

DATA EVALUATION REPORT
Degradate Adsorption/Desorption by Batch Equilibrium (Mobility: 163-1)

AC 312,094: Adsorption/Desorption
[Metabolite of AC 303,630 (PIRATE)]
MRID 434928-48

CITATION: Mangels, G.. AC 312,094: Adsorption/Desorption. 9 Sep 1994. Laboratory Project ID: E 94-06. American Cyanamid Report Number ENV 94-025. Performing Laboratory: American Cyanamid Company; Agricultural Research Division; P.O. Box 400; Princeton, NJ 08543-0400. Sponsored by American Cyanamid Company; Agricultural Research Division; P.O. Box 400; Princeton, NJ 08543-0400.

REVIEWER: Alex T. Clem, Environmental Scientist, CRS 3
EFGWB/EFED/OPP/OPPTS/USEPA

Alex Clem
10/21/96

CONCLUSIONS. *This study is acceptable and satisfies the data requirement. However, the registrant is advised to regard carefully the comment section below before submitting future studies.*

Batch equilibrium sorption coefficients for the major soil metabolite AC 312,094 (formula in attached Table I) of AC 303,630 (PIRATE) in the four test soils Arkansas loamy sand (ARLSa), Indiana silt loam (INSiL), New Jersey sandy loam (NJSaL), and Wisconsin loam (WSSL) are given in the table below. Soil characterization data are in attached Table II. These soils were the same as used in an earlier ads/des study for parent. Although the registrant did not provide a correct error analysis, the individual K_d values probably have a 95% confidence interval of around ± 20 to 40%. Variation in K_{oc} could be considerably more based on unspecified uncertainty in soil organic content which is usually relatively large from sample to sample (thus the number of significant digits recorded in the table below should be disregarded). As can be seen, within probable experimental error K_{oc} is similar for all the soils. *The median K_{oc} value of about 2200 is therefore a useful number for modeling purposes.*

Soil	<u>K_d_{ads}</u>	<u>K_d_{des}</u>	<u>K_{oc}_{ads}</u>	<u>K_f</u>	<u>1/n</u>	<u>R²</u>
ARLSa	14	25	5000	16	1.03	0.99
INSiL	22	50	2095	26	1.03	0.99+
NJSaL	20	41	2352	22	1.02	0.99+
WSSL	38	95	2774	34	0.98	0.99+

* The number of significant digits tabulated above should not be taken as an indication of experimental precision, but are the values as presented by the registrant. Use of more than one or two significant figures probably cannot be justified in most cases. (See also text above.)

These intermediate sorption coefficients mean that, coupled with persistence, this metabolite has high potential for runoff into surface water with comparable amounts in solution and on eroding soil.

MATERIALS/METHODS

Adsorption. Triplicate one gram soil samples in 50 mL screw-capped centrifuge tubes were treated with 30 mL aliquots of standardized solutions of carbon-14 radiolabeled AC 312,094 (80.41 $\mu\text{Ci}/\text{mg}$) at each of the four concentrations: 99.5, 49.6, 9.6, and 4.7 ppb in 0.01M calcium chloride.

The samples were shaken continuously for 2.5 days, after which time it was assumed equilibrium had been reached. Although, the temperature was not explicitly stated for this time period, since subsequent centrifugation of samples for one hour at 2500 rpm was said to be at 25°C, we assume the test was carried out at a controlled 25°C also. Aliquots of the supernatant were removed for the analysis described below. Remaining free standing water was removed by pipette.

Desorption. Thirty mLs of fresh 0.01M calcium chloride solution were added to the remaining soil in each tube. Then the same procedure as for the adsorption phase was repeated.

Soil Extraction. After the desorption water was removed, the soil samples were extracted with 10 mL of methanol by shaking for one hour, then centrifuged as before.

Radioassay. Aliquots of the adsorption and desorption solutions and the soil extracts were radioassayed by liquid scintillation.

Soil samples were air-dried, pulverized, and analyzed for adsorbed radioactivity by combustion followed by liquid scintillation counting of trapped C-14 carbon dioxide.

Thin-Layer Chromatography (TLC). Ethyl acetate extracts from the high concentration of extracted soil (combined samples from the adsorption phase) were co-chromatographed with non-labeled reference AC 312,094 by TLC on silica-gel using three different solvent systems. Location of the reference was by UV light; visualization of radioactivity was by autoradiography on X-ray film; and quantitation of scraped zones by liquid scintillation.

Results and Discussion (see also conclusions above)

The total mass balance for any replicate ranged from about 95 to 108% (Tables III-VII).

Three TLC systems showed one major spot which co-chromatographed with reference AC 312,094. This is an indication of the presence of only AC 312,094, and shows that this compound was stable during the course of the study.

COMMENTS

- ▶ Size of Soil Samples. Using soil samples of such small size (one gram) usually requires special processing and handling techniques to avoid segregation of soil separates and to further make certain that the size (number of heterogeneous particles) is sufficiently large to insure a reliable sample population distribution. Were the soils sieved and split? EFGWB assumes a 2 mm sieve was used as in a previous study for parent. What precautions were followed, and what assurance can you give that bulk soil containers and the selected one gram subsamples were handled such that they were representative of the chosen soils when placed in the test tubes? This situation presents a general problem and should be considered in all future studies when choosing samples and sample sizes.
- ▶ Where and when were the soil samples collected, and how were they stored.
- ▶ Range of Test Solutions. Ideally, test concentrations should span a range covering at least two orders of magnitude. Here the factor was only about 20.
- ▶ The error in the originally stated aqueous solubility of AC 312,094 was disconcerting. The solubility was reported as both 369 mg/L and 369 ppb which are mutually exclusive by a factor of a thousand. Amendments or corrections should be prominently called to the reviewer's attention by special, separate note or critical placement. In this case an amendment *not included in the table of contents* was buried three pages from the end of the report. The amended value at 25°C is 369 µg/L or 369 ppb.
- ▶ At least one *complete sample calculation* of each type leading to final results should be worked out *using actual numbers* from clearly indicated data tables. Only in this way can the reviewer quickly verify basic calculations. In a previously submitted study for parent, for example, an error was made in the use of the density factor for the extraction solution which led to an erroneous material balance and higher sorption coefficients. In the Appendix for the present study the statement is made that calculations were adjusted for density, but no density factor appeared in any of the general equations. This is a good example why numerical sample calculations should be provided.
- ▶ Reliability of Data (Error treatment). Is the uncertainty in the final values reported for the various sorption coefficients correctly represented by the use of two to four significant figures? No other indication of experimental error was given for the final tabulated numerical results. In all studies an error analysis, with stated assumptions, should be given for all determined values and results prominently displayed in final tabulations.

In Tables III-VI the standard deviations given for Kds are not based on a proper analysis and disregard nuclear statistics.

What uncertainty is associated with soil organic carbon and what is the impact on results?

Concerning laboratory precision only, conventional use of significant figures should be observed in reporting final numerical results with error limits indicated for individual results. Hypothetical expected errors can be calculated based on general experimental limitations for the various procedures, concentrations, methods, etc. For example, calculation of a maximum expected error is often a simple procedure, and would be appropriate for many studies. Pooling of precision data from similar samples or established methodologies taken over the course of time (even from other studies or sources) can often be used effectively. Material balance which was determined in the present study serves as a useful adjunct. Radioactivity measurements require nuclear statistics for each sample, and are especially sensitive when the number of counts collected are few. Only with an estimate of uncertainty can apparent results, variations, and trends be meaningfully interpreted.

It is not unreasonable to expect that considerable effort be devoted to experimental design, sample selection and characterization, and assessment of the reliability of experimental results (perhaps as much as data collection?). Otherwise, the data could legitimately be regarded as worthless.

TABLES, FIGURES, AND OTHER PERTINENT INFORMATION

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input to the fields and soil water redistribution are critical to the understanding of field dissipation studies because water affects both degradation and mobility. EFGWB likes rainfall and irrigation amounts to be plotted on the same figures which show time vs. dissipation so critical periods are easily identified.

It is important that an estimate of the maximum leaching potential (water movement or movement of an unretained component in the soil profile) be made with methods such as water balance, field moisture instrumentation, or use of tracers. Systematically measured soil moisture in the sampled cores is a useful adjunct which can be used as a primary input for a water balance and as an indicator of leaching potential. Consult a soil physicist for appropriate methods.

- ▶ Whether there was runoff, spray drift, or wind erosion from the test plot was not addressed. Did soil drift and pile up in the dense rows of cotton or elsewhere? Slope was stated to be less than 3%. Were buffer areas, especially downslope, sampled in an attempt to locate missing pesticide? What about in-row sampling as opposed to between the rows? Many things can happen in the course of a long field trial.
- ▶ Sample storage stability tests for collected samples needs to be formally completed and reported. (However, this is not really an issue unless one wants to argue very precisely about the degree of stability and half-lives because of the already demonstrated persistence and stability of this pesticide in these and other experiments.)
- ▶ Soil core diameters were only one to two inches. Much larger cores are recommended to reduce spatial variability and to minimize handling and subsampling errors. Some measure of variation and hence reliability of the data must be demonstrated (see Error treatment below).
- ▶ Error treatment. No error limits were given for final numerical results and no error bars were indicated in data plots. In all studies an error analysis should be given for all determined values. All data points should be used and plotted. As is almost always true for analytical results, precision in laboratory manipulation and quantitative procedures is secondary or tertiary when compared to choice of representative samples to analyze. Of utmost importance is some measure of variation of samples collected in complex environmental matrices.

Concerning laboratory precision only, conventional use of significant figures should be observed in reporting final numerical results with error limits indicated for individual results. Hypothetical expected errors can be calculated based on general experimental limitations for the various procedures, concentrations, methods, etc. For example, calculation of a maximum expected error is often a simple procedure, and would be appropriate for many studies. Pooling of precision data from similar samples or established methodologies taken over the course of time (even from other studies or sources) can often be used effectively. Only in this way can the apparent results, variations, and trends be meaningfully interpreted.

It is not unreasonable to expect that considerable effort be devoted to experimental design, sample selection, and assessment of the reliability of experimental results (perhaps as much as data collection?). Otherwise, the data could legitimately be regarded as worthless.

- ▶ "Gainesville", not "Gainsville", is the correct spelling for Gainesville, FL. Melrose and Gainesville are in Alachua County, not Slackua County (which does not exist in Florida). (The reviewer is a former longtime resident of Gainesville.)

PERTINENT DATA AND OTHER EXPERIMENTAL INFORMATION

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DATA EVALUATION REPORT
Terrestrial Field Dissipation (164-1)

AC 303,630 (PIRATE): Residues of AC 303,630 in Soil
Five Field Dissipation Studies on Soil in Cotton Fields
(Formulations AC 303,630 2SC or 3SC)
MRID 434928-50

CITATION: Schaefer, T.; Stout, S.; Babbitt, B.. CL 303, 630: Residues of CL 303,630 in Soil. 4 Nov 1994. Laboratory Project Report Numbers: RES 93-177, RES 93-177.01, RES 93-182, RES 94-069, RES 94-084, RES 94-128, C 3928, RES 93-039, RES 94-114, RES 94-141. Performing Laboratories: 1) ABC Laboratories, Inc.; Field and Analytical Chemistry Programs; 7200 E. ABC Lane; Colombia, MO 65202-8015; 2) American Cyanamid Company; Agricultural Research Division; P.O. Box 400; Princeton, NJ 08543-0400. Sponsored by American Cyanamid Company; Agricultural Research Division; P.O. Box 400; Princeton, NJ 08543-0400.

REVIEWER: Alex T. Clem, Environmental Scientist, CRS 3
EFGWB/EFED/OPP/OPPTS/USEPA

Alex T. Clem
8/27/96

CONCLUSIONS. *The five terrestrial field dissipation studies are upgradable and partially satisfy the data requirement. However, unless old soil samples are still available for analysis and proved stable, it may be necessary to consider new studies in order to account for routes and rates of dissipation.*

The five studies all suffer from the same major deficiency: *degradation was not investigated and there was no attempt whatsoever to identify degradates.* Consequently, the integrity or internal consistency of the studies and routes of field dissipation cannot be established. *However, it is clear from these studies that parent pesticide AC 303, 630 is indeed persistent, as defined below, and does not leach.* Because of the deficient manner in which the studies were conducted, EFGWB can only estimate *minimum* ranges of field dissipation "half-lives" (which are not to be confused with *degradation* "half-lives"), as is put forth below. Degradation could be slower with half-lives correspondingly longer.

The reason(s) for the apparent loss of parent pesticide--whether it was due to degradation, physical removal from the area sampled or procedural artifacts (for example, by off-site transport on soil particles by wind or rain driven erosion, or by soil particles drifting and piling up in the dense rows of cotton plants where no sampling took place, or by volatilization)--was not determined. Therefore, apparent field dissipation "half-lives" cannot be assumed to be due to degradation. In fact, EFGWB's statistical analysis of the data (no such analysis or estimate of data quality was presented by the study authors) shows that the field dissipation pattern is not explained very well by the usually applied first order degradation kinetics. *Unexplained* statistical variations calculated from $1-r^2$, where r^2 is the coefficient of determination, in the States of MS (Greenville), CA (Madera), CA (Hickman), TX (Uvalde), and FL (Melrose, near

Gainesville) were approximately 30, 40, 70, 70, and 70 percent, respectively. This is *prima facie* evidence that other dissipative processes, such as off-site transport, or systematic bias were operational. Minimum ranges of dissipation half-lives based on the first order model and a 95% confidence interval are in the table below. These values were computed starting with residues present at 0.1 day after the fifth application and ending with the last samples taken 540 days later. All available samples at all sampling intervals, not averages, were used. In some cases minor amounts of pesticide below the top six inches of soil were not included in the analyses, but the effect is inconsequential. Based on study results and necessary assumptions, these ranges could be shifted to even longer apparent half-lives. Simple regression plots and statistical figures of merit for the data from each state are attached. Even on a logarithmic scale for concentration, the large scatter in the data points is evident. As a further indication of scatter, EFGWB estimated percent of recoveries of initial target application rates after each of the five applications are also included in the table below.

Table of Initial Recoveries and Minimum Ranges of Dissipation Half-Lives
(Not to be confused with *degradation*, as explained in text)

	<u>Application Recovery (%)</u>	<u>Half-Life (years)</u>	<u>Unexplained Variation</u>
CA (Madera)	35, 0, 45, 25, 30 25(avg)	0.4-0.6	40%
CA (Hickman)	75, -5, 65, 35, 110 55(avg)	0.4-0.8	70%
MS (Greenville)	50, 80, 65, 40, 90 65(avg)	0.6-0.9	30%
TX (Uvalde)	45, 65, 115, 120, 35 75(avg)	0.6-1.4	70%
FL (Gainesville)	55, 5, 90, 25, 20 40(avg)	0.8-2.1	70%

Except for sporadic amounts detected below the six inch sampling interval (probably caused by contamination during sample collection and handling), leaching of PIRATE did not contribute appreciably towards dissipation in any of the sites except Uvalde, TX. At this Texas site significant concentrations at greater depths (once as deep as 24-30 inches) on several uncorrelated occasions are easily explained as contamination during core removal caused by wet, muddy and rocky soil. No water balance was attempted and no tracer of water movement was used to indicate whether there was opportunity for leaching at any of the test sites. However,

because PIRATE is so persistent and there were convenient episodic rainfall/irrigation events during the long course of the studies, it can be concluded from the data at opportunistic sampling times that leaching did not contribute appreciably towards dissipation.

It is important to realize the inherent uncertainties associated with guideline field studies. Length of study, vagaries of weather with increased opportunity for punctuated physical dispersal (not necessarily random) with longer time intervals, detection limits, etc., impart limitations which prevent precise definition of lifetimes in the field, especially for more persistent compounds. In other words, for persistent compounds the usual design, duration, and expense of field studies, and the physical aspects of dissipation generally preclude reliable extrapolation of half-lives beyond about six months. What is clear from these studies, however, is that

1. PIRATE is among the group of pesticides with the greatest persistence, and that there is large carryover from year to year. In agricultural areas where multicropping is practiced (several different crops harvested during the same year), there would be increased opportunity for build up.
2. PIRATE does not leach.
3. Since there was no information provided whatsoever on degradation or other possible dissipative processes besides leaching, from these studies we do not know how PIRATE disperses or dissipates.

DESCRIPTION OF STUDIES (for additional details consult the original two large volumes of MRID 434928-50)

Since all five field dissipation studies were conducted with virtually the same protocol and study design, they will be described as one. The study authors wisely formatted their summary information and data from all five sites the same way. The following description is nearly verbatim or paraphrased from summaries in the original submission. The five representative study sites (nearest familiar place name), soil textural classes, dates of study initiation, date of first pesticidal application, experimental termination date, and formulation, respectively, were 1) Uvalde, Texas; clay loam; 03 Jun 91, 14 Aug 91, 24 May 93; 2SC (24% a.i.); 2) Madera, California (San Joaquin Valley); loamy sand; 03 Jun 91, 11 Sep 91, 18 Jun 93; 2SC; 3) Greenville, Mississippi; silt loam; 22 Jun 92, 28 Jul 92, 21 Mar 94; 3SC (30.5% a.i.); 4) Hickman, California (San Joaquin Valley); sandy loam; 22 Jun 92, 14 Aug 92, 07 Apr 94; 3SC; 5) Gainesville, Florida; sand; 22 Jun 92, 4 Sep 92, 12 Apr 94; 3SC. Regions and soils chosen adequately represent potential use areas. Conventional or regional cultural practices seem to have been observed. There were no quantitative or descriptive indications of how the well the cotton grew.

All studies were *unreplicated*. Each study consisted of two plots: an untreated control plot and a plot treated with five weekly applications (with minor exception) of the insecticide-miticide AC 303,630 2SC or 3SC. For each, application rates were nominally 0.4 lb ai/acre (total rate

of 2.0 lb/acre), or twice the anticipated typical field rate. At a given location both plots had the same rectangular dimensions and were divided into six equal subplots. At the different sites plots had different dimensions, some long and narrow (80 x 240 ft), others nearly square in shape (95 x 115 ft) which varied in area from about 0.25 to 0.44 acre. Buffers between plots at the different sites varied from 100 to 464 ft. Cotton was planted in 2:2 skip-row fashion (described as alternating two rows of cotton with two unplanted rows). Row spacing and in-row spacing of cotton plants in inches were, respectively, TX: 40, 2; CA (Madera): 30, 3-5; MS: 38, 3; CA (Hickman): 30, 3; FL: 30, 3. Formulations mixed with water were broadcast sprayed on to the bare soil between the rows of cotton with backpack sprayers, except in Madera, CA, where the entire plot, including cotton plants, was sprayed with a sprayer driven by tractor. Spraying was done during the critical periods of late flowering and/or fruit formation and development. Tank mix analyses showed that the intended theoretical amount was essentially in the spray mixtures. Actual application recoveries in soil were not provided by the study authors.

One pretreatment soil sample composed of 18 soil cores (1 to 1.75 inches in diameter and 36 inches long) were taken from the test sites before the application of AC 303,630. Likewise, untreated control samples also composed of 18 cores were collected at appropriate intervals. Three replicated soil samples consisting of six 1 x 36 inch cores (one taken from each subplot) were collected from the treated plot at specified intervals. Soil samples were prepared for analysis by segmenting and compositing the soil cores into six separate layers at six inch intervals from top to bottom. Soil samples were analyzed for AC 303,630 using American Cyanamid Method M 2201, which is a GC method with a validated sensitivity (LOQ) of 10 ppb. The detection limit was stated to be 1 ppb. Sampling intervals and summarized results of soil analyses are attached.

COMMENTS

- ▶ No degradates or degradative processes were measured or identified. Therefore, except for the reasonable elimination of leaching, we do not know how AC 303, 630 disperses or dissipates. There was no attempt to account for the large scatter in the data or estimate reliability of "half-lives".
- ▶ There were no treatment replications.
- ▶ Verifications of the application rates to soil were not given (only tank mix information was provided). EFGWB made its own estimates from the data provided.
- ▶ Criteria for multiple or additional lab analyses beyond the three replicates for numerous soil samples were not given. Casual inspection seems to indicate a preponderant bias to resample when concentrations were highest.
- ▶ Water balance, movement and redistribution in the soil profile were not provided. Water

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