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河北省近岸贝类中麻痹性贝毒污染特征 及风险评估*

李晓康^{1,2} 吴海燕² 程玲³ 车瀚钰²
刘丽娟³ 牟海津⁴ 谭志军^{2,5} 郑关超^{2①}

(1. 上海海洋大学食品学院 上海 201306; 2. 农业部水产品质量安全检测与评价重点实验室
中国水产科学研究院黄海水产研究所 山东 青岛 266071; 3. 山东省海洋生态修复重点实验室
山东省海洋资源与环境研究院 山东 烟台 264006; 4. 中国海洋大学食品科学与工程学院
山东 青岛 266003; 5. 海水养殖生物育种与可持续产出全国重点实验室
中国水产科学研究院黄海水产研究所 山东 青岛 266071)

摘要 自2016年河北省发生贻贝中麻痹性贝毒(paralytic shellfish toxins, PSTs)超标且中毒事件以来, 该区域主产贝类中PSTs安全风险受到研究者和管理部门的密切关注。以2022年3—6月在河北省近岸采集的6种主产贝类为研究对象, 采用液相色谱质谱联用法(LC-MS/MS)分析了PSTs的残留状况并进行急性暴露评估, 以了解河北省近岸贝类中PSTs污染的变化情况及消费风险。整体来看, 不同贝类样品中均有PSTs检出, 且4月份贝类样品风险最高, 但所有样品均未超过安全限量标准; 该区域贝类中PSTs主要组分为GTx1&4和GTx2&3, 且紫贻贝(*Mytilus galloprovincialis*)中含量最高, 其次为毛蚶(*Scapharca subcrenata*); 采用最高含量进行急性暴露评估发现, 所有贝类样品均处于安全可接受状态。虽然河北近岸贝类中PSTs最高含量呈降低趋势, 但仍存在一定残留及安全风险, 后续需持续围绕该海域进行长期性调查研究, 为我国贝类毒素监管和食用安全提供基础参考数据。

关键词 麻痹性贝毒; 河北; 贝类; 污染特征; 安全评估

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麻痹性贝毒(paralytic shellfish toxins, PSTs)是一类急性神经毒素, 具有近60种同系物(Qiu *et al.*, 2018), 根据R4位点取代基的差异, 可将PSTs分为3类: 氨基甲酸酯类毒素(STX、NEO、GTx1&4和GTx2&3)、脱氨甲酰基类毒素(dcSTX、dcNEO、

dcGTx1&4和dcGTx2&3), N-磺酰氨基甲酰基类毒素(C1&2、C3&4、GTx5和GTx6)。PSTs主要由海洋甲藻和淡水蓝绿藻产生, 其中, 海洋甲藻包括亚历山大藻属(*Alexandrium*)多个物种、链状裸甲藻(*Gymnodinium catenatum*)、巴哈马梨甲藻(*Pyrodinium*

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① 通信作者: 郑关超, 工程师, E-mail: zhenggc@ysfri.ac.cn

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bahamense)(Yu *et al.*, 2021)。双壳贝类滤食产毒藻后,造成 PSTs 在体内积累,食用有毒贝类对人体健康造成巨大威胁。PSTs 中毒后会出现头晕、恶心、肌肉麻痹、呼吸困难等症状,甚至死亡(Liu *et al.*, 2017)。据估计,全球每年约发生 2 000 起 PSTs 中毒事件(Wang *et al.*, 2016; Brown *et al.*, 2019)。我国是世界上最大的水产品养殖国家,2022 年贝类产量约为 1589 万 t(农业农村部渔业渔政管理局等, 2023),同时也有庞大的贝类消费者。近几年因食用有毒贝类造成的中毒事件频发,例如福建贻贝中毒事件和香港虾夷扇贝中毒事件等(梁玉波等, 2019)。我国 PSTs 中毒事件发生呈现出分布区域广、区域性风险反复、产毒藻多样性、季节性差异明显等特点,可造成多人出现急性中毒症状,甚至死亡,致死率较高,不仅严重威胁我国消费者健康,也不利于地区的社会稳定(包振民等, 2021; 范礼强等, 2021)。

河北省位于我国华北地区,海岸线长 484 km,具有丰富的渔业资源,其中,2022 年海水养殖产量约为 58 万 t(农业农村部渔业渔政管理局等, 2023)。近年来,河北近岸尤其是秦皇岛沿岸,多次在双壳贝类中检测到 PSTs。其中,2016 年秦皇岛发生严重的贝类中毒事件,毒素含量超出安全限量标准 800 μg STXeq/kg 的 65 倍,引起该中毒事件的主要肇事藻种为链状亚历山大藻(*Alexandrium catenella*)(Yu *et al.*, 2021)。Wu 等(2022)研究发现,近 5 年来,每年 4 月份秦皇岛地区易发生链状亚历山大藻大量繁殖,并在贻贝、扇贝中多次检出 PSTs。Cao 等(2023)研究表明,2021 年 5 月和 2022 年 5 月秦皇岛地区紫贻贝(*Mytilus galloprovincialis*)、栉孔扇贝(*Azumapecten farreri*)和脉红螺(*Rapana venosa*)样品均检出 PSTs。

目前,对河北省 PSTs 污染情况调查主要集中在秦皇岛山海关海域,且主要是贻贝和扇贝样品,还缺少对河北省近岸其他城市以及多种不同贝类样品的调查,风险评估研究也较少(Liu *et al.*, 2017; 郑旭颖等, 2023)。本研究在 2022 年对唐山和秦皇岛两地多个海域采集的贻贝、扇贝、牡蛎、蚶类、蛤类 5 类 6 个品种贝类进行连续 PSTs 调查,通过液相色谱-质谱联用法(LC-MS/MS)检测,探究河北省近岸 PSTs 污染特征以及对消费者的危害,旨在为我国贝类毒素监管和食用安全提供基础数据。

1 材料与方法

1.1 样品采集

2022 年 3—6 月份在秦皇岛山海关海域(39.93°~

39.96°N, 119.77°~119.81°E)(39 个贝样)、北戴河海域(39.74°~39.84°N, 119.40°~119.54°E)(37 个贝样)、南戴河海域(39.78°~39.79°N, 119.44°~119.51°E)(3 个贝样)和河北唐山曹妃甸海域(39.02°~39.97°N, 118.33°~118.62°E)(24 个贝样)4 个海域自行网捕采集 5 类 6 个品种贝类样品,包括紫贻贝、海湾扇贝(*Argopecten irradians*)、太平洋牡蛎(*Crassostrea gigas*)、毛蚶(*Scapharca subcrenata*)、魁蚶(*Scapharca broughtonii*)和菲律宾蛤仔(*Ruditapes philippinarum*),共 103 个样品,依照《水产品抽样规范》(GB/T 30891-2014)要求进行贝类样品采样,贻贝、扇贝、蚶类和蛤类样品质量不少于 3 kg,牡蛎样品质量不少于 5 kg。去除贝壳后,能够用于检测的样品量不少于 700 g。采集样品后在 0~4 °C 冷藏情况下运至实验室后,于 -20 °C 保存待测。

1.2 实验材料

AB-5500 QTRAP 液相色谱-四极杆/离子阱复合质谱(AB SCIEX 公司,美国),配有电喷雾离子源(ESI); Himac CR 22G II 高速离心机(Hitachi 公司,日本); XW-80A 旋涡混合器(上海医大仪器厂); 恒温水浴锅(上海蓝凯仪器仪表有限公司); Milli-Q 超纯水仪(Millipore 公司,美国); 固相萃取装置(Supelco 公司,美国)。

甲酸、甲酸铵(色谱级,瑞士 Fluka 公司); 乙酸(色谱级, Thermo 公司,美国); 乙腈(质谱级, Merck 公司,美国); 超纯水(18.2 M Ω cm); 氨水(色谱级, Sigma 公司,美国); 石墨化碳黑固相萃取柱(ENVI-CarbTM, 250 mg/3 mL, Supelco 公司,美国); 其他未作特殊说明试剂均为分析纯。

毒素标准溶液(STX、NEO、dcSTX、dcNEO、dcGTx2&3、GTx1&4、GTx2&3、GTx5 和 C1&2)购自加拿大国家研究理事会海洋生物研究所。

1.3 毒素检测

1.3.1 贝类样品前处理 在室温下,使冷冻的样品呈半冷冻状态,用清水将贝壳外表洗净后去壳匀浆,准确称取(5.00 $\pm$ 0.05) g 试样于 50 mL 离心管中,加入 5 mL 1%乙酸水溶液,涡旋混合 90 s。将样品置于沸水中煮沸 5 min,取出置于流水下迅速冷却至室温。4 500 r/min 离心 10 min,移取上清液于 10 mL 容量瓶中,向残渣中加入 3 mL 1%乙酸水溶液,充分均匀后,4 500 r/min 离心合并上清液,定容 10 mL。移取上述提取液 1 mL 于 2 mL 离心管中,加入 5 μL 氨水,涡旋混匀,10 000 r/min 离心 5 min。依次用 3 mL 乙腈、

3 mL 20%乙腈水溶液、3 mL 0.1%氨水溶液活化 Supelco ENVI-Carb 固相萃取柱,加入 500 μ L 提取液,再用 700 μ L 超纯水淋洗,正压挤干,最后用 1 mL 75% 乙腈水溶液洗脱混匀,定容 1 mL,过 0.22 μ m 滤膜于进样小瓶中,4 $^{\circ}$ C 下保存,供 LC-MS/MS 分析。

1.3.2 LC-MS/MS 分析 液相色谱柱为 TSK-Amide-80 柱(2.0 mm $\times$ 15.0 cm, 3 μ m);进样量为 5 μ L,柱温 40 $^{\circ}$ C;流动相 A 为含 2 mmol/L 甲酸铵、50 mmol/L 甲酸的水溶液;流动相 B 为含 2 mmol/L 甲酸铵、

50 mmol/L 甲酸的 95%乙腈溶液。梯度洗脱条件参考 张海涛等(2023): 0~3.0 min, 80% B; 3.1~5.0 min, 80%~40% B; 5.1~10.0 min, 40% B; 10.1~11.0 min, 40%~80% B; 11.1~13.0 min, 80% B; 流速: 0.35 mL/min。采用多反应监测(MRM)检测方式,离子源温度为 550 $^{\circ}$ C,喷雾电压为 5 000 V、-4 500 V,气帘气压力为 20 psi,雾化气压力为 30 psi,辅助加热器压力为 30 psi,碰撞气 Medium。目标化合物质谱条件参数见表 1。

表 1 目标化合物质谱条件参数
Tab.1 Parameters of MS conditions for target compounds

麻痹性贝类毒素组分 PSTs component	定性离子对 Qualitative ion pair /(m/z)	碰撞能量 Collision energy /(eV)	定量离子对 Quantitative ion pair/(m/z)	碰撞能量 Collision energy /(eV)	离子模式 Ionisation mode
STX	300.2/221.0	35	300.2/204.0	30	正离子 Cation
dcSTX	257.1/239.1	22	257.1/126.1	30	正离子 Cation
NEO	316.1/298.2	34	316.1/126.1	34	正离子 Cation
dcNEO	273.1/225.2	35	273.1/126.1	35	正离子 Cation
GTX5	380.1/300.1	-15	380.1/282.1	-35	负离子 Anion
GTX2	394.0/333.1	-22	394.0/351.1	-16	负离子 Anion
GTX3	394.0/351.1	-16	394.0/333.1	-22	负离子 Anion
GTX1	410.1/349.1	-22	410.1/367.1	-15	负离子 Anion
GTX4	410.1/367.1	-15	410.1/349.1	-22	负离子 Anion
C1	474.1/351.1	-25	474.1/122.0	-30	负离子 Anion
C2	474.1/122.0	-30	474.1/351.1	-25	负离子 Anion
dcGTX2	351.1/333.1	-17	351.1/164.0	-30	负离子 Anion
dcGTX3	351.1/164.0	-30	351.1/333.1	-17	负离子 Anion

1.4 风险评估

1.4.1 风险评估

PSTs 膳食暴露量(μ g STXeq/kg b.w./d) =

$$\frac{\text{贝类中PSTs浓度}(\mu\text{g STXeq/kg}) \times \text{贝类消费量}(\text{g/d})}{\text{体重}(\text{kg})} \times 10^{-3}$$

1.4.2 贝类中 PSTs 浓度数据处理 风险评估中通过替代方法进行左删失数据处理,当 PSTs 组分含量低于检出限时,左删失数据处理可以定量组分含量,不会产生大量删失数据,从而保证急性暴露评估信息的完整性。在下界(lower bound, LB)方案中,将所有低于检出限浓度设为 0,而在上界(upper bound, UB)方案中,将低于检出限浓度设为每种毒素的 1/2 检出限(LOD/2)。在急性暴露评估的情况下,本研究使用获得的最大毒素水平。

2 结果

2.1 3—6 月贝类样品 PSTs 组分与含量分析

在采集的 103 份贝类样品中,全部检出 PSTs,检出率为 100%,均未超过欧盟限量标准,3—6 月份贝类样品的均值中,4 月份均值含量最高(300.2 μ g STXeq/kg)、其次 5 月、3 月,6 月均值含量最低,仅为 18.4 μ g STXeq/kg (图 1)。3—6 月贝类样品检出的主要组分为 GTX1&4 和 GTX2&3(图 2)。4 月检出的含量最高,其中, GTX1 含量为 140.2 μ g/kg、GTX4 含量为 68.6 μ g/kg、GTX2 含量为 120.1 μ g/kg、GTX3 含量为 55.8 μ g/kg。除 3 月外,4—6 月均有高毒性的 STX、dcNEO 检出。5—6 月检出了 3、4 月未检出的 dcGTX2。秦皇岛附近海域比唐山附近海域污染严重(唐山附近海域 3—6 月 PSTs 均值含量变化不明显,未放图),秦皇岛附近海域 3—6 月 PSTs 含量分布如图 3。

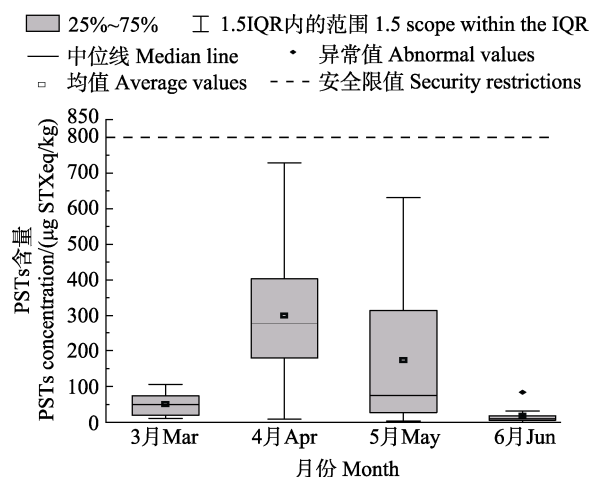


图1 2022年3—6月份贝类样品中PSTs平均含量对比
Fig.1 Comparison of average PSTs concentration in shellfish samples from March to June, 2022

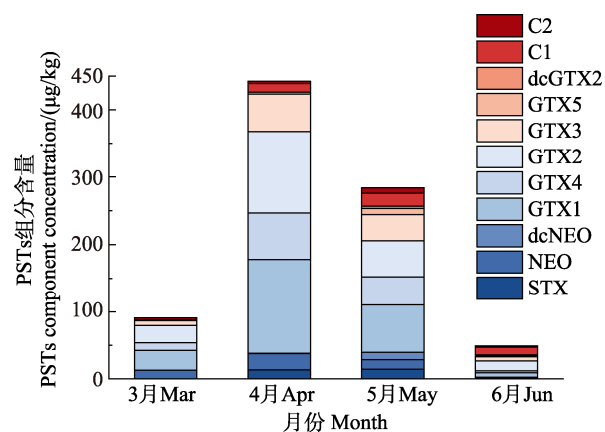


图2 2022年3—6月份贝类样品中PSTs组分与含量
Fig.2 Components and concentration of PSTs in shellfish samples from March to June, 2022

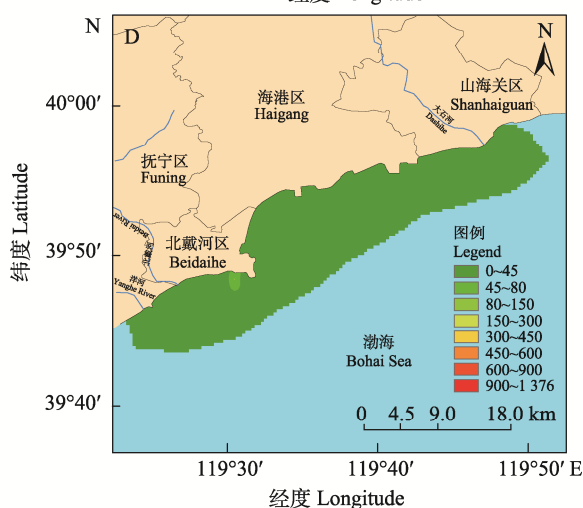
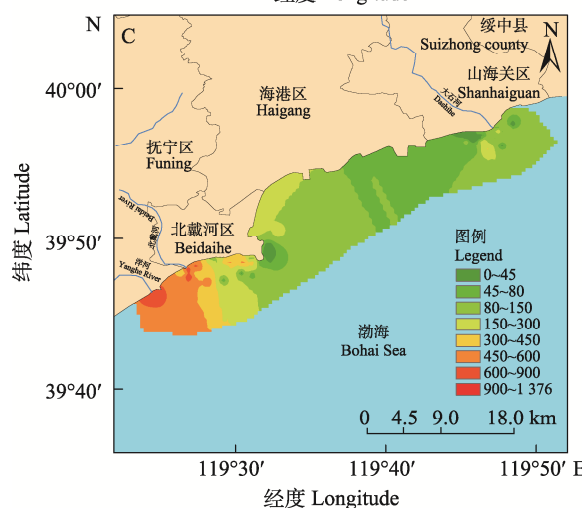
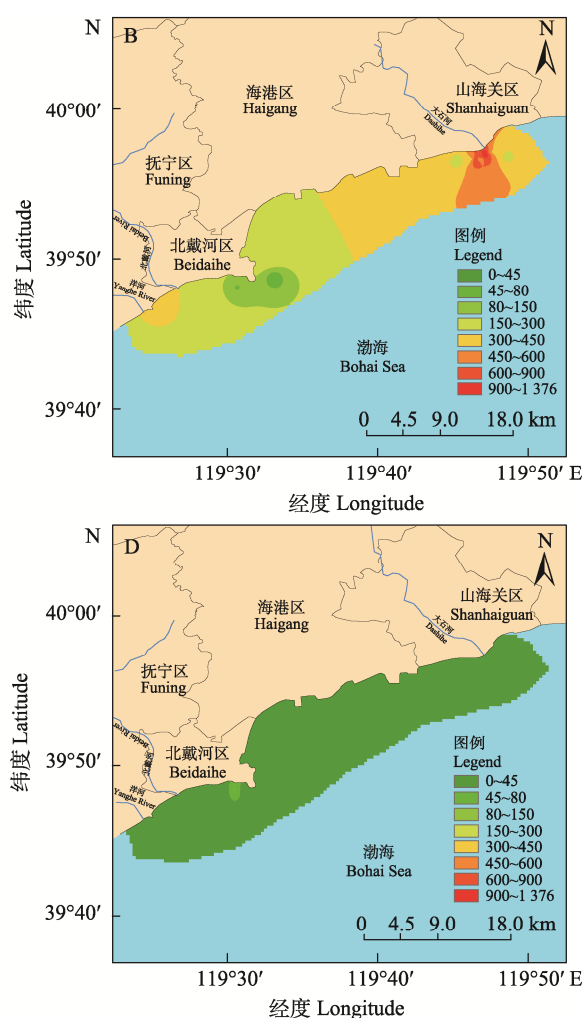
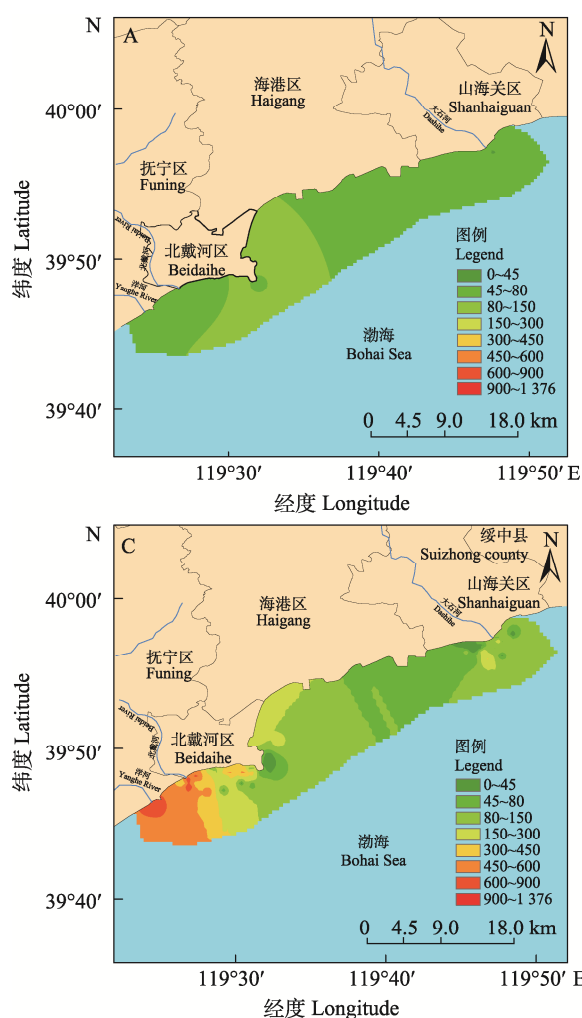


图3 2022年秦皇岛贝类样品PSTs污染分布

Fig.3 Distribution of PSTs contamination in shellfish samples from Qinhuangdao, 2022

A、B、C、D分别为河北省近岸秦皇岛附近海域3月、4月、5月和6月PSTs污染分布。

A, B, C, and D were the distribution of PSTs in the sea area near Qinhuangdao in the nearshore of Hebei Province in March, April, May and June, respectively.

2.2 不同品种贝类样品 PSTs 组分与含量分析

在采集的贝类样品中,不同品种的贝类样品 PSTs 均值含量差异明显(图 4)。紫贻贝均值含量最高为 250.8 $\mu\text{g STXeq/kg}$, 其次为毛蚶、海湾扇贝、魁蚶、菲律宾蛤仔和太平洋牡蛎, 含量分别为 229.9、80.7、59.1、27.3 和 17.6 $\mu\text{g STXeq/kg}$ 。

6 种贝类蓄积的 11 种 PSTs 组分存在较大差别(图 5), 其中, GTX1-4 和 C1&2 为 6 种贝类共同的检出组分, GTX1&4 最高含量在紫贻贝样品检出, GTX1 为 114.7 $\mu\text{g/kg}$, GTX4 为 63.8 $\mu\text{g/kg}$; GTX2&3 最高含量在毛蚶样品检出, GTX2 为 155.1 $\mu\text{g/kg}$, GTX3 为 70.5 $\mu\text{g/kg}$; C1&2 最高含量在海湾扇贝样品检出, C1 为 73.1 $\mu\text{g/kg}$, C2 为 20.3 $\mu\text{g/kg}$ 。样品中高毒性的 STX、NEO 检出量较少, 除紫贻贝样品和毛蚶样品中 11 种 PSTs 均有检出外, 其余 4 种贝类样品仅检出部分组分, 如魁蚶样品中未检出 dcNEO、GTX5 和 dcGTX2, 太平洋牡蛎样品中未检出 STX 和 NEO, 菲律宾蛤仔样品中未检出 GTX5 和 dcGTX2。

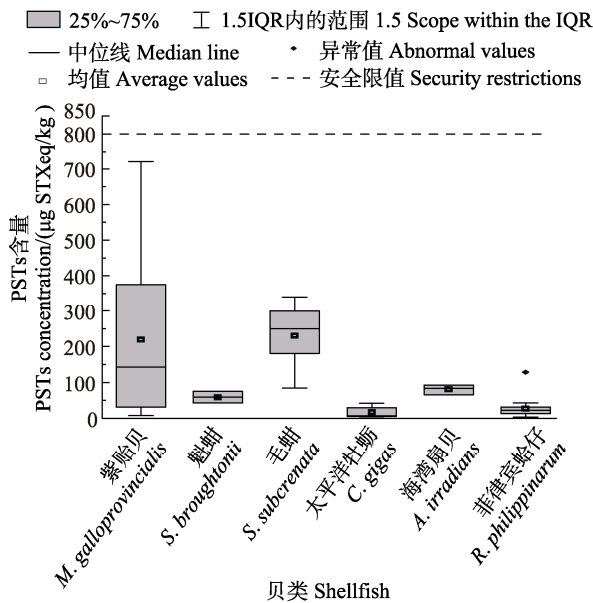


图 4 不同品种贝类样品 PSTs 平均含量对比
Fig.4 Comparison of average PSTs concentration in different species of shellfish samples

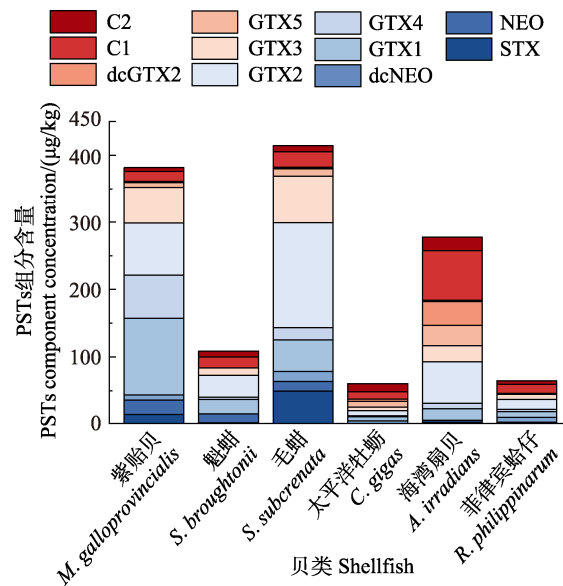


图 5 不同品种贝类样品 PSTs 组分与含量
Fig.5 Components and concentration of PSTs in different species of shellfish samples

2.3 双壳贝类中 PSTs 膳食暴露风险评估

近年来, 河北省近岸贝类中 PSTs 最高含量如表 2 所示, 其中, 2018 年为 $>4\,000\ \mu\text{g STXeq/kg}$, 2019 年为 $985\ \mu\text{g STXeq/kg}$, 2020 年为 $9\,147\ \mu\text{g STXeq/kg}$, 2021 年为 $1\,200\ \mu\text{g STXeq/kg}$ 。为保护消费者健康, 评估膳食暴露风险, 本研究采用 PSTs 最大值进行急性暴露评估(Shin *et al*, 2018; Zhou *et al*, 2022)(表 3), 基于 PSTs 的危险特征, FAO/IOC/WHO 推荐最低观察水平(LOAEL)PSTs 参考值为 $2.0\ \mu\text{g/kg b.w.}$, 使用安全系数 3 得出急性参考剂量(ARfD) $0.7\ \mu\text{g/kg b.w.}$ 。欧洲食品安全局(EFSA)规定 ARfD 为 $0.5\ \mu\text{g/kg b.w.}$, 观察到的 LOAEL 为 $1.5\ \mu\text{g/kg b.w.}$ 。两种急性参考剂量均可作为急性膳食暴露参考限值(Zhou *et al*, 2022)。本研究以成年人均体重 $60\ \text{kg}$ 、我国人均每日水产品食用量 $38.9\ \text{g}$ (Guo *et al*, 2023)进行急性暴露评估, 6 种贝类急性暴露评估结果见图 6。根据贝类样品最大值的下界数据和上界数据, 得出的急性暴露评估结果均未超过 FAO/IOC/WHO 和 EFSA 推荐的 ARfD 值, 处于安全可接受状态。

表 2 不同年份河北近岸贝类样品 PSTs 含量

Tab.2 Concentration of PSTs in nearshore shellfish samples from Hebei in different years

年份 Year	PSTs 最高含量 Maximum PSTs concentration /($\mu\text{g STXeq/kg}$)	参考文献 Reference
2018	$>4\,000$	Wu <i>et al</i> , 2022
2019	985	张亚亚等, 2020
2020	9 147	张海涛, 2022
2021	1 200	Tang <i>et al</i> , 2022

表3 不同贝类样品 PSTs 含量
Tab.3 Concentration of PSTs in different shellfish samples

毒素 Toxin	品种 Species	最大值 Maximum /($\mu\text{g STXeq/kg}$)	
		下界 LB	上界 UB
总毒素 Total toxin	紫贻贝 <i>M. galloprovincialis</i>	721.4	728.1
	魁蚶 <i>S. broughtonii</i>	69.5	85.6
	毛蚶 <i>S. subcrenata</i>	340.0	347.2
	太平洋牡蛎 <i>C. gigas</i>	29.4	59.5
	海湾扇贝 <i>A. irradians</i>	92.6	110.4
	菲律宾蛤仔 <i>R. philippinarum</i>	128.6	136.3

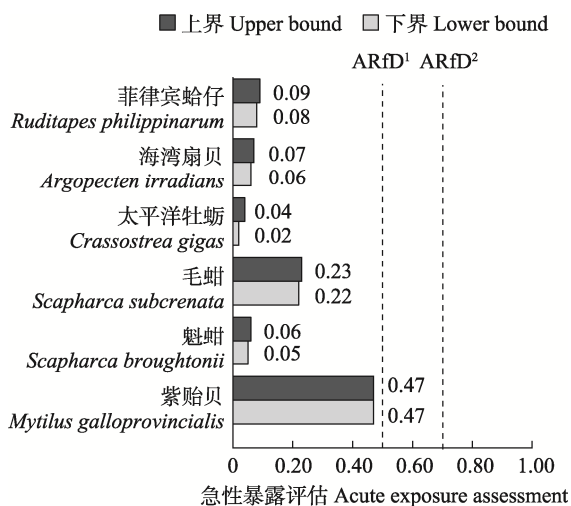


图6 不同品种贝类样品急性暴露评估数据
Fig.6 Acute exposure assessment data in different species of shellfish samples

ARfD¹: 0.5 $\mu\text{g STXeq/kg b.w.}$ (EFSA);
ARfD²: 0.7 $\mu\text{g STXeq/kg b.w.}$ (FAO/IOC/WHO)。

3 讨论

3.1 3—6月贝类样品 PSTs 含量差异

3—6月之间贝类样品中 PSTs 均值含量存在较大差异，贝类样品均值含量呈先上升、后下降趋势，4月 PSTs 均值含量最高，为 300.2 $\mu\text{g STXeq/kg}$ 。Tang 等(2022)研究表明，3—6月秦皇岛海域贝类样品中4月份 PSTs 风险最高，与本研究结果一致。温度可能是影响不同月份贝类样品 PSTs 含量差异的主要原因。研究表明，秦皇岛海域 PSTs 产毒藻主要为链状亚历山大藻(Yu *et al.*, 2021)，链状亚历山大藻最适生长温度为 10~13 $^{\circ}\text{C}$ (Tobin *et al.*, 2019)，而根据中国近海海洋气候检测月报数据，秦皇岛海域4月温度会升高至 4~9.5 $^{\circ}\text{C}$ 。Natsuike 等(2017)研究表明，亚历山大藻在水温接近最适生长温度即可大量繁殖，从而可能导致链状亚历山大藻细胞数量在4月达到峰值。此外，Wu 等(2022)研究也表明，秦皇岛近海海域链状

亚历山大藻在4月16日达到高峰期，5月藻类急剧减少，5月中旬浮游植物 PSTs 含量降低至0。根据中国近海海洋气候检测月报数据显示，秦皇岛海域在2022年3月温度仅为 1.5~4.5 $^{\circ}\text{C}$ ，而5月秦皇岛海水温度却已达到 17~18 $^{\circ}\text{C}$ (Cao *et al.*, 2023)，不适合链状亚历山大藻生存，导致链状亚历山大藻大量减少(Miyazono *et al.*, 2012)，最终链状亚历山大藻形成休眠包囊，沉积于海水底部。

3.2 不同品种贝类样品 PSTs 组分含量差异

双壳贝类是 PSTs 的主要水生动物载体，本研究发现，紫贻贝和毛蚶的 PSTs 均值含量远高于海湾扇贝、魁蚶、菲律宾蛤仔和太平洋牡蛎。Liu 等(2017)研究表明，紫贻贝和毛蚶均值含量高于太平洋牡蛎，与本研究结论相符。首先，不同贝类蓄积速度存在差异可能是影响贝类样品 PSTs 含量差异的原因。Tang 等(2022)研究表明，扇贝与贻贝相比，扇贝积累毒素的速度低得多，PSTs 含量和毒性水平低于贻贝。此外，也有研究发现，与贻贝相比，牡蛎和菲律宾蛤仔蓄积量少(Samsur *et al.*, 2006)。STX 含量升高后，贻贝中的过氧化氢酶和铁蛋白等转录水平升高，这可能是贻贝能够快速蓄积 STX 的保护机制(Núñez-Acuña *et al.*, 2013; Detree *et al.*, 2016)。其次，不同贝类品种摄食产毒藻细胞和吸收速度可能是影响含量差异的另外一个原因，与菲律宾蛤仔相比，紫贻贝具有更快的摄食速率，并且菲律宾蛤仔吸收速率低，在摄入大量藻细胞后菲律宾蛤仔会明显产生假性粪便(Li *et al.*, 2001; 包振民等, 2021)。最后，不同贝类 PSTs 的来源也会导致含量差异，毛蚶这类底栖贝类可以积累来自底栖亚历山大藻包囊的毒素，包囊中的毒素含量比营养细胞高达6倍，约有 28.9%~35.2%的包囊被底栖贝类摄食(Oshima *et al.*, 1992; Tsujino *et al.*, 2002)，这可能是其 PSTs 毒素含量较高的原因之一(Wang *et al.*, 2004; Liu *et al.*, 2017)。

贝类中蓄积的 PSTs 主要来源于摄入的产毒藻细胞

胞, 贝类中的毒素转化也会明显改变毒素组成(Raposo *et al*, 2020), 这是造成不同贝类中毒素组分含量差异较大的重要原因。双壳贝类体内的酶和细菌可促进不同结构、不同种类的 PSTs 发生转化, 从而导致贝类体内 PSTs 含量和组分不同(宋维佳等, 2022)。如在贝类体内可发生 C1→GTX2, C2→GTX3, 使低毒性的 N-磺酰氨基类毒素转化为高毒性的氨基甲酸酯类毒素(Ding *et al*, 2017)。贝类中产生的 C1&2 是由摄入产 N-磺酰氨基类毒素的亚历山大藻属造成的(Gao *et al*, 2015)。Kim 等(2015)研究表明, 随着紫贻贝在塔玛亚历山大藻 (*Alexandrium tamarense*) 中暴露时间的延长, 通过酶促紫贻贝中的 C1 和 GTX1, 逐渐转化为 C2 和 GTX4。与扇贝和牡蛎相比, 贻贝的 PSTs 代谢转化率低(Botelho *et al*, 2020), 从而使紫贻贝与扇贝、牡蛎中的毒素组分含量出现差异。林卓如等(2022)研究表明, 毛蚶体内缺乏磺胺甲酰基类水解酶和氨甲酰基水解酶, 无法进行相应转化反应, 同时, 在毛蚶体内没有明显的 β 型毒素通过差向异构化转化为 α 型毒素, 从而导致毛蚶与其他贝类之间在组分含量上存在差异。

3.3 贝类食用安全评估

随着河北省入海河流全流域系统治理、入海排污口分类治理和强力推动海洋垃圾污染防治等措施的落实, 河北省海洋生态环境逐渐变好(刘明等, 2018)。自 2020 年后, 河北近岸 PSTs 最高含量呈降低趋势, 本研究 2022 年贝类样品 PSTs 最高含量未超过安全限量标准。根据不同品种的贝类样品 PSTs 含量, 对河北近岸居民进行膳食暴露评估, 6 种贝类未超过 ARfD, 处于安全可接受状态, 其中, 紫贻贝膳食暴露风险最高, 存在部分残留, 大量摄入紫贻贝后可能会出现头晕、恶心等 PSTs 中毒症状。对于紫贻贝、毛蚶等膳食暴露评估数值较大的贝类, 应加强关注。考虑到 PSTs 对不同人群的不同影响, 应更多关注水产养殖户和海岛居民, 他们的水产品膳食摄入量要高于普通人群, 存在更高的食用风险(Wu *et al*, 2014)。

4 结论

本研究通过对河北省近岸贝类中 PSTs 调查, 结果发现 3—6 月贝类样品均有 PSTs 检出, 4 月均值含量最高, 其次为 5 月和 3 月, 6 月份均值含量最低; 另外贝类样品检出的主要组分为 GTX1&4 和 GTX2&3。对不同品种贝类 PSTs 含量的研究显示, 紫贻贝均值含量最高, 其次为毛蚶、海湾扇贝、魁蚶、

菲律宾蛤仔和太平洋牡蛎; 6 种贝类蓄积的 PSTs 组分中, GTX1~4、C1&2 为共同的检出组分。对河北近岸居民进行膳食暴露评估, 结果显示毒素风险均处于安全可接受状态。但由于对河北省近岸不同城市以及多种不同贝类样品的调查较少, 后续还需持续进行调查。

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Pollution Characteristics and Risk Assessment of Paralytic Shellfish Toxins in Shellfish from Hebei coastal Waters

LI Xiaokang^{1,2}, WU Haiyan², CHENG Ling³, CHE Hanyu²,
LIU Lijuan³, MOU Haijin⁴, TAN Zhijun^{2,5}, ZHENG Guanchao^{2①}

(1. Collage of Food Sciences & Technology, Shanghai Ocean University, Shanghai 201306, China; 2. Key Laboratory of Testing and Evaluation for Aquatic Product Safety and Quality, Ministry of Agriculture and Rural Affairs, Yellow Sea Fisheries Research Institute, Chinese Academy of Fishery Sciences, Qingdao 266071, China; 3. Shandong Key Laboratory of Marine Ecological Restoration, Shandong Marine Resources and Environment Research Institute, Yantai 264006, China; 4. College of Food Science and Engineering, Ocean University of China, Qingdao, 266003, China; 5. State Key Laboratory of Mariculture Biobreeding and Sustainable Goods, Yellow Sea Fisheries Research Institute, Chinese Academy of Fishery Sciences, Qingdao 266071, China)

Abstract Paralytic shellfish toxins (PSTs) are a class of acute neurotoxins with nearly 60 congeners. Shellfish that filter feed on toxin-producing algae exhibit PST accumulation in tissues, and the consumption of toxic shellfish poses a major threat to human health. China has the largest aquaculture industry in the world, with shellfish production of approximately 15.89 million tons in 2022 and many shellfish consumers. The PST poisoning incidents in China exhibit the characteristics of a wide distribution area, recurring regional risk, diverse toxin sources, and seasonal differences. PST consumption causes acute symptoms of poisoning and even death in many people, with a high lethality rate. This is a serious threat to the health of consumers and detrimental to the social stability of the region. In northern China, Hebei Province has rich fisheries resources, with a mariculture output of approximately 580,000 tons in 2022. In recent years, PSTs have been detected several times in bivalve shellfish inshore in Hebei Province, especially along the coast of Qinhuangdao. A serious shellfish poisoning episode was reported in Qinhuangdao in 2016, with PST concentrations exceeding the safety limit of 800 µgSTX

① Corresponding author: ZHENG Guanchao, E-mail: zhenggc@ysfri.ac.cn

equivalents/kg ($\mu\text{g STXeq/kg}$) by a factor of 65. The main algal species responsible for the poisoning was *Alexandrium catenella*. However, the current investigations of PST pollution in Hebei Province mainly focus on the shellfish species *Mytilus galloprovincialis* and *Argopecten irradians* in the sea area of Shanhaiguan, Qinhuangdao, and investigations on other coastal cities of Hebei Province and a wide range of different shellfish species are lacking. Moreover, few risk assessment studies have been conducted.

A continuous PST survey was conducted in 2022 on six species of shellfish, namely *M. galloprovincialis*, *Scapharca subcrenata*, *A. irradians*, *Scapharca broughtonii*, *Ruditapes philippinarum*, and *Crassostrea gigas*, collected by netting in Tangshan and Qinhuangdao, and the residual status of PSTs was assessed for acute exposure using liquid chromatography-tandem mass spectrometry. The results showed that PSTs were detected in shellfish samples collected from March to June, with a detection rate of 100%. However, no values exceeded the European Union limit. Among the shellfish samples collected from March to June, those assessed in April had the highest average concentration, followed by those in May, March, and June, which had the lowest average concentration. The main components detected in shellfish samples from March to June were gonyautoxins (GTX) 1–4; the highest concentrations were detected in April. Highly toxic saxitoxin (STX) and decarbamoylneosaxitoxin (dcNEO) were detected from April to June and not in March. Decarbamoylgonyautoxin (dcGTX) 2 was not detected in March or April; however, it was detected in May and June. The sea area near Qinhuangdao was more polluted than that near Tangshan. Among the collected shellfish samples, significant differences were observed in the average concentration of PSTs in shellfish samples of different species, and the concentration ranged from highest to lowest in species as follows: *M. galloprovincialis* > *S. subcrenata* > *A. irradians* > *S. broughtonii* > *R. philippinarum* > *C. gigas*. Large differences were observed between the six shellfish species regarding the accumulation of 11 PST components, among which GTX1–4 and carbamate toxin (C) 1 and 2 were the most commonly detected components. The highest concentrations of GTX1 and 4 were observed in *M. galloprovincialis*, the highest concentrations of GTX2 and 3 were observed in *S. subcrenata*, and the highest concentrations of C1 and 2 were observed in *A. irradians*. A low detection rate was recorded for highly toxic STX and neosaxitoxin (NEO) in samples, except in *M. galloprovincialis* and *S. subcrenata*, in which all 11 PSTs were detected. In the other four shellfish species, only certain of the components were detected. Statistical analysis of the highest levels of PSTs in nearshore shellfish in Hebei Province in recent years showed a decreasing trend. Acute exposure assessments using the maximum value of PSTs showed that none of the six shellfish species exceeded the acute reference dose values recommended by the Food and Agriculture Organization of the United Nations/World Health Organization and European Food Safety Authority, suggesting that toxin levels were safe and acceptable. *M. galloprovincialis* had the highest dietary exposure risk, as a few residues were present, and symptoms of PST poisoning, such as dizziness and nausea, may occur after ingesting large quantities of *M. galloprovincialis*. Increased attention should be paid to shellfish with high dietary exposure assessment values, such as *M. galloprovincialis* and *S. subcrenata*.

In this study, we investigated PSTs in shellfish from Hebei coastal waters and observed that PSTs were detected in shellfish samples from March to June, with the highest average concentration in April, followed by May and March, with the lowest average concentration in June. In addition, the main components detected in shellfish samples were GTX1–4. The analysis of different shellfish species showed that *M. galloprovincialis* had the highest average PST concentration, followed by *S. subcrenata*, *A. irradians*, *S. broughtonii*, *R. philippinarum*, and *C. gigas*; GTX1–4 and C1 and 2 were detected in all six shellfish species. Dietary exposure assessment for consumers in Hebei Province showed that the toxin levels were safe and acceptable. However, follow-up surveys and studies are necessary due to the paucity of surveys for different cities and species on the coast of Hebei.

Key words Paralytic shellfish toxins; Hebei Province; Shellfish; Contamination characteristics; Safety assessment