



Nutrients: Ken Bruland Lab Summary for CIMT Ship Surveys  
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The Bruland lab has participated in the ship surveys since November, 2002. Samples are collected during these surveys at ten stations (T100, T101, T102, T301, T401, T402, T501, T601, T701 and T702) for analysis of particulate and dissolved iron and manganese. The Bruland lab is investigating the temporal and spatial distribution of these trace metals in surface bay waters. Iron and manganese are essential phytoplankton micronutrients, and their concentration at the surface varies with seasons and location throughout the bay. During the upwelling season the supply of macronutrients (nitrate, phosphate, and silicic acid) to surface waters is sufficient to support high productivity in the bay, but without an adequate supply of micronutrients (such as iron), the potential high productivity brought about by the upwelling of macronutrients is not realized. The Bruland lab is interested in understanding processes responsible for the seasonally variable supply of micronutrients in order to assess if they are limiting productivity in different regions of the bay.

Trace metal clean equipment and techniques are employed during the collection, processing, and analysis of samples. The sampling assembly (Figure 1) consists of a vane and weight, tubing, a peristaltic pump, and a protecting plastic bell. The bell acts as a shield to protect the samples from sea spray, rain, and dust during collection. The intake of the tubing is attached to the vane which is positioned at least 10 feet away from the boat to prevent contamination from the hull during sampling. Collection of samples is done at approximately 5m depth while the boat is underway during zooplankton net tows. Two samples are collected at each station; an unfiltered 2L sample which is stored cold during the duration of the cruise, and a filtered (0.45  $\mu$ m) 500ml sample, which is acidified to pH 1.7 back in the lab and stored as an archived sample.

Once the unfiltered samples arrive in the lab, they are immediately filtered. The filtration apparatus (Figure 1) is connected to the lab's argon supply. Gas pressure (<10 psi) is used to pass the sample through the filters. Different size fractions are collected from each sample. A 10  $\mu$ m pore size filter is position in line above a 0.4  $\mu$ m pore size filter. The top filter collects particles 10  $\mu$ m in size and above, while the bottom filter collects particles between 0.4  $\mu$ m and 10  $\mu$ m. A duplicate particulate sample is collected on a 0.4  $\mu$ m filter (filtering out particles of 0.4  $\mu$ m and above). Anything smaller than 0.4  $\mu$ m is considered dissolved. The filtrate is collected in a 500ml bottle, acidified to pH ~1.7, and stored until further analysis, while the filters are stored frozen until further analysis.

Extraction of trace metals from the collected particles is done in a sequential manner (Figure 1). First, particles are leached using 25% acetic acid for two hours. This leached fraction is considered to be the labile fraction available to phytoplankton. The acetic acid containing the leachate is taken to dryness, and the residue is re-dissolved in 1M nitric acid. Leached filters are stored cold until further extraction. The final extraction step is total digestion of the remaining "refractory" particulates considered to be unavailable to phytoplankton. Total digestion is carried out with aqua regia under heat and pressure using a microwave oven and special high pressure Teflon containers.

The concentration of trace metals in the leachate solutions, the digested solutions, and the dissolved fraction are determined by inductively coupled plasma-sector field mass spectrometry (ICP-SFMS). The leachate and digested solutions are introduced directly into the plasma, but due to the extremely low concentration of metals in the dissolved fraction, filtrates are pre-concentrated in line (using a chelating resin) prior to analysis.

The trace metal data, together with macronutrient and hydrographic data, is then used to interpret the processes influencing the spatial and temporal distribution of trace metals in Monterey Bay, and to assess whether productivity is being limited in different regions of the bay by the availability of trace metals.

Figure 1. Sampling, processing and analysis of trace metals in Monterey Bay

