Geophysical Research Abstracts, Vol. 9, 00658, 2007
SRef-ID: 1607-7962/gra/EGU2007-A-00658

Chemical Controls Upon Carbon Monoxide Photoproduction

A. Stubbins (1), K. Mopper (1), G. Uher (2), R.C. Upstill-Goddard (2), C.S. Law (3)

(1) Old Dominion University, VA, USA, (2) University of Newcastle-upon-Tyne, UK, (3) NIWA, Wellington, NZ

A suite of natural dissolved organic matter isolates (i.e., humic substances; HS) and chemically related model aromatic compounds were irradiated in a solar simulator to investigate the chemical controls upon carbon monoxide (CO) photoproduction in aquatic environments. In the first set of experiments eleven HS isolates from sea, lake and river waters were dissolved in ultra-pure laboratory water producing aqueous samples with identical HS concentrations. HS from waters with large terrestrial inputs showed higher CO photoproduction than those from waters containing predominantly autochthonous carbon. Further investigation revealed CO photoproduction to be positively correlated with HS aromaticity, as determined by ^{13}C-NMR, and absorbance coefficient indicating that observed variations in CO photoproduction rates were a function of aromatic chromophore concentration. It is also noteworthy that CO photoproduction was not correlated to carbonyl carbon levels, suggesting these moieties to be of limited significance in the photoformation of CO from DOM. Once aromatic compounds were implicated as the prime photoreactant for the production of CO a second set of irradiations were conducted using solutions of chemically related aromatic compounds (10 μM in buffered, ultra-pure water) to investigate the role of functional side groups in determining photoreactivity. Photoproduction rates were divided by the absorbed light (i.e., the cross-product of the absorbance of the model aromatic solution and the irradiance in the solar simulator) to take into account different molar absorptivities, thus yielding an approximate measure of their CO photoproduction efficiencies. These experiments yielded some significant results. Firstly, aromatic compounds that are common constituents of lignin, humic substances and brown algae exhibit marked variations in photoreactivity depending upon the nature and location of substituents on the ring. Specifically, electron donating substituents in-

creased photoreactivity, while electron withdrawing groups decreased CO production. For example, production of CO increased in the order aldehyde $<$ methoxy $<$ phenol, when one group was present, and from aldehyde+phenol $<$ aldehyde+methoxy $<$ phenol+methoxy, when two groups were present. Interestingly, and in agreement with our HS studies above, the presence of carbonyl functionality did not enhance CO photoproduction. In fact, the presence of an aldehyde group on the ring strongly inhibited CO photoproduction, possibly because of its electron withdrawing properties. The implications of these studies are discussed in terms of impact upon the fundamental understanding of environmental photo-processes and how future studies might aim to shed more light upon these reactions.