

Water Quality Workshop Held at Olympic NP

Measurement of pH, conductivity, and alkalinity is fundamental to most studies of water resources. Yet, accurate measurement of these parameters, particularly of pH, is not simple in low-ionic strength waters. Waters of upland streams and lakes in the Pacific Northwest generally have very low solute concentrations (i.e. are "pure" waters). In these waters, errors in measurement of pH of 0.10 to 2.00 pH units are common using traditional techniques. These errors may seem of no consequence until one recognizes that pH is a *logarithmic* scale, representing the negative log of hydrogen ion activity. Thus, a small change in pH (0.10 pH unit) reflects a large change in hydrogen ion concentration (26% error). In national parks, achieving accurate results in pH measurement is important, particularly in establishing baseline conditions.

In September, 1987 a 2-day workshop on the measurement of pH, conductivity, and alkalinity was held at Olympic NP, led by Dr. Richard Metcalf, a Senior Geochemist in the Acid Deposition Department, Lockheed-EMSO. (Lockheed is under contract to EPA for the National Surface Water Survey, Episodic Response Project, and Watershed Manipulation Programs).

Attendants were from the large, natural area parks in the region, the Pacific Northwest Regional Office, CPSU at Oregon State University, Water Resources Branch in Fort Collins, and Washington State Department of Ecology. Topics covered included the theory and practice of pH measurement (types of electrodes, liquid junction potential errors, stirring potential errors,

use of dilute standards), applied conductivity measurements, determination of alkalinity, QA/QC, and hints on evaluating water chemistry research or contract work.

In an afternoon session, participants, using their own field pH meters, measured an unknown solution having a pH not revealed until the experiment's end. Results of this experiment are shown in Table 1.

The "mystery" solution was $1.00 \pm 0.01 \times 10^{-4}$ M HCl, with a pH of 4.005 at 25°C. For this solution, uncalibrated liquid junction potential errors cause a change in the value the electrode *should* read to 4.06 at 25°C. The experiment illustrated the importance of careful choice of equipment, and strict attention to methodology. It also made clear the need for "enlightened" evaluation of current and past research results. The trial indicated that no agreement closer than ± 0.16 pH unit should be expected (45% error in hydrogen ion concentration) for different people measuring the same water!

As a result of the workshop, water quality monitoring programs in the Pacific Northwest Region will be evaluated for appropriateness of equipment, field, and lab methodology. Meaningful, accurate results in the measurement of pH, conductivity, and alkalinity should be the end product in these parks.

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Table 1
pH Reading, Three Measurement Trials

Individual or team	Trial 1	Trial 2	Trial 3
A	3.93	3.85	3.82
B	4.03	4.02	4.02
C	3.98	3.99	4.00
D	4.09	4.07	4.08
E	4.36	4.05	4.03
F	4.02	4.07	3.97
G	4.01	3.96	3.99
mean	4.06	4.00	3.99
2 std. dev.	0.28	0.16	0.16