Behavior and Fate of Imidacloprid in Croatian Olive Orchard Soils Under Laboratory Conditions

Broznić, Dalibor; Marinić, Jelena; Milin, Čedomila

Source / Izvornik: **Pesticides in the Modern World - Risks and Benefits, 2011, 490 - 518**

Book chapter / Poglavlje u knjizi

https://doi.org/10.5772/949

Behavior and Fate of Imidacloprid in Croatian Olive Orchard Soils Under Laboratory Conditions

Dalibor Broznić, Jelena Marinić and Čedomila Milin
Department of Chemistry and Biochemistry, School of Medicine, University of Rijeka, Croatia

1. Introduction

Over the last two decades, the worldwide production and use of pesticides have greatly increased, causing great concern about their fate in the soil environment, as well as their adverse effects on nontarget organisms, including human beings. An important thing to realize it that only a small part of the pesticide doses used reaches its intended target (< 0.1%), while the major part (over 99%) of it is distributed into the ecosystem (Pimentel & Levitan, 1986), where it can cause difficulties through its toxicity to nontarget species, and cause serious environmental problems, such as groundwater contamination, food contamination, and air pollution (Larson et al., 1997; Mathys, 1994). There is also increasing interest in their transformation products, because they can be present at higher levels in the soil than the parent itself. In some instances, transformation products are more toxic, so they represent a greater risk to the environment than the parent molecule. Therefore, it is essential to study the residue and degradation pattern of pesticide in crop, soils and water systematically in order to generate meaningful data from the point of view of plant protection, public health and environmental safety.

In the past few decades, three major groups of insecticides have dominated the market: organophosphates, carbamates and pyrethroids. Nevertheless, pests resistance limited their use and caused a need for the synthesis of a new group that will be effective and nontoxic to the environment and to mammals. The results was "the birth" of neonicotinoids which exhibited high insecticidity and low toxicity to the environment (Maienfisch et al., 2001). But because neonicotinoids are becoming extensively used, both in agriculture and for home use, the chance of their polluting water is still present despite the low application rates.

Imidacloprid [1-(6-chloro-3pyridylmethyl)-N-nitroimidazolidin-2-ylideneamine; IMI] was the first neonicotinoid registered by the United States Environmental Protection Agency (USEPA) for use as a pesticide through its actions as an agonist on the nicotinic acetylcholine receptor (nAChR) (Bai et al., 1991). The mode of action of IMI in the brain is shown in Figure 1. The toxicity of IMI is largely due to interference of the neurotransmission in the nicotinic cholinergic nervous system. Prolonged activation of the nAChR by IMI causes desensitization and blocking of the receptor, and leads to incoordination, tremors, decreased activity, reduced body temperature and death. IMI's favorable selective toxicity to insects versus mammals makes it safer for insect control than other neurotoxins (Tomizawa & Casida, 2003) and enables its diverse use in soil and foliar treatment in different crops, as well as in non-agricultural practice. Thus, IMI is found in a variety of commercial insecticides. Its major manufacturer is Bayer Corporation that markets IMI products with the brand names Admire®, Confidor®, Gaucho®, Premier®, Premise®, Provado®, and Marathon®. However, one of the drawbacks of IMI's usage is a high toxicity in honeybees. In France, between 1994 and 1996, greatly increased mortality in honeybees was noticed when sunflowers were treated with a new pesticide Gaucho®. In addition Maxim & van der Sluijs (2007, 2010) and Suchail et al. (2004) found that IMI at very low doses causes bees mortality and adverse effects on laboratory-conditioned behavioral responses associated with feeding.

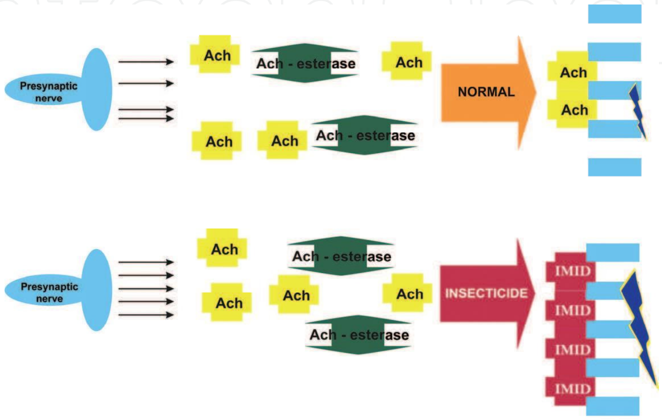


Fig. 1. IMI mode of action.

In Croatian coastal regions, IMI is increasingly being used in olive growing areas, including Istria and Kvarner islands, as an effective means of olive fruit fly infestation control. Although used at low dose rates (Capri et al., 2001), it is usually applied more than once during the growing season. Thus, intensive use of IMI, in addition to its high water solubility (510 mg/L, 20 °C) (Tomlin, 2001) might impose a great risk of water resources contamination which is consistent with USEPA statement regarding IMI's potential to leach to groundwater (USEPA, 1993). The review of literature revealed that few reports are available on leaching of IMI in soil (Carbo et al., 2008; Felsot et al., 1998; Gonzalez-Pradas et al., 2002; Gupta et al., 2002; Schmidt, 2010). For these reasons, there is a need for a more complete insight into IMI's fate in the soil (USEPA, 1993).

Among the processes that determine the behavior and fate of pesticides in the soil/water environment, sorption-desorption and degradation processes are the key processes affecting pesticide persistence, transport and bioavailability determining the amount of pesticide that can reach the target organism and that can be volatilized, or leached. Information regarding the sorption and desorption characteristics of IMI are essential for predicting its fate within the soil environment (Cox et al., 1998a; Cox et al., 1998b; Cox et al., 2001; Fernandez-Bayo et al., 2007; Liu et al., 2006; Ping et al., 2010). Capri et al. (2001) and Cox et al. (1998c) investigated the effect of selected soil properties on the sorption of IMI using the batch equilibrium technique. Their results indicated that IMI retention was highly dependent on the amount of the pesticide applied and on the physicochemical properties of the pesticide, but the key factor governing pesticide sorption-desorption were soil characteristics, including soil texture, organic carbon content (OC), cation exchange capacity (CEC), pH and temperature. Field and laboratory studies have determined that IMI sorption to soil particles increases as the concentration of the insecticide decreases (Cox et al., 1998a; Kamble & Saran, 2005; Oi, 1999). Cox et al. (1997; 1998b; 1998c) have found that the potential for IMI to leach would decrease, as the OC levels and laminar silicate clay content in the soil increase. In contrast, IMI sorption in a calcerous soil was found to decrease with the addition of OC (obtained from peat and tannic acid) (Flores-Cespedes et al. 2002), which increased the mobility and leaching potential of IMI. In the study of Cox et al. (1998a) positive correlation between IMI sorption and CEC have observed, while the effect of soil pH did not significantly contributed to the sorption. The effect of temperature is of special importance in greenhouses, where higher temperatures are used for cultivation (Cox et al., 1997; Fernandez-Bayo et al., 2007; Gonzalez-Pradas et al., 2002; ten Hulscher & Cornelissen, 1996). On the other hand, desorption governs the release of IMI from the soil and several studies have reported irreversible sorption and the occurrence of hysteresis phenomena; i.e. less desorption than predicted by sorption isotherms (Cox et al., 1997; Fernandez-Bayo et al., 2007; Papiernik et al., 2006). This behavior can be attributed to a portion of the sorbed compound that is bound irreversibly to soil surfaces (Celis & Koskinen, 1999; Cox et al., 1997; Cox et al., 1998b). Numerous studies indicated that values for IMI half-lives (DT_{50}) are highly dependent on experimental conditions; namely field or laboratory, (Krohn & Hellpointner, 2002). In fact, DT_{50}s for IMI have been reported ranging from approximately 80 days to 2 years. Examples of laboratory experiments include Krohn & Hellpointner (2002) who reported a DT_{50} of 156 days, representing the geometric mean value of five studies. In a field experiment, Krohn & Hellpointner (2002) reported a DT_{50} of 96 days for the 11 bare soils in Northern and Southern Europe. However, lengthier DTs have also been determined from field studies. Mulye (1996) reviewed a two-year field investigation in Germany using IMI and from the study results calculated a DT_{50} of approximately 2 years, indicating that the compound would persist in soil.

Since a variability of pesticide sorption-desorption and persistence can occur among regions and even within the areas with the same geological and climatic characteristics, additional knowledge is needed to improve IMI's applicability in conditions which cover the Croatian climate. Consequently, the objective of this study is to analyze sorption-desorption characteristics as well as persistence of IMI in four soils, representative of northern Adriatic region, namely an island Krk and a coastal Istrian region. For a better understanding of factors governing IMI's behavior and fate in these regions, the relationship between selected soil properties, IMI's concentration and soil sorption-desorption coefficients as well as persistence was determined for the soils among and within regions. Additionally, applicability of mathematical models to predict IMI's sorption-desorption and degradation was tested.

2. The behavior and fate of pesticides in the soil

The behavior and fate of pesticides in the soil environment is controlled by their physico-chemical properties and by various complex dynamic physical, chemical and biological processes, among which are the most important sorption-desorption interactions of pesticide molecules with natural sorbents: soil organic matter and soil minerals, as well as degradation processes. These processes directly control the transport, retention and transformation of pesticides within the soil matrix and their transfer from the soil to other environmental compartments, and also determine the efficacy of pesticides in controlling target organisms and their potential for adverse effects on non target organisms (Pimentel &

Levitan, 1986). Once a pesticide molecule is bound to soil particles in the soil, the main processes in the soil cause its loss and transformation. Significant losses of pesticides can occur during application, with the amount of loss affected by the nature of the pesticide, formulation, atmospheric conditions, method of application, and application characteristics. High vapor pressure, photodegradability, and weak sorption by the soil contribute to losses of pesticides after application (Navarro et al., 2007). Retention does not affect the amount of pesticide present in the soil, but can decrease the amount available for transport; whereas transformation reduces the amount of pesticide present in the soil. Transport processes include leaching, surface runoff, volatilization, and uptake by plants. Figure 2 shows the main processes of pesticides inactivation in the soil.

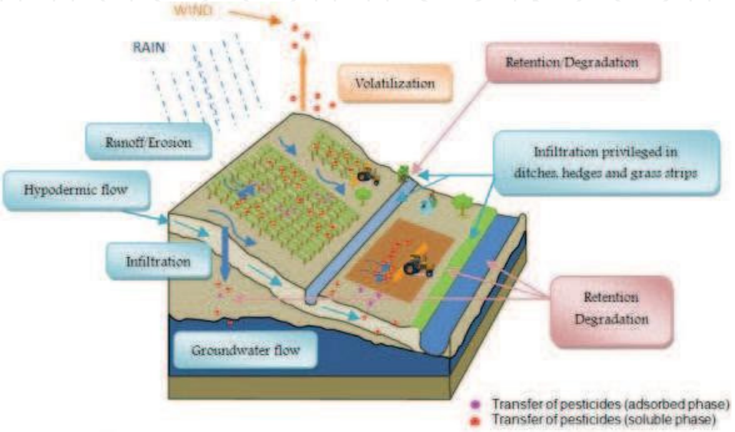


Fig. 2. The behavior and fate of pesticides in the environment.

2.1 Sorption-desorption processes

Sorption-desorption is a dynamic process in which molecules are continually transferred between the bulk liquid and solid surface (Koskinen & Harper, 1990). Sorption is the binding of the pesticide molecules by the surface of the treated soil, whereas desorption implies detachment of the molecules to the liquid medium. The ability of pesticides to sorb on soils and their tendency to desorb are the most important factors affecting soil and water contamination.

Several sorption models have been developed to describe, quantify and explain the sorptive process of pesticides on soils. The simplest one is the linear model depicted by the equation:

$$q_e^{sor/des} = K_D^{sor/des} \gamma_e \tag{1}$$

where $q_e^{sor/des}$ is the sorbed pesticide amount (mg/kg), γ_e is the equilibrium concentration in solution (mg/L) and $K_D^{sor/des}$ is the sorption-desorption partition coefficient (L/kg). Because $K_D^{sor/des}$ values for pesticides are soil specific and the $K_D^{sor/des}$ of one pesticide can differ considerably from soil to soil or with depth in a soil profile, the more widely accepted partition coefficient normalized to the fraction of OC content in the soil, K_{OC} was used. The K_{OC} was determined using the equation:

$$K_{OC} = \frac{K_D{}^{sor/des}}{f_{OC}} \times 100 \tag{2}$$

where f_{OC} represents the percentage of the OC content in the soil. High K_{OC} values (greater than 1000) indicate a tendency for the pesticide molecule to be sorbed by soil particles rather than remain in the soil solution (McCall et al., 1980). Since pesticide bond mainly to soil OC, the division by the percentage OC in soil makes the sorption coefficient a pesticide-specific property, independent of soil type. Sorption coefficients less than 500 indicate a considerable potential for losses through leaching.

This linear model is adequate if the sorption sites are of the same nature and in great amount to accommodate the chemical as the concentration increases. But in many cases, due to the heterogeneity of the soil, deviations from the linear sorption model are predictable and are effectively observed for pesticides (Delle Site, 2001; Wauchope et al., 2002). Two other nonlinear sorption isotherm models, the Freundlich and the Langmuir model, are frequently used when the amount of contaminant retained by the soil is abundant enough to impact the linear sorption.

The Freundlich isotherm is derived by assuming a heterogeneous surface with a non-uniform distribution of heat of sorption over the surface and it is represented by the equation:

$$q_e{}^{sor/des} = K_F{}^{sor/des}\,\gamma_e{}^{1/n} \tag{3}$$

where $K_F{}^{sor/des}$ is the Freundlich partition coefficient (coefficient of sorption-desorption capacity)(mg/kg)(mg/L)$^{1/n}$) and $1/n$ is the Freundlich's exponent (coefficient of nonlinearity), usually in the range $0<1/n\leq1$.

Sorption isotherm data could also be fitted to the Langmuir model given by Equation 4, with the assumption that soils have a finite number of sorption sites of uniform energy.

$$q_e{}^{sor/des} = \frac{q_{max}^{sor/des} K_L^{sor/des} \gamma_e}{1 + K_L^{sor/des} \gamma_e} \tag{4}$$

In Equation 4, $q_{max}{}^{sor/des}$ designates the maximum amount of sorbed IMI per unit mass of soil (mg/kg) to form a monolayer and $K_L{}^{sor/des}$ is the constant which depends on the enthalpy of sorption.

Although sorption processes of pesticides are usually characterized by a partition mechanism, in many cases, significant deviations between sorption and desorption isotherms have been observed. Typically, desorption is strongly delayed or hindered relative to the sorption (Huang & Weber, 1997; Lesan & Bhandari, 2003). In this phenomenon, called hysteresis, the Freundlich exponent $1/n_{sor}$ for desorption can be greater than the $1/n_{des}$ measured for desorption at a constant γ_e concentration (Huang et al., 2003). Sorption-desorption hysteresis can usually be explained by irreversible chemical binding, sequestration of a pesticide molecule into specific components of the organic matter, or entrapment of the pesticide into microporous structures or into the organic matter matrix (Pignatello & Xing, 1996). The extent of sorption-desorption hysteresis can be quantified for each pair of sorption and desorption isotherms using the hysteresis coefficient H (Cox et al., 1997). This coefficient is calculated using Freundlich exponent (coefficient of nonlinearity, 1/n) estimated from the sorption and desorption isotherms and it can be expressed by following equation:

$$H = \frac{1/n^{des}}{1/n^{sor}} \tag{5}$$

where, $1/n^{sor}$ and $1/n^{des}$ are Freundlich coefficients of nonlinearity for sorption and desorption, respectively. The lower the value of H is, the stronger the soil will sequestrate the pesticide molecule. Value $H = 1$ indicates that the hysteresis is insignificant and the sorption is reversible.

2.2 Degradation processes

Concern about the persistence of pesticides in soils has led to increased efforts to identify the nature, mechanisms, and factors affecting degradation processes, to identify the degradation products, and to predict persistence. Soil is an ideal medium for supporting degradation reactions of pesticides, which include photochemical, chemical, and biological reactions (Chen et al., 2005; Kuhad et al.; Ward & Singh).

Many published degradation studies assume that the degradation of pesticides follows simple first-order degradation kinetics (Baskaran et al., 1999; Calderon et al., 2004; Krohn & Hellpointner, 2002; Sarkar et al., 2001) which is represented with the following mathematical equation:

$$C(t) = ae^{-k_1 t} \tag{6}$$

where C is the amount of pesticide remaining at the time t (mg/kg), a is initial amount of pesticide degraded through one 1^{st} order process, t is the time (days) and k is degradation rate constant (1/days). First-order kinetics is advantageous for use in modeling as a constant degradation rate and allows estimation of a pesticide's half-life, DT_{50} (the time at which the concentration reaches half the initial concentration), which can be estimated according to equation:

$$DT_{50} = \frac{ln2}{k} \tag{7}$$

DT_{50} values are important in understanding the potential environmental impact of a pesticide. In fact, a molecule which degrades quickly has a low DT_{50} value and thus the impact of this species on the environment is reduced if the degradation products are harmless. On the contrary, the environmental impact of species with a high DT_{50} value can be substantial even if the molecule is only moderately toxic. Gavrilescu (2005) classified persistence of pesticides according to the DT_{50} value into three groups, where pesticides with $DT_{50} < 30$ days are non-persistent pesticides, compared to pesticides with $DT_{50} > 100$ days which are persistent.

However, deviations from the first-order degradation of pesticides have been reported. Typically, a fast initial degradation is followed by a gradual decrease in the degradation rate and eventually a very slow degradation. The gradual change in degradation rate may be better described by using two rate constants instead of one (Beulke & Brown, 2001; Henriksen et al., 2004; Ma et al., 2004; Sanchez et al., 2003). The two-compartment model (Equation 8) describes the degradation process as shared between two different compartments, where degradation proceeds at different rates (k_1 and k_2). The two constants, *a*, and *b*, express the quantitative partition between the two compartments, where a + b is approximately equal to C_0 (mg/kg):

$$C(t) = ae^{-k_1 t} + be^{-k_2 t} \tag{8}$$

The fast degradation in the first compartment occurs when the pesticide is in the soil-water phase and readily available for microorganisms. In the second compartment the pesticide is sorbed to soil particles. Degradation is, therefore, controlled by the rate of desorption-diffusion into the soil-water phase. The partition between the two compartments depends on the pesticide sorption properties and soil characteristics. These characteristics suggest that a single DT_{50} may not be sufficient as an index of persistence. Beulke & Brown (2001) recomended using DT_{90} as a risk index to indicate the persistence, where the DT_{90} represents the time for 90% of the initial residues to dissipate; whereas Grover et al. (1997) and Wolt (1997) used both DT_{50} and DT_{90} as indices of persistence.

2.2.1 Metabolites

The proposed metabolic pathway of IMI in the soil is shown in Figure 3. Two main routes of metabolism responsible for the degradation of IMI were identified. The first step is hydroxylation of the imidazolidine ring leading to the mono- and dihydroxylated compounds, followed by loss of water to yield the olefinic compound. The second important degradation step starts with dehydrogenation of the imidazolidine ring to form desnitro-metabolit with further oxidation to 6-chloronicotinic acid (6-CNA).

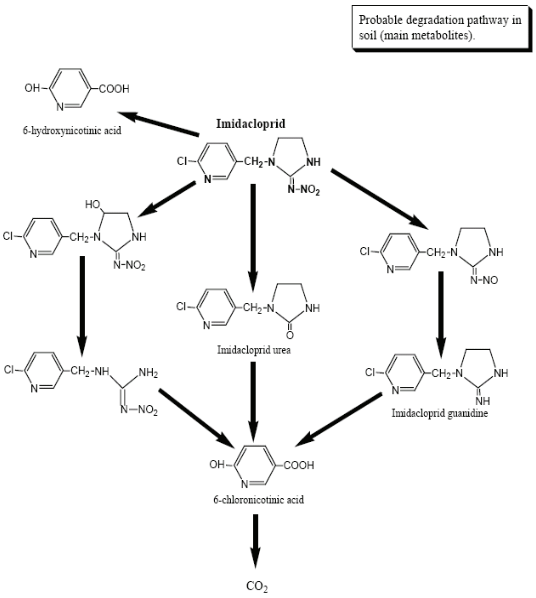


Fig. 3. The proposed metabolic pathway of IMI in the soil.

The main metabolites of IMI which have been identified in the soil include IMI-urea, 6-CNA, and 6-hydroxynicotinic acid (Rouchaud et al., 1996), which ultimately degrades to CO_2 (Scholz & Spiteller, 1992). For instance, depending on the soil type, IMI labeled with imidazolidin-^{14}C had a maximum mineralization to CO_2 of 8.8% or 14% after incubation for 12 weeks (Anderson, 1995; as reviewed in Mulye, 1996). In soils, when conditions were anaerobic and without light exposure, IMI was found to be readily decomposed, resulting in desnitro-IMI as the main transformation metabolite (Heim et al., 1996; as reviewed in Mulye, 1996). The desnitro-IMI produced under dark, anaerobic conditions has been found to be more persistent than its parent compound (Fritz & Hellpointner, 1991; as reviewed in Mulye, 1995). The major transformation products resulting from incubation under non-sterile, aerobic conditions and light exposure were desnitro-IMI, IMI-urea, 6-CNA and an unknown compound. Both desnitro-IMI and IMI-urea are highly water soluble, with solubility of 180 – 230 g/L and 9.3 g/L at 20°C, respectively (Krohn, 1996a, 1996b; as reviewed in Mulye, 1996), which is much higher than IMI's solubility, while 6-CNA has been found to be more toxic to honey bees than IMI itself.

3. Materials and methods

3.1 Chemicals

Analytical IMI at purity 99.9% (from Riedel-de Haën, Germany) and 6-CNA (chemical purity 99%, from Acros-Organics, USA) were used in this tudy. IMI's chemical structure and some selected physicochemical properties are shown in Figure 4 (Tomlin, 2001). Stock standard solutions of IMI and 6-CNA (1 mg/mL) were prepared by disolving the required amount in HPLC grade acetonitrile and stored at 4˚C. All other chemicals used were analytical grade, except acetonitrile which was of HPLC-grade (J.T.Baker, Holland). Sodium pyrophosphate, sulphuric acid, potassium dichromate, sodium hydroxide, sodium acetate and calcium chloride were purchased from Kemika (Croatia), while ammonium acetate, mercury chloride and methanol were from Alkaloid (Macedonia).

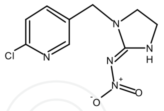
Structural formula	
Molecular formula	$C_9H_{10}ClN_5O_2$
Molecular weight (g/mol)	255.7
Water solubility, 20° C (g/L)	0.51
Log K_{OW}	0.57
Sorption coefficient, K_D (L/kg)	2.46
pK_a	11.2

Fig. 4. Chemical structure and physicochemical properties of IMI.

3.2 Experimental soils

Four agricultural soil samples, having different characteristics, from two coastal regions of Croatia, namely Istria and Kvarner, were used in this study. All soils were collected from the A horizon at depths of 0-30 cm following the standard methodology of soil sampling (USEPA, 2000), air-dried for 24 hours, ground (porcelain mortar + rubber pestle) and passed through a 2-mm sieve prior to use. They were selected on the basis of their texture (mechanical composition), pH values, OC content and CEC. The soils have never been treated with IMI, as verified by analyzing its residues in the soil. Selected physicochemical properties of the tested soils are given in Table 1.

Soil	Textural classes	Clay (%)	pH	CEC[a] (cmol/kg)	HA[b] (cmol/kg)	OC[c] (%)
Krk I	sandy clay	21.12	7.12	25.67 (±0.74)	2.98 (±0.90)	0.55
Krk II	sandy loam	15.38	6.88	14.01 (±0.63)	1.93 (±0.23)	0.42
Istria I	clay loam	34.28	4.76	34.19 (±0.99)	5.65 (±0.45)	1.30
Istria II	clay	47.21	6.35	49.16 (±0.31)	16.21 (±0.09)	1.91

[a] cation exchange capacity; [b] hydrolitic acidity; [c] organic carbon content.

Table 1. Physicochemical properties of the tested soils.

The mechanical composition of the soil samples was determined by sedimentation using the "pipet method" (Kroetsch & Wang, 2007). Soil samples pH values were measured in a soil + deionised water and in a soil + 0.01 M calcium chloride suspension (1:2.5, w/v). The MP 220 laboratory pH meter (Metler Toledo, Germany) was used for pH determination in aqueous phase. Hydrolitic acidity (HA) was determined by the Kappen method (Hendershot et al., 2007), CEC was measured using ammonium replacement (Sumner & Miller, 1996), while Na, K, Mg and Ca were analyzed by Atomic Absorption Spectrophotometer (Perkin Elmer Analyst, USA). The OC content of the soils was determined spectrophotometrically (Cary 100 Bio WINUV, Varian, Australia) by dichromate method (Darrel & Nelson, 1996).

3.3 Batch sorption-desorption experiments

In the present study, the IMI sorption by soils was quantified using the standard batch equilibrium method (OECD, 2000). The predetermined mass of each soil (5 g), in triplicate, was equilibrated with 25 mL of aqueous solutions of IMI by shaking in an rotary agitator (Unimax 1010, Heidolph, Germany) at 20 (±1)° C for 48 h to achieve equilibrium. The equilibrium time was determined according to previous sorption kinetics studies of the IMI sorption (Capri et al., 2001; Nemeth-Konda et al., 2002). Initial insecticide solutions, in the concentration range of 0.1, 0.25, 0.5, 1, 2.5, 5, and 10 mg/L respectively, were prepared in the background 0.01 M calcium chloride and 100 mg/L mercury chloride solution from stock IMI solutions prepared in HPLC-grade acetonitrile. Calcium chloride solution was used as background electrolyte in order to minimize ionic strength changes and to promote flocculation. Mercury chloride was added to the pesticide solution as a biocide to prevent any microbial activity during the sorption experiment. After equilibration, the suspensions were centrifuged at 4000 rpm for 30 min at 20 (±1) °C (BR4i Multifunction, Thermo electron corporation, France) to separate the liquid and solid phases. After filtration through a polypropylene hydrophilic filter of 0.45 µm (Whatman, Puradisc 25 TF, USA) the aqueous phase was analyzed by High Performance Liquid Chromatography (HPLC) using a Thermo Separation Products (Spectra System, USA) liquid chromatographic system, as described in the section 3.6. Blank samples without soil were also prepared in the same way and used to account for possible losses due to the volatilization and sorption of IMI to the cuvette walls. The average system losses were shown to be consistently lower than 3.4% of the initial solute concentrations, therefore no correction was required. Control samples, containing no IMI, only soil and 0.1 M calcium chloride, were used for each series of experiment. The amount of IMI sorbed to soil after equilibration was calculated from the difference between the initial and equilibrium solution concentration using the mass-balance equation:

$$q_e^{sor} = (\gamma_i - \gamma_e)\frac{V}{m} \tag{9}$$

where q_e^{sor} is the amount of IMI sorbed at equilibrium (mg/kg), m is the mass of soil (g), γ_i is the initial concentration of IMI (mg/L), γ_e is the equilibrium concentration of IMI (mg/L), V is the volume of the solution (L) from which sorption occurs.

Desorption experiments were conducted on triplicate soil samples immediately after the sorption experiments with the same initial concentrations of IMI. After completing the sorption process, the supernatant (25 mL) were removed and replaced with the same volume of 0.01 M calcium chloride and 100 mg/L mercury chloride solution. After shaking for 24 h, the suspensions were centrifuged under the conditions described previously, and the concentration of IMI was determined in the supernatants using the HPLC. This desorption procedure was repeated five times for each soil sample. The amount of pesticide remaining sorbed by the soil was calculated as the difference between the equilibrium sorbed and the desorbed amount by the following equation:

$$q_e^{des} = (\gamma_e^{sor} - \gamma_e^{des})\frac{V}{m} \tag{10}$$

where q_e^{des} is the amount of IMI remaining sorbed by the soil (mg/kg), γ_e^{sor} is the equilibrium sorption concentration of IMI (mg/L) and γ_e^{des} is the equilibrium desorption concentration of IMI (mg/L). The percentage of IMI desorbed was calculated as follows:

$$P^{des} = \frac{\sum_{a=1}^{5} q_e^{des}}{q_e^{sor}} \times 100 \tag{11}$$

3.4 Degradation experiments

The persistence of IMI in the tested soils was studied at two concentration levels, 0.5 and 5 mg/kg under laboratory conditions at room temperature (20±1˚C). For fortification of the soil at 50 mg/kg level, 100 g weighted, air-dried and sieved soil was taken in a baker and 10 mL of standard solution of IMI (1 mg/mL, in acetonitrile) was added. Additional methanol was added to dip the soil completely. The soil suspension was mixed well using a rotary agitator (Unimax 1010, Heidolph, Germany) for 1 hour and then left at room temperature for 24 hours to allow complete solvent evaporation. After the complete evaporation of the solvent, the fortified soil was again mixed and then serially diluted with untreated soil to get a 5 and 0.5 mg/kg level of fortification. For 5 mg/kg treatment, 1350 g untreated soil was taken in a polythene bag and 150 g of fortified soil (50 mg/kg) was added and thoroughly mixed for homogeneity. For the 0.5 mg/kg treatment, 5 mg/kg treated soil was mixed with untreated soil in the ratio 1:9. The treated soils were maintained at 60% of the maximum water holding capacity (WHC) and stored in a dark at room temperature (20±1˚C). Moisture contents were maintained at a constant level throughout the experiment by adding distilled water as necessary. Three parallel soil samples (25 g) at both concentration level including unspiked controls were used for analysis of IMI residues and its metabolite (6-CNA) at intervals of 0, 7, 15, 30, 45, 60, 75, 90, 105, 120, 150 and 180 days after application.

3.5 Extraction of IMI and 6-CNA from soil samples

IMI and 6-CNA were extracted from soil samples according to the method of Baskaran et al. (1997). At each sampling time, a 25 g sample of spiked and homogenized soil was extracted with 40 mL of acetonitrile-water (80:20, v/v) and shaken vigorously for 2 h using a rotary agitator (Unimax 1010, Heidolph, Germany) at 20 (±1)°C. After this time every sample was centrifuged for 20 min at 6000 rpm (BR4i Multifunction, Thermo electron corporation, France) and filtered through a polypropylene hydrophilic filter of 0.45 µm (Whatman, Puradisc 25 TF, USA). The operation of shaking and filtration was repeated three times and supernatants from each extraction were pooled. The solution was evaporated to dryness on a rotary evaporator (Laborota 4002/03 Control, Heidolph, Germany). The residue was dissolved in 1 mL of mobile phase (acetonitrile-water, 20:80, v/v). Three replicates of both level, including unspiked controls, were extracted and analyzed by HPLC.

3.6 Analysis of IMI and 6-CNA by HPLC

The concentration of IMI and 6-CNA in aqueous solutions was determined using a reverse-phase HPLC system (Thermo Separation Products, Spectra System, USA) equipped with a UV/VIS detector. All analyzes were performed on a Supelco reverse phase C_{18} column (150 mm length, 46 mm ID, 5 µm particle size). The mobile phase of acetonitrile and water (20:80 v/v) was used under isocratic conditions at a flow rate of 1.2 mL/min. The analytes were analyzed at 270 nm wavelength. The injection volume and the column temperature were 20 µL and 25° C, respectively. Under these conditions the retention times of IMI and 6-CNA were 4.3 and 1.6 min, respectively.

Calibration curves for both of chemicals were linear from 0.05 to 10 mg/L with regression coefficients of $R^2 > 0.999$ (six calibration points, in triplicate). The detection limits of IMI and 6-CNA were 0.001 mg/L and 0.003 mg/L, while the lower limits of quantification (LOQ) were 0.005 mg/L and 0.01 mg/L. The mean recoveries for IMI and 6-CNA were 91.4% and 87.8 % with a relative standard deviation lover than 5%.

3.7 Statistical analysis

Relationship between soil properties and sorption as well as degradation behavior of IMI was tested by a nonparametric correlation test, Kendall-Tau. Except nonparametric tests, multiple linear regression analysis was used, which combines the relationship between different soil parameters and the sorption coefficients, as well as DT_{50}, allowing the assumption of linear models for these parameters (Boivin et al., 2005). Differences in the soil sorption capacity among and within regions were analyzed using Mann-Whitney U test, while the DT_{50} values were tested by one-way ANOVA test with *post hoc* comparison (Tukey HSD test) to determine the effect of initial concentration and soil on the DT_{50} of IMI. Data are reported as mean ± standard deviations. The results were considered statistically significant at $p < 0.05$. The data were analyzed using Statistica® software package Version 7.0 and Wolfram Research Mathematica® software package Version 7.0.

4. Results and discussion

Sorption-desorption processes have a significant effect on pesticide persistence, pesticide concentration level in the soil solution and on the transport of pesticides from agricultural field to other environmental compartments (Arias-Estevez et al., 2008). An understanding of the variability of pesticide persistence and sorption-desorption processes within and among regions can improve the accuracy of estimates of the behavior and fate of pesticide in the soil and provide an additional support in design of intervention strategies against groundwater pollution.

4.1 Sorption-desorption study

4.1.1 Kinetic study

Sorption-desorption kinetic of IMI on the selected Croatian soils were studied using the initial IMI concentration of 10 mg/L in order to estimate the time needed to achieve the sorption and desorption equilibrium. The results for the case of Istria II soil are presented in Figure 5. Similar trends were observed in all tested soils. Equilibrium time for sorption process was reached at 48h, while for desorption process equilibration was achieved within 144h.

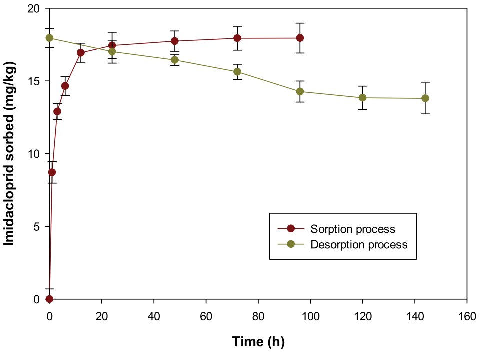


Fig. 5. Sorption-desorption kinetic of IMI on Istria II soil sample. The initial concentration of IMI was 10 mg/L.

4.1.2 Sorption equilibrium study

Figure 6a shows the sorption isotherms for IMI in the tested soils. All of the sorption isotherms are of L-type (Giles; et al., 1960) showing a convex initial curvature. This isotherm type indicates a decrease in specific sorption sites when the concentration of insecticide increases; however, in the case of IMI the curves did not reach the plateau of saturation.

In Table 2 the sorbed amount of IMI during the sorption processes in the tested soils is presented. The percentage of IMI sorbed on the Istria II soil was 35.96, 36.00, 37.13 and 37.88% at concentrations of 10, 5, 2.5 and 1 mg/L, respectively, whereas in the Istria I, Krk II and Krk I soil, the percentage sorbed ranged from: 30.41-33.01, 18.45-23.68 and 16.50-19.75% at the same respective concentrations. The percentage IMI sorbed was higher in Istria II soil than in the other soils.

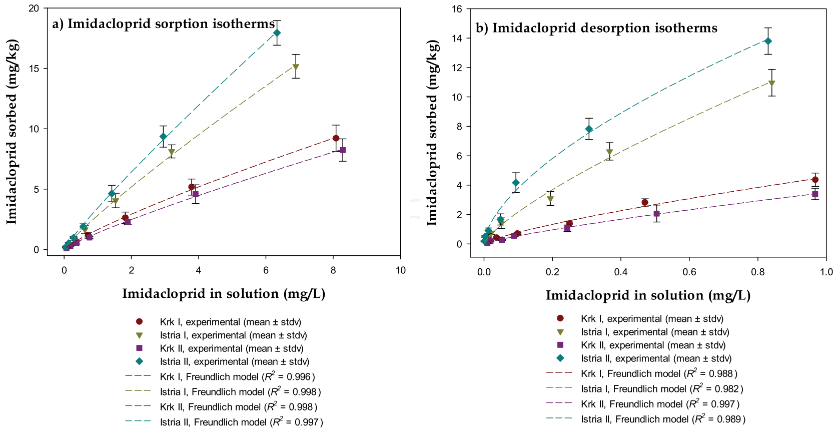


Fig. 6. a) Sorption and b) desorption isotherms of IMI in the tested soils represented by the Freundlich model. Values are means ± standard deviations. Symbols represent the experimental data, while lines represent the theoretical curves described by the Freundlich model.

Soil	Initial concentration, γ (mg/L)	Sorbed amount[a] (mg/kg)	Sorbed amount (%)	Desorbed amount[b] (mg/kg)	Desorbed amount (%)
Krk I	10	9.21	18.45	4.84	52.57
Istria I		15.17	30.41	4.20	27.71
Krk II		8.23	16.50	4.84	58.75
Istria II		17.94	35.96	4.15	23.12
Krk I	5	5.17	19.89	2.35	45.46
Istria I		8.13	31.26	1.84	22.58
Krk II		4.59	17.65	2.52	55.01
Istria II		9.36	36.00	1.53	16.39
Krk I	2.5	2.63	21.06	1.25	47.60
Istria I		4.06	32.54	0.97	23.90
Krk II		2.29	18.34	1.22	53.27
Istria II		4.63	37.13	0.47	10.04
Krk I	1	1.19	23.68	0.49	41.05
Istria I		1.66	33.01	0.25	15.12
Krk II		0.99	19.75	0.44	43.98
Istria II		1.91	37.88	0.24	12.70

[a] sorbed amount of IMI after 48 h of sorption reaction time; [b] desorbed amount of IMI after 144 h of desorption reaction time.

Table 2. The sorbed and desorbed amount of IMI in the tested soils in relation to the initial concentration.

All sorption data fit the Freundlich equation ($R^2 > 0.966$) and Table 3 summarizes the sorption capacity (K_F^{sor}) and intensity ($1/n_{sor}$) values. The K_F^{sor} values obtained from the Freundlich isotherm model were 1.28, 1.53, 2.60 and 3.28 $(mg/kg)/(mg/L)^{1/n}$ for Krk II, Krk I, Istria I and Istria II soil, respectively. The highest K_F^{sor} value for IMI, is indicative of the strongest retention by the soil matrix. A primary consequence of strong retention of IMI is its limited mobility in the Istria II soil profile and thus lower risk of ground water contamination.

Soil	K_F^{sor} $(mg/kg)/(mg/L)^{1/n}$	$1/n_{sor}$	R^2	K_{OC}^{sor} (L/kg)	ΔG (kJ/mol)
Krk I	1.53 (± 0.06)	0.894 (± 0.019)	0.996	278.18	-13.72
Krk II	(1.28 ± 0.06)	0.907 (± 0.022)	0.998	304.76	-13.94
Istria I	(2.60 ± 0.10)	0.945 (± 0.021)	0.998	200.00	-12.91
Istria II	(3.28 ± 0.09)	0.937 (± 0.016)	0.997	171.73	-12.54

Table 3. The Freundlich sorption parameters, values of organic carbon/partition coefficient (K_{OC}) and Gibbs free energy (ΔG^0) for IMI in the tested soils.

In our study, the behavior of sorption was nonlinear. This is based on the best-fit estimated parameter *1/n* under the value of one ($1/n < 1$) (Table 3). In fact, for the Krk soils, *1/n* values were lower (0.894 and 0.907) than for the Istria soils (0.937 and 0.945). Nonlinear isotherm behavior is a measure of the extent of heterogeneity of retention reactions and the presence of sites having variable affinities for sorption of IMI by the soil matrix surface. Based on the estimated *1/n* values, an increased amount sorbed by soil is anticipated in all soils at low IMI concentration. A higher initial insecticide solution concentration led to the change of the affinity between insecticide molecules and soil, probably due to decreased accessibility to the free sorption sites (Kamble & Saran, 2005).

In the present study, K_F^{sor} values varied between the tested soils, indicating that the differences between the soils strongly influence the sorption. Several studies have shown that soil properties, particularly the soil organic matter and clay content play a key role in the performance of applied pesticides (Cox et al., 1998a; Fernandez-Bayo et al., 2007; Kamble & Saran, 2005; Liu et al., 2006; ten Hulscher & Cornelissen, 1996). In order to elucidate the factors that affect sorption of IMI on the soils, the K_F^{sor} values were correlated with the OC and clay content, CEC, and pH using a nonparametric Kendall-Tau correlation test. Correlation analysis between sorption coefficients (K_F^{sor}) and selected soil properties showed a significant correlation between K_F^{sor} and the OC content, CEC and clay, but the correlation between K_F^{sor} and pH was not significant (Table 4). It has been postulated that soil pH has an influence on pesticide sorption only when the pK_a or pK_b are within approximately two units of the soil pH (Farenhorst, 2006). As the pH value in examined soils ranged from 4.76 to 7.12, which was significantly below the pK_a value of IMI (pK_a =11.2), the effect of soil pH was not noticeable. Thus, these results suggest that the OC content and CEC had the major influence on the IMI sorption in these soils.

In addition to nonparametric test, multiple linear regression was used, which simultaneously compares various soil properties and sorption coefficients (K_F^{sor}), and leads to a linear predictive model for K_F^{sor} value (Golfinopoulos & Arhonditsis, 2002). These models may be useful for identifying areas (homogeneous soil types) where surface water resources could be threatened by pesticide contamination and for identification of pesticides which are more easily leached through the soil profile (Golfinopoulos & Arhonditsis, 2002). Multiple liner regression resulted in the following correlation:

$$K_F^{sor} = 0.4177\,OC + 0.0037\,CEC + 0.0398\,clay - 0.0866\,pH + 1.009\left(R^2 = 0.989\right) \quad (12)$$

	pH	clay	CEC	OC
pH	1.00	-0.21	-0.24	-0.15
clay	-0.21	1.00	**0.85**	**0.82**
CEC	-0.24	**0.85**	1.00	**0.79**
OC	-0.15	**0.82**	**0.79**	1.00
K_F^{sor}	-0.24	**0.79**	**0.82**	**0.85**
DT_{50}	0.21	**-0.67**	**-0.76**	**-0.64**

OC – organic carbon content; CEC – cation exchange capacity;
K_F^{sor}– Freundlich coefficient of sorption;
DT_{50}- time for 50% of the initial residue to degrade.

Table 4. Kendall-Tau correlation test for soil properties and sorption and degradation parameters of IMI, n = 12 (Bold typeface indicates significant correlations with $p < 0.05$).

Nonparametric regression showed that the amount of OC in the soil, the CEC and clay amount affected the sorption processes, but multiple linear regression equations suggested that the OC content predominantly influenced IMI sorption on the tested soils.

Given the difference between tested soils in the studied regions, statistically significant differences in soil sorption coefficients, K_F^{sor} were found among the studied regions, i.e. Krk and Istria region ($p = 0.004$). In addition, results of sorption study within the regions showed a statistically significant diffrence in K_F^{sor} values between the soils Istria I and Istria II ($p = 0.049$), as well as between soils Krk I and Krk II ($p = 0.050$).

The OC partition coefficient, K_{OC}^{sor} (Equation 2) usually illustrate the hydrophobicity of the pesticide and may be used to estimate or predict the migration and behavior of an organic pesticide in the environment (Xue et al., 2006). Thus, defined coefficient, normalized to the proportion of OC, should have a constant value for each pesticide molecule and the same values in the soils with different content of organic matter. However, variability in K_{OC}^{sor} values for the soils of different type and characteristics, and even for the soils with the same content of organic matter, indicated that not only organic matter content, but also its structure, aromaticity and polarity, affected the distribution of pesticide molecules in the soil/water system (Schwarzenbach et al., 2002). The values of K_{OC}^{sor} coefficient for IMI in the tested soils varied from 172 to 305 L/kg (Table 3), and they are consistent with reported K_{OC}^{sor} values (Cox et al., 1998b; Krohn & Hellpointner, 2002), especially for soils with similar textural characteristics. Estimated values of our study prove that, according to the McCall classification for the mobility of pesticides (McCall et al., 1980), IMI can be categorized as having a medium mobility (K_{OC}^{sor} 150 - 500 L/kg) (Comfort et al., 1994), showing less tendency to be sorbed by the examined soils. Therefore, these K_{OC}^{sor} values, together with reported K_{OW} values (3.7) (Krohn & Hellpointner, 2002) and a great water solubility (0.51g/L) (Tomlin, 2001) suggest a potential of IMI to leach to groundwater. However, the results of field studies have showed the lack of leaching for IMI, which could be due to a larger sorption potential at a lower concentration compared to higher concentration range (Kamble & Saran, 2005), or as a result of an increase in the sorption of IMI with time in the soil (Oi, 1999).

At equilibrium, the pesticide distribution between the solid and aqueous phases is ultimately governed by the sorption Gibbs free energy ($\Delta G°$). The change in the $\Delta G°$ as a result of sorption process, was calculated from the thermodynamic relationship:

$$\Delta G^0 = -RTlnK_{OC} \tag{13}$$

where, $\Delta G°$ is the free energy change (kJ/mol), T is the absolute temperature (K), R is the universal gas constant (8.314 J/molK). $\Delta G°$ values of sorption processes ranged from -13.94 to -12.54 kJ/mol and are listed in Table 3. The $\Delta G°$ values obtained in the present study indicate that the sorption capacity of the soils would be in the order of Istria II soil > Istria I soil > Krk I soil > Krk II soil. The greater the absolute magnitude of $\Delta G°$ value, the greater is the extent to which the sorption reaction may take place. A small negative value of $\Delta G°$ indicated the exothermic nature of the reaction and a spontaneous process. In such cases, it can be inferred that the sorption of IMI takes place via physical processes involving weak attractive forces (ten Hulscher & Cornelissen, 1996), primarily by dissolution-like partition of IMI into soil organic matter (Sheng et al., 2001).

4.1.3 Desorption equilibrium study

Plot of the desorption isotherms for IMI are shown in Figure 6b. It can be seen that the slopes of the desorption isotherms are clearly different from those of the sorption isotherms. The characteristic steep slopes of all isotherms are observed at the low equilibrium concentrations of IMI corresponding to the low initial IMI content in solutions. With increase of the IMI concentrations in solutions the curve slopes become less steep.

The desorption data are also shown in Table 2, where desorbed amount was expressed as a percentage of the total amount sorbed. In all the tested soils significant differences of the amount desorbed between different concentrations and between the tested soils were observed. As the initial IMI concentration increased from 1 to 10 mg/L, the desorbed amount, as a percentage of the total sorbed, increased from 12.70 to 27.71% for the Istrian soils and from 41.05 to 58.75% for the Krk soils. The highest percentage of desorption was achieved for the Krk II soil, where actual amounts of recovery ranged from 43.98 to 58.75%of that sorbed by soil. This suggests that half of the amount sorbed was retained by the Krk II soil regardless of initial concentration. The lowest measured recovery of the amount of the desorbed IMI was observed for the Istria II soil. The higher release for Krk II than Istria II soil is likely due to difference in OC content. In a desorption study of IMI on a Hungarian soil, (Nemeth-Konda et al., 2002) found that the amount of IMI desorbed following three desorption steps (average the initial concentrations) was 62±15%. In their study, a similar background solution ($CaCl_2$) was used except that sorption was limited 24h.

The Freundlich desorption coefficient values (K_F^{des}) for the tested soils were higher than sorption values (K_F^{sor}), while desorption $1/n$ values were lower than the Freundlich sorption equilibrium values (Table 5). K_F^{des} value was highest for the Istria II soil (clay soil with 1.91% OC) followed by the Istria I, Krk I and the Krk II soil (sandy loam soil with 0.42 % OC) which exhibited the lowest K_F^{des}. A higher K_F^{des} value indicated a stronger affinity for the IMI. In our study, *1/n* constants ranged from 0.654 to 0.836 with deviations from the linear function ranging from 16.4% (Krk II soil) to 34.6% (Istria II soil). Fernandez-Bayo et al. (2007) made similar observations for IMI in Spain soils. This could be explained by a possible hysteresis effect taking place during desorption, involving various forces that caused the amount of IMI retained to be higher after desorption than after sorption at the unit equilibrium concentration. Hysteresis is manifested by an increase in the difference between the sorption and desorption isotherm slopes. Conceptually, the lack of similarity between sorption and desorption due to the hysteresis is likely a results of binding to organic matter and clay particles. Clay fraction is of great importance because it can enter into interactions with natural organic matter in the soil and it can control its structural configuration (Gunasekara & Xing, 2003). Particularly, in the interaction of organic matter with the clay fraction crystal-amorphous complexes are formed which can increase the nonlinearity of the sorption isotherm. Several studies have illustrated hysteretic behavior of IMI (Fernandez-Bayo et al., 2007; Papiernik et al., 2006).

Soil	K_F^{des} (mg/kg)/ (mg/L)$^{1/n}$	$1/n_{des}$	R^2	K_{OC}^{des} (L/kg)	H
Krk I	4.66 (± 0.16)	0.786 (± 0.049)	0.988	847.27	0.879
Krk II	3.65 (± 0.05)	0.836 (± 0.023)	0.982	869.05	0.922
Istria I	12.41 (±0.39)	0.749 (± 0.041)	0.997	954.61	0.793
Istria II	16.05 (±0.54)	0.654 (± 0.036)	0.989	840.31	0.698

Table 5. The Freundlich desorption parameters and hysteresis index (H) for IMI in the tested soils.

For the Krk II soil, the Freundlich K_F^{sor} was 1.28 (mg/kg)/(mg/L)$^{1/n}$ and the K_F^{des} was 3.65 (mg/kg)/(mg/L)$^{1/n}$, while the K_{OC}^{sor} and K_{OC}^{des} were 304.76 and 869.05 L/kg. These findings indicated that IMI was weakly sorbed, but slightly held by the soil. In contrast, the K_F^{sor} and K_F^{des} values for the Istria II soil were 3.28 and 16.05 (mg/kg)/(mg/L)$^{1/n}$, while the K_{OC}^{sor} and K_{OC}^{des} were 171.73 and 840.31 L/kg. The IMI was sorbed firmer by the Istria II soil and retained, though surprisingly the low K_{OC}^{sor} values of Istria II soil suggested that OC played less of role in sorption than with the lower OC content in Krk II soil. The difference may lie in the different pH values for the soils. The pH for the Krk II soil was 6.88 (nearly neutral) while the Istria II soil pH was 4.76 (acidic). Ping et al. (2010) found that IMI was sorbed more strongly at pH 4.5 than at pH 7.5. The effect of pH is probably due to the increased polarity of the humic material and the electrostatic interaction of the pesticide with soil particles at higher pH.

4.1.4 Sorption-desorption hysteresis

In order to estimate the discrepancies between sorption and desorption isotherms hysteresis coefficient *H* was calculated, and its values for the tested soils are presented in Table 5. When the value of *H* is lower, sorption-desorption hysteresis is more pronounced. We can see that the highest hystersis effect (the lowest *H*) was observed in the Istria II soil.

In Krk soils, no higher differences between sorption-desorption isotherm slopes were found, and therefore, hysteresis coefficients near to unit ($1/n_{des} \approx 1/n_{sor}$) indicates the high reversibility of IMI sorption by these two soils. Coefficient H was lower for Istrian soils than for Krk soils ($1/n_{des}<1/n_{sor}$). This indicates that a significant amount of the sorbed IMI is very difficult to desorb from Istrian soils which may have been caused by a higher amount of OC and clay content in Istria soils, leading to a higher sorption capacity than for Krk soils.

According to the dual model for the sorption of organic pesticides on the soil organic matter, sorption takes place through two sorption mechanisms: the partition and the sorption (Pignatello & Xing, 1996). Soil organic matter has not a uniform continuous phase and is rather represented as a three dimensional matrix, in which the condensed and amorphous phases form separated microenvironment. According to the proposed mechanism, at low concentrations of IMI, the sorption sites in the condensed aromatic area are occupied first, while at higher concentrations of IMI the sorption sites in the amorphous and aliphatic regions start to fill. This effect caused a pronounced hysteresis in the range of lower concentrations, which is consistent with the results obtained for the sorption of IMI. Since sorption area contains a limited number of high-energy sorption sites, molecules of sorbate occupy first these places at low concentrations, meaning that at low concentration the sorption mechanism dominates over the partition (Gunasekara et al., 2003). In addition, de Jonge & Mittelmejer-Hazeleger, 1996) showed that natural organic matter, has high microporosity, with a radius of pores <20 Å, and, therefore, the authors assumed that the observed sorption-desorption hysteresis can be the result of irreversible "trapping" of IMI molecules in the pores of natural organic matter. If we assume that the pore radius is 10 Å, than the calculated pore volume is about 4200 Å^3. Since the volume of one IMI molecule is 275 Å^3, it is possible that "irreversible entrapment" caused the observed sorption-desorption hysteresis.

4.2 Degradation study

4.2.1 Persistence of IMI

Results of degradation studies for IMI at two concentration levels (0.5 and 5 mg/kg) in four Croatian soils at various times are plotted in Figures 7 and 8. A visual examination of degradation pattern for the IMI in all tested soils suggests significant deviation from the first-order kinetic (R^2 range from 0.95 to 0.98). Consequently, alternative two-compartment model was used to describe the observed two-phase kinetic and to derive DT_{50} and DT_{90} (50 and 90 % degradation time) values. In our study, therefore, we presented the experimental data as a concentration of IMI degraded from the initial application on soil, and the corresponding values for DT_{50} and DT_{90}, were graphically estimated from Figures 7 and 8.

Following the treatment of soils at 0.5 and 5 mg/kg concentration level, the average initial concentration varied from 0.43 to 0.49 and 4.71 to 5.43 mg/kg (Figure 7 and 8). In all the tested soils, the residues persisted beyond 180 days at both levels and 4.7-13.8 % loss was recorded on day 7, 12.0-39.9 % on day 30, 32.7-65.2 % on day 90, and 55.0-82.6 % on day 180. The greatest loss of IMI was found in a clay soil with a higher OC content (Istria II soil, 75.4 -82.61 %) and the lowest in a sandy loam soil with a lower OC content (Krk II soil, 55.0-58.1 %).

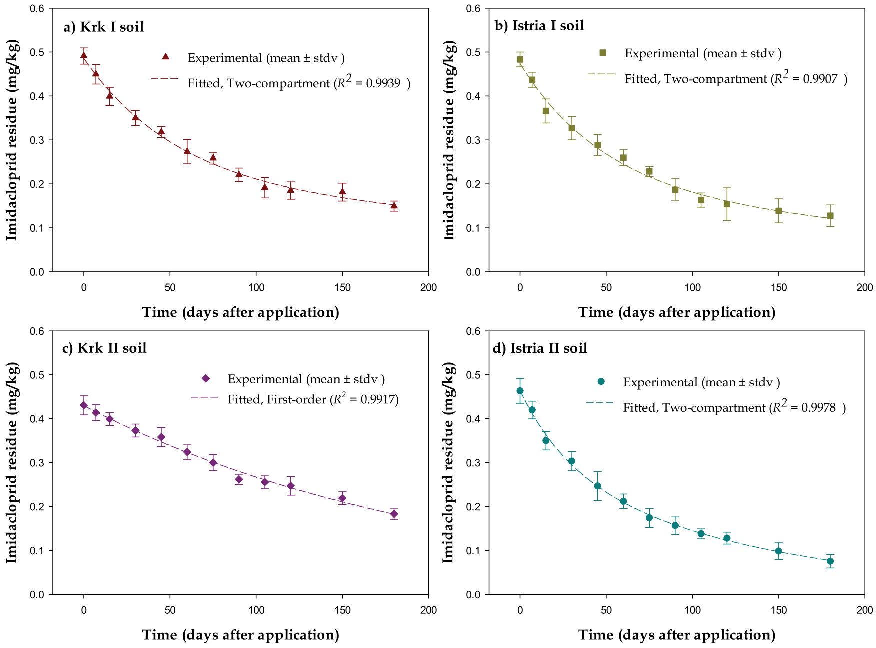


Fig. 7. Degradation of IMI in the tested soils at 0.5 mg/kg concentration level. Values are means ± standard deviations. Symbols represent the experimental data, while lines represent the theoretical curves fitted by the first-order kinetics model or two-compartment model.

The results from the curve fitting analysis are shown in Figure 7 and 8. In each figure, the measured data are shown together with the curves simulated by the first-order kinetic model or by two-compartment model. IMI degradation in all tested soils at the low concentration level appears to be adequately described by two-compartment model. In contrast, at the high concentration level the experimental data were better described using the first-order kinetic model rather than the two-compartment model, except for Istria II soil, where biphasic kinetic was observed (Figure 8d). In fitting two-compartment model, we assumed that the fast degradation phase occurred from 0 to 15 days after application and that the slow degradation phase occurred thereafter. This was visually determined based on the changes of the slopes of the degradation curves. Capri et al. (2001), who studied the degradation of IMI in Italian soils, found that IMI concentration decreased rapidly in the first 10 days followed by a slower decrease in the total amount recovered. The derived rate constants as well as DT_{50} and DT_{90} for each model are shown in Table 6 together with the correlation coefficient for each curve (R^2) and with root mean square error (RMSE). Both statistical indices (R^2 and RMSE) indicated that the first-order kinetic model better described IMI degradation at the high concentration level in all tested soils, except in Istria II soil, than at the low concentration level (Table 6). At the low concentration level, the more complex two-compartment model generated smaller RMSE.

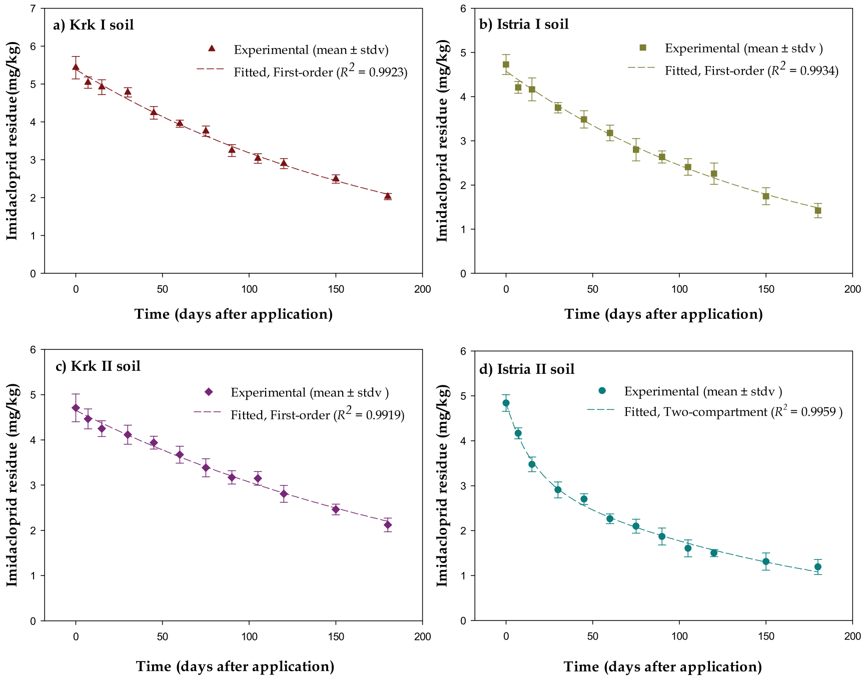


Fig. 8. Degradation of IMI in the tested soils at 5 mg/kg concentration level. Values are means ± standard deviations. Symbols represent the experimental data, while lines represent the theoretical curves fitted by the first-order kinetics model or two-compartment model.

The adequacy of the first-order kinetic model description at the high concentration level can be seen by comparing the fitted rate constants (Table 6). The fitted k_1 for the first-order kinetic model was equal (except the Istria II soil) to that in the rapid degradation pool of the two-compartment model. Moreover, the two-compartment model had the same rate constant in the rapid and slow degradation pools, which is also equal to k_1 of the first-order kinetic model. The rate of degradation was highest in the Istria II soil and the lowest in the Krk II soil. The higher degradation rate in Istria II soil than in Krk II soil could be due to the higher OC content of Istria II soil vs Krk II soil.

The calculated DT$_{50}$ and DT$_{90}$ values for the tested soils ranged from 50.18-145.97 and 247.38-914.97 days at the low concentration level respectively, and from 54.86-165.04 and 345.76-548.23 days at the high concentration level, respectively (Table 6). The DT$_{50}$ and DT$_{90}$ values were highest (for both concentration levels) for the Krk II soil, which were significantly higher than that in the other soils. The lowest DT$_{50}$ and DT$_{90}$ were observed in the Istria II soil. Estimated values for DT$_{50}$ in our study prove that IMI can be categorized as moderately persistent pesticide (DT$_{50}$ from 30 - 100 days) (Gavrilescu, 2005). Previous studies of IMI degradation at laboratory and at field conditions have reported DT$_{50}$ values in the range from 40 to 229 days (first-order kinetic) (Sarkar et al., 2001; Schad, 2001). However, high values of 156 days (Krohn & Hellpointner, 2002) and a greater than a year (Baskaran et al., 1999) have been measured. The DT$_{50}$ values for IMI degradation in the present study are comparable with those reported under field conditions (Schad, 2001; 96 days) and degradation was slower than in other study at laboratory conditions (Sarkar et al., 2001; 40 days). If we compare the DT$_{50}$ values derived from the used kinetic models between the two examined initial concentration levels, we can see that these values differed significantly. Higher persistence of IMI was observed at higher initial concentration level (mean DT$_{50}$ = 118.46 days) compared to lower concentration (mean DT$_{50}$ = 90.62 days), which was statistically significant ($p = 0.020$). This seems to lead to the conclusion that concentration level significantly affected IMI degradation.

Fitted parameter or index*	Model I				Model II			
	Krk I	Istria I	Krk II	Istria II	Krk I	Istria I	Krk II	Istria II
Concentration level 0.5 mg/kg								
k_1 (1/d)	0.0076	0.0090	0.0048	0.0114	0.0187	0.0210	0.0055	0.0353
k_2 (1/d)					0.0020	0.0031	$2.21 \cdot 10^{-11}$	0.0075
a (mg/kg)	0.4613	0.4507	0.4297	0.4407	0.2798	0.2928	0.2209	0.2965
b (mg/kg)					0.2060	0.1814	0.2106	0.1675
DT$_{50}$ (d)	91.20	77.02	144.41	60.80	82.39	63.60	145.97	50.18
DT$_{90}$ (d)	302.97	255.84	479.71	201.98	722.10	466.64	914.97	247.38
R^2	0.9679	0.9695	0.9917	0.9844	0.9939	0.9907	0.9823	0.9978
RMSE	0.0212	0.0219	0.0077	0.0167	0.0103	0.0135	0.0084	0.0071
Concentration level 5 mg/kg								
k_1 (1/d)	0.0053	0.0063	0.0042	0.0093	0.0053	0.0063	0.0042	0.0356
k_2 (1/d)					0.0053	0.0063	0.0042	0.0051
a (mg/kg)	5.3848	4.5780	4.6514	4.3303	3.1555	2.9662	2.5149	3.4221
b (mg/kg)					2.2293	1.6118	2.1365	1.4170
DT$_{50}$ (d)	130.78	110.02	165.04	74.53	130.78	110.02	165.04	54.86
DT$_{90}$ (d)	434.45	365.49	548.23	247.59	434.45	365.49	548.23	345.76
R^2	0.9923	0.9934	0.9919	0.9483	0.9923	0.9934	0.9919	0.9959
RMSE	0.1010	0.0889	0.0769	0.2779	0.1130	0.0984	0.0859	0.0727

* DT$_{50}$ and DT$_{90}$ are times for 50 and 90% of the initial residues to degrade; k_1 and k_2 are first-order rate constants in the rapid and slow degradation pools; a and b are initial concentrations in the rapid and slow degradation pools; R^2 is the coefficient of determination; RMSE is the root mean square error

Table 6. Fitted parameters for the first-order kinetics model and two-compartment model for describing IMI degradation in the tested soils.

These results suggested that the persistence of IMI was significantly influenced by soil properties. Kendal-Tau correlation analysis between DT$_{50}$ and selected soil properties demonstrated that IMI persistence in the tested soils was inversely connected to CEC, clay and OC content, with a strongest relationship between DT$_{50}$ and CEC (Table 4). The analysis showed the positive, but very weak correlation between DT$_{50}$ with soil pH. Other studies have found reasonable correlation between DT$_{50}$ and pH. For example, Sarkar et al. (2001) showed that the persistence of IMI tended to increase as soil pH increased. In addition, multiple liner regression confirmed that IMI persistence was primarily correlated with OC content, with a regression equation of:

$$DT_{50} = 72.7581\,OC - 4.9850\,CEC - 0.4689\,clay + 11.8127\,pH + 116.50\left(R^2 = 0.825\right) \tag{14}$$

The DT_{50} values were further tested to determine the effects of soil type on the DT_{50} of IMI. Statistically significant differences in soil persistence, were found among the Krk (mean DT_{50} = 132.09 days) and Istria (mean DT_{50} = 77.00 days) region (p = 0.000002). In addition, results of degradation study within the regions showed a statistically significant difference in DT_{50} values between the soils Istria I (mean DT_{50} = 92.53 days) and Istria II (mean DT_{50} = 61.46 days) (p = 0.002), as well as between soils Krk I (mean DT_{50} = 108.16 days) and Krk II (mean DT_{50} = 156.02 days) (p = 0.00001).

Examining the soil properties reveals that the most contrasting difference between tested soils, with respect to IMI degradation, is soil OC content, which was in the range from 1.30 to 1.91% for Istrian soils and from 0.42 to 0.55% for Krk soils. Higher OC content in Istrian soils would cause more IMI sorption by the soil based on the concept proposed by (Park et al., 2003). An equilibrium sorption study, conducted to verify this hypothesis showed that IMI equilibrium sorption constants were higher for the Istrian soils than for the Krk soils (2.60 and 3.28 for the Istria I soil and Istria II soil; 1.28 and 1.53 for the Krk II soil and Krk I soil). Higher OC content in Istrian soils might have been accompanied by higher microbial population and activities that promoted biodegradation processes of IMI (Cox et al., 1997; Getenga et al., 2004; Park et al., 2003). In describing degradation of 2,4-D (2,4-dichlorpphenoxyacetic acid) Picton & Farenhorst (2004) hypothesized a mechanism according to which initially readily available chemical resulted in apparent rapid degradation, while subsequent increased binding to soil caused noticeable reduction in degradation rate. When comparing IMI degradation in all the tested soils, we observed that IMI degraded faster in Istrian soils than in Krk soils, although more IMI was sorbed in Istrian soils. Thus, it appears that sorption did not significantly inhibit IMI degradation in the soil. Otherwise, IMI should have degraded faster in the Krk soils than in the Istrian soils. Fitting two-compartment model to the measured data showed that the degradation rate constants in the rapid degradation pool in the Istrian soils were greater than those in the Krk soils at both concentration level (Table 6). Calculations using two compartment model based on the data in Table 6 revealed that readily available IMI amount in the rapid degradation pool initially represented 51-58 and 54-59% of the applied IMI in Krk soils and 62-64 and 65-71% in Istria soils at the low and high concentration level, respectively. These results suggested that IMI in the rapid degradation pool is not equivalent to the dissolved IMI molecule, as Wolt, (1997) proposed. Although pesticide molecule in soil solution is generally thought to be readily available to microorganisms for biodegradation, there is evidence that sorption can accelerate pesticide degradation (Park et al., 2003).

4.2.2 6-CNA formation

Metabolism of IMI was also studied in four Croatian soils at both concentration levels. The amount of 6-CNA, which was detected in all the tested soils as a metabolic product, varied irregularly with the time (Figure 9). The maximum concentration of 6-CNA in the tested soils was in the range from 280 to 720 µg/kg for the 5 mg/kg concentration level, while the corresponding concentration of 6-CNA was from 36.2 to 54.9 µg/kg for the 0.5 mg/kg concentration level during the period of 150-180 days after application. Formation of the 6-CNA from IMI in soil has been reported earlier (Scholz, 1992). 6-CNA accounted for a maximum of about 15 and 10% of the initial concentration of IMI for the 5 and 0.5 mg/kg, respectively, in the Istria II soil. The corresponding minimum values for 6-CNA were 6 and 9%.

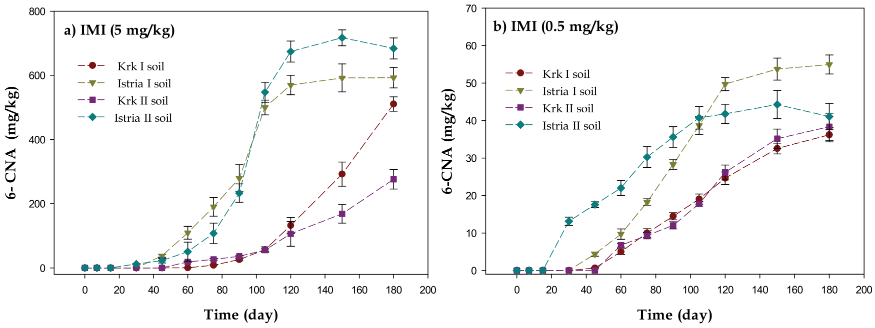


Fig. 9. Formation of 6-CNA in the tested soils at concentration level of: a) 5 and b) 0.5 mg/kg. Values are means ± standard deviations. Symbols represent the experimental data, while vertical bars represent the standard deviation in the triplicate samples.

5. Conclusions

The sorption-desorption and degradation of IMI was examined to understand the influence of concentration and soil properties on its behavior and fate in soils of Croatian coastal regions. The experimental data revealed that the sorption and desorption isotherms of IMI in the tested soils were nonlinear over the concentration range used, which can be best described by the Freundlich equation. Soil sorption capacity of IMI depended significantly on the soil properties. Especially, the sorption behavior of IMI was largely dependent on the soil OC content, where the soils with higher OC content (Istria soils) showed higher sorption capacity and less potential mobility of IMI. Given the spatial difference between tested soils, statistically significant differences in soil sorption capacity were found among and within soils of Istrian and Krk region. According to calculated K_{OC} values, IMI can be categorized as a medium mobility pesticide indicating that rational use of IMI entails little danger of the ground-water contamination. In all soils, a higher sorption capacity was observed at lower IMI concentrations, indicating that the percentage of desorbed amount of pesticide increased with increasing initial solution concentration. Desorption experimental data deviated significantly from the sorption data, indicating that these processes were distinctly different in tested soils. It can be assumed, that the desorption process appeared to be the result of a complex, time dependent interplay of several chemical and physical processes and irreversible binding of IMI to soil surfaces, leading to hysteresis. The negative and low values of the Gibbs free energy of the IMI sorption indicated exotermic characteristics of sorption reaction and corresponded to the physical process, suggesting that partitioning into soil organic matter was the main mechanism of IMI sorption in the soils used. IMI kinetic behavior in all tested soils at the high concentration level can be described by the first-order kinetic degradation model, except for Istria II soil, where biphasic kinetics was observed. In contrast, at the low concentration level, the two-compartment kinetic model took place, characterized by the fast initial phase in the first 15 days of degradation followed by a slow degradation phase up to 180 days. According to the pesticide persistence classification, IMI can be categorized as moderately persistent pesticide (DT_{50} from 50 – 165 days), showing that the slow degradation of IMI in the tested soils further enlarges the danger of environmental damage. Concentration level significantly affected IMI's degradation, where higher persistence of IMI at higher initial concentration level was observed. In all tested soils, organic matter provided an accelerating effect on the degradation rate.

The study results emphasize the need for controlled IMI usage, especially in soils with low humus content (Krk soils), thus avoiding a risk of IMI leeching. Considering the abundant current use of IMI in the Croatian olive growing areas, regular monitoring is needed to evolve a strategy to manage the environmental hazards due to the IMI and its degradation products. Further research, aided also with the actual field data, will be directed to investigate the IMI's metabolism and binding mechanisms in order to better understand degradation pathway and the causes for hysteresis phenomena.

6. Acknowledgment

This work was supported by the Croatian Ministry of Science, Education and Sport (grant number 062-0621341-0061).

7. References

Anderson, J. P. E. (1995). Mineralization of [imidazolidin-4,5-^{14}C] NTN 33893 to $^{14}CO_2$ in sterile and microbiologically active samples of 2 agricultural soils. Bayer AG, Leverkusen, Germany, pp. 6, Report No. 107300, (Reviewed in Mulye 1996)

Arias-Estevez, M.; Lopez-Periago, E.; Martinez-Carballo, E.; Simal-Gandara, J.; Mejuto, J. C. & Garcia-Rio, L. (2008). The mobility and degradation of pesticides in soils and the pollution of groundwater resources [Review]. *Agriculture Ecosystems & Environment*, Vol.123, No.4, (February 2008), pp. 247-260, ISSN 0167-8809

Bai, D.;Lummis, S. C. R.; Leicht, V.; Breer, H. & Sattele, B. D. (1991.). Actions of imidacloprid and a related nitromethylene on cholinergic receptors of a identified insect motor neurone. *Pest Management Science*, Vol.33, No.2, (April 1991), pp. 197-204

Baskaran, S.; Kookana, R. S; & Naidu, R. (1997). Determination of the Insecticide Imidacloprid in Water and Soil Using High-Performance Liquid Chromatography. *Journal of Chromatography A*, Vol.787, No.1-2, (November 1997), pp. 271-275, ISSN 0021-9673

Baskaran, S.; Kookana, R. S. & Naidu, R. (1999). Degradation of bifenthrin, chlorpyrifos and imidacloprid in soil and bedding materials at termiticidal application rates. *Pesticide Science*, Vol.55, No.12, (December 1999), pp. 1222-1228, ISSN 0031-613X

Beulke, S. & Brown, C. D. (2001). Evaluation of methods to derive pesticide degradation parameters for regulatory modelling. *Biology & Fertility of Soils* , Vol.33, No.6, (June 2001), pp. 558-564, ISSN 0178-2762

Boivin, A.; Cherrier, R. & Schiavon, M. (2005). A comparison of five pesticides adsorption and desorption processes in thirteen contrasting field soils. *Chemosphere*, Vol.61, No.5, (November), pp. 668-676, ISSN 0045-6535

Giles, C.H.; Macevans, T. H.; Nakhwa, S. N. & Smith, D. (1960). Studies in adsorption: Part XI. A system of classification of solution adsorption isotherms and its use in diagnosis of adsorption isotherms mechanisms and in measurement of specific surface areas of solids. *Journal of the Chemical Society*, Vol.111, No.3, (January 1960), pp. 3973-3993

Calderon, M. J.; Ortega, M.; Hermosin, M. C.; Garcia-Baudin, J. & Cornejo, J. (2004). Hexazinone and simazine dissipation in forestry field nurseries. *Chemosphere*, Vol.54, No.1, (January 2004), pp. 1-8, ISSN 0045-6535

Capri, E.; Camisa, M. G.; Flores-Cespedes, F.; Glass, C. R.; Gonzalez-Pradas, E. & Trevisan, M. (2001). Imidacloprid and pyrimethanil soil sorption. *Agronomie*, Vol.21, No.1, (January-February 2001), pp. 57-64, ISSN 0249-5627

Carbo, L.; Souza, V.; Dores, E. & Ribeiro, M. L. (2008). Determination of pesticides multiresidues in shallow groundwater in a cotton-growing region of Mato Grosso, Brazil. *Journal of the Brazilian Chemical Society*, Vol.19, No.6, (July 2008), pp. 1111-1117, ISSN 0103-5053

Celis, R. & Koskinen, W. C. (1999). An isotopic exchange method for the characterization of the irreversibility of pesticide sorption-desorption in soil. *Journal of Agricultural & Food Chemistry*, Vol.47, No.2, (Fabruary 1999), pp. 782-790, ISSN 0021-8561

Chen, W.; Mulchandani, A. & Deshusses, M. A. (2005). Environmental biotechnology: Challenges and opportunities for chemical engineers. *AICHE Journal*, Vol.51, No.3, (March 2005), pp. 690-695, ISSN 0001-1541

Comfort, S. D.; Shea, P. J. & Roeth, F. W. (1994). *Understanding Pesticides and Water Quality in Nebraska,* (Extension Circular, EC 94-135), Institute of Agriculture and Natural Resources, University of Nebraska, ASIN: B0006PBUMG, Lincoln, USA

Cox, L.; Koskinen, W. C. & Yen, P. Y. (1997). Sorption-desorption of imidacloprid and its metabolites in soils. *Journal of Agricultural & Food Chemistry*, Vol.45, No.4, (April 1997), pp. 1468-1472, ISSN 0021-8561

Cox, L.; Koskinen, W. C.; Celis, R.; Yen, P. Y.; Hermosin, M. C. & Cornejo, J. (1998a). Sorption of imidacloprid on soil clay mineral and organic components, *Soil Science Society of America Journal*, Vol.62, No.4, (July-August 1998), pp. 911-915, ISSN 0361-5995

Cox, L.; Koskinen, W. C. & Yen, P. Y. (1998b). Changes in sorption of imidacloprid with incubation time. *Soil Science Society of America Journal*, Vol.62, No.2, (March-April 1998), pp. 342-347, ISSN 0361-5995

Cox, L.; Koskinen, W. C. & Yen, P. Y. (1998c). Influence of soil properties on sorption-desorption of imidacloprid. *Journal of Environmental Science & Health - Part B (Pesticides)*, Vol.33, No.2, (May-Jun 1998), pp. 123-134, ISSN 0360-1234

Cox, L.; Hermosin, M. C.; Koskinen, W. C. & Cornejo, J. (2001). Interactions of imidacloprid with organic-and inorganic-exchanged smectites. *Clay Minerals*, Vol.36, No.2, (June 2004), pp. 267-274, ISSN 0009-8558

Darrel, W. N. & Nelson, L. E. (1996). Total Organic Carbon and Organic Matter, In: *Methods of soil analysis*, D.L. Sparks, (Ed.), pp. 982-991, Soil Science Society of America: American Society of Agronomy, ISBN 978-0891188254, Madison, Wisconsin, USA

de Jonge, H. & Mittelmejer-Hazeleger, M. C. (1996). Adsorption of CO_2 and N_2 on soil organic matter: nature of porosity, surface area, and diffudion mechanisms. *Environmental Science & Technology* , Vol.30, No.2, (January 1996), pp. 408-413, ISSN 0013-936X

Delle Site, A. (2001). Factors affecting sorption of organic compounds in natural sorbent/water systems and sorption coefficients for selected pollutants. A review [Review]. *Journal of Physical & Chemical Reference Data*, Vol.30, No.1, (January-February 2001), pp. 187-439, ISSN 0047-2689

Farenhorst, A. (2006). Importance of soil organic matter fractions in soil-landscape and regional assessments of pesticide sorption and leaching in soil [Review]. *Soil Science Society of America Journal*, Vol.70, No.3, (May-June 2006), pp. 1005-1012, ISSN 0361-5995

Felsot, A. S.; Cone, W.; Yu, J. & Ruppert, J. R. (1998). Distribution of imidacloprid in soil following subsurface drip chemigation. *Bulletin of Environmental Contamination & Toxicology*, Vol.60, No.3, (Mart 1998), pp. 363-370, ISSN 0007-4861

Fernandez-Bayo, J. D.; Nogales, R. & Romero, E. (2007). Improved retention of imidacloprid (Confidor ((R))) in soils by adding vermicompost from spent grape marc. *Science of the Total Environment*, Vol.378, No.1-2, (May 2007), pp. 95-100, ISSN 0048-9697

Flores-Cespedes, F.; Gonzalez-Pradas, E.; Fernandez-Perez, M.; Villafranca-Sanchez, M.; Socias-Viciana, M. & Urena-Amate, M. D. (2002). Effects of dissolved organic carbon on sorption and mobility of imidacloprid in soil. *Journal of Environmental Quality*, Vol.31, No.3, (May-Jun 2002), pp. 880-888, ISSN 0047-2425

Fritz, R., & Hellpointner, E. (1991). Degradation of pesticides under anaerobic conditions in the water/sediment system: imidacloprid. Miles Report No. 101346. Bayer AG, Leverkusen, Germany, pp. 69 (Reviewed in Mulye 1995)

Gavrilescu, M. (2005). Fate of pesticides in the environment and its bioremediation. *Engineering in Life Sciences*, Vol.5, No.6, (October 2005), pp. 497-526, DOI: 10.1002/elsc.200520098

Getenga, Z. M.; Madadi, V. & Wandiga, S. O. (2004). Studies on biodegradation of 2,4-D and metribuzin in soil under controlled conditions. *Bulletin of Environmental Contamination & Toxicology*, Vol.72, No.3, (March 2004), pp. 504-513, ISSN 0007-4861

Golfinopoulos, S. K. & Arhonditsis, G. B. (2002). Multiple regression models: A methodology for evaluating trihalomethane concentrations in drinking water from raw water characteristics. *Chemosphere*, Vol.47, No.9, (June 2002), pp. 1007-1018, ISSN 0045-6535

Gonzalez-Pradas, E.; Urena-Amate, M. D.; Flores-Cespedes, F.; Fernandez-Perez, M.; Garratt, J. & Wilkins, R. (2002). Leaching of imidacloprid and procymidone in a greenhouse of southeast of Spain. *Soil Science Society of America Journal*, Vol.66, No. 6, (November-December 2002), pp. 1821-1828, ISSN 0361-5995

Grover, R.; Wolt, J. D.; Cessna, A. J. & Schiefer, H. B. (1997). Environmental fate of trifluralin. *Reviews of Environmental Contamination & Toxicology*, Vol.153, (May-Jun 1997), pp. 1-64, ISSN 0179-5953

Gunasekara, A. S.; Simpson, M. J. & Xing, B. S. (2003). Identification and characterization of sorption domains in soil organic matter using structurally modified humic acids. *Environmental Science & Technology*, Vol.37, No.5, (March 2003), pp. 852-858, ISSN 0013-936X

Gunasekara, A. S. & Xing, B. S. (2003). Sorption and desorption of naphthalene by soil organic matter: Importance of aromatic and aliphatic components. *Journal of Environmental Quality*, Vol.32, No.1, (January-February 2003), pp. 240-246, ISSN 0047-2425

Gupta, S.; Gajbhiye, V. T.; Kalpana & Agnihotri, N. P. (2002). Leaching behavior of imidacloprid formulations in soil. *Bulletin of Environmental Contamination & Toxicology*, Vol.68, No.4, (April 2002), pp. 502-508, ISSN 0007-4861

Heim, D.; Yan, Z. & Halarnkar, P. P. (1996). Anaerobic aquatic biotransformation of [pyridinyl-14C-methyl] imidacloprid at 5°C. Bayer Corporation, Kansas City, Missouri. Report No. 107546, pp. 138 (Reviewed in Mulye 1996).

Hendershot, W.H.; Lalande, H & Duquette M. (2007). Soil Reaction and Exchangeable Acidity, In: *Soil Sampling and Methods of Analysis*, M. R. Carter & Gregorich E. G., (Eds.), pp. 173-179, CRC Press, ISBN 978-0849335860, Boca Raton, USA

Henriksen, T.; Svensmark, B. & Juhler, R. K. (2004). Degradation and sorption of metribuzin and primary metabolites in a sandy soil. *Journal of Environmental Quality*, Vol.33, No.2, (March-April 2004), pp. 619-627, ISSN 0047-2425

Huang, W. L. & Weber, W. J. (1997). A distributed reactivity model for sorption by soils and sediments .10. Relationships between desorption, hysteresis, and the chemical characteristics of organic domains. *Environmental Science & Technology*, Vol.31, No.9, (September 1997), pp. 2562-2569, ISSN 0013-936X

Huang, W. L.; Ping, P. A.; Yu, Z. Q. & Fu, H. M. (2003). Effects of organic matter heterogeneity on sorption and desorption of organic contaminants by soils and sediments [Review]. *Applied Geochemistry*, Vol.18, No.7, (July 2003), pp. 955-972, ISSN 0883-2927

Kamble, S. T. & Saran, R. K. (2005). Effect of concentration on the adsorption of three termiticides in soil. *Bulletin of Environmental Contamination & Toxicology*, Vol.75, No.6, (December 2005), pp. 1077-1085, ISSN 0007-4861

Koskinen, W. C. & Harper, S. S. (1990). The retention process: mechanisms, In: *Pesticides in the soil environment : processes, impacts, and modeling*, H.H. Cheng (Ed.), pp. 51-77, Soil Science Society of America, ISBN 978-0891187912, Madison, Wisconsin, USA

Kroetsch, D. & Wang, C. (2007). Particle Size Distribution, In: *Soil Sampling and Methods of Analysis*, M. R. Carter & Gregorich E. G., (Eds.), pp. 713-727, CRC Press, ISBN 978-0849335860, Boca Raton, USA

Krohn, J. (1996a). Water solubility and partition coefficient of desnitro compound. Bayer Corporation, Kansas City, Missouri. Report No. 107676, (Reviewed in Mulye 1996)

Krohn, J. (1996b). Water solubility and partition coefficient of urea compound. Bayer Corporation, Kansas City, Missouri. Report No. 107677, pp. 15 (Reviewed in Mulye 1996)

Krohn, J. & Hellpointner, E. (2002). Environmental fate of imidacloprid. *Pflanzenschutz-Nachrichten Bayer (Special edition)*, Vol. 55, No. 73, (January 2002), pp. 1-25, ISSN 0340-1723

Kuhad, R. C.; Johri, A. K.; Singh, A. & Ward, O. P. (2004) Bioremediation of pesticide-contaminated soils, In: *Applied bioremediation and phytoremediation*, A. Singh & O. P. Ward, (Eds), pp. 35-54, Springer-Verlag, ISBN 978-3540210207, Berlin, Germany

Larson, S. J.; Capel, P. D. & Majewski, M. S. (1997). *Pesticides in Surface Waters: Distribution, Trends, and Governing Factors* (1 edition), Ann Arbor Press, ISBN 978-1575040066, Chelsea, Michigan, USA

Lesan, H. M. & Bhandari, A. (2003). Atrazine sorption on surface soils: time-dependent phase distribution and apparent desorption hysteresis. *Water Research*, Vol.37, No.7, (April 2003), pp. 1644-1654, ISSN 0043-1354

Liu, W. P.; Zheng, W.; Ma, Y. & Liu, K. K. (2006). Sorption and degradation of imidacloprid in soil and water. *Journal of Environmental Science & Health - Part B (Pesticides)*, Vol.41, No.5, (October 2006), pp. 623-634, ISSN 0360-1234

Ma, Q. L.; Rahman, A.; Holland, P. T.; James, T. K. & McNaughton, D. E. (2004). Field dissipation of acetochlor in two New Zealand soils at two application rates. *Journal of Environmental Quality*, Vol.33, No.3, (May-June 2004), pp. 930-938, ISSN 0047-2425

Maienfisch, P.; Angst, M.; Brandl, F.; Fischer, W.; Hofer, D.; Kayser, H.; Kobel, W.; Rindlisbacher, A.; Senn, R.; Steinemann, A. & Widmer, H. (2001). Chemistry and biology of thiamethoxam: a second generation neonicotinoid. *Pest Management Science*, Vol.57, No.10, (October 2001), pp. 906-913, ISSN 1526-498X

Mathys, W. (1994). Pesticide pollution of ground- and public drinking waters caused by artificial groundwater recharge or bank filtration - underestimated sources for water contamination [German]. *Zentralblatt fur Hygiene und Umweltmedizin*, Vol.1964,No. 4, (December 1994), pp. 338-359, ISSN 0934-8859

Maxim, L. & van der Sluijs, J. P. (2007). Uncertainty: cause or effect of stakeholders' debates? Analysis of a case study: the risk for honeybees of the insecticide Gaucho. *Science of the Total Environment*, Vol.376, No.1-3, (April 2007), pp. 1-17, ISSN 0048-9697

Maxim, L. & van der Sluijs, J. P. (2010). Expert explanations of honeybee losses in areas of extensive agriculture in France: Gaucho (R) compared with other supposed causal factors - art. no. 014006. *Environmental Research Letters*, Vol.5, No.1, (January-March 2010), pp. 14006, ISSN 1748-9326

McCall, P. J.; Swann, R. L.; Laskowski, D. A.; Unger, S. M.; Vrona, S. A. & Dishburger, H. J. (1980). Estimation of the chemical mobility in the soil from the liquid chromatographic retention times. *Bulletin of Environmental Contamination and Toxicology*, Vol.24, No.1, (November, 1980), pp. 190-195, ISSN 0007-4861, DOI 10.1007/BF01608096

Mulye, H. S. (1995). . Environmental evaluation of imidacloprid insecticide and the end-use product Admire 240F. Submission Numbers: 94-1706 and 94-1705. Pesticides Division, Commercial Chemicals Evaluation Branch, Environmental Protection Service, Environment Canada

Mulye, H. S. (1996). Supplementary review of imidacloprid technical and the end-use product, Admire 240F insecticide. Submission Numbers: 94-1706 and 94-1705, Environmental Evaluation Division, Pest Management Regulatory Agency, Health Canada

Navarro, S.; Vela, N. & Navarro, G. (2007). Review. An overview on the environmental behaviour of pesticide residues in soils [Review]. *Spanish Journal of Agricultural Research*, Vol.5, No.3, (September 2007), pp. 357-375, ISSN 1695-971X

Nemeth-Konda, L.; Fuleky, G.; Morovjan, G. & Csokan, P. (2002). Sorption behaviour of acetochlor, atrazine, carbendazim, diazinon, imidacloprid and isoproturon on Hungarian agricultural soil. *Chemosphere*, Vol.48, No.5, (August 2002), pp. 545-552, ISSN 0045-6535

OECD. (2000). Test No 106: Adsorption-Desorption Using a Batch Equilibrium Method, In: *OECD Guidelines for the Testing of Chemicals, Section 1: Physical-Chemical Properties,* pp. 1-45, ISBN 9789264069602, Paris, France, 03.04.2011, Available from http://www.oecd-ilibrary.org/environment/test-no-106-adsorption-desorption-using-a-batch-equilibrium-method_9789264069602-en

Oi, M. (1999). Time-dependent sorption of imidacloprid in two different soils. *Journal of Agricultural & Food Chemistry*, Vol.47, No.1, (January 1999), pp. 327-332, ISSN 0021-8561

Papiernik, S. K.; Koskinen, W. C.; Cox, L.; Rice; P. J., Clay, S. A.; Werdin-Pfisterer, N. R. & Norberg, K. A. (2006). Sorption-desorption of imidacloprid and its metabolites in soil and vadose zone materials. *Journal of Agricultural & Food Chemistry*, Vol.54, No. 21, (October 2006), pp. 8163-8170, ISSN 0021-8561

Park, J. H.; Feng, Y. C.; Ji, P. S.; Voice, T. C. & Boyd, S. A. (2003). Assessment of bioavailability of soil-sorbed atrazine. *Applied & Environmental Microbiology*, Vol.69, No.6, (June 2003), pp. 3288-3298, ISSN 0099-2240

Picton, P. & Farenhorst, A. (2004) Factors influencing 2,4-D sorption and mineralization in soil. *Journal of Environmental Science & Health - Part B (Pesticides)*, Vol.39, No.3, (January 2004), pp. 1-11, ISSN 0360-1234

Pignatello, J. J. & Xing, B. S. (1996). Mechanisms of slow sorption of organic chemicals to natural particles [Review]. *Environmental Science & Technology*, Vol.30, No.1, (January 1996), pp. 1-11, ISSN 0013-936X

Pimentel, D. & Levitan, L. (1986). Pesticides: amounts applied and amounts reaching pests. *BioScience - American Institute of Biological Sciences*, Vol.36, No.2, (February 1986), pp. 86-91

Ping, L.; Zhang, C.; Zhu, Y.; Wu, M.; Dai, F.; Hu, X.;, Zhao, H. & Li, Z. (2010). Imidacloprid adsorption by soils treated with humic substances under different pH and temperature conditions. *African Journal of Biotechnology*, Vol.9, No.13, (March 2010), pp. 1935-1940, ISSN 1684–5315

Rouchaud, J.; Gustin, F. & Wauters, A. (1996). Imidacloprid Insecticide Soil Metabolism in Sugar Beet Field Crops. *Bulletin of Environmental Contamination & Toxicology*, Vol.56, No.1, (January 1996), pp. 29-36, ISSN 0007-4861

Sanchez, L.; Pena, A.; Sanchez-Rasero, F. & Romero, E. (2003). Methidathion degradation in soil amended with biosolids and a cationic surfactant: use of different kinetic models. *Biology & Fertility of Soils*, Vol.37, No.5, (May 2003), pp. 319-323, ISSN 0178-2762

Sarkar, M. A.; Roy, S.; Kole, R. K. & Chowdhury, A. (2001). Persistence and metabolism of imidacloprid in different soils of West Bengal. *Pest Management Science*, Vol.57, No.7, (July 2001), pp. 598-602, ISSN 1526-498X

Schad, T. (2001). Calculation of Temperature Referenced First Order DT_{50} of Imidacloprid Based on Field Dissipation Studies Conducted in Europe. In: *Internal Report Bayer AG*, Leverkusen (Cited in Krohn & Hellpointner, 2002)

Schmidt, C. (April 2010). Groundwater and surface water monitoring for pesticides and nitrate, East Shore, Flathead lake, Montana, In: *Department of Agriculture Helena*: *Current and Past Groundwater Reports*, 03.04.2011, Available from: <http://agr.mt.gov/pestfert/groundwater/GWcherries.pdf >

Scholz, K. & Spiteller, M. (1992). Influence of groundcover on the degradation of ^{14}C-imidacloprid in soil, *Proceedings of Crop Protection Conference – Pests and Diseases*, Vol 2, Brighton pp. 883-888, October 1992, (Cited in Rouchaud et al., 1996)

Schwarzenbach, R. P.; Gschwend, P.M. & Imboden, D.M. (2002). *Environmental Organic Chemistry* (2nd Edition), John Wiley and Sons, ISBN 978-0471357506, New Jersey, USA

Sheng, G. Y.; Johnston, C. T.; Teppen, B. J & Boyd, S. A. (2001). Potential contributions of smectite clays and organic matter to pesticide retention in soils. *Journal of*

Agricultural & Food Chemistry, Vol.49, No.6, (June 2004), pp. 2899-2907, ISSN 0021-8561

Suchail, S.; Debrauwer, L. & Belzunces, L. P. (2004). Metabolism of imidacloprid in Apis mellifera. *Pest Management Science*, Vol.60, No.3, (March 2004), pp. 291-296, ISSN 1526-498X

Sumner, M. E. & Miller, W.P. (1996). Cation Exchange Capacity and Exchange Coefficients. I In: *Methods of soil analysis*, D.L. Sparks, (Ed.), pp. 1201-1231, Soil Science Society of America: American Society of Agronomy, ISBN 978-0891188254, Medison, Wisconsin, USA

ten Hulscher, T. E. M. & Cornelissen, G. (1996). Effect of temperature on sorption equilibrium and sorption kinetics of organic micropolutants [Review]. *Chemosphere*, Vol.32, No.4, (October 1995), pp. 609-626, ISSN 0045-6535

Tomizawa, M. & Casida, J. E. (2003). Selective toxicity of neonicotinoids attributable to specificity of insect and mammalian nicotinic receptors [Review]. *Annual Review of Entomology*, Vol.48, (September 2002), pp. 339-364, ISSN 0066-4170

Tomlin, C. (2001). *Pesticide Manual* (10th Revised edition), British Crop Protection Council, ISBN 978-1901396126, Surrey, UK

USEPA. (1993). *A Review of Methods for Assessing Aquifer Sensitivity and Ground Water Vulnerability to Pesticide Contamination,* USEPA, Retrieved from: < http://nepis.epa.gov >

USEPA. (2000). *Standard OperatingProcedures: Soil Sampling*. USEPA, Retrieved from: <http://www.ecy.wa.gov/programs/eap/qa/docs/QAPPtool/Mod7%20EPA%20SOPs/Soil%20Sampling/ERTSOP2012%20Soil%20Sampling.pdf>

Ward, O. P. & Singh, A. (2004). Soil bioremediation and phytoremediation, In: *Applied Bioremediation and Phytoremediation*, A. Singh & O. P. Ward, (Eds.), pp. 1-12, Springer-Verlag, ISBN 978-3540210207, Berlin, Germany

Wauchope, R. D.; Yeh, S.; Linders, J.;Kloskowski, R.; Tanaka, K.; Rubin, B.; Katayama, A.; Kordel, W.; Gerstl, Z.; Lane, M. & Unsworth, J. B. (2002). Pesticide soil sorption parameters: theory, measurement, uses, limitations and reliability [Review]. *Pest Management Science*, Vol.58, No.5, (May 2002), pp. 419-445, ISSN 1526-498X

Wolt, J. D. (1997). Environmental fate of trifluralin. *Reviews of Environmental Contamination &Toxicology*, Vol.153, (May 1997), pp. 65-90, ISSN 0179-5953

Xue, N.; Yang, R.; Xu, X.; Seip, H. M. & Zang, Q. (2006). Adsorption and degradation of benfuracarb in three soils in hunan, people's Republic of China. *Bulletin of Environmental Contamination & Toxicology*, Vol.76, No.4, (April 2006), pp. 720-727, ISSN 0007-4861

Pesticides in the Modern World - Risks and Benefits
Edited by Dr. Margarita Stoytcheva

ISBN 978-953-307-458-0
Hard cover, 560 pages
Publisher InTech
Published online 03, October, 2011
Published in print edition October, 2011

This book is a compilation of 29 chapters focused on: pesticides and food production, environmental effects of pesticides, and pesticides mobility, transport and fate. The first book section addresses the benefits of the pest control for crop protection and food supply increasing, and the associated risks of food contamination. The second book section is dedicated to the effects of pesticides on the non-target organisms and the environment such as: effects involving pollinators, effects on nutrient cycling in ecosystems, effects on soil erosion, structure and fertility, effects on water quality, and pesticides resistance development. The third book section furnishes numerous data contributing to the better understanding of the pesticides mobility, transport and fate. The addressed in this book issues should attract the public concern to support rational decisions to pesticides use.

How to reference
In order to correctly reference this scholarly work, feel free to copy and paste the following:

Dalibor Broznić, Jelena Marinić and Čedomila Milin (2011). Behavior and Fate of Imidacloprid in Croatian Olive Orchard Soils Under Laboratory Conditions, Pesticides in the Modern World - Risks and Benefits, Dr. Margarita Stoytcheva (Ed.), ISBN: 978-953-307-458-0, InTech, Available from: http://www.intechopen.com/books/pesticides-in-the-modern-world-risks-and-benefits/behavior-and-fate-of-imidacloprid-in-croatian-olive-orchard-soils-under-laboratory-conditions

INTECH
open science | open minds

InTech Europe
University Campus STeP Ri
Slavka Krautzeka 83/A
51000 Rijeka, Croatia
Phone: +385 (51) 770 447
Fax: +385 (51) 686 166
www.intechopen.com

InTech China
Unit 405, Office Block, Hotel Equatorial Shanghai
No.65, Yan An Road (West), Shanghai, 200040, China
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
Fax: +86-21-62489821