

Supplementary Materials

Seasonal Single-Site Sampling Reveals Large Diversity of Marine Algal Toxins in Coastal Waters and Shellfish of New Caledonia (Southwestern Pacific)

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Table S1. Average amount (mean \pm standard deviation, $n = 3$) with coefficient of variation (CV %) of toxin accumulated by SPATT bag during the two seasons after one week of exposure in Lemon Bay, Noumea.

Season	Toxicity in ng SPATT ⁻¹				
	PTX2	AZA2	PnTx-G	OA	hYTX
<i>Cold</i>	3.0 \pm 0.5	0.3 \pm 0.1	0.6 \pm 0.0	37.3 \pm 4.2	12.6 \pm 1.4
	19%	17%	4%	11%	11%
<i>Warm</i>	51.6 \pm 10.1	0.6 \pm 0.2	3.5 \pm 0.7	37.2 \pm 2.4	16.4 \pm 2.6
	20%	28%	21%	7%	16%

Table S2. Quantitative results of the LC-MS/MS analysis obtained on the whole tissue of the shellfish collected in the bays of Noumea.

Sample Code	Toxicity in $\mu\text{g kg}^{-1}$ of WT									
	hYTX	h45-OH-YTX	hCOOH-YTX	OA	PTX2	PTX2sa	AZA2	GYM-A	PnTX-G	BTX3
WT N°1	6	1.8	1.5	ND ¹	ND	ND	0.5	1	3.7	2.9
WT N°2	ND	ND	ND	ND	ND	ND	ND	2.3	8.3	ND
WT N°3	ND	ND	ND	ND	2.7	2.7	ND	1.3	1.0	ND
WT N°4	6.7	ND	0.6	0.6	0.0	2.2	1.3	1.5	7.0	ND
WT N°5	ND	ND	ND	ND	ND	ND	ND	8.0	16.0	ND
WT N°6	ND	ND	3.9	3.9	ND	ND	ND	8.4	0.8	ND
WT N°7	ND	ND	6.2	6.2	ND	2.6	0.2	0.7	22.6	ND
WT N°8	0.6	ND	ND	ND	ND	ND	ND	0.5	0.1	ND
WT N°9	ND	ND	ND	ND	ND	ND	ND	7.8	2.8	ND
WT N°10	ND	ND	ND	ND	ND	ND	ND	22.6	6.0	ND

Table S3. List of the selected MRM transitions and the MS parameters used for the detection of lipophilic toxins in negative ionization mode (**method 1**) and in positive ionization mode (**method 2 and method 3**).

Ionization mode	Compound	Parent ion (m/z)	Fragment ion (m/z)	DP (V)	CE (eV)	CXP (eV)
ESI ⁻	<i>OA & DTX2</i>	803.4	113.1	-170	-92	-9
			255.1*		-62	-16
	<i>DTX1</i>	817.5	255.1*	-170	-68	-13
			113.1		-92	-5
	<i>YTX</i>	1141.4	1061.6*	-120	-48	-17
			855.6		-98	-19
	<i>Homo-YTX</i>	1155.5	1075.6*	-120	-48	-17
			869.4		-98	-19
	<i>45-OH YTX</i>	1157.5	1077.5*	-120	-48	-17
			855.5		-98	-19
	<i>45-OH homo YTX</i>	1171.5	1091.5*	-120	-48	-17
			869.4		-98	-19
	<i>COOH YTX</i>	1173.5	1093.5*	-120	-48	-17
			855.5		-98	-19
	<i>Homo COOH YTX</i>	1187.5	1107.5*	-120	-48	-17
			869.4		-98	-19
ESI ⁺	<i>Portimine</i>	402.5	246.5*	100	58	10
			134.1		69	8
	<i>GYM-A</i>	508.4	490.2*	86	33	12
			162.4		69	10
	<i>GYM-B/-C</i>	524.4	506.4*	86	33	12
			162.4		69	10
	<i>SPX-A / SPX desMe-C</i>	692.7	444.3	121	53	26
	<i>SPX-A</i>		150.0*		69	8
	<i>SPX desMe-C</i>		164.2*		69	8
	<i>SPX-B / SPX desMe-D</i>	694.3	444.3	121	53	26
	<i>SPX-B</i>		150.0*		69	8
	<i>SPX desMe-D</i>		164.2*		69	8
	<i>PnTX-G</i>	694.4	440.2	125	60	10
			164.1*		80	8
	<i>PnTX-A</i>	712.4	440.2	125	60	10
			164.1*		80	8
	<i>PtTX-A /-B /-C</i>	831.5	458.5	125	60	10
			164.2*		80	8
	<i>AZA 1</i>	842.6	824.6*	116	41	12
			672.3		69	16
			654.4		69	16
	<i>AZA2</i>	856.6	838.6*	116	41	12
			672.4		69	16
			654.4		69	16
	<i>AZA3</i>	828.6	792.6*	116	41	12
			658.4		69	16
			640.4		69	16
	<i>PTX2</i>	876.6	823.3*	91	31	12
			805.6		37	12
	<i>PTX2 sa</i>	894.6	823.5*	91	31	12

			805.6		37	12
	<i>PTX1</i>	892.6	821.4*	91	31	12
			839.5		37	12
	<i>PTX6</i>	906.6	871.6*	91	31	12
			853.6		37	12
ESI ⁺	<i>BTX1</i>	867.6	849.5*	151	21	22
			831.5		25	24
			813.6		27	20
	<i>BTX2</i>	895.6	877.5*	161	23	24
			859.6		29	24
			455.4		39	12
	<i>BTX3</i>	897.6	725.4*	151	29	18
			825.4		17	24
			807.5		19	24
	<i>BTX-B5</i>	911.6	893.6*	141	25	14
			875.6		27	14
			431.1		37	24
	<i>BTX6</i>	911.6	893.6*	120	30	20
			875.6		35	20
	<i>BTX7</i>	869.4	779.4*	120	25	20
			151.2		45	20
	<i>BTX9</i>	899.4	863.5*	120	35	20
			157.1		45	20
	<i>Brevenal</i>	657.4	639.3*	120	35	20
			579.3		35	20
			267.2		35	20

*transition used for quantification