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Safety and quality of the green tide algal species *Ulva prolifera* for option of human consumption: A nutrition and contamination study

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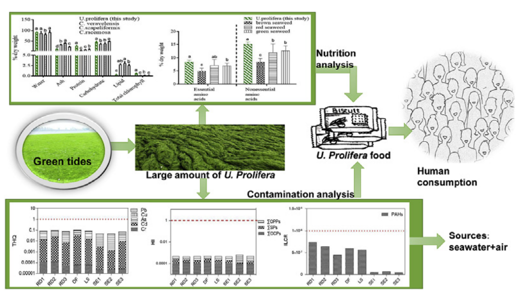
HIGHLIGHTS

- *U. prolifera* as a low-fat, high-protein food resource.
- Acceptable health risks due to heavy metals, pesticides and PAHs in *U. prolifera*.
- Different PAH composition profiles in the floating and grown-on-raft *U. prolifera*.

GRAPHICAL ABSTRACT



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ABSTRACT

This study sampled *U. prolifera* and surface seawater from the same locations where green tide broke out in the southern Yellow Sea, in both the year 2016 and 2017. The revealed nutritive components of *U. prolifera* samples characterized *U. prolifera* as a high-protein, high-Fe, high ratio of unsaturated lipid acids and low-fat seaweed food, with an ideal ratio of essential and nonessential amino acids. The concentrations and health risk assessment of major micropollutants (heavy metals, pesticides and polycyclic aromatic hydrocarbon (PAHs)) in *U. prolifera* were also analyzed, respectively. The results showed that the Target Hazard Quotient values of five heavy metals ($<1.0 \times 10^{-1}$) and the total hazard index of 13 pesticides ($<1.5 \times 10^{-8}$) were lower than the unity, respectively, and the incremental lifetime cancer risk values of PAHs ($<7.4 \times 10^{-7}$) were lower than the USEPA limit (1.0×10^{-6}). It suggested that consuming *U. prolifera* is safe as a food-source option, with PAHs causing relatively higher risks. PAHs from the sites closer to the shore were also found more originated from pyrolysis. We further confirmed the PAH congeners were partly in equilibrium between seawater and *U. prolifera*. It suggested the possibility that the food safety-risk turned to be above the USEPA limit was not high regardless of the sample collecting time. However, the sources of PAHs and their contributions to the accumulation in *U. prolifera* need further investigation. This study favored that *U. prolifera* of the green tide from the southern Yellow Sea has a potential for a nutritious-food production.

1. Introduction

Green tides usually refer to the abnormal proliferation of floating macroalgae in the phylum of Chlorophyta (Alstyne et al.,

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2015; Wang et al., 2015). There have been reports of occurrence of green tides at the Cadiz Bay and Palmones estuaries in Spain (Palomo et al., 2004), Tokyo Bay in Japan (Yabe et al., 2009), the Brittany coast in France (Perrot et al., 2007), the northeast Pacific coast (Alstyne et al., 2006), the South Korean coast (Kim et al., 2004), and the southern coast of England (Taylor et al., 2001). As the largest green tide events in the world to date, green tides in the Yellow Sea happened in ten consecutive years from 2007 (Hu et al., 2014). The maximum distribution area of the floating macroalgae mats of each event ranged from 1.0×10^4 to $6.0 \times 10^4\,km^2$, which was approximately one-tenth of the total area of the Yellow Sea (Wang et al., 2015). The large-scale green tides can cause negative impacts on the local ecosystem, and are destructive to the coastal landscapes and mariculture, incurring significant economic losses (Wang et al., 2018). Morphological and molecular analyses have revealed *Ulva prolifera* as the dominant species of green tides in the Yellow Sea (Liu et al., 2013). The precaution of the green tides is requiring more investment. Meanwhile, removing the massive floating mats from the Yellow Sea by human and machines has been at considerable expense to the government of China every year. Effective utilization of the massive amount of the collected *U. prolifera* has therefore become a focus of research.

U. prolifera can be processed into bio-oil and bio-char products, as a viable eco-friendly, green feedstock substitute for biofuels and chemicals production (Zhuang et al., 2012). Nowadays, the yield of *U. prolifera* is approximate 20% of wet weight for bio-oil and 40% for bio-char (Wang et al., 2018; Zhou et al., 2010; Chow et al., 2013). The utilization rate of *U. prolifera* can be enhanced through developing high value products such as food, feed ingredients (Michalak and Chojnacka, 2009).

Being a low-calorie food rich in vitamins, minerals and dietary fiber, *U. prolifera* has been used as raw material or additives for fertilizers and animal feeds for decades (Liu et al., 2013). Large-scale production of seaweed feed has been achieved (Sun et al., 2011). *U. prolifera* has also received a lot of attention as functional food ingredients, being used widely for centuries in Asia, mostly as food to provide nutrition and a characteristic taste (Lordan et al., 2011; Collins et al., 2016). Fresh dried seaweed is extensively consumed, especially by people living in coastal areas in China. Moreover, polysaccharide, as the major component of *U. prolifera*, was found to be of high hypolipidemic activities, potent immunomodulatory properties and antibacterial activities (Zhao et al., 2016). Processing *U. prolifera* into functional ingredients of food for human consumption and the related food safety have consequently gained increasing attention (Zhao et al., 2016; Michalak et al., 2017). To the best of our knowledge, the nutritional composition of *U. prolifera* has not been systematically analyzed and reported, however.

The cell wall of *U. prolifera* contains functional groups such as hydroxyl, carboxyl, amino, thiol and phosphate, and thus the cell wall is negatively charged and can attract heavy metal ions in water through ion exchange (Flores et al., 2015). The equilibrium between *U. prolifera* and water can be achieved very soon when the concentration of heavy metals in the seawater is not high (Sheng et al., 2004). Besides, *U. prolifera* consists of filamentous shoots with monostromatic hollow cylinders and have high ratio of surface to volume (S/V), which enables them to absorb particles-bounded polycyclic aromatic hydrocarbons (PAHs) and pesticides abundantly when exposed to contaminated aquatic environment (Zhang et al., 2017). Several kinds of seaweed were reported to be contaminated by toxic compounds such as heavy metals, pesticides and PAHs (Besada et al., 2009; Kamala-Kannan et al., 2008; Rubio et al., 2017). Marine macroalage were even selected as novel materials for the removal and monitoring of heavy metals from water (Khan et al., 2015; Khaled et al., 2014; Huan et al., 2018). In comparison, the reports regarding the uptake rate of PAHs and pesticides by *U. prolifera* were not found (García-Rodríguez et al., 2012; Pavoni et al., 2003).

The key aims of this study were: (1) to assess the nutritive components and the concentrations of the PAHs, pesticides and heavy metals in *U. prolifera* collected from the southern Yellow Sea during the outbreak of green tides in 2016 and 2017; (2) to evaluate the health risk of *U. prolifera* by human consumption based on contamination levels; and (3) to investigate the possible sources of the contaminants that would result in high food safety risk and their bioconcentration potentials into *U. prolifera*. This study was in hope of providing supporting data for the advanced utilization of the green tide algae from the southern Yellow Sea in China.

2. Materials and methods

2.1. Sample collection

According to the distribution pattern and growth status of *U. prolifera* along and off the coast of Jiangsu Province, site-matched samples of *U. prolifera* and surface water were collected between May and August in 2016 and 2017, respectively, from three Porphyra culturing rafts at the coast of Rudong City (RD1, RD2, and RD3), one at the coast of Lvsi City (LS) and one at the coast of Dafeng City (DF). In 2017, *U. prolifera* and water samples were collected from three sampling sites following the direction of algae floating in the southern Yellow Sea (SE1, SE2, and SE3) (Fig. 1). In total, 65 *U. prolifera* samples were collected in this study, with five replicate samples collected from each sampling site in each year. The collected *U. prolifera* samples (2 kg for each site) were stored in a cool box with ice packs and transferred to a $-20\,^{\circ}C$ freezer in the lab until analysis. Water samples (2 L for each site) were collected into pre-cleaned glass bottles and transferred to a $-4\,^{\circ}C$ fridge in the lab until analysis. *U. prolifera* samples were freeze-dried within 48 h and all sample analysis were completed within 7 days.

2.2. Sample analysis

Water content was determined *via* oven-drying at $105\,^{\circ}C$; crude ash content was determined *via* heating at $550\,^{\circ}C$; crude fat content was determined using the Soxhlet extraction method; chlorophyll content was determined using the N, N′-dimethylformamide extraction method (Kumar et al., 2011). The crude protein, phosphate, iron, copper, manganese, zinc, carbohydrate, fatty acid and amino acid content were determined according to the methods published previously (Ortiz et al., 2006; Kumar et al., 2011). PAHs, heavy metals, organochlorine pesticides (OCPs), pyrethroid pesticides (PEs) and organophosphorus pesticides (OPPs) in the samples (seawater and *U. prolifera*) were measured following methodologies published previously (Li et al., 2015a, 2015b; Khan et al., 2015). Details of the instrumental method were provided in Supplementary Information. The target compound list was presented in Table S1.

2.3. Quality control

Quality control procedures for sample analysis included duplicate analysis, method blanks and spiked samples. For duplicate analysis of each sample, the relative standard deviation (RSD) of the analytical results was less than 15%. For every ten samples analyzed, a blank sample was included to check laboratory contamination. Pre-extracted *U. prolifera* were used as the blank samples. For recovery analysis, the pre-extracted *U. prolifera* samples were spiked with heavy metals, pesticides and PAHs of 0.1, 1.0, 10 μg/g dw, 0.5, 5.0, 50 ng/g dw and 0.1, 1.0, 10, 100 ng/g dw,