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Method for the determination of the organic speciation of iron (ligand concentration and conditional stability constant of the ligand with iron).

The organic complexation of iron was determined by cathodic stripping voltammetry (CSV). The method used derives from the method described in Boyé et al., 2001; with an exception is that TAC (2-(2-thiazolylazo)-p-cresol, an electroactive added ligand) was used instead of NN (1-nitroso-2-naphthol), as being adapted from the method of Croot and Johansson, 2000.

The following reagent concentrations were used:

Titration were carried out at pH 8.1 using borate buffer (H<sub>3</sub>BO<sub>3</sub>, BDH) with 10 µM of TAC. The borate stock solution (1 M boric acid/0.3 M ammonia) was cleaned by equilibration with TAC (40 µM), followed by extraction using a Sep-Pak C18 cartridge (activated with methanol) and was used to a final concentration of 5 mM. A methanolic solution of 2-(2-thiazolylazo)-p-cresol (TAC) (C<sub>10</sub>H<sub>8</sub>OH.N<sub>3</sub>.S, Aldrich Product) was prepared containing 0.02 M TAC using 3-times quartz-distilled methanol and was used to a final concentration of 10 µM.

All samples were collected in 100-ml HDPE bottles which were filled with 0.01 nM acidified MQ. Bottles were rinsed 3 times with sample before filled.

#### Procedure

Samples were titrated with iron (using a stock solution of 10<sup>-6</sup> M Fe<sup>III</sup> prepared in 0.01 M quartz-distilled hydrochloric acid) which was added in 11 increments on the order of 0.25 nM to 1 nM Fe ranging between 0 and 8 nM. There to 250 ml sea water was placed in a teflon bottle; borate buffer (5 mM) and TAC (10 µM) were added, and the sample was mixed. The Fe<sup>III</sup> standard was added to 11 conditioned teflon vials, and subsequently a 20 ml aliquot of the sample/buffer/ligand mixture was pipetted into each vial. Any remaining sample was pipetted into a 12th Sterilin tube, and used for the first measurement to condition the voltammetric cell. The solutions were equilibrated at least 7 h (often overnight: 12-15 h), at room temperature in a laminar-flow hood.

The equilibrated solutions were sequentially (starting from the lowest concentration) transferred to the voltammetric teflon-cell. Each solution was purged (200 s) with O<sub>2</sub>-free nitrogen. A new mercury drop was made, and FeTAC<sub>2</sub> complex species were adsorbed using an adsorption time of 200 to 400 s, at an adsorption potential of - 0.4 V, whilst stirring using a rotating PTFE rod (2500 rpm). The stirrer was switched off for a 10 s quiescence period whereafter the potential was scanned from - 0.4 to - 0.9 V using the fast linear sweep waveform (10.1 V.s<sup>-1</sup>, step potential 1.98 mV) [Croot and Johansson, 2000]. The voltammetric cell was not rinsed during the titration to maintain the cell conditioned to the iron and TAC concentrations. The Teflon-vials were rinsed once with MQ-water between titrations, and the same order of tubes was maintained.

Calculation of the organic and inorganic speciation of iron

The ligand concentrations ([L]) and conditional stability constants (K) were calculated by linear least-squares regression of the data fitted to a linear equation (van den Berg and Kramer, 1979; Ruzic, 1982; van den Berg, 1982).

The inorganic side reaction coefficient for iron was taken as log (Fe' = 10 (Hudson et al., 1992), and for FeTAC<sub>2</sub> as log FeTAC<sub>2</sub> = 12.4 (using log (FeTAC<sub>2</sub> = 22.4 [Croot and Johansson, 2000] and [TAC] = 10 µM), giving a detection window (van den Berg and Donat, 1992) of 10E+11.4 to 10E+13.4. Dissolved and soluble Fe-concentrations measured by FIA-Chemiluminescence by Jun Nishioka (CRIEPI) were used to calculate the organic complexation of iron in the dissolved and soluble-fractions respectively. The free metal ion concentration [Fe<sup>3+</sup>], the inorganic metal concentration [Fe'], the concentration of organic metal complexes [FeL] were calculated at the thermodynamic equilibrium, as described in Boyé et al. (2001).