Dissolved Cadmium – values in pmol/kg
Consensus values (± 1 std. dev.) for North Atlantic GEOTRACES Reference Samples as of May 2013

GEOTRACES GS = 2.1 ± 0.6 pmol/kg

GEOTRACES GD = 271 ± 6 pmol/kg

These are considered to be the consensus values for the GEOTRACES Atlantic Reference Samples as of May 2013. The surface water value is below the detection limit of some of the labs.

Labs participating in the analysis of the North Atlantic GEOTRACES reference samples to determine a consensus value for dissolved Cd:

Yoshiki Sohrin (U Kyoto, Japan):
Off line concentration using the Nobias PA-1 EDTriA-type chelating resin with subsequent analyses by ICP-MS using the method of Sohrin et al. (2008).

Michael Ellwood (Australian National U, Australia):
Cadmium was concentrated by solvent extraction (Bruland et al., 1979) and analyzed by ICPMS. 100 g seawater samples were buffered to a pH of 4.5 with purified ammonium acetate buffer. Purified ammonium pyrrolidinedithiocarbamate (PDC) and sodium diethyldithiocarbamate (DDC) were added to the samples which were then extracted twice by shaking following the addition of purified chloroform. The two chloroform extracts obtained were combined, acidified with nitric acid, shaken for 1 min and then diluted with purified water. Trace metal concentrations were determined by ICP-MS (820-MS Varian, Australia) with hydrogen introduced into the collision reaction interface to reduce the interference of $^{40}Ar^{16}O$ on ^{56}Fe.

Ana Aguilar-Islas/Jingfeng Wu (UAF, U.S.):
$Mg(OH)_2$ coprecipitation and analysis by isotope dilution ICP-MS (Wu and Boyle, 1997). Cd was analyzed using the ratio between the natural abundance of ^{114}Cd and an added ^{110}Cd spike. Interferences from MoO, ^{110}Pd and ^{114}Sn (using ^{95}Mo, ^{106}Pd, ^{118}Sn) were monitored and used to correct Cd counts.
Deep samples: 1.6 ml of acidified sample and spike were allowed to equilibrate for several minutes. A single co-precipitation step was carried out followed by dilution of the precipitate with 4% HNO_3. Blanks were done using 50 µl of low Cd seawater instead of 1.6ml.
Surface samples: Multi-step method consists of a single co-precipitation using 50ml of sample and spike. The precipitate was dissolved in 2 ml 4% nitric, and the pH was adjusted with ammonium acetate to pH 5.5. This solution was loaded off-line onto a rinsed (pH 5.5) Chelex 100 micro-column and eluted with 0.5% nitric. This is an important step because it removes Mo (Cd is eluted readily off the column, but Mo is not). The collected eluent (~ 1 ml) was evaporated to dryness in a Teflon conical vial and the dried salts diluted with 4% nitric. Blanks were done by loading the column with all reagents (pH 5.5) and carrying out all other steps.

Ed Boyle (MIT, U.S.):
400-bead NTA-type resin with isotope dilution ICP-MS (Lee et al., 2011). The 1.3 ml samples in 1.5 cc microcentrifuge tubes were spiked with ^{110}Cd-, the solution pH was raised to 6 using ammonium acetate. The beads were added, and left to equilibrate overnight on a shaker table. The samples were centrifuged and supernatant siphoned off. The beads were washed/centrifuged/siphoned three times with high purity distilled water to eliminate salt. 150 μl of 0.1N HNO_3 was added and allowed at least one day to release the Cd into the acid. The Cd 114/110 ratio was then determined by quadrupole ICP-MS using a low-flow micromist nebulizer. Mo was monitored to check for possible MoO^+ interference but it was never significant.

Peter Croot/Peter Streu (IMF/GEOMAR, Germany);
Samples were analyzed according to the method described in Kremling and Streu (2001). For the analysis of Cd, Co, Cu, Fe, Ni, Pb and Zn, 300–500 g portions of the samples were subjected to a dithiocarbamate–freon extraction modified from the procedure by Danielsson et al. (1978) implying maximum concentration factors of 500. The final extracts with the metals were measured by electrothermal atomic absorption spectrometry with Zeeman background correction (ETAAS; Perkin-Elmer Model 4100 ZL).

Christa Pohl (Warnemunde, Germany):
Samples were analyzed according to the method described in Kremling and Streu (2001). The final extracts with the metals were measured by electrothermal atomic absorption spectrometry.

Dondra Biller/Ken Bruland (UCSC, U.S.):
Off-line concentration using the Nobias PA-1 EDTriA-type chelating resin with subsequent analyses by ICP-MS (Biller and Bruland, 2012) based upon the method of Sohrin et al. (2008). The method entails an eight column manifold enabling eight separate ~ 40 mL samples to be processed simultaneously.

Bill Landing/Angie Milne (FSU, U.S.):
Off-line extraction using IDA Toyopearl AF-Chelate-650 M resin followed by analysis using isotope dilution ICP-MS (Milne et al., 2010). Prior to extraction the samples (12 mL) were UV oxidized and buffered to pH ~6.2. Mo interference on Cd is corrected by monitoring Mo during ICPMS analyses.

Geoff Smith/Ken Bruland (UCSC, U.S.):
In-line flow injection analysis Nobias PA-1 EDTriA-type chelating resin at pH 6 utilizing purified ammonium acetate buffer and eluting analytes with 1.5 M HNO_3 followed by detection with ICP-MS. The Mo interference and correction were greatly reduced with the use of a water cooled Scott glass spray chamber. Mo95 was monitored and used to further correct for remaining MoO interference on ^{111}Cd and ^{113}Cd counts. Results for ^{111}Cd and ^{113}Cd were averaged together.

Mark Rehkamper (Imperial College, London, UK)
Isotope dilution mass spectrometry. Concentrations determined as part of measuring cadmium isotope ratios.

Wafa Abouchami (Max Planck Institute, Mainz, Germany)
Isotope dilution mass spectrometry with a variety of concentration steps. Concentrations determined as part of measuring cadmium isotope ratios (Milne et al. (2010).

Eric Achterberg (Plymouth, UK)
Off-line extraction using IDA Toyopearl AF-Chelate resin followed by analysis using isotope

dilution ICP-MS (Milne et al. 2010). Prior to extraction the samples (12 mL) were buffered to pH ~6.2. Samples were not UV oxidized.

Celine Gallon, Cheryl Zurbrick, Russ Flegal (UCSC, U.S.)

In-line IDA chelating resin concentration with ICP-MS (Ndung'u et al. 2003).

Christian Schlosser and Eric Achterberg (Plymouth, UK)

Off-line extraction using a WAKO chelating resin (Kagaya, 2009) followed by analysis on an Element XR ICP-MS. Samples were UV digested for 3 hours.

Jingfeng Wu (U. Miami, U.S.)

$Mg(OH)_2$ coprecipitation and analysis by isotope dilution ICP-MS (Wu and Boyle, 1997).

Rob Middag and Ken Bruland (UCSC, US)

Off-line extraction with Nobias PA-1 chelating resin and analysis on an Element XR ICP-MS Middag et al., submitted).

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