

Supplementary material

**Metal speciation from stream to open ocean: modelling v. measurement**

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**Table S1. Summary of pH and DOC data and numbers of values**

Numbers of values used in the analysis are given, and total data before rejection of unrealistic results are in parentheses. Italicised DOC values were estimated. Data sources are given in Table S2

	<i>n</i>	Fresh water pH	DOC (mg L <sup>-1</sup> )	<i>n</i>	Estuarine and coastal pH	DOC (mg L <sup>-1</sup> )	<i>n</i>	Open ocean pH	DOC (mg L <sup>-1</sup> )
Metal									
Al	402 (402)	5.08 3.71–6.42	5.70 1.00–32.00	–	–	–	–	–	–
Fe	–	–	–	34 (34)	7.09 6.90–8.00	2.4	329 (330)	8.03 8.00–8.10	0.64 0.50–0.91
Co	5 (6)	7.95 (no range)	2.30 1.00–3.40	–	–	–	41 (41)	9.10 (no range)	0.68 0.50–0.80
Ni	48 (54)	7.36 4.09–8.66	4.94 0.57–23.60	57 (57)	8.31 8.30–8.40	4.86 0.93–10.63	7 (8)	8.00 (no range)	0.84 (no range)
Cu	129 (135)	7.49 40.90–8.66	4.12 0.30–15.00	533 (533)	8.01 7.30–8.50	2.05 0.14–16.03	53 (53)	7.89 7.30–8.35	0.70 0.48–0.89
Zn	57 (84)	7.32 4.09–8.47	5.24 0.57–13.90	18 (18)	8.01 7.80–8.40	4.43 3.00–10.63	45 (45)	8.03 7.70–8.20	0.66 0.48–0.86
Cd	78 (86)	7.42 4.09–8.8	5.99 0.57–15.00	17 (24)	8.10 7.80–8.20	1.52 1.20–3.00	42 (45)	7.94 7.80–8.20	0.63 0.48–0.86
Hg	–	–	–	11 (11)	8.20 (no range)	2.17 0.66–3.34	–	–	–
Pb	68 (75)	7.14 4.09–8.66	3.38 0.30–15.00	24 (25)	8.08 7.80–8.20	1.8 1.20–3.60	22 (22)	7.89 7.80–8.00	0.69 0.54–0.88
Method									
CED	402 (402)	5.08 3.71–6.42	5.70 1.00–32.00	–	–	–	–	–	–
CL-ASV	32 (32)	8.10 7.30–8.80	5.70 3.20–15.00	38 (38)	8.16 7.90–8.40	1.62 1.20–3.20	–	–	–
CL-CSV	107 (112)	7.47 5.30–8.43	2.75 0.30–10.38	168 (168)	7.85 6.90–8.40	4.31 0.66–16.03	398 (400)	8.14 7.30–9.10	0.65 0.48–0.91
DMT	191 (222)	7.33 4.09–8.66	4.47 0.57–15.0	–	–	–	–	–	–
DPASV	3 (4)	7.45 7.30–7.60	8.59 6.70–10.38	323 (323)	8.06 7.30–8.50	1.43 0.14–3.20	141 (144)	7.94 7.50–8.20	0.67 0.48–0.89
IET	46 (63)	6.99 5.22–8.00	7.07 2.14–13.90	–	–	–	–	–	–
ISE	–	–	–	152 (152)	8.00 7.60–8.20	2.24 0.88–9.19	–	–	–
PLM	6 (7)	8.36 8.09–8.66	7.30 1.90–15.00	13 (21)	8.03 7.90–8.10	3.28 2.80–3.60	–	–	–

**Table S2. Data sources**

Surface water type	Metals	Method	Reference
Fresh waters	Ni, Cu, Zn, Cd, Pb	DMT	[1]
Fresh waters	Cd	CL-ASV	[2]
Fresh waters	Cu, Zn, Cd	IET	[3]
Fresh waters	Ni	IET	[4]
Fresh waters	Cu, Zn, Cd	CL-CSV (Cu, Cd); DPASV (Zn)	[5]
Fresh waters	Ni, Cu, Zn, Cd, Pb	DMT	[6]
Fresh waters	Cu, Zn	CL-CSV (Cu); CL-ASV (Zn)	[7]
Fresh waters	Al	CE	[8]
Fresh waters	Cu, Pb	CL-CSV	[9]
Fresh waters	Co	CL-CSV	[10]
Fresh waters	Ni, Cu, Cd, Pb	DMT (Ni, Cu, Cd, Pb); PLM (Cu, Cd, Pb)	[11]
Fresh waters	Ni	DMT	[12]
Fresh waters	Cu	CL-CSV	[13]
Fresh waters	Zn	CL-ASV	[14]
Fresh waters	Cu	CL-CSV	[15]
Estuarine & coastal	Fe <sup>III</sup>	CL-CSV	[16]
Estuarine & coastal	Ni	CL-CSV	[17–18]
Estuarine & coastal	Cu, Zn, Cd, Pb	DPASV	[19]
Estuarine & coastal	Cu, Cd, Pb	PLM	[20]
Estuarine & coastal	Cu	DPASV	[21–22]
Estuarine & coastal	Cu	ISE	[23–24]
Estuarine & coastal	Cu	CL-CSV	[25–27]
Estuarine & coastal	Cu, Zn	CL-ASV	[28]
Estuarine & coastal	Cu, Cd, Pb	CL-ASV	[29]
Estuarine & coastal	Cu	ISE	[30]
Estuarine & coastal	Hg	CL-CSV	[31]
Estuarine & coastal	Zn	CL-CSV	[32]
Open ocean	Fe <sup>III</sup>	CL-CSV	[33–39]
Open ocean	Cu	CL-CSV	[40–41]
Open ocean	Cu	DPASV	[42]
Open ocean	Zn	CL-CSV	[43]
Open ocean	Zn	DPASV	[44]
Open ocean	Zn, Cd	DPASV	[45]
Open ocean	Cd	DPASV	[46]
Open ocean	Cd, Pb	DPASV	[47]
Open ocean	Pb	DPASV	[48]
Open ocean	Co	CL-CSV	[49–50]
Open ocean	Ni	CL-CSV	[51]

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