Predicting Anionic Pharmaceutical Sorption to Soils Using Probe Compounds

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The ability to predict the fate of chemicals released into the environment is crucial in protecting both human and ecosystem health. More pharmaceuticals are being found at detectable levels in the environment, with prolonged exposure leading to antibiotic resistance, endocrine disruption, and other adverse health effects. When a chemical is released into the environment, it can transfer between different earth system compartments. While there are well-established predictive models for how a chemical will partition between water and air and between water and biota, there is not a very well-established model for water-soil partitioning of all chemicals.

Sorption, the transfer of chemicals from a liquid, such as water, to solid interface, such as soils, is quantified using K_d, which is equal to the concentration of a compound in soil divided by its remaining concentration in water. While sorption can occur through a variety of different mechanisms, the two most relevant to my work are surface complexation (SC), the formation of a covalent bond between the iron or aluminum atoms on the soil surface and the carboxyl or hydroxyl groups on an organic compound, and cation bridging (CB), the electrostatic attraction between a negatively charged functional group on an organic compound and the naturally occurring cations on the soil surface. Since soils are so complex and variable in terms of their composition, we use pure phase minerals, which are synthesized or isolated from soils to contain only specific receptor sites, to determine the dominant sorption mechanisms.

To avoid measuring the sorption of every pharmaceutical to every soil, MacKay and Vasudevan (2012) have developed a predictive model that uses probe compounds and scaling factors to anticipate the sorption of any compound. Type I interactions, which include hydrophobic partitioning and electron donor and acceptor interactions have a well-established predictive model. Cationic and anionic contributions to sorption require additional study. The goal is to find a cheap and accessible universal probe that will work for cationic pharmaceuticals and one that will work for anionic pharmaceuticals. While a cationic universal probe has been established, we are still searching for an anionic probe.

$$K_d^{pharma} = K_{Type\ I} + f\left(K_{CE}^{probe}, K_{CE}^{XS}\right) + f\left(K_{CB+SC}^{probe}, K_{CB+SC}^{XS}\right)$$

Prior work has shown that it is difficult to find one anionic probe that can adequately capture the extent of both CB and SC, which are both included in the anionic section of the predictive equation noted above. With that in mind, my work this summer explored an alternative method of separating the predictive equation: constituting the equation by sorption mechanism rather than by Type I, cations, and anions.

Since 2,3-dihydroxynaphthalene (2,3-DHN) is a neutral compound, I expected it to sorb primarily if not entirely via surface complexation. My pure phase data show that sorption to Hematite (affords sites for SC) was greatest, followed by sorption to calcium and aluminum montmorillonite (Ca-MMT and Al-MMT) (Figure 1). This indicates that SC is likely the primary sorption mechanism, but there is also evidence that it may not be the only important mechanism. Since 2,3-DHN is not charged, it lacks the ability to sorb via CB. However, since the hydroxyl groups are electron donating, it could allow for negative charge delocalization within the aromatic rings. This can create an electrostatic attraction to the positive charge on the Ca-MMT and Al-MMT, offering an explanation as to why we see notable sorption to these pure phases despite the lack of charge on 2,3-DHN. Since the charge of the calcium ion is more defocused and softer than aluminum, similar to the delocalized negative charge on 2,3-DHN, it makes sense that we would see greater sorption to Ca-MMT than Al-MMT.

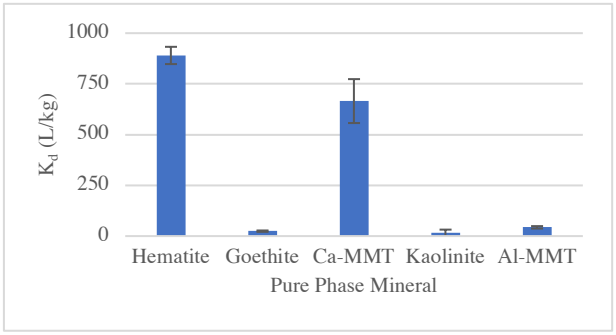

Figure 1. Graph depicting the sorption, quantified using K_d, of 2,3-DHN to five pure phase minerals. Error bars represent +/- standard deviation.

Examining 2,3-DHN sorption to a range of soils showed a general increase in K_d with an increase in DCB Fe content of the soil, which is an indicator of sorption via SC. In cases where this trend did not hold true – where a soil had a high Kd but relatively low DCB Fe – the soil typically had above average exchangeable calcium or aluminum content (Ex Ca or Ex Al). This shows that SC is the dominant sorption mechanism, but electrostatic attraction to Ex Ca and Ex Al plays a secondary role, with the 2,3-DHN likely sorbing parallel to the surface.

Using the limited number of soils on which 2,3-DHN sorption was quantified, a preliminary comparison of log K_d values shows that 2,3-DHN sorption is correlated to hydratropic acid sorption (R^2=0.8671, excluding Goldsboro and Tunbridge soils), but not to any of the other pharmaceuticals or probes previously studied. A more complete data set will help to determine this with more confidence.

Future Work: measure 2,3-DHN sorption to remaining soils, compare the data from all 30 soils to other probes and pharmaceuticals previously studied in the Vasudevan lab, quantify K_d for 2,3-DHN sorption to Na-MMT to help verify the idea that 2,3-DHN sorbs to a higher extent when charge is softer and more spread rather than concentrated.

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