

Technical Notes – Sampling and Metals Analysis

Chemical analysis of environmental samples can be used as a first step in understanding potential impacts of an exposure to environmental contaminants. The minimum goals of chemical analysis should be to identify what contaminants are present and at what concentrations. This study focused on two metals, As (arsenic) and Cd (cadmium). Both were identified as being potential contaminants in surface water based upon the geology of the San Juan Islands and both are known aquatic toxicants.

With metals analysis, the concentrations that are determined are *total metals*, and so all of the metal species present in the sample being analyzed are included in the final concentration. Research has shown that only certain metal species actually contribute to toxicity. The chemical analysis, therefore, may overestimate toxicity when chemical speciation is not accounted for. There are several ways to account for speciation, including thermodynamic models, correction factors based on empirically collected data (such as the *hardness correction* for Cd), and actual toxicity tests using the whole sample. Since the goals of this study were to provide a screening level understanding of potential impacts as a result of As or Cd exposure to aquatic organisms in San Juan county, acute toxicity experiments were conducted as a way of indirectly assessing the concentration of toxic metal species present in the surface water samples. These tests were not designed to assess chronic toxicity, however.

Under Section 304(a)(1) of the Clean Water Act, the Environmental Protection Agency (EPA) is required to develop criteria for priority pollutants for water quality that accurately reflect the latest scientific knowledge. National Recommended Water Quality Criteria (NRWQC) are based on data and scientific judgments on pollutant concentrations and environmental or human health effects using on an extensive database of toxicity experiments conducted in controlled laboratory situations with each priority pollutant. NRWQC are based on the *LC50 value* that is protective of 95% of the genera for which these toxicity tests have been conducted, for acute exposures (CMC) and for chronic exposures (CCC). NRWQC can be adopted as Water Quality Standards (WQS) without change by a state or can be modified with EPA approval and are available for the protection of human health or the protection of aquatic life. The CMCs and CCCs listed below are all for the protection of aquatic life.

The EPA freshwater CMC for As is 340 µg/L and the CCC is 150 µg/L. The As CMC and CCC are based upon As (III) toxicity, there is not a distinction made for As(V) versus As(III) in the samples, although both may be present in a sample. The EPA freshwater CMC for Cd is 2 µg/L and the CCC is 0.25 µg/L. For Cd, there is a correction that is done for water hardness, which may increase the CMC and CCC if the hardness is greater than 100 mg/L as CaCO₃ and will decrease if the hardness is less than 100 mg/L as CaCO₃. In all cases, the CMC and CCC are based upon dissolved metal concentrations (US EPA, 2006). Dissolved metal concentrations are all of the metal species that are present in a filtered water sample. Washington State adopted CMC values of 360 µg/L and CCC values of 190 µg/L for the WQS (Washington State Department of Ecology, 2006) prior to the new NRWQC for As. The Washington state WQS for Cd is based on hardness (Equations 1 and 2) and is 3.7 µg/L and 1.03 µg/L at 100 mg/L hardness as CaCO₃ for the CMC and CCC, respectively (Washington State Department of Ecology, 2006).

$$\text{CMC} \leq (0.944)(e^{(1.128[\ln(\text{hardness})]-3.828)}) \text{ at hardness} = 100.$$

Equation 1

Conversion factor (CF) of 0.944 is hardness dependent. CF is calculated for other hardnesses as follows: $CF = 1.136672 - [(\ln \text{ hardness})(0.041838)]$.

$$CCC \leq (0.909)(e^{(0.7852[\ln(\text{hardness})]-3.490)}) \text{ at hardness} = 100. \quad \text{Equation 2}$$

Conversions factor (CF) of 0.909 is hardness dependent. CF is calculated for other hardnesses as follows: $CF = 1.101672 - [(\ln \text{ hardness})(0.041838)]$.

Materials and Methods

Streams (flowing water) and lakes on Orcas, Lopez, and San Juan Islands were sampled July 12-13 and October 20-21, 2007, by submerging the mouth of the pre-cleaned sampling bottle, as far as possible without disturbing sediments. Each bottle was filled and emptied three times and the fourth volume was collected. A minimum of 150 ml of samples was filtered through a 0.45 μm pore size MF-Millipore membrane. This filtered sample was acidified to $\text{pH} < 2$ with trace metal grade HNO_3 and stored in the closed bottle until acid digestion; this sample is later referred to as the *dissolved* metal sample. A minimum of 150 ml of sample, collected directly from the stream or pond/lake, was also acidified to $\text{pH} < 2$ with trace metal grade HNO_3 and stored in the closed bottle until acid digestion; this sample is referred to as the *total* metal sample.

For toxicity assays, large pre-cleaned bottles were filled and emptied three times and the fourth volume was collected, a minimum of 150 mL leaving no headspace. Samples were stored on ice in the field and at 4°C in the laboratory.

Mountain Lake and Cascade Lake samples were collected at the approximate middle of the lakes accessed via canoe. In addition to surface samples, samples were collected just above the sediment of the lake (at 19.5 m and 5.9 m for Mountain and Cascade lakes, respectively), and at middle depth (11.1 m for Mountain lake) with a Niskin bottle. These samples were treated as described above for dissolved metal samples, total metal samples, and toxicity assay samples.

Physicochemical measures were collected in the field for each of the sampling sites. With the exception of the Niskin collected samples, dissolved oxygen (DO), temperature, and conductivity (μs) were measured by submerging a YSI model 85 probe under water (in flowing water where possible). DO and conductivity were measured in sub-samples from the Niskin bottle for the three lake samples. All other measurements were conducted in the field on a sample of water collected (as described above) in a wide mouth container. A field calibrated YSI (model pH10) meter was used to measure pH. Turbidity was measured with an HF Scientific MicroTPI Field Turbidimeter. Ammonia (NH_4) was measured with Baker Test strips for Ammonium (J.T. Baker, Phillipsburg, NJ). Alkalinity was measured according to manufacturer's instructions with CHEMetrics (Calverton, VA) Total Alkalinity Titrets® (10-100 ppm) and total hardness was measured according to manufacturer's instructions with CHEMetrics Inc. (Calverton, VA) Total Hardness Titrets (20-200 ppm).

Both dissolved (filtered) and total (unfiltered) samples were digested according to EPA Method 3005A. EPA Method 3020 is the recommended digestion method for analyses using a Graphite Furnace Atomic Absorption Spectrometer (GFAA). The main difference between EPA Method 3005A and Method 3020 is that hydrochloric acid is not used in Method 3020. This may result in an increase in background and alter the sensitivity of the instrument.

A Varian SpectrAA 220Z GFAA with UltraAA lamps was used to analyze the digested water samples. A 5-point calibration curve was established for each element using stock solution made with certified AAS standards. All samples were re-measured twice (July samples) or three times (October samples) as the peak area. Samples that had an RSD > 20% were either reanalyzed or not included in the results (identified as NA). Palladium (Inorganic Ventures, Lakewood, NJ) was added as a modifier during the analysis of the October 2007 samples. Zeeman background correction was used for all samples. Cd was measured at 228.8 nm and As at 193.7 nm. A continuing calibration blank (CCB) and continuing calibration verification (CCV) (CCV= 0.75 µg/L for Cd and 5.0 µg/L for As) was measured immediately after the calibration curve and after every 10 samples. If the CCV was not within ± 20%, the instrument was recalibrated.

The Limit of Detection (LOD) was calculated as three times the standard deviation of multiple measurements of Barnstead NanoPure water. The Limit of Quantification (LOQ) was calculated as 10 times the standard deviation of multiple measurements of Barnstead NanoPure water. The following LOD and LOQ data are expressed in micrograms per liter of water (µg/L):

	July 2007		October 2007	
	LOD	LOQ	LOD	LOQ
Arsenic	0.44	1.48	0.29	0.98
Cadmium	0.10	0.34	0.036	0.12

References

- US Environmental Protection Agency. 2006. *National Recommended Water Quality Criteria*. Office of Science and Technology; Office of Water. 4304T.
- Washington State Department of Ecology. 2006. *Water Quality Standards for Surface Waters of the State of Washington*. WAC 173-201A. Publication # 06-10-091.