Charge delocalization in heterocyclic amines and its impact on sorption mechanisms
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In both the environment and the material world, pesticides, pharmaceuticals, and personal care products have become more prevalent and accessible. Consequently, these compounds are found in groundwater, food, soil, and air. The transport, transfer, and transformation of these compounds informs their environmental fate and potential harm: in particular, my work in the Vasudevan lab examines the transfer or sorption of compounds with ionizable cationic (positively charged) amine groups from water to soil (Vasudevan et.al., 2013). Sorption is quantified by the soil-water partitioning coefficient K_d (L/kg) and is calculated by dividing the concentration of the compound sorbed onto soil (mol/kg) by the concentration of the compound in water (M).

Cationic amines are attracted to negatively charged sites on soils prevalent in soil, quantified as ECEC – effective cation exchange capacity. Soil organic matter (OM) and aluminosilicates (AS) and metal oxides–possess negative charges at environmentally relevant pH (3-8).

Previous studies in the Vasudevan lab explored how amine order (ao) affects heterocyclic amine sorption to AS and OM by using 1,2,3,4-tetrahydorisoquinoline (1,2,3,4-THIQ) (ao =2) and 5,6,7,8-tetrahydroisoquinoline (5,6,7,8-THIQ) (ao =2.5) shown in Figure 1. They found that alicyclic heterocyclic amines (1,2,3,4- THIQ) with a less delocalized charge prefer to sorb to soils with high OM and moderate to low ECEC and aromatic heterocyclic amines (5,6,7,8 -THIQ) show preference for sorption to AS because of the greater defocused charge.
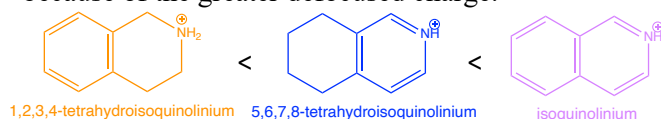

Figure 1 Charge delocalization prediction for ISQN, 5,6,7,8-THIQ, and 1,2,3,4-THIQ in their protonated form

1,2,3,4-tetrahydroisoquinolinium < 5,6,7,8-tetrahydroisoquinolinium < isoquinolinium

Building on this work, I studied charge delocalization with isoquinoline (ISQN) by measuring ISQN sorption to 30 soils, comparing ISQN sorption to 5,67,8 sorption, and conducting regression analysis to a range of soil properties. Under my experimental conditions, soil OM site will be neutral, hence I am able to assume that sorption is primarily to AS which possess permanent negative charge.

The soil properties include percent organic carbon (%OC), surface area (SA), ECEC, exchangeable magnesium (ExMg), sodium (ExNa), potassium (ExK), calcium (ExCa), and aluminum (ExAl).

As shown in Figure 2, Twenty-two of 27 soils have higher sorption for ISQN, 2 of 27 soils prefer 5,6,7,8-THIQ, and 3 of 27 soils have no preference of amine: furthermore supporting that a more delocalized compound has higher sorption AS due to is defocused charge and affinity to high negative charge sites. Regression results showed log %OC, SA, and ExAl as not statistically significant when correlated with log ISQN K_d for the 27 soils. Log ECEC, ExCa, ExMg, and ExNa are moderately correlated with log ISQN K_d - R^2= 0.61, 0.61, 0.69, and 0.65, respectively. The moderate correlation indicates there are other factors to consider; nonetheless, the regressions show the importance of negative sites within the soil and indirectly indicates that the exchangeable cations listed above are most likely found in copious quantities in AS, given that OM sites are neutral at my experiment's pH. ExK had a weak but significant correlation of 0.26 suggesting that ExK is not a principal factor with delocalized heterocyclic amine sorption.

Future work: Collecting data with more delocalized compounds on all 30 soils, further analysis on cation sorption to AS and OM by redoing 1,2,3,4-THIQ at pH 3, and relating these results to previous environmental fate work
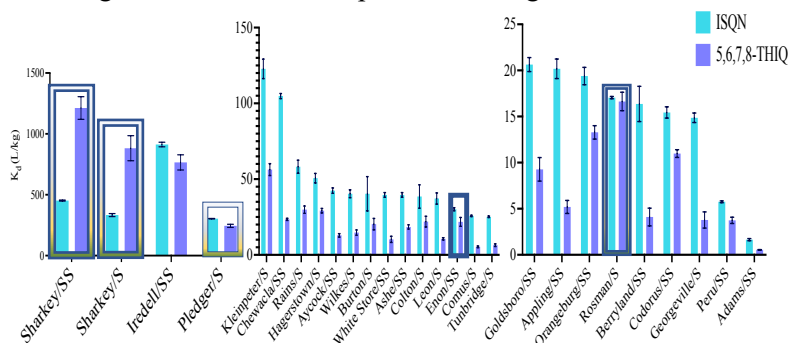

Figure 2 Charge delocalization comparison of ISQN and 5,6,7,8-THIQ separated by decreasing Kd- ISQN Kd > 150 L/kg, ISQN Kd > 25 < 150 L/kg, and ISQN Kd < 25 L/kg. Kd (L/kg) is on the y-axis and soils are on the x-axis.