

and their feedbacks to regional and global climate conditions. Boreal and arctic regions form a complex land cover mosaic where vegetation structure, condition and distribution are strongly regulated by environmental factors such as moisture availability, permafrost, growing season length, disturbance and soil nutrients. The timing of spring thaw in particular, can influence boreal carbon uptake dramatically. With boreal forests accumulating 1% of their annual total accumulated carbon each day of the growing season, variability in timing of spring thaw can trigger total interannual variability in carbon uptake on the order of 30%. The ability to quantitatively apply multi-year observations of landscape freeze-thaw status of 1- to 2-day temporal fidelity to ecosystem process studies in high-latitude regions will allow improved assessment of modeled processes for long-term monitoring. We utilize brightness temperature measurements from the Special Sensor Microwave Imager (SSM/I) and the Scanning Multichannel Microwave Radiometer (SMMR) to examine trends in the timing of springtime thaw across the pan-boreal high latitudes since 1979. We apply a temporal discrimination technique to these data sets to determine the timing of the primary springtime thaw events across the pan-boreal high latitudes. We apply data from biophysical monitoring stations to quantify the sensitivity to surface freeze-thaw state transitions and associated vegetation biophysical processes under a variety of terrain and landcover conditions. We develop a time series of landscape freeze-thaw products at regional and pan-boreal scales across multiple years. These time series products demonstrate the highly complex spatial and temporal nature associated with these critical processes. Results show a trend toward an advance in pan-boreal springtime thaw over the past years, corroborating similar findings relating to advance in vegetation green-up. The continued capability for monitoring seasonal freeze-thaw cycles across the pan-boreal region provides a means for assessing interannual variability and, eventually, longer-term trends in ecosystem function. This work was performed at the Jet Propulsion Laboratory, California Institute of Technology, and the University of Montana under contract with the National Aeronautics and Space Administration.

B31D MCC: Level 1 Wednesday 0830h

Ecosystems in Flux: Isotopes as Indicators of Ecosystem Change I Posters (joint with A, H, OS)

Presiding: H Jahren, Johns Hopkins University; T W Boutton, Texas A&M University

B31D-0324 0830h POSTER

Examination of an Oligocene Lacustrine Ecosystem Using C and N Stable Isotopes

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Stable isotopes of C and N are used to reconstruct the fossil Oligocene (25.8Ma) ecosystem at Lake Enspel, Westerwald, Germany. Enspel was a steep-sided, deep maar lake with anoxic bottom waters. Upon drying, terrestrial and aquatic organisms sank into the sediment where they were colonized by bacteria. These bacteria quickly became fossilized, preserving morphological detail and large amounts of organic matter from the original macroorganism. Carbon and nitrogen are sufficiently preserved in these fossils to permit stable isotope analysis. Stable isotopic signatures identify several trophic levels, including primary producers (terrestrial and aquatic plants, diatoms), primary consumers (tadpoles, some insects), and secondary consumers (carnivores such as fish). Primary producers are associated with depleted $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values, primary consumers such as flies are one trophic shift higher, and fish are another shift higher. Signatures for the fish species show heavy-isotope enrichment correlated with increasing length, indicating an increasingly carnivorous diet. This study marks the first attempt

to reconstruct a complete fossil ecosystem using stable isotope analysis, and confirms that techniques used to study modern food webs can be applied to extinct webs as well.

B31D-0325 0830h POSTER

Distribution and Sources of Lignin Monomers in Late Quaternary Sediments From Southwestern Coastal Plain of Taiwan

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In an effort to understand paleoenvironmental changes of the southwestern coastal plain of Taiwan over the past 50K years, we employed molecular and stable isotope techniques to sediment cores to study shifts in organic carbon input and plant communities. Preliminary results show that, during the Holocene (the last 10K yrs), large shifts in bulk stable carbon isotope values are observed suggesting either shifts C_3/C_4 communities or changes in algal productivity. Moreover, lithologic variations in lignin monomer proxies indicate wide a variation in the degree of microbial oxidation based on elevated vanillyl Acid/Aldehyde ratios. The carbon-normalized yield of 8 vanillyl, syringyl, and cinnamyl phenols shows wide variation during periods in the late Pleistocene and Holocene. The Holocene-Pleistocene boundary exhibits a sharp change of TOC, vanillyl Acid/Aldehyde ratio, and lignin yield. However, variations still exist between cores due to different regional sedimentary environments. Studies are ongoing to relate nitrogen and sulfur cycling to organic carbon input.

B31D-0326 0830h POSTER

Soil gas ^{13}C Values and CO_2 Concentrations on the Southeast Slope of Mauna Kea: Implications for Palaeoclimate and Hydrogeology

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As part of the Hawai'i Scientific Drilling Project (HSDP), an elevational transect on the southeast slope of Mauna Kea Volcano, Hawai'i, was sampled for soil gas CO_2 ^{13}C over a one-year study interval. Our objective is to determine the principle influences on the ^{13}C values of dissolved inorganic carbon (DIC) that is contributed to groundwater recharged in the area. Groundwater DIC from the HSDP drill hole, dated to 2200 B.P., had a carbon isotopic value of -12‰ . The D/H and ^{18}O values of the water indicate that the average elevation of recharge is at 2000 m on Mauna Kea. It was postulated that this ^{13}C was controlled mainly by the photosynthetic pathway of the predominant vegetation at this elevation at the time of recharge. If this is true, the current ^{13}C values should have changed as a result of the conversion of the formerly forested Mauna Kea slopes to grassland in the past 2200 years. Preliminary results support this hypothesis. Present day ^{13}C values range from -12‰ in grasslands at 2000 m ASL to -24‰ in the lower elevation forested areas. With the soil gas values of -12‰ in the grasslands, fractionation between soil gas and bicarbonate in groundwater would cause the DIC in groundwater to have values of -4‰ today. The conversion of this area to grassland approximately 2000 years ago and the introduction of exotic C_4 grasses are assumed to be the causes of the difference, as C_3 trees have lighter values than C_4 grasses. Other areas of the transect follow predicted patterns for vegetation type. Analysis of the data is continuing in order to elucidate diurnal and annual trends in the soil gas $\delta^{13}\text{C}$ values and CO_2 concentrations.

B31D-0327 0830h POSTER

Drought Cycles in Northern New Mexico, Isotopic Evidence of Forest Stress

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Severe droughts in the southwestern United States are shown to occur about every 50 years. Accompanying these droughts, disturbance varieties such as fire or insect infestation produce ecosystem shifts in forest species composition. Specifically, in the Jemez Mountains of northern New Mexico Mountains shifts from Ponderosa pine (*Pinus ponderosa*) to pinon (*Pinus edulis*)/juniper (*Juniperus monosperma*) to juniper forests have occurred in the last 100 years. Stable carbon isotope ratios of needle tissues and cellulose from tree rings were measured to determine the periodicity and the severity of regional drought in the Jemez Mountains. Pinon and Ponderosa pines were investigated over an elevation gradient to determine the temperature and precipitation thresholds necessary to cause significant changes in water use efficiency, in isotope ratios, and in large-scale species die-off. Samples of organic $\delta^{13}\text{C}$ in whole leaf tissue were collected from pinon species from attached cohorts where a total of 7 years could be measured. The $\delta^{13}\text{C}$ of cellulose from tree ring samples were collected from both pinon and Ponderosa species where select years over the past 100 years were analyzed. During periods of intense drought, greater than 4 successive years, steady enrichments in ^{13}C were observed with highest levels of stress occurring at the lowest elevation sites. These results suggest that $\delta^{13}\text{C}$ can be used as a marker for drought in both needle and wood tissues, that the threshold for stress and large scale forest die-off occur at low elevation, and that there is about a 50 year periodicity in severe drought observed in the northern New Mexico region.

B31D-0328 0830h POSTER

Tree-ring Indices and Isotope Signatures of *Pinus ponderosa* Related to Historic Ozone Changes Outside Los Angeles

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Ozone concentrations in the Los Angeles (LA) basin were at historic highs in the late 1970s. Since that time Clean Air regulations have helped lower ozone, but little is known of the long-term vegetation responses. Extensive research has used tree-ring indices together with the physiological and environmental information stored in the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ signatures of tree-ring cellulose to understand past climates. Here, we used the forty-year ozone record from Camp Paivika, CA, the site in the San Bernardino mountains of the LA basin with both the longest record and the highest values, to determine climate versus ozone impacts on basal area increment and $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ signatures for Ponderosa Pine. Annual growth increment was significantly related to ozone and temperature but not precipitation. $\delta^{13}\text{C}$ showed the typical climatic pattern of becoming more enriched in warm dry years, but was more strongly related to ozone independent of climate effects. $\delta^{18}\text{O}$ was also enriched in warm, dry years, but was most strongly related to annual growth increment and showed no relationship with ozone. The relationship between $\delta^{18}\text{O}$ and growth is likely due to alterations in evaporative enrichment within the foliar tissues. Our results will be discussed in light of physiological processes and environmental variation responsible for alterations in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ signatures.

B31D-0329 0830h POSTER

Tracking Urban Air Deterioration in San Francisco: Carbon and Nitrogen Isotope Study of Weedy Plants.

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Stable isotopes of carbon and nitrogen have long been used as indicators of ecosystem structure and nutrient cycling in natural and anthropogenically disturbed terrestrial ecosystems. However, relatively few of these studies have targeted urban environments, where nitrogen and CO₂ emissions dramatically impact atmospheric composition. Here we present the results of carbon and nitrogen isotope analyses of herbaceous plants growing in and around San Francisco. These plants were collected mainly as part of a public outreach walking tour of San Francisco ("The Weed Walk - Concrete Jungle") sponsored by the San Francisco Exploratorium. In all cases, the plants were sampled in areas with negligible forest canopy. A consortium of species was collected at each of several distinct sites to examine the localized and regional impact of automobile traffic and proximity to the ocean on isotopic compositions of carbon and nitrogen. $\delta^{13}\text{C}$ measurements trend towards relatively light values in the range of -26 to -36 permil. In comparison, the leaves from similar types of herbaceous species in relatively unpolluted and unforested environments typically have $\delta^{13}\text{C}$ values in the range of -22 to -28 permil. The observed light carbon isotopic compositions potentially reflect input of isotopically light CO₂ emissions from fossil fuel burning, boosting atmospheric CO₂ concentrations to >10 % above background. $\delta^{15}\text{N}$ values range from +4 to +9 permil. This is substantially offset from the -4 to +1 permil values that typify vegetation in regions where nitrogen oxides from fossil fuel combustion dominate the nitrogen inputs. The nitrogen isotope compositions might suggest nitrogen contributions from a marine source (typically +6 permil).

B31D-0330 0830h POSTER

Woody Plant Invasion of Grassland: Changes in Whole-Soil Carbon Storage and Dynamics

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Woody plant encroachment into grass-dominated ecosystems has been a globally significant land cover change over the past century, but its biogeochemical consequences remain largely unquantified. In the Rio Grande Plains of Texas, grasslands and savannas dominated by C4 grasses (d13C = -14 o/oo) have undergone succession over the past 150 y to subtropical thorn woodlands dominated by C3 trees/shrubs (d13C = -27 o/oo). To evaluate soil organic carbon (SOC) storage and dynamics in these woodlands, we measured the mass and isotopic composition (d13C) of SOC in chronosequences consisting of remnant grasslands (Time 0) and woody plant stands ranging in age from 10-130 y in upland (clusters and groves) and lowland (drainage woodlands) landscape elements. Carbon storage in surface litter increased linearly from 100 g C/m² in woody plant stands less than 30 y old to nearly 500 g C/m² in stands more than 60 y old. Similarly, carbon storage in root biomass (0-30 cm) increased linearly from 400 g C/m² in remnant grasslands to more than 2000 g C/m² in some of the older (i.e. 60-130 y) woody plant stands. Increased litter and root carbon were associated with significant increases in SOC storage (0-30 cm) from 2000 g C/m² in grasslands to more than 5000 g C/m² in older woodlands. Over the past century, SOC accumulation rates (0-30 cm) have ranged from 12.5 g C/m²/y in upland clusters to 41.5 g C/m²/y in low-lying drainage woodlands. d13C of SOC at 0-15 cm decreased exponentially from -18 o/oo in grasslands to -23 o/oo in woodlands older than 60 y. At 15-30 cm, d13C of SOC decreased from -15 o/oo in grasslands to -19 o/oo in woodlands older than 60 y. These C-13 dynamics yielded SOC mean residence times of 40-80 y at 0-15 cm and 150-500 y at 15-30 cm, consistent with results from C-14 dating. Therefore, soils in this region have been a net sink for atmospheric carbon over the past century. Most of this newly sequestered carbon is stored in the upper 15 cm of the profile and has mean residence times less than

100 y. Given the geographically extensive nature of this vegetation shift, changes in SOC dynamics and storage documented here could have significance for regional and global carbon cycles.

B31D-0331 0830h POSTER

Woody Plant Invasion of Grassland: Storage and Turnover of Carbon in Soil Physical Fractions

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Woody plant encroachment is common in many grassland and savanna regions around the world. In the Rio Grande Plains of southern Texas, subtropical thorn woodlands dominated by C3 trees and shrubs (d13C = -27 o/oo) have largely replaced C4 grasslands (d13C = -14 o/oo) over the past 150 y. This vegetation change has resulted in increased soil organic carbon (SOC) storage. To elucidate mechanisms of SOC sequestration and turnover in this system, we separated soil organic matter into specific physical (size, density) fractions and determined natural d13C values of carbon in these fractions. Using a chronosequence approach, soils were collected from remnant grasslands (Time 0) and from woody plant stands ranging in age from 10-130 y. The free light-fraction (density less than 1 g/cm³) increased from 1 o/o of whole-soil weight in grasslands to 2-4 o/o of whole-soil weight in wooded landscape elements. The macroaggregate fraction (greater than 250 um) of soil in the 0-15 cm depth increment increased from less than 10 o/o of whole-soil dry weight in grasslands to more than 30 o/o of whole-soil weight in older woodlands. In contrast, the microaggregate fraction (53-250 um) decreased from 80 o/o of whole-soil weight in grasslands to 60 o/o of whole-soil weight after 80-130 y of woodland development. The decrease in microaggregates with increasing stand age likely reflects their incorporation into the macroaggregate fraction. Carbon contents (g C within a fraction per kg of whole soil) of all soil physical fractions (except free silt and clay) increased linearly with increasing woodland age, and were greatest in macroaggregates. Based on changes in natural C-13 abundance, mean residence times (1/k) for microaggregate carbon (326 y) were significantly greater than those for macroaggregate carbon (76 y), indicating that the older carbon associated with microaggregates is biochemically recalcitrant and/or physically protected. These results indicate that the interactions between SOC and soil aggregation may provide a mechanistic explanation for carbon processes and dynamics following land cover changes in terrestrial ecosystems.

B31D-0332 0830h POSTER

Woody Plant Invasion of Grassland: Lignin and Aliphatic Biopolymer Chemistry and Carbon Isotope Composition in Physical Fractions

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Significant changes in the apportionment of organic carbon in grassland and savanna soils have been documented as a result of woody plant encroachment. In the Rio Grande Plains of Texas, C4 grasslands (d13C = -14 o/oo) have undergone succession to trees and shrubs of a subtropical thorn woodland (d13C = -27 o/oo) over the past 150 y which has resulted in increased soil organic carbon storage. Large differences in the turnover times of physical fractions in this system indicate selective preservation mechanisms which may include physical protection or inherent biochemical recalcitrance. To elucidate mechanisms of SOC sequestration during woody plant succession in this system, we are investigating the chemistry and compound-specific stable carbon isotope composition of lignin and

aliphatic biopolymers in specific physical (size, density) soil fractions within a chronosequence that includes remnant grasslands (Time 0) and woody plant stands ranging in age from 10-130 y. The soil fraction data is being compared to biopolymer and isotope chemistry of the root, stem and/or leaf tissue of 20 of the dominant genus of plants in the system. Lignin phenols and suberin and cutin-derived hydroxyfatty acids are being isolated using alkaline CuO oxidation and tetramethylammonium hydroxide thermochemolysis. A comparison of the macroaggregate (greater than 250 um), microaggregate (53-250 um), and free silt and clay fractions in the oldest stand indicates that lignin is the most concentrated (organic carbon normalized values) in macroaggregates and is significantly less degraded, as determined by relative yields of oxidized and reduced lignin phenols. Additionally, the intra-aggregate silt and clay fraction from the macroaggregates contains less than half of the organic carbon normalized lignin phenols and is relatively more oxidized than what is found in the total macroaggregate pool. From these preliminary results it appears that the bulk macroaggregate pool contains the least degraded/freshest lignin of the physical fractions. This is consistent with the relatively shorter residence times determined for this fraction in this system. Continuing work includes compound specific isotope analysis of isolated lignin and hydroxyl fatty acids to elucidate biopolymer-specific turnover times which will provide important clues into the mechanisms of SOM storage and biopolymer recalcitrance.

B31D-0333 0830h POSTER

A Soil Carbon Cycle Without Life?: The Content and Residence Times of Organic and Inorganic Carbon in the Atacama Desert of Chile

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The central Atacama Desert of Chile is nearly rainless and virtually devoid of biota. Precipitation increases steadily as one moves to more southern latitudes, providing a natural experiment to assess the role of water in the soil C cycle. We have established three research sites along this gradient, where the mean annual precipitation varies from nearly 0 to about 15 mm y⁻¹. At the driest site, where plants are completely absent and soil microorganisms quite rare, trace quantities of organic C (OC) are present (~0.009 +/- 0.0038%), and OC increases slightly with precipitation (and the increasing presence of vegetation) to 0.053%. The apparent radiocarbon age of the organic matter at the driest site is exceedingly old (> 7,000 y), suggesting C cycling rates on the order of 10⁴ y. The source of the incoming C is being investigated, and may include a combination of marine aerosols and exceedingly rare cyanobacteria on the undersides of quartz clasts ("hypoliths"). Radiocarbon-based turnover times appear to increase to decadal scales with increasing rainfall, with annually cycling OC concentrated in coppice dunes (0.32% OC) and hypolith-associated soils (0.39% OC). The radiocarbon age of co-existing soil carbonate was ~12,000 years at the driest site and thus older than that of the OC, suggesting limited weathering and incorporation of modern atmospheric CO₂ with increasing precipitation. The character of the organic matter present in the soil was analyzed by pyrolysis-GC-MS. The main organic molecules released at 750°C in an inert atmosphere are benzene and formic acid. Their concentrations in the driest soil are in the ppb range, and decrease by about an order of magnitude with depth. This suggests that either the environmental conditions in the past were much more severe or else that there are slow downward fluxes of organic materials accompanied by decomposition (either biological or abiotic). In contrast, soil organic matter from the other two southern sites released an order of magnitude more pyrolysis product at depth with respect to the surface, suggesting higher C inputs and differing decomposition processes. The ratio of formic acid to benzene was highest at the driest site, indicating more oxidized organic matter. Moving south, this ratio drops rapidly. At the driest site, the high formic acid/benzene ratio appears to remain constant with depth. At the two more southern sites, this ratio is quite low in the surface and then goes up with depth, suggesting that the organic matter at greater depths is more oxidized than at the surface.

B31D-0334 0830h POSTER

Large Scale Structural Sequestration of Subsurface Soil Organic Carbon

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Aggregation of soil particles can have a profound influence on the retention and turnover of soil organic carbon. Most research on this topic has been focused on aggregates < 2 mm in diameter, thus neglecting the mega-scale structure (often 20-50 mm or greater in size) observable in situ in the field. These large soil units have the potential to create distinct spatial distributions of soil C pools that vary in both age and recalcitrance. In a 60-day controlled laboratory incubation of sieved and homogenized soil, we observed a large initial pulse of old (14C depleted) CO₂ followed by decreasing effluxes of progressively younger CO₂ in both surface and subsurface samples of an undisturbed grassland in central California. $\Delta^{14}\text{C}$ values of -147 and -596 per mil for these initial pulses from the surface and subsurface incubations, respectively, indicate a pool of potentially labile but physically protected organic matter. In subsoil ped samples (65-85 cm depth) from a similar soil, we found that the ped surfaces had significantly higher C and N percentages, C/N ratios and $\Delta^{14}\text{C}$ values than the material in the ped interiors. In fact, a $\Delta^{14}\text{C}$ value of -550 per mil for the subsurface interior C closely matched the $\Delta^{14}\text{C}$ value of the initial CO₂ pulse from the subsurface incubation experiment, lending additional support to the hypothesis that these large soil aggregates are effective in protecting otherwise easily degraded organic matter for long periods of time. The lack of clear spatial trends (for both total C and 14C) in the surface horizon samples is likely a result of frequent disruptions to soil structure due to enhanced biological mixing activity, and low residence times of entrapped organic matter. These two complementary studies demonstrate that aggregate stabilization of organic C likely occurs at all levels of a cascading scale of soil aggregates, and that large-scale subsurface physical structure is likely a far more important control on C cycling rates than previously assumed.

B31D-0335 0830h POSTER

N isotope fractionation and measures of organic matter alteration during decomposition

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Most soil organic matter (SOM) derives from plant material but there are substantial gaps in our understanding of its transformation mechanisms. Alterations that occur as SOM decays and is stabilized have proven difficult to study owing largely to its diverse initial chemical composition and stable isotope values. We examined SOM stable isotope ratios in relation to composition using solid-state ¹³C CPMAS nuclear magnetic resonance (NMR) in sequentially deeper organic and mineral horizon soil samples collected from an unpolluted ecosystem in southeast Alaska dominated by C₃ vegetation. We found that as humified carbon (C)-C not respired as CO₂ during decomposition-increased in aliphaticity (ratio of unsubstituted aliphatics to carbohydrates), it also increased in ¹⁵N (P<0.0001) but showed no clear trend in ¹³C or C:N ratio. These results imply that humification (and the concomitant stabilization of soil C) at our site resulted from microbial alteration of organics rather than from accumulation of recalcitrant compounds. The strong, and previously unreported, relation between ¹⁵N and SOM composition found at our study site suggests that degree of

SOM humification may be correlated with an increase in $\delta^{15}\text{N}$ SOM values relative to $\delta^{15}\text{N}$ for fresh litter and other source material.

B31D-0336 0830h POSTER

Differentiating Nitrification and Denitrification Sources of Nitrous Oxide Based on the Isotopomeric Composition

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Atmospheric concentrations of nitrous oxide (N₂O) are steadily increasing primarily due to microbial activity in the environment. This has prompted efforts to apportion microbial sources of N₂O to specific microbial processes. We investigated the isotopomeric composition N₂O as a possible aid in differentiating microbial production mechanisms. Isotopomer refers not only to the isotopic abundance of N₂O ($\delta^{15}\text{N}$ and $\delta^{18}\text{O}$), but also to the ¹⁵N abundance within each of the nitrogen atoms comprising this molecule. In the linear N₂O molecule, the central atom is referred to as alpha (α) and the terminal nitrogen atom is referred to as beta (β). The site preference refers to the difference between $\delta^{15}\text{N}_{\alpha}$ and $\delta^{15}\text{N}_{\beta}$. We conducted experiments with pure bacterial cultures and agricultural soil mesocosms. Four microbial pathways for the production of N₂O were investigated including hydroxylamine oxidation via autotrophic nitrifiers and methane oxidizers and nitrite reduction via denitrifiers and autotrophic nitrifiers. We used concentrated cell suspensions of a nitrifier (*Nitrosomonas europaea*), a methane oxidizer (*Methylococcus capsulatus* Bath) and a denitrifier that lacks N₂O reductase (*Pseudomonas chlororaphis*). The average site preference of N₂O produced by the oxidation of hydroxylamine by *M. capsulatus* Bath (5.5 +/- 3.5 per mil) and *N. europaea* (-2.3 +/- 1.9 per mil) was significantly different. Nitrous oxide produced by the reduction of nitrite by *N. europaea* and *P. chlororaphis* had a site preference of -8.3 +/- 3.6 per mil and -8.1 +/- 3.4 per mil, respectively. These results demonstrate that site preference can distinguish N₂O produced by hydroxylamine oxidation by two distinct organisms. Furthermore, N₂O derived by hydroxylamine oxidation differed significantly from that derived from nitrite reduction by the same nitrifying organism. Soil mesocosm experiments were used to determine that consumption of N₂O did not change the isotopomeric composition. Since the site preference of the distinct pathways differ and N₂O reduction does not affect site preference, we have demonstrated that isotopomers can be used to apportion the production of N₂O by nitrification and denitrification in agricultural systems.

B31D-0337 0830h POSTER

Nitrogen Addition Reduces Decomposition of Native Recalcitrant Soil Carbon Under Plants With High Root Lignin and Low Cell Soluble Content

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The effect of increased atmospheric nitrogen (N) deposition on long-term soil carbon (C) storage remains unclear. Both enhanced and retarded decomposition of lignin and other recalcitrant C substrates in the soil have been reported with N addition. We examined the

effect of N addition on soil C pools under 12 different grassland species planted as monoculture plots treated with 560 ppm atmospheric CO₂ concentrations, and 0 and 4 g N fertilizer m⁻² yr⁻¹ in Minnesota, USA. After 5 years of treatment we separated soil C into light and heavy fractions and used the distinct ¹³C isotopic signature of C3 plants in elevated CO₂ plots to separate the more recalcitrant native or pre-treatment C from newly formed C. As fertilizer N was labeled with ¹⁵N, we also calculated the amount of N fertilizer retained in the soil. Nitrogen addition significantly increased the pre-treatment C pool of the light soil fraction by 18% compared to plots receiving no N addition, suggesting reduced decomposition of C with added N. Added N did not affect the more stable heavy soil C fraction. In plots with added N, the pre-treatment C pool of the light fraction was especially high for plants that produced roots high in lignin and low in cell soluble content. These results suggest that high lignin content interacted with high levels of N to stimulate chemical stabilization of native soil C. The amount of fertilizer N retained in the light fraction was significantly positively related to pre-treatment soil C content, further evidence that N fertilization promoted stabilization of pre-treatment C. We conclude that plant species composition (via its effects on root lignin concentrations) determines the influence of atmospheric N deposition on the decomposition of soil organic matter under elevated CO₂.

B31D-0338 0830h POSTER

¹⁵N/¹⁴N Variation in CalCOFI Zooplankton: A 51 year history of Marine Nitrogen Dynamics and Climate Variability off Central CaliforniaGreg H Rau¹ (925-423-7990; rau4@llnl.gov)Mark D Ohman²Annelies Pierrot-Bults³¹Institute of Marine Sciences, University of California, Santa Cruz, CA 95064, United States²Integrative Oceanography Division, Scripps Institution of Oceanography, La Jolla, CA 92093, United States³Institute for Biodiversity and Ecosystem Dynamics,, Zoological Museum, University of Amsterdam, Amsterdam 2000, Netherlands

Long-term variability in marine zooplankton ¹⁵N/¹⁴N was investigated in two species of calanoid copepods (*Calanus pacificus* and *Eucalanus californicus*) and two chaetognaths (*Sagitta bierri* and *Sagitta euneritica*) sampled in the spring of selected years from 1951 to 2001 near Monterey Bay, California. No statistically significant trend in ¹⁵N/¹⁴N was detected for any of the four species, with isotopic ratios in 2001 resembling those in copepods and chaetognaths sampled from the same area five decades earlier. With respect to proposed oceanographic regime shifts in this region, heterogeneity in ¹⁵N/¹⁴N was detected only for *S. bierri* when comparing the periods 1951-1975, 1978-1998, and 1999-2001. In this species the ¹⁵N/¹⁴N in the most recent, brief period (1999-2001) averaged slightly lower than in the previous period. Three of the four species (*C. pacificus*, *S. bierri*, and *S. euneritica*) showed significant increases in ¹⁵N/¹⁴N during major El Ninos. El Nino-related enrichment in ¹⁵N could arise as a consequence of increased nitrate demand/supply at the base of the food web or advection of ¹⁵N-enriched nitrate from more southerly waters. While a range of physical and climate indices were evaluated, anomalies of ¹⁵N/¹⁴N from the long-term mean were found to be significantly related only to: i) the Southern Oscillation Index in the case of both chaetognath species, ii) a regional surface water temperature record (*S. bierri* only), iii) an index of wind-driven coastal upwelling for the surface-dwelling *C. pacificus*, and iv) variability in the Pacific Decadal Oscillation for the somewhat deeper-dwelling *E. californicus*.

B31D-0339 0830h POSTER

Nitrogen and Oxygen Isotopic Detection of Nitrate in Seawater by Chemical Conversion of Nitrate to Nitrous Oxide

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A fast, easy, and reliable method for nitrogen and oxygen isotopic detection of nitrate would be beneficial to many in the biogeochemical society. Here we

present a novel method capable of natural isotopic detection in the nM range. In addition to a fast analysis time (batch preparation in less than one hour for nitrogen isotopes), this method is capable of very low blanks (less than 1 nanomole) with sample precision of 0.2 permil for nitrogen and 0.5 permil for oxygen. The first step of the method is reduction of nitrate to nitrite by use of either spongy cadmium or UV light. UV light reduction has the advantage of a short reaction time (13 minutes), but is not capable of oxygen isotope analysis due to exchange with water. Reduction using spongy cadmium retains the oxygen isotopic signature, but requires up to 3 hours to react. Both reactions are non-fractionating with respect to nitrogen. The next step is the reduction of nitrite to nitrous oxide using either hydroxylamine or azide. The hydroxylamine has the advantage of being nontoxic, but the reaction time is 2 hours and oxygen is exchanged with water. The azide-nitrite reaction is complete in only 3 minutes and retains both nitrogen and oxygen isotopes of nitrate. The produced nitrous oxide is then purged and trapped in liquid nitrogen, then released into a capillary GC column connected to an isotope ratio mass spectrometer.

B31D-0340 0830h POSTER

Stable Isotope Analyses of Phosphate Oxygen From Micro-samples of Biological Apatite: A new Routine Procedure for Silverphosphate Micro-precipitation and the Removal of Organic Contamination

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Oxygen isotope analyses in bone and teeth of living and fossil animals are widely used for testing hypotheses about variability of diet and habitat. For the analysis of environmental or dietary changes in the past, tooth enamel has become the preferred study material, because its mineral content is higher than bone and dentine, and the relatively large size of the carbonate-apatite crystals of enamel make it more stable against *post mortem* diagenetic alteration than dentine or bone. Intra-tooth sampling of dental enamel is increasingly used for the investigation of seasonal climate variability, taking advantage of both the high correlation between an animal's drinking water and the $\delta^{18}\text{O}$ in its mineralized tissues and the incremental growth pattern of tooth enamel. The different oxygen-containing ions of bioapatite (phosphate, carbonate, and hydroxyl group) incorporate into the mineral lattice at different rates during enamel mineralization, and differ in their susceptibility against *post mortem* diagenetic alteration. In addition, it is difficult to account for the different reaction chemistries of phosphate, carbonate, and hydroxyl group using isotope analysis techniques that include all oxygen contained in the enamel (e.g., laser ablation). These problems can be addressed analyzing phosphate oxygen only. However, two major factors limit the potential of $\delta^{18}\text{O}$ analyses in dental enamel: A) the starting sample size for isotope analyses often precludes the use of small teeth or the intra-tooth sampling of a given tooth; B) Small amounts of biogenic organic material in tooth enamel (less than 1% by wt) can reduce the precision and lead to anomalous analytical results in $\delta^{18}\text{O}$ measurements on Ag_3PO_4 produced from tooth enamel. A new procedure was developed for the pre-treatment and $\delta^{18}\text{O}$ analysis of phosphate from small samples (500 μg) of tooth enamel containing organic matter. Ag_3PO_4 was precipitated quantitatively for analysis of $\delta^{18}\text{O}$ phosphate using a Thermoquest-Finnigan TC/EA coupled to Delta^{Plus} XL. A sodium hypochlorite sample pre-treatment step was determined to remove organic matter quantitatively without altering the isotopic composition of the phosphate oxygen. The reproducibility of $\delta^{18}\text{O}$ values for pretreated samples (0.2-0.3 ‰/‰, 1 σ) is much better than for samples without pre-treatment (1.2 ‰/‰, 1 σ). Phosphate oxygen isotope standards processed using this technique gave measured values indistinguishable from the standard composition, demonstrating the accuracy of the new technique.

B31D-0341 0830h POSTER

A Time Series Investigation of the Oxygen Isotopic Composition of Dissolved Inorganic Phosphate in Monterey Bay Seawater

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Phosphorous is an essential and limiting macro-nutrient for productivity in marine ecosystems. Because the P-O bond in phosphate is resistant to inorganic hydrolysis and the fractionation and exchange of oxygen isotopes will only occur due to intracellular biological cycling, the oxygen isotopic composition of dissolved inorganic phosphate (DIP) in seawater may be used as a tracer for modern phosphate recycling in aquatic ecosystems. The degree of disequilibrium between the $\text{d}18\text{O}$ of DIP and that of the surrounding water will act as a proxy for the extent of phosphate recycling through the biomass in a particular system. A time series investigation of a dynamic system such as the Monterey Bay could indicate how ecosystems vary the extent of phosphate turnover as the system becomes nutrient stressed following a bloom period. The nutrient dynamics in the Monterey Bay vary temporally and are characterized by seasonal upwelling from March to September which supplies nutrients to the surface waters and sustains high productivity during these months. We conducted monthly depth profiles for a year at MBARI stations C1, M1 and M2 to assess the variation in $\text{d}18\text{O}$ of DIP over the course of the onset of the upwelling season and less productive seasons which follow. The results of this time series investigation were compared to estimates of primary productivity, chlorophyll concentrations, temperature, salinity, and nutrient concentrations to determine if phosphate turnover varies with these seasonal ecosystem changes and if during periods of higher nutrient availability phosphate is utilized less efficiently than during periods of lower nutrient availability.

B31D-0342 0830h POSTER

Sulfur Biogeochemistry and Isotope Fractionation in Shallow Groundwater of Owens Dry Lake, California

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The redox status of hypersaline, strongly alkaline groundwaters at Owens Dry Lake was investigated to help guide mitigation efforts for attenuating dust generated from the dry lakebed. Shallow (<1 m), anoxic groundwaters have been identified as a major limitation to vegetation establishment on the lakebed due to the inability of roots to grow in anoxic conditions. Previous work indicates that sulfate reduction is the dominant reaction regulating the redox status of shallow groundwaters. The purpose of this study was to evaluate sulfur biogeochemistry and formation of solid-phase sulfides in the shallow groundwater/sediments using selective sulfur speciation techniques coupled with isotopic measurements. In addition to groundwater and subsurface sediment samples (1-2 m depth) at sites representative of different groundwater pathways, selected sediment samples at 5 different depths (from oxic to anoxic layers) were collected. Sediment samples were examined for monosulfide, pyrite, sulfate, organic sulfur, and total sulfur. Organic sulfur was less than 0.01% of the total, and pyrite was the predominant sulfur-bearing phase below the groundwater capillary zone (~20cm depth) where anoxic conditions were developed. The concentration of monosulfide and pyrite were less than detection limits above

the capillary zone as these unsaturated layers were exposed to oxygen. High concentrations of dissolved sulfide (4.81 to 134.7 mg/L) and low concentrations of dissolved Fe (generally <0.5 mg/L) indicate that the availability of Fe limits pyrite formation. The high values (~50‰) of isotopic fractionations between $\delta^{34}\text{S}_{\text{pyrite}}$ and $\delta^{34}\text{S}_{\text{sulfate}}$ ($\Delta_{\text{sulfate-pyrite}}$) in anoxic zones suggest that bioavailability of organic carbon is a limiting factor for the reduction of sulfate. The values of $\Delta_{\text{sulfate-pyrite}}$ along the hydrologic flowpath indicate that the isotopic fractionations were significantly correlated with dissolved sulfate concentration, which was strongly controlled by evaporation. This indicates that spatial variations in the concentration of dissolved sulfate due to evaporation can be reflected in the pyrite content of sediments in groundwater. The important role of evaporation on the concentration of sulfate in groundwater was confirmed using hydrogen and oxygen isotope values of pore fluids.

B31D-0343 0830h POSTER

Analysis of growth and tissue replacement rates by stable sulfur isotope turnover.

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Stable isotope analysis has become a powerful tool to study animal ecology. Analysis of stable isotope ratios of elements such as carbon, nitrogen, sulfur, hydrogen, oxygen and others have been used to trace migratory routes, reconstruct dietary sources and determine the physiological condition of individual animals. The isotopes most commonly used are carbon, due to differential carbon fractionation in C3 and C4 plants, and nitrogen, due to the approximately 3‰ enrichment in ^{15}N per trophic level. Although all cells express sulfur-containing compounds, such as cysteine, methionine, and coenzyme A, the turnover rate of sulfur in tissues has not been examined in most studies, owing to the difficulty in determining the $\delta^{34}\text{S}$ signature. In this study, we have assessed the rate of sulfur isotopic turnover in mouse tissues following a diet change from terrestrial (7%) to marine (19%) source. Turnover models reflecting both growth rate and metabolic tissue replacement will be developed for blood, liver, fat and muscle tissues.

B31E MCC: Level 1 Wednesday 0830h

Regional-Scale Isotopic Interactions Between the Biosphere and the

Atmosphere I Posters (joint with A, H, OS)

Presiding: M J Kohn, University of
South Carolina; J van Haren,
Columbia University Biosphere 2Center

B31E-0344 0830h POSTER

A New Perspective on the Temperature-Dependence of Stable Isotopes in Modern Precipitation

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Distillation of water vapor from the atmosphere is primarily temperature-dependent, as illustrated by the well-known correlation between the stable isotope composition of precipitation and temperature. However, reevaluation of modern precipitation, temperature, and isotope data indicates major errors in the assignment of temperature dependencies. This has a profound impact on use of stable isotopes of precipitation for ecosystem studies, models of atmospheric circulation, and continental paleoclimate investigations. Past analysis has