



Long-term Oxidation and Development of Surface Charge of Black Carbon along a Climosequence

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Although black carbon (BC) is perceived as a very recalcitrant fraction of organic matter, it is clear that BC is ultimately oxidized to CO₂ over long periods of time. Such oxidation may not only mineralize BC to carbon dioxide but also alter the chemical properties of BC. Since decomposition rates are strongly influenced by temperature, these changes in BC properties may be more pronounced in warmer climates. The objectives of this study were to investigate the changes of BC properties as influenced by temperature. BC samples were taken from 16 historic charcoal blast furnaces, from Quebec to Alabama, with mean annual temperatures (MAT) from 4°C to 17°C to study long-term decomposition. These furnaces were in operation in the mid 19th century and decommissioned in the 1880s. For investigating short-term effects on BC properties, fresh BC samples were incubated at different temperatures, -22°C, 4°C, 30°C, 70°C, and 105°C, for 6 and 12 months. The incubation data showed that pH values decreased from 8 to 4 with higher incubation temperature and longer incubation time. Fourier Transform Infrared Spectroscopy (FT-IR) spectra and X-ray Photoelectron Spectroscopy (XPS) indicated that the decrease in pH values was due to the formation of carboxylic and phenolic functional groups specifically on particle surfaces. At the same time, the positive charge decreased and the negative surface charge increased. The point of zero net charge (PZNC) dropped from pH 7 to below 3 when BC was incubated at 70°C or 105°C. Compared to the incubated BC samples, the historic BC samples showed a much greater oxidation. Their XPS C1s spectra shifted to highly oxidized states and FTIR spectra showed intense bands of OH bonds, carboxylic, aromatic, carboxylate, and phenolic functional groups. Positive surface charge of all historic BC samples was absent and negative surface charge increased from 100 mmole kg⁻¹ C in incubated BC samples to over 1,000 mmole kg⁻¹ C in historic BC samples. Higher MAT led to more negative charge. The PZNC of all historic

BC samples was below pH 3. With presence of BC, soils had much higher negative surface charge, base cations, and base saturation than the adjacent non BC-containing soils. Oxidation processes play an important role in changing BC properties which was significantly enhanced by greater MAT.