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

GEOTRACES GS = 0.041 ± 0.007 nmol/kg

GEOTRACES GD = 1.71 ± 0.12 nmol/kg

The above concentrations are consensus values for the GEOTRACES Reference Samples as of May 2013. The surface water concentration was below the detection limit for some labs.

Labs participating in the analysis of the North Atlantic GEOTRACES reference samples to determine consensus values for dissolved Zn:

Ana Aguilar-Islas/Jingfeng Wu (UAF, U.S.):
Concentrated off-line with the $Mg(OH)_2$ coprecipitation method (Wu and Boyle, 1997) and analyzed by ICPMS. Zinc was analyzed using the ratio between the natural abundance of ^{64}Zn and an added ^{68}Zn spike. Interferences from ^{64}Ni were monitored (using ^{60}Ni) and used to correct ^{64}Zn counts.
Deep samples: 1.6ml of 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 quantified by co-precipitating increasing volumes of deep seawater (300, 600, 900, and 1200 ul), and creating a regression line to calculate the 0 ml sample blank.
Surface samples: Double co-precipitation method (Wu, 2007).
Yoshiki Sohrin (U. Kyoto, Japan):
Off line concentration using an EDTriA-type chelating resin with subsequent analyses by ICP-MS using the method of Sohrin et al. (2008).
Michael Ellwood (Australian National U, Australia):
Zinc 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.
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.
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 an EDTri-A-type chelating resin with subsequent analyses by ICP-MS 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. The samples were UV oxidized for 1.5 hrs, amended with H_2O_2 (final concentration of 10 μM), and adjusted to pH 6.5 with ammonium acetate prior to the concentration step. The resin columns were rinsed with a weak ammonium acetate buffer at a pH of 6.5 and eluted with 3 mL of 1 N nitric acid for a concentration factor of ~13, with subsequent analyses by ICP-MS.

Angie Milne/Bill Landing (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.

Geoff Smith/Ken Bruland (UCSC, U.S.):

On-line flow injection analysis of 4 ml of sea water using an EDTA-type chelating resin (Sohrin et al., 2008) at pH 6 utilizing purified ammonium acetate buffer and eluting analytes with 1.5M HNO_3 followed by detection with ICPMS.

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.

Rob Middag, 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).

Tim Conway and Seth John (U. South Carolina, US)

Off-line extraction by batch extraction using Nobias PA-1 chelating resin and analysis on a Neptune multi-collector ICP-MS for isotope ratios and concentrations using a double spike isotope dilution.

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

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

Taejin Kim and Hajime Obata (Atmosphere and Ocean Research Group, University of Tokyo, Japan)

Adsorptive cathodic stripping voltammetry after UV-oxidation with PDC as the added ligand.

Maria Lagerstrom and Rob Sherrell (Rutgers University, US)

On-line flow injection with a modified seaFAST system, the Nobias PA-1 resin, **isotope dilution** and ICP-MS detection.

References:

1. Milne, A., W. Landing, M. Bizimis and P. Morton. Determination of Mn, Fe, Co, Ni, Cu, Zn, Cd and Pb in seawater using high resolution magnetic sector inductively coupled mass spectrometry (HR-ICP-MS). *Analytica Chimica Acta*, **665**: 200-207 (2010).
2. Bruland, K.W., R.P. Franks, G. Knauer and J. Martin. Sampling and analytical methods for the determination of copper, cadmium, zinc, and nickel in seawater. *Analytica Chimica Acta*, Vol. **105**: 233-245 (1979).

3. Danielsson, L.G., B. Magnusson, and S. Westerlund. An improved metal extraction procedure for the determination of trace metals in seawater by atomic absorption spectrometry with electrothermal atomization. *Analytica Chimica Acta,* **98**: 47-57 (1978).
4. Kremling, K. and P. Streu. Behaviour of dissolved Cd, Co, Zn, and Pb in North Atlantic near-surface waters (30°N/60°W to 60°N/2°W). *Deep Sea Research I*, **48**(12): 2541-2567 (2001).
5. Sohrin, Y., S. Urushihara, S. Nakatsuka, T. Kono, E. Higo, T. Minami, K. Norisuye, and S. Umetani. Multielemental determination of GEOTRACES key trace metals in seawater by ICP-MS after preconcentration using an ethylenediaminetriacetic acid chelating resin. *Analytical Chemistry*, **80**: 6267-6273 (2008).
6. Wu, J., and E.A. Boyle. Low blank preconcentration technique for the determination of lead, copper and cadmium in small-volume seawater samples by isotope dilution ICP-MS. *Anal. Chem.,* **69**:2464-2470 (1997).
7. Wu, J. Determination of picomolar iron in seawater by double Mg(OH)2 precipitation isotope dilution high-resolution ICPMS. *Marine Chemistry*, 1**03**: 370–381 (2007).
8. 8. Biller, D.V. and K.W. Bruland. Analysis of eight trace metals in seawater using the Nobias-chelate PA-1 resin and magnetic sector inductively coupled plasma mass spectrometry. *Marine Chemistry,* **130/131**: 12-20 (2012).
9. Kagaya et al. A soid phased extraction using a chelate resin immobilizing …, *Talanta*, **79**: 146-152 (2009).
10. Middag, R., K.W. Bruland and H.J.W. de Baar. GEOTRACES intercomparison of dissolved trace metals at the Bermuda Atlantic Time Series station. Submitted to Limnology and Oceanography: Methods.