TECHNICAL TRANSACTIONS | **CZASOPISMO TECHNICZNE**
CIVIL ENGINEERING | BUDOWNICTWO

4-B/2015

GABRIELA ZEMEŁKA *

FATE OF THREE HERBICIDES (TEMBOTRIONE, NICOSULFURON AND S-METOLACHLOR) ON SOIL FROM LIMAGNE REGION (FRANCE)

WPŁYW TRZECH HERBICYDÓW (TEMBOTRION, NICOSULFURON I S-METOLACHLOR) NA GLEBĘ Z REGIONU LIMAGNE (FRANCJA)

A b s t r a c t

The laboratory studies of pesticides involves a number of ways and methods. It has become especially important nowadays when pesticides is common for people to use. The increasing risk of these chemicals has forced the Legislating Authorities in France to set up recommendations on the use of pesticides and established *Ecophyto 2018* program. This paper and research are the part of an interdisciplinary project funded by CPER (Contract between the State and Region), FEDER and the Région Auvergne.

The objective of this research is to characterize the fate of 3 herbicides (tembotrion, S-metolachlor, nicosulfuron) belonging to different chemical families on soil from Limagne region in France. The author have performed the experiments with the dry samples of soil which were polluted in the laboratory by spraying pesticide solutions. The work focused on one of the main processes governing the adsorption on surface of solid phase. The results of the research shown that the impact of pesticides is greatly dependent on their family origin as well as on the environmental conditions and the type of soil. Further studies have to be carried out to better understand actions and behaviour of the pesticides in the soil.

Keywords: herbicide, black soil, Limagne – France

S t r e s z c z e n i e

Naukowe badania pestycydów obejmują wiele sposobów i metod badań laboratoryjnych. Są one szczególnie istotne w dzisiejszych czasach, kiedy popularne stało się stosowanie pestycydów. Wzrost zagrożenia tymi substancjami, zmusił organy prawa we Francji do utworzenia zaleceń dotyczących ich stosowania i wprowadzenia programu *Ecophyto 2018*. Artykuł i przedstawione w nim badania są częścią interdyscyplinarnego projektu sponsorowanego przez CPER (Umowa między Państwem i Regionem), FEDER i Région Auvergne.

Celem badań jest scharakteryzowanie losów 3 herbicydów (tembotrion, S- metolachlor, nikosulfuron), należących do różnych rodzin chemicznych w glebie z regionu Limagne we Francji. Autor prowadził badania na glebie zanieczyszczonej roztworami pestycydów. Badania te skoncentrowane były na jednym z głównych procesów dotyczących adsorpcji na powierzchni fazy stałej. Wyniki badań pokazały, że wpływ pestycydów jest znacznie uzależniony od ich pochodzenia chemicznego, jak również od warunków środowiskowych i gleby. Dalsze badania powinny być prowadzone w celu lepszego zrozumienia działania i zachowania pestycydów w glebie.

Słowa kluczowe: herbicyd, czarna ziemia, Limagne – Francja

DOI: 10.4467/2353737XCT.15.405.5036

* MSc. Eng. Gabriela Zemełka, PhD student, Cracow University of Technology.

1. Introduction

One of the main processes governing the dissemination and fate of pesticides in agricultural soils is adsorption on surface of the solid phase. These interactions play a key role not only in the transport of pesticides but also in their biodegradation, by acting on their bioavailability and on the microbial metabolic activity. Therefore the understanding and measurement of the pesticide retention and degradation are the key steps in risk assessments of their persistence and contribution to pollution [10].

The objective of laboratory studies was to characterise the fate of 3 pesticides belonging to different chemical families in soils from Limagne region. Nicosulfuron (sulfonylurea), S-metolachlor (acetanilide) and tembotrione (triketone), known to be usually applied sequentially during the growing season of maize [4, 13, 14, 16]. Soil from Limagne region (Auvergne, France) was formed under continental climate, very cold in winter, very wet during the spring thaw and very hot and dry in summer. That soil was classified as Vertisol which is very fertile and lead to high production yields [3, 9]. That is why monitoring the fate of pesticides in this area is a major environmental and health concern. In order to better understand the mechanism involved in transfer/transformation processes of pesticides, research was carried to identify the role of the soil component on the different pesticide adsorption. Laboratory microcosm experiments were conducted to assess the dissipation of each pesticide in this soil.

2. Materials and methods

2.1. Preparation of soil sample

Samples were separated into 3 fractions depending on their size by physical treatments (50 µm < Φ < 500 µm; 2 µm < Φ < 50 µm; Φ < 2µm) according to the procedure described on Figure 1. Bulk soil (air-dried and sieved at 2mm) was used.

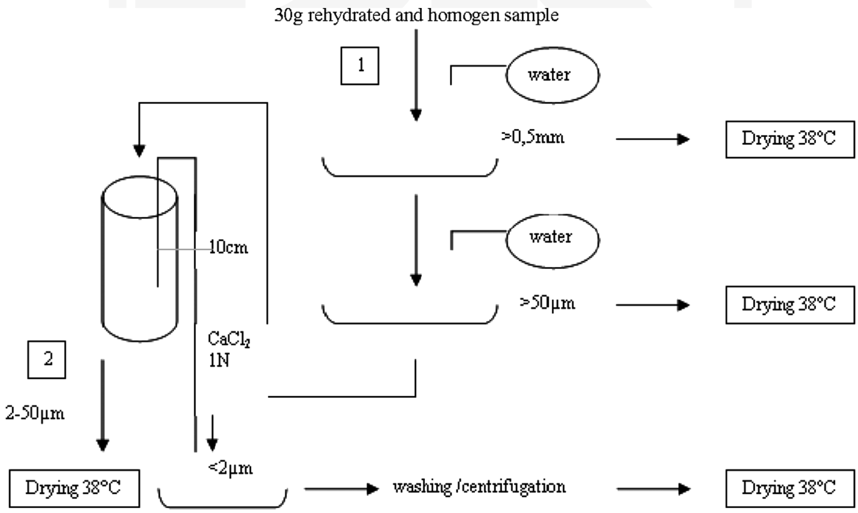


Fig 1. Steps of the soil fractioning [17]

30 g of soil were put into container and cover sample with 2L of water. Fraction obtained contained carbonates and organic matter. Water was removed every 8 hours by special pipe and a vacuum pump and moved to the other container. $CaCl_2$ 1N was put to accelerate settling. After 1 week the fraction <0.5 mm was placed in a plastic pot and an ultrasonic bath for 15 minutes and sow in 50 μm and 5μm sieve. The fraction < 2 μm should be washed to remove Cl-ions made during the addition of $CaCl_2$ 1N. It was centrifuged twice during 15 minutes and speed 4000 rpm. The samples were placed in a crystallizer and dried at 38°C.

2.2. Stability of pesticides

Three different solution pesticides of tembotrione, nicosulfuron, S-metolachlor with the same concentration (100 μM) were prepared. The solutions were kept 7 days in Infors HT Multitron Incubator. They were shaken with a speed 140rpm in 27°C under lights simulating the solar spectra. Every day solutions were weighted. Distilled water was given in amount which disappeared from the flask. 1ml of solutions were taken by automatic pipette and moved into the eppendorf. The solutions were weighed again. New weight was recorded. Samples were frozen at –20°C until HPLC analyses.

2.3. Microcosms

Six microcosms were prepared, two for each pesticide with two moisture contents (25 and 35%). Therefore six different solutions of pesticides: tembotrione 35% (142 μM) and 25% (200 μM), nicosulfuron 35% (142 μM) and 25% (200 μM), S-metolachlor 35% (142 μM) and 25% (200 μM) were prepared. Each one was sprayed on 200g of air-dried and sieved bulk soil into different containers. Control of water content was checked every week, the day before sampling (Fig. 2). Soil (3.5 g) was contaminated with 1.5 mL of pesticide at different concentrations in centrifuge tubes. After 15 minutes (T0) and 20 hours (T20), 20 mL of solvent was added and the suspension was shaken for 24 h. After centrifugation (1200 rpm for 15 min), supernatants were put in a freezer (–20°C) until HPLC analyses (Fig. 2.). The same protocol was carried out with a soil samples of each microcosm once a week (samples taken in triplicate) and extracted with ultra pure water for tembotrione and nicosulfuron and a mixture of MeOH/H_2O 4/1 for S-metolachlor [11].

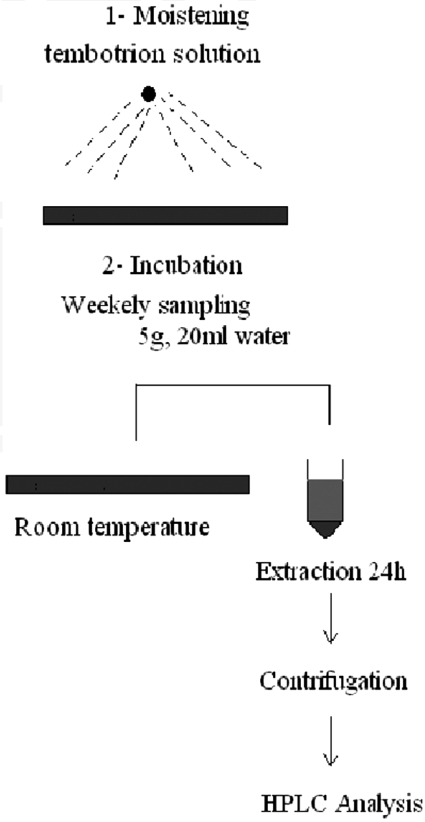


Fig. 2. Microcosm experiments on the example of tembotrione [17]

2.4. Sorption experiment-Kinetics

1 g of dry soil with 3mL of Volvic® water (natural mineral water from France) was used. The soil samples were shaken (Heidolph Reax2) for 12 hours in 20°C before the day of experiment. The supernatant was removed after centrifugation (Thermo KR22i Jouan) at 12000 rpm for 15 min. 3 mL of pesticide solution in distilled water (pH = 6) was pipetted into the container. The samples were shaken again for 1/2, 1, 1 1/2, 2, 3, 4, 6, 8, 20 and 24 hours in 20°C. Centrifugation was used again. HPLC analysis of supernatant was conducted. Each measurement was performed three times.

2.5. Sorption experiment-Isotherms

The author prepared various concentrations solution of pesticide were prepared (10 μM, 20 μM, 30 μM, 50 μM, 70 μM, 10 0μM). The process of preparing samples is the same like in adsorption kinetics.

1 g of clay was used and preconditioning with 3 mL of Volvic water (natural mineral water from France). Samples were shaken (Heidolph Reax2) for 12 hours in 20°C before the day of experiment. Centrifugation (Thermo electron corporation KR22i Jouan) 12000 rpm for 15 min was used. Then supernatant was removed. 3mL of various concentrations solution pesticide were pipetted into the 6 containers. Samples were shaken in 20°C for 4 or 6 hours according to the pesticide studied. HPLC analysis of supernatant was conducted. Each measurement was performed three times.

3. Results

The results of pesticide stability showed that a strong decrease of S-metolachlor was observed within the first day. Almost 70% has disappeared. Tembotrione and nicosulfuron were stable.

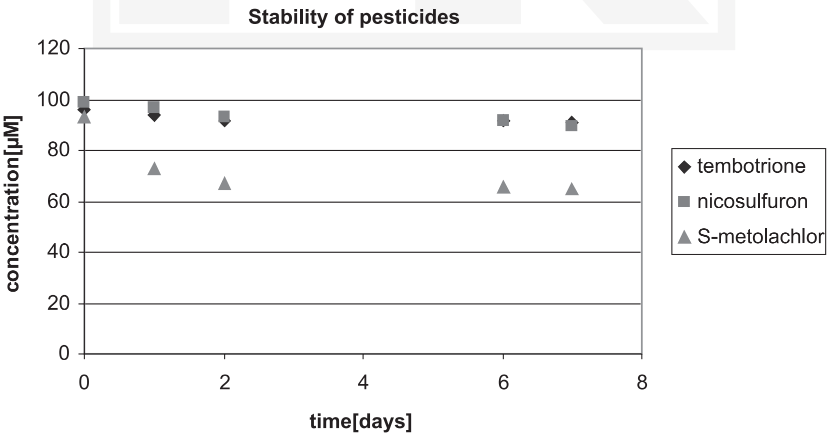


Fig. 3. Photostability of tembotrione, S-metolachlor and nicosulfuron (100 μM) [17]

The results of pesticide dissipation in microcosms are presented on Fig 4.

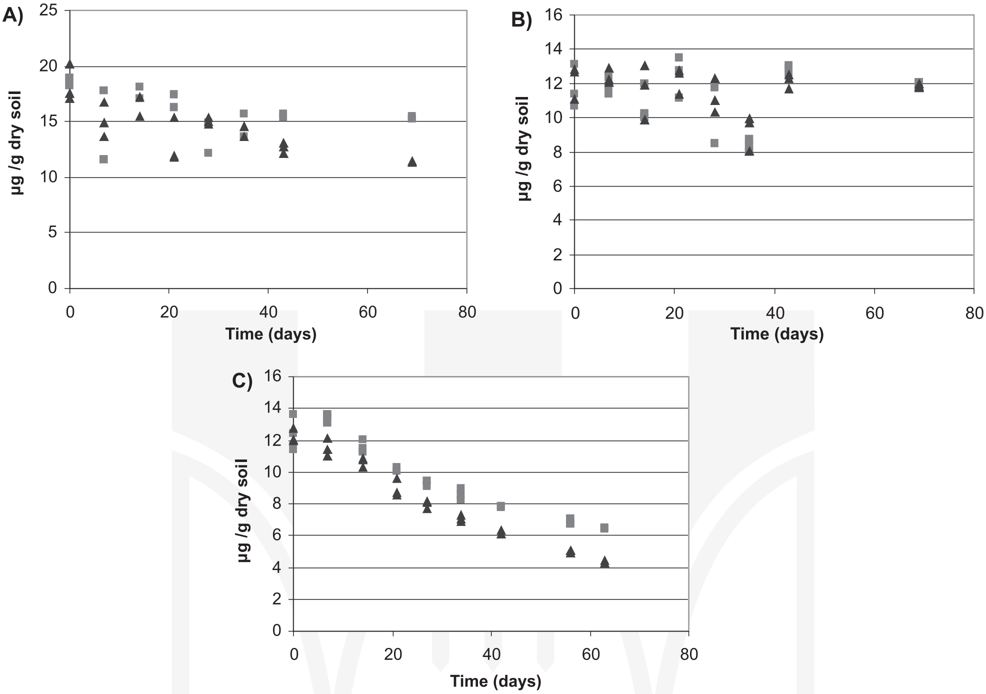
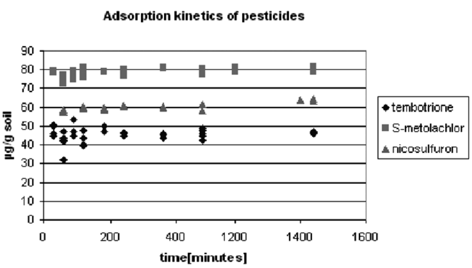


Fig. 4. Dissipation of (A) tembotrione, (B) nicosulfuron and (C) S-metolachlor in microcosms with 25% (■) and 35% (▲) soil moisture [17]

Nicosulfuron is persistent as the final concentration after 69 days of incubation is the same as the initial one. Tembotrione dissipated very slowly but a decreasing tendency of its concentration is observed with time. The less persistent herbicide is nicosulfuron as 50% and 70% have disappeared within 69 days of incubation for 25 and 35% of soil moisture, respectively [10].



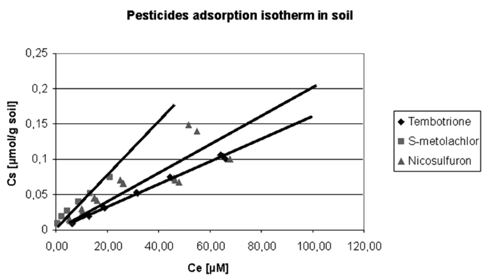


Fig. 5. Adsorption kinetic of pesticides Fig 6. Adsorption isotherms of pesticide in soil [17] in soil [17]

Kinetics studies showed a quick adsorption, and equilibrium soon reached which is shown on the graphs (Fig. 5). The graph of tembotrione adsorption kinetics shows that the most stable time of adsorption is 6 hours and for nicosulfuron and S-metolachlor is 4 hours. After that time concentration of the analytes did not change.

The results of pesticide adsorption isotherms showed that tembotrione displays the lowest adsorption capacity and S-metolachlor displays the greater adsorption behavior (Fig. 6).

4. Discussion

Degradation is the process of pesticide breakdown after application. This can be done by microorganisms, chemical reactions and light or photodegradation [2,6]. S-metolachlor and nicosulfuron have the potential to move into the water due to their highwater solubility [12]. These three pesticides are quite stable under those conditions (temperature, light, humidity). Degradation from irradiation was comparatively slow. The contribution of a photolytic mechanism of degradation is therefore limited. Moreover, no other chemical degradation was observed (hydrolysis).

The dissipation could be observed due to sorption process on soil particles or organic matter and/or to biodegradation by microorganisms present in soil. To discriminate both these processes and to understand better the role of the different components of soil, adsorption experiments were carried out with each pesticide.

Kinetics studied showed that the diffusion through the heterogeneous matter and accessibility to the adsorption sites are high. Consequently, 4h and 6h of pesticide/soil contact time were chosen for adsorption isotherm experiments [1, 5, 8].

Adsorption coefficients (K_d) of the 3 herbicides adsorbed on soil from Limagne region follows the variation: K_d (S-metolachlor) > K_d (nicosulfuron) > K_d (tembotrione). The same behavior is observed than reported in the literature [7, 15]. The most soluble herbicide, tembotrione displays the lowest adsorption capacity. Because of the negative charge of its ionic form, interaction of tembotrione with surface of metal oxides, carbonates and clays is unfavorable. Differently, S-metolachlor displays the greater adsorption behavior. Due to its low solubility and its high K_{OC}, this herbicide has a greater tendency to be adsorbed by the soil organic matter. This is probably the reason why, it has great capability to be immobilized on Limagne Vertisol. The major components are soil organic matter and clays. In Vertisols, clays mineral is vermiculite, which is very specific.

5. Conclusion

In summary, the present results show that the fate of pesticides is greatly dependent on their chemical structure and corresponding physico-chemical properties as well as on the environmental conditions and type of soil. In this soil, our work focused on one of the main processes governing the fate of pesticide: adsorption/desorption with solid particles that was studied in detail but also on a global view of the pesticide dissipation under environmental conditions. Tembotrione, S-metolachlor and nicosulfuron were not strong adsorbed by the soil. The results showed that S-metolachlor had the highest percentage of adsorption. Nicosulfuron and tembotrione that were much less sorbed were found to be respectively, persistent and slightly dissipated in soil. We can then assume that biodegradation by soil microorganisms, known to be another important dissipation process in the soil, is not very active for both these pesticides under theconditions used in the experiments. To conclude, Further studies have to be carried out to better understand actions and behaviour of the pesticides in the soil.

Acknowledgment

This work is part of an interdisciplinary project funded by CPER (Contract between the State and Region), FEDER and the Région Auvergne.

I would like to thank my supervisors Dr. Pascale Besse-Hoggan and Pr. Claude Forano for help at my scientific research during my stay at University Blaise Pascale in Clermont-Ferrand in France (Erasmus research program).

I would like to thank the reviewer of this paper for his valuable comments.

References

[1] Bedmar F., Daniel, P. Costa J., Giménez D., *Sorption of acetochlor, S-metolachlor, and atrazine in surface and subsurface soil horizons of Argentina,* Environ. Toxicol. Chem., vol. 30, 2011, 1990–1996.

[2] Benzi, M., Robotti, E., Gianotti, V., *HPLC-DAD-MSn to investigate the photodegradation pathway of nicosulfuron in aqueous solution*, Anal. Bioanal. Chem., vol. 399, 2011, 1705–1714.

[3] Bornand M., Dejou J., Robert M., Roger L., *Composition minéralogique de la phase argileuse des Terres noires de Limagne (Puy de Dôme). Le problème des liaisons argiles-matière organique*, Agronomie, vol. 4 (1), 1984, 47–62.

[4] Bowman, B.T., *Mobility and persistence of the herbicides atrazine, metolachlor and terbuthylazine in plainfield sand lysimeters*, Environ. Toxicol. Chem., vol. 8, 1989, 485–491.

[5] Cao P., Wang X., Liu F., Zhao E., Han L., *Dissipation and residue of S-metolachlor in maize and soil*, Bull Environ Contam Toxicol, vol. 80, 2008, 391–394.

[6] Dimou A.D., Sakkas, V.A., Albanis, T.A., *Metolachlor photodegradation study in aqueous media under natural and simulated solar irradiation*, J. Agric. Food Chem., vol. 53, 2005, 694–701.

[7] Foo K.Y., Hameed B.H., (2010) *Insights into the modeling of adsorption isotherm systems*, Chem.Eng. J., 156, 2-10.

[8] Gonzalez J.M., Ukrainczyk L., *Adsorption and desorption of nicosulfuron in soils*, J. Environ. Qual., vol. 25(6), 1996, 1186–1192.

[9] IUSS Working Group WRB, *World Reference Base for Soil Resources 2014. International soil classification system for naming soils and creating legends for soil maps*, 2014, 97–100.

[10] Mamy L., Barriuso E., Gabrielle B., *Environmental fate of herbicides trifluralin, metolachlor, metamitron and sulcotrione compared with that of glyphosate, a substitute broad spectrum herbicide for different glyphosate-resistant crops*, Pest Management Science, vol. 61, 2005, 905–916.

[11] Nelieu S., Perreau F., Guichon R., Seguin F., Bry Ch., Einhorn J., *Monitoring and effects of nicosulfuron in aquatic mesocosms: development of a simple analytical procedure and evidence for low toxicity to phytoplankton communities,* Anal Bioanal Chem, vol. 382, 2005, 108–114.

[12] PPDB=Pesticide Properties Database-University of Hertfordshire, (online) homepage: http://sitem.herts.ac.uk/ (date of access: 2013-06-20).

[13] Regitano J. B., Koskinen W. C., *Characterization of Nicosulfuron Avalibility In Aged Soils*, Journal of Agricultural and Food Chemistry, vol. 56, 2008, 5801–5805.

[14] Santel H.J., *Laudis® OD – a new herbicide for selective post-emergence weed control in corn (Zea mays L.),* Bayer CropScience Journal, vol. 62, 2009, 95–108.

[15] Si Y., Takagi K., Iwasakid A., Zhoub D., *Adsorption, desorption and dissipation of metolachlor in surface and subsurface soils*, Willey Interscience, vol. 65, 2009, 956–962.

[16] Tarara G., Fliege R. Desmarteau D., Kley C., Peters B., *Environmental fate of tembotrione*, Bayer CropScience Journal, vol. 62, 2009, 63–73.

[17] Zemełka G., *Fate of three herbicides (tembotrione, nicosulfuron and S-metolachlor), alone or in mixture, in Limagne plane soil*, Rapport de Stage Master 2, Institut de Chimie de Clermont-Ferrand, 2013.