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Review Article

Innovative adsorbent materials for the mitigation and analysis of paralytic shellfish toxin contamination: An updated mini review 2023-2025

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Abstract
Paralytic shellfish toxins (PSTs), potent neurotoxins produced by harmful algal blooms, threaten marine ecosystems, human health and seafood safety. Saxitoxin and its analogues are particularly concerning due to their extreme toxicity, persistence and bioaccumulation potential. Effective methods for removing and analyzing PSTs in contaminated water and seafood are urgently needed. This mini-review highlights recent innovations in solid-phase adsorption (SPA) as a promising solution. Novel adsorbents, including covalent organic polymers, biochar and silica-chitosan composites, have shown excellent selectivity and efficiency for PST removal. Integration of SPA into analytical processes via solid-phase extraction has significantly improved detection sensitivity and accuracy, supporting more reliable PST monitoring. However, challenges remain, such as adsorbent regeneration and reuse, scalability for large applications and matrix interferences affecting adsorption efficiency. Future research should optimize adsorbent designs for enhanced selectivity and durability, clarify underlying adsorption mechanisms and establish integrated strategies combining SPA with other methods. Addressing these challenges will enhance SPA's role in mitigating PST risks, ultimately leading to safer water and seafood supplies.

Keywords: adsorption, extraction, paralytic shellfish toxins, saxitoxin

Introduction on the toxin contamination trend

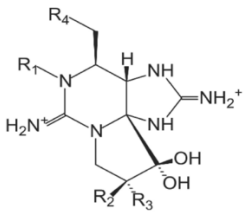
A harmful algal bloom (HAB) is a natural event that adversely affects other living creatures through the generation of toxins by noxious phytoplankton, benthic algae, macroalgae or cyanobacteria. This event has been observed as early as the 19th century and has not attracted international attention until the end of the 20th century [1]. Since it has cause massive fish mortalities and/or economic losses in a number of nations, including Philippines [2], Malaysia [2], Indonesia [2], China [3], New Zealand [4], the United State [5] and other countries around the world [6], addressing the issue of HABs has become a global priority. For instance, the most harmful bloom observed in New Zealand was caused by a paralytic shellfish toxin (PST)-producing species, *Gymnodinium catenatum* [7], started from May 2000 to 2003, resulted in widespread contamination and closure of shellfish harvesting areas. Fish-killing algal blooms caused by *Prorocentrum cordatum, Karlodinium, Margalefidinium (Cochlodinium) polykrikoides and Chattonella* also have been an increasing concern in Malaysia and the Philippines [8]. The Atlantic and Pacific coast of the United State, Canada and the United Kingdom are the primary regions affected by amnesic shellfish poisoning-related problems; despite significant *Pseudo-nitzschia* blooms, the levels of domoic acid in seafood often remain below legal bounds. Neurotoxic shellfish toxins are most reported in Florida (the southeast part of the United States [5], but only one outbreak observed in New England [6].Though no cases of Ciguatera fish poisoning (CFP) from eating fish from New Zealand have been documented as CFP was the most common seafood toxin

illness in Australia [6]. Among toxins generated by HABs, PSTs can be especially concerning due to their severe health effects on both humans and marine life [9].

Overview of paralytic shellfish toxins (PSTs)

Essentially, PSTs are a group of toxins that block voltage-gated sodium channels. Among over 50 PSTs, saxitoxin (STX) is the most well-known member of PSTs [9]. STX and its analogues, or simply as the STXs-group, are mainly produced by a variety of cyanobacteria and microalgae, including *Alexandrium minutum, Dolichospermium circinalis, Cylindrospermopsis raciborskii* (also known as *Raphidiopsis raciborskii*) and *Aphanizomenon spp*. They are classified in a group because all members of this group share a central framework, with different substituents arranged by subgroups. In **Figure 1**, 3 subgroups of PSTs are shown [10]. They are carbamate (STX, neosaxitoxin (NeoSTX) and gonyautoxins (GTX1-4)), *N*-sulfo-carbamoyl (GTX5-6, C1-4) and decarbamoyl (dc-) (dcSTX, dc-NeoSTX, dcGTX1-4), ranked from the most to the least toxic. Given the variety of PST analogues and their varied toxicities, it is critical to translate them into a standardized unit of measurement, STX equivalents (STX eq), to facilitate health hazard evaluation and ensure regulatory compliance. This conversion is made easier with toxicity equivalency factors, which have been determined through electrophysiological tests in cultured neurons. In other words, the reported levels of STX eq includes the contributions from different forms of PSTs. As reported by the World Health Organization (WHO), guideline values of STX are set at 3 µg/L in drinking water and 30 µg/L in recreational water [11]. While the current European Union (EU) limit of PSTs in shellfish meat is set at 800 µg STX eq/kg [12]. This limit is stated in Regulation (EC) No 853/2004 to ensure shellfishes sold for human consumption adhere to strict safety and health regulations [13]. However, when a 60 kg adult consumes a 400 g portion of shellfish meat containing STX at the EU limit of 800 µg/kg, the adult might ingest STX at 320 µg, which is far above the recommended safety level of 30 µg (obtained from an acute reference dose at 0.5 µg STX eq per kilogram of body weight). That is to say, people may still exceed acceptable STX exposure levels if they consume a large portion of shellfish meats. To meet an acceptable risk to health, a 400 g shellfish serving should have no more than 75 µg of STX eq per kilogram of shellfish.

When bivalves or water contaminated by PSTs are consumed, they pose a considerable danger to human health by causing paralytic shellfish poisoning (PSP) [15, 16], with symptoms like numbness, paralysis and, in severe cases, respiratory failure or death within few hours [9]. Increasing evidence also indicated that bivalves are not only transporters of PSTs generated by HAB species, but that HAB species and their released toxins may also change bivalves' behaviour, physiology, cellular responses, immunity, resistance to environmental changes or even kill them [17]. Additionally, excessive PSTs in water bodies can cause negative impact to aquatic life by interrupting food chains and triggering ecological imbalances [3, 18]. For example, migration of PSTs along the food chain, particularly via zooplankton, allows the transmission and buildup of toxins in higher trophic levels (e.g. fish), impacting the population of affected species and predators who rely on these species for food. Therefore, threats to human populations and marine ecosystems must be addressed by eliminating PSTs from water sources, protecting the well-being of human health and aquatic habitats.



R_1	R_2	R_3	R_4	Toxin
H	H	H	$COONH_2$	STX
OH	H	H	$COONH_2$	neoSTX
OH	H	OSO_3^-	$COONH_2$	GTX1
OH	OSO_3^-	H	$COONH_2$	GTX4
H	H	OSO_3^-	$COONH_2$	GTX2
H	OSO_3^-	H	$COONH_2$	GTX3
H	H	H	$COONHSO_3^-$	GTX5
OH	H	H	$COONHSO_3^-$	GTX6
H	H	OSO_3^-	$COONHSO_3^-$	C1
H	OSO_3^-	H	$COONHSO_3^-$	C2
OH	H	OSO_3^-	$COONHSO_3^-$	C3
OH	OSO_3^-	H	$COONHSO_3^-$	C4
H	H	H	OH	dcSTX
OH	H	H	OH	dcNEO
OH	H	OSO_3^-	OH	dcGTX1
OH	OSO_3^-	H	OH	dcGTX 2
H	H	OSO_3^-	OH	dcGTX 3
H	OSO_3^-	H	OH	dcGTX 4

Figure 1. Classification of paralytic shellfish toxins (PSTs) into three structural analogues: carbamate (STX, neosaxitoxin (NeoSTX) and gonyautoxins (GTX1-4)), N-sulfo-carbamoyl (GTX5-6, C1-4) and decarbamoyl (dc-) (dcSTX, dc-NeoSTX, dcGTX1-4)

Challenges in PST detection and mitigation

Applying a comprehensive strategy to risk assessment, including natural resources, biota and human can provide more informed risk management for PST-producing HABs. The costs associated with eliminating STXs can be decreased if the stresses and potential growth of HABs are avoided or controlled by manipulating several ecological changes, such as avoiding farm soil runoff, reducing rising temperatures due to climate change, reducing deposition of nitrogen and phosphorus in the water environment and wetlands mitigation [19]. Ineffective or failed risk management measures could result to HAB formation in water systems and potential contamination of seafood, drinking water and surrounding environment. To guarantee the safety and quality of water, multiple engineering measures are required. Various measures such as biological, chemical and physical approaches have been used to manage HABs and their toxins [20].

Biological approaches utilize microorganisms for toxin degradation while chemical approaches employ chlorination, ozonation and UV irradiation. Physical approaches involve membrane filtration (nanofiltration, ultrafiltration, microfiltration) and adsorption [20]. Since most of the PSTs are cell-bound, any approach that removes PST-bound cells without causing cell harm is a viable alternative [20]. Various methods, including coagulation/sedimentation/filtration, membrane filtration and pre-treatment oxidation, are used as control methods to remove intracellular PSTs [20]. Pre-oxidation techniques such as ozonation, chlorine and potassium permanganate are frequently employed to render algal cells inactive. Nonetheless, these precursors may cause harm to the algal cells without oxidising the released PSTs, raising the possibility of disinfection byproducts production in water treatment plant [21]. Cell-bound PSTs and algal cells can be eliminated by coagulation procedures, which frequently employ organic polymers, ferric and aluminium salts, or both, but coagulation operations are ineffective for removing dissolved toxins [20].

Reverse osmosis and membrane filtration are efficient in eliminating algal cells [22]; however, they also have drawbacks like membrane fouling and the leakage of bound toxins during the filtration process. Although the majority of PSTs are cell-bound, it is critical to implement effective measures to address extracellular PSTs. This is because extracellular PSTs are readily dissolved in water. Thus, removing only cell-bound PSTs may not be adequate since the release of PSTs into the water is possible due to their cellular breakdown. This is supported by a study conducted by [23], where dissolved PSTs were discovered widely distributed in water columns in the Bohai and Yellow Seas. To guarantee proper PST contamination control, effective water treatment must target both intracellular and extracellular PSTs. This dual strategy is critical for ensuring regulatory compliance, preserving public health and shielding aquatic habitats from the negative impacts of PSTs.

There are several methods suitable for the removal of extracellular or dissolved PSTs, namely adsorption, membrane filtration, chlorination, ozonation and UV radiation [20]. While membrane filtration like reverse osmosis and nanofiltration are efficient at eliminating extracellular toxins, they are expensive and need more testing to ensure thorough toxin removal. Other removal methods such as UV radiation, ozone treatment and chlorination are known particularly useful in eliminating dissolved PSTs but these methods also have disadvantages, including operating cost, scalability, effectiveness and the generation of disinfection byproducts [20]. As a result, their suitability for PST-removal should be considered and determined based on several factors like water quality, PST concentration and treatment objectives. Among these strategies, adsorption stands out as a fascinating strategy due to its capability to selectively remove targeted toxins from water by attaching these molecules to the adsorbent surfaces [19, 24].

Adsorption also has other benefits like high efficacy, simple and high adaptability in handling various water sources. However, it has drawbacks, including the need for regular adsorbent replacement or regeneration and the possibility of adsorption site saturation over time. Notwithstanding these obstacles, continuous developments in adsorption technology such as the fabrication of novel adsorbents and the improvement of existing adsorbents' performances will further enhance the technology's efficacy in the removal of PSTs [25]. These aforementioned methods have been commonly used in water treatment facilities. Yet, degree of these treatments are highly depending on the water source, characteristics of the water and operational factors such as temperature, pH and the types/amount of toxin in water [20]. As it is currently not possible to effectively remove all intact cells or dissolved PSTs from water bodies with a single approach, employing combined water treatment approaches are highly recommended to mitigate HABs effectively [19,

24]. Public awareness to seafood quality and safety is rising with the increasedseafood consumption. Since the presence of marine toxins in various shellfish has caused numerous cases of poisoning [16, 26-28], efforts have been made to understand their effective elimination from shellfish. Adsorption [29, 30], advanced oxidation processes (AOPs, such as ozone degradation, photolysis and photocatalysis) [31, 32] and biodegradation [32, 33] are examples of marine toxin removal technologies for shellfish that have gotten a lot of attention in recent years. Each of these methods has its pros and cons [32], as mentioned in the previous paragraph. However, removal methods for marine toxins like PSTs are mostly proposed to remove PSTs from water or microalgae cultures that produce them [25, 34]. The shellfish depuration methods are also slow and ineffective at removing PST [35]. It is crucial to investigate and create more effective methods for removing PSTs from shellfish due to the health hazards of consuming shellfish poses to the general public. Besides their application in water and microalgal cultures, these removal strategies are also relevant when dealing with contaminated shellfish and other seafood, where subsequent analytical extraction is required to accurately determine PST levels and to evaluate the effectiveness of any mitigation approach.

Within the overall PST removal and management framework, extraction represents a critical analytical step because the toxins must be transferred from complex matrices into a workable phase. Extraction methods that commonly employed for PSTs are liquid-liquid extraction (LLE) and solid-phase extraction (SPE) [36]. LLE is versatile and able to extract a broad range of compounds (both polar and non-polar compounds); nevertheless, it is time-consuming, needs plenty of organic solvents and may have limited reproducibility. SPE, on the other hand, has greater selectivity, fast and requires less organic solvent, making it more environmentally friendly and cost-effective. However, it is constrained by smaller sample volume and the cost of specialised sorbents. As analysing PSTs can be challenging due to their instability and potential to convert into many analogues [37, 38], selecting the most appropriate analytical methods requires careful consideration of sample matrices. Since the demand for more efficient and sustainable analytical methods for PSTs increases, several adsorption-based extraction methods have been developed [39-41]. These methods, especially those employed in SPE or modified form of SPE, are essential because of their great selectivity, efficiency and capacity to work with intricate matrices. In this review, the efficacy of adsorption as a strategy for extracting pollutants, notably PSTs, from contaminated water and shellfish are investigated and discussed. This review also focuses on the use of adsorption in analytical methods, notably SPE or other form of SPE, where it plays an important role in improving the sensitivity and accuracy of PSTs detection. The main goal of this review is to present a thorough analysis of recently developed adsorbents or adsorption processes from 2023 to 2025, including their mechanism, their performances in the shellfish and water treatment and their analytical performances in detecting PSTs.

Adsorptive approaches for the removal of paralytic shellfish toxins from water and shellfish

Water is an essential resource for life, but its quality is under growing danger from a variety of environmental pollutants, including PSTs. As PSTs are potent neurotoxins that endanger aquatic ecosystems, human health and drinking water sources, this highlights the needs of progressing research on effective PST removal from water. In response to this challenge, a few sophisticated adsorbent materials have been developed. In our previous study, we used humic acid (extracted from goat dung) as a key functional component in the design of an adsorbent that targets STX [42], taking advantage of its rich functional groups such as carboxyl, amino, phenyl, carbonyl and phenolic hydroxyl that act as effective adsorption sites for STX removal. To ease the separation process, humic acid functionalized with magnetite nanoparticles (HAM) was developed. At optimum condition, STX removal efficiency reached 71.04% at slightly alkaline pH (7.94), by using 30 mg of HAM for 8 min at an initial STX concentration of 100 µg/L. A kinetic study showed that the adsorption process followed a pseudo-second-order model (R^2 = 0.9983; adsorption capacity at equilibrium, Q_e=0.0022 mg/g), confirming chemisorption as the dominant mechanism. Strong electrostatic interactions are expected during the adsorption as the negatively charged HAM and the cationic fraction of STX are dominant at pH 7.94, while other interactions like hydrogen bonding and π-π interactions (between aromatic rings of humic acid and STX) are also proposed. After rigorous calculation, our analytical Eco-Scale assessment yielded a score of 81, supporting the eco-friendliness of the method. As compared to existing methods, Fe_3O_4–HA demonstrated superior adsorption efficiency, rapid performance and environmental sustainability. These results imply that HAM is a potential

adsorbent for the practical remediation of water contaminated by STX and should be further studied for practical scalability and use. [43] Furthermore, also presented an innovative solution for the adsorption of STX by using a carboxyl-functionalized covalent organic polymer. Initially, two β-keto-enamine-based materials were prepared by self-assembly of 2,4,6-triformylphloroglucinol (Tp) with 2,5-diaminobenzoic acid (Pa-COOH) to give TpPa-COOH and with 2,5-diaminotoluene (Pa-CH_3) to give TpPa-CH_3. Their efficiencies in adsorbing STX from water were evaluated and compared. TpPa-COOH (96 ± 0.23%) was found to outperform TpPa-CH_3 (8.6 ± 1.31%), despite having a smaller BET surface area (177 m^2/g for TpPa-COOH; 531 m^2/g for TpPa-CH_3) and poorer long-range order. This might be due to the presence of carboxylic acid groups in TpPa-COOH that create strong hydrogen-bonding interactions with STX. Moreover, guanidium moieties of STX, which have pK_a values of 8.24 and 11.5 [44], are protonated at the working pH range of 6–7, this enables them to establish strong cation-π interactions with the aromatic groups of TpPa-COOH. High affinity and favourable monolayer adsorption of STX onto the TpPa-COOH surface are also well explained by the Langmuir isotherm model, as supported by its correlation coefficients (close to 1), notable maximum adsorption capacity (Q_m) of 5.69 mg/g and separation factor, R_L of 0.3259. On the other hand, the adsorption process exhibits pseudo-second-order kinetics with Q_e of 1.82 mg/g, indicating that the TpPa-COOH and STX have strong chemical interactions that cause fast adsorption. During real sample analysis, TpPa-COOH showed better STX adsorption efficiencies in real river and lake water samples (95.0-99.7%) than in ultrapure water (94.9%). Equally noteworthy is TpPa-COOH's ability to maintain its structural integrity and adsorption efficiency for at least 3 consecutive cycles of STX adsorption-desorption, highlighting its potential for long-term and sustainable applications. The extension of the study to include the adsorption of dcSTX with Q_m of 4.1 mg/g, further accentuate the versatility of TpPa-COOH. A remarkable 91% adsorption efficiency for dcSTX demonstrates the material's potential in broad applicability to various saxitoxin analogues.

In a recent study conducted by [45], they investigated the effectiveness of powdered activated carbon (PAC) for STX removal from distilled and source water treated by different settings of wastewater treatment plants (WWTP) in the city of Akron and Alliance, Ohio, USA. For distilled water sample treated by Akron, the water prepared at pH 6 shows negligible elimination of STX by PAC. In contrast, for distilled water prepared at pH 7, 8 and 9, the adsorption rates for STX at a concentration of 0.3 µg/L were 37%, 48% and 48%, respectively. The results show that the elimination of STX was higher at pH 8 and 9 than at pH 6. This is congruent with the findings of [46], who discovered the STX removal efficiencies increased with a rising water pH when PAC adsorbent was used. For distilled water samples treated by Alliance, insignificant STX adsorption by PAC was observed at pH 6. While additional investigation showed that PAC successfully eliminated 57% and 47% of STX at pH 8 and 9, respectively, with no significant difference in the adsorption rates. When 0.3 µg/L of STX was introduced into the source water treated by Akron, PAC removed STX significantly at all pH levels (pH 6, 7 and 9), with removal efficiencies of 13-31%. The lower STX removal efficiencies in source water than distilled water could be attributed to the competing effects of natural organic matter and other elements in the source water. For source water treated by Alliance, PAC eliminated 52-79% STX in the pH range from 6 to 9. This higher STX removal was due to a larger PAC dosage and longer contact duration used in the WWTP of the City of Alliance than the city of Akron. Interestingly, PAC considerably improved the elimination of STX in the presence of microcystin-LR (MC-LR). The removal of 0.3 µg/L STX from Akron's source water was 53-89% (at pH 6-9) in the presence of 20 µg/L MC-LR (with co-removal rates of 25-91%). This might be due to the synergistic electrostatic interactions between STX and MC-LR, where the negatively charged MC-LR promoted the STX adsorption onto the PAC. Similarly, PAC successfully eliminated STX from source water in the presence of cyanobacteria, with removal rates ranging from 23% to 57% at a pH range of 6 to 9. However, the presence of cyanobacteria in the water had resulted in slightly lower removal rates of STX. This may be due to the possibility of cell breakage and the release of intracellular toxins. Overall, this study is novel as it shows that PAC can effectively remove STX even when MC-LR and cyanobacteria cells are present.

Moreover, [47] also conducted a similar study on the adsorption of STX and MC-LR on a commercial pine-derived biochar, showing the potential of biochar under complex water treatment scenarios. Under optimized circumstances, the biochar demonstrated great efficiencies in removing STX and MC-LR from aqueous samples. The ideal dosage of biochar to achieve over 90% removal efficiencies was 0.02

g/L for STX and 0.4 g/L for MC-LR. STX needs lower biochar dosage as it has a lower molecular weight (299.3 g/mol for STX and 995.2 g/mol for MC-LR) which allow it to exhibit better diffusion and faster interactions with the biochar surface. This is further validated by a shorter equilibrium time to adsorb STX (1-8 hours) than MC-LR (20-22 hours). When investigating impact of solution pH on their removal efficiency, STX adsorption appeared the best at pH 10 with 99.85% removal efficiency while MC-LR adsorption appeared the best at pH 4 with 97.92% removal efficiency. This is because the biochar surface has a positive charge at pH 4, enable an electrostatic attraction to the negatively charged MC-LR molecule, leading to greater adsorption. In contrast, at pH 10, the biochar surface becomes negatively charged, promoting electrostatic attraction with the positively charged STX at this pH. A kinetic study revealed that both MC-LR and STX were well explained by the Elovich model, while STX was also well explained with the pseudo-first order and pseudo-second order models, indicating the participation of both physical and chemical adsorption processes. In the binary system of these components, the pseudo-second order model better fit MC-LR, whereas the Elovich model was more suitable for STX, indicating that chemisorption is the dominant mechanism of toxin elimination. For isotherm study, the Langmuir-Freundlich model offered the best match, showing heterogeneous adsorption behaviour, with Q_m of 3507.46 μg/g for STX and 622.53 μg/g for MCLR. The study demonstrated different adsorption processes for MCLR and STX on biochar, such as hydrogen bonding, hydrophobic contacts, electrostatic interactions and π-π interactions for MCLR and hydrogen bonding, pore filling and dispersive interactions for STX. Both work of [45, 47] highlighted the capacity of carbon-based adsorbents to address multiple cyanotoxins in complex water matrices at the same time and enhance water treatment procedures by tackling the problem of co-occurring contaminants. The same research group [48] also investigated relationship between the adsorption performance of loblolly pine-derived biochars for STX and their pyrolysis temperature. Generally, there was a decrease in oxygen elements (from 21.16±0.13 to 0.42±0.00 wt%) and an increase in surface area (from 7.26±0.2 to 408.15±6.19 m^2/g) as the pyrolysis temperature of biochar rose from 400 to 800°C. Among these biochars, biochar prepared at 400°C (P400) showed the best Q_m (314.37 μg/g) for STX due to its higher abundance of oxygen-containing functional groups and negative surface charge, reaching over 90% STX adsorption with a lower biochar dosage (0.01 g/L). In contrast, biochars prepared at 600°C (P600) and 800°C (P800) demonstrated lower Q_m at 303 μg/g and 251.3 μg/g, respectively. These Q_m values are significantly different with the Q_m of 3507.46 μg/g [47] when a commercial pine-derived biochar was employed for STX adsorption. This might be due to the difference in their activation procedure and the source material of biochar [49] since the effectiveness of pine biochar is highly dependent on the species of pine employed and pyrolysis temperature.

Efforts to develop efficient and practical detoxification techniques for live bivalve mollusks have been ongoing. However, a genuinely successful and viable solution within a short timeframe has yet to be discovered. [50] had investigated the potential of using cation-exchange resins (in both H-form and Na^+-form) to remove PSTs from live mussels, *Mytilus edulis*. The H-form cation-exchange resin demonstrated a slight acceleration in PST clearance after 24 hours, which was attributable to lower dcSTX concentrations, but the results were not statistically significant. Furthermore, the H-form cation-exchange resin acidified the water, lowering the pH to 3, which had a detrimental influence on mussel health by causing a defensive shell-closing reaction and limiting PST clearance. Interestingly, a further experiment discovered that the mussels could gradually return the acidic conditions to neutral through the interaction between their calcium carbonate shells and the acidic environment. To address the acidification issue, a Na^+-form cation-exchange resin was explored for PST clearance, which abled it to maintain a stable pH range (pH 7.83-7.98) and was less harmful to mussels and the environment. Despite this improvement, the Na^+-form cation-exchange resin did not considerably increase PST clearance rates, most likely due to competition from cations found in seawater, interference from organic matter and the limited capacity of the mussels to filter the resin. In addition, the study assessed the elimination of PSTs from *Gymnodinium catenatum* cultures using the H-form cation-exchange resin for 48 hours. There was no elimination of C1&2 and GTX6 by the resin. While dcSTX and GTX5 were eliminated by 100% and 55%, respectively, resulting in an 80% drop in total toxicity equivalent to STX. The resin demonstrated high efficiency in eliminating dcSTX, most likely due to its less sterically hindered structure and positive charge, which aid in adsorption. Unlike dcSTX, toxin C1&2 and GTX6 have a bulky structure (due to *N*-sulfocarbamoyl groups in C1&2 and GTX6, *O*-sulphate group in C1&2 and extra hydroxyl

groups in GTX6) that showed limited adsorption owing to steric and electrical effects. Overall, the resin-based depuration in natural environments did not significantly enhance the PST clearance process as compared to those without resin. Additional work such as modifying the functional groups of resin to customize the physicochemical features of the system, are required in future.

Silica-malic acid chitosan hydrogel adsorbent (SMC) was prepared by physical cross-linking of malic acid and chitosan, followed by the incorporation of SiO_2 by [51]. The synthesised SMC was explored for its adsorption potential for PSTs from aqueous sample and scallop (*Argopecten irradians*) exposed to *Alexandrium minutum*. The results showed that SMC had considerable adsorption effects on GTX3 and GTX4, lowering the total toxicity of the aqueous sample (consisting 2.5 mg/mL of GTX1, GTX2, GTX3 and GTX4) by 54.42% in terms of STX eq. Specifically, SMC showed the highest adsorption efficiency for GTX4 in aqueous sample at a rate of up to 78.12%. On the other hand, the study discovered that the SMC group (scallop samples treated with SMC) significantly facilitated PST detoxification in scallops, lowering total PST toxicity in the hepatopancreas by 54.56% and kidneys by 55.30%. In comparison, the starving group, which did not receive any detoxifying treatment, had a substantially weaker detoxification effect, with only a 44.83% drop in total PST toxicity in the hepatopancreas and no significant reduction in the kidney. The lack of considerable detoxification effect in the starving group can be related to the presence of extremely toxic STX. After five days of depuration, the SMC group demonstrated a 17.60% drop in hepatopancreas toxicity and a 56.50% reduction in kidney toxicity, when compared to the starving group. In general, the starving group did not demonstrate substantial detoxification, while the SMC group efficiently lowered PST toxicity levels by 55.29%, suggesting the potential detoxifying capacity of SMC in facilitating the depuration of scallop samples.

In addition to experimental studies, several authors have employed computational approaches to gain molecular-level insight into how PSTs interact with carbon-based adsorbents. Such studies help rationalise the observed adsorption capacities and selectivity and can guide the future design of more efficient materials. To predict how PSTs will behave with different types of adsorbents, it would be advantages to conduct a computational study to obtain detailed insights into their molecular interactions at the surface level, which are frequently challenging to observe experimentally The following works illustrate how modelling and experiment can complement each other for PST removal. Alvarez et al. [52] performed a computational study using MMFF94 Force Field to determine supramolecular adsorption of hydroxybenzoate derivates of STX (GC toxins) to a pristine graphene surface. A basic model was employed to allow GC centred on the graphene surface to replicate the stacking of GC molecules on the graphene without interacting with the graphene edges. They discovered that the interactions of graphene and GCs are favourable, primarily driven by non-covalent interactions such as ion-π and π-π stacking interactions. While the aromatic GCs tend to show noticeably greater adsorption energies than the non-aromatic GCs, the enhanced adsorption strength is due to the π-π stacking interactions between the aromatic GCs and the graphene surface. The model also showed that best adsorption occurs when the guanidinium and sulphate groups of GCs were positioned near to the graphene surface. Overall, the study stresses that graphene's surface structure and polarity are important elements in influencing the adsorption intensity of GC toxins and the MMFF94 force field was a helpful tool for generating and analyzing such interactions. Concurrently, an experimental study performed by [53] revealed that mesoporous graphene nanoplatelets (GnPs) have quick adsorption kinetics for STX, reaching equilibrium in 1 hour when an adsorbent dosage of 50 mg/L was employed, whereas granular activated carbon (GAC) took up to 72 hours when a higher adsorbent dosage was used (2500 mg/L). For Langmuir isotherm study, GnPs showed a 93.5-fold greater Q_m (51.14 mg/g) than GAC (0.548 mg/g), while Freundlich isotherm affirmed the greater Q of GnPs due to the presence of various adsorption sites (edges, basal planes and defects) with a 157-fold higher Freundlich constant, K_F value. Basically, the exceptional performance of GnPs is due to their mesoporous structure, high specific surface area (750 m^2/g) and sp^2-hybridized carbon atoms, which enable effective adsorption via chemisorption mechanisms. This study is consistent with the predictions of [52] on the interactions between graphene and GCs, which highlighted the importance of surface characteristics of graphene in aiding adsorption with PSTs. Both studies revealed that π-π stacking and electrostatic interactions of graphene with PSTs play an important role in adsorption processes. Furthermore, higher pH and lower ionic strength enhanced STX adsorption because of greater electrostatic interactions between STX and GnP. In simulated

field water study, 90% STX were successfully removed by GnPs in 1 hour and this result demonstrates potential of GnPs in real-world water treatment. In short, these works advance our understanding of graphene's potential in the adsorption of PSTs, providing insights for the development of more efficient separation approaches. All adsorbents discussed in this section are tabulated in **Table 1** to provide a concise overview for readers.

Table 1. Novel adsorbents for the elimination of PSTs from water and shellfish

Adsorbate	Adsorbent	Adsorption Capacity	Removal (%)	Sample	Reference
STX	Magnetic humic acid-functionalized adsorbent	Q_e= 0.0022 mg/g	71.04	Aqueous sample	[42]
STX	Covalent organic polymer TpPa-COOH	Q_m= 5.69 mg/g	95.0-99.7	River and lake water	[43]
STX, MC-LR, cyanobacteria	Powdered activated carbon	NM	City of Akron: 13-89 for source water, nearly 0-76 for distilled water; City of Alliance: 23- 79 for source water, ~20-81 for distilled water	Source and distilled water	[45]
C1, C2, dcSTX, GTX5, GTX6	Cation-exchange resin	NM	55 of GTX5 removal and 100 of dcSTX removal from *G ymnodinium catenatum* cultures for 48 hours	*Gymnodinium catenatum* cultures and *Mytilus edulis*	[50]
STX, MC-LR	Pine-derived biochar	Q_m= 376.84–3507.46 µg/g for STX; Q_m= 210.23–622.53 µg/g for MC-LR	> 90	Aqueous sample	[47]
GTX1, GTX2, GTX3, GTX4, NEO, STX, dcSTX, dcGTX2, dcGTX3, C1, C2	Silica-malic acid chitosan	NM	≤78.12 for GTX1, GTX2, GTX3 and GTX4 from aqueous sample	Aqueous sample and *Argopecten irradians*	[51]
Hydroxybenzoate derivates of STX	Graphene	NA	NA	NA	[52]
STX	Loblolly pine derived biochar	Q_m= 314.37 µg/g	>90	Aqueous sample	[48]
STX	Graphene nanoplatelets (GnPs) and granular activated carbon (GAC)	Q_m of GnPs= 51.14 mg/g; Q_m of GAC=0.548 mg/g	GnPs: >90 removal in 1 hour; GAC: 64% removal in 1 hour	Surface water	[53]

NM= not mentioned; NA= not available; Q_e=adsorption capacity at equilibrium; Q_m=maximum adsorption capacity

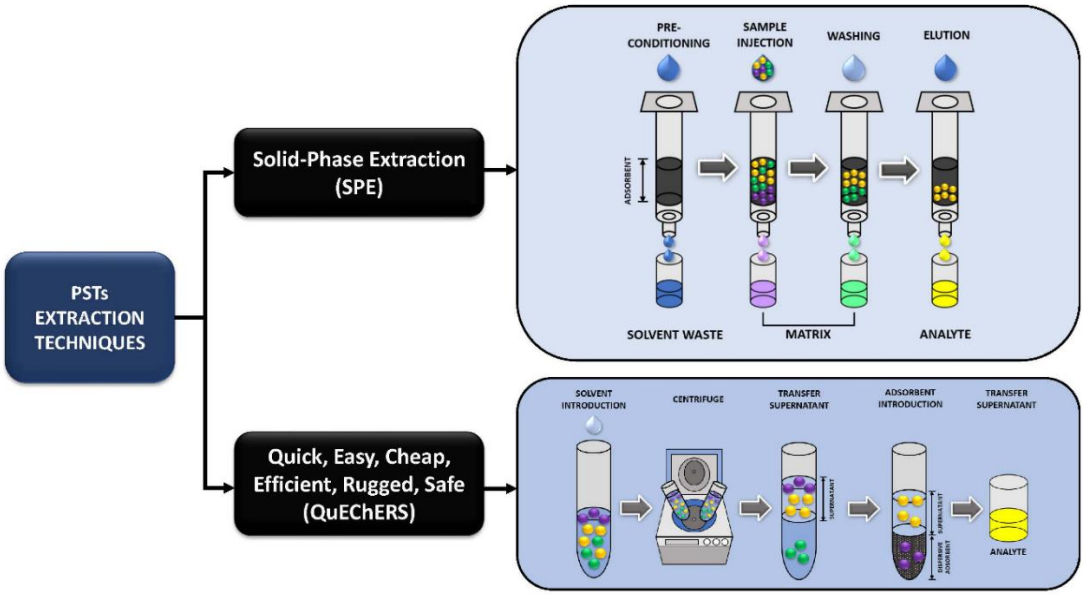


Figure 2. Common analytical workflows for PSTs extraction

Adsorptive approaches for the extraction of paralytic shellfish toxins

The persistence and high toxicity of PSTs, along with their potential to contaminate food and water sources, pose significant risks to the eco-system and public health. Regulatory agencies have established stringent guideline values to mitigate these risks and ensure the safety of consumables. Therefore, adopting effective pre-analytical workflows is critical for compliance with these standards, with adsorptive techniques playing a pivotal role in sample extraction and preparation. These methods enable the efficient removal of interference matrix and enrichment of the concentration of PSTs, thereby facilitating sensitive, accurate and reliable analysis. Solid-phase extraction (SPE) remains the most widely used adsorptive technique for PST analysis because it offers high selectivity, efficient clean-up and compatibility with LC–MS workflows. In this subsection, SPE-based workflows are first outlined, followed by recent developments in innovative adsorbent materials that further improve extraction performance. In **Figure 2**, two common analytical workflows for PSTs extraction using adsorptive techniques such as SPE and quick, easy, cheap, efficient, rugged, safe (QuEChERS) are presented.

SPE is a conventional method that uses a solid sorbent to selectively adsorb PSTs from a sample matrix, thereby facilitating their separation and concentration. For instance, [54] utilized porous graphitic carbon (PGC, Hypersep Hypercarb) as SPE sorbent for the extraction of nine PSTs and tetrodotoxin (TTX) from contaminated urine sample. PGC was employed due to its ability to form charge-induced dipolar and hydrophobic interactions with the PSTs and TTX. The method performance was evaluated using a novel desorption electrospray ionization mass spectrometry hyphenation with ultra-high-performance hydrophilic interaction liquid chromatography (UPHILIC) triple quadrupole mass spectrometry (QqQ/MS) method. The results demonstrated by satisfactory recovery rates of 83.8-95.4% for PSTs and 83.7% for TTX, respectively. Additionally, intra-day and inter-day precisions of the method were below 9.8 %, underscoring the consistency of the analytical method. Other than that, the method demonstrated LOQs for PSTs and TTX below 49.7 µg/L and 23.0 µg/L, respectively, confirming its high sensitivity for the PSTs and TTX quantification in urine sample.

A similar study conducted by [55] had evaluated the extraction performance of TTX and 12 PSTs by comparing PGC and graphitized carbon black (GCB, Supelclean ENVI-Carb) SPE cartridges in the influence of mussel, oyster and scallop matrix based on the extraction recovery rate. With the introduction of ion-paring reagent (method A), specifically tridecafluoroheptanoic acid (TDFHA), the extraction performance of most toxins (TTX, neoSTX, STX, dcSTX, GTX1, GTX4, GTX2, dcGTX2, dcGTX3 and C2) using PGC sorbent was better than GCB sorbent. As compared to GCB sorbent, the porous sponge structure in PGC provided relatively larger specific surface area and enable better entrapment of TDFHA, which could adsorb the hydrophilic TTX and PSTs through ion-pairing, significantly improved the extraction

performance. In contrast, the overall extraction performances of both SPE cartridges diminished when ion-pairing reagent was omitted (method B), with the performance trends varying between both cartridges. Interestingly, GCB sorbent exhibited better extraction performance for certain toxins, including STX, dcSTX, GTX1, dcGTX2 and C2 meanwhile GTX5 and C1 showed better recovery with PGC under method B condition. Furthermore, the authors discovered the concentration of the elution solution substantially impacted the extraction performance of SPE cartridges. The finding showed that only 40 % acidified acetonitrile solution could effectively elute all targeted toxins from the SPE cartridge. The overall extraction performance of PGC sorbent was determined using UPHILIC tandem triple quadrupole mass spectrometry (UPHILIC-QqQ/MS/MS), yielding reliable recovery ranges of 79.5-95.5% for PSTs and 76.5-84.1% for TTX in the influence of sample matrix. This analytical method demonstrated high precision, as reflected by RSD values below 12.0 %. Moreover, the LOQs for PSTs and TTX were below 41.0 µg/kg and 10.0 µg/kg, respectively, underscoring its high sensitivity in detecting PSTs and TTX in the seafood matrixes. As a result, this extraction performance of PGC sorbent was comparable to the study by [54], with both demonstrating high recovery rates and similar RSD for PSTs and TTX, despite slight differences in values were observed due to variations in the sample matrixes, separation and detection methods, indicating that the performance of PGC sorbent remained consistent under different conditions.

A recent study conducted by [56] used GPC sorbent for the extraction of 13 PSTs from the same sample matrix showed different extraction performances as compared to the findings of [55]. In the similar separation and quantification conditions, [56] achieved notably higher extraction performance with recovery range of 96.57-103.57%. Plus, the sensitivity and precision were relatively higher as well, exploiting to lower LOQs (≤4.97 µg/kg) and RSD values (≤2.27 %). These advancements might attribute to the variations in SPE procedure such as the washing volume. When a lower washing volume (700 µL) was employed, it prevented premature elution of PSTs, meanwhile maintaining the efficiency of matrix removal as compared to a higher washing volume (2 mL) that used in the extraction work of [55]. Additionally, other parameters might have contributed to these advancements, including the differences in conditioning solvent, the matrix interference (e.g. TTX) and the setting up of the liquid chromatography and mass spectrometry instrumentations. Further investigation is critically important to study the influence of these parameters and provide a comprehensive understanding of their impact on the extraction performance. Besides, a study by [57] investigated SPE performance of 14 PSTs in shellfish sample using four different sorbents, including hydrophilic N-vinyl-pyrrolidone and lipophilic divinylbenzene balance (HLB) sorbent, GPC sorbent, high purity silica (Si) sorbent and mixed cation exchange (MCX) sorbent. Among these, the GPC sorbent demonstrated the highest extraction recovery rates for PSTs, with 78% of the compounds achieving recoveries between 60% and 120%. In comparison, extraction recoveries were lower for HLB (43%), MCX (42%) and Si (7%), highlighting GPC as the most effective sorbent for extracting PSTs from shellfish samples. The overall extraction performances of the GPC sorbents were evaluated using UPHILIC-high resolution mass spectrometry, yielding recovery rates between 81.50-118.36%. This analytical method exhibited high sensitivity and high precision with low LODs for each PSTs (≤8.78 µg/kg) and low RSDs (≤15.48%) for all the PSTs in shellfish matrix. [58] introduced a two-step enrichment analytical approach by combining off-line GPC SPE and on-line zwitterionic SPE cartridges prior for the extraction of 13 PSTs from the seawater samples. In this study, the sample loading volume effect on the enrichment efficiency was evaluated at three different levels (50, 80 and 120 mL). The results revealed that the extraction performance increased with the sample loading volume in certain toxins (C1, C2, GTX1, GTX4 and GTX2). However, the extraction efficiencies exhibited a dumbbell-shaped trend for most toxins (dcGTX2, dcGTX3, GTX5, STX, NEO, dcSTX and dcNEO), which might be due to the premature elution of weakly adsorbed toxins at higher sample injection volume (120 mL). Besides that, the study also assessed the matrix effect (seawater and pure water) on the extraction performance. Notably, the extraction performance was significantly higher in seawater than pure water for all PSTs. This enhancement was attributed to the high salt content in the seawater sample, which created a strong salting effect and dampened the availability of the water molecule, thus facilitated the toxins transfer from sample to the enrichment phase. During the separation stage, the PSTs enrichment was further achieved through the zwitterionic SPE cartridge, which was integrated in a valve distinct from the separation column. However, the optimization detail of the on-line SPE setup was not reported. Overall, the extraction performance was evaluated using on-line SPE-UPHILIC-MS/MS

and reported with satisfactory recovery rates (63.4-102.4%) in three different sample matrixes. The combination of off-line and on-line SPE effectively enriched PSTs, achieved extremely low LOD and LOQ (≤2.33 ng/L) and satisfactory RSD value (≤ 11.32 %), underscoring its potential for precise and sensitive PSTs analysis in seawater sample. In addition to SPE, alternative adsorptive approach prior to the PSTs extraction was also reported. For instance, [14] presented a modified QuEChERS method utilizing octadecylsilane (C_{18})/GCB dispersive sorbent for the extraction of 10 PSTs and 2 TTXs from the human serum samples. In this study, the effect of the dispersive adsorbent composition on the extraction performance was evaluated by comparing pure GCB, pure C_{18} and GCB/C_{18} with 1:1 mass ratio. C_{18} demonstrated strong adsorption of non-polar matrix through hydrophobic interaction by its long hydrophobic chains. Conversely, GCB provided excellent retention for planar and planar aromatic molecules, exploiting to its hexagonal microstructure. The combination of both C_{18} and GCB enabled comprehensive matrix retention and removal from the supernatant, resulting in better extraction performance with relatively higher extraction recovery rate for all PSTs and TTXs (81.2-106.0%) when compared to the use of C_{18} (41.1-105.2%) and GCB (60.3-102.7%) sorbents alone. The overall extraction performance of the modulated dispersive sorbent was further validated using the modified QuEChERS coupled with UPHILIC Q-Exactive Orbitrap high resolution mass spectrometry. This approach achieved recovery ranges of 85.3-118.2% for PSTs and 89.3-105.9% for TTXs, indicating high extraction performance. The analytical method demonstrated acceptable precision with RSD values below 12.1 % for PSTs and 11.2% for TTXs. Moreover, the method exhibited high sensitivity by achieving low LODs and LOQs of ≤8.69 ng/mL for PSTs and ≤3.28 ng/mL for TTXs. The summary of adsorptive approaches that used PSTs extraction, along with their analytical performance is presented in **Table 2**.

Conclusion and future insights

Adsorbent-based methods have shown to be one of the most promising methods for removing PSTs from aquatic systems among the methodologies investigated. It provides a useful way to lower marine toxin levels by accumulating PSTs onto the surface of adsorbent. The optimisation of adsorbent materials, the scalability of treatment methods and the cost-effectiveness of implementation are some of the problems that still need to be overcome despite its potential. Furthermore, the dynamic nature of aquatic ecosystems, as well as the intricate interactions among PSTs, co-contaminant and other water elements, make it difficult to effectively predict and respond to marine toxins. Therefore, future research should concentrate on tackling these issues and developing novel approaches to improve the efficiency of adsorbent-based PST removal methods.

Currently, there is still no viable method for eliminating PSTs from shellfish, owing to uncontrollable variables that complicate the detoxification process. While adsorption-based approaches have potential, their efficacy is governed by parameters such as adsorbent stability and species-specific circumstances, making it challenging to produce reliable and consistent treatments. Despite these difficulties, adsorption has advantages in terms of simplicity and cost-effectiveness. However, economic, political and technological challenges remain, including the need for more optimisation and overcoming legal impediments to detoxifying live contaminated shellfish. Future study should improve these approaches by considering the influence of uncontrollable factors and guarantee that adsorption-based detoxification is both economically viable and scalable to provide a safe approach for lowering PSTs in seafood.

Adsorption-based methods, notably SPE, are critical for the effective extraction of PSTs. This adsorption approach employs the interaction of PSTs with a solid phase adsorbent to isolate, preconcentrate and purify them from complex sample matrices like water and shellfish tissues. It is very useful for boosting the sensitivity and accuracy of PST detection since it minimises sample amount while eliminating matrix interferences. Advances in SPE have resulted in the development of novel adsorbents, such as C_{18}/GCB dispersive sorbents in QuEChERS method, which improve the selective adsorption of PSTs. Furthermore, optimising adsorbent materials, such as C_{18} resins or graphitized carbon-based sorbent, has boosted toxin recovery efficiency and rates from diverse matrices. While fine-tuning adsorption procedures to account for various PST analogues is difficult, adsorption remains an important toxin monitoring approach. It offers a cost-effective and ecologically friendly alternative to more sophisticated extraction procedures, as well as a scalable strategy for PST detection across a wide range of sample types.

Establishing comprehensive management plans that incorporate monitoring, mitigation and

Table 2. List of adsorbents for PSTs extraction and their analytical performances

Adsorbate	Adsorbent (Brand)	Extraction Method	Sensitivity	Relative Recovery	Relative Standard Deviation	Sample	Reference
TTX, neoSTX, STX, dcSTX, GTX1, GTX2, GTX 3, GTX4, dcGTX2, dcGTX3	Porous graphitic carbon (Hypersep Hypercarb)	SPE	PSTs 2.2-14.9 ug/L [a] 7.3-49.7 ug/L [b] TTX 6.9 ug/L [a] 23.0 ug/L [b]	PSTs 83.7 – 95.4 % TTX 83.7 %	PSTs 4.8 – 9.2 % [c] 5.5 – 9.8 % [d] TTX 6.9 % [c] 23.0 % [d]	Urine	[54]
TTX, NEO, STX, dcSTX. GTX5, GTX1, GTX4, GTX2, GTX3, dcGTX2, dcGTX3, C1, C2	Porous graphitic carbon (Hypersep Hypercarb)	SPE	PSTs 1.7-13.7 ug/kg [a] 5.2-41.0 ug/kg [b] TTX 3.3 ug/kg [a] 10.0 ug/kg [b]	PSTs Mussel: 80.5-91.6 % Oyster: 81.6-95.4 % Scallop:79.5-95.5 % TTX Mussel: 77.6-83.2 % Oyster: 76.5-81.6 % Scallop:79.5-80.2 %	PSTs Mussel: 3.1-12.0 % Oyster: 3.6-9.7 % Scallop: 4.0-10.0 % TTX Mussel: 4.2-10.8 % Oyster: 5.1-5.6 % Scallop: 3.9-7.2%	Mussel, oyster and scallop	[55]
STX, NEO, GTX5, dcNEO, C1, C2, GTX2, GTX3, dcGTX2, dcGTX3, dcSTX, GTX1, GTX4	Graphitized carbon black (Supelclean ENVI-Carb)	SPE	Mussel 0.16-1.49 ug/kg [a] 0.54-4.97 ug/kg [b] Oyster 0.33-1.92 ug/kg [a] 1.09-6.41 ug/kg [b] Clam 0.20-1.46 ug/kg [a] 0.65-4.86 ug/kg [b]	Mussel 97.17-103.57 % [c] 97.64-101.81 % [d] Oyster 97.13-102.10 % [c] 97.58-101.56 % [d] Clam 96.57-102.07 % [c] 97.64-101.81 % [d]	Mussel 0.014-2.22 % [c] 0.14-2.27 % [d] Oyster 0.09-2.07 % [c] 0.12-1.98 % [d] Clam 0.02-2.10 % [c] 0.11-1.86 % [d]	Mussel, oyster and, clam	[56]
STX, NEO, GTX1, GTX2, GTX3, GTX4, GTX5, GTX6, C1, C2, dcSTX, dcNEO, dcGTX2, dcGTX3	Graphitized carbon black (Supelclean ENVI-Carb)	SPE	0.20-8.78 µg/kg [a]	86.99-118.36% [c] 81.50-118.29% [d]	0.19-9.54% [c] 1.30-15.48% [d]	Shellfish	[57]
C1, C2, GTX1, GTX4, GTX2, GTX3, GTX5, dcGTX2, dcGTX3, NEO, STX, dcNEO, dcSTX	Graphitized carbon black (Supelclean ENVI-Carb) + zwitterionic polymer (ZIC-HILIC guard column)	Off-line SPE + on-line SPE	0.13-1.05 ng/L [a] 0.38-2.33 ng/L [b]	60.59-108.76 %	1.17-8.85 % [c] 2.28-11.32 % [d]	Seawater	[58]
TTX, 4,9-anhydroTTX, STX, dcSTX, neoSTX, dcGTX2, dcGTX3, GTX5, GTX2, GTX3, GTX1, GTX4	Mixture of C_{18} and graphitized carbon black	QuEChERS	PSTs 0.90-2.61 ng/mL [a] 2.98-8.69 ng/mL [b] TTXs 0.67-0.98 ng/mL [a] 2.23-3.28 ng/mL [b]	PSTs 85.3-118.2% TTXs 89.3-105.9%	PSTs 1.2-5.4% [c] 5.6-12.1% [d] TTXs 2.0-3.1% [c] 7.4-11.2% [d]	Human serum	[10]

[a]= LOD; [b]= LOQ; [c]= Intra-day; [d]= Inter-day

public awareness campaigns are significant and it requires interdisciplinary cooperation (among scientists, policymakers and stakeholders from different disciplines) and regional alliances. It is necessary for knowledge exchange across disciplines to stimulate innovation and implement evidence-based management practices. Regulatory bodies also play a pivotal part in establishing water quality standards, monitoring procedures and responses systems. However, differences in regulations among jurisdictions, limitations in enforcement and evolving toxin profiles will highlight the need for adaptive and standardised procedures to enforce regulations by improving regulatory frameworks necessitates ongoing evaluation and change based on scientific evidence, stakeholder feedback and developing PST dynamics.

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