ADSORPTION OF HERBICIDE ATRAZINE ONTO COMPLEXES OF KAOLIN WITH HUMIC SUBSTANCES

N. Kulikova* and I. Perminova**
* Dept. of Soil Science, Lomonosov Moscow State University,
Leninskie Gory, 119992 Moscow, Russia
** Dept. of Chemistry, Lomonosov Moscow State University,
Leninskie Gory, 119992 Moscow, Russia
iperm@org.chem.msu.ru

Atrazine is one of the most widely applied and persistent herbicides. Its fate in the environment is greatly affected by binding to humic substances (HS) affecting degradation and toxicity of the herbicide. In soil media it associates with various soil components, mainly with organo-mineral complexes (OMC) containing immobilized HS. This study focused on atrazine interactions with model OMC synthesized using clay mineral kaolin and HS.

Eleven samples of humic (HA) and fulvic (FA) acids used in this study were isolated from different environments, nominally, soil, peat, brown coal and lake water. All HS samples were characterized using elemental and 13C solution-state NMR analysis and potentiometric titration. The model OMC were prepared by adsorption of HS (250 mg/L, pH 5.6, 0.1M NaCl, 12 h) onto kaolin clay (Kaolin CF 70, Caminauer Kaolinwerk GmbH, Germany) of particle size less than 20 μm. The obtained OMC were washed, dried, and stored for further use. Mass percent organic carbon (OC) in coated samples ranged from 0.06 to 0.18%.

Adsorption-desorption experiments were conducted in centrifuge tubes at atrazine concentrations 2–20 μM. 0.5 g of OMC was dispersed in 10 mL of atrazine solution (pH 5.6, 0.1M NaCl). The samples were equilibrated for 12 h by means of a rotary shaker. The probes were then centrifuged (10 min, 4000 rpm) and the equilibrium concentration of atrazine in supernatant was determined by HPLC (acetonitrile:water (50:50, v/v), pH 2.5, 220 nm).

Both adsorption and desorption isotherms for all the complexes used were near linear and fitted quite well by a Freundlich equation. To estimate a hysteresis effects, a hysteresis indices (H) were calculated as a ratio nf/nfd, where nf and nfd are the Freundlich linearity coefficients calculated from the adsorption (nf) and desorption (nfd) isotherms, respectively. The minimum value of H was observed for kaolin clay (1.21) demonstrating a possibility of completed atrazine desorption. However, H values for the model OMC laid in the range from 2.31 (peat HA) to 9.24 (aquatic HA). This fact showed that atrazine adsorption onto kaolin-HS complexes was only partly reversible. Correlation between H and O/C ratio of HS used (r=0.75) demonstrated that irreversibly adsorbed atrazine was probably bound to the O-containing groups of HS. Carboxylic groups seemed to play the leading role: the correlation coefficient between their content in HS and H values was 0.93.

The calculated distribution coefficient (Kd) for adsorption of atrazine onto kaolin clay was 172, while that for OMC varied from 193 (soil FA) to 248 (coal HA) L/kg. Values of Kd increased alone with increasing OC content in the OMC. However, not only quantity of OC, but also properties of adsorbed HS influenced the atrazine binding. A significant (P=95%) relationship between Kd and the content of aromatic fragments in HS was established (r=0.76). This is indicative for the role of aromatic structures of HS in atrazine binding and for hydrophobic mechanism of the interaction.

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