Supporting information

Environmental chemistry

Temporal and intra-thallus variation in arsenic in the brown macroalga *Laminaria digitata*

Rebecca Sim , Jörg Feldmann, Dagmar B. Stengel and Ásta H. Pétursdóttir

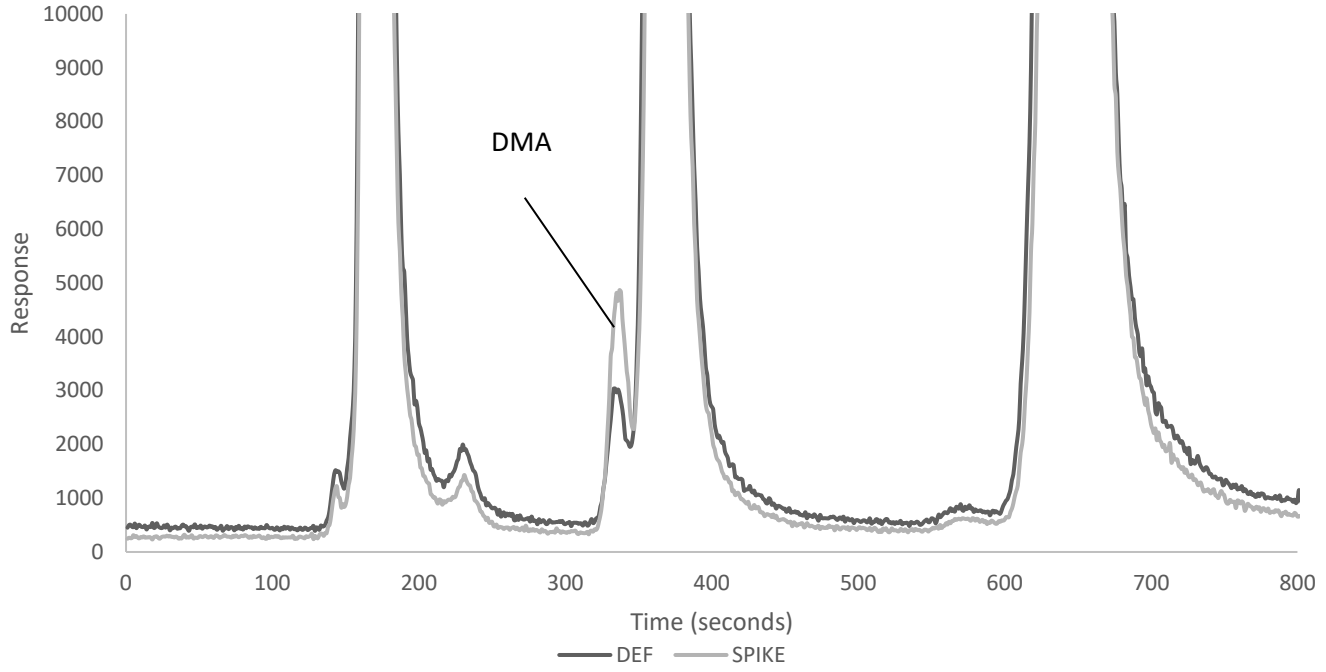
Table of contents

Table 1 – The instrumental operating parameters for the ICP-MS and HPLC-ICP-MS.

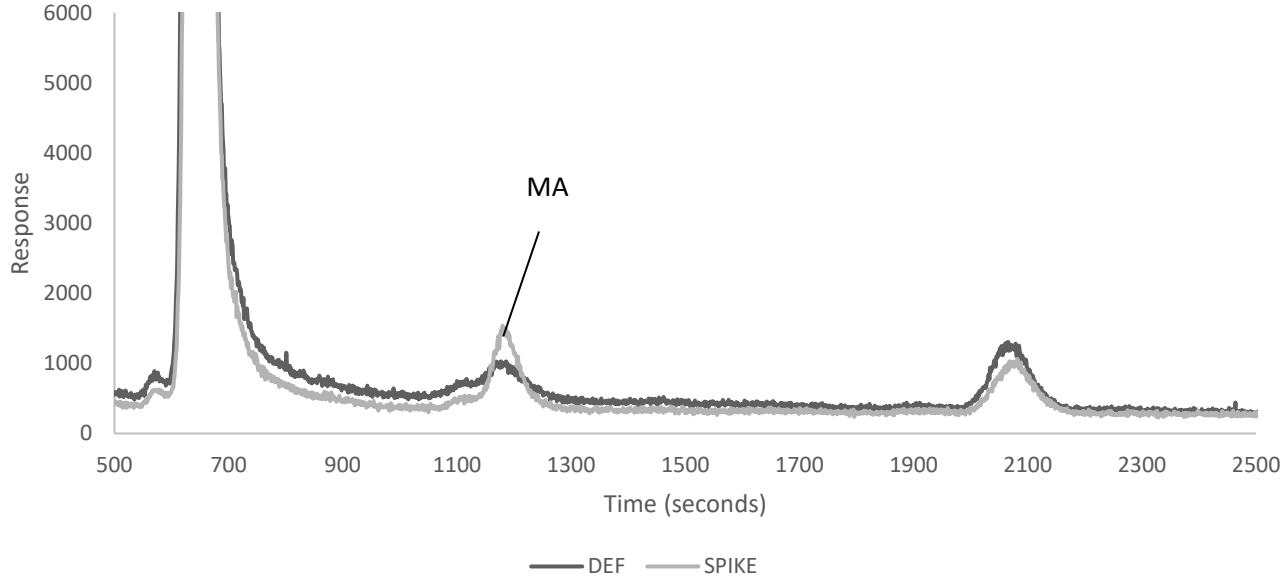
Instrument operating parameters	
ICP-MS settings	Agilent 7900 ICP-MS
RF power	1550 W
RF matching	1.25 V
Plasma gas flow	15.0 $Lmin^{-1}$
Carrier gas flow	1.07 $Lmin^{-1}$
Make-up gas flow	0.8 $Lmin^{-1}$
He gas flow	5.0 $Lmin^{-1}$
Spray chamber temperature	2 °C
Isotopes monitored	As^{75}, In^{115} (internal standard)
HPLC-ICP-MS settings	Agilent 1290 Infinity II HPLC and Agilent 7900 ICP-MS
Isotopes monitored	As^{75}, Se^{77}, Se^{82} Ge^{73} (internal standard
Anion exchange column	PRP-X100 (250 x 4.6 mm, 10 µm)
Guard column	PRP-X100 Guard cartridge
Mobile phase	20 mM $(NH_4)_2CO_3$, 3% MeOH
Flow rate	1 $mLmin^{-1}$
Injection volume	40 µL

Table 2 – The total As concentrations in thallus sections for both February and May. All concentrations are expressed per kg of dry sample weight. Errors are 1 SD (n=3).

Thallus Section	**February (mg kg^{-1})**	**May (mg kg^{-1})**
Holdfast/stipe	73±2.9	39±1.3
Meristem	125±7.5	55±1.3
Young frond	112±1.0	62±1.3
Old frond	151±24	63±3.7
Decaying frond	130±13	74±4.7

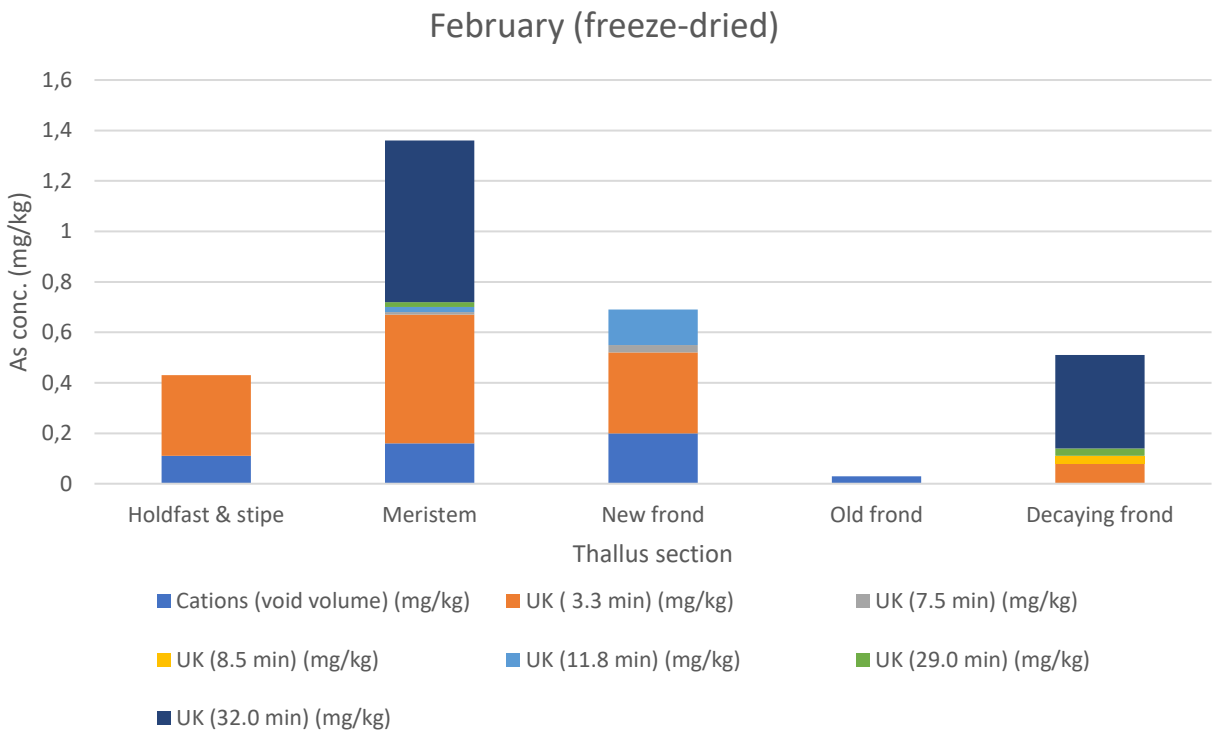


A)

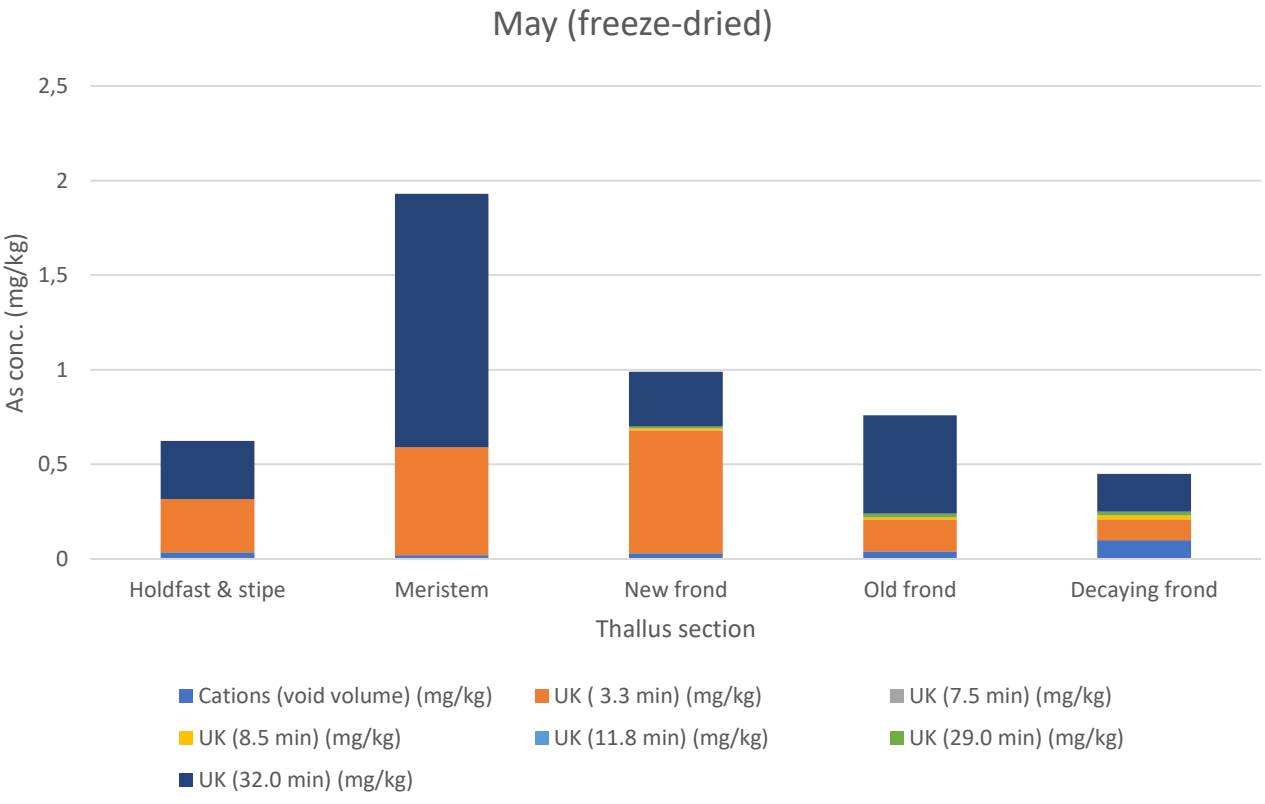


B)

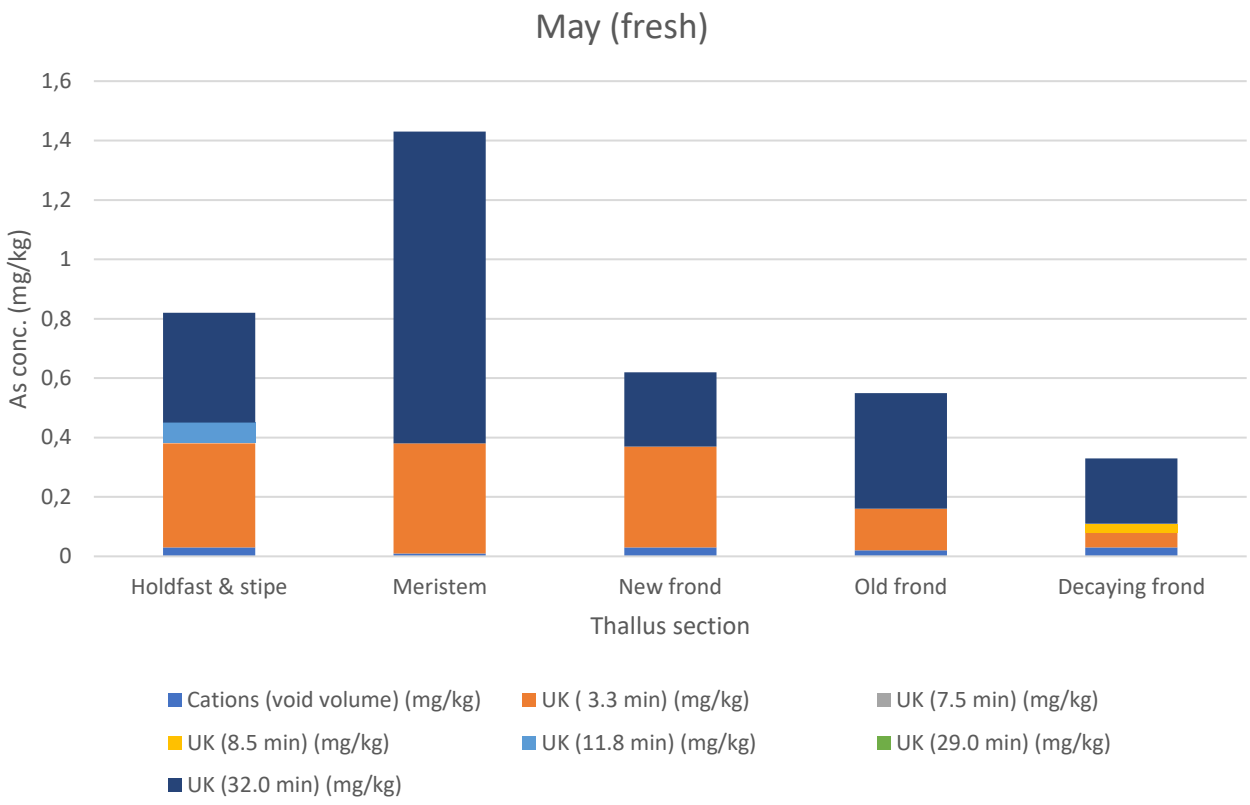
Fig 1 – A) Decaying frond sample, normal and spiked with 50 µg L^{-1} DMA solution, B) Decaying frond sample, normal and spiked with 20 µg L^{-1} MA solution.


February (freeze-dried)
As conc. (mg/kg)
1,6
1,4
1,2
1
0,8
0,6
0,4
0,2
0
Holdfast & stipe
Meristem
New frond
Old frond
Decaying frond
Thallus section
Cations (void volume) (mg/kg)
UK (3.3 min) (mg/kg)
UK (7.5 min) (mg/kg)
UK (8.5 min) (mg/kg)
UK (11.8 min) (mg/kg)
UK (29.0 min) (mg/kg)
UK (32.0 min) (mg/kg)

A)


May (freeze-dried)
As conc. (mg/kg)
2,5
2
1,5
1
0,5
0
Holdfast & stipe
Meristem
New frond
Old frond
Decaying frond
Thallus section
Cations (void volume) (mg/kg)
UK (3.3 min) (mg/kg)
UK (7.5 min) (mg/kg)
UK (8.5 min) (mg/kg)
UK (11.8 min) (mg/kg)
UK (29.0 min) (mg/kg)
UK (32.0 min) (mg/kg)

B)



C)

Fig 2 – Barcharts displaying the concentrations of the unknown compounds in each thallus section during both months. Compounds are labelled by their retention time, A) February (freeze-dried), B) May (freeze-dried), C) May (fresh).

Table 3 - The average concentration of AsSugars and other water-soluble As species in each thallus section during both months.

Month (drying method)	Thallus section	AsSug-gly/As(III) (mg kg^{-1})	DMA (mg kg^{-1})	AsSug-PO_4 (mg kg^{-1})	AsSug-SO_3 (mg kg^{-1})	MA (mg kg^{-1})	As(V) (mg kg^{-1})	Unknown (sum) (mg kg^{-1})
February (freeze-dried)	Holdfast/stipe	3.19	0.19	4.21	25.38	0.05	1.82	0.47
	Meristem	3.12	0.22	9.89	41.92	0.09	2.19	1.50
	New frond	2.78	0.28	12.89	35.27	0.05	24.56	1.02
	Old frond	1.97	0.32	9.55	22.67	0.03	59.28	0.85
	Decaying frond	14.75	0.19	13.40	13.63	0.05	60.97	0.71
May (freeze-dried)	Holdfast/stipe	11.45	0.05	5.55	20.78	0.06	0.78	0.65
	Meristem	15.88	0.07	5.72	33.26	0.07	2.46	1.90
	New frond	15.71	0.06	4.47	23.03	0.06	7.82	0.77
	Old frond	17.14	0.12	4.57	11.31	0.07	35.54	0.75
	Decaying frond	2.25	0.26	7.55	16.46	0.04	44.42	0.43
May (fresh)	Holdfast/stipe	6.41	0.03	3.79	14.13	0.03	0.63	0.86
	Meristem	11.69	0.03	6.40	24.18	0.03	1.65	1.43
	New frond	7.54	0.06	1.75	12.72	<LOQ	5.69	0.62
	Old frond	9.09	0.08	2.30	6.54	0.02	19.14	0.59
	Decaying frond	5.56	0.09	3.74	6.00	0.13	27.71	0.37

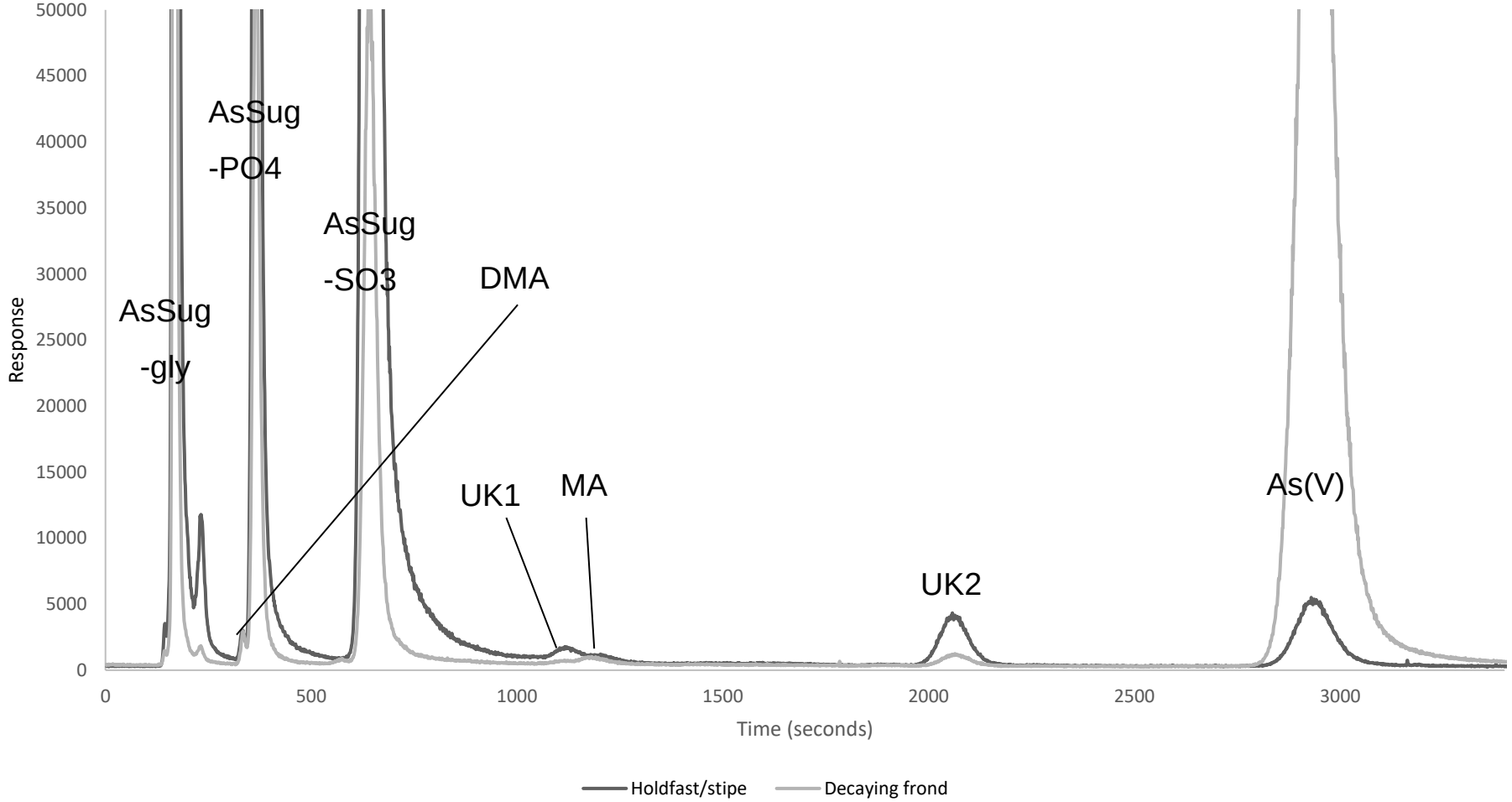


Fig 3 – Chromatographs of the holdfast/stipe and decaying thallus sections from extractions with fresh sample material.

Table 4 – The As(III) concentrations present all samples, analysed using a different HPLC-ICP-MS method.

Thallus section (n =2)	As (III) conc. in February (mg kg^{-1})	As (III) conc. in May (mg kg^{-1})
Holdfast/stipe	0.12	0.10
Meristem	0.12	0.13
Young frond	0.15	0.13
Old frond	0.06	0.05
Decaying frond	0.07	0.03

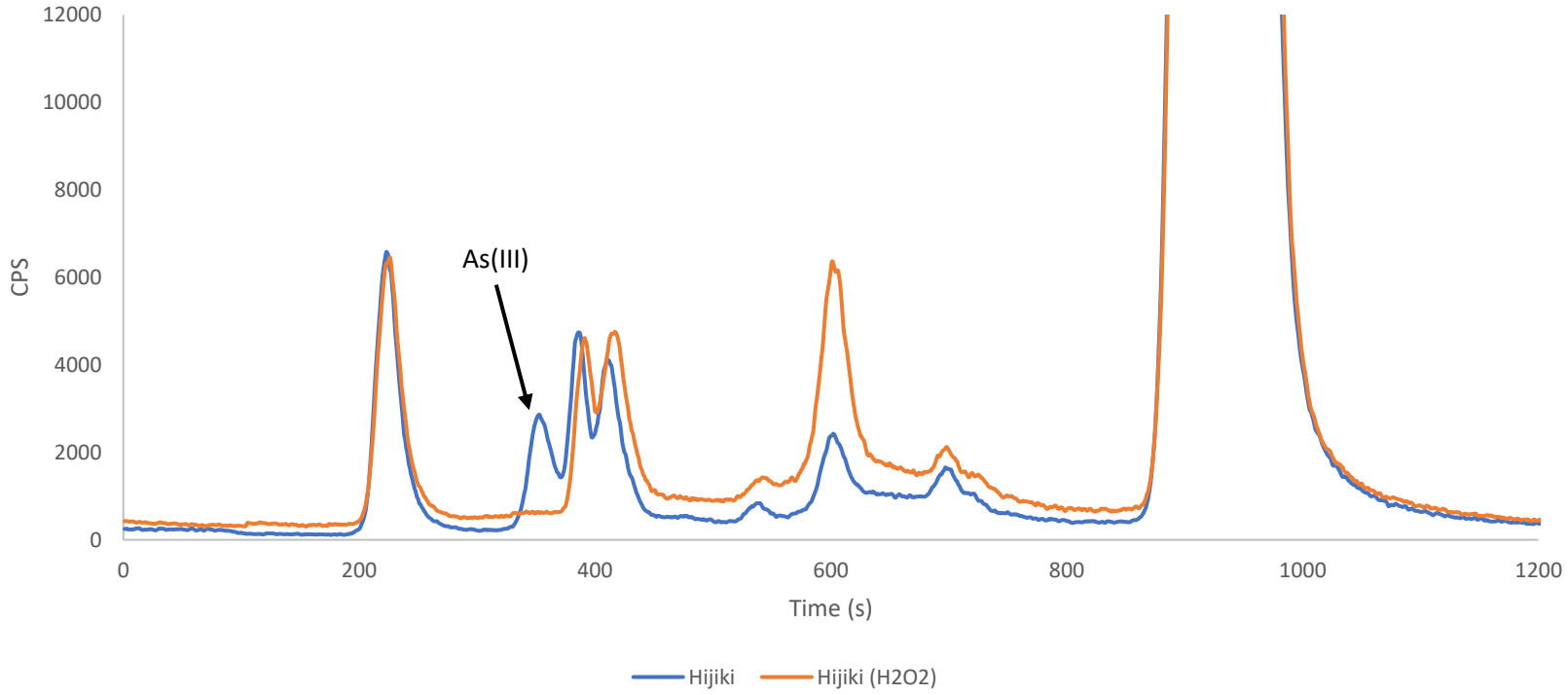


Fig 4 – Identification of As(III) by spiking with hydrogen peroxide. The As(III) concentration in hijiki (CRM 7405-b) was found to be 0.2 ± 0.001 (n =3).