

# Cyclodextrins as capture agents of lipophilic marine toxins

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## Introduction

• **Harmful algal blooms (HABs)** caused by proliferation of the phytoplankton are increasing geographically and in frequency. Phytoplankton releases toxins in the water that may accumulate in seafood, specially in filter feeding bivalves, causing seafood intoxication in humans. Contamination of seafood by marine toxins is an international public health issue.



• **Lipophilic marine toxins** are produced by dinoflagellates, such as *Dinophysis* spp. and *Prorocentrum* spp.: okadaic acid (OA), its derivatives dinophysistoxins (DTXs) and pectenotoxin (PTX2).

• Many countries have **monitoring programs** for:

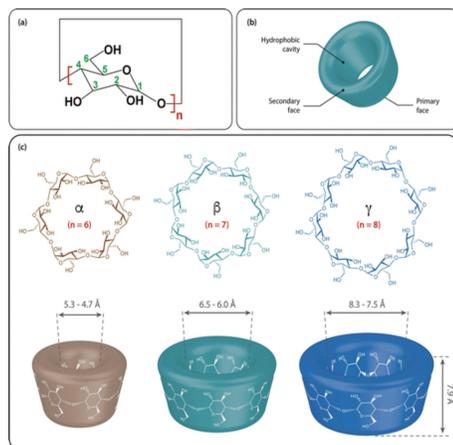
- Toxins in shellfish flesh
- Toxic phytoplankton counts



• New method since 2004:

- Toxins in seawater: solid phase adsorption and toxin tracking (SPATT)

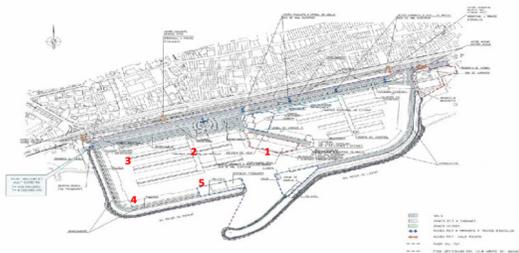
• **Cyclodextrins** are cyclic oligosaccharides composed of six, seven or eight ( $\alpha$ ,  $\beta$  or  $\gamma$ ) glucose units linked together by glucosidic bonds, with a hydrophobic inner cavity that allows guest molecules to enter and be captured.



**OUR PROPOSAL: USE CYCLODEXTRINS AS CAPTURE AGENTS IN SPATT**

## Methodology

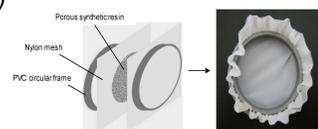
- Preparation of **SPATT** discs:
  - $\beta$ -epichlorohydrin ( $\beta$ -EPI)
  - $\gamma$ -epichlorohydrin ( $\gamma$ -EPI)
  - $\beta$ -hexamethylene diisocyanate ( $\beta$ -HDI)
  - $\gamma$ -hexamethylene diisocyanate ( $\gamma$ -HDI)
  - Commercial Diaion® (HP-20) (as a control)



- SPATT deployment**
  - Masnou harbour (NW Mediterranean)
  - Five sampling points and two depths

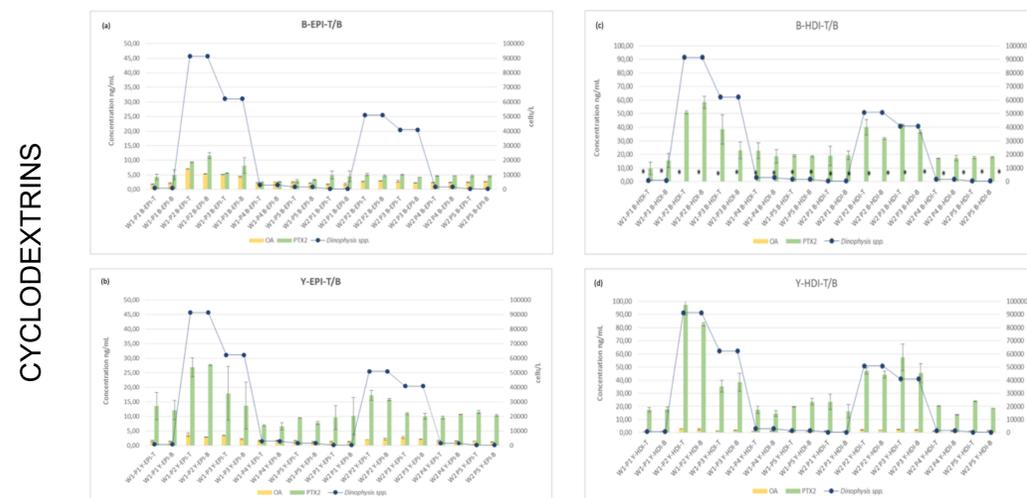
- Toxin **extraction** in methanol

- Toxin analysis with liquid chromatography tandem mass spectrometry (**LC-MS/MS**)

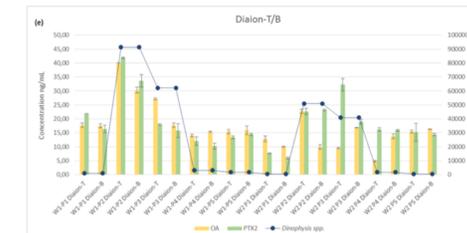


## Results

### 1. Toxin accumulation per resin

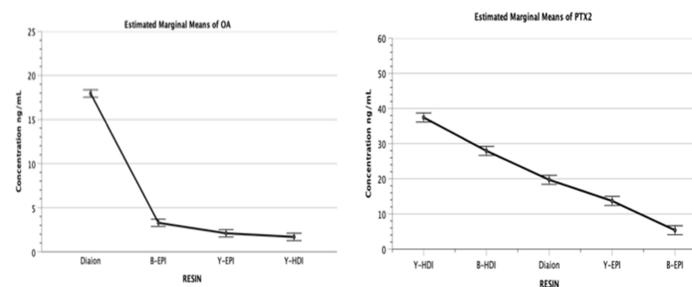


### CONTROL



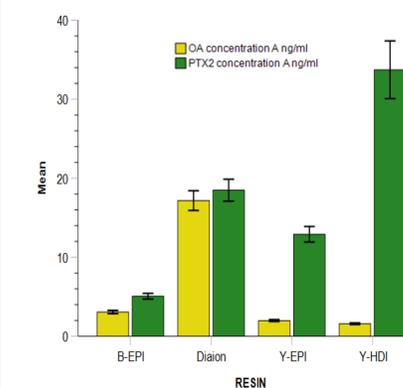
Clear correlation between phytoplankton cell abundance and toxin accumulation for each resin can be observed.

### 2. Resin size and material



- The Diaion is the predominant adsorber of OA, where no significant differences were observed between  $\beta$ -EPI,  $\gamma$ -EPI and  $\gamma$ -HDI ( $\beta$ -HDI was not quantifiable by LC-MS/MS).
- $\gamma$ -HDI and  $\beta$ -HDI provided the best adsorptions for PTX2, followed by Diaion and then  $\gamma$ -EPI and  $\beta$ -EPI.
- The cyclodextrin material play a more crucial role than size.

### 3. Toxin adsorption



- Cyclodextrins showed higher adsorption of PTX2 than OA, differences being very evident for  $\gamma$ -cyclodextrins.

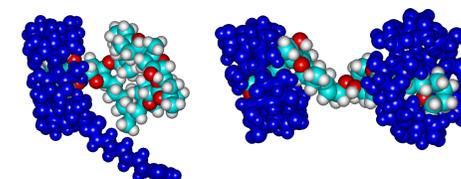
### 4. In vitro assay (spiked seawater)



- All resins showed good recoveries for both OA and PTX2 and no competition was observed.

## Conclusions

- Good correlation between *Dinophysis* spp. cell abundances and toxin content was observed, indicating that cyclodextrins have proven efficient and reliable as a monitoring tool.
- Cyclodextrins have proven extremely sensitive PTX2 adsorbers.
- Resin type and resin size matters.
- Cyclodextrins are able to adsorb lipophilic marine toxins and therefore can be used as novel materials in SPATT technology.



- Studies about the relationship between toxin accumulation in cyclodextrins and toxin accumulation in shellfish have to be performed.

## Acknowledgements

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