INVESTIGATION ON ADSORPTION OF CHLOROACETANILIDE HERBICIDES ON HUNGARIAN SOILS

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ABSTRACT

Herbicides used by the agriculture can contaminate our drinking water resources through the soil-soil solution-groundwater system. That is the reason why it is important to get more information on their adsorption behavior.

Equilibrium batch expriments were carried out with five chloroacetanilide type herbicides (acetochlor, alachlor, metolachlor, propachlor, propisochlor). Typical Hungarian soils (chernozem, brown forest and sandy) with different humic contents were used as adsorbents. The experiments were carried out at pH = 7 in phosphate buffer and in 0.1M $NaNO_3$ solution in order to maintain the ionic strength at the same value. Adsorbed amounts were calculated from the equilibrium concentration measured by gas- and liquid chromatography (GC and HPLC).

Adsorption isotherms have one or two steps. The curves were fitted using a newly described theory and adsorption coefficients were calculated by means of suitable equation. The meaning of the parameters in the adsorption equation is given. A comparison of the parameter values was also completed. According to the measurements the greatest amount adsorbed on the chermozem, having the highest content of organic matter of the soils used while the least amount is bounded by sandy soil.

INTRODUCTION

Using pesticides people enter the processes of the nature. (Of course that is the reason why they are produced.) More amounts of pesticides than necessary cause an environmental contamination of a sort that can be reduced when a kind of sorption happens in the soils. This immobilisation has two different consequences. One is that the effect of the retained active ingredient lasts longer and the other is that this molecule can be decomposed or transformed into another compound or can be bonded to the humic substances. These are the reasons to know more about the adsorption features of pesticides.

In the present work we made experiments with five chloroacetanilide type herbicides (alachlor, acetochlor, metolachlor, propachlor and propisochlor) used widely in Hungary.

METHODS

Adsorption:

- Equilibrium batch experiments.

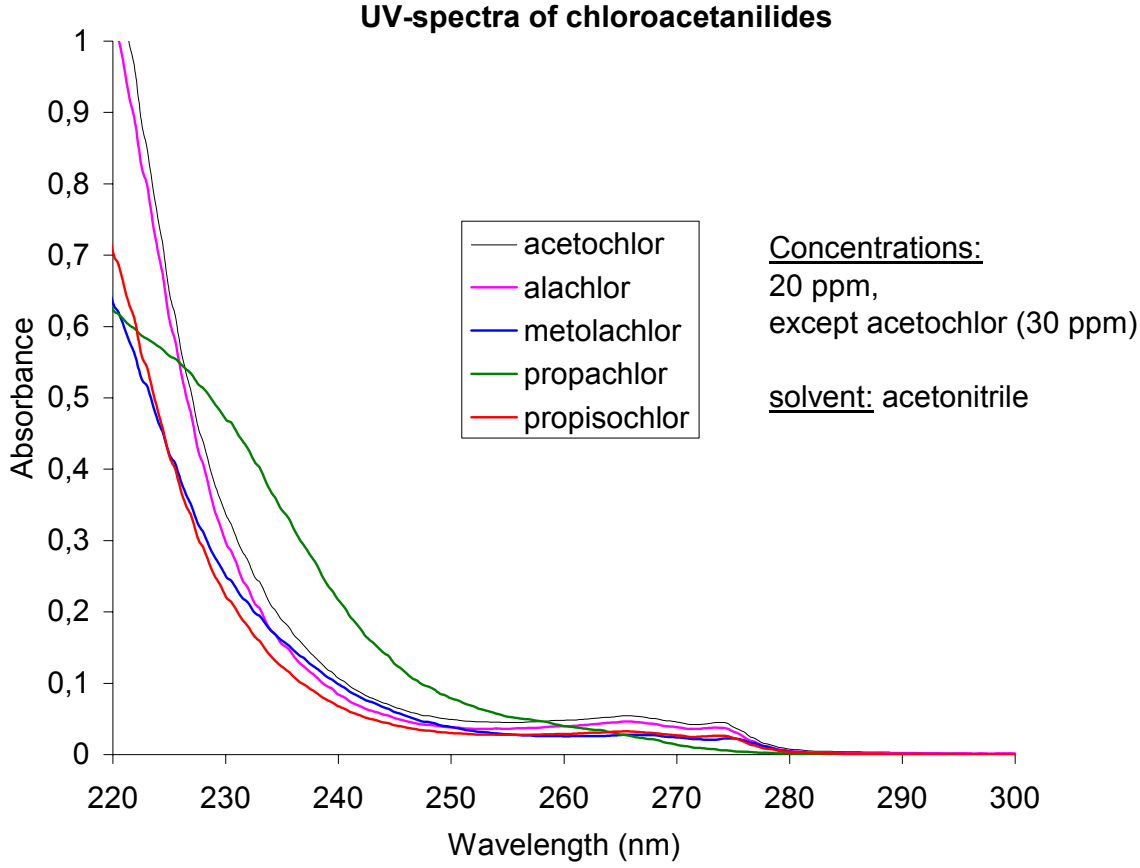
- Medium: 0.1 mol/L $NaNO_3$ and 0.01 mol/L Na_2HPO_4/NaH_2PO_4 buffer (pH = 7).
- After equilibration (24 hours) and centrifugation of the samples the aqueous phase was analysed (in case of the GC measurements an extraction step was inserted).
- Adsorbed amounts were calculated from the equilibrium concentration of the compound.

Analythical methods used were GC:
Fisons 2000 Series, with a JSZW Scientific column (DB-1 stationary phase) 26.4 m*0.537 mm, 5 μm film thickness; ECD pure N_2 carrier gas (24 cm^3/min.); ECD detector. The temperature programme was isotherm 230 ^oC in case of alachlor and metolachlor and 170 ^oC in case of propachlor. The injector and the detector was also

and RP-HPLC with a Merck Hitachi LaChrom 7000 series instrument equipped with a LiChrospher 100 RP-18 (15 μm) column; isocratric separation, 1 mL/min.; mobile phase: acetonitrile/water: 65/35; detection: UV detector:

Compound	**Alachlor**	**Acetochlor**	**Metolachlor**	**Propachlor**	**Propisochlor**
Wavelength	240	265	233	233	265

based on these spectra:

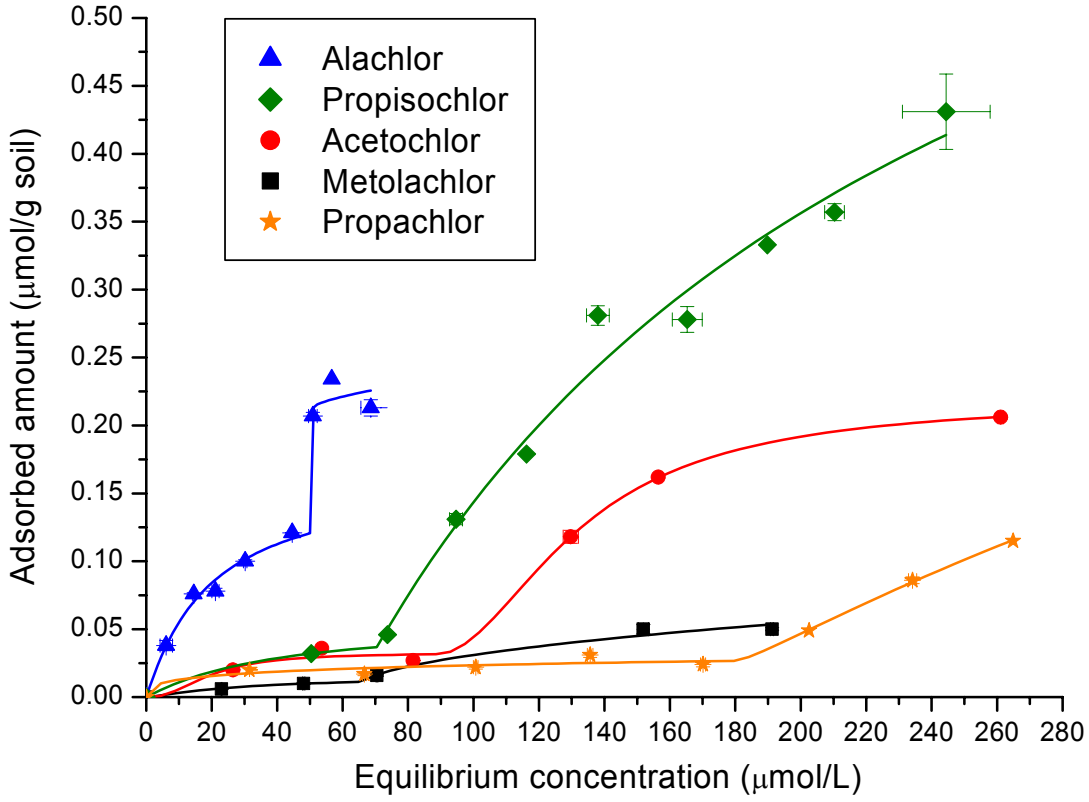


The equation used for fitting was:

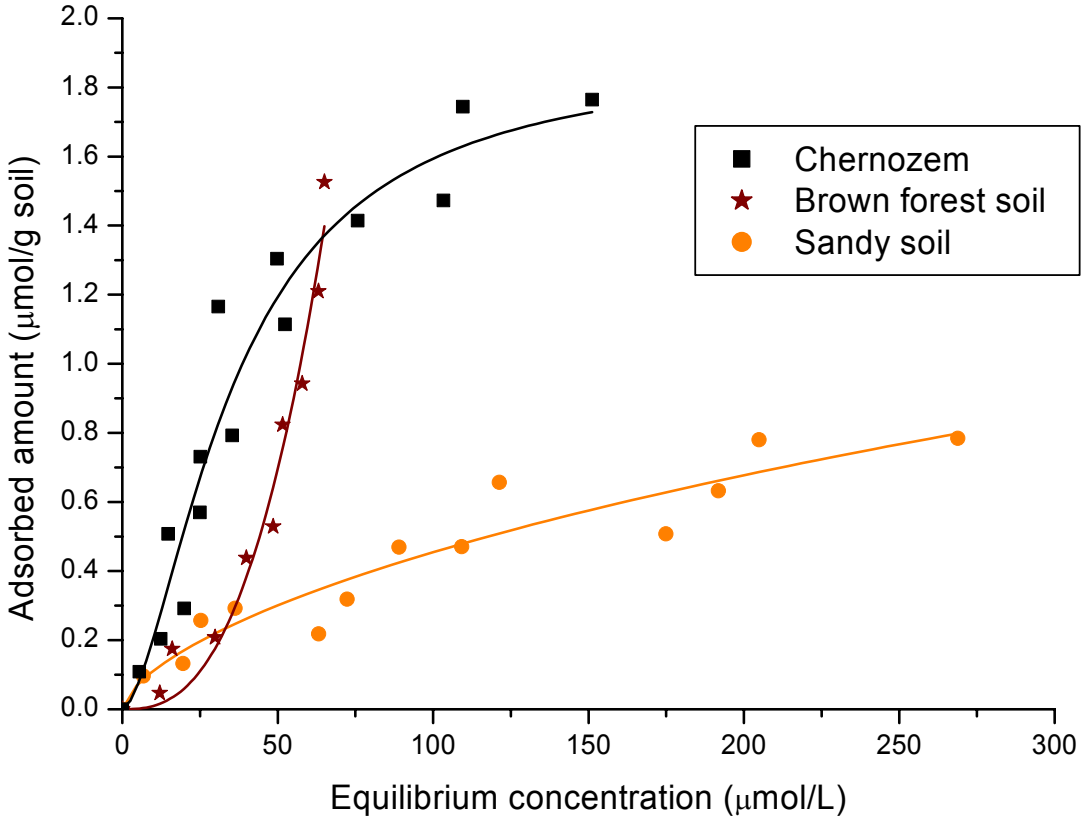
$$q = \sum_{i=1}^{s} \left\{ \frac{q_{Ti} \cdot K_i \cdot (c - b_i + |c - b_i|)^{n_i}}{2^{n_i} + K_i \cdot (c - b_i + |c - b_i|)^{n_i}} \right\}$$

Where q, mmol/g adsorbed amount,
c, mmol/L equlibrium concentration,
q_{Ti}, mmol/g adsorption capacity,
K_i, $(L/mmol)^{n_i}$ equilibrium constant, showing the adsorption activity of the active centrums,
b_i, mmol/L critical concentration limit of the i^{th} step of the curve,
n_i average degree of association of the i^{th} step of the curve [1].

Our results on brown forest soil were:



Illustrating the organic matter dependency we would like to introduce the isotherms of metolachlor on different soils:



DISCUSSION

In the process of GC we used lower temperature in case of propachlor, because of the risk of decomposition. On the grounds of the spectra of herbicides we could choose the best wavelength to detect them by UV in the case of HPLC (we could not do that on lower wavelengths because the nitrate would disturb the correct detection).

Observing the relation between the soil organic matter and the adsorption we can find that the greater is the organic matter portion the greater is the adsorption [2]. It should not be forgotten anyway that the surface of the mineral constituents also has non-polar regions. This is completed by the fact that the sandy soil has quartz (not so good sorbent) in the greatest and clay component in the least portion [3].

Most of the isotherms have two steps. Having a look at the parameters we can see that in general K_1 constant is higher than the K_2 and that is what everyone expects. A possible interpretation of the “wrong” order in case of the propachlor can be: the second layer starts to be created before the first layer is built up completely.

CONCLUSIONS

Adsorbed amounts of the herbicides were in the next order:
alachlor > propisochlor > acetochlor > metolachlor > propachlor → the mobility increases in this order.
Greatest amount is adsorbed on chernozem. (Having the highest organic matter content.)
The fitting according to the equation is quite good: R^2 is between 0.988 and 0.998.

REFERENCES

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