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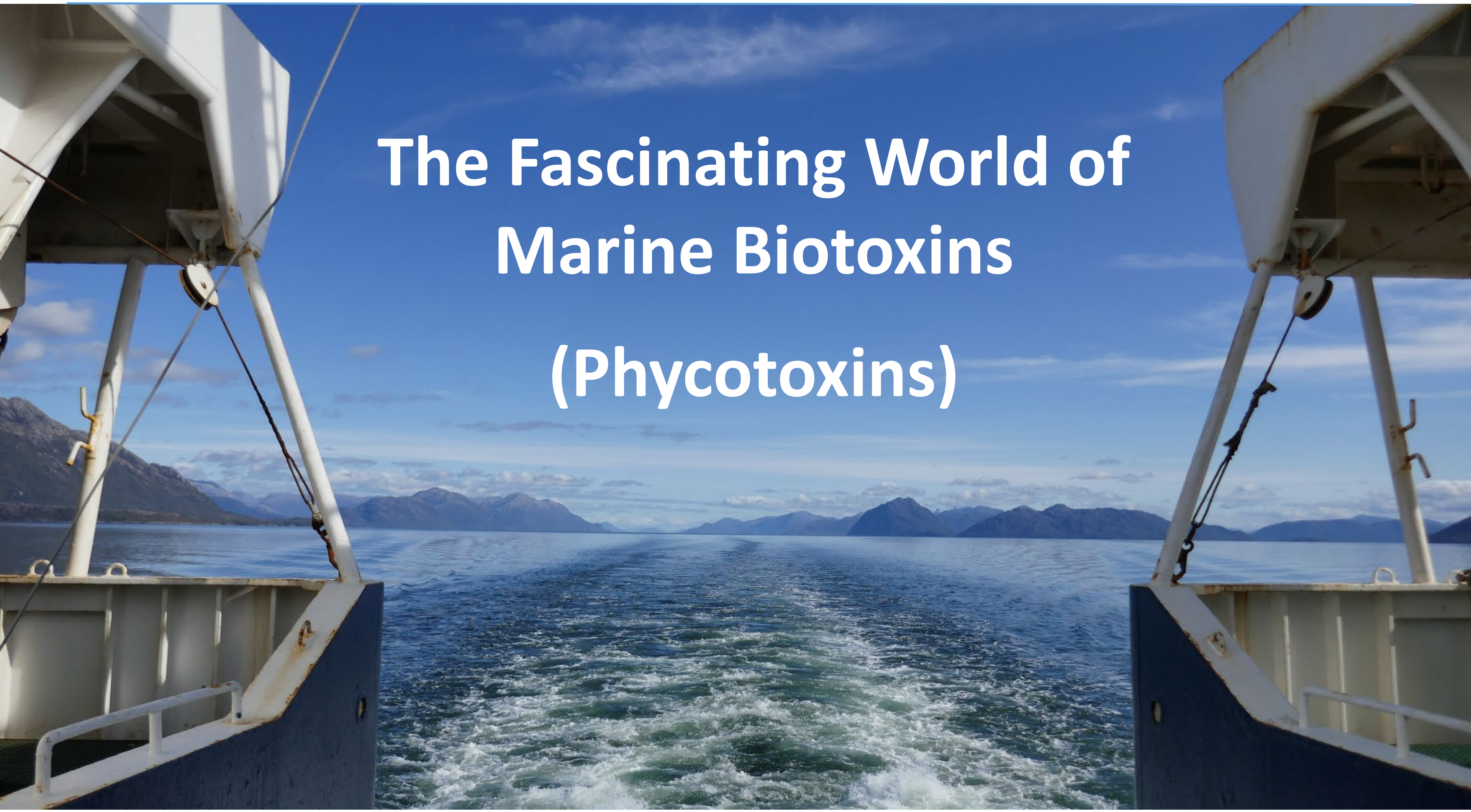
The Fascinating World of Marine Biotoxins

(Phycotoxins)



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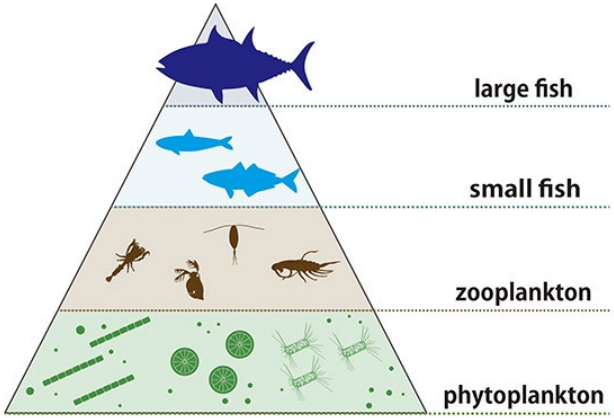
Bernd Krock, HABTUPORE, Istanbul University, 07.05.2024

Introduction

- Marine toxins = Phycotoxins are toxic chemicals produced by photosynthetic plankton-species
- Dinoflagellates are the principle producers of phycotoxins
  → Also toxigenic diatoms or cyanobacteria amongst others
- Accumulate in a variety of filter feeding bivalves or shellfish and can reach high concentrations during algal blooms
  → "Harmful algal blooms" = HABs

Algal Bloom Lake Erie



Introduction

February/March 2016, Regíon de Los Lagos, Chile:
massive bloom of *Pseudochattonella* cf. *verruculosa* associated with fish kills

Introduction

April/May 2016, Región de Los Lagos, Chile:
massive bloom event of *Alexandrium catenella* associated with high shellfish contamination

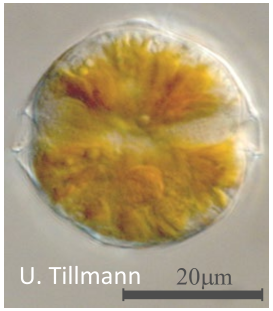
Introduction

Both blooms were almost coinciding in time and space and caused mass mortality of marine life, especially in salmon aquaculture

Mechanistically both blooms were differrent:

Pseudochattonella cf. *verriculosa*:
Ichthyotoxic

Alexandrium catenella:
Paralytic Shellfish Poisoning Toxin producer



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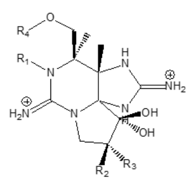
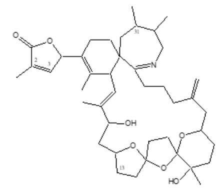
Organism | **Chemical compound** | **Ecological Function**

Alexandrium spp.

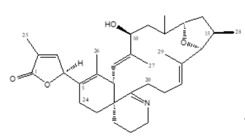
PSP-Toxins



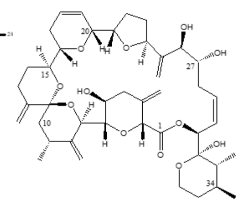
Spirolides



Gymnodimines



Goniodomins



?

Pseudochattonella cf. *verriculosa*

(*Alexandrium* spp.)

?

Defense against Predators

Elimination of Competitors

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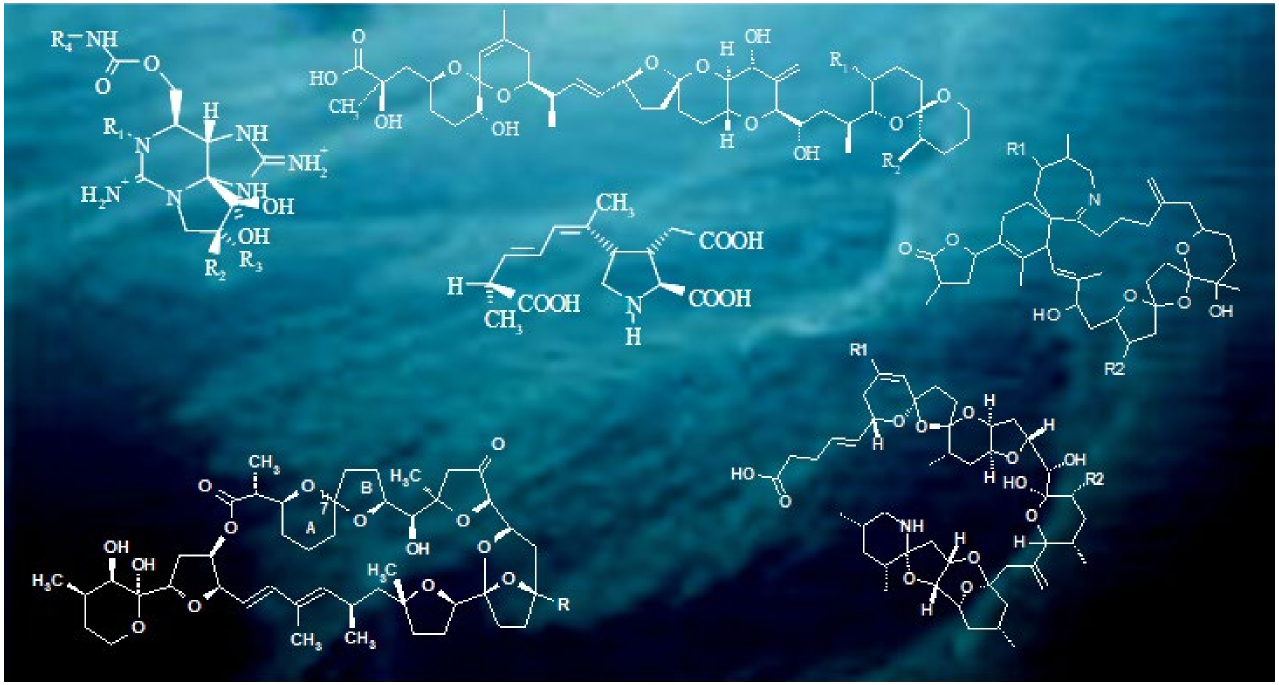
High variability of phycotoxin classes

- Amphidinol
- Anatoxin
- Azaspiracid
- Brevetoxin
- Ciguatoxin
- Cylindrospermopsin
- Domoic Acid
- Goniodomin
- Gymnocin
- Gymnodimine
- Karenia brevisulcata toxin
- Karlotoxin
- Lyngbyatoxin
- Microcystin
- Nodularin
- Okadaic acid
- Palytoxin
- Pectenotoxin
- Pinnatoxin
- Prymnesin
- Saxitoxin
- Spirolide
- Yessotoxin



Need of monitoring for seafood safety

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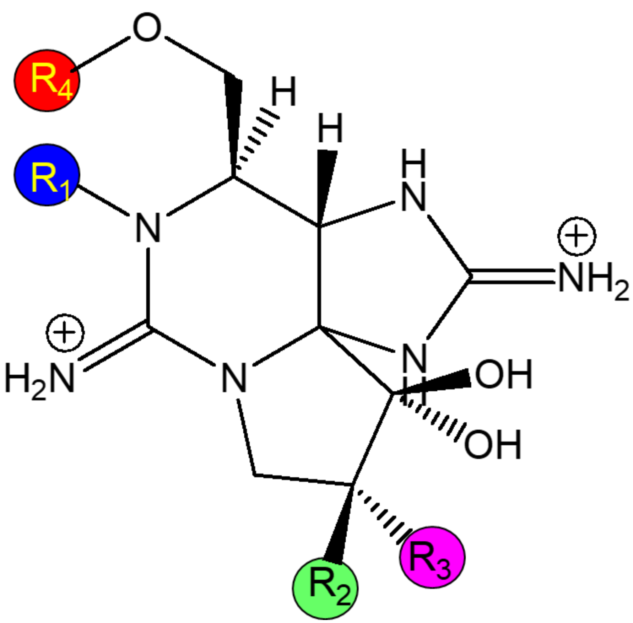
Paralytic Shellfish Poisoning (PSP) Toxins

PSP: structures and charges



Double charged PSP-toxins (no sulfonyl/sulfate group)

Single charged PSP-toxins (1 sulfonyl/sulfate group)

Neutral PSP-toxins (1 sulfonyl & 1 sulfate group)

Toxin	R1	R2	R3	R4	Toxictity factor
STX	H	H	H	$CO\text{-}NH_2$ (Carbamoyl-)	1.00
NEO	OH	H	H		1.10
GTX1	OH	H	OSO_3^-		0.90
GTX2	H	H	OSO_3^-		0.48
GTX3	H	OSO_3^-	H		0.76
GTX4	OH	OSO_3^-	H		0.90
B1= GTX5	H	H	H	$CO\text{-}NH\text{-}SO_3^-$ (*N*-Sulfo-carbamoyl-)	0.07
B2= GTX6	OH	H	H		0.07
C3	OH	H	OSO_3^-		<0.01
C1	H	H	OSO_3^-		0.01
C2	H	OSO_3^-	H		-
C4	OH	OSO_3^-	H		-
dc-STX	H	H	H	H (De-carbamoyl-)	0.43
dc-NEO	OH	H	H		0.43
dc-GTX1	OH	H	OSO_3^-		0.45
dc-GTX2	H	H	OSO_3^-		0.15
dc-GTX3	H	OSO_3^-	H		0.18
dc-GTX4	OH	OSO_3^-	H		0.45

STX = Saxitoxin, NEO = Neosaxitoxin, GTX = Gonyautoxin

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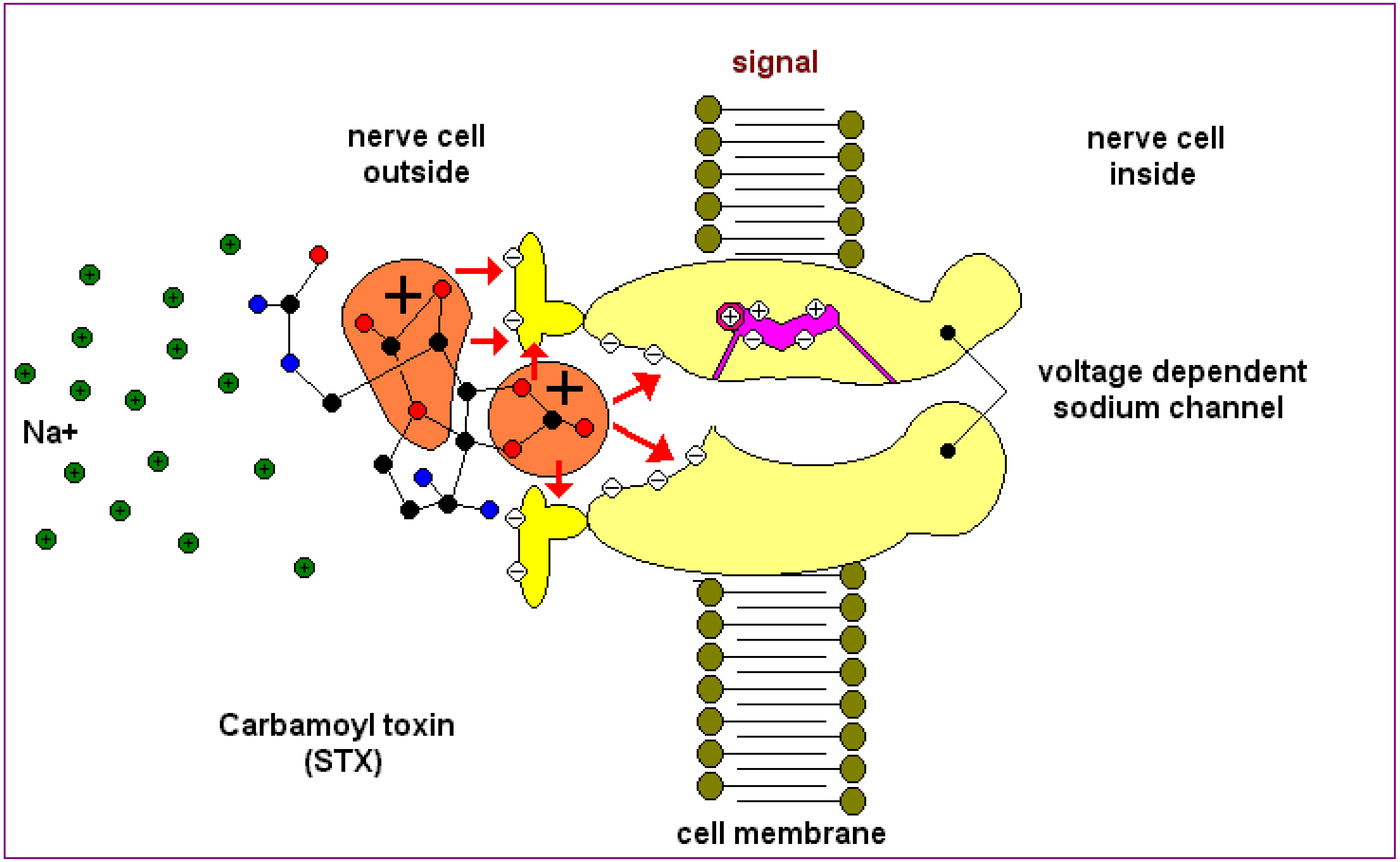
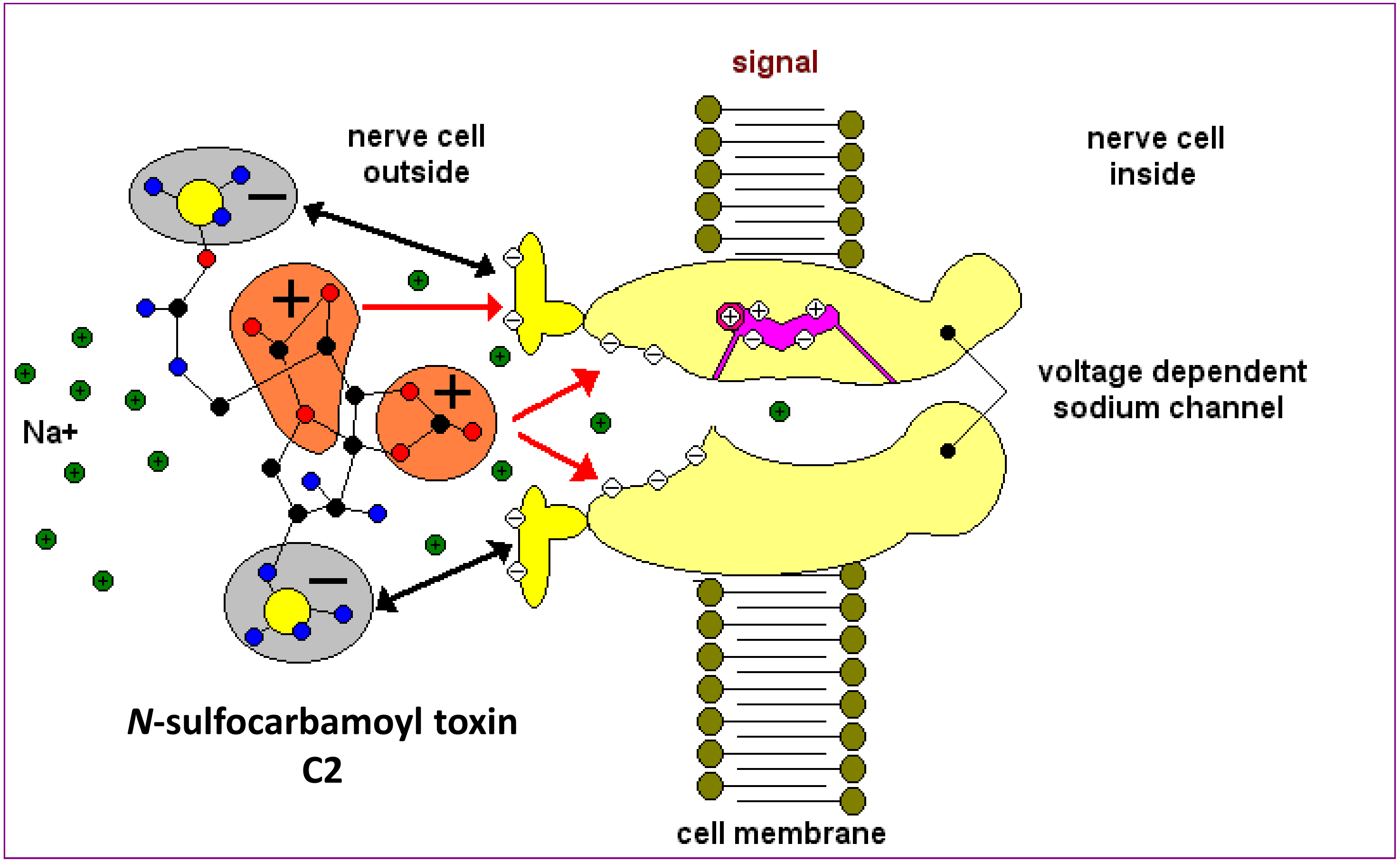
Paralytic Shellfish Poisoning (PSP) Toxins

PSP: charges and toxicity



Paralytic Shellfish Poisoning (PSP) Toxins

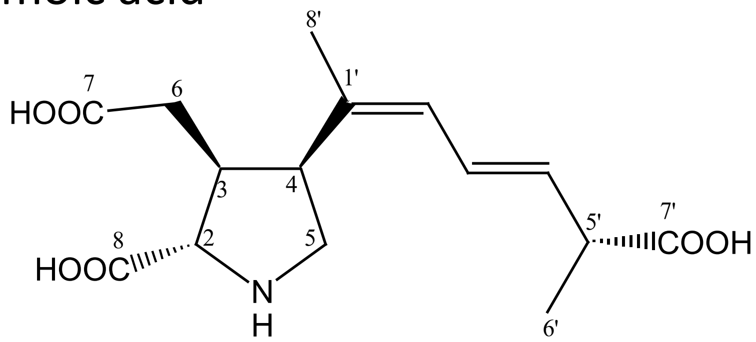
PSP: charges and toxicity



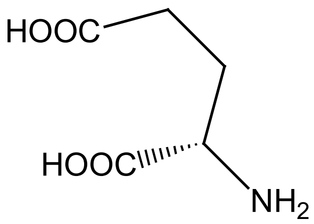
***N*-sulfocarbamoyl toxin**
C2

Amnesic Shellfish Poisoning (ASP) Toxin

Domoic acid



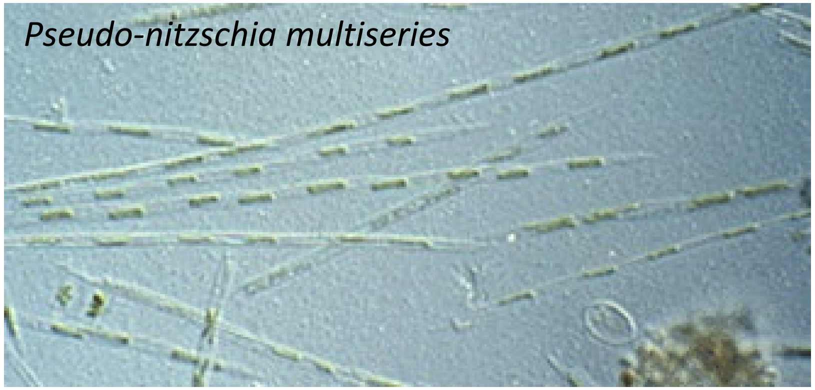
Domoic acid



Glutamic acid

Toxicity:
LD_{50}: 2.4 mg/kg (ip; mice)

Pseudo-nitzschia spp.



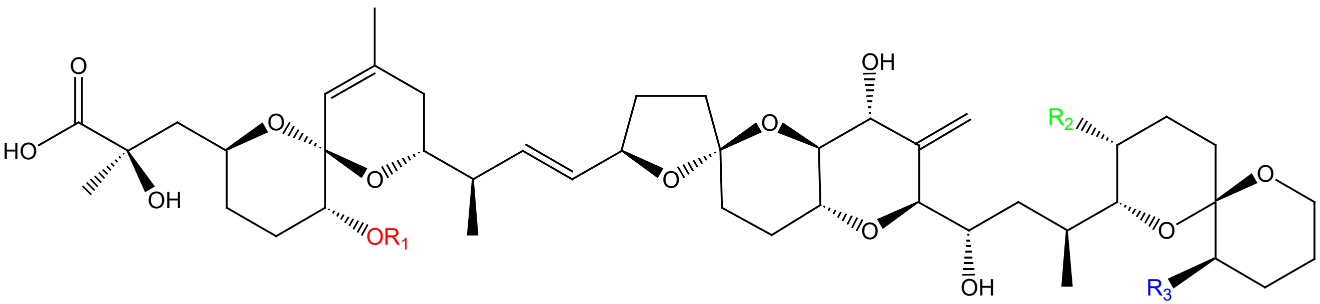
Mode of Action:

Glutamic acid agonist, binds to certain glutamic acid receptors (kainate receptors) in the brain and causes neuronal firing due to the inability of glutamate transporters to clear DA from the synaptic cleft, thus prolonging neuronal excitation.

Neurotoxic, causes neurobehavioural effects, loss of short term memory

Diarrheic Shellfish Poisoning (DSP) Toxins

Dinophysistoxins/okadaic acid



Dinophysis spp.
Prorocentrum spp.

	R1	R2	R3
OA	H	CH_3	H
DTX1	H	CH_3	CH_3
DTX2	H	H	CH_3
DTX3	CH_3CO	CH_3	CH_3
Acyl-OA	CH_3CO	CH_3	H

Dinophysis acuminata

Prorocentrum lima

OA: Okadaic acid (first isolated from the sponge *Halichondria okadaii*)

Diarrheic Shellfish Poisoning (DSP) Toxins

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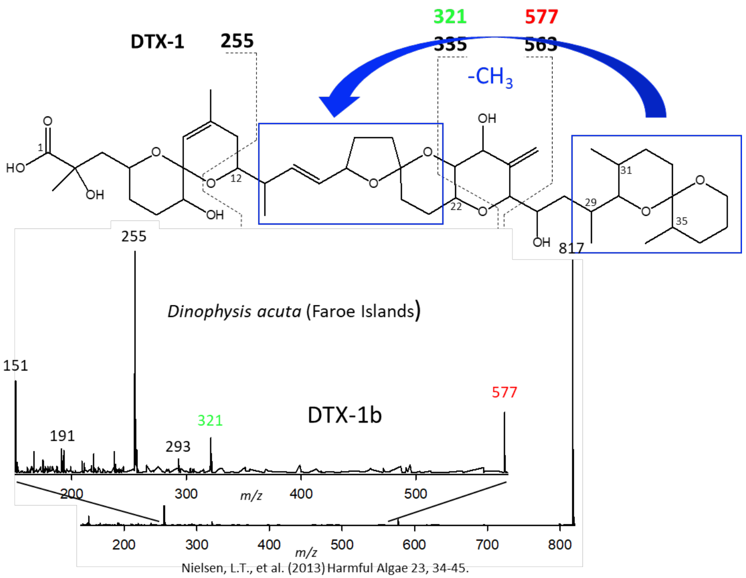
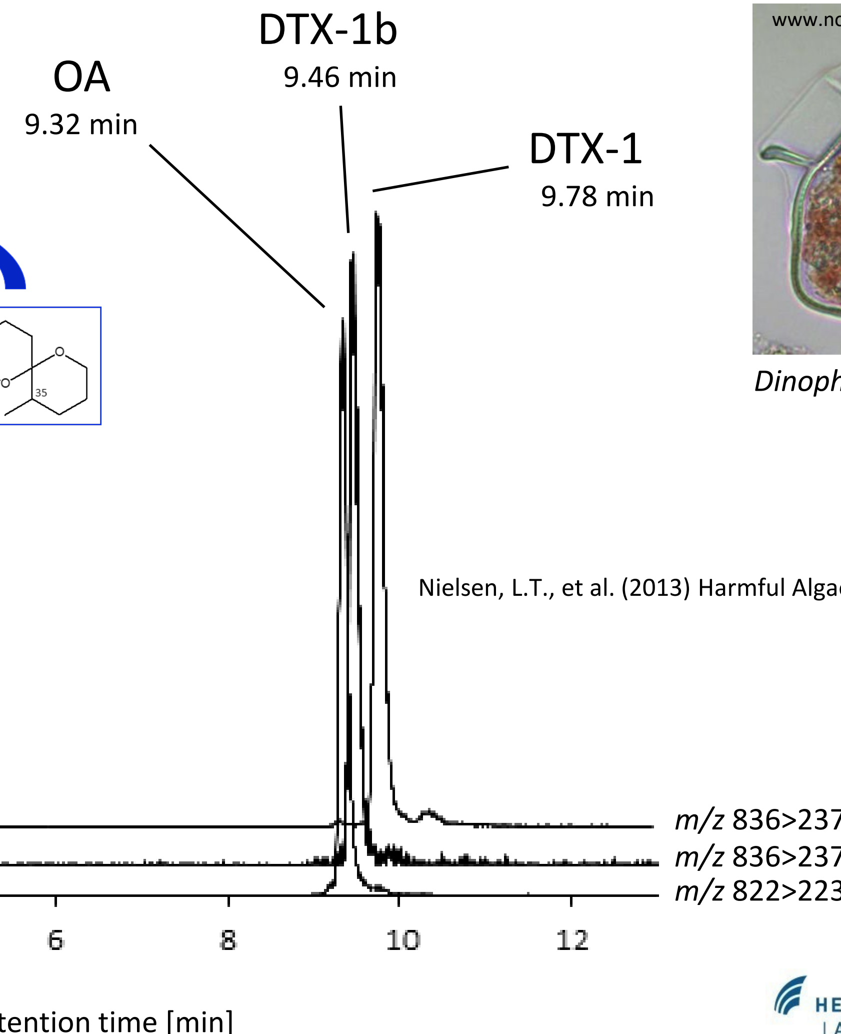
Dinophysistoxin variants: DTX1 isomer





Dinophysis acuta

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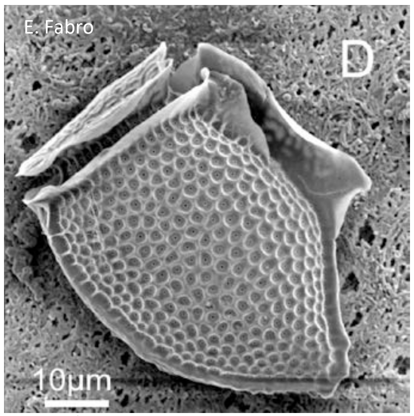
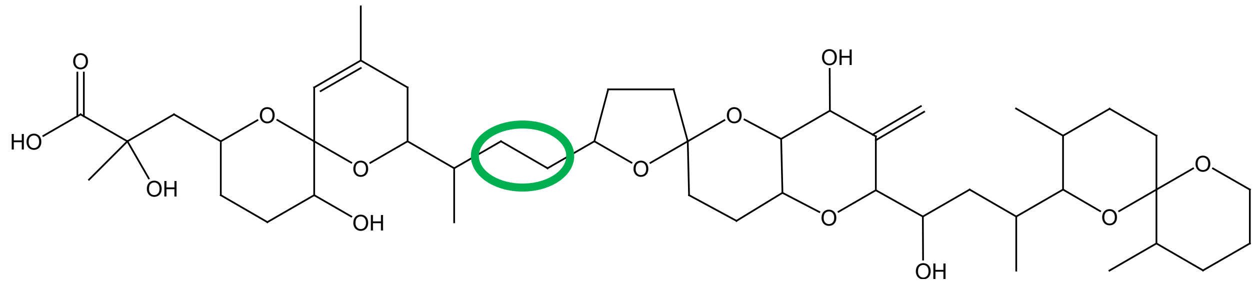
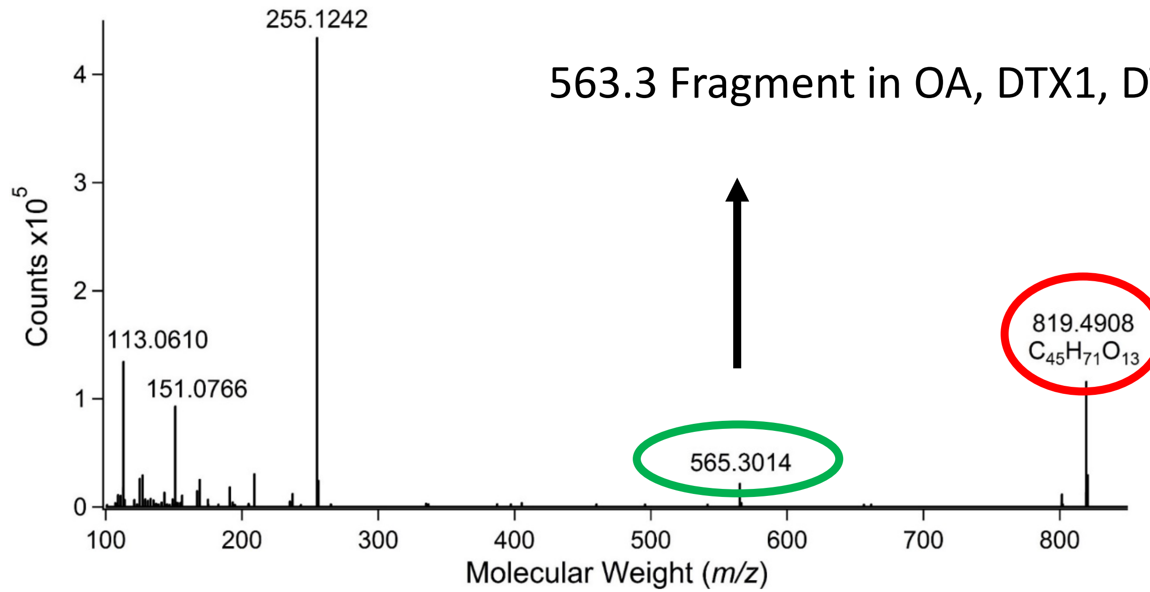
Diarrheic Shellfish Poisoning (DSP) Toxins

Dinophysistoxin variants: dihydro-DTX1



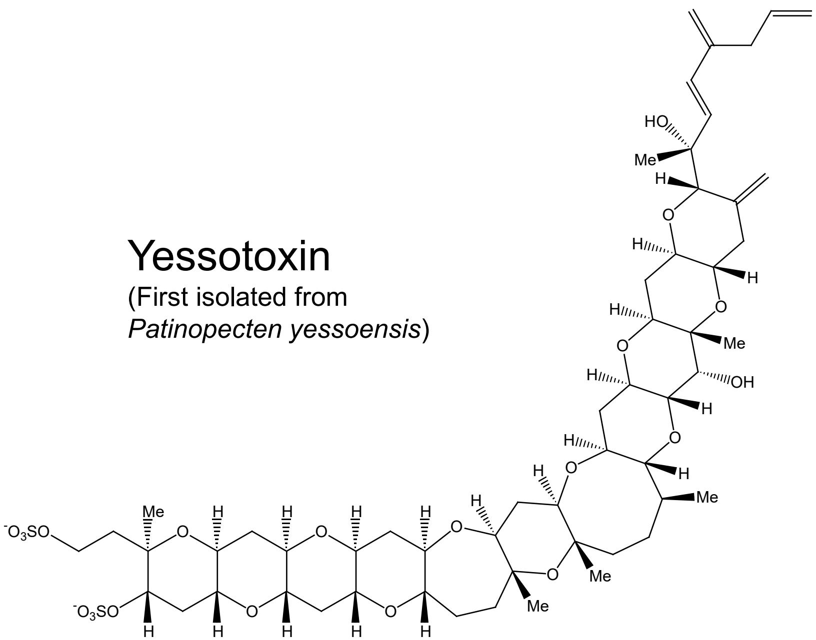
Dinophysis norvegica





Deeds, J.R., et al. (2020). Toxins 12(9): 533.

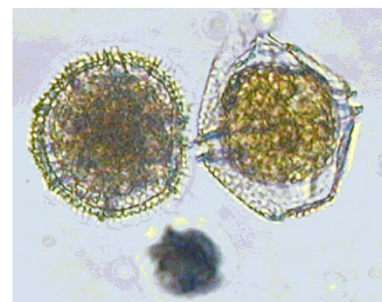
Yessotoxins (YTX)



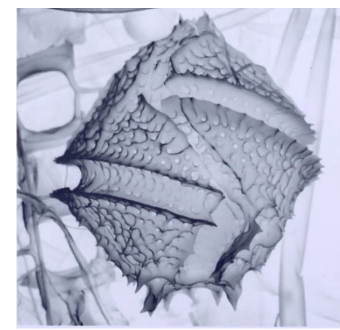
Yessotoxin
(First isolated from
Patinopecten yessoensis)

Protoceratium reticulatum

Gonyaulax spinifera
Gonyaulax taylori
Lingulodinium polyedra
Protoceratium reticulatum



Lingulodinium polyedra



Gonyaulax spinifera

Toxicity:
LD_{50} (ip): 286 µg/kg (mice)
LD_{50} (oral): > 54 mg/kg

Mode of Action:

mechanism unknown

Tubaro, A., et al. (2010). Toxicon 56(2): 163-172.

Yessotoxins (YTX)

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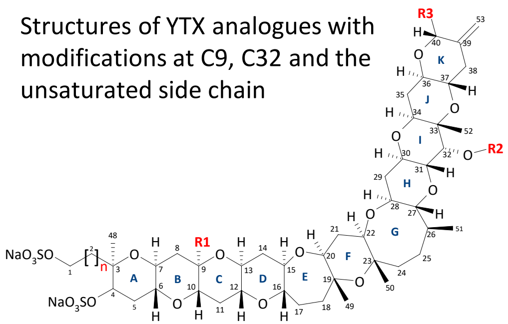
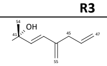
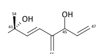
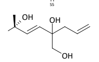
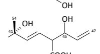
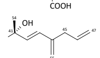
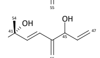
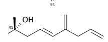
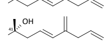
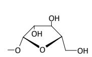
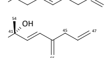
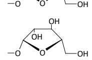
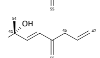
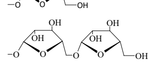
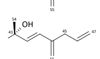
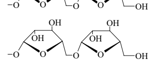
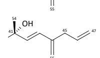
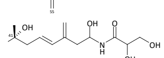
YTX variants

Structures of YTX analogues with modifications at C9, C32 and the unsaturated side chain



Name	n	R1	R2	R3
YTX	1	H	H	
45-OH YTX	1	H	H	
44,55-di OH YTX	1	H	H	
COOH YTX	1	H	H	
1a-homo YTX (Protoceratin I)	2	H	H	
45-OH homo YTX	2	H	H	
41a-homo YTX	1	H	H	
9-Me-41a-homo YTX	1	CH_3	H	
arabinofuaranosyl YTX	1	H		
Protoceratin II	2	H		
diarabonofuranosyl YTX	1	H		
Protoceratin III	2	H		
41a-homo YTX amide	1	H	H	

Miles, C.O., et al. (2005) Harmful Algae 4, 1075-1091

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Harmful Algae 4 (2005) 1075–1091

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Evidence for numerous analogs of yessotoxin in *Protoceratium reticulatum*

YTX analogs detected by LC–MS^3 analysis of a fractionated extract of *Protoceratium reticulatum*

Entry	M_{wt}	R_t	$[M-H]^-$	MS^2	MS^3 (see Fig. 5)	$[M-2H]^{2-}$	Relative intensity[a]	MS^2	MS^3	Structure[b]
1	956[c]	3.2	955	**875**	**831**, 795	477.3	++	–	–	
2	984	3.3	983	**903**, 869, 653, 599	–	–	–	–	–	
3	986	2.2	985	905, **815**, 771	**797**, 772, 645, 627, 583	439.0	+	–	–	
4	992	5.2	991	**911**	868, **799**, 757, 729, 688, 575	–	–	–	–	**17**
5	992	6.1	991	**911**	**868**, 657	–	–	–	–	**18**
6	992	7.1	991	**911**	**827**	–	–	–	–	**19**
7	1008	3.2	1007	**927**	919, 912, **855**, 759	–	–	–	–	
8	1010	3.3	1009	**929**, 922, 850, 799	–	–	–	–	–	
9	1012[d]	2.7	1011	**931**	**887**, 851, **807**, 696	505.2	+	–	–	
10	1020[e]	4.4	1019	**939**, 799	**939**	–	–	–	–	
11	1022[f]	4.1	1021	980, **941**, 925	–	–	–	–	–	
12	1026[g]	2.8	1025	**945**, 875, 847, 786	**927**, 758	512.0	+	–	–	
13	1026	3.1	1025	**945**	**927**, 864	–	–	–	–	
14	1038	3.3	1037	**957**	**939**, 877	518.3	++	–	–	
15	1038	4.0	1037	**957**	**929**	–	–	–	–	
16	1040	5.4	1039	**959**, 929, 847, 598	**927**	519.5	+	–	–	
17	1042	2.6	1041	**961**	946, **943**, 917, 915, 881	520.4	+	–	–	
18	1048	5.2	1047	**967**	924, 907, 895, **855**, 713, 671	–	–	–	–	**6**
19	1048	5.9	1047	**967**	924, 895, **855**, 713, 671, 659	–	–	–	–	**7**
20	1048	6.8	1047	**967**	**883**	–	–	–	–	**8**
21	1062	3.2	1061	**981**	**951**	–	–	–	–	
22	1062[h]	6.3	1061	**981**, 924, 855, 713	–	–	–	–	–	
23	1082	3.0	1081	**1001**	970, 927, **885**, 855, 799, 713	–	–	–	–	
24	1082	3.4	1081	**1001**	983, 957, 927, 869, **855**, 713	–	–	–	–	
25	1086	8.8	1085	**1005**, 868	921, **868**, 851, 822, 799, 773, 657	–	–	–	–	**16**
26	1090	7.5	1089	**1009**	981, 967, **925**, 855, 799, 671	–	–	–	–	
27	1118[i]	5.7	1117	**1037**	**924**, 895, 855, 713	–	–	–	–	
28	1120	4.6	1119	**1039**	**959**, 895, 855, 799, 713, 687	559.4	++	–	–	
29	1120[j]	5.3	1119	**1039**	1021, 941, **924**, 895, 855, 713	559.4	+	–	–	
30	1134	5.8	1133	**1053**	967, **925**, 855, 713	–	–	–	–	

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Yessotoxins (YTX)

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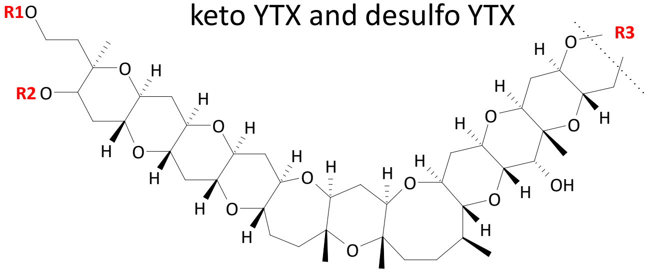
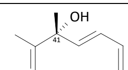
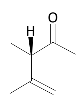
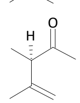
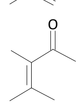
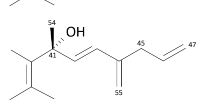
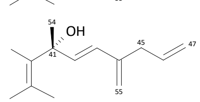
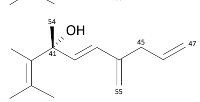
YTX variants

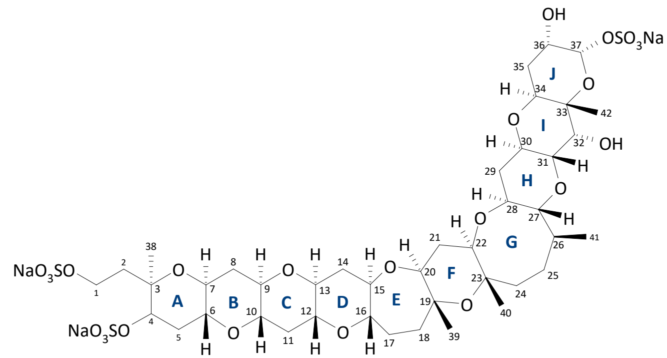
Structures of trinor YTX,
keto YTX and desulfo YTX



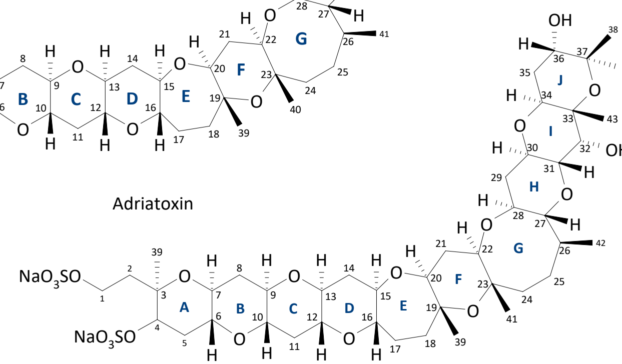
Name	R1	R2	R3
45,46,47 trinor YTX	SO_3Na	SO_3Na	
41-keto YTX (heptanor-41 oxo YTX)	SO_3Na	SO_3Na	
40-*epi* 41-keto YTX (heptanor-41 oxo YTX)	SO_3Na	SO_3Na	
41-keto YTX 1,3enone	SO_3Na	SO_3Na	
1-desulfo YTX	H	SO_3Na	
4-desulfo YTX	SO_3Na	H	
1,4-desulfo YTX	H	H	

Miles, C.O., et al. (2005) Harmful Algae 4, 1075-1091

Adriatoxins
Structures ATX and ATX B



Adriatoxin



Adriatoxin B

Ciminiello, P., et al. (1998) Tetrahedron Letters 39 (48), 8897-8900

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Azaspiracid Shellfish Poisoning (AZP)

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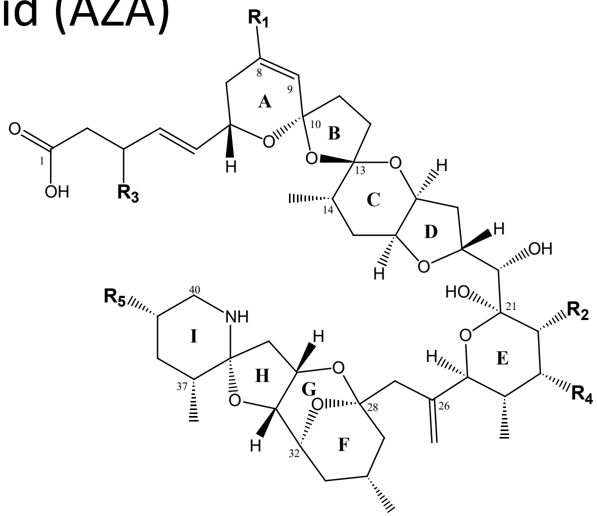
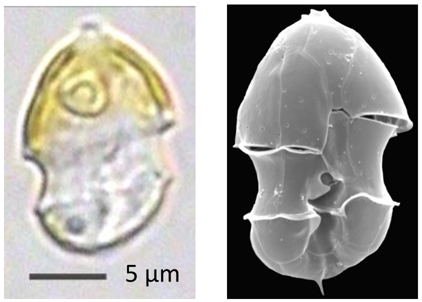
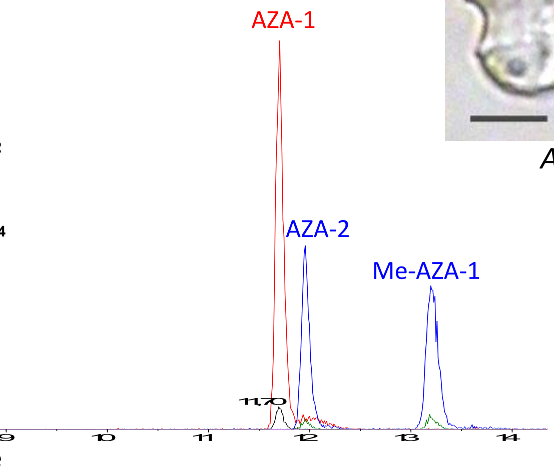
Azaspiracid (AZA)



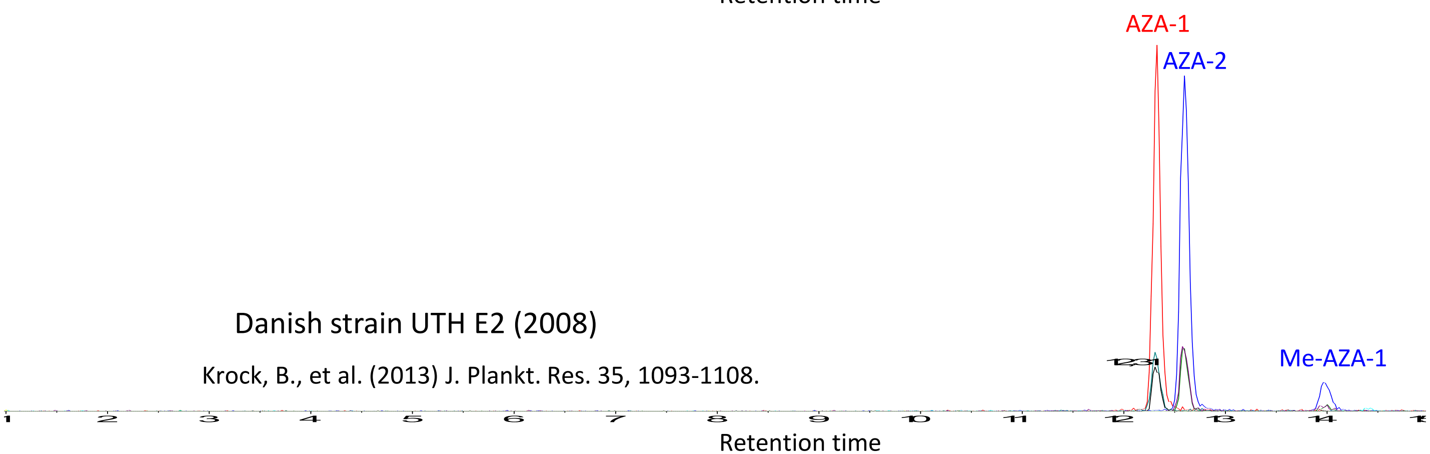


A. spinosum



Scottish strain 3D9 (2007)

Krock, B., et al. (2009) Harmful Algae 8, 254-263.



Danish strain UTH E2 (2008)

Krock, B., et al. (2013) J. Plankt. Res. 35, 1093-1108.

m/z 842>824

m/z 856>838

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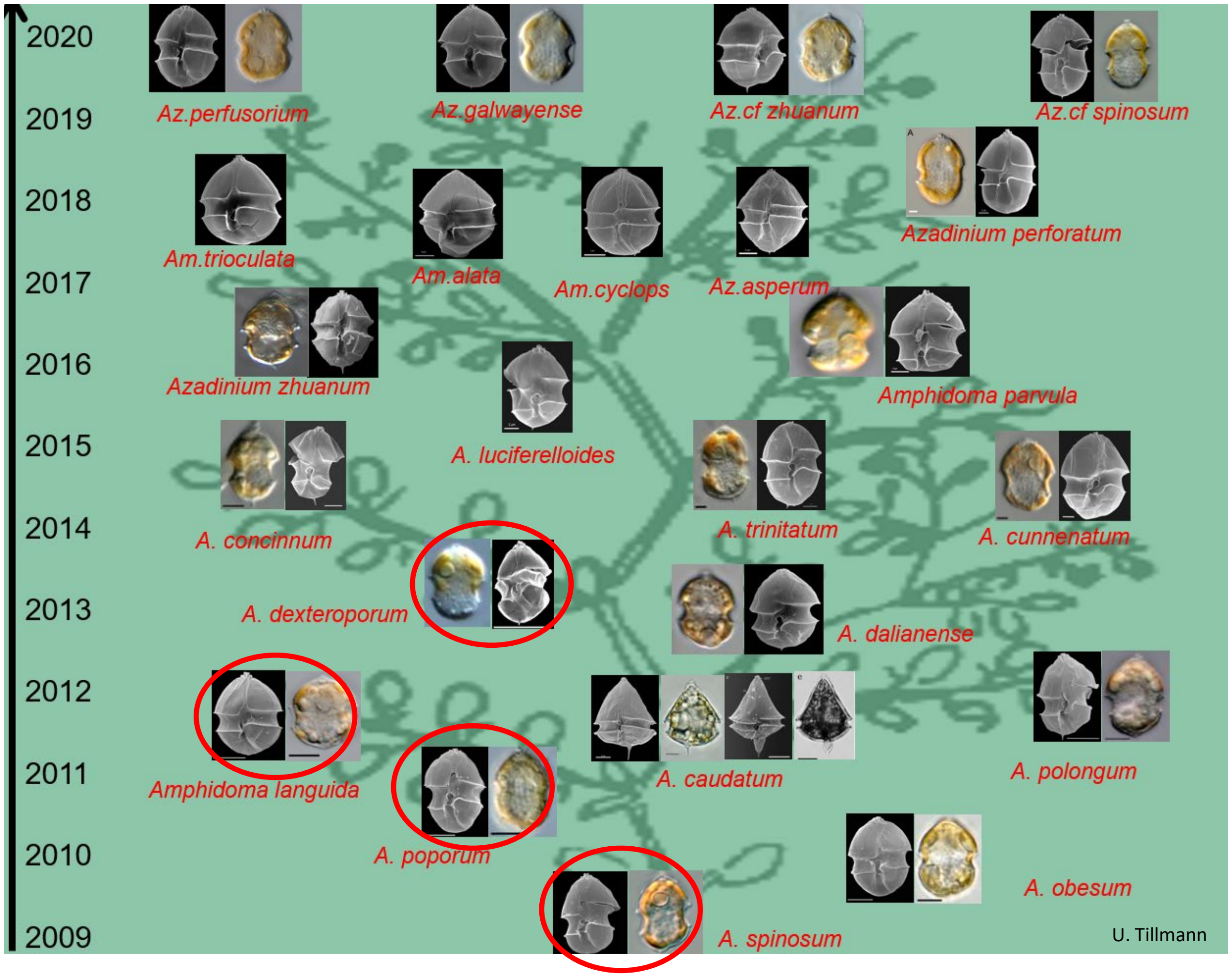

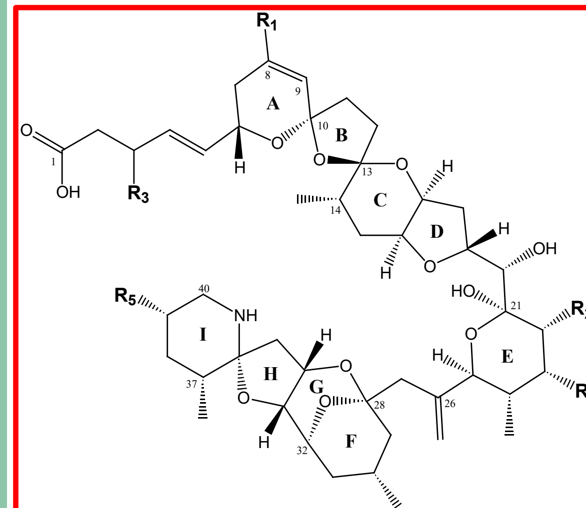

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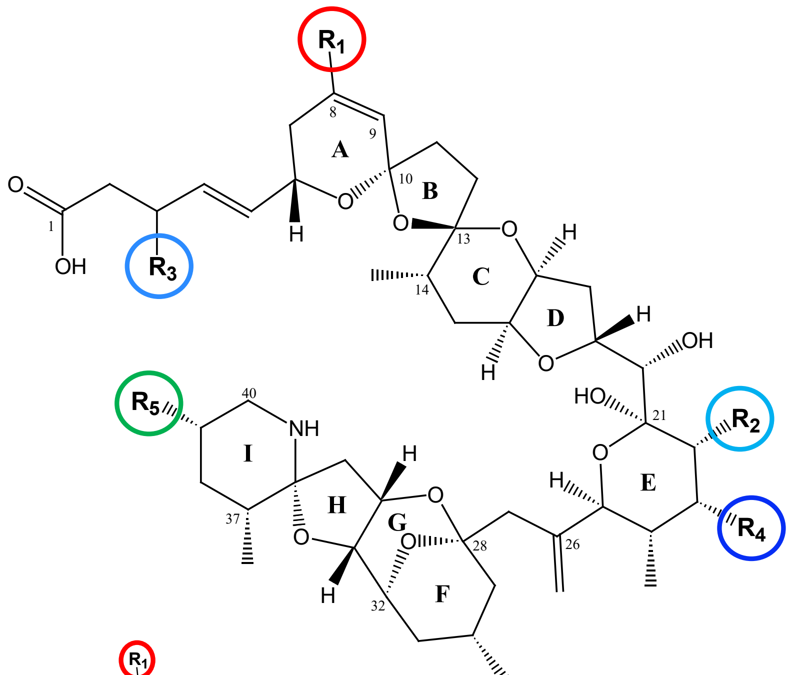
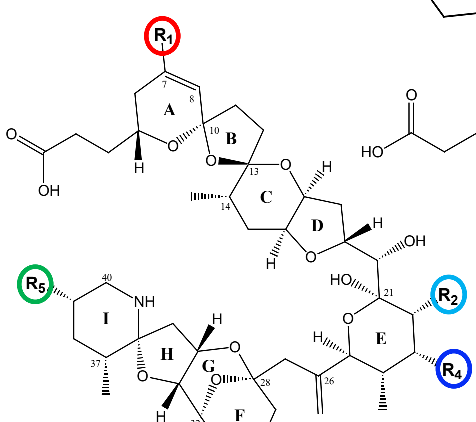
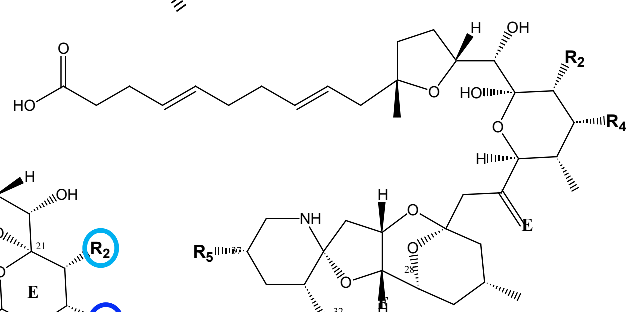
AZA variants





AZA-34/35



AZA-33

Toxin	R_1	R_2	R_3	R_4	R_5	$\Delta_{7,8}$	$[M+H]^+$
AZA-1	H	CH_3	H	H	CH_3	√	842
AZA-2	CH_3	CH_3	H	H	CH_3	√	856
AZA-3	H	H	H	H	CH_3	√	828
AZA-4	H	H	OH	H	CH_3	√	844
AZA-5	H	H	H	OH	CH_3	√	844
AZA-6	CH_3	H	H	H	CH_3	√	842
AZA-7	H	CH_3	OH	H	CH_3	√	858
AZA-8	H	CH_3	H	OH	CH_3	√	858
AZA-9	CH_3	H	OH	H	CH_3	√	858
AZA-10	CH_3	H	H	OH	CH_3	√	858
AZA-11	CH_3	CH_3	OH	H	CH_3	√	872
AZA-33	-	CH_3	H	H	CH_3	-	716
AZA-34	H	CH_3	-	H	CH_3	√	816
AZA-35	CH_3	CH_3	-	H	CH_3	√	830
AZA-36	CH_3	CH_3	OH	H	H	√	858
AZA-37	H	CH_3	OH	H	H	-	846
AZA-38	nd	nd	nd	nd	H	nd	830
AZA-39	nd	nd	nd	nd	H	nd	816
AZA-40	CH_3	CH_3	H	H	H	√	842

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AZA variants

Currently Known AZA from Dinoflagellate (Algal) Origin

#	AZA	*m/z* [M+H]$^+$	*m/z* group 4 fragment	*m/z* group 5 fragment	Producer	Reference
1	AZA-1	842	362	262	*A. spinosum*	Krock et al. 2009
2	AZA-2	856	362	262	*A. spinosum* *A. poporum* *Am. languida*	Krock et al. 2009 Krock et al. 2014 Tillmann et al. 2017
3	epi-AZ[illegible]	[illegible]	[illegible]	[illegible]	*A. dexteroporum*	Rossi et al. 2017
4	AZA-1[illegible]	[illegible]	[illegible]	[illegible]	*A. poporum*	Krock et al. 2014
5	AZA-3[illegible]	[illegible]	[illegible]	[illegible]	*A. spinosum*	Kilcoyne et al. 2014
6	AZA-3[illegible]	[illegible]	[illegible]	[illegible]	*A. spinosum*	{Kilcoyne et al. 2014
7	AZA-35	830	362	262	*A. spinosum* *A. dexteroporum*	Kilcoyne et al. 2014 Rossi et al. 2017
8	AZA-36	858	348	248	*A. poporum*	Krock et al. 2015
9	AZA-3[illegible]	[illegible]	[illegible]	[illegible]	*A. poporum*	Krock et al. 2015
10	AZA-3[illegible]	[illegible]	[illegible]	[illegible]	*Am. languida*	Krock et al. 2012
11	AZA-3[illegible]	[illegible]	[illegible]	[illegible]	*Am. languida*	Krock et al. 2012
12	AZA-4[illegible]	[illegible]	[illegible]	[illegible]	*A. poporum*	Krock et al. 2014
13	AZA-41	854	360	260	*A. poporum*	Krock et al. 2014
14	AZA-42	870	360	260	*A. poporum*	Krock et al. under review
15	AZA-43	828	360	260	*Am. languida*	Tillmann et al. 2017
16	AZA-5[illegible]	[illegible]	[illegible]	[illegible]	*A. spinosum*	Tillmann et al. 2018
17	AZA-5[illegible]	[illegible]	[illegible]	[illegible]	*A. spinosum*	Tillmann et al. 2018
18	AZA-5[illegible]	[illegible]	[illegible]	[illegible]	*Am. languida*	Tillmann et al. 2018
19	AZA-5[illegible]	[illegible]	[illegible]	[illegible]	*Am. languida*	Tillmann et al. 2018
20	AZA-5[illegible]	[illegible]	[illegible]	[illegible]	*A. dexteroporum*	Rossi et al. 2017
21	AZA-5[illegible]	[illegible]	[illegible]	[illegible]	*A. dexteroporum*	Rossi et al. 2017
22	AZA-5[illegible]	[illegible]	[illegible]	[illegible]	*A. dexteroporum*	Rossi et al. 2017
23	AZA-57	844	362	262	*A. dexteroporum*	Rossi et al. 2017
24	AZA-58	828	362	262	*A. dexteroporum*	Rossi et al. 2017
25	AZA-59	860	362	262	*A. poporum*	Kim et al. 2017
26	AZA-62	870	362	262	*A. poporum*	Krock et al. 2019

26 AZAs from planktonic origin

Currently 62 published AZAs

And at least additional 10 known AZAs

Azaspiracid Shellfish Poisoning (AZP)

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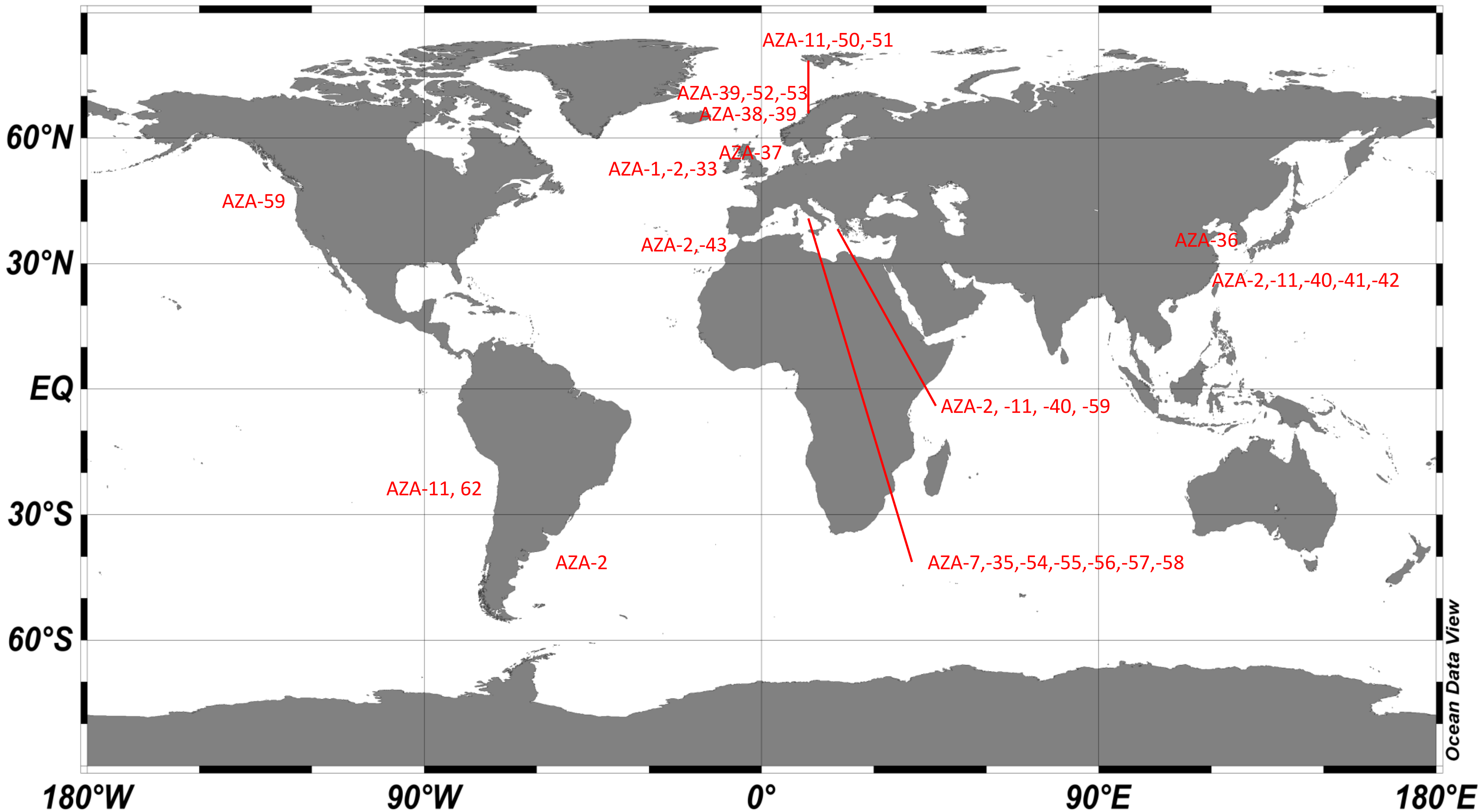
AZA variants: geographic distribution



Bernd Krock, HABTUPORE, Istanbul University, 07.05.2024

Azaspiracid Shellfish Poisoning (AZP)

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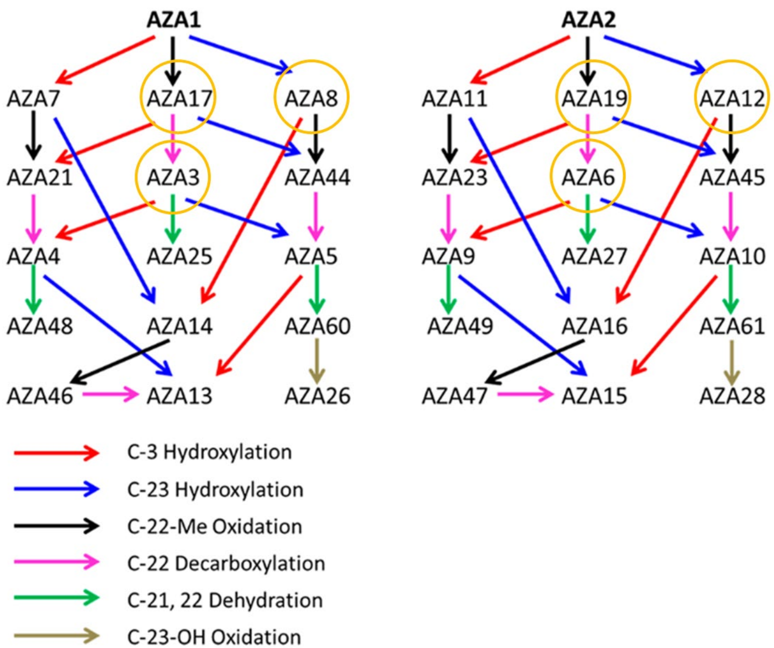
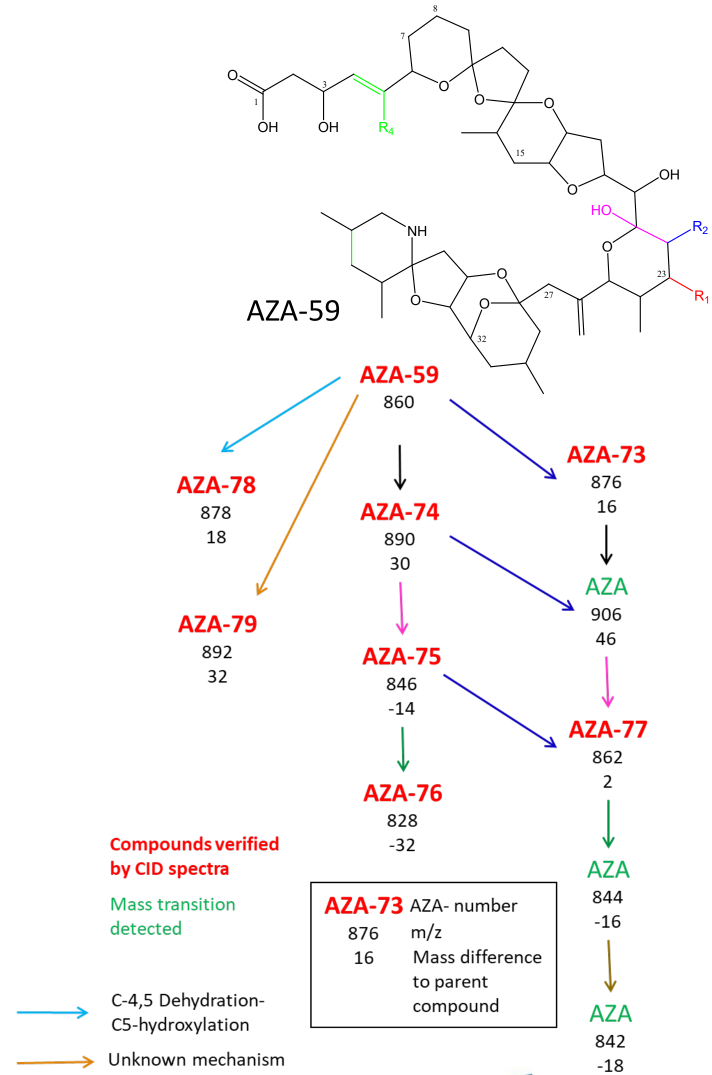
AZA variants: Metabolism in Bivalves



Kilcoyne, J., et al. (2018) J. Nat. Prod. 81(4), 885-893.



Krock, B., et al. (in prep.).

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Bernd Krock, HABTUPORE, Istanbul University, 07.05.2024

Azaspiracid Shellfish Poisoning (AZP)

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AZA variants

AZAs produced by algae

AZA-1	AZA-41
AZA-2	AZA-42
epi-AZA-7	AZA-43
AZA-11	AZA-50
AZA-33	AZA-51
AZA-34	AZA-52
AZA-35	AZA-53
AZA-36	AZA-54
AZA-37	AZA-55
AZA-38	AZA-56
AZA-39	AZA-57
AZA-40	AZA-58
AZA-59	AZA-62

Krock, B., et al. (2019) Harmful Algae 82, 1-8.

AZA shellfish metabolites of AZA-1 and -2

AZA-3	AZA-14	AZA-25	AZA-47
AZA-4	AZA-15	AZA-26	AZA-48
AZA-5	AZA-16	AZA-27	AZA-49
AZA-6	AZA-17	AZA-28	AZA-60
AZA-7	AZA-18	AZA-29	AZA-61
AZA-8	AZA-19	AZA-30	
AZA-9	AZA-20	AZA-31	
AZA-10	AZA-21	AZA-32	
AZA-11	AZA-22	AZA-44	
AZA-12	AZA-23	AZA-45	
AZA-13	AZA-24	AZA-46	

2 AZAs of phytoplankton origin result in
38 shellfish metabolites!

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Summary regulated toxins

Toxin group	Analogue	TEF	Regulatory limits
OA-group toxins (OA-equivalents)	OA	1	160 µg OA eq/kg
	DTX1	1	
	DTX2	0.6	
AZA-group toxins (AZA-equivalents)	AZA1	1	160 µg AZA-1 eq/kg
	AZA2	1.8	
	AZA3	1.4	
YTX-group toxins (YTX-equivalents)	YTX	1	3.75 mg YTX eq/kg
	1a-homoYTX	1	
	45-hydroxyYTX	1	
	45-hydroxy-1a-homoYTX	0.5	
STX-group toxins (STX-equivalents)	STX	1	800 µg STX eq 2HCl/kg
	NeoSTX	1	
	GTX1	1	
	GTX2	0.4	
	GTX3	0.6	
	GTX4	0.7	
	GTX5	0.1	
	GTX6	0.1	
	C2	0.1	
	C4	0.1	
	dc-STX = 1	1	
	dc-NeoSTX	0.4	
	dc GTX2	0.2	
	dc GTX3	0.4	
PTX-group toxins (PTX2-equivalents)	PTX1	1	Regulation suspended
	PTX2	1	
	PTX3	1	
	PTX4	1	
	PTX6	1	
	PTX11	1	
DA and its isomers	None established	-	20 µg DA/kg

The EFSA Journal (2009) 1306, 1-23

Ichthyotoxins

Massive Fish Kill in the Oder River in August 2022

https://www.tagesschau.de/ausland/fischsterben-oder-115.html

produced by the haptophyte („Golden Alga“) *Prymnesium parvum*

Ichthyotoxins

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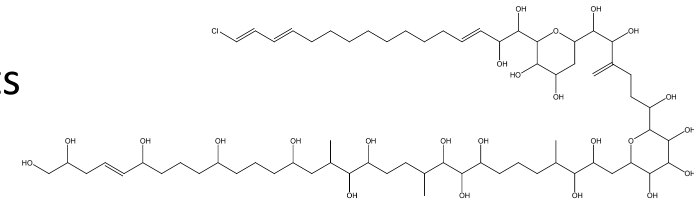
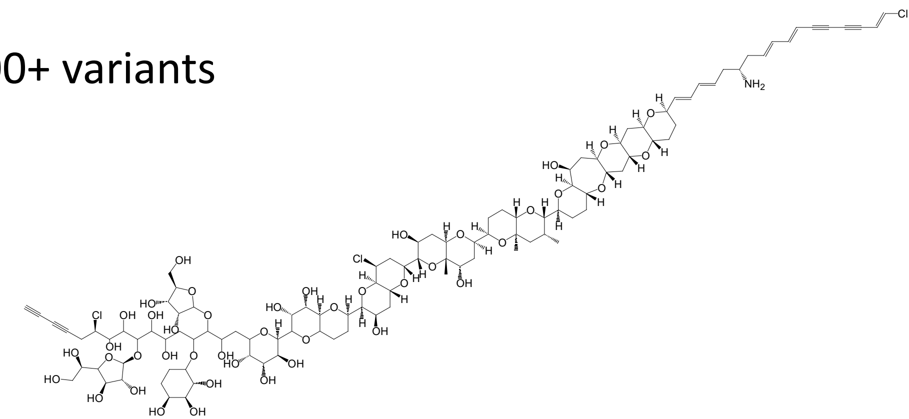
Variability

Amphidinium spp.: Amphidinols - 20+ known variants
Karlodinium spp.: Karlotoxins - 20+ known variants



Prymnesium parvum: Prymnesins - 100+ variants



Other ichthyotoxic species:

Alexandrium spp.
Chattonella spp.
Chrysocromulina spp.
Fibrocapsa japonica
Heterosigma akashiwo
Protoceratium reticulatum
Pseudochattonella cf. *verruculosa*

Ichthyotoxins:

Unknown !!

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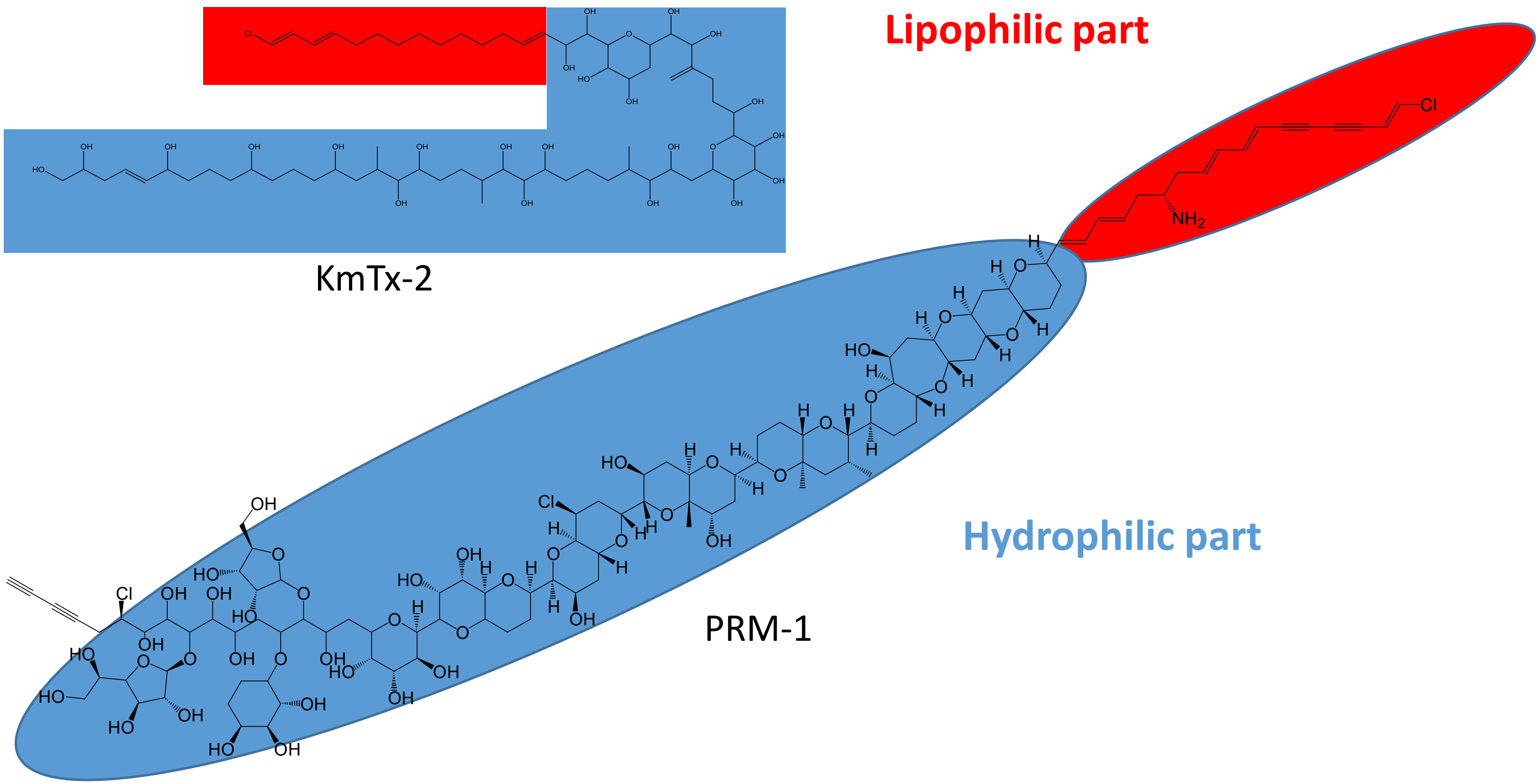
Ichthyotoxins

Known Ichthyotoxins



Ichthyotoxins

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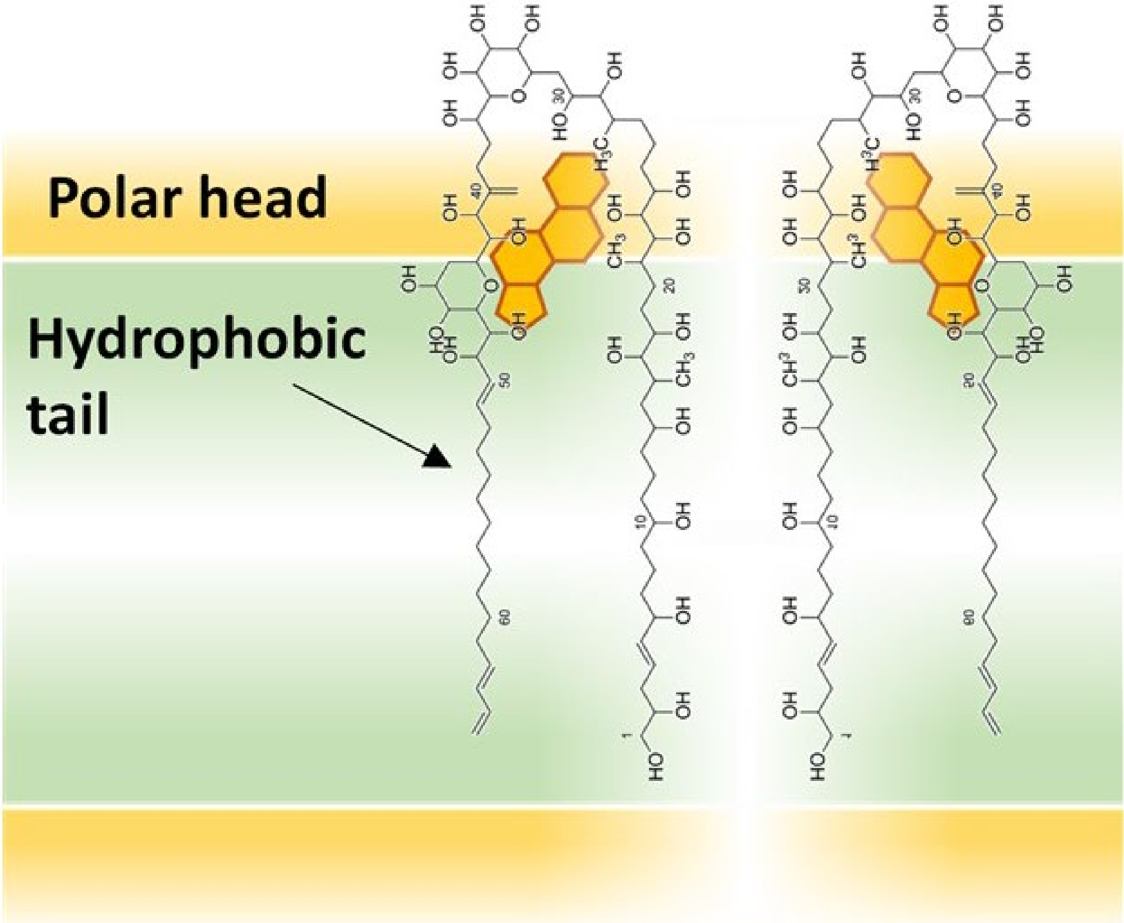
Mode of action



Long, M., et al. (2021) Toxins 13(12): 905.

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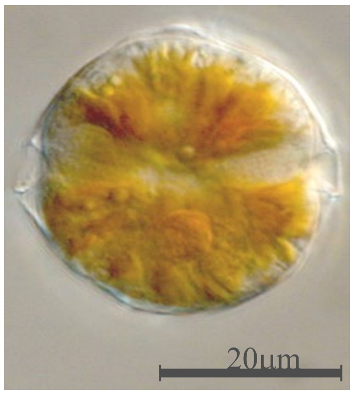
Lytic Effect



Alexandrium catenella strain 2 (Alex2)

Rhodomonas salina

Rhodomonas salina exposed to *A. catenella* supernatant (cell free)

Video: U. Tillmann

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Ichthyotoxins

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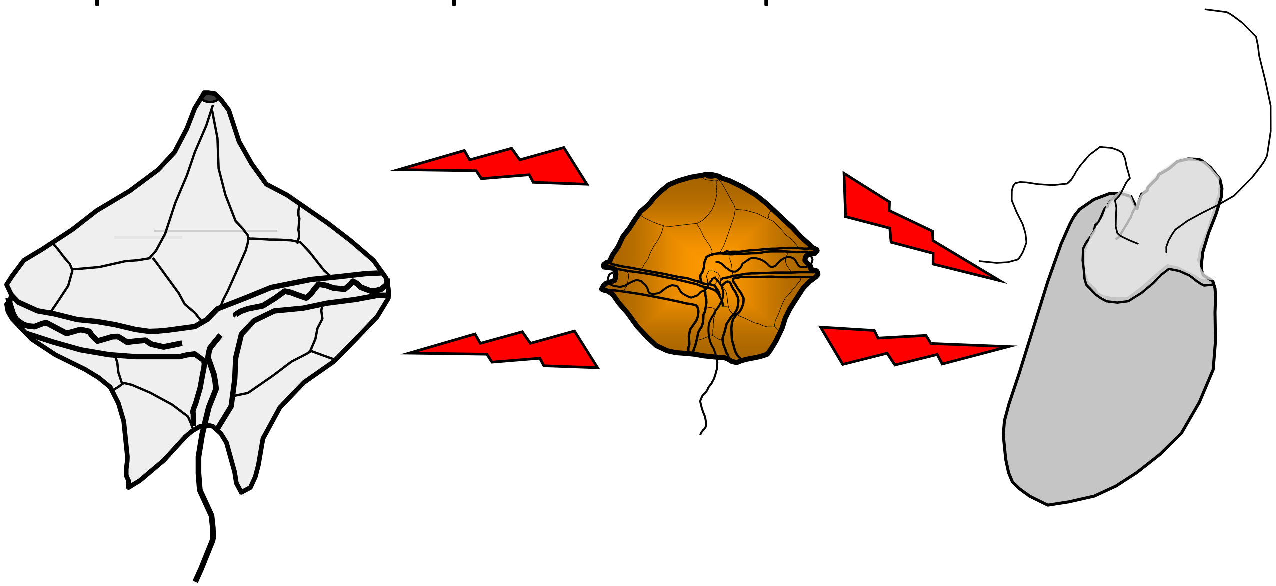
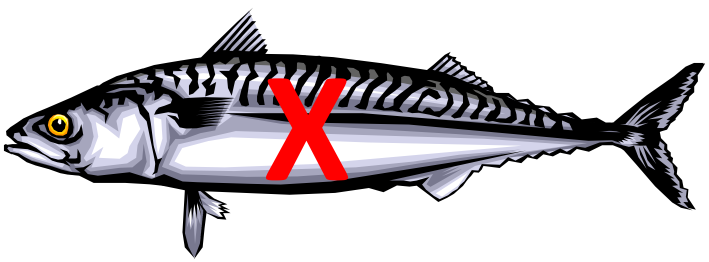
Current Hypothesis:

Lytic compounds of marine protists are weapons of chemical warfare among protists



Ichthyotoxicity is a collateral damage of protistan allelochemistry



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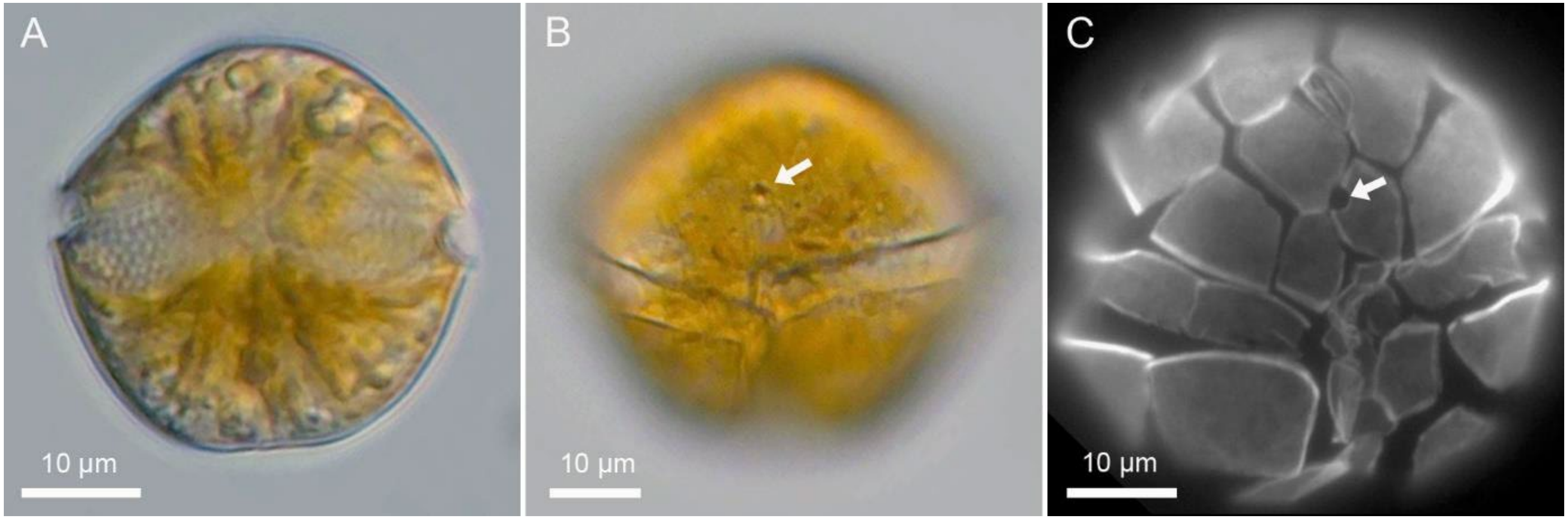
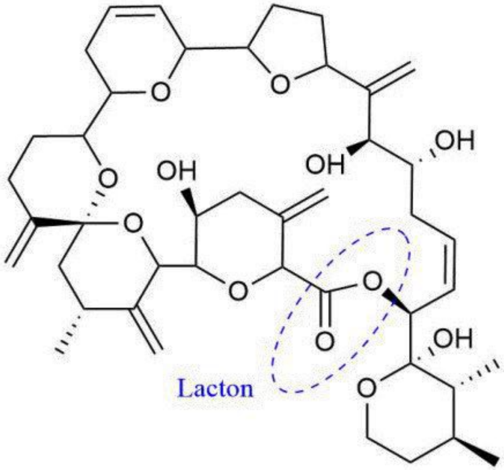
Alexandrium pseudogonyaulax



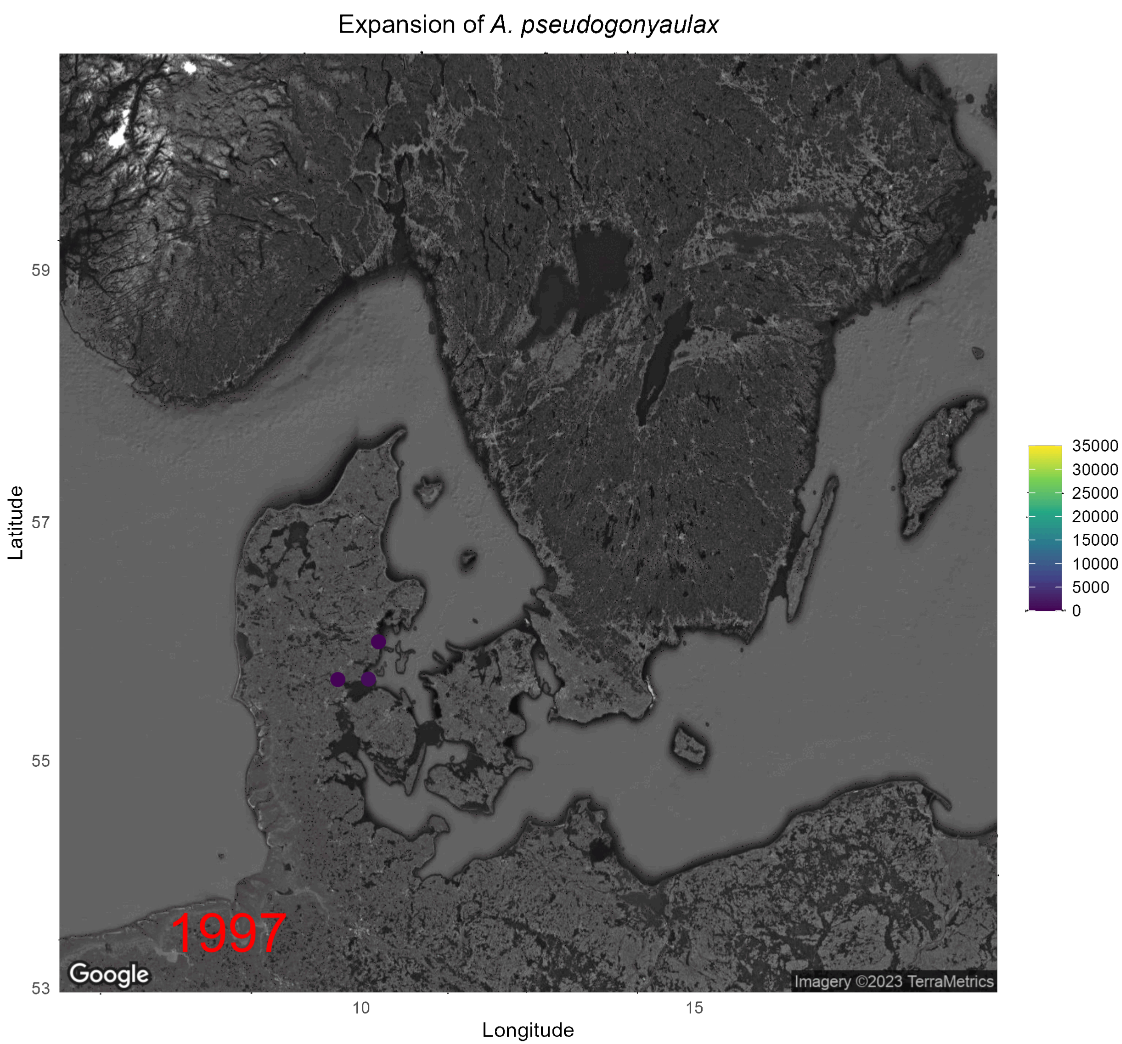
Photos: Urban Tillmann

- Thecate dinoflagellate
- Producer of goniodomins (GDs)
- Producer of bioactive extracellular compounds (BEC)
- Suspected to be ichthyotoxic



Goniodomin A (GDA)

Alexandrium pseudogonyaulax



PhD thesis:
Causes of the spread of the harmful and potentially fish-toxic microalgae *Alexandrium pseudogonyaulax* (Dinophyceae) in German coastal waters and assessment of the future risk potential

Kristof Möller

Alexandrium pseudogonyaulax

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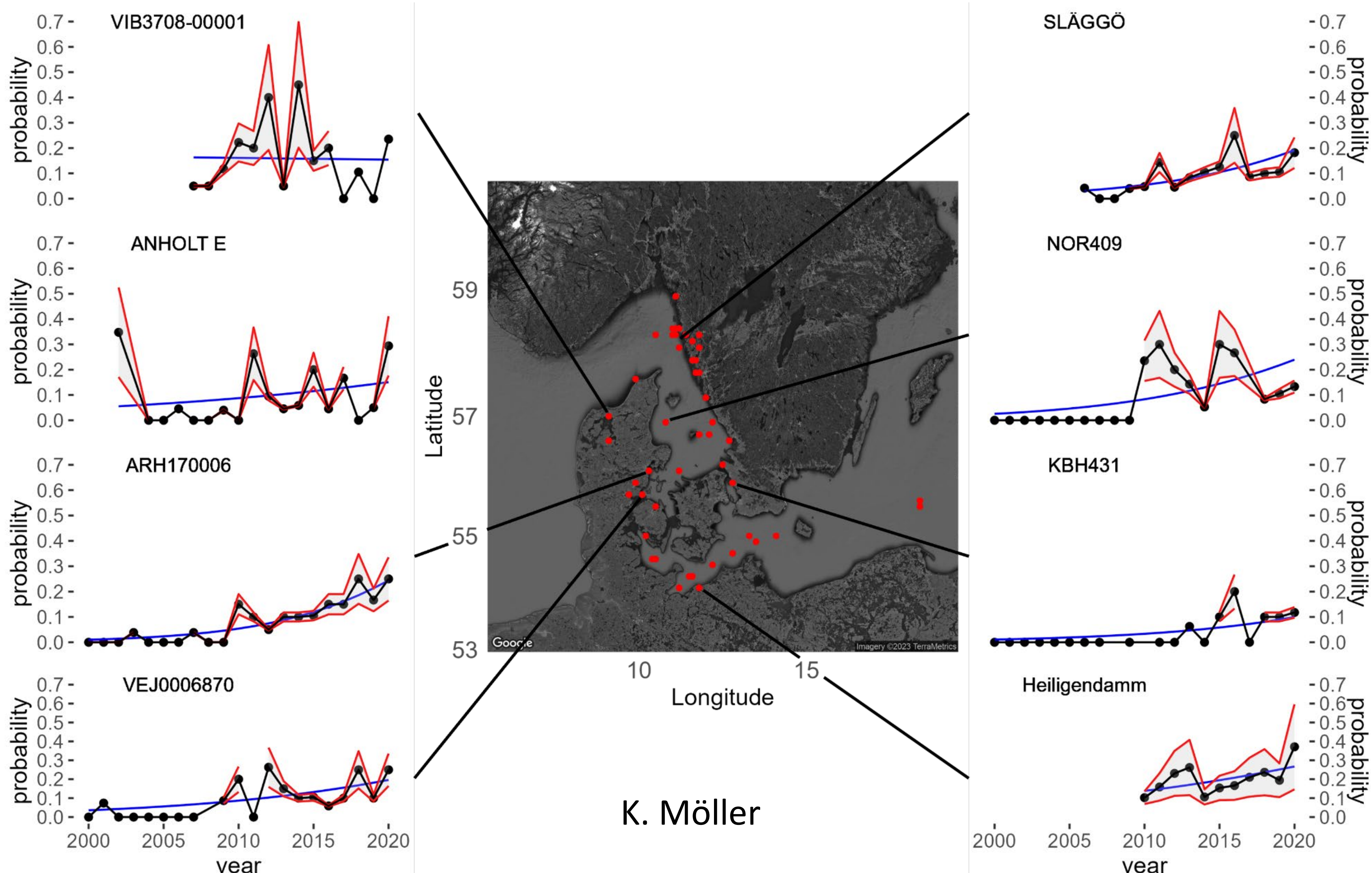
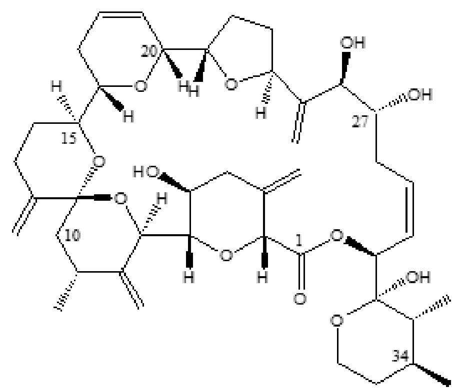


K. Möller

Introduction

Organism	Chemical compound	Ecological Function
Alexandrium pseudogonyaulax	Goniodomins 	?
Alexandrium pseudogonyaulax	? Bioactive Extracellular Compound (BEC)	Defense against Predators Elimination of Competitors

Alexandrium pseudogonyaulax

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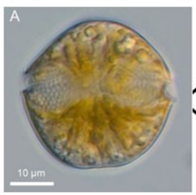
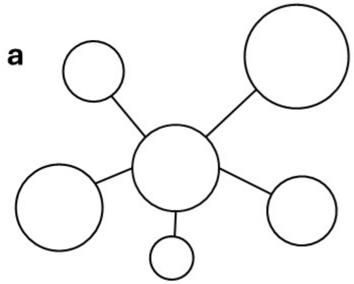
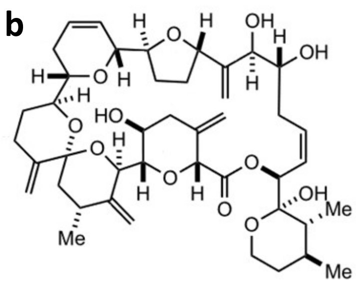
Background:

Alexandrium pseudogonyaulax





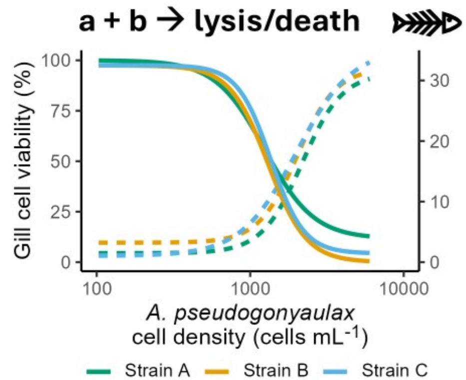
unknown Bioactive Extracellular Compounds (BECs)

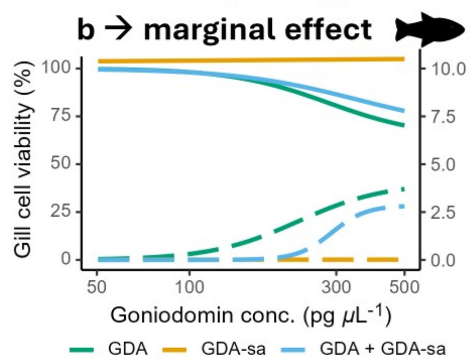


Goniodomins (Goniodomin A)

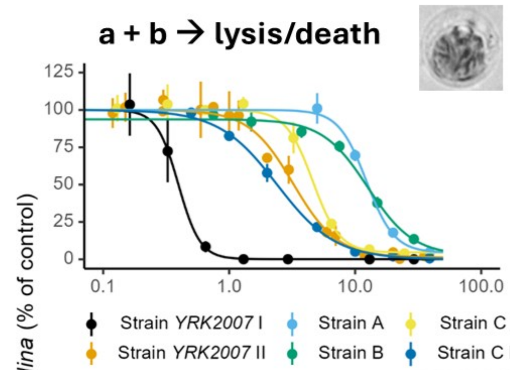
Results:

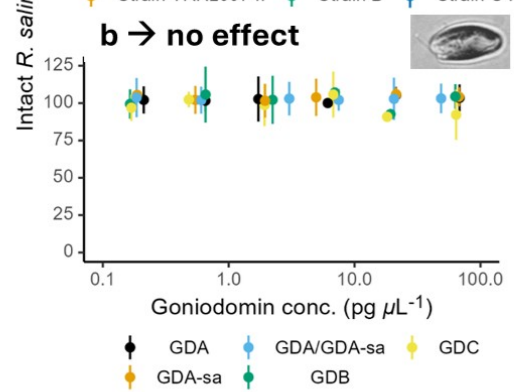
Bioassays Rtgill-W1 (fish cells)





Bioassays *R. salina* (microalgae)





Conclusion: Toxic effects of *Alexandrium pseudogonyaulax* are likely driven by BECs and not by goniodomins

K. Möller

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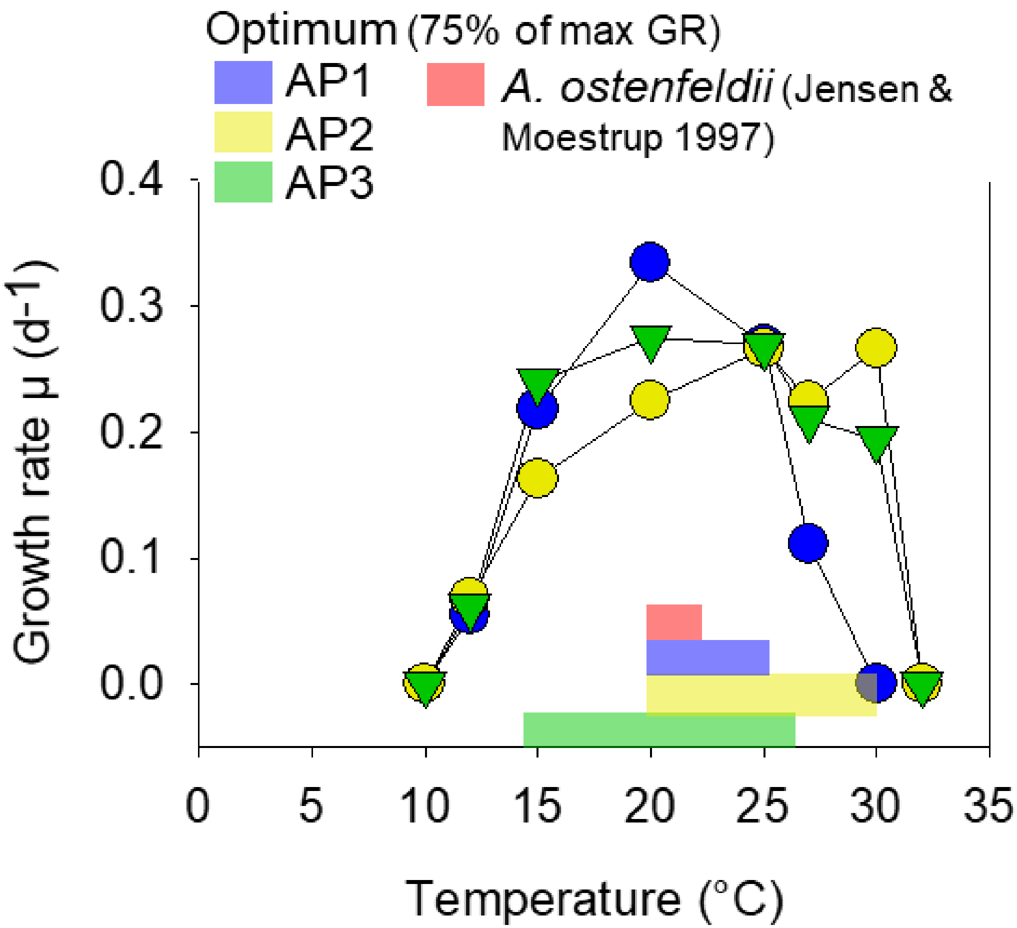
Alexandrium pseudogonyaulax

Temperature tolerance

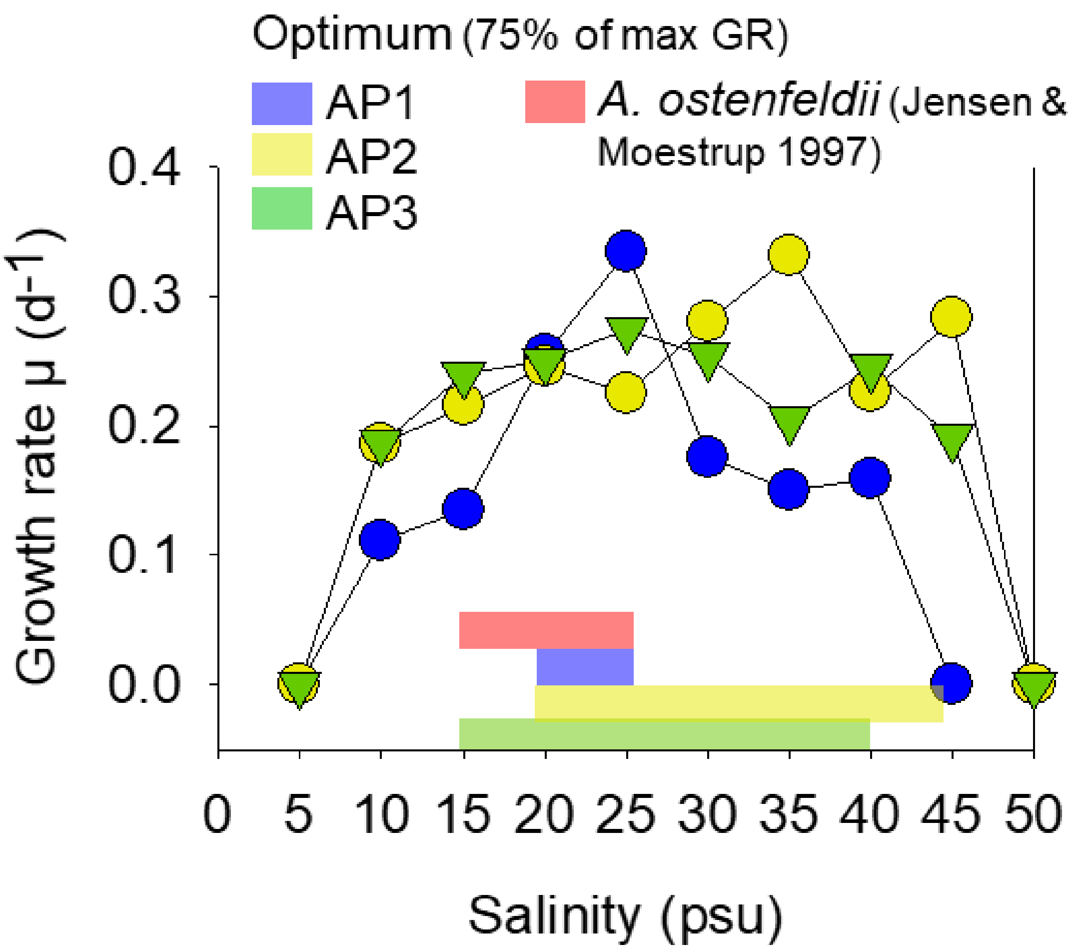


PhD thesis:
Response of Harmful Dinoflagellates to Climate Change

Simon Tulatz

Alexandrium pseudogonyaulax

Salinity tolerance



S. Tulatz

Alexandrium pseudogonyaulax

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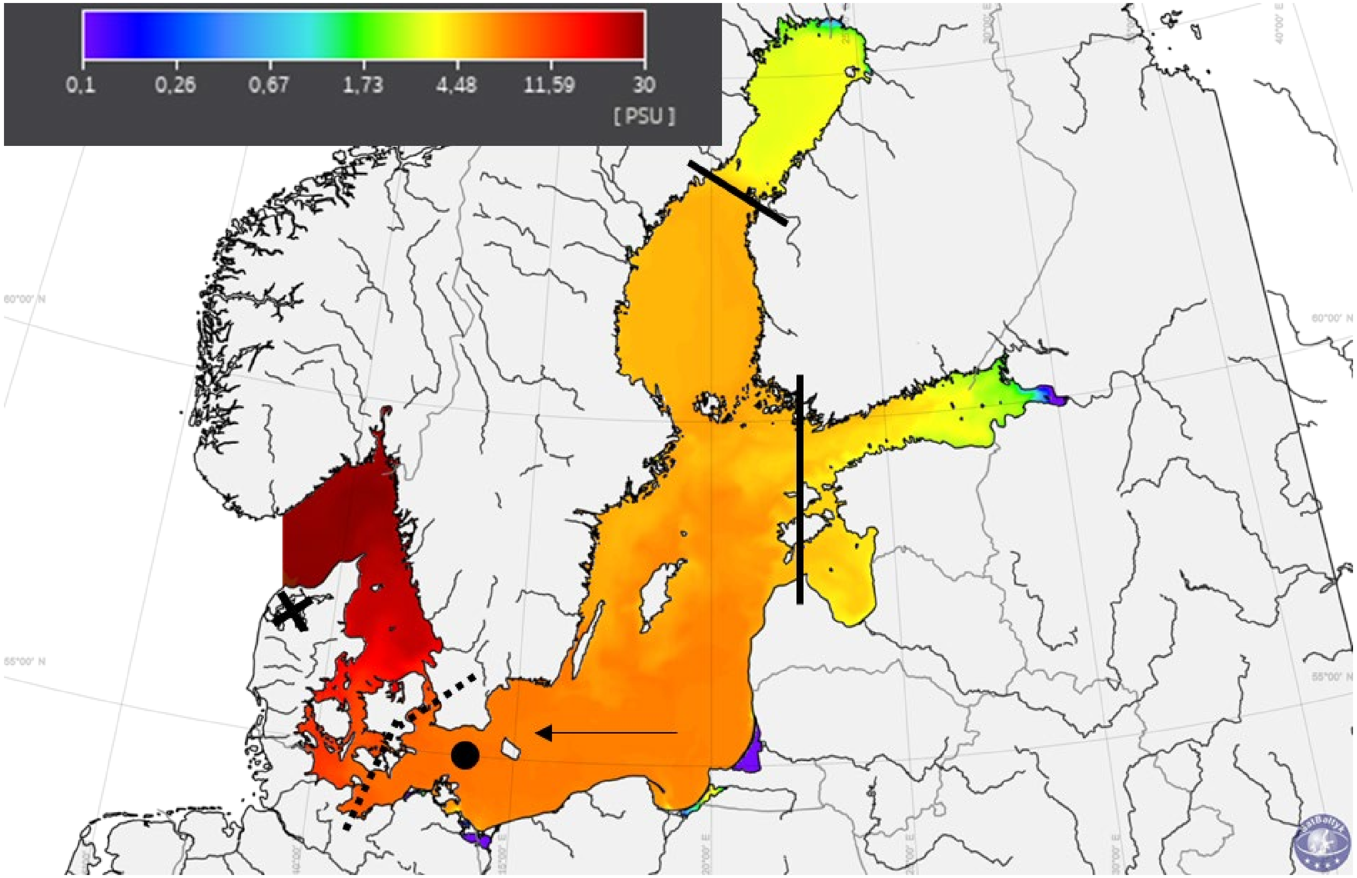
Potential distribution range



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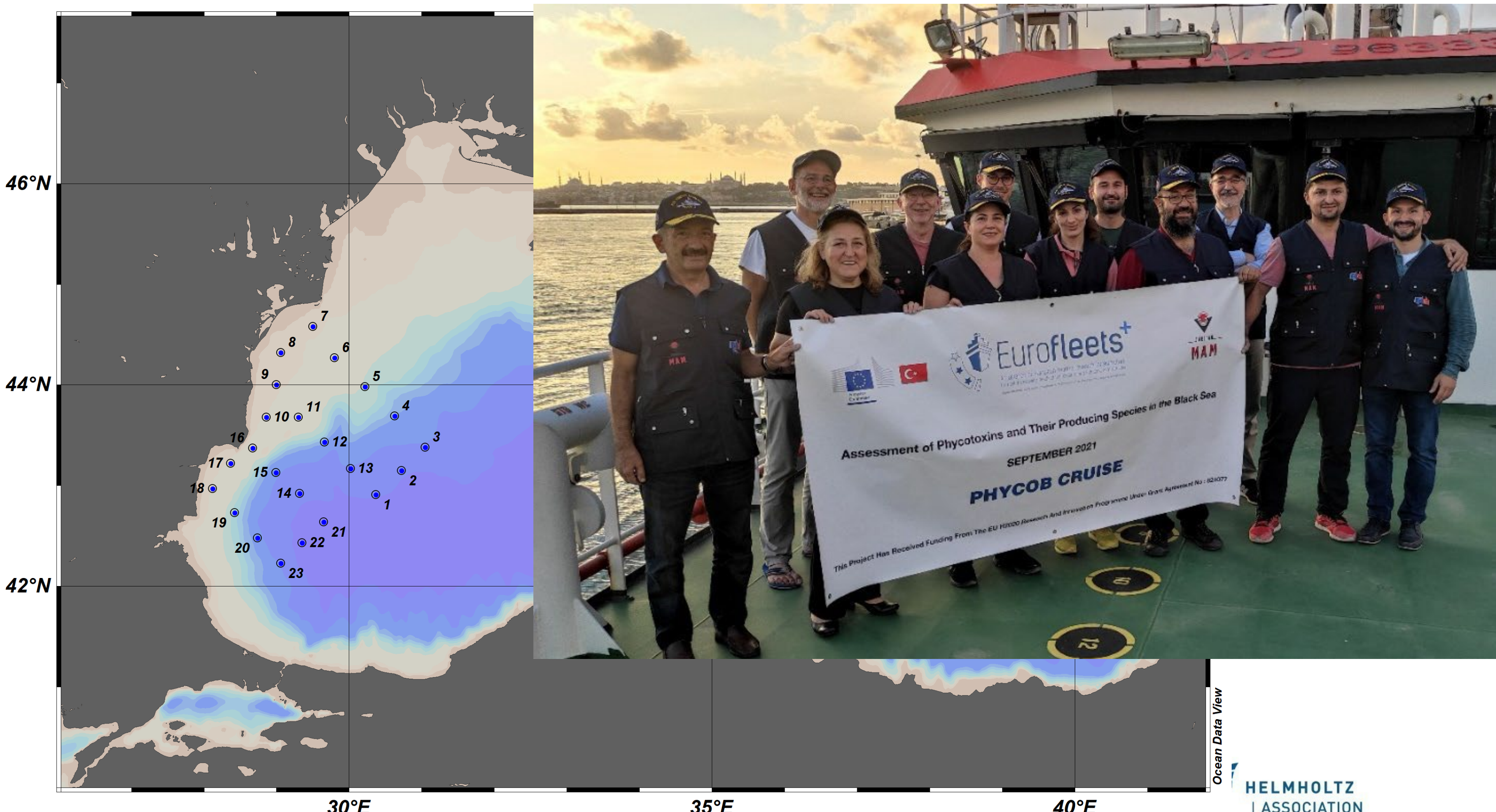
PHYCOB cruise September 2021 (Western Black Sea)



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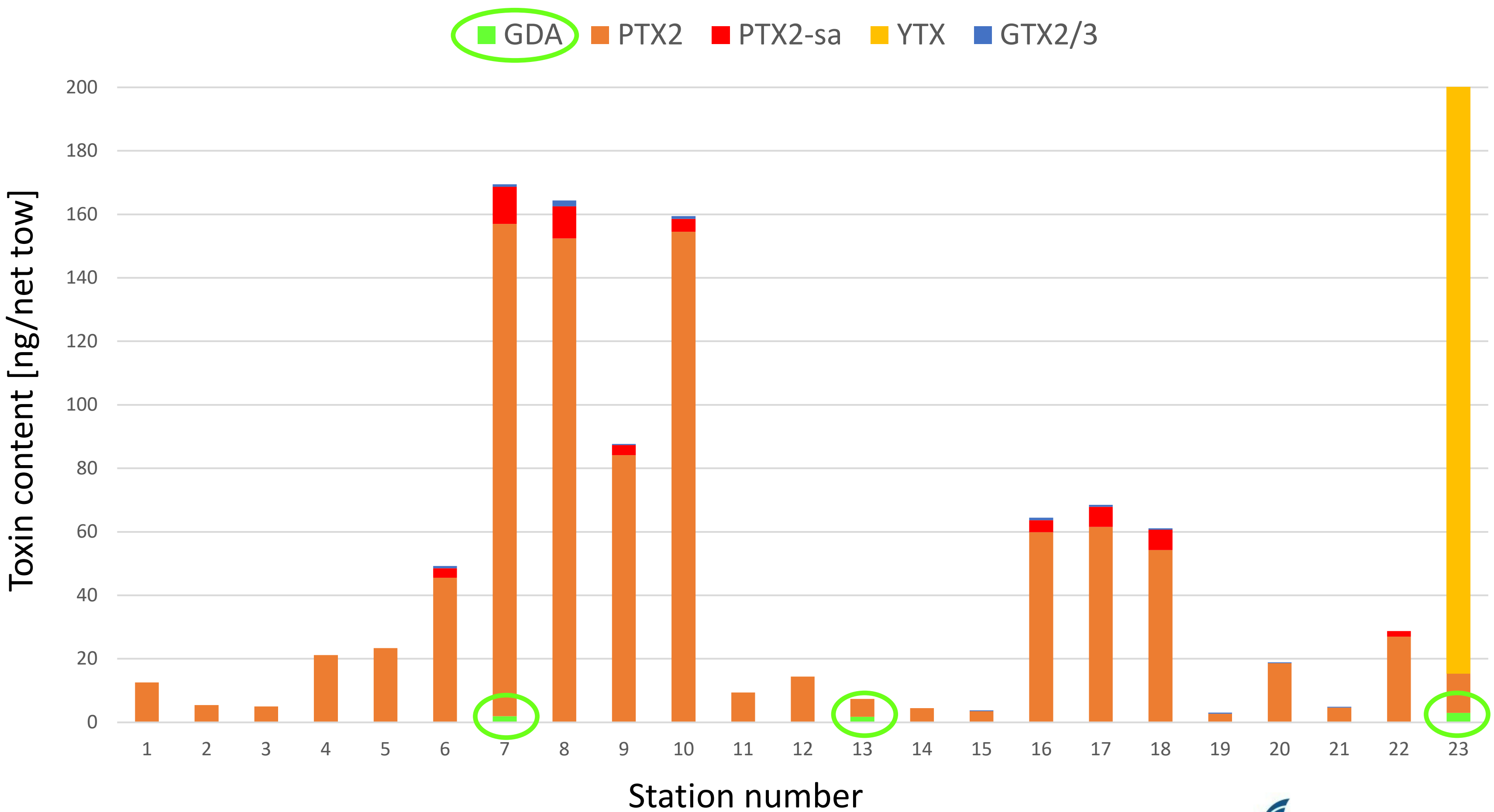
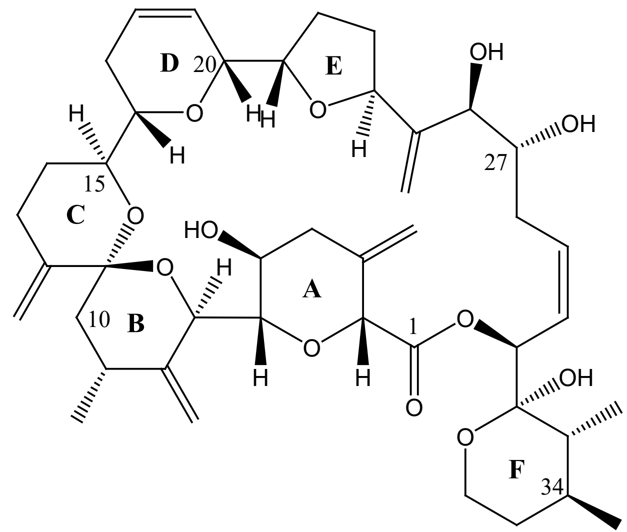
PHYCOB toxin results (Western Black Sea)



A. pseudogonyaulax strain 6D-1

isolated in the Black Sea
in September 2021

A. pseudogonyaulax



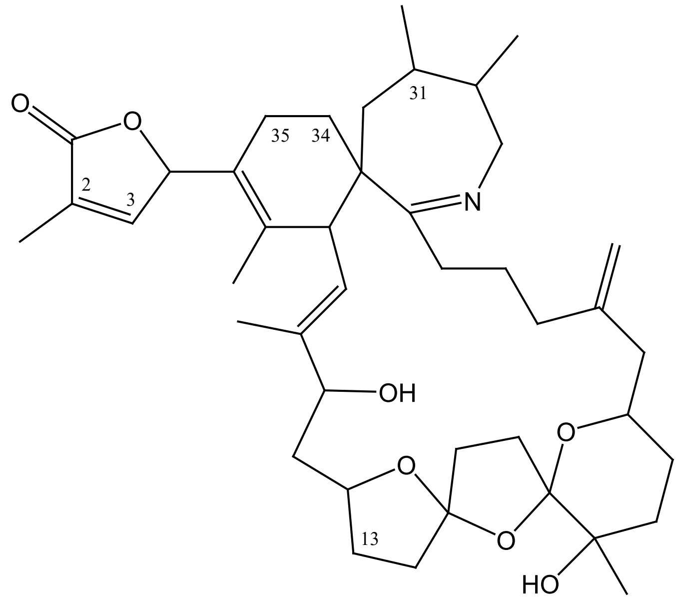
Goniodomin A (GDA)

=> GDA can be used as a chemotaxonomic marker
for *A. pseudogonyaulax* in the Black Sea

A. ostenfeldii strain 5D-3

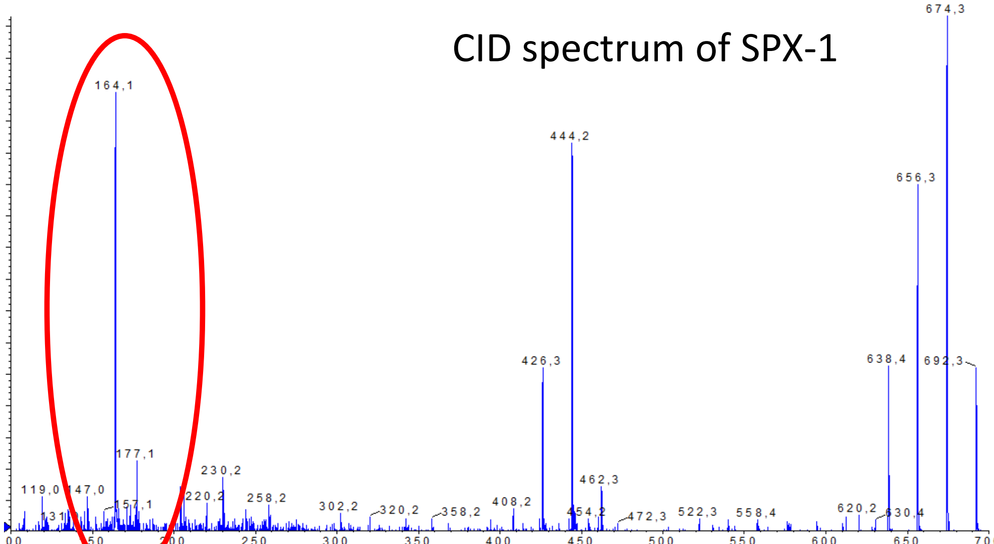
isolated in the Black Sea
in September 2021

Alexandrium ostenfeldii

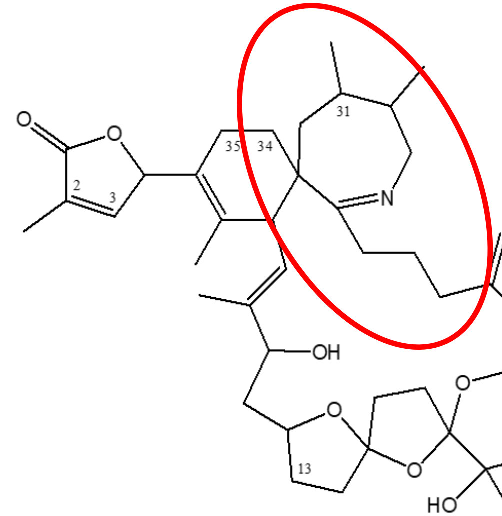


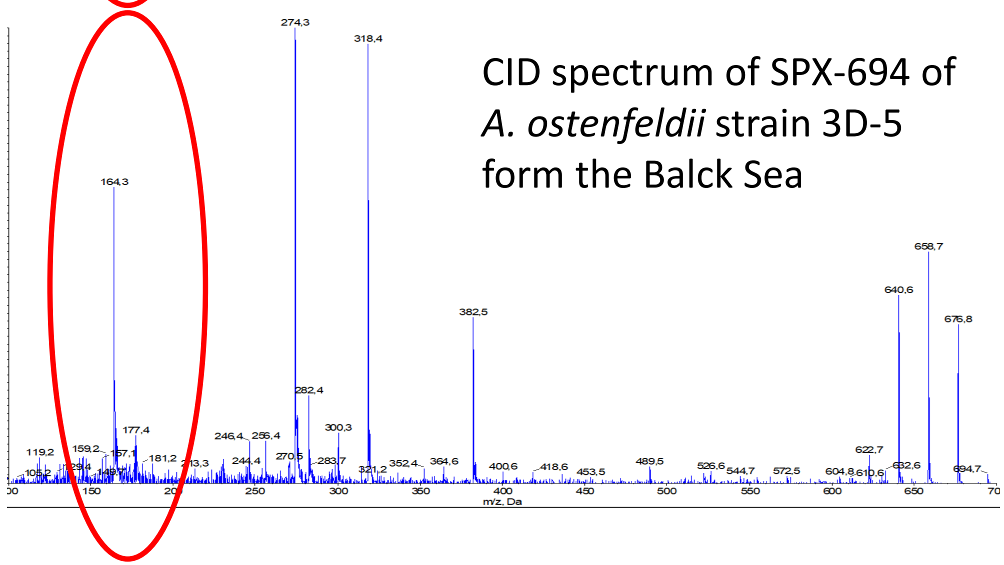
13-desmethyl-spirolide C (SPX-1)

Alexandrium ostenfeldii



CID spectrum of SPX-1





CID spectrum of SPX-694 of *A. ostenfeldii* strain 3D-5 form the Balck Sea

?

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