

# **Metadynamics based molecular dynamics simulation and experimental study of the adsorption of phthalate esters on smectite clay surfaces**

JENNIFER WILLEMSSEN<sup>1</sup>, SATISH MYNENI<sup>2</sup>, IAN C. BOURG<sup>3</sup>

<sup>1</sup>jarw@princeton.edu

<sup>2</sup>smyneni@princeton.edu

<sup>3</sup>bourg@princeton.edu

Phthalate esters are widely used plasticizers with known or suspected endocrine disrupting properties. Understanding the processes fundamental to the transport and persistence of phthalates in the environment is essential for developing effective remediation strategies. Central to this is the adsorption of phthalates by soils and sediments, which can strongly hinder contaminant mobility and bacterial and photodegradation. Studies have indicated that the clay content of a given soil can play a substantial role in the partitioning, but the relevant mineral-organic interactions are not fully understood. To further understand these interactions, we have developed a molecular dynamics (MD) simulation methodology to model a stack of flexible Ca-smectite clay sheets with cleaved edges in contact with a bulk aqueous reservoir containing phthalate molecules. Our methodology uses the metadynamics technique to facilitate the exploration of the entire free energy landscape of our simulation box. The simulation output provides detailed insight into the coordination and energetics of phthalate adsorption. In particular, we calculate the free energy of adsorption, the enthalpy of adsorption, the affinity of the phthalate esters for different clay adsorption sites (interlayer, edge, external basal surface), and the impact of phthalate adsorption on clay basal spacing. This research examines the six phthalate esters listed on the EPA priority pollutant list (dimethyl phthalate, diethyl phthalate, di-n-butyl phthalate, di-n-octyl phthalate, bis(2-ethylhexyl) phthalate, and butyl benzyl phthalate) that span a range of sizes and hydrophobicities. Simulation results are compared to collected experimental adsorption and x-ray diffraction (XRD) data.