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Uptake of PCBs contained in marine sediments by the green macroalga *Ulva rigida*

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ABSTRACT

The uptake of PCBs contained in marine sediments by the green macroalga *Ulva rigida* was investigated in both laboratory and field experiments. Under laboratory conditions, total PCBs (tPCBs) uptake was significantly greater in live vs dead plants. The concentration of tPCB taken up in live plants was greatest in the first 24 h (1580 μg kg^{-1} dry weight), and then increased at a lower rate from day 2 to 14. Dead plants had a significantly lower tPCB concentration after 24 h (609 μg kg^{-1} dry weight) and lower uptake rate through day 14. Lesser chlorinated PCB congeners (below 123) made up the majority of PCBs taken up. Congener composition in both laboratory and field experiments was correlated to congener logK_{ow} value and sediment content. Field experiments showed that *Ulva* plants could concentrate PCBs to 3.9 mg kg^{-1} in 24 h. Thus, *U. rigida* is capable of removing PCBs in sediments at a rapid rate.

1. Introduction

Because of their location near centers of high human population and/or manufacturing, a large number of estuaries in the United States are polluted with toxic heavy metals and organic compounds (Long, 2000; USEPA National Coastal Condition Report, 2005). The two most widespread persistent organic pollutants (POPs) in estuarine and coastal river sediments are PCBs and PAHs. While both pollutants are known to be hazardous to a wide range of organisms, PCBs are of particular concern because of their greater capacity to bioaccumulate up the food chain and the toxicity of some of their non-ortho and mono-ortho substituted dioxin-like congeners (De Voogt et al., 1990; Wolska et al., 2012). PCBs are highly hydrophobic, partition strongly in non-aqueous phases, and are very slowly biodegraded (Erickson, 2001). In addition, PCBs accumulate in organically rich sediments, are taken up by primary producers and consumers, and then transferred up the food chain to fish species that dominate mid and top tropic levels where they may be bioaccumulated to extremely high levels (e.g. Lake et al., 1995).

PCBs have been shown to be harmful to a wide variety of aquatic organisms, including fish, bird and mammal species (Tanabe et al., 1994; Thurberg and Gould, 2005), as well as to humans (Kimbrough, 1987). They are considered to be carcinogenic to animals, as well as agents of neurodevelopmental, immune and reproductive damage (Kimbrough, 1987; Ribsd-Fito et al., 2001). One of the major methods they are acquired by humans is through the consumption of contaminated fish (Alcock et al., 1998). Not surprisingly, the consumption of fish from various rivers and estuaries in the Northeast US has been banned, in many cases due to PCB contamination (US DOI, 2001; USEPA National Coastal Condition Report, 2005).

Remediation of PCB-contaminated estuarine and coastal river sediments is far more difficult than that on land due to the overlying water column and associated ecosystem, and the potential for resuspension of contaminants during clean-up operations (Gomes et al., 2013). The most common remediation method used today involves dredging of the contaminated sediment and transferring it to landfills or handling via confined aquatic disposal, which are both extremely costly and potentially harmful to the environment in the long-term (Eggleton and Thomas, 2004; Perelo, 2010). There is no low-cost and sustainable method available today to clean up PCB-contaminated sediments found in estuaries and coastal rivers. Phytoremediation has proven effective in the elimination of a wide range of pollutants from terrestrial soils, including mercury, explosives, chlorinated solvents, PAHs and PCBs (McCutcheon and Schnoor, 2004; Pilon-Smith, 2005), however, the technology of using Angiosperm plants or algae to remove PCBs and other organic pollutants from marine sediments is undeveloped.

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While there is extensive information on the capacity of freshwater aquatic plants and marine micro- and macroalgae to take up and concentrate heavy metals and radionuclides, relatively little is known about their capacity to take up and concentrate PCBs and PAHs. For example, freshwater submergent Angiosperm plants such as water hyacinth, duckweed, water milfoil and parrot's feather have been shown to have a great capacity for taking up heavy metals such as lead, copper, cadmium, iron, selenium, and mercury (Kamal et al., 2004). Similarly, both freshwater macroalgae (e.g. *Spirogyra*, *Nitella and Ulva*) and marine micro- and macroalgae (e.g. *Chlorella*, *Ulva*, *Sargassum*, *Fucus* and *Ascophyllum*) have also demonstrated a similar capacity to take up and concentrate lead, nickel, copper, cadmium, strontium, chromium, mercury and U(VI) (Davis et al., 2003; Maeda and Sakaguchi, 1990; Rybak et al., 2012; Yu et al., 1999).

There have been very few studies, however, that have examined the ability of Angiosperm plants or micro- and macroalgae to take up persistent organic pollutants from marine waters or sediments. Only two marine Angiosperms have been shown to take up and concentrate PAHs or PCBs: the salt marsh plant *Spartina alterniflora* and the seagrass *Zostera marina*. Using containers filled with contaminated sediment, Watts et al. (2006) showed that *Spartina* was able to concentrate PAHs in their root tissue to levels as high as 43 $\mu g\, g^{-1}$, but showed little uptake in leaves. Using a similar approach, Mrozek et al. (1982) showed that *Spartina alterniflora* can also take up Aroclor 1254 PCB congeners in its roots and stem, with a selectivity towards lesser chlorinated congeners. The uptake of PAHs and PCBs by the seagrass *Zostera* has been examined by Huesemann et al. (2009), who grew plants for up to 60 weeks in containers with contaminated estuarine sediments. Huesemann et al. (2009) showed a significant increase in selected PCB congeners being removed from sediment containers planted with *Zostera* compared to unplanted sediment containers. They hypothesize that PCB-degrading microorganismal activity stimulated by root exudates and/or catabolic reactions mediated by plant enzymes released into the sediment was responsible for the transformation of PCBs observed.

The earliest report of a macroalga (or seaweed) taking up and concentrating PCBs from sediment is that of Larsson (1987), who described the ability of a freshwater green macroalga, *Cladophora glomerata*, to take up and concentrate PCBs to a level of 3.6 $\mu g\, g^{-1}$ dry weight from an artificial fresh water pool containing sediment with a PCB concentration of 2.7 $\mu g\, g^{-1}$ dry weight after two months. The ability of marine macroalgae to take up PCBs from contaminated sediments in the field has been reported in several studies from the Venice Lagoon, Italy (Maroli et al., 1993; Micheli et al., 1995; Pavoni et al., 2003). The highest seaweed PCB concentration reported from these studies was that of 120 $\mu g\, kg^{-1}$ for the green, bloom-forming macroalga *Ulva laetevirens* from sediments with PCB levels of 1.6 $mg\, kg^{-1}$ (Micheli et al., 1995). There is only one report on the uptake of PAHs by a seaweed, that of Wang and Zhao (2007) for the brown macroalga *Laminaria japonica* under laboratory conditions.

One of the most common macroalgae used in past studies of heavy metal biosorption from the environment, as well as for the removal of nitrogen and ammonia in fish aquaculture is the green alga *Ulva* (Neori et al., 2003; Rybak et al., 2012). *Ulva* grows as one cell-thick tubes or two cell-thick sheets that have a high surface area to weight ratio and can grow unattached. *Ulva* species are common causes of seaweed blooms (called "Green Tides") around the world (Hu et al., 2010; Menesguen and Piriou, 1995; Ye et al., 2011), in part because of their fast growth rates, high nitrogen uptake efficiency, and broad physiological tolerances. In a preliminary report of an *Ulva rigida* bloom discovered in the PCB-contaminated Superfund Site of New Bedford Harbor, MA (eg. Nelson and Bergen, 2012), Cheney et al. (2007) collected samples of *U. rigida* lying on top of the sediment with total PCB (tPCB) levels as high as 99 $mg\, kg^{-1}$ dry weight, and a corresponding bioconcentration factor (ratio of concentration in the alga to concentration in surrounding water) of approximately 100,000. Based upon these preliminary results, *U. rigida* was chosen as a potential seaweed component in the development of a new type of marine sediment remediation system that would expand on the reactive core mat concept described in Meric et al. (2012) and Sheahan et al. (2003). The overall goal of the present study was to determine the rates at which living and dead *U. rigida* plants take up PCBs contained in contaminated marine sediment, and their congener composition. We chose to examine *Ulva*'s ability to take up PCBs contained in sediment because of its relevance to both bioremediation applications and what we have observed in the field. That is, during the time that *U. rigida* forms a bloom in the Superfund Site of New Bedford Harbor (Cheney et al., 2007), sheets of *Ulva* form a thick mat that lies on the top of and in contact with the sediment.

2. Materials and methods

2.1. Materials

The PCB mixture used to inoculate sediment in our laboratory experiments, Aroclor 1248 (C-248N-50MG), was obtained from AccuStandard Inc. (New Haven, CT). Acetone and hexane were purchased from Fisher Scientific. All chemicals were of analytical grade. Synthetic saltwater was made from sea salt mixture that was purchased from Instant Ocean.

Seaweed samples for laboratory experiments consisted of small sheets (10–20 cm dia.) of the green macroalga *U. rigida* collected in July and August, 2012, from a site 200 m north of the Coggeshall St. bridge at the bottom of the upper harbor of New Bedford Harbor, MA. Preliminary PCB analysis showed the total PCB concentration in these plants to be 85 $\mu g\, kg^{-1}$ dry weight. Immediately after collection, plants were brought back to the laboratory where they were washed repeatedly with sterilized seawater and scrubbed with paper towels to remove surface algal and bacterial contaminants. Plants were cultured overnight in an incubator at 15 °C and used in experiments the next day. For dry weight calculations, premeasured fresh *Ulva* was dried inside an oven at 103 °C for 16 h and determined to have a 16.5% dry weight content and 83.5% water content. For the dead plant experiments, *Ulva* plants were dried in an oven at 50 °C for 18 h to obtain a final average water content of 11.5%.

Seaweed samples for field experiments consisted of sheets of *U. rigida* 20–30 cm in diameter collected just inside the Hurricane Barrier at the entrance to New Bedford Harbor (MA). These plants were shown to have a PCB concentration of 24 $\mu g\, kg^{-1}$ dry weight or less. After collection, the plants were immediately moved to stainless steel mesh cages in the upper harbor as described below.

The sediment used in the laboratory microcosm experiments was collected from the Neponset River in Quincy, MA, behind the Tilestone & Hollingsworth Dam using an Ekman dredge sampler. The sediment had an average total organic carbon content (Schumacher, 2002) of 10.4% and a 75.2% dry weight and was similar to that of New Bedford Harbor, whose organic carbon content varies between 4.1% to 11.3% (Hansen et al., 1986). The sediment dry weight was determined by weighing fresh sediment after drying in an oven at 103 °C until the constant mass was reached. The homolog composition in the initial sediment and total PCB concentration are given in Table 1. Fourteen days prior to initiation of laboratory experiments, the sediment sample was spiked with Aroclor 1248 to obtain a nominal target PCB concentration of 50 $mg\, kg^{-1}$. A high volume solvent spiking method (Northcott and Jones, 2000) was used with 8 mL acetone per 50 mg of Aroclor