Dynamics and copper content analysis of ulvoid blooms in New Haven Harbor

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Introduction

Ulvoids & Heavy Metals

- Ulvoids are a type of green macroalgae that when found in large abundance, or blooms, are known as green tides (See Figure 1 for examples from New Haven Harbor).
- Green tides are a nuisance to the surrounding environment and are caused by eutrophication, geothermal emissions, sewage, industrial inputs, decomposition, and other anthropogenic means (Paerl 1997).
- Heavy metal inputs from onshore industrial factories has become an increasing concern within many near shore coastal systems due to the effect the inputs have on both the surface and ground water systems as well as sediment.
- Biosorption by ulvoids has been found to be a productive and cost effective mechanism to remove these pollutants (Mackenzie 2005; Karthikeyan et al. 2007).
- Among such heavy metal pollutants, copper is a prominent metal found within these industrial inputs being introduced into the environment through extensive mining as well as landfills and waste disposal sites (ATSDR 2000).
- The Energy Dispersive X-Ray Fluorescence (EDXRF) is used for the purpose of measuring the chemical content within organic material by projecting x-ray radiation through the samples and recording the intensities of each element or compound.

Study Objectives

- Determine the average ulvoid biomass throughout New Haven Harbor to interpret distribution of overall blooms.
- Develop a method to quantify the copper content within the tissue of *Ulva* spp.

Figure 1 *Ulva* spp. samples collected from Long Wharf, West Haven, CT.

Materials and Methods

Figure 2 Overview of sampling sites throughout New Haven Harbor, New Haven, CT.

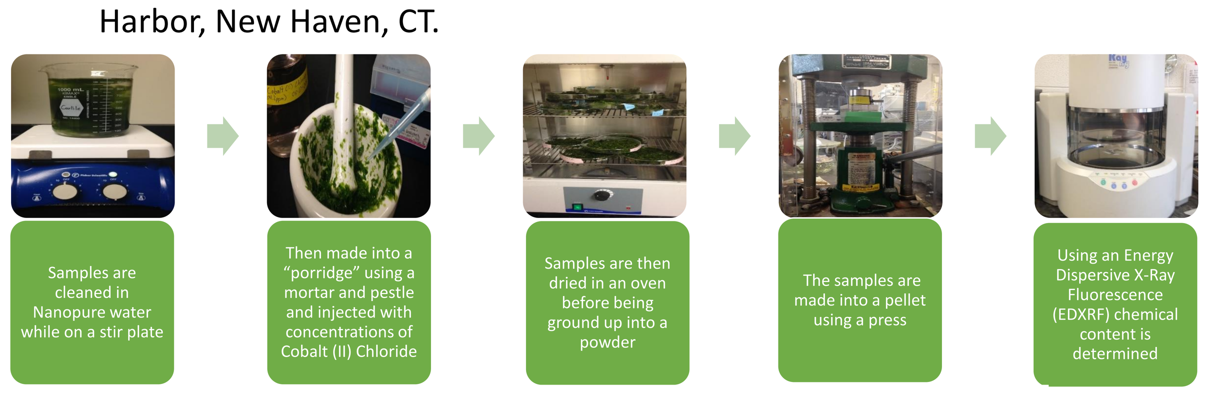


Figure 3 Method of preparing ulvoid samples for EDXRF testing.

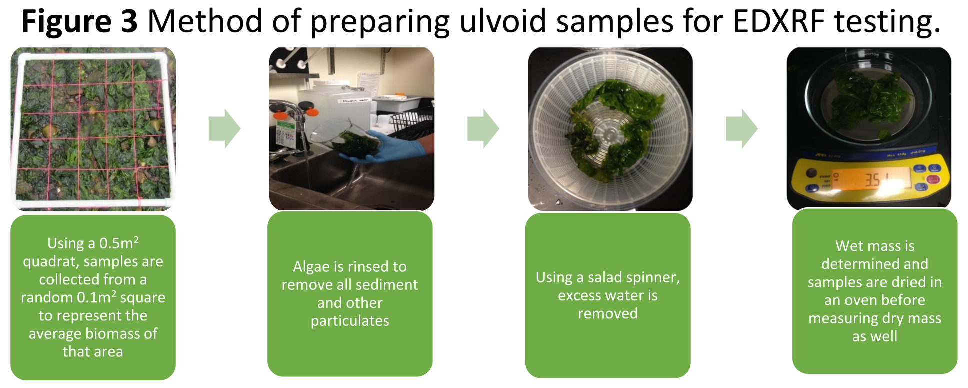


Figure 4 Method of measuring wet and dry mass of average biomass.

Results

Biomass Variability

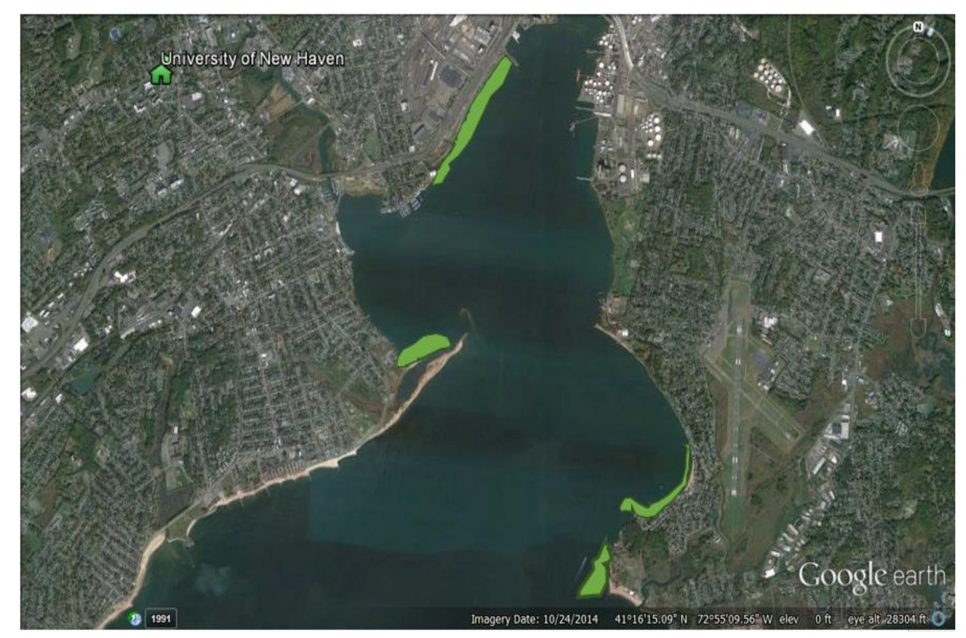


Figure 5 Ulvoid bloom outline, indicated by the green fields, throughout New Haven Harbor, New Haven, CT.

Figure 6 Average wet mass biomass variability throughout New Haven Harbor, New Haven, CT.

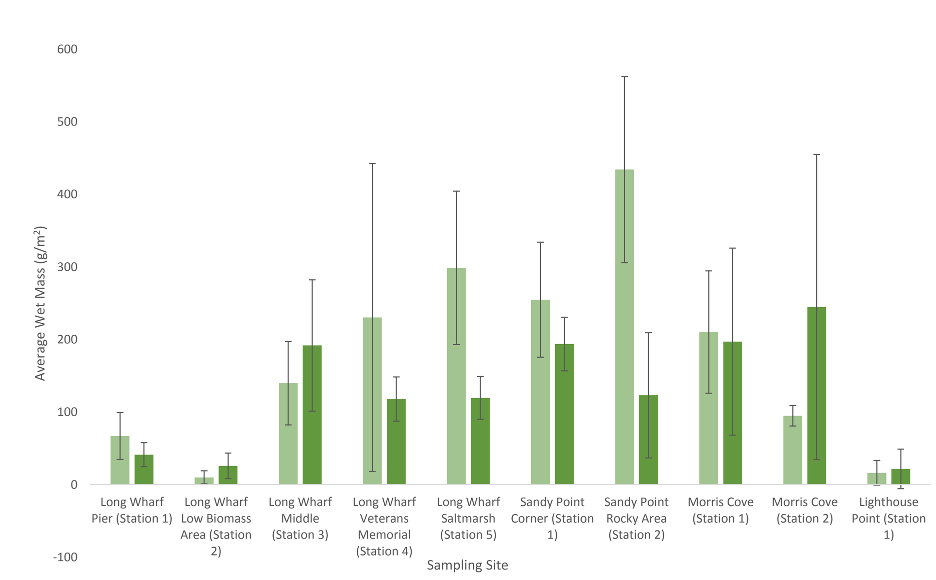


Figure 7 Average wet mass for sampling sites throughout New Haven Harbor at the low tide line (light green) and high tide line (dark green).

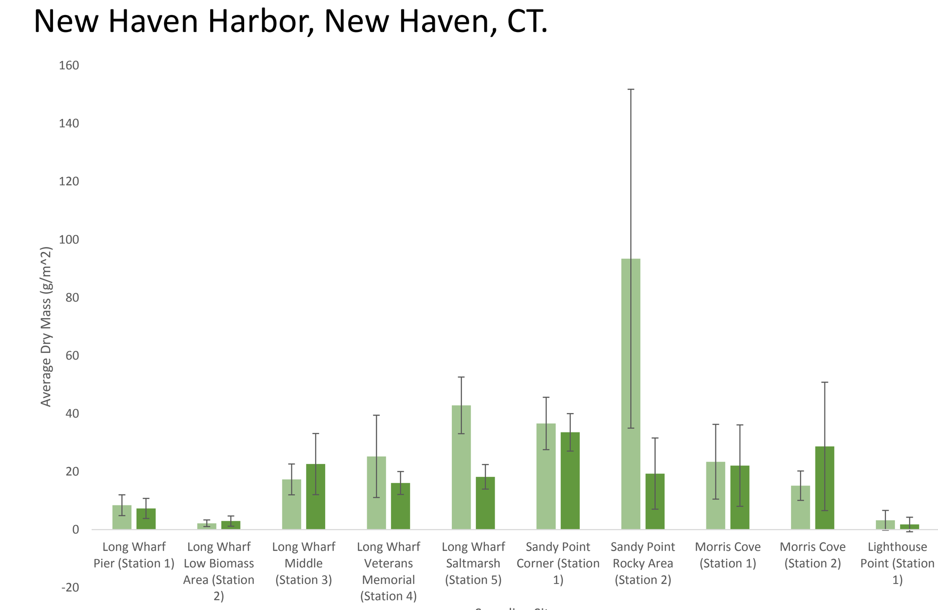
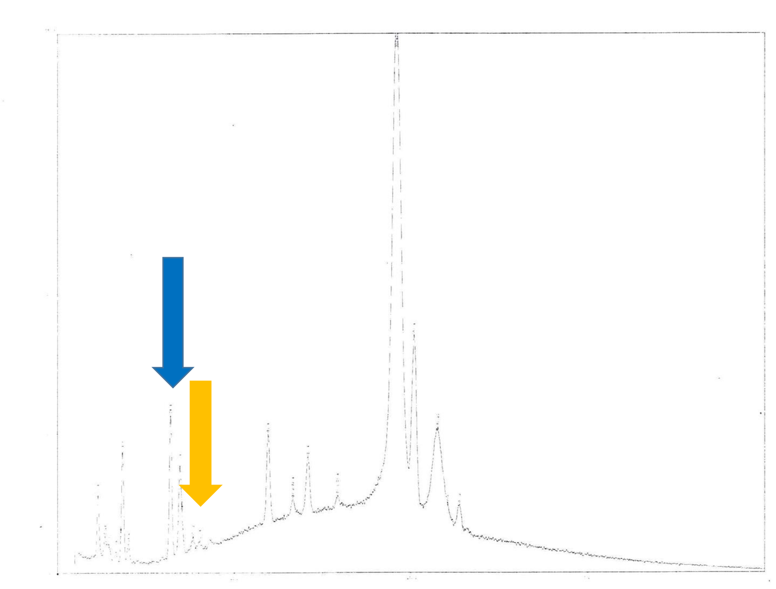


Figure 8 Average dry mass for sampling sites throughout New Haven Harbor at the low tide line (light green) and high tide line (dark green).

Presence of Copper

Table 1 The species and morphology of various samples as well as whether they were attached to a substrate at the sampling site and if copper was present in the tissue.

Site	Species	Sample	Morphology	Attached	Unattached	Presence of Copper
Long Wharf	U. compressa	AC 459	Blade		X	
		AC 553	Blade		X	X
	U. prolifera	AC 458	Tubular	X		X
	U. spp.	AC 557	Blade		X	X
		AC 587	Blade		X	X
		AC 598	Blade		X	X
		AC 611	Blade		X	X
		AC 662	Blade		X	X
		AC 679	Blade		X	X
Sandy Point	U. compressa	AC 467	Blade	X		
		AC 473	Blade	X		X
		AC 474	Blade	X		
		AC 475	Blade		X	X
		AC 482	Blade	X		
	U. rigida	AC 469	Blade		X	X
		AC 472	Blade	X		X
	U. spp.	AC 476	Blade		X	X
		AC 483	Blade	X		
Morris Cove	U. compressa	AC 505	Blade		X	X
	U. linza	AC 510	Tubular	X		X
	U. spp.	AC 509	Tubular	X		X
		AC 511	Tubular	X		X
Lighthouse Point	U. compressa	AC 515	Tubular	X		X
	U. lactuca	AC 516	Blade		X	X
		AC 523	Blade		X	X
		AC 524	Blade		X	X
	U. prolifera	AC 517	Blade		X	X
		AC 520	Tubular	X		X



Quantitative Result

Analyte	Result	(Std.Dev.)	Proc.-Calc.	Line	Int.(cps/uA)
SO3	61.954 %	(0.187)	Quan-FP	S Ka	1.8678
CaO	22.484 %	(0.057)	Quan-FP	CaKa	2.5827
Fe2O3	4.694 %	(0.032)	Quan-FP	FeKa	9.0309
P2O5	4.596 %	(0.137)	Quan-FP	P Ka	0.0538
Co2O3	2.219 %	(0.024)	Quan-FP	CoKa	5.2501
K2O	2.167 %	(0.027)	Quan-FP	K Ka	0.1902
Br	0.770 %	(0.008)	Quan-FP	BrKa	7.5517
SrO	0.487 %	(0.007)	Quan-FP	SrKa	5.1469
Sc2O3	0.396 %	(0.024)	Quan-FP	ScKa	0.0521
CuO	0.179 %	(0.011)	Quan-FP	CuKa	0.6386
Rb2O	0.035 %	(0.006)	Quan-FP	RbKa	0.3778
ZrO2	0.020 %	(0.006)	Quan-FP	ZrKa	0.2162

Figure 9 EDXRF scan of chemical content of *Ulva* sp. tissue sample AC 472 with an internal standard of cobalt (II) chloride emphasizing the measured intensity and peak heights of the standard (blue) and copper (yellow).

Results

- Large ulvoid blooms were found in all sampling sites throughout New Haven Harbor (Figure 5).
- Wet mass biomass increased at Long Wharf from North to South; however, at Station 2 biomass was much lower than other stations. Sandy Point exhibited the largest biomass throughout the harbor (Figure 6).
- Biomass was higher at the low tide line than high tide, with some exceptions throughout the harbor (Figure 7 and 8).
- *Ulva compressa* was the only species present at all sampling sites and exhibited both types of morphology: tubular and blade (Table 1).
- Copper was present in ulvoid tissue from all sampling sites and in samples that were either attached or unattached (Table 1).
- The EDXRF scan shows the measured intensities of the cobalt internal standard and copper which can be compared to quantify copper (Figure 9).

Discussion

- Blooms became larger from North to South on the western side of the harbor. This may be due to movement from the Mill, West, and Quinnipiac Rivers, which move algae as they flow south in the harbor, causing it to collect at the Sandy Point spit. On the eastern side of the harbor there is much less biomass present.
- Ulvoids are effective at uptaking nutrients, including ammonia and nitrate, leading to an increase in bloom size which may explain the thick mats present at Long Wharf and Sandy Point (Guidone and Thornber 2013; Littler and Littler 1980; Pedersen and Borum 1997; Mackenzie 2005). Nitrate concentration at these sampling sites were higher than those at Morris Cove or Lighthouse Point (data not shown).
- Most *Ulva* spp. samples contained copper and all sediment samples contained copper. The copper present in the ulvoids may have been absorbed from the sediment due to most samples being in close proximity to the sediment. These algae have also been observed to uptake PCBs, lead, and cadmium from sediment (Sari and Tuzen 2008).
- Ulvoids are productive at uptaking heavy metals because these macroalgae contain polysaccharides which have functional groups that may act as sites for metal binding (Sari and Tuzen 2008; Karthikeyan et al. 2007).
- There is no observable correlation between presence of copper and attached vs. unattached, species, or sampling site.
- Copper quantification is conducted by comparing the measured intensity of copper to that of the cobalt (II) chloride internal standard. Some progress has been made in developing this method of copper quantification, but further testing using the EDXRF is needed. Quantifying this copper may show different concentrations within samples and sites; however, there is still a constant presence of it throughout the harbor.

References

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