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EFB File

DYNAMAC CORPORATION

AMITRAZ

TASK 2: ENVIRONMENTAL FATE AND EXPOSURE ASSESSMENT

Contract No. 68-01-6679

Final Report

September 19, 1984

SUBMITTED TO:

Environmental Protection Agency
Arlington, Virginia 22202

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Environmental Fate and Exposure Assessment

Amitraz

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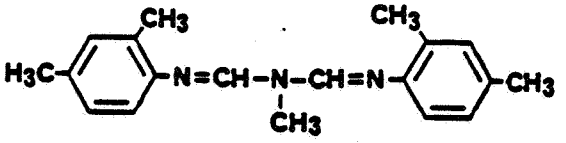

N'-(2,4-dimethylphenyl)-N-[[(2,4-dimethylphenyl)imino]methyl]-N-methylmethanimidamide

Amitraz is an insecticide/acaricide registered for use on pears. About two-fifths of the domestic pear acreage are treated with amitraz. Application rates range from 0.75 to 1.5 lb ai/A. Amitraz is only formulated as single active ingredient products. Single active ingredient formulations of amitraz consist of 50% WP and 1.5 lb/gal EC. Amitraz may be applied to pears in either a dilute or concentrated form as a foliar spray using air or ground equipment. The most commonly used equipment is the air blast sprayer for ground application. Applicators must be certified or under the direct supervision of applicators certified to apply amitraz.

Available data are insufficient to fully assess the environmental fate of amitraz and the exposure of humans and nontarget organisms to amitraz.

Under aerobic conditions, [^{14}C]amitraz (purity unspecified), at 1.25 ppm, degraded with a half-life of 6-12 weeks in a loam soil incubated at 21-26 C and ~12% moisture content (Somerville, 00030462). N-(2,4-dimethylphenyl)formamide (BTS-27,919) was the major degradate formed, and accounted for 27-44% of the applied radioactivity from day 4 to week 24. N'-(2,4-dimethylphenyl)-N-methylmethanimidamide (BTS-27,271) and 2,4-dimethylbenzenamine (BTS-24,868), were found at maximum levels of 13 and 25% of the applied radioactivity, respectively.

[^{14}C]Amitraz (95% pure), at 6 ppm, degraded with a half-life of <1 day in sterile and nonsterile sandy loam and silt loam soils, maintained at 50% of moisture holding capacity and an unspecified temperature (Newby, et al., 00114301). The major degradate formed was N-(2,4-dimethylphenyl)formamide

(BTS-27,919), reaching maximum concentrations of ~1.9-2.0 (1 day after treatment) and ~3.3-3.7 ppm (14 days after treatment) in the nonsterile and sterile soils, respectively. Concentrations of N'-(2,4-dimethylphenyl)-N-methylmethanimidamide (BTS-27,271) and 2,4-dimethylbenzenamine (BTS-24;868) were ≤1.3 ppm at any sampling interval. In the nonsterile soils, ~22-31% of the applied radioactivity had evolved as $^{14}CO_2$ at 1 year after treatment. No $^{14}CO_2$ was produced from the sterile soils.

Amitraz (technical, purity unspecified) at 5 ppm, degraded in two Japanese soils with a half-life of 2-4 hours (Takano, 00030475). The soils were incubated at 60% of water holding capacity and 30 C.

Under anaerobic conditions, [^{14}C]amitraz (96% pure), at 6 ppm, was relatively stable in sandy loam and silt loam soils during 60 days of anaerobic incubation at an unspecified temperature and 50% of moisture holding capacity (Newby, et al., 00114301). Following a 30-day aerobic aging period, [^{14}C]amitraz concentrations ranged from ~0.01 to 0.06 ppm during the 60-day anaerobic test period. Concentrations of N'-(2,4-dimethylphenyl)-N-methylmethanimidamide (BTS-27,271), N-(2,4-dimethylphenyl)formamide (BTS-27,919), and 2,4-dimethylbenzenamine (BTS-24,868) were <0.7 ppm at any sampling interval. Up to 11.8% of the applied radioactivity was evolved as $^{14}CO_2$.

[^{14}C]Amitraz residues (unaged, test substance 97% pure) were intermediately mobile in sandy loam, silt loam, and clay soils (R_f 0.36-0.48) and very mobile in sand (R_f 0.91), based on soil TLC tests (Leake, et al., 00114299). [^{14}C]Amitraz residues (aged 30 days, purity of test substance unspecified) were mobile in Florida sand and Nottinghamshire sandy loam soil columns; after leaching 30.5-cm soil columns with 58.5 cm of water, 11.28 and 5.00% of the applied radioactivity, respectively, was found in the leachate (Somerville and Nicholson, 00030466). In the soil columns, ~46-89% of the applied radioactivity remained within the top 5 cm. [^{14}C]Amitraz residues (aged 30 days, test substance 96% pure) were slightly mobile in a sandy loam soil; after leaching 32-cm high soil columns with 22.5 cm of 0.01 M $CaCl_2$, ~20% of the applied radioactivity was bound to the soil in the 2.5-cm soil segment adjacent to the treated segment, and ~3-5% was found in the remainder of the soil column (Leake, et al., 00114300). Less than 1% of the applied radioactivity was found in the leachate. Extractable radioactivity accounted for ~5-6% of the applied. N'-(2,4-dimethyl-

phenyl)-N-methylmethanimidamide (BTS-27,271) and N-(2,4-dimethylphenyl)formamide (BTS-27,919) were identified, but were not quantified. No amitraz was detected.

Amitraz residues dissipated with a half-life of <29 days in an uncharacterized field soil (0- to 3-inch depth) in Michigan (Lee, et al., 00051731; Nappier and Hornish, 00051730). Residues at the 3- to 6-inch depth were 1.09 ppm on day 0, and <0.49 ppm at intervals up to 84 days after treatment. Amitraz (1.66 lb/gal EC) was applied at 10 lb ai/A. Following up to three applications of amitraz (1.66 lb/gal EC) to apple or pear trees in Michigan at 1.3 lb ai/A, amitraz residues were relatively stable at the 0- to 3-inch soil depth, and were <0.10 ppm at the 3- to 6-inch depth.

[^{14}C]Amitraz residues accumulated in bluegill sunfish exposed to [^{14}C]amitraz (99.7% pure) at 0.01 ppm for 30 days, with maximum bioconcentration factors of ~280x, 2118x, 1467x, and 933x in muscle, viscera, carcass, and whole fish, respectively (EG & G Bionomics, 00072503). Of the [^{14}C]amitraz residues accumulated in fish tissue by day 30, ~83-88% had been eliminated after a 14-day depuration period.

Dermal, ocular, and inhalation exposures to workers may occur during application. The primary potential for exposure from the EC formulation is during mixing and loading where both dermal and ocular exposure can occur via splashing. Inhalation and dermal exposure may occur during opening and pouring of the WP formulation; splashing during dilution, mixing, and loading operations may result in dermal, ocular, and ingestion exposures. Application from aircraft or use of air-blast sprayers increases the potential for exposure of humans and nontarget organisms to amitraz due to spray drift and volatilization. Human exposure to amitraz during handling, mixing, and application operations could be minimized by the use of approved respirators and protective clothing. However, no data are available to assess such exposures. No federal reentry intervals have been established for amitraz. No PIMS data were available.

In summary, amitraz degrades with a half-life of <1 day-12 weeks in aerobic soils under both laboratory and field conditions, and is relatively stable under anaerobic conditions. The primary degradate under aerobic conditions is N-(2,4-dimethylphenyl)formamide (BTS-27,919), with smaller amounts of

BTS-27,271 and BTS-24,868 being formed. All three degradates remain at low levels in anaerobic soils. Amitraz is intermediately mobile to very mobile in soils, and therefore possesses a considerable potential for groundwater contamination. Amitraz residues have a low potential to bioaccumulate in the tissue of bluegill sunfish, and are depurated rapidly.

The following data are required (EPA Data Requirements for Registering Pesticides, 1983) to fully assess the environmental fate and transport of, and the potential exposure to amitraz: hydrolysis studies; photodegradation studies in water and air, and on soil; aerobic and anaerobic soil metabolism studies; leaching and adsorption/desorption studies; laboratory and field volatility studies; terrestrial and possibly long-term field dissipation studies; accumulation studies in fish; and reentry studies.

Hydrolysis studies: No data were submitted, but all data are required.

Photodegradation studies in water: Two studies were reviewed; one study (Golding, 00051761) is scientifically invalid because a dark control was not used, the analytical methods were inadequately described, the sampling protocol was inadequate to accurately assess the photodegradation of amitraz in water, and the materials balance was too low (~50% of the applied amount was accounted for after 16 days of irradiation). In addition, this study would not fulfill data requirements because the test substance was not technical grade or purer, the experiment was not conducted in a buffered solution and the pH was not specified, the temperature was not specified, UV wavelengths <290 nm were used, and the intensity of the UV light was not reported. The second study (Golding, 00111860) is scientifically invalid because a dark control was not used, the analytical methods were inadequately described, and the materials balance was too low (~55% of the applied amount was accounted for after 13 days of irradiation). In addition, this study would not fulfill data requirements because the test substance was uncharacterized, the experiment was not conducted in a buffered solution and the pH was not specified, and the wavelength and intensity of the light source were not provided. All data are required.

Photodegradation studies on soil: Three studies were reviewed; one study (Golding, 00051761) is scientifically invalid because the analytical methods were inadequately described, and the materials balance was too low (46.3% of the applied amount was accounted for after 28 days of irradiation). In addition, this study would not fulfill data requirements because the test substance was uncharacterized, the wavelength and intensity of the light source was not reported, and the experiment was conducted on aluminum plates and not on soil. A second study (Golding, 00111860) is scientifically invalid because a dark control was not used, the analytical methods were inadequately described, the sampling protocol was inadequate to accurately assess the photodegradation of amitraz on soil, and the materials balance was too low (~54% of the applied amount was accounted for at day 212). In addition, this study would not fulfill data requirements because the test substance was uncharacterized, the experiment was conducted on glass and not on soil, and the intensity and duration of the sunlight were not provided. A third study (McCarthy, 00030471) is scientifically invalid because the materials balance was too low (<60% of the applied amount was accounted for by 72 hours after treatment). In addition, this study would not fulfill data requirements because the purity of the test substance was not reported. All data are required.

Photodegradation studies in air: No data were submitted, but no data are required because there is no greenhouse use.

Aerobic soil metabolism studies: Five studies were reviewed; one study (Somerville, 00030461) is scientifically invalid because the parent compound accounted for <47% of the extractable radioactivity on day 0, and the data were too variable to allow an accurate assessment of the metabolism of amitraz in soil. In addition, this study would not fulfill data requirements because the test substance was uncharacterized, complete soil characteristics were not provided, a materials balance was not conducted, and the analytical methods were inadequately described. A second study (Somerville and Nicholson, 00030465; Somerville, et al., 00030464) is scientifically invalid because: Experiment 1 - the parent compound accounted for <3.5% of the extractable radioactivity on day 0, the materials balance was too low (<28% of the applied amount was accounted for at the end of the test period), and the data were too variable to allow an accurate

assessment of the metabolism of amitraz in soil; Experiment 2 - the parent compound accounted for <1.3% of the extractable radioactivity at the first sampling interval, the materials balance was too low (47% of the applied amount was accounted for at the end of the test period), and the data were too variable to allow an accurate assessment of the metabolism of amitraz in soil; Experiment 3 - the parent compound accounted for <11% of the extractable radioactivity at the first sampling interval, and the sampling protocol was inadequate to provide data for assessing the metabolism of amitraz in soil. In addition, this study (all experiments) would not fulfill data requirements because the test substance was uncharacterized, and the incubation temperature was not reported. The three remaining studies are scientifically valid, but do not fulfill data requirements because: the test soil was not completely characterized, the purity of the test substance was not reported, and a materials balance was not conducted (Somerville, 00030462); the incubation temperature was not reported (Newby, et al., 00114301); and the purity of the test substance was not reported, the soil extraction procedure was not described, the test soils were inadequately characterized, and degradates were not identified (Takano, 00030475). All data are required.

Anaerobic soil metabolism studies: Two studies were reviewed; one study (Somerville and Nicholson, 00030465; Somerville et al., 00030464) is scientifically invalid because the materials balance was too low (~34-65% of the applied radioactivity was accounted for at the end of the test period), and the data were too variable to allow an accurate assessment of the metabolism of amitraz in soil. In addition, this study would not fulfill data requirements because the test substance was uncharacterized, the incubation temperature was not reported, and the radioactive residues were not characterized. The second study (Newby, et al., 00114301) is scientifically valid, but does not fulfill data requirements because the incubation temperature was not reported. All data are required.

Anaerobic aquatic metabolism studies: No data were submitted; however, no data are required because amitraz has no aquatic, forestry, or aquatic impact use.

Aerobic aquatic metabolism studies: No data were submitted; however, no data are required because amitraz has no aquatic or aquatic impact use.

Leaching and adsorption/desorption studies: Three studies were reviewed, and all are scientifically valid. One study (Somerville and Nicholson, 00030466) does not fulfill data requirements because the purity of the test substance was not reported, the test soils were not completely characterized, the incubation temperature during the 30-day aging period was not reported, radioactive residues were not characterized, and K_d values were not reported. A second study (Leake, et al., 00114300) does not fulfill data requirements because radioactive residues were identified but not quantified, the distribution of extractable radioactivity in the soil column was not reported, soil was inadequately characterized, and K_d values were not provided. The remaining valid study (Leake, et al., 0011-4299) partially fulfills data requirements by providing data on the mobility of amitraz in sand, sandy loam, silt loam, and clay soils. A study is needed providing data on the mobility of amitraz aged under aerobic conditions for 30 days or one half-life in a sandy loam soil.

Laboratory volatility studies: No data were submitted, but all data are required.

Field volatility studies: No data were submitted, but all data are required.

Terrestrial field dissipation studies: One study was reviewed (Lee, et al., 00051731; Nappier and Hornish, 00051730). Experiments 1, 2, and 4 of this study are scientifically valid. Experiment 3, however is scientifically invalid because the sampling protocol was inadequate to accurately assess the dissipation of amitraz in soil. This study does not fulfill data requirements because a nonspecific analytical method was used (all experiments), the test soil was uncharacterized (Experiments 1, 2, and 4) or incompletely characterized (Experiment 3), and no rainfall data were provided for Experiment 3. All data are required.

Aquatic field dissipation studies: No data were submitted; however, no data are required because amitraz has no aquatic food crop, aquatic non-crop, or aquatic impact use.

Forestry dissipation studies: No data were submitted; however, no data are required because amitraz does not have a forestry use.

Dissipation studies for combination products and tank mix uses: No data were submitted; however, no data are required because data requirements for combination products and tank mix uses are currently not being imposed for this Standard.

Long-term field dissipation studies: No data were submitted, but all data may be required based on the results from the terrestrial field dissipation/ aerobic soil metabolism studies.

Confined accumulation studies on rotational crops: No data were submitted; however, no data are required because no crops are rotated with pears.

Field accumulation studies on rotational crops: No data were submitted; however, no data are required because no crops are rotated with pears.

Accumulation studies on irrigated crops: No data were submitted; however, no data are required because amitraz does not have an aquatic food crop or aquatic noncrop use, is not used in and around holding ponds used for irrigation purposes, and has no use involving effluents or discharges to water used for crop irrigation.

Laboratory studies on pesticide accumulation in fish: Two studies were reviewed; one study (Barrows, 00030469) cannot be validated because of an unexplained increase in [^{14}C]amitraz residues in the treated soil during the test period. In addition, this study would not fulfill data requirements because radioactive residues were not characterized, a flow-through aquatic exposure system was not used, and residues in whole fish were not determined. The second study (EG & G Bionomics, 00072503) is scientifically valid, but does not fulfill data requirements because the [^{14}C]amitraz residues in fish tissue were not characterized. All data are required.

Field accumulation studies on aquatic nontarget organisms: No data were submitted; however, no data are required because amitraz has no forestry, aquatic noncrop, or aquatic impact use.

Reentry studies: No data were submitted, and foliar dissipation data are required.

Label Restrictions

Products labeled for terrestrial use(s) must be classified for "Restricted Use" and the labels must bear the following groundwater precautionary statements: "Amitraz is known to leach through soil. Users are advised to apply this product only where groundwater contamination is unlikely. Do not apply in recharge areas of designated Sole Source Aquifers, or in areas with well-drained soils as defined by Class A of the Soil Conservation Service classification system which overlay shallow aquifers or which are not protected by an overlying impervious layer. Consult the proper state regulatory officials in your area for information on the location of soil source recharge areas, and the local agent of the Soil Conservation Service for information on your specific soil characteristics." "Do not re-enter treated areas for 24-hours without protective clothing."

References (All Studies Reviewed)

Barrows, M.E. 1976. Kinetics of aged ^{14}C-amitraz in model aquatic ecosystem: AX 76008. Unpublished study received Apr. 9, 1980 under 43142-EX-1; prepared by EG & G, Bionomics, submitted by Boots Hercules Agrochemicals Co., Wilmington, DE; CDL:099370-L. (00030469)

EG & G Bionomics. 1980. Accumulation and elimination of ^{14}C residues by bluegill sunfish (Lepomis macrochirus) exposed to ^{14}C-labeled amitraz. Report No. BW-80-10760. (00072503)

Golding, P.B. 1973. BTS 27 419: Stability to light. Unpublished study received Dec. 1975 under 1023-EX-34; submitted by Upjohn Co., Kalamazoo, MI; CDL: 094994-C. (00051761)

Golding, P.B. 1973. Further work on the photodegradation of BTS 27 419. Compilation; unpublished study received June 24, 1976 under 6F1817; CDL:098096-A. (00111860)

Leake, C., L. Somerville, D. Lines, et al. 1982. The leaching of amitraz in four soil types using soil TLC: METAB/82/16. Unpublished study received Sep. 8, 1982 under 45639-49; prepared by FBC, Ltd., Eng., submitted by BFC Chemicals, Inc., Wilmington, DE; CDL:248318-B. (00114299)

Leake, C., L. Somerville, and K. Tiffen. 1982. The degradation and leaching of amitraz in a sandy loam soil: METAB/82/19. Unpublished study received Sep. 8, 1982 under 45639-49; prepared by FBC, Ltd., Eng., submitted by BFC Chemicals, Inc., Wilmington, DE; CDL:248318-C. (00114300)

Lee, B.L., W.J.H. Stone, C. Pitts, et al. 1976. Soil residue determination for U-36,059 and metabolites: Report No. 315-9760-66. Unpublished study including report nos. 315-9760-68 and 315-9760-69, received June 24, 1976 under 6F1817; submitted by Upjohn Co., Kalamazoo, MI; CDL:096420-R. (00051731)

McCarthy, J.F. 1975. The effect of artificial sunlight on traces of amitraz deposited on soil: AC 75 035. Unpublished study received Apr. 9, 1980 under 43142-EX-1; submitted by Boots Hercules Agrochemicals Co., Wilmington, DE; CDL:099370-N. (00030471)

Nappier, J.L., and R.E. Hornish. 1975. Total residue method for U-36,059 [1,5-di-(2,4-dimethylphenyl)-3-methyl-1,3,5-triazapenta-1,4-diene] in apples, pears and soils: Report No. 315-9760-32. Method dated Sep. 26, 1975. Unpublished study received June 24, 1976 under 6F1817; submitted by Upjohn Co., Kalamazoo, MI; CDL:096420-Q. (00051730)

Newby, S., L. Somerville, K. Tiffen, et al. 1982. The laboratory decline of amitraz in two soils, a sandy loam, and a silt loam under aerobic, anaerobic, and sterile conditions: METAB/82/34. Unpublished study received Sep. 8, 1982 under 45639-49; prepared by GBC, Ltd., Eng., submitted by BFC Chemicals, Inc., Wilmington, DE; CDL:246318-D. (00114301)

Somerville, L. 1973. BTS 27 419: Soil degradation studies: A preliminary report: AX 73001. Unpublished study received Apr. 9, 1980 under 43142-EX-1; submitted by Boots Hercules Agrochemicals Co., Wilmington, DE; CDL:099370-C. (00030461)

Somerville, L. 1975. Amitraz--Soil degradation studies: AX 74 013. Unpublished study received Apr. 9, 1980 under 43142-EX-1; submitted by Boots Hercules Agrochemicals Co., Wilmington, DE; CDL:099370-D. (00030462)

Somerville, L., and J.E. Nicholson. 1976. Amitraz (BTS 27 419): Degradation studies in an American sandy loam soil: Part 2: AX 76002. Unpublished study received Apr. 9, 1980 under 43142-EX-1; submitted by Boots Hercules Agrochemicals Co., Wilmington, DE; CDL:099370-G. (00030465)

Somerville, L., and J.E. Nicholson. 1976. The leaching of amitraz in soil: AX 76001. Unpublished study received Apr. 9, 1980 under 43142-EX-1; submitted by Boots Hercules Agrochemicals Co., Wilmington, DE; CDL:099370-H. (00030466)

Somerville, L., J.E. Nicholson, and J. Taylor. 1975. Amitraz (BTS 27 419): Degradation studies in an American sandy loam soil: AX 75021. Unpublished study received Apr. 9, 1980 under 43142-EX-1; prepared in cooperation with Michigan State Univ., Soil Testing Laboratory, submitted by Boots Hercules Agrochemicals Co., Wilmington, DE; CDL:099370-F. (00030464)

Takano, J. 1972. Residue analysis of soil (JA-119 Technical). Appendix 15; unpublished study received Apr. 9, 1980 under 43142-EX-1; prepared by Nissan Chemical Industries, Ltd., submitted by Boots Hercules Agrochemicals Co., Wilmington, DE; CDL:099370-P. (00030475)