Comparison of Trace Metals in Coastal Sediments Located Near Urban and Protected Areas.

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Introduction

St. Augustine is the oldest city in the United States, with a long history of anthropogenic impact on the surrounding waterways. Heavy Metals in Sediments have attracted global attention in many studies due to the potential biological and health risk they pose. In this study, we examined the trace metals Lead, Nickel, Chromium, Copper, and Zinc. Heavy metals are often the focus of many studies due to the health issues they can cause at high concentrations (Lin et al., 2013). Here, we employed X-Ray fluorescence to compare the concentrations of these metals in sediment near both developed areas including downtown St. Augustine and surrounding suburbs as well as protected areas with limited development, using X-Ray fluorescence. We then compared our findings to the sediment quality guidelines used for marine sediment by the National Oceanic and Atmospheric Administration (NOAA). With the major industries in St. Augustine being based on tourism and boating, we expected the main sources of trace metals to be runoff from roads and residential housing and from the anti-spoiling paint used on boats. Once in the waterway, metals will attach to particles in the water and eventually settle on the bottom (Abrahim & Parker, 2008). Over time, these metals will accumulate, leading to higher concentrations of metal in the sediment.

We compared our results to sediment quality guidelines (SQGs) used by the National Oceanographic and Atmospheric Administration (NOAA), including the threshold effect level (TEL), effects range low (ERL), probably effect level (PEL) and effects range medium (ERM) (Long et al., 1995; Long et al., 1998). The TEL is the concentration below which adverse effects are not expected. The ERL is the 10^{th} percentile of concentrations where biological effects are expected to occur. The PEL is the minimal concentration at which adverse effects are expected to occur. The ERM is the 50^{th} percentile concentration where biological effects are expected occur. We hypothesized that the urban section of our study area will have higher concentrations of trace metals than the undeveloped section due to the increased runoff from the more highly concentrated human population.

Methods

Sampling Site Selection:

In this study we sampled from 140 sites within the Guana, Tolomato, and Matanzas Rivers and its saltmarshes and tidal creeks from north of St. Augustine, Florida to the urban border of Palm Coast Florida. We selected our sampling sites by outlining the research area and cutting it into two sections. The urban section is adjacent to the more developed area of St. Augustine, and the undeveloped section is adjacent to the protected areas of the Matanzas State Forest and Pellicer Creek Corridor Conservation Area. These areas were selected to enable a comparison of the levels of trace metals in sediments adjacent to developed areas against sediments located next to protected areas. Once the research area was outlined and divided, we ran a random point generator to randomly select 100 points in both the urban and undeveloped sections. We supplemented these sites by sampling at points where there were larger gaps between sites. The outline of the research area and the sampling sites can be seen in figure 1.

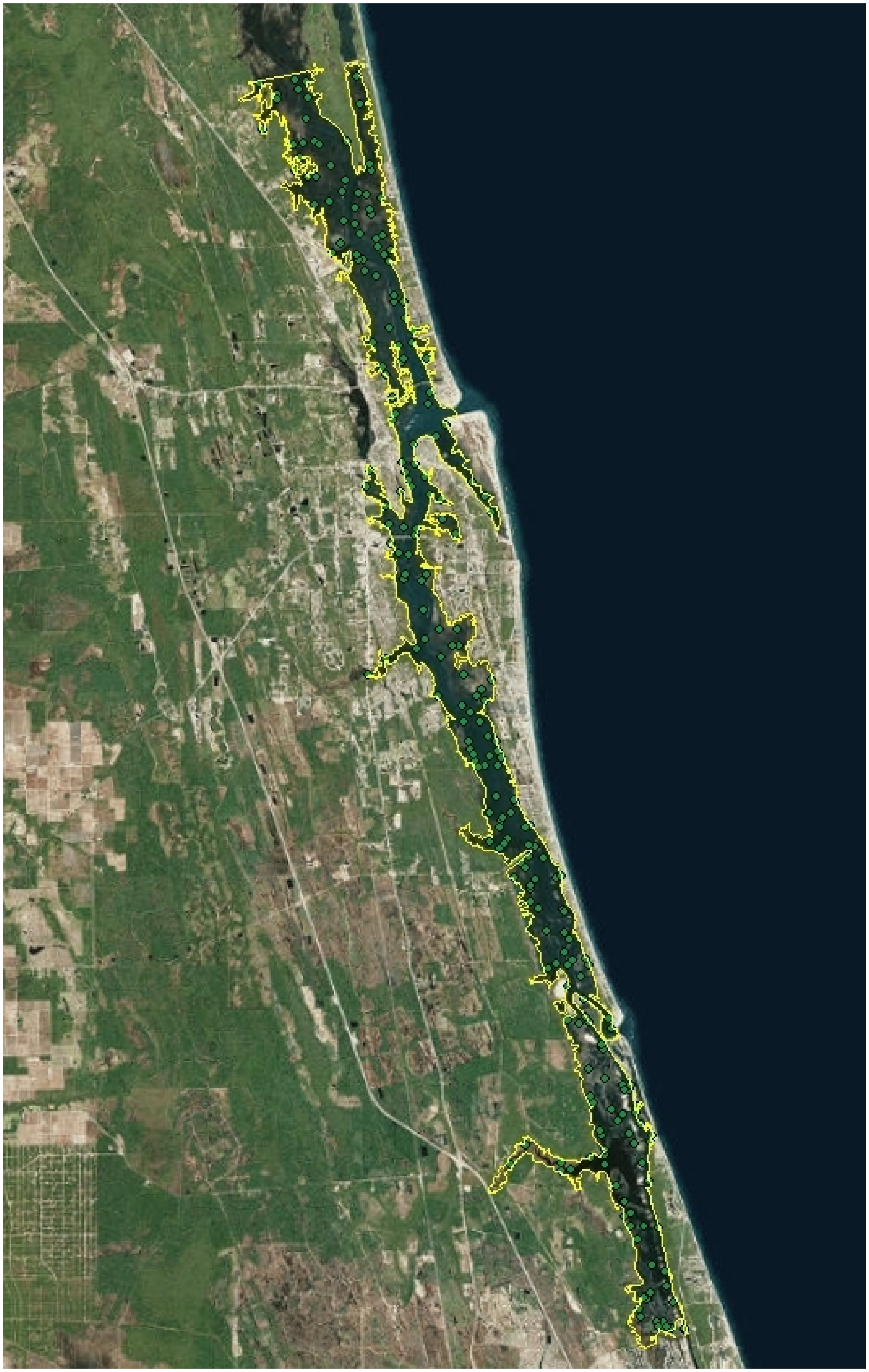

Figure 1 Shows an outline of the study area, and marks all of the sampling locations.

Sample collection and processing:

Samples were collected by using a push core and, for cores too deep to reach by hand, a piston core. The top 10 cm of each core was stored it in a polyethylene bag. Once collected samples were weighed, then a subsample was dried to calculate bulk density. After calculating bulk density, the dried subsamples were ground using a ball mill. All samples were subjected to X-Ray fluorescence to calculate the concentrations of the trace metals (Shackley, 2011). Four standards of known concentrations were run four times each to create and validate our calibration curve, with the y intercept indicating the limit of detection (LOD). The LOD is the lowest concentration that can be reliably reported with the calibration curve we calculated. This curve was used to calculate the concentration of the trace metals in our samples based on their intensity. One unknown sample was run 8 times to calculate our error rate.

Data Analysis:

The degree of contamination (mC_d) was calculated using the equation created by (Abrahim & Parker, 2008), which is a modified version of the equation used in (Tomlinson et al, 1980), namely it is the sum of the C_f divided by the number of elements, where C_f is the contamination factor, calculated by dividing the concentration of the contaminant by the background concentration (Tomlinson et al, 1980) . The contamination factor was calculated using the minimum detection limit for elements below the detection limit. The degree of contamination indicates how contaminated each sample is compared to the natural value for the samples as a whole. The risk index (RI) was calculated by calculating the sum of the contamination factor divided by the toxicity response coefficient of each element (Cr = 2, Zn = 1, Pb, Ni, and Cu = 5).

The risk index helps determine how the combined impact of the contaminants may be a risk to the environment for each sample (Duodu et al., 2016). Once all the calculations were finished we used inverse distance weighting in GIS software to create a spatial gradient of all the metals tested for and the mC_d. When running the interpolation, we set all samples under the LOD at 0.

Table 1

$mC_d < 1.5$	Very low degree of contamination	RI < 110	Low Risk
$1.5 \le mC_d < 2$	Low degree of contamination	110 ≤ RI ≤ 200	Moderate Risk
$2 \le mC_d < 4$	Moderate degree of contamination	200 ≤ RI ≤ 400	Considerable Risk
$4 \le mC_d < 8$	High degree of contamination	RI ≥ 400	Severe Risk
$8 \le mC_d < 16$	Very high degree of contamination		
$16 \le mC_d < 32$	Extremely High degree of contamination		
$mC_d \ge 32$	Ultra-high degree of contamination		

Results and Discussion

For every element tested the sediments adjacent to the urban areas had the sample with the highest concentration. The urban area also had a higher percentage of samples that were above the LOD for all metals tested except for copper. Based on the results, we concluded that the urban area had higher average concentrations of every metal tested for, and also a higher percentage of samples over the ERL. However, our results also revealed that only one sample collected and only one element in this sample was over the effects range median (ERM) and probable effects level (PEL). We conclude that, even though there are more trace metals in the urban section, the overall contamination levels do not indicate a significant biological impact as a result of the contaminants tested for. After calculating the degree of contamination only one sample had over a low degree of contamination. The undeveloped section was found to have 96.64% of samples with a very low degree of contamination and 3.36% with a low degree of contamination. The urban section yielded 75.63% of samples with a very low degree of contamination, 23.53% with a low degree of contamination, and 0.84% with a high degree of contamination. Figure 2 is a map of the spatial gradient of the distribution of

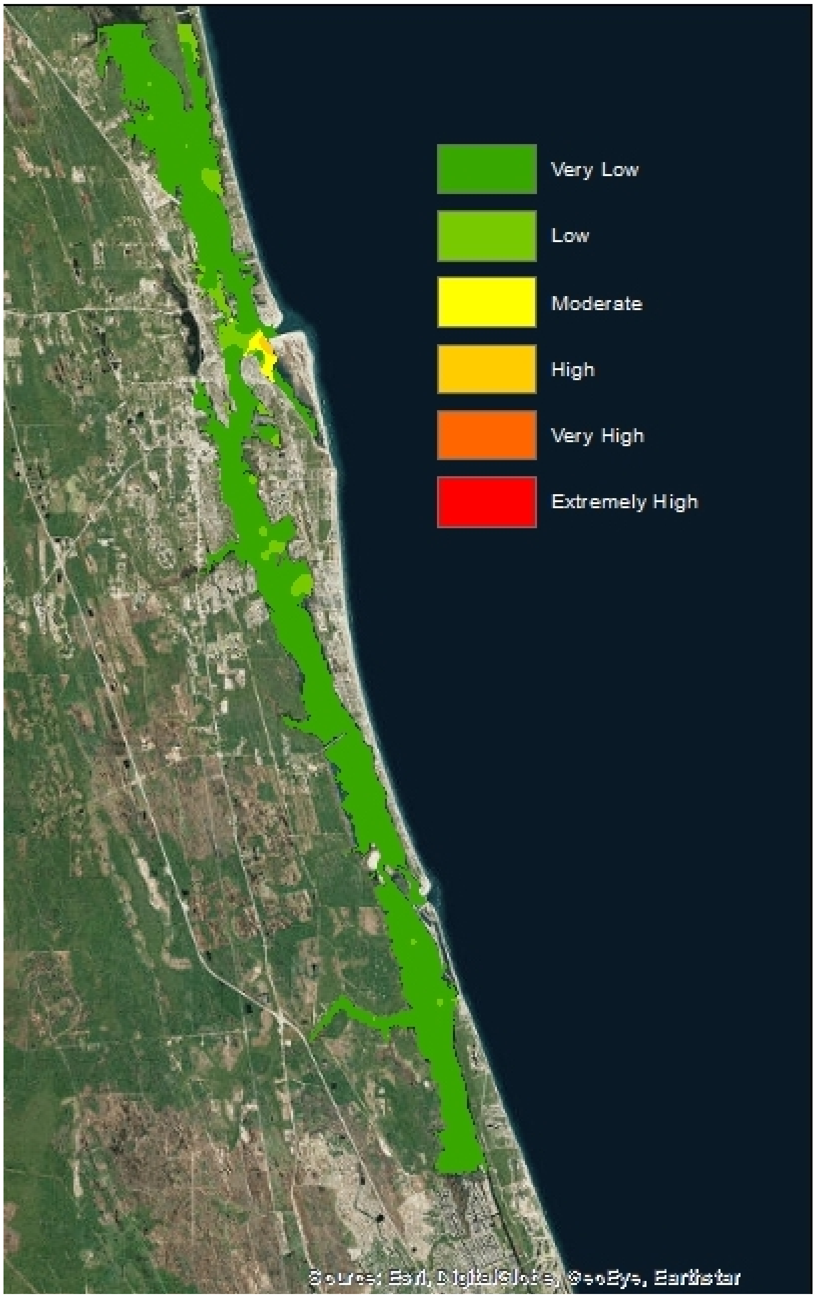

Figure 2 show a spatial distribution of the degree of contamination

contaminant levels. Most of the study area is illustrated as having a very low degree of contamination. As expected, areas with the highest degree of contamination were near the highest density of development. These results demonstrate that, while the urban areas do have a higher degree of contamination most of the study area had low concentrations of the tested elements. The Risk index for all but one sample was low risk. However, the one sample that was above low was a severe risk, most likely due to an extremely high level of nickel in this sample.

Table 2

Metal	LOD	Undeveloped Max	Undeveloped Min	Urban Max	Urban Min	Undeveloped % over LOD	Urban % over LOD
Chromium, Cr	6.36	67.53 +/- 7.91	LOD	68.86 +/- 7.91	LOD	70.25	78.99
Copper, Cu	21.35	44.83 +/-4.50	LOD	61.46 +/- 4.50	LOD	90.08	94.12
Lead, Pb	5.79	22.76 +/- 5.36	LOD	66.15 +/- 5.36	LOD	64.46	71.43
Nickel, Ni	4.11	23.76 +/- 2.76	LOD	1292.26 +/- 2.76	LOD	58.68	64.71
Zinc, Zn	33.58	98.28 +/-4.22	LOD	89.05 +/- 4.22	LOD	54.55	59.66

Table 3

Metal	Chromium, Cr	Copper, Cu	Lead, Pb	Nickel, Ni	Zinc, Zn
TEL (ppm)[b]	52.3	18.70	30.24	15.9	124
ERL (ppm)[a]	81	34	46.7	20.9	150
PEL (ppm)[b]	160.	108.20	112.18	42.80	271
ERM (ppm)[a]	370	270	218	51.6	410
Undeveloped % over TEL[c]	11.76	100	0	38.03	0
Urban % over TEL[c]	20.21	100	2.35	62.34	0
Undeveloped % over ERL[c]	0	4.59	0	7.04	0
Urban % over ERL[c]	0	10.71	1.18	17.39	0
Undeveloped Average (ppm)[c]	37.42	26.66	16.45	10.37	53.05
Urban Average (ppm)[c]	40.81	28.92	19.43	16.13	63.10

a) Effects Range Low (ERL); Effects Range Medium (ERM) SQGs used to measure sediment toxicity (Long et al., 1995)
b) Threshold Effect Level TEL; Probably Effect Level (PEL) SQGs used to measure sediment toxicity (Long et al., 1998)
c) These values are calculated without samples under LOD.

Chromium:

Chromium is an essential nutrient for humans, but in large concentrations it can be toxic. In this study no sample was found to have a concentration over the ERL. The urban section had a higher percentage of samples over the TEL at 20.21% compared to the undeveloped section at 11.76%. The urban section also had a higher average concentration at 40.81 ppm compared to 37.42 ppm for undeveloped section, and a higher percentage of samples over the LOD. Neither section had any sample over the ERL, thus we would expect that only the most sensitive species to be affected by these levels of chromium. In Figure 3, areas over the TEL for chromium are shaded in red. There are some smaller red areas in the undeveloped section that are above the TEL, but most are

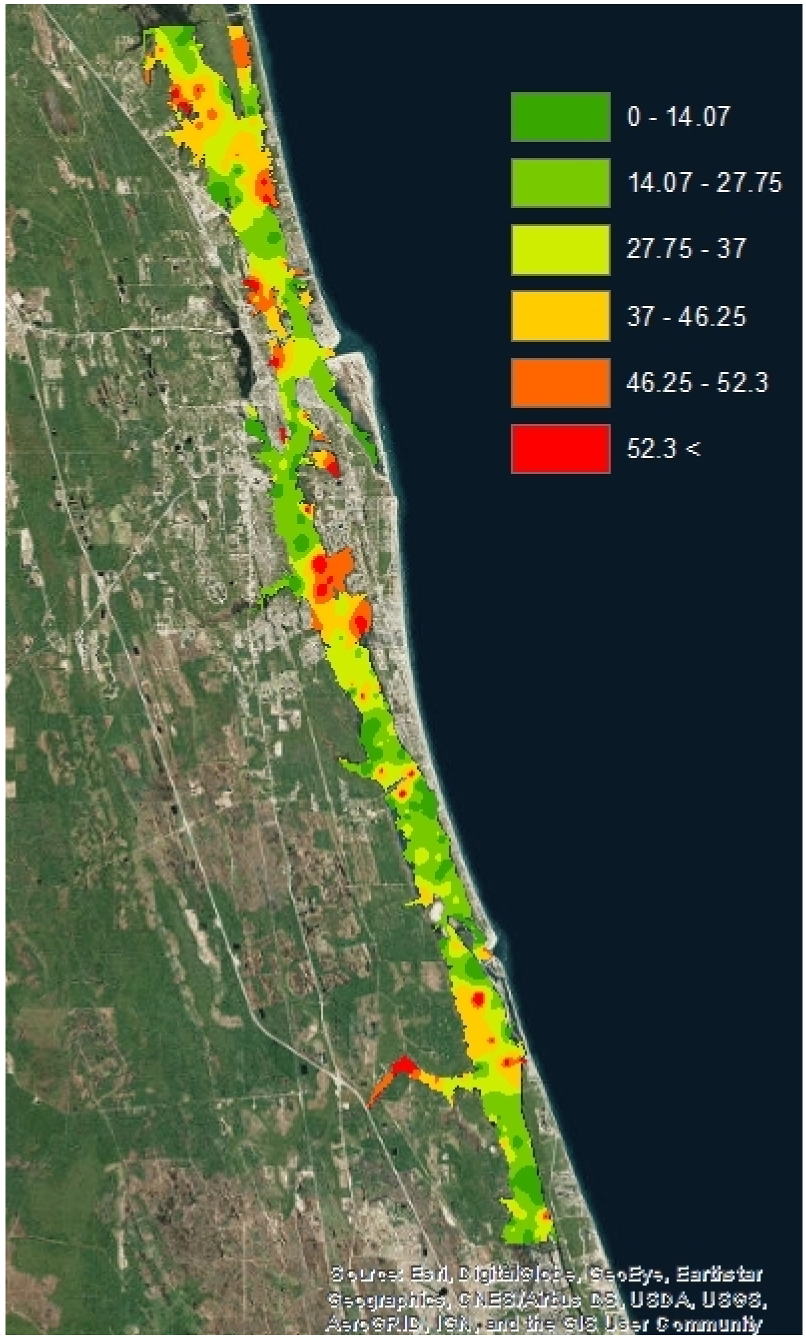

Figure 3 Shows the spatial distribution of chromium in the study area

located near more developed areas. The main sources of chromium pollution are paint, metal coating and leather industries (Lin et al., 2013), which are not prominent in this area. Thus, it is not surprising that the chromium levels are low. The area surrounding the study area did not have much industry areas other than the boat yards.

<u>Copper:</u>

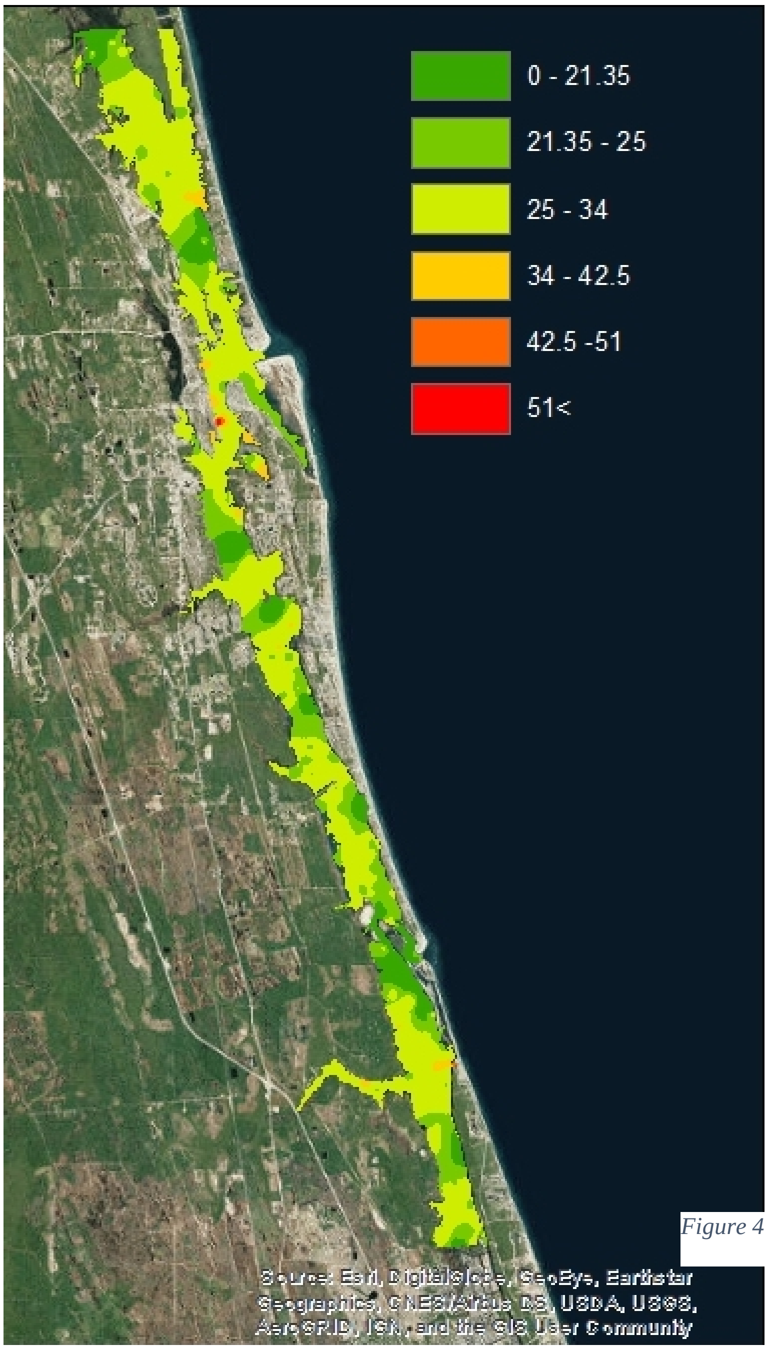

Figure 4 Shows the spatial distribution of copper in the study area

Copper is another essential element that is toxic in high concentrations. Exposure to high levels of copper can lead to interference with cell processes such as cell division as well as damage the liver and kidneys. (Lin et al., 2013). For both sections, over 90% of samples were over the detection limit, and of the samples over the detection limit, all were over the TEL. This shows that sensitive organism has a high chance of being negatively affected by copper throughout section for copper also had the higher average (28.92 ppm), as well as the higher percent over the ERL (10.71%). The protected area had lower concentrations with their average being 26.66 ppm and their percent over ERL only 4.13%. The source of this contamination is most likely due to anti-spoiling marine paint, building materials, and pesticides (Yuchao & Trefry, 2014, Mulligan et al., 2001). As shown in Figure 4 there were a few pockets of areas over the ERL primarily in the urban sections of the study area, with the highest concentrations being located closest to most densely populated areas. In the undeveloped area the largest section shaded as over the ERL is located at a marina, indicating that the most likely source of this copper is the antifouling paint from the boats stored in the marina.

Lead:

Lead can be released into the environment from waste, pesticides, and automobiles (Mulligan et al., 2001). Although lead had the third highest percentage over the LOD for the metals tested, no samples collected from the undeveloped section were above the TEL for lead, and the urban section only had 2.35% over the TEL and 1.18% over the ERL. While lead was present in a concentration high enough to be detected in most samples, the amount of lead present was not at an alarming level. The concentrations were higher in the urban section most likely due to runoff from roadways. As shown in Figure 5, only a few locations exhibited concentrations over 24 ppm and one small area had levels over 32 ppm. This indicates that while the levels of lead are not high, the concentrations are highest near the developed areas.

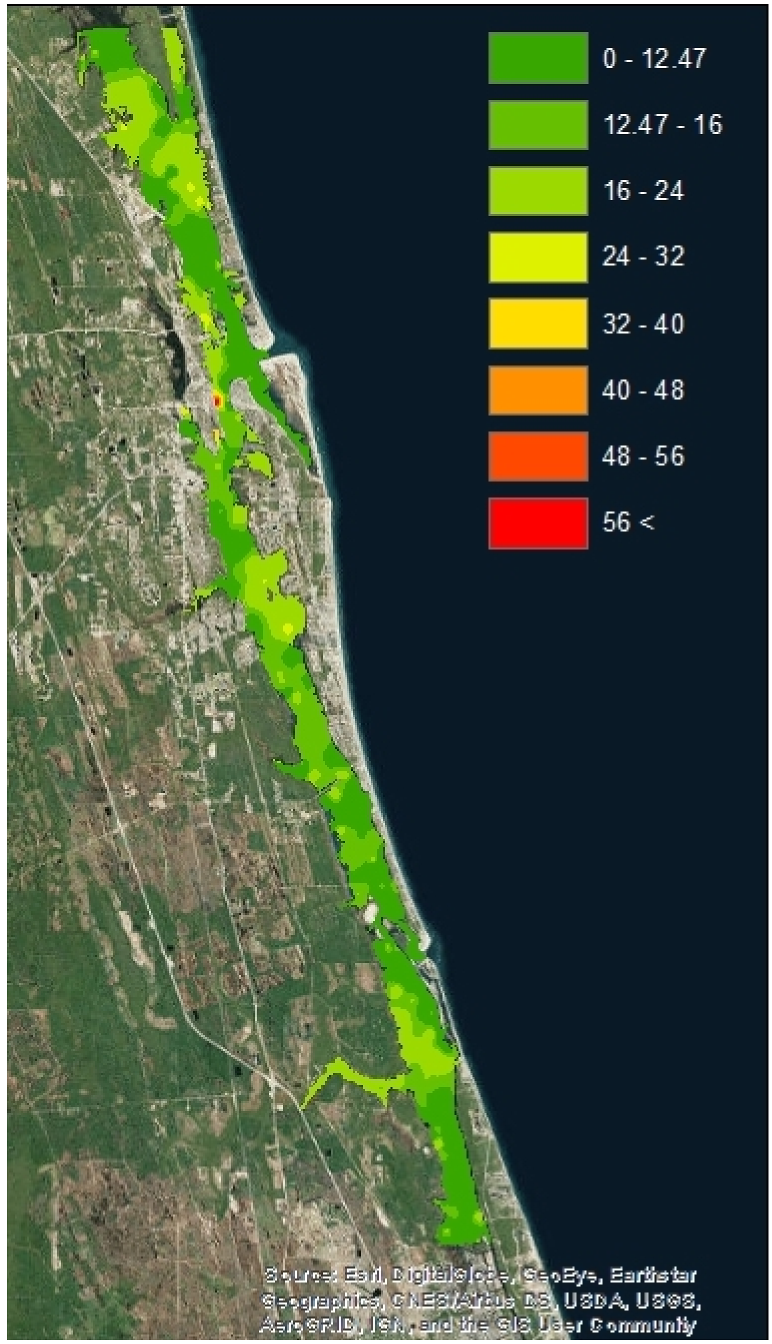

Figure 5 Shows the spatial distribution of lead in the study area

<u>Nickel:</u>

Only the urban section of the study area was reported to have an average concentration of nickel over the TEL, with an average of 16.9 ppm. The undeveloped section had 38.03% of samples over the TEL and 7.04% over the ERL, while the urban section was 62.34% over the TEL and 17.39% over the ERL. This indicates that the more sensitive species may be affected by nickel especially in the urban section. The most likely source of this nickel is atmospheric deposition from the exhaust created by the combustion of fossil fuels. Most of the study area was over the detection limit, but under the TEL. There is a pocket of the study area that was highly contaminated. This may be skewed on the map due to one sample being found to have a concentration of 1292.26 ppm. The area with elevated concentrations is located near downtown St. Augustine. These elevated levels may be due to a local source of nickel, or the fact that the area

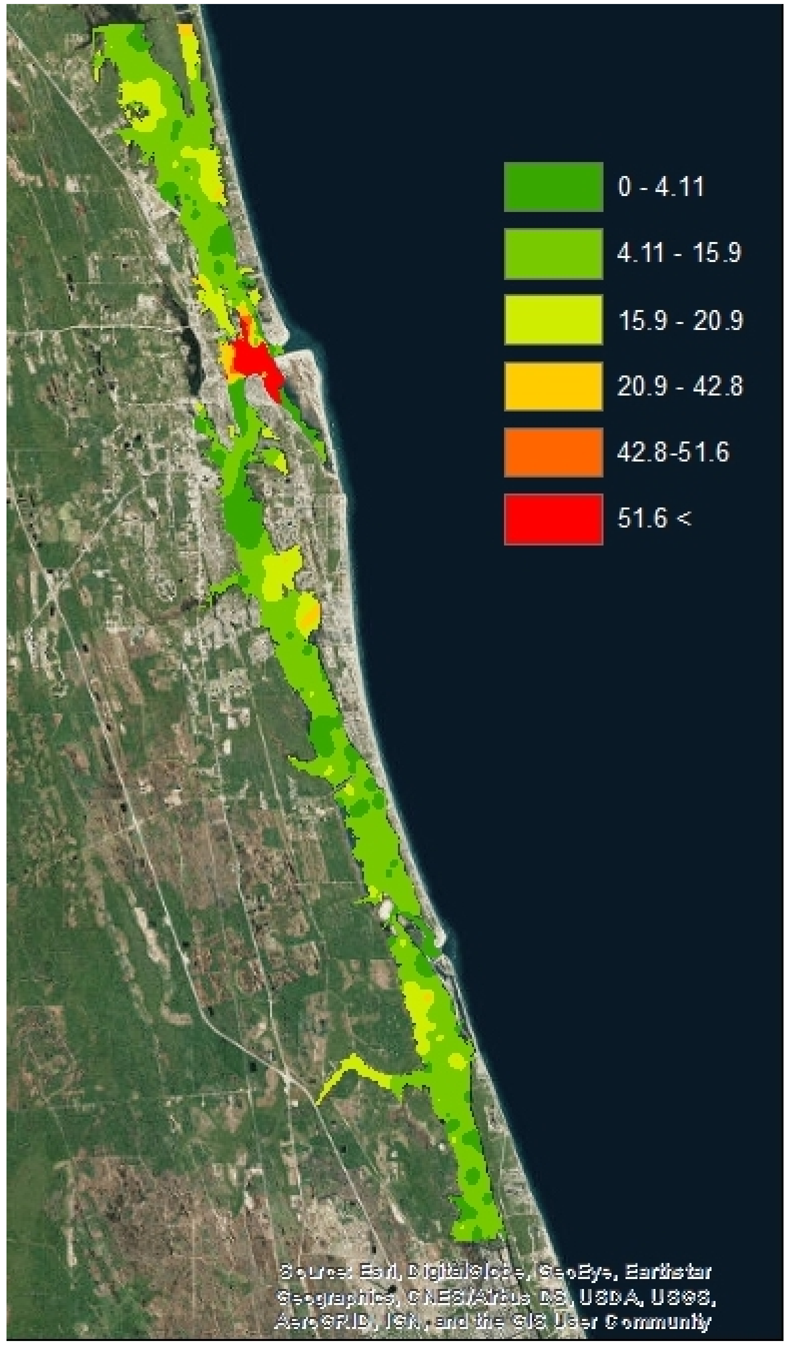

Figure 6 Shows the spatial distribution of nickel in the study area

was in the process of being dredged when the sample was collected. When sediment is dredged any contaminants that were previously buried can be brought to the surface.

Zinc:

The contamination levels for zinc were some of the lowest we found in comparison to the sediment quality guidelines. No sample

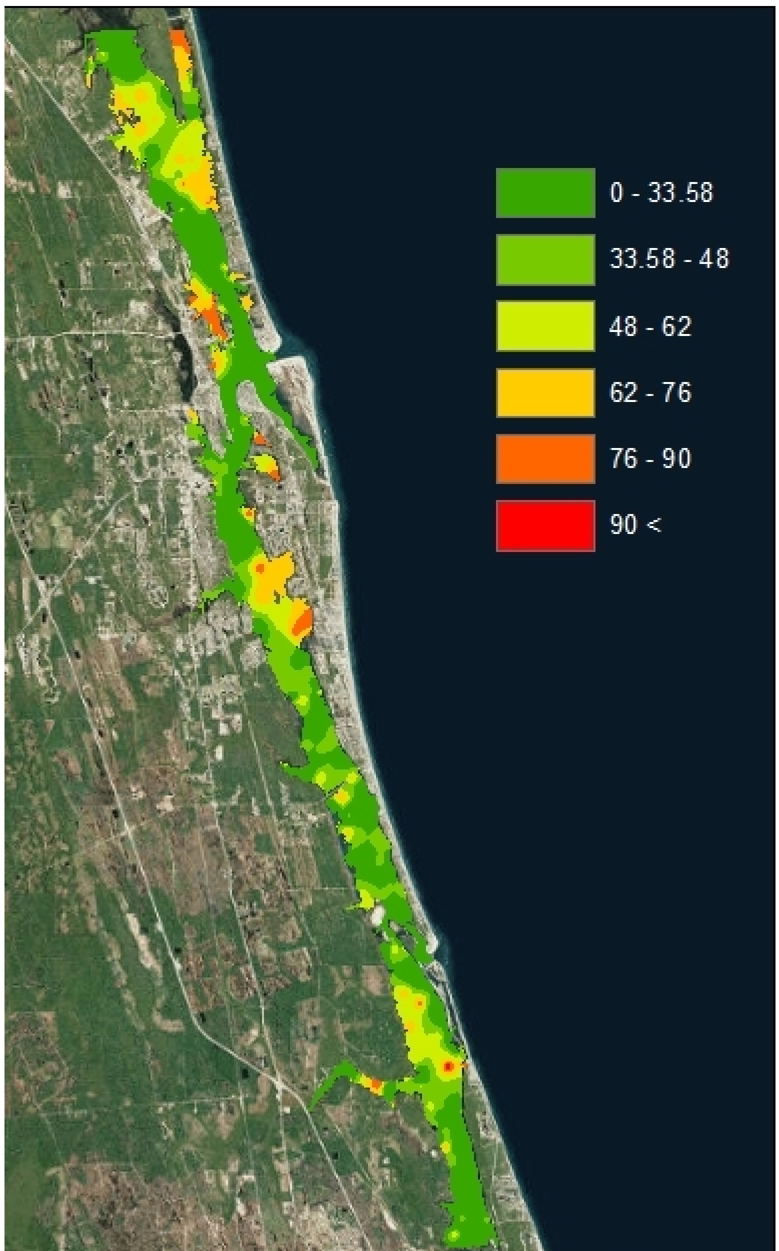

Figure 7 Shows the spatial distribution of Zinc in the study area

was above the TEL indicating that there is low risk to even the most sensitive species. The TEL is listed at 124 ppm while our sample with the highest concentration was at 98.28 ppm, indicating that the zinc present in the area is slightly natural levels where there is limited impact from the surrounding area. This is not surprising given that one of the biggest source of zinc pollution is metal production factories, and there are no metal factories near the study area. While none of the samples were over the TEL the spatial gradient shown in Figure 7 illustrates that even though the sample with the highest concentration was in the undeveloped section, the urban section had a higher average concentration.

Metal	Urban Area[a] (ppm)	Undeveloped Area[a] (ppm)	Pearl River estuary[b]	Pearl River Coastal zone[b]	San Pedrito Lagoon[c]	Dhamara Estuary[d]	Kennebec/ Androscoggin River system[e]
Cr mean +/- SD	40.81 ± 12.12	37.42 ± 11.20	87.6 ± 22.0	47.1± 10.5	79.54 ± 31.12	347.04 ± 51.10	73.2 ± 41.4
Cr Range	19.49 – 68.86	17.91 - 67.53	33.8 - 135	20.3-84.5	61.96 – 126.11	298.0 – 416.10	25.6 - 218.5
Cu +/- SD	28.92 ± 5.41	26.66 ± 4.21	46.8 ± 17.0	10.4 ± 6.0		18.94 ± 6.36	38.4 ± 19.6
Cu Range	21.57 – 61.46	21.70 – 44.83	6.2 - 100	2.71-49.1		10.21 – 27.89	13.5 - 98.4
Pb +/- SD	19.43 ± 6.79	16.45 ± 2.85	47.9 ± 13.7	21.7 ± 7.7	20.87 ± 5.81	31.91 ± 3.95	41.7 ± 49.0
Pb Range	12.51 – 66.15	13.69 – 22.76	16.0 – 96.3	4.6 -73.8	16.31 – 29.28	27.10 – 36.18	9.5 - 284.7
Ni +/- SD	33.08± 145.45 (16.51 ± 4.25)[f]	14.77 ± 3.69	34.8 ± 10.1	30.4 ± 5.6	119.97 ± 22.61	64.68 ± 10.71	50.3 ± 34.8
Ni Range	7.58 - 1292.26	7.25 – 23.76	10.6 – 54.1	13.9 – 48.5	104.90 - 153.34	54.34 – 79.70	18.8 – 184.2
Zn +/- SD	63.10 ± 15.69	53.05 ± 14.69	140 ± 42	72.1 ± 17.0	36.61 ± 32.99	41.70 ± 12.42	170.4 ± 109.7
Zn Range	34.15 – 89.05	34.97 – 98.28	55.1 - 268	32.2 - 161	19.28 – 86.08	55.80 – 84.20	39.8 – 474.6

a) These values are calculated without samples under LOD.
b) Concentrations of trace metals in sediment in study by (ip et al., 2007)
c) Concentrations of trace metals in sediment in study by (Mendoza-Carranza et al., 2007)
d) Concentrations of trace metals in sediment in study by (Asa et al., 2013)
e) Concentrations of trace metals in sediment in study by (Larsen & Gaudette., 2010)
f) This was calculated without the outlier sample.

After comparing the results of our study to results of different similar studies from around the world we found that the samples from our study area were considerably lower than other studies. For chromium, lead, and nickel no other study had an average concentration lower than either of our study areas. The area with the closest average concentration to our concentrations for chromium, lead, and nickel was the Pearl River coastal area. This area most likely had levels this close to ours because many of the samples were taken off shore which lessens their exposure to anthropogenic sources of pollution. Copper and zinc were the metals that we found the concentrations in our samples that were the highest relative to the other studies looked at. Of the studies looked at only the Pearl River Estuary and Kennebec Androscoggin River systems had higher concentrations of copper. For zinc the only study areas that had lower average concentrations were the San Pedrito Lagoon and the Dhamara Estuary. While some elements tested had lower concentrations when compared to other studies when all samples are taken into account the contamination of even the urban area is lower than the comparable studies. The area that had the closest concentrations to our study area was the Pearl River Coastal Zone. This shows how low the concentrations we found were because The Pearl River Coastal Zone had many samples taken offshore. With those samples being offshore the contaminant levels will decrease the further they are from the source.

Conclusion:

Our results demonstrate that while the urban more developed section of the study does have higher contaminant levels, overall the contaminant levels were not high enough to warrant a large concern. Based on the metrics measured all but one sampling spot had a low degree of contamination and low ecological risk. The element that has the biggest cause for concern would be copper. This was the metal with the most samples over the TEL and the ERL. We would recommend that there is a continued monitoring of copper in the area and consideration put into reducing the amount pesticides used in the area. With every metal tested indicating a higher level in the sediments near the urban and residential areas than the sediments near the protected areas the source of these elevated levels are indicated as anthropogenic.

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