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Going beyond the ring trial - seeking a measure of BC condensation

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The results of the BC ring trial, in which the various BC quantification methods gave widely varying BC contents, bring into question the very concept of the "BC content" of a sample. It is now absolutely clear that these methods measure different things – all of which come under the umbrella definition "black carbon". The notion that BC is not a single entity but a range or spectrum of materials has been around for a while. It is now time to deal with the implications of this reality: (i) we need to develop methods for BC characterization, i.e. methods that can place a where the BC in a sample lies on the "BC spectrum"; and (ii) we need to identify relationships between these measures of "BC quality" and function (e.g. decomposition rates).

One concept of BC quality is the notion of the degree of aromatic condensation or degree of graphitization. Graphite itself consists of very large sheets of sp^2-hydridized carbons in a hexagonal array. BC is known to contain similar structures, but these "graphitic domains" are believed to be much smaller – there is more "edge" and less "middle" and there are imperfections in their structure. In theory, one would expect the larger graphitic domains to have the most graphitic properties, i.e. be the most stable to chemical, thermal and biological degradation. If the degree of aromatic condensation is the key property that controls its key functions, we need to be able to measure it. And I think I know how – ring currents!

Extended planar aromatic structures enable the movement of electrons through the conjugated orbitals to set up so-called ring currents. One consequence of the ring currents is that they affect the chemical shift of the ^{13}C nuclei. This is well-documented for chars produced at high temperature – beyond a certain temperature there is a shift in ^{13}C chemical shift to high field (lower ppm values). This effect in itself is less useful

than it sounds, because these ^{13}C nuclei become harder to detect as they become more remote from nearest ^{1}H neighbours. However, we have found that molecules sorbed to these surfaces are also affected by the ring current, i.e. their ^{13}C signal is shifted – substantially – to lower ppm values. For example, we found that the chemical shift of benzene sorbed to a char produced at 850˚C was $\sim$3 ppm lower than that of benzene sorbed to a char produced at 450˚C. Crucially, benzene sorbed to two chars collected from recent wildfires gave intermediate values, suggesting a degree of aromatic condensation somewhere between the two lab-produced chars. More recent results show that the technique works just as well for sorbed phenanthrene. Finally the technique has been applied to some of the ring trial materials, but alas I have run out of space to tell you what happened. You'll just have to come along to find out.