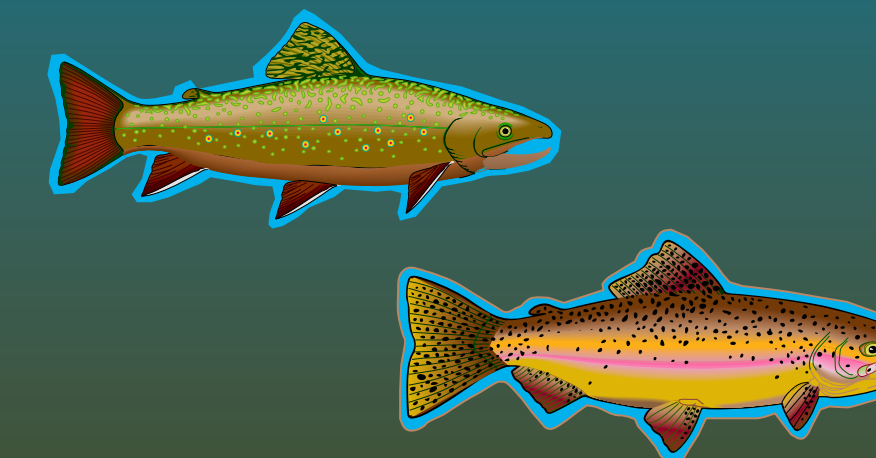# National Park Aquatic Samples: Multielement Analysis by Inductively Coupled Plasma Mass Spectrometry

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1. INTRODUCTION

The U.S. Environmental Protection Agency and the National Park Service have instituted a joint long-term research program, the Park Research and Intensive Monitoring of Ecosystems Network (PRIMENet)[1], which utilizes 12 National Park index sites as platforms for intensive ecological research. As part of PRIMENet, EPA's Environmental Sciences Division is studying the distribution of anthropogenic chemical contamination in aquatic ecosystems at the 12 index sites. Freshwater streams were the primary target ecosystems, although a freshwater lake was sampled instead at one index site (Acadia N.P.), because of the absence of streams. As part of that study, ESD is evaluating the distribution of trace elements in the multiple media. Samples of water, sediments, and fish were collected during Summer and Fall of 1998 and Spring of 1999 from areas in the parks that are minimally impacted by direct human activity. A suite of target trace-element analytes (Be, V, Cr, Co, Zn, Cu, As, Se, Cd, Sn, Sb, Ba, Ce, Tl, Pb, and U) was selected based on potential toxicity to aquatic life.

Inductively coupled plasma-mass spectrometry (ICPMS) was the technique of choice for the analysis of trace-element contaminants because of its capability of multielement analysis and excellent detection limits. Sampling and analysis techniques were tailored to minimize contamination, given the constraint of non-cleanroom conditions. The objectives of this trace-element survey of multiple media at the PRIMENet sites are:

- To establish suitable sampling, storage, and processing protocols for trace-element distribution studies that may be components of future ecological research programs.
- To determine the suitability of ICPMS as a determinative method for trace-element screening of multiple media in relatively pristine ecosystems.
- To evaluate trace-element concentrations in fish at PRIMENet sites, using distributions from statistically sampled similar ecosystems of a large geographic region of the U.S. Fish samples collected in the Environmental Monitoring and Assessment Program's Mid-Atlantic Integrated Assessment are being used to establish the reference distribution.[3]
- To establish baseline data for trace-element concentrations at the PRIMENet sites.

This poster presents the results of the initial analyses of water and fish samples from several PRIMENet Sites. The performance of the methods used, including the ICPMS analysis, will be discussed, along with a preliminary analysis of the results from individual parks.

2. METHODS

Sample Collection, Storage, and Preparation

Water samples were collected in trace-cleaned polyethylene bottles using a "clean hands/dirty hands" sampling protocol.[2] Fish samples were collected and categorized as primary (bottom feeders) and secondary (predators). Both water and fish samples were shipped in ice coolers to the laboratory within 24 hours. Water samples were stored in a refrigerator at 4°C, while fish were kept in a freezer at -75°C. Fish of the same class (primary or secondary) were composited and homogenized. Samples of whole fish homogenate were suspended in nitric acid and digested in a microwave oven (CEM™ MDS 2100 microwave oven). Two digestion procedures were used: the recommended CEM procedure in which 10 mL of nitric acid was added to the sample, and a slightly modified version using less acid (10 mL of 70% HNO₃). One gram of each fish homogenate was digested and diluted to 500 mL total volume for analysis.

Rainbow Trout
Oncorhynchus mykiss

Stoneroller
Hypentelium nigricans

Water samples from 8 PRIMENet sites have been analyzed. Homogenates of two fish classes from three PRIMENet Parks (Great Smoky Mountains, Sequoia-Kings Canyon, and Shenandoah) have been digested and analyzed thus far. The Great Smoky Mountains homogenates have been analyzed using both microwave digestion methods.

Analysis

Acidified water samples and fish digests were analyzed for trace-element concentrations by inductively coupled plasma-mass spectrometry, using a PQ II STE instrument (VG Elemental), equipped with a conventional Meinhard™ nebulizer and water-cooled Scott spray chamber and Gilson™ autosampler. ICP-MS operating parameters were optimized for maximum detector response of ¹¹⁵In, while maintaining reasonably even response across the mass range. Data were collected in the scanning mode, which permitted non-target elements to be evaluated semiquantitatively, and facilitated evaluation of interferences. Stock and working standards were prepared in 1% sub-boiling-distilled nitric acid from commercial ICP standard solutions. For these initial analyses, only water samples without visible suspended sediment were analyzed. No sample preparation, other than acidification with nitric acid to ph < 2, was employed for the water samples. To minimize potential for contamination, and because of the low dissolved solids of the water samples, internal standards were not used. Internal standards were employed for the fish analyses.

Brook Trout
Salvelinus fontinalis

Evaluation of Method Performance

Instrumental limits of detection (LODs) were established on the 3σ basis using the results of 15 reagent blanks scattered throughout the analysis runs. Separate LODs were established for the water analyses and the fish analyses. Quality assurance methods used for the water analyses included trip blanks (laboratory water exposed to the same transportation, sample-handling, and processing regime as the samples), duplicate analysis (100% frequency), and analysis of quality control solutions (NIST water CRM - 10% frequency). Quality assurance methods for fish analyses included duplicate digestion and analysis (100% frequency), and digestion and analysis of dogfish muscle reference material (DORM-2, NRC, Canada - 10% frequency).

3. RESULTS AND DISCUSSION

Method Performance

Water Analyses

The instrumental LODs for the analytes (Table 1) were low enough to allow detection of 8 of the 12 target analytes in 7 of 8 water samples. The LODs for Cu, Zn, and Pb were probably adversely affected by laboratory contamination, but the concentrations of Cu and Zn found in virtually all samples were still significantly above the LODs. Be and Cd were below the LOD in the majority of samples (6 of 8, and 7 of 8, respectively). Analyses of quality control samples were uniformly within ±15% control limits.

Table 2 shows the results of analyses of water trip blanks that exceeded the LOD. Zinc was detectable in all trip blanks. In addition, low concentrations of lead and copper were detectable in several trip blanks. It is believed that these contamination problems were the result of out-of-control deionized water used to prepare the trip blanks, which would not affect the quality of the data from actual samples. Unfortunately, samples of the water used to prepare the trip blanks were not saved to allow confirmation of this assessment. A retrospective study of field sampling contamination with new trip blanks will be performed.

Fish Analyses

The instrumental LODs (Table 3) were low enough to allow detection of 12 of the 16 target analytes in all 8 fish homogenates analyzed. The number of samples in which U, Cd, Be, and Sb could be detected were 5, 4, 1, and 0, respectively.

Table 4 shows the accuracy and precision of the total method (digestion and analyses), using the DORM-2 material. Fourteen of 16 elements were detected in the reference material. Of the 12 elements for which a certified value is reported, both microwave methods recovered 8 within the 75-125% control limits. Poor recovery for Cd can be attributed to the very low concentration. The poor precision for the Cu recovery by the modified method, as well as for Pb recoveries by both methods, indicates that these high recoveries were probably due to one contaminated digest. The high selenium recoveries by both methods could be due to interference from BrH⁺ at m/z 82. Very large peaks of similar intensity were observed at m/z 79 and 81. Previous studies (T. A. Hinners, personal communication) indicate interference at m/z 82 approximately equivalent to 1% of the m/z 81 intensity. If this correction is made to the DORM data, the recovery falls within control limits. Of course, application of correction factors based on MH⁺/M⁺ ratios is problematic unless matrices are well matched, as Se should probably be re-analyzed, using the method of standard additions (adding Br) to correct the BrH⁺ interference.

The standard CEM microwave digestion method gave significantly higher recoveries than the modified method for vanadium, chromium, copper, and barium. Of these elements, Cr and Co have certified values. Both digestion methods were within the 75-125% control limits for Cr. The CEM method gave a recovery that was 170% of the certified Co value. No explanation is available at this time. The precision for both digestion methods was good (RPDs < 10%).

Analyses of PRIMENet Samples

Water Analyses

The concentrations of target transition elements (Cr, Co, Cu, and Zn) in waters collected from 8 PRIMENet sites are shown in Figure 1. Zinc had the highest concentration of these elements in all the waters, generally followed by copper, chromium, and cobalt. Of the latter three elements, the western U.S. park waters generally had higher transition element concentrations than the eastern park waters. This might be partly due to the generally lower organic content of soils in the western U.S. The water from Olympic N.P. had the lowest concentrations among the western parks, and the soil in the Sol Duc watershed, the source of the Olympic sample, has a high organic content.
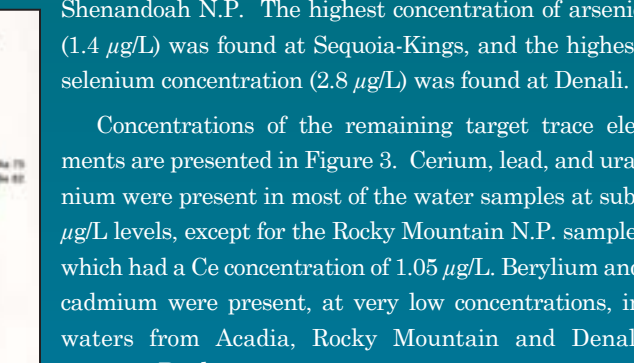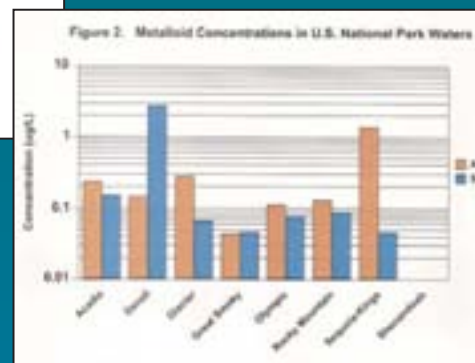
Figure 2 presents the concentrations of arsenic and selenium found in the water samples. Arsenic and selenium were detected in all the parks except Shenandoah N.P. The highest concentration of arsenic (1.4 μg/L) was found at Sequoia-Kings, and the highest selenium concentration (2.8 μg/L) was found at Denali.

Concentrations of the remaining target trace elements are presented in Figure 3. Cerium, lead, and uranium were present in most of the water samples at sub-μg/L levels, except for the Rocky Mountain N.P. sample, which had a Ce concentration of 1.05 μg/L. Beryllium and cadmium were present, at very low concentrations, in waters from Acadia, Rocky Mountain and Denali National Parks.

Analyses of PRIMENet Samples
(Continued)

Fish Analyses

The analytical results of the fish samples, expressed as mg/kg (wet weight) of whole-fish homogenate, are summarized in Figures 4-6. In these figures, a point above the equal-concentration line represents an element that was present in higher concentration in the predator class, while a point below that line represents an element with a higher concentration in the bottom-feeder class. Beryllium was only detected in the bottom-feeder homogenate from Shenandoah N.P., and only slightly above the LOD (0.006 mg/kg vs. 0.005 mg/kg), so it is not shown in any of the figures. Cadmium was detected only at Great Smoky Mountains N.P., in both classes, so it appears in Figure 4. Antimony was not detected in any homogenates. Although the uranium concentration measured was below the LOD of 0.002 mg/kg in the secondary (predator) fish homogenates from Shenandoah and Great Smoky Mountain N.P., it was significantly above that level in all the primary (bottom-feeder) fish, and in the secondary fish from Sequoia-Kings Canyon. It is shown in all three figures, using the secondary fish concentrations reported by the instrument.
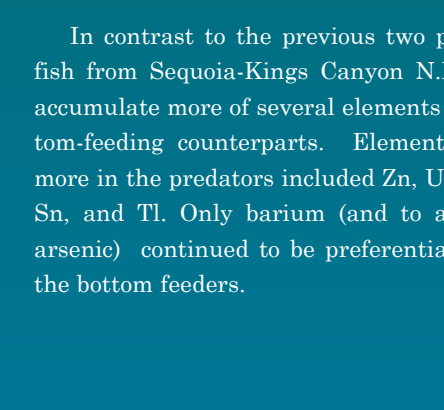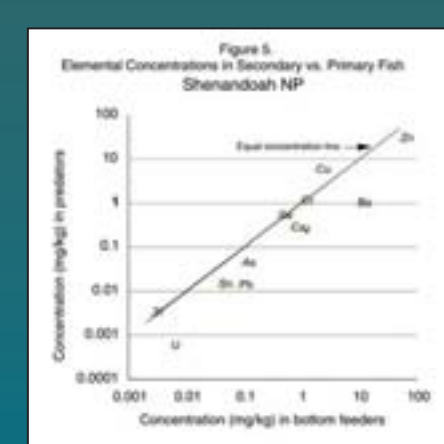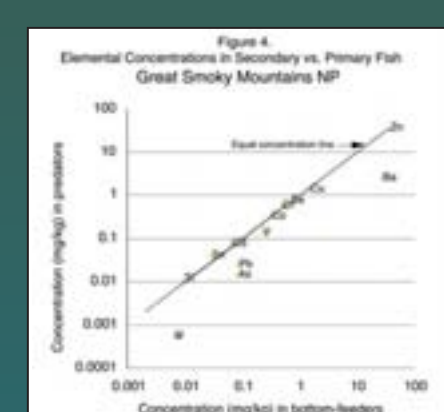
Of the elements detected in the fish from Great Smoky Mountains N.P. (Figure 4), Ba, U, As, Pb, and V were present in significantly higher concentrations in the bottom-feeder (stoneroller, *Hypentelium nigricans*) homogenate. Only tin was present in an appreciably higher concentration in the predator fish. Although biomagnification (accumulation of higher concentrations of chemicals at higher trophic levels) can occur for some trace elements, it will only be apparent when comparing fish in the same food chain. The predator fish at Great Smoky Mountains N.P. was rainbow trout, *Oncorhynchus mykiss*, the diet of which is varied and largely dependent on insects. Trout were the predators as at most of these sites, so biomagnification may not be evident in these figures.

The tendency for higher trace element concentrations in the primary (bottom-feeder) homogenate is even more pronounced for the fish from Shenandoah N.P. (Figure 5). In addition to the same elements found preferentially in the fish from Great Smoky bottom feeders, that class at Shenandoah (torrent sucker, *Moxostoma rhothoecum*) also had higher concentrations of Zn, Sn, and Co. The Cu concentration was significantly higher in the predator class fish (brook trout) than in the bottom feeders.

In contrast to the previous two parks, predator fish from Sequoia-Kings Canyon N.P. appeared to accumulate more of several elements than their bottom-feeding counterparts. Elements accumulated more in the predators included Zn, U, Pb, Co, Cr, V, Sn, and Tl. Only barium (and to a small extent, arsenic) continued to be preferentially retained in the bottom feeders.

Bioaccumulation

Apparent bioaccumulation factors can be calculated as the ratios of the fish trace-element concentrations to the corresponding water concentrations. This bioaccumulation factor includes accumulation of an element from all pathways (dermal and gill sorption, as well as from diet), and it is always higher than the bioconcentration factor, which reflects sorption from the water column only. While bioaccumulation is more relevant to exposure of an organism, it depends upon a number of factors that are specific to a site and situation. Therefore, bioconcentration factors are more often reported in the literature. Table 5 lists the bioaccumulation factors determined for the bottom-feeder class fish at the three PRIMENet sites, along with a range of bioconcentration factors found in the literature. Two conclusions can be drawn from Table 5. First, uptake via the diet is an important mechanism for accumulation of trace elements at all three parks. Second, bioaccumulation is much less pronounced at Sequoia-Kings Canyon than at the other parks. It should be noted that the concentrations measured in water in this study represent that fraction of the total element concentration that can be efficiently sampled and nebulized after acidification with nitric acid. The apparent bioaccumulation factors could be different for different sample treatments. There is no one correct method for measurement of bioaccumulation.

4. CONCLUSIONS

ICPMS has been used to study the trace element distributions in two media (water and fish) from several stream ecosystems in the U.S. that are minimally impacted by direct human activity. It has the sensitivity required to provide useful data for most elements of concern in the majority of samples. A relatively simple sampling, processing, and analytical regime has been effective in producing data of acceptable quality. The project is continuing with the analysis of water and fish from more PRIMENet index sites, and the analysis of bed sediment from the sites. Fish from a statistically sampled set of streams from the Mid-Atlantic region of the U.S. will also be analyzed to provide a reference distribution against which to compare the PRIMENet trace-element concentrations.

References

1. National Park Service, 1999. http://www2.nature.nps.gov/ard/prime/primeres.htm
2. Horowitz, A.J., Demas, C.R., Fitzgerald, K.K., Miller, T.L., and Rickert, D.A., 1994. U.S. Geological Survey protocol for collection and processing of surface-water samples for the subsequent determination of inorganic constituents in filtered water: U.S. Geological Survey Open-File Report 94-539, 57 p.
3. U.S. Environmental Protection Agency, 1999. Information home page for the Mid-Atlantic Integrated Assessment. http://www.epa.gov/maia/
4. Nuclear Task Force of the International Joint Commission (U.S. and Canada), 1999. "Report on Bioaccumulation of Elements to Accompany the Inventory of Radionuclides in the Great Lakes Basin." http://www.ijc.org/boards/nuclear/bio/index.html
5. Tetra Tech, 1985, Bioaccumulation monitoring guidance: 1. Estimating the potential for bioaccumulation of priority pollutants and 301(h) pesticides discharged into marine and estuarine waters. Final report prepared by Tetra Tech, Inc., for the U.S. Environmental Protection Agency under Contract No. 68-01-6938.
6. Campbell, Diane E., 1998. "The Identification and Assessment of Hazards Associated with Minerals and Metals" in Proceedings of the Pan-American Workshop on the Safe Use of Minerals and Metals. Lima, Peru July 1-3, 1998.

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