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Formulation approaches to reduce post-application pesticide volatilisation from glass surfaces

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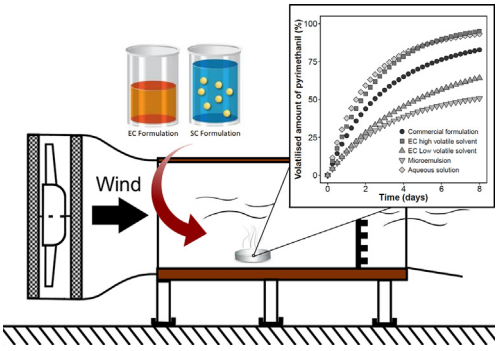
HIGHLIGHTS

- Pesticide formulations with different adjuvants were produced in the lab.
- Active ingredient volatilisation was measured in wind tunnel experiments.
- Effective vapour pressure were measured using SPME-GC/MS.
- Adjuvants and formulation types affected volatilisation.
- Volatilisation rates and effective vapour pressure were correlated.

GRAPHICAL ABSTRACT



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ABSTRACT

Volatilisation is one of the main pathways for pesticide emission to the atmosphere. While formulation strategies and adjuvants are known to affect the fate of active ingredient, no general volatilisation reducing guidelines exist for formulation purposes. Moreover, as limited information on formulation effects is available, current pesticide fate models lack parameters characterising reduction of active ingredient volatilisation. The objective of this study was to investigate the volatilisation reducing potential of formulation types and adjuvants, and to propose an effective vapour pressure for pesticide fate modelling. Several formulations of fenpropimorph, pyrimethanil and tebuconazole were produced and tested in a wind tunnel to evaluate the effect of formulation on active ingredient volatilisation. Produced emulsifiable concentrates with high volatile solvents did not offer any reduction in volatilisation, while the low volatile solvent reduced the volatilisation of pyrimethanil and fenpropimorph with 79.2 and 52.9%, respectively. The microemulsion reduced the volatilisation of fenpropimorph, pyrimethanil and tebuconazole with 57.6, 57.8 and 49.8%, respectively. High surfactant-active ingredient ratios (100:1) reduced the volatilisation of applied amount of pyrimethanil with 50%, on average. The effective vapour pressure of pyrimethanil formulated as a commercial available suspension concentrate was reduced by 33.8%. The commercial available emulsifiable concentrate did not reduce volatilisation of fenpropimorph. Effective vapour pressures of formulated fenpropimorph and pyrimethanil were determined and showed a high correlation with the amount volatilised within 48 h. The saturated vapour pressure is useful when comparing the volatility of active ingredients, but effective vapour pressures are more appropriate to be used in pesticide fate models.

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1. Introduction

Active ingredient (a.i.) volatilisation from soil range from 1 to 30% of the applied dosage (Bedos et al., 2002; Gish et al., 2011; Prueger et al., 2017; Yates, 2006). Vapour losses from plant surfaces range from 1 to 50% for highly volatile active a.i.'s (Bedos et al., 2010; Leistra et al., 2006; Leistra and Van Den Berg, 2007; Rudel, 1997; Willis and McDowell, 1987). While an extensive amount of research has been conducted on the quantification of the volatilisation of either formulated or technical a.i., only a few studies (Da Silva and Da Silva, 1998; Da Silva et al., 2001; De Ruiter et al., 2003; Kubiak, 1999; Stevens and Bukovac, 1987) specifically focus on the influence of the formulation type and adjuvants. Volatilisation reducing strategies often consist of producing controlled release formulations (Chen et al., 1994; Dailey, 2004; Fernandez-Perez et al., 2014). Several coating materials exist for producing capsules around the a.i. of interest (e.g. ethyl cellulose polyvinyl alcohol, gelatin, sodium alginate, polyurea). More recently, the ability of cyclodextrins to alter the physical, chemical, and biological properties of guest molecules upon complexation, has been considered as an innovative way to improve and/or develop new capsule formulations for crop protection products (Morillo, 2006). Formulation as a salt increases the water solubility of the a.i. and provides a lower vapour pressure by the rigid crystallographic structure, which is useful for certain formulation types.

To reduce the volatilisation rate and stability of volatile molecules, fixatives are often used in perfume formulations. A fixative lowers the vapour pressure, and thus, the volatility of the raw material in a perfume oil (Martinez-Guido et al., 2014). Although fixatives are common in perfumery and personal care products [e.g. with DEET (Syed and Leal, 2008)], they are currently not included in agricultural formulations. However, built-in adjuvants have been found to influence the volatilisation of the formulated a.i.'s. Octylphenol surfactants reduce the volatilisation of DDT on polytetrafluoroethylene dishes up to 70% (Stevens and Bukovac, 1987). Moreover, when endosulfan is formulated as an emulsifiable concentrate (EC), volatilisation from *Phaseolus vulgaris* L. (common bean) leaves is distinctly higher than the volatilisation of endosulfan formulated as a water dispersible powder (Kubiak, 1999). Da Silva et al. (2001) observed that volatilisation of technical triadimefon is slightly higher than the volatilisation of triadimefon formulated as a wettable powder. Moreover, when chlorpyrifos is formulated on modified natural nanoclay, volatilisation is clearly reduced (Xiang et al., 2014; Xiang et al., 2013). This is explained by the opening of clogged pores in the clay, resulting in many micro-nanopores, which foster chlorpyrifos adsorption.

Affected volatility is often characterised by an apparent or effective vapour pressure of the a.i. in formulation compared to the saturated vapour pressure of the unformulated or technical a.i. (De Ruiter et al., 2003; Lichiheb et al., 2016; Spencer and Cliath, 1970). However, only the saturated vapour pressure of the technical a.i.'s is available in literature.

Several models [PEARL, SURFATM-pesticide model, Pesticide emission model (PEM), PELMO] exist to estimate the volatilisation based on meteorological data (temperature, humidity, precipitation and solar radiation), physicochemical properties of the a.i. (vapour pressure and molecular weight) and agricultural practices (crop type, application method, application rate) (Lichiheb et al., 2016; Scholtz et al., 2002; van den Berg et al., 2016). All models use the saturated vapour pressure of the a.i. to estimate the volatilisation. However, a.i.'s are formulated with several adjuvants to ensure a stable and efficient product. While the effect of these adjuvants on plant penetration is incorporated in models, their effect on the volatilisation is often neglected or omitted as limited information is available. The SURFATM-Pesticide is one of the rare models including a factor accounting for the effect of formulation on the volatilisation (Lichiheb et al., 2016). However, limited data are available to account for the formulation effect nor is there a validated quantification technique.

In-flight a.i. volatilisation is limited to the smallest droplets and to only a limited time window. Volatilisation from a.i. deposits on soil is calculated to be 5 to 13 times lower than from a.i. deposits on plants (Rudel, 1997) due to the increased turbulence above the foliage and the poor adsorptive capacity of leaf surfaces (Boehncke et al., 1990; Waymann and Rudel, 1995). Hence, the main focus in this study is the reduction of the volatilisation of a.i., present as dried spray deposits, through formulation. In this study, fenpropimorpf, pyrimethanil, and tebuconazole are formulated with several adjuvants. Active ingredient volatilisation is studied in wind tunnel experiments. Vapour pressure measurments are performed using headspace solid-phase microextraction. Active ingredients included in the study were selected based on volatility, relevance for agriculture, stability on crop and in air. The aims of this research is (i) to investigate the volatilisation reducing potential of some formulation types, adjuvants and solvents which are commonly used in commercial crop protection products, (ii) to propose an effective vapour pressure to be used in environmental fate models to improve the modelling of the volatilisation process.

2. Materials and methods

2.1. Reagents and materials

2.1.1. Active ingredients

Analytical standards of bifenthrin, diflufenican, fenpropimorph, metalaxyl, pendimethalin, pyrimethanil, tebuconazole and tolylfluanid were purchased from Sigma-Aldrich (Bornem, Belgium). Stock solutions of analytical standards (1 mg a.i. L^{-1}) of pendimethalin, bifenthrin, metalaxyl, diflufenican, tolylfluanid, tebuconazole, fenpropimorph and pyrimethanil were prepared in hexane for use in the headspace analysis. Stock solutions of fenpropimorph, pyrimethanil and tebuconazole were also prepared in acetonitrile for use in the residue determination. Methanol and acetonitrile were LC–MS grade, hexane was GC–MS grade and were purchased from Merck (Darmstadt, Germany). Water was produced locally though a Milli-Q purification system.

Commercial formulations of fenpropimorph (Corbel™, 750 g a.i. L^{-1}, emulsifiable concentrate, BASF), tebuconazole (Horizon™, 250 g a.i. L^{-1}, emulsifiable concentrate, Oxon Italia) and pyrimethanil (Scala™, 400 g a.i. L^{-1}, suspension concentrate, BASF) were purchased. Technical product of fenpropimorph and pyrimethanil was supplied by BASF (Antwerp, Belgium). Technical product of tebuconazole was supplied by Bayer (Diegem, Belgium). Physicochemical properties of a.i.'s included in this research are shown in Supplementary Data, Table S1.

2.1.2. Adjuvants

An esterified canola oil (ethyl esterified seed oil, ESO) with emulsifiers (Hasten™) was supplied by Surfaplus (Wageningen, The Netherlands). Three alcohol ethoxylate surfactants with 3, 11 and 20 ethylene oxide (EO) additions (respectively Synperonic™ A3, Synperonic™ A11 and Synperonic™ A20), a polymeric surfactant combined with a nonionic surfactant blend (Atlox™ 4913 & 4894) and an alkoxylated phosphate ester (Atplus™ 310) were provided by Croda Crop Care (Goole, United Kingdom). A pinolene-based film-forming emulsion (Spraygard™), an antitranspirant, was supplied by Eastman (Ghent, Belgium). An aromatic solvent (Solvesso™ 200ND) was supplied by ExxonMobil (Antwerp, Belgium). All adjuvants are commonly used in the formulation of crop protection products.

2.2. Preparation of formulations

Stock solutions of fenpropimorph, pyrimethanil and tebuconazole were prepared in methanol (10,000 mg a.i. L^{-1}) to keep concentration equal over all trials. Stock solutions of adjuvants were prepared in Milli-Q water (10,000 mg adjuvant L^{-1}). Different amounts of a.i. and adjuvant stock solution were combined to prepare the formulations. All stock solutions were stored at 4 °C. Concentrations were used to