Ground-Water Leaching Potential of DRIVE 75 DF (EPAReg. No. 7969-130) with the New Active Ingredient 3,7-dichloro-8-quinolinecarboxylic acid

Introduction: Registration request for the use of Drive 75 DF herbicide were filed to the Hawaii Department of Agriculture by the BASF corporation. The herbicide is primarily used for weed control in turf grass, rice, soybeans, and grain sorghum. It is a post-emergent herbicide for use in residential and nonresidential turf grasses. The common turf grasses are moderate to highly tolerant of this compound. Grasses such as bahia, centipede, dichondra, and St. Augustine seem to be susceptible. The herbicide is effective against barnyard grass, clover, crabgrass, dandelion, dollarweed, foxtails, torpedograss, black medic and a variety of others. The application rate varies from 0.37 to 1.0 lb/acre and the common additives are methylated seed oil (1.5 pints/acre) or crop oil concentrate (2 pints/acre). Application is made through standard hydraulic sprayer or a pressurized system. The herbicide is **absorbed** by the **foliage** and the **roots** and translocated throughout the plant. For broadleaf weeds, the control symptoms are stem curl or twisting and chlorosis. Susceptible grasses demonstrate stunting, chlorosis, and gradual reddening followed by necrosis and death

Summary of Physical/Chemical Properties for DRIVE 75:

Molecular weight:	242.05 g/mole
Molecular formula:	$C_{10}H_5O_2NCl_2$
Common name:	Quinclorac
Aqueous solubility:	62 mg/1000g of water at 20 ^{0}C, which is approximately 60 mg/L.
Other data on solubility (25 ^{0}C):	890 ppm (pH 5), 6500 ppm (pH 7), 20,000 ppm (pH 9 (what media?)
Solubility in nonaqueous media: acetone:	0.2%
ethanol	0.2%
n-hexane	<0.1%
Vapor pressure:	not given
Dissociation constant:	not given
Henry Law constant:	not given/was unable to calculate
Octanol water partition coefficient (P_{ow}):	not given
Density:	not given

Environmental Fate Data:

Photodegradation in Soil The photodegradation studies were conducted on soil using artificial light. The soil (solution?) had a pH of 6.4. The intensity of light was 1800 $\mu Em^{-2}s^{-1}$ and the wavelength of the light less than 290 nm were filtered out to simulate natural light. The soil was exposed to 12 hours light followed by 12 hours dark. The soil was a silt loam collected from

Savoy, IL. The same soil was also used for aerobic soil metabolism study. The following are the soil properties:

pH   6.4
CEC (meq/100 g)   24.8
Bulk density (g/cc)   1.12
Organic matter (%)   2.5
Water content @1/3 bar   29.6% (what basis? gravimetric??)
Sand/silt/clay: 14.8/65.2/20 percent

The soil was air-dried and sieved through a 2-mm screen prior to use and the soil was not sterilized.

The equipment setups are in Figures 1 and 2 and they are **missing** in the report. The light source was a xenon lamp and described before, the small wavelengths were filtered out. Temperature of a water bath that held the soil containers was maintained at 18 ^{0}C during dark and 26 ^{0}C during photolysis. The photolyzed samples were analyzed after 0, 7.08, 14.16, 19.44, and 30.99 days and dark control samples were analyzed after 14 and 30 days. Tables showing material balance and other data are missing. The photolysis data are supposed to have 11 tables and the same number of figures. It was reported that the photolytic degradation half -life to vary between 122 to 162 days for reaction order of zero or 1st, respectively. For dark controls, the respective half-lives were 382 and 529 days.

Photodegradation in Water
An aqueous solution of Quinclorac as well as that containing 0.5% acetone were buffered at pH 7 and exposed to simulated sunlight at an intensity of 805±33 w/m^2 for a duration of 697 hours over a 35-day period. The temperature of the solution maintained close to 25 ^{0}C. Light exposure was 15 hours light and 9 hours dark with continuous weekend illuminations. (Why were the weekends illuminated??). At the end of 35 days, 64% of initial quinclorac remained in the solution that contained acetone compared to 86% in the simple aqueous solution. The estimated half-life was 100 days for the aqueous solution and 45 days for that contained acetone.

Aerobic Soil metabolism
Two soils were tested for the aerobic soil metabolism using the radio-labeled product. The first soil is a loamy sand from Holly Springs, NC and the second soil was a clay from Leland, MS. The organic carbon for the loamy sand was 1.2 percent and that for clay it was 1.6 percent. For the loamy sand, the half-life was 391 days compared to 168 days for clay

Two methods were used for extracting the bound residues from soil. It was suggested that ^{14}C-residues extracted from soil refluxing with NaOH solution were considered bound. It was also suggested that the pesticide became strongly adsorbed to soil or organic matter with the progress of time. The ^{14}C-residues extracted from soil refluxing with borate buffer solution were considered "available" residues which can move in the soil water.

Anaerobic Aquatic Metabolism
Metabolism, under anaerobic aquatic conditions was concluded to be negligible.

Laboratory Volatility

Volatilization was studied on the Mississippi clay at 21 $\pm$1 ^{0}C with a wind speed of 1 m/s, 66-100 percent relative humidity and an air exchange rate of 100 and 200 L/min. Within 7 days, 2.3 to 3.4 percent of applied active ingredient was volatilized yielding an average volatilization rate of 0.8 to 1.1 ng $cm^{-2} h^{-1}$. The corresponding air concentrations were 0.09 to 0.13 ng m^{-3}. The volatility data appears to be insufficient. The vapor pressure and Henry law constants are also missing.

Sorption Studies

Sorption potential of quinclorac was evaluated on five U.S. soils. The soils were sand, sandy loam, loam, clay, and silty-clay. The organic matter percentage for sand was 0.2 (%) lowest and for silty clay it was 2.5% (highest). The respective organic carbon percentage will be 0.12 and 1.47%, respectively. The K_d values ranged from a low of 0.067 (mL/g **unit??**) for sand to 0.6 for clay soil. The approximate K_{oc} values ranged from 13 mL/g for sandy loam to 54 mL/g for clay. The registrant states "These low K_{oc} values indicate a low binding tendency of BAS 514 H to any of the soil types tested in this report". For sand, the K_d values value was so small that the calculated K_{oc} value was negligible.

Evaluation of Leaching Potential to Ground Water

The retardation factor (RF) is a relative mobility indicator, which is based upon pesticide sorption property, soil porosity, and bulk density. Recharge and dissipation half-lives are not included in calculating RF. The Attenuation Factor (AF) approach (see Rao et al., 1985), as used by the Hawaii Department of Agriculture, provides the relative mobility of a chemical for the given soil conditions, pesticide properties, and recharge rates. Khan and Liang (1989) have assigned numerical values to RF and AF indices to indicate the relative leaching classes of pesticides. Loague et al. (1990) suggested that such numeric values are arbitrary and these classes only indicate relative retardation or attenuation of a chemical. In Khan and Liang (1989), a pesticide that is moderately mobile was assigned a RF between 2 and 3 and an AF between 0.01 and 0.1. As per Khan and Liang (1989) a compound with RF values between 0-1, 1-2, and 2-3 would be listed as very mobile, mobile, moderately mobile, respectively. A RF value between 3 and 10 would suggest a compound to be moderately immobile and that higher than 10 as very immobile. As discussed above, sorption properties (affected by organic carbon) and soil porosity and bulk density are expected to provide differing RF values based upon the location. Similarly, AF maps for values 0.0001-0.01, 0.01-0.1, 0.1-0.25, and 0.25-1 were listed by Khan and Liang (1989) as unlikely, moderately likely, likely, and very likely to leach to ground water. RF and AF maps for Kauai were prepared for Drive 75 using the following data in the HNRIS system. In the following table, the K_{oc} values ranged from 0,013 to 54. It was unclear about the units involved in reporting the K_{oc} values and for this reason, the registration specialist use these high numbers. The normal reporting unit for K_{oc} is mL/g. In such case, the K_{oc} values will only range from 0.013 to 0.054 mL/g. The registrant also has admitted to low sorption capacity of the compound in the adsorption/desorption study. Just for comparison, these high K_{oc} values have been used.

K_{oc} (m³/kg)	Henry constant* (atm m³/mole)	Pesticide half-life (days)	Depth to water (m)
0.054	0	391	0.4572
54	0	391	0.4572
13	0	391	0.4572
13	0	168	0.4572
0.013	0	391	0.4572
0.013	0	168	0.4572

* Assumed value (actual data not given)

The HNRIS predictions for cases with low K_{oc} values (<1) produced sensitivity indices that were between 0.01 and 1.0 (moderately likely to very likely to leach).

In order to make sure that the above AF values adequately address the concerns of uncertainty in parameters, an improvement to the method suggested by Loague et al. (1990) was examined. The impact of parameter uncertainty on predicting leaching of nearly 40 pesticides by the AF approach was addressed by Li et al. (1998). In this approach, DBCP and diuron were used as two reference chemicals in which DBCP was listed as a probable leacher and diruon was listed to be a probable non-leacher. This was based upon the observation that many water supply wells in Oahu have been contaminated by DBCP in areas where depth to water easily exceeds 500 ft. A log-transformed attenuation factor (AFR) was used to set the scales for these pesticides. An AFR score close to or less than DBCP classifies a chemical to be a probable leacher on this scale. A set of exercises was carried out for Drive 75 for the same soil and hydrologic conditions in which Li et al. (1998) made their analyses. Two soils were considered: Eutrustox and Oxisol (both are Wahiawa series) on 0-3% slope. The following table provides the characteristics of the two soils:

Soil type	Bulk density (m³/kg)	Fraction organic carbon (f_{oc})	Field capacity (θ_{fc})	Depth to water (d) in m	Recharge rate (q) in m day⁻¹
Eutrustox	1116	0.0184	0.451	0.5	0.001
Oxisol	1107	0.026	0.456	0.5	0.001

The database in Li et al. (1998) contains information for standard deviation for soil properties such as bulk density, organic carbon, and field capacity. The K_{oc}, depth to water, and recharge rates and their standard deviations are user-supplied input in the model. Since we do not have adequate data on these parameters, standard deviations that are 10 to 50 percent of the mean values were considered. For comparison against two reference chemicals (DBCP and diuron), we used a K_{oc} value of 0.013 m³/kg with a standard deviation of 0.0026 m³/kg. The standard deviations for the depth to water and recharge rate were assumed to be 0.25 m and 0.002m/day, respectively. Similarly, the field dissipation half-life used for this analysis was 391 days with a standard deviation of 100 days. The predicted AFR value for DRIVE 75 for the given conditions for Eutrustox was 0.911 with a standard deviation of 0.608. For the DBCP and diuron, the respective AFR scores were 3.11 and 6.02, respectively. The retardation factor for DRIVE 75 was 1.59. From this analysis, it is clear that the DRIVE 75 has a leaching potential worse than DBCP, which is a potential leacher. With a K_{oc} value of 0.054 m³/kg (standard deviation 0.01

m^3/kg) and a half-life of 168 days (standard deviation of 50 days), the AFR value was 2.53 with a standard deviation of 0.65. The computed retardation factor was 3.43. The pesticide will be moderately mobile with an AFR score less than that for DBCP (3.11).

Other Issues of Importance

Some of the other issues of importance for ground water contamination are: acreage to be treated with the given pesticide, the rate and frequency of application, and the timing of application with respect to the local rainy season. Since the pesticide is a golf course chemical and there are nearly three dozen golf courses in Oahu alone, there is potential for its use in thousands of acres of land. The AF model does not account for photolysis. Further, photolysis may not be significant if there is a significant storm event soon after the application of the pesticide. Golf courses do irrigate in regular intervals and if photodegradation is not significant in the first day, potential exist for leaching.

Health advisory levels (HALs) or the maximum contaminant levels (MCLs) often force the regulating agencies to take actions on a chemical once the chemical concentrations reach these values. If a chemical is applied at a lower rate, it is likely that it will be observed at a lower concentration in ground water than a chemical that is applied at a higher rate and has similar chemical properties. However, if the chemical with a lower application rate has a lower HAL or MCL, the regulator will be forced to take action if the respective contaminant reaches that level. Even at lower applications rates, a compound with low sorption potential and higher field dissipation half-life could appear in ground water at low concentrations.

Possible Use Plan

The above compound (DRIVE 75), based upon the company provided field dissipation half-life and K_{oc} data, appears to a potential leacher. However, one advantage of this product is that it is a post-emergent herbicide and applied at smaller rate than many agricultural herbicides. However, the toxicity data for this compound and the proposed HALs are not available. If a user wants to field-test this product, it will be ideal to monitor the leachate emanating from the root zone and the residual concentration of the pesticide in the soil in shallow vadose zone. The leachate water samples can easily be collected via suction lysimeters installed prior to pesticide application. Porous stainless steel suction cups may be installed at 45 cm and 1.0 m to collect the samples. Many golf courses appear to have suction lysimeters within their property. Stainless steel lysimeters are not subject to sorption by pesticides. Based upon the findings from the first one or two seasons of operation a second evaluation using the acreage, application rate, and HAL for the compound should be performed. At present, the state may permit the compound as a "restricted use" chemical.

References

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