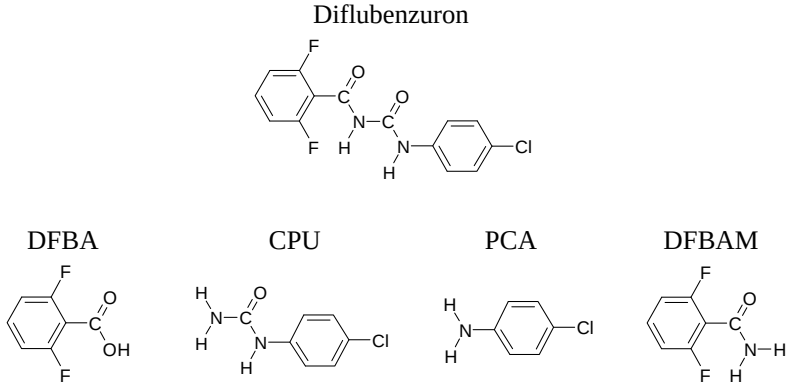
Appendix D. Supplemental Fate Information for Diflubenzuron

Diflubenzuron and Degradate Chemical Structures

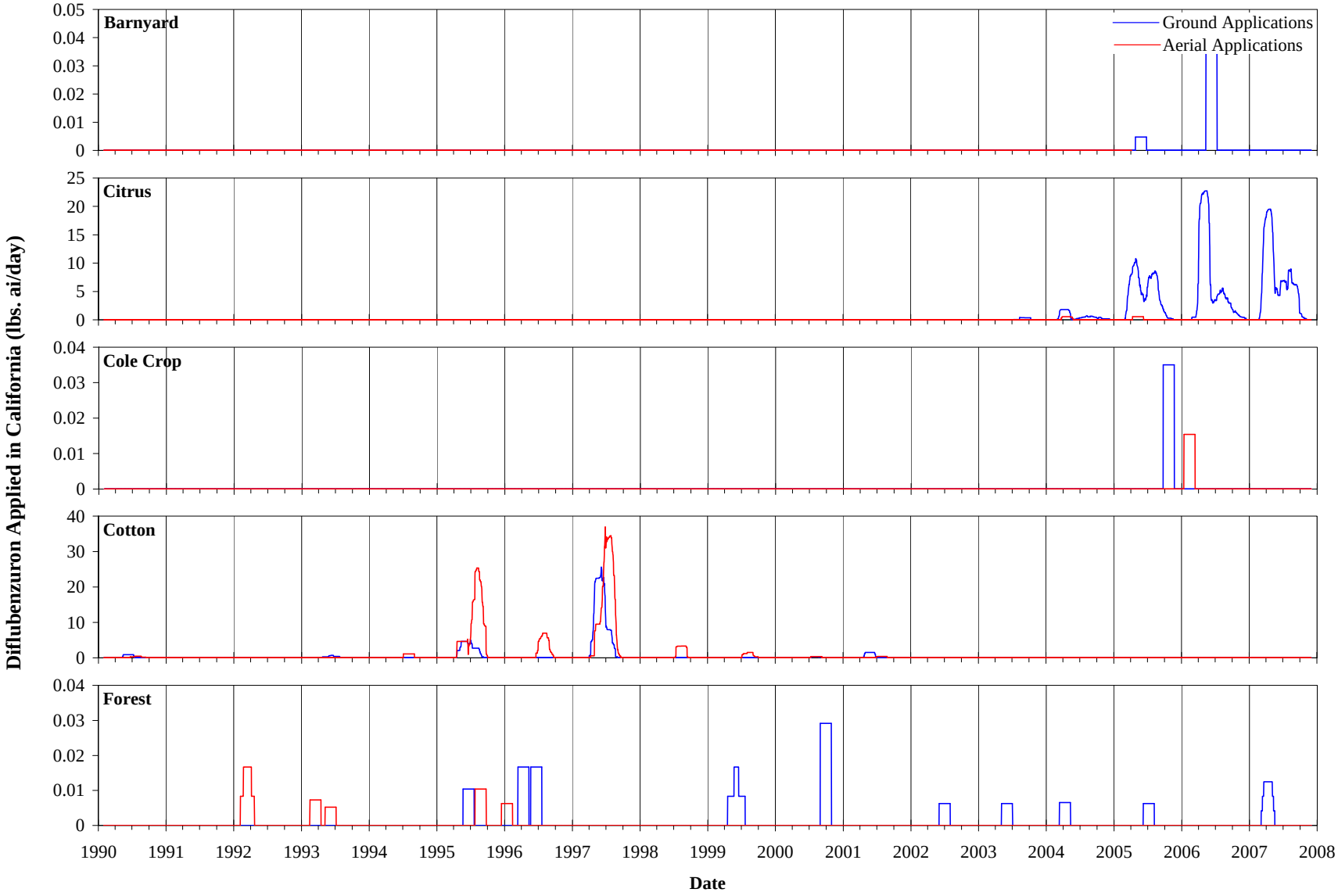
Chemical structure diagrams for diflubenzuron and four of its degradates identified in fate studies are shown in Appendix Figure B1 – 2,6-diflubenzoic acid (DFBA), 4-chlorophenylurea (CPU), 4-chloroaniline (PCA), and 2,6-diflubenzamide (DFBAM). Discussion of degradates occurs in Section 2.2 of the main document. Maximum degradate yields from each fate study are included in Table 2-1 of the main document.



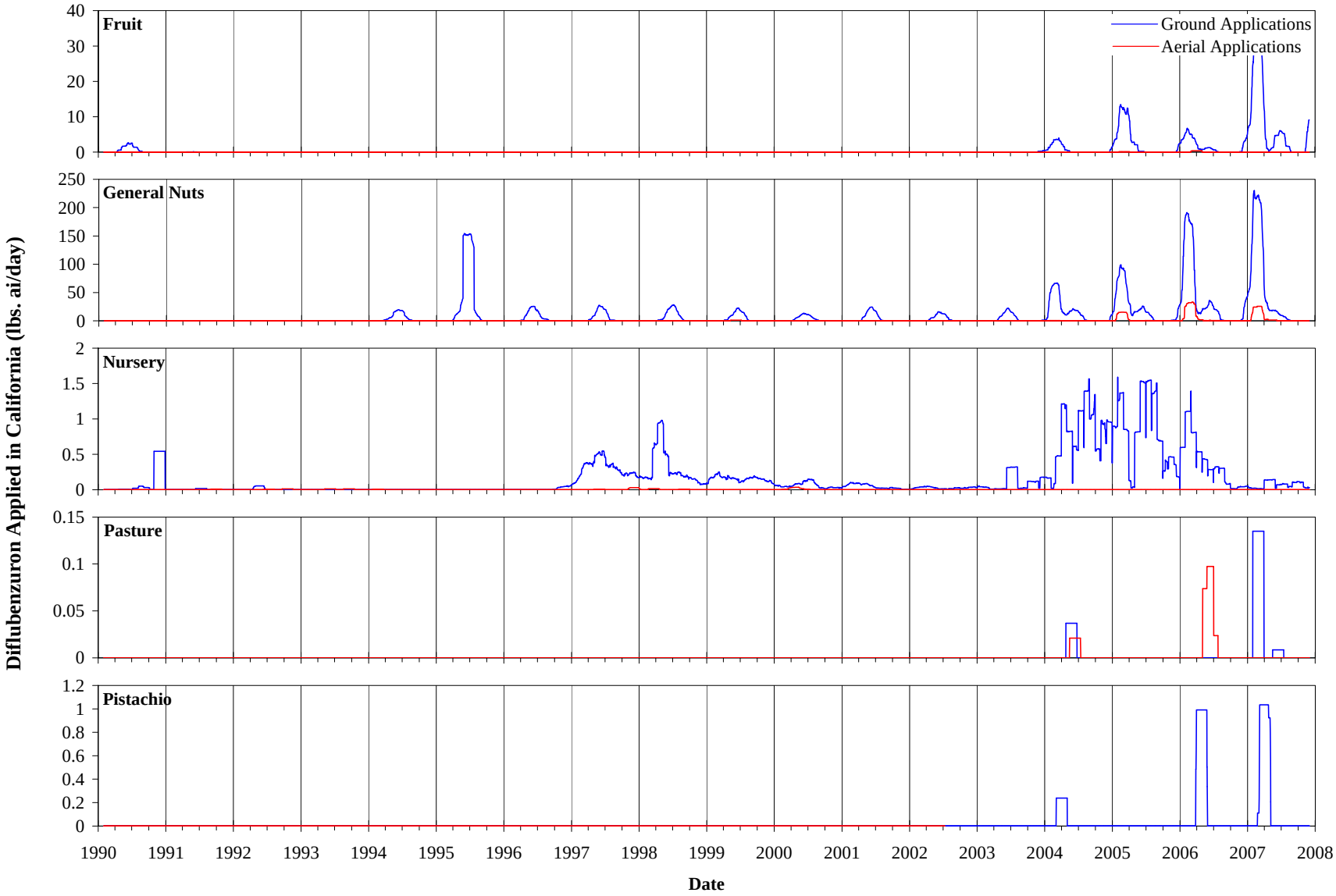
Appendix Figure D1. Diflubenzuron and degradate chemical structures as discussed in Section 2.2 of the main document.

Historical Diflubenzuron Use

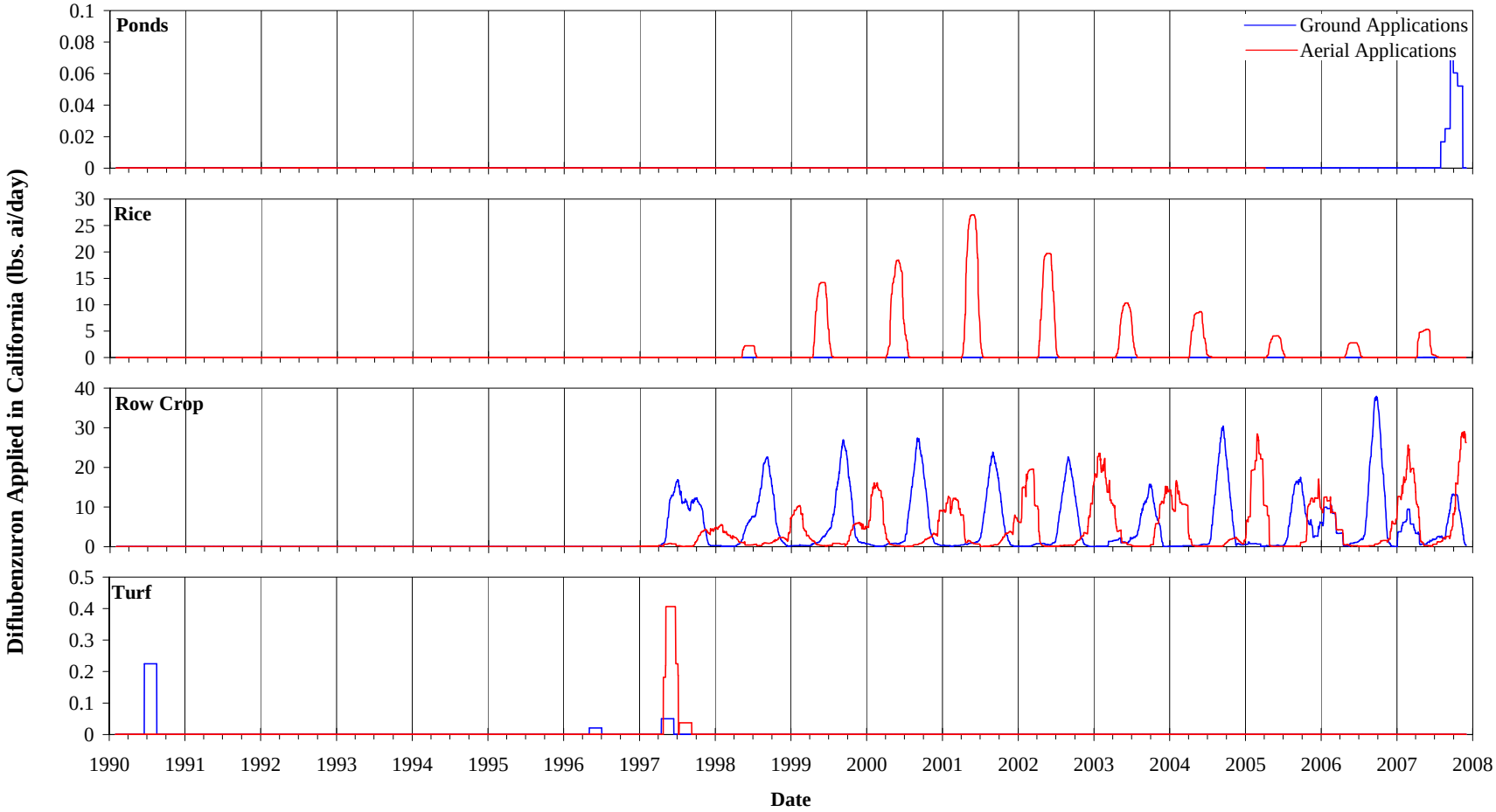
Information on the historical usage of diflubenzuron in California was obtained California Department of Pesticide's Pesticide Use Reporting (CDPR PUR) data set. The full CDPR PUR data set contains pesticide use data from 1990 through 2007. This data is summarized in the following graph (Appendix Figure D1). For each exposure scenario group, trends in propargite application (lbs/day) were obtained using moving averages. Inter-year variation in propargite application are depicted using a 60-day moving average for CDPR PUR data from 1990-2007. This graph provides some indication of whether intra-annual temporal trends in propargite applications are consistent between years and how propargite usage has changed across years.



Appendix Figure D2. Variation in the rate of diflubenzuron application from 1990 through 2007 in California by use.



Appendix Figure D2. Continued.



Appendix Figure D2. Continued.

Fate Properties

Hydrolysis

Diflubenzuron appears to be stable to hydrolysis at pH 5 and pH 7 (90% unchanged after 4 weeks). At pH 9, a 32 day hydrolytic half-life was reported. (MRID 40859801 and 41087801)

Aqueous Photolysis

Diflubenzuron appears stable to unsensitized aqueous photolysis at pH 7. An extrapolated natural light half-life of 80 days was reported in the data. (MRID 40816301 and 41087802)

Soil Photolysis

Diflubenzuron had a reported half-life of 11.3 and 3.7 days for light exposed and control samples, respectively. Five degradates, p-chlorophenyl urea (CPU), 2,6-difluorobenzoic acid (DFBA), two unidentified degradates (labeled SP1 and PK1), and $^{14}C0_2$, were discernible in the light exposed and control samples. The maximum concentration reported for DFBA, CPU, SP1, and PK1 in the light exposed samples were 3.0% (Day 7), 12.9 % (Day l0), 0.6% (Day 10), and 0.1% (Day 16) of applied radioactivity, respectively. The maximum concentration for DFBA, CPU, SPl, and PKl (2.1% at Day 2, 21.1% at Day 7, 3.5% at Day 10, and 0.2% at Day 10 & 16, respectively) in the control samples were similar. (MRID 42251201)

Aerobic Soil Metabolism

Diflubenzuron, applied to sandy loam soil, was calculated to have a half-life of 2-14 days (depending on soil texture) when incubated at 24 ± 1°C and maintained at 77% of 0.33 bar moisture capacity. The major degradate, 4-chlorophenyl urea, reached a maximum concentration of 30.8% to 37% of the applied radioactivity at 7 to 14 days post-treatment. The other major degradate, CO_2, reached a maximum concentration of 26.3 % of applied radioactivity by day 21 post-treatment. Three minor degradates, 2,6-difluorobenzobenzoic acid, 2,6, difluorobenzamide, and 4-chloroaniline, which each had a maximum concentration of <10 % of applied radioactivity were identified, as well. (MRIDs 00039473, 00039474, and 41722801)

Anaerobic Soil Metabolism

Diflubenzuron degraded with a half-life of 2 to 14 days when applied to sandy loam soil and incubated at 14°C and 24°C. The major degradate, 4-chlorophenyl urea, reached a maximum concentration of 37% of the applied radioactivity at days 2 to 14 (depending on temperature). The other major degradate, 2,6-difluorobenzoic acid, increased to a maximum concentration of 23% of the applied radioactivity. However, bound residues increased to 37% of the applied radioactivity as extractable residues decreased during the testing period. (MRID 00040782 and 41837601)

Anaerobic Aquatic Metabolism

A half-life of 34 days was reported for diflubenzuron when applied to silt loam soil and incubated at 24°C under anaerobic conditions. Three degradates (2,6-difluorobenzoic acid, 4-chlorophenyl urea, and 4-chloroaniline) were identified at maximum concentrations of 0.42, 0.33, and 0.004 µg/g in floodwater and maximum concentrations of 0.38, 1.15, and 0.02 µg/g in soils, respectively. (MRID 41837601)

Aerobic Aquatic Metabolism

The route and rate of degradation of ^{14}C-diflubenzuron was investigated in two equilibrated water/sediment systems with water and sediment from the Rhine river and Ormalingenl/Switzerland pond. Whole system half-lives of 5.4 (river) and 3.7 (pond) days were reported for diflubenzuron, 1.6 (river) and 4.4 (pond) days for DFBA, and 26.9 (river) and 52.5 (pond) days for CPU. Degradate maximum concentrations of 7.3 (DFBA), 2.6 (DFBAM), and 31.1 (CPU) %AR in water and 3.7 (DFBA), not detected (DFBAM), and 15.9 (CPU) %AR in sediment, respectively for the river system, and 13.1 (DFBA), 2.4 (DFBAM), and 31.1 (CPU) %AR in water and 3.7 (DFBA), 1.1 (DFBAM), and 21.0 (CPU) %AR in sediment, respectively for the pond system. In addition to these compounds, up to 10 additional minor degradates were detected. These degradates did not exceed 2.9% of the applied radioactivity. In addition, 33.1% and 37.5% of the applied radioactivity for river and pond, respectively, was mineralized to CO_2. (MRID 46888707)

Mobility

Four mobility studies were submitted. One contained thin layer chromatography (TLC) data which is no longer acceptable for a guideline study. Two mobility studies contained column leaching data and one adsorption/desorption data. The column leaching and adsorption/desorption data combined fulfilled the requirement for leaching, adsorption/desorption (163-1). Adsorption values (40, 40, 20, 25, 130, 110, 150, and 3500 for a sand clay, a silty clay loam, a silt loam, a sand loam, a sandy clay loam, a , clay, a clay hydro-soil, and a peat hydro-soil, respectively) reported for diflubenzuron indicate that diflubenzuron is relatively immobile and adsorbs preferentially to soil organic matter over remaining in solution. There did appear to be some desorption, but desorption was not quantified as percent of adsorption.

^{14}C-Diflubenzuron residues (mainly CPU) were mobile in sandy loam-loamy sand, sandy loam, silt loam, and clay loam-clay soils treated with ^{14}C-diflubenzuron at ~2.2 lb ai/A and leached with 30 inches of water over a 20 day period. Of the applied radioactivity (residues not identified in top areas), 36.4-56.9% remained within 1 inch of the treated surface, 78.2-102.9% remained in the soil, and 18.9-34.3% leached from the 24 inch columns. More than 90% of the radioactivity in the each leachate was in the form of p-chlorophenyl urea.

^{14}C-diflubenzuron was immobile in clay loam and silty clay loam soils (Rfs = 0.01 - 0.07) and had a low mobility in sandy loam soils (Rfs = 0.14 - 0.34), as well, based on TLC test. (MRID 00039476, 00039477, 00040777, and 00157842)

Accumulation

Diflubenzuron appears to accumulate and to depurate from all fish tissues. Bluegill sunfish exposed to 0.0093 (±0.0021) ppm for 28 days were reported to have bioconcentration factors of 34 to 200X for fillet, 78 to 360X for whole fish, and 100, to 550X for viscera. By day 3 to 7 of the uptake phase, the accumulation ^{14}C-residues appeared to have reached their maximum and leveled to a steady state concentration in all tissues. The maximum uptake tissue concentrations of ^{14}C-diflubenzuron were 1.7 mg/kg for fillet, 3.3 mg/kg for whole fish, and 4.7 mg/kg for viscera. A depuration of 99% of accumulated ^{14}C-residues from all sampled tissue was reported for the 14 day depuration period. During the depuration period, ^{14}C-residues dropped to <0.06 mg/kg in fish tissues. (MRID 42258401)

Terrestrial Field Dissipation

Eight guideline terrestrial field dissipation studies were submitted. The field dissipation studies included three performed in California (one orchard and two field dissaption studies), two in Oregon (one orchard and one bare ground), one on a Louisianna soil, one on an Arkansas soil, one on a Florida citrus orchard, and one on a New York apple orchard. The combined studies fulfill the bare soil and orchard terrestrial field dissipation requirement.

The orchard and bare ground data had similar reported and/or observed half-lives (half-life of approximately 5.8 to 13.2 days). However, the calculated half-lives for the California citrus and the Oregon apple orchards (half-life of approximately 68.2 to 78 days) were higher.

P-Chlorophenyl urea appears to be the major degradate in field dissipation data with maximum concentrations ranging from <0.02 to 0.06 ppm. Another discernible degradate, 2,6-difluorobenzoic acid, had reported concentrations ranging from not detected (ND) to 0.01 ppm. Diflubenzuron and its degradates were not detected below the top 30 cm soil depth.

Forestry Dissipation

One guideline forestry dissipation study furnished supplemental data but did not fulfill the data requirement for forestry dissipation (164-3). Addenda to this study partially addressed concerns in the original review and analytical methodology; however, the storage stability data could not address the storage stability of diflubenzuron and its degradates when applied to soil, litter, and leaves. Further storage stability data are needed for diflubenzuron and its degradates using the same type of soil, litter, and leaves that were used in the forestry dissipation study.

Residues of diflubenzuron either did not occur or did not persist in flowing water or ponds, sediment, or soil. In addition, the degradate, CPU, was not detected in exposed soil samples. Residues in leaf litter increased for 60 days post-treatment to a peak of 1.5 ppm, and then declined slowly with an apparent calculated half-life of 70 days. Residues

in laurel leaves reached a maximum concentration of 1.3 ppm at 14 days post-treatment, and then declined steadily with an apparent calculated half-life of 30days. Conifer and hardwood leaf residues declined steadily with an apparent calculated half-life of 30 to 35 days, respectively. (MRID 00163853, 41922201-41922210)

Aquatic Field Dissipation

The study indicates that Diflubenzuron degrades between 2 to 6 days of application on pond water at sites in Arkansas and California (MRIDs 45009601 and 45197601).

Droplet Size Spectrum

The droplet size spectrum data indicated that smaller droplets are more likely to move off target. Droplets 122 µm and .smaller are readily airborne and transported in the atmosphere as drift-loss. (MRID 42151701-addendum)

Drift Field Evaluation

The spray drift data indicate that approximately 4% of applied diflubenzuron drifted 110 feet from the edge of a citrus orchard sprayed with DIMILIN 25W at a rate of 1.25 lb ai/250 gallons (4X max label rate) by air blast orchard sprayers. At a distance of 300 feet, drift was only 0.5% of applied. The concentration of diflubenzuron collected by high volume air samplers during the course of the event at 300, 600, and 1200 ft. was 0.22 $\mu g/ft^3$, and 0.02 $\mu g/ft^3$, respectively. (MRID 42151701 and 42151702)

Label Requirements Concerning Drift

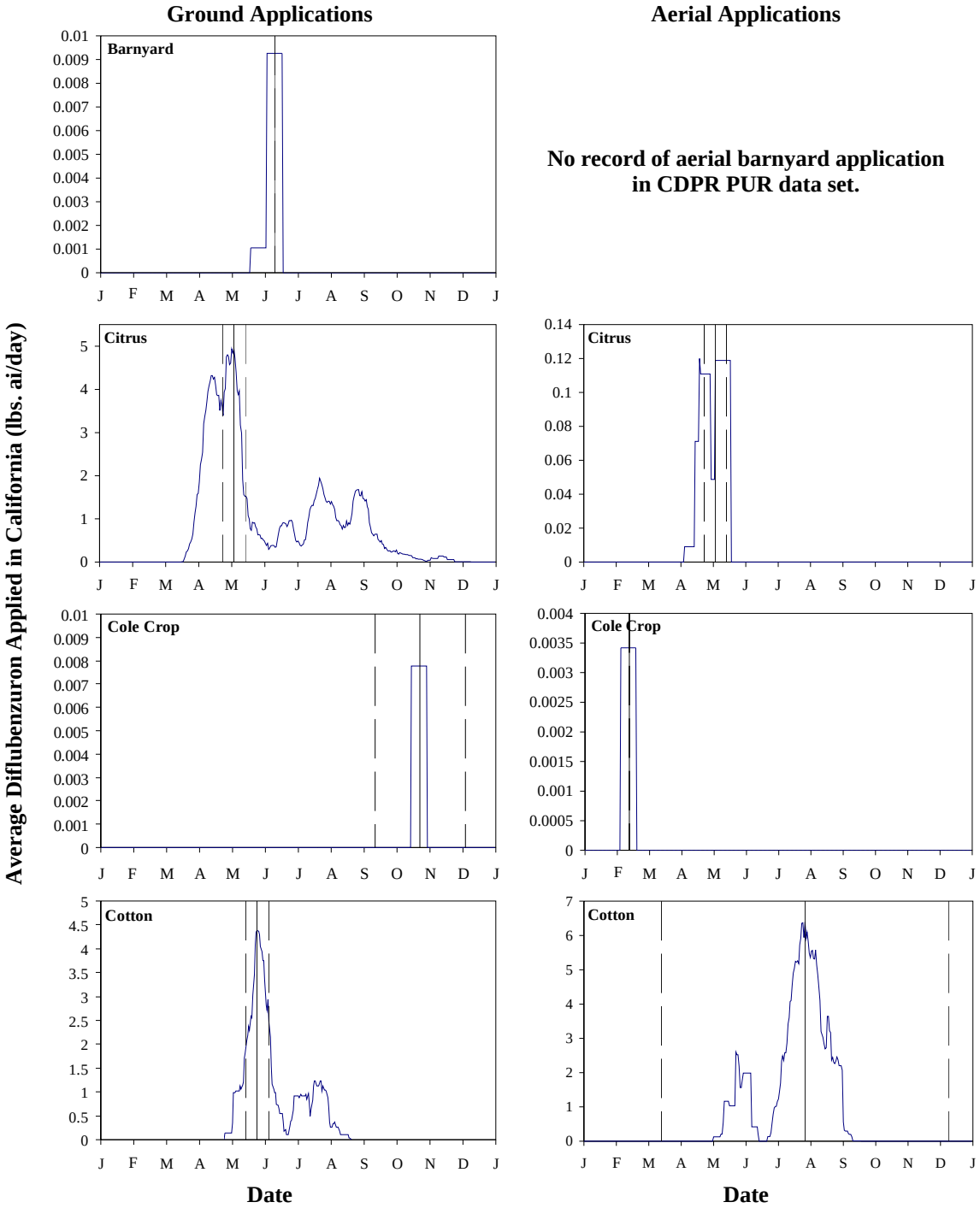
Product (Registration Number)	Spray Drift Restrictions
Bi-Larv H&G (400-543)	No aerial applications. No spray drift buffers specified for ground applications.
Dimilin 25W for Cotton/Soybean (CA97001900)	No aerial applications. Application is directly to water - spray drift issues do not apply.
Dimilin 25W for Cotton/Soybean (CA97002100)	No aerial applications. Application is directly to water - spray drift issues do not apply.
Dimilin 25W for Cotton/Soybean (CA97000900)	**For Field Crops, Row Crops, Orchard Uses, Grassland and Non-Crop Areas:** Do not apply within 25 feet by ground or 150 feet by air of bodies of water such as lakes, reservoirs, rivers, permanent streams, natural ponds, marshes or estuaries. All applications must include a 25 foot vegetative buffer strip within the buffer zone to decrease runoff.
Dimilin 2L (400-461)	
Dimilin 4L for use on Forests (400-474)	Standard Spray Drift language without spray drift buffers specified for air or ground applications.
Dimilin 80Wgs (400-511)	Do not apply by air. Do not apply within 25 feet by ground of bodies of water such as lakes, reservoirs, rivers, permanent streams, natural ponds, marshes or estuaries. All applications must be include a 25 foot vegetative buffer strip within the buffer zone to decrease runoff.
Dimilin W-25 for Cotton/Soybean (400-465)	Do not apply within 25 feet by ground or 150 feet by air of bodies of water such as lakes, reservoirs, rivers, permanent streams, natural ponds, marshes or estuaries. All applications must include a 25 foot vegetative buffer strip within the buffer zone to decrease runoff.
Dimilin W-25 for Mushrooms (400-469)	No aerial applications. Application is directly to water or within enclosed structures - spray drift issues do not apply.
Dimlin W-25 for Pasture, Grass,	Standard Spray Drift language without spray drift buffers specified for air

& Mosquitoes (400-470)	or ground applications.
Micromite 25Ws (400-471)	**Ground Application:** Do not apply within 25 feet of bodies of water such as lakes, reservoirs, rivers, permanent streams, natural ponds, marshes or estuaries. **In the State of Florida**, do not apply within 100 feet of estuarine/marine bodies of water. **Aerial Application:** Do not apply within 150 feet of bodies of water such as lakes, reservoirs, rivers, permanent streams, natural ponds, marshes or estuaries. **In the State of Florida**, do not apply within 1000 feet of estuarine/marine bodies of water.
Micromite 25Ws (400-476)	
Micromite 25Ws (400-487)	
Pond Care Dimilin (8709-009)	No aerial applications. Application is directly to water - spray drift issues do not apply.
Truth Termite Bait (499-488)	Enclosed bait stations - aerial and ground spray drift issues do not apply.
Truth Termite Bait (499-500)	
Truth Termite Bait (68850-002)	
Truth Termite Bait (75313-002)	

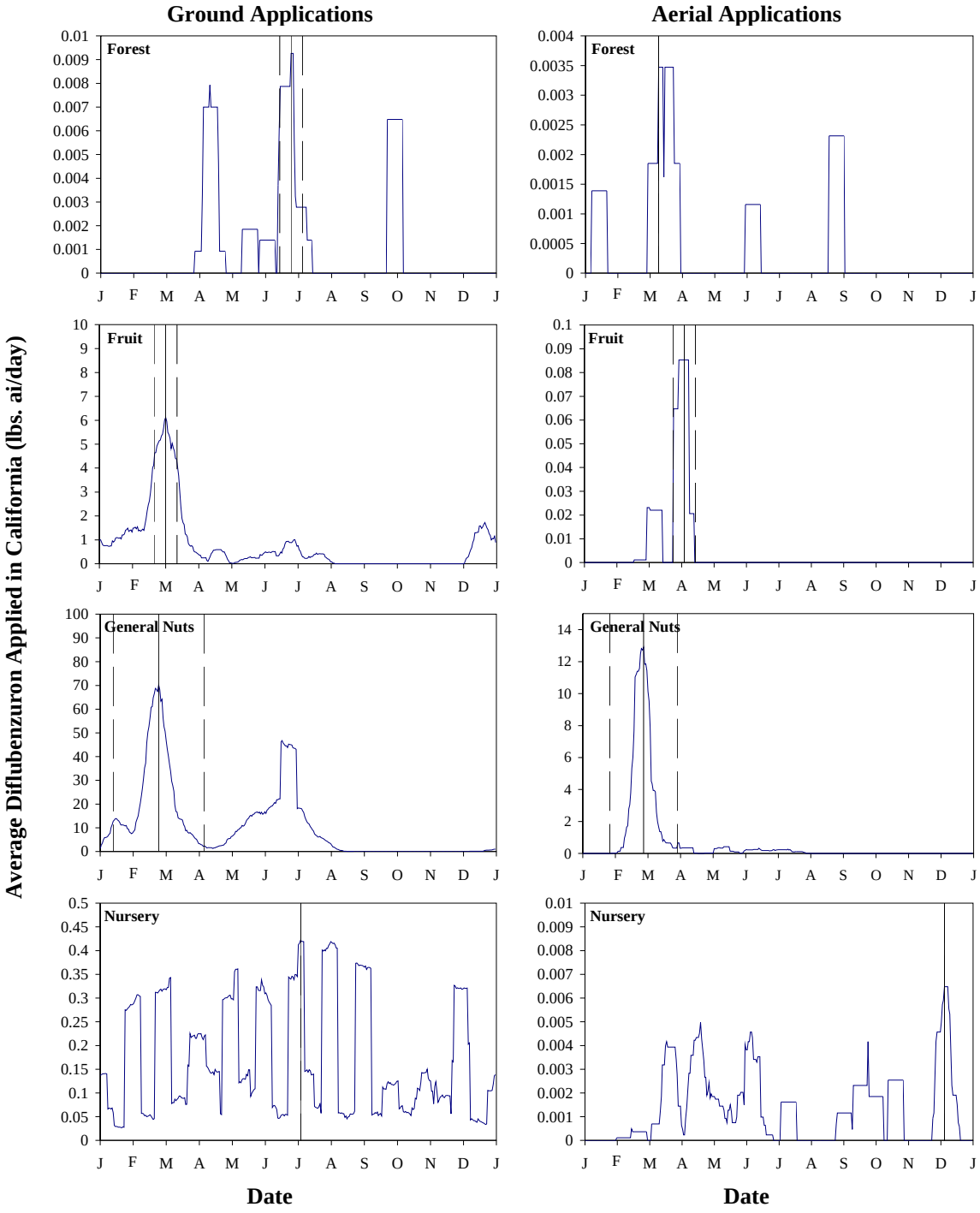
Application Timing

Two different sources of information were used to approximate the timing of diflubenzuron applications for each scenario. The maximum number of applications per growing season and minimum days before re-treatment with propargite were obtained from the Label Use Information System (LUIS) report produced by OPP, BEAD. Because some of the current labels do not provide this information, the maximum number of applications and minimum days before re-treatment provided on any of the labels listed for each exposure scenario were used (missing values excluded). Where no label relevant to the exposure scenario group provides this information, the applications per growing season and re-treatment interval were estimated using professional judgment (Appendix Table D1).

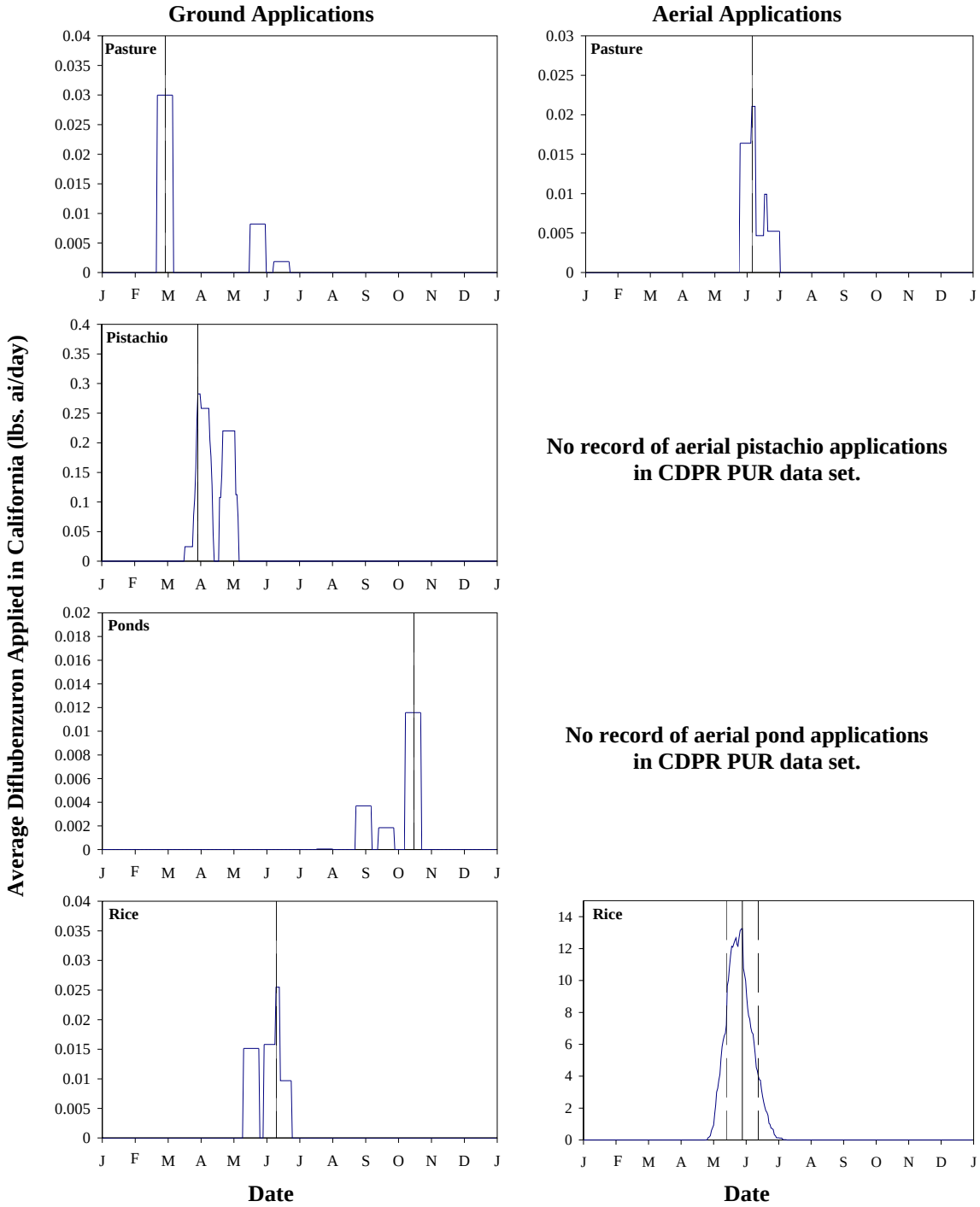
Application dates for each crop/site were derived from the CDPR PUR data set. Appendix Figure D3 shows a 16-day moving average calculated across all 17 years (1990 – 2007) of CDPR PUR data. (This can be thought of as the *average* of the moving-averages for all years in Appendix Figure D2.) The peak of the right graph is used to calculate the midpoint of the propargite application period used in each PRZM scenario. Using this peak value and the applications per growing season and re-treatment intervals from Appendix Table 1, the first and last scenario application days (dashed lines in Appendix Figure D3) are calculated to bracket the peak of the diflubenzuron application for each exposure scenario group.



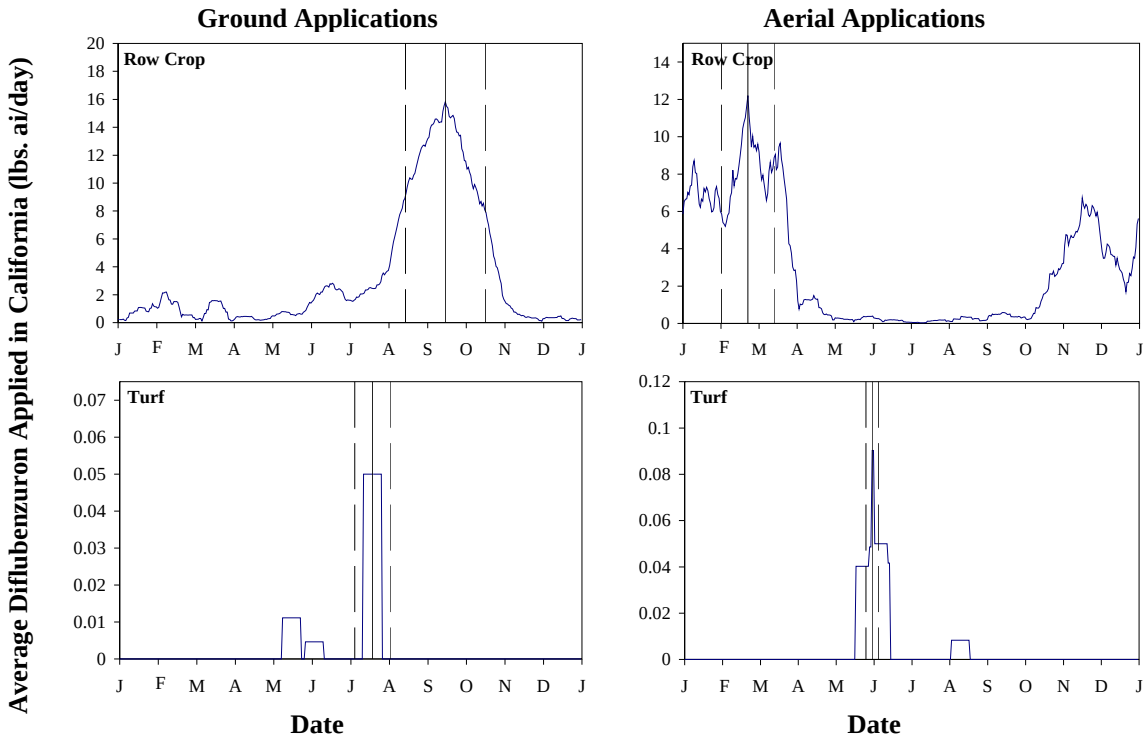
Appendix Figure D3. Generalized within-year diflubenzuron application by crop use according to the CDPR PUR data. Vertical lines indicate the date of propargite application in the single application scenarios (solid line) and first to last applications in the multiple application scenarios (dashed lines).



Appendix Figure D3. Continued.



Appendix Figure D3. Continued.



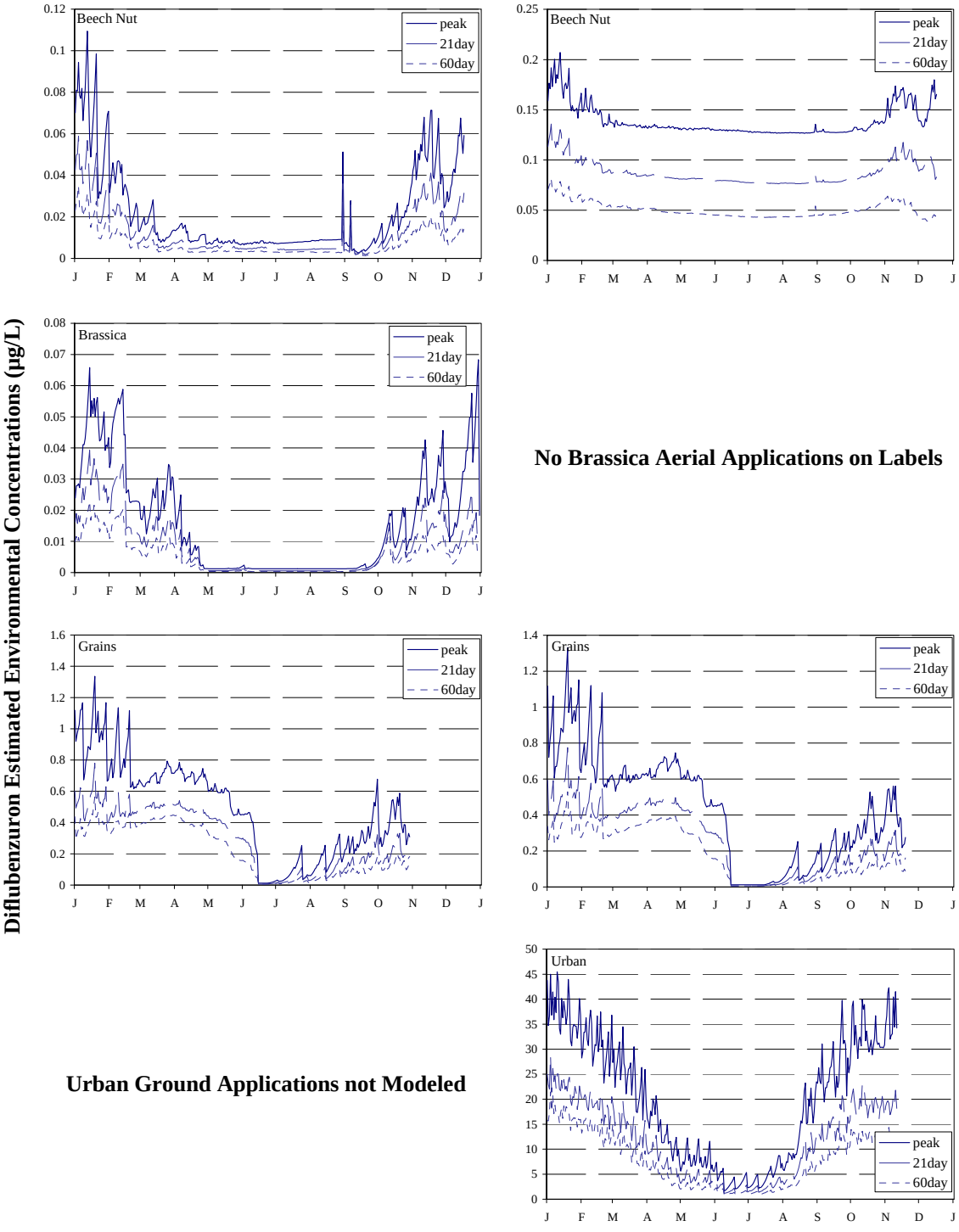
Appendix Figure D3. Continued.

Appendix Table D1. Summary of scenario group information.

Scenario Group	Application Type	Appl. Rate (lbs. ai/A)	Number of Appl.	Appl. Interval	Max. Annual (lbs. ai/Yr)	1st – last Appl. Date	Spray Drift Fraction (%) / Buffer Width (ft)	PRZM Scenario Name - Meteorological Station (Station Identifier)
1. Barnyard	Ground	8.508	NS (17)	NS (21)	NS (2.125)	Year-round	0.8% / 25 ft	Manure Scenario
2. Beech Nut	Ground	0.0408	3	7	0.0938	NPUR (1/12)	0.07% / 25 ft	CA almond STD – Sacramento, CA (W23232)
	Air	0.0408	3	7	0.0938		3.9% / 150 ft	
3. Brassica	Ground	0.0313	1	NA	0.0313	NPUR (1/14)	0.07% / 25 ft	CA cole crop RLF – Santa Maria Valley Area, CA (W23234)
4. Citrus	Ground	0.3125	3	21	0.9375	4/23 – 5/14	0.07% / 25 ft	CA citrus_WirrigSTD Fresno County, CA (W23155)
	Air	0.125	3	7	0.375	4/23 – 5/14	3.9% / 150 ft	
5. Cole Crop	Ground	0.25	4	21	1	9/11 – 12/4	0.07% / 25 ft	CA cole crop RLF – Santa Maria Valley Area, CA (W23234)
6. Cotton	Ground	0.3125	3	7	0.9375	5/14 – 6/4	0.07% / 25 ft	CA cotton STD Fresno, CA (W93193)
	Air	0.3125	3	90	0.9375	3/14 – 12/9	3.9% / 150 ft	
7. Forest	Ground	0.22048	NS (4)	14	0.88192	6/14 – 7/5	0.07% / 25 ft	CA forestry RLF Shasta County, CA (W24283)
	Air	0.25	1	NA	0.25	3/10	3.9% / 150 ft	
8. Fruit	Ground	0.3125	3	7	0.9375	2/20 – 3/12	0.07% / 25 ft	CA fruit STD Fresno, CA (W93193)
	Airblast	0.3125	3	7	0.9375	2/20 – 3/12	1.5% / 25 ft	
	Air	0.3125	3	7	0.9375	3/24 – 4/14	3.9% / 150 ft	
9. General Nuts	Ground	0.3125	3	7	0.9375	1/13 – 4/6	0.07% / 25 ft	CA almond STD Sacramento, CA (W23232)
	Airblast	0.3125	3	7	0.9375	1/13 – 4/6	1.5% / 25 ft	
	Air	0.3125	3	90	0.9375	1/26 – 3/29	3.9% / 150 ft	
10. Grains	Ground	0.25	4	21	1	NPUR (1/19)	0.07% / 25 ft	CA wheat RLF Fresno, CA (W93193)
	Air	0.125	3	NS (21)	0.375		3.9% / 150 ft	
11. Nursery	Ground	0.25	1	NA	0.25	7/4	0.07% / 25 ft	CA Nursery STD San Diego, CA (W23188)
	Air	0.25	1	NA	0.25	12/5	3.9% / 150 ft	
12. Pasture	Ground	0.25	1	NA	0.25	2/28	0.07% / 25 ft	Carangelandhay RLF San Francisco Bay Area, CA (W23232)
	Airblast	0.25	1	NA	0.25	2/28	1.5% / 25 ft	
	Air	0.25	1	NA	0.25	6/6	3.9% / 150 ft	
13. Pistachio	Ground	0.75	2	14	1	3/30	0.07% / 25 ft	CA almond STD Sacramento, CA (W23232)
14. Residential	Ground	0.25	1	NA	0.25	NPUR (1/12)	0.07% / 25 ft	CA residental RLF

Scenario Group	Application Type	Appl. Rate (lbs. ai/A)	Number of Appl.	Appl. Interval	Max. Annual (lbs. ai/Yr)	1st – last Appl. Date	Spray Drift Fraction (%) / Buffer Width (ft)	PRZM Scenario Name - Meteorological Station (Station Identifier)
	Air	0.25	6	10	1.5		3.9% / 150 ft	
15. Rice	Air	0.625	6	5	3.75	5/14 – 6/13	NA	Rice Model
16. Rights-of-way	Ground	0.25	2	5	0.375	NPUR (1/12)	0.07% / 25 ft	CArightofway RLF Central/Coastal California (W23234)
	Airblast	0.25	2	5	0.375		1.5% / 25 ft	
	Air	0.25	2	5	0.375		3.9% / 150 ft	
17. Row Crop	Ground	0.3125	3	21	0.9375	8/14 – 10/16	0.07% / 25 ft	CA row crop RLF Monterey County, California (Santa Maria) (W23234)
	Air	0.3125	3	14	0.9375	2/1 – 3/14	3.9% / 150 ft	
18. Urban	Air	0.25	6	NS (10)	1.5	NPUR (1/12)	3.9% / 150 ft	CA Impervious RLF San Francisco Bay Area, CA (W23234)
19. Squash	Ground	0.25	4	15	1	NPUR (1/10)	0.07% / 25 ft	CA melons RLF Fresno, Kern, Kings, Madera, and Merced Counties, CA (W93193)
	Air	0.25	4	15	1		3.9% / 150 ft	
20. Turf (High Application Rate)	Ground	0.25	2	14	0.375	7/5 – 8/2	0.07% / 25 ft	CA turf RLF San Francisco, CA (W23234)
	Airblast	0.25	2	14	0.375	7/5 – 8/2	1.5% / 25 ft	
	Air	0.25	2	5	0.375	5/26 – 6/5	3.9% / 150 ft	
21. Turf (Low Application Rate)	Ground	0.0313	3	7	0.0939	7/5 – 8/2	0.07% / 25 ft	CA turf RLF San Francisco, CA (W23234)
	Airblast	0.0313	3	7	0.0939	7/5 – 8/2	1.5% / 25 ft	
	Air	0.0313	3	7	0.0939	5/26 – 6/5	3.9% / 150 ft	
22. Turnip	Ground	0.25	2	21	0.5	NPUR (1/18)	0.07% / 25 ft	CA Potato RLF Lewkalb (Kern County, CA) (W23155)

Ground Applications **Aerial Applications**



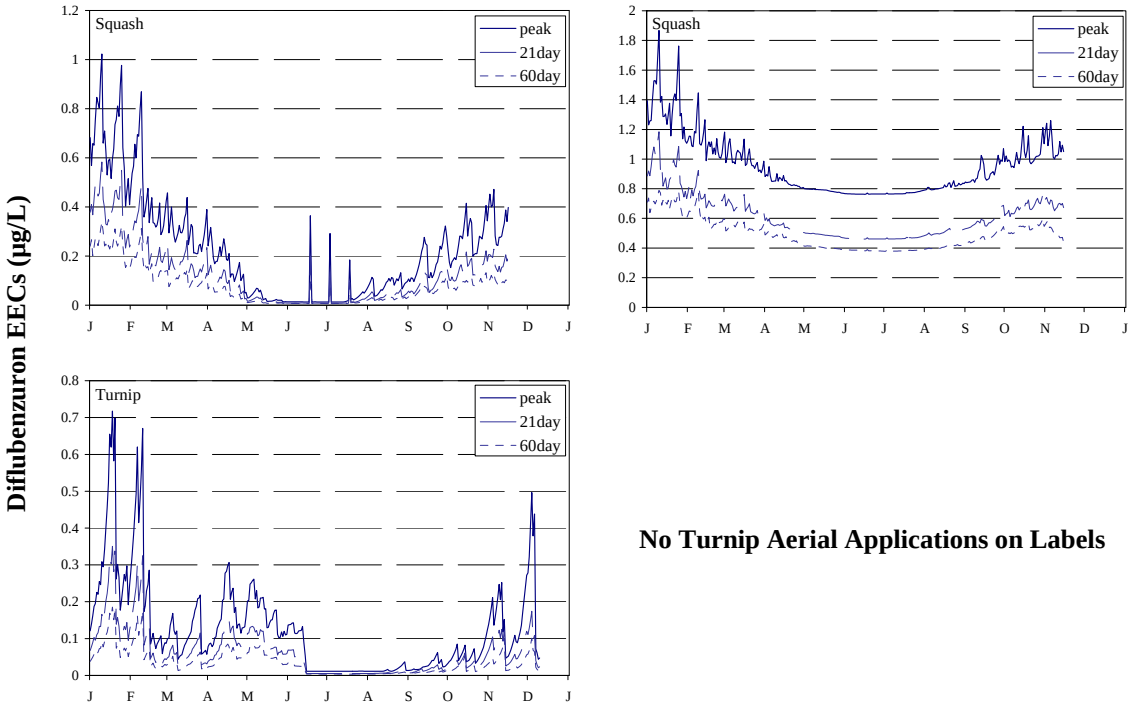
No Brassica Aerial Applications on Labels

Urban Ground Applications not Modeled

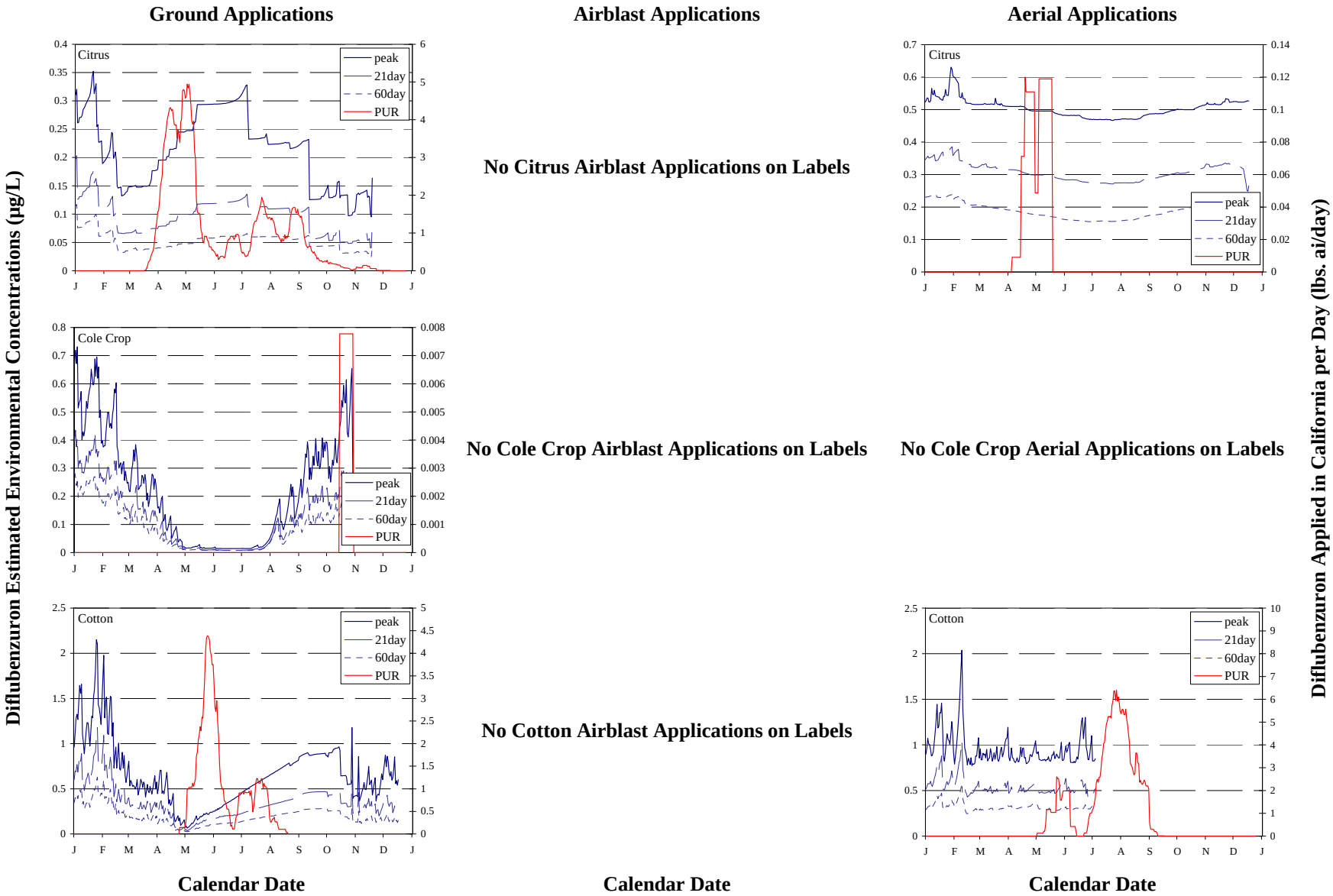
Calendar Date **Calendar Date**

Appendix Figure D4. Variation in diflubenzuron EECs (peak, 21-day, and 60-day) as function of application date (first application date for scenarios with multiple applications).

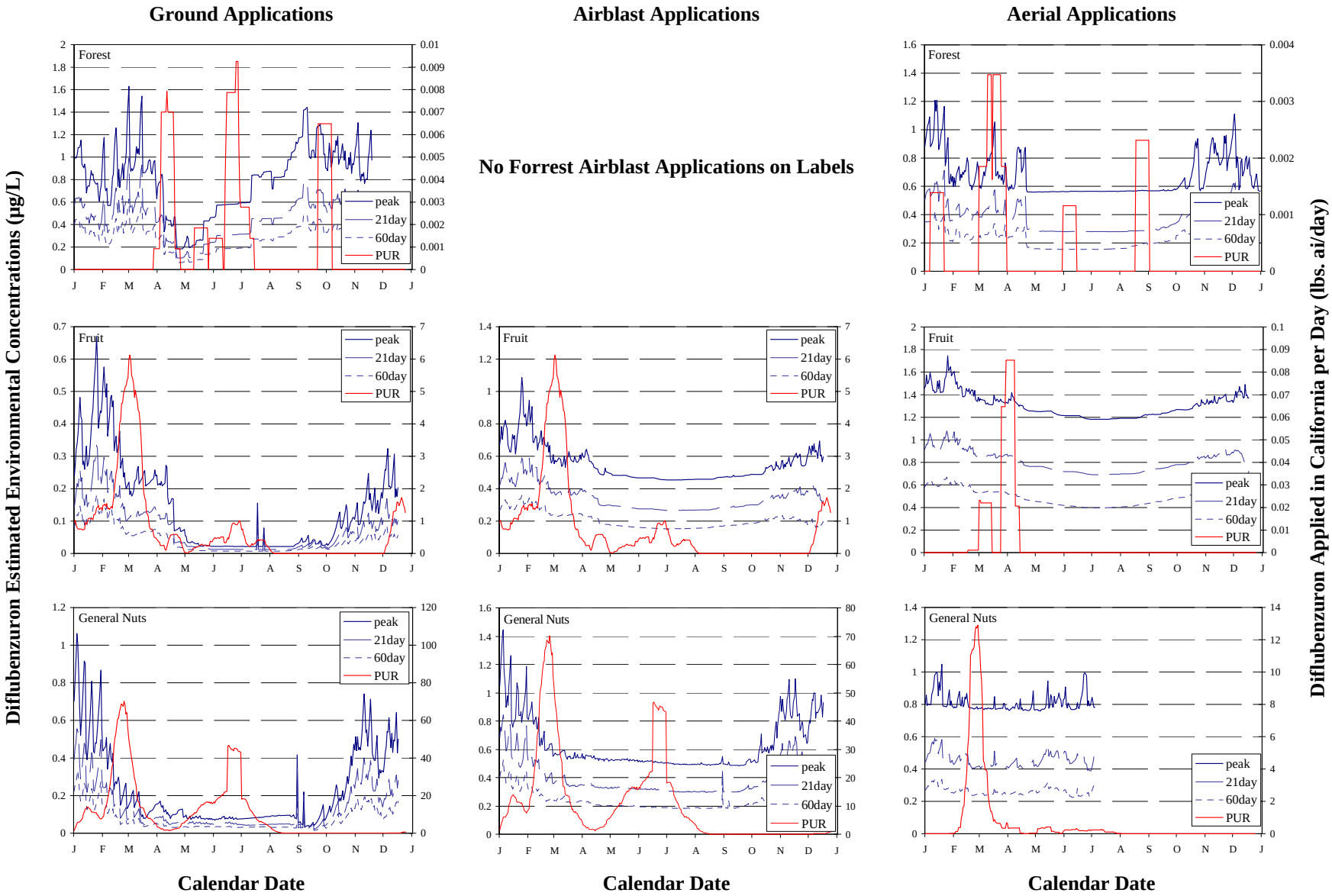
Ground Applications **Aerial Applications**



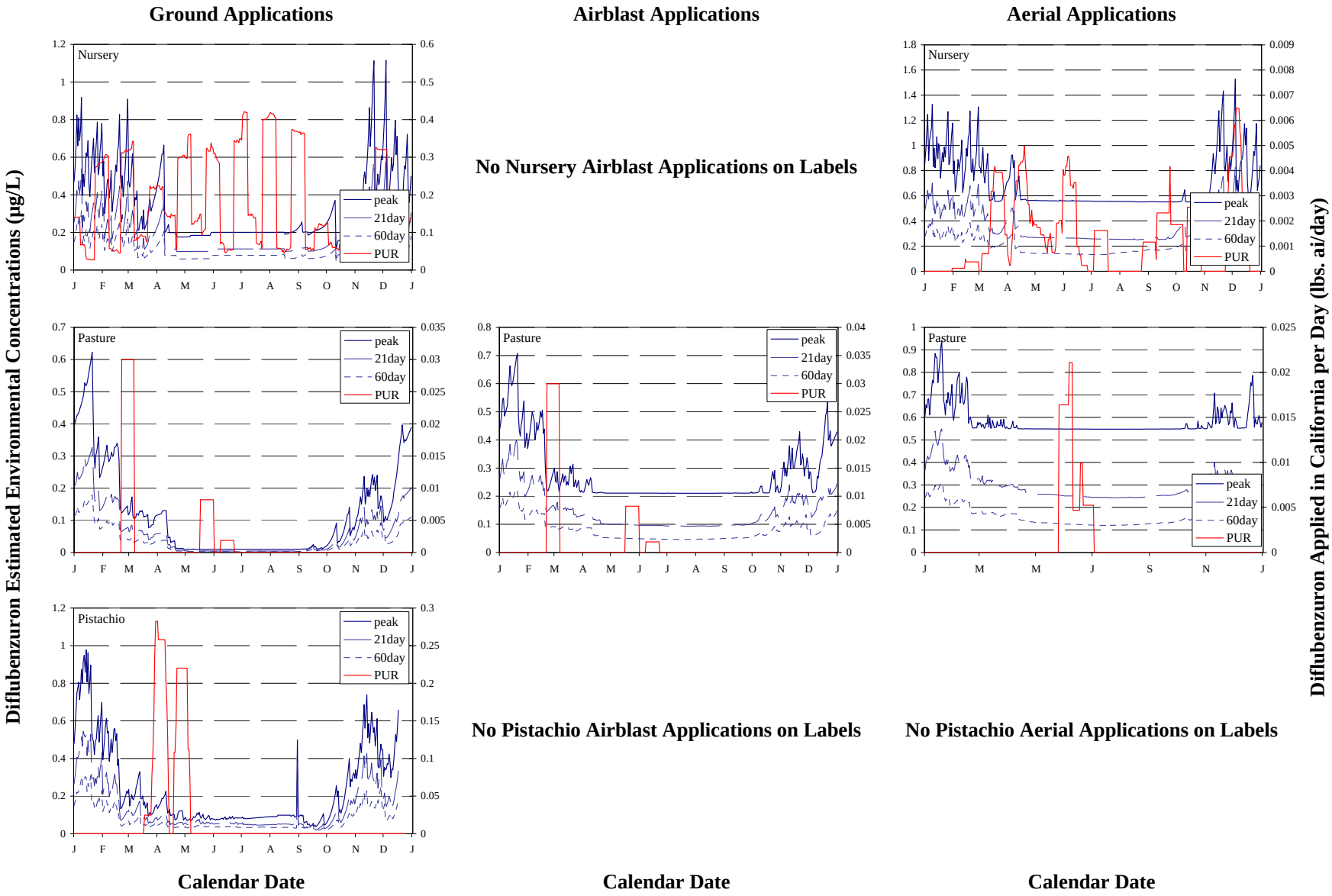
Appendix Figure D4. Continued.



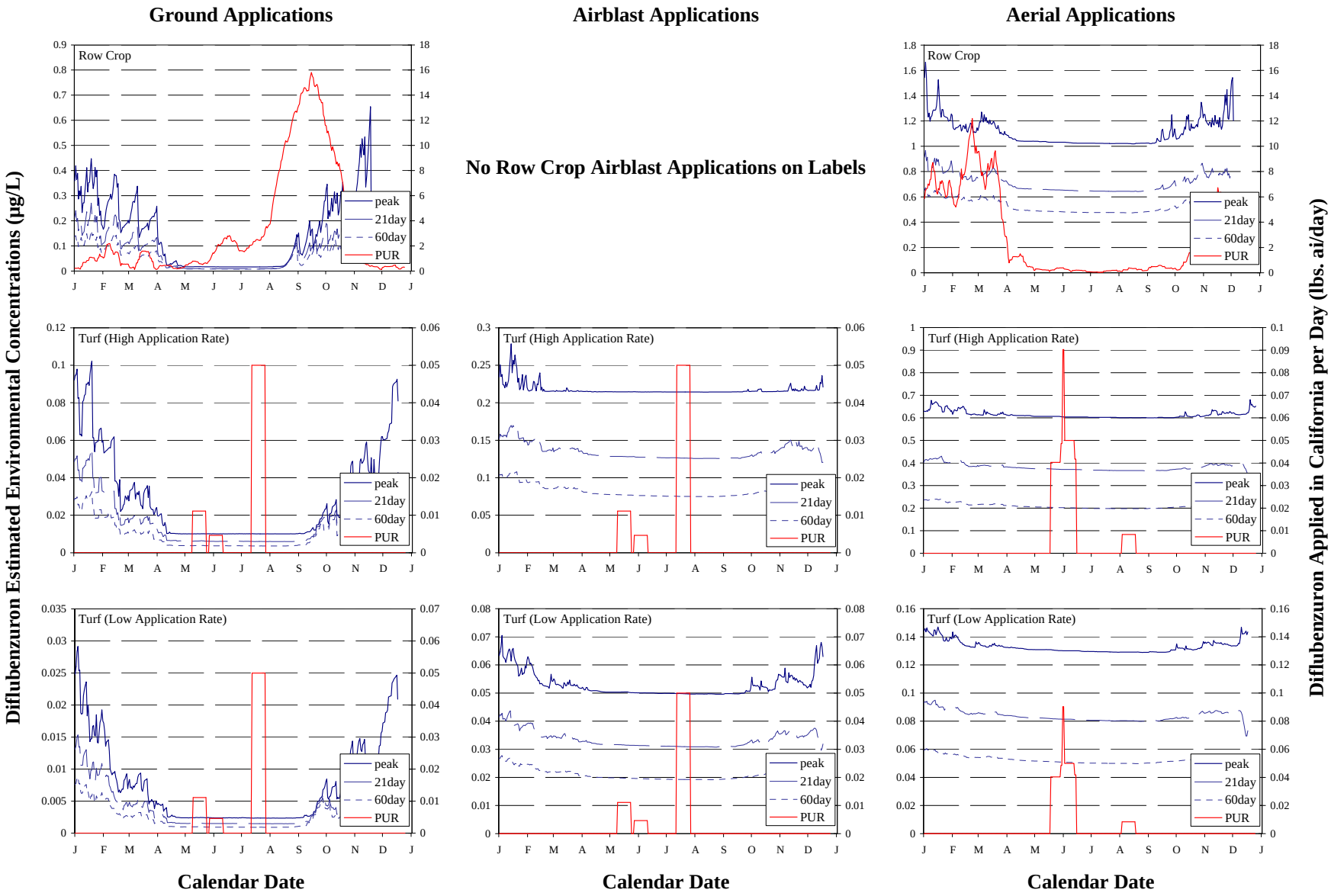
Appendix Figure D5. Variation in diflubenzuron EECs (peak, 21-day, and 60-day) as function of application date (first application date for scenarios with multiple applications) compared to variation in the amount of diflubenzuron applied (lbs. ai/day) per day in California for each use.



Appendix Figure D5. Continued.



Appendix Figure D5. Continued.



Appendix Figure D5. Continued.