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Leaching kinetics of atrazine and inorganic chemicals in tilled and orchard soils

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A b s t r a c t. The aim of this study was to verify first-order kinetic reaction rate model performance in predicting of leaching of atrazine and inorganic compounds (K^{+1}, Fe^{+3}, Mg^{+2}, Mn^{+2}, NH_4^+, NO_3^- and PO_4^{-3}) from tilled and orchard silty loam soils. This model provided an excellent fit to the experimental concentration changes of the compounds vs. time data during leaching. Calculated values of the first-order reaction rate constants for the changes of all chemicals were from 3.8 to 19.0 times higher in orchard than in tilled soil. Higher first-order reaction constants for orchard than tilled soil correspond with both higher total porosity and contribution of biological pores in the former. The first order reaction constants for the leaching of chemical compounds enables prediction of the actual compound concentration and the interactions between compound and soil as affected by management system. The study demonstrates the effectiveness of simultaneous chemical and physical analyses as a tool for the understanding of leaching in variously managed soils.

K e y w o r d s: leaching, kinetics, atrazine, inorganic chemicals, tilled and orchard soils

INTRODUCTION

Atrazine, a derivative of the S-triazine group of herbicides, is one of the most widely used pesticides in the world, due to the lowest cost associated with ease of application. This substance is one of the most effective soil-applied herbicides for control of narrow- and broad-leaved weeds in cereal crops, fruit orchards, vegetables, maize, sugar cane, vines, citrus groves, grassland and forestry. High mobility of atrazine in soil (Tindall and Vencil, 1995) and its potential contamination of ground waters (Ritter *et al.,* 1994) represent a serious human health hazard because of the potential carcinogenic effects. Taking into account atrazine toxicity, high mobility, long life-time (10 to 12 months), the rate of leaching in every soil system should be of great interest.

Leaching and concentration of chemicals in variously managed soil is largely associated with aggregate and pore structure (Holland *et al.,* 2004; Lipiec *et al.,* 2011). In general, orchard grassed soils, in comparison with tilled soils are characterized by a greater contribution of continuous biological pores made by soil fauna and plant roots that raise infiltration under ponded conditions (Słowińska-Jurkiewicz *et al.,* 2001). Quantification of pore size distribution over a wide range of pore size revealed that the nature of the pore system is more heterogeneous in untilled orchard than in tilled soil (Hajnos *et al.,* 2006). There is substantial evidence that increased root growth in the grassed soil enhances soil aggregation and produces lines of weakness along which the clod or soil mass break into smaller aggregates that are stabilized by root exudation and associated microbial activity (Six *et al.,* 2004). Change of land use from tilled to grass or no-till system leads further to a higher soil organic carbon content and modified soil acidity (Lipiec *et al.,* 2011). The differences in aggregate and pore structure and soil chemistry affect pore water residence time and sorption capacity and thereby leaching kinetics of agricultural chemicals (Siczek *et al.,* 2008).

It was shown that the presence of macropores made by earthworms can lessen the potential for leaching of pesticides due to adsorption in organic burrow linings, and contribute to preferential flow and thereby permit solutes to bypass large parts of soil (Stehouwer *et al.,* 1994). Moreover, earthworm feeding motion, due to ingesting and carrying herbicide residues away from the soil surface, can increase the amount of non-leachable herbicide residues in the soil (Farenhorst *et al.,* 2000).

Jalali and Rowell (2003) postulated that the leaching of potassium increased with increasing calcium concentrations due to the capability of calcium ions to move potassium ions

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from exchange pools into the solution. However, manganese in comparison with iron is mobilised under higher pH and less reductive conditions (McDaniel and Buol, 1991). Less intense tillage in comparison with conventionally tilled soil declines nitrate concentration in drainage water and total N losses and can be more advantageous from the point of view of N conservation, recycling and quality of the ground water (Holland, 2004; Lipiec and Stępniewski, 1995). In addition, the studies of Shipitalo *et al.* (1990) revealed that no-till, in comparison with tilled soil, stimulated more losses of NH_4^+ than of NO_3^-. Brye and Norman (2004) reported that nitrate leaching losses were positively correlated with leaching losses of K^{+1}, Ca^{+2}, Mg^{+2}, and Na^{+1} in the maize agroecosystems, but not for the prairie. It indicates that nitrate-N leaching affects the concomitant loss of cations. Leaching of phosphate is relatively small (<1 kg ha^{-1} $year^{-1}$) but it can be environmentally important when joined with the surface run-off losses (Puustinen *et al.,* 2005) and may go beyond the critical concentration levels for eutrophication. Ionic mechanism for phosphorus sorption onto metal oxides (which are oppositely charged) was suggested, but this will not apply for sorption onto organic material since phosphate anions will not be attracted to negatively charged organic colloids. Feiza *et al.* (2003) reported that the sorption of phosphorus can be increased by a decrease in the size of the aggregates due to the type of land use, which would be affected by soil disturbance.

Although general information about atrazine conversions is available, however the specific pathways in different soils are not yet clearly defined. Therefore, the understanding of the rate of leaching of agricultural chemicals under different land uses is important in predicting the effect of management practices on environmental quality. The aim of this study was to verify first-order kinetic reaction rate model performance in predicting of leaching of atrazine and inorganic compounds (K^{+1}, Fe^{+3}, Mg^{+2}, Mn^{+2}, NH_4^+, NO_3^- and PO_4^{-3}) in tilled and orchard silty loam soils.

MATERIALS AND METHODS

The experiment was performed on an Orthic Luvisol developed from loess, over limestone, at the experimental field of the University of Life Sciences in Lublin (51°15'N, 22°35'E), Poland. Long-term annual mean temperature and precipitations at the site are 7.4°C and 572 mm, respectively. The experimental objects included: tilled field (100 x 150 m) with main tillage operations including pre-plough (0.1 m depth) + harrowing, mould-board ploughing (0.2 m depth) and crop rotation involving selected cereals, root crops and legume crops, and orchard 35 year-old apple orchard (100 x 200 m) with permanent sward that was mown in the interrows during the growing season (Lipiec *et al.,* 2011; Siczek *et al.*, 2008). The management practices on tilled were used for 30 years. Both field sites were close to each other. The research area is characterized by rather uniform soils with respect to genesis and textural composition (Dobrzański and Zawadzki, 1951). Core samples of 100 ml volume, 0.05 m diameter from the top layer of 0-0.1 and 0.1-0.2 m depths (four replicates) were used to determine bulk density. Total organic carbon was estimated by TOC 5050A with Solid Sample Module (SSM-5000A, Shimadzu, Japan).

Leaching of atrazine and inorganic compounds (K^{+1}, Fe^{+3}, Mg^{+2}, Mn^{+2}, NH_4^+, NO_3^- and PO_4^{-3}) was determined in soil columns with undisturbed structure, taken with steel cylinders of 0.215 m diameter and 0.2 m height from the depth of 0-0.20 m (three replicates). The sampling was performed in the autumn, under tilled it was done after cropping of wheat and 10 days after shallow cultivation to a depth of approximately 0.10 m. In order to avoid soil damage, the cylinders were slowly pressed into the soil with a hydraulic jack. This method of sampling is suggested for laboratory studies for a realistic assessment of chemical dissipation and movement in soils (Farenhorst *et al.,* 2000).

Afterwards all columns were saturated with water and allowed to stay for drainage to obtain field water capacity. 48 h later 28 mg (7.85 kg ha^{-1}) of atrazine (purity 97.5%) was suspended in 6.5 ml of distilled water and dripped uniformly onto the surface of each column without plain residue. The rate and way of application of atrazine were similar to those used by Shipitalo *et al.* (2000). 24 h after atrazine application, 0.5 g of granular NH_4NO_3 (140 kg ha^{-1}) was placed uniformly on the surface of each column. All the chemicals used in this study were of analytical grade. 24 h later all the columns were subjected to watering at an amount of 30 mm (1 100 ml) of distilled water per each column. Long-term data indicate that on average rainfalls of such a size occur in the experimental area four times a year (Rejman, 2006). Water was applied with a manual irrigation system, in 100 ml doses, to maintain only a few millimetres ponding during infiltration. To avoid damage of soil structure by water, filter paper was used on the soil surface during the irrigation. Breakthrough times and infiltration rates were recorded as soon as the column began to produce leachate. All the leachates were collected in 50 ml increments from each column separately, and the time of percolation was noted. In all cases leaching lasted longer than filtration.

Atrazine in leachates was analysed by means of HPLC Dionex with a UV-VIS (254 nm) detector and the following operating conditions: the column was Nucleosil CC 250/4 50-5 Macherey Nagel C_{18}, 150 mm long, the mobile phase consisted of a mixture of methanol and water (60:40), the flow rate was set at 1 ml min^{-1}. Separation was carried out at a constant temperature (30°C). The correlation coefficient of calibration function was 0.994 (Baran and Oleszczuk, 2003). NH_4^+ NO_3^- and PO_4^{-3} were assayed using ion chromatograph HIC-6A Shimadzu (Japan) equipped with a LP-6A isocratic HPLC pump, conductivity detector CDD-6A, a rotary valve fitted with 20 µl sample loop, protected with a guard column of the same material (25 x 2.3 mm I.D.). The detection was monitored at the range of sensitivity of 1 µS.

The column was operated at a temperature of 25°C (Szajdak and Jaskulska, 2011). For NH_4^+ determination the mobile phase consisted of 4mM nitric acid at the ratio 7:3 water: methanol, and the column Hamilton PRP X-200 was used. For NO_3^- and PO_4^{-3} measurements we used the column Hamilton PRP X-100, and mobile phase 4 mM p-hydroxy benzoic acid in 2.5% methanol at pH=8.5 (Szajdak and Gaca, 2010). The contents of inorganic elements including K^{+1}, Mg^{+2}, Mn^{+2} and Fe^{+3} in the 0-0.2 m depth of soil were determined by ICP-AES using high pressure system-sealed microwave digestion. The samples of soil were digested with HNO_3-HF-H_2O_2 acids system.

Infiltration of water into the soil was determined by the double ring infiltrometer with a 0.215 m diameter inner and 0.3 m diameter outer cylinder inserted 0.14 m into the soil (3 replicates). Water entering the soil was measured with a calibrated Mariotte bottle. A constant water head of 0.015 m was maintained in both rings. The measurements were done at the soil water content corresponding to approximately field water capacity in both the treatments. This allowed minimization of the effect of different water content. The water infiltration was described according to Philip-type equation (Philip, 1957).

RESULTS AND DISCUSSION

The management systems under study revealed very high impact on the chemical and physical properties of soil (Table 1). The concentration of soil organic matter (SOM) in soil under tilled ranged from 1.13 to 1.17% and was 1.51 and 1.41-times higher under orchard at the depths of 0-0.1 and 0.1-0.2 m, respectively. The soil under tilled was more acidic (pH 5.80-5.91) than orchard (pH 6.36-6.40), tilled in comparison with orchard soil was less porous as shown by higher bulk density and had less biological pores made by soil fauna and/or plant roots. The concentrations of NO^{-3}, PO_4^{-3}, K^{+1}, Mg^{+2}, and Fe^{+3} were lower, and NH_4^+ and Mn^{+2} higher in orchard than in tilled (Table 2).

For better understanding of the time-dependent behaviour of a system of interacting species a first-order kinetics reaction model was used. The model proceeds at a rate that depends linearly only on one reactant concentration *A*. The differential equation describing first order kinetics is:

$$-\frac{d(A)}{(A)} = \mathrm{K}(A)\,. \qquad (1)$$

We can rearrange the above equation to:

$$\ln(A) = \ln(A_0) - \mathrm{K}t\,. \qquad (2)$$

The reaction rate unit is molar/time and K is the first-order rate constant (in units of 1/time). However, the units can vary with other order reactions. The statistical parameters in Table 3 indicate that the first-order kinetics reaction model provided an excellent fit for the measured concentration changes *vs*. time data (Fig. 1), with low values of coefficient of variation (CV) ranging from 3.2 to 14.8%.

T a b l e 1. Some properties of tilled and orchard soils

Depth (m)	Particle size (mm) distribution (%, w/w)			Bulk density (Mg m^{-3})	Soil organic carbon	Organic matter	pH_{H_2O}
	2-0.02	0.02-0.002	< 0.002		(%)		
				Tilled			
0-0.1	66	28	6	1.38	1.17	2.02	5.91
0.1-0.2	62	29	9	1.62	1.13	1.95	5.80
				Orchard			
0-0.1	71	27	2	1.33	1.77	3.05	6.36
0.1-0.2	70	23	7	1.34	1.59	2.74	6.40

T a b l e 2. Mean concentrations of the chemicals in the 0-0.02 m soil layer under tilled and orchard soils

Management system	NO_3^-	NH_4^+	PO_4^{-3}	K^{+1}	Mg^{+2}	Fe^{+3}	Mn^{+2}
	(mg kg^{-1})			(g kg^{-1})			
Tilled	61.1	12.1	2.01	2.31	1.61	10.10	0.35
Orchard	45.6	14.2	0.71	2.00	1.45	8.10	0.46

T a b l e 3. Statistical evaluation of the pseudo first-order reaction rate constants (K) for the leaching of investigated compounds under tilled and orchard soils

Management system	Investigated compounds	10^{-4} (k±Dk) (s^{-1})	$t_{0.5}$ (h)	R	b	CV (%)
Tilled	Atrazine	0.756±0.061	2.55	-0.969	6.455	6.5
	Mn^{+2}	0.758±0.068	2.54	-0.966	-2.747	6.9
	Fe^{+3}	0.641±0.058	3.00	-0.985	0.867	5.9
	NH_4^+	0.633±0.051	3.04	-0.993	-0.773	3.2
	Mg^{+2}	0.539±0.048	3.57	-0.972	2.946	5.8
	K^{+1}	0.526±0.067	3.66	-0.807	1.444	14.8
	NO_3^-	0.540±0.043	3.57	-0.967	4.391	6.8
	PO_4^{-3}	0.221±0.018	8.7	-0.958	0.867	7.1
Orchard	Atrazine	8.587±0.773	0.22	-0.943	6.861	7.1
	Mn^{+2}	2.911±0.378	0.66	-0.873	-3.177	13.6
	Fe^{+3}	4.978±0.428	0.39	-0.952	0.192	5.8
	NH_4^+	5.313±0.288	0.36	-0.947	0.838	6.8
	Mg^{+2}	3.848±0.343	0.50	-0.955	2.990	6.7
	K^{+1}	3.897±0.335	0.49	-0.954	2.128	7.0
	NO_3^-	3.947±0.355	0.49	-0.955	4.741	6.9
	PO_4^{-3}	4.209±0.379	0.46	-0.910	-1.135	8.2

k±Δk - confidence limits for pseudo-first-order reaction rate of soil samples at α-0.05 and (n-2) degrees of freedom, $t_{0.5}$ – half-life, R – correlation coefficient, b – the constant term – the *y*-intercept, equal ln (c_∞ - c_t) at t=0, CV – coefficient of variation.

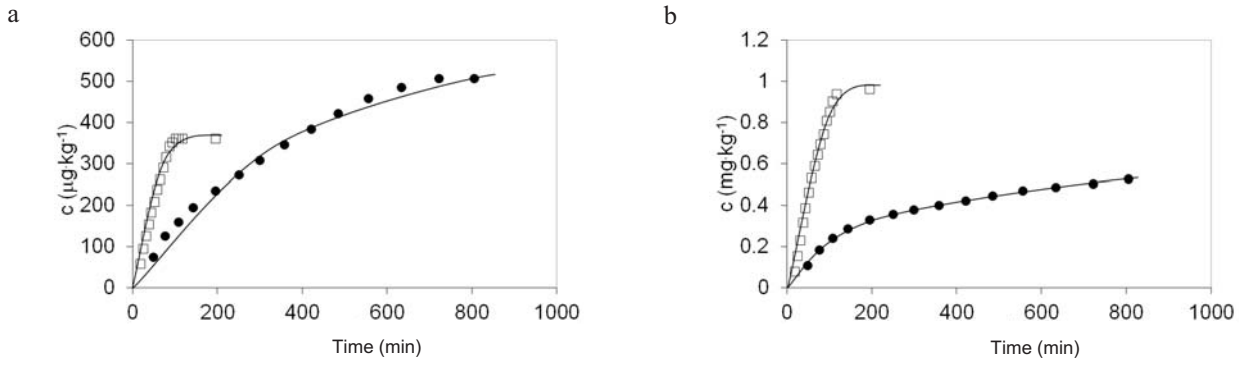

Fig. 1. Cumulative concentrations of: a – atrazine, b – amonium in soil under orchard (square) and tilled (circle).

The cumulative concentrations of atrazine and inorganic compounds (K^{+1}, Fe^{+3}, Mg^{+2}, Mn^{+2}, NH_4^+, NO_3^- and PO_4^{-3}) in tilled and orchard silty loam soils as a function of time were characterized by exponential Eq. (3), (Fig. 2):

$$(c_t) = (c_\infty)(1 - e^{-Kt}), \quad (3)$$

where: c_t – substance concentration, c_∞ – maximum of the substance concentrations, t – reaction time, and e – the base of natural logarithm.

The half-life times $t_{0.5}$ of studied compounds were calculated according to Eq. (4) at a substrate concentration $c_t = 0.5c_\infty$:

$$t_{0.5} = K^{-1} \ln 2. \quad (4)$$

Semilogarithmic function of the concentrations measured *vs.* time showed linear curves. It agrees well with the first-order kinetics reaction model with respect to all compounds studied (Reemtsma *et al.,* 1999). Selected examples for atrazine and ammonium are presented in Fig. 2.

$$\ln(c_\infty - c_t) = \ln(c_\infty) - Kt \,. \quad (5)$$

The first-order reaction rate constants (K) were calculated as the slope of Eq. (5) by means of the least squares formulas. The slopes of Eq. (5) describe the rates of the chemical concentration changes. The correlation coefficients (r) calculated between the decrease in the concentrations of the chemicals $\ln(c_\infty - c_t)$ and time elapsed varied from -0.807 to -0.993 (Table 3). In general, the first-order reaction rate constants for the changes of all the chemicals in the leachates under orchard were shown to be significantly higher than under tilled where they ranged from 0.221 10^{-4} s^{-1} for phosphate to 0.758 10^{-4} s^{-1} for manganese. The corresponding half-life values for these compounds were 8.70 and 2.54 h, respectively. However, the first-order kinetics reaction rate constants were greater under orchard than tilled and ranged from 2.911 10^{-4} s^{-1} for manganese to 8.587 10^{-4} s^{-1} for atrazine, the respective half-life values being 0.66 h and 0.22 h. In general, higher values of the first-order reaction rate constants under orchard than tilled soils were associated with higher concentration of organic matter and pH and lower bulk density (Tables 1 and 3). In addition, the ratios (K) of the first-order reaction constants under orchard and tilled for the leaching of all compounds were from 3.8 for manganese to 19.0 times higher for phosphates (Table 4).

Higher first-order reaction rate constants and lower half-life values of the chemicals under orchard than tilled can be due to higher total porosity and contribution of biological pores made by soil fauna and/or plant roots. Additionally, under orchard the biological pores were surface-open. These were reflected in leachate percolation rate. The same quantity of percolate (800 ml) under orchard and tilled was obtained after 200 and 800 min, respectively. Corresponding break-through times were 8 and 23 min. A greater infiltrability of orchard than tilled soil was confirmed by field measurements of water infiltration that was described by the Philip-type Eq. (6), (Philip, 1957):

$$I = Bt + St^{0.5} \,, \quad (6)$$

where: I – cumulative infiltration (cm), B – coefficient related to saturated soil conductivity, S – describes soil sorptivity. The value of A is proportional to saturated soil conductivity, multiplied by coefficient varying from 0.2 to 0.67 (Kutílek and Nielsen, 1994). Both B and S were greater under orchard than tilled, A calculated for orchard soil was about twenty times higher than for tilled, while the differences for S were much smaller (Fig. 3, Table 5). Both factors were related to water infiltration: the proportion of the soil through which the water passes and the residence time of the water in the soil affect the process of chemicals sorption (Mohsen and Zahra, 2006). The greater infiltrability of orchard than tilled soil can be largely a result of higher contribution of large and more continuous and conductive pores under orchard where they are not disturbed by tillage. The differences in pore structure agree well with all the values of the first-order reaction rate constants (Table 4). The first-order reaction rate constants under orchard and tilled can be influenced by different acidity and SOM content (Table 1). Therefore, the first-order reaction rate constant (Table 3) and the parameters of Philip-type equation (Table 5) have shown agreement.

Our results indicate that the half-life of atrazine leaching from 0-20 cm soil layer (0.2-8.7 h) (Table 3) is significantly shorter than the half-life of enzymatic conversion of

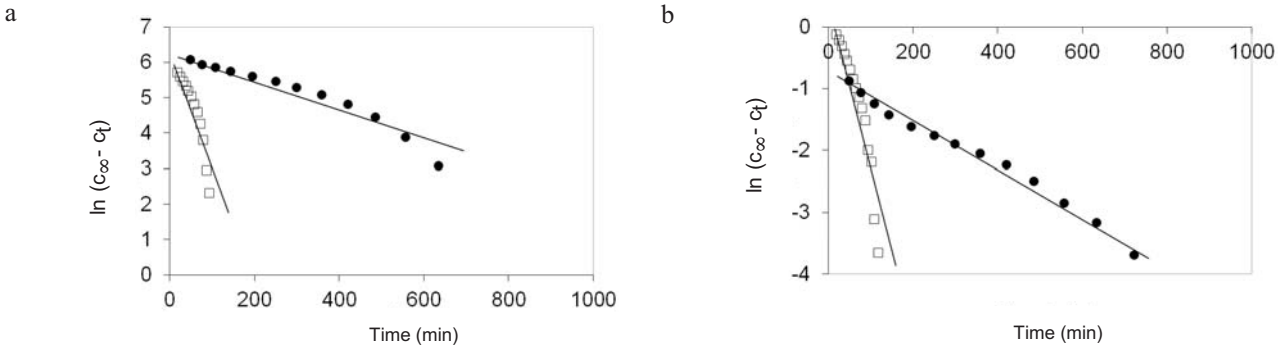

Fig. 2. Semilogarithmic function of: a – atrazine changes, b – ammonium in soil under orchard (square) and tilled (circle).

T a b l e 4. Ratios (K) of the first-order reaction rate constant for the leaching of chemicals under orchard and tilled soils

	Cations					Anions	
Atrazine	NH_4^+	Fe^{+3}	K^{+1}	Mg^{+2}	Mn^{+2}	PO_4^{-3}	NO_3^-
11.4	8.4	7.8	7.4	7.2	3.8	19.0	7.3

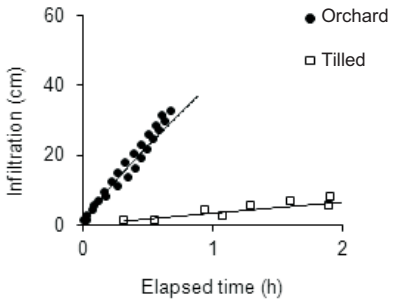

Fig. 3. Philip-type model fitted to infiltration data measured in the orchard and in the tilled soil under field conditions. Parameters of the model are presented in Table 5.

T a b l e 5. Parameters and coefficient of determination R of a Philip-type Eq. (3) for tilled and orchard soils

Management system	B ($cm\ h^{-1}$)	S ($cm\ h^{-0.5}$)	R
Tilled	2.44	1.49	0.97
Orchard	44.55	1.71	0.99

B – coefficient related to saturated soil conductivity, S – describes soil sorptivity, R – correlation coefficient.

atrazine by microorganisms in soils (10-12 months). Therefore, leaching leads to a significant decrease in the quantity of atrazine that should act against weeds. Thus analyses of acting time of atrazine must take into account the fast leaching of this herbicide.

In the less acidic soil orchard than soil tilled, the first-order reaction rate constants of Fe, Mg and Mn cations can be indirectly influenced by a greater conversion into insoluble hydroxides $Fe(OH)_2$, $Fe(OH)_3$, $Mg(OH)_2$, $Mn(OH)_2$. As for atrazine, the constants can be modified by greater sorption of atrazine in orchard than tilled due to the greater SOM content in the former (Table 1). The fate and mobility of atrazine in the environment involve complex mechanism that are influenced by many processes, including leaching, adsorption, volatilization as well as chemical and biological degradation. Of these processes, adsorption is the key process in soil because the detoxification mechanisms, such as degradation, metabolism, microbial uptake and mobilization, involve only the non-sorbed fraction of molecules (Durovic *et al*., 2009).

The knowledge of the first order reaction constant for the leaching of chemical compound calculated in field condition has a practical meaning. It enables the researcher to perform the calculations of the actual concentration of the compound to predict the effectiveness action of the substance in any soil conditions. Our model-derived results demonstrate the feasibility of using the kinetic technique to determine the persistence of chemicals in the environment. This approach could be used to obtain information on the persistence of degradable leachates in soil.

CONCLUSIONS

1. The first-order kinetics reaction model is adequate to describe the process of leaching of agricultural chemicals under different soil management systems. The first-order rate constants reflected different leaching potential of the chemicals from orchard and tilled soil. In general, the first-order reaction rate constants for the changes of all chemicals in leachates under orchard were shown to be significantly higher than in tilled soil. The contrary was shown for half-lives that were lower in orchard soil.

2. The ratios of the first-order reaction constants between orchard and tilled soil for the leaching of cations and anions ranged from 3.8 to 8.4 and from 7.3 to 19, respectively.

3. Higher first-order reaction constants and lower half-life values of the compounds under orchard than in tilled soil correspond with both higher total porosity and contribution of biological pores, created by soil fauna and plant roots.

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