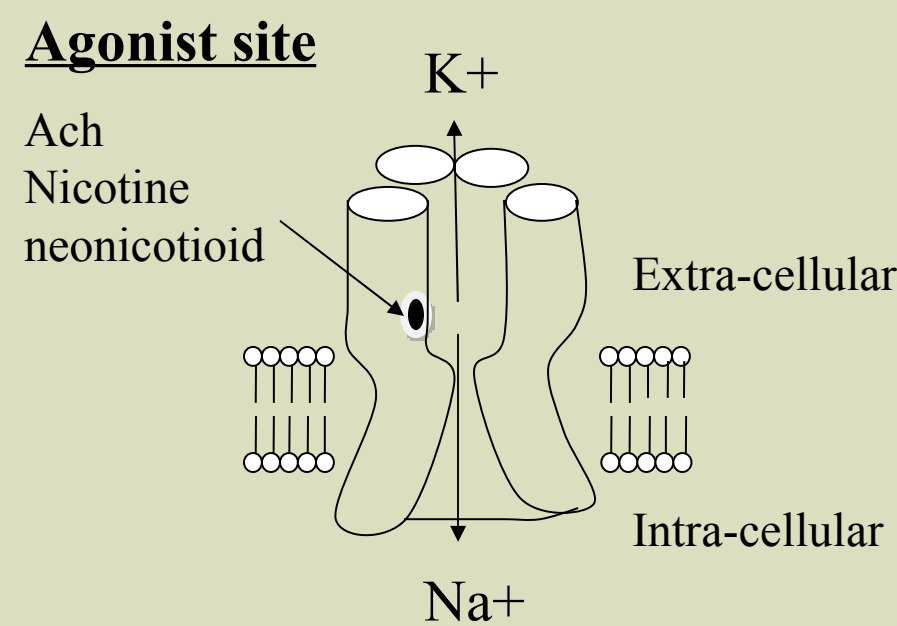


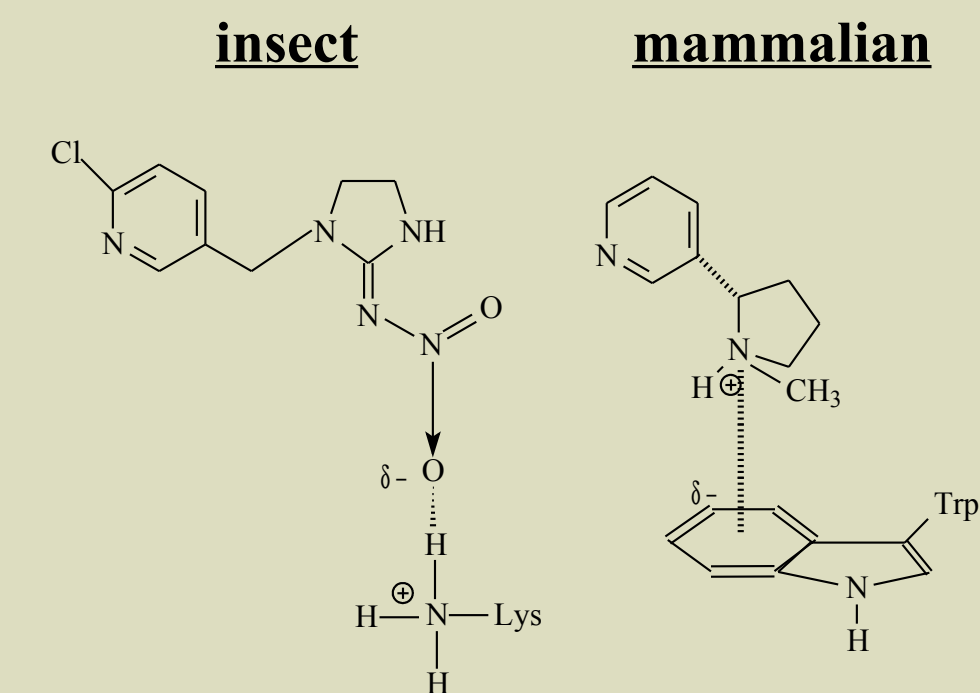
INTRODUCTION

Imidacloprid is a relatively new systemic chloronicotinyl insecticide having a mode of action based on interference of the transmission of impulses in insect nerve system (Elbert et al., 1991). Imidacloprid works by interfering with the transmission of stimuli in the insect nervous system. Specifically, it causes a blockage in a type of neuronal pathway (nicotinic) which is often found in insect nervous systems. It is distinguished for its relatively low toxicity to most mammals other than insects (Casida and Quistad, 2004; Tomizawa, 2004).

Acetylcholine (ACh)-mediated excitatory synapse



Subsite specificity confers selective toxicity



Imidacloprid electronegative tip interactions with basic amino acid residues

Nicotine cation- π interaction

In this study, we focus on the kinetics of imidacloprid adsorption with time and over wide range of imidacloprid concentrations in several different soils. Subsequent to adsorption, release or desorption was also quantified with time to assess the kinetics of reactions during release as well as to measure the extent of hysteresis for several soils. Specifically, our objectives were; **(i) to quantify the extent of kinetics on imidacloprid adsorption in soils having different properties; (ii) to assess the extent of hysteresis of imidacloprid and its irreversibility over time during desorption or release; and (iii) to evaluate multireaction models in their capability of describing kinetic retention as well as desorption behavior of applied imidacloprid, over a wide range of concentrations.** Such information is a prerequisite in predicting the fate of applied insecticides and the implementation of corrective actions needed to reduce their off-target movement from agricultural lands.

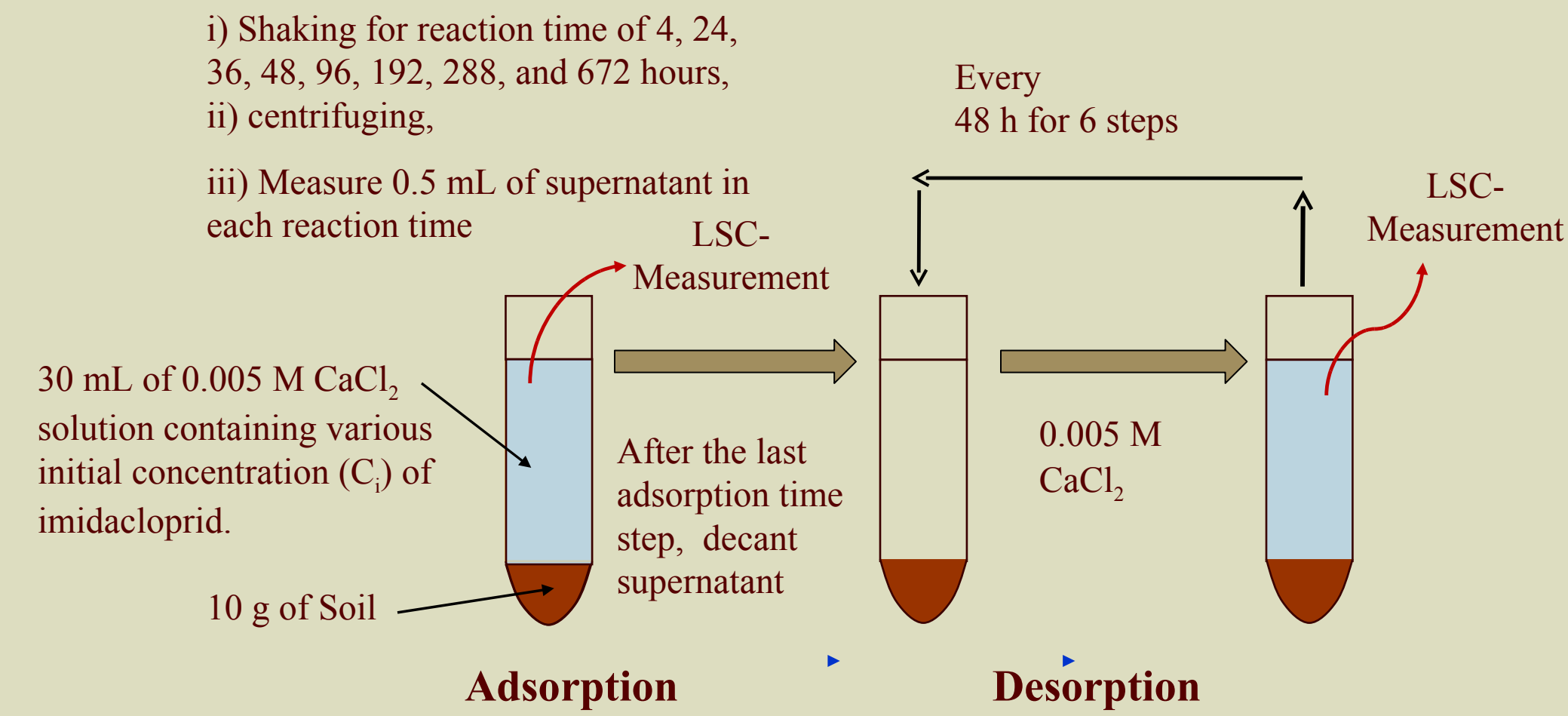
Table 1. Selected Physical and Chemical Properties of the Studied Soils.

Soils	pH	CEC meq/100g	O.M	Sand	Silt	Clay	DOC $\mu\text{g/mL}$
Mahan	6.1	7.00	0.96	49	20	31	153.0
Mhooon	6.4	43.3	4.15	10	55	35	537.6
Sharkey	5.9	39.4	1.41	3	36	61	80.95
Vacherie	7.6	16.2	2.51	50	48	2	261.3
Sand	6.3	0	0	81	19	0	

MATERIAL AND METHODS

In this study, four soils, Mahan, Mhooon, Sharkey, and Vacherie, having different characteristics were used. Selected chemical and physical as well as soil classification information of the soils are given in Table 1.

Adsorption-Desorption experiments



Multireaction model (MRM)

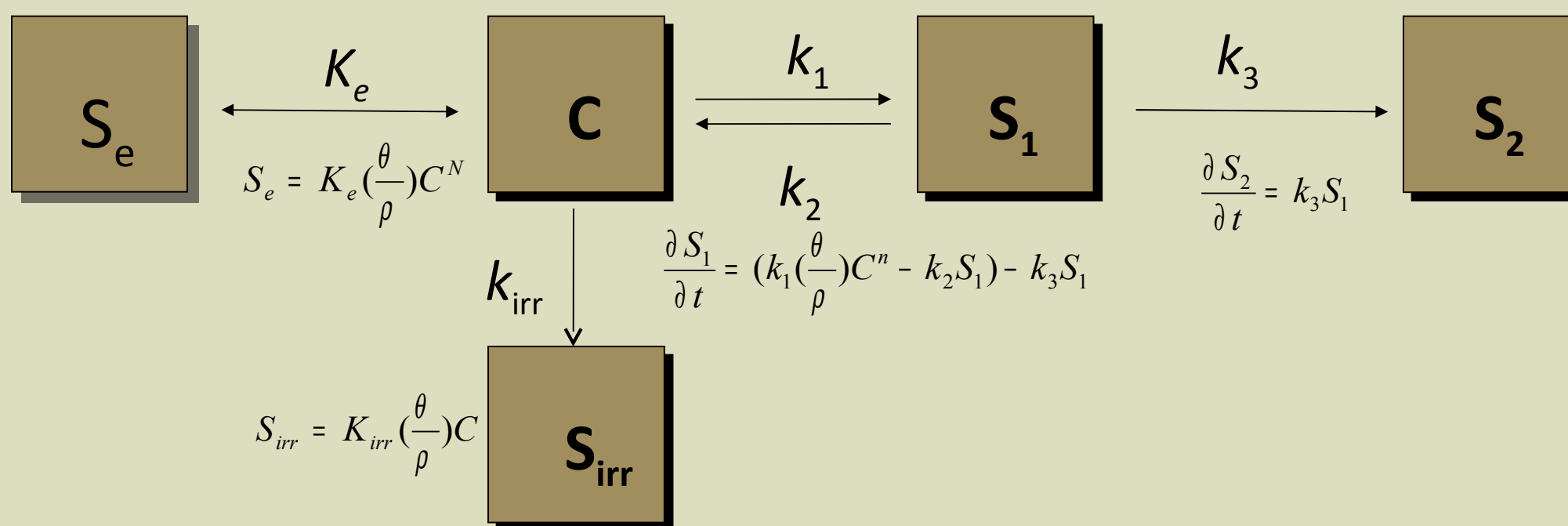


Figure 1. Schematic diagram of the multireaction model (MRM) where C is imidacloprid concentration in soil solution, and S_e and S_1 are the amount sorbed with reversible way on equilibrium- and kinetic-type sites, respectively. The S_{irr} and S_2 are irreversibly sorbed amount on the soil matrix with the concurrent and consecutive type, respectively. The parameters k_e , k_1 , k_2 , k_3 , and k_{irr} are the reaction rate associated with the binding reactions.

RESULTS AND DISCUSSION

Adsorption equilibrium

A comparison of the adsorption capacities of the different soils shows that imidacloprid sorption followed the sequence; Mhooon > Sharkey > Vacherie > Mahan soil after 24 h, and Mhooon > Vacherie > Sharkey > Mahan soil after 672 h.

Isotherm results shown in Fig. 3 reflect adsorption characteristics of imidacloprid with time of reaction for the soils chosen for this study. The organic matter content of Vacherie was higher than that of Sharkey soil (1.4% vs 2.51 %) and the opposite for the clay contents (2% versus 61%). Therefore, it is most likely that organic matter is the major contributor for imidacloprid adsorption for these soils.

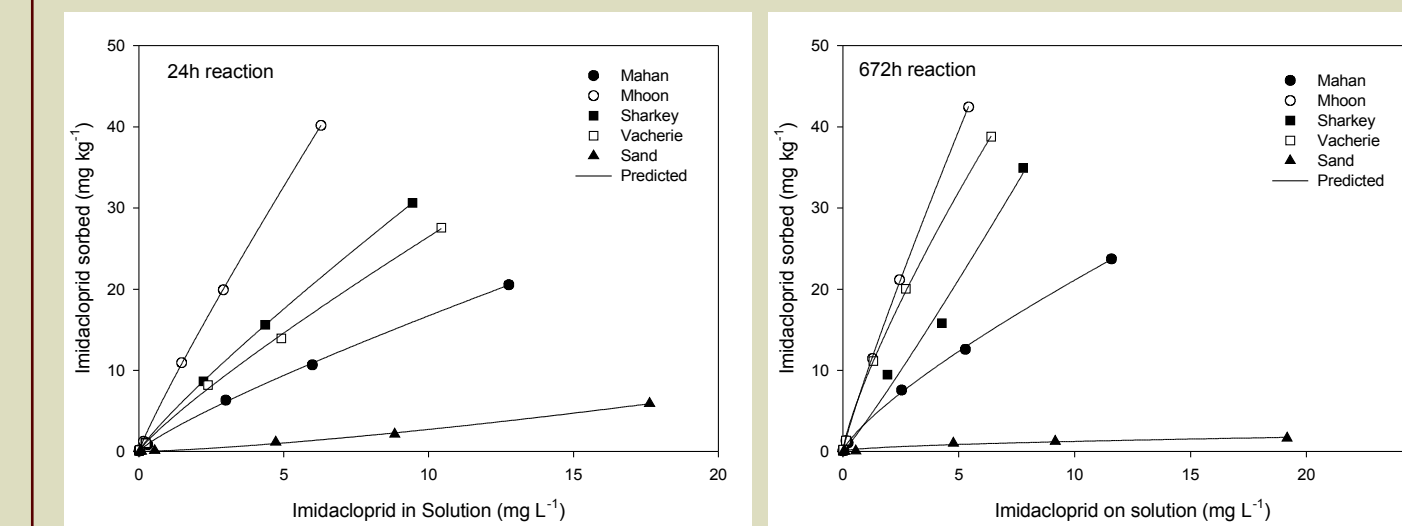


Figure 2. Imidacloprid adsorption isotherms for Mahan, Mhooon, Sharkey, and Vacherie soils after 24 h and 672h of reaction time. Soil curves depict results of curve-fitting with Freundlich equation.

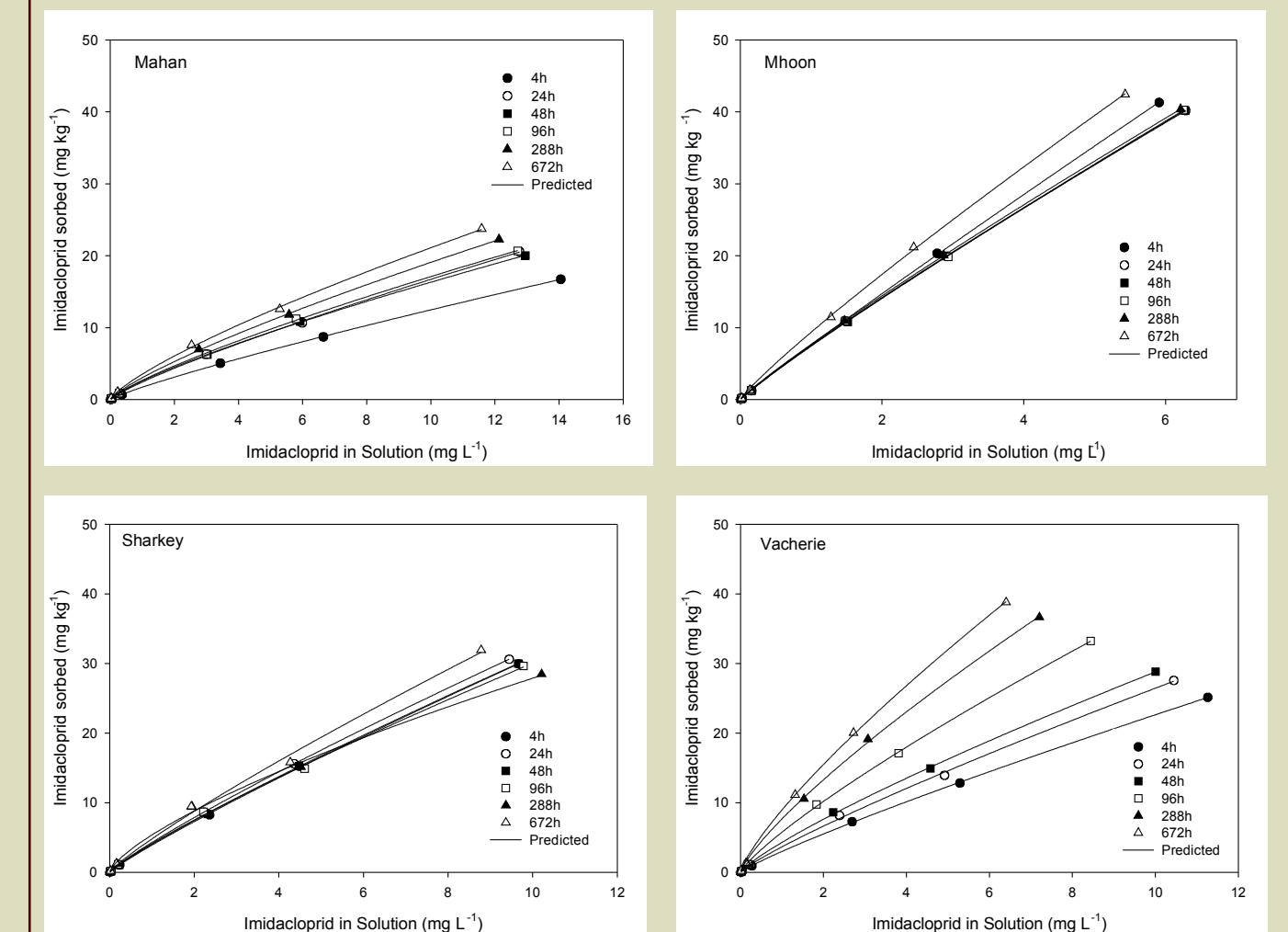


Figure 3. Adsorption isotherms of imidacloprid by the Mahan, Mhooon, Sharkey, Vacherie, and reference sand soil with different reaction times. The solid curves are fitting to Freundlich equation.

Kinetics

Imidacloprid adsorption & adsorption-desorption of experimental and model (MRM) predictions exhibited kinetic behavior for all soils as shown in Fig.4. Overall the observed change in imidacloprid concentration in the soil solution was rapid during the initial stages of adsorption reaction and was then followed by slow and continued reactions.

Desorption hysteresis

Desorption or release results of imidacloprid which followed adsorption, are presented as isotherms in the traditional manner in Figs. 5 for all soils. Distinct discrepancies between adsorption and successive desorption isotherms are clearly observed in the figures and indicate considerable hysteresis for imidacloprid release the extent of which varied among the soils.

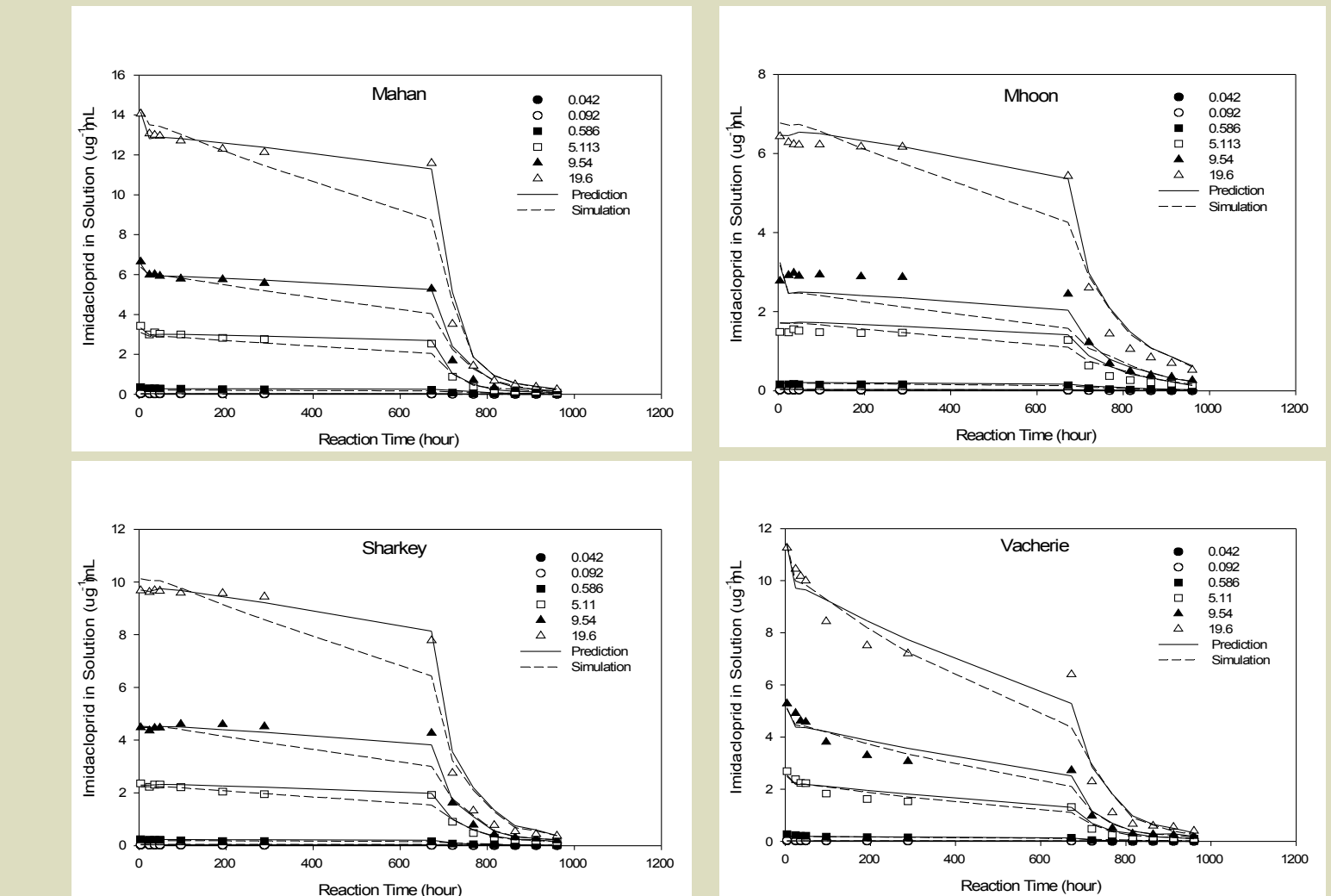


Figure 4. Imidacloprid concentration in soil solution with time during adsorption and desorption for Mahan, Mhooon, Sharkey, and Vacherie soil with different initial concentrations. Solid curves present multireaction model (MRM) prediction using values from only adsorption data set and predicted desorption, and dashed curves present simulation using MRM model based on adsorption-desorption data sets.

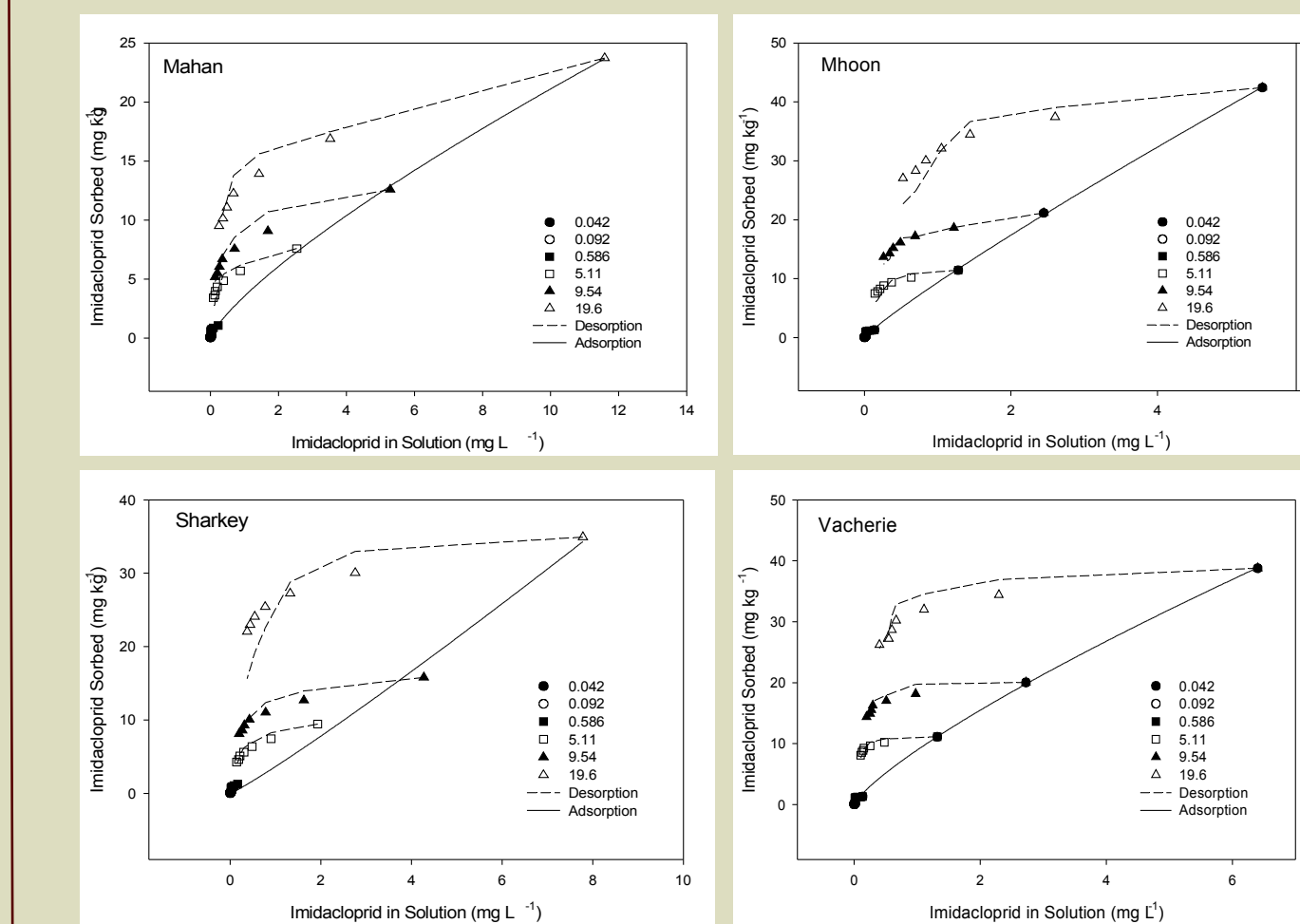


Figure 5. Isotherms of Imidacloprid desorption from different soils based on successive dilution after the last adsorption step for different initial concentrations. The solid line presents the results of curve-fitting with the Freundlich equation for 672-h adsorption and the dashed lines with desorption indicate the results of prediction based on values from only adsorption data with multireaction model (MRM).

CONCLUSIONS

The hysteresis behavior was observed from the desorption procedure, and the total recovery of imidacloprid was calculated, and it ranged from 79.3 % for the Mahan soil to as low as 41.1 % for the Vacherie soils. Particularly, the dominant clay contents in the Sharkey soil were not a critical factor for the hysteresis behavior on imidacloprid bindings compared to the organic matter factor in the Vacherie soil. Imidacloprid may be classified as moderately or weakly polar pesticide in its polarity, and it contains in its molecular structural substituent which cause relatively high water solubility and a low affinity to hydrophobic structures. Conclusively, the potential leaching of imidacloprid through land application with normal rate would possibly reduce or decrease with the contents of soil organic matter increase.