STATE OF MAINE
DEPARTMENT OF AGRICULTURE, CONSERVATION AND FORESTRY
BOARD OF PESTICIDES CONTROL
28 STATE HOUSE STATION
AUGUSTA, MAINE 04333

JANET T. MILLS
GOVERNOR

AMANDA E. BEAL
COMMISSIONER

Memorandum

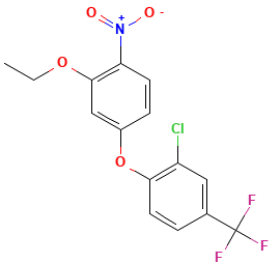
To: Board of Pesticides Control

From: Pamela J. Bryer, Ph.D. | Pesticides Toxicologist | Maine Board of Pesticides Control

Subject: Goal Tender FIFRA 24(c) Special Local Need registration

Date: February 18, 2022

Oxyfluorfen, the active ingredient in Goal Tender, is an herbicide that has been in use since the late 1970's. It works as a contact herbicide that inhibits a cellular enzyme leading to damage of the cell membrane. It is in Group 14 of the Herbicide Resistance Action Committee Mode of Action Classification (2021 Edition).[1] It is immobile in soil and, depending on circumstances, is considered to be moderately persistent to persistent. Laboratory studies indicate low toxicity to mammals, honeybees, some sediment-dwelling organisms, and some algae. Moderate toxicity is seen for birds, earthworms, fish, some sediment-dwelling organisms, some aquatic invertebrates, and some algae. High toxicity was seen for acute exposures to aquatic plants and aquatic invertebrates.



Exposed applicators have found the product is an irritant to eyes, skin, and occasionally respiratory tract tissues. Data from the California Pesticide Illness Surveillance Program provides an example of a human exposure incident; a group of agricultural workers entered a field 30 minutes following application (a violation of the 24-hour restricted entry interval (REI)) and nine out of 15 experienced symptoms of chemical conjunctivitis, eye irritation, tingling and itching of the skin, nausea, dizziness, headache, and vomiting.[2]

The WHO Recommended Classification of Pesticides by Hazard identifies oxyfluorfen as unlikely to present an acute hazard in normal use.[3]

Risks associated with oxyfluorfen:
Managing risk with pesticides is largely a function of controlling exposure. Current-use pesticides often degrade quickly and reach low or non-detectable concentrations by the time the treated commodity reaches the market. This document explores if there are currently ongoing exposures of oxyfluorfen and how use on broccoli might add to those exposures.

MEGAN PATTERSON, DIRECTOR
90 BLOSSOM LANE, MARQUARDT BUILDING

PHONE: (207) 287-2731
WWW.THINKFIRSTSPRAYLAST.ORG

Current occurrences in the marketplace:
USDA testing routinely includes oxyfluorfen as part of the Pesticide Data Program (PDP). Out of 141,238 samples tested 106 samples have tested positive for oxyfluorfen which is 0.1% of all tests.[4] The highest detection found to date is 0.011 ppm. The only violative tests occurred when the active ingredient was found on crops lacking established tolerances. Detections have been made on cilantro, celery, spinach, rice, raisins, green onions, and mustard greens, none of the detections exceeded the established tolerances. The current tolerance for broccoli is 0.05 ppm.[5] The PDP testing has included over 7,400 samples of broccoli and cauliflower, none of the samples contained detectable concentrations of oxyfluorfen.

Potential exposure from broccoli consumption:
The highest concentration representing use on broccoli was found to be 0.0168 ppm following use at the 0.25 lbs a.i./A rate.[6] These data were submitted as part of IR-4 tolerance setting. Experiments found no residues in broccoli samples treated with 0.125 lbs a.i./A but did find detectable residues in one out of seven fields at the 0.25 lbs a.i./A rate. The maximum detected broccoli residue in that one field is the 0.0168 ppm mentioned above.

The average daily consumption of broccoli is 7.5 lbs/yr which corresponds to 9.3 grams/day.[7] If an adult consumes this amount of broccoli that was treated with oxyfluorfen (and that broccoli ended up with the maximum detected residue of 0.0168 ppm) they would be expected to be exposed to 0.00000195 mg oxyfluorfen/ kg body weight per day. This is lower than the established acceptable daily intake (ADI) of 0.003 mg oxyfluorfen/ kg body weight per day.[8] This value is conservatively based on 100% of the broccoli weight even though it is understood that oxyfluorfen is only going to be present in fatty-type tissues of the plant (based on its K_{ow} of 4.86 and that broccoli is 0.4% fat).[9,10] Additionally, this is based on 100% uptake into the body even though rat studies have shown that only 18% is expected to cross the GI tract and into the body.[11]

Oxyfluorfen is classified as likely to be carcinogenic to humans with an exposure level for cancer risk set at 0.0732 mg oxyfluorfen/kg body weight per day.[12] Based on the above calculation an individual would have to eat over 37,000 daily equivalents to reach this exposure level for cancer risk. This value overestimates the exposure potential by using the highest known concentration of oxyfluorfen in broccoli or any other commodity tested in USDA's PDP program, overestimating the partitioning into the broccoli, and overestimating the potential for crossing out of the GI tract.

Fate and transfer in the environment:
As previously discussed oxyfluorfen has a high K_{ow} indicating it is likely to partition into fatty tissues. That together with the low solubility in water indicates leaching into groundwater is not a likely concern for this compound. The vapor pressure and Henry's law constant (0.026 mPa and 0.0238 Pa/ m^3 mol^{-1} respectively) indicate low and non-volatility, together with the K_{ow} and solubility values, indicate that movement off-site is unlikely.[13,14]

In studies looking at the depth of penetration into the soil horizon oxyfluorfen has been found to travel short distances.[15] One study found the compound stayed within the top ten centimeters at 28 days after application. Another study found after three to twelve centimeters of rain the product traveled to five to nine centimeters deep.

Degradation:
Soil half-life data are variable. The range for laboratory-derived half-life data averages from 35 to 138 days, though the full range went up to 438 days. Soil field-derived half-life data were also variable and ranged from 31 to 172 days, averaging at 73 days.[16] Using the five half-lives rule of thumb, under the most extreme persistence (438 days) this chemical would take approximately six years until the product would be eliminated

from the environment, or more specifically 97.5% degraded. Under more normal or average conditions, the product would be expected to be eliminated from the soil environment in one year, again at the 97.5% eliminated threshold.

Sunlight appears to have significant degradation effects on the chemical which are reflected in shorter half-lives when the compound is in or on the plant or in sun-lit water. Water itself does not cause the compound to break down. On the surface of a plant, the breakdown half-life is 1.6 days. When the product is measured as on and in the plant tissues the half-life is 3.6 days.[16]

Long term soil dynamics:
Due to the combination of persistence in the soil and bioaccumulation potential the long-term patterns of oxyfluorfen are of concern. Soils of differing compositions will differ in their behavior, however, some studies indicate that oxyfluorfen does not accumulate in soils significantly. Figure 1 shows the soil concentration of oxyfluorfen on the same parcel over a four-year period.[17] Given the typical half-life 95.5% elimination from the soil is expected at the one-year point and you can see from the graph that the prediction is pretty accurate. The soil concentration at day 150 is approximately 0.8 mg/kg and the soil concentration at day 1350 (or 150 days after the fourth application) is approximately 1 mg/kg. While this is clearly an increase it does not follow the typical patterns of additive exposures which increase over time. Additionally, the soil maximum concentrations do not increase over time.

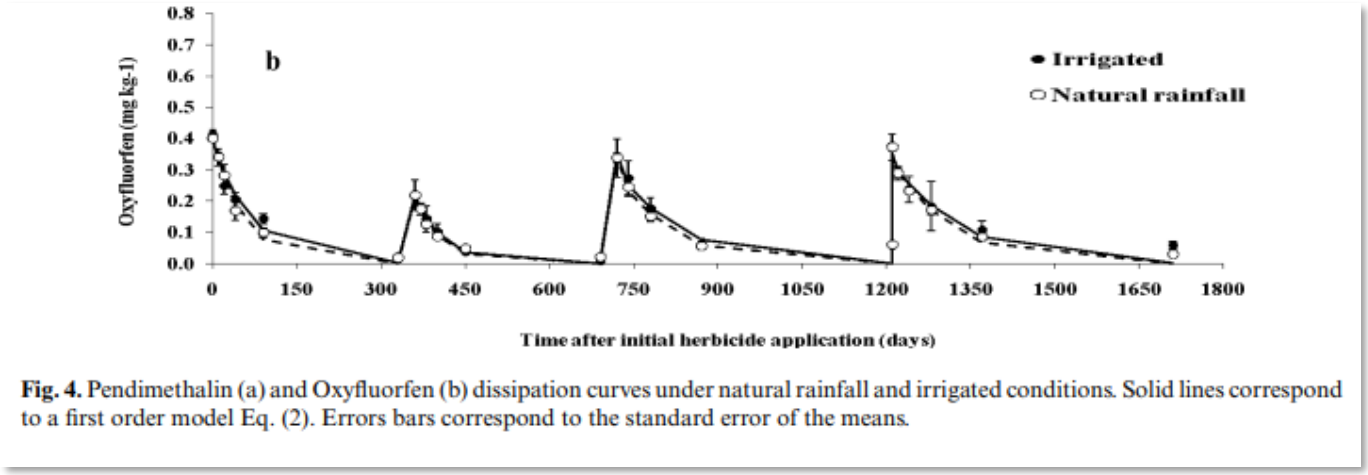


Fig. 4. Pendimethalin (a) and Oxyfluorfen (b) dissipation curves under natural rainfall and irrigated conditions. Solid lines correspond to a first order model Eq. (2). Errors bars correspond to the standard error of the means.

Figure 1. Excerpt from the paper by Claudio et al. 2009 showing soil concentrations of oxyfluorfen following repeated applications over a four-year period.

Another study has shown that oxyfluorfen residues that become entrapped by the soil stay bound to the soil particles.[18] Forty-two percent of the applied oxyfluorfen was found in the top two centimeters of soil 109 days following a wintertime application in a Mediterranean olive orchard under natural rainfall conditions. Of the oxyfluorfen found offsite it was found in the sediment, not the rainwater accumulated offsite. This reaffirms the data suggesting oxyfluorfen is unlikely to leach while reminding us that offsite transport can still occur. The residues are not considered to be active when they are bound.

Technical consideration:
It is of note that oxyfluorfen may be considered as a PFAS compound under the State of Maine's PFAS definition as per 38 MRS §1614(1)(f). Oyxfluorfen does not meet the Office of Pesticide Pollution's working definition of PFAS, nor does it fit into the Buck et al. 2011 classification scheme.[19,20]

Details of this SLN application:
The Goal Tender supplemental label states that the required amount of time following application that harvest activities are allowed is 35 days. There are 10 specific restrictions on the supplemental label. Use under this label does not allow rates that exceed those tested in the IR-4 testing program (0.25 lbs per acre), meaning the estimates of how much oxyfluorfen may enter the food supply would likely not exceed those estimated by the analysis performed. Similar SLN registrations have been issued in AZ, DE, MI, NY, PA, & TX.

The EPA Office of Pesticide Program's webpage indicates that the oxyfluorfen registration reevaluation interim decision is to be released in the first quarter of 2022.[21]

References

[1]Resistance classification group: https://hracglobal.com/tools/hrac-mode-of-action-classification-2021-map

[2]Applicator hazards: https://pubchem.ncbi.nlm.nih.gov/compound/39327#section=Skin-Eye-and-Respiratory-Irritations & https://pubchem.ncbi.nlm.nih.gov/compound/39327#section=Human-Toxicity-Excerpts

[3]Hazard classification: WHO (2005) The WHO Recommended Classification of Pesticides by Hazard and Guidelines to Classification 2004, International Programme on Chemical Safety, p.34

[4]USDA PDP: https://www.ams.usda.gov/datasets/pdp

[5]Tolerance for broccoli: https://www.ecfr.gov/current/title-40/chapter-I/subchapter-E/part-180/subpart-C/section-180.381

[6]Broccoli test residues: Submitted test results in 2009 SLN review, data generated by IR-4 National Pesticide Clearance Protocol oxyfluorfen/broccoli. PR No 08806. Analytical results Report Date 08/02/05.

[7]Broccoli consumption: https://www.statista.com/statistics/257338/per-capita-consumption-of-fresh-broccoli-in-the-us/

[8]ADI for oxyfluorfen: https://comptox.epa.gov/dashboard/chemical/executive-summary/DTXSID7024241

[9]Oxyfluorfen K_{ow} value: https://sitem.herts.ac.uk/aeru/ppdb/en/Reports/502.htm

[10]Broccoli fat content: https://www.healthline.com/nutrition/foods/broccoli#nutrients

[11]Uptake rate: EPA 2014. Oxyfluorfen: Human Health Assessment Scoping Document in Support of Registration Review. PC Code 111601. Decision No. 489866. Nieves et al.

[12]Cancer risk: EPA 2014. Oxyfluorfen: Human Health Assessment Scoping Document in Support of Registration Review. PC Code 111601. Decision No. 489866. Nieves et al.

[13]Water solubility: https://sitem.herts.ac.uk/aeru/ppdb/en/Reports/502.htm

[14]Vapor pressure: https://sitem.herts.ac.uk/aeru/ppdb/en/Reports/502.htm

[15]Oxyfluorfen soil mobility: https://pubchem.ncbi.nlm.nih.gov/compound/39327#section=Environmental-Fate-Exposure-Summary

[16]Half-live values: https://sitem.herts.ac.uk/aeru/ppdb/en/Reports/502.htm

[17]Figure of oxyfluorfen applications over four years: Claudio A. Alister , Patricio A. Gomez , Sandra Rojas & Marcelo Kogan (2009) Pendimethalin and oxyfluorfen degradation under two irrigation conditions over four years application, Journal of Environmental Science and Health Part B, 44:4, 337-343, DOI: 10.1080/03601230902800986

[18]Oxyfluorfen in olive orchard: Calderon MJ, De Luna E, Gomez JA, Hermosin MC. Herbicide monitoring in soil, runoff waters and sediments in an olive orchard. Sci Total Environ. 2016 Nov 1;569-570:416-422. doi: 10.1016/j.scitotenv.2016.06.126. Epub 2016 Jun 25. PMID: 27351146.

[19] EPA PFAS definition: https://www.epa.gov/pesticides/pfas-packaging

[20]Buck, R.C., Franklin, J., Berger, U., Conder, J.M., Cousins, I.T., de Voogt, P., Jensen, A.A., Kannan, K., Mabury, S.A. and van Leeuwen, S.P. (2011), Perfluoroalkyl and polyfluoroalkyl substances in the environment: Terminology, classification, and origins. Integr Environ Assess Manag, 7: 513-541. https://doi.org/10.1002/ieam.258

[21]OPP renewal schedule: https://www.epa.gov/pesticide-reevaluation/upcoming-registration-review-actions