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INFLUENCE OF COMMERCIAL FORMULATION ON THE SORPTION AND LEACHING BEHAVIOUR OF PROPYZAMIDE IN SOIL

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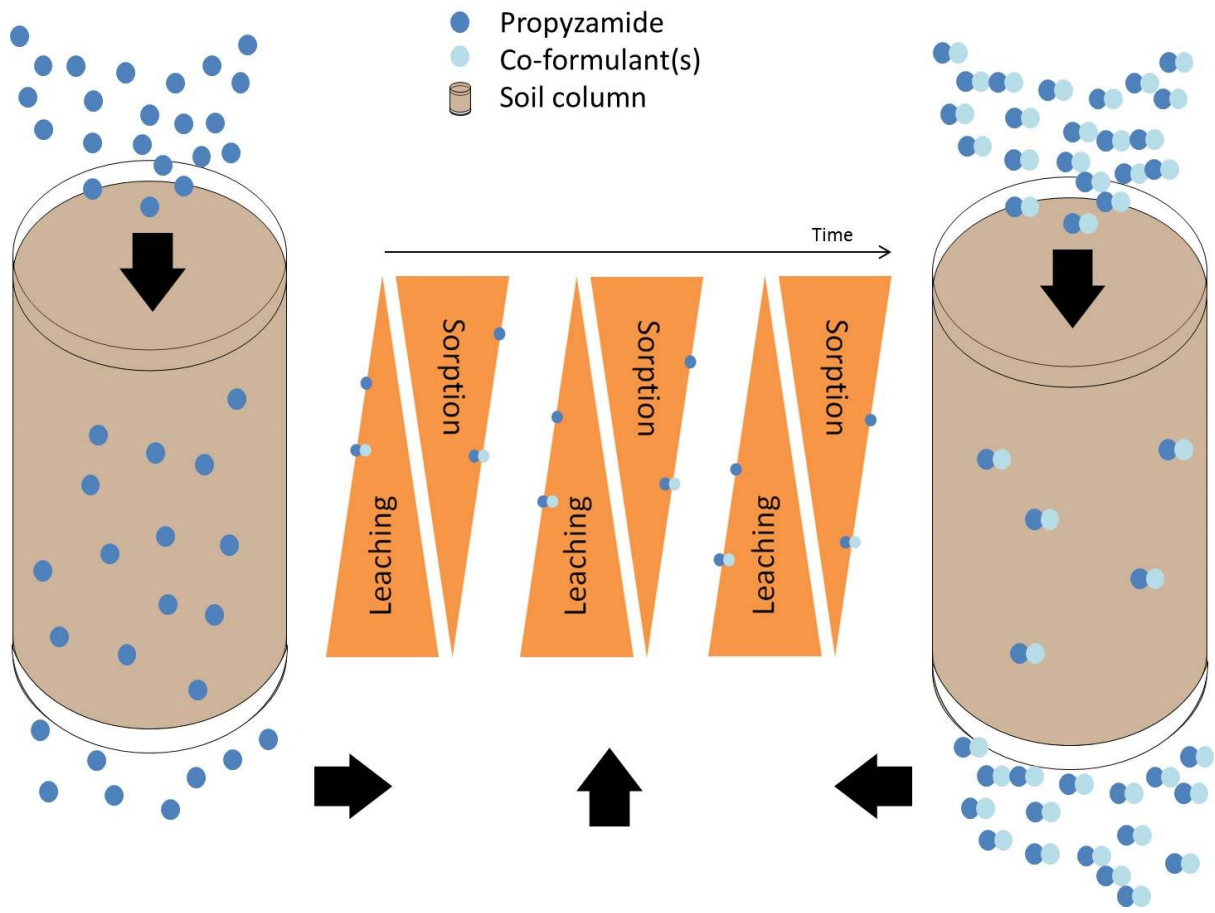
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Highlights

- 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



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.

Keywords: Pesticide; co-formulants; environmental fate;

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 $<5^{\circ}\text{C}$ 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.

2.2. Measurement of sorption-desorption by standard batch equilibrium method

Sorption of propyzamide in the two soils was determined for technical and commercial formulation of propyzamide using a standard batch equilibrium method following OECD guideline 106 (OECD, 2000). Preliminary studies identified an optimal soil-to-solution ratio of 1:5 and an equilibration period of 24 hours (data not shown). Soil (2 g dry weight equivalent) was transferred into 50 mL PTFE centrifuge tubes and was pre-equilibrated with 9.5 mL of 0.001M CaCl₂ solution by shaking on an orbital shaker at 250 rpm for 15 hours. After pre-equilibration, the soil suspensions were spiked with either 2 to 10 µL of a 1000 µg active substance (a.s.) mL⁻¹ stock solution of technical grade propyzamide in methanol or 0.1 to 0.5 mL of a 20 µg a.s. mL⁻¹ stock solution of Kerb® Flo in 0.001M CaCl₂. The volume of 0.001M CaCl₂ solution was adjusted by weight to achieve the required soil to solution ratio of 1:5, giving starting concentrations (in triplicate) of 0.2, 0.3, 0.4, 0.5 and 1.0 µg a.s. mL⁻¹ for both technical material and formulated product. Duplicate control tubes comprised soil with herbicide-free 0.001M CaCl₂ solution or 1.0 µg a.s. mL⁻¹ solutions of technical and formulated materials in 0.001M CaCl₂ with no soil. Centrifuge tubes were returned to shaking for a period of 24 hours. Thereafter, soil suspensions were centrifuged at 4000g for 15 minutes to separate the two phases. Supernatant (1.0 mL) was evaporated to dryness under a gentle stream of nitrogen at room temperature and the pesticide was re-dissolved into 1 mL (tubes with initial concentrations of 0.2 and 0.3 µg mL⁻¹ propyzamide) or 1.4 mL (remaining initial concentrations) of hexane. Samples were analysed by GC-MS to determine the concentration of propyzamide remaining in the solution at equilibrium (C_e, µg mL⁻¹). The concentration of pesticide in the solid phase C_s (µg g⁻¹), was calculated by difference and a Freundlich sorption isotherm was fitted to the data using SigmaPlot (Systat Software Inc):

$$C_s = K_f C_e^{n_f}$$

where K_f is the Freundlich sorption coefficient (mL g^{-1}), and n_f is the Freundlich exponent.

Samples spiked with the highest initial concentrations in the sorption experiment ($1 \mu\text{g mL}^{-1}$) were used for the desorption study (five replicates). Following centrifugation after 24 h of shaking as described above, the supernatant was removed as completely as possible and replaced by weight with an equivalent volume of herbicide-free 0.001M CaCl_2 solution. The soil was re-suspended and the suspensions were shaken for 24 hours. After this, the soil suspensions were centrifuged and an aliquot of the supernatant was analysed to quantify the amount of propyzamide desorbed. The desorption process was repeated a further two times. Desorption isotherms were described using the non-linear form of the Freundlich equation:

$$C_s = K_{fd} C_e^{n_{fd}}$$

where K_{fd} and n_{fd} are parameters related to the capacity to desorb and to the intensity of desorption, respectively. The hysteresis index, HI was then calculated as the ratio of the slope of the sorption curve to the slope of the desorption curve.

2.3. Measurement of sorption by centrifugation

Soil (10 g dry weight equivalent) was weighed into separate 60-mL glass jars for each treatment and replicate. Soil was wetted to 0.25 mL below field capacity (Table 1) by addition of 0.001M CaCl_2 and pre-incubated for 24 hours at $<5^\circ\text{C}$ in the dark. Soil samples were then treated with 50 μg active substance per 10 g of soil (the same pesticide-to-soil ratio as in subsequent leaching experiments). Technical grade propyzamide was added as 0.1 mL of a 500 $\mu\text{g a.s. mL}^{-1}$ stock in acetone followed, after allowing acetone to evaporate, by 0.25 mL of 0.001M CaCl_2 . Formulated product was added as 0.25 mL of a 200 $\mu\text{g a.s. mL}^{-1}$ stock made up from Kerb® Flo in 0.001M CaCl_2 . Soil samples were thoroughly mixed with a spatula for a few minutes and then incubated at $<5^\circ\text{C}$ in the dark for a period of up to 28 days. Controls comprised soil treated in the same way but without addition of propyzamide.

Water contents were checked and re-adjusted by weight for any water losses every 2-3 days. Water contents were also checked and re-adjusted at time of sampling.

To assess the availability of pesticide in soil solution, soil samples were taken 1, 7, 14, 21 or 28 days after treatment and the entire sample was transferred into the insert of a 50-mL centrifuge tube (Vivaspin 20 polypropylene, 0.2 μm PES) fitted with a glass microfibre filter (Whatman GF/F, 25 mm diameter, 0.45 μm pore). At each sampling interval, four replicate samples for each treatment plus two controls without pesticide addition were centrifuged for 30 minutes to collect an aliquot of soil pore water. Samples were centrifuged at 1500g corresponding to a pressure of ca. 200 kPa following the protocol proposed by Kah and Brown (2007). The pressure of 200 kPa was also proposed by Walker and Jurado-Exposito (1998) to extract soil solution on the assumption that this corresponds to the boundary between mobile and immobile water. 0.5 mL of the extracted soil solution was evaporated to dryness under a gentle stream of nitrogen at room temperature and the pesticide was re-dissolved into 0.7 mL (1 and 7 day samples) or 1.0 mL (14, 21 and 28 day intervals) hexane prior to analysis by GC-MS.

A separate degradation check was carried out with soil (5 g dry-weight basis) transferred into 30-mL glass bottles and treated as described above but with 25 μg technical or formulated propyzamide. Samples were incubated at field capacity, $<5^{\circ}\text{C}$ and in the dark and four replicates per treatment were sampled after 1, 7, 14, 21 or 28 days. At sampling, soils were air-dried in a fan oven at 20°C for 24 hours, then sequentially extracted by vigorous shaking with acetonitrile. The soil was allowed to settle and supernatant was removed, combined and centrifuged at 4000g for 20 minutes. 0.3 mL of the supernatant was evaporated under a gentle stream of nitrogen and the chemical was re-dissolved in 2 mL hexane for analysis by GC-MS.

2.4. Leaching experiments

Leaching experiments were carried out in PVC columns (2 cm i.d. x 10 cm length). Each column was manually packed with 20 g of soil on an oven-dry weight basis with glass wool at the bottom to prevent loss of soil. Four replicate columns were prepared per treatment and for each leaching interval. Either sandy loam or sandy silt loam soil was added to the columns in steps followed by gentle tapping to ensure uniform packing and achieve the same height of soil within each column. Columns were then saturated from the base with 0.01M CaCl₂ and allowed to drain freely for 24 h under gravity. After this time, water held within the glass wool plug was evacuated by applying a small suction to the base of the column using a plastic syringe. The bulk density of the packed column was 1.18 and 1.12 g cm⁻³ for sandy loam and sandy silt loam soils, respectively, and these values were used to determine total porosity of 0.54 and 0.56 cm³ cm⁻³, respectively, based on an assumed particle density for topsoil of 2.55 g cm⁻³ (Avery and Bascomb, 1982). One pore volume for each soil column was thus equivalent to 9.2 cm³ for the sandy loam soil and 10.0 cm³ for the sandy silt loam soil.

Soil columns were treated with either technical or formulated propyzamide, giving a total of 80 treated columns (40 per soil type). A further 20 columns (10 per soil type) were untreated to act as controls. Each treated column received 100 µg of the respective pesticide. This is equivalent to 3.2 kg a.s. ha⁻¹ which is larger than typical field application rates for propyzamide and was selected to facilitate analysis for pesticide in leachate. Columns receiving technical pesticide were treated with 0.1 mL of a 1000 µg a.s. mL⁻¹ solution in acetone; the solvent was allowed to evaporate before the addition of 0.5 mL deionised water. Columns receiving formulated pesticide were treated with 0.5 mL of a 200 µg a.s. mL⁻¹ solution of the commercial formulation in deionised water. Immediately after treatment, a 1-

cm layer of acid-washed sand was added to the top of each column. All columns were incubated in the dark and at $<5^{\circ}\text{C}$ until leaching.

Separate columns were leached either 1, 7, 14, 21 or 28 days after pesticide application. On each leaching event, one set of four replicates from each treatment together with two control columns per soil type were irrigated with 55.2 mL of 0.01 M CaCl_2 solution using a 323S Watson Marlow peristaltic pump at the rate of 12.6 mL hr^{-1} . This is equivalent to 6.0 and 5.5 pore volumes for sandy loam and sandy silt loam soils, respectively. Leachate was collected as a single fraction at the bottom of each column and quantified by weight. A 1-mL aliquot of each leachate sample was evaporated to dryness under nitrogen and re-dissolved in 1 mL of hexane prior to analysis.

2.5. Analytical methods

Propyzamide samples were analysed by GC-MS. A PerkinElmer (Cambridge, UK) Clarus 680 gas chromatograph equipped with a Clarus 600 mass spectrometer and automatic split-splitless injector was operated in electron impact ionization mode with an ionizing energy of 70eV, scanning from m/z 50-500 at 0.2 s per scan. The ion source temperature was 180°C . The electron multiplier voltage was maintained at 323 V, and a solvent delay of 3 min was employed. An Elite-5MS fused silica capillary column (30 m x $0.25 \mu\text{m}$ i.d. and $0.25 \mu\text{m}$ film thickness) supplied by PerkinElmer was used. The oven temperature was maintained at 90°C for 1 min, followed by a ramp to 270°C at a rate of $20^{\circ}\text{C min}^{-1}$ for propyzamide. Helium was used as carrier gas with a flow rate of 20 mL min^{-1} . Sample ($1 \mu\text{L}$) was injected in splitless mode and the injector temperature was maintained at 250°C . Pre- and post-injection needle washes were programmed at six. Analysis was performed with selected ion monitoring (SIM) mode using primary mass ions of m/z 173 for quantification of propyzamide. The target and qualifier abundances were determined by injection of

propryzamide standards under the same chromatographic conditions using full scan with the mass/charge ratio ranging from m/z 50-500. Compound was confirmed by retention time and the identification of target and qualifier ion. Retention times had to be within 0.2 min of the expected time, and qualifier-to-target ratios had to be within a 10% range for positive confirmation. The concentrations of the compound were determined by comparing the peak area in the samples to those found for pesticide standards of known concentrations. The limits of detection and quantification were 0.02 and 0.05 $\mu\text{g mL}^{-1}$, respectively. Recovery of propryzamide from spiked water samples was $99.5 \pm 5.6\%$, whilst recoveries from spiked samples of the sandy loam and sandy silt loam soils were $99.9 \pm 4.4\%$ and $102.9 \pm 1.5\%$, respectively.

2.6. Data analysis

Leaching behaviour was assessed based on the total mass of pesticide lost in leachate from individual soil columns. Datasets were tested for normality using the Shapiro-Wilk test. Two-sided t-tests were used to investigate differences in sorption measured by centrifugation and leaching losses from columns treated with technical grade and commercial formulations of propryzamide. Two-way and multi-way ANOVA was carried out to test the significance of formulation, residence time and soil type on the sorption and leaching behaviour of pesticides. Tukey post-hoc tests were undertaken to test for differences between individual treatments over time; this is a pairwise comparison, similar to a t-test, but designed to compensate for the increased likelihood of a significant result occurring due to chance as the number of comparisons increases. All statistical analyses were undertaken with SPSS (IBM Analytics).

3. Results

3.1. Sorption studies by batch-equilibrium method

Sorption and desorption isotherms for technical grade and formulated propyzamide in the two soils are shown in Figure 1 whilst Table 2 gives sorption parameters and goodness-of-fit values. Sorption isotherms were relatively well described by the Freundlich equation with regression coefficients (r^2) ranging between 0.93 and 0.95. Sorption behaviour for formulated and technical material was similar in both soils. Fitted values for the Freundlich coefficient and Freundlich exponent were smaller for the technical material in both soils. Differences between means were less than the fitting error for the sandy loam soil but not for the sandy silt loam (Table 2). Sorption behaviour in all treatments was strongly non-linear ($n_f \leq 0.70$); values for the Freundlich exponent were smaller for the technical material in both soils, but differences were less than the fitting error (Table 2).

Desorption isotherms were strongly hysteretic for all treatments (Fig. 1). There was more uncertainty associated with the fitting of desorption parameters (r^2 0.62-0.87, Table 2) and results indicated that there were no significant differences between Freundlich desorption parameters for the different treatments. Hysteresis indices were much less than one for all treatments, with somewhat smaller values for the formulated product in both soils. Between 30 and 35% of the propyzamide sorbed to soil after 24 hours was desorbed across the three desorption steps.

3.2. Sorption studies by centrifugation method

There was no degradation over the duration of the study, with degradation checks yielding recoveries between 97.8 and 103.5% of the applied amount. Changes in the availability of propyzamide in soil pore water over time are shown in Fig 2. Concentrations in soil pore water for the sandy loam soil were consistently and significantly larger (two-sided t-

tests, $p < 0.05$) for the formulated product compared to the technical material. Mean concentrations for the formulated product were 31-80% larger than those for the technical material across the different time intervals. In contrast, there were no significant differences (two-sided t-tests, $p > 0.05$) for the two treatments in the sandy silt loam soil.

The mass of propyzamide in pore water decreased rapidly and consistently with time for all treatments (shown by the letters in Fig. 2 indicating statistical differences determined with a Tukey post-hoc test). For example, the mass of propyzamide extracted from pore water at day 7 and day 28 was only 39-61% and 14-19%, respectively, of that extracted at day 1. Nevertheless, the overwhelming majority of propyzamide was sorbed to soil constituents throughout; across the various treatments, sorbed material represented 97.2-97.9 and 99.5-99.7% of the total propyzamide present at days 1 and 28, respectively.

A multi-way ANOVA showed that the effects of formulation, residence time and soil type on the availability of propyzamide in pore water were highly statistically significant ($p < 0.001$). There was a highly significant interaction between formulation and soil type ($p < 0.001$), but not between residence time and formulation ($p = 0.713$) or between residence time and soil type ($p = 0.079$).

Fig. 3 shows the change in point values for partition coefficients (K_d , mL g^{-1}) over time calculated as concentration sorbed divided by concentration in soil solution from the centrifugation experiment. Partition coefficients were very similar across the two soils and for technical and formulated material (range 8.09 ± 1.34 to $10.63 \pm 1.12 \text{ mL g}^{-1}$). Notably, distribution coefficients for the centrifugation experiment at 1 day after treatment matched linear partition coefficients calculated for the 24-hr batch-equilibrium study (range 9.21 ± 1.43 to $10.88 \pm 2.30 \text{ mL g}^{-1}$). Thereafter, partition coefficients for the centrifugation experiment increased markedly with time, increasing by factors of 5.3 to 7.5 over the 28-day experiment. Partition coefficients were always larger for the technical material than for the formulated

product; these differences were significant at all time intervals for the sandy loam soil (Fig. 3a; two-sided t-tests, $p < 0.05$), but only significant for samples taken 21 days after treatment in the sandy silt loam (Fig. 3b; two-sided t-tests, $p < 0.05$).

3.3. *Leaching behaviour of propyzamide*

Figure 4 presents the results of leaching through small soil columns. The leached mass of propyzamide across the whole dataset 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 average mass of propyzamide leached from the columns was greater for the formulated product than for the technical material and this difference was significant in every case except for day 7 in the sandy silt loam soil and day 14 in the sandy loam (two-sided t-tests, $p < 0.05$). Leached losses decreased consistently with time in the sandy loam soil (shown by the letters in Fig. 4 indicating statistical differences determined with a Tukey post-hoc test) and losses after 28 days were only 14 and 17% of those after 1 day for the technical and formulated material, respectively. Losses in leachate also decreased up to 14 days after treatment in the sandy silt loam soil (Fig. 4), but there was a marked increase in leaching at the final (technical grade) or final two (formulation) sampling intervals. A multi-way ANOVA confirmed that there was a highly significant effect of formulation on the leaching behaviour of propyzamide in soil ($p < 0.001$) as well as highly significant effects of both time and soil type ($p < 0.001$). There were significant interactions ($p < 0.05$) between all three factors evaluated.

4. Discussion

Although the environmental fate of pesticides has been investigated over at least 40 years, there are relatively few studies that directly investigate the effect of formulation on pesticide behaviour in soil. One exception is the influence of controlled-release formulations

that are expressly designed to restrict leaching and/or maintain efficacy in soil over a prolonged time period (Dubey et al., 2011). For pesticide formulations designed to be sprayed onto plant or soil surfaces, the limited information available primarily comprises batch-equilibrium studies comparing sorption of formulated material with that of the pure active substance. This is a relevant experiment because the batch-equilibrium test (e.g. OECD 106) undertaken with technical grade active substance is a bedrock both for our understanding of pesticide fate and for risk assessment to ensure the safe use of plant protection products.

Our results challenge the existing literature on effects of formulation on pesticide fate. Whilst there were no significant differences in sorption measured in batch-equilibrium studies, we identified clear effects of the commercial formulation on both concentrations of propyzamide present in soil pore water at realistic soil water contents and on leaching through small soil columns. The batch-equilibrium study involves addition of excess water to create a soil-slurry that will likely reduce and mask any interactions between pesticides, co-formulants and soil constituents. In contrast, the centrifugation technique was developed to measure pesticide sorption under realistic soil water contents where formulation effects should be much closer to those occurring in the field (Walker et al., 2005). The soil is maintained at field capacity throughout the experiment and there is minimal disturbance to soil structure once the initial air-drying and sieving to 2-mm is complete.

We found a highly significant effect of pesticide formulation on the fate of propyzamide that resulted in weaker sorption to sandy loam soil incubated at field capacity and greater leaching through small columns of both soil types. These effects were consistent across all time intervals studied. Whilst we have not investigated the mechanisms underpinning this finding, it is likely that the surfactants within the Kerb® Flo formulation remained associated with the active substance, keeping a greater proportion in soil solution and acting to retard extent of sorption to soil and thus to exacerbate leaching (Beigel and

Barriuso, 2000; Oukali-Haouchine *et al.*, 2013). The findings are consistent with the literature whereby propyzamide is found reasonably frequently in water quality monitoring studies despite the relatively strong sorption to soil constituents within the literature. This paradox has confounded attempts to simulate the environmental behaviour of propyzamide. Two recent studies at different scales and using different models reported that it was necessary to decrease soil organic carbon partition coefficients used as input by a factor of ca. 3 relative to published values in order to match observations for transport via drainflow in a 15.5-ha headwater catchment (Tediosi *et al.*, 2013) and occurrence of propyzamide in a river draining a 650-km² catchment (Villamizar & Brown, 2017); initial simulations in both studies used the published K_{oc} (840 mL g⁻¹), but this had to be reduced to 250 and 292 mL g⁻¹ to fit observed behaviour in the two studies, respectively.

The partition coefficients (K_d) values we measured for technical propyzamide are smaller than those reported in regulatory data (University of Hertfordshire, 2016), but are in line with those reported by Pederson *et al.* (1995); in four soils ranging in organic carbon content between 0.6 and 2.3%, the authors reported K_d values of 1.4-5.6 mL g⁻¹, equivalent to K_{oc} values of 228 to 335 mL g⁻¹. The partition values for the technical grade and commercial formulation of propyzamide obtained by the centrifugation method after one day of equilibration were similar to partition coefficients obtained after 24 hours by the batch method (Table 2 and Fig.3). Previous studies suggest that the partition coefficients obtained by batch method are generally greater than those from extraction using centrifugation (Walker and Jurado-Exposito, 1998; Yazgan *et al.*, 2005; Kah and Brown, 2007; Folberth *et al.*, 2009). This is attributed to the action of shaking in batch systems causing disaggregation and thus more intimate contact between pesticide molecules and sorption sites on soil. (Kah and Brown, 2007; Folberth *et al.*, 2009). The distribution coefficients measured by

centrifugation show a large increase in the strength of sorption of propyzamide over time for both soils and for both technical and formulated material (Fig. 3).

Time-dependent sorption is attributed in the literature both to physical control on the migration of pesticide molecules to binding sites within the soil matrix and to preferential degradation of pesticide in solution compared to that sorbed to soil (Beulke *et al.* 2004). Pesticide degradation was inhibited by the incubation conditions throughout the four-week experiments reported here, implying that the former of these two mechanisms predominated. The increases in strength of sorption measured here (partition coefficients increased by factors of 5.3-7.5 over 28 days incubation) are towards the top end of the range of increases reported in the literature. For example, relative increases in sorption have been reported as 1.6-1.7 for isoproturon and linuron over 28 days (Cox and Walker, 1999), 3.2-3.8 for imidacloprid over 100 days (Oi, 1999), and 4.5-6.6 for sulfonylaminocarbonyltriazolinone over 84 days (Koskinen *et al.*, 2002).

In sandy loam soil, the increase in strength of sorption over time was matched by a decrease in the mass of pesticide lost during leaching (Figs. 2 and 4). The behaviour is consistent with field observations that the time between pesticide application and the first leaching event is an important control on leaching behaviour (Renaud *et al.*, 2004; Brown and van Beinum, 2009). Mass of propyzamide leached through soil also decreased over the first 14 days of the experiments with the sandy silt loam (Fig. 4). Thereafter, an increase in leached mass was observed. This is an unexpected behaviour that might be caused by facilitated transport with colloidal material. We do not have direct evidence, but there could have been some breakdown of soil aggregates in this finer textured soil that did not occur in the sandy loam.

Fig. 5 compares changes in propyzamide concentration in pore water over time with changes in leached mass for events occurring at corresponding intervals after treatment.

There is a rapid decrease in pore water concentrations that is relatively consistent across the two soils and for both formulated and technical propyzamide. Fitting simple first-order kinetics to these soil pore water concentrations yielded times for 50% reduction of pore water concentrations of 10.2-11.8 days (r^2 0.89-0.98). Applying the same approach to leaching behaviour yielded times for 50% reduction in leached load of 10.0 days (technical) and 18.4 days (formulated) in the sandy loam soil. Changes in leaching over time were less consistent in the sandy silt loam, and here data yield times for 50% reduction in leached load of 44-51 days. The mass of propyzamide lost in leachate was much greater than that present in pore water at the onset of leaching (Fig. 5). This indicates significant desorption of the herbicide over the course of the 4.4-hour leaching period and implies a need to investigate whether commercial formulation influences the desorption process under natural soil conditions. Figure 5 also confirms the significantly greater availability of formulated than technical propyzamide in the sandy loam soil, but not in the sandy silt loam. Similar behaviour for the sandy silt loam under batch and centrifugation conditions suggests that controls on sorption were similar in the two systems, possibly due to a greater role for dissolved and colloidal organic matter in sorption relative to that in the sandy loam soil which has less organic matter.

Every aspect of the experiments reported here was identical for treatments with technical and formulated propyzamide except for the initial addition of test material to soil. The only named co-formulant in Kerb® Flo is propylene glycol (<5%) which acts as a solvent to aid solubility. The formulated treatments were thus made up directly in CaCl_2 solution for addition to soil. In contrast, the technical pesticide had to be made up in a solvent due to the low solubility of propyzamide in water (9 mg L^{-1}). For batch sorption experiments, technical pesticide was added to 10 mL soil solution in <10 μL methanol, so solvent effects would be negligible. For centrifugation and leaching experiments, technical pesticide was

added in 0.1 mL acetone which was allowed to evaporate prior to adding pesticide-free CaCl₂ solution to match that added in the formulated treatments. Dosing in acetone is a possible source for experimental artefacts if, for example, the solvent resulted in enhanced transfer of pesticide into soil aggregates or precipitation of propyzamide on soil surfaces.

Whilst the effect of formulation was very consistent across both centrifugation and leaching experiments, the soil columns were small and the rate of irrigation was high. The experimental set-up for leaching tests was selected to accommodate the large number of replicates, but an alternative would have been to run standard regulatory leaching studies such as the OECD 312 test (OECD, 2004). We have demonstrated an effect of commercial formulation on sorption and leaching in these systems, but further work is needed to assess the relevance to field conditions. For example, the influence of co-formulants on sorption and leaching may be significant in the immediate topsoil but may become less important as the pesticide moves to depth. Alternatively, the effect may be significant in the first leaching event(s) after application, but may become less important over time. Finally, it will also be important to investigate the extent to which the effect of commercial formulation demonstrated here for propyzamide can be generalised to other compounds. We have undertaken leaching experiments with a further three pesticides to start addressing this requirement (Khan and Brown, 2016).

5. Conclusion

Experiments have demonstrated a highly significant effect of commercial formulation on the leaching behaviour of the herbicide propyzamide relative to the pure technical active substance. Co-formulants did not influence sorption in batch-slurry systems. Centrifugation experiments that extracted pore water from soil incubated at field capacity identified significantly greater sorption of technical material compared to formulation for one of the

two soils studied. There were very strong increases in strength of sorption over time and this resulted in significantly reduced leaching as the time between treatment and irrigation increased. Results are reported for small, controlled systems and these need to be scaled up to investigate behaviour under conditions closer to the field. Nevertheless, the observations are in accordance with recent modelling exercises for propyzamide. Potentially, there are important implications for the assessment of environmental fate of pesticides which has been based to date on the assumption that sprayable formulations do not influence behaviour of the active substance in soil.

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Table 1

Main properties of the two soils studied (mean plus standard deviation in parentheses for three determinations).

Soil texture	pH in water	Sand (%)	Silt (%)	Clay (%)	Water content at field capacity (g g ⁻¹)	Water holding capacity (g g ⁻¹)	Organic matter (%)
Sandy loam	5.14 (0.03)	62.3 (0.39)	36.5 (0.40)	1.2 (0.01)	0.22 (0.01)	0.37 (0.02)	2.7 (0.58)
Sandy silt loam	6.71 (0.03)	39.4 (0.15)	56.8 (0.15)	3.8 (0.1)	0.29 (0.01)	0.42 (0.03)	4.30 (0.58)

Table 2

Freundlich sorption coefficients and partition coefficients calculated for technical grade and commercial formulation of propyzamide. Values in parentheses are the standard errors associated with the model fit.

Treatment	Sorption			Desorption				
	K_f (ml g^{-1})	n_f	r^2	K_{fdes}	n_{fdes}	r^2	HI	Desorbed proportion %
Sandy loam								
<i>Technical material</i>	6.13 (0.61)	0.64 (0.06)	0.93	3.83 (0.23)	0.168 (0.03)	0.68	0.26	32.9
<i>Formulated product</i>	6.50 (0.63)	0.70 (0.06)	0.94	3.60 (0.14)	0.146 (0.02)	0.87	0.22	31.9
Sandy silt loam								
<i>Technical material</i>	5.54 (0.44)	0.55 (0.05)	0.95	3.62 (0.20)	0.170 (0.02)	0.74	0.31	34.5
<i>Formulated product</i>	6.91 (0.71)	0.66 (0.06)	0.94	3.61 (0.19)	0.104 (0.02)	0.62	0.16	30.6

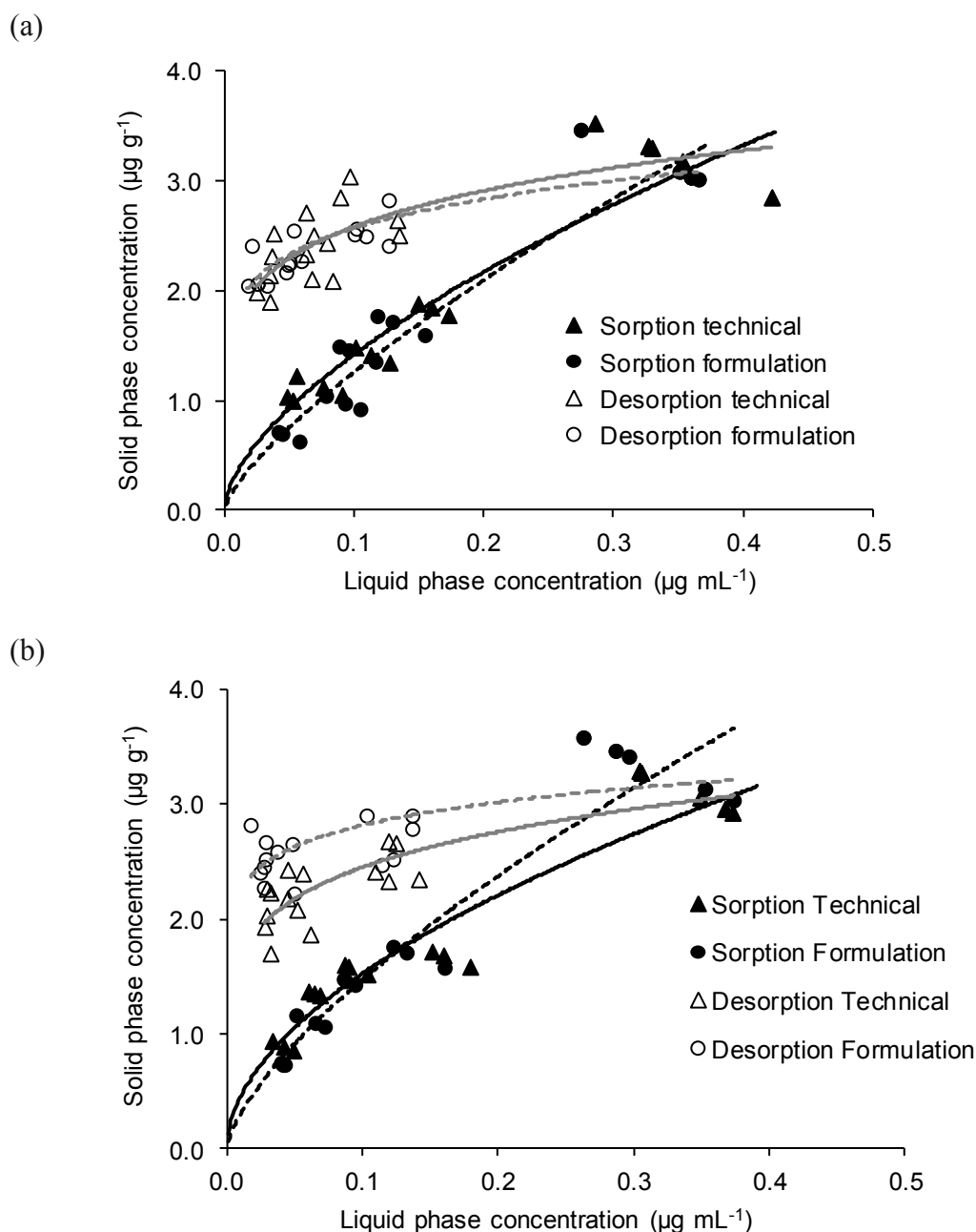


Fig. 1. Batch sorption (closed symbols) and desorption (open symbols) isotherms of technical grade (triangles) and commercial formulation (circles) of propyzamide in (a) sandy loam soil and (b) sandy silt loam soil. The black and grey solid and dotted lines represent the sorption and desorption isotherms from the technical grade material and formulated product, respectively. All points are individual replicates; there were three replicates for each sorption measurement and five replicates for each desorption measurement (Section 2.2).

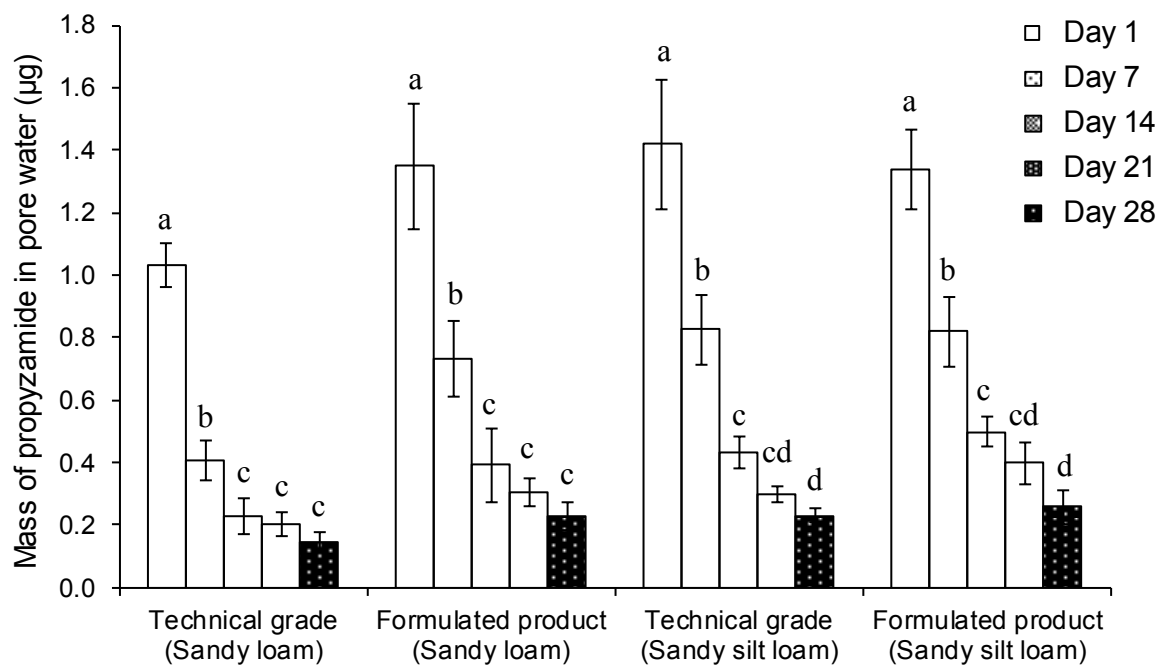


Fig. 2. Mass of propyzamide found in pore water in sandy loam and sandy silt loam soils treated with technical grade and commercial formulation of propyzamide (Kerb® Flo). Values are means \pm standard deviations of four replicates. Letters on the bars show significant differences between time intervals within the treatments (Tukey post-hoc test).

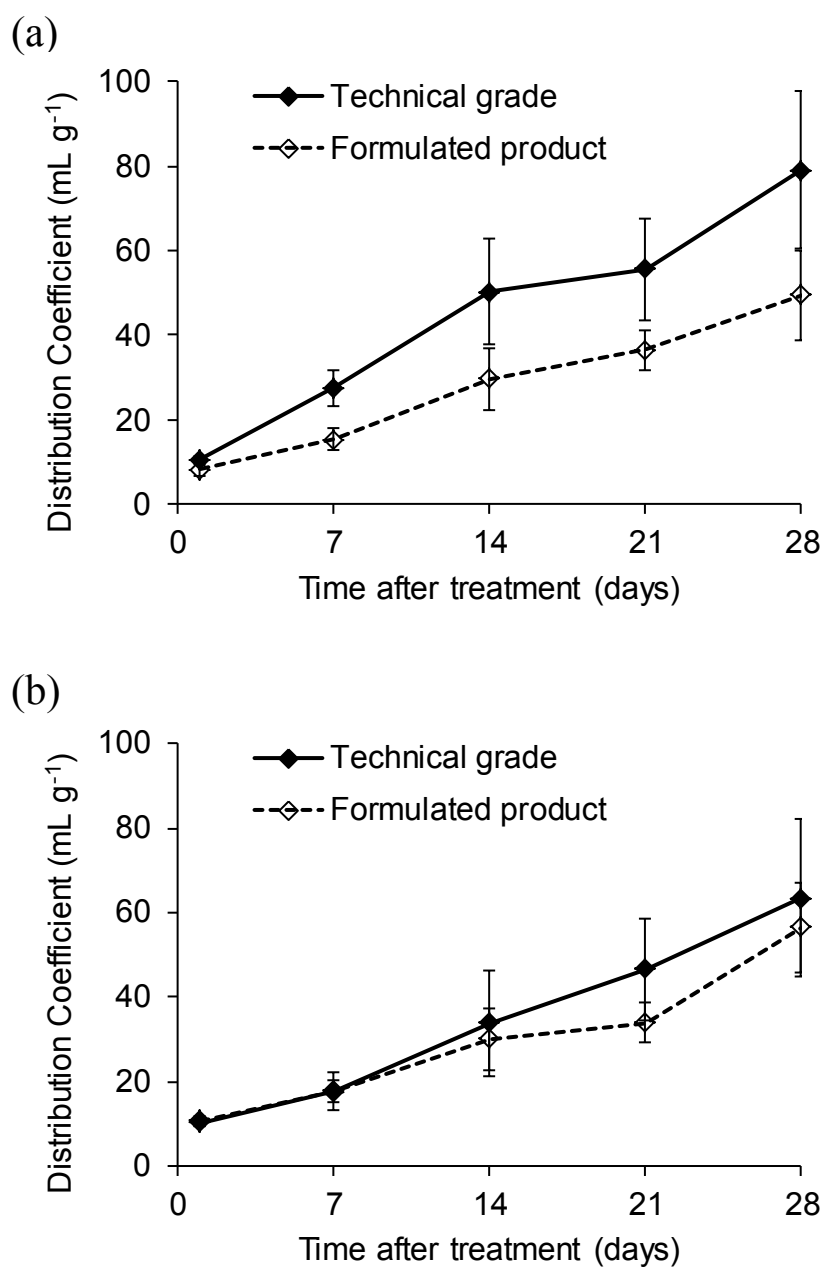


Fig. 3. Change in distribution coefficients of technical grade and commercial formulation of propyzamide over time in sandy loam soil (a) and sandy silt loam soil (b). Values are the means ± 1 standard deviation of four replicates.

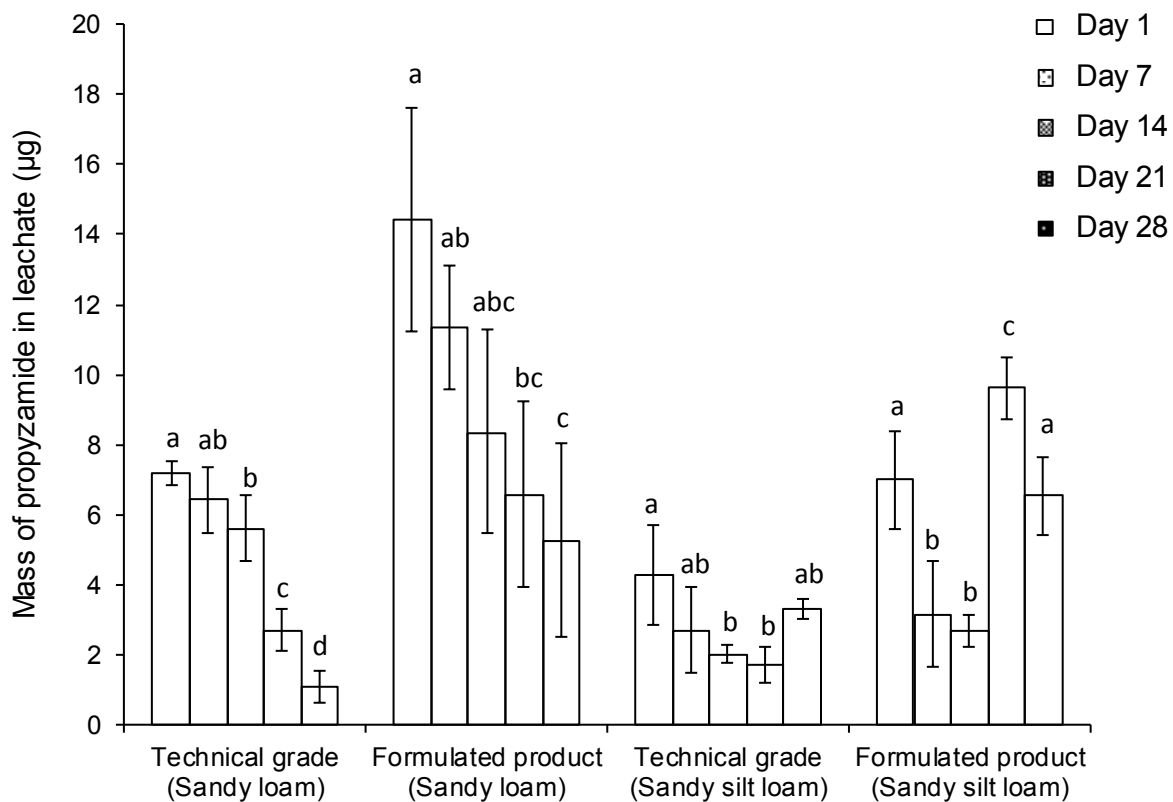


Fig. 4. Mass of propyzamide leached through sandy loam and sandy silt loam soils treated with technical grade and commercial formulation of propyzamide (Kerb® Flo). Values are the means \pm 1 standard deviation of four replicates. Letters on the bars show significant differences within the treatments (Tukey post-hoc test).

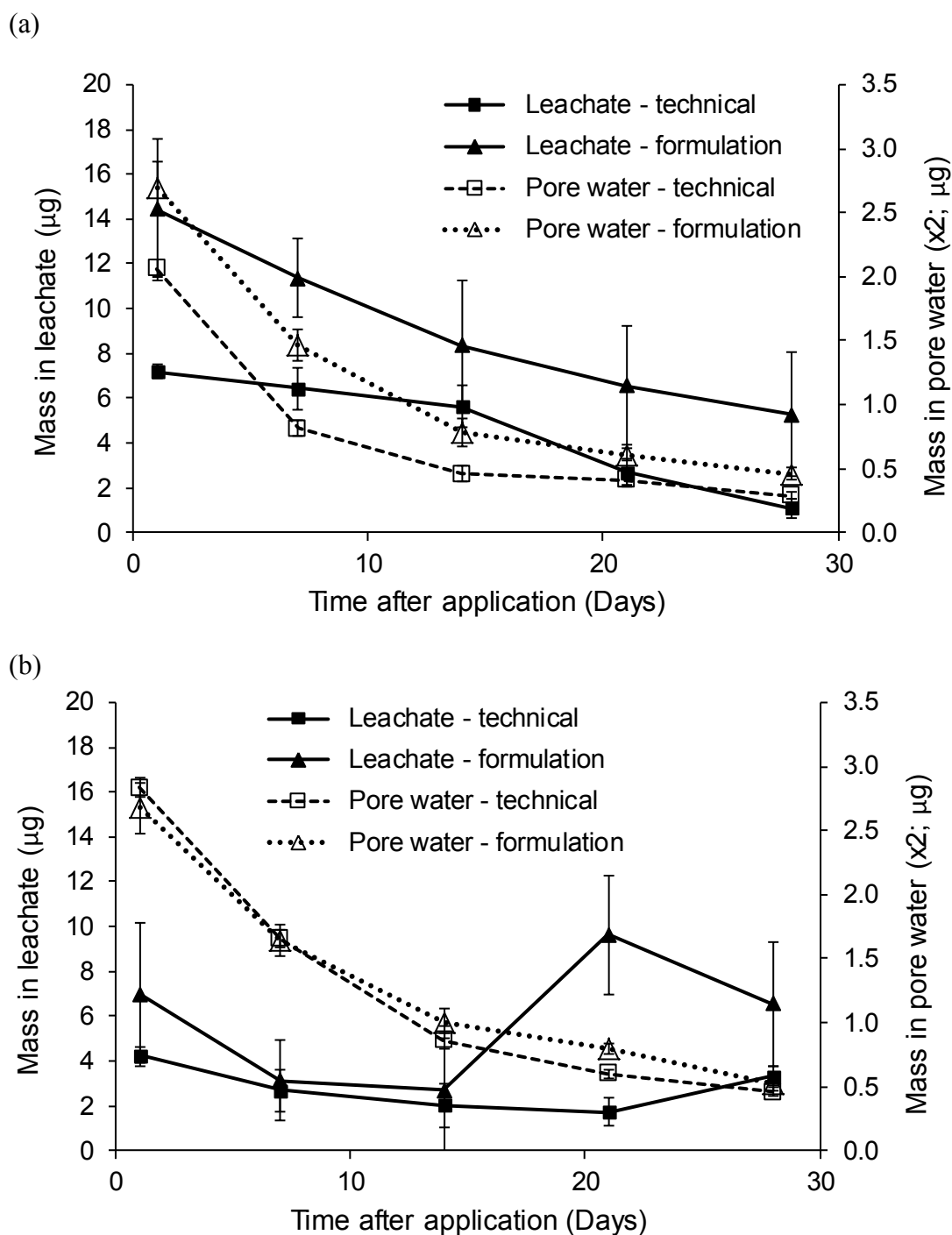


Fig. 5. Masses of technical grade and commercial formulation of propyzamide in leachate and soil pore water extracted by centrifugation (means and standard deviations of four replicates) over several time intervals in (a) sandy loam soil and (b) sandy silt loam soil. Values are the mean ± 1 standard deviation of four replicates. Masses in pore water are multiplied by two to correct for initial mass (50 μg in 10 g soil for centrifugation experiments, 100 μg in 20 g soil for leaching experiments).