

Sources of Calcium in Northern Hardwood Forests:

Implications for Repeated Harvest and Calcium Depletion

Michigan Subcontract

Principal Investigator: Ruth D. Yanai, SUNY College of Environmental Science and Forestry, Syracuse, NY 13210. phone: 315 470-6955 fax: 315 470-6954 e-mail: rdyanai@mailbox.syr.edu

Subcontractor: Joel D. Blum, University of Michigan, Department of Geological Sciences, Ann Arbor, MI 48109. phone: 734 615-3242 e-mail: jdblum@umich.edu

Michigan Subcontract Work Statement

The laboratory of Joel D Blum at the University of Michigan is responsible for all of the sample preparation, sample digestion, and chemical analyses associated with this project.

Tissue analysis – Samples of litter (0.4 to 1 g dry weight) will be digested in concentrated nitric acid using high pressure microwave digestion (Milestone Ethos 1600; 3 min ramp to 85°C, 9 min ramp to 145°C, 4 min ramp to 200°C, 14 min at 200°C, then cool down) and then diluted to a 10% nitric acid solution for analysis using ICP-OES.

Sequential extractions of soil Ca pools – We will analyze four operationally defined soil base-cation pools. Each pool is extracted in sequence from a 5 gram soil sample, and the solid residue is separated from the solution by centrifugation after each of four steps. (1) First the soil is exchanged overnight with 5 ml of 1M NH₄Cl (ph=7) to remove the exchangeable cations. (2) The residue is treated overnight with 10 ml H₂O₂ to oxidize organic matter. This solution dissolves most (but not all) organic matter and allows us to determine the relative ratios of cations in organic matter. We choose not to ash the sample because some non-silicate minerals would be dissolved in the process of dissolving the ash into solution. (3) The residue is next leached overnight in 5 ml of 1M HNO₃ to remove non-silicate minerals such as apatite and calcite. Our previous studies have shown that this treatment dissolves >75% of the apatite and calcite in Hubbard Brook soils, yet dissolves <0.3% of the silicate fraction. (4) Finally, the residue is totally digested in 10 ml of a mixture of concentrated HF, HNO₃ and HCl at high pressure and 210°C in a microwave digestion apparatus to digest the silicate mineral fraction. Analyses of major and trace elements will be carried out on all of the solutions using ICP-OES and ICP-MS with both internal and external calibration.

Strontium Isotope Analyses – Subsets of all types of samples analyzed for Ca will be analyzed for Sr concentration by ICP-MS and then analyzed for ⁸⁷Sr/⁸⁶Sr ratio. Digested sample solutions will be evaporated to dryness and re-dissolved in 1 ml of 3 N HNO₃. Strontium will be separated by ion exchange chromatography in quartz columns using Sr-Spec ion specific resin, and loaded on to tungsten filaments with Ta₂O₅ powder. The ⁸⁷Sr/⁸⁶Sr ratio will be measured using a multi-collector thermal ionization mass spectrometry in static mode (Finnigan MAT 262) and normalized to ⁸⁶Sr/⁸⁸Sr = 0.1194.

Michigan Subcontract Budget Explanation

Analytical and technical services are budgeted at \$20,000 per year for three years for the analysis of soil and tissue samples at the University of Michigan. The recharge rate for sample digestions is \$5 per sample, the rate for major element analysis by ICP-OES is \$5 per sample and the rate for trace element analysis by ICP-MS is \$14 per sample. The established rate for clean room sample digestion, Sr separation by cation exchange chromatography, and thermal ionization mass spectrometric analysis is \$86 per sample. All of these rates are exclusive of labor. A senior research associate will work two months per year on these analyses.

We plan on an analytical load of about 450 samples for major and trace element analysis over three years: 50 sites explored in Phase 1 (1 C-horizon sample from each) and 20 sites in Phase 2 (20 samples: 4 composite soil samples by depth, with 4 fractions of each, plus leaves of the four dominant species at each site). A subset of these samples will be analyzed for Sr isotopic composition.

	Year 1	Year 2	Year 3	
Research Associate				
Salary (2 months/yr)	7000	7210	7426	
Benefits (33%)	2310	2380	2450	
Laboratory Charges				
Digestion (\$5)	770	760	740	
ICP-OES (\$5)	770	760	750	
ICP-MS (\$14)	2100	2100	2100	
TIMS (\$86)	7050	6790	6534	
TOTAL	20000	20000	20000	60000