

Supplementary Material

A comprehensive analysis of water-soluble arsenicals in Icelandic macroalgae

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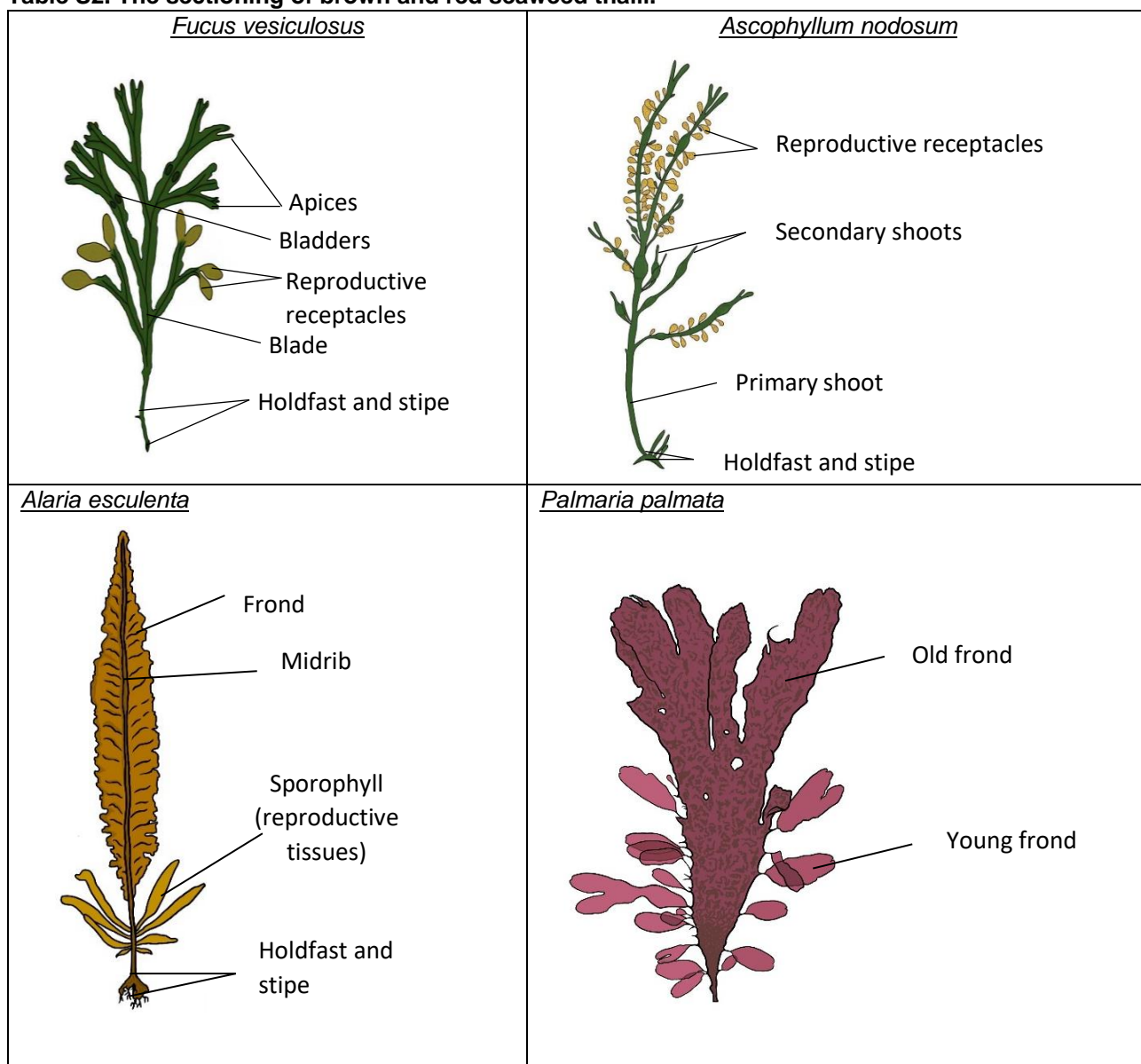
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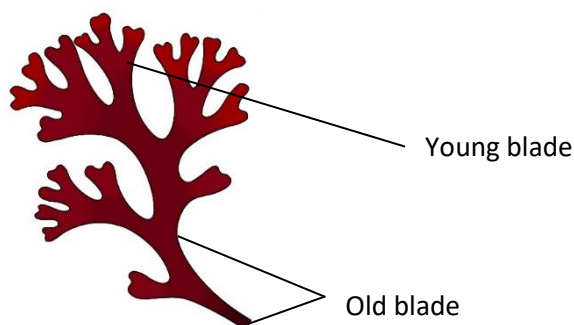
Table S1. The species of seaweed collected in May 2021 and February 2022.

	Grindavík, Iceland (63°50'55.5"N, 22°18'23.5"W)	Kjalarnes, Iceland (64°13'34.2"N, 21°48'50.7"W)
May 2021	<i>Fucus vesiculosus</i> , <i>Ascophyllum nodosum</i> , <i>Alaria esculenta</i> <i>Palmaria palmata</i> , <i>Mastocarpus stellatus</i> <i>Acropsiphona arcta</i> , <i>Ulva prolifera</i> , <i>Ulva intestinalis</i>	<i>Fucus vesiculosus</i> , <i>Ascophyllum nodosum</i> , <i>Palmaria palmata</i> , <i>Devaleraea ramentacea</i> , <i>Cystoclonium purpureum</i> , <i>Chondrus crispus</i> <i>Acrosiphonia arcta</i> , <i>Ulva intestinalis</i>
February 2022	<i>Fucus vesiculosus</i> , <i>Ascophyllum nodosum</i> , <i>Alaria esculenta</i> <i>Palmaria palmata</i> , <i>Mastocarpus stellatus</i> , <i>Vertebrata lanosa</i> , <i>Chondrus crispus</i> <i>Acrosiphonia</i> sp. (<i>arcta</i> or <i>coalita</i>)	<i>Fucus vesiculosus</i> , <i>Laminaria hyperborea</i> , <i>Ascophyllum nodosum</i> <i>Palmaria palmata</i> , <i>Chondrus crispus</i> -

Table S2. The sectioning of brown and red seaweed thalli.



Chondrus crispus–Mastocarpus stellatus



Fucus vesiculosus

Holdfast and stipe – distinct tissues tethering thallus to rock. Blade – thin, dark green tissue which makes up majority of thallus, photosynthetic. Bladders – found in pairs on blade, used for buoyancy. Apices – ends of blades which are not reproductively mature and have not formed reproductive receptacles. Reproductive receptacles – swollen, light green/yellow structures on ends of blade, reproduction.

Ascophyllum nodosum

Holdfast and stipe – distinct tissues tethering thallus to rock. Primary shoot – older shoot directly attached to stipe from which secondary shoots branch, thick and contain bladders, photosynthetic. Secondary shoot – younger, thinner branches from primary shoot, photosynthetic. Reproductive receptacles – swollen, yellow structures on ends of shoots, reproduction.

Alaria esculenta

Holdfast and stipe – distinct tissues tethering thallus to rock. Midrib – tough, vein-like structure running through centre of thallus, support. Frond – thin brown tissue surrounding midrib, photosynthetic. Sporophyll – distinct reproductive tissues that grow from the sides of the stipe, reproduction.

Palmaria palmata

Old frond tissues were thick and weathered. New fronds were small, thin growths occurring from the sides of the old frond.

Chondrus crispus–Mastocarpus stellatus

The old blade tissue was identified as the blade directly attached to the holdfast from which new growth branches from. Young blades were identified as branches from the primary growth, as new growth is apical and occurs from the ends of the blade.

Table S3. Instrument parameters for analysis with the ICP-MS.

ICP-MS operating conditions	Agilent 7900 ICP-MS (He gas mode)
RF power	1550 W
RF matching	1.20 V
Plasma gas	15 L min ⁻¹
Carrier gas	1.07 L min ⁻¹
Make-up gas	0.80 Lmin ⁻¹
Spray chamber temperature	2°C
Octopole collision cell	Pressurised, He gas (5 mL min ⁻¹)
Isotopes monitored	As ⁷⁵ , In ¹¹⁵ (internal std)

Table S4. Instrument parameters for analysis with the HPLC-ICP-MS set-up.

HPLC-ICP-MS settings	Agilent Infinity II 1290 HPLC and Agilent 7900 ICP-MS (No gas mode)
RF power	1530 W
RF matching	1.25 V
Nebuliser gas flow	1.07 L min ⁻¹
Plasma gas flow	15.0 L min ⁻¹
Spray chamber temperature	2°C
Isotopes monitored	⁷⁵ As, ⁷⁷ Se, & ⁷² Ge (internal standard)
Integration time	1 s
Guard column	Hamilton PRP-X100 Guard cartridge
Analytical column	Hamilton PRP-X100 (250 × 4.6 mm; 10 µm)
Mobile phase	A: Ammonium carbonate (0.05 mM, pH 9.2) 3% MeOH B: Ammonium carbonate (50 mM, pH 9.2) 3% MeOH
Gradient	0-6 min: A 80% B 20% 6-17 min 100% B 17-23 min A 80% B 20%
Flow rate	1 mL min ⁻¹
Injection volume	40 µL

Table S5. The water-soluble arsenic speciation of all samples measured.

Species	Location	Season	Section	Total As	Total As error	Total As extract	Cations	AsSug-gy	DMA	AsSug-PO ₄	AsSug-SO ₃	MMA	AsSug-SO ₄	As ^v (iAs)	Unknown sum	Column recovery	Extraction efficiency
<i>Acrosiphonia arcta</i>	K	May 2021	Whole	6.47	0.31	3.34	0.16	0.71	0.10	1.15	0.15	<LOQ	0.12	0.43	0.06	86	51
<i>Ulva prolifera</i>	K	May 2021	Whole	5.27	0.62	1.87	0.11	0.44	0.03	0.45	0.04	<LOQ	<LOQ	0.40	0.04	81	35
<i>Ulva intestinalis</i>	K	May 2021	Whole	9.45	0.38	3.89	0.22	0.56	0.12	1.05	0.08	<LOQ	0.31	1.06	0.03	89	41
<i>Acrosiphonia arcta</i>	G	May 2021	Whole	6.05	0.56	2.19	0.06	0.36	0.11	0.78	0.07	<LOQ	0.06	0.22	0.07	80	36
<i>Porphyra dioica</i>	G	May 2021	Whole	21.59	0.93	21.46	0.10	0.87	0.15	20.13	<LOQ	<LOQ	0.02	<LOQ	0.15	100	99
<i>Ulva intestinalis</i>	G	May 2021	Whole	3.76	0.37	2.99	0.28	1.32	0.07	0.41	0.15	<LOQ	0.02	0.41	0.08	92	80
<i>Acrosiphonia (arcta or coalita)</i>	G	Feb 2022	Whole	7.68	0.21	4.51	1.25	0.86	0.11	1.04	0.44	0.12	0.17	0.84	0.08	109	59
<i>Chondrus crispus</i>	K	May 2021	Old blade	6.48	0.26	4.35	0.05	0.41	0.06	4.09	<LOQ	<LOQ	<LOQ	0.07	<LOQ	107	67
<i>Chondrus crispus</i>	K	Feb 2022	Old blade	22.6	0.51	12.30	0.11	0.68	0.07	10.11	0.02	<LOQ	<LOQ	0.11	<LOQ	91	54
<i>Chondrus crispus</i>	G	Feb 2022	Holdfast and stipe	49.02	2.57	22.88	0.17	1.85	0.07	21.16	<LOQ	0.19	<LOQ	0.02	<LOQ	103	47
<i>Chondrus crispus</i>	G	Feb 2022	Blade	32.24	4.56	21.03	0.16	1.55	0.06	20.68	<LOQ	0.05	<LOQ	0.04	<LOQ	107	65
<i>Cystoclonium purpureum</i>	K	May 2021	Whole	5.62	0.16	2.81	0.12	0.45	0.11	1.00	0.34	0.06	0.08	0.10	<LOQ	80	50
<i>Develararea ramentacea</i>	K	May 2021	Whole	7.60	0.92	1.99	<LOQ	0.13	<LOQ	0.89	0.16	<LOQ	0.09	<LOQ	<LOQ	89	26
<i>Mastocarpus stellatus</i>	G	May 2021	Holdfast and stipe	16.87	2.67	8.02	0.10	0.40	0.07	4.47	<LOQ	<LOQ	0.04	<LOQ	3.59	109	48
<i>Mastocarpus stellatus</i>	G	May 2021	Blade	15.63	0.83	12.75	<LOQ	1.15	0.13	9.49	<LOQ	<LOQ	0.03	<LOQ	2.86	107	82
<i>Mastocarpus stellatus</i>	G	Feb 2022	Holdfast and stipe	21.57	2.04	14.92	0.28	0.44	0.13	6.87	<LOQ	<LOQ	0.07	<LOQ	6.40	96	69
<i>Mastocarpus stellatus</i>	G	Feb 2022	Blade	30.16	3.83	16.88	0.37	0.55	0.11	9.32	<LOQ	<LOQ	0.05	0.03	6.61	101	56
<i>Vertebrata lanosa</i>	G	Feb 2022	Whole	10.20	1.15	7.25	0.31	1.79	0.13	1.53	0.58	0.03	1.70	0.39	<LOQ	90	71
<i>Palmaria palmata</i>	K	May 2021	Green	4.96	0.48	2.31	0.07	0.98	0.07	1.07	0.03	<LOQ	<LOQ	0.12	<LOQ	103	46
<i>Palmaria palmata</i>	K	May 2021	Red	5.53	0.08	2.54	0.08	1.06	0.05	1.08	0.04	<LOQ	0.02	0.22	<LOQ	100	46
<i>Palmaria palmata</i>	K	May 2021	Whole	8.30	0.21	5.51	0.09	1.81	0.16	3.54	0.10	<LOQ	0.02	0.14	0.04	107	66
<i>Palmaria palmata</i>	G	May 2021	Whole	9.11	0.06	6.54	0.07	1.55	0.19	4.37	0.37	<LOQ	0.05	0.08	0.02	103	72
<i>Palmaria palmata</i>	K	Feb 2022	Young frond	10.43	0.49	6.65	0.19	2.35	0.21	3.89	0.10	<LOQ	<LOQ	0.34	0.07	108	64
<i>Palmaria palmata</i>	K	Feb 2022	Old frond	13.70	1.83	9.02	0.25	3.08	0.27	5.42	0.16	<LOQ	<LOQ	0.38	0.12	108	66
<i>Palmaria palmata</i>	K	Feb 2022	Whole	11.81	1.62	6.30	0.23	1.96	0.13	3.25	0.08	0.02	<LOQ	0.21	<LOQ	92	53
<i>Palmaria palmata</i>	G	Feb 2022	Young frond	7.04	0.60	10.35	0.37	3.30	0.20	5.60	0.06	0.08	0.02	0.32	<LOQ	98	147
<i>Palmaria palmata</i>	G	Feb 2022	Old frond	13.90	2.30	8.88	0.20	2.50	0.15	5.72	0.23	0.04	0.02	0.10	<LOQ	101	64
<i>Palmaria palmata</i>	G	Feb 2022	Whole	13.17	1.5	9.37	0.15	2.61	0.14	6.41	0.40	0.05	<LOQ	0.06	<LOQ	105	71
<i>Alaria esculenta</i>	G	May 2021	Frond	34.97	4.03	26.55	0.05	1.12	0.15	5.20	21.36	0.02	<LOQ	0.34	0.11	107	76
<i>Alaria esculenta</i>	G	May 2021	Midrib	34.08	0.99	26.54	0.04	1.15	0.11	5.32	20.42	0.02	<LOQ	0.21	0.08	103	78
<i>Alaria esculenta</i>	G	May 2021	Sporophyll	54.31	0.38	39.42	0.04	0.90	0.21	8.72	28.83	0.03	<LOQ	0.11	0.17	99	73
<i>Alaria esculenta</i>	G	May 2021	Holdfast and stipe	44.39	1.58	36.96	0.05	0.70	0.19	8.79	24.91	<LOQ	<LOQ	0.06	0.15	94	83
<i>Alaria esculenta</i>	G	Feb 2022	Frond	125.98	5.04	95.61	0.03	1.04	0.46	12.11	73.28	<LOQ	<LOQ	0.10	0.55	92	76
<i>Alaria esculenta</i>	G	Feb 2022	Midrib	65.74	1.43	45.55	0.04	0.56	0.16	6.84	33.72	<LOQ	<LOQ	0.03	0.20	91	69
<i>Alaria esculenta</i>	G	Feb 2022	Sporophyll	265.33	9.91	108	0.09	1.18	0.24	14.67	87.82	<LOQ	<LOQ	0.07	0.62	97	41
<i>Alaria esculenta</i>	G	Feb 2022	Holdfast and stipe	47.50	2.52	37.32	0.07	0.48	0.17	10.46	24.43	<LOQ	<LOQ	0.08	0.23	96	79
<i>Ascophyllum nodosum</i>	K	May 2021	Holdfast and stipe	40.75	1.36	27.84	<LOQ	2.33	0.49	2.26	2.97	<LOQ	16.82	0.08	0.11	88	68
<i>Ascophyllum nodosum</i>	K	May 2021	Primary shoot	42.77	0.30	16.30	<LOQ	1.99	0.12	1.22	1.50	<LOQ	8.58	0.07	0.16	82	38
<i>Ascophyllum nodosum</i>	K	May 2021	Secondary shoot	32.63	1.77	17.67	<LOQ	1.54	0.10	1.69	1.14	<LOQ	11.25	0.02	0.15	87	54
<i>Ascophyllum nodosum</i>	K	May 2021	Reproductive receptacle	41.63	3.41	29.15	<LOQ	1.57	0.21	2.26	3.71	<LOQ	19.91	<LOQ	0.14	93	70
<i>Ascophyllum nodosum</i>	K	Feb 2022	Holdfast and stipe	60.76	3.03	19.08	<LOQ	2.45	0.09	0.98	1.74	<LOQ	5.44	0.03	0.02	97	31
<i>Ascophyllum nodosum</i>	K	Feb 2022	Primary shoot	34.51	4.59	18.72	<LOQ	6.34	0.15	1.55	2.04	<LOQ	6.35	0.04	0.09	89	54
<i>Ascophyllum nodosum</i>	K	Feb 2022	Secondary shoot	87.69	4.31	23.11	<LOQ	3.30	0.20	1.82	4.34	<LOQ	13.39	0.08	0.15	99	26
<i>Ascophyllum nodosum</i>	K	Feb 2022	Reproductive receptacle	195.16	11.11	43.17	<LOQ	1.88	0.31	2.27	7.85	<LOQ	31.68	0.09	0.28	102	22
<i>Ascophyllum nodosum</i>	G	May 2021	Primary shoot	29.66	1.33	17.39	0.04	3.00	0.08	1.17	1.81	0.03	9.44	0.06	0.11	91	58
<i>Ascophyllum nodosum</i>	G	May 2021	Secondary shoot	34.58	0.40	17.23	0.03	2.30	0.05	1.29	2.18	0.03	10.21	0.11	0.09	96	50
<i>Ascophyllum nodosum</i>	G	May 2021	Reproductive receptacle	50.78	0.66	29.78	0.05	1.36	0.22	1.55	4.20	0.07	21.05	0.14	0.18	97	59
<i>Ascophyllum nodosum</i>	G	May 2021	Holdfast and stipe	39.70	2.98	23.18	0.04	2.47	0.13	1.81	3.27	0.03	16.16	0.17	0.17	107	58
<i>Ascophyllum nodosum</i>	G	Feb 2022	Secondary shoot	47.72	2.26	23.31	<LOQ	1.68	0.17	1.64	3.63	<LOQ	15.47	0.08	0.18	98	37

Species	Location	Season	Section	Total As	Total As error	Total As extract	Cations	AsSug-gy	DMA	AsSug-PO ₄	AsSug-SO ₃	MMA	AsSug-SO ₄	As(V) (iAs)	Unknown sum	Column recovery	Extraction efficiency
<i>Ascophyllum nodosum</i>	G	Feb 2022	Primary shoot	33.0	1.1	17.51	0.02	2.70	0.13	1.24	2.56	0.03	9.65	0.08	0.24	94	71
<i>Ascophyllum nodosum</i>	G	Feb 2022	Reproductive receptacle	130	8.1	67.99	<LOQ	1.42	0.42	2.82	10.38	<LOQ	53.80	0.35	0.42	103	52
<i>Ascophyllum nodosum</i>	G	Feb 2022	Holdfast and stipe	73.31	8.46	35.49	0.12	2.26	0.29	3.06	4.11	0.06	23.77	0.26	0.23	97	48
<i>Fucus vesiculosus</i> ^A	G	May 2021	Blade	26.43	3.40	12.45	<LOQ	0.68	0.09	0.76	7.83	0.03	2.18	<LOQ	0.06	94	47
<i>Fucus vesiculosus</i> ^A	G	May 2021	Apice	49.80	7.19	25.06	<LOQ	0.66	0.13	1.10	19.54	0.07	3.27	<LOQ	0.05	99	50
<i>Fucus vesiculosus</i> ^A	G	May 2021	Reproductive receptacle	39.97	8.52	22.50	<LOQ	0.90	0.10	0.84	14.53	<LOQ	3.70	<LOQ	0.13	90	56
<i>Fucus vesiculosus</i> ^A	G	Feb 2022	Blade	81.82	4.65	29.53	<LOQ	0.74	0.16	0.93	21.10	0.05	5.67	<LOQ	0.10	97	36
<i>Fucus vesiculosus</i> ^A	G	Feb 2022	Apice	122.91	3.27	53.43	<LOQ	0.54	0.30	0.94	46.09	0.09	5.49	<LOQ	0.36	101	43
<i>Fucus vesiculosus</i> ^A	G	Feb 2022	Holdfast and stipe	100.93	3.85	53.05	<LOQ	0.61	0.18	1.36	41.88	<LOQ	10.62	0.03	0.34	103	53
<i>Fucus vesiculosus</i> ^A	G	May 2021	Holdfast and stipe	36.56	4.53	29.75	0.03	0.76	0.08	1.07	16.91	1.07	6.88	0.05	0.13	91	81
<i>Fucus vesiculosus</i>	K	May 2021	Holdfast and stipe	48.62	0.66	44.55	0.02	0.50	0.30	1.24	34.11	<LOQ	2.28	<LOQ	0.11	87	92
<i>Fucus vesiculosus</i>	K	May 2021	Blade	46.58	7.30	26.78	0.03	0.39	0.17	1.69	18.02	<LOQ	2.46	<LOQ	0.07	85	58
<i>Fucus vesiculosus</i>	K	May 2021	Bladder	31.44	1.57	25.24	<LOQ	0.41	0.14	1.66	17.62	<LOQ	4.15	<LOQ	0.06	95	80
<i>Fucus vesiculosus</i>	K	May 2021	Apice	71.15	4.72	48.65	<LOQ	0.32	0.14	1.97	39.63	0.03	3.75	<LOQ	0.10	93	68
<i>Fucus vesiculosus</i>	K	May 2021	Reproductive receptacle	96.03	25.01	40.37	<LOQ	0.60	0.07	3.23	32.57	<LOQ	5.65	<LOQ	0.20	105	42
<i>Fucus vesiculosus</i>	K	Feb 2022	Holdfast and stipe	43.36	2.51	38.16	<LOQ	0.85	0.23	1.33	30.87	<LOQ	5.53	0.06	0.11	102	88
<i>Fucus vesiculosus</i>	K	Feb 2022	Blade	73.95	5.72	28.32	<LOQ	0.84	0.24	1.47	19.65	0.03	3.79	0.04	0.10	92	38
<i>Fucus vesiculosus</i>	K	Feb 2022	Bladder	36.92	2.09	27.16	<LOQ	0.83	0.20	1.44	21.07	0.02	3.73	0.03	0.12	101	74
<i>Fucus vesiculosus</i>	K	Feb 2022	Apice	92.72	8.00	53.10	<LOQ	1.24	0.40	2.12	52.84	<LOQ	4.96	0.06	0.17	116	57
<i>Fucus vesiculosus</i>	K	Feb 2022	Reproductive receptacle	115.10	13.12	67.32	<LOQ	1.08	0.38	2.46	55.92	0.02	6.73	0.03	0.32	99	58
<i>Fucus vesiculosus</i>	G	May 2021	Bladder	33.44	4.56	21.70	0.02	0.37	0.11	1.56	12.84	0.02	3.72	0.08	0.09	87	65
<i>Fucus vesiculosus</i>	G	May 2021	Blade	27.64	0.77	20.53	<LOQ	0.41	0.09	1.69	11.36	0.02	3.23	0.05	0.11	83	74
<i>Fucus vesiculosus</i>	G	May 2021	Apice	83.41	13.97	45.31	0.02	0.28	0.16	3.32	33.69	<LOQ	5.43	<LOQ	0.21	95	61
<i>Fucus vesiculosus</i>	G	May 2021	Reproductive receptacle	46.26	0.51	40.21	<LOQ	0.57	0.10	2.76	27.04	<LOQ	5.75	<LOQ	0.30	91	87
<i>Fucus vesiculosus</i>	G	May 2021	Holdfast and stipe	32.21	1.27	28.74	<LOQ	0.33	0.10	0.83	18.39	<LOQ	5.26	<LOQ	0.08	87	88
<i>Fucus vesiculosus</i>	G	Feb 2022	Bladder	32.15	3.61	12.96	<LOQ	0.55	0.12	0.67	7.76	<LOQ	2.74	<LOQ	0.02	92	40
<i>Fucus vesiculosus</i>	G	Feb 2022	Blade	31.60	4.54	21.09	0.05	0.82	0.15	1.13	11.97	<LOQ	5.02	<LOQ	0.05	91	67
<i>Fucus vesiculosus</i>	G	Feb 2022	Apice	78.40	0.74	62.50	0.04	1.30	0.38	2.56	53.00	0.07	8.65	<LOQ	0.27	106	80
<i>Fucus vesiculosus</i>	G	Feb 2022	Reproductive receptacle	122.84	2.86	55.58	0.02	1.40	0.27	1.25	46.68	0.05	7.68	<LOQ	0.29	104	45
<i>Fucus vesiculosus</i>	G	Feb 2022	Holdfast and stipe	59.25	12.75	52.38	0.04	0.72	0.20	1.38	41.60	<LOQ	10.35	<LOQ	0.30	105	88

Extraction: water and hydrogen peroxide (3% v/v). Analysis. HPLC-ICP-MS with anion exchange column and ammonium carbonate buffer (gradient elution). All concentrations in milligrams per kilogram. LOQ, limit of quantification.

^ANo bladders due to wave action.