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Absorption or adsorption? Characterization of nonpolar organic compound sorption in soils using normal and cyclic alkanes as molecular probes

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Carbonaceous materials (CMs), thermally or diagenetically altered carbon-rich materials including black carbons, “ad”sorb organic compounds strongly on the surface and are therefore said to significantly influence the sorption behavior of organic chemicals in soils and sediments, even if the content of CMs may be small. For example, frequently observed nonlinear sorption isotherms of nonpolar oraganic compounds on soils are explained as a combination of recent organic matter, which “ab”sorbs the sorbate compound and contributes to the linear sorption at high solute concentrations, and CMs, being responsible for the nonlinear, stronger sorption at low concentrations. The influence of CMs on soil sorption is, however, not easy to evaluate, because (i) in soils CMs are present with recent organic matter and quantification of the content of CMs in soils is not simple, and (ii) sorption by recent organic matter often shows nonlinear sorption isotherms as well.

As a tool to assess CM sorption in natural soils, we propose a new experimental approach using normal and cyclic alkanes as molecular probes. Empirically, it is known that a cycloalkane is “ab”sorbed more strongly than the n-alkane of the same number of carbon atoms. However, in the case of “ad”sorption, cycloalkanes are just equally or even less attracted than n-alkanes. Indeed, organic solvent-air partitioning coefficients of cyclohexane are always ca. 2 to 3 times greater than those of n-hexane, while surface-air adsorption coefficients are equal or greater for n-hexane by a factor of up to 5, or sometimes more. This behavior can be explained by the difference of the sorbate transfer processes between ad- and absorption. We studied sorption of nor-

mal and cyclic alkanes of five to eight carbon atoms on five carbon-rich geosorbents ĄEpeat soil, lignite, charcoal, lignite coke and graphite. As expected, the sorption of the former two preferred cycloalkanes, signifying “ab”sorption, while the other three sorbed normal alkanes more indicating the dominance of “ad”sorption. These results suggest that investigation on n- and cycloalkane sorption in natural soils will be useful to identify significant contribution of CMs to soil sorption.