UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

20 JUL 1993

OFFICE OF PREVENTION, PESTICIDES AND TOXIC SUBSTANCES

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EFGWB Out:

MEMORANDUM

SUBJECT: EFGWB Review of Two Coumaphos Studies

FROM: Richard J. Mahler, Hydrologist Richard J. Mahler
Environmental Chemistry Review Section 1

THRU: Paul J. Mastradone, Chief Paul J. Mastradone
Environmental Chemistry Review Section #1
Environmental Fate and Groundwater Branch
Environmental Fate and Effects Division (H7507C)

Henry Jacoby, Chief Henry Jacoby 7/26/93
Environmental Fate and Groundwater Branch
Environmental Fate and Effects Division (H7507C)

TO: Anthony Maciorowski, Chief
Ecological Effects Branch
Environmental Fate and Effects Division (H7507C)

Enclosed are the reviews of two cattle hide studies (MRIDs 425126-01 and 425126-02) which you requested be performed by EFGWB in a memorandum sent on January 14, 1993. One study used an 11.6% emulsifiable liquid product and the other a 25% wettable powder.

The ultimate goal of these two studies was to estimate how much coumaphos may end up in an aquatic environment as a result of wash-off from a herd of treated cattle when they enter a body of water. The studies were conducted so that only leaching of coumaphos from the exterior of the hide was measured; therefore, as far as we can determine, there was little potential absorption or other interference by the flesh side of the hide.

The factors tested as affecting coumaphos loading levels were drying time (0.5, 3 and 24 hours) after treatment and soaking time (0.5, 1.0, 2.0 or 4.0 hours) of the hides. The study design was to treat fresh cattle hides with coumaphos and then determine

the amount of active ingredient that, after drying, could be removed with water under greenhouse conditions.

In the emulsifiable liquid study, approximately 11.6% of the applied coumaphos would be expected to wash off the treated hides and be recovered in water after a minimum of drying time (0.5 hr). Similarly, drying times of 3 and 24 hours would result in 4.6 and 2.7% of the applied material being recovered from the water, respectively. Significant differences were found between the 0.5 hr drying time and the other two drying times; but not between the 3.0- or 24.0-hr drying times.

In the 25% WP study, significant differences were found among the drying times since approximately 38% of the applied coumaphos would be expected to wash off the treated hides and be recovered in water after a minimum of drying time (0.5 hr); while, drying times of 3 and 24 hours resulted in 21 and 2.0% of the applied material being washed off the hides into the water, respectively.

Although the study authors' did not test the statistical significance of formulation in these two studies, it appears that the formulation has a significant influence on the amount of coumaphos that can wash off an animal. For example, averaged over all drying and soaking times, the amount of coumaphos washed off cattle hides when the emulsifiable liquid product was used could be as much as 60% less than if the wettable powder product is used (i.e., 6.3% vs. 20.4%). However, it should be mentioned that after drying 24 hours, there was little difference between formulations in the percent (2.0 and 2.7%) of coumaphos in solution.

Based on these studies, the maximum and minimum amount of coumaphos that may be expected to wash off a unit area of hide will depend on formulation used and length of drying time before submersion. For example, if the emulsifiable liquid product is used, then it could be expected that the range of wash off per square foot of cattle hide would be 4.86 to 20.88 mg; however, if the wettable powder is used then the range to be expected would be 4.8 to 91.2 mg per square foot. Based on 48.5 square feet of hide surface area per animal, minimum and maximum wash off figures for EEB to use in calculations would be 0.24 g and 4.4 g of coumaphos per animal, respectively.

The above numbers assume that the cattle are completely submerged when they go into water to cool themselves. It should be noted that according to the study authors, cattle usually enter water only knee deep or up to the underneath side of their body trunk, and sometimes half-way up their body side on extremely hot days. They seldom submerge to any greater depth. Therefore, the above estimates probably should be reduced by one-half before using them for determination of how much coumaphos may end up in an aquatic environment.

The total amount of coumaphos that leaches from cattle hides appears to be independent of the amount of time the hides were submersed in water, since there were no significant differences in coumaphos residues in solution among the four soaking times of 0.5, 1.0, 2.0 or 4.0 hours in either study. Therefore, the total amount released is available almost immediately upon submersion, and consequently there does not appear to be a release or leaching rate that can be determined from the present data.

For further details of these reviews please refer to the attached Data Evaluation Records. If you have any questions related to these reviews, please contact me at 305-7991.

cc: Linda Propst/Joanne Edwards, PM Team #73
SRRD (H7508W)

DATA EVALUATION RECORD

STUDY 5

CHEM 036501 COUMAPHOS

FORMULATION--00--ACTIVE INGREDIENT

STUDY MRID 425126-01
Judy, D. and F. Kaiser. September 29, 1992. Removal of coumaphos active ingredient from cattle hides treated with Co-Ral[R] emulsifiable liquid insecticide (E.L.I.). Unpublished study performed by ABC, Laboratories, Columbia, MO and submitted by Miles, Inc., Animal Health Division, Merriam, KS (ABC Final Report 40329).

DIRECT REVIEW TIME = 5

REVIEWED BY: Richard J. Mahler, Hydrologist
Environmental Chemistry Review Section 1, EFGWB

SIGNATURE: Richard J. Mahler

DATE: 20 JUL 1993

APPROVED BY: Paul J. Mastradone, Chief
Environmental Chemistry Review Section 1, EFGWB

SIGNATURE: Paul J Mastradone

DATE: 20 JUL 1993

This study was requested by EEB. The purpose of this study was to estimate levels of contamination of water bodies by cattle treated with a coumaphos application. The factors tested as affecting coumaphos loading levels were drying time after treatment and soaking time of the animal. The study design was to treat fresh cattle hides with coumaphos and then determine the amount of active ingredient that, after drying, could be removed with water under greenhouse conditions.

CONCLUSIONS:

1. Cattle hide wash off studies are not specifically required by Subdivision N guidelines. However, these studies were requested by EEB

to obtain some estimate of the amount and rate at which coumaphos may be washed or leached off cowhide. This study was subsequently sent to EFGWB for review. The ultimate goal of the study is to estimate how much coumaphos may end up in an aquatic environment as a result of wash-off from a herd of treated cattle when they enter a body of water.

2. EFGWB concludes that this study is scientifically valid and provides supplemental information that shows approximately 11.6% of the applied coumaphos would be expected to wash off the treated hides and be recovered in water after a minimum of drying time (0.5 hr). Similarly, drying times of 3 and 24 hours would result in 4.6 and 2.7% of the applied material being recovered from the water, respectively. Significant differences were found between the 0.5 hr drying time and the other two drying times; but not between the 3.0- or 24.0-hr drying times. No significant differences were found in coumaphos residues among the four soaking times of 0.5, 1.0, 2.0 or 4.0 hours.

3. Based on the study authors' calculation that 2500 ml (0.66 gal) of pesticide solution would adhere to each animal, it is possible to determine an amount of pesticide that could be expected to wash off a treated animal using 11.6% (the amount of applied expected to be washed off). EFGWB notes that the 50ml spray solution used to spray each 1-ft^2 of hide contained 180 mg ai which is equivalent to the 12 qt/100 gal label rate. Therefore, if 11.6% of the applied washes off, this represents 11.6% times 180 mg = 20.8 mg washed off each square foot of a cattle hide. Based on the 4.5 m^2 (48.4 ft^2) of hide surface area, this would represent a total wash off per animal of 48.4 ft^2 times 20.8 mg = 1.01 g. This represents the maximum if the animal is totally submerged. However, based on information presented in the report, cattle seldom totally submerge and usually enter water only knee deep or up to the underneath side of their body trunk, and sometimes half-way up their body side on extremely hot days.

4. The spray solution and filter paper verification samples recovered, respectively, 71 and 69%, of the theoretical amount. The study authors did not offer an explanation of why the target application rate of 34 mg/filter paper was not attained. EFGWB believes that at a minimum, the spray solution values should have been closer to theoretical. If the actual amount of material applied, as determined by the verification samples, was less than the target amount then perhaps recalculation of the wash off percentages should have been performed. This recalculation probably will increase the wash off calculation by 30%. Therefore, the amount of coumaphos that could wash off each animal may be as high as 1.3 g when applied as the emulsifiable liquid product.

5. EFGWB notes that the amount of coumaphos washed off cattle when the 25% wettable powder product is used could be as much as 4.4 g per animal (see DER for Study 6 attached). It appears that the formulation has a significant influence on the amount of coumaphos that can wash off an animal.

METHODOLOGY:

Coumaphos (0,0-dimethyl O-(3-chloro-4-methyl-2-oxo-2H-1-benzopyranyl-7-yl phosphorothioate, purity = 97.02%) was applied, as an emulsifiable liquid product (11.6% ai), to cattle hides at a rate of 12 qt/100 gal for grub control in one application. A CO_2-powered sprayer was used to spray 1-ft^2 sections of a 7 day-old cattle hide in a 50 mL volume that approximated the amount normally applied to live cattle. After applications were made, the hide sections were allowed to dry at intervals of 0.5, 3.0 and 24.0 hours. At the completion of each drying interval, the cattle hides were clamped to the base of stainless steel cylinders (18-in. long and 8-in. diameter, Figure 1), and filled with 5 gal/ft^2 soaking water. After filling the cylinders with deionized water, the hides were soaked for 0.5, 1.0, 2.0 and 4.0 hours. At the end of each soaking time, a sample was withdrawn from the water and analyzed for the presence of coumaphos.

In order to verify the application rate, 5 application measurement samples were taken after the hides were treated. The application samples consisted of 15-cm diameter filter papers that were placed in the center of a 1-ft^2 hide sample, which were then sprayed with the same 50-mL volume as the treated hide samples.

Two water spike tanks, containing the theoretical amount of active ingredient which was absorbed by the 8-in. diameter of the hide in contact with the water, were prepared each day and run concurrently with the tanks containing the treated hides. Two control tanks with untreated cattle hides were exposed to the same soaking volume and were sampled at the same times as the treated hides during the experiment.

Twelve tanks were designated as treated tanks and two as untreated controls. The 12 tanks were arranged in 4 replicates in a completely randomized design. The main plot factor was drying times and the subplot factors were the four soaking times. A split plot in time analysis of variance procedure (ANOVA) was used to statistically evaluate the data with Tukey's HD test used to separate the means at the 0.05 level of significance.

Fifty ml of treated water were added to a 250-ml separatory funnel along with 2 ml of pH 6 phosphate buffer, and 100 ml of methylene chloride, shaken for 12 minutes and the methylene chloride rinse was drained through methylene chloride/hexane/acetone-rinsed sodium sulfate. The water was extracted with two additional volumes of methylene chloride and the methylene chloride portions were combined in the same flask, taken to dryness under a partial vacuum using a rotary evaporator and dissolved in mobile phase solution (acetonitrile:water, 70:30, v/v, 0.05 M phosphate buffer, pH 2).

Extracted water samples were analyzed by high performance liquid chromatography (HPLC) with UV detection. The validation consisted of fortifying control samples in duplicate on 2 different days in order to assess precision and accuracy at levels of 0.001, 0.01, 0.5, 2.1 and 5.1 ppm for coumaphos.

The collected water samples were stored in a refrigerator at 6°C for up to 7 days before analysis.

The study was conducted in a climate-controlled greenhouse with shadecloth applied to remove interference from sunlight. Tank water temperatures ranged from 22 to 28°C, air temperatures from 27 to 33°C, while relative humidity from 28 to 60%.

Residues found in the treated samples were corrected for procedural recovery only if % recovery was <100%.

DATA SUMMARY:

The method was validated by analyzing nontreated water and nontreated fortified water samples at five different fortification levels. Results are given in Table 3. The overall average was 103 ± 3%.

Recovery from fortified samples analyzed concurrently with authentic samples are reported in Table 4. The overall average percent recovery for coumaphos was 97% ± 6%.

The calculated theoretical amount of coumaphos in a spray solution is 3595.2 mg/L. The values obtained from the spray solutions ranged from 67 to 73% of theoretical (average = 71 ± 2%, Table 5).

The calculated theoretical amount of coumaphos expected in the treated samples is 34.2 mg/filter paper. The values recovered from the filter papers used to verify the application rate ranged from 62 to 74% of theoretical (average 69 ± 5%, Table 6). The study authors maintain that the generally close agreement (70%) with theoretical levels expected in the spray solutions and application measurement samples provide supportive data for the application at the intended rate to the treated hides.

Table 7 and 8 and Graphs 1 and 2 present the results from the analysis of the treated and control water samples, respectively. The calculated theoretical amount of coumaphos in a treated water sample, if 100% of the material leached from the hide into the soaking water, is 9.52 ppm. As can be seen, residues found at the 0.5 hr drying time (1.10 ppm) were higher than those at the 3.0- or 24.0-hr drying times (0.44 ppm and 0.26 ppm, respectively), and were statistically significantly different from the results found at 3.0- and 24.0 hr drying times. Although not significantly different, the amount leached from the 24.0 hr drying time was approximately 40% lower than the amount leached from the 3.0 hr drying time.

When averaged over soaking time, the data indicate that approximately 11.6% of the applied coumaphos was recovered from the water after immediate exposure. After the active ingredient on the hide had dried for 3 hr, then 4.6% was recovered from the water. Approximately 2.7% of the active ingredient was recovered from the hides that were dried 24 hr before the addition of water.

No significant differences were found in coumaphos residues among soaking times (0.5, 1.0, 2.0 or 4.0 hours).

REVIEWER'S COMMENTS:

EFGWB notes that according to the study authors, treated cattle may enter ponds and streams after application of coumaphos, which may result in the chemical entering the water due to "wash off" or "leaching" from the surface of the animals. Cattle usually enter water only knee deep or up to the underneath side of their body trunk, and sometimes half-way up their body side on extremely hot days. They seldom submerge to any greater depth.

RIN 3189-94

EFGWB REVIEW FOR COUMAPHOS

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____ Identity of product impurities.

____ Description of the product manufacturing process.

____ Description of quality control procedures.

____ Identity of the source of product ingredients.

____ Sales or other commercial/financial information.

____ A draft product label.

____ The product confidential statement of formula.

____ Information about a pending registration action.

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STUDY AUTHORS' RESULTS, DISCUSSION AND CONCLUSIONS

DATA EVALUATION RECORD

STUDY 6

CHEM 036501 COUMAPHOS

FORMULATION--00--ACTIVE INGREDIENT

STUDY MRID 425126-02
Judy, D. and F. Kaiser. September 29, 1992. Removal of coumaphos active ingredient from cattle hides treated with Co-Ral[R] 25% wettable powder insecticide. Unpublished study performed by ABC, Laboratories, Columbia, MO and submitted by Miles, Inc., Animal Health Division, Merriam, KS (ABC Final Report 40329).

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This study was requested by EEB. The purpose of this study was to estimate levels of contamination of water bodies by cattle treated with a coumaphos application. The factors tested as affecting coumaphos loading levels were drying time after treatment and soaking time of the animal. The study design was to treat fresh cattle hides with coumaphos and then determine the amount of active ingredient that, after drying, could be removed with water under greenhouse conditions.

CONCLUSIONS:

1. Cattle hide wash off studies are not specifically required by Subdivision N guidelines. However, these studies were requested by EEB

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to obtain some estimate of the amount and rate at which coumaphos may be washed or leached off cowhide. This study was subsequently sent to EFGWB for their review. The ultimate goal of the study is to estimate how much coumaphos may end up in an aquatic environment as a result of wash-off from a herd of treated cattle when they enter a body of water.

2. EFGWB concludes that this study is scientifically valid and provides supplemental information. Significant differences were found amoung the drying times since approximately 38% of the applied coumaphos would be expected to wash off the treated hides and be recovered in water after a minimum of drying time (0.5 hr); while, drying times of 3 and 24 hours resulted in 21 and 2.0% of the applied material being washed off the hides into the water, respectively. However, no significant differences were found in coumaphos residues among the four soaking times of 0.5, 1.0, 2.0 or 4.0 hours.

3. Based on the study authors' calculation that 2500 ml (0.66 gal) of pesticide solution would adhere to each animal, it is possible to determine an amount of pesticide that could be expected to wash off a treated animal using 38% (the amount of applied expected to be washed off after minimal drying time). EFGWB notes that the 50 ml spray solution used to spray each 1-ft^2 of hide contained 240 mg a.i. which is equivalent to the 16 lb/100 gal label rate. Therefore, if 38% of the applied washes off, this represents 38% times 240 mg = 91.2 mg washed off each square foot of a cattle hide. Based on the 4.5 m^2 (48.4 ft^2) of hide surface area, this would represent a total wash off per animal of 48.4 ft^2 times 91.2 mg = 4.4 g. This represents the maximum if the animal is totally submerged. However, based on information presented in the report, cattle seldom totally submerge and usually enter water only knee deep or up to the underneath side of their body trunk, and sometimes half-way up their body side on extremely hot days.

4. EFGWB notes that the amount of coumaphos washed off cattle when the emulsifiable concentrate product is used could be as much as 1.01 g per animal (see DER for Study 5 attached). It appears that the formulation has a significant influence on the amount of coumaphos that can wash off an animal.

METHODOLOGY:

Coumaphos (O,O-dimethyl O-(3-chloro-4-methyl-2-oxo-2H-1-benzopyranyl-7-yl phosphorothioate, purity = 97.02%), as a 25% wettable powder, was applied to cattle hides at a rate of 16 qt/100 gal for grub control in one application. A CO_2-powered sprayer was used to spray I-ft^2 sections of a 3 day-old cattle hide in a 50 ml volume that approximated the amount normally applied to live cattle. After applications were made, the hide sections were allowed to dry at intervals of 0.5, 3.0 and 24.0 hours. At the completion of each drying interval, the cattle hides were clamped to the base of stainless steel cylinders (18-in. long and 8-in. diameter, Figure 1), and filled with the equivalent of 5 gal/ft^2 soaking water. After filling the cylinders with deionized water, the hides were soaked for 0.5, 1.0, 2.0 and 4.0 hours. At

the end of each soaking time, a sample was withdrawn from the water and analyzed for the presence of coumaphos.

In order to verify the application rate, 5 application measurement samples were taken after the hides were treated. The application samples consisted of 15-cm diameter filter papers that were placed in the center of a 1-ft^2 hide sample, which were then sprayed with the same 50-mL volume as the treated hide samples.

Two water spike tanks, containing the theoretical amount of active ingredient which was absorbed by the 8-in. diameter of the hide in contact with the water, were prepared each day and run concurrently with the tanks containing the treated hides. Two control tanks with untreated cattle hides were exposed to the same soaking volume and were sampled at the same times as the treated hides during the experiment.

Twelve tanks were designated as treated tanks, two as untreated controls and four tanks for water spikes. The 12 tanks were arranged in 4 replicates in a completely randomized design. The main plot factor was drying times and the subplot factors were the four soaking times. A split plot in time analysis of variance procedure (ANOVA) was used to statistically evaluate the data with Tukey's HD test used to separate the means at the 0.05 level of significance.

Fifty ml of treated water were added to a 250-ml separatory funnel along with 2 ml of pH 6 phosphate buffer, and 100 ml of methylene chloride,shaken for 12 minute and the methylene chloride rinse was drained through methylene chloride/hexane/acetone-rinsed sodium sulfate. The water was extracted with two additional volumes of methylene chloride and the methylene chloride portions were combined in the same flask, taken to dryness under a partial vacuum using a rotary evaporator and dissolved in mobile phase solution (acetonitrile:water, 70:30, v/v, 0.05 M phosphate buffer, pH 2).

Extracted water samples were analyzed by high performance liquid chromatography (HPLC) with UV detection. The validation consisted of fortifying control samples in duplicate on 2 different days in order to assess precision and accuracy at levels of 0.001, 0.01, 0.5, 2.1 and 5.1 ppm for coumaphos.

The collected water samples were stored in a refrigerator at 6°C for up to 7 days before analysis.

The study was conducted in a climate-controlled greenhouse with shadecloth applied to remove interference from sunlight. Tank water temperatures ranged from 22 to 28°C, air temperatures from 27 to 33°C, while relative humidity from 28 to 60%.

Residues found in the treated samples were corrected for procedural recovery only if % recovery was <100%.

DATA SUMMARY:

The method was validated by analyzing nontreated water and nontreated fortified water samples at five different fortification levels. Results are given in Table 3. The overall average was 103 ± 3%.

Recovery from fortified samples analyzed concurrently with authentic samples are reported in Table 4. The overall average percent recovery for coumaphos was 98% ± 6%.

The calculated theoretical amount of coumaphos in a spray solution was 4798 mg/L. The values obtained from the spray solutions ranged from 76 to 89% of theoretical (average = 83 ± 5%, Table 5).

The calculated theoretical amount of coumaphos expected in the treated samples was 45.6 mg/filter paper. The values recovered from the filter papers used to verify the application rate ranged from 83 to 95% of theoretical (average 90 ± 5%, Table 6). The study authors maintain that the generally close agreement with theoretical levels expected in the spray solutions and application measurement samples provide supportive data for the application at the intended rate to the treated hides.

Table 7 and 8 and Graphs 1 and 2 present the results from the analysis of the treated and control water samples, respectively. The calculated theoretical amount of coumaphos in a treated water sample, if 100% of the material leached from the hide into the soaking water, is 12.7 ppm. As can be seen, residues found at the 0.5 hr drying time (4.86 ppm) were higher than those at the 3.0- or 24.0-hr drying times (2.70 ppm and 0.46 ppm, respectively), and were statistically significantly different from the results found at 3.0- and the 24.0 hr drying times.

When averaged over soaking time, the data indicate that approximately 38% of the applied coumaphos was recovered from the water after immediate exposure. After the active ingredient on the hide had dried for 3 hr, then 21% was recovered from the water. Approximately 2.0% of the active ingredient was recovered from the hides that were dried 24 hr before the addition of water.

No significant differences were found in coumaphos residues among soaking times (0.5, 1.0, 2.0 or 4.0).

REVIEWER'S COMMENTS:

1. EFGWB notes that according to the study authors, treated cattle may enter ponds and streams after application of coumaphos, which may result in the chemical entering the water due to "wash off" or "leaching" from the surface of the animals. Cattle usually enter water only knee deep or up to the underneath side of their body trunk, and sometimes half-way up their body side on extemely hot days. They seldom submerge to any greater depth.

2. The spray solution and filter paper verification samples recovered, respectively, 83 and 90%, of the theoretical amount.

RIN 3189-94

EFGWB REVIEW FOR COUMAPHOS

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