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Screening of lipophilic marine toxins in marine aquaculture environment using liquid chromatography–mass spectrometry

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HIGHLIGHTS

- Development of a LC-TOF/MS method for screening of different classes of lipophilic marine toxins.
- Analysis of lipophilic marine toxins in different environmental samples of Jiaozhou Bay was achieved.
- Two types of lipophilic marine toxins were found in the analyzed samples from mariculture environment.
- Environmental risks of the mariculture area posed by lipophilic marine toxins need more attention.

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ABSTRACT

This study aimed to develop an exact mass suspect screening approach to perform finding of multiple lipophilic marine toxins (LMTs) in seawater, suspended particulate matter (SPM), and marine sediment from marine aquaculture area using liquid chromatography-time of flight mass spectrometry (LC-TOF/MS). The method was validated and proven to be reliable for the screening of various LMTs. Then, the method was applied to screen LMTs in marine environmental samples collected from mariculture area of Jiaozhou Bay, China. Okadaic acid (OA), pectenotoxin 2 (PTX2), etc were detected and tentatively identified. Positive detection results were confirmed by liquid chromatography-tandem mass spectrometry (LC–MS/MS), and contents of OA and PTX2 in seawater, SPM and marine sediment were also quantified. The mean concentration of OA ranged from 2.71 to 14.06 ng L^{-1} in seawater and from 0.78 to 3.34 ng g^{-1} dry weight in marine sediment. The mean concentration of PTX2 ranged from 0.86 to 7.90 ng L^{-1} in seawater, from 1.56 to 10.67 ng in SPM obtained from 1 L seawater sample and from 0.95 to 2.23 ng g^{-1} dry weight in marine sediment. The above results suggested that the proposed method was convenient and reliable for the screening of LMTs in different marine environmental samples. In addition, typical LMTs exist in different marine environmental media of the mariculture area of Jiaozhou Bay, China. Follow-up studies should focus on improving current understanding on the environmental behavior of these LMTs in the marine aquaculture environment.

1. Introduction

Although harmful algae bloom events are natural phenomena, their impacts on the human health and on the coastal economy appeared to have increased in frequency, intensity, and extension (Facca et al., 2014). Contamination with marine toxins produced by planktonic and benthic micro-algae has also become a global problem for public health and quality assurance of shellfish products (Botana, 2008). As always, substantial effort has been focused on research on marine toxins in contaminated bivalves and toxic algae (Fux et al., 2011; These et al., 2011). To date, however, little is

Abbreviations: LMTs, lipophilic marine toxins; SPM, suspended particulate matter; LC-TOF/MS, liquid chromatography– time of flight mass spectrometry; OA, okadaic acid; PTX2, pectenotoxin 2; HAB, harmful algal bloom; ASE, accelerated solvent extraction; MRM, multiple reaction monitoring; SPE, solid phase extraction.

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known about the pollution levels of marine toxins in marine aquaculture environment in which shellfish and fish need to live. Considering the high toxicity of marine toxins for human health, the detection, occurrence, environmental behavior and bioavailability of marine toxins in different marine environmental medium is expected to garner more attention.

On the basis of their chemical properties, marine toxins can be divided into two broad classes: hydrophilic and lipophilic toxins (Table S1, Supplementary Materials). At present, a large number (>260) of marine toxins have been described in the previous literature (Gerssen et al., 2011; Pierce et al., 2005; Mendoza et al., 2008; Rundberget et al., 2011), but lipophilic marine toxins (LMTs) accounted for more than 90% of the total marine toxins (Wang et al., 2015). Therefore, studies on LMTs in marine environment are of considerable significance to both human health and marine ecological environment protection. Only during the last decade, marine toxins in marine environments have gained increasing attention (MacKenzie et al., 2004; Rundberget et al., 2009; Li et al., 2010, 2014; McCarthy et al., 2014). A wide range of LMTs, including OA, DTX, PTX, YTX, GYM, AZA, SPX, and so on, has been detected in seawater of different areas of the world (Lane et al., 2010; MacKenzie, 2010). Research work by Mendoza et al (Mendoza et al., 2008). has shown that brevetoxin group toxins were determined in marine sediments from three sites along the southwest Florida coastline. Moreover, the occurrence of brevetoxins in Florida coast sediments can be durable in marine ecosystems (Hitchcock et al., 2012). In addition, a recent study (Jauffrais et al., 2013) shows that dissolved AZAs in seawater were bioavailable for mussels, and that AZA accumulation may reach concentrations above the regulatory limit and thus may be considered as a food safety issue. The existing literature shows that various LMTs exist in different marine environmental media. In addition, previous studies show that some toxins are persistent and bioavailable. Thus, LMTs presented in marine aquaculture area are a potential menace to the cultured species and human health.

Until now, LC-MS/MS remains the most used technique in the identification and quantification of lipophilic marine toxins in seawater and sediment samples (Mendoza et al., 2008; Wang et al., 2015; Li et al., 2014). In these studies, almost all of mass spectrometers used for toxin determination were of low resolution, in either single ion monitoring (SIM) or multi reaction monitoring (MRM) mode. However, such methods fail to detect toxins that are not preset in SIM or MRM mode and are thus unable to detect non-target toxins in marine environmental samples. Moreover, the fact that most classes of marine toxins consist of numerous analogues, as well as the lack of certified standards and reference materials, renders the use of target analytical methods for detecting all LMTs extremely difficult, if not impossible. Therefore, developing suitable alternative test methods to screen various LMT contaminations, both those that are currently known and those which might emerge, in marine environmental samples is urgently needed.

The evolution of high resolution (HR) MS coupled with LC has opened up new windows of opportunity for monitoring expected and unexpected compounds together in a sample with full scan acquisition methods (Schymanski et al., 2014). Recently, the use of LC–HRMS has increased (Schymanski et al., 2014; Moschet et al., 2013). Several researchers successfully utilized HRMS for simultaneously screening multiple contaminants in different environmental samples (Boix et al., 2014; Haddad and Kümmerer, 2014; Blanco et al., 2016; Chen et al., 2016b). Several suspect screening approaches based on LC–HRMS were also developed for LMTs in shellfish and toxin producing microalgae (Facca et al., 2014; Gerssen et al., 2011; Blay et al., 2011; Domènech et al., 2014; Zendong et al., 2015; Rúbies et al., 2015; Orellana et al., 2015; Chen et al., 2016a), which demonstrated that the LC–HRMS was a useful tool for the simultaneous screening of LMTs. To the best of our knowledge, no previous research has focused on the use of LC–HRMS to screen LMT contaminations in different marine environmental media such as seawater and marine sediment. However, the properties and composition of marine environmental samples are different from those of shellfish samples. So a suitable pretreatment method combined with LC–HRMS would be a powerful method for the simultaneous screening of LMTs in marine environmental samples.

Jiaozhou Bay is a typical semi-enclosed bay with a channel 3.1 km in width that connects with the Yellow Sea, situated in the southern part of Shandong Peninsula (35°58′–36°18′N, 120°04′–120°23′E), China. It has an area of 380 km^2 and an average water depth of 6–7 m. More than ten rivers flow into the bay, the largest one is the Dagu River. The bay serves multiple functions, such as a port, transportation, aquaculture, tourism, and fishing, among them aquaculture is the main economic activity (Wang et al., 2016b). Given rapid progresses in industrial and aquaculture development, Jiaozhou Bay is significantly affected by anthropogenic activities and it has been suffering algae blooms in summer in recent years (Yuan et al., 2016). In our previous research (Wang et al., 2015; Li et al., 2014), LC–MS/MS was developed to determine the concentrations of some typical LMTs in seawater and marine sediment. Based on the previous research, this study aimed to develop an approach of target analysis and suspect screening to perform rapid identification of multiple LMTs in seawater, SPM, and marine sediment samples by LC–HRMS, and the proposed method was applied to screen LMTs in real marine environmental samples collected from Jiaozhou Bay, China (Fig. 1).

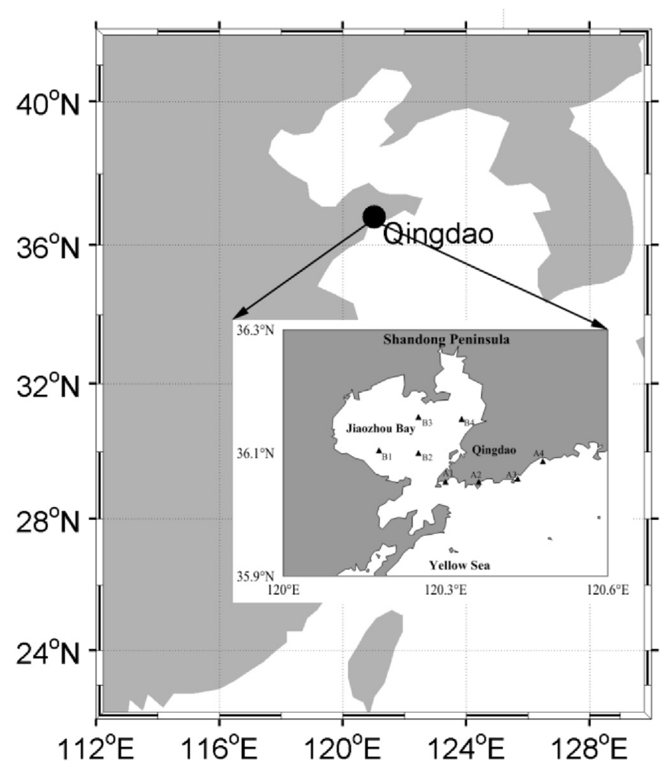

Fig. 1. Sampling locations for seawater, SPM and marine sediment samples in Jiaozhou Bay, China.