## Supplementary material

## Metal complexation by organic ligands (L) in near-pristine estuarine waters: evidence for the identity of L

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## Table S1. Comparison of sample handling and treatment methods for spiked artificial seawater and seawater samples collected from the Lough Furnace estuary, for total dissolved labile metal concentration (mean $\pm$ s.d., n = 5)

Methods tested include: (A) filtration and immediate analysis (conventional); (B) filtration, freezing, thawing, then analysis (conventional) and (C) freezing, thawing, filtration, then analysis (unconventional and employed in this study). Asterisks denote significant difference in labile metal concentration between methods, within a water type

Element	Artificial seawater [M] <sub>L</sub> (nM)			Lough Furnace seawater [M] <sub>L</sub> (nM)		
	А	В	С	А	В	С
Cd	$1.11 \pm 0.19$	$1.03\pm0.05$	$1.07\pm0.05$	$0.69\pm0.19$	$0.66\pm0.04$	$0.66 \pm 0.03$
Zn	$4.57\pm0.20$	$4.40\pm0.62$	$5.20\pm0.16$	$2.42\pm0.28$	$2.16\pm0.25$	$3.34 \pm 0.09^{*}$

## Table S2. Accuracy of the analytical procedures employed for seaweed metal concentration and seawater total dissolved metal concentration (mean $\pm$ s.d., n = 3)

The algal CRM (NIES number 9) certified by the National Institute for Environmental Studies, Japan Environment Agency and the near-shore seawater CRM (CASS-5) certified by the National Research Council of Canada

	NI	ES number	9		CASS-5	
Element	Measured	RSD	Certified	Measured (nM)	RSD	Certified
	$(\mu g g^{-1} DW)$	(%)	(µg g <sup>-1</sup> DW)		(%)	(nM)
Cd	$0.17\pm0.026$	15.3	$0.15\pm0.002$	$0.20\pm0.02$	10.5	$0.19\pm0.02$
Cu	$5.00\pm0.58$	11.59	$4.9 \pm 0.2$	$6.16 \pm 0.21$	3.41	$5.97 \pm 0.44$
Pb	$1.31 \pm 0.15$	11.5	$1.35 \pm 0.05$	$0.052 \pm 0.001^{\mathrm{A}}$	1.92	$0.053\pm0.01$
Zn	$16.13\pm0.21$	1.31	$15.6 \pm 1.2$	$12.01\pm0.25$	2.1	$10.92 \pm 1.03$

<sup>A</sup>Deposition time was increased from 1 to 5 min