

US EPA ARCHIVE DOCUMENT

PMSP/TS



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

SEP 19 1986

OFFICE OF
PESTICIDES AND TOXIC SUBSTANCES

MEMORANDUM

SUBJECT: EPA Reg. Nos. 279-3052, -3053, and -3054. Command.
Data on Off-Target Incidents. Accession Nos. 263995,
263996, 2636027, 2638055, and 264000. RCB Nos. 1265,
1266, and 1267.

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FMC Corporation, Agricultural Chemical Group, has submitted additional data on Command off-target incidents from the 1986 growing season. This package includes descriptions of incidents, sample analyses, volatility data, and an analytical method for crops other than soybeans.

The data in the folder labeled "volatility" respond to EAB requests. Information on the volatility of inert ingredients in the formulation was reported as requested. All inerts have vapor pressures in the range of [redacted]. We are unable to determine who requested this information on inert ingredients, but EAB has the expertise to evaluate it (personal communication with Bob Holst, 9/5/86). Since this same package sent to EAB, we are not formally deferring to them for evaluation of these data, since their normal review is expected to cover it.

The incident descriptions are not especially relevant to RCB's area of concern and we are not discussing them further. The analytical results of samples from the various locations and crops are reported in summary tables only, accompanied by individual records of analysis, (a statement signed by the Lab Director -- presumably, to take the place of raw data). Of several hundred analyses (6 pages), only occasional samples showed detectable residues of Command, per se, in the range 30 ppb to 1 ppm. A list of crops and residue ranges follows:

EX 728

Analysis of Samples for Command

crop	# original samples	# detectable residues	residue range
alfalfa	77	25	30 ppb - 32 ppm
apple foliage and fruit	7	4	30 - 60 ppb
asparagus	2	1	35 ppb
beets	1	---	
blackberries	1	---	
broccoli	2	---	
cabbage	5	---	
carrot	2	---	
cauliflower	2	---	
chinese cabbage	2	---	
cherries	2	---	
clover	11	2	32 - 229 ppb
corn (various types/parts)	8	---	
eggplant	2	---	
elderberry	2	---	
garlic	4	2	33 - 633 ppb
grapes	5	---	
grass	5	1	82 ppb
green beans	4	---	
hay (unspecified)	8	2	37 - 106 ppb
horseradish	1	1	233 ppb
kale	1	---	
lettuce	17	---	
milk	2	---	
oats	35	8	34 - 1617 ppb
onion	6	1	82 ppb
parsley	1	1	54 - 56 ppb
peas	10	2	48 - 87 ppb
potato leaves	2	---	
radish parts	3	---	
raspberry (fruit & leaves)	15	6(leaves only)	
rhubarb	2	2	210 - 239 ppb
spinach	3	---	
strawberries, fruit & leaves	19	3 (2 fruit)	31-52 ppb
swiss chard	1	not yet analyzed	
tomato	6	---	
triticale	1	1	105 ppb
water (cistern, well, tap, pond and pool)	22	1 (pond)	759 ppb
wheat	7	1	40 ppb

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Many of the samples showing detectable residues were resampled; later sample analyses invariably show lower or non-detectable residue levels.

Alfalfa samples more often had detectable Command residues, ranging as high as 30 ppm; FMC indicates there may be reason to question several of the alfalfa samples having high residues. The GC chromatograms did not match normal alfalfa samples, and both re-extraction and resampling showed far lower or non-detectable residue levels.

We have insufficient information to evaluate the significance of the residue levels found. Only metabolism studies by soil uptake are available; no studies on foliar application have been submitted. Thus, we cannot determine whether the residue quantitated (Command, per se) is the entire residue of concern. Clearly, however, the parent compound has moved on to non-target plants. Preliminary results of plant metabolism studies being done by FMC were presented in a meeting 9/15/86. The studies are not yet complete, but FMC is exploring the metabolism in both plants and animals.

The analytical method submitted is for milk, soil, water and r.a.c.s. other than soybeans. An early version, marked as CBI, was submitted 6/30/86 (Acc. No. 263627) and a later version (Acc. No. 263855), submitted 7/16/86, is described as "validated", and is not marked CBI. The earlier method was sent by FMC to various other agencies and institutions involved in handling the off-target incidents, and a list of those persons is provided. We had sent the soybean method (with modifications from the EPA method trial) to several labs, also. FMC states that the soybean method is used for soil and crops, while different extraction procedures are used for milk and water.

The soybean method has not yet been submitted to PAM-II. EPA requested incorporation of the revisions required during EPA's method trial into a revised write-up which is being prepared by FMC (telecon, E. Cuirle, 8/29/86). When received, that revised procedure will be forwarded for incorporation into PAM-II, along with the validated method for other commodities as a supplementary method.

The method for soil and other crops involves acid hydrolysis of samples, then partitioning of residues into hexane; the hexane extract is then washed with sodium bicarbonate. Extract from soil samples is quantitated by GC/NPD at this stage, while crop samples are further cleaned up on florisil before quantitation by GC/NPD or GC/MS. This is the same as for soybeans. This method write up describes parameters suitable for four different gas

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chromatographs. Minimum levels of quantification are given as 30 ppb for crops and 100 ppb for soil. Recovery values for 33 crops at levels of 50 ppb to 500 ppm range from 64 to 130%. Soil recoveries are equally acceptable.

The method for water involves extracting residues twice with hexane by mixing in a separatory funnel, then concentrating the hexane first over a steambath and then under nitrogen. Quantitation is by GC/N-P FID. Recoveries from distilled water were 68-120% at 5 to 100 ppb.

The milk method requires homogenizing milk with acetone, filtering, and partially evaporating the solution on a Kunderna-Danish evaporater. Hexane is added, and the mixture further evaporated. Two layers will form as the volume reduces; the lower (aqueous) layer is removed and the remaining hexane dried with Na₂SO₄. The hexane is chromatographed on a Florisil Sep-Pak which was prepared by washing with 30% ethyl acetate in hexane, and the solution concentrated under nitrogen. Quantitation is by GC/N-P FID. Method sensitivity is given as 20 ppb, and recoveries were 52-81% over the range 20 ppb to 2 ppm.

Since no animal metabolism studies have been submitted, we do not know if Command would occur in milk as a result of treated (or contaminated) animal feed.

Conclusions

The analytical methods submitted are adequate to determine residues of Command, per se, in various crops, water, milk, and soil. Both the soybean method (when resubmitted) and this new method for other crops will be submitted for publication in PAM-II.

The residue data presented indicate that the active ingredient can transfer to off-target crops, although not all commodities had detectable residue levels of Command. Lack of foliar and animal metabolism data prevents us from reaching firm conclusions about the total residue levels.

cc:R.F., Circu, Reviewer, PP#4F3128, EAB, TOX, Command S.F
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