Science of the Total Environment 898 (2023) 165472

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Monthly distribution of lipophilic marine biotoxins and associated microalgae in the South Sea Coast of Korea throughout 2021

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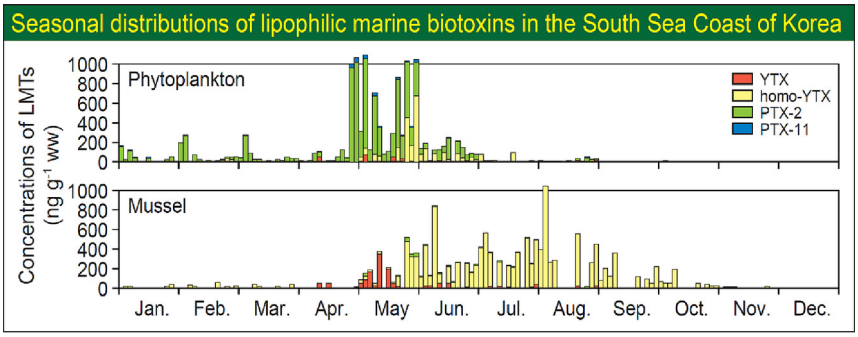
HIGHLIGHTS

- Various biotoxin-producing microalgae were found on the South Sea Coast of Korea.
- Relatively high concentrations of homo-YTX and PTX-2 were detected in phytoplankton.
- YTXs tended to accumulate for a more extended period compared to other LMTs.
- LMT compositions in SPATT varied compared to those in phytoplankton and mussels.
- SPATT is useful for monitoring trace concentrations of LMTs in the marine environment.

GRAPHICAL ABSTRACT



ARTICLE INFO

Editor: Julian Blasco

Keywords:
Shellfish
Causative microalgae
Lipophilic marine toxins
Passive sampler
Risk assessment

ABSTRACT

Aquaculture farms have been established along the South Sea Coast of Korea, supplying most of the seafood consumed domestically. However, annual harmful algal blooms pose a potential threat to seafood safety. This study aimed to determine the spatial and seasonal distributions of 12 lipophilic marine biotoxins (LMTs) in phytoplankton and mussels in the region in 2021. Solid-phase adsorption toxin tracking (SPATT) was used to monitor the cumulative compositions of LMTs in seawater. LMT concentrations were also determined in twelve commercially available species of domestic shellfish to evaluate the potential risks to human health. *Gonyaulux spinifera* and *Dinophysis acuminata*, causative microalgae of yessotoxins (YTXs) and pectenotoxins (PTXs), respectively, showed high densities in the region from May to July. This period corresponded to high LMT concentrations in phytoplankton and mussels. Phytoplankton mainly contained PTX-2 and homo-YTX, with a maximum concentration of 2300 ng g^{-1} wet weight (ww) in May. In contrast, mussels mainly contained homo-YTX and YTX, with a maximum concentration of 1300 ng g^{-1} ww in July. LMTs-producing microalgae showed low densities and concentrations after July, whereas mussels accumulated toxins until September. In the SPATT sampler, more diverse LMTs were detected than in seawater, phytoplankton, and mussels. For example, dinophysistoxin-1 and azaspiracid-2 were detected only in SPATT. YTXs were detected in domestic seafood samples, including mussels, red scallops, and pen shells, but the concentrations were below the European Food Safety Agency recommended standard of 3.75 mg YTX-eq. kg^{-1}. Moreover, the hazard quotient was less than 100 in all scenarios, indicating that the human health risk was not significant. This study provides valuable data on monthly distribution patterns of LMTs in the South Sea Coast of Korea and can serve as baseline data for future management policies of marine biotoxins.

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http://dx.doi.org/10.1016/j.scitotenv.2023.165472
Received 7 May 2023; Received in revised form 26 June 2023; Accepted 9 July 2023
Available online 12 July 2023

1. Introduction

Marine biotoxins are naturally produced by microalgae, which can cause harmful algal blooms (HABs). The occurrence and frequency of HABs have increased in recent decades due to changes in global climate, seawater circulation, and nutrient inputs (Griffith and Gobler, 2020; Tester et al., 2020). As a result, the regional scope, frequency, and intensity of shellfish toxin contamination are increasing (Hallegraeff et al., 2021). More than 200 shellfish toxins have been reported to date (Gerssen et al., 2011), and these toxins can accumulate in organisms, such as crustaceans, fishes, and bivalves through the food chain (Liu et al., 2019; Zhao et al., 2022). Human consumption of shellfish contaminated with highly toxic biotoxins can pose a significant health risk (Young et al., 2020). Shellfish toxins can be classified based on their symptoms as paralytic shellfish poisoning (PSP), diarrheic shellfish poisoning (DSP), neurotoxic shellfish poisoning, and amnesic shellfish poisoning (ASP) (Nicolas et al., 2017). They can also be divided into hydrophilic and lipophilic biotoxins based on their physicochemical properties (Chen et al., 2017). The hydrophilic biotoxins, such as saxitoxins and domoic acid, cause PSP and ASP, respectively. Lipophilic marine biotoxins (LMTs) include a diverse group of toxins, such as okadaic acid (OA), dinophysistoxins (DTXs), yessotoxins (YTXs), pectenotoxins (PTXs), brevetoxins, and azaspiracids (AZAs). It has been reported that LMTs account for 90% of all known biotoxins (Wang et al., 2015).

Various LMTs, including OA, DTXs, PTXs, YTXs, and AZAs, have been detected in seawater and organisms worldwide using traditional sampling methods (i.e., grab sampling) (Lane et al., 2010; Li et al., 2014; Liu et al., 2019). However, these methods only provide information at the time of sampling and lack temporal representativeness (Allan et al., 2006). Moreover, they may have difficulty detecting LMTs present in low concentrations in seawater. To overcome these limitations, a passive sampler called solid-phase adsorption toxin tracking (SPATT) was developed by MacKenzie et al. (2004). SPATT has been used to monitor various LMTs, such as OA, DTXs, PTXs, YTXs, and AZAs, in seawater (Fux et al., 2009; Pizarro et al., 2013; Rundberget et al., 2009; Zendong et al., 2016). Since SPATT accumulates LMTs throughout the deployment period, it is possible to detect toxins that exist only temporarily and therefore simulate the bioaccumulation of toxins in shellfish. Compared to monitoring shellfish, SPATT is relatively easy to extract and has fewer matrix effects, which helps avoid interference during the analytical process (Fux et al., 2008; Zendong et al., 2015). It offers the advantages of relatively good temporal resolution and low detection limits (Lane et al., 2010; MacKenzie et al., 2004).

HABs have occurred repeatedly on the South Sea Coast of Korea (Baek et al., 2020; Kim et al., 2019), where numerous fish and shellfish aquaculture farms are located (Lee et al., 2019). Most of the seafood consumed in Korea is farmed on the South Sea Coast; thus, biotoxin contamination can threaten human health. Various toxic planktons, such as *Alexandrium* spp., *Dinophysis acuminata*, *Gonyaulax spinifera*, and *Pseudo-nitzchia* spp., appear on the South Sea Coast (Kim et al., 2022). Among them, *G. spinifera* and *D. acuminata* are known as representative microalgae that produce YTXs and PTXs, respectively. Microalgae such as *Protoceratium reticulatum*, *Lingulodinium polyedrum*, *D. fortii*, and *D. caudata* are also known to produce LMTs (Paz et al., 2007; Pizarro et al., 2008).

Due to the frequent occurrence of HABs on the South Sea Coast, shellfish samples are regularly monitored for biotoxins to protect human health. However, regulations for other LMTs, such as YTXs, AZAs, and PTXs, have not yet been established, and regular monitoring has not been conducted. As global warming causes seawater temperatures to increase, the habitat range of harmful microalgae and poisonous subtropical marine organisms is expanding (Gobler et al., 2017). For instance, certain dinoflagellates that inhabit tropical and subtropical regions, such as *Gambierdiscus*, *Ostreopsis*, *Coolia*, and *Prorocentrum*, have been documented to produce various LMTs, such as ciguatoxins, spirolides, and YTXs, respectively (Steidinger and Tangen, 1997) In fact, the presence of these species was reported first in Korean coastal waters in 2009 (Kim et al., 2011). Therefore, there is a possibility that subtropical poisonous microalgae may appear in the coastal waters of South Korea, and new shellfish toxins may emerge. However, monitoring of YTXs, PTXs, and AZAs has been infrequent in Korea, and studies on their distributions in the environment are also insufficient.

The research hypothesis of the present study is that LMTs accumulated in phytoplankton and mussels in the South Sea Coast of Korea show seasonal distribution characteristics, which may be related to the appearance of causative microalgae. This study aims to investigate the spatiotemporal distribution of LMTs-producing microalgae on the South Sea Coast of Korea throughout 2021. It also aims to determine the distribution characteristics of LMTs in phytoplankton and mussels inhabiting the South Sea, and apply SPATT for LMTs monitoring. Finally, this study will investigate LMTs contamination in domestic seafood and evaluate the potential risk to human health.

2. Materials and methods

2.1. Water quality monitoring and sample collections

Field sampling was conducted at 13 sites along the South Sea Coast of Korea every month from January to December 2021 (see Fig. 1). Phytoplankton samples ($n = 156$) were collected using a 20-μm mesh size phytoplankton net and filtered through a 200-μm mesh to remove zooplankton and large suspended particles. The 20–200 μm suspended particulate matter (SPM) was then filtered again through 20-μm nylon net filters (Millipore, Merck, Darmstadt, Germany). Mussels ($n = 121$) were also collected monthly at the sites where phytoplankton was collected. More than ten individuals were collected per sampling site and pooled. Phytoplankton and mussels were immediately frozen and transported to the laboratory.

Seawater temperature, salinity, pH, and dissolved oxygen (DO) were measured in the field using a multi-sensor (YSI 6600v2, YSI Inc., Yellow Springs, OH). Dissolved inorganic nutrients, such as NO_2^-, NO_3^-, NH_4^+, PO_4^{3-}, and SiO_2, were analyzed using a nutrient auto-analyzer (LACHAT Quikchem 8000, Hach Company, Loveland, CO). Chlorophyll-a (chl-a) was extracted using 90% acetone in a dark room for 24 h and measured using a Turner-designed fluorometer (Turner BioSystems, Sunnyvale, CA) (Table S2) (Lim et al., 2019).

Domestic shellfish were obtained monthly from two seafood markets from March to October 2021 (Fig. 1). Twelve bivalve species, including mussels, red scallops, pen shells, oyster, and clams cultivated from the coast of Korea were purchased, transported to the laboratory, and shell length and shell width were measured ($n = 121$) (Table S1 of the Supplementary materials). The domestic bivalve samples were stored at −20 °C until analysis.

2.2. Preparation and field deployment of SPATT

To prepare the SPATT, 3 g of Diaion HP20 resin (Sigma-Aldrich, St. Louis, MO) was added between two 30-μm nylon meshes using a stainless holder washer. The surface area of the SPATT was approximately 47.5 cm^2 on both sides. To activate the resin, the SPATT was soaked in 100% methanol (MeOH) for 48 h. The MeOH was then removed using Milli-Q water, and sonication was performed to remove any remaining MeOH residue. The SPATT was stored in Milli-Q water at 4 °C until deployment (Lane et al., 2010). The SPATT was deployed at four sites (S2, S4, S7, and S12) at two-week intervals from July to September 2021 (Fig. 1). Surface seawater, phytoplankton, and mussels were collected during the deployment and retrieval of the SPATT. The collected samples and SPATT were placed in a cool box for transportation to the laboratory and stored at −20 °C until extraction.

2.3. Identification of phytoplankton species

To confirm the abundance and species composition of phytoplankton, 500 mL of seawater was collected and fixed with Lugol's solution (final concentration 3%). The fixed seawater was then concentrated to 50 mL. A

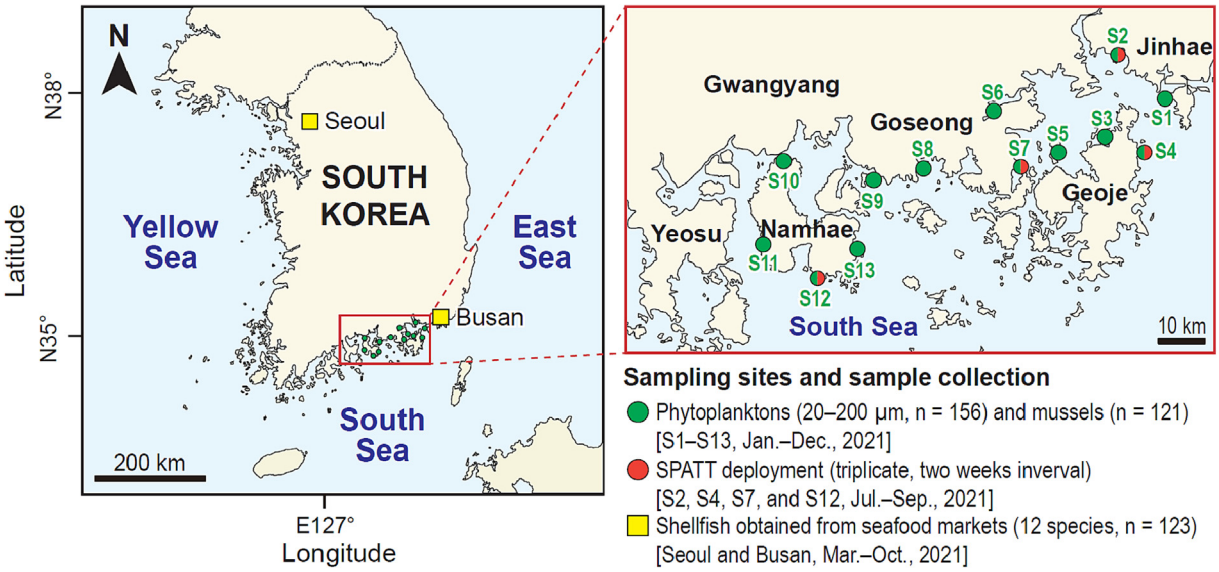

Fig. 1. Map showing the sampling sites of phytoplankton (20–200 μm suspended particulate matter), mussels, and domestic shellfish. Phytoplankton and mussels were collected monthly from sites S1–S13 along the South Sea Coast of Korea from January to December 2021. Domestic shellfish samples were obtained monthly from two seafood markets located in Seoul and Busan from March to October 2021. SPATT was deployed at sites S2, S4, S7, and S12 in two-week intervals from July to September 2021.

portion of the concentrated sample was transferred to a Sedgewick-Rafter Chamber for settling and species counting, and an optical microscope was used for analysis. Species that could be distinguished morphologically were identified at the species or genus levels.

2.4. Extraction and purification of LMTs

Analysis of LMTs in biological samples was performed following previously established methods (Kim et al., 2022). Briefly, the shells of the bivalves were removed, soft tissues were homogenized, and more than 20 samples were pooled and homogenized together. For extraction, 2 g of tissues were added to a centrifuge tube with 9 mL of MeOH. After swirling for 1 min, sonication was performed to increase extraction efficiency. The supernatant was collected by centrifugation and repeated twice to a final volume of 20 mL. The purification was performed to remove interfering substances using a solid phase extraction (SPE) cartridge (Strata-X, 30 mg, 3 mL, Phenomenex, Torrance, CA). The SPE cartridge was first conditioned by adding 3 mL of MeOH and Milli-Q water. The extract was diluted with Milli-Q water so that the MeOH:water ratio was less than 20%. After sample loading, 3 mL of 15% MeOH was added to rinse the cartridge. Three milliliters of MeOH containing 1% ammonium hydroxide were added and eluted, then dried under N_2 gas. Finally, the eluent was redissolved in 1 mL of MeOH containing 1% ammonium hydroxide and stored at −20 °C until analysis.

LMTs in seawater samples were extracted using SPE (Oasis HLB cartridges, 500 mg, 6 cc, Waters, Ireland) after removing SPM using GF/F filters (47 mm, Whatman, Maidstone, UK) (Li et al., 2014). One liter of filtered seawater was loaded onto the cartridge, and the cartridge was washed with 3 mL of 15% MeOH. The sample was eluted with 3 mL of MeOH containing 1% ammonium hydroxide and dried under N_2 gas. Finally, it was redissolved in 1 mL of MeOH containing 1% ammonium hydroxide and stored at −20 until analysis.

For LMTs analysis in phytoplankton (20–200 μm SPM), the frozen filters were defrosted and placed in a centrifuge tube. Then, 3 mL of MeOH was added to the tube, and it was swirled for 1 min. The extract was sonicated for 5 min, then centrifuged at 3500 rpm for 10 min to obtain the supernatant. This procedure was repeated three times to yield a final volume of 10 mL. The extract was passed through a 0.22-μm syringe filter and stored at −20 °C until analysis.

The retrieved SPATT was washed with Milli-Q water to remove suspended solids and salts and was then disassembled in the laboratory. The HP-20 resin was carefully transferred to an empty SPE cartridge and extracted with 24 mL of MeOH, as described previously (Fux et al., 2009; Zendong et al., 2016). The extract was concentrated under N_2 gas at 40 °C, redissolved in 1 mL of 100% MeOH, and stored at −20 °C until analysis.

2.5. Instrumental analysis

Certified reference standards of OA, DTX-1, DTX-2, YTX, homo-YTX (h-YTX), PTX-2, AZA-1, AZA-2, and AZA-3 were purchased from the National Research Council Canada (Ottawa, ON, Canada). PTX-11 was purchased from Sigma-Aldrich, and AZA-4 and AZA-5 were obtained from Cifga (Lugo, Spain). Target LMTs were analyzed using an Agilent 1290 infinity II LC system (Agilent Technologies, Santa Clara, CA) coupled with an Agilent 6470 triple quadrupole mass spectrometer (Agilent Technologies). Chromatographic separation was performed by a Waters X-Bridge C18 column (3.0 mm × 150 mm, 5.0 μm), and the column temperature was set at 25 °C (Fig. S1). The binary mobile phase consisted of (A) water and (B) 90% ACN/water (90:10, v/v), each containing 0.05% ammonium hydroxide. The target LMTs were quantitatively and qualitatively determined in multiple reaction monitoring (MRM) mode. Detailed LC conditions and MRM transitions are shown in Tables S3 and S4.

2.6. Quality control

To ensure the quality of the analytical results, linearity, limit of detection (LOD), limit of quantification (LOQ), recovery, and coefficient of variation were confirmed (Table S5). Calibration curves in the range of 1, 2, 5, 10, 25, and 50 ng mL^{-1} were used, and samples outside the range of the calibration curve were further diluted and analyzed. The LOD of LMTs was calculated as 3.143 times the standard deviation (SD) of mussels spiked with a standard (1 ng, $n = 7$), and the LOQ was calculated as 10 times the SD of mussels spiked with a standard. The recovery rate of each toxin was confirmed by spiking the standard material into blank mussels and then following the extraction method described above (25 ng, $n = 4$).

2.7. Statistical analysis

To confirm the normality of the sample, Shapiro-Wilks test was performed using R software version 4.1.3. In this study, the data did not follow a normal distribution. Spearman correlation analysis was performed to

assess any significant relationship between LMTs concentrations, environmental factors, and causative microalgae populations. The Mantel test based on Spearman's rank correlation was executed using the R packages vegan and dplyr. Significance levels were set at 0.01 and 0.05. LMTs concentrations less than the LOD were analyzed by treating them as LOD/2.

2.8. Exposure assessment of LMTs through shellfish consumption

The exposure assessment of LMTs was based on the consumption of bivalves, which was estimated from the Korean National Health and Nutrition Examination Survey (KNHANES, 2016–2018) (KDCA, 2020). In this study, risk assessment was performed on red scallops, clams, and mussels in which LMT was detected. To assess human exposure to shellfish toxins, consumption scenarios (S1–S4) were established according to the FAO/WHO guidelines (FAO/WHO, 2011; Kim et al., 2022). To estimate human exposure to shellfish toxins, the estimated daily intake (EDI) was calculated according to Eq. (1).

$$EDI = (Cs \times DIs)/BW \quad (1)$$

where Cs (ng g^{-1} ww), DIs (g d^{-1}), and BW (kg) are the concentration of LMTs in bivalves, daily intake of bivalves, and body weight, respectively. A value of 60 kg was used for body weight as suggested by KNHANES. To evaluate chronic effects of LMTs, the hazard quotient (HQ) and hazard index (HI) were calculated according to Eqs. (2) and (3).

$$HQ = (EDI/HbGV) \times 100 \quad (2)$$

$$HI = \Sigma_{n=1}^{i} HQ_n\% \quad (3)$$

Here, the health-based guidance value (HbGV) was calculated as 1500 μg YTX-eq. d^{-1} by multiplying the Korean mean BW (60 kg) with 25 μg YTX-eq. bw kg^{-1} d^{-1}, which is the acute reference dose (aRfD) value of YTX suggested by EFSA (EFSA, 2008). The HI was calculated by adding the HQ_n values estimated in each scenario.

3. Results and discussion

3.1. Spatiotemporal distributions of LMTs-producing microalgae

In the South Sea, the phytoplankton community was composed of Bacillariophyceae, Dinophyceae, Cryptophyceae, Raphidophyceae, and Dictyochophyceae, which made up an average of 59%, 12%, 28%, 0.07%, and 0.64%, respectively (Fig. S2 and Table S6). Diatoms were the dominant group throughout the South Sea Coast, and an increased abundance of Cryptophyceae was observed during the autumn season. This trend is consistent with previous studies (Baek et al., 2015, 2019), which suggest that Cryptophyceae thrive in environments where nutrients are not limiting and competition is low, such as during the autumn season (Baek et al., 2015; Klaveness, 1989).

The causative algae of YTXs and PTXs, *G. spinifera* and *D. acuminata*, respectively, were identified along the South Sea Coast of Korea (Fig. 2 and Table S7). *G. spinifera* appeared in February and reached its maximum density of 21 cells mL^{-1} in June. Its density subsequently decreased, and it was not observed at any of the sites after August. *D. acuminata* started to appear in April, and its maximum density was also observed in June (6 cell mL^{-1}). The density of *D. acuminata* remained relatively low until September and was not observed at any of the sites after October. A similar trend was observed in a study conducted in the same area in 2020, which reported a relatively high density of LMTs-producing microalgae during the summer (Kim et al., 2022). *Alexandrium* spp. and *Pseudo-nitzschia* spp., the potentially causative microalgae of PSP and ASP, respectively, were also observed. *Pseudo-nitzschia* spp. showed a relatively high density (up to 2150 cells mL^{-1}), suggesting potential contamination by ASP in the South Sea Coast of Korea.

Statistical analysis was conducted to identify environmental factors associated with the occurrence of LMTs-producing microalgae. A significant relationship was found between *D. acuminata* and water temperature ($p < 0.01$), but not between *G. spinifera* and water temperature ($p > 0.05$). During the period from April to June, when the density of *D. acuminata* was relatively high, the average water temperature ranged from 16 to 22 °C. This temperature range is known to be optimal for the growth of *D. acuminata*, and previous studies have shown that *D. acuminata* has a

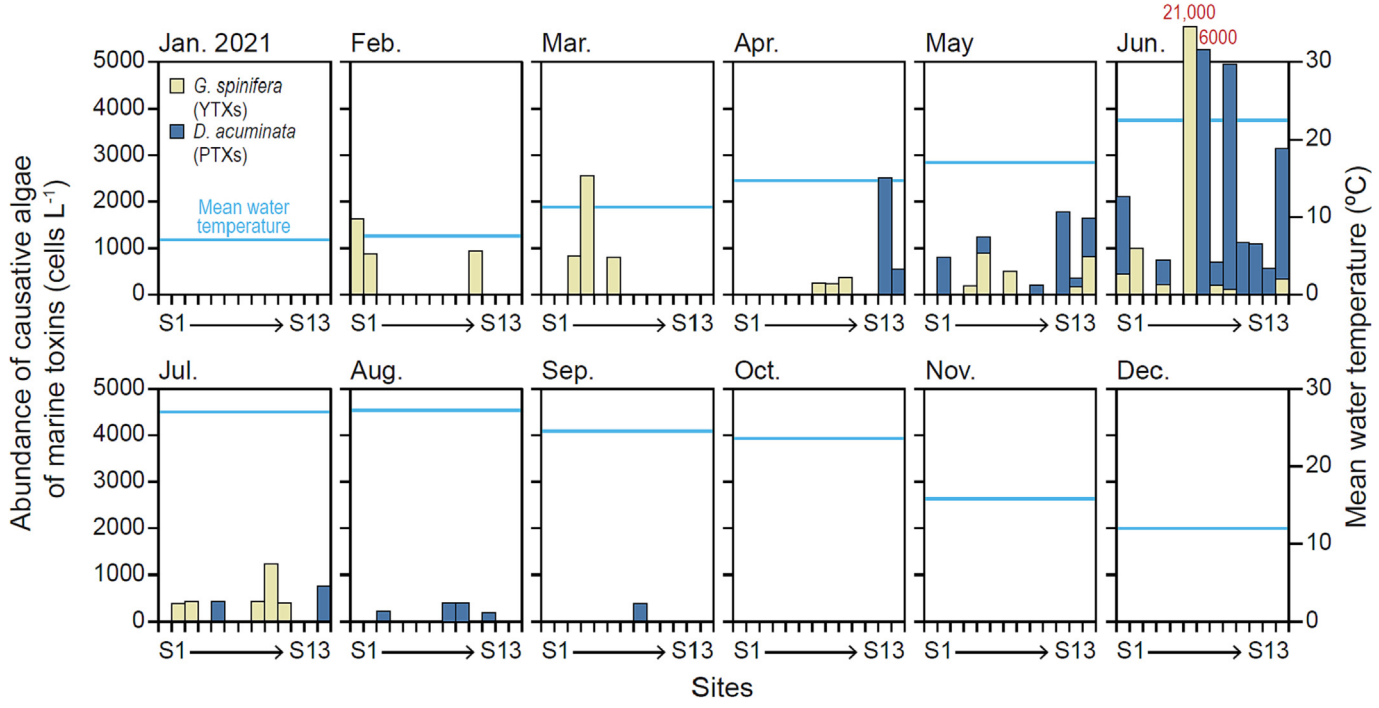

Fig. 2. Abundance of *Gonyaulux spinifera* and *Dinophysis acuminata*, the causative microalgae of YTXs and PTXs, respectively, along the South Sea Coast of Korea from January to December 2021. Blue lines represent the average seawater temperature.

higher growth rate and the highest toxin production at temperatures ranging from 18 to 24 °C (Fiorendino et al., 2020; Kamiyama et al., 2010). On the other hand, *G. spinifera* is a photophilic organism that can thrive in a wide range of water temperatures (5–25 °C), which may explain why no significant relationship was observed between this species and water temperature (Kim et al., 2022). As relatively high densities of LMTs-causative microalgae were observed during the summer season, it is expected that LMTs contamination will also be relatively high during this period and that this trend may be repeated every year.

3.2. Distribution characteristics of LMTs in phytoplankton

Out of the 12 LMTs analyzed, YTX, h-YTX, PTX-2, and PTX-11 were detected in phytoplankton samples, and OA, DTXs, and AZAs were not detected in any of the samples (Fig. 3a and Table S8). The concentrations of YTX, h-YTX, PTX-2, and PTX-11 in phytoplankton ranged from <LOD to 0.06 μg g^{-1} wet weight (ww), <LOD to 0.64 μg g^{-1} ww, <LOD to 2.2 μg g^{-1} ww, and <LOD to 0.3 μg g^{-1} ww, respectively. YTXs were detected in phytoplankton samples beginning in February, and decreased after reaching their maximum concentrations in May. This trend is thought to be related to the density of the causative microalgae. In this study, a significant relationship was found between the concentration of YTXs in phytoplankton and the density of *G. spinifera* (Fig. 4a, $p < 0.01$), a result that is consistent with previous studies (Kim et al., 2022). YTX was detected in phytoplankton samples in April and May but not afterward. In contrast, h-YTX concentrations were higher in May and June. These changes in composition are likely due to population changes in the microalgae that produce YTXs. Although not confirmed in this study, it is possible that *P. reticulatum* or *L. polyedrum*, known producers of YTXs, may have appeared (Liu et al., 2019). According to previous studies, *L. polyedrum* was reported to appear at a density of less than 1 cells mL^{-1} (Yoon et al., 2020), and *P. reticulatum* was found in the form of a cyst in the South Sea Coast (Pospelova and Kim, 2010).

PTXs were detected in phytoplankton beginning in the winter (January and February), peaking in late spring (April and May), and continuing until summer. This distribution pattern is similar to that of YTXs described above, and appears to be related to the density of causative microalgae. In this study, *D. acuminata* was first identified in late spring (April), and its density decreased after reaching the maximum in summer. Similarly, PTXs in phytoplankton were detected in relatively high concentrations from April to May, continued until June, and then decreased. A previous study also confirmed a significant relationship between the concentration of PTXs in phytoplankton and the density of microalgae that cause PTXs ($p < 0.01$) (Kim et al., 2010). The composition of LMTs in phytoplankton of the South Sea Coast of Korea showed monthly variations. PTX-2 was detected in March and April, and YTX was detected in small amounts in April and May. From May to June, h-YTX was the predominant LMTs.

This study reported lower LMT concentrations from June to December than those reported in 2020 from the same region (Kim et al., 2022). This might be due to the lower densities of *G. spinifera* and *D. acuminata* compared to 2020. In 2020, the average densities of *G. spinifera* and *D. acuminata* were 1.2 cells mL^{-1} and 0.3 cells mL^{-1}, respectively, whereas in 2021 they were 0.4 cells mL^{-1} and 0.26 cells mL^{-1}. Overall, the spatio-temporal distribution of LMT concentrations in phytoplankton is thought to be significantly influenced by the density of the causative algae. In the South Sea Coast of Korea, a relatively high concentration of LMTs is observed in the spring and summer seasons every year due to correspondingly high densities of LMTs-producing microalgae.

3.3. Bioaccumulation of LMTs in mussels

YTX, h-YTX, and PTX-2 were detected in mussels inhabiting the South Sea Coast (Fig. 3b and Table S9). The concentrations of YTX, h-YTX, and PTX-2 in mussels ranged from <LOD to 0.14 μg g^{-1} ww, <LOD to 1.3 μg g^{-1} ww, and <LOD to 0.017 μg g^{-1} ww, respectively. LMTs in

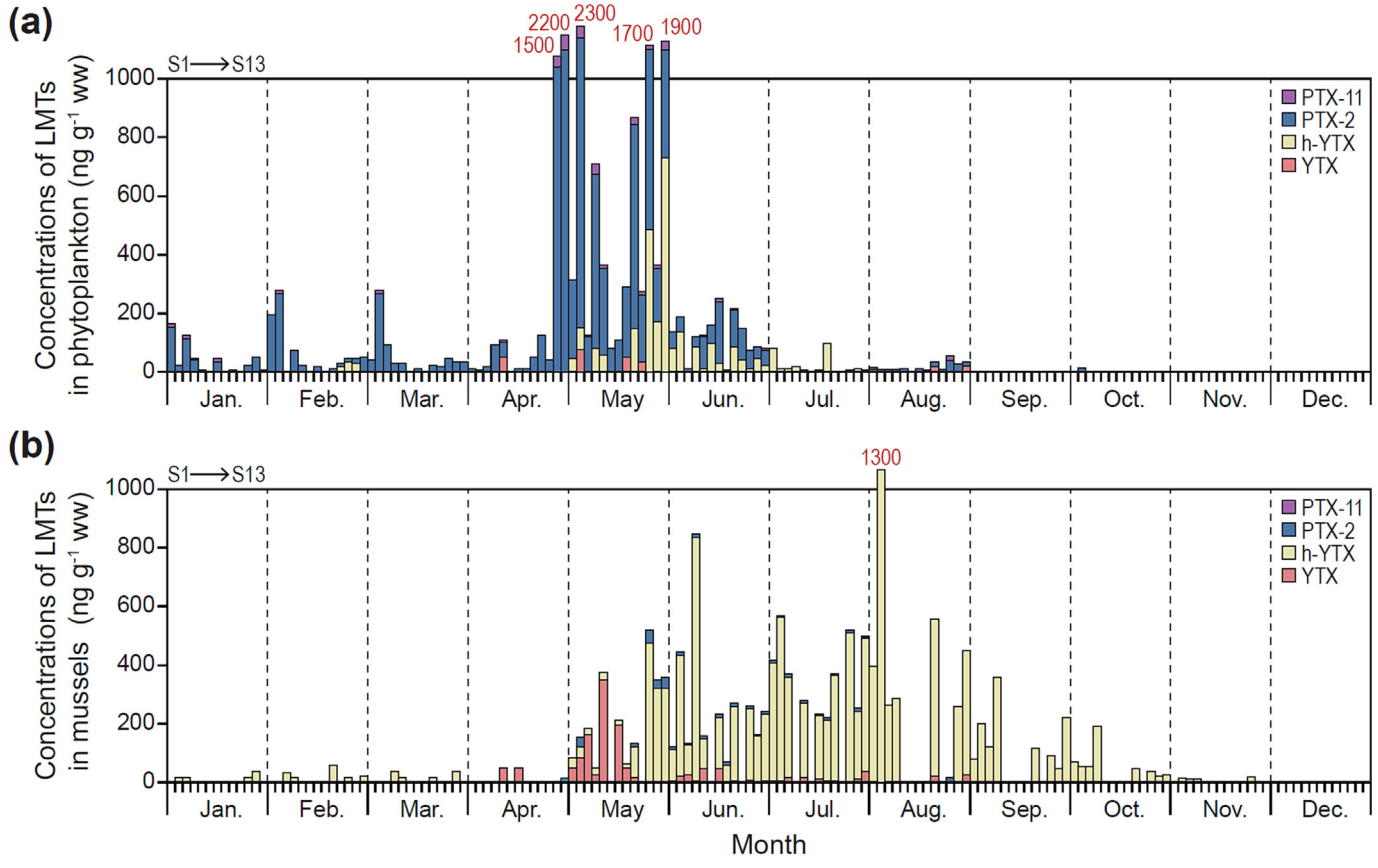

Fig. 3. Concentrations of LMTs in (a) phytoplankton (20–200 μm SPM) and (b) mussels collected from the South Sea Coast of Korea from January to December 2021.

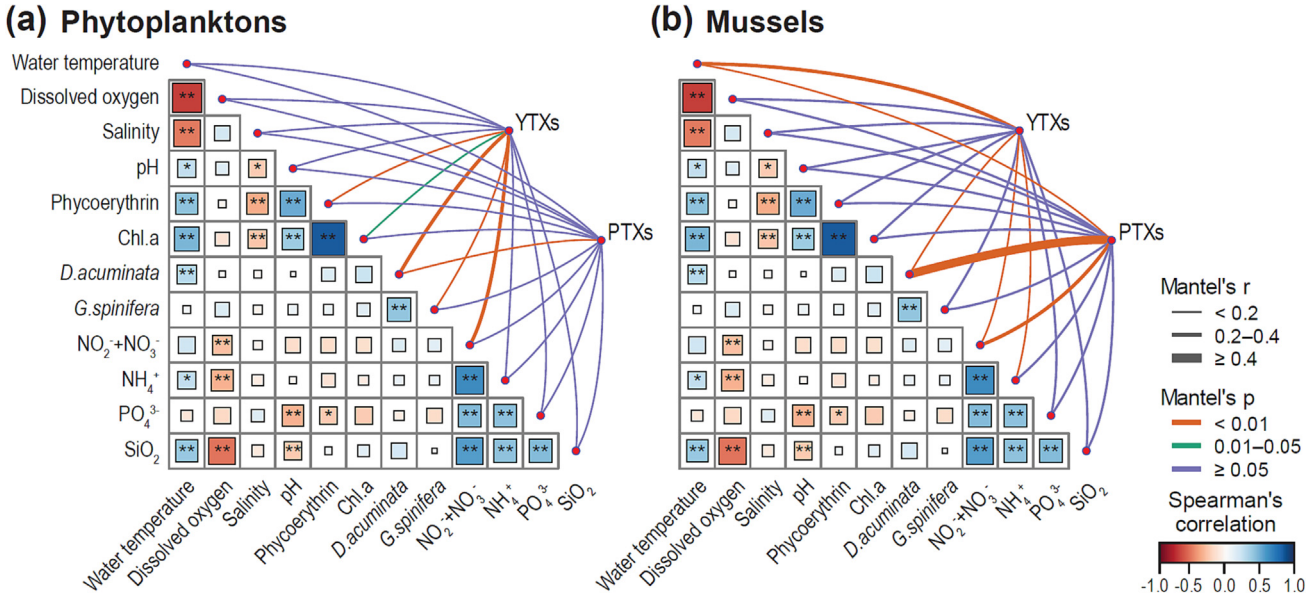

Fig. 4. Relationships between environmental factors and concentrations of LMTs in (a) phytoplankton (20–200 μm SPM) and (b) mussels along the South Sea Coast of Korea from January to December 2021. Spearman's rank correlation coefficient is shown as a color gradient, and an asterisk indicates the statistical significance ($*p < 0.05$ and $**p < 0.01$). Line width corresponds to Mantel's r statistic, and line color denotes the statistical significance based on 99 permutations.

mussels were first detected in spring (April–May) and showed the highest concentration in summer (August). This trend is similar to that observed for LMTs in phytoplankton. Thus, the concentration of YTXs in mussels showed significant relationships with both the density of causative microalgae ($p < 0.05$) and the concentration of YTXs in phytoplankton ($p < 0.01$). In the case of PTX concentrations in mussels, a significant relationship was confirmed with *D. acuminata* through the Mantel test ($p < 0.01$, Fig. 4b). A significant relationship between the density of causative microalgae and toxin concentrations in shellfish has also been reported in previous studies (Hassoun et al., 2021; Kim et al., 2022). Thus, the density of causative microalgae and the concentration of LMTs in phytoplankton appear to be important factors for the accumulation of LMTs in mussels.

The composition of YTXs in mussels was found to be similar to that in phytoplankton. A relatively high concentration of YTX appeared from April to May, and the concentration of h-YTX increased after May. Thus, the concentration and composition of YTXs in mussels seem to accurately reflect those in phytoplankton. In contrast, the concentration of PTXs in mussels was relatively low compared to that in phytoplankton, and in most sites, it was not detected. This finding is consistent with previous studies (Kim et al., 2022) and can be attributed to the difference in the half-lives of YTXs and PTXs in mussels. The half-life of PTXs in mussels is known to be 2.9 d, whereas the half-life of YTXs ranges from 20 to 24 d (Aasen et al., 2005; Nielsen et al., 2016). Thus, PTXs are metabolized in mussels and excreted rapidly, while YTXs accumulate over longer periods of time. In addition, the result of the present study indicated that, in shellfish, h-YTX accumulated for longer periods of time than YTX.

The maximum concentration of LMTs in mussels was observed approximately two months later than the maximum concentration in phytoplankton (Fig. S3). This phase lag has also been reported in previous studies (Kim et al., 2022; Li et al., 2017), indicating that LMTs accumulate for a longer period in mussels than in phytoplankton. Thus, continuous monitoring is necessary because shellfish toxin contamination may occur not only during the phytoplankton bloom but also after it subsides. Data from the same area in 2020 also showed relatively high concentrations of LMTs in shellfish during the summer, suggesting that this trend may occur every year. Therefore, consuming shellfish produced on the South Sea Coast in the summer season may pose a potential health risk.

3.4. Compositions of LMTs in SPATT and environmental samples

OA, DTX-1, YTX, h-YTX, PTX-2, and AZA-2 were detected in the SPATT, with concentrations ranging from 1.9 to 120 ng g^{-1}, 2.6 to 31 ng g^{-1}, <LOD to 3.5 ng g^{-1}, 4.9 to 152 ng g^{-1}, 3.9 to 84 ng g^{-1}, and <LOD to 2.0 ng g^{-1}, respectively (Fig. 5a and Table S10). The concentration of LMTs in the SPATT did not show a clear seasonal trend. In a previous study, it was demonstrated that LMT concentrations in SPATT reflect the densities of causative microalgae (García-Altares et al., 2016), and the results of the present study were thought to follow a similar pattern.

LMTs were detected in all seawater samples collected during the SPATT deployment (Fig. 5b). The concentration of LMTs varied depending on the sampling period, but none of the differences between times and sites were significant ($p > 0.05$). The LMTs in seawater were confirmed to be OA, h-YTX, and PTX-2, with concentrations ranging from 1 to 1.7 ng L^{-1}, 0.63 to 1.1 ng L^{-1}, and 0.13 to 1.3 ng L^{-1}, respectively. Notably, OA was detected in seawater, but not in phytoplankton or mussels, and had an average composition of 40% during the deployment period (Fig. 5b). These results suggest that OA is present in trace amounts in seawater rather than phytoplankton because it is a relatively water-soluble compound compared to other LMTs (Wu et al., 2019). PTX-2 has been reported to be the most hydrophobic among the LMTs (Wu et al., 2019). Thus, PTX-2 has a high affinity for SPM and exhibits lower concentrations in seawater. LMTs are initially produced by microalgae and exist in particulate form within cells, and they can be released into seawater through cell destruction. Dissolved LMTs can be degraded by microorganisms, with the persistence of these biotoxins varying depending on their specific properties (Shetty et al., 2010).

LMTs were detected in all phytoplankton and mussels collected during the SPATT deployment period (Fig. 5c and d). h-YTX and PTX-2 were detected in phytoplankton (Fig. 5c), and YTX and h-YTX in mussels (Fig. 5d). In the phytoplankton and mussel samples collected during the SPATT deployment period, higher LMT concentrations were observed in the samples collected first, and then the concentrations tended to decrease over time. h-YTX was the most abundant LMT detected in phytoplankton and mussels, comprising an average of 89.2% and 98.4%, respectively, during the deployment period. LMT concentrations decreased as the density of causative algae decreased from summer to autumn, and the relative composition of h-YTX likewise decreased; however, the relative composition of PTX-2 increased.

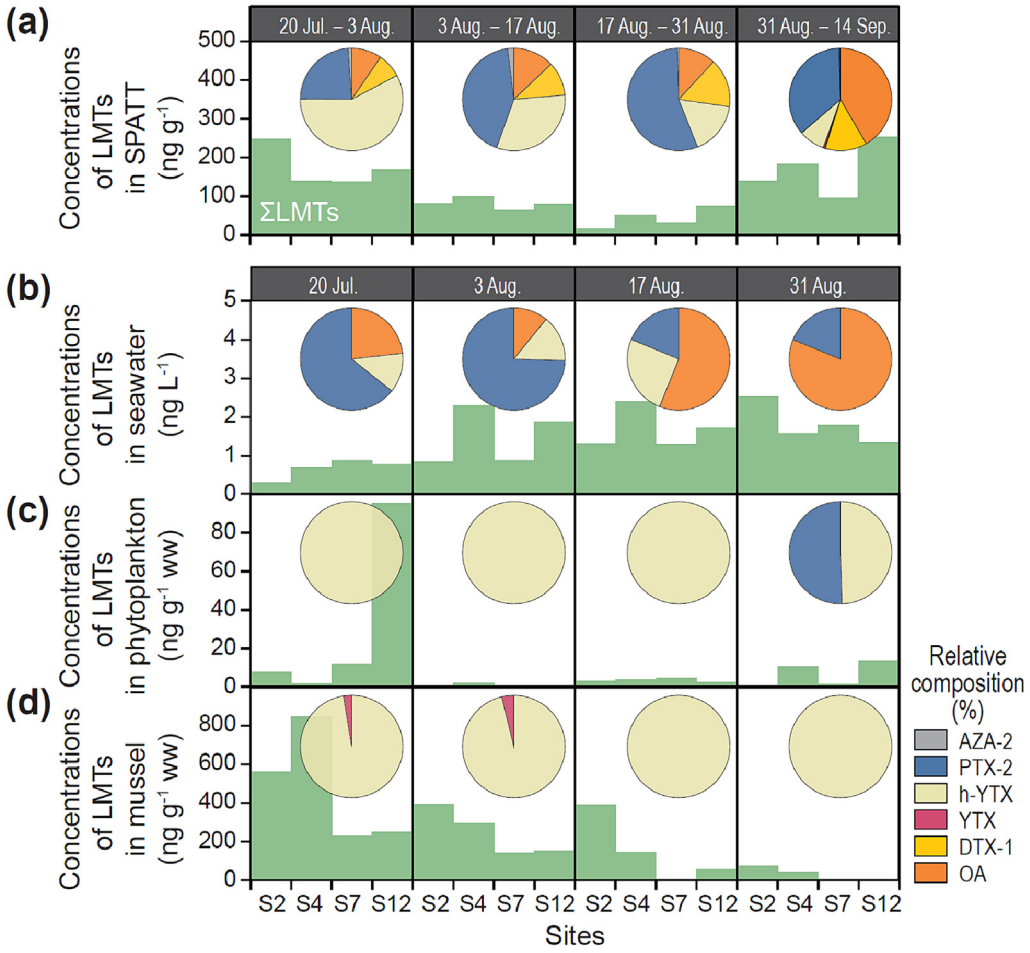

Fig. 5. (a) Concentrations of LMTs in SPATT deployed at sites S2, S4, S7, and S12 from 20 July to 14 September 2021. Concentrations of LMTs in (b) seawater, (c) phytoplankton (20–200 μm SPM), and (d) mussels collected from sites S2, S4, S7, and S12 along the South Sea Coast of Korea during deployment and retrieval of SPATT.

Compared to biological and seawater samples, a wider range of LMTs were detected in the SPATT extracts. During the deployment period, the average compositions of OA, DTX-1, YTX, h-YTX, PTX-2, and AZA-2 were 19%, 12%, 0.16%, 29%, 40%, and 0.90%, respectively. DTX-1 and AZA-2 were detected in the SPATT for the first time and were present in lower concentrations than other LMTs. This suggests that passive sampling devices such as SPATT can accumulate even trace amounts of dissolved toxins in seawater, since they are exposed over a longer period of time than grab sampling (Kim et al., 2021). Moreover, since SPATT resin does not undergo biotransformation or metabolism, it is thought to better reflect the composition of LMTs in the environment compared to biological samples. Thus, simultaneous analysis of SPATT and multimedia samples (i.e., seawater and biota) is expected to provide useful data for understanding the dynamic behavior of LMTs in the marine environment.

3.5. Exposure assessment of LMTs through shellfish consumption

Out of 121 seafood samples, YTX and h-YTX were detected in 20 samples and the other LMTs were not detected at all. Among the 12 species tested, YTXs were only detected in three species (pen shells, mussels, and red scallops), in concentrations as high as 36 ng YTX-eq. g^{-1} ww, 91 ng YTX-eq. g^{-1} ww, and 143 ng YTX-eq. g^{-1} ww, respectively (Table 1). YTXs were first detected in domestic seafood in March and showed a trend similar to that in mussels collected from the South Sea, reaching its maximum concentration during the summer season. Previous studies of YTXs in domestic seafood have also reported higher concentrations in summer (Kim et al., 2022). This is likely because much domestic seafood originates in Yeosu, Tongyeong, and Myeongji, which are all located on the South Sea Coast. Thus it is not surprising that LMT concentrations in domestic seafood reflect LMT concentrations in phytoplankton.

Monthly risk assessment was conducted for the domestic shellfish in which LMTs were detected. Consumption rates of pen shells, mussels, and red scallops ranged 0.03–6.97 g d^{-1}, 1.1–15.19 g d^{-1}, and 0.24–23.73 g d^{-1}, respectively (Table S11). Considering risk assessment as a function of shellfish consumption, higher HQs were found in May–August, and higher HQs were found in mussels and red scallops than in pen shells. However, in all intake scenarios, the HQ did not exceed 100 and the HI was less than 1 (Table 1), indicating no risk to human health (Evans et al., 2015). In addition, since the concentration detected in this study was lower than the EFSA guideline of 3.75 mg YTX-eq. kg^{-1}, there was no toxicity risk (EFSA, 2008). Overall, the concentration of LMTs in domestic bivalves seems to reflect the concentration of organisms inhabiting the origin (South Sea). Although toxins were detected in domestic seafood during spring and summer, the risk was considered low because they were detected at low concentrations. However, because seafood is a staple for many people, continuous monitoring is necessary to prevent possible human poisoning accidents and protect public health.

4. Conclusions

This study investigated the occurrence of LMT-causative microalgae and the bioaccumulation characteristics of LMTs in phytoplankton and mussels on the South Sea Coast of Korea. Additionally, SPATT was applied

Table 1
Concentrations and hazard quotient (HQ) of LMTs in domestic seafood samples.

Month	Origin	Species	YTX (ng g^{-1} ww)	homo-YTX (ng g^{-1} ww)	Sum of YTXs (ng YTX-eq. g^{-1} ww)	HQ (%) S1	S2	S3	S4	HI
March	Yeosu	Pen shell	<LOD[a]	11	11	0.00002	0.0051	0.00006	0.0001	0.00528
	Myeongji	Pen shell	<LOD	20	20	0.00004	0.0093	0.0001	0.00014	0.00958
April	Yeosu	Pen shell	<LOD	17	17	0.00003	0.0079	0.00009	0.00012	0.00814
		Mussel	<LOD	22	22	0.0016	0.022	0.003	0.014	0.0406
		Red scallop	<LOD	16	16	0.00026	0.025	0.00064	0.0009	0.0268
	Tongyoung	Red scallop	<LOD	14	14	0.00022	0.022	0.00056	0.0008	0.02358
	Myeongji	Mussel	<LOD	14	14	0.00103	0.014	0.0019	0.0089	0.02583
May	Yeosu	Pen shell	12	12	24	0.00005	0.011	0.00012	0.00017	0.01134
		Mussel	<LOD	38	38	0.0028	0.038	0.0051	0.024	0.0699
		Red scallop	<LOD	93	93	0.0015	0.15	0.0037	0.0052	0.1604
	Tongyoung	Red scallop	<LOD	32	32	0.00051	0.051	0.0013	0.0018	0.05461
	Myeongji	Mussel	27	51	78	0.0057	0.079	0.011	0.049	0.1447
June	Yeosu	Mussel	<LOD	44	44	0.0032	0.045	0.006	0.028	0.0822
	Tongyoung	Red scallop	<LOD	143	143	0.0023	0.23	0.0057	0.008	0.246
	Myeongji	Pen shell	17	19	36	0.00007	0.017	0.0002	0.00025	0.01752
	Tongyoung	Red scallop	<LOD	74	74	0.0012	0.12	0.003	0.0041	0.1283
	Myeongji	Mussel	<LOD	15	15	0.0011	0.015	0.002	0.0095	0.0276
August	Yeosu	Mussel	37	51	88	0.0065	0.089	0.012	0.056	0.1635
		Red scallop	<LOD	71	71	0.0011	0.11	0.0028	0.0039	0.1178
	Myeongji	Mussel	16	75	91	0.0067	0.092	0.012	0.058	0.1687

[a] <LOD: Below limit of detection.

to monitor LMTs, and trace amounts of LMTs that were not detected by biological monitoring were found in SPATT. High concentrations of LMTs were detected in the summer months, and accordingly, LMTs were also detected in domestic seafood. Although the concentration of LMTs detected in domestic seafood was low, previously undetected toxins were also identified. To date, there are no regulations on these toxins in South Korea. Therefore, it is necessary to establish regulations and continuously monitor these LMTs, and SPATT is expected to be effective at monitoring such trace LMTs.

CRediT authorship contribution statement

Mungi Kim: Conceptualization, Investigation, Formal analysis, Data curation, Visualization, Writing - original draft. **Seongjin Hong:** Conceptualization, Methods development, Writing - review & editing, Project administration, Funding acquisition, Supervision. **Young Kyun Lim:** Investigation, Formal analysis, Data curation. **Jihyun Cha:** Investigation, Formal analysis, Data curation. **Youngnam Kim:** Investigation, Formal analysis, Data curation. **Chang-Eon Lee:** Investigation, Formal analysis. **Ji Nam Yoon:** Investigation, Formal analysis, Data curation. **Hee-Seok Lee:** Investigation, Data curation, Writing - review & editing. **Seung Ho Baek:** Conceptualization, Investigation, Formal analysis, Data curation, Writing - review & editing.

Data availability

Data will be made available on request.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This research was supported by grant (20163MFDS641) from the Ministry of Food and Drug Safety, Korea.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2023.165472.

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