

we report on the effects of the MR-1 biofilm formation on the more slowly dissolving end-member plagioclase feldspar, anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$). The influence of organisms on feldspar weathering rates, in particular the Ca-rich plagioclases, has been the subject of considerable interest because of their crustal abundance and role in the maintenance of atmospheric CO_2 . (Schwartzman and Volk, 1989, Schwartzman, 1995 and others). Our methodology of direct observation of microbial attachment, biofilm propagation and effects on mineral dissolution provides a quantitative measure of biological contribution to weathering of single crystal minerals for subsequent use in biogeochemical modeling.

B12D-05 1440h

Mineral Surfaces and Their Implications for Microbial Attachment: Results from Monte Carlo Simulations and Direct Surface Observations

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Mineral surfaces in contact with aqueous solutions form the interface at which microbial attachment and development is likely to occur and reactions will progress. Therefore, it is key to understand how microbes attach to crystal surfaces, and how they eventually impact mineral reaction kinetics. A prerequisite for any attempt to define these processes is the understanding and quantification of surface area. For practical reasons, we use the total surface area, even if we agreed that it would be more correct to use the reactive surface area, which is understood to be a fraction of the total. Surprisingly, recent computer based Monte Carlo (MC) simulations of mineral dissolution reactions have indicated that this concept might be flawed. The following questions elucidate this conclusion: How large is the reactive surface area? AND: How reactive is it? The first answer will be given in units of surface area, the second answer, however, can not be given in this unit. This has the unfortunate consequence that the reactivity term is embedded within the rate constant itself. A comparison of reactive versus total surface area implies that one part of the surface is reactive while the other is not. This concept is arbitrary and otherwise incorrect, as shown by analytical techniques like AFM and VSI that provide spatially resolved information. Additional evidence comes from model calculations that indicate that every locus the crystal surface has a certain reactivity. Expressed in terms of a MC model, these reactivities are expressed as probabilities; - otherwise, parts of the surface would be inert. Focusing at the molecular scale, we understand that each surface molecule has a certain probability to leave the structure and that every adatom has a probability to become a new member of the structure. The probabilities for the processes to occur depend, beside other factors, on the energy configuration at each location. Therefore, it is the number, type, and distribution of surface sites that define the average reactivity of a crystalline surface at any given time. This insight has large implications for a number of topics: (1) reactive surface area can not be expressed solely in units of area, (2) nor can it be compared directly with total surface area. (3) Even more important, the distribution of sites at a given surface have the inherent potential for dynamic change. Therefore, we can not expect a unique rate for a dissolution process, but a range of rates. This conclusion is in agreement with many very well constrained experimental results. An attempt to model microorganisms on mineral surfaces and their interactions should address this problem because all interactions occur at the molecular scale. For example, Shewanella MR-1 attaches to specific sites at carbonate surfaces, i.e., the outcrops of line defects. By blocking these sites MR-1 modifies the reactivity of the surface and therefore the dissolution or growth kinetics.

B12D-06 1455h

Molecular Modeling of Biogenic Manganese Oxides Using ab Initio Density Functional Theory

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Layer type manganese oxides with short-range crystalline order (birnessites) are produced by many species

of bacteria. Deposits of these oxides form a highly reactive catalytic surface that plays a major role in the destruction and sequestration of organic compounds and metals. Biogenic oxides also contain vacant Mn(IV) sites; these sites, with their associated negative charge, are the probable main cause of the high sorptive reactivity of the oxide surfaces. In order to acquire a deeper understanding of the molecular mechanisms involved in these processes, a model of a biogenic oxide was built and its structure was optimized using the CASTEP three-dimensional periodic system computational package. The resulting crystal structure shows good agreement with EXAFS data from crystals formed by a strain of the common soil and freshwater bacterium, *Pseudomonas putida*. The greatest challenge in modeling Mn oxides (like other transition metal oxides) comes in dealing with the electronic factors that lead to their magnetic and catalytic properties: they are highly correlated systems where the spin must be taken into account in order to obtain accurate predictions of their properties.

B12D-07 1510h

Cesium Interactions With Illite in the Presence of Bacterial Exudates

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Biogeochemical processes in the rhizosphere can significantly alter chemical reactions between contaminants and soil minerals. Several strains of bacteria that exude aluminum-chelating compounds were isolated from the rhizosphere of crested wheatgrass (*Agropyron desertorum*) collected from the Idaho National Engineering and Environmental Laboratory (IN-EEL). We examined the effect of exudates from the rhizosphere bacteria on cesium desorption from illite. The exudates from some strains of rhizosphere bacteria significantly enhanced Cs desorption from illite. In addition, Cs desorption from illite increased with increasing concentration of exudates from one selected bacterial strain. There was no obvious relationship between Cs desorption and the Al-chelating ability of the exudates. Both mobilization of Al from illite and changes in the density of frayed edge sites on the illite were monitored as a function of exudate type and concentration. Results suggest that exudates from rhizosphere bacteria may play an important role in Cs interactions with illite and, therefore, could alter Cs availability in micaceous soils.

B12D-08 1525h

Studies On The Influence Of Soil Components On Adsorption-Desorption Of Hazardous Organics And Their Insitu Biodegradation

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Currently approximately 155 cubic yards of soil is contaminated with hazardous organics at Patancheru Industrial area (Hyderabad, India). These hazardous organic contaminants are frequently part of hazardous waste disposed on land and the study of waste site interaction is the key to assess the potential for offsite and onsite contamination. In the present study the authors report the results on the adsorption, soil leaching potential and persistence of phenol, p-nitrophenol, 2,4-dichlorophenol and 4-chloro-2-nitrophenol which are the common constituents of the hazardous waste generated. The role of soil components like organic matter, clay, iron and aluminium oxides in the adsorption capacity has been studied. Desorption isotherms of soil adsorbed hazardous organics exhibited hysteresis at high initial concentration indicating the degree of irreversibility of adsorption-desorption process. Leaching potential of the hazardous organics decreases with their increasing hydrophobicity and soil organic matter content while their persistence in terms of half life time (DT50) increases. Insitu biodegradation has been carried out by developing mixed culture systems which can

degrade the phenols to complete mineralisation by utilizing them as the sole source of carbon and their corresponding biodegradation kinetic constants were evaluated. Based on the above data generated preparation of hazardous waste dumpsites with suitable soil surface having high holding capacity for organics and their insitu biodegradation by mixing with specific bacterial cultures enriched from different soils can be exploited as a cost effective technology for reclamation of contaminated sites.

B12E MCC: 3014 Monday 1340h

Disturbance, Climate, and Management Impacts on Carbon Budgets of Forested Ecosystems II

(joint with A, GC)

Presiding: K A Hibbard, Oregon State University; M Apps, Canadian Forest Service; D J Barrett, CSIRO Plant Industry

B12E-01 1340h INVITED

Fire and Carbon in Canadian Forests

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Fire is the major stand-renewing agent in Canadian forests, affecting carbon sources and sinks. On average over the past 40 years, about 27 Tg carbon have been emitted directly through combustion of Canadian forest fires annually, but in some years, this can be over 100 Tg carbon. The overall impact is much greater because fire-killed vegetation decomposes and releases carbon through heterotrophic respiration. In addition, very young successional vegetation that replaces the burned forest is usually a weaker carbon sink until the forest canopy develops. The magnitude of these post-fire effects has not been well quantified, but models suggest that it is of a similar magnitude to the direct combustion emissions. Post-fire carbon fluxes are being measured using eddy covariance as part of FLUXNET-Canada on a chronosequence of burned forests. These long-term measurements, in conjunction with short-term aircraft measurements and modelling are helping to reduce the uncertainty in our estimates of the effect of fire on the forest carbon balance. The impact of fire on forest carbon is expected to become more important in the future since global circulation models and regional climate models suggest that the area burned could double in Canada under a 3xCO₂ climate. This will be caused by warmer and drier conditions throughout much of the country. Although climate is a main driver of fire, landscape and fuel changes also need to be considered. Ongoing research is aimed at evaluating the potential to mitigate fire through landscape modifications and other fire management options. However it is most likely that we will need to adapt to the economic, social and ecological impacts of fire in a changing climate.

B12E-02 1355h

Climatic Variability, Fire Regimes and Carbon Dynamics in Dry Forest Ecosystems of the Western US

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Historical variability of fire regimes in the western Americas is associated with climatic phenomena such as ENSO. We describe the relationship between fire occurrence and interannual to decadal climatic variability (Palmer Drought Severity Index [PDSI],

El Niño/Southern Oscillation [ENSO] and the Pacific Decadal Oscillation [PDO]) and explain how land use changes in the 20th century affected these relationships. Ongoing research uses these past changes to understand the influence of fire regimes on the regional carbon balance. We used 1701 fire-scarred trees collected in five study sites in central and eastern Washington to investigate current year, lagged, and low frequency relationships between composite fire histories and PDSI, PDO, and ENSO (using the Southern Oscillation Index [SOI] as a measure of ENSO variability) using superposed epoch analysis and cross-spectral analysis. Fires tended to occur during dry summers and during the positive phase of the PDO. Cross-spectral analysis indicates that percentage of trees scarred by fire and the PDO are spectrally coherent at 47 years, the approximate cycle of the PDO. Similarly, percentage scarred and ENSO are spectrally coherent at 6 years, the approximate cycle of ENSO. However other results suggest that ENSO was only a weak driver of fire occurrence in the past three centuries. While drought and fire appear to be tightly linked between 1700-1900, the relationship between drought and fire occurrence was disrupted during the 20th century as a result of land use changes. We suggest that long-term fire planning using the PDO may be possible in the PNW, potentially allowing decadal-scale management of fire regimes, prescribed fire and potentially, carbon emissions. Future work will quantify the changes in carbon emissions associated with a return to natural fire regimes and compares them with estimates of carbon emissions associated with current management. To model past, present and future emissions from fire in Washington's dry forest system we will use: (1) our network of fire-history records for the Pacific Northwest, (2) a fuelbed classification system (FCCs), (3) state-of-the-art computer models for predicting biomass consumption (CONSUME and EPM), and (4) an emission/dispersion modeling framework (BlueSky) to build an integrated model for spatially explicit estimates to guide fire management and policy.

B12E-03 1410h

Effect of Climate Variability and Management Practices on Carbon, Water and Energy Fluxes of a Young Ponderosa Pine Plantation at the Blodgett Forest Ameriflux Site

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Our research at Blodgett Forest in the Sierra Nevada mountains of California seeks to better understand how fluxes of CO₂, H₂O, and energy in a mid-elevation, young pine plantation change interannually in response to climate variability, and how they are impacted by management practices such as shrub removal and thinning. Ecosystem scale fluxes have been measured by the eddy covariance method since 1997, along with meteorological parameters. During winter, the young Ponderosa pine plantation at Blodgett acted mainly as a sink of carbon. Strong variations in winter carbon sequestration occurred due to changes in leaf area index and frequency of freezing temperatures. Inter-annual variations in springtime carbon flux occurred mainly due to differences in the timing of seasonally increasing temperatures. Drought is a regular feature of the California climate, making water availability the major controller of gas exchange in summer and fall. In late summer 2001, drought stress reduced ecosystem carbon uptake by 1/5, while the Bowen ratio increased by 1/3. Thinning is a widespread procedure in plantation management carried out to reduce stand density, improve forest health, and optimize tree growth. In spring 2000, 2/3 of the trees were removed by mastication, the process of mechanically chewing up unwanted trees, which is becoming a widespread method for pre-commercial thinning in the U.S. During and after thinning, the plantation remained a sink of carbon. Thinning at the Blodgett site reduced the leaf area index from 3 to 1.5 m² m⁻², and created branch and stem debris of 400-500 g m⁻². During summer 2000, mastication decreased ecosystem carbon uptake by 1/3. Ecosystem water use efficiency decreased by 1/5 and the Bowen ratio increased by 1/3. This indicates the increasing heat lost as sensible versus latent heat as the water flux decreased due to the reduction in leaf area index. After thinning, leaf area index rapidly increased to 2.5 m² m⁻² by the end of 2000, and to 3.5 m² m⁻² in 2001. As a result, the uptake of carbon by the ecosystem increased by 1/3 in early summer 2001 in comparison to the pre-thinning value. By summer 2001 the Bowen ratio returned to its pre-thinning value, and the ecosystem water use efficiency increased by 1/3. Higher ecosystem water use efficiency was maintained in summer 2002 and 2003, indicating that the thinning led to better optimization of ecosystem water use for at least the following three years, increasing the ratio of carbon gained to water lost over the growing season.

B12E-04 1425h

Reconstructing the Recent Disturbance History of North America Using the AVHRR Satellite Record

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Ecosystem structure and function are strongly impacted by disturbance events, many of which in North America are associated with seasonal temperature extremes, droughts, and tropical storms. This study was conducted to evaluate patterns in a 19-year record of global satellite observations of vegetation phenology from the Advanced Very High Resolution Radiometer (AVHRR) as a means to characterize major ecosystem disturbance events and regimes. The fraction absorbed of photosynthetically active radiation (FPAR) by vegetation canopies worldwide has been computed at a monthly time interval from 1982 to 2000 and gridded at a spatial resolution of 8-km globally. Potential disturbance events were identified in the FPAR time series by locating anomalously low values (FPAR-LO) that lasted longer than 12 consecutive months at any 8-km pixel. We find verifiable evidence of numerous disturbance types on the long-term carbon fluxes of North America, including major regional patterns of cold and heat waves, several major droughts and tropical storms, and large-scale forest logging. This study approach readily enables the integration of field observations, remote sensing, and ecosystem modeling to better understanding the trajectories of change in global ecosystems over time.

URL: <http://geo.arc.nasa.gov/sge/casa/>

B12E-05 1440h

Rapid decomposition of labile soil organic matter inputs obscures sensitivity of heterotrophic respiration to temperature: A model analysis.

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Labile carbon, although often a small fraction of soil organic matter (SOM), significantly affects heterotrophic respiration at short time scales because of its rapid decomposition. However, in the current literature, most soil respiration measurements are interpreted without simultaneous information on labile carbon pool dynamics. Sensitivity of soil respiration to temperature is routinely derived directly from field observations and such relationships have been used to extrapolate effects of global change (e.g. warming) on the carbon emission from SOM. Here we used a multi-pool SOM model to demonstrate the impacts of seasonal fluctuations in labile carbon pools. Labile carbon pool sizes varied widely in response to seasonal changes in representative plant material inputs and temperature even though the model was operating at an equilibrium state (in terms of annual means). Convolution of the dynamics of fast turnover carbon pools and temporal progression in temperature led to misrepresentation and misinterpretation of the heterotrophic respiration - temperature relationships estimated from bulk soil CO₂ exchanges. Temperature sensitivity was overestimated when the variations of labile carbon pools and temperature were in phase and underestimated when they were out of phase. Furthermore, with normally used observation time windows (weeks to a year), temperature sensitivity was more likely to be underestimated. A distortion of temperature sensitivity (Q₁₀) from 2 (actual, sensitive dependence on temperature) to nearly 1 (false, no dependence on temperature) was shown. Our analysis indicates that cautions must be taken when soil respiration - temperature relationships are evaluated based on bulk soil observations and that sensitivity of soil respiration to temperature estimated directly under field conditions should not be used to predict future carbon cycle climate feedbacks.

B12E-06 1455h

Soil Mineralogical Control of Aggregate-Protected Carbon in a Mature Secondary Conifer Forest in Northern California

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Forest systems have the potential to act as sinks for atmospheric carbon dioxide, as shown by the role of secondary forest growth in the North American C sink. We investigated the role of soil mineralogy as a key parameter in controlling long-term soil C storage and aggregate-protection of C in secondary growth forests of California. Soil pedons were sampled to a depth of one meter on granitic and andesitic parent materials in 80 year old ponderosa pine forests. Soil samples were characterized for total C and N, pH, clay content and clay mineralogy. The latter were determined by X-ray diffraction (XRD) and selective dissolution (SD) techniques. The andesitic soils contain 50% more C than the granitic soils (19.6 vs 12.8 kg m⁻²) mainly due to significant differences in surface horizon C content. No significant difference was observed in subsurface C concentration between parent materials. XRD data indicates only slight differences in clay species between parent materials. In both soils, clay crystallinity increases with depth, with an increased dominance of kaolinite and gibbsite, while amorphous material decreases with depth. The main soil mineralogy difference between the parent materials is greater crystalline (38.7 vs 22.8 g kg⁻¹) and short range order (1.0 vs 0.5 g kg⁻¹) iron oxide content in the andesite derived soils. Chemical and physical indices of C differed significantly between parent materials. Both soils had similar amounts of Na-pyrophosphate (pH 10) extractable C (Cp), but significantly more Cp in the andesite soil was stabilized in Al and Fe organo-metal complexes ([Alp-Fep]/Cp; 1.0 vs 0.7). In addition, a greater portion of the total C was contained in aggregate fractions in the andesitic soils (17.8 vs 9.4 gC kg soil⁻¹). Radiocarbon analyses will be carried out on three C fractions separated by density and ultrasonic dispersion techniques to isolate inter-aggregate, intra-aggregate and organo-mineral pools for modeling C dynamics. Preliminary data suggest a longer mean residence time of C in andesite than granite derived soils. We hypothesize that the enhanced aggregate C storage and slower turnover time of C in andesitic soils is a function of iron oxides acting to stabilize soil aggregates and of short range order aluminosilicates providing greater reactive surface area to bind organic compounds. These results suggest that the potential for natural soil C storage and sequestration management in secondary growth forests may be sensitive to parent material and soil development.

B12E-07 1510h

Changes in Carbon Storage and Net Carbon Exchange After a Shelterwood Harvest at Howland Forest, Maine

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While many forests are actively sequestering carbon, little research has examined the direct effects of forest management practices on carbon sequestration. This is a critical issue in North America, where a large proportion of forests are managed. At the Howland Forest in Maine, we are using eddy covariance, biometric techniques and modeling to evaluate changes in carbon storage following a shelterwood cut that removed

just under 30% of aboveground biomass. This management regime is becoming increasingly common throughout the region. Prior to harvest, the stand contained about 76 Mg C ha^{-1} ($30 \text{ m}^2 \text{ ha}^{-1}$ basal area) in above- and below-ground live biomass. Harvesting removed about 15 Mg C ha^{-1} ($\text{SEM}=2.1$), and created about 5.3 Mg C ha^{-1} ($\text{SEM}=1.1$) of aboveground and 5.2 Mg C ha^{-1} ($\text{SEM}=0.7$) of root/stump detritus. Leaf-area index and litterfall declined by about 40% with harvest. Approximately half of the harvested wood was used for paper products (half-life of 3.5 years) and half for longer-lived wood products (half-life of 45 years). In a nearby, unharvested stand, eddy covariance measurements indicated that net ecosystem exchange (NEE) averages about $1.8 \text{ Mg C ha}^{-1} \text{ y}^{-1}$. A comparison of NEE at unharvested and harvested stands, both pre- and post-harvest, indicated that NEE declined following the harvest by about 18%, which is less than expected based on basal area and LAI changes. Both daily uptake and nocturnal respiration declined after harvest. Soil respiration declined slightly with harvest, suggesting no major soil C loss after harvest; harvesting had little effect on soil moisture and temperature. When decay of paper and wood products is included in a preliminary carbon budget, we predict that the forest will be a net C source to the atmosphere for at least 5 years, assuming pre-harvest growth rates of trees. How quickly the carbon balance becomes positive will depend largely on whether post-harvest tree growth rates increase.

B12E-08 1525h

Assessing Biogeochemical Cycling in Forested Ecosystems Through Integration of Remotely-Sensed Forest Structure with an Ecosystem Model

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Forested landscapes are generally composed of a heterogeneous mixture of patches that reflect the complex interaction of processes occurring at many spatial and temporal scales. Whether caused by natural disturbances, such as blow downs and fire, management practices, such as logging and agriculture, or varying climatic factors, both ecosystem structure and carbon fluxes will vary strongly as a result of differences in successional stage. Forest structural measurements, such as canopy characteristics and biomass, are key elements in furthering our understanding of the carbon budgets of forested ecosystems because they provide the observational evidence from which the impacts of various processes may be assessed. They also provide what is often the only means of determining successional status and edaphic controls, and are thus critical for both initialization and validation of carbon modeling approaches. Identifying and tracking these structural differences through space and time has been extraordinarily difficult, given the burden and limited scope of field-based methods, and the limited efficacy of most remote sensing approaches. In this paper we explore the potential for assessments of biogeochemical cycling in forests using a combined field, remote sensing and modeling approach. Our focus is on the fusion of various remote sensing data, including lidar and multispectral methods, with limited field based observations, to provide trajectories of successional status that can then be used to initialize and validate ecosystem models. We provide examples using the Ecosystem Demography (ED) model for both tropical and temperate forests. Our results in these areas show that initialization of the ED model with remotely sensed data on forest structure, in particular canopy height, allows for estimates of carbon stocks within few percent of field-based methods, greatly constrains consequent estimates of carbon flux. This approach thus provides a promising means for observing the effects of various disturbance and management regimes on forested ecosystem structure and associated carbon fluxes.

B12F MCC: 2000 Monday 1600h

Environmental Assessment From the Width, Anatomy, and Chemical Composition of Tree Rings II (*joint with A, H, GC*)

Presiding: T E Lewis, U.S.

Environmental Protection Agency; T Yanosky, U.S. Geological Survey

B12F-01 1600h

Tree-Ring Evidence for Volcanic Eruption Effects on Temperate and Boreal Tree Net Primary Productivity

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The 1991 Pinatubo eruption and the apparent increased terrestrial carbon uptake in 1992 and 1993 have motivated interest in understanding the impact on plant productivity of the climate and radiative change resulting from volcanic eruptions that generate large stratospheric aerosol loadings. We used tree ring width series to look for anomalously high or low tree growth following 10 large eruptions since 1500 (not including Pinatubo) that resulted in stratospheric aerosol loadings comparable to Pinatubo's. We obtained cross-dated ring width series from the International Tree Ring Data Bank, developed regional mean width indices, and used a Monte Carlo approach to test for significant departures in the indices following eruptions. Boreal zone trees (north of 50°N) showed significantly reduced widths ($\sim 5\%$ below average) for several years centered around years 4-6 after eruptions. Temperate zone ($35^\circ\text{--}50^\circ\text{N}$) trees in eastern North America showed significantly increased (by $\sim 6\%$) widths on years 0-2 after eruptions. Temperate zone trees in western North America showed a smaller increase, and trees in Europe showed no increase. We tentatively suggest that eruption-induced cooling causes the growth reduction in boreal trees, whereas the differing regional patterns found in temperate trees could be due to a combination of differences in eruption climate effects between regions, temperature versus moisture limited growth depending on ambient climate, and enhancement of tree light use efficiency in closed-canopy forest because of an increase in diffuse light fraction. Our findings invite additional research to clarify how regional climate and ecology modulate the effects of eruptions on tree growth and to assess the net effect of eruptions on global plant productivity. A series of annual tree carbon increment compiled from coring in plots of Harvard Forest, Massachusetts (42.5°N , 72.2°W), as well as other series for eastern North America do not show increased growth following the Pinatubo or the 1982 El Chichón eruptions. For this region, non-volcanic climate variation may be more important than any eruption effects in causing interannual variability in net primary productivity after any individual eruption.

B12F-02 1615h INVITED

Paleoflood records from anatomical tree-ring signatures

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Records derived from trees growing in temperate regions have provided annually resolved paleohydrological data that span the last several hundred or thousand years. Unfortunately, conventional tree-ring parameters are often insensitive to shorter-term hydrological fluctuations, such as floods, that occur too quickly to be recorded in ringwidth or isotopic series. Paleoflood reconstructions derived from tree rings have been more successful developing flood records using anatomical signatures (flood rings) caused by defoliation or inundation. Although paleoflood records developed from tree rings are much shorter than those developed from geological evidence, their brevity is offset by their exceptional utility for dating floods to a specific year. Like other flood proxies, flood-ring records can shed light on the past frequency of extreme floods, thereby

providing a long-term context for contemporary observations. In some situations, flood-ring records enable one to infer the magnitude of paleofloods based on analogy with more recent floods for which stage and discharge measurements are available. The annual resolution of tree rings also allows flood-ring records to provide credible evidence for synchronized flooding in separate drainage basins, and to tightly constrain linkages between extreme floods and potential forcing mechanisms. With complementary records from tributary rivers and streams, it is possible to obtain additional details concerning the relative contributions of individual sub-basins to past extreme floods. Ultimately, extended flood records derived from tree-ring data may be used to test assumptions of stationarity in annual flood series data, and to develop more accurate estimates of the probability of extreme flooding.

B12F-03 1630h

Interpreting Environmental Change and Nutrient Cycling Using Major Element and Strontium Isotope Ratios in Tree Rings

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In northeastern US forest ecosystems affected by acid deposition, calcium and other base cations have been leached from the soil exchange complex thereby increasing the possibility that calcium could become a limiting nutrient and negatively affect ecosystem health. Three of the most significant contributions of calcium to the soil exchange complex are atmospheric deposition, silicate mineral weathering, and non-silicate weathering. Strontium isotope and Ca/Sr ratios can be used to identify the relative inputs from these sources and determine whether they have changed over time. Strontium isotopic compositions and Ca/Sr ratios of tree rings hold promise for interpreting and understanding changes in calcium sources and availability in forest ecosystems. However, before tree rings can be used as a reliable archive for environmental perturbations several important issues must be resolved. These include 1) the degree of differential uptake of Ca and Sr by different tree species, and 2) the degree of translocation of Ca and Sr between growth rings. A manipulation experiment at the Hubbard Brook Experimental Forest (HBEF), NH was conducted, in which wollastonite pellets were applied to an experimental watershed. The wollastonite, with Ca/Sr and $87\text{Sr}/86\text{Sr}$ ratios distinct from sources to the soil exchange complex, serves as an environmental tracer. By monitoring the uptake of wollastonite into foliage we demonstrate that the degree of fractionation between Ca and Sr is small and that Ca/Sr ratios provide a good monitor of Ca sources to trees. Uptake into roots of selected species suggests there is not significant physiological discrimination against strontium assimilation in favor of calcium. We also explored the degree of mobility of Ca and Sr once it is incorporated into growth increments by determining the presence of the tracer in older growth increments. We developed a multi-step chemical leaching procedure to isolate a reservoir of Ca in wood that represents Ca utilized by the tree during the time of cell wall formation. Applying these methods to tree cores of sugar maple and red spruce allows us to establish a long-term chemical record, indicating that there has been a significant change in calcium sources to northern forests over the past 80 years. In conjunction with decades of foliar, forest floor, and soil chemistry data at HBEF, and one of the longest watershed water chemistry records in the world, the dendrochemical record provides a powerful addition to our understanding of past watershed chemistry.

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Dendrochemistry of base cations in red spruce: the fallacy of the passive recorder

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Chemical analysis of red spruce (*Picea rubens* Sarg.) was conducted as part of a regional investigation on