

ENVR

Changing Atmospheric Chemistry: Environmental Implications of Land-Air Interactions

247th ACS National Meeting, Dallas, TX

Wednesday, March 19 2014

8:30 a.m. *Opening Remarks (Bassam Shkhashiri)*

8:35 a.m. *Climate Change Challenges: Responsibilities of Chemists and the ACS*
(Bassam Shkhashiri, Professor of Chemistry, UW-Madison)

Everyone and everything on Earth is affected by the climate. ACS has a clear position statement on global climate change (www.acs.org/policy). The ACS Climate Science Initiative includes a toolkit for use by members, a challenge grant program for local sections and divisions, and narratives for communicating the science of climate change to a variety of audiences. I will discuss strategies aimed at enriching and expanding on the ACS position statement on climate change and related ACS programs and activities.

8:55 a.m. *The ACS Climate Science Toolkit (Jerry Bell, Faculty Associate, WISL, UW-Madison)*

As context for this symposium, this will be a brief history of the development of the ACS Climate Science Toolkit and its present contents. We will consider the rationale for including the concepts there now and also what is missing that might provide a more complete picture of the major factors that affect the climate and the changes it is undergoing. One that has been identified is the interaction of land and air, especially the large seasonal fluxes of carbon dioxide, their causes, and the reasons for the changes that may be occurring. These are the subjects of this symposium that will inform additions to the Toolkit.

9:15 a.m. *Organic emissions from terrestrial ecosystems: Their role in the Climate System and interactions with emissions from human activities (Alex Guenther, Laboratory Fellow, Pacific Northwest National Laboratory)*

Atmospheric levels of secondary organic aerosol (SOA) and ozone have increased considerably since the beginning of the industrial age and they are important contributors to the radiative forcing that drives climate change. These two atmospheric constituents are formed in the atmosphere from chemical reactions involving volatile organic compounds (VOC) emitted primarily from terrestrial ecosystems. Ozone is a significant greenhouse gas and SOA can directly and indirectly (cloud albedo) influence solar radiation and thus change light and temperature at the Earth's surface. Since VOC emissions from terrestrial ecosystems are extremely temperature sensitive, and can respond to light, this can lead to a feedback between temperature/light and VOC emissions. Another potential feedback is associated with the water cycle since SOA can influence precipitation by serving as cloud condensation nuclei and because VOC emissions are sensitive to water availability. Human activities, primarily fossil fuel combustion, add to the complexity of these coupled systems by amplifying the production of ozone and SOA from biogenic VOC. There is limited or no production of SOA and ozone when biogenic VOC are emitted into a pristine atmosphere. Thus it is incorrect to conclude that trees are a source of SOA and ozone. It is only when biogenic VOC emissions mix with polluted air that SOA and ozone are produced at levels that have a significant impact on air quality and climate. Our current understanding of the role of VOC in the climate system and potential feedback couplings will be presented and the major uncertainties will be discussed. The influence of air pollution on the natural Earth System will be described along with the implications for climate change.

9:45 a.m. *Disruption of Forest-Atmosphere Interactions Related to Changing Atmospheric Chemistry (Walter Shortle, Forest Service, Northern Research Station, U.S. Department of Agriculture)*

Both land and oceans have equal carbon fluxes with the atmosphere. These fluxes both slow the accumulating carbon dioxide and other greenhouse gases which increase radiative forcing and alter the climate of Earth adversely affecting life on the planet. The major source of carbon flux on land are forests which cover about 30% of the land surface, but

contain 90% of the biomass comprised in large part by cellulose and lignin, the two most abundant organic compounds on Earth. Forest land is where a never-ending cycle of biosynthesis and biodecomposition takes place and the balance of these forces determines losses and gains of carbon dioxide in the atmosphere. Disruption of the biogeochemical cycling of calcium has occurred in forests exposed to acid deposition by emission of sulfur and nitrogen oxides. How this disruption alters the biosynthesis of lignified cellulose and water use efficiency of forest trees will be considered.

10:15 a.m. **BREAK**

10:25 a.m. *Adaptation of higher plants to changes in atmospheric carbon dioxide concentration* (**James Bunce, Crop Systems and Global Change Laboratory, USDA-ARS**)

The concentration of carbon dioxide in earth's atmosphere has varied greatly over geologic time, from about 3000 to 4000 parts per million by volume (ppm) when plants invaded land about 400 million years ago, to less than 200 ppm several times within the last half-million years. Such changes in concentration would have profound effects on photosynthesis and stomatal conductance of plants, which are the most obvious plant processes which respond directly to carbon dioxide concentration. Low carbon dioxide concentrations have been implicated in the evolution of C₄ photosynthesis, which uses metabolic energy to concentrate carbon dioxide at the site of the first enzymatic step in the C₃ photosynthesis pathway. Despite the fact that modern gymnosperms and angiosperms evolved when the carbon dioxide concentration was about 2000 ppm, there is some evidence that these higher plants are currently adapted to the lower concentrations of the more recent past. Efforts are currently underway to determine what traits would improve the adaptation of crops and other plants to projected changes in atmospheric carbon dioxide concentration. Results suggest that more subtle changes than altered properties of photosynthesis and stomatal conductance may be important.

10:55 a.m. *Non-enzymatic decomposition of lignocellulose by brown rot fungi and the role it plays in carbon sequestration and cycling* (**Barry Goodell, Department of Sustainable Biomaterials, Virginia Tech**)

Forests contain 90% of terrestrial biomass and are a significant contributor to carbon flux. Much of this biomass is lignocellulose, which is decomposed by basidiomycetous fungi. Brown rot fungi are unique in that they have evolved several times to develop non-enzymatic free radical systems which has permitted them to reduce the physiologically-expensive process of producing large extracellular enzymes for plant cell wall deconstruction. The first non-enzymatic system to be identified in *Gloeophyllum trabeum* (Pers.) Murrill, and now found in several other brown rot species, is the chelator mediated Fenton system (CMFS). The mechanism involves low molecular weight compounds, typically catecholates (hydroxybenzene derivatives) such as 2, 5-dimethoxyhydroquinone, that bind and reduce iron in the wood cell wall. This mechanism has been demonstrated to be dependent on pH and oxalate concentration. Iron is bound by oxalate, found in the low pH, immediate environment of the fungal hyphae. Ironoxalate and free fungal catecholate diffuse into the highly buffered environment of the wood cell wall, where iron from the oxalate will transfer to the catecholate chelator. Iron in the catecholate-bound form will react with peroxide within the cell wall to generate short-lived, but powerful, hydroxyl radicals via Fenton chemistry. This mechanism explains how reactive oxygen species can be generated at a distance from the fungal hyphae to protect the fungus from damage. Further, it provides a basis to explain how both cellulose and lignin are modified by brown rot fungi, with the cellulosic components being metabolized by the fungus and the lignin components re-polymerized to produce a highly recalcitrant "brown rot modified lignin" that has been reported to persist for centuries in the environment. The role of low molecular weight fungal metabolites in association with iron will be discussed in the context wood cell structure, cellulose crystallinity, and carbon cycling.

11:25 a.m. **Panel Discussion**