Australian Government

Australian Pesticides and Veterinary Medicines Authority

Fipronil Review

Phase 2
Environmental Assessment Report:

Fipronil Fate technical report

prepared by

Department of the Environment, Water, Heritage and the Arts
Environmental Branch

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1. Introductory comments

The Australian Pesticides and Veterinary Medicines Authority (APVMA) has assessed Fipronil for a number of end-use products since its original registration in the mid-1990s. At the time of the initial assessment for agricultural products, a data package addressing the environmental fate of fipronil was received and relied on in the assessment.

While some additional data were received with subsequent registration applications, these could not be applied to earlier assessments that had already concluded.

In addition, a number of studies have not previously been provided to the APVMA, including those relied on in international assessments of fipronil. These data have the potential to alter previous conclusions relating to the environmental risk of fipronil through changes in our understanding of how fipronil behaves in the environment. The primary source document in this case is the draft assessment report (DAR) from the European Food Safety Authority (EFSA) review of fipronil[1].

This Appendix provides in a step-wise format: data that were available and relied on for different assessments of fipronil at the time; data that became available with later assessments but could not be applied to earlier assessments; and data the APVMA and Department of the Environment, Water, heritage and the Arts (DEWHA) is now aware of that will lead to a revision of the environmental risk of fipronil.

Data are reported under three potential headings. The first, *'Original data package'* provides information relied on in assessing registrations for fipronil use on brassicas, rice (seed treatment only), cotton (seed treatment and spray), pasture, sorghum, young pine plantations, sugarcane, recreational turf and commercial turf (latest consolidated report, 29 September 1998). In addition, sunflower and sorghum seed treatments, and assessment of fipronil for stonefruit (bait) used this same data package. These data are incorporated in this Appendix as they were used and reported at the time of the DEWHA assessment. They are not rated further.

[1] Draft Assessment Report (DAR) – public version. Initial Risk Assessment Provided by the Rapporteur Member State France for the Existing Active Substance FIPRONIL of the second stage of the review programme referred to in Article 8(2) of Council Directive 91/414/EEC. Volume 3, Annex B, B.8. January 2005.

The second data set, *'Data available for later assessments,'* provides information provided in support of later assessments (primarily with applications for termiticide use) that could not be used at the time to reassess end points from earlier assessments undertaken using previously available data. These data are incorporated in this Appendix as they were used and reported at the time of the DEWHA assessment. They are not rated further.

The third heading, *'Additional data not previously available'* provides information on data that are reported, either in international assessments or in the literature, that were not available for consideration in Australian assessments of fipronil. Where studies reported in the EFSA review have not been requested, the full text for these studies, as assessed by the European Rapporteur Member State, are included here for context. These data were rated using DEWHA's data rating system as follows:

1	**Fully reliable:**	GLP-compliant and fully compliant with the test guideline specified.
2:	**Reliable with restrictions:**	GLP-compliant but not fully compliant with the test guideline specified, but nevertheless judged to provide a reliable basis for regulatory decision-making. An asterisk is to be added to identify studies that are not standard but judged to be reliable for the purpose conducted (such as mechanistic studies).
3	**Not reliable:**	Not GLP-compliant and/or not compliant with the test guideline specified, and judged to not provide a reliable basis for regulatory decision-making.
4	**Not assignable:**	Insufficient information provided to allow the reliability of the test or study report to be assessed (such as published literature).

It should be noted these ratings are derived from the Organisation for Economic Co-operation and Development (OECD). Australia does not have mandatory GLP and consequently some allowances need to be made in addressing the validity of a study. For example, non-GLP studies cannot be considered unreliable on these grounds alone. Therefore, a degree of expert judgement was used in applying the validity rankings associated with studies assessed.

Data provided in the EFSA review were automatically rated as '4'. Where these studies are required (due to their results leading to a change in the risk assessment), the results only are included here and used within the risk assessment. Where they are not requested, further context from the studies is reported from the summaries in the EFSA review. This is proposed to be the final text for these and the studies summarised from the literature.

Under this third and final heading, it needs to be realised that not all new data are reported in this Appendix. Many literature reports were considered by DEWHA. However, not all are useable or reported. For example, there are a number of literature reports on soil degradation of fipronil, and some also provide pertinent information relating to metabolite formation and decline. However, quality, regulatory studies that follow standard guidelines will take

precedence for use in the risk assessment. One of the main problems with using the literature reports is there is generally insufficient detail available in the paper to allow a full analysis of rate and/or route of degradation in terms of understanding mass balance, the ability to adequately 'follow' the parent molecule through the study, or contribution of metabolites such as their peak levels and times at which they are formed. This is not to impugn in any way the quality of the studies underpinning the literature papers. However, for consistency wherever possible, they will not be relied on **except** where there are no contemporary, guideline and GLP studies available to base the risk assessment on.

Where new data are likely to result in a change to the risk assessment, these will be identified and should be provided, if not already available, for independent review. In the meantime, their results will be taken as given for use in the scoping risk assessment.

For chemical structures of fipronil and its metabolites, see Attachment 1, Volume 1.

2. Physicochemical degradation

2.1. Hydrolysis

2.1.1. *Original data package*

No degradation of fipronil (0.89 mg/L in sterile aqueous buffers) was observed during 30 days at pH 5 and 7. At pH 9, the calculated half-life was about 28 days. A single hydrolysis product, the amide RPA200766 arising from nitrile hydrolysis, was detected. No volatile compounds were detected at any pH in traps attached to the hydrolysis vessels for 1 year. Very little of the recovered radioactivity was found in the aqueous phase after extraction with dichloromethane. The radioactivity balance in all samples ranged from 96.4–101.6% of applied (Corgier & Plewa 1992 (a)).

2.1.2. *Data considered in later assessments*

The following studies were available for assessment for registration of fipronil as a termiticide.

Hydrolysis studies were carried out by Bobé et al. (1998 (a)), who kept 2.5 mg/L aqueous solutions (2.5% methanol) in the dark with frequent shaking. Tests were carried out at 22^{o}C at different pH values, 5.5, 7.0, 9.0, 10.0, 11.0 and 12.0, adjusted using 0.2–1M NaOH or HCl solutions and left from 20 (pH 12.0) to 2500 hours (pH 5.5 to 9.0). The influence of temperature was also investigated at pH 10, where solutions were heated at 30^{o}C, 37^{o}C and 45^{o}C. As above, fipronil was shown to be stable in acid and neutral solution (80% remaining unchanged after 100 days in both cases) but under alkaline conditions degradation increased in direct proportion to the rise in pH.

Degradation of fipronil at pH 12 was 300 times faster than at pH 9, with half-life values of 2.4 and 700 hours respectively. As expected the rate of hydrolysis increased with the rise in temperature, and was first-order in respect of the OH^- ion. As above, the amide RPA 200766 was formed almost quantitatively.

Ngim and Crosby (2001) also studied the hydrolysis of fipronil in deionised water and in buffers of pH 5.15, 7.07 and 9.00 at 24°C for 2200 hours. Again fipronil was stable under acidic and neutral conditions (<5 and <1% of fipronil sulfide formed respectively after 2200 hours). The half-life of 542 hours at pH 9 was slightly faster than that of Bobé et al. (1998) above, put down to the higher concentration used (0.425 versus 2.5 mg/L) in the latter.

2.1.3. *Additional data not previously available*

The EFSA review provides hydrolysis results for the main metabolites. Results from these studies may be applied in the scoping risk assessment, but the studies are not necessary to obtain for independent review. The summaries below are the EFSA report text.

Title	The Determination of the Hydrolytic Stability of [^{14}C]-M&B 046136
Authors	Mackie
Date	2000a
Test guideline	EC Directive 91/414 according to SETAC; US EPA 161-1
Title	Hydrolysis of [^{14}C]-M&B 46513 at pH 4, 5, 7 and 9
Authors	Mamouni
Date	1998
Test guideline	US EPA 161-1; EC Directive 92/69/EC Part C7
Title	The Determination of the Hydrolytic Stability of [^{14}C]-M&B 045950
Authors	Mackie
Date	2000b
Test guideline	EC Directive 91/414 according to SETAC; US EPA 161-1
Data validity	4 (studies reported in source document – not reviewed independently)
Data relied on	Yes

(Mackie 2000a): The sulfone ^{14}C-MB46136 (99% purity) was dissolved in acetonitrile and studied at a concentration of around 0.3 mg/L in sterile buffers at pH 4, 5, 7 and 9 at 25°C for 30 days and 50°C for 5 days. Samples were analysed at 13 different times from 0–30 days by TLC and HPLC; structural confirmation was obtained by LC/MS. The total radioactive recovery ranged from 93.7–112.1% at 25°C and 99.86–112.2% at 50°C. The corresponding overall mean recoveries ranged from 100–107%, which is acceptable. At 50°C, MB46136 was stable at pH 4, 5 and 7. At 25°C it was stable at pH 4 and 5; at pH 7 no degradation product was detected up to and including 24 days, but the amide, RPA 105320 was detected on day 30 at 11.5%. At pH 9, MB46136 was rapidly transformed to RPA 105320 (34.96% at 30 days); the incubation period was extended to 63 days when RPA 105320 increased to 41.75%. A half-life of 50 days at 25°C was estimated (DT90 of 166 days). At 50°C and pH 9, degradation was faster (DT50 3 days, DT90 9 days) resulting in the same degradation product (82.6% after 5 days). No other radiolabelled component was detected.

(Mamouni 1998): The desulfinyl ^{14}C-MB46513 (99% purity) was dissolved in acetonitrile and studied at a concentration around 0.5 mg/L in sterile buffers at pH 4, 5, 7 and 9, at 25^{o}C for 30 days. Duplicate samples of solution were analysed at seven different times from 0–30 days by TLC and HPLC. Structural confirmation was obtained by LC/MS/MS. The radioactive recovery for each individual sample ranged from 94.8–103.2%. The corresponding overall mean recoveries ranged from 96.7–100.7%, which is acceptable. MB46513 was stable at pH 4, 5 and 7. At pH 9 it was hydrolysed and decreased to 20.9% at 30 days. Two main products were detected, an acid metabolite MB46400 reaching 79.1% at 30 days and RPA 105048 never exceeding 4%. The DT50 was calculated to be 10.9 days.

(Mackie 2000b): The sulfide ^{14}C-MB45950 (99% purity) was dissolved in acetonitrile and studied at concentrations around 0.3 mg/L in sterile buffers at pH 4, 5, 7 and 9 at 25^{o}C for 30 days and 50^{o}C for 5 days. Samples were analysed at 13 different times from 0–30 days by TLC and HPLC; structural confirmation was obtained by LC/MS. The radioactive recovery for each individual sample ranged from 91.43–118.8% at 25^{o}C and from 94.58–120.9% at 50^{o}C. The corresponding overall mean recoveries ranged from 103–107%, which is acceptable. MB45950 was stable at pH 4, 5 and 7 at both temperatures. At pH 9 it was transformed to an unknown product, further identified as MB46126 (at 25^{o}C, max 10.45% at 24 days decreasing to 4.81% at 30 days; at 50^{o}C, max 27.55% at 5 days). At 50^{o}C, the notifier estimated a DT50 of 11 days.

2.2. Photolysis/Photodegradation

2.2.1. Aqueous photolysis

2.2.1.1. Original data package

Photodegradation of fipronil (0.89 mg/L) in sterile aqueous buffer (pH 5) containing 1% acetonitrile proceeded rapidly under xenon lamp irradiation (half-life about 3.5 hours, equivalent to 0.33 days of summer sunlight in Florida) to form three photoproducts. Two of these were identified by comparison with authentic standards as the corresponding trifluoromethyl pyrazole MB46513 (lacking the sulfoxide link) and the sulfonate RPV204615, in roughly 5:1 ratio and found in organic extracts and aqueous phases, respectively. The structure of a third minor photoproduct, also recovered from the organic extracts, could not be determined. The radioactivity balance ranged from 99.1–103.5% of applied, and no significant levels of volatile products were found. Dark controls were stable (Corgier & Plewa 1992 (b)).

2.2.1.2. Data available for later assessments

The following studies were available for assessment for registration of fipronil as a termiticide.

Photolysis was studied by Bobé et al. (1998 (a)), who subjected 2.5 mg/L aqueous (2.5% methanol) solutions adjusted to pH 5.5 in quartz capsules to irradiation with a Suntest solar simulator for up to 24 hours. Again with direct excitation fipronil degraded rapidly with a rate constant of 0.17/h and a calculated half-life of 4.1 hours. As above, two photo products were formed: the trifluoromethyl pyrazole MB46513 (the major and most rapidly formed) and the sulfonate (RPA 104615).

Ngim and Crosby (2001) irradiated 0.9 mg/L solutions of fipronil and desthiofipronil (MB46513) in deionised water in borosilicate glass photoreactors with fluorescent lamps producing 285–480 nm radiation (with maximum output at 365 nm but <300 nm filtered out) at 35^{o}C with or without aeration. Indirect photolysis was also measured by adding H_2O_2 at 50:1, 200:1 and 500:1 molar ratios. Trials were run until about 5% of starting material remained and a minimum of five time points were sampled. Desthiofipronil was clearly more persistent under the conditions with half-life values of 120 and 149 hours for aerated and static trials respectively, compared with 7.97 and 9.42 hours for fipronil. The slightly slower photodegradation compared with Bobé et al. (1998 (a)) above was attributed to the different light sources and the acidic methanolic solutions used by the latter. Photolysis of fipronil to desthiofipronil started almost immediately, but the maximum yield was about 50%. While the sulfonate was also observed, together with minor quantities of the sulfone and amide, a mass balance was not achieved. By contrast indirect photolysis was much more rapid with half-life values for fipronil of 4.51, 1.09 and 0.874 hours for 50:1, 200:1 and 500:1 molar ratios of H_2O_2 respectively, with again desthiofipronil the main photodegradate. The corresponding half-life values for desthiofipronil were 3.76, 1.44 and 0.853 hours, but degradation products were not investigated in this case.

2.2.1.3. Additional data not previously available

Title	A Brief Investigation of [^{14}C]-Fipronil in Natural Water under Artificial Sunlight
Authors	Mackie
Date	2000c
Test guideline	EC Directive 91/414, SETAC; US EPA 161-2
Data validity	4 (studies reported in source document – not reviewed independently)
Data relied on	Yes

The EFSA review provides an additional aqueous photodegradation result for fipronil (Mackie 2000c). In this study, ^{14}C-fipronil, in acetonitrile, was studied at 25^{o}C in a natural water under artificial sunlight for 48 hours. Two major photoproducts were detected. MB46513 was found at 52.1% after 24 hours and 47.5% after 48 hours while RPA 104615 was found at 10.6% after 24 hours and 15.6% after 48 hours. MB45950 was found at 4% after 24 hours. The half-life was calculated at 12.5 hours and no degradation was observed in the dark control.

This is considered a significant new study and should be provided. It provides additional information on the breakdown pattern of fipronil under sunlight and may be important for refining the risk assessment.

The EFSA review also provides information on photolysis of some fipronil metabolites.

Title	Artificial Sunlight Photodegradation of [^{14}C]-M&B 045950 in buffered aqueous solution
Authors	Keirs
Date	2001a
Test guideline	EC Directive 91/414; US EPA 161-2
Title	Artificial Sunlight Photodegradation of [^{14}C]-M&B 046136 in buffered aqueous solution
Authors	Keirs
Date	2001b
Test guideline	EC Directive 91/414; US EPA 161-2
Title	Artificial Sunlight Photodegradation of [^{14}C]-M&B 046513 in buffered aqueous solution
Authors	Keirs
Date	2001c
Test guideline	EC Directive 91/414; US EPA 161-2
Data validity	4 (studies reported in source document – not reviewed independently)
Data relied on	Yes

The photodegradation of the major metabolites the sulphide, MB45950 (Keirs 2001a), the sulfone, MB46136 (Keirs 2001b) and the desulfinyl MB46513 (Kiers 2001c) was rapid with half-lives of 6.0 hours, 13.0 hours and 38.9 hours respectively (continuous artificial irradiation, first-order kinetics, linear regression).

These studies are considered important for the purpose of refining the risk assessment and they should be provided.

Title	Phototransformation of the Insecticide Fipronil: Identification of Novel Photoproducts and Evidence for an Alternative Pathway of Photodegradation
Authors	Raveton et al.
Date	2006
Test guideline	None identified
Data validity	4
Data relied on	No – information only

Fipronil was solubilised in a water/ethanol mixture. The photodegradation was studied in solution at low light intensities (sunlight or UV lamp). The major metabolite found was MB46513 at levels around 40%. Following exposure to constant UV light for 170 hours, the authors observed the formation of a wide range of photoproducts. Six main photoproduct groups could be identified based on similarities in chemical structures. These groups included 4-unsubstituted derivatives, sulphide derivatives, aniline derivatives and sulfone derivatives. The authors note these findings disagree with other studies that suggest the existence of a single phototransformation pathway with MB46513 as the only product.

Regulatory studies described above note MB46513 is the major photoproduct, but is not the only one formed. Further, there is no indication in this study as to levels of formation of individual metabolites with the exception of MB46513. As a group, the sulphide derivatives and the 4-unsubstituted derivatives accounted for around 15% at the end of the study. Sulfone and aniline derivatives accounted for <5%. However, it is unclear how many individual chemicals formed these groups, or whether any single molecule would have accounted for >10%, which would deem it a major metabolite.

Title	Role of Dissolved Organic Matter, Nitrate, and Bicarbonate inthe Photolysis of Aqueous Fipronil
Authors	Walse et al.
Date	2004a
Test guideline	Modelling study
Data validity	4
Data relied on	No – information only

A multivariate kinetic model of aqueous fipronil photodegradation was developed as a function of dissolved organic matter (DOM), bicarbonate and nitrate. Several pathways were available for fipronil photodegradation in this system, including direct photolysis and indirect photooxidation by species produced during the illumination of natural waters. Product studies indicated that fipronil was quantitatively converted to fipronil desulfinyl (MB46513). DOM was the only variable that affected fipronil degradation. It decreased the rate of photodegradation primarily through competitive light adsorption. The addition of sodium chloride resulted in a more rapid rate (~20%) of fipronil loss in comparison to equivalent experiments performed without sodium chloride, implying that fipronil may be more photolabile in marine environments.

2.2.2. *Soil photolysis*

2.2.2.1. Original data package

Photodegradation was observed when radiolabelled fipronil was applied as acetone solution to the surface of a clay loam soil at a nominal application rate of 0.25 kg/ha and subjected to 30 days of xenon lamp irradiation, said to be equivalent in intensity to bright natural sunlight. The radioactivity balance ranged from 90.3–101.3% of applied in irradiated samples and dark controls. Estimated half-lives were 49 days in controls and 34 days under irradiation, indicating a contribution from photolysis (Burr & Austin 1992).

Fipronil degraded in dark controls to the corresponding sulfide MB45950, amide RPA200766 and sulfone MB46136, each reaching about 10% of applied after 30 days. The metabolite profile differed under irradiation, with unique products (the trifluoromethyl pyrazole MB46513 and sulfonate RPV204615, each amounting to about 7% of applied after 30 days) formed as above in aqueous solution and only traces (<2%) of the sulfide detected. Production of $^{14}CO_2$ reached 2.5% of applied after 30 days irradiation but remained below 0.3% in dark controls (note that the radiolabel occurred at the 5 position of the pyrazole ring in this study).

Susceptibility of fipronil to photolysis was confirmed (Buddle et al. 1991) by exposing a granular formulation (2% on Sepiolite) to artificial sunlight for 14 days, during which time the fipronil content declined to 0.5% with the concomitant formation of 0.4% each (based on the granule) of the trifluoromethyl pyrazole MB46513 and sulfonate RPV204615. Traces of the sulfide MB45950 were also detected, as well as two sulfonyl derivatives carrying methoxy and fluoro substituents, the former deriving rapidly from the latter in methanolic solution. The rate of degradation slowed with time as the level of fipronil available for surface reaction declined. Dark controls and granules exposed to filtered sunlight on a windowsill proved stable.

2.2.2.2. Data available for later assessments

The following study was available for assessment for registration of fipronil as a termiticide.

Bobé et al. (1998 (a)) subjected samples containing 2.5 mg/kg fipronil evenly distributed throughout the soil in quartz capsules to irradiation using a Xenon lamp for up to 196 hours. Half-lives were much slower than in solution being 147 and 178 hours for two Sahelian soils and 217 hours for a Mediterranean soil (attributed to the light shielding effect but much faster than for surface samples above), with a possible correlation with the strength of adsorption. Only the trifluoromethylpyrazole MB46513 was observed as a degradation product, the sulfonate RPV204615 found under aqueous conditions (and on soil above) could not be detected.

3. Biodegradation

3.1. Aerobic soil metabolism

3.1.1. *Original data package*

The aerobic metabolism of radiolabelled fipronil was investigated (Humphreys et al. 1993) over a 12-month period in four laboratory soils, the properties of which are tabulated below. Soils were fortified by dropwise addition of a dosing solution in acetone to around 0.4 mg/kg (equivalent to an application of about 200 g/ha dispersed through 4 cm of soil) and incubated at 22^{o}C in the dark. Samples were taken periodically and stored in the freezer prior to soxhlet extraction with acetonitrile.

Table V2.1 Soil characteristics and half-lives from Humphreys et al. (1993)

Soil type	pH	% oc	% sand	% silt	% clay	CEC	Half-life	Kinetics
Loamy sand	6.3	3.3	83	9	8	9.0	62 days	2nd order
Sandy loam	6.4	0.4	80	11	9	6.7	117 days	1st order
Sandy clay loam	6.2	0.7	47	27	26	14.1	18 days	1.5 order
Sandy clay loam	6.2	1.3	50	26	24	20.6	40 days	1st order

The radioactivity balance in individual samples ranged from 88.1–108.4% of applied or 91.9–108.1 %as the mean of duplicate samples. Most remained extractable, with bound residues remaining below 10% and carbon dioxide the only volatile product found, reaching 1.4% of applied in the loamy sand and sandy loam.

As in the photolysis and hydrolysis studies, metabolites derived from transformations of the substituents at the 3 and 4 positions of the pyrazole ring. The dominant metabolite, reaching levels in the order of 40–50% of applied, was the amide hydrolysis product RPA200766. Significant amounts of the sulfone (MB46136) and sulfide (MB45950) analogues of fipronil were also detected from between 1 week and 1 month after dosing. Smaller amounts of two further metabolites, one (MB45897) with the trifluoromethylsulfoxide group displaced completely (labelled the displacement product in this report) and the other carrying both trifluoromethylsulfone and carboxamide substituents, were also detected in the latter half of the study. The displacement product MB 45897 is thought to arise via the photochemically-derived sulfonate RPV204615.

The sulfone (MB46136) and sulfide metabolites (MB45950) exhibited similar retention times to fipronil when analysed by reverse phase HPLC. Principal and minor metabolites, most of which carry carboxamide substituents, eluted much more rapidly and exhibited only slightly longer retention times than the hydrophilic sulfonate.

Several polar metabolites, together comprising up to 30% of applied in the two sandy clay loams, remained unidentified. The authors speculate these arose because of high soil moisture content, although they were not detected in studies on flooded soil. Soil moisture content in these studies, conducted according to Dutch guidelines, was maintained at 0.1 bar moisture holding capacity, which exceeded 0.33 bar moisture holding capacity by some 50% for the two sandy clay loams. The US EPA (Fletcher & Creeger 1985) recommends maintenance within 10–12% of 75% of 0.33 bar moisture holding capacity. The higher moisture levels used under Dutch guidelines presumably reflect the generally wet state of Dutch soils, but are of limited relevance to Australian conditions.

The final report for this study (Humphreys et al. 1994) identifies the polar metabolites and includes data for degradation at 10^{o}C. The polar metabolites were found to be carboxylates arising from complete hydrolysis of the nitrile

substituent in fipronil and metabolites. Only the carboxylate analogue of fipronil was present at more than 10% of applied.

Degradation slows markedly at the lower temperature in two of the soils, with half-lives extending to 246, 163, 61 and 62 days respectively in the four soils studied.

Half-lives tabulated above were calculated using a computer model which also determined the order of the reaction. The apparent departure from first-order kinetics may reflect changing experimental conditions as microbial biomass declined significantly over the course of the study.

A separate study (Waring, 1993) conducted in two soils spiked at 0.2 mg/kg and incubated in the dark at 25^{o}C and 75% of 33 kPa (0.33 bar) moisture capacity for 11 months found two major metabolites, the amide hydrolysis product RPA200766 (up to 38% and 27%, respectively) and the sulfone MB46136 (up to 24% and 14%, respectively). The sulfide MB45950 (<5%) and trifluoromethyl pyrazole MB46513 (1%) were detected in all soils, and the displacement product MB45897 (1%) in the sand. Six unidentified degradation products (each <4%) were also detected in the sandy loam, and four in the sand. Production of volatiles was limited, with <3% $14CO_2$ and <2% non-polar metabolites recovered from traps. Bound residues increased slowly but steadily to reach 15% and 6% of applied, respectively. Half lives of fipronil were calculated graphically from HPLC data. Note the sandy loam in this study is the same standard soil as used in the previous; half-lives (117 days and 128 days) are well correlated.

Table V2.2: Soil properties and half-lives from Waring (1993)

Soil type	pH	% oc	% sand	% silt	% clay	CEC	First half-life
Sandy loam	7.8	1.0	56	35	9	6.4	128 days
Sand	6.1	1.9	88	9	3	3.3	308 days

3.1.2. *Additional data not previously available*

Title	[^{14}C]-Fipronil: Degradation in Four Soils at 20^{o}C and Two Soils at 10^{o}C
Authors	Fitzmaurice and Mackenzie
Date	2002
Test guideline	EC Commission Directive 95/36/EC of 14th July 1995 – Section 7.1.1
Data validity	4 (study reported in source document – not reviewed independently)
Data relied on	Yes – the data were relied on for this scoping assessment

Test system

The EFSA review reports a newer laboratory aerobic soil degradation study (Fitzmaurice & Mackenzie 2002). The study was performed using ^{14}C-fipronil in four soils at 20^{o}C, with two soils then tested at 10^{o}C. This study appears to have been performed as results of a 1994 study (presumably, Humphreys et al. 1994 above) was not considered reliable by the EU. The study was performed to EU guidelines. The following soil characteristics are reported:

Table V2.3: Soil characteristics from Fitzmaurice and Mackenzie (2002)

Soil location Soil classification	Chazay (F) Clay loam	Ongar (UK) Clay loam	Royston Clay loam	Levington Sandy loam
% sand	41.55	33.43	20.07	73.36
% silt	25.09	34.43	45.54	15.80
% clay	33.36	29.14	34.40	10.83
% OC	1.1	2.0	4.1	1.3
CEC (mEq/100 g)	12.8	18.1	45.3	3.8
pH (water)	8.2	7.3	8.3	6.6
Water holding capacity, % w/w	45.32	60.11	104.67	39.27
Initial microbial biomass, µg C/g	176	359	1093	145
Final microbial biomass, µg C/g, 20^{o}C	63	265	957	58
Final microbial biomass, µg C/g, 10^{o}C	113	327		

Application was at a dose equivalent to 184 g/ha. Soils were incubated in the dark for up to 219 days and volatiles were trapped. Following extraction, solvent extracts were analysed by reverse phase HPLC against known certified reference standards. Unextractable residues were analysed after combustion. Structural confirmation of the species present was obtained by LC-MS/MS.

Findings

The EFSA report provides extensive tables reporting the findings. These were not replicated for this scoping assessment report. Overall recovery was acceptable (95.9–106.5%) and mineralisation was low (<1% AR). Maximum unextractable soil residues were 5.4–10.7%. Three major metabolites were detected being RPA200766 (amide), MB46136 (sulfone) and MB45950 (sulphide). Maximum levels found for soils incubated at 20^{o}C are summarised in the following table:

Table V2.4: Summary of metabolite findings from Fitzmaurice and Mackenzie (2002)

Soil	Chazay (F)	Ongar (UK)	Royston	Levington
Maximum found (%AR) (RPA200766)	19.31*	38.44*	25.17	29.01*
Days after treatment	219	219	162	219
Maximum found (%AR) (MB46136)	11.06	22.43	34.34	13.25
Days after treatment	162	153	162	153
Maximum found (%AR) (MB45950)	2.07	8.63	16.99	3.99
Days after treatment	219	162	91	28

* No plateau of residues apparent

In the two soils incubated at 10^{o}C, RPA200766 and MB46136 still dominated but were generally <10% AR.

The rate of fipronil degradation was dependent on temperature and soil microbial biomass, being more rapid at 20^{o}C and more rapid with higher microbial biomass. The following table summarises the half-life calculations using the KIM model, and using linear 1st order kinetics as calculated by the European Union (EU) rapporteur Member State (France).

Table V2.5: Summary of results from Fitzmaurice and Mackenzie (2002)

	KIM model		Linear 1st order	
	DT50 (days)	Fit criteria	DT50 (days)	R^2
	20^{o}C			
Chazay (F)	304	0.99	382	0.84
Ongar (UK)	102	0.99	123	0.97
Royston	31	0.99	42	0.97
Levington	221	0.99	288	0.80
	10^{o}C			
Chazay (F)	686	0.99	747	0.50
Ongar (UK)	358	0.99	515	0.73

Conclusion with respect to this study:

The results show substantially longer half-lives than those observed in the Humphreys et al. (1993) and Humphreys et al. (1994) studies previously relied on above. Further, there appears to be much better characterisation of radioactivity than that in Humphreys et al. (1993) where up to 30% applied radioactivity in the two sandy clay loams remained unidentified. This study should be considered as significant new information and half-lives of parent fipronil in some soils exceed 6 months. Applying the Australian PBT (persistent, bioaccumulative, toxic) criteria (EPHC 2009), and those outlined in Annex D to the Stockholm Convention for persistent organic pollutants, this indicates fipronil is very persistent in soils. This study should be provided for proper review.

Some other results were considered from the literature.

Title	The Sorption and Degradation of the Rice Pesticides Fipronil and Thiobencarb on Two Australian Rice Soils
Authors	Doran, Eberbach and Helliwell
Date	2006
Test guideline	None identified
Data validity	4
Data relied on	No – information only

Test system

An Australian study is reported in the literature (Doran et al. 2006). Degradation of fipronil along with formation of MB45950 was tested in triplicate in aerobic soil microcosms (50 g sieved soil) from two rice growing regions: Coleambally and Yanco. The application is stated as 'normal field rate'. Incubation was in the dark at around 25^{o}C for 45 days. Soils were extracted in their entirety at 30 minutes, then 1, 2, 5, 10, 20 and 45 days after application. Extraction was done using acetonitrile with 2 hours shaking following by centrifugation. Analysis was undertaken by GC-ECD.

Findings

The results showed an initial rapid decrease in fipronil concentrations in both soils (30–50% by day 5) with a slowing thereafter. Levels of MB45950 increased over time, and reached a maximum of 17% in both soils. The authors did not calculate soil half-lives. DEWHA has calculated first-order half-lives (assuming first-order kinetics, but the data were not strongly correlated due to the rapid initial loss of fipronil) of around 26–34 days.

Conclusions

These are much lower than results found in the laboratory studies described above. However, the results here will not be relied on. After 45 days, recovery of fipronil and MB45950 totalled 41–45% of the applied amount indicating a very large amount of bound residues that were not characterised. This suggests the extraction process may not have been efficient, or the aerobic soil metabolite, MB46136, could have been present in significant quantities, but was not looked for.

Title	Laboratory and Field Studies on the Degradation of Fipronil in a Soil
Authors	Ying and Kookana
Date	2002
Test guideline	None identified
Data validity	4
Data relied on	No – information only

Test system

A further Australian study (Ying & Kookana 2002) considered degradation of fipronil in a single soil under laboratory conditions, but at three different moisture levels (15%, 30% and 60% maximum water holding capacity). Incubation was undertaken at 20^{o}C in the dark for up to 182 days. Fipronil was

added to the test soil at 2 mg/kg (1500 g ac/ha if distributed in top 5 cm soil with density of 1500 kg/m^3).

Findings

The results tended to show that fipronil degradation followed first-order kinetics. Degradation was fastest at the highest moisture content (half-life 68 days) with greatest production of the sulphide MB45950 (increased reducing conditions at the higher moisture content). This metabolite was found at around 0.6 mg/kg after 182 days. At 30% and 15% moisture, degradation slowed with half-lives of 161 and 198 days respectively. Under these moisture conditions, the sulfone, MB46436, was the dominant metabolite being found at around 0.12 and 0.14 mg/kg after 182 days at 30% and 15% moisture respectively.

In corresponding field studies under natural conditions with fipronil applied at either 1500 g ac/ha or 750 g ac/ha, the half-life of fipronil was 139 and 124 days respectively. However, when 'total residues' were considered to account for the metabolites, the average half-life in the field was 188 days.

Conclusions

These results are within the higher end of the range of half-lives found in regulatory studies.

Title	Degradation of Fipronil under Laboratory Conditions in a Tropical Soil from Sirinhaem Pernambuco, Brazil
Authors	Masutti and Mermut
Date	2007
Test guideline	None identified
Data validity	4
Data relied on	No – information only

Test system

Masutti and Mermut (2007) investigated the degradation of fipronil and its metabolite formation under laboratory conditions in a tropical soil from Brazil. Soil samples (50 g, air dry) were spiked with fipronil at an initial concentration of 0.689 mg/kg (non-autoclaved) and 0.601 mg/kg (autoclaved) for long-term experiments (120 days) and 0.978 mg/kg (non-autoclaved) for a short-term study (30 days). Soils were incubated at around 25^{o}C in the dark. Soil analysis was performed at 0, 2.54, 5, 7.5, 15 and 30 days (short-term) and 0, 15, 30, 60, 90 and 120 days (long-term) with samples analysed in duplicate.

Findings

In the short-term experiment, there didn't seem to be a great difference in fipronil losses from the non-sterile soil (16% after 30 days) compared with the sterile soil (12% after 30 days). The short-term experiment resulted in an estimated half-life of 83 days, but this needs to be treated with caution as it is well outside the duration of the experiment.

In the long-term experiment, fipronil levels decreased 42% after 120 days compared with only 19% under sterile conditions. The zero-order model resulted in a predicted half-life of 200 days (poor $r^2 = 0.69$), and faster degradation was observed after 90 days that likely contributed to this poor correlation. Again, the result needs to be treated with caution as the half-life is well outside the experimental period. The data are not reported sufficiently for DEWHA to undertake additional half-life calculations.

Three main metabolites were identified. MB46513 was only found at trace amounts. The major metabolite found in the non-sterile soils (120-day study) was the sulfone, MB46136, at maximum levels of around 1.7 mg/kg (values read from a graph) at days 60, 90 and 120. The sulphide, MB45950, was found at a maximum level around 0.5 mg/kg (value read from a graph) at 120 days, and its presence indicates some more anaerobic soil sites were present during the study.

Conclusions

The results of this study in terms of tentative soil half-lives for parent fipronil and corresponding metabolite formation tend to support the other regulatory studies reported above. These results will not be relied on further in the risk assessment.

Title	Microbial Degradation of Fipronil in Clay Loam Soil
Authors	Zhu, Wu, Guo and Kimaro
Date	2004
Test guideline	None identified
Data validity	4
Data relied on	No – information only

A further study on microbial soil degradation is reported by Zhu et al. (2004) on a single clay loam soil in China. The study was performed over 35 days of incubation, and demonstrated the ability of soil microbes to increase the degradation rate of fipronil. Incubation was undertaken at 25^{o}C and 35^{o}C, and there was not a great difference in degradation rates at these two temperatures. However, even in the sterile soils, the half-life was calculated at around 33 days, which is much faster than other aerobic degradation studies and the reason for this is unclear. In the non-sterile soils, the fipronil half-life was 9–10 days, which is very fast compared with other data. The main metabolite is reported as MB45950, which indicates anaerobic conditions, and the levels of this metabolite are not reported. However, the authors do state there was no further degradation of this metabolite. These results will not be relied on further in the risk assessment.

Title	Concentration-Dependent Degradation of Three Termiticides in Soil Under Laboratory Conditions and their Bioavailability to Eastern Subterranean Termites (Isotera: Rhinotermitidae)
Authors	Saran and Kamble
Date	2008
Test guideline	None identified
Data validity	4
Data relied on	No – information only

Saran and Kamble (2008) demonstrated the concentration dependence of fipronil degradation in aerobic soil when considering efficacy of fipronil as a termiticide. Briefly for the persistence component of the study, test soil was sieved (2 mm) and adjusted to 25% moisture content. Three fipronil concentrations (60, 95 and 125 mg/kg soil) were tested. If these concentrations are indicative of soil levels when distributed through the top 5 cm soil with a density of 1500 kg/m^3, approximate application rates correspond to 45, 71 and 167 kg ac/ha. Four replicates were used for each concentration. Soils were incubated at around 25^{o}C, it is unclear whether this was in the dark. Soils were analysed at 0, 8, 31, 65, 90, 135, 150 and 180 days after treatment. Extraction efficiency for fipronil was demonstrated with a mean recovery rate of 95%. The calculated half-lives for each concentration was longer than the incubation period, so need to be treated with some caution. However, the data were reasonably well correlated to first-order degradation kinetics. At the low, medium and high application rates, the calculated half-lives for fipronil were around 223, 365 and 544 days respectively, demonstrating the increase in degradation time as concentration increased. No metabolite formation or decline was considered in this experiment.

This report supports the persistence of fipronil at the high termiticide rate.

3.2. Anaerobic soil metabolism

3.2.1. *Original data package*

Anaerobic studies were conducted for about 1 year on the sandy loam described in Table V2.1, which was held in glass cylinders as a 5 cm layer covered by 12 cm of water for 52 days before treatment by dropwise addition to the water surface with a solution of radiolabelled fipronil (0.0160 mg in 480 µL of acetonitrile; Lowden et al. 1993).

Recovery of radioactivity ranged from 79–102%. Applied radioactivity detected in the surface water declined from 93% initially to 13–21% over 365 days, with a concurrent increase in soil from 4–69% over the test period. At least 62% of soil radioactivity was extracted with acetonitrile, with bound residues increasing from <0.2% initially to a peak of about 18% after 179 days before declining to about 10% by study end. Polar and non-polar volatiles, and carbon dioxide traps all returned radioactivity levels of <0.1%.

Major degradation products were the sulfide analogue (MB45950) of fipronil and the amide hydrolysis product RPA200766, detected at levels of 32–47% and 18%, respectively, at the end of the study period. The former was predominantly

found in the soil, whilst the latter was present in both phases. Small amounts (<1%) of the displacement product MB45897, the trifluoromethyl pyrazole MB46513 and the sulfone MB46136 were also detected in surface water and soil samples. TLC analyses detected five unidentified degradation products in soil samples (all <1%) and five in water samples (one at 6%, the others all <2%). The first half-life was about 123 days.

3.2.2. *Additional data not previously available*

Title	The Sorption and Degradation of the Rice Pesticides Fipronil and Thiobencarb on Two Australian Rice Soils
Authors	Doran, Eberbach and Helliwell
Date	2006
Test guideline	None identified
Data validity	4
Data relied on	No – information only

An Australian study is reported in the literature (Doran et al. 2006). Degradation of fipronil along with formation of MB45950 was tested in triplicate in anaerobic soil microcosms (50 g sieved soil) from two rice growing regions: Coleambally and Yanco. Two separate systems were used. One with anaerobic soil (purged with nitrogen) and the other with a flooded soil. The application is stated as 'normal field rate'. Incubation was in the dark at around 25^{o}C for 45 days. Soils were extracted in their entirety at 30 minutes, then 1, 2, 5, 10, 20 and 45 days after application. Extraction was done using acetonitrile with 2 hours shaking following by centrifugation. Analysis was undertaken by GC-ECD. Anaerobicity was not measured, for example, through redox potentials.

The results showed an initial rapid decrease in fipronil concentrations in both soils in both test systems (40–55% by day 5) with a slowing thereafter. Levels of MB45950 increased over time. In the non-flooded systems, this metabolite was found at a maximum of 12–18%, which was similar to levels found in aerobic soils. However, in the flooded soils, MB45950 reached a maximum of 30–32% in both soils. The authors did not calculate soil half-lives. DEWHA has calculated first-order half-lives (assuming first-order kinetics, but the data were not strongly correlated due to the rapid initial loss of fipronil) of around 29–45 days from both systems. When combined residues of fipronil and MB45950 are considered, half-lives in the flooded soils increase to around 70 days due to the much higher formation of MB45950 in this system.

These results will not be relied on. After 45 days, recovery of fipronil and MB45950 totalled 37–58% of the applied amount indicating a very large amount of bound residues that were not characterised. This suggests the extraction process may not have been efficient.

3.3. Aerobic aquatic metabolism

3.3.1. *Original data package*

There were no standard laboratory data available to address this end point.

3.3.2. *Additional data not previously available*

The EFSA review describes several studies that consider the metabolism of fipronil and some metabolites in water/sediment systems. The EFSA report provides quite detailed information on the findings of these studies. They are not reproduced here for this scoping assessment, but the results are summarised below.

Title	Fipronil – aerobic aquatic metabolism
Authors	Feung and Yenne
Date	1997
Test guideline	US EPA Pesticide Assessment Guidelines – Subdivision N, 162-4
Data validity	4 (study reported in source document – not reviewed independently)
Data relied on	Yes – the data were relied on for this scoping assessment

The earliest of these studies (Feung & Yenne 1997) provides limited information with testing in a single system over 365 days. Fipronil degradation in the whole system followed first-order kinetics with a half-life of 14.5 days. The major metabolite was MB45950, accounting for over 83% applied radioactivity in the sediments at the study end. However, measurements were taken weekly, and there is insufficient detail to determine fipronil persistence in the water column.

Title	[^{14}C]-Fipronil – Degradation and Retention in Two Water/Sediment Systems
Authors	Ayliffe
Date	1998
Test guideline	EU Directive 95/35/EC Annex 1 SETAC Guidelines
Title	[^{14}C]-Fipronil – Degradation in Two Water/Sediment Systems
Authors	Roohi and Buntain
Date	2002
Test guideline	EU Directive 91/414, as amended by 95/36/EC of July 1995, Section 7.2.1.3.2 and SETAC Guidelines
Data validity	4 (studies reported in source document – not reviewed independently)
Data relied on	Yes – the data were relied on for this scoping assessment

The other two studies (Ayliffe 1998; Roohi & Buntain 2002) allow a much better analysis of fipronil behaviour in an aerobic aquatic system. Both studies tested two different water/sediment systems with a much greater sampling intensity during the early stages of the studies. Again, MB45950 was the dominant metabolite in both water and sediment. Loss of radioactivity tended to follow first-order kinetics, and the following table summarises the results of these studies with results calculated by DEWHA based on information in the EFSA review.

Table V2.6: Summary of results from Ayliffe (1998) and Roohi and Buntain (2002)

Reference	System	Water		Whole system	
		DT50 (d)	r^2	DT50 (d)	r^2
Ayliffe, 1998	Ongar	16.3	0.996	16.3	0.987
	Manningtree	14.4	0.963	35.9	0.960
Roohi and	Iron Hatch	93.6	0.898	119.5	0.912

Buntain, 2002	Ongar	29.6	0.963	31.5	0.902

Fipronil degradation in the Iron Hatch system appeared biphasic. The first half-life (0–28 days) was 28.6 days (r^2 = 0.963), which is in much better agreement with water half-lives of fipronil in the other systems. The second phase (days 28–244) half-life was much longer at 117 days (r^2 = 0.937).

There is significant new information on toxicity of various fipronil metabolites to aquatic organisms, and these data suggest the main metabolites are highly biologically active. The dominant metabolite in the water/sediment systems was MB45950, and toxicity data suggest this metabolite to be as potent as the parent compound to some organisms. Therefore, it is appropriate to consider loss from the tests systems in terms of combined fipronil and MB45950. DEWHA has performed these calculations based on the information in the EFSA review, and they are summarised in the following table.

Table V2.7: Results of dissipation of 'Total Residues', results from Ayliffe (1998) and Roohi and Buntain (2002); calculated by DEWHA

Reference	System	Water		Whole system	
		DT50 (d)	r^2	DT50 (d)	r^2
Ayliffe, 1998	Ongar	32.1	0.945	2310	0.576
	Manningtree	17.8	0.950	2310	0.1723
Roohi and Buntain, 2002	Iron Hatch	121.6	0.877	231	0.917
	Ongar	48.8	0.944	301	0.961

Water half-lives of the sum of residues ranged from around 1–3 months indicating the potential to persist in water. Again, the actual degradation in the Iron Hatch system was biphasic and the first half-life for combined residues was 30.1 days (r^2 = 0.970) with the second phase half-life being 192 days (r^2 = 0.918).

The very long half-life estimations in the whole system from Ayliffe (1998) are not reliable given the low correlation coefficient. However, at the end of the study, in both test systems around 80% of the initially-applied radioactivity was still present in the sediments as MB45950 indicating very slow degradation in these systems.

In the two systems investigated in Roohi and Buntain (2002), losses from the whole system of the combined residues demonstrated persistence with a range of 231–301 days.

Conclusion regarding the need for these studies: At the time of assessing broadacre use patterns, no aerobic aquatic metabolism data were available. The risk assessment at that time could only consider the single study on

anaerobic soil, where some information on fipronil behaviour could be gleaned. However, in view of the results above, that information is inadequate to remain satisfied, and the studies noted here as not being available should be provided for review to gain appropriate knowledge of the potential for both the rate and route of degradation in water/sediment environments. This is particularly important given the more advanced knowledge of metabolite toxicity available since broadacre use risk assessments in Australia. The information from these studies indicates half-lives of total residues in water may exceed 2 months, and in sediments, can exceed 6 months. The use of total residues as an approach to the risk assessment is appropriate given new toxicity data showing effects of major metabolites on environmental organisms. Applying the Australian PBT (persistent, bioaccumulative, toxic) criteria (EPHC 2009), and those outlined in Annex D to the Stockholm Convention for persistent organic pollutants, the data in these studies indicates fipronil (in terms of total residues) is very persistent in sediments, and potentially, in the water column.

Title	The Fate of Fipronil in Modular Estuarine Mesocosms
Authors	Walse, Pennington, Scott and Ferry
Date	2004b
Test guideline	None identified
Data validity	4
Data relied on	No – information only

Walse et al. (2004b) report results on the fate of fipronil and metabolites in modular estuarine mesocosms, designed to approximate coastal conditions typical of the south eastern United States of America (USA). The mesocosms were designed to allow simulation of tidal movement with fipronil and major metabolites measured routinely in water and sediment up to 28 days following application. Fipronil was introduced in acetone stock solutions at 5 µg/L around 1 hour prior to flow tide. Water half-lives of fipronil in this system were biphasic, and much faster than those reported above, probably due to 'tidal' movement of the water in and out of reservoirs. The initial rapid loss of fipronil (0–96 hours) had half-lives around 2 days, with the second phase half-life being 7.4–10 days. The major metabolite was MB45950 found at almost 20% initial fipronil levels and all in the sediment after 28 days. The photolysis metabolite, MB46513, was found in sediment at 7.3% initial fipronil levels after 28 days and was still in water at 4.1% initial fipronil levels at this time. The dominant metabolite in the water column was the sulfone (MB46136), which remained at about 10.4% initial fipronil levels after 28 days.

Apart from the parent compound, the EFSA review also reports studies of aquatic metabolism for one of the main fipronil metabolites.

Title	[^{14}C]-MB46513 – Degradation in Two Water/Sediment Systems
Authors	Lowden and Mahay
Date	2002
Test guideline	EU 95/36/EC of July 1995, Section 7.2.1.3.2; US EPA N 162-4
Data validity	4 (studies reported in source document – not reviewed independently)
Data relied on	Yes – the data were relied on for this scoping assessment

The desulfinyl, MB46513, was tested in two water/sediment systems. The test substance was applied to the surface water at a dose equivalent to 100 g ac/ha. The system (aerobic water and anaerobic sediment, although no measurements confirming anaerobicity were included) was incubated in the dark at 20^{o}C for 1 year. Volatile products were trapped.

DEWHA has performed half-life calculations based on the dissipation data as described in the EFSA report:

Table V2.7: Results of dissipation of MB46513 in two water/sediment systems; calculated by DEWHA

System	Water		Whole system	
	DT50 (d)	r^2	DT50 (d)	r^2
Ongar	77.9	0.68	533	0.36
Manningtree	92.4	0.66	770	0.45

In the water system, degradation of MB46513 was rapid first, then slowed. Without reviewing the whole study, first-order half-lives are reported above, but the correlation was not strong due to this faster initial degradation (initial degradation half-life in water <10 days). Nonetheless, after 100 days in both systems, more than 10% of the initially-applied chemical was still found in the water. There was a poor correlation of degradation data from the whole system for both systems. However, the test substance was persistent and was still found at >60% applied in the whole system, almost all in sediment, at the end of the 365-day incubation period. Half-lives exceeded 1 year in both systems, and levels in sediment had only just appeared to plateau by the end of the study. No metabolite accounted for more than 5% applied.

Conclusions for this study: The study should be provided for review as it provides pertinent information on persistence for one of the main fipronil metabolites in aquatic systems.

3.4. Anaerobic aquatic metabolism

3.4.1. *Original data package*

There were no standard laboratory data available to address this end point.

3.4.2. *Additional data not previously available*

Title	Enantioselective Microbial Transformation of the Phenylpyrazole Insecticide Fipronil in Anoxic Sediments
Authors	Jones, Mazur, Kenneke and Garrison
Date	2007
Test guideline	None identified
Data validity	2* – reliable with restrictions
Data relied on	Yes – this non-standard study provides results that can be used in the risk assessment

Jones et al. (2007) provide further results on the transformation kinetics along with product of the fipronil in anoxic sediments with an aim to determine if the process was enantioselective. Briefly, two sediments of differing characteristics were sieved (1 mm) and mixed with either anoxic (N_2 sparged) site water or half-strength artificial seawater to achieve a sediment solids concentration of approximately 100 g/L. The initial target concentration of fipronil was ~3.3 mg/L. Microcosm bottles were incubated at 25^{o}C. Control microcosms were prepared by autoclaving sediment slurries. Triplicate samples were collected at selected time points to assess fipronil transformation.

In the sulfidogenic sediment (seawater microcosm), following a short lag of around 5 days, fipronil transformation was observed with almost stoichiometric production of the sulphide MB45950. The half-life of fipronil was determined to be around 35 days. MB45950 reached a maximum (3.4 mg/L) on day 62 and from there, an appreciable loss of this metabolite was evident to the end of the 88-day incubation period. In the autoclaved control, only minor loss (<5% of the amended fipronil) was observed over the incubation period. A similar result was found in the methanogenic microcosm (N_2 sparged). Following an initial lag period of around 13 days, fipronil was transformed primarily to MB45950 with a half-life around 40 days. MB45950 reached a maximum, at day 60 and decreased by around 65% over the next 25 days of incubation. Again, in the autoclaved system, fipronil loss was <5% over the course of the study.

The differences in the systems was in the enantioselectivity of the transformation. The enantiomeric fraction (EF) of fipronil decreased from an initial racemic EF value of 0.46 to a value of 0.22 in the sulfidogenic sediment slurry. The opposite was found in the methanogenic slurry the EF mean value increased from the initial 0.46 to 0.76 at days 24 and 46 indicating that in this sediment, the rate of transformation of the R-(-) enantiomer was faster than that of the S-(+) enantiomer.

Conclusion for this study: There are no regulatory data available for degradation of fipronil and its metabolites in anaerobic water/sediment systems. This study provides some useful information and has reported degradation half-lives of parent fipronil in two anoxic sediment systems. In both systems, however, there was a corresponding increase in the sulphide, MB45950. The data are not reported in a way that allows an assessment of degradation of ‘total residues’, and this is important for the fipronil assessment. Nonetheless, in

the absence of other data, the results of this study will need to be used in the risk assessment.

4. Mobility

4.1. Volatility

4.1.1. *Original data package*

No laboratory data were available for these assessments.

While the fate of fipronil in the atmosphere was not considered in the original assessments, DEWHA has calculated the rate constant for reactions of fipronil with OH radicals (photochemical oxidative degradation) in the atmosphere using the AOP program [AOPWIN Program (Atmospheric Oxidation Program for Microsoft Windows 3.1) Version 1.8, Syracuse Research Corp. 1988–97]. The structure of fipronil (pure) was entered into the program with the following SMILES notation: FC(F)(F)S(=O)c1c(N)n(nc1N)c2c(Cl)cc(cc2Cl)C(F)(F)F. No reference compounds were modelled.

First, the rate constant k_{OH} of the active substance was estimated based on the chemical structure. The resulting value was:

k_{OH} 96.1043^{-12} cm^3/molecule.s

The half-life of this process is calculated by the following equation:

$t_{½}$ = ln2/k' = ln2/k_{OH} X [OH radicals]

The diurnally and seasonally-averaged concentration of tropospheric hydroxyl radicals used by the AOP program is 1.5 X 10^6 cm^{-3}. Therefore, half-life for the degradation of fipronil by hydroxyl radicals was calculated to be 1.3 hours.

4.1.2. *Data available for later assessments*

The following study was available for assessment for registration of fipronil as a termiticide.

- Volatilisation from water

Borosilicate glass jugs containing de-ionised solutions of 0.8 mg/L of fipronil and desthiofipronil were sparged with 200–220 mL/min of N_2 through a coarse dispersion tube at 24^{o}C for 800 hours (Ngim & Crosby 2001). Henry's Law constants were derived from these experiments using a literature method and compared with calculated values. The Hcalc for fipronil and desthiofipronil (8.5X10^{-10} and 1.6X10^{-8} respectively) indicated that water would volatilise more rapidly, predicting that both compounds would concentrate in field water in the absence of other loss mechanisms. However, the Hexp for fipronil of 6.6X10^{-6} indicated it would volatilise slowly from rice fields. The four orders of magnitude

difference between experimental and calculated values were put down to possible errors in solubility and vapour pressure estimations – both are very low.

4.2. Soil adsorption/desorption

4.2.1. *Original data package*

Standard batch adsorption/desorption studies were conducted in duplicate on 2.5 g samples of five soils treated with solutions of radiolabelled fipronil (10 mL) at nominal concentrations of 0.01, 0.05, 0.2 and 1 µg/L and shaken in the dark for 24 hours. Five sequential desorptions of residual soil were conducted, each for over 1 hour, at the same soil/water ratio (Godward et al. 1992 (a), Godward et al. 1996).

Table V2.8: Soil characteristics and Koc findings from Godward et al. 1996

Soil type	pH	% oc	% sand	% silt	% clay	CEC	Koc
Loamy sand	6.3	3.3	83	9	8	10.8	427
Sandy loam	6.1	0.3	77	11	12	7.1	1248
Loam	6.9	4.2	46	29	25	36.5	486
Sandy clay loam	6.2	1.1	58	18	24	12.6	800
Sandy clay loam	6.3	1.6	47	19	34	20.4	673

Chromatographic analysis indicated that fipronil was stable over the course of the study. Adsorption and desorption data were well correlated with the Freundlich equation in all soils, and returned soil organic carbon adsorption coefficients from 400–1300, characteristic of low mobility in soils. Desorption coefficients were generally slightly higher than those for adsorption (markedly so for the sandy loam) and generally exhibited a gradually increasing trend through the five desorption cycles (marked increases occurred in the sandy loam).

4.2.2. *Data available for later assessments*

The following study was available for assessment for registration of fipronil as a termiticide.

Soil sorption coefficients of fipronil and its two main metabolites were measured, using a batch equilibrium method, on eight South Australian soils (Ying & Kookana 2001) ranging from sandy to clayey.

Table V2.9: Details of the soils used by Ying and Kookana, and the Kf/Koc values for fipronil in 5% acetonitrile/water

Soil type	pH	% oc	% fine sand	% silt	% clay	% coarse sand	Kf	Koc
Pt Wakefield	8.0	0.95	25	4	20	40	2.64	278
Mintaro	5.9	1.67	35	27	33	5	4.84	290
Mountadam	4.5	0.68	36	2	3	58	3.71	546
Turretfield	7.4	1.77	27	23	48	2	4.75	268
Nuriootpa	6.8	0.82	58	6	5	29	3.36	410
Roseworthy Farm	5.4	0.51	41	4	10	43	1.94	380
O'Halloran Hill	7.5	1.86	17	9	60	8	4.72	254
Roseworthy Campus	7.2	1.31	37	1.4	12	47	4.83	369

A 2 g soil sample was shaken with 5 mL of 5% acetonitrile/water solutions containing 1–15 mg/L fipronil on a mechanical shaker for about 4 hours. After centrifugation the aqueous supernatants were passed through a C18 cartridge and then analysed by GC. The sorption coefficients were also measured, for fipronil only, in a 5% methanol/water mixture, as well in different fractions of acetonitrile (or methanol)/water ranging from 5–40% (Turretfield soil only). Desorption was not studied.

The average Koc values for fipronil, its sulfide and desulfinyl metabolites (presumably MB45950 and MB45897 or MB46513 respectively) in 5% acetonitrile/water were 349, 1665 and 814 respectively. Values for fipronil were in general lower than those generated using more standard methodology above (attributed to the presence of the cosolvent). Sorption was better correlated with soil organic carbon than soil clay contents, but soil pH had no effect.

In 5% methanol/water the average Koc values for fipronil, its sulfide and desulfinyl metabolites were higher at 825, 3946 and 2010 respectively. Sorption coefficients decreased sharply with increasing fraction of cosolvent. This was said to be relevant as commercial termiticides contain solvents or surfactants, as is the case with Termidor.

4.2.3. *Additional data not previously available*

The EFSA review reports study results for adsorption and desorption of several of the main fipronil metabolites. These studies provide information on the mobility of the main fipronil metabolites not available to the APVMA for other assessments. The studies (with the exception of the amide, RPA200766) should be provided for review as the results are required for use in the risk assessment to revise predicted environmental concentrations. Results are summarised below:

Title	[^{14}C]-M&B45950: Adsorption/Desorption to and from Four Soils and One Sediment
Authors	Burr
Date	1997
Test guideline	EU Commission Directive 95/36/EC Section 7.1.2; US EPA 163-1
Data validity	4 (source document – study not independently reviewed)
Data relied on	Yes – the results were relied on for this scoping report

The following summarises the results of a standard batch equilibrium test for the sulphide MB45950.

Table V2.10: Summary of adsorption and desorption of MB45950 to four soils and one sediment

Soil type	pH (water)	OC (%)	Adsorption			Desorption (1st cycle)		
			Kf	1/n	Koc	Kf	1/n	Koc
Silt loam	6.2	0.5	28.10	1.05	5621	27.87	0.96	5574
Sandy loam	6.7	1.2	42.36	0.95	3530	48.48	0.95	4040
Loam	7.0	2.2	95.97	0.99	4362	94.59	0.97	4300
Sandy clay loam*	8.2	2.3	100.02	0.97	4349	97.59	0.95	4243
Silt loam	8.1	1.9	32.20	0.93	1695	37.92	0.92	1996

* - Sediment

Title	[^{14}C]-M&B46136: Adsorption/Desorption to and from Four Soils and One Sediment
Authors	McMillan-Staff
Date	1997a
Test guideline	EU Commission Directive 95/36/EC Section 7.1.2; US EPA 163-1
Data validity	4 (source document – study not independently reviewed)
Data relied on	Yes – the results were relied on for this scoping report

The following summarises the results of a standard batch equilibrium test for the sulfone MB46136.

Table V2.11: Summary of adsorption and desorption of MB46136 to four soils and one sediment

Soil type	pH (water)	OC (%)	Adsorption			Desorption (1st cycle)		
			Kf	1/n	Koc	Kf	1/n	Koc
Silt loam	6.2	0.5	26.55	1.14	5310			
Sandy loam	6.7	1.2	48.64	0.99	4054	72.1	1.02	6008
Loam	7.0	2.2	148.40	1.05	6745	231.0	1.08	10500
Sandy clay loam*	8.2	2.3	80.18	0.97	3486	95.1	0.98	4136
Silt loam	8.1	1.9	27.51	0.94	1448	33.8	0.95	1777

* Sediment

Title	Fipronil metabolite MB46513: Soil adsorption/Desorption
Authors	Feung and Mislankar
Date	1996
Test guideline	US EPA Subdivision N Guideline 163-1
Data validity	4 (source document – study not independently reviewed)
Data relied on	Yes – the results were relied on for this scoping report

The following summarises the results of a standard batch equilibrium test for the desulfinyl MB46513.

Table V2.12: Summary of adsorption and desorption of MB46513 to four soils and one Ssediment (Feung & Mislankar 1996)

Soil type	pH (water)	OC	Adsorption			Desorption (1st cycle)		
		(%)	Kf	1/n	Koc	Kf	1/n	Koc
Silt loam	6.5	0.47	5.47	0.92	1164	6.21	0.93	1321
Clay	6.2	1.22	15.24	0.94	1245	14.65	0.92	1201
Sand	6.8	0.38	4.34	0.92	1150	5.77	0.93	1518
Loamy sand	6.4	0.34	5.13	0.95	1498	5.93	0.95	1744
Pond sediment	5.6	4.98	69.34	0.94	1392	66.22	0.91	1329

Title	[^{14}C]-RPA200766: Adsorption/Desorption to and from Four Soils and One Sediment
Authors	McMillan-Staff
Date	1997b
Test guideline	EU Commission Directive 95/36/EC Section 7.1.2; US EPA 163-1
Data validity	4 (source document – study not independently reviewed)
Data relied on	Yes – the results were relied on for this scoping report

The following summarises the results of a standard batch equilibrium test for the amide RPA200766.

Table V2.13: Summary of adsorption and desorption of RPA200766 to four soils and one sediment

Soil type	pH (water)	OC	Adsorption			Desorption (1st cycle)		
		(%)	Kf	1/n	Koc	Kf	1/n	Koc
Silt loam	6.2	0.5	0.86	0.89	173	1.42	0.88	284
Sandy loam	6.7	1.2	2.25	0.91	188	3.21	0.94	267
Loam	7.0	2.2	3.90	0.94	177	4.52	0.93	205
Sandy clay loam*	8.2	2.3	4.68	0.93	203	5.38	0.93	234
Silt loam	8.1	1.9	1.83	0.91	96	2.55	0.92	134

* - Sediment

The following report was also considered from the literature:

Title	The Sorption and Degradation of the Rice Pesticides Fipronil and Thiobencarb on Two Australian Rice Soils
Authors	Doran, Eberbach and Helliwell
Date	2006
Test guideline	None identified
Data validity	4
Data relied on	No – information only

This study was conducted, in part, to compare the sorption of fipronil on two representative Australian rice growing soils. The two soils were from the Coleambally (TOC 2.2%, pH 6.2, sand 14%, silt 37% clay 49%) and Yanco (TOC 2.5%, pH 6.5, sand 36%, silt 29%, clay 35%). Batch studies were conducted using a constant soil:water ratio. The fipronil formulation Cosmos (500 g ac/L) was serially diluted in water to prepare working standards in the range of 4.1–29.0 µg/L. Technical grade fipronil and fipronil sulphide (assumed to be MB45950) were also prepared as aqueous standards at concentrations of 25–60 µg/L and 30–80 µg/L respectively. Soil (~1.5 g) from the 0–10 and 10–20 mm depths was sieved (<0.2 mm). To each test vessel, 10 mL of the aqueous standards was added and shaken for 12 hours. Supernatants were recovered and extracts analysed.

From the 0–10 cm soil layers, the following results are reported:

Soil	Cosmos			Fipronil			Fipronil sulfide		
	Kf	n	Koc	Kf	n	Koc	Kf	n	Koc
Coleambally	83	0.84	3725	7	1.46	320	30	1.31	1342
Yanko	40	1.03	1568	7	1.51	292	14	1.66	540

The amount of fipronil in the Cosmos treatment sorbed by both soils began to reach saturation and as the concentration of fipronil remaining in solution at equilibrium increased rapidly, that adsorbed to soil increased only a small amount. This suggested the sorption capacity of the soil was becoming saturated due to a low number of specific fipronil sorption sites, or more likely, competition between the emulsifiers in the formulation and fipronil for these sorption sites.

Title	Sorption of Fipronil in Tropical Soils
Authors	Mukherjee and Kalpana
Date	2006
Test guideline	None identified
Data validity	4
Data relied on	No – information only

Sorption/desorption experiments for fipronil were carried out by the batch equilibrium method in triplicate in three soils. Five different concentrations were used with 0.01 N $CaCl_2$ as a solvent. Fipronil was dissolved in 20 mL 0.01 N $CaCl_2$. To this solution, 10 g air-dried soil was added. The soil solutions were shaken for 4 hours then kept to equilibrate (presumably without shaking) for 24 hours. After this time, samples were centrifuged for 10 minutes prior to analysis.

The data were fitted to the logarithmic form of the Freundlich equation.

The soils used had the following properties:

Property	Delhi	Ranchi	Nagpur

Texture	Sandy loam	Sandy loam	Clayey
Organic matter	0.951	0.072	0.734
CEC (meq/100 g)	7.43	4.21	14.27
pH	8.04	5.57	8.28
OC[1]	0.553	0.042	0.427

[1] Converted by DEWHA by OC = %OM/1.72

The authors determined the following Kd values based on different concentrations tested. The corresponding Koc values, determined by DEWHA (Koc = KdX100/%OC) were calculated:

Concentration (mg/kg)	Delhi		Ranchi		Nagpur	
	Kd	Koc	Kd	Koc	Kd	Koc
0.01	0.64	116	0.85	2023	1.50	351
0.05	0.32	58	0.61	1452	1.00	234
0.1	0.39	70	0.69	1642	0.82	192
0.15	0.36	65	0.63	1500	0.64	149
0.2	0.40	72	0.60	1428	0.64	150

The authors make the following conclusions with respect to this study:

- fipronil, being non-polar, has more affinity towards organic matter
- sorption was slow and irreversible (desorption data not reported)
- sorption of fipronil at low concentrations is low because it faces strong competition from water molecules for adsorption sites
- fipronil adsorbed increasingly to soil with increasing organic content as is evident from the adsorption coefficient on different soil types.

There appears to be some problem with the data as reported in the paper, compared with the interpretation. In this study, the Kd values generally don't appear to relate to organic matter as reported in the paper. The lowest organic matter soil (Ranchi) has higher Kd values for all tested concentrations than the highest OM soil (Delhi). Corresponding Koc values are around 20 times higher in the Ranchi soil compared with the Delhi soil.

Sorption based on Koc values was higher at lower concentrations based on the results as reported in this paper.

4.3. Soil column leaching studies

4.3.1. *Original data package*

A low leaching potential is apparent from leaching studies (Godward et al. 1992 (b)) conducted in duplicate on packed columns (36 x 5 cm) of the same five soils used in the adsorption study. Radiolabelled fipronil was either freshly applied to the columns, or adsorbed to 20 g loamy sand (for the loamy sand columns) or sandy loam (for remaining columns) for 35 days of aerobic incubation before application, at rates approximating 200 g/ha. Columns were leached with the equivalent of 50.8 cm of rainfall over 2–7 days.

Radioactivity in leachates from fresh columns was generally below 1%, although it reached 8% in one sandy loam sample (an apparent artifact as the leachate from the other contained <1%). Most residual radioactivity (73–99%) was detected in the top 6 cm of the soil columns, with the exception of the sandy loam columns where most (82–91%) of the residual radioactivity was found in the top 12 cm. Formation of bound residues was only significant in the first of the two sandy clay loams, where 25–36% of applied radioactivity became unextractable.

Unchanged fipronil was the major component found in soil extracts, with the amide hydrolysis product RPA200766, sulfide MB45950 and sulfone MB46136 present in minor amounts. The amide and sulfone were most frequently detected, the latter reaching 19% of applied in the top 6 cm of the loam. No metabolites were detected in the sandy loam.

Analysis of the aged samples indicated that only those on sandy loam had undergone detectable degradation (about 6%) but the HPLC chromatogram is uninformative concerning the nature of the metabolites. Leachates from columns loaded with aged samples of fipronil contained up to 4% of applied radiolabel, and the soil fractions contained similar levels of radiolabel to those observed on fresh columns. Unchanged fipronil was the main component extracted, but the amide RPA200766, sulfide MB45950 and sulfone MB46136 were also found, in larger amounts than on the fresh columns (around 20% of radiolabel was recovered as the amide RPA200766 from the top 6 cm of the second sandy clay loam, for example). Small amounts of the sulfonate RPV204615 were also apparent in the loam.

Results indicate that both fresh and aged samples of fipronil have low mobility in soils.

4.3.2. *Additional data not previously available*

Title	Persistence and Movement of Fipronil Termiticide with Under-Slab and Trenching Treatments
Authors	Ying and Kookana
Date	2006
Test guideline	None identified
Data validity	4
Data relied on	No – information only

Ying and Kookana (2006) assessed the mobility of fipronil in soil under intermittent wetting and drying periods. Two soils were used with each air-dried and sieved (2 mm). Two columns (15 cm inner diameter, 30 cm length) were packed and fipronil applied to the surface at a rate of 3 g ac/m^2 with bromide as a tracer, in 5 L water/m^2. This high application rate (30 kg ac/ha) corresponds to equivalent rates when used as a termiticide. Following application, the packed columns were left for 7 days prior to applying water by a dripping system equivalent to 20 mm rain. This sequence of drying and wetting was repeated five times. The soil columns were then sectioned (5 cm) for analysis.

The results showed fipronil was not mobile in either soil under the simulated weather conditions of wetting and drying cycles. Fipronil remained in the top 5 cm of the packed columns at very high concentrations (62.25–72.98 mg/kg). Trace amounts (levels not reported) were found deeper in the profile.

5. Field dissipation

5.1. Terrestrial field dissipation studies

5.1.1. *Original data package*

- Exploratory studies in Europe

These studies involved spray application at 50 g/ha to prepared seed beds at Sevilla and broadcast of 0.1% Biodac granules at the same rate at Bologna. Soils were loamy. Plots were maintained as bare ground using mechanical and chemical (paraquat, glyphosate) weeding, apart from one-third of the Spanish site which was planted with cotton. Soil samples were taken for 18 months after early summer application (Boussemart 1995).

Significant amounts of the photochemically-derived trifluoromethyl pyrazole MB46513 were found at Sevilla, including at the first sampling within hours of application, but very little of this metabolite was detected at Bologna, perhaps because spray applications are more susceptible to photolysis than granular. This degradation product was only detected for the first 2 months after application. The dominant metabolite at Sevilla was the oxidised sulfone MB46136, with traces of the sulfonate RPV204615 at one sampling but no sulfide MB45950 or amide RPA200766 at any time. The sulfone also dominated at Bologna, where no sulfonate was found but small amounts of sulfide and amide also formed.

A similar model to that employed in the laboratory studies was used to obtain the best estimations of dissipation rate and order of reaction. First half-lives of fipronil were 5.6 days at Bologna and 7.9 days at Sevilla, extending to 14.4 and 46.2 days for total residues. The half-life at Bologna for total residues when data were forced to fit first-order kinetics was 182 days, but could not be determined for fipronil itself because of major departures from first-order kinetics. At Sevilla, the half-life of fipronil extended to 22 days when forced to fit first-order kinetics, but remained unchanged for total residues. These half-lives should be regarded as indicative only because of high variability within and between plots at the prevailing low residue levels.

The increasing metabolite levels represented only a fraction of the concomitant declines in fipronil levels. The authors suggest this reflects further degradation into smaller molecules.

No residues were detected below 10 cm at Sevilla, notwithstanding irrigation during the first months of the study. At Bologna, traces (1–2% of applied) were

found in the 20–30 cm soil segment, as trifluoromethyl pyrazole MB46513 at 1 month and sulfone MB46136 at 4 months after application.

- Definitive studies in Europe

Field dissipation was studied at four locations in Italy, Spain and France, where fipronil was applied in May 1992 (July for one site) at 200 g/ha as granules (2% on sepiolite) in furrow to maize. Levels of unchanged fipronil and metabolites were monitored in 10 cm soil segments to 30 cm, and in the 30–60 cm segment, for 24 months after application (Boussemart 1993; Boussemart & Wicks 1995).

Soil properties for the surface 10 cm are tabulated below. The two French soils were underlaid at depths below 60 cm by sandy loam subsoil. Plots were generally flat (a 0.15% slope at Sevilla) and undrained, and were irrigated to a minimum of 110% historical rainfall. In furrow samples (each a composite of five cores) were taken from four sub-plots. Some samples were also taken at the quarter and halfway points between the furrows, at 2, 6, 12, 18 and 24 months after application, to investigate possible lateral movement. Samples were analysed for fipronil and its primary metabolites (amide, sulfide, sulfone, trifluoromethyl pyrazole and sulfonate) with a limit of quantitation of 2 µg/kg. Selected samples (a total of 27) were also analysed for the corresponding carboxylic acids of fipronil and its sulfide and sulfone, with a limit of determination of 5 µg/kg.

Table V2.14: Soil properties from Boussemart (1993); Boussemart and Wicks (1995)

Location	Soil type	pH	% oc	% sand	% silt	% clay	CEC
Bologna	Loam	8.5	0.8	42	45	14	19
Sevilla	Silt loam	7.3	0.9	35	51	14	15.6
Chazay	Loam	6.1	1.3	27	57	15	23
Mereville	Silt loam	8.1	1.4	30	46	21	24.8

Total residues found at the first sampling ranged from 1.5–4.2 mg/kg, significantly higher than the theoretical concentration of about 0.17 mg/kg from dispersing 200 g/ha through 10 cm of soil. The high residues reflect confinement of fipronil to the furrow. Significant variability was observed between sub-plots, reflecting a heterogenous distribution of residues through the soil, but data are adequate to determine dissipation trends.

A rapid decline in the levels of fipronil and total residues was evident during the first month or two of the studies, but total residues appeared relatively static beyond this time. The sulfone MB46136 was the main metabolite detected, followed by lesser amounts of amide RPA200766 and sulfide MB45950. Traces of the photochemically-derived trifluoromethyl pyrazole MB46513 were detected sporadically at all sites. The sulfonate RPV204615 was also detected in trace amounts. Low levels of the two photochemically-derived metabolites probably reflect spillage of granules at the soil surface. The first three metabolites (sulfone, amide and sulfide) were found at combined levels of 3–13% of the

fipronil levels at the first sampling, and gradually increased in proportion. The increasing metabolite levels represented only a fraction of the concomitant declines in fipronil levels. This may reflect extensive leaching of hydrophilic metabolites, such as the carboxylates discussed below, as well as the further degradation into smaller molecules suggested in the exploratory study.

As noted above, selected samples were also analysed for the carboxylic acids formed by hydrolysis of the nitrile substituent of fipronil and its sulfide and sulfone analogues. These metabolites would be expected to be hydrophilic and leachable. The carboxylate derivative of fipronil was most frequently detected, reaching levels of 37 µg/kg after 12 months at Sevilla, followed by that of the sulfone analogue, which reached 21 µg/kg after 24 months at the same location. These levels equate to 1–2% of applied fipronil. Note that these detections occurred in individual sub-plots only. The carboxylate of fipronil's sulfide analogue was not detected at any location.

Most residues were recovered from the surface 20 cm of soil. Mobility was most apparent at Mereville where a combination of frequent rain and well-drained, coarse-textured soil resulted in some 6% of total residues at 6 months being found in the 20–30 cm horizon, as well as traces (<1%) deeper in the profile.

The most commonly detected metabolite in the 30–60 cm segment was the amide RPA200766, generally near the limit of quantitation but reaching 7.8 µg/kg in one subplot 24 months after application.

Metabolites appear more mobile than fipronil as their combined concentration was much less than that of the parent in the surface 10 cm but exceeded it deeper in the soil. The main metabolite, the amide RPA200766, appears to be the dominant contributor to this increased mobility, being the predominant species in the 20–30 cm horizon at Mereville after the first 6 months of the study. This metabolite was also found in significant concentrations (0.01 mg/kg, or some 80% of total residues) in the 20–30 cm horizon at Bologna 6 months after application, consistent with its enhanced mobility on HPLC, and was also the only contaminant detected in the 20–30 cm horizon at Sevilla after 6 months, at levels near the detection limit of 2–3 µg/kg. This metabolite continued to be detected in the 20–30 cm segment at all sites to the end of the study. The amide is evidently slightly more mobile than fipronil.

No significant lateral movement of fipronil and metabolites was apparent at any site except the final sampling at Chazay when significant amounts of fipronil and its sulfone, sulfide and amide metabolites were found at the quarterway point between the rows. About 25% of total residues were detected at this point, compared with less than 10% at all other locations and sampling times. This behaviour is thought to reflect high rainfall (some 380 mm in 2 months) at the start of the second year of the study and consequent water saturation on the plot. Note that no 18-month samples were taken between the rows at this site.

The first half-life for degradation of fipronil as calculated by linear regression ranged between a minimum of 3.2 months at Bologna to a maximum of 4.5

months at Chazay. An estimated 10.5–14.8 months is needed for 90% degradation of fipronil. In terms of total residues, these ranges extend to 6.5–11.4 months and 21.6–38.0 months respectively.

- Definitive studies in North America

These studies were conducted in the States of California, Nebraska, North Carolina and Washington, using a 1.5% granular formulation of fipronil applied in furrow at 1.12 g active per 100-metre row (equivalent to 147 g/ha) when corn was planted. Soil properties for the surface 15 cm are tabulated below (Norris 1994).

Table V2.15: Summary of soil characteristics from Norris (1994)

Location	Soil type	pH	% oc	% sand	% silt	% clay	CEC
California	Loam	7.4	0.8	46.2	39.8	14.0	17.3
Nebraska	Clay loam	5.9	1.3	27.0	42.3	30.7	21.8
N Carolina	Sand	5.6	0.5	85.7	9.8	4.5	4.6
Washington	Loamy sand	7.7	0.6	83.7	14.6	1.8	11.3

Three metabolites were observed, the sulfone MB46136, sulfide MB45950 and amide RPA200766. The sulfone was the dominant metabolite, accompanied by significant amounts of the amide and smaller amounts of the sulfide. Photochemical breakdown products (trifluoromethylpyrazole MB46513 and sulfonate RPV204615) were not seen.

The first half-life of fipronil as estimated using linear regression ranged from 3.0–7.3 months. Half-lives for the metabolites could not be computed because of their continuing formation, but appear somewhat longer than for fipronil.

Residues were only found in the surface 45 cm throughout 18 months of sampling at three sites, generally with only the amide found in quantifiable amounts (>5 µg/kg) below 15 cm. At the Washington site, detection in the 30–45 cm segment correlated with the spring thaw and consequent saturated soils, and one metabolite (the amide RPA200766) was found at concentrations of 5–10 µg/kg in the 45–60 cm segment at 14 months after application and subsequent samplings. Traces (below the limit of quantitation) were also found to 90 cm at the 16 and 18-month samplings. No significant lateral movement was observed.

- Turf studies in North America

Studies were conducted for 4 months on bare soil and established turf plots in Florida (sand) and North Carolina (sandy loam) using a 0.1% granular formulation applied beneath the surface through slits at a rate of 56 g/ha fipronil (within the range used in Australia). Soils were sampled in 15 cm increments to a depth of 0.9 m and analysed for fipronil and its major soil metabolites and photochemical breakdown products (sulfide MB45950, sulfone MB46136, trifluoromethyl pyrazole MB46513 and amide RPA200766) (Chancey & Norris 1994).

Only fipronil and its sulfone and amide metabolites (MB46136 and RPA200766) were consistently found at levels above the limit of detection (2 µg/kg, equivalent to about 6% of applied), with occasional detections of the sulfide MB45950. Some samples with significant sulfone levels werre also analysed for the sulfonate RPV204615, but with negative results. The amide RPA200766 was only found in the bare soil plots. Detections only occurred in the surface 15 cm, notwithstanding adequate rainfall and irrigation to ensure good soil penetration. The half-life of fipronil was about 2 weeks under turf and 4–6 weeks in bare soil, the more favourable results under turf probably a reflection of larger and more active microbial populations.

5.1.2. *Data in later assessments*

The following study was available for assessment for registration of fipronil as a termiticide.

- Behaviour under Sahelian Plain field conditions

Bobé et al. (1998(b)) studied the behaviour of fipronil under sub-Saharan conditions which are relevant to local use for locust control and as a termiticide.

Two plots of 1600 and 1215 m^2 respectively in the Niamey region of Niger were treated with 2 L of Adonis 4UL, corresponding to a rate of 8 g/ha, double the recommended locust dose, using a battery-powered rotary sprayer. Plots were manually weeded prior to application and had the properties listed in Table V2.16 for the top 10 cm (note that data for the 10–20 cm and 20–30 cm layers are also available in the paper). The average maximum temperatures were 37.5 and 38.3^{o}C respectively. Heavy rains (64 mm) fell at the first site on the day after treatment, whereas at Saguia no rainfall occurred after application.

Table V2.16: Details of the soils used by Bobé et al. (1998(b))

Location	Soil type	pH	% oc	% fine sand	% coarse sand	% fine silt	% coarse silt	% clay	CEC (meq/100 g)
Banizoumbou	Loam	5.8	0.15	25.6	53.8	1.8	16.4	2.4	0.74
Saguia	Clay loam	5.3	0.05	47.3	50.7	0.6	0.8	0.6	0.72

A composite sample, consisting of sub-samples at various points along the diagonal of the plots, was taken for up to 53–57 days after treatment and analysed by GC. Despite the sandy soils, fipronil was not found below the 0–10 cm soil layer, and within this layer was noticeably higher in the 0–5 cm than 5–10 cm depths when examined on days 14 and 28. These levels were used to determine the rate of degradation. At Banizoumbou a half-life of close to 36 hours was estimated. While for the Saguia soil the half-life estimate was made difficult due to the delay of day 0 sampling for 8 hours, it was very similar. These are more rapid than that observed under temperate climates (3.2–4.5

months in Europe and 3.0–7.3 months in the United States respectively from above).

Three days after treatment fipronil was 75% degraded at Banizoumbou, and four metabolites were identifiable, the dessulfinyl photodegradate (MB46513), the sulfide (MB45950), the sulfone (MB46136) and the amide (RPA200766), of which only the amide could be detected in the 10–20 cm layer. The same metabolites appeared in the Saguia soil, apart from the sulfide which was relatively abundant at Banizoumbou. After the third day, fipronil and its metabolites degraded more slowly at Sanguia, with the process seeming to stabilise (attributed to the absence of rainfall).

- Sugar cane runoff study

The following study was provided as part of the agreement made at the time of registration for the company to monitor residues from sugar cane use.

Two sites representative of typical sugar cane growing country were selected with drainage either directly towards brackish water (Redlynch, near Cairns) or into watercourses (Mourilyan, 120 km south of Cairns) which lead more or less directly marine water (Liddell 2000). Only the latter site was treated with fipronil in the previous year. Soil types at both sites are said to be typical of the alluvial flood and coastal plains in the area, with the former an alluvial red clay and the latter a dark grey very coarse sand, and had the properties listed in the table below. Sediment samples were said to be very variable in nature, generally containing large amounts of organic matter and variable amounts of fine material.

Table V2.17: Details of the soils used by Liddell (2000)

Location	Soil type	pH	% om	% fine sand	% coarse sand	% silt	% clay	CEC (meq/100 g)
Mourilyan	Coarse sand	6.0	1.6	26	67	5	2	2.00
Redlynch	Red clay	5.1	1.0	42	1	35	22	3.84

Spraying was performed with Regent 200 SC at the rate of 375 mL/ha, based on the recommended (registered) application rate of up to 5.7 mL/100 m of row, with a treated row width of 20 cm under correct weather conditions and crop height.

During the experiment extensive flooding occurred in both areas, with significant rainfall events (>10 mm precipitation) occurring at Mourilyan on, or immediately prior to days 7, 21, 56 and 85 of sampling (1903 mm total). At Redlynch significant rainfall fell on or prior to days 6, 15, 28 and 42 of sampling, with a total of 333 mm.

At the Mourilyan site a field drain bordered an area of cane with the three rows with a trash blanket in between that were sprayed. Soil samples were collected up to 40 cm from the base of the cane. Sediment and water samples were collected in the field drain which leads through a small creek to the Moresby

River which travels a short distance into Mourilyan Harbour. Sediment, soil and water samples were also collected at intervals along this water course on days 0, 3, 7, 14, 21, 28, 42, 56 and 84 post treatment.

At Redlynch an intermittent field drain bordered the three rows of cane with a mixture of trash and weeds in between that were sprayed. At the end of the field the drain empties into Freshwater Creek which feeds into the Barron River and then into Trinity Bay. Water and sediment from the creek were sampled on days 0, 3, 7, 14, 21, 28 and 42 post treatment. Initially the field drain was dry but once it filled with water the sediment were sampled. Note that collection was only conducted for 42 days as the site was badly disturbed by a tropical cyclone after this period.

Analysis of samples for fipronil and its metabolites was carried out by GC-MS using a published method (Bobe et al. 1998(b)) for soils and sediments adapted for use in Australia. The concentrations for fipronil and its metabolites MB46136 (sulfone), MB46513 (trifluoromethyl pyrazole) and MB 45950 (sulfide) in the matrix were converted to fipronil equivalents and the sum of these reported as fipronil$_{total}$. The Limit of Quantitation (LOQ) for fipronil was set at 10 ppb, but a 'concentration factor' of 1.25 in the water sample extraction allowed the LOQ to be revised down to 8 ppb for both fipronil and its metabolites in water. However, during the extraction procedure for soils and sediments a much greater 'concentration factor' of about 22.5 was achieved, allowing a much more sensitive LOQ of 0.4 ppb for fipronil and its metabolites in these solid media. These LOQ are the reverse of the usual much greater sensitivity in the cleaner water samples.

As a result, the LOQ of 8 ppb was not exceeded in any of the water samples, said to indicate that concentrations of fipronil and its metabolites in water were <8 ppb, which the author notes would be as expected given the low water solubility of fipronil (and its presumably its metabolites) and the low concentrations of fipronil$_{total}$ in sediments of the creek and field drain (but see comments below). However, given that fipronil's water solubility is in the order of 1–2 mg/L (ppm) (that is, nearly three orders of magnitude higher than the LOQ) it would not be unexpected to find fipronil dissolved in water in the very low ppb range. That fipronil will not completely partition to soil/sediment is supported by both lab and field studies. When this is coupled with the fact that fipronil and several of its metabolites are toxic in the low to sub-ppb range to a variety of aquatic invertebrates, the lack of a sufficiently sensitive assay to detect fipronil levels in water is a serious deficiency in the study.

While the recovery for the water assays was acceptable at >76%, this was not so for soils and in particular sediments, where they were in the order of 40–50% for fipronil$_{total}$ and only 25–30% for fipronil itself. This is of real concern, especially as the reported results are uncorrected, and therefore may have been up to four times as high if recovery is accounted for. These would be raised even further if the amount of water (ranging from 5–50%) in the soil/sediment samples was also accounted for. The author did not dry his soils

or sediments (compared with Bobe et al. (1998(b) who used air-dried soils) for fear of an unacceptable amount of further reaction and/or volatilisation.

The uncorrected values for fipronil$_{total}$ in the Redlynch soil ranged from >45 ppb (another deficiency in the study resulting from an exceedance of the upper limit of the calibration curve) to 1 ppb over the course of 42 days. The decline of fipronil did not follow first-order kinetics and at the end of 42 days the trifluoromethyl pyrazole photolysis product MB46513 was present at 46% (said to be in contrast to literature studies where it was a minor metabolite or absent entirely, but note its presence in some Spanish and Sahelian soils above), with a similar amount of the sulfone MB46136 (35%), and much smaller amounts of fipronil (16%) and the sulfone MB 45950 (3%). A possible work up effect leading to MB46513 was discounted and it was concluded that a major pathway for the transformation of fipronil under far north Queensland summer conditions is via photochemical reaction (note it was 18 ppb on day 0).

Uncorrected fipronil$_{total}$ concentrations in the Mourilyan soil samples ranged from >45–2 ppb with a very uneven decline over 85 days. For example fipronil$_{total}$ was >45 and 68 ppb after 14 and 21 days respectively, based largely on contributions of >45 and 43.8 ppb fipronil which was only 5.5 ppb on day 7 and <LOQ on day 28. The author notes that replicate samples taken from <0.5 m away in the field showed considerable variation, suggesting that either the presence of the dense trash blanket or the directional nature of the spraying resulted in a heterogeneous lateral distribution of pesticide residues in the soil. Again the predominant metabolite after 85 days was the photolyis product MB46513 (53%), with smaller and near-equal amounts of fipronil (15%) and the other metabolites.

The fipronil$_{total}$ concentrations in the Redlynch sediment samples (apparently taken only from the entry point of the nearby creek) were low (0.0–0.8 ppb), with all individual values below the LOQ of 0.4 ppb and thus indicative only. The author concluded that small amounts of fipronil and/or its metabolites, supported on soil particles or organic matter, were finding their way into the nearby creek. For the Mourilyan sediment samples fipronil$_{total}$ concentrations were all below 1 ppb, with the levels of the individual components nearly all below the LOQ. The author claims this justified the decision not to collect samples further downstream, although as noted, these levels may have been seriously underestimated. Again it was concluded that small amounts of fipronil and/or its metabolites were making their way into the field drain at low levels, which was not surprising since it was immediately adjacent to the sprayed area and very high rainfall (>100 mm per day on several occasions) meant the field was often completely submerged, allowing for considerable transport of surface soil into the field drain.

Given the deficiencies in this study outlined above, but that the potential for off site movement in sugar cane use has been clearly demonstrated, the author's recommendation that the study should be repeated on a commercial-size plot using more sensitive assay methods to clarify the actual extent of loss of fipronil and its metabolites from the sugar cane paddock is supported.

- Levels in Australian soils after treatment with Termidor

Four different sites across Australia were chosen to encompass the different climatic conditions and soil types (McBeath undated). Fifty soil pads or plots were treated at each site with five different treatment regimes, including fipronil applied at 1.5, 3.0 and 6.0 g ac/m^2, equivalent to 50–200% of the proposed rate. Details of soil properties are in Table V2.18 (note the rather sandy natures of three sites). The soil was scarified to a depth of 150 mm prior to application, either by hand or the use of a mechanical backhoe and not compacted. It appears an experimental 25 g/L formulation of fipronil was used.

Table V2.18: Details of the soils used in McBeath, undated

Soil type	pH[a]	% oc	% coarse sand	% fine sand	% silt	% clay	Electrical conductivity (dS/m)[a]
Adelaide	6.8	3.0	21	30	20	27	0.12
Sydney	6.0	3.9	59	21	5.9	8.2	0.20
Townsville	6.2	0.3	79	10	4.6	5.0	0.74
Walpeup (Vic)	7.8	1.0	47	26	8.8	17	0.02

a) of a 1:5 soil:water extract

Ten soil pads with an individual area of 0.25 m^2 were used for each treatment. After dilution in water, these were applied according to AS 3660.1 using a hand-held watering can, adding approx 1.25 L of emulsion per plot. Five of the pads were covered with a concrete slab to simulate soil beneath a structure, while the other five were exposed to the environment, simulating a perimeter horizontal barrier.

Four 80 mm soil cores were taken at random from each plot at each site at sampling intervals of 0, 6, 12, 24, 36, 48 and 60 months. Two samples used for residue analysis, and the other two for bioassay exposure to determine the distance termites would tunnel through each soil core.

Residue analysis was only carried out on up to and including the 24-month samples. Analysis was carried out, presumably by HPLC, for fipronil and the metabolites MB45950 (sulfide), MB45513 (presumably the trifluoromethyl pyrazole MB46513) and MB45136 (again presumably the sulfone MB46136, the major metabolite in other field tests – note no analysis for the amide RPA200766, the third major degradation product). However, fipronil and MB45136 so dominated that the results are quoted in total ‘fiprole’ levels comprising of these two, for the top, middle and bottom section of each core.

Both raw and mean data (individual or combined for all sites) are presented. The latter indicate a clear decline in total fipronil over time, with protection from weathering reducing the rate. For example over 24 months at the highest 6 g ac/m^2 rate the combined mean values for the entire core dropped from 1025 mg/kg to 240 and 399 mg/kg for uncovered and covered sites, respectively. This was most noticeable at the lowest rates, where after 24 months mean levels at uncovered sites were 33–38% of those at the intermediate rate, which

in turn were 53–73% of those at the top rate at the same sites. Degradation was also faster in the top sections, which at the highest rate had dropped to a mean of 150 (uncovered, ~20% of initial) to 245 (covered, ~33% of initial) mg/kg after 24 months, compared with the bottom sections which were round 15–20 mg/kg at 0 and 24 months. The latter had maximum combined mean levels of 55 (uncovered) and 126 (covered) mg/kg after 6 months, indicative of some movement down the soil column. Note however, that at 8 cm, cores sampled were relatively shallow.

The above analysis masks some of the variability in levels observed between sites. For example after treatment soil levels in Victoria were significantly higher than at the other three sites, being a mean of 2280 mg/kg at the highest rate compared with 1191 mg/kg for Sydney soil and 376 and 345 mg/kg for Adelaide and Townsville respectively. Degradation was also consistently slower in Victoria than at the other three sites, with either South Australia or Queensland the second slowest and Sydney clearly the fastest. However, due to the variability no half-life determinations were done, though examination suggests that in some cases greater than half 'total fipronil' remained after 24 months (Victoria and South Australia covered plots at proposed and highest rate respectively), as compared with <5% remaining for uncovered New South Wales plots at all rates.

The influence of climate and soil type on persistence was also examined. Rainfall clearly did not have a significant effect on degradation rates, as Townsville had by far the greatest total rain, but ranked below Sydney in terms of loss of activity (a surprise in view of the Sahelian data above). In the author's view this supports the low leaching rate of fipronil from soil. In covered plots (where the effect of rainfall and exposure are removed) the Victoria and Adelaide sites favoured persistence over Sydney and Townsville, which could be due to a temperature effect. There was some correlation between retention and levels of fine soil particles, due to the greater surface area. It is hypothesised higher levels at lower depth in these soils could be explained by settling of fine particles, note that the soil was scarified prior to treatment (see above). However, it is agreed with the author that the influence of soil type on persistence is not clear.

- Levels in United States soils after treatment with Termidor

Details of an study looking at persistence and movement of fipronil in five United States soils, after pretreatment (horizontal spray) and trench application, are also included in the submission (Anonymous undated; Essig 2002). Sites were in Arizona, California, Florida and North Carolina (sand and clay), but no details of soils properties or climate are available.

The Termidor SC formulation was used and electron capture GC and HPLC analysis of ppm fipronil, ppm metabolites and ppm 'total fiproles' was carried out.

Table V2.19: Details of the soils used in Essig (2002)

Site	Soil type	pH	% oc	% sand	% silt	% clay
Arizona (AZ)	desert clay loam	8.2	0.0	38.5	38.75	22.75
California (CA)	Hanford fine sandy loam	7.0	0.05	71	19	10
Florida (FL)	medium, fine sand	5.6	1.9	91.5	5.2	3.1
North Carolina (NC)	loamy sand	6.0	0.6	84	8	8
North Carolina (NC)	clay	4.9	0.4	36	8	56

Approximately 3 X 3 m (10 X 10 feet) pre-treatment plots were established by spraying 3.79 L (1 gallon) of 0.06% ai liquid per square metre (10 square feet), which is slightly higher than proposed for Australia (5 L per m^2 at the same dilution). Core samples of 5 cm (2 inch) were taken throughout the treated plots (four samples from each of four replicate plots). Trenches measuring 15 X 15 cm (6 X 6 inches) were also established by applying 15.2 L (4 gallons) of the same strength liquid per 3 (10 feet) of depth, which appears to be over two times the proposed Australian rate (at 100 L per m^3 the equivalent is 6.75 L). One 12.5 cm core was taken from the middle of each trench (four replicates at each site except for 16 in Arizona).

One day after treatment the amount of fipronil in soil in pretreament plots was fairly consistent across three sites (average range 22.3–31.7 ppm) except for the sandy North Carolina plot (9.2 ppm). This was attributed to uneven depth of application [most could be shown to be in the top 1.25 cm (0.5 inches)] and/or sampling, rocks or organic debris in plots, varying soil moisture or analytical method variation. One month later under uncovered conditions fipronil levels ranged from 34.8% (North Carolina clay) to 82.0% (Arizona) of initial. However, in terms of 'total fiproles' remaining levels were 47.4% (North Carolina clay) to 138% (California) of initial fipronil.

One day after trench application, average levels ranged from 53.9 (Florida) ppm to 94.8 (California) ppm, with the variation explained as above. However, 1 month later these were still 98.9% (North Carolina sand) to 196.7% (Florida) of initial levels in terms of fipronil, or 104.1–213.2% (same sites) in terms of 'total fiproles'.

Lateral movement was also examined by taking four 5 cm (2 inch) core samples (one from each edge of the square) 30 cm (12 inches) outside of the edge of the Californian and Florida pretreatment plots. Average levels were 1.0–1.7 ppm after one day and 0.6–1.3 ppm after 1 month, or a maximum of 5.5% of the levels within the plots. Single samples (12.5 cm cores) were also taken 7.5 cm (3 inches) from the outside of each trench, with 1-day samples ranging from 'not detected' (California) to 9.4 ppm (North Carolina clay, or 13.4% of the mean levels within the plot, but with a maximum individual sample of 25.4%) and 1-month levels being 0.1 (North Carolina sand) to 2.92 ppm (Florida, 5.4% of the initial trench level, but with an individual sample result of 33.1%). While the paper concludes this indicates no significant movement of fipronil occurred

laterally over 1 month following trench application, levels are very variable, attributed to sampling location difficulties.

5.1.3. *Additional data not previously available*

Title	Laboratory and Field Studies on the Degradation of Fipronil in a Soil
Authors	Ying and Kookana
Date	2002
Test guideline	None identified
Data validity	4
Data relied on	No – information only

The study, in part, considered degradation of fipronil in the field under natural weather conditions. Two small plots (2 X 2 m) were weeded, levelled and fenced. Fipronil, as a commercial termiticide (Termidor), was applied at a high rate of 1.5 kg ac/ha and a low rate of 0.75 kg ac/ha. Fipronil in the top 30 cm was sampled at 2 days, then 1, 3, 6 and 12 months after treatment. Soil cores were sectioned into 5 cm layers for analysis.

Three metabolites, desulfinyl, sulphide and sulfone derivatives (taken to be MB46513, MB45950 and MB46136 respectively, but not stated in the report) were identified from both plots. The desulfinyl derivative was detected at the highest concentrations at 2 days. This decreased over time and the sulfone increased. However, actual residue findings are not reported. In the first half of the year, most residues stayed in the top 15 cm soil, but by 6 and 12 months, trace amounts (0.004–0.006 mg/kg) were detected below 15 cm.

In the top 5 cm, the dissipation half-lives of fipronil in the field were 139 days (high treatment) and 124 days (low treatment).

The following study is specific to termiticide use.

Title	Persistence and Movement of Fipronil Termiticide with Under-Slab and Trenching Treatments
Authors	Ying and Kookana
Date	2006
Test guideline	None identified
Data validity	2* – reliable with restrictions
Data relied on	Yes – specific to termiticide application

One literature study provides useful information on persistence of fipronil in aerobic soils when applied specifically as a termiticide. Ying and Kookana (2006) assessed the persistence and movement of fipronil in soil profiles with time following treatment by standard termiticide application methods.

Persistence was measured through surface application under a simulated slab. Two small plots (2 X 2 m) of three different soil types (six plots in all) with grasses cleared were bordered and quartzite sand (~5 cm thick) laid on the soil surface. Termidor (100 g/L fipronil) was applied to the surface at rates equivalent to 3, 0.75 and 0.15 g ac/m^2 with two plots for each application. After application, each plot was covered with plastic liners and 1 cm fibre cement. The quartzite sand layer and soil layers in 5 cm increments to 15 cm depth were

sampled (four samples, but mixed to produce a bulk sample) at 2, 30, 90, 180, 360, 480, 730 and 1095 days after treatment.

There was slow dissipation and little movement of fipronil in all plots with the majority of residues remaining in the top quartzite sand layer or the 0–5 cm soil layer. Extra analysis of deeper soil samples (15–30 cm) showed no or little amounts of fipronil or its metabolites. Over the 3-year study, fipronil dissipated significantly from all three field sites. While there was no statistically-significant effect of soil type (site) on the half-life of fipronil, there was a marked effect based on application rate. The following table summarises the findings from the three sites in the top 0–5 cm sand quartzite layer for fipronil and total residues:

Table V2.20: Half lives (days) of fipronil and total residues in the quartzite sand layer

	Site 1		Site 2		Site 3	
Application rate	Fipronil	Total residues	Fipronil	Total residues	Fipronil	Total residues
Low	166	227	145	200	161	326
Medium	309	340	529	589	382	563
High	578	633	613	652	514	674

While these half-lives are for the quartzite layer only (dissipation, not strictly degradation), losses were not really the result of movement to lower soil layers. Within 3 years of this study, average fipronil concentrations in the soil profile (0–20 cm including the quartzite layer) decreased from by ~73 to 91% at the medium application rate with negligible (values not reported) amounts of fipronil or metabolites found below 20 cm.

5.2. Aquatic field dissipation studies

5.2.1. *Original data package*

- Rice paddy studies in Thailand

Following a single application (50 g/ha) of fipronil in granular form in a rice paddy environment, the only compound found in significant quantities in the paddy water was fipronil, at 23 µg/L on the day following application, declining to 3.7 µg/L by 56 days after application. The trifluoromethyl pyrazole MB46513, sulfone MB46136 and sulfide MB45950 remained below 2 µg/L, and the displacement product MB45897 and amide RPA200766 below 1 µg/L. Fipronil could be found in the top 5 cm of paddy soil 7 days after application, at levels of 5.4–13 µg/kg. The main soil metabolite under these reducing conditions was the sulfide MB45950, which was found in some (but not all) samples taken to 56 days, at concentrations in the order of 10 µg/kg (Maycey et al. 1994).

Fipronil could also be detected in the water at significant levels (in the order of 20 µg/L) for a brief period immediately following foliar application to rice 20 days after transplanting, but not when applied 50 days after transplanting. The photochemical metabolite MB46513 was also found in the water at the first sampling, at about 3 µg/L. Fipronil continued to be detected in later samples of

paddy water, at levels of 3–6 µg/L, together with the sulfone MB46136 (about 3 µg/L) in one of the later samples. Neither fipronil nor metabolites could be detected in paddy soil following these applications which may be the result of increased crop cover intercepting the spray.

- Rice paddy study in Thailand

Similar results were found from an earlier study with the exception that the sulfone MB46136 was present at a higher concentration of 7.6–17 µg/L 15 days after application (Adams et al. 1991).

Within the same study, foliar applications of fipronil as a suspension concentrate were carried out around 15 days apart, with fipronil present at 1–1.6 µg/L 31 days after the fourth foliar application. The trifluoromethyl pyrazole MB46513 was present in significant levels (8.4–11 µg/L) on the day of the first foliar application. By day 15, this had decreased to 1–1.5 µg/L, with levels similar to this obtained at later sampling periods after the second and fourth application. Quantifiable levels of MB45950 were found only following the fourth application (1.3–2.9 µg/L), whilst measurable levels of MB46136 were only found on day 0 and day 15 (2.5–6.5 µg/L). At all sampling times, MB45897 was below detection limits. RPA 200766 and RPA 104615 were less than 1 and 5 µg/L respectively.

- Evaluation of fipronil seed treatments

A field evaluation of fipronil seed treatments was conducted in Australia (Yanco Agricultural Institute). Part of this study measured residues in paddy water following an application of fipronil as a seed treatment. Rates equivalent to 12.5, 25, 50 and 100 g/ha were applied to pre-germinated rice. Samples of paddy water were collected at intervals after broadcast sowing (1–22 days), and fipronil levels measured by gas chromatography (Stevens & Helliwell 1996).

Use of fipronil at the lowest rate resulted in approximately treble the plant establishment of malathion treated bays. Twenty-four hours after application, fipronil levels in the water column were 18.3–23.2% of initial application rates as applied to the seed (that is, 14.88 µg/L at 100 g ac/ha down to 2.11 µg/L at 12.5 g ac/ha), and fell rapidly thereafter. After 22 days, fipronil was still detectable in the water column (0.05–0.01 µg/L) at initial application rates of 100–25 g/ha, but was below detection limits (0.005 µg/L) at 12.5 g/ha. An irregularity in the decline of fipronil levels between days 3–5 is explained as a consequence of rainfall during that period.

- Levels in paddy water after application to nursery boxes

A Japanese study where fipronil was applied as a 1% w/w granular treatment to rice nursery boxes at 50 g and 100 g formulation per box, tested levels of fipronil and four metabolites in paddy water. Rice was transplanted on the day of application, with rates equivalent to 2.5 g/ha and 5 g/ha. Five days after

transplanting, fipronil levels were at a maximum of 1.1–1.8 µg./L, declining to 0.5 µg/L by day 28 (Oguchi & Hirata 1994).

MB46513 was detected in paddy water from 3 days after transplanting (0.5–0.9 µg/L) declining to less than detection limits by day 28. The sulfide, MB45950 was found from 14 days through to 49 days after transplanting at levels of 0.5–0.9 µg/L. The metabolites MB46136 and RPA200766 were less than detection limits (0.5 µg/L) over the period of the study.

5.2.2. *Data available for later assessments*

The following study was provided for assessment for registration of fipronil as a termiticide.

- Rice field studies in California

Ngim and Crosby (2001) studied the fate of fipronil under Californian growing conditions, and inclusion in this report is relevant in view of the likely close similarity to those in New South Wales.

Three different formulations of fipronil were applied to 18.6 metre^2 (6.1 X 3.05 m) plots enclosed by sheet metal walls within paddies at the Rice Experimental Station in Biggs, California, a dry flowable at 28 and 560 g ac/ha, a granular at 28 g ac/ha and a soluble concentrate at 42.6 g /ha. The dry flowable was also applied at 36.4 g ac/ha to a similar 83.6 m^2 (9.14 X 9.14 m) plot in Richvale California, as well as to an unconfined 10 700 m^2 field at Pleasant Grove, California, whereas the soluble concentrate was applied at 42.6 g ac/ha to a pair of unconfined fields (4090 and 12 100 m^2 respectively) at Sheridan CA. Dry flowable and soluble concentrates were applied by back-pack sprayer to the smaller enclosures and by ground rig to commercial fields, while granules were distributed by hand. Treatments to unflooded soil prior to rice seeding were followed by incorporation with hand raking or a tractor-pulled roller, while soil of previously-flooded (about 2 weeks earlier) basins sustaining three-leaf maturation stage rice were not disturbed after treatment. Fields were maintained at a typical water depth of 4–6 cm (pH 6.8–8.3) over the June to October growing season, during which they were subjected to intense summer sunlight and temperature fluctuations (14–34^{o}C).

Field sampling began 15 minutes to 24 hours following application or flooding and were analysed by GC. An equilibration period of up to 36 hours in water and 100 hours in soil was necessary to reach maximum concentrations, attributed to time needed to allow release from the formulations (note some trials were discontinued as fipronil was not detected in soil and/or water within 24 hours of treatment). Dissipation was shown to generally follow pseudo first-order kinetics resulting in half-lives of 10.5–125 hours in water, and 44.5–533 hours in soil, with granules the most persistent (half-life 125 hours in water, 438 hours in soil) and the soluble concentrate the least (half-lives 10.5–77.8 hours in water, 44.5–95.9 hours in soil). The dry flowable treatment was among the least persistent in water (half-lives 22.1–67.6 hours) but the most stable in soil (half-

lives 462–533 hours). These differences were attributed, at least in part, to the rate of release from, and soil sorption of, the formulations; some support is given by the fact that persistence was greater in confined plots compared with commercial fields where greater mixing may occur. Unfortunately there is no information provided about the rate of movement from water to soil for those treatments to flooded fields.

The major degradation products found were the desthio product (trifluoromethyl pyrazole, MB 46513) in water and the sulfide (MB45950) in soil, while the sulfone and the amide (MB46136 and RPA200766 respectively) were detected only intermittently in water and appeared to be minor. MB46513 was formed (by photolysis) within 24 hours of application in all treatments, attaining maximum concentrations of 1–2.3 µg/L, and was more persistent than fipronil, though it dissipated to undetectable levels about 150 hours after soluble concentrate applications to both the enclosed plots and the large unconfined paddies (this was not the case with the other two formulations). The maximum levels of MB45950 were 14 µg/kg in soil treated with the granular formulation, attributed to the reducing conditions.

These results are consistent with those obtained in Thailand.

6. Accumulation

6.1. Bioaccumulation

6.1.1. *Original data package*

Bioaccumulation factors in bluegill sunfish (*Lepomis macrochirus*) exposed for 35 days under flow-through conditions to a nominal concentration of 0.85 µg/L radiolabelled fipronil were 321, 164 and 575 in whole fish, muscle and viscera, respectively, indicating a moderate bioaccumulation potential. Steady state conditions were apparent after 14 days. Accumulated residues were rapidly depurated, with almost complete elimination (>96%) after 14 days in clean water (Chapelo & Hall 1992).

Investigation of the metabolite profile at steady state found roughly equal amounts of fipronil, its sulfone analogue MB46136 and the displacement product MB45897, together with smaller amounts of the sulfide analogue MB45950 (Roohi et al. 1993). These metabolites were all found at much higher concentrations in viscera than in muscle. Similar results were obtained during the early depuration phase. The report states that the higher concentrations in viscera are consistent with the octanol/water partition coefficients of these compounds. Small amounts of the amide hydrolysis product RPA200766 were also found in fish, but the report is silent concerning the relative concentrations in muscle and viscera. The smaller amounts found may reflect a more rapid

depuration of this metabolite, which appears from HPLC to be significantly more hydrophilic than the main metabolites detected.

A separate report detailing the octanol-water partition coefficients of fipronil and metabolites, as determined by HPLC, is provided (Holmsen & Edens 1995). The result for fipronil (logPow = 2.80) is a little lower than that determined by the shake-flask method, but results are adequate for comparative purposes. The sulfide MB45950, sulfone MB46136 and trifluoromethyl pyrazole MB46513 are all more lipophilic than fipronil (logPow = 3.45, 3.32, 3.14, respectively) while the amide RPA200766 is less lipophilic (logPow = 1.47), consistent with its greater mobility in soil. A similar amide (lacking the sulfur linkage between the trifluoromethyl group and the pyrazole ring) exhibited similar properties (logPow = 1.24). As expected, the sulfonate RPV204615 is hydrophilic (logPow < 0).

6.1.2. *Additional data not previously available*

Title	Bioaccumulation, Biotransformation and Metabolite Formation of Fipronil and Chiral Legacy Pesticides in Rainbow Trout
Authors	Konwick et al.
Date	2006
Test guideline	None identified
Data validity	2*
Data relied on	Yes - this non-standard study provides results that can be used in the assessment

Test system

Fipronil bioaccumulation and biotransformation were assessed in rainbow trout (*Oncorhynchus mykiss*), exposed to fipronil through their diet. Juvenile trout were assigned to 800 L aquaria (45 fish per tank) with recirculating dechlorinated tap water at 12^{o}C. Fish were maintained on a 12-hour light: 12-hour dark photoperiod. Single aquaria were used for fipronil exposure and control fish. Fish were exposed to the spiked food for 32 days (uptake) followed by 96 days of clean food (depuration). Three fish were randomly sampled from each treatment on days 2, 4, 8, 16 and 32 of the uptake phase, and on days 34, 36, 40, 48, 64 and 128 of the depuration phase. Fish were separated into liver, GI tract and carcass (being the whole fish minus liver and GI tract to avoid analytes in the undigested food). Only carcass results were used in calculating bioaccumulation parameters and enantionmer fractions (EFs).

Findings

Fipronil appeared to reach steady state in the carcass at around day 15 of the uptake phase (graphical interpretation). In addition, it was rapidly biotransformed with EFs indicating relative abundance of fipronil enantiomers changing quickly over time. After 2 days, the (-) enantiomer was more prominent. The detection of fipronil sulfone (assumed to be MB46136) on the first sampling day and at higher concentrations than parent fipronil throughout the uptake phase confirmed rapid biotransformation (compared with ~3% sulfone in the spiked food).

Fipronil was rapidly eliminated by the fish with an elimination half-life ~0.6 days. The sulfone was more recalcitrant, although still quickly eliminated, with an elimination half-life of around 2 days.

The paper reported a biomagnification factor (BMF) of 0.02 for fipronil indicating it is unlikely to accumulate in aquatic food webs. The BMF of fipronil sulfone (4.8) would suggest this substance may accumulate, however, the authors consider this to be unrealistic based on its elimination half-life.

Conclusion

Fipronil and it sulfone metabolite are not expected to accumulate in aquatic food chains. Fipronil rapidly biotransforms in rainbow trout based on a change in EF and the rapid formation of fipronil sulfone.

Title	Toxicity and Bioaccumulation of Fipronil in the Nontarget Arthropodan Fauna Associated with Subalpine Mosquito Breeding Sites
Authors	Chaton, Ravanel, Tissut and Meyran
Date	2002
Test guideline	None identified
Data validity	4
Data relied on	No – information only

One literature paper (Chaton et al. 2002), considered bioaccumulation of fipronil in nontarget arthropodan fauna associated with subalpine mosquito breeding sites. Fipronil accumulation was studied on 800 specimens for each species, being *Daphnia pulex* (Cladocera), *Acanthocyclops robustus and Diaptomus castor* (Copepoda), *Eucypris virens* (Ostacoda), *Chaoborus crystallinus* (Chaoboridae) and *Chironomus annularius* (Chironomidae). Each assay was performed for 48 hours on 20 specimens placed in plastic vials containing 20 mL of water solutions of ^{14}C-fipronil at concentrations of 1–2000 nM. The accumulation factor (AF) was the ration between the [^{14}C] concentration per gram fresh weight of animal and per mL of medium.

After 48 hours, the AF varied among the species. Among Dipteral larvae, the AF was <1 for *C. crystallinus* and more than 60 for *C. annularius*. Among Crustacea, the AF was around 10 for *E. virens*, 30 for *D. pulex* and *D. castor* and more than 40 for *A. robustus*.

6.2. Soil accumulation

6.2.1. *Additional data not previously available*

The following study provides results specific to seed coating uses.

Title	Soil Distribution of Fipronil and its Metabolites Originating from a Seed-Coated Formulation
Authors	Raveton, Aajoud, Willison, Cherifi, Tissut and Ravanel.
Date	2007
Test guideline	None identified
Data validity	2*
Data relied on	Yes – this non-standard study provides results that can be used in the assessment

A non-standard, but important study relating to environmental fate of fipronil when exposed to the environment as a seed coating was reported by Raveton et al. (2007). These authors investigated the soil distribution and fate of fipronil from a sunflower seed-coating (Regent TS formulation) in the field. ^{14}C-fipronil distribution in soil in laboratory experiments were considered where sunflower seeds were coated with unlabelled fipronil (0.437 mg/seed) and with ^{14}C-fipronil (0.030 mg/seed). Seeds were planted in about 800 g dry weight soil and moisture content brought up to 35% soil weight. The experiment was carried out at 26^{o}C with a 16-hour light: 8-hour dark photoperiod. Soil samples and plants were collected weekly for 6 months. Three spherical soil layers of diameter 1.8 cm (4 g), 5 cm (80 g) and 11 cm (800 g) were delimited around the seed. The soil layer closest to the seed showed the highest concentration of fipronil at around 2.3 mg/kg after 19 days increasing to 3.1 mg/kg after 35 days cultivation. Very low levels of radioactivity were found in the 5 cm and 11 cm diameter soil samples demonstrating low mobility. These results were compared with those under field conditions (using non-radiolabelled fipronil). Sunflower seeds were coated with 0.437 mg fipronil. Seed-coating and soil samples were collected at 0, 13, 63, 98, 128 and 178 days in the vicinity of the seed at a depth of 0–11 cm. The average water content of the soil was around 15.9%, varying as a function of rainfall. The fipronil concentrations in the first soil layer (1.8 cm diameter) increased over time from 0–2 months reaching 6.5 mg/kg freshweight, confirming that fipronil was released from the seed-coat to this layer. Fipronil was detected in the 5 cm diameter layer after 1 month cultivation. The concentration increased from 0.1 to 0.7 mg/kg with a general tendency showing a slight increase in fipronil concentration in this layer from 0–4 months followed by a stabilisation. The most distant layer (11 cm diameter) was free of fipronil until 2–3 months cultivation. After this time, a very low concentration of 0.05–0.08 mg/kg was measured.

The two major metabolites found were the sulfone, MB46136 (0.881 mg/kg at 1.8 cm diameter after 174 days down to 0.054 mg/kg at 11 cm diameter after 174 days) and the sulphide, MB45950 (0.523 mg/kg soil at 1.8 cm diameter after 174 days down to 0.014 mg/kg at 11 cm diameter after 174 days). At the end of the cultivation period, 42% of fipronil and metabolites remained in the seed coat with 51% being found in the soil. About 7% was absorbed by the sunflower plant.

7. Environmental monitoring

At the time of initial assessments for fipronil end-use products in Australia, no monitoring data were available as it was a new molecule being considered for registration (not review). Some monitoring data are now available. These are reported below, but their relevance for the environmental risk assessment will be considered in the overview report.

Title	Fipronil and Degradation Products in the Rice-Producing Areas of the Mermentau River Basin, Louisiana, February–September 2000
Authors	United States Geological Survey (USGS)
Date	2003
Test guideline	None identified
Data validity	2*
Data relied on	Yes – monitoring data for comparison with modelled values in the risk assessment

This report presents a study of the analytes of fipronil and three of its degradation products (desulfinyl, MB46513; sulphide, MB45950; and sulfone, MB46136) in water, suspended sediment and bed sediment. Samples were collected from 17 sites in the rice-producing areas of the Mermentau River Basin from February to September 2000. Depth-integrated sampling methods were used to collect water samples, while grab sampling was used for sediments.

From a total of 17 sites, 91 water samples were collected (limit of detection 0.0044 µg/L for parent fipronil). The following results were summarised by DEWHA.Table V2.21: Summary of surface water monitoring data from USGS, 2003

	Number	Number of detections	% of detections	Range where detected		90th percentile (µg/L)
				Low (µg/L)	High (µg/L)	
Fipronil	91	72	79	0.004	5.29	2.690
MB46513	72	72	100	0.004	1.13	0.481
MB45950	72	72	100	0.007	0.214	0.162
MB46136	91	90	99	0.004	0.205	0.132
TOTAL	91	90	99	0.004	5.945	3.570

In suspended sediment, fipronil and degradation products ranged from 1–10% of the concentrations in water. In the bed sediment, fipronil was not found at any of the 17 sites. However, MB45950 and MB46513 were detected at all sites. MB45950 had the highest range of concentrations from 0.636–24.8 µg/kg.

In the region sampled, fipronil use was primarily as a rice seed treatment. The maximum concentrations found in water occurred during March through April, corresponding to the release of ricefield tailwater. Nonetheless, outside this period, fipronil and its main metabolites were consistently detected in surface waters.

Title	Water-Quality, Sediment-Quality, Stream-Habitat and Biological Data for Mustang Bayou Near Houston, Texas
Authors	United States Geological Survey (USGS)
Date	2007
Test guideline	None identified
Data validity	2*
Data relied on	Yes – monitoring data for comparison with modelled values in the risk assessment

The United States (US) Geological Survey collected water quality data from six sites primarily in Brazoria County, southeast of Houston, Texas, during September 2004 and August 2005. The study area is described as including grassland (~51%), woody land (~20%) and low-intensity developed. Land use primarily is rural agriculture where channelized streams and irrigation canals are common.

Over the course of the year (September 2004–August 2005), water samples were analysed for fipronil and its three major on four occasions (September 2004, January 2005, June 2005 and August 2005) at six sites. From these 24 samples, fipronil was detected in seven samples (29%). All concentrations were reported as estimated due to the relatively poor recovery during analysis. The maximum concentration found was 0.033 µg/L. Fipronil sulphide (MB45950) and sulfone (MB46136) were found at maximum concentrations of 0.075 µg/L and 0.024 µg/L respectively.

Title	Environmental Fate of Fipronil
Authors	Gunasekara and Troung
Date	2007
Test guideline	None identified
Data validity	2*
Data relied on	Yes – monitoring data for comparison with modelled values in the risk assessment

Gunasekara and Troung (2007) summarise information from the US Geological Survey monitoring work that demonstrated, since 2002, the presence of fipronil and its major metabolites occurring in the low µg/L range of water bodies in urban and agricultural areas throughout the USA (data from 2002–06). The highest recorded concentration for fipronil was found in Louisiana (0.117 µg/L, while for MB46136, MB46513, MB45950 and RPA200766, the highest detections were 0.038 µg/L (Colarado), 0.015 µg/L (Louisiana), 0.158 µg/L (California) and 0.011 µg/L (Louisiana) respectively. The Louisiana detections were made in surface water from mainly agricultural areas.

Title	Pesticide Detections in Dry and Wet Weather Surface Runoff from Single-Family Residences
Authors	Haver et al
Date	2008
Test guideline	None identified
Data validity	2*
Data relied on	Yes – monitoring data for comparison with modelled values in the risk assessment

Haver et al. (2008) report pesticide detections in dry and wet weather surface runoff from single family residences in California. This monitoring program included eight single-family residential drainsheds (four in Sacramento County and four in Orange County) with 150–450 parcels (presumably house blocks) per site. Pesticide sampling was undertaken for various OPs, synthetic pyrethroids and fipronil. Weekly grab samples were taken from October 2006–December 2007 in Orange County, and from July 2006–December 2007 in Sacremento. In addition, biweekly grab samples were taken in both counties from January 2008–September 2008. In the Orange Country samples, for dry weather runoff, fipronil was detected in 98.5% of samples (194/197). The maximum level was 10 µg/L, although the median concentration found was much lower at 91 ng/L. In wet weather runoff (26 samples), fipronil was found in all samples with a median concentration of 183 ng/L and a maximum concentration of 1.1 µg/L.

Title	Analysis, Occurrence and Toxic Potential of Pyrethroids and Fipronil in Sediments from an Urban Estuary
Authors	Lao et al
Date	2010
Test guideline	None identified
Data validity	2*
Data relied on	Yes – monitoring data for comparison with modelled values in the risk assessment

Lao et al. (2010) report on the occurrence of fipronil in sediments from the Ballona Creek estuary. This creek is described as a nine mile-long (14.4 km) flood-control channel that drains a highly urbanised 329 km^2 watershed within the city of Los Angeles. Given the information from Moran (2007), it must be assumed that fipronil exposed to sediments in this region is the result of runoff from urban uses as a pest control. Six sampling stations along a 4 km tidally-influenced stretch of this water way were utilised and sediment samples collected during three dry season events (September 2007, June 2008 and October 2008). Samples were collected to a depth of 5 cm. Fipronil desulfinyl (MB46513), sulphide (MB45950) and sulfone (MB46136) were detected in samples from each of the three sampling events. In contrast, parent fipronil was detected infrequently (4 of 18 samples). MB46136 was the most abundant metabolite (100% of samples) at concentrations ranging up to 9.8 µg/kg. The other two metabolites were found in all 2008 samples but at lower concentrations, generally <1 µg/kg. For the September 2007 event, these metabolites were found at a maximum concentration of 6.2 µg/kg (MB45950) and 1.5 µg/kg (MB46513). MB46136 accounted for >50% total residues

compared with around 20% each for MB45950 and MB46513, and <10% total residues was attributed to the parent compound.

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