



## Thermodynamics of imidacloprid sorption in Croatian soils

Čedomila Milin and Dalibor Broznić

Rijeka, School of Medicine, Chemistry and biochemistry, Croatia (cedomila.milin@medri.uniri.hr)

Neonicotinoids are increasingly replacing the organophosphate and methylcarbamate acetylcholinesterase inhibitors which are losing their effectiveness because of selection for resistant pest populations. Imidacloprid is the most important neonicotinoid with low soil persistence, high insecticidal potency and relatively low mammalian toxicity. In Croatia, imidacloprid is most commonly used in olive growing areas, including Istria and Kvarner islands, as an effective means of olive fruit fly infestation control. Sorption-desorption behavior of imidacloprid in six soils collected from five coastal regions in Croatia at 20, 30 and 40°C was investigated using batch equilibrium technique. Isothermal data were applied to Freundlich, Langmuir and Temkin equation, and the thermodynamic parameters  $\Delta H^\circ$ ,  $\Delta G^\circ$ ,  $\Delta S^\circ$  were calculated. The sorption isotherm curves were of non-linear and may be classified as L-type suggesting a relatively high sorption capacity for imidacloprid. Our results showed that the  $K_F$  values decreased for all the tested soils as the temperature increases, indicating that the temperature strongly influence the sorption. Values of  $\Delta G^\circ$  were negative (-4.65 to -2.00 kJ/mol) indicating that at all experimental temperatures the interactions of imidacloprid with soils were spontaneous process. The negative and small  $\Delta H^\circ$  values (-19.79 to -8.89 kJ/mol) were in the range of weak forces, such as H-bonds, consistent with interactions and partitioning of the imidacloprid molecules into soil organic matter. The  $\Delta S^\circ$  values followed the range of -57.12 to -14.51 J/molK, suggesting that imidacloprid molecules lose entropy during transition from the solution phase to soil surface. It was found that imidacloprid desorption from soil was concentration and temperature dependent, i.e. at lower imidacloprid concentrations and temperature, lower desorption percentage occurred. Desorption studies revealed that hysteric behavior under different temperature treatments existed, and it was more pronounced at 20°C in the soils with higher organic carbon content. The study results emphasize the importance of thermodynamic parameters in controlling soil pesticide mobility in different geographical locations, seasons and greenhouses condition.