

Targeted and suspect screening of contaminants in coastal water and sediment samples in Qatar



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Introduction

In recent years, high-resolution mass spectrometry (HRMS) combined with separation techniques is a valuable tool for a more comprehensive analysis of contaminants of emerging concern (CECs) in the environment via retrospective screening. However, to date, only a few suspect or non-targeted studies have been reported on the occurrence of CECs in marine aquatic systems.

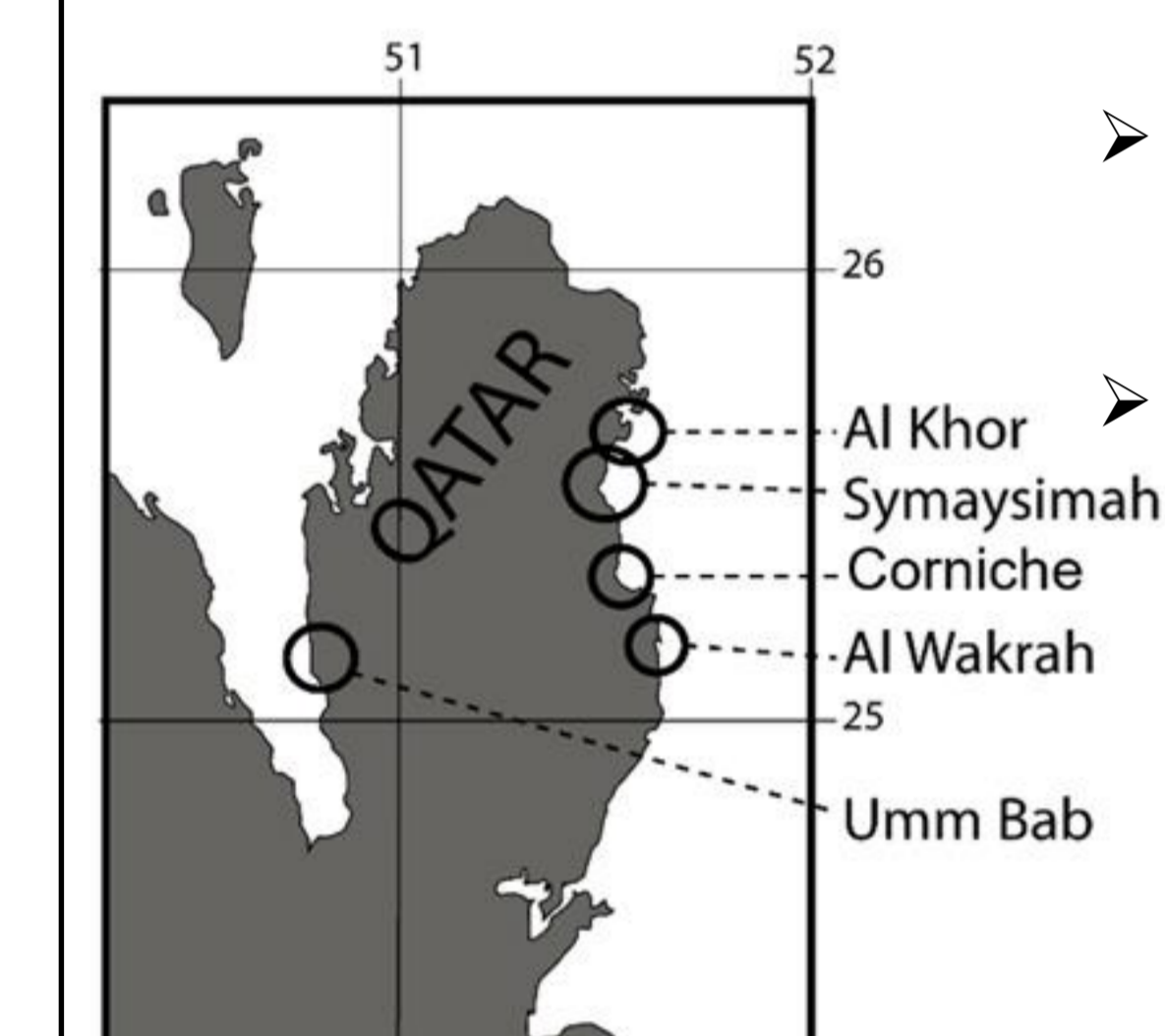
The aim of this study was to analyze seawater and sediment samples collected at four sites around Qatar coastal area in 2017-2018 by combining both targeted and suspect screening on data acquired via liquid chromatography-quadrupole-time-of-flight-mass spectrometry (LC-Q-TOF-MS). Suspect screening was also performed on two additional matrices: seawater with stormwater inputs and particulates from sediment traps.

A targeted method based on sample pre-treatment and pre-concentration followed by direct injection into LC-QTOF-MS was first validated for the targeted analysis of a range of compounds of emerging concern, including pharmaceutically active compounds. Method performances (incl. method detection limits, method quantification limits, recoveries and matrix effects) are presented. The method was then applied to coastal water and sediment samples collected around the Qatari coast. Full MS scan and All Ions MS/MS data were further mined for other contaminants using a library of >1000 suspect contaminants (suspect screening).

Experimental

Sampling and sample preparation:

Four sampling rounds from 2017 to 2018.
Four sites – 3 batches per site.
Two additional matrices from Corniche: seawater with stormwater inputs and particulates from sediment traps



- Seawater samples were spiked with internal standards followed by syringe filtration.
- Sediment samples spiked with internal standards were extracted using acetonitrile. The supernatant was filtrated and concentrated under nitrogen flow to less than 100 µL. The extract was reconstituted to around 500 µL using methanol before injection.

LC-QTOF-analysis:

- Agilent 1290 Infinity II LC system coupled to the 6545 Q-TOF-MS.
- Mobile phase A: Water with 5mM NH₄Ac;
- Mobile phase B: AcN/MeOH, (50:50 v/v) with 5mM NH₄Ac.
- Injection volume: 20 µL for seawater seawater samples and 6 µL for sediment extracts.
- Column: EC-C18 (3X100mm, 2.7µm).
- ESI-MS full scan and all ion MS/MS were performed.

Post-data analysis:

- Target analysis: Quantitative Analysis B.10.00 from Agilent MassHunter Workstation Software.
- Suspect screening: MassHunter Profinder B.10.0. Library: Environmental Water Screening PCDL (Agilent Technologies).

Conclusions

- A simple method, based on sample pre-treatment followed by data acquisition using LC-QTOF-MS, was developed for the targeted analysis of 21 contaminants in coastal seawater and sediment samples and for the suspect screening of other contaminants using the same data.
- Caffeine and cotinine were detected in coastal seawater samples as well as in seawater with stormwater inputs.
- Trimethoprim and carbamazepine were mainly detected in the sediment samples collected at four sites in 2017.
- In suspect screening, 12 molecular features were tentatively identified through suspect screening at concentration levels significantly higher than that in procedural blanks. These features tentatively corresponded to plasticizers (4), pesticide (1), drugs (2), antimicrobial agents (2) and industrial chemicals (3).
- The presence of the four plasticizers and the pesticide were further confirmed using reference analytical standards. Diethyl phthalate (DEP), dibutyl phthalate (DBP), and tributyl phosphate (TEP) were detected in seawater samples; Bis(2-ethylhexyl) phthalate (DEHP) in sediment and particulate samples; and dinoterb in seawater after storm event and particulate samples.

Acknowledgement

This publication was made possible by the NPRP award [NPRP9-394-1-090 "The Pearl Oyster: from national icon to guardian of Qatar's marine environment"] from the Qatar National Research Fund (a member of Qatar Foundation). The statements made herein are solely the responsibility of the authors. We wish to acknowledge financial support from the Canada Foundation for Innovation / John R. Evans Leaders Fund grant (Project #35318) of S. Bayen. DBP and TBOEP standards were purchased under the grant Endocrine Disrupting Chemicals – Towards Responsible Replacement (PI: Prof. B. Hales).

Results

Targeted analysis of 21 analytes

Table 1: Method validation for the LC-MS analysis of the 21 target analytes in simulated seawater and solvent.

Target analytes	Simulated seawater							Solvent				
	RT (min)	Quantifier m/z	MDLs (ng/L)	MQLs (ng/L)	Mean relative recoveries (% n=9)	Matrix effects (%)	Intraday precision (RSD,%, n=6)	RT (min)	MDLs (ng/g ww)	MQLs (ng/g ww)	Mean relative recoveries (% n=9)	Intraday precision (RSD,%, n=6)
ESI+												
Acetaminophen	3.322	152.0712	34	110	103±9	-14%	1.0	2.98	0.25	0.84	104±7	5.3
Atrazine	6.465	216.1016	28	90	100±2	-8%	0.9	4.63	0.15	0.49	105±6	0.7
Caffeine	3.853	195.0882	67	220	92±4	-5%	0.6	3.20	0.052	0.17	99±6	1.0
Carbamazepine	6.067	237.1028	15	50	96±2	2%	1.4	4.37	0.22	0.72	112±5	3.3
Cotinine	3.721	177.1028	12	40	96±3	2%	2.0	3.13	0.032	0.11	106±9	1.4
Diuron	6.540	233.0249	47	160	101±5	-1%	1.0	4.65	0.016	0.052	107±4	0.4
Fluoxetine	6.457	310.1419	56	190	95±1	3%	1.2	4.54	0.004	0.012	105±5	0.7
Lincomycin	5.536	407.2216	23	80	85±8	1%	3.5	4.09	0.096	0.32	94±15	3.4
Monocrotophos	3.994	224.0688	10	30	102±2	-18%	1.2	3.26	0.008	0.028	100±8	0.9
Paroxetine	6.134	330.1506	140	470	98±4	-5%	1.1	4.37	0.04	0.13	102±7	0.5
Sulfadimethoxine	4.807	311.0814	16	50	90±6	23%	4.6	3.71	0.02	0.068	97±10	3.8
Sulfamethazine	4.326	279.0916	6	20	102±6	18%	2.5	3.46	0.012	0.04	107±9	2.9
Sulfamethoxazole	3.986	254.06	16	50	93±7	-17%	1.2	3.34	0.084	0.28	111±10	1.5
Trimethoprim	4.533	291.1457	13	40	98±1	1%	1.8	3.50	0.008	0.028	103±6	0.5
Tylosin A	7.054	916.5271	100	330	0*	-48%	6.3	4.85	0.012	0.04	108±8	2.3
Tylosin B	6.125	772.4484	150	500	0*	-2%	4.4	4.33	0.13	0.44	101±7	3.4
Venlafaxine	5.545	278.212	26	90	100±3	-14%	0.8	4.10	0.004	0.012	101±8	1.5
ESI-												
Bisphenol A	5.244	227.1072	940	3130	91±6	-4%	3.6	4.54	0.59	1.97	107±7	7.3
Gemfibrozil	5.883	249.1491	160	530	95±6	-5%	11.7	5.16	0.072	0.24	107±9	3.9
Ibuprofen	5.286	205.1229	370	1230	88±7	-20%	6.2	4.55	0.14	0.47	103±18	7.9
Triclosan	6.107	286.9433	940	3130	96±3	14%	1.4	5.39	0.75	2.5	104±8	7.2

*Tylosin A and B almost had no recovery in simulated sea water after filtration

- For simulated seawater, MDLs and MQLs via direct injection were within the range of 6-940 ng/L and 20-3130 ng/L, respectively. The relative recoveries for 19 target analytes ranged from 85 to 103 %. Matrix effects ranged from -48% (tylosin A) to 23 % (sulfadimethoxine) in simulated seawater.
- In solvent, MDLs and MQLs were in the range or in some cases lower than reported values for the same compounds from sediments samples in mangrove, Singapore.¹ Relative recoveries ranged from 94 to 111 %.

Suspect screening of contaminants

Table 3: Tentative compounds identified in all matrices by suspect screening with concentration level significantly higher than that in blank (fold change >2).

Tentative compound name	Class of compound	Chemical formula	ESI mode	Exact mass (mass error)	Retention time (min)	Fragment ions	Identification level ²	logP
Sea water samples								
Diethyl phthalate (DEP)	Plasticizer	C12H14O4	+	222.0898 (0.95)	6.78*	177.0552/149.0238/121.0647	1	2.42
Dibutyl phthalate (DBP)	Plasticizer	C16H22O4	+	278.1524 (0.8)	8.09*	279.1607/205.0868/149.0240/121.0290/93.0342/57.0700	1	4.5
Tributyl phosphate (TBP)	Plasticizer	C12H27O4P	+	266.1651(0.72)	7.99*	267.1731/211.1089/98.9821/80.9480	1	4
Bezonic acid	Antimicrobial agent	C7H6O2	-	122.0367 (2.93)	3.28	77.0395	2a	1.87
Sediment samples								
2,6-Xylidine	Industry chemicals	C8 H11 N	+	121.0891 (1.88)	3.07	105.0702/79.0543/77.0387/51.0227	2a	1.84
Phenylalanine	Industry chemicals	C9 H11 N O2	+	165.0787 (3.62)	2.73	120.0806/149.0590/131.0490/103.0540/91.0541/77.0384	2a	-1.38
Bis(2-ethylhexyl) phthalate (DEHP)	Plasticizer	C24 H38 O4	+	390.2769 (1.0)	6.99*	279.1592/167.0339/149.0236/113.1327/71.0856	1	7.6
Cytarabine	drug	C9 H13 N3 O5	+	243.0863 (5.56)	2.37	112.0507/95.0530	2a	-2.8
Valproic acid	drug	C8 H16 O2	-	144.1149 (1.02)	4.16	71.0137	2a	2.8
4-Nitrophenol	Industry chemicals	C6 H5 N O3	-	139.0268 (0.65)	3.95	108.0216/92.0267	2a	1.61
Seawater samples with stormwater inputs								
Dinoterb	Pesticide	C10 H12 N2 O5	-	240.0751(1.63)	5.07*	224.0416/207.0399/194.0444/177.0419/164.0708/151.0757/136.0526/123.0322/107.0867	1	3.64
Dichlorophen	Antimicrobial agent	C13 H10 Cl2 O2	-	268.0058 (2.04)	5.69	126.9954	2a	4.26
Particle samples								
Bis(2-ethylhexyl) phthalate (DEHP)	Plasticizer	C24 H38 O4	+	390.2766 (1.72)	6.94*	279.1580/167.0332/149.0228/113.1320	1	7.6
2,6-Xylidine	Industry chemicals	C8 H11 N	+	121.0887 (0.61)	3.12	105.0696	2a	1.84
Dinoterb	Pesticide	C10 H12 N2 O5	-	240.0753 (0.62)	4.43*	207.0697/194.0453/177.8696/164.0762/151.0762/123.0451/107.0504	1	3.64
Valproic acid	drug	C8 H16 O2	-	144.1153 (0.54)	4.254	71.0133	2a	2.8
4-Nitrophenol	Industry chemicals	C6 H5 N O3	-	139.0272 (05)	3.99	108.0215/92.0264	2a	1.61
Dichlorophen	Antimicrobial agent	C13 H10 Cl2 O2	-	268.0075 (10.14)	5.05	126.9051	2a	4.26

*Retention time was confirmed by reference standard.

- Samples and blanks were aligned and extracted by Agilent Profinder (B10.00) under "Targeted Feature Extraction" mode using the Agilent Environmental Water Screening PCDL for environmental contaminants (1452 compounds).
- Suspect screening parameters were first validated using the 21 targeted analytes at low concentration range. Molecular features with overall match score >70% were subjected to MS/MS fragment comparison with spectral library.
- In seawater samples, four molecular features were tentatively identified. Three plasticizers were confirmed with standards. DEP showed the significantly high fold change in the range of 182-713, compared with that of DEP (2-8) and TBP(3-12).
- In sediment samples, six molecular features were tentatively identified. The presence of DEHP was confirmed using standard with high fold change values (21-84) in samples collected at four sampling sites in 17/12, 18/05 and 18/11. The DEHP has been detected in oyster samples collected at the same sampling sites and time in previous studies.³
- For seawaters with stormwater inputs and small particles samples collected at Corniche, totally 6 molecular features were tentatively identified. DEHP was confirmed to presence in particulate samples with mean fold change of 12. The identification of dinoterb, a pesticide, was confirmed using its standard, with concentration around 2000ng/L and 4 ng/g dry weight (dw) in seawater after storm event and particle samples, respectively.

Reference

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