carbon and nitrogen cycling and the responses of vegetation physiology, structure, and distribution to climate, atmospheric CO2, nitrogen deposition, and land use change on time scales of minutes to centuries. All processes are unified through a consistent conceptual structure: the vertical attenuation of light through the plant canopy. This attenuation is responsible for the biophysics of spatial variation in photosynthesis and stomatal conductance, the land surface albedo, the biochemical partitioning of nitrogen to photosynthetic and non-photosynthetic pools, and the long-term biogeographical dynamics of competition between plants for light and soil resources. The new biophysical model of photosynthesis and plant canopy gas conductance uses simple parameterizations derived from a ground-based network of water, carbon, and energy flux measurements, and incorporates realistic responses by vegetation type to atmospheric humidity, light (consistent with photosynthetic nitrogen), and temperature. Results include: significant improvement in the GISS GCM's calculation of surface temperatures; realistic annual global gross primary productivity of 116 Gt-C for the current climate; response to doubled atmospheric CO2 concentrations increasing CO2 uptake by 48%, and surface temperatures in some regions by up to 2 °C due to stomatal closure. The model of individual plant growth includes a mechanistic treatment of carbon and nitrogen allocation, morphological changes with development and environment, and process-based foliage dynamics. The model has been tested off-line and is being implemented within the GISS GCM. Prognostic albedos will be obtained from a fast, analytical calculation that can account for different levels of clumping of foliage and plants. Disturbance and vegetation competition will be handled through a theoretically sound approach that overcomes computational challenges by solving for these individual-based phenomena as plant size- and gap age-structured ensemble behaviors. The above improvements advance the science of coupled global vegetation-climate modeling through the novel use of data, introduction of recent theories in plant dynamics, and development of computationally efficient algorithms for parallelized computing in GCMs.

B23A-02 1330h POSTER

Modelling environmental controls on leaf phenology

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The exchanges of energy and CO2 fluxes between the biosphere and the atmosphere, via the biophysical and biogeochemical pathways, respectively, are strongly influenced by the phenology (timing of onset and offset) of the leaves. Leaf phenology regularly alters land-surface boundary conditions by changing surface albedo, roughness, and the dynamics of the surface water and energy fluxes. Yet, phenology remains one of the most difficult processes to parameterize because our understanding of physical processes that are involved in initiating leaf onset and senescence is incomplete. A lack of understanding of processes that control leaf phenology has led to development of various empirical formulations that have been used with varying degree of success in terrestrial ecosystem models for both extra-tropical and tropical biomes. Of these formulations, the use of growing degree days (GDDs) to initiate leaf onset has received fair recognition and this formulation is used in a number of models. GDD-based and other empirical formulations suffer from a number of limitations when used at the global scale and in transient climate change simulations. A phenology scheme built for the Canadian Terrestrial Ecosystem Model (CTEM) that is currently being developed for inclusion in Canadian Centre for Climate Modelling and Analysis (CCCma) coupled general circulation model (GCM) is presented. Our goal was to develop a scheme that is general enough to be applied at a global scale and sufficiently robust so that it can be used in transient climate change simulations. CTEM uses a carbon-gain based scheme that initiates leaf onset only when it is beneficial for the leaves in carbon terms to grow new leaves. For leaf offset the conventional day length, temperature, and soil moisture controls are used. Comparison of simulated leaf onset and offset times with observation-based estimates for temperature and boreal deciduous, tropical evergreen, and tropical deciduous plant functional types (PFTs) at selected locations indicates that the phenology scheme performs satisfactorily. Model simulated leaf area index (LAI) and stem and root biomass are also compared with observational estimates to illustrate that the overall performance of CTEM is reasonable.

B23A-03 1330h POSTER

Energy, Moisture and Carbon Flux at the ARM/SGP Site: Model Simulations using the CSU General Circulation Model coupled to the Simple Biosphere Model (SiB).

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Year 2000 simulations of surface fluxes at the Atmospheric Radiation Measurement Program Southern Great Plains (ARM/SGP) site made with SiB Version 2.5 coupled to the Colorado State University GCM (CSU-BUGS5) in Single Column Mode (SCM) result in a spuriously large Bowen Ratio and anomalously low precipitable water during several periods over the summer. While initially thought to be a result of soil water stress on transpiration, anomalously dry intervals during the summer months were instead the result of pathological relationships between energy, moisture and carbon fluxes as simulated in this numerical model. We have replaced SiB2.5 with the latest version of the Simple Biosphere model (SiB3.0) in the coupled BUGS5-SiB model system, and repeated the simulations. SiB3.0 provides a more realistic treatment of fluxes within the surface layer, as well as a more sophisticated soil module. The resultant fluxes of latent heat, sensible heat and carbon more accurately reproduce the observations.

B23A-04 1330h POSTER

Interannual Variability In the Atmospheric CO2 Rectification Over Boreal Forests Based On A Coupled Ecosystem-Atmosphere Model

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Ecosystem CO2 exchange and the planetary boundary layer (PBL) are correlated diurnally and seasonally. The simulation of this atmospheric rectifier effect is important in understanding the global CO2 distribution pattern. A 12-year (1990-1996, 1999-2003), continuous CO2 measurement record from Fraserdale, Ontario (located 150 km north of Timmons), along with a coupled Vertical Diffusion Scheme (VDS) and ecosystem model (Boreal Ecosystem Productivity Simulator, BEPS), is used to investigate the interannual variability in this effect over a boreal forest region. The coupled model performed well in simulating CO2 vertical diffusion processes. Simulated annual atmospheric rectifier effects, (including seasonal and diurnal), quantified as the variation in the mean CO2 concentration from the surface to the top of the PBL, varied from 2.8 to 4.1 ppm, even though the modeled seasonal variations in the PBL depth were similar throughout the 12-year period. The differences in the interannual rectifier effect primarily resulted from changes in the biospheric CO2 uptake and heterotrophic respiration. Correlations in the year-to year variations of the CO2 rectification were found with mean annual air temperatures, simulated gross primary productivity (GPP) and heterotrophic respiration (Rh) (r2=0.5, 0.46, 0.42, respectively). A small increasing trend in the CO2 rectification was also observed. The year-to-year variation in the vertical distribution of the monthly mean CO2 mixing ratios (reflecting differences in the diurnal rectifier effect) was related to interannual climate variability, however, the seasonal rectifier effects were found to be more sensitive to climate variability than the diurnal rectifier effects.

B23B CC: 524 A Tuesday 1330h

Mercury Biogeochemistry at the Terrestrial-Aquatic Interface II *(joint with H)*

Presiding: **B A Branfireun,** University of Toronto at Mississauga**; M Marvin-DiPasquale,** U.S. Geological Survey

B23B-01 1330h

Factors Influencing Enhanced Mercury Bioaccumulation in Riverine Mixing Zones of Lake Superior

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Very low concentrations of total mercury (HgT - less than 0.6 ng/L)) and methyl mercury (MeHg 0 - 13 pg/L) have been measured in the offshore waters of Lake Superior, while inflowing tributaries reflected higher HgT (up to 20 ng/L) and MeHg (50 to 220 pg/L) concentrations, depending on the individual watershed characteristics and flow regimes. Watershed export of HgT and MeHg is function of not only land use/land cover, slope and soil characteristics but for MeHg, also a function of hyporheic zone transformations. In regions influenced by forest and wetland areas, Hg is effectively transported with dissolved organic carbon. In agricultural regions and clay-dominated soils, Hg is mainly delivered on the particulate phase. A preliminary mass balance suggests that about 30 percent of HgT and 50 percent of the MeHg is exported in the colloidal phase from rivers in the basin. Transformations of dissolved, colloidal and particulate phases within riverine mixing zones lead to enhanced bioaccumulation of MeHg in phytoplankton and zooplankton relative to offshore regions of the lake.

B23B-02 1400h

An Assessment of Aquifer Storage and Recovery and Mercury Methylation in the south Florida Everglades Ecosystem

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In an attempt to restore natural hydroperiods, vital to the Everglades ecosystem, Aquifer Storage and Recovery (ASR) technology is proposed in south Florida. ASR is used to store excess surface water and shallow groundwater during wet periods for recovery during seasonal or longer-term dry periods. Studies suggest methylmercury is formed in anoxic environments where there is active sulfate reduction; however, no known published studies have considered methylmercury formation in deep subsurface environments. Similarly, few studies evaluate ASR and water chemistry. The proposed storage zone is the Upper Floridan Aquifer, which is anaerobic, suggesting the potential for mercury methylation during storage periods. Additionally, the recovered water may stimulate mercury methylation when released to the Everglades. Using water samples from Florida municipal wells and cores from pre-existing ASR wells to simulate ASR conditions, a series of 9 columns were set up using Floridan Aquifer materials, native surface water, and mercury isotopes. Five

columns were set up as anaerobic by introducing nitrogen gas, and 4 columns aerobic with oxygen gas. Seven columns contain 500 mL by volume of aquifer core and 1,500 mL native surface water, 2 columns contain native surface water to serve as controls. Two columns contain sterilized core, and 1 column contains native core with deionized water. Each column was sampled at 2, 4, 8, 12, and 16 weeks. The objectives of the experiments are to determine potential chemical reactions, to evaluate the potential for ASR injection to methylate mercury, to determine the time required for stored water to methylate mercury, and the conditions under which methylation may occur in ASR stored water.

B23B-03 1415h

Hg Deposition to Lakes in Northern New England Inferred at Multiple Scales From ^{210}Pb-Dated Sediment Cores

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Mercury (Hg) contamination of aquatic systems is recognized to be a problem of global consequence, and Hg bioaccumulation poses significant risks to piscivorous animals and humans who consume gamefish. In order to quantify historical and current Hg deposition to the northern New England landscape, we dated and performed Hg analyses on sediments cores from various lakes at local and regional scales. In this presentation, we contrast results of three studies: a regional assessment of Hg deposition to the VT-NH landscape (10 lakes); a localized study of deposition to the Lye Brook Wilderness of southern VT (four lakes); and the first-ever dated assessment of sediment Hg deposition history for Lake Champlain (three sites + one adjacent inland lake). At the VT-NH scale, total Hg (HgT) fluxes to sediments ranged from 5 to 17 $\mu g.m^{-2}.yr^{-1}$ during pre-industrial times, and from 21 to 83 $\mu g.m^{-2}.yr^{-1}$ presently. Present-day HgT fluxes are between 2.1 to 6.9 times greater than pre-1850 fluxes, and atmospheric Hg deposition to the VT-NH region was estimated at 21 $\mu g.m^{-2}.yr^{-1}$. This agrees well with measured HgT deposition, when re-evasion of Hg is accounted for. Hg fluxes to lake sediments have declined in recent decades, owing to reductions in atmospheric Hg deposition to the lake surfaces. In the high-elevation Lye Brook Wilderness landscape, baseline, peak, and present accumulations were higher than those estimated from the VT-NH dataset, a finding that highlights the roles of elevation, watershed size, and dissolved organic carbon export in mediating Hg transport. Available data from the Lake Champlain Basin show the influence of historical and current watershed sediment delivery due to land cultivation, and more recently to land-use conversion. These studies jointly indicate that watershed export of legacy Hg continues despite declines in present-day deposition rates, contributing to the impression that Hg retention by watershed soils has declined.

B23B-04 1430h

Increases in methylmercury export from a sulfate-amended peatland: A consequence of an altered microbial consortia?

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An experiment at the Marcell Experimental Forest, Minnesota is ongoing to test the hypothesis that increased atmospheric sulfate deposition to northern peatlands is responsible for increased methylmercury yields from these ecosystems. A peatland, divided into an upslope control portion and a downslope experimental portion, has had elevated levels of sulfate applied to the experimental portion using an extensive irrigation network for several seasons. Increases in methylmercury yield from the system were apparent early in the experimental manipulation. In 2002, peat cores were extracted from the control and experimental areas of the peatland to evaluate whether or not changes in the peat sulfur geochemistry, microbial community structure, and/or mercury methylation potential could be attributed to the sulfate additions. Mercury methylation potential was assessed using a stable isotope addition to incubated intact peat cores, which were subsequently sliced and frozen until analyses. The microbial community structure was assessed using a modified solid-phase extraction followed by phospholipid fatty acid (PLFA) analyses. Although only minor differences in sulfur geochemistry and methylation potential were detected, the treatment cores had increased abundances of Desulfovibrio-group and Desulfobacter-group biomarkers compared to the control cores, and the effect was greatest in the near surface peat. In the control cores, the abundances of sulfate-reducers in both groups increased with depth. These results suggest that increased sulfate loading may cause a shift in microbial community structure and abundance in favour of known mercury methylators.

B23B-05 1445h

Are uplands the key to understanding possible lag times for ecosystem recovery to reduced mercury loading? Results from the first two years of mercury stable isotope additions to the uplands of the METAALICUS project

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The Mercury Experiment to Assess Atmospheric Loadings in Canada and the US (METAALICUS) is a whole-watershed Hg loading experiment being conducted at the Experimental Lakes Area in northwest Ontario. Many of the response metrics that attract attention to this project are focused on methylmercury (MeHg) formation and bioaccumulation. However, some of the most difficult questions to answer at the study site, and watersheds elsewhere, relate to responses in the uplands and wetlands, and connections to down-gradient aquatic ecosystems. Mercury studies in upland areas are in part motivated by the observation that the vast majority of past emissions now resides in soils and sediments across the globe, yet we know relatively little about the stability of this large Hg reservoir. For this aspect of METAALICUS, we applied a traceable stable isotope (200Hg) to the upland areas of the watershed at about 4 to 5 times the ambient rate in an attempt to answer these difficult questions. Results from the first two years of applications to the uplands and monitoring have showed several interesting, and somewhat unexpected results. The estimated annual total Hg flux (about 98% inorganic Hg) from upland runoff to the study lake (about 1500 mg) exceeds the rate of direct atmospheric Hg deposition flux by a factor of about three to four, illustrating the importance of including upland studies for aquatic ecosystems. This upland mercury flux is the dominant ambient inorganic Hg source for the study lake. In contrast, very little of this flux was MeHg.

B24A CC: 524 A Tuesday 1530h

Mercury Biogeochemistry at the Terrestrial-Aquatic Interface III

Presiding: **B A Branfireun,** University of Toronto at Mississauga**; M Marvin-DiPasquale,** U.S. Geological Survey

B24A-01 1530h INVITED

Methymercury Formation in Marine and Freshwater Systems: Sediment Characteristics, Microbial Activity and SRB Phylogeny Control Formation Rates and Food-Chain Exposure

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Mercury research in freshwater and marine systems suggests that sediment characteristics such as organic substrate, mercury speciation, and sulfate/sulfide concentrations influence availability of inorganic mercury for methylation. Similarly, sediment characteristics also influence sulfate-reducing bacterial (SRB) respiration as well as the presence/distribution of phylogenetic groups responsible for mercury methylation. Our work illustrates that the process of methylmercury formation in freshwater and marine systems are not dissimilar. Rather, the same geochemical parameters and SRB phylogenetic groups determine the propensity for methylmercury formation and are applicable in both fresh- and marine-water systems. The presentation will include our integration of sediment geochemical and microbial parameters affecting mercury methylation in specific freshwater and marine systems. Constructed wetlands planted with *Schoenoplectus californicus* and amended with gypsum ($CaSO_4$) have demonstrated a capacity to remove inorganic mercury from industrial outfalls. However, bioaccumulation studies of periphyton, eastern mosquitofish (*Gambusia holbrooki*) and lake chubsucker (*Erimyzon sucetta*) were conducted in order to ascertain the availability of wetland-generated methylmercury to biota. Total mercury concentrations in mosquitofish from non-sulfate treated controls and the reference location were significantly lower than those from the low and high sulfate treatments while mean total mercury concentrations in lake chubsuckers were also significantly elevated in the high sulfate treatment compared to the low sulfate, control and reference populations. Methylmercury concentrations in periphyton also corresponded with mercury levels found in the tissue of the lake chubsuckers, and these findings fit well given the trophic levels identified for both species of fish. Overall, data from this study suggest that the initial use of gypsum to accelerate the maturity of a constructed wetland may not prove beneficial with respect to the ultimate objective of mercury sequestration. Current regulations place strict requirements on dredge material placed in confined disposal facilities (CDF) as well as associated effluent waters. Although regulatory guidelines typically address total mercury concentrations, historical data specific to bioaccumulation of mercury suggest that methylmercury concentrations found in sediments and water require attention. Resource agencies are now interested in knowing the likelihood of methylmercury formation in dredge spoil since birds and fish are frequently found feeding in CDFs and the associated mixing zones. Mechanisms that influence methylmercury formation in sediments dictate that dredging of mercury-containing sediments will result in an increased availability of inorganic mercury for methylation. Prior to dredging, the undisturbed sediment contains inorganic mercury complexed to sulfide in an insoluble, unavailable form. However, hydraulic or clamshell dredging can result in an oxidation of sediments and remobilization of mercury-sulfide species thus increasing its availability for methylation. Once sediments are disposed in a CDF, sulfate-reducing bacteria profiles are re-established vertically in dredge spoil and methylmercury synthesis can readily occur.