

How to examine soil sorption of ionizable organic compounds and avoid varying pH?

Mikhail Borisover

The Volcani Center, Institute of Soil, Water and Environmental Sciences, Israel (vwmichel@volcani.agri.gov.il)

Multiple natural and anthropogenic organic compounds including new and emerging pollutants undergo ionization in aqueous solutions, and their sorption by soils and sediments is contributed by presence of both molecular and ionized species. Better understanding of environmental fate of organic chemicals requires taking into account interactions of molecular and ionized species with environmental sorbents. A "standard" (and undoubtedly important) procedure for differentiating contributions of molecular and ionized species into the overall soil sorption of an organic compound involves varying pH of solution in batch sorption experiments. However, varying pH is (1) often not possible, without destroying a sorbent, e.g., due to the buffer capacity of soils containing carbonates, (2) difficult for further interpretation, since it changes not only the ionization status of a solute in a solution but also the sorbent structure, e.g., a conformation of organic matter, and/or ionization of surface functional groups, (3) making difficult (or even impossible) to explicitly evaluate the role of dissolved species-bulk water interactions, directly affecting the affinity of a sorbate to distribute between water and a sorbent. Indeed, both molecular and ionized species undergo interactions with the solvent bulk and, at least in the case of the ionized ones, there was no a simple way to quantify organic ion-water interactions and their role in organic ion distribution between soil and water phases. This paper presents a "counter-intuitive" approach to examine sorption interactions of an ionizable compound, without experimenting with varied pH. The approach is based on an idea of replacing an initial state in sorption transfer of an ionizable compound from the solvent bulk to a solvated (hydrated) sorbed state: a traditional coefficient describing distribution of a partially ionized compound between a hydrated sorbent and a co-equilibrated aqueous phase is converted to the coefficient describing the transfer of the sorbing compound from its initial molecular (non-ionized) state (in a solution or in the gas phase) to the final hydrated sorbed state equilibrated with the actual aqueous solution of this ionizable compound. In this way, any contributions from the bulk solvent-organic ion interactions into the sorption transfer may be excluded; in addition, further any solute-solvent interactions may be taken out of the consideration. Therefore, compound's sorption characteristics "cleared" of solute-solvent interactions may be obtained, and a better understanding of relations between interactions in a sorbed phase and a molecular structure of organic sorbates can be reached. The approach is illustrated by examining sorption of variously ionized organic compounds, i.e. those belonging to the pharmaceuticals and personal care products (triclosan, gemfibrozil, galaxolide), and aliphatic organic acids on natural and organic amendment-enriched soils. Specifically, it is demonstrated how the greater H-donating ability of trifluoroacetic acid, as compared with acetic acid, strengthens the acid interactions in the soil phase. In another series of examples, it is shown how hydrophobic and non-ionizing galaxolide interacts weakly with soils, as compared with partially ionized triclosan and almost fully ionized gemfibrozil, i.e. leading to the conclusions not reachable based only on the direct comparison of experimentally measured distribution coefficients.