ENVIRONMENTAL ANALYTICAL ASPECTS OF MOSQUITO CONTROL PRACTICE

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Abstract
Aerial application of insecticides was monitored by determination of the active ingredient (deltamethrin) using a gas chromatograph coupled to an electron capture detector. The amount of pesticide active ingredient settled to trays after an hour indicated uneven distribution patterns influenced by micrometeorological conditions as well. Maximum half and typically about 30% of the applied insecticide settled in one hour after the treatment. Pesticide drift observed 50 meters away from the target treatment zone was significant in all cases. The measured values ranged between 7% and 31% of the applied deltamethrin and the highest value was observed for K-OTHRIN 10 ULV formulation. Parallel determination of the spray droplet size distribution and specific droplet numbers also confirmed that the drops reach the soil surface and indicated a substantial spray drift.

Introduction
Nowadays pyrethroids are the most widely used insecticide active ingredients to control mosquitoes. Formerly, aerial application of pesticides containing deltamethrin used to be typical in Hungary, and reduction of larvae population by larvicides (*Bacillus thuringiensis* var. *israelensis*) as a targeted biological control has been less significant [1,2]. Adulticides are applied either using aerial applications by aircraft or on the ground by truck-mounted sprayers, which produce small particles by a thermal or a cold (ULV, ultra-low volume) fogger. The authorization of all products formulated for aerial application for imago control was expired in 2019, and only a single product, applied by thermal fog formation, remained temporarily on the market [3]. Ground-based applications are suitable for the treatment of smaller areas, but their drawback is that mosquitoes are easily replaced from nearby regions. Currently a single formulation containing deltamethrin as an active ingredient is provisionally authorized for aerial application [4], and another deltamethrin-based formulation and a formulation containing etofenprox and natural pyrethrins (0.1%) are authorized for ground-based spraying in thermal foggers [1]. Two formulations as spraying agents, restricted for use only by certified experts (category II), containing either cypermethrin or a combination of cypermethrin, tetramethrin and pyriproxyfen are available, the latter also containing piperonyl butoxide as a synergistic additive [5]. In addition, other pyrethroid active ingredients (bioallethrin, cyfluthrin, cyhalothrin, transfluthrin, etc.) are available for home use [1]. According to a European pesticide database [6], deltamethrin, alpha-cypermethrin (aka alphamethrin) and pyrethrins are currently authorized pesticide active ingredients, but tetramethrin is no longer approved in plant protection in the European Union. It is misfortunate that authorization of the active ingredients in mosquito control and agricultural uses are not synchronized, neither in respect of the actual active ingredients, nor for their approval expiration dates.

Gas chromatography (GC) coupled with electron capture detection (ECD) provides a convenient instrumental analytical method with sufficient analytical sensitivity to determine pyrethroids from different matrices [7-9]. In the present work, we studied the settling, drift, as well as the droplet size distribution of the previously used formulations applied in aerial treatments. Settling of the formulation was characterized by laboratory measurement of the active ingredient content (deltamethrin).

Experimental

Eleven trays (size 37.5x26 cm) were placed every 5 meters on the target treatment zone to sample the insecticide settled. Three trays were placed 50 m from the treatment line to determine the pesticide drift. The typical dosages of deltamethrin were between 0.5 and 1.0 g/ha. One hour after application, the material settled to the surface of the trays was dissolved by washing in two subsequent steps by 2x50 ml of a suitably chosen organic solvent. Solutions were stored at 4 °C until instrumental analysis. Several solvents (e.g., hexane, ethanol) were tested for analytical efficacy. Ten milliliters of the organic solutions were evaporated to the dryness in the laboratory and redissolved in 1 ml of isooctane prior to determination.

The active ingredient (deltamethrin) content in ten-fold concentrated samples was measured by the developed GC method. ECD was used for detection; thus, interferences with the white oil matrix used as a carrier for the application or with other components were minimal. The limit of detection is 10 ng/ml, which considering the concentration factor, allows the detection of up to 1 ng of active substance per tray. Sample analyses were carried out on a HP 5890 GC instrument equipped with a HP 7673 autosampler. A Chrompack CP-Sil 8 CB column (30 m x 0.25 mm, 0.25 μm) was used for the separation applying hydrogen 5.0 as a carrier gas and nitrogen 6.0 as make up gas. Injector and detector temperatures were 280 and 300 °C, respectively. The temperature program started with initial oven temperature of 80 °C for 1 min, then increased by the rate of 30 °C/min to 260 °C, followed by the rate of 6 °C/min to 287 °C, and was held for 2 min. Quantification was performed by external calibration with solutions containing 100, 200, 300, 500, 700 and 1000 ng/ml of deltamethrin (Pestanal).

Relative coverage (%) and specific droplet number (number/cm^2) values, as indicators of spray dispersal characteristics, were determined by using oil sensitive papers (TeeJet 52 x 76 mm) placed on the ground along with the sampling trays (see above) to catch the fall-off of the aerial spray reaching ground level. Fifty papers were placed perpendicular to flying direction in every 1 meter, and to follow the spray drift eight papers were placed in every 5 meters up to 50 meters. Result were digitally recorded and statistically (Statistica, ANOVA) evaluated.

Results and discussion

Regarding the solvents to remove the ingredient from the tray surfaces, there were no significant differences between the efficiency of hexane and ethanol, and 4% of water in ethanol did not influence the results either. On-site application of methanol is not recommended due to its toxicity, and in addition resulted in the appearance of a further, unidentified peak in the chromatogram of the extract.

The GC-ECD method allowed a sensitive detection mode of the target analyte and no significant interference with the matrix occurred (Figure 1). In the above concentration range the calibration curve was linear, but calculation in some cases of lower concentrations resulted in negative estimated values due to the nonlinear characteristics of ECD as a function of the analyte concentration. Data were calculated from three parallel injections. Additional points are required in the low region to determine the levels below 100 ng/ml.

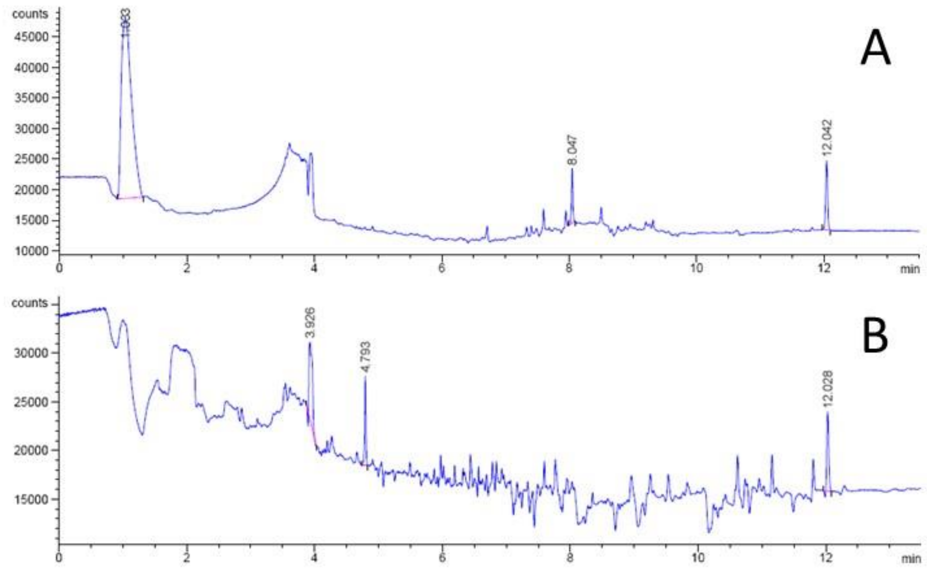

Figure 1. Chromatograms of a calibration solution (A) and a field sample (B), containing 100 and 461 ng/ml of deltamethrin, respectively. The retention time was at 12 min.

Results for a commercially available formulation K-OTHRIN 10 ULV (see Figure 2) showed a smooth distribution pattern indicating a significant drift of deltamethrin. The pesticide drift determined at 50 meters was the highest (31%), whereas 49% of the sprayed active ingredient (0.96 g/ha) settled to the treated area. Thus, this formulation containing oil as carrier medium settled intensively upon 1 hr, and its levels were practically even among the trays, yet this formulation was found to be prone to drift.

Relative coverage values varied between 0.2-0.5%, whereas the specific droplet numbers (see Figure 2) were between 6-27 droplets/cm^2 as an average on the treatment target area. The corresponding values ranged between 0.11-0.42% and 10-22 droplets/cm^2 for non-target areas (50 meters from the flight line). Thus, the untreated area sampled received the same order of magnitude from the spray (and therefore, the active ingredient) than the treated area. Spray drift determined at each point was significant up to 50 meters, which is objectionable from environmental point of view.

Worthy of note that application of large amount of insecticides against the mosquitoes contaminates the aquatic environment and via pesticide drift nearby soils are also polluted. This latter effect gains agricultural importance when the drift settles on cultivated crops. Through this, deltamethrin can occur as an unintended pesticide residue on the crop, which can be problematic in agrochemicals-based technologies, but can cause an irreconcilable problem in organic farming, were to occurrence of synthetic pesticide residues (deltamethrin in this case), even in trace amounts, is strictly prohibited. Although the dosage of deltamethrin for mosquito control is about one tenth (0.96 g/ha) of the recommended dosages in intensive crop protection (7.5-12.5 g/ha), residues may appear e.g. on the surface of organic produce. Thus, spray drift from mosquito control with active ingredients also registered as pesticides can make organic farming, if affected, unmanageable. Moreover, formulating agents (e.g. cyclohexanone added to finished preparations in a proportion as high as 1.7%) or the carrier mineral oil simultaneously appear and pollute the soil surface.

As the investigated compound is highly toxic not only to insects and aquatic organisms but also to humans and vertebrates [5], besides exposure to mosquitoes, its use can damage non-target organisms as well. The determined ecotoxicological parameters, for example the acute EC_{50} values are 0.00056 mg/l and 0.00015 mg/l for for *Daphnia magna* and *Oncorhynchus mykiss*, respectively.

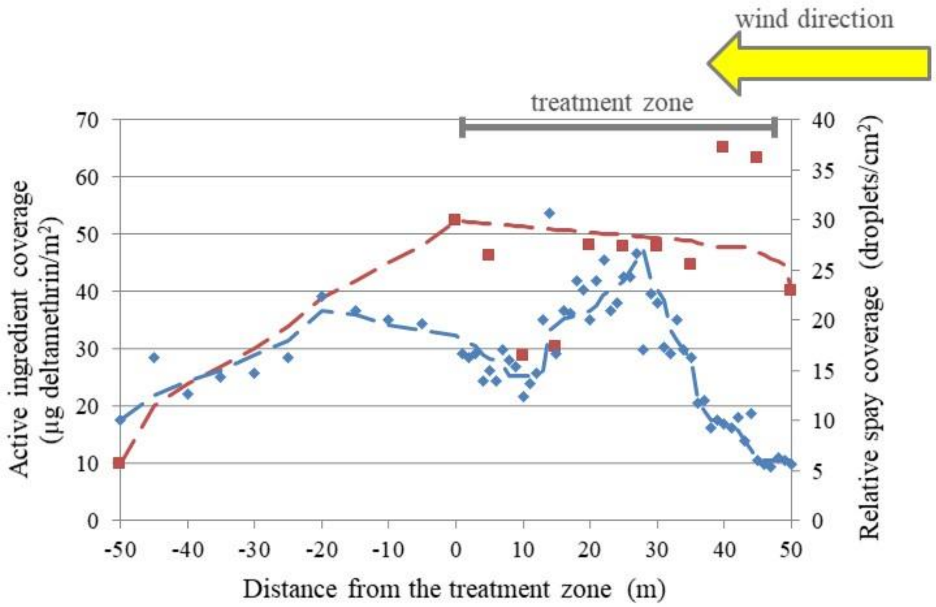

Figure 2. Amounts of deltamethrin (µg/m^2) (■) spray droplet coverage (♦) settled on the ground one hour after the aerial application of K-OTHRIN 10 ULV.

Due to their poor water solubility (e.g., 0.2 µg/l for deltamethrin), pyrethroids are rarely detected in water resources, but contamination of surface waters is more pronounced by the metabolites. Decomposition of deltamethrin results in a smaller compound containing a cyclopropanecarboxylic acid moiety and the remaining phenoxybenzyl derivative, both are enough volatile to be detected by GC-MS. According to our monitoring results, the two corresponding metabolites were observed in June in the Danube River water and in Lake Balaton. Lack of standards prevented the quantification, but they were present not at trace levels.

Conclusion

Physical measurements of the pesticide spray droplet size and their distribution as well as the chemical instrumental analysis of the active ingredient confirmed that spray droplets in aerial application of deltamethrin as an active ingredient adulticide in mosquito control reached the surface of the soil, and the survey also evidenced a substantial spray drift. The amount of the insecticide settled one hour after the treatment varied between 8 and 48%. The results confirmed that the drift of the airborne agent at 50 meters can be significant, up to 31%. In the process, micrometeorological factors play a key role, which is mostly influenced by local vegetation cover. Comparing the two application technologies, it can be concluded that in aerial application, lower concentrations can be measured due to scattering over a larger area, while the thermal foggers (where field dosages maybe higher) result in higher concentrations locally. The large amounts of aerially applied active ingredient pollute surface waters, and despite of its extremely low water solubility, its metabolites were detected in Danube water samples. In addition, in the case of aerial application, the contamination of the agricultural areas over which the aircraft applies or to which the applied agent drifts must not be neglected. Over intensive agricultural areas, this effect is not severe, as the doses used for mosquito control are lower than the dosages of the given active ingredient used against the insects in agriculture, nonetheless, low dosage exposures of pest insects can promote the development of resistance of agricultural pests. However, this type of involvement of organically grown areas is serious, as no synthetic active substance is allowed in this agricultural management practice at all. Formulating agents and solvents of formulations are usually synthetic chemicals, which can also gain significance when they affect organic farming.

Despite of developments in chemical mosquito control technology as well as in spraying machines, pesticide drift upon aerial application is still of concern. Applying the more targeted biological control (reduction of larvae populations), off-target exposure can be eliminated for many aquatic species. Numerous treatments in every year lead to detrimental environmental effects and to unintended contamination of surrounding agricultural areas by synthetic insecticides, which hinders organic farming. Therefore, restriction of aerial applications of insecticide active ingredients is justified and biological control of mosquitoes is recommended.

Acknowledgements
This work was supported by OTKA 112978.

References

[1] B. Darvas, V. Zöldi, M. Mörtl, A. Székács, Abs. IX. Ökotoxikológiai Konf. 9 (2019) 6.
[2] A. Székács, szerk. (2006) Környezetbarát védekezési technológiák csípőszúnyogok ellen. MTA Növényvédelmi Kutatóintézet, Budapest. https://mek.oszk.hu/09900/09992
[3] V. Zöldi (2019) https://index.hu/velemeny/2019/11/28/miert_korszerutlen_a_szunyoggyeritesunk
[4] http://www.hort.hu/2020/szunyogirtas_korlevel_onkormanyzatoknak.pdf
[5] Irtószerek Kereshető Adatbázisa, http://www.oek.hu/ika
[6] Hertfordshire University, Pesticide Properties DataBase, https://sitem.herts.ac.uk/aeru/ppdb/en/atoz.htm
[7] V. Nardelli, F. Casamassima, G. Gesualdo, et al. J Agric. Food Chem. 66(39) (2018)10267 .
[8] A. Kretschmann, N. Cedergreen, J.H. Christensen, Anal. Bioanal. Chem. 408(4) (2016) 1055.
[9] M. Paramasivam, S. Chandrasekaran, Chemosphere 111 (2014)291 .