

Dissolved Cadmium – all values in pM – labs are anonymous

	<u>SAFe S</u>	<u>SAFe D2</u>	<u>Blank</u>	<u>Detect. Lim.</u>
Lab A	1.02 ± 0.15		0.023 ± 0.003	0.01
		984 ± 12	6.0 ± 0.8	2.4
Lab B	< 10	1065 ± 10	< 10	~ 10
Lab C	≤ 1	952 ± 31	3.6 ± 0.5	~ 1.5
Lab D	6 ± 3	986 ± 47	20 ± 3	10
Lab E	4 ± 1	966 ± 24	1.3 ± 1.2	3
Lab F	1.0 ± 0.1	1017 ± 28	1.1 ± 0.1	0.4
Lab G	7 ± 2	988 ± 40		
Lab H	1 ± 2	977 ± 25	0 ± 2	6

Lab I	6	920	6 ± 2	5

SAFe S = 1 pM

SAFe D2 = 992 ± 35 pM

SAFe D1 = 1027 ± 55 pM

These are considered to be the consensus values for the SAFe reference samples at this time. The average value for SAFe D2 (and ± 1 standard deviation) was determined using the data from Labs A to H. For the surface sample, Lab A and F were the only labs that appeared to have adequate sensitivity and a low enough detection limit to determine a concentration at the 1 pM level. We need more labs with a better detection limit to further evaluate the surface water concentration. It is currently suggested to be 1 pM, although others could argue the concentration is closer to ~ 6 pM. Less data (not shown) is available for the SAFe D1 sample. Labs using ICP-MS for the determination of cadmium in surface samples need to examine the potential of significant MoO⁺ interference.

Labs have not noticed a significant difference between UV treatment and non-UV treated samples for dissolved Cd.

References:

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3. Hurst, M.P. and K.W. Bruland. The effects of the San Francisco Bay plume on trace metal and nutrient distributions in the Gulf of the Farallones. *Geochimica et Cosmochimica Acta*, **72**: 395-411 (2008).
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).
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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. *Analytical Chemistry*, **69**:2464-2470 (1997).

Labs participating in the analysis of the SAFe reference samples to determine a consensus value for dissolved Cd (listed in random order):

Yoshiki Sohrin (U Kyoto, Japan):

Off line concentration using an EDTA-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 $^{40}\text{Ar}^{16}\text{O}$ 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% HNO₃. 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 a very 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. 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).

Dondra Biller/Ken Bruland (UCSC, U.S.):

Off-line concentration using an EDTA-type chelating resin with subsequent analyses by ICP-MS based upon the method of Sohrin et al. (2008). The method entails a six column manifold enabling six separate ~ 75 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 ~ 25 , with subsequent analyses by ICP-MS. The Mo interference and correction were greatly reduced with the use of a PC3-SSI Peltier, water-cooled, spray chamber (Elemental Scientific Inc.). Results for ^{111}Cd and ^{113}Cd were averaged together.

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. 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.):

On-line flow injection analysis of 6 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 1.5 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.

Matt Hurst (HSU, U.S.):

On-line flow injection using IDA Toyopearl AF-Chelate resin with analyses by ICP-MS (Hurst and Bruland, 2008).

The figure below presents unpublished data from the SAFe station in fall 2004 (Jingfeng Wu's data from samples collected with the UAF Vane sampler and Bill Landing's data with samples collected in the upper 1000 meters with the CLIVAR sampler) compared with historical data from a nearby station (Bruland, 1980). The consensus values for the SAFe reference samples are shown as evidence that the SAFe reference samples are representative of this station in the eastern North Pacific. Note that the concentrations are in nmol/kg units, rather than pM.

