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Interactions of hydrophobic fractions of dissolved organic matter with

Fe $^{3+}$- and Cu^{2+}-montmorillonite

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Interactions of dissolved organic matter (DOM) with clays can significantly affect soil processes. We studied adsorption and fractionation of DOM hydrophobic fractions (hydrophobic acid, HoA and hydrophobic neutral, HoN) by Cu^{2+}- and Fe^{3+} -montmorillonite. We also used fulvic acid (FA) as a reference material to evaluate the adsorptive behavior of the investigated DOM samples. Adsorption of both HoA and HoN on Fe^{3+}-montmorillonite were higher than that on Cu^{2+}-montmorillonite. Adsorption amounts of HoN were greater than that of HoA due to the higher hydrophobicity and the larger molecular size of HoN as compared to HoA. The isotherms of HoA and FA adsorption by Fe^{3+}-montmorillonite was best fitted by Langmuir equation. The pH increased by one unit following HoA and FA adsorption by Fe^{3+}-montmorillonite. This suggested exchange of negatively charged HoA and FA groups on surface hydroxyls of Fe^{3+}-montmorillonite followed by decrease in adsorptive surface sites. Isotherms of HoA adsorption by Cu^{2+}- montmorillonite and isotherms of HoN adsorption on both clays were best fitted by Freundlich equation, which indicated significant van der Waals interactions participating in adsorption; the pH did not change following HoN adsorption on clays. Spectroscopic analyses showed a distinct HoA and FA fractionation by molecular size and aromaticity only by Fe^{3+}-montmorillonite: E_2/E_3 ratio decreased from 11.6 to 5.9 and from 10.3 to 3.5 following HoA and FA adsorption, respectively, whereas molar absorptivity (at 280 nm) enhanced: the $\varepsilon/\varepsilon_0$ ratio increased from 0.39 to 1 and from 0.27 to 0.89 followed by

HoA and FA adsorption, respectively. Since analogous fractionation of bulk DOM was previously observed for goethite we suggested that saturation of montmorillonite with Fe^{3+} changes clay surface properties and makes it similar to goethite.