Science of the Total Environment 578 (2017) 158–166

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Influence of commercial formulation on the sorption and leaching behaviour of propyzamide in soil

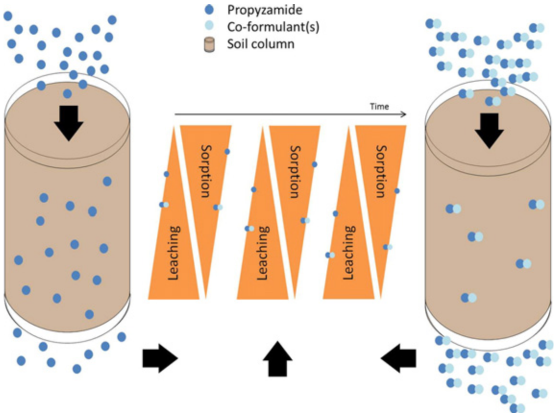
Majid Ali Khan, Colin D. Brown *

Environment Department, University of York, Heslington, York YO10 5NG, UK

HIGHLIGHTS

- Weaker sorption of formulated pesticide for centrifugation method but not for batch.
- Greater leaching of propyzamide from commercial formulation than for technical.
- Enhanced leaching from formulation consistent across soils and time points.
- Very strong increase in sorption and decrease in leaching with time.
- Assessments of pesticide fate that ignore co-formulants may be over-simplified.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 9 July 2016
Received in revised form 25 October 2016
Accepted 1 November 2016
Available online 12 November 2016

Keywords:
Pesticide
Co-formulants
Environmental fate

ABSTRACT

Experiments compared sorption and leaching behaviour for the herbicide propyzamide when applied to two soils either as technical material or in the commercial formulation Kerb® Flo. Sorption was investigated in batch systems as well as using a centrifugation technique to investigate changes in pesticide concentration in soil pore water over incubation periods of up to 28 days. Studies with small soil columns compared leaching of technical and formulated pesticide for irrigation events (6 pore volumes) 1, 7, 14, 21 and 28 days after treatment. There were no differences in sorption of technical and formulated propyzamide when measured by batch systems. Sorption of technical material was significantly greater than that of formulated pesticide in sandy loam ($p < 0.05$), but not in sandy silt loam when measured by centrifugation of soil incubated at field capacity. Partition coefficients measured by batch and centrifugation methods were similar after 1 day and those measured by centrifugation increased by factors of 5.3 to 7.5 over the next 4 weeks. The mass of propyzamide leached from soil columns ranged between $1.1 \pm 0.33\%$ and $14.4 \pm 3.2\%$ of the applied amount. For all time intervals and in both soils, the mass of propyzamide leached was significantly greater (two-sided t-tests, $p < 0.001$) for the formulated product than for the technical material. Leached losses decreased consistently with time in the sandy loam soil (losses after 28 days were 14–17% of those after 1 day), but with less consistency in the sandy silt loam. There was a highly significant effect of formulation on the leaching of propyzamide through soil (two-way ANOVA, $p < 0.001$) as well as highly significant effects of time and soil type ($p < 0.001$). Results are consistent with modelling studies where leaching from commercial products in the field could only be simulated by reducing sorption coefficients relative to those measured with technical material in the laboratory.

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* Corresponding author.
E-mail address: colin.brown@york.ac.uk (C.D. Brown).

http://dx.doi.org/10.1016/j.scitotenv.2016.11.011
0048-9697/

1. Introduction

There has been extensive research over the last four decades into the environmental fate and behaviour of pesticides. The quantification of processes and influencing factors that determine pesticide fate underpins work to ensure their safe use in agriculture. Sorption to soil constituents is a key process that controls the availability of pesticides in the liquid phase, hence their susceptibility to transport within the soil environment and potential for leaching to groundwater (Flury, 1996). Sorption is a time-dependent process, with extent of sorption often increasing with pesticide residence time in soil (Cox and Walker, 1999; Beulke et al., 2004; Mamy and Barriuso, 2007).

The influence of various physico-chemical properties of soil as well as properties of pesticides on their fate and behaviour within soil is well established (Flury, 1996). Nevertheless, there has been limited research into the effect of formulating pesticides into commercial products on fate of the active substance in soil. A range of product additives including solvents, surfactants, spreaders and stickers can be included as co-formulants to improve the performance of an active substance by modifying the physical and chemical characteristics of the spray mixture. Co-formulants can act within formulations to solubilise or emulsify the active substances for better spray application (Rial-Otero et al., 2003) and hence to enhance their effectiveness and bioavailability (Krogh et al., 2003). Liquid products incorporating pesticides with relatively low water solubility usually require use of a water-miscible organic solvent and adjuvants including surfactants to solubilise, suspend, or disperse the active substance of pesticide in the spray mixture (Katagi, 2008).

Studies into the influence of commercial co-formulants on pesticide fate in soil have primarily investigated sorption using batch-equilibrium experiments. Yet, there are conflicting results even for this highly standardised and unrealistic test system. Beigel and Barriuso (2000) and Oukali-Haouchine et al. (2013) suggested that co-formulants may favour maintaining pesticide molecules in solution, thus weakening sorption relative to that of the technical pesticide material. It has also been suggested that slow separation of the pesticide molecule from the surrounding co-formulants within soil may slow the rate of sorption processes relative to technical material (Pose-Juan et al., 2011). Földényi et al. (2013) reported that adsorption of chlorosulfuron on sandy soil decreased markedly in the presence of the forming agent Supragil. However, some studies show an opposite behaviour where sorption in batch systems is greater from the formulated product than from pure active substance (Beigel et al., 1998; Pose-Juan et al., 2010a, 2010b); it has been postulated that co-formulants may enhance the sorption of active substance due either to a layering effect or to enhanced penetration of pesticide onto the less polar sites of soil organic matter (Pose-Juan et al., 2010b). Cox and Walker (1999) provided a rare example where sorption of a 50% wettable powder formulation of linuron was compared with that of technical material based on soil incubation at field capacity and centrifugation to extract pore water at intervals up to 28 days. They reported no significant differences in sorption of the formulated and technical materials.

In addition to the limitations imposed by only studying the influence of sprayable formulations on sorption in unrealistic batch-slurry systems, work on sorption has only very rarely been extended to consider influence of commercial formulation on leaching through soil (Wybieralski, 1992; Sharma et al., 2013). The aim of the present work was to study the influence of formulation and residence time on the sorption and leaching behaviour of propyzamide (3,5-dichloro-N-(1,1-dimethyl-2-propynyl)benzamide, CAS 23950-58-5), a residual benzamide herbicide for control of a range of weeds including blackgrass in oilseed rape, field beans and other crops. This was done by comparing sorption of technical grade propyzamide and a commercial formulation (Kerb® Flo) in two soil types and in systems comprising either a standard batch sorption experiment or a centrifugation approach to measure changes in concentrations of pesticide in soil pore water over time. This was followed by experiments to compare leaching of technical and formulated pesticide through small soil leaching columns at different intervals after application.

Propyzamide was selected for this study because of an apparent anomaly in its reported behaviour. The compound is characterised as having low potential for leaching through soil and is not expected to contaminate groundwater (English Nature, 2003; Dow, 2012). Propyzamide is reported to have a mean soil organic carbon partition coefficient of 840 mL g^{-1} with a range of 548–1340 mL g^{-1} ($n = 6$; University of Hertfordshire, 2016) Irrespective of its physicochemical properties, propyzamide has been detected in surface and groundwater monitoring studies (USEPA, 2008). Moreno-González et al. (2013) identified propyzamide as one of the most frequently detected contaminants in a Spanish coastal lagoon, alongside triazine herbicides and chlorpyrifos; propyzamide was detected in 25 to 100% of samples according to season, with the absolute maximum concentration detected being 0.27 μg L^{-1}. Five priority surface water catchments in the UK were monitored over four seasons starting in 2006/07 for nine pesticides, including propyzamide, that were selected on the basis of usage and previous occurrence in surface water (Environment Agency, 2011); between 2.2 and 5.9% of all samples within a year contained individual pesticides at >0.1 μg L^{-1} with propyzamide a significant contributor over the winter months (maximum concentration 0.66 μg L^{-1}). Much of the contamination in the UK results from leaching through upper soil layers prior to transfer to streams and ditches via subsurface drainage systems; Tediosi et al. (2012) measured peak concentrations of propyzamide in drainflow from a heavy clay soil in the range 24 to 60 μg L^{-1} and calculated total losses to surface water in the month following application of 1.1% of the applied amount. The relatively regular detection of a strongly sorbed pesticide in water monitoring campaigns indicates the need for work to investigate the causal factors. Here we hypothesise that formulation of the active substance into a commercial product may enhance potential for transport within the environment.

2. Materials and methods

2.1. Test materials

Two soils from York, UK were used in experiments. A sandy loam soil of the Blackwood association was collected from the upper 5–15 cm of an arable field margin (national grid reference 4648 4478), and a sandy silt loam soil of the Bishampton association was collected from the upper 5–15 cm of an organic allotment (national grid reference 4597 4473). Check analyses confirmed that neither soil contained residues of propyzamide prior to use. Properties of the two soils are given in Table 1. Soils were air dried at room temperature, passed through a 2-mm mesh sieve, and stored at <5 °C in the dark prior to use.

Chemical properties of propyzamide (University of Hertfordshire, 2016) are: molecular weight 256.1; solubility in water 9 mg L^{-1} at 20 °C; log P 3.3 at pH 7 and 20 °C; and organic carbon partition coefficient 840 mL g^{-1}. Propyzamide is stable to hydrolysis, has a half-life for photolysis in water of 41 days, and a half-life for degradation in aerobic soil at 20 °C of 47 days. Analytical grade propyzamide (purity 99.6%) was purchased from Sigma-Aldrich Ltd. (Dorset, UK), while the commercial formulation Kerb® Flo (suspension concentrate, 400 g L^{-1} (35.3% w/w) propyzamide) was supplied by the Food and Environment Research Agency, York, UK. The declared co-formulant in Kerb® Flo is <5% propylene glycol, a solvent used to aid solubility.

Deionised water was used to make up $CaCl_2$ solution for leaching experiments. All solvents used throughout were HPLC grade.