastidas and Garcia 2004).

Concentration in Tinian Corals: Mercury was not detected in coral tissue samples in Tinian.

Discussion: Mercury has been detected in other coral species in other locations (Table 4; Pait et al. 2009; Whitall et al. 2010; Whitall et al. 2014; Apeti et al. 2014), and in *P. damicornis* in Guam (Denton et al. 1999) but was not found in this study. This could be due to a lack of anthropogenic mercury use in Tinian or the geologic makeup of the island.
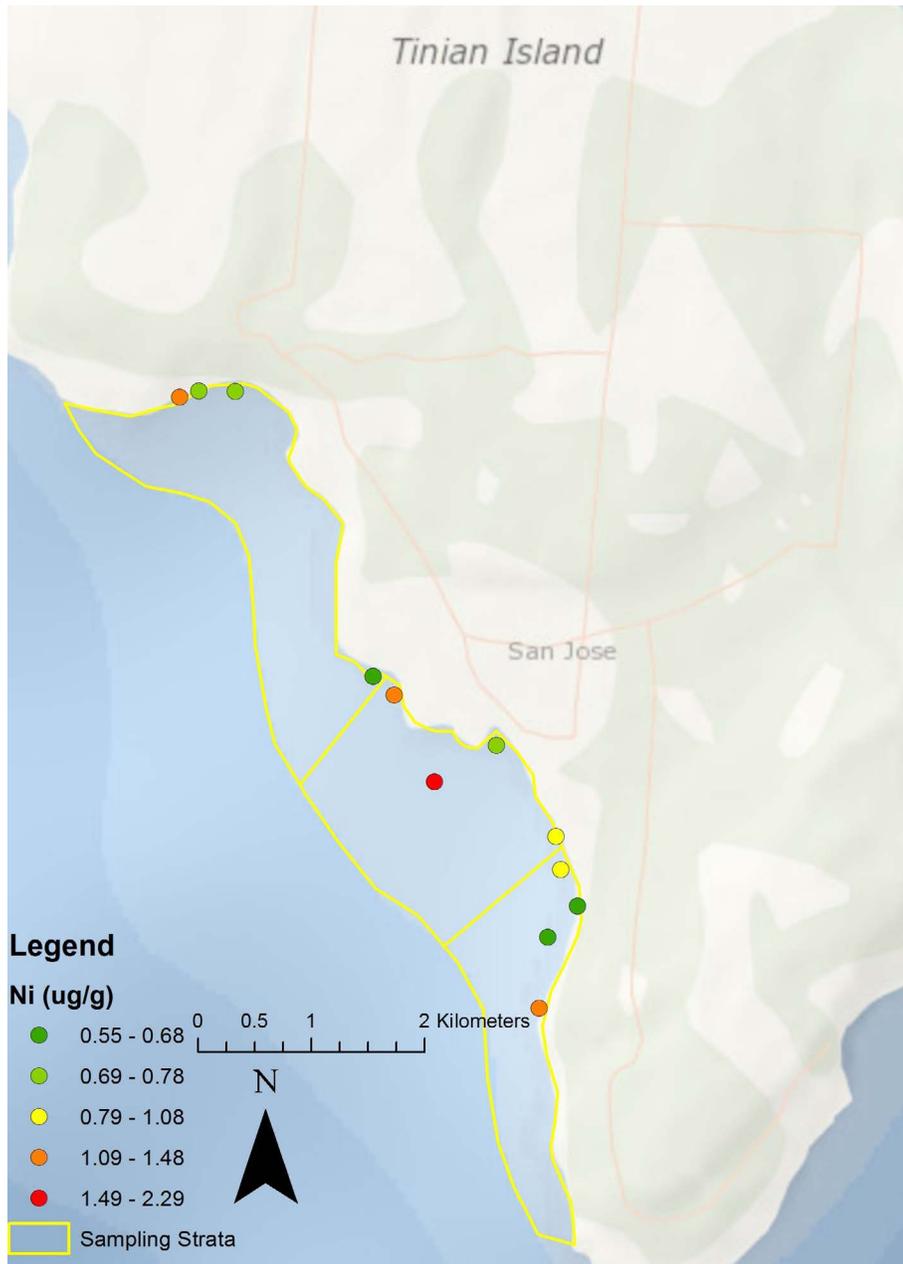
Figure 31. Nickel concentrations in coral.

Legend

Ni (ug/g)
- 0.55 - 0.68
- 0.69 - 0.78
- 0.79 - 1.08
- 1.09 - 1.48
- 1.49 - 2.29
- ☐ Sampling Strata

Nickel

Background: Nickel (Ni) is a metallic element that naturally occurs in the Earth's crust. Mining and use of nickel has increased the amount of nickel present in the environment.

Uses: Nickel is used in batteries, coins, metal plating and a variety of alloys (e.g. stainless steel).

Environmental effects: Nickel has been shown to have adverse effects on sea urchins (Novellini et al. 2003), crustaceans and fish (Hunt et al. 2002). Previous studies (e.g. Esselmont 2000; Whitall et al. 2014) have shown that nickel accumulates in coral tissues, and that water column concentrations of 9 mg/L cause mortality in Pocilopora damicornis larvae (Goh 1991). Reichelt-Brushett and Harrison (2005) showed that nickel had moderate effects on fertilization success in Goniastrea aspera.

Concentration in Tinian Corals: Coral concentrations of nickel in Tinian ranged from 0.55 µg/g to 2.29 µg/g, with a mean of 1.05 µg/g.

Spatial Patterns: There were no statistically significant differences between the strata (Dunn's test, **α**=0.05).

Discussion: Ni levels measured here were an order of magnitude higher than the maximum reported values for nickel in P. damicornis in Guam (Table 4; Denton et al. 1999). Like all metals, nickel has both natural and anthropogenic uses. While there are no clear sources of nickel on modern Tinian, historical land use, including military activities, may have contributed to the observed Ni levels. High nickel levels are of concern, especially given research showing the direct effect of nickel on coral health (Goh 1991). More research is needed to establish body burden threshold above which corals are adversely affected by Ni and other pollutants.
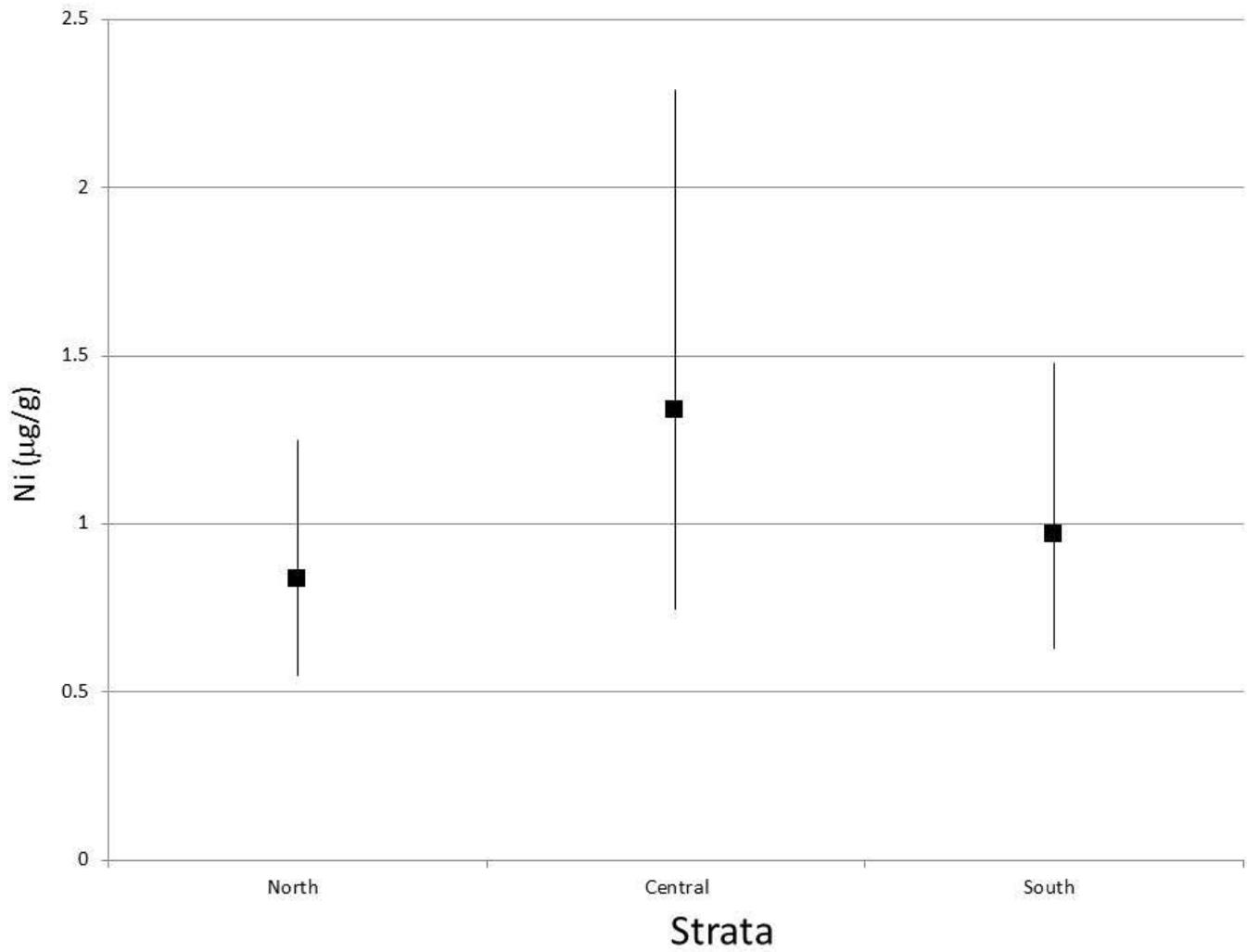
Figure 32: Coral nickel concentrations by strata. Squares are mean values; lines show maximum and minimum values. There were no statistically significant differences between the strata (Dunn's test, α=0.05)
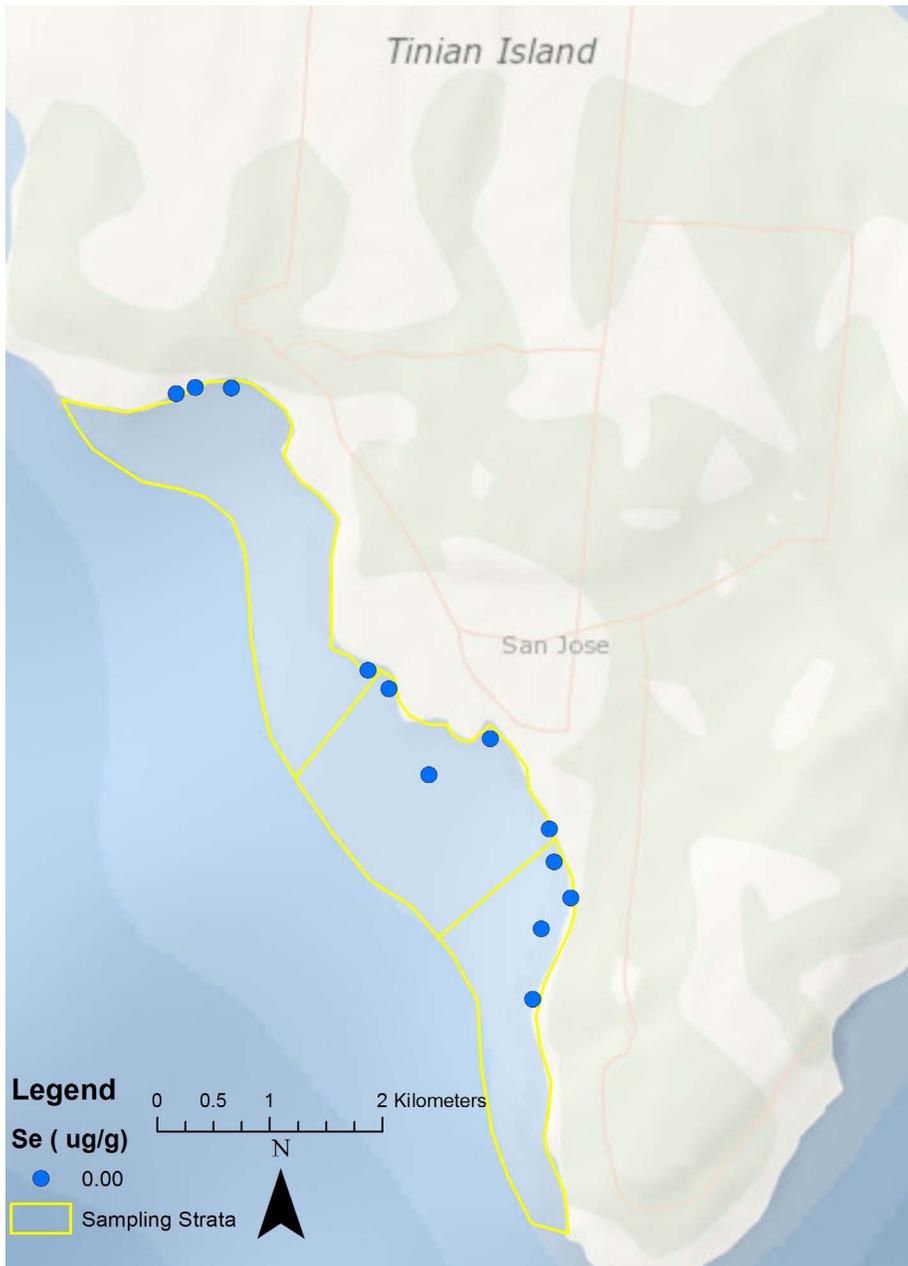
Figure 33. Selenium concentrations in coral.

Legend

Se (ug/g)

● 0.00

☐ Sampling Strata

0   0.5   1   2 Kilometers

N

Selenium

Background: Selenium (Se) is a trace element (semi-metal) that naturally occurs in the Earth's crust. Mining and use of selenium has increased the amount of selenium present in the environment.

Uses: Selenium has a range of uses including as an additive in glass production, as a fungicide and in photocells, solar cells, photocopiers and rectifiers (RCS 2014g).

Environmental effects: Selenium is a micronutrient for some organisms including humans. Selenium can bioaccumulate and has been shown to be toxic to both invertebrates and fish at elevated concentrations (EPA 2014). Selenium's effect on corals has not been well documented.

Concentration in Tinian Corals: Selenium was not detected in coral tissue samples in Tinian.

Discussion: Selenium has been detected in other coral species in other locations (Table 4;Pait et al. 2009; Whitall et al. 2010; Whitall et al. 2014; Apeti et al. 2014) but was not found in this study. This could be due to differences in species uptake (Porites astreoides vs P. damicornis) or a lack of anthropogenic selenium use in Tinian. The geologic makeup of the island may also play a role in the lack of observed Se in these samples.
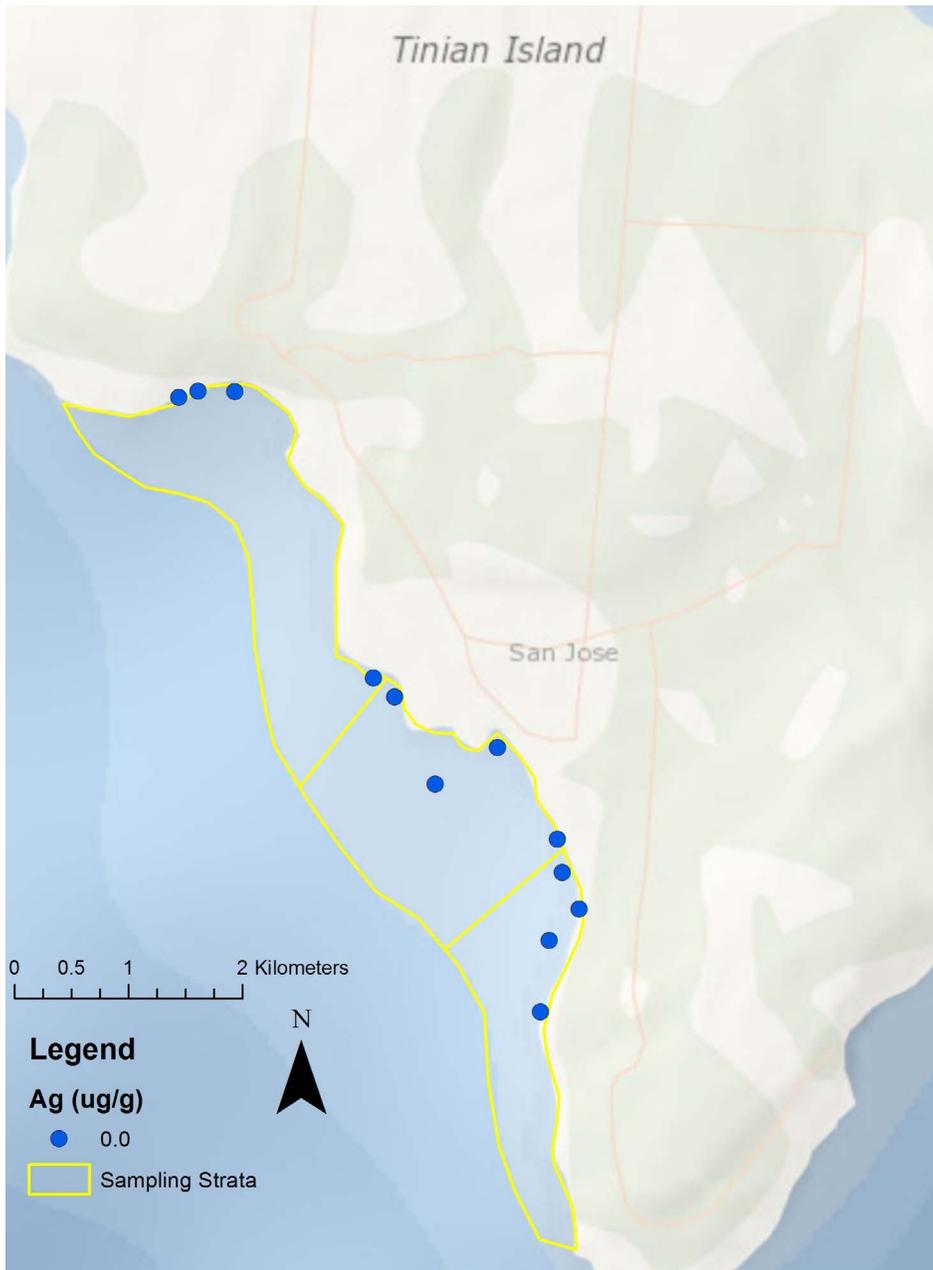
Figure 34: Silver concentrations in coral.

Silver

Background: Silver (Ag) is a metallic element that naturally occurs in the Earth's crust. Mining and use of silver has increased the amount of silver present in the environment.

Uses: Silver is widely used including in jewelry, dental alloys, solder and brazing alloys, electrical contacts, batteries, circuits, photography and nanoparticles (RSC 2016h).

Environmental effects: Silver is one of the more toxic elements to plants and animals in the marine environment (Bryan 1984) including toxicity to bivalves, fish and phytoplankton. Previous studies (e.g. Whitall et al. 2014) have reported relatively low levels of silver in coral tissues, which is consistent with the finding that silver was primarily accumulated in coral skeletons in *Stylophora pistillata* (Metian et al. 2014).

Concentration in Tinian Corals: Silver was not detected in coral tissue samples in Tinian.

Discussion: Silver has been detected in other coral species in other locations (Table 4; Pait et al. 2009; Whitall et al. 2014; Apeti et al. 2014) and in *P. damicornis* in Guam (Denton et al. 1999), but was not found in this study. This could be due to negligible anthropogenic sources of silver on Tinian or low levels of crustal silver in the geology of the island.

Figure 35: Tin concentrations in coral.

Tin

Background: Tin (Sn) is a pliable metallic element that naturally occurs in the Earth's crust. It can exist as either as an inorganic or organic compound. Mining and use of tin has increased the amount of tin present in the environment.

Uses: Tin is used in metal coatings to prevent corrosion (e.g. tin-coated steel), a variety of alloys, window glass, fire retardants and in anti-foulant boat paints (RSC 2016i).

Environmental effects: Tin has no known biological role and the elemental metal is generally non-toxic. However, organic forms, especially butyltins used in boat paints, can be very toxic to marine organisms (RSC 2016i). Because of this toxicity, butyltins have been banned for most uses. Tin has been show to accumulate in coral skeletons (Inoue 2004; Whitall et al. 2014).

Concentration in Tinian Corals: Coral concentrations of tin in Tinian ranged from below limits of detection to 16.3 µg/g, with a mean of 2.99 µg/g.

Spatial Patterns: There are no statistically significant (Dunn's test, α=0.05) differences between the strata for tin.

Discussion: Tin has been detected in other coral species in other locations (Table 4; Pait et al. 2009; Whitall et al. 2010; Whitall et al. 2014; Apeti et al. 2014), and in *P. damicornis* in Guam (Denton et al. 1999), although at lower concentrations than what was found here. This could be due to a larger source of tin on Tinian, or geologic differences among the study areas. Based on the military history of Tinian, a logical source of this tin could be tributyltin (TBT) which was used as an anti-fouling boat paint. TBT breaks down in the environment to elemental tin. However, neither TBT, nor its organic breakdown products (dibutyltin and mononutyltin), were detected in coral tissues in this study. It is possible that *P. damicornis* does not sequester butyltins. Further environmental sampling (e.g. sediments) could test the hypothesis that butyltins are present in the environment and responsible for the Sn levels in coral in the study. The spatial pattern (Figure 34) while not statistically significant, does not support the hypothesis that boat traffic (and associated TBT) have led to enhanced tin in the system. Alternatively, the source of tin could be related to the geology of the island (i.e. crustal erosion as a source).
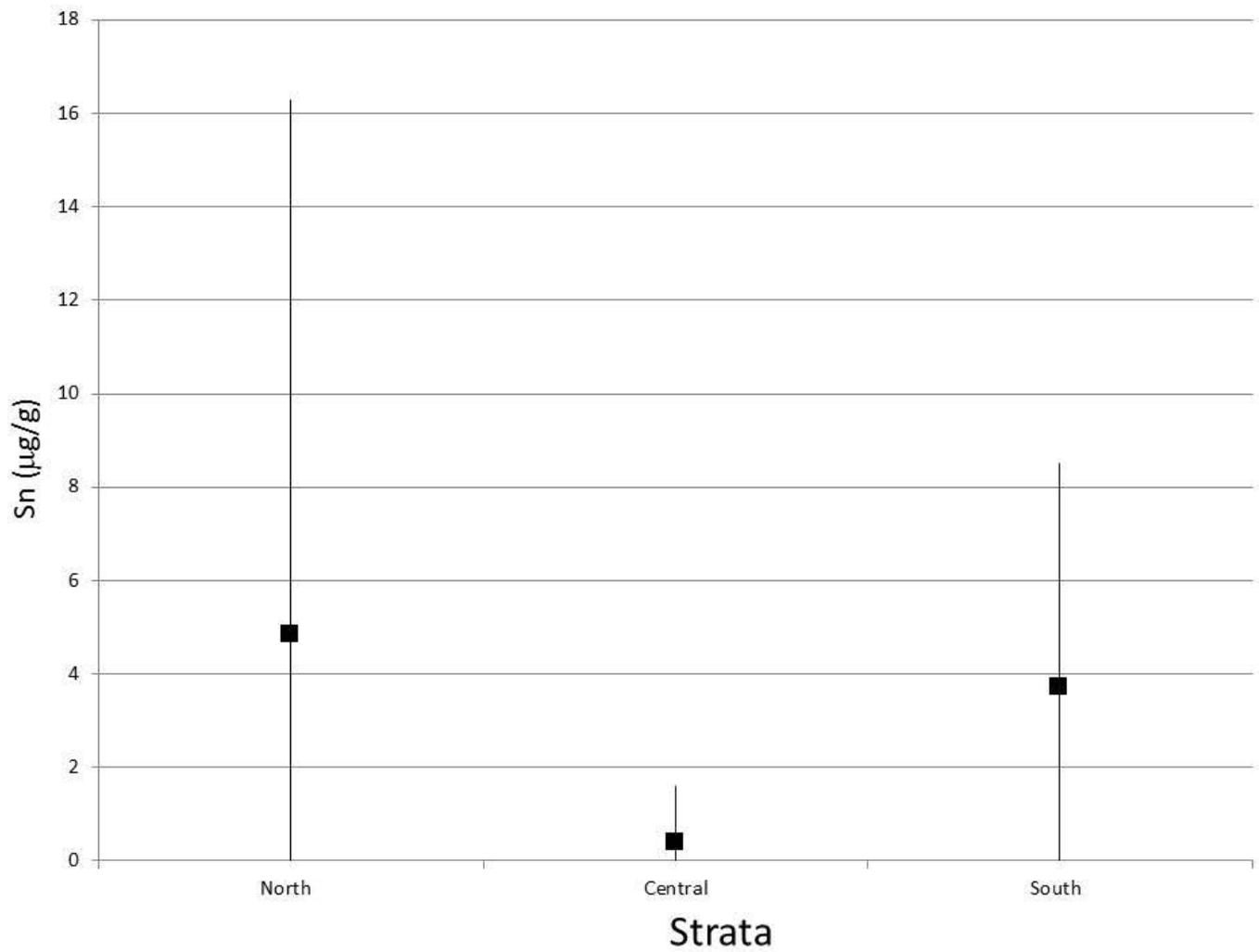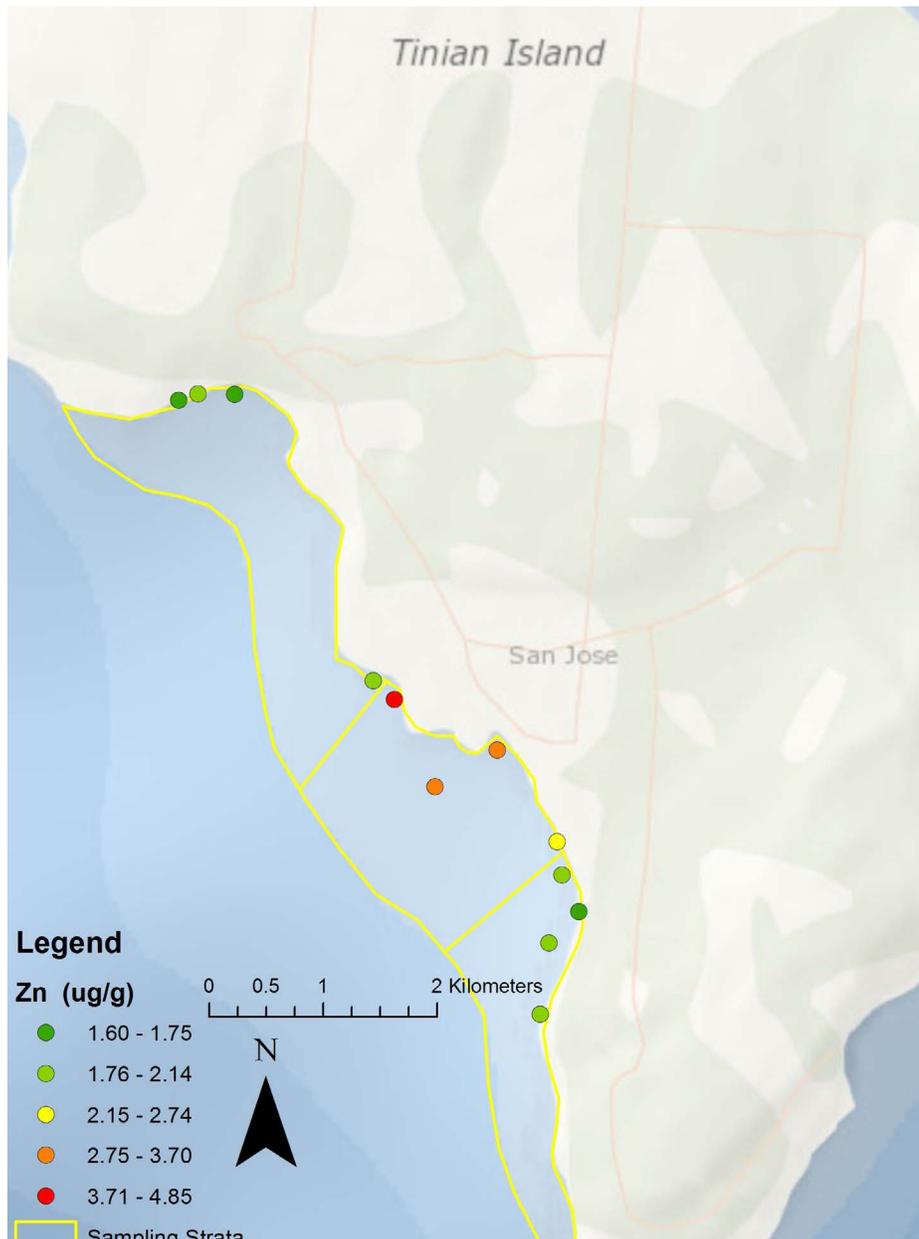
Figure 36: Coral tin concentrations by strata. Squares are mean values; lines show maximum and minimum values. There were no statistically significant differences (Dunn's test, α=0.05) between strata.

Figure 37: Zinc concentrations in coral.

Zinc

Background: Zinc (Zn) is a metallic element that naturally occurs in the Earth's crust. Mining and use of zinc has increased the amount of zinc present in the environment.

Uses: Zinc is used in brass, bronze, die castings metal, alloys, rubbers, paints, wood preservation, catalysts, corrosion control in drinking water systems, photographic paper, vulcanization acceleration for rubber (including automobile tires), ceramics, textiles, fertilizers, pigments, batteries, and as nutritional supplements or medicines (EPA 2005).

Environmental effects: Zinc is a micronutrient for both plants and animals, but can be toxic in excess. Zinc has been shown to be toxic to aquatic invertebrates, including sea urchins (Novellini et al. 2003; Dermeche et al. 2012; Edullantes and Galapate, 2014), and fish (Besser and Lieb, 2007), but relative less toxic to mammals and birds (US-DOI 1998). Zinc accumulates in coral tissues (Denton et al. 1999), primarily in the tissues of corals rather than the skeletons (Metian et al. 2014) and can cause reduction in fertilization success in scleractinian corals (Reichelt-Brushett and Harrison, 2005).

Concentration in Tinian Corals: Concentrations of zinc in corals in Tinian ranged from 1.6 µg/g to 4.85 µg/g, with a mean of 2.48 µg/g.

Spatial Patterns: Statistically, the central stratum had higher zinc concentrations than the north stratum (Dunn's test, **α**=0.05).

Discussion: Zn levels measured here were within the range of values reported elsewhere for Zn in P. damicornis tissue (Table 4; Denton et al. 1999). Like all metals, zinc has both natural and anthropogenic uses. While there are no clear sources of zinc on modern Tinian, historical land use, including military activities, may have contributed to the observed Zn levels. Potentially elevated zinc in the harbor area may be related to boat traffic, specifically emissions from fossil fuel combustion (Isakson et al., 2001). More research is needed to establish body burden threshold above which corals are adversely affected by Zn and other pollutants.
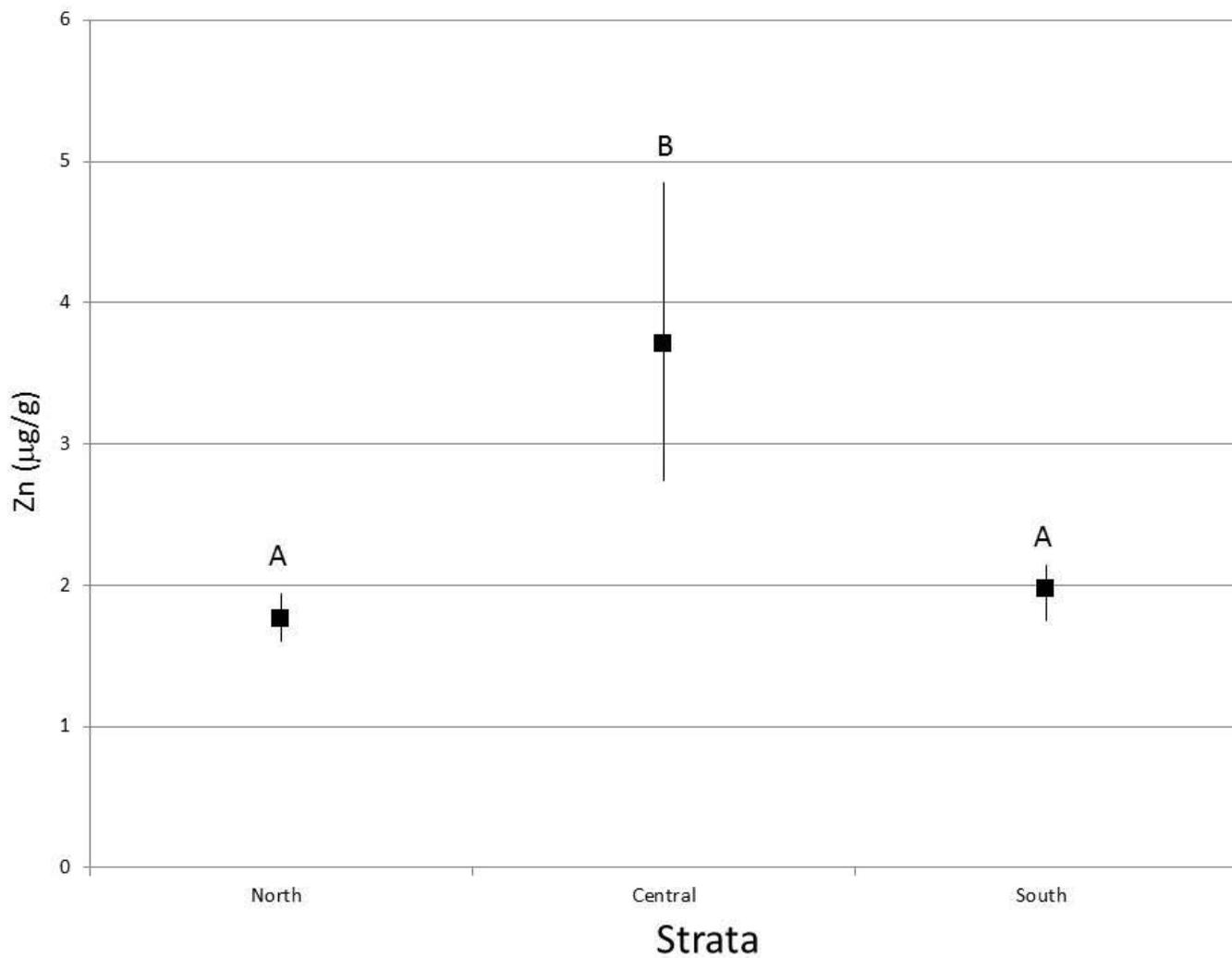
Figure 38: Coral zinc concentrations by strata. Squares are mean values; lines show maximum and minimum values. Letter show statistical differences between strata (Dunn's test, α=0.05).
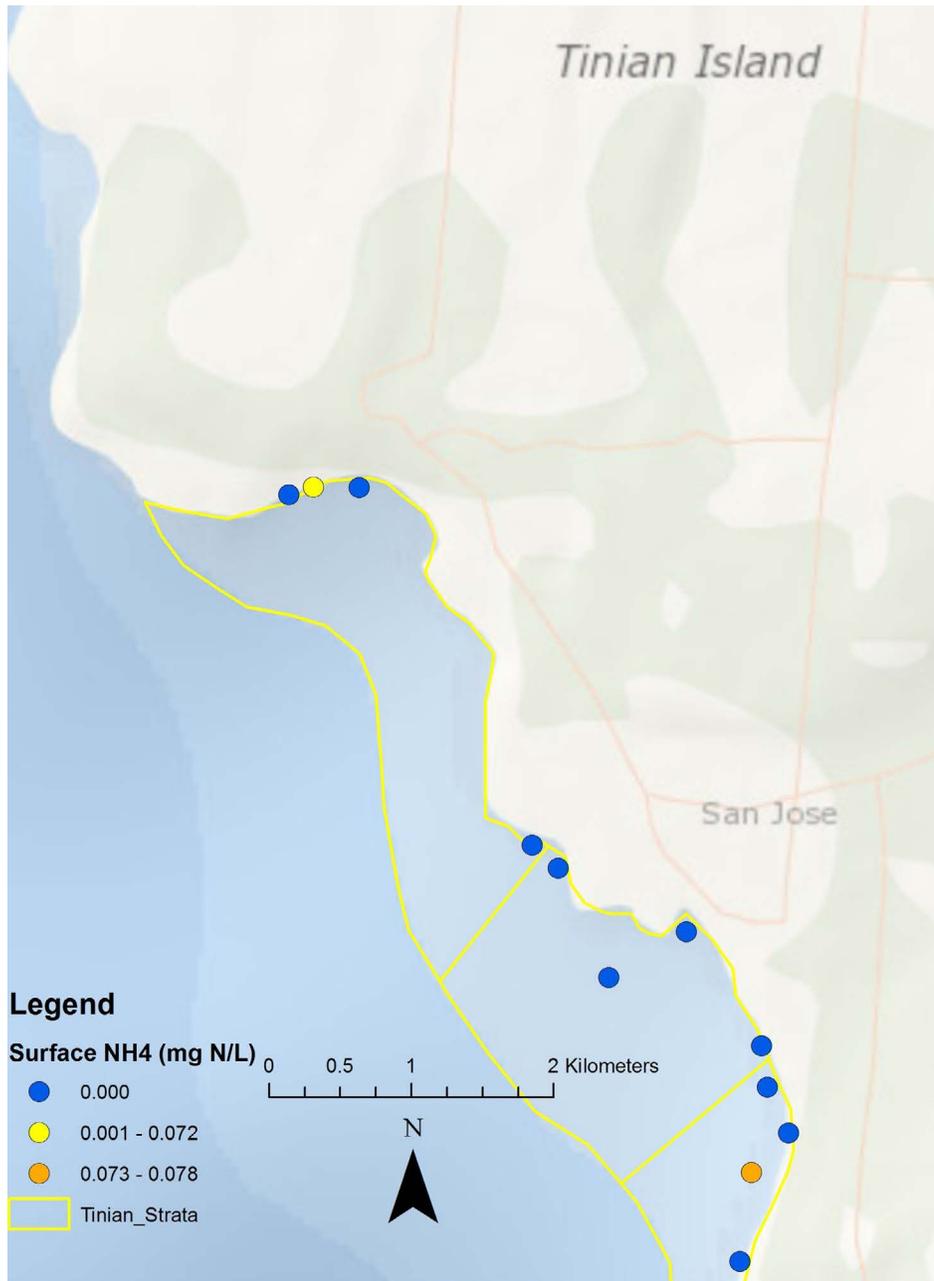
Figure 39: Surface water ammonium concentrations (mg N/L) August 2013.

Water Column Nutrients

Background: Nutrients, including both inorganic (nitrate, nitrite, ammonium, and orthophosphate) and organic forms (e.g. urea, amino acids), are both essential building blocks of plant and animal life, as well as byproducts (waste) of human and animal functions. Nutrients in the environment are both naturally occurring (i.e. from biogeochemical cycling), as well as from human activities.

Uses: Nutrients can enter the environment from a wide variety of anthropogenic sources (Whitall et al. 2012), including fertilizers, animal waste, human waste (from both septic systems and wastewater treatment plants), fossil fuel combustion, industry and mining (i.e. of phosphate).

Environmental effects: Too few nutrients in a marine environment can stifle primary productivity, but the excess of nutrients (eutrophication) can lead to a cascade of environmental effects including algal blooms, hypoxia and deleterious effects on corals (D'Angelo and Wiedenmann 2014). Nutrients can indirectly affect corals by causing increases in macroalgae which can outcompete and overgrow corals (McCook et al. 2001) or by reductions in water transparency (Hallock and Schlager, 1986). Corals can be directly impacted by elevated levels of nitrogen and phosphorus by lowering fertilization success (Harrison and Ward, 2001), and reducing both photosynthesis and calcification rates (Marubini and Davis, 1996).

Table 6: Surface water nutrient concentrations (mg N/L or mg P/L) August 2013.

Surface		Mean	Median	Min	Max	StDev
	NH4	0.012	0	0	0.078	0.027
	NO2/NO3	0.013	0	0	0.104	0.028
	PO4	0	0	0	0	0
	TN	0.052	0.037	0.029	0.160	0.035
	TP	0	0	0	0	0
Bottom						
	NH4	0.011	0	0	0.050	0.019
	NO2/NO3	0.004	0	0	0.038	0.012
	PO4	0	0	0	0	0
	TN	0.040	0.034	0.028	0.077	0.015
	TP	0	0	0	0	0

Concentrations of nutrients in Tinian: Concentrations of each analyte (minimum, maximum, mean, standard deviation) are shown in Table 6. Phosphorus was not detected in any samples.

Spatial Patterns: There were no statistically significant differences between the strata (Dunn's test, **α**=0.05), nor between surface and bottom samples. Qualitatively, there are a few sites that have higher nitrogen values than others, but there are no clear spatial patterns.

Discussion: Care should be taken in interpreting these data because there is only one time point. Nutrient concentrations are likely to change on the time scale of hours to days, and this "snapshot" of nutrient conditions provides only limited utility. A more robust event based nutrient monitoring program would be necessary to tease out spatiotemporal variability which may be useful to managers. However, with those caveats, several observations of these data can be made. The lack of phosphorus may reflect nutrient delivery mechanisms, as phosphorus tends to reach coastal waters primarily through runoff, and there are no major streams/rivers within the study areas. Conversely, the delivery mechanism for nitrate is more commonly groundwater. However, it is also possible that spatial differences in nutrient uptake or sequestration by primary producers may be influencing spatial patterns in nutrient concentrations. Although widely agreed upon threshold values for nutrients in coral reef ecosystems have not been established, several publications should be noted. De'ath and Fabricus (2008) proposed nutrient threshold values for the Great Barrier Reef, but only for particulate nutrients (i.e. particulate nitrogen and particulate phosphorus) which are not comparable with the data presented here. Lapointe (1997) proposed nutrient threshold values for dissolved constituents in Caribbean coral reef ecosystems (1 αM DIN and 0.1 αM soluble reactive phosphorus). Acknowledging that there may be regional and species differences in nutrient responses, values observed in this study exceed those thresholds for DIN. This suggests that more research is needed to better quantify temporal patterns in nutrient biogeochemistry and its potential effect on coral reef health.
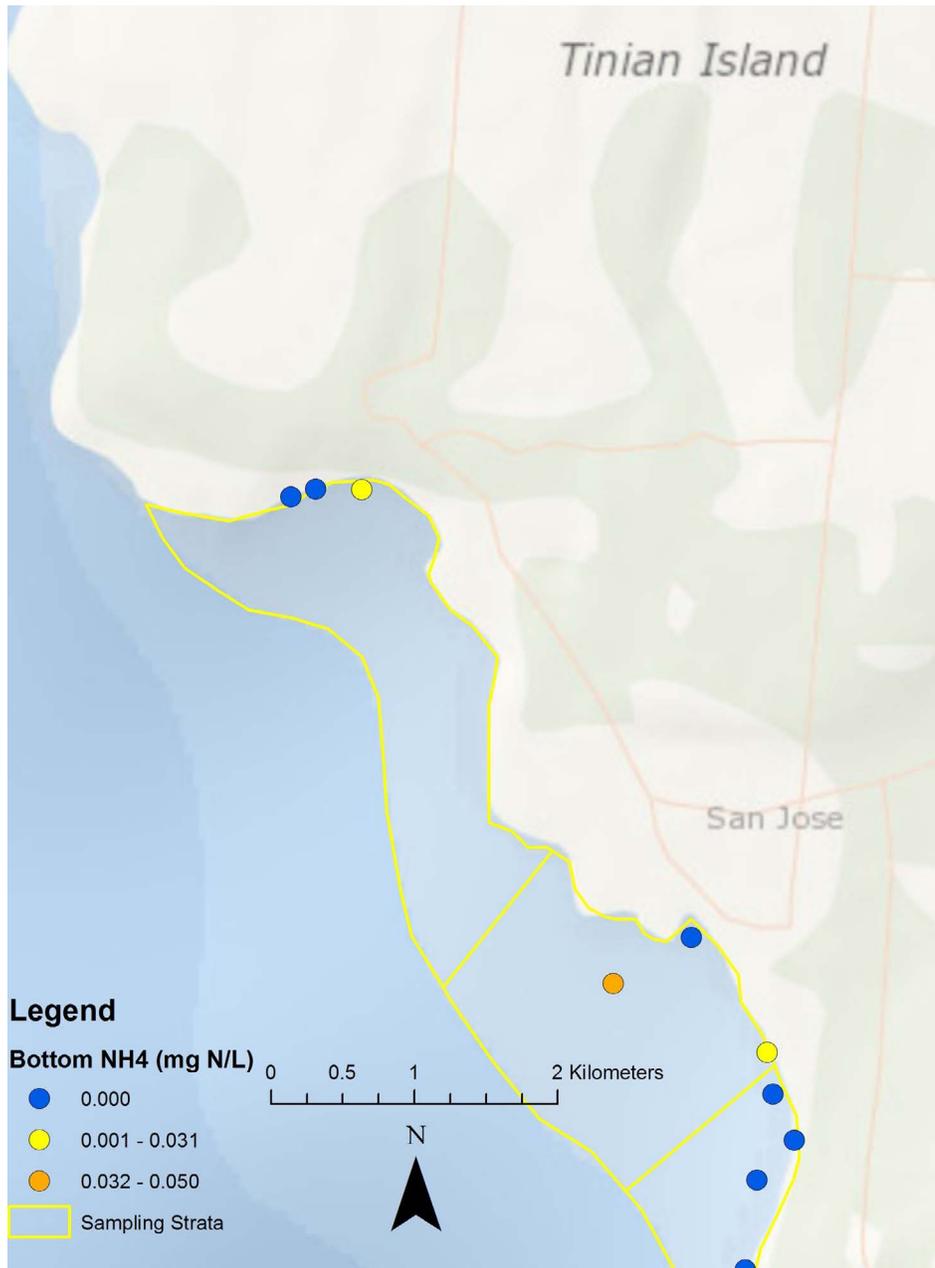
Figure 40: Bottom water ammonium concentrations (mg N/L) August 2013.

Legend

Bottom NH4 (mg N/L)
- 0.000
- 0.001 - 0.031
- 0.032 - 0.050
- Sampling Strata

0   0.5   1   2 Kilometers

N

Additional Analysis: Crustal Element Ratios

Another way to potentially examine the nature of the source of metals quantified in corals is to look at the relationship of crustal elements to each other. This has been applied previously to sediment metals analysis (see Apeti et al. 2012b). Applying this to corals should be approached cautiously, as potential differences in metal uptake rates could confound these relationships. For the purposes of this comparison, we have operationally defined Al, Mn and Si as "reference elements" because they are plentiful in the earth's crust and are generally not considered to be pollutants. By comparing these reference elements with other metals that are widely used by humans, patterns may emerge which can shed light on whether these metals exist in enriched (i.e. greater than natural) quantities, or if their presence is merely due to natural crustal erosion. In order to make this comparison, each metal was correlated with the reference elements using a Spearman rank correlation. "Well correlated" is operationally defined here as a statistically significant relationship with a rho value of greater than 0.7. If a metal is well correlated with one or more reference elements, it is more likely to have a natural (erosional) source. Not surprisingly, Al and Mn are well correlated. More interestingly, Cr is also well correlated with Mn. This may suggest that Cr is from natural sources.

Conclusions

This data set serves as an important baseline of coral contaminants against which to measure future change, which might result from coastal development, more military training activities and other land use alterations.

Pollution in the corals sampled in this study is generally lower than or comparable to other published data from U.S. jurisdictions. Exceptions to this pattern are tin, which is two orders of magnitude higher in Tinian than elsewhere, and PAHs, which is at the high end of what has been reported elsewhere. Both tin (as the ultimate breakdown product of TBT) and PAHs are associated with boating activities.
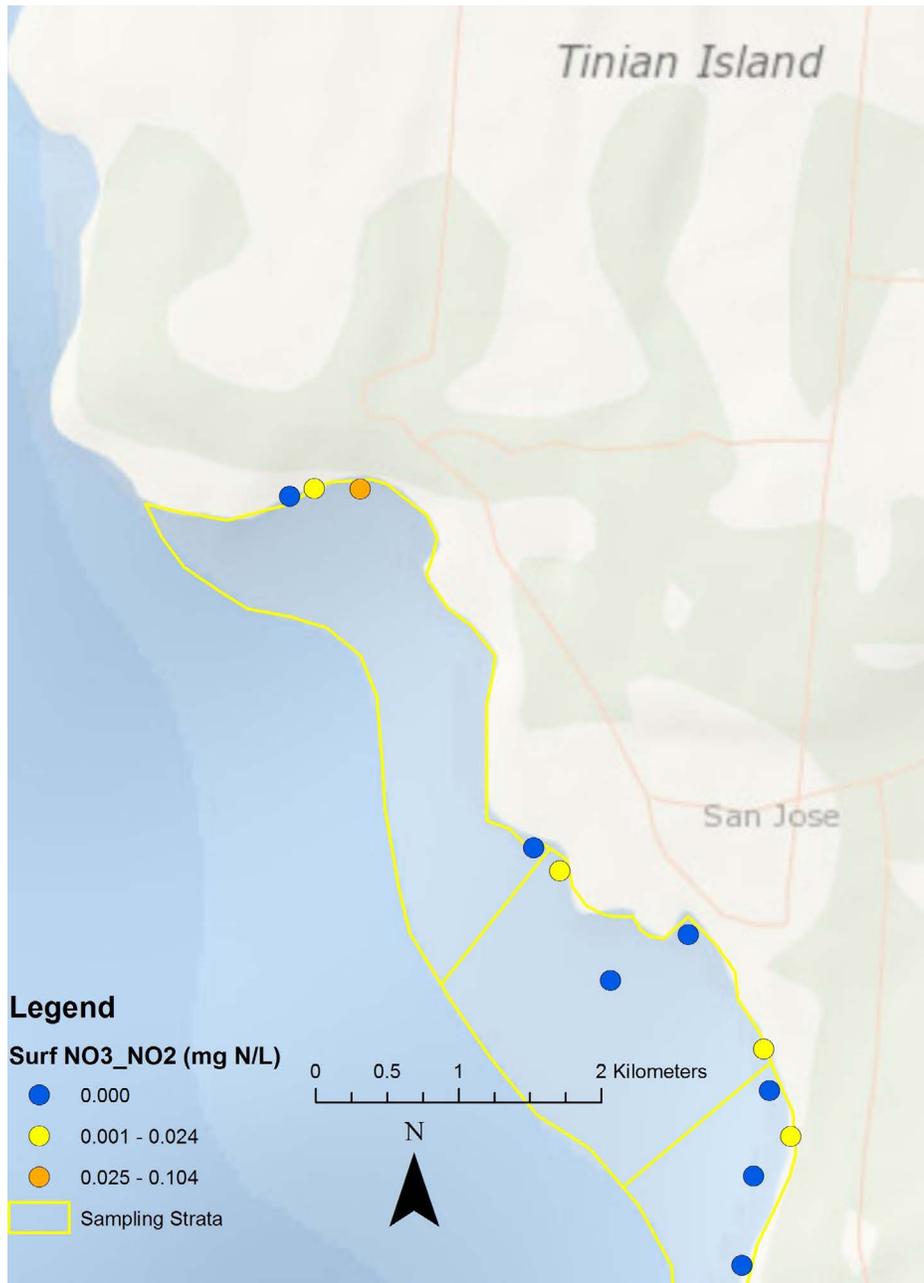
Figure 41: Surface water nitrate+nitrite concentrations (mg N/L) August 2013.

Table 7: Correlations (Spearman rho) for metal contaminants with crustal "non-pollutant" metals. Only relationships with strong (rho>0.7) relationships are shown.

Analyte	Analyte	Spearman rho	p value
Mn	Al	0.8682	0.0002
Mn	Cr	0.7875	0.0024

Possible future studies could explore the extent to which these contaminants are being taken up by other species, including those which may be harvested for human consumption such as octopus, sea cucumbers or fish. Additionally, future work could quantify the toxicity to benthic infauna through laboratory experiments. New techniques (e.g. transcriptomics) should be considered when making the functional link between stressor exposure and biological effect. The development of coral tissue body burden guidelines would be an impor-
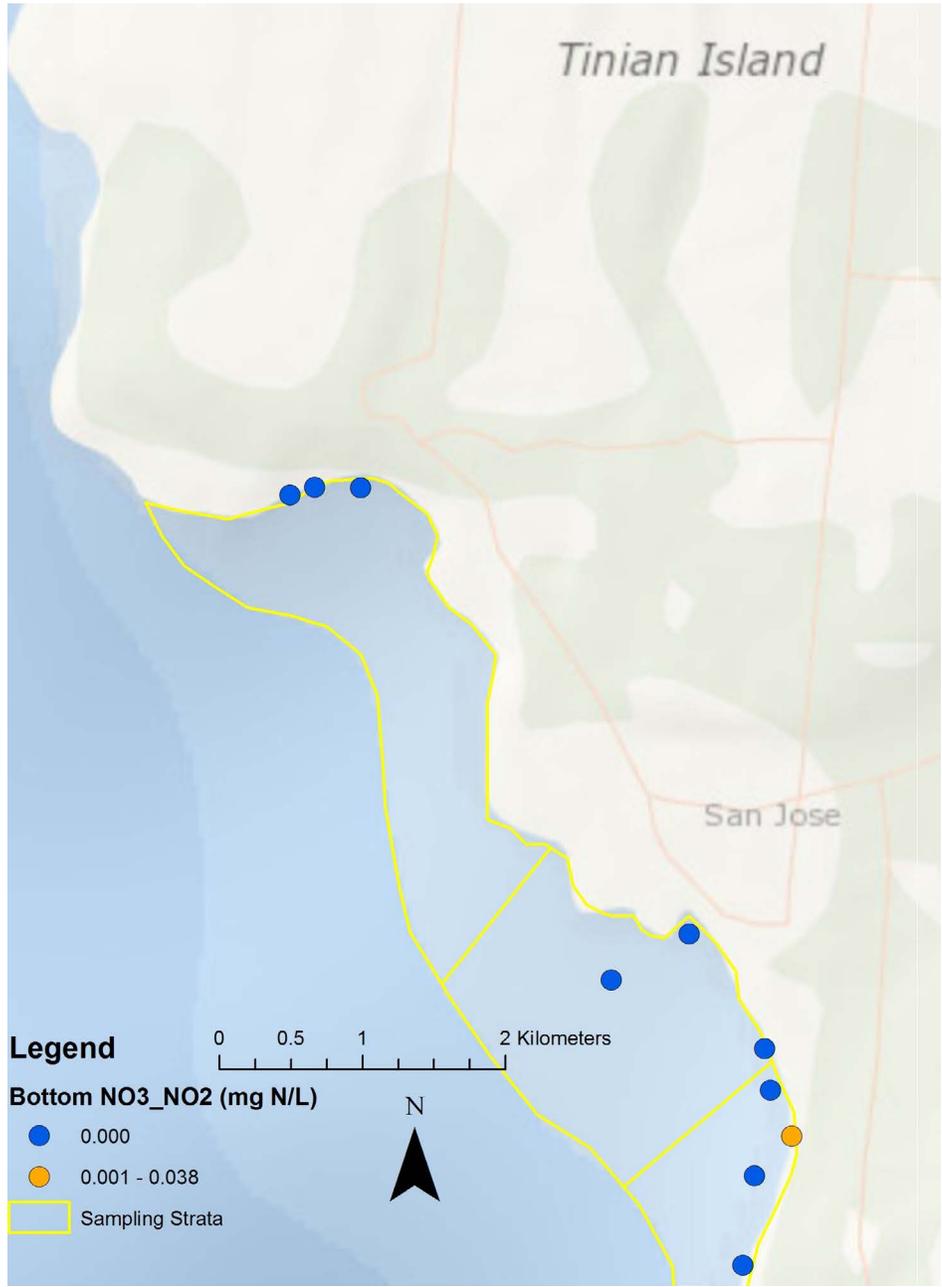
Figure 42: Bottom water nitrate+nitrite concentrations (mg N/L) August 2013.
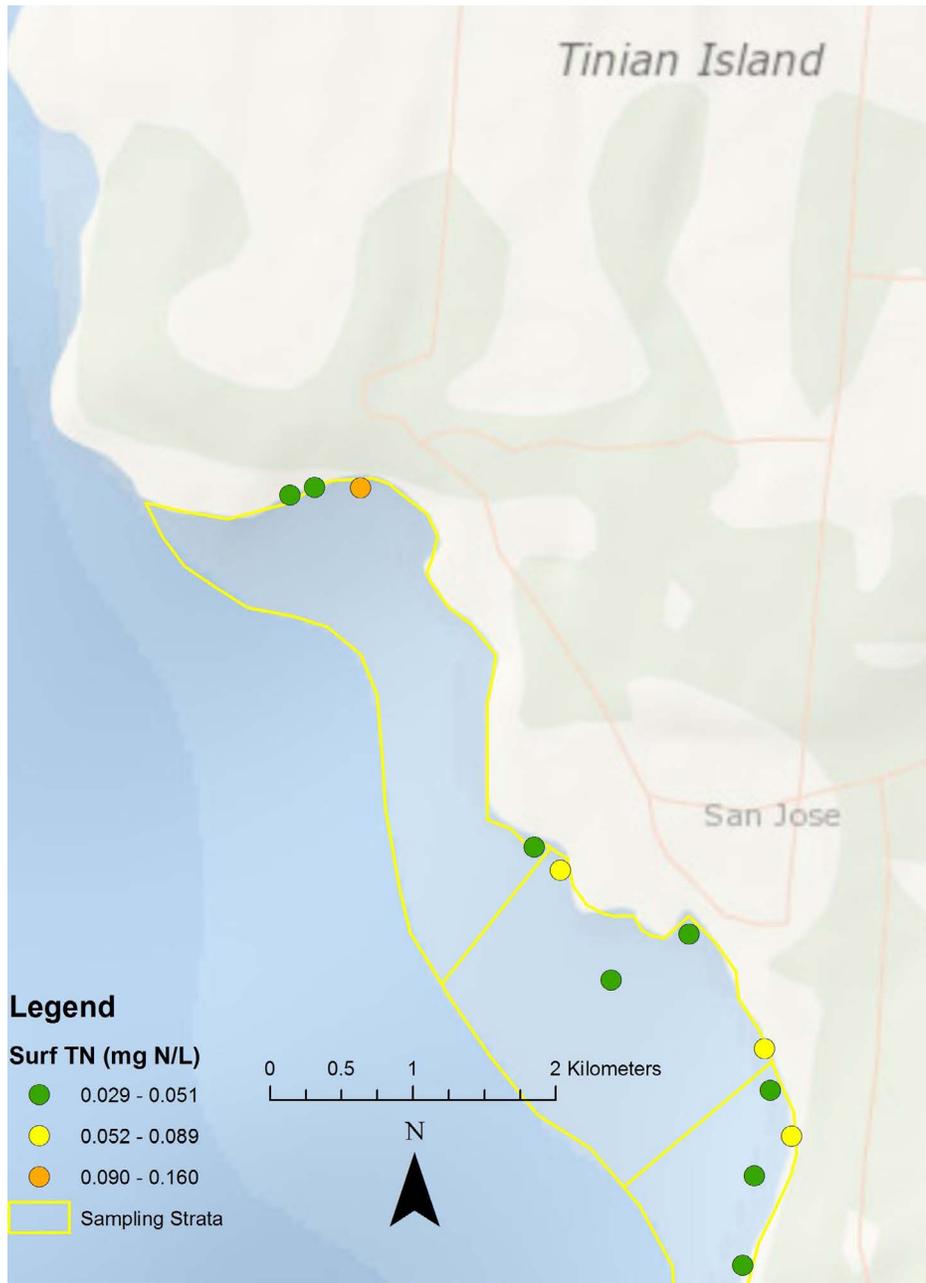
Figure 43: Surface water total nitrogen concentrations (mg N/L) August 2013.
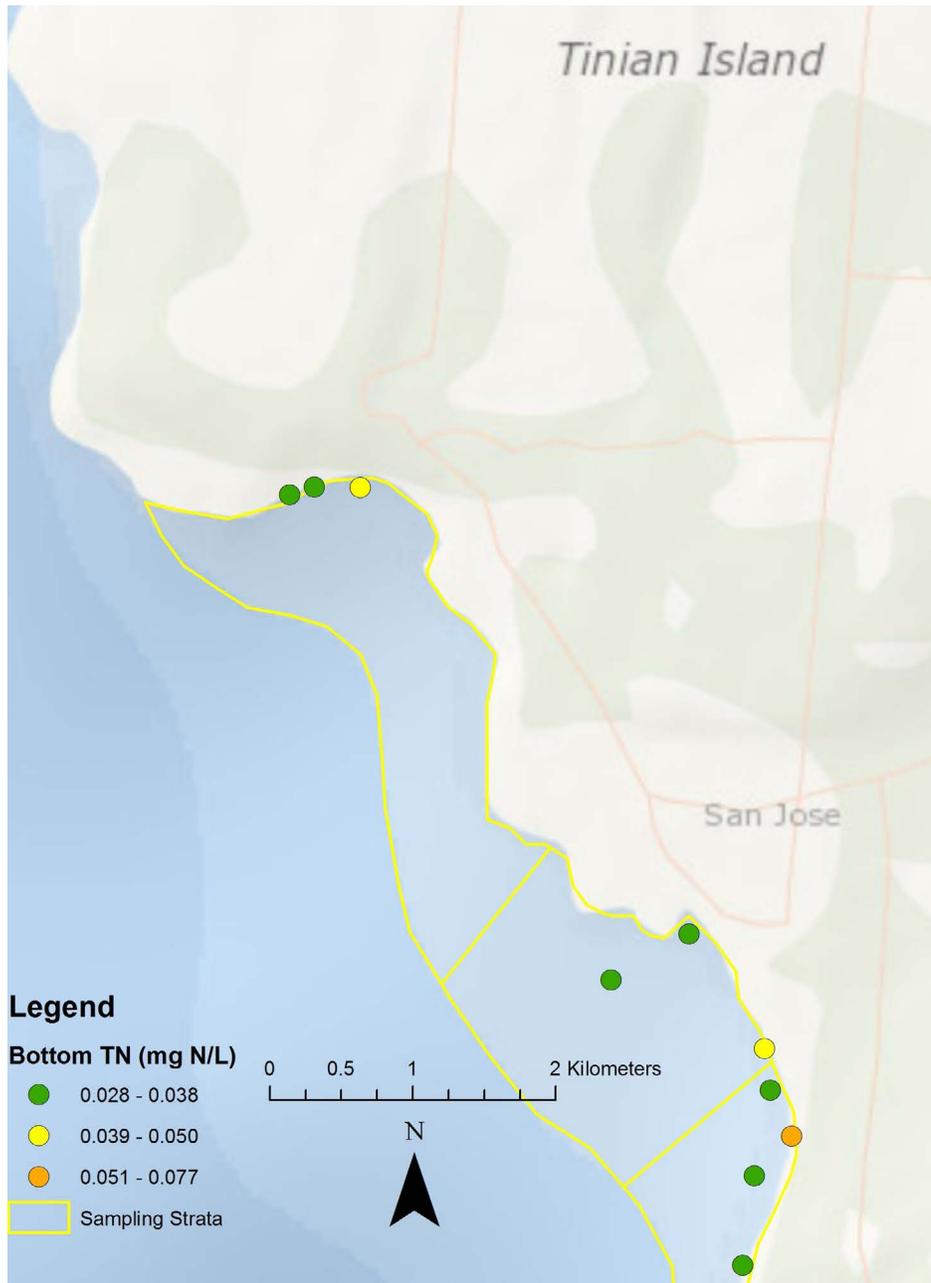
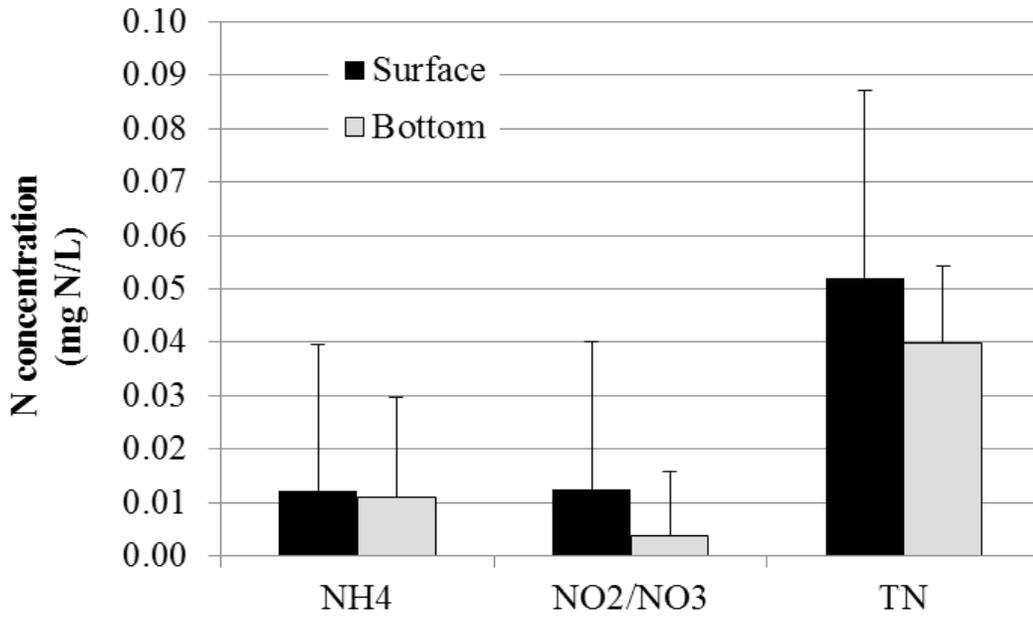**Figure 44: Bottom water total nitrogen concentrations (mg N/L) August 2013.**

Figure 45: Mean nitrogen concentrations (mg N/L) August 2013. Error bars are one standard deviation.

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