DYNAMAC CORPORATION

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ALDICARB

TASK 2: ENVIRONMENTAL FATE AND EXPOSURE ASSESSMENT

Contract No. 68-01-6679

Final Report

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SUBMITTED TO:

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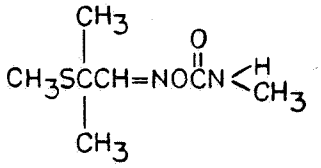
Environmental Fate and Exposure Assessment

Aldicarb

ALDICARB, TEMIK, UC-21149



2-Methyl-2-(methylthio)propionaldehyde
O-(methylcarbamoyl)oxime

Aldicarb is a systemic carbamate insecticide, acaricide, and nematicide registered for use on various field and vegetable crops, orchard crops, turf, and ornamentals (i.e., commercial field grown and nursery plantings, greenhouse crops, potted plants). Approximately 3.05 - 4.72 million pounds of the active ingredient are used annually in the United States. Of the total domestic aldicarb usage, ~29, 25, 14, 12, and 10% is applied to cotton, potatoes, peanuts, soybeans, and pecans, respectively. Application rates range from 0.3 to 10 lb ai/A. Aldicarb 5% G is formulated with Terrazole and Terraclor. Single active ingredient formulations of aldicarb consist of 10 and 15% G. Aldicarb may be applied as a pre- or post-emergent treatment by banding or sidedressing the row, and is soil incorporated immediately after application. Applicators must be certified or under the direct supervision of applicators certified to apply aldicarb.

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

[^{14}C]Aldicarb hydrolyzes at 25 C under alkaline conditions (pH 9), with ~24% hydrolyzed over a 28-day period (00102065). Under these conditions, the degradate aldicarb sulfoxide undergoes rapid hydrolysis, with a half-life of 2.3 days (00102066). At pH 7, aldicarb sulfoxide is stable (<8% hydrolyzed after 28 days), whereas no hydrolysis of aldicarb occurs. Both aldicarb and aldicarb sulfoxide are stable to hydrolysis at pH 5. Aldicarb, at pH 9, hydrolyzes primarily to aldicarb oxime, and in lesser amounts to aldicarb nitrile, aldicarb

sulfoxide, and aldicarb sulfoxide oxime. Aldicarb sulfoxide oxime and aldicarb sulfoxide nitrile were identified as minor hydrolysis products of aldicarb sulfoxide at pH 9 (00102065, 00102066).

[^{14}C]Aldicarb sulfoxide is relatively stable in water (uncharacterized) when exposed to UV light at 20-25 C, with ~93% of the applied ^{14}C remaining as parent compound after 14 days (00102068).

Under aerobic conditions at 25-28 C and 100% of field capacity, aldicarb degrades with half-lives of 9-12 days in clay, silt loam, and sand soils (00093642, 00080820, 00093640, 00053366), and <15 days in sandy loam, loamy sand, and sand soils incubated at an unspecified temperature and moisture content (00102051). At 22 C and 75% of field capacity, aldicarb, at 2.7 ppm, was degraded completely within 60 days in aerobic silt loam soil (00102054). [^{14}C]Aldicarb degrades with half-lives of >56 days in four dry soils (pure sand, fine sandy loam, clay, and muck), in sand at 50 and 100% of field capacity, and in fine sandy loam at 50% of field capacity. Degradation rates increase in fine sandy loam, clay, and muck soils (half-lives <1 to 28 days) with an increase in moisture content up to field capacity. Soil pH (6, 7, or 8) had no appreciable effect on the rate of degradation (00101934, 00035365, 00102071). The major identified degradates were aldicarb sulfoxide and aldicarb sulfone with half-lives ranging from ~1 to 3 weeks (00093642, 00080820, 00093640, 00053366, 00102051, 00053370). Aldicarb sulfoxide acid, aldicarb sulfoxide oxime, aldicarb sulfoxide alcohol, aldicarb sulfoxide amide, aldicarb sulfoxide nitrile, aldicarb sulfone acid, aldicarb sulfone alcohol, aldicarb sulfone amide, aldicarb sulfone nitrile, aldicarb sulfone oxime, aldicarb oxime, and methane sulfonic acid were identified as minor degradates, representing ≤8.5% of the applied radioactivity up to 3 months after treatment (00093642, 00080820, 00093640, 00053366, 00102054, 00101934, 00035365, 00102071). Evolved $^{14}CO_2$ accounted for the majority of the applied radioactivity over the test periods and was greatest in soils treated with N-methyl-labeled [^{14}C]aldicarb (as compared to S-methyl- or tertiary-labeled [^{14}C]aldicarb) (00102051).

[^{14}C]Aldicarb sulfone degrades to CO_2 and noncarbamate products in aerobic sandy loam, sand, and silt loam soils, with half-lives ranging from <1 week to <1 month. The majority of the applied radioactivity (54-72%) evolved as $^{14}CO_2$ after ≥28 days of incubation at 22 ± 2 C in all three soils. Aldicarb sulfone al-

cohol, aldicarb sulfone amide, aldicarb sulfone nitrile, aldicarb sulfone aldehyde were present at >0.01 ppm (00053370).

Insecticidal residues dissipate with half-lives of ~2 weeks in a modified sandy loam soil (2:1 Norfolk sandy loam and "UC mix") treated with aldicarb, aldicarb sulfoxide, or aldicarb sulfone at ≤20 lb/A, and are generally more persistent at 40 lb/A (00093641). Total carbamate residues (aldicarb, aldicarb sulfoxide, and aldicarb sulfone) degrade with half-lives of ~2 to 5 weeks in clay loam soil treated with aldicarb at 5-50 ppm and maintained at an unspecified moisture content and 23-32 C (00102050), and with half-lives of ~1 to 3 weeks in greenhouse soils composed of sandy loam, peat, and/or perlite treated with aldicarb at 4-20 lb ai/A (00101915).

Under anaerobic conditions, [^{14}C]aldicarb, at 2.7 ppm, degrades completely in silt loam soil incubated aerobically for 30 days followed by 60 days of anaerobic incubation at 22 C and 75% of field capacity. The majority of the applied radioactivity was associated with $^{14}CO_2$ (76.9%). Aldicarb sulfoxide acid, aldicarb sulfoxide alcohol, aldicarb sulfoxide amide, aldicarb sulfoxide oxime, aldicarb sulfone, aldicarb sulfone acid, aldicarb sulfone alcohol, aldicarb sulfone amide, and methane sulfonic acid were present at >0.01 ppm (00102054). Under identical incubation conditions, [^{14}C]aldicarb sulfone, at 2.7 ppm, degrades in silt loam soil, declining from ~23% of the applied radioactivity at the onset of anaerobic conditions to <4% 61 days later. The majority of the applied radioactivity was associated with $^{14}CO_2$ (~58%). The following degradates were present at maximum concentrations of >0.01 ppm: aldicarb sulfone amide (~31% of applied), aldicarb sulfone acid, aldicarb sulfone alcohol, aldicarb sulfone nitrile, and aldicarb sulfone oxime (00053370).

Aldicarb, aldicarb sulfone, and aldicarb sulfoxide are mobile in sandy loam, sandy clay loam, and fine sand soils. Aldicarb is also mobile in clay loam, silt loam, humic sand, muck, and loam soils. After applying 1 inch of water, 50% of the radioactivity applied as aldicarb, aldicarb sulfoxide, or aldicarb sulfone leached 2.1-2.6 inches in sandy loam, sandy clay loam, and fine sand soils.

In muck soil, 50% of the applied [^{14}C]aldicarb (only compound tested in muck soil) leached 0.3 inches after elution with 1-inch of water (00053380). Total

residues in the leachate of 28- to 50-cm silt loam, humic sand, and loam soil columns were equivalent to 20-72% of the applied aldicarb after applying ~11-26 inches of water. Aldicarb sulfoxide represented the major portion of residues in the leachate (00102079). Aldicarb moved readily upward in a 10-inch fine sand soil column (treated with [^{14}C]aldicarb at a 4-inch depth) that had been saturated and then heated to 38 C on its top surface to evaporate the water. Following evaporation of 49% of the water in the soil, 47.6% of the applied radioactivity moved ~3 inches upward in the soil column. Aldicarb sulfoxide was associated with ~75% of the extracted radioactivity (00053381). After application of 7-8 inches of water to 5-inch fine sand and fine sandy loam soil columns treated with [^{14}C]aldicarb sulfone, ~90 and 19% of the applied radioactivity was eluted from the respective columns. The majority of the radioactivity in the leachate was associated with aldicarb sulfone; aldicarb sulfone amide, aldicarb sulfone alcohol, aldicarb sulfone oxime, aldicarb sulfone aldehyde, and aldicarb sulfone nitrile represented ≤1.86% of the applied radioactivity (00053370). Carbamate residues are mobile in clay soil columns (25 cm height) with ~77% of applied recovered in the first 450 ml of leachate, and in sandy loam and muck soils, leaching .6 inches in soil columns eluted with 1 and 3 inches of water, respectively (00102050, 00053385). Carbamate residues do not move horizontally from a bare, sloping field (1% slope) irrigated to runoff, following treatment with aldicarb (10% G) at 10 lb ai/A (00101939, 00101926).

[^{14}C]Aldicarb and [^{35}S]aldicarb dissipate with a half-life of <7 days in cultivated sandy loam soil and fine sandy loam soil sampled to a depth of 20 cm (00102064, 00101935, 00101937, 00053364). In uncultivated sandy loam soil sampled to the same depth, [^{14}C]aldicarb dissipates more slowly with a half-life of 14-30 days. Aldicarb degraded quickly, with only 82% of the radioactivity recovered as parent compound when sampled immediately after treatment. In both cultivated and uncultivated soils, the major degradate was aldicarb sulfoxide (12-76% of recovered radioactivity). Minor degradates found include aldicarb sulfone, aldicarb sulfoxide oxime, aldicarb sulfoxide nitrile, and aldicarb sulfone nitrile (00102064, 00101935, 00101937). Total carbamate residues dissipate rapidly from sand, sandy loam, fine sandy loam, and mineral soils sampled at depths up to 8 feet with half-lives ranging from 1 to 7 days (00101934, 00035365, 00102071, 00101939, 00101926, 00068252), and more slowly in a high organic matter (85%) muck soil (half-life of 30-60 days; sampling depth unspecified) and a fine loam

soil planted with Scotch pine trees (half-life of 15-36 days; sampled to a 12-inch depth) (00101939, 00101936, 00102078). Insecticidal aldicarb residues dissipated within 1 year in an unspecified field soil treated with aldicarb (10% G) at <6 lb ai/A, as determined by a Colorado potato beetle bioassay (00101936). Due to the mobility of aldicarb in soil, loss of applied aldicarb in these field dissipation studies may have partly resulted from leaching of aldicarb beyond the sampling depth.

[^{14}C]Aldicarb residues are taken up by rotational crops, ranging from <0.01 to 0.06 ppm in tomato plants rotated to a sandy loam soil 90 days after treatment with [^{14}C] aldicarb at 3 lb ai/A. The tomato plants were analyzed 7 days following planting into the treated soil (00102064, 00101935, 00101937).

Aldicarb residues have been found in well water from wells near aldicarb-treated fields. Aldicarb residues <50 ppb were found in well water samples from New York (Long Island), Wisconsin, Florida, Maine, Virginia, and North Carolina; aldicarb residues <200 ppb were found in 2-8% of the private wells sampled in Suffolk County, Long Island, New York between November 1979 and May 1981 (00025511, 00096543, Union Carbide Agricultural Products Company, Inc., 1981, No MRID, Union Carbide Corp., 1983, No MRID).

Dermal and inhalation exposures to workers may occur during application of aldicarb. Exposure from the G formulations is expected to be mainly dermal. Human exposure to aldicarb during handling, application, and soil incorporation operations could be minimized by the use of gloves, approved respirators, and other protective clothing. However, data are not available to fully assess such exposures.

Although aldicarb meets Subpart K (Reentry) requirements, exposure during reentry operations is expected to be minimal for current uses, as aldicarb is soil incorporated immediately after application. However, data are not available to fully assess such exposures. Currently, no federal reentry intervals have been established; however, California has a 24-hour reentry interval established for all pesticides in Toxicity Category I, which includes aldicarb.

Reported pesticide incidents involving aldicarb alone between 1966 and 1982 include 165 involving human injury, and 6 each involving animals, environmental contamination, and nontarget plants and crops. In the incidents involving human injury, there were 2 fatalities, and 137 individuals were hospitalized and/or received medical attention. Most of the human incidents resulted from failure to use safety equipment while applying aldicarb. Other incidents were the result of accidental spillage and ingestion of aldicarb or food improperly treated with aldicarb.

Accumulation of aldicarb in aquatic nontarget organisms is expected to be minimal, based on an octanol/water partition coefficient of 5 and an ecological magnification value of 42 (Metcalf, R.L., 1978, Partition Coefficients as Measures of Bioaccumulation Potential for Organic Compounds).

In summary, aldicarb hydrolyzes fairly rapidly under alkaline conditions (pH 9), but is essentially stable at pH 5 and 7. Aldicarb sulfoxide undergoes rapid hydrolysis at pH 9, is fairly stable at pH 7, and stable at pH 5. Aldicarb sulfoxide is relatively stable to photolysis, with ~93% of the applied compound remaining unchanged in water after 14 days of irradiation. Under aerobic conditions, aldicarb degrades rapidly in moist soil, with half-lives ranging from <1 to 28 days, and slowly (half-lives of <58 days) in dry soils. Soil pH has no appreciable effect on the rate of degradation. Aldicarb sulfone rapidly degrades to CO_2 and noncarbamate products in aerobic soils, with half-lives of <1 week to <1 month. Insecticidal residues dissipate fairly rapidly from aerobic soils treated with aldicarb, aldicarb sulfoxide, or aldicarb sulfone at 20 lb/A (half-lives of ~2 weeks), and are generally more persistent at 40 lb/A. Total carbamate residues degrade fairly rapidly with half-lives of ~1 to 5 weeks in aerobic soils treated with aldicarb at 5-50 ppm or 4-20 lb ai/A. Under anaerobic conditions, aldicarb and aldicarb sulfone degrade rapidly in silt loam soil incubated aerobically for 30 days followed by 60 days of anaerobic incubation at 22 C and 75% of field capacity. Evolved $^{14}CO_2$ accounted for the majority of the applied radioactivity over the test periods in both aerobic and anaerobic soils. Aldicarb, aldicarb sulfoxide, and aldicarb sulfone are mobile in fine to coarse textured soils, including those with high organic matter content. Carbamate residues do not move horizontally from a bare, sloping field (1% slope) irrigated to runoff, following treatment with aldicarb at 10 lb ai/A. Aldicarb dissipates rapidly with a half-life of <7 days in culti-

vated field soils, and more slowly (half-life of 14-30 days) in uncultivated soil. In both cultivated and uncultivated soils the major degradate was aldicarb sulfoxide. Total carbamate residues dissipate from field soils with half-lives of 1-7 days. Dissipation of carbamate residues is slowed in highly organic field soils and in soil planted with pine trees (half-lives of 15-60 days). Due to the mobility of aldicarb in soil, loss of applied aldicarb from these field soils may have partly resulted from leaching of aldicarb beyond the sampling depth. [^{14}]Aldicarb residues are taken up by rotational crops, ranging from <0.01 to 0.06 ppm in tomato plants rotated to aldicarb-treated soil 90 days post-treatment. Aldicarb residues have been found in well water from wells near aldicarb-treated fields, as determined by monitoring studies in New York (Long Island), Wisconsin, Florida, Maine, Virginia, and North Carolina.

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 aldicarb: photodegradation studies in water; anaerobic soil metabolism studies; aerobic and anaerobic aquatic metabolism studies; leaching and adsorption/desorption studies; laboratory and field volatility studies; terrestrial and long-term field dissipation studies; accumulation studies in rotational crops; and possibly reentry studies.

Hydrolysis studies: Eight studies were reviewed; six could not be validated because they were not stated to have been conducted in darkness (00102072, 00102057, 00102011, 00053377) and the analytical method was not presented (00102048, 00096547). One study (00102066) partially fulfills data requirements by providing data on the hydrolysis of aldicarb sulfoxide at pH 5, 7, and 9 at 25 C. The remaining study (00102065) fulfills data requirements by providing data on the hydrolysis of aldicarb at pH 5, 7, and 9 at 25 C and by identifying aldicarb oxime as a major hydrolysis product of aldicarb at pH 9. Together, these two studies (00102065, 00102066) completely fulfill data requirements.

Photodegradation studies in water: Three studies were reviewed; one is scientifically invalid because precautions were not taken to minimize and/or account for the loss of [^{14}C]aldicarb residues (≤33% of applied) during the test (00102067), and one could not be validated because the analytical method for determining aldicarb residues was not presented (00102048). The remaining

valid study (00102068) investigated the photodegradation of aldicarb sulfoxide (a degradate of aldicarb) in water. This study does not partially fulfill data requirements because the experiment was not carried out for a sufficient length of time to assess the decline of aldicarb sulfoxide in UV irradiated water and no dark controls were monitored. All data are required.

Photodegradation studies on soil: No studies were submitted; however, all data are waived because aldicarb is soil incorporated.

Photodegradation studies in air: No studies were submitted; however, all data are waived because aldicarb is soil incorporated.

Aerobic soil metabolism studies: Fifteen studies were reviewed; one was scientifically invalid because the sampling protocol was insufficient to confirm the stated application rates or to establish decline curves for aldicarb in soil (00029989), and one could not be validated bacause the analytical method was not presented and the soil moisture content was not reported (00096968). Three of the thirteen valid studies do not fulfill data requirements because nonspecific analytical methods were used (00093641, 00102050, 00101915), the test substance used was not technical grade or purer (00101915), a materials balance was not provided (00102050), and insufficient information was provided regarding characteristics of the test soils, the purity of the test substance, and soil moisture content and/or temperature during incubation (00093641, 00102050, 00101915). Six of the remaining valid studies partially fulfill data requirements by providing half-life estimates for aldicarb and aldicarb sulfone in a wide range of soils and by identifying 13 aldicarb degradates and 6 aldicarb sulfone degradates (00102051, 00101934, 00035365, 00101071, 00102054, 0053370). The four remaining studies (00093642, 00080820, 00093640, 00053366) completely fulfill data requirements by establishing quantitative decline curves for aldicarb in three soils, and by identifying and establishing rates of formation and decline of aldicarb degradates.

Anaerobic soil metabolism studies: Two studies were reviewed (00053370, 00102054) that partially fulfill data requirements by identifying degradates of aldicarb and aldicarb sulfone. A study is needed to establish a quantita-

tive decline curve and half-life data for aldicarb, and the pattern of formation and decline of degradates.

Anaerobic aquatic metabolism studies: No data were submitted; however, all data are required based on the results of groundwater monitoring (exposure studies) and leaching studies.

Aerobic aquatic metabolism studies: Two studies were reviewed; one study (00102050) is scientifically invalid because the sampling protocols were inappropriate to assess the decline of aldicarb residues in water. The second study (00102048) could not be validated because the analytical method for determining aldicarb residues was not presented. However, all data are required based on the results of groundwater monitoring (exposure studies) and leaching studies.

Leaching and adsorption/desorption studies: Twelve studies were reviewed; three studies (00101934, 00035365, 00102071) are scientifically invalid because the experimental design was inadequate to assess the mobility of aldicarb in soil, and one study (00101915) could not be validated because the procedures and protocols were incompletely described. Two of the eight valid studies are runoff studies (00101939, 00101926) that do not fulfill data requirements for leaching and adsorption/desorption studies because the procedure used was not one of the three acceptable methods for assessing pesticide mobility in soil (column leaching, soil TLC, or batch equilibrium), a technical grade or purer test substance was not used, and a nonspecific colorimetric method was employed. The six remaining valid studies do not fulfill data requirements because the soil columns used were too short and/or were not eluted with a sufficient amount of water (00053380, 00053385, 00053370); the procedure used was not an EPA acceptable method for assessing pesticide mobility (00053381); the test substance was uncharacterized or not a technical or purer grade (00102079, 00053380, 00053385); the test soils were not characterized (00102050, 00053385); and a nonspecific analytical method was used (00102050, 00053385). All data are required.

Laboratory volatility studies: Three studies were reviewed (00101934, 00035365, 00101071) and considered scientifically invalid because a large portion of the applied radioactivity was not recovered by the end of the test period and volatiles were not trapped, precluding any accurate assessment of aldicarb volatility from soil. All data are required.

Field volatility studies: No data were submitted, but all data may be required based on results from laboratory volatility studies.

Terrestrial field dissipation studies: Twenty studies were reviewed; eight studies are scientifically invalid because sampling intervals were insufficient to establish an aldicarb residue decline curve (00101915, 00036313, 00101910, 00053379, 00101968); procedures and analytical methods were inadequately described (00080815, 00101923); and the data were extremely variable (00102061). One of the twelve valid studies is a monitoring study (00101936) that does not fulfill data requirements because a nonspecific bioassay was used, the field soil was uncharacterized, rainfall and irrigation data were not provided, and soil from the treated area was not sampled at any time. The eleven remaining valid studies do not fulfill data requirements because a nonspecific analytical method was used (00102078, 00101939, 00101936, 00068252); soil characteristics were incompletely described (00102078, 00053364, 00102064, 00101935, 00101937, 00101939, 00101926); rainfall and irrigation data were incompletely reported (00102078, 00053364, 00101939, 00101926); the test substance used was not a typical end-use product (00101934, 00035365, 00102071, 00053364, 00102064, 00101935, 00101937); and soil samples were not taken in increments to a depth >15 cm and/or to a depth sufficient to define the extent of leaching (00101934, 00035365, 00102071, 00053364, 00101939, 00101926). All data are required.

Aquatic field dissipation studies: Two studies were reviewed; one study (00101940) is scientifically invalid because the experimental design did not allow for an accurate assessment of aldicarb dissipation from an aquatic environment. The second study (00094799) could not be validated because the analytical methodology was not reported. However, no data are required because aldicarb does not have aquatic or aquatic impact uses.

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

Dissipation studies for combination products and tank mix uses: No data were submitted; however, 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; however, all data may be required based on results from terrestrial field dissipation studies.

Confined accumulation studies on rotational crops: Four studies were reviewed; one study (00102073) could not be evaluated because the document reviewed was incomplete. The remaining three studies (00102064, 00101935, 00101937) were considered scientifically valid, but do not fulfill data requirements because the rotational crop was not analyzed at the time of harvest, irrigation and rainfall data were not provided for the specified sampling interval, and aldicarb residues were not characterized. All data are required.

Field accumulation studies on rotational crops: No data were submitted; however, all data may be required based on results from confined accumulation studies on rotational crops.

Accumulation studies on irrigated crops: No data were submitted; however, no data are required because crops are not expected to be irrigated with aldicarb-contaminated water.

Laboratory studies of pesticide accumulation in fish: One study was reviewed and considered scientifically invalid (00026981) because the procedures and protocols used were not adequate for assessing the accumulation potential of aldicarb in fish. All data are waived because aldicarb has an octanol/water partition coefficient of 5 and is not expected to bioaccumulate in fish.

Field accumulation studies of aquatic nontarget organisms: No data were submitted; data are waived because aldicarb has a very low octanol/water partition coefficient (5) and is not expected to bioaccumulate in aquatic nontarget organisms.

Reentry studies: No data were submitted; however, all data may be required.

Exposure studies: Five studies were reviewed; one study could not be evaluated (00080705) because the methods were not sufficiently described. The remaining four studies (00025511; 00096543; Union Carbide Agricultural Products Company, Inc., 1981, No MRID; Union Carbide Corp., 1983, No MRID) were considered scientifically valid.

Label Restriction

Do not plant any crop not registered for use with aldicarb within 10 days of last application. Based on the available data, it is suggested that aldicarb not be applied in areas with shallow and unconfined aquifers, and a total precipitation and irrigation recharge greater than 10 in/yr.

References (All Studies Reviewed)

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