

Decomposition of clopyralid, tribenuron-methyl and pendimethalin in different organic substrates

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Herbicide decomposition dependence on herbicide formulation and substrate type was in the focus of this research. Well known cereal crop herbicides were selected: Lontrel (active ingredient clopyralid), Granstar (active ingredient tribenuron-methyl), and Stomp (active ingredient pendimethalin). These herbicides were sprayed and mixed into organic substrates of three types: wheat straw chop, high moor peat substrate prepared for plant growing, and pine wood sawdust. The spraying rate was 100 mg of herbicide's active ingredient per 1 kg of substrate. Three variants of every substrate were made: pure substrate, substrate in combination with humate 2 ml per 1 kg of dry substrate, and substrate in combination with the microbial preparation Septic Gobbler, 50 mg per 1 kg of dry substrate. According to the experimental results, the bulk of clopyralid (64–73%), tribenuron-methyl (59–63%) is decomposed within the first 30 days. The decomposition of pendimethalin depended on the type of substrate more than of the other two active ingredients. Within 30 days, 72% of pendimethalin was decomposed in straw chop, 47% in peat and 34% in wood sawdust. In other words, wood sawdust was 2.1 times less effective than straw.

Clopyralid half-life in straw and peat substrates was 23 days and in wood sawdust less than 21 days. Tribenuron-methyl half-life was somewhat longer – 24 days in peat, 26 days in wood sawdust, 30 days in straw. Pendimethalin half-life in straw was 21 days, in peat 63 days and in wood sawdust 98 days. The process of herbicide decomposition in later stages continued in a similar way. 450 days after spraying the herbicides, there were no traces of clopyralid found, while tribenuron-methyl was still present in all substrates: in straw 2.0 mg kg⁻¹ of dry substrate, in peat 19 mg kg⁻¹, in wood sawdust 18 mg kg⁻¹; pendimethalin: 1.3 mg kg⁻¹ of dry substrate in straw, 17 mg kg⁻¹ in peat, 22 mg kg⁻¹ in wood sawdust.

Addition of humate to the substrates did not result in a consistent effect on herbicide decomposition. Addition of the microbial preparation Septic Gobbler to the substrates resulted in substantially decreased tribenuron-methyl and pendimethalin concentrations within the period of 360 days, but 450 days after herbicide spraying these active ingredients were still present in the substrates.

Key words: herbicide decomposition, clopyralid, tribenuron-methyl, pendimethalin

INTRODUCTION

The monitoring and evaluation of different chemical compounds' emission and impact on the environment is an integral part of chemical control indicators, since it reveals the long-term pollution trends. The chemical of soil, plant and water content in agricultural landscape is strongly influenced by the economic activities, and this impact is both positive and negative (Morril et al., 1982; Shoen., Winterlin, 1987; Šakalienė, Puzinaitė, 1994; Лунев, 1992; Lubytė, Adomaitis, 1996; Lukauskas et al., 2005).

Plant diseases, pests and weeds can decrease the crop yield by 50%, therefore pesticides have long ago become one of the crop productivity of means increasing (Cramer, 1967). 2 mln. tons of pesticides' active substances are yearly produced in the world; 900 kinds of active ingredients in the form of 60 thousand

kinds of pesticides are used in the agricultural sector. Lithuania has registered 175 plant protection means containing 130 kinds of active ingredients.

One of the main features of the EU Common Agricultural Policy Reform is the focus on environmental protection.

Based on a commonly agreed assumption, the environment outside the sprayed area is considered to be almost not contaminated, on the condition that pesticides have been applied strictly in accordance with the given recommendations, using modern spraying equipment and complying with good farming practice (Torstensson, 1994). On the other hand, pesticide residues are detected in the surface and ground waters from time to time even when all the preconditions are met. The reason is the pollution sources – sites where the sprayers are checked, filled and washed. High concentrations of pes-

icide residues were found in these places (Helweg, 1994). Even very little amounts (just a few ml of a product) of spilled pesticide may cause a serious environmental contamination (Torstensson, Castillo, 1997).

20–70% of the total pesticide amount reaching surface waters in arable areas is coming from the sites where pesticides are handled and sprayers parked or washed (Mason et al., 1999, Carter, 2000). There is little or no data on their impact on groundwater.

In order to assess the potential risk in terms of occupational exposure, the presence of 13 pesticides on the external surfaces of agricultural sprayers was investigated. Pesticides were detected with a greater frequency and at higher doses on the bottom, nozzles and spray tank, five pesticides being detected above 1000 mg m⁻². Ten of the 13 pesticides were detected at >10 mg m⁻² on the tractor body. To prevent environmental contamination from such pollution sources, farmers of North-Western European countries have started installation of bio-beds recommended by the specialists.

It is already known that pesticide decomposition in the environment depends on the class of pesticide compounds, pesticide concentration, soil type, organic mixture, sorption, microbial biomass and the amount of soprotropic micro-organisms (Aspelin, 1994; Freedman, 1989; Alexander, 1980; Eagle, 1988; Bollag, Liu, 1990; Coleman, 1992; Torstensson, Castillo, 1997; Fogg et al., 2003a, 2003b; Henriksen et al., 2003; Fogg et al., 2004a, 2004b).

Laboratory experiments were carried out in Sweden with the aim to test the suitability of different mixtures of top soil, peat and straw for use as bio-bed filling. A larger share of straw in a mixture increased the microbial activity and consequently the degree of herbicide decomposition. Soil used in a mixture should be humus-rich (for a better binding of pesticides), with a low content of clay (pesticides stay in the micropores). Peat functions as a pesticide binding and mixture humidity regulating material.

UK researchers have indicated in their papers (Fogg et al., 2003a, 2003b) that the rate of isoproturon and chlorothalonil decomposition was slowed down by higher concentrations of pesticides in bio-mixtures (concentrations applied in the experiments exceeded the highest recommended application rate up to 20 times). Pesticides were decomposed in a bio-mixture (plough layer soil, compost and wheat straw) more rapidly than in a plough layer soil. Pesticide mixture impact on decomposi-

tion rate was studied. Presence of chlorothalonil extended the half-life (DT₅₀) of isoproturon in the plough layer soil from 18.5 to 71.5 days, while in the bio-mixture the half-life of isoproturon or chlorothalonil did not increase. A pesticide mixture (isoproturon, pendimethalin, chlorpyrifos, chlorothalonil, epoxyconazole and dinethoat) was applied 3 times at 30-day intervals, and decomposition rate was slowed down each time, probably because of the toxic impact of the pesticide mixture on micro-organisms.

It took 120 days to mineralise 18% of isoproturon and 50% of mecoprop in biobeds (application rate 500 mg l⁻¹) (Henriksen et al., 2003).

Based on the results of a number of various experiments, it can be concluded that after 8 months about 30% of the most persistent compounds (pendimethalin, chlorothalonil, epoxyconazole) will still be present in bio-beds (Fogg et al., 2004a). On the other hand, these compounds were not leached from the test bio-mixture – they were still in the process of decomposition.

Persistence of separate pesticides and pesticide mixtures was studied using different matrices (straw, compost and different soils) with different physical, chemical, and microbiological characteristics. Isoproturon, chlorothalonil, mecoprop-P and metsulfuron-methyl compounds were applied at four times the maximum approved rate; DT₅₀ values in different bio-mixtures were similar and less than (or equal to) the known DT₅₀ values for soil treated at approved rates. When the aforementioned compounds were applied as a mixture, DT₅₀ values increased in all bio-mixtures, but DT₉₀ values remained below 167 days in all cases with practically no risk of accumulation (Fogg et al., 2004b).

According to the recent findings, 2.4 D decomposition rate (DT₅₀) is lower when soil organic carbon content is higher; this has to do with an increased adsorption – the rate of desorption decreases and the concentration of 2.4 D in soil solution (where the compound is accessible for the microorganisms) becomes low. On the other hand, of the rate both adsorption and decomposition increased when the content of organic carbon exceeded 12% (Baskaran et al., 1996).

The main aim of this research was to select an organic mixture which would be the best to use in a bio-bed for a sprayer washing site. Such organic mixture should stimulate pesticide decomposition into environmentally not harmful or less harmful compounds, thus decreasing the contamination of surface and ground waters with pesticides.

Table. Characteristics of straw, peat and sawdust used for degradation experiments

Characteristics	Wheat straw chop	Peat substrate	Pine sawdust
Water content % ¹	9.2	45.5	37.2
Organic material content % ²	93.5	89.9	99.1
Water volume (maximum water holding capacity) % w/w ³	75.0	94.7	80.4
Texture: ⁴			
% (1–2 mm)			13
% (2–4 mm)			85
% (>4 mm)			2
% (<10 mm)		15	
% (10–20 mm)		56	
% (20–30 mm)		29	
% (50 mm)	100		

MATERIALS AND METHODS

Three organic substrates were selected for the research: (1) wheat straw chop, (2) high moor peat substrate prepared for plant growing (3) pine sawdust (Table).

Well known cereal crop herbicides were selected: Lontrel 300 g/l water-soluble concentrate (SL), active ingredient clopyralid; Granstar 75% water-soluble granules (DF), active ingredient tribenuronmethyl; and Stomp 330 g/l emulsifiable concentrate (EC), active ingredient pendimethalin. The structural formulas of the herbicides are presented in Fig. 1.

Each substrate was tested in three variants: pure substrate (no additives); substrate complemented with humate (10% solution of humic acids, producer Lenmatch, UK) 2 ml per 1 kg of dry substrate; substrate complemented with microbial preparation Septic-Gobbler 50 mg per 1 kg of dry substrate (Septic-Gobbler, produced in March 2004, producer American Biotech Labs – is a highly concentrated microbial formulation of aerobic bacteria; this product eliminates the build up of many organic wastes found in septic systems. Septic-Gobbler contains an amazing number – 10 millions of microorganisms in each 1 ml of the product).

Herbicide solution was prepared for the whole experiment concentration of 1 mg ml⁻¹. The solution was divided into portions using a cylinder to make sure that every 1 kg of the dry substrate mass would get 100 ml of each active ingredient. Before spraying, the solution was diluted with water to 500 ml volume. The humidity of the substrates was set at the level of 60% of water holding capacity (water volume) by adding an appropriate amount of water, then herbicides were applied. After the spraying of herbicides, substrates were thoroughly mixed and kept in aerobic conditions. The experiment was carried out in three replications. After the treatment, the substrates (3 kg of dry matter) were put into polyethylene bags (40 × 60 × 80 cm) and placed open in a shelter outside. Experiment was conducted in aerobic conditions. Once per week the substrates were weighed and replenished with an appropriate amount of water compensating the losses caused by evaporation. Monthly air temperature means in 2004: 12.3 °C in May, 15.5 °C in June, 17.5 °C in July, 16.4 °C in August, 12.2 °C in September, 8.2 °C in October and 1.3 °C in November–December. The year 2005 was warmer than 2004. The mean air temperature for December–March was minus 2.1 °C, and it was higher than the multi-annual mean (minus 3.2 °C); the mean for April was 7.6 °C (multi-annual mean

1.3 °C); the mean for May was 12.1 °C, for June 15.5 °C – both months matching the multi-annual means. The means for July, August and September were exceeding the multi-annual means by 2.5 °C, 0.3 °C and 2 °C, respectively.

Substrate sampling took place 30, 60, 120, 360 and 450 days after the spraying of herbicides. The substrates were tipped out from the bags, mixed thoroughly, and then 200 g substrate samples were taken for testing for herbicide residues. The concentration of herbicide residues was determined in the naturally humid substrate; substrate humidity was determined as well. The determined concentrations of herbicide residues were recalculated into the content of residues in the dry matter of a substrate. Recoveries for all the extraction methods were >80%. Herbicide concentrations were determined in substrate samples taken from all three replications of the experiment; means and standard deviations were calculated.

Tribenuron-methyl and pendimethalin were extracted from samples using ethylacetate. The extracts were cleaned using aluminium oxide columns. Clopyralid was extracted into 1M NaCl and then re-extracted into ethylacetate. The extracts were dried using anhydrous sodium sulphate followed by rotary evaporation (at 40 °C). The remainder was dissolved in ethyl alcohol, etherified and extracted into hexane.

Tribenuronmethyl, pendimethalin and clopyralid concentrations were measured using a Hewlett Packard HP 5890 gas chromatograph fitted with a split injector. Tribenuron-methyl was determined using a 30.0 m × 320 μm × DB-35MS (35%-phenyl-methylpolysiloxane) capillary column and a nitrogen-phosphorus detector, and for pendimethalin and clopyralid 30.0 m × 250 μm × 0.25 μm HP-5 (5% phenyl methyl siloxane) capillary column and an electron capture detection were used. Data obtained from the experiment were processed by mathematical statistical methods.

RESULTS AND DISCUSSION

25–40% of applied clopyralid, 38–50% of applied tribenuron-methyl and 28–66% of applied pendimethalin were found in the substrate samples taken 30 days after spraying (Fig. 2). Clopyralid data are more dispersed, the variation among the repetitions being 0.5% to 38%. Pendimethalin data dispersion was from 4% to 25% and tribenuron-methyl from 5% to 23%. Trends remained the same for the later measurements, too.

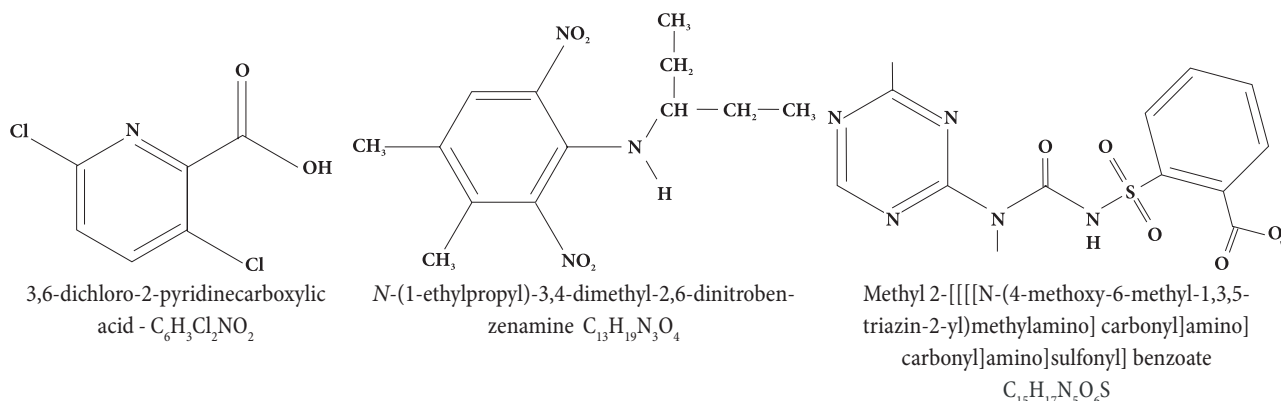


Fig. 1. Structural formulas of Clopyralid, Pendimethalin and Tribenuron-methyl

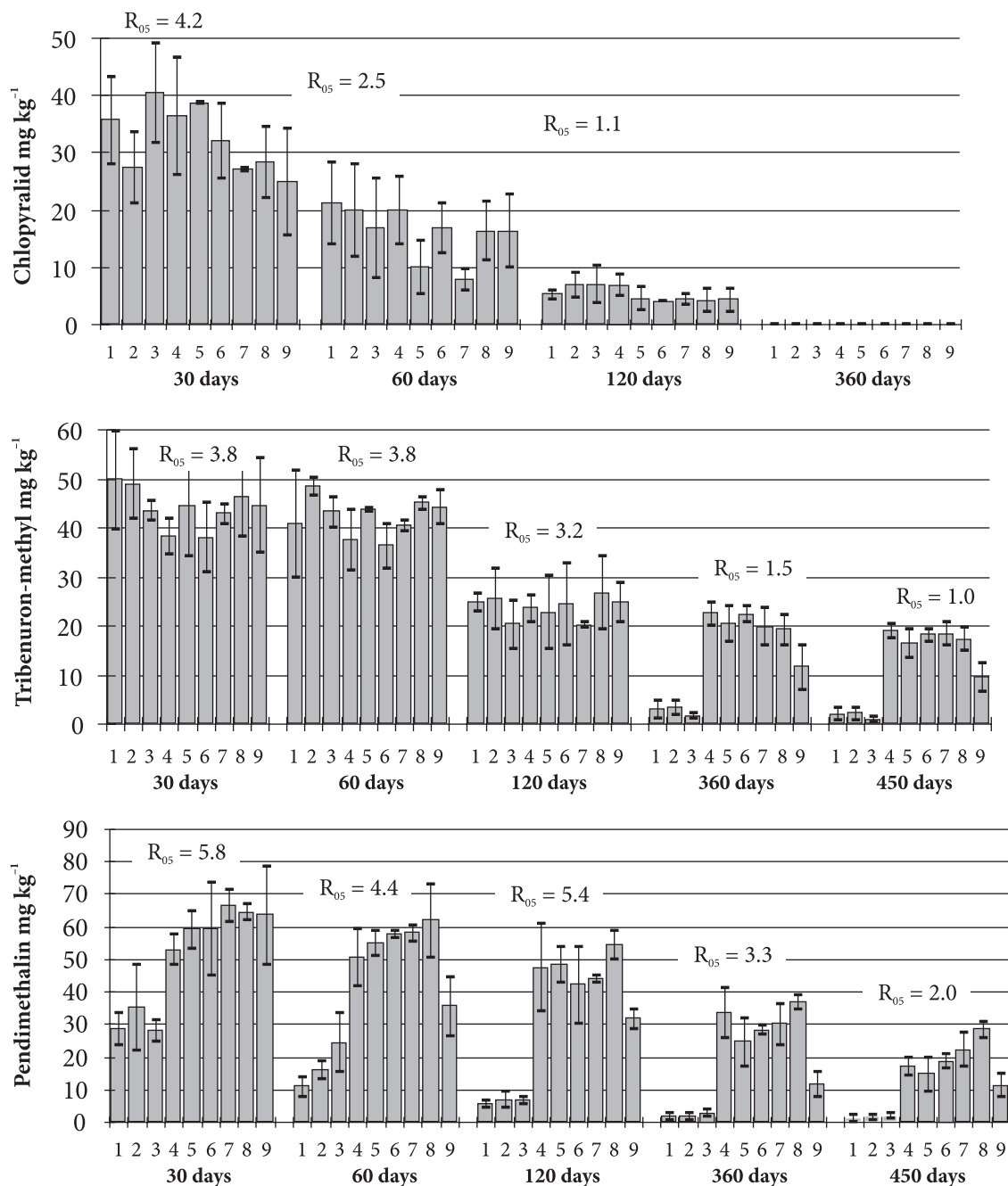


Fig. 2. Decomposition of Lontrel (clopyralid), Granstar (tribenuron-methyl) and Stomp (pendimethalin) in different substrates. Average data and standard deviation for 2004–2005

1 – wheat straw chop; 2 – wheat straw chop + humate; 3 – wheat straw chop + microbial preparation Septic Gobbler; 4 – peat substrate; 5 – peat substrate + humate; 6 – peat substrate + microbial preparation Septic Gobbler; 7 – wood sawdust; 8 – wood sawdust + humate; 9 – wood sawdust + microbial preparation Septic Gobbler

Herbicide decomposition trends and regularities were different in separate variants of the experiment. Addition of humate did not result in a consistent effect on the decomposition of herbicides. The slower decomposition (because of added humate) of pendimethalin in straw chop and peat and tribenuron-methyl in peat during the first 0–60 days was statistically reliable, but later the rate of decomposition increased: the results of testings after 120, 360 and 450 days showed similar decomposition rate for the pure substrate and the substrate complemented with humate. Several studies showed that increasing amounts

of compost or brown coal-derived humic acid stimulated aerobic bacterial growth, but had only slight effects on actinomycetes and no effect on filamentous fungi (Vallini et al., 1993; Valdrighi et al., 1995, 1996). Russian researchers have found humate to stimulate the activity of soil micro-organisms and thus to increase the degree of decomposition of the plant protection products applied (Bezuglov et al., 2002). In our experiment, the regularities differed in the course of the experiment; at its end (after 450 days) there were no consistent differences caused by humate application.

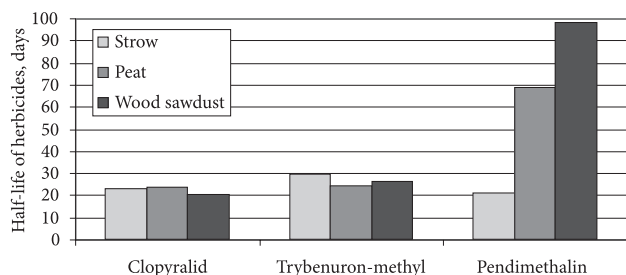


Fig. 3. Lontrel (clopyralid), Granstar (tribenuron-methyl) and Stomp (pendimethalin) half-life in different substrates

Herbicide decomposition under the influence of the microbial preparation Septic-Gobbler depended on the kind of a substrate. Dependence of clopyralid decomposition on the application of the microbial preparation Septic-Gobbler was statistically not reliable. The application of Septic-Gobbler resulted only in a slight trend of Lontrel residue decrease in peat substrate.

The decomposition of pendimethalin under the influence of the microbial preparation Septic-Gobbler depended on the kind of a substrate. A statistically reliable decrease of pendimethalin was determined in wood sawdust substrate 60 and 120 days after the application of Stomp and the microbial preparation – 1.6 and 1.4 times respectively, versus the variant of pure substrate.

Addition of Septic-Gobbler resulted in a significant decrease of tribenuron-methyl and further decrease of pendimethalin (1.7 and 2.9 times, respectively, versus the variant of pure substrate) in wood sawdust substrate 360 days after the application. No positive influence was recorded in wheat straw chop and peat. Similar trends were recorded 450 days after the application. The least amounts of residues were determined in straw, larger being in peat and the largest in wood sawdust. Septic Gobbler statistically significantly decreased the content of tribenuron-methyl and pendimethalin (approximately 2 times) in wood sawdust 450 days after the application.

The largest share of herbicides is decomposed within 30 days (64–73% of clopyralid, 59–63% of tribenuronmethyl), the rest remaining in the substrate for a longer time. Pendimethalin decomposition depended on the substrate more than that of other herbicides (Fig. 2). 30 days after the application, 72% of pendimethalin was decomposed in straw, 47% in peat and 34% in wood sawdust (2.1 times less than in straw). The content of clopyralid in the samples taken 60 days after herbicide application was less in all substrates as compared with the clopyralid content in samples taken 30 days after herbicide application, while pendimethalin content decrease was recorded only in the wheat straw chop. After 60 days (in comparison to 30 days) clopyralid content in wheat straw chop was 1.7 times, in peat 1.8 times and in wood sawdust 3.4 times less.

During the same period, tribenuron-methyl decomposition was much slower in all substrates; in 60 days its amount was only 1.1–1.2 times lower than in 30 days. The decomposition of pendimethalin in peat and wood sawdust was about equally slow – it decreased only 1.1 times. On the other hand, it was intensively decomposed in straw, and its content decreased 2.7 times. The decomposition pattern in later stages was about the same. Clopyralid was decomposed faster in all substrates and pendimethalin in straw, the decomposition of tribenuron-methyl was

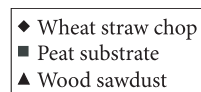
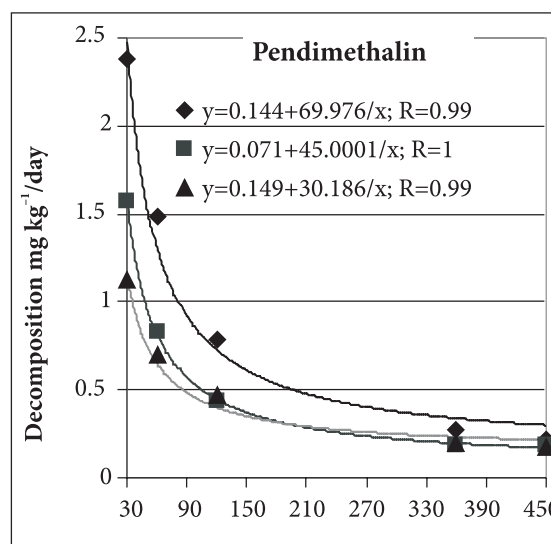
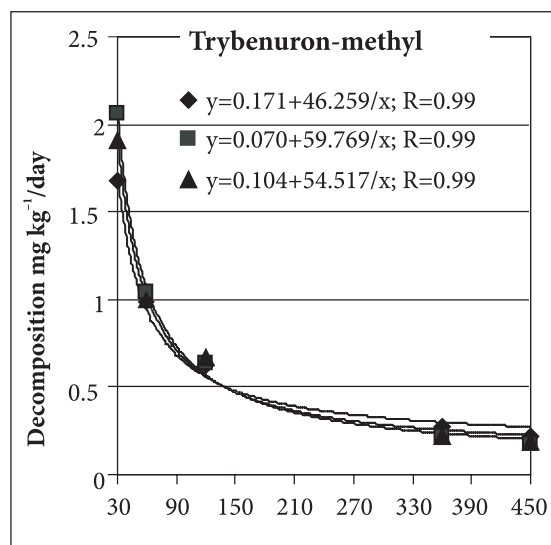
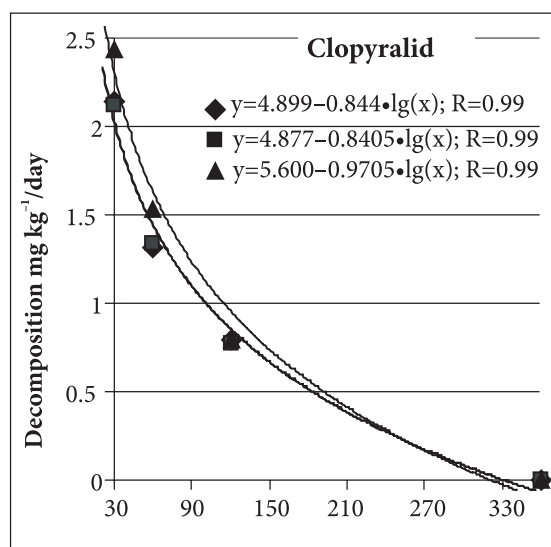


Fig. 4. Rate of decomposition of Lontrel (clopyralid), Granstar (tribenuron-methyl) and Stomp (pendimethalin) in different substrates

slower, followed by the slowest decomposition of pendimethalin in peat and wood sawdust.

For example, in 2004, 120 days after the experiment was over, the following content of pesticide residues was found in substrates (mg per kg of dry substrate): clopyralid in wheat straw chop 5.1, in peat 6.9, in wood sawdust 4.3; tribenuron-methyl in wheat straw chop 25, in peat 24, in wood sawdust 20; pendimethalin in wheat straw chop 5.5, in peat 47, in wood sawdust 44.

Our experimental data suggest that half-life of clopyralid in straw and peat substrates was 23 days and of wood sawdust less than 21 days (Fig. 3). Tribenuron-methyl half-life was longer: 24 days in peat, 26 days in wood sawdust and 30 days in straw. Pendimethalin half-life in straw was 21 days, but in other two substrates it was much longer: in peat 63 days and in wood sawdust 98 days.

In spring 2005, before the spraying season, no clopyralid residues were found in any of the substrates (Fig. 2). The content of tribenuron-methyl and pendimethalin residues in the test substrates was more different: much less in straw chop than in wood sawdust and peat. 360 days after the application, was compared to the testing data at the 120-day point, the content of tribenuron-methyl significantly decreased only in straw (1.7 times) and of pendimethalin in all substrates: 3.6 times in straw, 1.4 times in peat and 1.5 times in wood sawdust.

450 days after the application (late autumn) there were no clopyralid residues found, the other two pesticides being still present (mg per 1 kg of dry substrate): tribenuron-methyl – 2.0 in straw chop, 19 in peat and 18 in wood sawdust; pendimethalin – 1.3 in straw chop, 17 in peat and 22 in wood sawdust.

The experimental data show that the decomposition of herbicides depended on the substrate. In general, the decomposition was fastest in straw, slower in peat and slowest in wood sawdust.

There are three distinctive time span phases concerning the change of herbicide concentration in substrates (Fig. 4). The first phase of 30 days is the most intensive one, here the concentration of herbicides was decreasing by 1.12–2.43 mg kg⁻¹ of substrate every day. The second phase (60, 120 days) is less intensive; the concentration was decreasing by 0.03–0.59 mg kg⁻¹ (measured in 30 and 60 days). The third phase (360, 450 days) is the slowest one, here the concentration was decreasing by 0.003–0.18 mg kg⁻¹ of substrate every day (measured in 240 and 90 days).

The experimental data show that the decomposition of herbicides depended on the substrate. In general, the decomposition was fastest in straw, slower in peat and slowest in wood sawdust.

CONCLUSIONS

1. The rate of clopyralid, tribenuron-methyl and pendimethalin decomposition in substrates depended on the composition of herbicide and the type of substrate. Lontrel (in all the test substrates) and pendimethalin (in straw chop) decomposed faster, tribenuron-methyl more slowly, and the decomposition of pendimethalin in peat and wood sawdust was the slowest one.

2. The decomposition of the major part of herbicide (64–73% of clopyralid, 59–63% of tribenuron-methyl and 34–72% of pendimethalin) takes place within the first 30 days, and the rest remains in substrate for a longer time.

3. There are three distinctive time span phases concerning the change of herbicide concentration in substrates. The first phase is the most intensive one, here the concentration of herbicides (30 days) was decreasing by 1.12–2.43 mg kg⁻¹ of substrate every day. The second phase was less intensive (60, 120 days); the concentration was decreasing by 0.03–0.59 mg kg⁻¹. The third phase was the slowest one (360, 450 days), here concentration was decreasing by 0.003–0.18 mg kg⁻¹ of substrate every day.

4. 450 days after the application of herbicides there were no clopyralid residues found, tribenuron-methyl was still present in straw chop (2.0 mg per 1 kg of dry substrate), in peat (19 mg per 1 kg of dry substrate) and in wood sawdust (28 mg per 1 kg of dry substrate); pendimethalin: in straw chop 1.3 mg, in peat 17, and in wood sawdust 22 mg per 1 kg of dry substrate.

5. Complementing the substrates with humate did not result in a consistent effect on the decomposition of herbicides. The regularities were not the same in different sampling stages, and after the experiment was over (450 days after the spraying) no trends in the change of herbicide content due to the application of humate were revealed.

6. As a result of mixing the microbial preparation Septic-Gobbler into the wood sawdust substrate, in 60 days and later the concentration of pendimethalin decreased 1.4 and 2.0 times, respectively versus the variant of pure substrate, and the concentration of tribenuron-methyl in 360 and 450 days decreased 1.7 and 2.0 times, respectively.

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PESTICIDŲ SKILIMAS ĮVAIRIUOSE ORGANINIUOSE SUBSTRATUOSE

Santrauka

Tirtas herbicidų detoksikacijos greitis, atsižvelgus į jų sudėtį ir substrato tipą.

Tyrimams pasirinkti javų pasėliuose plačiai naudojami herbicidai: lontrelas, kurio veikloji medžiaga yra klopivalidas, granstaras – tribenuronmetilas bei stompas – pendimetalinas. Jie išpurkšti į tris organinius substratus: kvietinių šiaudų kapojus, aukštapelkių durpių substratą, paruoštą augalų auginimui, bei medžių pjuvenas. Kilogramme substrato sausos medžiagos įterpta po 100 mg herbicidų veikliųjų medžiagų. Kiekvienas substratas buvo tiriamas: grynas, su humatu po 2 ml/kg ir su mikrobiniu preparatu Septic Gobbler po 50 mg kg⁻¹ substrato sausos medžiagos.

Nustatyta, kad daugiausia klopivalido (64–73%), tribenuronmetilo (59–63%) suskyla per 30 d., o kita dalis laikosi ilgiau. Pendimetalino skilimas, lyginant su kitais herbicidais, labiau priklausė nuo naudojamo substrato. Kai jis buvo įterptas į šiaudų kapojus, per 30 d. suskilo 72%, durpėse – 47% ir pjuvenose – tik 34%, arba pastarasis 2,1 karto mažiau nei šiauduose.

Klopivalido skilimo pusperiodis šiaudų ir durpių substratuose buvo 23 dienos, pjuvenų – mažiau nei 21 diena. Tribenuronmetilo skilimo periodas – kiek ilgesnis, trumpesnis – durpėse (24 dienos), ilgesnis pjuvenose (26 dienos) ir ilgiausias šiauduose (30 dienų). Pendimetalino skilimo pusperiodis šiauduose ir klopivalido pjuvenose buvo vienodas (21 diena). Tuo tarpu durpėse jis skilo gana lėtai (63 dienos) ir lėčiausiai pjuvenose (98 dienos). Panašus herbicidų skilimo eiliškumas išliko ir toliau. Praėjus 450 dienų po herbicidų įterpimo, klopivalido liekanų substratuose neaptikta, tribenuronmetilo šiaudų kapojuose nustatyta 2,0, durpėse – 19 ir pjuvenose – 18, pendimetalino – atitinkamai 1,3, 17 ir 22 mg kg⁻¹ substrato sausos medžiagos.

Humatas, įmaišytas į substratus, neturėjo nuoseklios įtakos herbicidų skilimui. Dėl mikrobiologinio preparato Septic Gobbler per 360 d. itin sumažėjo tribenuronmetilo ir pendimetalino koncentracija, bet ir jie išsilaikė praėjus 450 d. po įterpimo.

Raktažodžiai: herbicidų skilimas, klopivalidas, tribenuronmetilas, pendimetalinas