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Original Research

Degradation of MCPA in Soil Horizons of Polish Agricultural Soils

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Abstract

Laboratory studies on degradation of MCPA were performed in different soil horizons of three Polish agricultural soils. Hyperdystric Arenosol (Ap, BwC, C), Haplic Luvisol (Ap, E, Bt) and Hypereutric Cambisol (Ap, Bw, BwC) were selected for investigations as representative of Polish agricultural soils. Degradation experiments were performed at 5 and 25°C. Fitting the data to the exponential form of the three-half kinetic model gave good results, worse in the case of a first-order kinetic equation due to the lag-phase observed. Therefore the zero-order kinetic equation was also used. The values of *DT50* at 25°C for Ap horizons of soils were in the range of 1.5-6.9 days, for BwC, E and Bw horizons 8.7-20.1 days, and for C, Bt and BwC 27.6-85.8 days. The activation energies for all horizons of all soils were in the range of 47.8-67.8 kJ mol^{-1}. The results showed significant correlations between the zero- and first-order rate coefficients for MCPA degradation and the contents of microbial biomass carbon, activity of the enzyme dehydrogenase and fluorescein diacetate hydrolyse in the studied soils.

Keywords: MCPA, soil horizons, degradation, temperature

Introduction

The phenoxyalkanoic acid herbicide MCPA (4-chloro-2-methylophenoxyacetic acid) is one of the most widely used pesticides for the control of broad-leaf weeds primarily in cereal and grass seed crops since World War II [1, 2]. Although herbicides from this group are applied as salts or esters, they are readily hydrolyzed and found in their acidic forms in soils [3]. MCPA is adsorbed weakly to soil, typically with K_d in the range 0.2-1 dm^3 kg^{-1} [4, 5] and it is rather quickly degraded with half-lives usually in the range of 3-16 days [6, 7]. However, adverse conditions such as acidic pH and low temperatures are known to increase its persistence [8].

Degradation processes are characterized by splitting of the pesticide molecule by chemical, photochemical, or biological processes [7]. For most pesticides, degradation in a soil is enzymatically catalyzed by microorganisms [9]. Microbial degradation of 2,4-D and MCPA has been widely studied because it serves as a model for understanding the mechanism of biodegradation of other, structurally related haloaromatic compounds [10, 11]. The main products of the oxidative degradation MCPA in soil is 4-chloro-2-methylphenol (CMP) and 4-chloro-2-methyl-6-nitrophenol (CMNP). CMP disappears about as quickly as MCPA, while CMNP seems to be environmentally more persistent, but they are found in the environment in much lesser concentrations than the parent compound [12].

Adsorption is often found to limit degradation, because it reduces the pesticide concentration in the aqueous solution. The fractionation study showed that MCPA degradation occurs almost entirely from the water extractable pool, which corresponds to MCPA in the solution or easily desorbed fractions [13].

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Table 1. Summary of the physical, chemical and biological characteristics of the soils.

Soil	Hyperdystric Arenosol Sandy soil			Haplic Luvisols Loamy soil			Hypereutric Cambisols Loess soil		
Soil horizon	Ap	BwC	C	Ap	E	Bt	Ap	Bw	BwC
Depth (cm)	5-15	35-45	65-75	5-15	35-45	65-75	10-20	35-50	65-75
Sand (%)	89	94	93	75	67	56	13	13	15
Silt (%)	9	5	6	21	26	18	77	75	73
Clay (%)	2	1	1	4	7	26	10	12	12
pH ($CaCl_2$)	4.3	4.5	4.5	5.2	4.7	4.8	6.5	6.0	6.0
C_{org}	0.73	0.08	0.02	0.89	0.09	0.06	1.17	0.50	0.44
WHC (%)	23.0	18.1	16.1	29.4	22.1	35.3	44.5	38.1	33.7
SIR – C_{mic} (μg g^{-1})	276	185	112	380	165	105	424	177	147
DHA – TPF (nm kg^{-1} min^{-1})	17.2	12.6	12.9	53.6	13.3	13.4	51.2	13.0	5.9
FDA (μg g^{-1} h^{-1})	1.64	0.19	0.1	2.71	0.56	0.13	1.72	0.48	0.14

MCPA has been found in groundwater at concentrations exceeding the maximum allowable concentration for drinking water in the European Union (EU) [14, 15]. The EU drinking water limit of 0.1 μg dm^{-3} corresponds to an amount leached that is in the order of 1 g ha^{-1} [16]. This is 0.04% of an MCPA dose of 2.5 kg ha^{-1}.

For assessing the leaching risk, EU directive 91/414 suggests the performance of simulation studies using simulation models [17]. Modeling of leaching at such low levels requires a rigorous understanding of all relevant pesticide transport and fate processes in soil [16]. An adequate description of pesticide degradation in soil is important to provide input for these models. Values of *DT50* (time required for 50% dissipation of initial concentration) for soil layers and E_a (activation energy from Arrhenius equation) are mostly used as main input degradation parameters. In cases when the measured *DT50* is known only for topsoil, values for the deeper soil layers are estimated on the basis of correlation with microbial biomass [18].

Generally, the soils from Poland and from a large part of Central Europe differ from the soils of Western and Southern Europe, as the former have lower organic matter and clay contents as well as lower soil pH than the latter. A colder climate in Poland and such soil characteristics may favour the leaching potential of pesticides. Therefore, detailed studies on pesticide degradation in soils are of great importance. The present study on the MCPA degradation in soil horizons of Polish agricultural soils is also of great importance, since evaluation of many chemicals is now coordinated within the EU and there is a need to compare results from different countries [7].

The objective of this study was to investigate degradation process of MCPA in typical Polish agricultural soils and their different horizons to provide accurate input data for simulation models.

Materials and Methods

Soils

Three soils, a Hyperdystric Arenosol from the locality of Olempin (22°14´N, 51°24´E), a Haplic Luvisol from Dęba (22°10´N, 51°26´E) and a Hypereutric Cambisol from Skierbieszów (23°22´N, 50°51´E), were selected for this study based on information from the database of the Institute of Agrophysics PAS as the representative Polish agricultural soils [19]. Due to the character of the bed-rock, they are called sandy, loamy and loess soils in the paper. Soil sampling was performed in different horizons, taking care that no contamination by other soil layers occurred. The depth of the soil samples was chosen, taking into account changes in soil microbial biomass. The main characteristics of the soils selected for the study is given in Table 1. The soil samples for incubation experiments were dried to 40% of their water holding capacity (WHC), passed through 2 mm sieve and stored in the dark at 4°C. The period between collecting from the field and beginning of the experiments was no longer than 1 month.

Substrate-induced respiration (SIR) was used for determination of soil microbial biomass (C_{mic}) [20]. Soil microbial activity was estimated on the basis of dehydrogenase (DHA) activity with triphenyltetrazolium chloride and $CaCO_3$ according to Casida et al. [21] and fluorescein diacetate (FDA) hydrolysis according to Schnürer and Rosswall [22].

Incubation Experiments

Duplicate incubation experiments were performed according to the OECD guideline [23]. Five days before the start of the experiments an amount of each soil stored at 4°C was pre-incubated for a 5-day period in the dark at 25°C.

Then 50 g dry weight soil samples were placed in incubation flasks and spiked with MCPA solution to obtain a herbicide concentration of 7 mg kg^{-1} dry weight. Analytical pure MCPA (certified purity 99.7 ± 0.1%) purchased from LGC Promochem (Łomianki, Poland) was used for the experiments. Finally, the water content was adjusted with the sterile redistilled water to 40% of water holding capacity of each soil. The last operation was repeated weekly.

At days 0, 4, 8, 15, 22, 30, 60, 90 and 120 the soil samples of 5 g dry weight were taken from the incubation flasks to polypropylene tubes. Then 5 cm^3 of a solution of methanol : 0.1 mol dm^3 NaOH (90:10 v/v) was injected and the tubes were agitated on a rotary shaker for 1 h and centrifuged (10 min, 4,000 rpm) to separate the liquid phase for analyses. The recoveries were in the range 70-100%. All degradation experiments were performed at 5 and 25ºC.

Analytical Methods

A 20 µl portion of MCPA solution was injected into a WellChrom HPLC (Knauer, Berlin, Germany) equipped with two K-500 pumps, a K-2500 UV-VIS detector and a Hypersil Gold C18 column (100 × 3.0 mm i.d., 3 µm particle size, Thermo Electron Corporation, Runcorn, United Kingdom) preceded by a Hypersil Gold C_{18} guard column (10 × 3.0 mm i.d., 3 µm particle size). The mobile phase was acetonitrile/0.25% H_3PO_4 (45:55 v/v). The flow rate of the mobile phase was 0.8 cm^3 min^{-1}, the run time was 5 min per sample and the detection wavelength 228 nm. All measurements were performed at least in duplicate. The detection limit was 10 µg dm^{-3} and the reproducibility of results with the relative standard deviation lower than 5%.

Degradation Models

The results of degradation experiments were fitted to the first-order kinetic equation:

$$C_t = C_o \exp(-k\,t) \quad (1)$$

...where C_o and C_t (mg kg^{-1}) are the masses of compound in the soil at the beginning of the experiment and at time *t* (d), respectively and *k* is the first-order degradation rate coefficient. Because $k = ln(2)/DT50$, values of *DT50* (d) were estimated after replacing *k*.

Degradation does not often follow simple first-order kinetics [7]. Therefore, a zero-order kinetic equation also was used:

$$C_t = C_o - k_o\,t \quad (2)$$

...where k_o is the zero-order degradation rate coefficient. Values of *DT50* were estimated after replacing k_o with $C_o/2DT50$.

The degradation process of MCPA is very often dependent on changes in microbial biomass. For this reason, the three-half kinetic model, which assumes either linear or exponential growth of the cell or enzyme concentration responsible for degradation, was taken into account [24]:

$$C_t = C_o \exp(-k_1 t - (k_2 t^2)/2) \quad (3)$$

$$C_t = C_o \exp(-k_1 t - E_o/\mu(\exp(\mu t)-1)) \quad (4)$$

...where k_1 is the initial rate constant, k_2 is the rate of increase of the first-order rate constant, μ is the growth rate constant and E_o is the starting cell concentration.

The influence of temperature on the degradation can be described by the well-known Arrhenius equation. Activation energy E_a (kJ mol^{-1}) was calculated from the transformed form of this equation [25]:

$$E_a = R\,ln(DT50_1/\,DT50_2)\,/(1/T_1 - 1/T_2) \quad (5)$$

...where $DT50_1$ and $DT50_2$ are the 50% dissipation times at T_1 and T_2 (K), and *R* is the gas constant (0.008314 kJ K^{-1} mol^{-1}).

All parameters of the above kinetic equations were determined by nonlinear regression (Marquardt method, Statgraphics, Manugistic).

Results and Discussion

The data from incubation studies at two different temperatures are plotted in Fig. 1 as a percentage of an amount detected at day 0 for each soil treatment. The rate of degradation was shown to decrease with increasing soil depth and with decreasing temperature. The first-order kinetic equation fit the measured degradation data (Table 2) with an exception of the deepest soil horizons at 5ºC, where r^2 was in the range of 0.380-0.892. However, it should also be noted that r^2 values are generally smaller where the exponential curves are relatively flat (i.e. where degradation is slow) [26]. In the sandy soil the solid line (Fig. 1) which shows the result of fitting with this equation in most cases fits the experimental data well enough. In the C horizon of sandy soil at 5ºC and in the loamy and loess soil (with the exception of Ap horizons at 25ºC) an initial lag-phase, where little or no degradation took place, can be observed. In such cases, degradation doesn't follow with first-order kinetics and the results of fitting are worse. Although the shape of the presented degradation curves is not unusual, a similar pattern of MCPA degradation was observed by Thorstensen et al. [7].

The lag-phase has been frequently observed during MCPA mineralization in soils. Mortensen et al. [1] observed a 12-15-day lag-phase during degradation at 10ºC in B and C horizons of sandy soil, Jensen et al. [13] observed 9 and 13-20-day lag-phases during degradation in A and C horizons of sandy soil at the same temperature. Usually the lag-phase is omitted during estimation of *k* and *DT50* values [1, 13]. In the presented studies the lag-phase was omitted in cases where it was very long (Table 2) and clearly overestimated the *DT50* values.

The results of fitting using the linear and simplified exponential form of the three-half kinetic model (equation (4) with assumption $k_1 = 0$ that can be made when growth is really exponential [1]) are presented in Table 3 and as

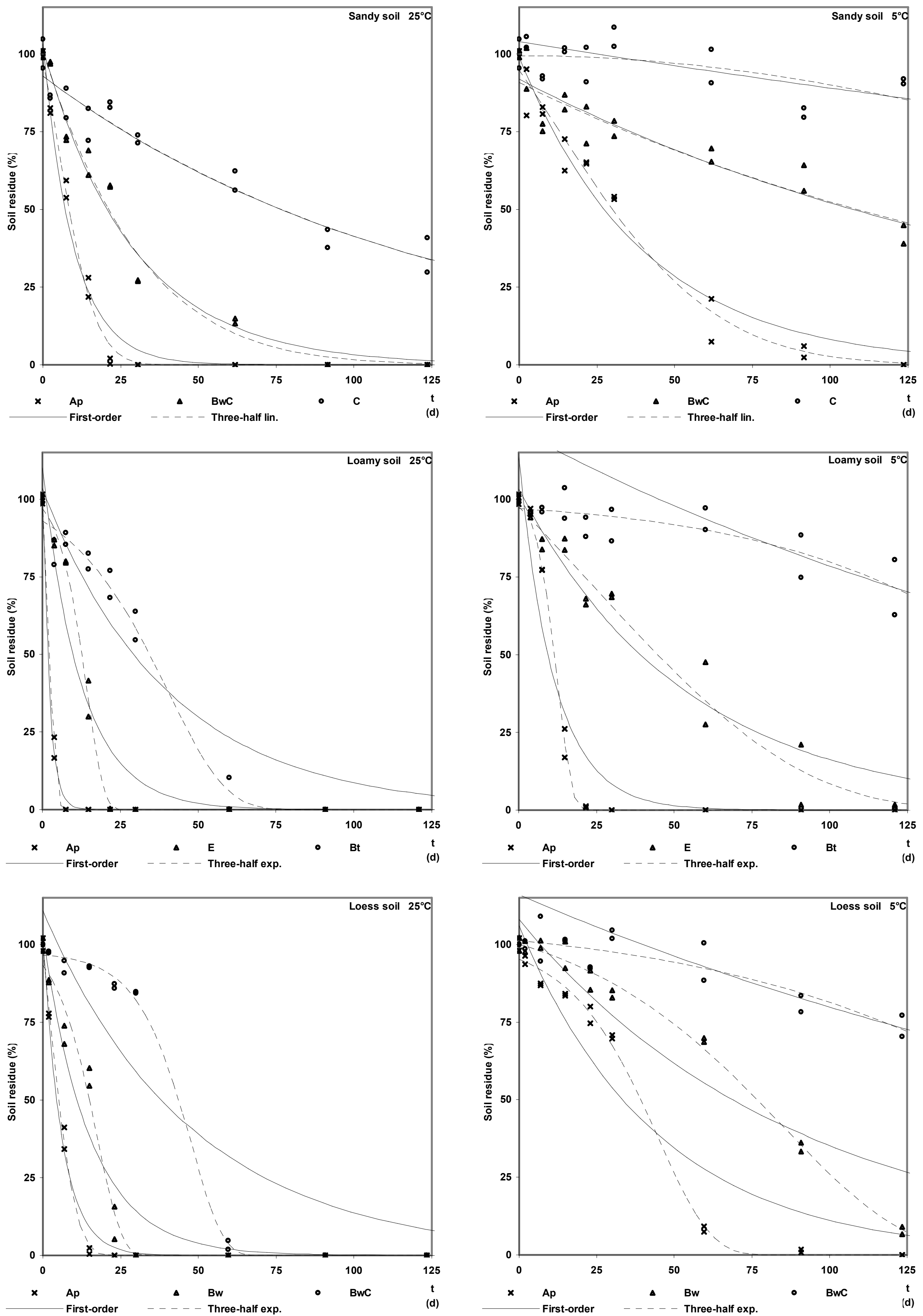

Fig. 1. Fit of first-order and three-half kinetic models to data of MCPA incubation experiments in soil horizons of sandy, loamy and loess soil at 25°C and 5°C.

Table 2. MCPA degradation rate estimates and their standard errors using the first-order kinetic equation.

Soil horizon/ Temp.	*k* (d^{-1})	*DT50* (d)	r^2	*RSS*	Lag-phase (d)	E_a (kJ mol^{-1})
Sandy soil						
Ap 25°C	0.1000±0.0073	6.9±0.5	0.982	1.87	0	
5°C	0.0250±0.0022	27.8±2.4	0.967	3.00	0	47.8
BwC 25°C	0.0344±0.0025	20.1±1.4	0.979	1.31	0	
5°C	0.0057±0.0007	122.3±15.3	0.842	2.13	0	62.2
C 25°C	0.0081±0.0007	85.8±7.5	0.926	0.91	0	
5°C	0.0016±0.0008	448.5±203.3	0.380	0.75	22	56.9
Loamy soil						
Ap 25°C	0.4496±0.0174	1.5±0.1	0.997	0.20	0	
5°C	0.0871±0.0125	7.9±1.1	0.926	8.91	0	56.6
E 25°C	0.0796±0.0108	8.7±1.2	0.932	7.60	0	
5°C	0.0185±0.0019	37.3±3.7	0.949	4.09	0	50.3
Bt 25°C	0.0249±0.0036	27.6±3.8	0.923	5.75	0	
5°C	0.0044±0.0017	157.1±59.8	0.640	0.76	30	60.0
Loess soil						
Ap 25°C	0.1618±0.0200	4.3±0.3	0.991	0.89	0	
5°C	0.0225±0.0069	30.7±4.3	0.915	10.27	0	67.8
Bw 25°C	0.0658±0.018	10,5±1.3	0.944	6.38	0	
5°C	0.0112±0.0029	61.5±7.1	0.906	6.51	0	61.0
BwC 25°C	0.0209±0.0093	33.1±6.7	0.835	16.69	0	
5°C	0.0037±0.0005	185.6.±26.9	0.892	0.43	22	59.9

dashed lines in Fig. 1. The r^2 and RSS values are in general higher and lower, respectively, than the corresponding values of the first-order kinetic equation. This suggests that changes in biomass really influence the degradation pattern of MCPA. The E_o values at 5°C were lowest in soil horizons of the loess soil, whereas the μ values were the highest. This suggests that the changes in microbial biomass related to the degradation of MCPA were probably the largest in the loess soil at 5°C. It could be also stated that the changes in biomass were better described by the exponential form of the three-half kinetic model for the loamy and loess soils, whereas these changes were approximately linear in the sandy soil. The three-half kinetic exponential model gives an excellent fit also in such case, where application of the first-order model was very problematic: at 25°C for the Bt horizon in the loamy soil and BwC horizon in the loess soil and at 5°C for the Ap and Bw horizons in the loess soil.

Table 2 shows the E_a values calculated from equation (5). The E_a values were in the range of 47.8-62.2, 50.3-60.0 and 59.9-67.8 kJ mol^{-1} in the sandy, loamy and loess soils, respectively.

Due to the difficulties with estimation of *DT50* and E_a values with using the first-order equation, the zero-order equation was used (Table 4). The lag-phase was omitted in the same cases as in Table 2. Comparison of the sum of RSS for zero-order and first-order equations in particular soils can serve as a measure of applicability of the equations for the experimental data. These values for the zero-order equation were 12.55, 8.71 and 18.38 in the sandy, loamy and loess soils, respectively, whereas they were 9.97, 27.31 and 41.17 for the first-order equation. This means that the first-order equation gave a better fit in the sandy soil whereas the zero-order equation in the loamy and loess soil. The values of E_a calculated from the zero-order equation were in the range of 47.1-48.7 kJ mol^{-1} in the sandy, 51.7-53.8 kJ mol^{-1} in the loamy and 54.0-60.8 kJ mol^{-1} in the loess soil. It can be noted that these values were scattered to a lesser extent than those calculated from estimates of the first-order equation (Table 2). It seems that the E_a values are slightly increasing in the order sandy soil<loamy soil<loess soil, which might be connected with the increasing soil C_{org} content.

Table 3. MCPA degradation rate estimates using the simplified exponential form (eq. (4) with assumption $k_1 = 0$) and linear form (eq. (3)) of the three-half kinetic model.

Soil horizon/	Temp.	Simplified exponential form				Linear form			
		E_o (d^{-1})	μ (d^{-1})	r^2	*RSS*	k_1 (d^{-1})	k_2 (d^{-1})	r^2	*RSS*
Sandy soil									
Ap	25°C	0.0532	0.0795	0.996	0.42	0.0480	0.0073	0.994	0.58
	5°C	0.0161	0.0165	0.980	1.81	0.0151	0.0004	0.979	1.89
BwC	25°C	0.0288	0.0079	0.980	1.30	0.0308	0.0002	0.980	1.24
	5°C	0.0044	0.0044	0.837	2.19	0.0055	5 10-7	0.842	2.15
C	25°C	0.0069	0.0024	0.925	0.93	0.0080	2 10-6	0.926	0.91
	5°C	0.0011	0.0011	0.364	1.09	3 10-7	2 10-5	0.338	1.14
Loamy soil									
Ap	25°C	0.2076	0.3566	0.998	0.10	-0.2826	0.3849	0.998	0.10
	5°C	0.0127	0.2253	0.998	0.24	-0.0312	0.0178	0.998	0.30
E	25°C	0.0128	0.1851	0.995	0.52	-0.0110	0.0114	0.988	1.42
	5°C	0.0105	0.0151	0.971	2.36	0.0095	0.0003	0.969	2.51
Bt	25°C	0.0063	0.0529	0.984	1.13	-0.0015	0.0012	0.978	1.64
	5°C	0.0007	0.0186	0.699	1.43	0.0041	0	0.645	6.09
Loess soil									
Ap	25°C	0.1029	0.0959	0.998	0.25	0.0995	0.0143	0.997	0.33
	5°C	0.0041	0.0596	0.995	0.64	-0.0043	0.0012	0.985	1.82
Bw	25°C	0.0139	0.1263	0.983	1.92	0.0085	0.0056	0.973	3.11
	5°C	0.0030	0.0250	0.991	0.63	0.0052	0.0002	0.966	3.21
BwC	25°C	0.0009	0.0997	0.997	0.30	0	0.0009	0.961	4.75
	5°C	0.0010	0.0144	0.789	1.39	3 10-12	4 10-5	0.796	1.34

The values of *DT50* for MCPA in this study are similar to those in other studies [6, 7, 13]. Degradation potential of the studied soils was high enough to degrade MCPA very quickly. Also, the values of E_a correspond well with the results of Helweg [5] (activation energy in the range of 76-87 kJ mol^{-1} for soils with larger amounts of C_{org} than investigated here) and with the mean activation energy of 54.1 kJ mol^{-1} calculated by Walker et al. [27] on the basis of 114 observations of various pesticides and proposed as a default value for EU.

Table 5 shows correlations between the degradation rate coefficient k_o (Table 4) or k (Table 2) and C_{mic}, DHA activity and FDA hydrolysis (Table 1). The results for individual soils at both temperatures have shown very good correlations with all above indicators of the microbiological activity. It is usually explained [18] that, the population of microorganisms within one soil is similar for the different soil layers as a result of their infiltration from surface to subsurface soil layers and an exchange between layers. Similar population patterns of microorganisms lead consequently to the same degradation pattern of the pesticides in the different soil horizons.

In the sandy and loamy soil the values of r at 25°C and 5°C were on the same level, in the loess soil r values at 5°C values were smaller. This is supposed to be caused by changes in the activity of microbial biomass and can be indirectly proved based on the values of E_o (starting cell concentration) and μ (growth rate) from exponential form of the three-half kinetic model (Table 3). It should be noted that Araújo et al. [28] indicated that after application of herbicide soil microbial activity increased significantly to the much higher levels than at the beginning of the experiment. Also, Mortensen et al. [1] observed this phenomenon. Moreover, in the presented studies, those changes caused difficulties with the estimation of k_o and k and additionally worsened the results of correlations.

When individual layers of different soils were combined and compared, the r values for SIR and DHA were much smaller. This was also found in other studies [18] and explained that different soils have different populations of

Table 4. MCPA degradation rate estimates and their standard errors using the zero-order kinetic equation.

Soil horizon/ Temp.		k_o (mg kg^{-1} d^{-1})	*DT50* (d)	r^2	*RSS*	Lag-phase (d)	E_a (kJ mol^{-1})
Sandy soil							
Ap	25°C	0.2841±0.0125	10.5±0.3	0.985	0.79	0	
	5°C	0.0651±0.0045	43.1±2.3	0.937	4.18	0	48.7
BwC	25°C	0.0718±0.0079	31.7±2.7	0.872	4.17	0	
	5°C	0.0176±0.0020	126.1±12.3	0.841	1.58	0	47.6
C	25°C	0.0191±0.0015	93.1±5.9	0.913	1.07	0	
	5°C	0.0056±0.0026	364.9±152.3	0.373	0.76	22	47.1
Loamy soil							
Ap	25°C	1.3248±0.0612	2.3±0.1	0.996	0.10	0	
	5°C	0.3128±0.0225	10.6±0.5	0.960	2.47	0	52.4
E	25°C	0.2857±0.0166	11.2±0.4	0.974	1.33	0	
	5°C	0.0584±0.0035	50.3±2.3	0.952	2.41	0	51.7
Bt	25°C	0.0781±0.0052	33.3±1.7	0.950	1.63	0	
	5°C	0.0191±0.0072	158.9±43.0	0.639	0.77	30	53.8
Loess soil							
Ap	25°C	0.4193±0.0338	7.2±0.4	0.962	1.82	0	
	5°C	0.0770±0.0052	41.9±2.1	0.941	5.24	0	60.8
Bw	25°C	0.2232±0.0186	13.9±0.8	0.947	2.02	0	
	5°C	0.0473±0.0018	69.6±2.1	0.977	1.58	0	55.6
BwC	25°C	0.0883±0.0108	36.1±3.4	0.847	7.28	0	
	5°C	0.0191±0.0027	172.8±19.6	0.890	0.44	22	54.0

Table 5. Values of *r* for correlations between k_o from zero- and *k* from first-order kinetic equations and microbial biomass determined by SIR, DHA activity or FDA hydrolysis (n = 3).

Soil/Horizon	Temp.	k_o - zero-order eq.			*k* - first-order eq.		
		SIR	DHA	FDA	SIR	DHA	FDA
Sandy	25°C	0.963	0.970	0.991	0.984	0.943	0.974
	5°C	0.964	0.969	0.990	0.957	0.975	0.994
Loamy	25°C	0.999	0.988	1.000	0.996	0.993	0.999
	5°C	0.996	0.992	0.999	0.999	0.987	1.000
Loess	25°C	0.950	0.963	0.978	0.976	0.985	0.994
	5°C	0.917	0.935	0.955	0.953	0.966	0.980
Ap-Ap-Ap	25°C	0.343	0.646	0.999	0.386	0.681	0.995
	5°C	0.269	0.585	1.000	0.195	0.521	0.995
BwC-E-Bw	25°C	-0.939	0.988	0.997	-0.944	0.990	0.995
	5°C	-0.931	0.985	0.998	-0.999	0.987	0.922
C-Bt-BwC	25°C	0.483	-0.565	0.994	0.137	-0.232	0.890
	5°C	0.359	-0.447	0.971	0.125	-0.220	0.885

microorganisms and different pattern of degradation. But the r values for FDA were similar to those found for correlation within one soil. Moreover, correlation between FDA and k_o was better than between FDA and k. This confirms again that the estimation of degradation parameters from the zero-order equation gave probably more reliable results. The hydrolysis of FDA is a simple, sensitive and rapid method for determining microbial activity in soils [22], but so far it has not been used very often in investigations concerning correlations between the rate of degradation and microbial activity in soil layers. It should be mentioned that significance levels of the correlations from Table 5 cannot be easily tested (n=3). Although the results clearly suggest that on the basis of FDA hydrolysis data it is possible to estimate the rate of degradation of MCPA not only for various layers of the same soil but even for the respective layers of different soils.

Conclusions

1. A fast degradation of MCPA occurred in the Ap horizons of the soils taken for the investigations and lower – but also significant – in the deeper horizons. Moreover, the E_a values were in the range of the mean default value for EU. This suggests that MCPA may not be a leacher in Polish soils, but the detailed adsorption/desorption studies should be performed as well as simulations based on the appropriate climatic data to verify this thesis.
2. Degradation data fitted very well to the exponential form of the three-half kinetic model and, to a much lesser extent to the first-order kinetic model. This was probably due to the changes in microbial activity of biomass during the degradation process. In the cases in which the lag-phase was observed, the zero-order kinetic equation was more useful for estimating degradation parameters than the first-order equation.
3. There were very good correlations between degradation parameters and microbial biomass content, dehydrogenase activity or fluorescein diacetate hydrolysis for individual soils. Significant correlations between degradation parameters and FDA were also found for individual layers of different soils. It seems that this method could be very useful in estimating *DT50* in cases when measured value is known only for the topsoil, but further studies with the use of other pesticides should be performed to confirm this finding.

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