Sampling:

During this expedition a so called 'Ultra Clean CTD' was used. This 'Ultra Clean CTD' is a CTD equipped with 24 polypropylene water samplers each with a volume of 24 liters. The samplers are closed using a butterfly-type closing mechanism powered using seawater hydraulics (Rijkenberg et al. Marine Chemistry 177 (2015) 501–509).

After deployment, the complete frame was pushed into an ISO Class 6 clean room container. Here samples for dissolved metals were filtered directly from the polypropylene samplers over < 0.2 µm Sartobran 300 cartridges (Sartorius) under mild pressure (0.7 bar) of filtered N2 applied via the top-connector of the polypropylene sampler. The filters were rinsed with approximately 700ml seawater before use. Samples for dissolved metals were acidified to a pH of 1.8 using a final concentration of 0.024M ultraclean Seastar Base-line HCl (Seastar Chemicals).

Analysis

Trace metals Cd, Co, Cu, Fe, Mn, Ni, Zn and Pb were analysed with a Thermo Finnigan HR-ICPMS element 2. A volume of 30 mL sample was pipetted into an acid cleaned FEP vial. An internal standard (lutetium and indium) was added at a final concentration of 5 nM prior to UV digestion (Middag et al., 2015). The samples were digested for 4h in a home-made UV box after which they were pre-concentrated with a factor of 40 using a seaFAST inline pre-concentration system, using Nobias PA1 resin as pre-concentration column (Lagerstrom et al., 2013; Bown et al., 2017). Samples were eluted in 1.5M teflon distilled HNO_3 that contained rhodium as a standard to easily identify any sample introduction issues in a run whereas the indium and lutetium were used as the internal standards in the quantification (Middag et al., 2015).

The system was calibrated via 7 standard additions using a home-made stock solution. The maximum standard additions were comparable to maximum concentrations in the marine environment. The recovery was verified in every analytical run by comparing the slope of the seawater calibration curve (multi-element standard added to seawater) and the eluent calibration curve (multi-element standard added directly to the elution acid) after Biller and Bruland (2012). Blank contributions from the sample handling, pre-concentration and analyses steps were determined by handling analysing acidified MQ water (~1.8 pH) as a sample. The accuracy and precision of the measurements were determined by measuring GEOTRACES community consensus reference materials SAFE D1 and S, as well as in-house reference seawater North Atlantic Surface water (Bay of Biscay) samples (Table 1).

References:

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Blank contributions from the sample handling, pre-concentration and analyses steps were determined by analyzing acidified MQ water (~1.8 pH) as a sample (Table 2). Detection limit was estimated as 3 times the standard deviation of the blank with exception of Cd. Cd detection limit was estimated from the value when Mo interference correction subtracts more than half of the cps. It is the lowest measured sample, in this case Surface Seawater (SSW).

The meaning of the quality flag follows the rules established for the WOCE Hydrographic Program. see: the WOCE Operations Manual, WOCE Report No. 67/91

Table 1: Concentrations with standard deviations and number of analyses of standard reference samples (GSP and SAFeD1) and in house reference water (NADW, North Atlantic Deep Water).

	GSP Determined							
#227	**Cd**	**Co**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**
	nM	**pM**	**nM**	**nM**	**nM**	**nM**	**pM**	**nM**
Mean	0.0015	8	0.568	0.25	0.761	2.542	62	0.067
±SD	0.0001	0.4	0.004	0.06	0.001	0.024	1	0.005
n	3	3	3	3	3	3	3	3
	Consensus							
	Cd		**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**
	nM		**nM**	**nM**	**nM**	**nM**	**pM**	**nM**
Mean	0.002	-	0.574	0.155	0.778	2.595	62	0.030
±SD	0.002	-	0.053	0.045	0.034	0.100	5	0.052
n	4	-	9	11	9	11	11	10
	NADW - In-house reference material							
	Cd	**Co**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**
	nM	**pM**	**nM**	**nM**	**nM**	**nM**	**pM**	**nM**
Mean	0.18	53	1.323	0.534	0.426	3.58	44	3.236
±SD	0.005	2	0.039	0.023	0.010	0.1	3	0.078
n	18	18	18	18	18	18	16	13
	SAFe D1							
	Determined							
#599	**Cd**	**Co**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**
	nM	**pM**	**nM**	**nM**	**nM**	**nM**	**pM**	**nM**
Mean	1.013	43	2.044	0.824	0.409	8.758	25	7.537
±SD	0.007	1	0.02	0.04	0.002	0.086	1	0.098
n	6	6	6	6	6	6	6	6
	Consensus							
	Cd	**Co**	**Cu**	**Fe**		**Ni**	**Pb**	**Zn**
	nM	**pM**	**nM**	**nM**		**nM**	**pM**	**nM**
Mean	1.016	46.5	2.33	0.69	-	8.79	28.4	7.59
±SD	32	4.8	0.11	0.04	-	0.27	2.7	0.36

*Ti was analysed separately, for Ti GSP #194 was used and SAFe D1 #190
SAFe consensus values were converted to molar units using a density of 1.025 kg/L

Table 2: Blank and Limit of detection concentrations in pM

Element	**Unit**	Blank	±SD	n	LOD (3xSD)
Cd	pM	0.41	2	20	8
Co	pM	1.5	1	20	3
Cu	pM	8.4	11	24	32
Fe	pM	21.7	8	21	24
Mn	pM	1.6	2.2	24	7
Ni	pM	7.6	4.1	24	13
Pb	pM	1.3	1	16	3
Zn	pM	25	18	13	55