Dermatoxins Report

Project: Florida Department of Environmental Protection

Submitted to:	FDEP Laboratory
Organization:	Florida Department of Environmental Protection
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Sample Receipt Date:	29 April 2022
Sample Condition:	4.1 ºC upon arrival
Report#	220426_FDEP
Date Prepared:	03 May 2022
Prepared by:	Amanda Foss

Table 1: Samples analyzed

Sample ID	Site/Description	Collection Date	Matrix
2322363	HAB-SD-04262022-100	26 April 2022	W-SURF-SLT

Analytes: Lyngbyatoxin-a (LA), Debromoaplysiatoxin (DAT), Aplysiatoxin (AT)

Abbreviations

MRL	Method Reporting Limit	FS	Field Sample
MDL	Method Detection Limit	LFSM	Lab Fortified Sample Matrix
Blank	Water/buffer free from interferences	LFSMD	Lab Fortified Sample Matrix Duplicate
LFB	Lab Fortified Blank	LD	Lab Duplicate
MB	Method Blank	IS	Internal Standard
CCC	Continued Calibration Check	—	Not Analyzed
ND	Not Detected above the MDL/MRL	NA	Not Applicable

Sample Preparation

Water Sample Sonication

LA/DAT/AT (Dermatoxins)

The sample was inverted to mix, and an aliquot (0.5 mL) was diluted in MeOH (0.5 mL) with a lab duplicate (LD; Table 3) and LFSM (Table 2). The aliquots were lysed by water bath sonication for 10 min followed by filtration (0.2 µm PVDF). A method blank (Blank) and spiked method blank (laboratory fortified blank - LFB) were prepared in the same manner and analyzed.

Analytical Techniques

Liquid chromatography mass spectrometry/mass spectrometry (LC-MS/MS)

Dermatoxins (LA/AT/DAT)

High performance chromatography coupled with tandem mass spectrometry was used for a targeted lyngbyatoxin-a, debromoaplysiatoxin, and aplysiatoxin analysis. The $[M+Na]^+$ ion for DAT (*m/z* 615) was fragmented and the product ions (*m/z* 597, 583, 481, and 393) were monitored. The $[M-H]^-$ ion for AT (*m/z* 670) was fragmented and product ions (*m/z* 509, 626) were monitored. The $[M+H]^+$ ion for LA (*m/z* 438) was fragmented and product ions (*m/z* 410, 395, 302, 271) were monitored. A S:N ratio of 3 was used to determine detection limits for DAT (0.3 ng/mL), LA (0.1 ng/mL), and AT (0.5 ng/mL). External standard curves were used to determine LFSM returns.

Qualifier	Flag
CL	Analytical result is estimated due to ineffective quenching.
J	Analyte was positively identified; the associated numerical value is estimated.
PT	The reported result is estimated because the sample was not analyzed within required holding time.
B	Analytical result is estimated. Analyte was detected in associated reagent blank as well as the samples.
E	Analytical result is estimated. Values achieved were outside calibration range.
N	Spiked sample control was outside limits
T	The reported result is estimated because the sample exceeded temperature threshold when received

Quality Control

Table 2: LFSM (lab fortified sample matrix), LFB (lab fortified blank), and MB (method blank) QC samples prepared for analyses.

Analyte	Concentration (ng/mL)	Sample ID	QC Type	Return
DAT	5.0	2322363	LFSM	96%
LA	5.0	2322363	LFSM	19%^{N}
AT	5.0	2322363	LFSM	13%^{N}
DAT	5.0	LFB	LFB	93%
LA	5.0	LFB	LFB	76%
AT	5.0	LFB	LFB	113%
DAT	0.0	MB	MB	< 0.3
LA	0.0	MB	MB	< 0.1
AT	0.0	MB	MB	< 0.5

**Control limits: water LFSM ± 30%; complicated matrix LFSM and when LFSM within 2x MDL ±50%; IS ± 50%*

N Qualifier: The N qualifier was used for the low (< 70%) LA & AT LFSM recoveries. All recoveries were taken into account when determining method detection/reporting limits.

Table 3: The percent reproducibility (%RPD) between lab duplicates (LDs) or LFSM/LFSMDs prepared and analyzed

QC Type	Sample ID	Analyte	Value 1	Value 2	% RPD	Pass/Fail (<40%)
LDs	2322363	DAT	< 0.3	< 0.3	NA	Pass
LDs	2322363	LA	< 0.1	< 0.1	NA	Pass
LDs	2322363	AT	< 0.5	< 0.5	NA	Pass

%RPD is NA when values are below the method reporting/detection limit

Summary of Results

Table 5: Summary of results in ng/mL for debromoaplysiatoxin (DAT), lyngbyatoxin-A (LA), and aplysiatoxin (AT)

Sample ID	DAT (ng/mL)	LA (ng/mL)	AT (ng/mL)
2322363	ND	ND	ND
MRL (ng/mL):	*1.0*	*1.0*	*1.0*
Analyst Initials:	*AF*	*AF*	*AF*
Date Analyzed:	*5/2/2022*	*5/2/2022*	*5/2/2022*
Analysis Time:	*1521 / 1534*	*1521 / 1534*	*1521 / 1534*
Extraction Date:	*5/2/2022*	*5/2/2022*	*5/2/2022*
Extraction time:	*1200*	*1200*	*1200*

Interpretations:

Dermatoxins (lyngbyatoxin-a, debromoaplysiatoxin aplysiatoxin) were not detected in the submitted samples above the method reporting limits.

Submitted by: 

Mark T. Aubel, Ph.D.
Lab Director
Date: May 3, 2022

The results in this report relate only to the samples listed above.
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