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INTRODUCTION

Time-dependent sorption has been attributed to several factors, including rate-limited sorption, diffusion, non-linear sorption and non-singularity. Physical nonequilibrium and intra-organic matter diffusion have been suggested to be the main causes for time-dependent sorption of hydrophobic compounds.

In previous work, a diffusion-based model was applied successfully to describe the behaviour of different pesticides on natural clay loam aggregates (Van Beinum et al., 2005). The present work goes further in order to test if those findings can be extrapolated to different types of soils for a longer sorption time.

MATERIALS AND METHODS

Pesticides: azoxystrobin, chlorotoluron, atrazine.

Some physico-chemical properties of the soils under study

Soil Series	Textural classification*	pH	OM (%)	Clay (%)	Silt (%)	Sand (%)
Evesham	Clay	7.9	5.89	59.2	33.5	7.3
Brockhurst	Silty Clay Loam	6.71	4.27	36.4	52.8	10.8
Ragdale	Clay Loam	7.02	4.42	33.7	44.5	21.8

Soil aggregates preparation. The aggregates were stabilised by coating them with alginate gel. Individual aggregates were dipped in alginate solution in a desiccator connected to a vacuum pump (~80 kPa) to avoid entrapped air (Figure 1) and then immersed in a 0.1 M CaCl₂ solution to cross-link the alginate gel.

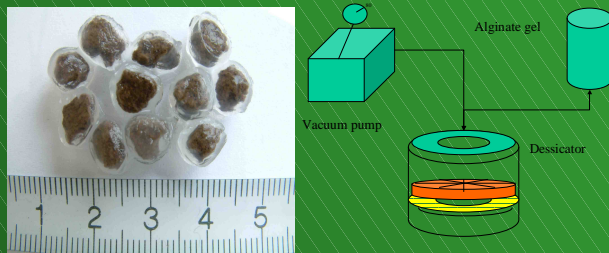


Figure 1. Gel coated soil aggregates. Preparation sketch

Sorption experiments. Ten coated soil aggregates (1 g) were weighed and placed in a 20 mL glass vial and 4 mL of pesticide solution in CaCl₂ was added to each vial. The aggregates were left on a shaker stirring gently for 1, 3, 9 hours and 1, 3, 7, 14, and 28 days.

Intra-aggregate diffusion model.

➤ The aggregates are assumed to be homogeneous and spherical with an identical radius.

➤ All sorption is controlled by diffusion into the aggregates, and there is no instantaneous fraction. - Sorption inside the aggregate is described by a Freundlich equation.

➤ Diffusion across the gel coating is not taken into account in the model.

Model equation:

Where D_e is the effective pore diffusion coefficient, D_w is the diffusion coefficient in water, τ is tortuosity, and θ is the aggregate porosity.

RESULTS AND DISCUSSION

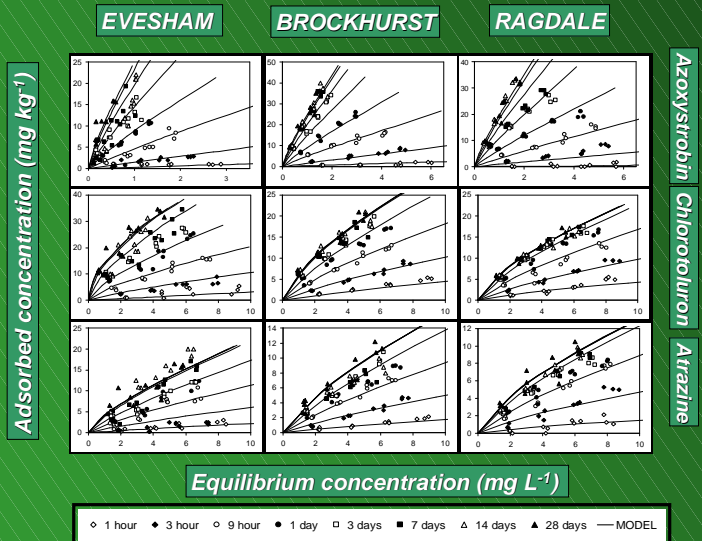


Figure 2. Adsorption of azoxystrobin, chlorotoluron and atrazine on coated soil aggregates after different equilibration times, measured (symbols) and simulated with the intra-aggregate diffusion model (solid lines)

• Equilibrium sorption was reached during the 28-day experiment for all pesticide-soil combination. The amount of sorption increased rapidly during the first three days. Overall, sorption seemed to reach equilibrium sooner for atrazine and chlorotoluron than for azoxystrobin.

• Most of the datasets could be described (diffusion model) with the same diffusion coefficient, which supports the theory that time-dependent sorption in the aggregates is controlled by pore diffusion into the aggregates. Each of the three pesticides was described despite strength of sorption differing between the pesticides by up to a factor ten. This suggests that the model describes the retardation caused by sorption correctly.

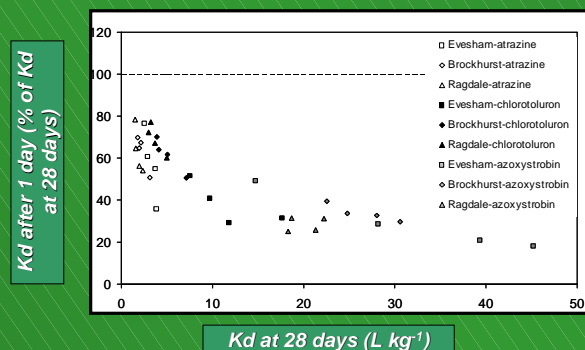


Figure 3. Relative difference in sorption after 1 and 28 days for different combinations of soil and pesticide.

• The results in Figure 3 confirmed that there is an inverse relationship between the speed of approach to sorption equilibrium and the strength of sorption. Sorption measured after 24 hours was further from equilibrium for those pesticides and soils that showed stronger sorption

REFERENCES

Van Beinum, W., Beulke, S., Brown, C.D., 2005. Pesticide sorption and diffusion in natural clay loam aggregates. *J. Agric. Food Chem.* 53, 9146-9154.