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**Beneficent Implications on Admixture of 'Biochar'
Carbons into Thermally-Treated Soils.**

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Typical benefits of thermally-treating soils.

- **Removal of organic contaminants from the soil:**
 - flux of volatilized soil $H_2O_{(g,l)}$ assists contam. removal (non-eqm. molr. entrainment);
 - the treatment temperature can be dialed-up to *ca.* 500 °C (*cf.* higher T_{bpt} compounds).
- **Uniformity of post-treatment particle sizing:**
 - rotary quench drum guides particle aggregation (*i.e.*, fines as a temporary 'glue');
 - uniformity provides for smooth backfilling and excellent compaction.
- **Boosting of inorganic nutrient availabilities post-treatment:**
 - thermal exfoliation of clay mineral crystal structures exposes basal-plane ions;
 - entrained woody plant materials are charred externally (esp. roots); '*biochar*'.

Applicability considerations for thermal:

Which Organics are present (i.e., re: 1°, likely derivatives & possible side-products):

- HCs, F1-F4 (BTEXs, C₆-C₁₀, C₁₀-C₁₆, C₁₆-C₃₄, C₃₄-C₅₀);
- polynuclear aromatic compounds, PNAs (incl. PAHs, PANHs, PASHs);
- oxygenates (glycols, dioxanes, alcohols, phenols, aldehydes, ketones, carboxylic acids, esters, ethers);
- chlorocarbons (chlorinated solvents, TCE, PCE, HCHs (“BHCs”), BHC, PCBs, PCDDs, PCDFs);
- Sulfur-contng spp.; Nitrogenates / amines / 4° ammonium ions; Phosphorus-contng spp.;
- herbicides (*e.g.*, *Tebuthiuron*, *Bromacil*).

What Inorganics are present (i.e., re: leachables-vs.-totals, redox effects/changes at Temp., emissions):

- metals (esp. re: electrochemical series, reducibility, volatility, toxicity, formation of M(O) carbonyls);
- ions (*e.g.*, phosphate, sulfate vs. ammonium, nitrate, sulfide, carbonate, chloride, fluoride);
- mineralogy (mineral catalysis (esp. re: clays), salinity, sedimentary rock permeation).

Other physical & chemical parameters of the soil:

- pH; both native/ambient, & as a site-specific function of Temp., H₂O (esp. re: HCl, HF, &c.);
- calorific values (calcd. from analyt., vs. total oxy-combustible energy content by bomb calorimetry);
- moisture content (% H₂O);
- redox condition/state/behaviour/expectations before, during, & after ΔT (reducing, oxidizing);
- Radioactives.

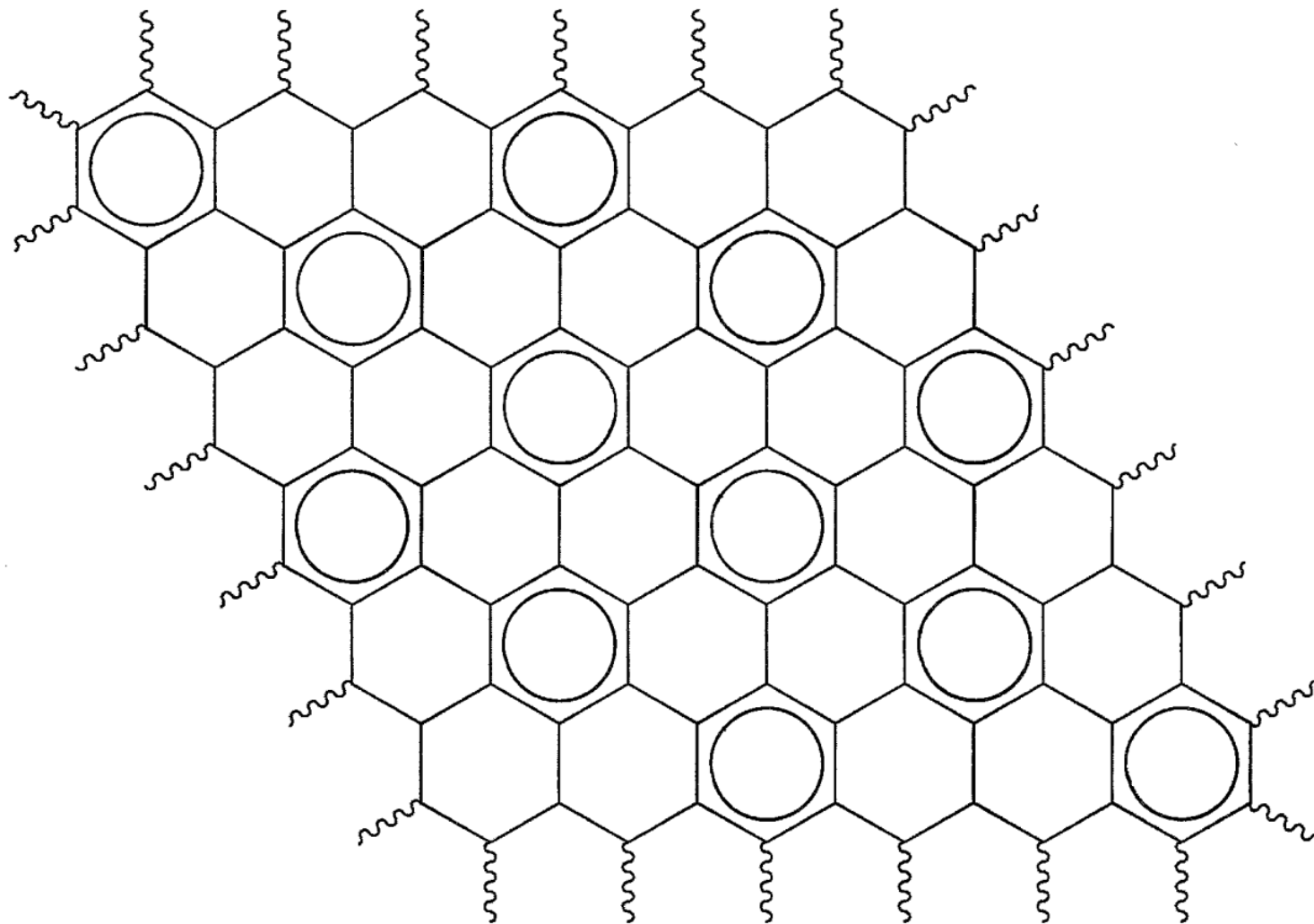
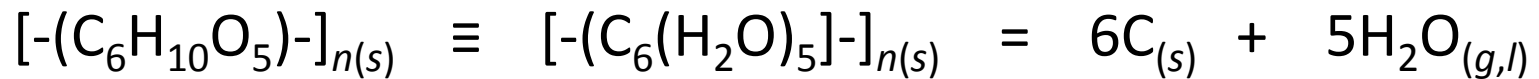


Figure 1. Diagram showing a 'cut-out' portion of a single ideal graphitic graphene sheet's (all-hexagonal) co-planar covalently-bonded network of sp^2 -hybridized carbon atoms (looking directly down the c -axis, onto the ab -plane); resonance delocalization of the $2p_z$ valence electrons in π -molecular orbitals is indicated by the use of the customary circles, that are understood to be general to all of the six-membered rings (*i.e.*, not polycyclically fixed as the kind of representationally-convenient 'snapshot' type of illustration above might suggest).



***'Biochars'* process-generated from plant materials.**

- *'biochar'* carbons can be generated inside a TDU's main drum by the thermal dehydration of entrained plant materials (esp. roots), classically from carbohydrates such as cellulose via:



- the rapidity of charring, under non-equilibrium conditions, together with abrasional forces (*i.e.*, rotary mechanical), is expected to favour the formation of ring-structure defects (*i.e.*, 5-membered & 7-mmbrd rings of carbon atoms).
- 5-mmbrd rings introduce *positive curvature* into a graphene sheet (*i.e.*, bowl-shaped), while 7-mmbrd rings impart *negative curvature* (saddle-shaped).

'Biochars' & amorphous carbons.

- **Graphenes** are polycyclic & aromatized HCs, incl. both planar (*i.e.*, ref. classical graphite structure: hexagons of sp^2 -hybridized carbons) & curvature-containing molecules (*i.e.*, 5-membrd & 7-membrd rings).
- **Fullerenes** are allotropes of Carbon, which are also polycyclic & aromatized, & closed-shell spp. are expected to always be curvature-containing (*i.e.*, since no valence-terminating elements are present).
- Aromatized polycyclic surfaces, planar & curved, all sorb (& on both sides).
- Generally, var.-curved graphene spp. can't associate/crystallize as easily as simpler/planar ones, so the presence of multiple ring-number 'defects' provides for long-lasting exposure & availability of carbon(0) surface areas.
- 'Flat-to-flattish' surface associations (via co-operative weak chemical bonding interactions) between graphenes & phyllosilicates interferes with the post-treatment re-crystallization of clay minerals, with basal exposures persisting longer.

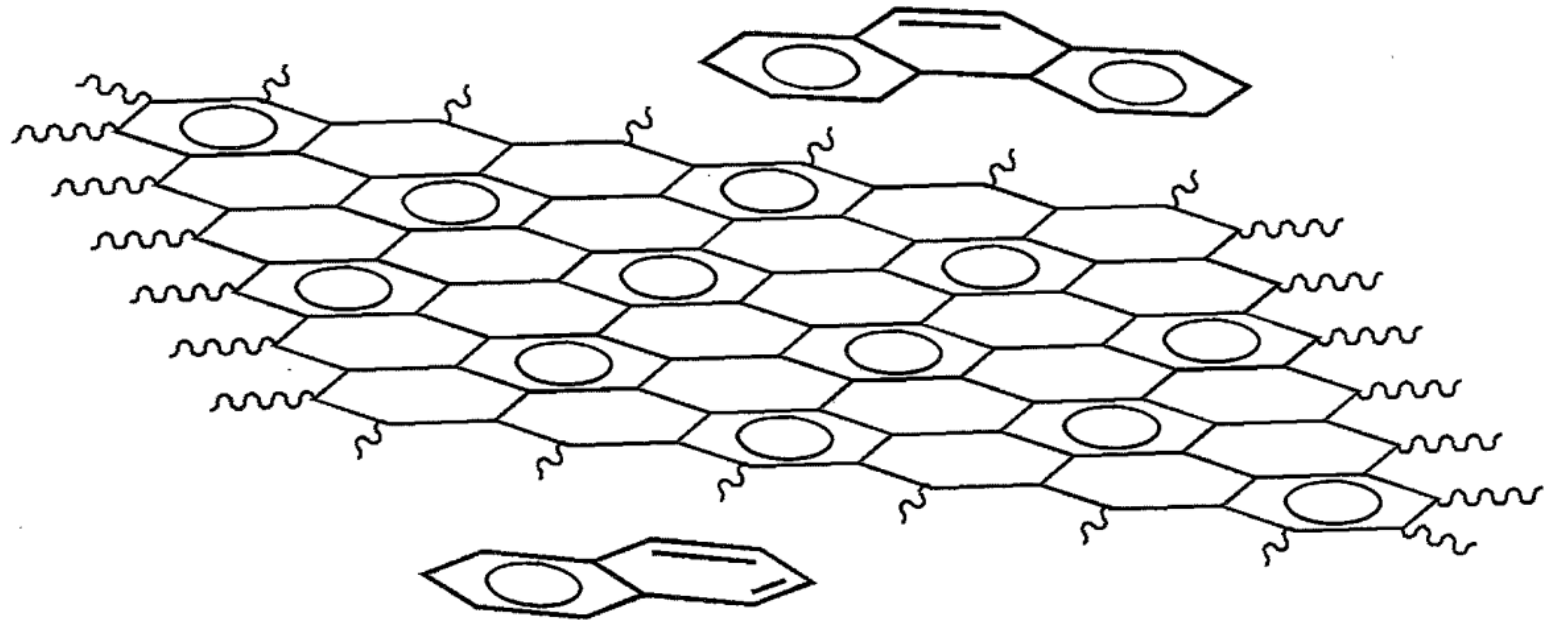


Figure 2. One environmental soil beneficence of biochars (incl. both *in situ* generated, as well as deliberately added): two exemplar small polynuclear aromatic compounds, naphthalene ($C_{10}H_8$) and phenanthrene ($C_{14}H_{10}$), are here shown within $\pi - \pi$ associative dispersive intermolecular bonding distances of a 'cut-out' portion of a single ideal graphitic graphene sheet's (all-hexagonal) coplanar covalently-bonded network of sp^2 -hybridized carbon atoms (looking obliquely down onto the *ab*-plane of the graphene); a naphthalene molecule is shown below the plane of the ideal graphene, and a phenanthrene molecule is shown above the plane of the ideal graphene. Very similar surficial-sorptive situations would obtain in the case of curved graphenes as well.

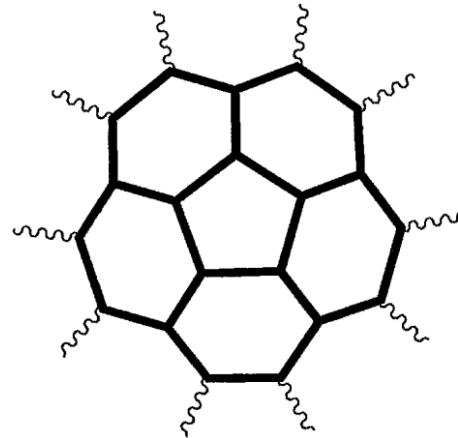
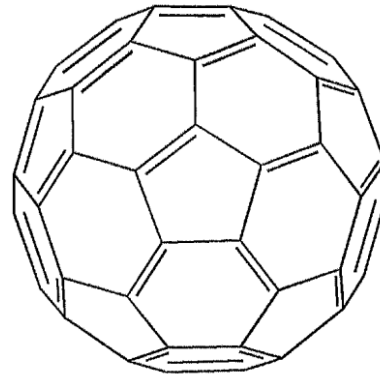
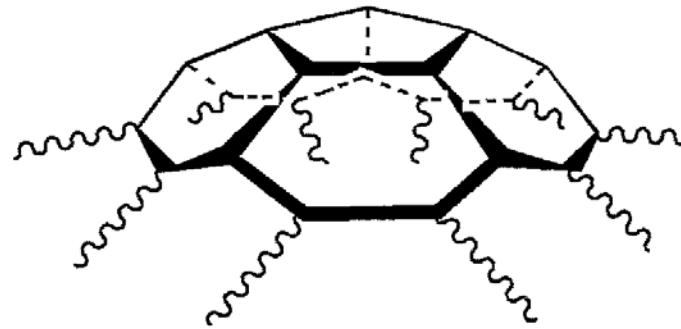


Figure 3. Introduction of the structural 'defect' (*i.e.*, versus the ideal of the classical all-hexagonal graphitic graphene) of a single five-membered ring of sp^2 -hybridized carbon atoms necessarily imparts positive curvature upon the covalently-bonded aromatized network of carbon atoms (as exemplified by the structure of the C_{60} molecule referenced above as a visual *aide-mémoire*). The concentration and distribution (symmetric or otherwise) of 5-membered rings within a (now curvature-containing) biochar graphene sheet will of course depend on the sample's history, including such variables as the original carbon source (*e.g.*, carbohydrate speciation), the (uniform / non-uniform) rate of heating to charring temperatures, the presence / absence of potentially structure-mediating / catalyzing species (*i.e.*, esp. inorganics / minerals), as well as the maximal temperatures reached, time durations at temperature (*i.e.*, with some similarities to metallurgical annealing). The importance of such 'defect' ring-number (*i.e.*, $\neq 6$) caused curvatures wasn't fully appreciated until after the mid-1980s.

An individual clay mineral aluminosilicate / phyllosilicate platelet.



An individual clay mineral aluminosilicate / phyllosilicate platelet.

Figure 4. An exemplar curvature-containing biochar graphene has become situated between two (thermally-separated / -exfoliated / '-exploded') clay mineral aluminosilicate / phyllosilicate platelets (*i.e.*, post-thermal soil treatment). The temporary (*i.e.*, non-equilibrium) physical 'flat-to-flattish' associations between flat individual clay platelets and flattish graphene sheets (*i.e.*, biochar carbons containing various concentrations of formal 'defect' 5-membered and 7-membered rings) provides for time-extended access to clay mineral surface areas bearing what were previously poorly-accessible (*i.e.*, previously interior crystalline) inorganic nutrients (*e.g.*, metal ions, ammonium ions, complex ions, chelates, *etc.*). The geological re-crystallization of clay mineral platelets is generally water-mediated, but the extent of plane-to-plane co-operativity of the weak chemical bonding interactions (incl. dispersional, and ion / induced-dipole) across significant surface areas, and with this being able to operate on both sides of each individual particle (*i.e.*, both for each aluminosilicate / phyllosilicate particle, as well as for each graphene particle), allows for a lengthening of the time taken by the system over which to approach equilibrium (*i.e.*, through true eventual re-crystallization of the soil's clay mineral components), and hence a longer agrological exposure time for crystal-structure plane-facial clay mineral inorganic nutrients.



Some beneficences of process-generated *biochars*:

- freshly-produced (*cf.* ‘activated’) carbon(0) surface areas for the binding of soil organics & nutrients;
- migratory retardation of residual CoCs (esp. PAHs);
- the sorbing of odoriferous spp.;
- soil water-retention;
- ‘sweetening’ (*i.e.*, co-generated Group I & II bases);
- textural ‘opening up’ (re: aeration, pore spaces, &c.) owing to graphene curvatures inhibiting self-association (towards crystallization), as well as inhibiting phyllosilicate re-crystallizations through co-operative ‘flat-to-flattish’ weak chemical bonding interactions.



Questions are welcome.

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