Adsorptive Behavior of Atrazine and Alachlor in Organic-Poor Sediments

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ABSTRACT

Atrazine and alachlor are commonly used herbicides in the mid-continent region of the United States. Atrazine is the single most widely used herbicide in this region and the one most commonly detected in groundwater. A key process affecting transport of herbicides to groundwater is sorption (adherence) to the solid matrix through which soil solution percolates. Sorption of herbicides retards the transport of these substances in solution. Hence a more in-depth understanding of the sorptive behavior of herbicides is important to the interpretation and prediction of their fate and movement in the subsurface. Numerous studies have demonstrated that sorption of herbicides and other non-ionic organic pollutants to soil is controlled by the organic carbon portion of the sediment. These observations have led to a model in which sorption of organic pollutants is assumed to be maximized in organic-rich topsoils and minimized in organic-poor subsoils. However, this model may be overly simplistic for organic molecules such as atrazine which are strongly hydrophilic (water loving), especially if the topsoils are organic-poor and clay-rich. A more rigorous model that incorporates the sorptive capacity of mineral surfaces (clay) was investigated to evaluate the relative contributions of each sorption mechanism. Batch experiments were performed on an organic-rich topsoil and an organic-poor subsoil typical of soils found in Southeastern Wisconsin. Sorption of atrazine to the mineral fraction accounts for 70% of total adsorption in the subsoil and 21% in the topsoil. Sorption to the mineral fraction of these soils is significant, even in the organic-rich topsoil. When modeling the movement of pollutants in groundwater systems, sorption data is often used to calculate retardation of pollutant movement with respect to bulk groundwater flow. The findings show that predicted retardation of atrazine in the subsoil is three times greater than calculated by ignoring sorption to the mineral portion of the sediment.

TECHNICAL SUMMARY

INTRODUCTION: In general, the sorptive behavior of organic pollutants in soils is controlled by partitioning into the organic carbon (oc) component of the sediment. This behavior arises as a consequence of hydrophobicity, i.e., (1) the hydrophobic repulsion of non-polar, non-ionic molecules out of the highly polar aqueous solution, and (2) the hydrophobic affinity of the oc component of sediments for these organic molecules. The hydrophobic nature of organic molecules is manifested by low water solubilities (S_w) and high octanol:water partition coefficients (K_{ow}). It is also well established that clay mineral surfaces can play a role in adsorption of organic pollutants. Their role is particularly important for organic herbicides such as atrazine and alachlor which have polar functional groups that allow hydrogen bonding to mineral surfaces. Atrazine and alachlor have relatively high water solubilities (S_w = 70 and 240 mg/L, respectively) and low octanol:water partition coefficients ($K_{ow} = 10^{2.7}$ and $10^{2.6}$, respectively). Hence, they are only poorly hydrophobic and are likely to be driven by less of a force to partition into the oc fraction of sediments, but by a greater force to complex with mineral surfaces. This study evaluates the contributions of mineral and oc surfaces of soils and sediments to sorb the two herbicides by typical topsoil and subsoil samples.

METHODS: Two soil samples, a topsoil and a subsoil directly beneath, were collected from the University of Wisconsin-Milwaukee campus and characterized as Kewaunee silt loam. The organic rich topsoil was collected from the top 10 cm and contained 3.2% oc and 24% clay while the organic poor subsoil was collected at a depth of 55 cm and contained 0.39% oc and 51% clay. The principal clay minerals in both soils were montmorillonite and illite. Batch sorption experiments were conducted in glass centrifuge tubes with aluminum foil cap liners. The soil:water ratio was 1:5 by weight, herbicide concentrations were <300 mg/L, and a 48 hour equilibration on a wrist action shaker was employed for the sorption process. Phase separation was accomplished by centrifugation at 2250 x g for 50 minutes. Aqueous concentrations of atrazine and alachlor in the supernatants were measured by direct injection into a HP-5890 gas chromatograph (GC) with a ^{63}Ni electron capture detector and a 25-m DB-5 capillary column. Herbicide concentration in the sediment was determined after triple extraction with HPLC grade methanol. Simazine and propachlor were used as internal standards for atrazine and alachlor determinations, respectively. Experiments were replicated a minimum of three times with data averaging and mass balances averaged 99% throughout the study.

RESULTS: The conceptual framework used to differentiate between the mineral and organic components of herbicide sorption centers around the following equation (Grundl, T. and G. Small (1993*), J. Contaminant Hydrology,* Vol. *14:117-128)*

$K_p = K_m(cm) + K_{oc}(oc)(1)$

where K_p is total partition coefficient to sediment (L/kg), K_m is intrinsic partition coefficient to mineral clay surfaces (L/kg), K_{oc} is intrinsic partition coefficient to organic matter measured as organic carbon (L/kg), cm is fractional sorptive mass of clay in the sediment (0 to 1), and oc is fractional sorptive mass of organic carbon matter in the sediment (0 to 1). Two independent (two different soil samples) determinations of K_p and oc were made for each herbicide. Since cm = 1-oc, the only unknowns are K_{oc} and K_m. Two independent equations can be written, one each for topsoil and subsoil, by dividing equation (1) by appropriate oc and cm values, respectively. The resulting equations (not shown) can be solved for K_{oc} and K_m by determining the slope of the K_p/oc vs. cm/oc and K_p/cm vs. oc/cm plotted lines. The resulting mineral and organic sorption coefficients are K_{oc} = 196 and 436 L/kg organic carbon for atrazine and alachlor respectively; and, K_m = 1.8 and 3.0 L/kg clay mineral, respectively. Although organic sorption appears dominant from the K_{oc} values, this is not the case when multiplied through by the relative amounts of organic and mineral matter. After normalization, the sorption of atrazine to the mineral fraction accounts for 70% of the total in the subsoil and 21% in the topsoil. Equivalent values for alachlor are 63% and 17%, respectively. Hence sorption to the mineral portion of these soils is significant, even in the topsoil with an organic carbon content of >3%.

DISCUSSION: Comparison with literature K_m (partition coefficient) values of atrazine to clean mineral surfaces at neutral pH reveal that clay in soils generally has lower values. The average of three citations for montmorillite was 11 ± 4 compared to 1.8 found here (Bailey et al., 1968, Proc. Soil Sci. Soc. Am., 32:222-234; Hance, 1969, Can. J. Soil Sci., 49:357-364; Talbert et al., 1965, Weeds, 13:46-52). The higher Km values to clean mineral surfaces supports the idea that these surfaces are not rigidly representative of naturally occurring clay mineral surfaces in soils. This is not unexpected since humic acid components of organic carbon matter are known to undergo ionic complexation with clay mineral ion-exchange sites. This leads to a diminution in the number of mineral surface reactive sites and to more restricted access to the sites still available for complexation. Nevertheless, it is clear that naturally occurring clay mineral surfaces still retain the capacity for significant sorption of moderately hydrophilic herbicides such as atrazine and alachlor. Therefore, when modeling movement of these herbicides in groundwater systems, it is important to incorporate sorption data for both organic carbon and clay mineral surface content. For example, retardation of atrazine and alachlor in the present subsoil calculated by ignoring sorption to the mineral portion are low by factors of 2.6 and 2.8. Actual retardation is about three times slower because of mineral sorption. This is important when trying to determine the extent and time course of groundwater contamination resulting from herbicide usage.

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