decades to centuries. The 8,500 ha Sylvania Wilderness in the upper peninsula of Michigan is one of several large tracts of old-growth forest in the Midwest. Trees range from 0-350 years old. Primary species are sugar maple, eastern hemlock and yellow birch. Catastrophic disturbance is rare. A research plot near the wilderness was established in late 2001 to measure the net ecosystem exchange (NEE) of carbon and water using eddy-flux, component flux and biometric methods. This site is part of the Chequamegon Ecosystem Atmosphere Study (ChEAS, http://cheas.psu.edu), a loose affiliation of researchers conducting carbon and water research in northern Wisconsin and upper Michigan. Another similar research plot within ChEAS and not far from Sylvania is the Willow Creek mature uplands site. This forest is about 70 years old and the primary species are sugar maple, basswood and green ash. The site had presettlement old-growth vegetation similar to what is currently seen in the Sylvania Wilderness. Thus, the carbon exchange seen at Sylvania may be representative of carbon uptake at Willow Creek had it not been logged in the early 20th century, and may also represent the future (or past) carbon uptake for similar forests in northern Wisconsin/upper Michigan. Initial results from 2002 show that both Sylvania and Willow Creek were sinks of carbon, though the annual NEE of carbon at Sylvania was only -72 gC/m2/yr, while it was -447 gC/m2/yr at Willow Creek. The lack of carbon balance at the old-growth site may be caused by growth enhancement due to carbon/nutrient fertilization, climate warming, or recent local-scale disturbances. A standard moving-window Arrenhius-style temperature-nighttime NEE relationship was used to separate total ecosystem respiration from gross ecosystem production (GEP). Total annual respiration was much greater at Sylvania (965 gC/m2/yr) than Willow Creek (667 gC/m2/yr), while GEP at Sylvania (1045 gC/m2/yr) was only slightly smaller than Willow Creek (1136 gC/m2/yr). The largest differences in respiration between the two sites occurred in early summer, whereas the largest difference in GEP occurred in late summer. The observed differences between the two sites matches well with theory. Ecosystem respiration is expected to increase steadily with stand age while gross ecosystem production is expected to increase rapidly as new species are established, but eventually level off. Current ongoing component flux measurements will help determine the mechanisms for the observed differences in carbon uptake at the two sites and provide insight on the causes of declining carbon exchange with stand age.

### B52D-05 1455h

## Pulse Effects of Soil Respiration After Rain Events in California


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We observed pulse effects of soil respiration following the first rain and second rain after the dry season in California savanna and forest ecosystems in 2002 and 2003. Soil respiration was measured by three different methods: soil CO2 profile measurements using solid-state CO2 sensors buried in several depths of soils, under-story eddy covariance measurements, and chamber measurements. In addition, we conducted laboratory soil incubation experiments and in situ watering experiments to simulate rain events to observe the pulse effects of soil respiration. The results indicated that soil microbes immediately responded to the rain events. The time lag is less than an hour. The pulse CO2 efflux was about 5-10 times larger than the efflux before the rain. Spatially, soil respiration under trees has smaller pulse than that in the open area. Surface soils provide more CO2 sources and more contribution to the pulse than deep soils. The pulse after the first rain was more significant than that after the second rain, probably due to the decrease in the labile carbon content. The pulse effects also influence the seasonal pattern of soil respiration. It is suggested that soil respiration models may need to consider these pulse effects of soil respiration.


### B52D-06 1510h

## Annual CO2 budget at arctic wet sedge tundra in Barrow and the contribution of winter fluxes


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Although the longer winter period in the arctic affects annual CO2 budget, there have been few direct flux observations because of the sever climate. We measured CO2 and energy fluxes by eddy correlation technique and the micrometeorology at wet sedge tundra in Barrow, Alaska from 1999 spring. The data obtained continuously provided huge upward fluxes during snow-covered period, which occurred during blizzard events. The measured upward fluxes during the strongest blizzard event in mid winter showed CO2 source of 198 g CO2 m-2, 12 MJ/ m-2 and16 MJ/ m-2 for sensible and latent heat fluxes. If the fluxes were facts, which might be large contributions on annual carbon and energy budgets. We analyzed the fluxes and the micrometeorology detailed and revealed that the upward fluxes in mid-winter resulted in sublimation during blizzard, thus the huge upward fluxes in winter were thought to be apparent, especially CO2 efflux was thought to be unpractical flux converted from carbonic acid in the snow. Average winter respiration between 1999-2002 (upward CO2 flux during October to May) was around 55 gC m-2 which was almost the same as ecosystem respiration during the growing period (June-September). The annual CO2 budget was sink of 16-102 gC m-2, in which the large deviation among three years resulted in different CO2 sink levels in growing periods caused by different climate in each year.


### B52D-07 1525h

## Evidence of a Positive Warming Effect on Boreal Productivity Derived From a 11-year Air CO2 Concentration Record at Fraserdale


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An 11-year long (1990-1996, 1999-2002), hourly air $CO_2$ concentration record measured on a 40-m tower at Fraserdale, northern Ontario, is used to retrieve information on the carbon cycle of boreal ecosystems at the landscape level. Using a model, the effects of ecosystem metabolism and atmospheric diffusion on the hourly $CO_2$ concentration are separated, and daily ecosystem respiration ($R_e$) and gross primary productivity (GPP) are estimated. Both $R_e$ and GPP increased with increasing air temperature. As the mean air temperature in the growing season (May to October) varied from 10.6 to 13.2°C within the 11-year period, seasonal mean GPP varied from 3.4 to 5.3 gC $m^{-2}d^{-1}$ and $R_e$ from 3.2 to 3.9 gC $m^{-2}d^{-1}$. The temperature sensitivity is higher for GPP than for $R_e$ because of additive direct and indirect warming effects on productivity. Faster nutrient mineralization in soil at higher temperatures is considered to be the main indirect factor according to model simulations. As the footprint area of the concentration measurements is of the order of $10^2$-$10^4$ $km^2$, the methodology allows for evaluation of the collective effects of climate change on ecosystems at the landscape level consisting of forests of different ages, species and densities as well as non-forest cover types. The atmospheric diffusion model only considers the vertical diffusion processes in the surface and mixed layers in both daytime unstable and nighttime stable conditions. In hourly simulations, such a model is in error under advection conditions associated with synoptic weather systems, but when averaged for ten-day periods, the error in the simulated $CO_2$ is less than 0.6 ppmv. The methodology of deriving fluxes from concentration was tested against a tower flux site in a black spruce forest in Saskatchewan for the year 1998. The correlation coefficient was 0.86 between concentration-derived daily GPP and those derived from eddy covariance flux measurements. When averaged for 10 days, the coefficient increased to 0.94.

URL: http://www.geog.utoronto.ca/info/facweb/Chen/Chen%27s%20homepage/home.htm


# B52E MCC: 3014 Friday 1600h

## Estimating Terrestrial Carbon, Water, and Energy Fluxes From Site to Region VI *(joint with A, H)*

***Presiding:*** **M Falk,** University of California, Berkeley**; J Wang,** Massachusetts Institute of Technology**; P Thornton,** National Center for Atmospheric Research

### B52E-01 1600h

## The Influences of Fresh Water co2 Effluxes and Mesoscale Circulations on Regional Carbon Balance in the Tapajos Region, Para, Brazil


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We have investigated mesoscale variations of atmospheric co2 over a heterogeneous landscape of forests, pastures, and large rivers during Santarem Mesoscale Campaign (SMC) during August 2001. We simulated the variations of surface fluxes and atmospheric concentration of co2 using the CSU Regional Atmospheric Modeling System (RAMS) on 4-level nested grids which including a 1-km finest grid centered on the Flona Tapajos. Surface fluxes of co2 were prescribed in the model using idealized diurnal cycles over forest and pasture vegetation, and over surface water using a value suggested by in-situ measurements in the Amazon River. Heterogeneous vegetation types were derived from the 1-km International Geosphere-Biosphere Programme (IGBP) land-cover dataset version 2.0. Our simulation ran from 1 through 15 August 2001, which was concurrent with our SMC. The results demonstrated that the local topography, the roughness length, the "T" shape juxtaposition of Amazon and Tapajos Rivers, and the resulting horizontal and vertical wind shears, all facilited the generation of local mesoscale circulations. The explanation for the mechanisms producing the lower level convergence line on the east bank of Tapajos River during the strong trade-wind days will also be presented. Meanwhile, we investigated the effects of surface water co2 effluxes on the regional carbon balance. The simulations with and without specifying co2 fluxes from the rivers and inundated land were performed. The result demonstrated that surface water co2 fluxes modify simulated co2 concentrations, especially at night. We are currently collecting and processing SMC measurement data, and hope that our modeling study can help the interpretation of [co2] distribution observed by towers and light aircraft.


### B52E-02 1615h

## Assimilation of Remotely Sensed Data into the Biome-BGC Ecosystem Model to Improve the Prediction of Energy and Carbon Exchange in Southwestern Mountain Island Forests


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Mountain island forest ecosystems populate high-altitude areas in the semi-arid southwestern U.S. and northwestern Mexico. In these regions, on average, the precipitation input exceeds the evapotranspiration loss. Therefore, they represent the primary source area for sustainable water resources, as well as making a major contribution to the regional carbon balance. During 2002 a 30-m tall micrometeorological tower was installed at a sky island forest site in the Santa Catalina Mountains, near Tucson AZ in order to characterize the surface exchanges of water, energy, and carbon. Measurements to date indicate that the surface fluxes are very sensitive to water status, for example, stomatal functioning totally closed down during the premonsoon period in 2002. Initial studies with the Biome Biogeochemical model (Biome-BGC) using driving data measured in the Santa Catalina Mountains provide reasonable simulations of the behavior of the mountain island forest. In order to obtain a regional estimate of the carbon exchange using a model such as Biome-BGC accurate estimates of the distributed forcing data particularly the precipitation are required. Alternatively, an estimate of the soil water status and the leaf area index can be used to improve model predictions. TERRA-MODIS leaf area index and fraction of photosynthetically active radiation (FPAR) are both sensitive to drought stress. Time periods during which there is a marked and sustained decrease in FPAR are shown to be symptomatic of a sustained period of low soil moisture that started 10-20 days earlier. Under these conditions the soil moisture status in Biome-BGC can be set to an arbitrary low value. Initial modeling studies demonstrate significant improvement in the prediction of surface exchange when using FPAR to diagnose periods of water stress.

## B52E-03 1635h

### Integration of MODIS-LAI with Sim-CYCLE to Estimate the Net Primary Productivity

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Net primary production (NPP) is a key component of the global carbon cycle. Among the pools and fluxes that make up the cycle, NPP accounts most of the annual carbon fluxes between the atmosphere and biosphere. To improve our understanding and estimating the NPP accurately at various spatial and temporal scales, there is a need for integration of multiple, complementary and independent methods and datasets. In this context, an ecosystem model plays an important role in synthesizing such desperate time/space data into single coherent analysis of terrestrial carbon fluxes. However, such models require a large number of biophysical and climatic parameters over a large area and their applicability to operational level is often limited by the fundamental drawback of large input parameter requirements. This is especially true for the parameters describing vegetation composition and structure, such as leaf area index (LAI), which is generally highly variable over space and time, and difficult to measure with conventional methods. However, recent advances in remote sensing, both in terms of new sensors (e.g., MODIS) as well as algorithm development for data processing have shown a promising future and now it is possible to do near real-time monitoring of the important biophysical parameters of vegetations like LAI to input into an ecosystem model. The current study aimed at the possibility of integrating remote sensing data to a processed based ecosystem model driven by conventional data. The ecosystem model selected for this study is Sim-CYCLE due to its portability for integrating data from different sources. Sim-CYCLE model is based on the dry-matter production theory and integrates ecophysiological findings into a simple scheme of plant growth to achieve the scaling-up from single-leaf to canopy level. The LAI derived from MODIS sensor (MODIS-LAI) was integrated with Sim-CYCLE and the model was renamed as MOD-Sim-CYCLE. Global annual NPP was estimated as 59.6 Gt C yr-1 by MOD-Sim-CYCLE, whereas it was 62.7 Gt C yr-1 in case of Sim-CYCLE. An intercomparison of LAI and NPP for world's major ecosystems was made for MOD-Sim-CYCLE and Sim-CYCLE. Differences both in magnitude and seasonality were observed in between MODIS-LAI and Sim-CYCLE simulated LAI for each biome. However, MOD-Sim-CYCLE LAI showed seasonality very accurately, synchronising with NPP and provided information on actual phenological conditions of the vegetations on the ground. A high correlation was also found between observed NPP and MOD-Sim-CYCLE NPP.

## B52E-04 1650h

### Carbon Cycle and Vegetation Dynamics in the GFDL-Princeton University Coupled Atmosphere-Biosphere Model

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Modeling global interactions between the atmosphere, hydrosphere and biosphere continues to pose a significant challenge, because of the tight and complex coupling of flows of water, energy, greenhouse gases, and ecosystem dynamics. We developed a comprehensive dynamic land surface model (LM3) able to simulate carbon and vegetation dynamics on time scales from minutes to centuries, as well as the exchange of water and energy among the land, LM3 predicts carbon dynamics in vegetation and soil in response to environmental conditions (weather, climate and soil type), ambient concentration of CO2, natural disturbances (e.g. fire), and anthropogenic land use changes (e.g. deforestation, agricultural cropland abandonment and forest management). A suite of the historical 300 years land cover change scenarios (developed at University of New Hampshire) is used to represent direct anthropogenic forcing on the terrestrial carbon system. Here we analyze the behavior of LM3 forced with observed atmospheric data and coupled with GFDL atmospheric circulation model AM2. The series of experiments indicates that our model adequately simulates climatic gradients of net primary productivity (NPP), leaf area index (LAI), biomass accumulation, evapotranspiration, and runoff. Additionally, analysis of the simulations suggests that anthropogenic land use has been a major forcing on the terrestrial carbon cycle, with large sources of CO2 caused primarily by deforestation and timber harvesting in the current tropics and past north temperate zone, and large current north temperate sinks caused primarily by secondary forest growth.

## B52E-05 1710h

### Linking Ocean-Atmosphere Dynamics to Precipitation-Vegetation Covariability

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Variability in precipitation regimes at seasonal and longer time scales strongly influences ecosystem dynamics in arid and semi-arid regions. We use time series of global precipitation and satellite normalized difference vegetation index (NDVI) data to analyze joint spatial and temporal variability between terrestrial ecosystems and precipitation regimes. Accumulated monthly rainfall anomalies are quantified using a standardized precipitation index (SPI), which provides a better measure of ecologically significant precipitation excess or deficit at growing season time scales relative to monthly precipitation data. Results from canonical correlation analysis reveal geographically extensive patterns of joint NDVI-SPI variability suggestive of strong climate-biosphere coupling. Further, leading modes of covariability are shown to be related to large-scale ocean-atmosphere circulation anomalies. These results illustrate the global extent and sensitivity of ecosystems susceptible to climate change-induced perturbations in precipitation regimes.

## B52E-06 1725h

### Can we detect interannual variability of summertime terrestrial photosynthesis from climatic and hydrological markers?

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Because plant physiology controls simultaneously the exchanges in carbon, energy and water between land surface and atmosphere, numerous climate variables are modified when changes in photosynthesis occur. Numerous models simulations or observations studies have already shown that a change in vegetation can strongly impact climate variables such as DTR (Diurnal Temperature Range) or Bowen ratio. We suggest that these atmospheric signals register not only vegetation's strong influence on climate, but they also constitute powerful proxies from which changes in photosynthesis activity could be quantified. We propose: (1) to identify the physical variables that can be used as "markers" of summertime photosynthesis variability using two long, pre-industrial simulations performed with the CCSM NCAR coupled global climate-carbon model; (2) to test the conditions under which the markers can be used; (3) to add a new dimension to this analysis in exploring ground-based and/or satellite measurements.

B

## B52E-07 1745h

### Mission Design for Continental-Scale Carbon Cycle Applications

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Carbon cycle scientific requirements in both land and ocean studies point toward the need for multiple spectrally detailed observations per day. For terrestrial research, accurate estimates of carbon, water and energy (CWE) exchange between the terrestrial biosphere and atmosphere are needed to identify the geographical locations of carbon sources/sinks and to improve regional climate models and global climate change assessments. It is an enormous challenge to estimate CWE exchange from the infrequent temporal coverage provided by most polar-orbiting satellites, and without benefit of spectral indices that capture vegetation responses to stress conditions that down-regulate photosynthesis. Physiological status can be better assessed with spectral indices based on narrow (<10 nm) bands. Sensors that can measure CWE exchange would also provide accurate biomass observations, although geosynchronous platforms are not required to observe the slowly changing land biomass and biomass change. A hyperspectral instrument (400-1000 nm) would enable improved estimates of seasonal and annual terrestrial productivity, using narrow band and red edge indices not available with current of near-future operational satellites. The overall goal for geosynchronous ocean observations is to predict the variability of carbon uptake in the ocean, and thereby evaluate its role in climate change scenarios. In the plan for developing new observations, we need to: 1)continue to improve estimates of ocean productivity; and 2 expand the emphasis of coastal ocean processes and specific regions of critical importance. Remote sensing of the coastal ocean represents a unique challenge due to the small-scale spatial variability and elevated concentrations of dissolved organic carbon, detritus and chlorophyll, which are difficult to distinguish, because they

absorb light intensely in the blue spectrum. Observations in the ultraviolet are essential to improve our capability to distinguish these ocean constituents. A hyperspectral instrument design capable of observing in the ultraviolet, in addition to the visible and near infrared spectrum, is essential to investigate the variability, dynamics and biogeochemical cycles of the world's coastal and open ocean regions. For both terrestrial and ocean carbon cycle science objectives, a hyperspectral geostationary sensor should enable the development of new remote sensing measurements for important but as yet unobservable variables, and with the overall goal of linking both terrestrial and ocean carbon cycle processes to climate variability. The GSFC Carbon Team has been pursuing a geosynchronous hyperspectral instrument, which would revolutionize our knowledge of biological processes on land, in the ocean, and along the coast by providing multiple, diurnal coverage. Preliminary studies in Goddard's Instrument Synthesis and Analysis Laboratory indicate that we can meet many of our science requirements: full spectral coverage (360-1000 nm); narrow bandwidths (5-10 nm); adequate ground resolution (100-200 m); and continental-scale coverage 4-6 times per day; all the while achieving a signal to noise ratio of between 500 and 1000 to 1. An innovative and bold focal plane design and a large mirror (1.8 meter diameter) will be required.

## B52F MCC: 3002 Friday 1600h

### Sulfur and Isotopic Biogeochemistry

*(joint with A, H, OS)*

***Presiding:*** **S Mylon,** Environment School, Yale University**; J H Scott,** Carnegie Institution of Washington

### B52F-01 1600h

#### Relative Changes in $C_3$ and $C_4$ Biomass Recorded by Carbon Isotopes of Lipid Biomarkers in the Maya Lowlands of Petén, Guatemala

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Forest disturbance in the Petén region of northern Guatemala, beginning approximately 3000 cal yrs BP, was associated with the agricultural practices of the Maya. Expansion of the Maya civilization during the Preclassic and Classic periods was accompanied by widespread deforestation of Petén watersheds and accelerated rates of soil erosion. Palynological data from the Petén region suggest the near elimination of high forest taxa during the period of Classic Maya occupation. The validity of pollen records has been questioned, however, because they represent only a small percentage of tropical vegetation that is pollinated by wind. To estimate changes in the proportion of $C_3$ to $C_4$ vegetation in the Maya forest, we measured the $\delta^{13}$C of long chain *n*-alkanes ($C_{29}$ and $C_{31}$) produced by higher terrestrial plants in a 4.1-m sediment core from Lake Sacnab, Guatemala. Deforestation during the period of Maya occupation is reflected in sediments cores by a distinct, clay-rich interval (termed the "Maya clay") that is characterized by low magnetic susceptibility and low organic carbon content. The $\delta^{13}$C of long chain *n*-alkanes average -28$^{o}/_{oo}$ within the Maya clay, and decreases by 10$^{o}/_{oo}$ above the clay unit following the demise of the Classic Maya civilization in the 9$^{th}$ century A.D. Our results suggest that vegetation was dominated by $C_4$ biomass during the Classic Maya period and is consistent with previous palynological interpretations. Reforestation following the demise of the Classic Maya is apparent in the pollen and compound-specific $\delta^{13}$C records and indicates a switch back to a $C_3$ dominated ecosystem once human pressures were curtailed. Compound-specific $\delta^{13}$C analyses of biomarkers in Lake Sacnab sediment provide further evidence that the Maya had a profound impact on their lowland neotropical environment.

### B52F-02 1615h

#### Carbon-Isotopic Analysis of Individual Pigments by HPLC-Moving Wire-IRMS

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We have developed a method for directly analyzing the carbon isotope ratios of individual pigments, including chlorophyll (chl) and its derivatives, by coupling a high-performance liquid chromatograph (HPLC) to an isotope-ratio mass spectrometer (IRMS) via a novel moving-wire' interface. Pigments were separated on a reversed-phase C18 column, using a binary gradient modified from Airs et al. (2001, J. Chrom. A 917, 167-177). The HPLC effluent was dried onto a continuously-spooling nickel wire, and the involatile sample residue was combusted to $CO_2$ and transferred to the IRMS for isotopic analysis. Replicate analyses of a standard solution yield precision for $delta^{13}$C of better than 0.2$^{o}/_{oo}$ for injections containing 5 $\mu$g of chl-a. A five-fold improvement in sensitivity should be attainable using capillary HPLC to further reduce solvent volumes. The biomarker potential of tetrapyrrole pigments, combined with the geochemical information recorded by isotopic compositions, makes this combination a potent tool for biogeochemical studies. As a demonstration, we analyzed chlorophyll degradation products in sediments from a lake and a salina. First, compounds derived from bacteriochlorophylls (bchl)-c and -d were extracted from sediment cores taken at Kirisjes Lake (Larsmann Hills, Antarctica). These pigments are products of green sulfur bacteria and indicate the presence of an anoxic photic zone. The $\delta^{13}$C values of bchl-related compounds are near -25$^{o}/_{oo}$. Using published fractionations for *Chlorobium* species to extrapolate, dissolved $CO_2$ in Kirisjes Lake probably had a $\delta^{13}$C value of -12 to -21$^{o}/_{oo}$ and was strongly influenced by the recycling of organic carbon, possibly including methane. Second, compounds derived from chl-a, bchl-c, and bchl-d were isolated from sediments taken below a living microbial mat in the hypersaline les Salines de la Trinital (South Catalonia, Spain). The sediments contain visible remnants of past microbial mats and pigment distributions that indicate the major primary producers have been cyanobacteria and green bacteria. Components derived from chl-*a* have $\delta^{13}$C values of about -9$^{o}/_{oo}$, and are derived mainly from cyanobacteria that lived near the surface of the mat. We estimate that dissolved $CO_2$ used by those cyanobacteria had $\delta^{13}$C near +11$^{o}/_{oo}$. Such a strongly enriched value would likely result from the drawdown of dissolved $CO_2$ by vigorous photosynthesis. In contrast, components derived from bchl-c and bchl-d have $\delta^{13}$C values ranging from -15 to -19$^{o}/_{oo}$, indicating dissolved $CO_2$ with $\delta^{13}$C of -2 to -12$^{o}/_{oo}$ and again suggesting a strong role for recycled organic carbon. These differing estimates of $CO_2$ isotopic composition likely reflect the different microhabitats of cyanobacteria (aerobic mat surface) versus green sulfur bacteria (lower, anoxic levels) and can be used to infer the biogeochemical structure of the mat community.

### B52F-03 1630h

#### Thiols in a Connecticut Stratified Freshwater Lake

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Thiols are an important class of dissolved reduced sulfur (DRS) species in aquatic environments. They are generally formed from biological processes or during diagenesis of biogenic matter. Thiols can affect the biogeochemistry of B-type metals as they form strong complexes that influence trace metal speciation, bioavailability and toxicity. While current literature focuses on the biogeochemistry of thiols in marine systems, little is known about the biogeochemistry of thiols in oxic freshwaters. We chose to study thiols in Linsley Pond a stratified freshwater lake that has been extensively studied by Hutchinson. Our goals were to identify and quantify the range of thiols present throughout this small lake. Additionally, we hoped to discern the environmental factors that influence the production and distribution of thiols in the water column, and to evaluate importance of thiols in trace metal speciation. To identify and quantify various thiols in freshwaters, we adopted a sensitive and selective analytical method, which involves precolumn fluorometric labeling coupled to high performance liquid chromatography and sensitive fluorescence detection. Using this method, our analytical detection limit is below one nanomolar. Among others, two thiol species were observed in Linsley Pond: 3-mercaptopropionic acid (3-MPA) and glutathione (GSH). 3-MPA exists in both oxic and anoxic water layers at nanomolar levels, and increases from surface to bottom. GSH is only detected in subsurface layer and co-varies with Chl a, indicating possible biological sources of GSH in these layers. There is a third, unidentified thiol species which is currently under investigation. The unidentified thiol species appears only in anoxic lake waters, and tests indicate that it is not PC2 (phytochelatin with 2 glutamic acid-cysteine units). Throughout the water column, concentrations of all three thiols are greater in whole water samples than in the dissolved phase (0.45 um).

### B52F-04 1645h INVITED

#### Determination of Strong Metal Ligands (S(II-))in Natural Waters

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Reduced sulfide (S(II-)) ligands have been measured in oxic freshwaters at 1-100s nM. "Group B" metals, such as Ag(I), Hg(II), Cu(I) and Pb(II) bind strongly to S(II-) ligands. Their role in aqueous metal speciation and suppression of metal toxicity make S(II-) ligands an important analytical challenge. S(II-) is probably stabilized in oxic environments as metal-sulfide (M-S) clusters within natural organic matter (NOM). S(II-) species are measured by Cr(II) reduction of M-S, acid reaction, purge and trap to capture H2S and measurement as the methylene diamine complex (CRS). But CRS may also detect other sulfur species. Silver is an excellent probe metal for determination of strong ligand sites(SLS)in NOM. A competitive ligand method, using Ag(I), is demonstrated. The bound Ag-ligand and the "free" silver ion concentration are measured during the titration. The total strong ligand (Lt) is determined by a Grans' approach. These values are used to determine the (Lt) and the conditional binding constant, K'. Measured Lt concentrations match CRS concentrations, and conditional stability constants for a 1:1 M-L stoichiometry range from log K'= 11+ to 13, consistent with known Ag-S(II-) values. Furthermore SLS and Lt correlate with water-effect ratios (WERs) for silver

### B52F-05 1700h

#### Metal-sulfide species in oxic waters: Complexes, clusters, or colloids?

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A weight-of-evidence approach is employed to characterize metal-sulfide species that have recently been suggested to be present in oxic waters. Sulfide in synthetic Cd-, Zn-, Pb-, Cu-sulfide solutions persists in oxic waters for a prolonged period of time (2 to more than 10 weeks) whereas it is oxidized rapidly in Fe-, Mn- and Ni-sulfide solutions. Direct mass spectrometric (MS) analysis and transmission electron microscopic (TEM) analysis revealed that the metal-sulfide species resistant to oxidation in oxic waters are not soluble molecular nanoclusters as suggested previously; instead, they are a mixture of truly dissolved metal-sulfide complexes and dynamic metal-sulfide colloids. The morphology and size of the colloids change significantly with time. Nanomolar to sub-micromolar levels of acid-volatile sulfide (AVS) and chromous-volatile sulfide (CVS) were measured in oxic surface waters of