

Shaughnessy No.: 125401

Date Out EAB: JUN 17 1985

TO: R. Taylor
Product Manager # 25
Registration Division
TS-767

FROM: Samuel M. Creeger, Chief *SM*
Environmental Chemistry Review Section No. 1
Exposure Assessment Branch
Hazard Evaluation Division

Attached please find the environmental fate review of:

Reg./File No.: 279-GLNU, -GNLE and -GNLE

Chemical: FMC-57020 (dimethazone - proposed common name)

Type Product: Herbicide

Product Name: Command®

Company Name: FMC

Submission Purpose: New chemical, registration on soybeans,
response to previous review

Action Code: 106

Date In: 2/20/85

EAB # 5394-5396

Date Completed: JUN 17 1985

TAIS (Level II)

Days

61

3.5

Deferrals To:

Ecological Effects Branch

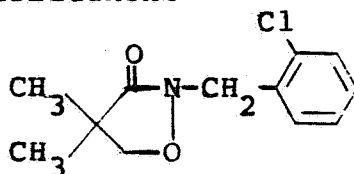
Residue Chemistry Branch

Toxicology Branch

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1. CHEMICAL:

- o Common name: dimethazone (proposed)
- o Trade name: Command
- o Company code: FMC 57020
- o Chemical name: 2-(2-chlorophenyl)methyl-4,4-dimethyl-3-isoxasolidinone
- o Chemical structure:

2. TEST MATERIAL: Not applicable.3. STUDY/ACTION TYPE: Response to the EAB review of 11/23/84 on the environmental fate data deficiencies.4. STUDY IDENTIFICATION: No new studies were submitted.5. REVIEWED BY:

Soobok Hong
Chemist

Environmental Chemistry Review Section 1/EAB/HED

6. APPROVED BY:

Samuel M. Creeger, Chief
Supervisory Chemist

Environmental Chemistry Review Section 1/EAB/HED

Soobok Hong
6-17-85
Sam M Creeger
JUN 17 1985

7. CONCLUSIONS:

7.1 EAB accepts FMC's response on Field mobility and Fish accumulation studies, but not on Aqueous photolysis, Soil Photolysis, and Field dissipation studies.

7.2 As of this review, the following environmental fate data requirements have been satisfied for Command® Herbicide:

- o Hydrolysis - FMC 57020 is stable to hydrolysis in acidic, neutral and basic solutions maintained at temperature of $25 \pm 0.5^\circ\text{C}$.
- o Aerobic soil metabolism - FMC 57020 is mineralized in soil under aerobic conditions. CO_2 evolution and soil binding increase with time. The rate and the degree of mineralization and soil binding vary with soil types. Both rings of the molecule are susceptible to the mineralization process. Unchanged FMC 57020 is the primary residue in soil, and polar/non-polar metabolites are minor residues. The estimated half-lives varied from 56 to 173 days depending on soil type.

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- o Anaerobic soil metabolism - FMC 57020 readily degrades to FMC 65317 as a major product under anaerobic conditions. Another 12 minor degradation products were detected. No CO₂ evolution was observed. Data indicate that FMC 65317 persists under anaerobic conditions.
- o Laboratory leaching - FMC 57020 appears to have a low to intermediate mobility in sandy loam, silt loam and clay loam soils but a high mobility in sand soil. FMC 65317, an anaerobic soil degradate of FMC 57020, has a very high mobility in all soil types.
- o Field leaching - FMC 57020 appears to have a low leaching potential under actual field conditions (loamy sand, 1.2 % OM, 2.0 lb ai/A, 13.9 inches of water in 61 days) since no detectable levels (less than 0.02 ppm) of the compound or its metabolites were found in soil samples taken deeper than 1 foot. FMC 65317 was not detected in any soil sample at any depth.
- o Rotational crops - The application of ¹⁴C-FMC 57020 at the rate of 2 lb ai/A (1.6-1.7x maximum label rate) results in low residues in rotational crops (corn, oat, cabbage and sugar beet) planted 10 months after chemical application. A majority of these residues are either plant tissue bound or polar. Organosolubles accounted for less than 0.02 ppm. Residue levels were higher in the mature rotational crops as compared to the immature ones. Total ¹⁴C did not exceed 0.063 ppm in corn, cabbage or sugar beet, but reached a maximum of 0.118 ppm in mature oat straw. The data support a 10 month rotational crop interval. Additional data will be needed if a shorter interval is desired.
- o Fish accumulation - FMC 57020 has a moderate tendency to bioaccumulate in bluegill sunfish under flow-through conditions. A bioaccumulation factor of 40x for whole fish was found, but depuration occurs rapidly to low but measurable levels upon removal of the fish to uncontaminated water. FMC 57020 appears to be metabolized in the fish by a variety of processes including oxidation, hydroxylation, heterocyclic ring opening, methylation, and decarboxylation. There are indications that the methylene carbon is incorporated into fats/oils and higher molecular weight lipophilic/polar conjugate.

8. RECOMMENDATIONS:

8.1 FMC's response on the deficiencies indicated in the review of 11/23/84 is not considered adequate to satisfy the following requirements:

- o Aqueous photolysis - A new study need to be done. The study should show a good material balance (i.e. volatile traps should be used).

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- o Soil photolysis - A new study need to be done. Volatile traps should be used, and soil temperature need to be controlled.
 - o Field dissipation - Recalculate the residue concentration in 0-12 inch soil depth, provide all the data points used for linear regression analyses, and recalculate half-lives.
- 8.2 Volatility data on FMC 57020 may need to be provided to EAB. Depending on the volatility data, air photolysis study may be required to support registration.

9. BACKGROUND:

A. Introduction

In response to the EAB review of 11/23/84 on Command Herbicide, FMC has submitted its response.

B. Directions for Use

No label was included with the submission. Previous reviews reveal that Command® Herbicide may be used alone, or in combination with other herbicide for pre-emergence and post-emergence control of broadleaf and grass weeds on soybeans. The maximum use rate when used alone is 1.2 lb ai/A. For detailed information, see the attachment (labels) of 11/23/84 review.

10. DISCUSSION OF INDIVIDUAL RESPONSES

10.1 A. Study Identification

Aqueous photolysis (FMC Report No. P-0869), Section 3.1 of EAB review of 11/23/84.

B. EPA Cited Deficiency

1. Half-lives were not derived in a consistent manner.
2. Actual recoveries of radioactivity (loss due to non-trapped volatiles) were not reported.

C. FMC's Response

1. FMC has revised its method of half-life estimation by assuming first-order kinetics for all photolytic experiments. The new half-lives were the same as estimated by EAB in its review.
2. Recoveries of radiocarbon which were inadvertently omitted from tests reported in FMC Report No. P-0869 are summarized below:

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SUMMARY OF ^{14}C RECOVERY FROM SOLUTION PHOTOLYSIS

Tests	Days of Exposure										
	0	1/3	1/2	1	2	3	4	5	7	14	30
OUTDOOR TESTS											
Irradiated	100	-	-	-	-	-	-	-	-	103.4	83.5
Dark Control	100	-	-	-	-	-	-	-	-	-	83.6
INDOOR TESTS											
#1	100	-	-	97.8	-	93.6	-	-	67.3	78.1	-
#4	100	95.9	91.3	89.7	78.6	72.6	65.9	61.9	54.4	-	-
#5	100	103.0	96.1	94.3	91.5	85.9	84.2	74.9	68.9	-	-
#6 ₁	100	-	-	85.4	-	82.3	-	-	71.1	75.6	-
#2 ₁	100	-	-	-	-	-	-	-	-	76.6	-
#3 ₁	100	-	-	-	-	-	-	-	71.1	-	-

$\frac{1}{2}$ Dark control

D. Reviewer's Comment

The estimated half-lives are meaningless because recovery rates are different from one sampling interval to another.

Also, it is not known what caused to the loss of radio-activity from the above recovery data.

FMC explained at the meeting with EAB held 3/5/85 that the loss was thought to be due to volatility of parent compound because the same recovery was obtained from the irradiated sample and from the dark control sample. However, the data are not reliable. According to the recovery data, radio-activity was not lost at all on day 14 of irradiation, but 16.5 % was lost on day 30 from the outdoor study.

Also, if the parent compound is relatively volatile, an air photolysis study may be required in support of registration.

In conclusion, it is recommended another aqueous photolysis study be conducted. Volatile compounds should be trapped.

10.2 A. Study Identification

Soil Photolysis (FMC Report No. P-0873), Section 3.2 of EAB review of 11/23/85.

B. EPA Cited Deficiencies

1. Volatile compounds were not trapped;
2. Soil was not sterilized;
3. The temperature of soil was not mentioned;
4. Degradation rate was neither reported nor can be estimated;
5. Identification of degradation products was not done;
6. The Mylar film may have excluded those wavelengths that could cause photodegradation.

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C. FMC's Response

1. Material balance

Levels of radioactivity lost due to volatility amounted to 25.6 % and 29 % of the applied ^{14}C chemical in irradiated soil at 14 days and 30 days, respectively, following initiation of irradiation.

2. Soil sterility

FMC believes that microorganisms were not a determining factor in breakdown of FMC 57020 in/on irradiated soil because of low moisture level. Also, data obtained from 30 day non-irradiated soil showed that a total of 95.7 % of the recovered radioactivity was parent chemical.

3. Soil temperatures

Soil temperatures for outdoor soil tests utilizing 250 u soil layers could not be accurately and precisely monitored.

4. Degradation rate

First-order half-life was estimated to be 96.7 days.

5. Product Identification

No extractable residue other than parent compound exceeded 10 % of the recovered radioactivity at any testing interval. No product identification was deemed necessary.

6. Mylar film

Use of Mylar film was not deleterious either to the conduct of the tests or the results obtained because of the transparent nature of the film and the negligible photochemical breakdown potential of FMC 57020 over the natural sunlight spectrum being studied.

D. Reviewer's Comments

FMC's justification cannot be accepted for the following reasons although some of the questions (items 2, 5, and 6) were adequately answered:

- o Volatile compounds (parent compound and degradation products) should be monitored quantitatively and qualitatively. There is no supporting evidence that

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the loss of radioactivity (25.6 % at 14 days and 29.0 % at 30 days) was totally due to volatilization of parent compound.

- o Soil temperature should be controlled so that thermal degradation should not interfere with the results of photodegradation.
- o The photodegradation rate estimated using only the recovered ^{14}C and recovered parent compound is not considered valid.

In conclusion, it is recommended a new soil photolysis study be conducted. Volatile compounds should be trapped, and soil temperature should be controlled.

10.3 A. Study Identification

Field leaching study (FMC Report No. P-0916), Section 3.11 of EAB review of 11/23/84.

B. EPA Comments

1. Residue decline plot (concentration vs. log time).
2. Soil residue extraction procedure.
3. No soil residue between detection limit (0.02 ppm) and the method sensitivity (0.1 ppm).

C. FMC's Response

1. Residue decline plot

First-order or second-order decay did not fit the data (very poor or no correlation). In order to find the best fit line for the data, an empirical approach was used. The empirical approach using concentration vs. log time plotting yielded a better correlation than any other technique tried.

2. Soil residue extraction procedure

FMC 57020 and FMC 65317 do not form respective salts with HCl and they are highly water soluble.

3. Soil residue

If there were any FMC 57020 or FMC 65317 residues present in the soil samples between 0.02 and 0.1 ppm, the analytical method would have detected them.

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D. Reviewer's Comments

The obtained data are not adequate to fit any rate law. FMC's approach seems very forceful. As FMC explains, the data points were highly scattered and very poorly correlated.

Since the purpose of the study was to measure the extent of leaching of FMC 57020 residues, it can be said that the study satisfies the field leaching monitoring. It can be concluded that FMC 57020 will not leach under the field conditions.

10.4 A. Study Identification

PESTANS modeling (FMC Report P-0904), Section 3.13 of EAB review of 11/23/84.

B. EPA Cited Summary/FMC's Response/EAB Comments (by M. Lorber)

"Four points were made in M. Lorber's initial review of the PESTANS modeling study conducted by FMC on the chemical FMC 57020. Three of the four comments made by M. Lorber essentially did not refute any conclusions FMC drew on the basis of their original PESTANS modeling. For example, the comment that FMC did not use the current version of PESTANS is somewhat insignificant since the use of the current version did not significantly change the results. However, one comment does significantly affect the conclusion of the study:

'The sand soil characterization in PESTANS is generous in favor of the registrant. I would not consider sand soil results reported valid, even if the correct version of PESTANS were used.'

FMC commented that changes in PESTANS modeling parameters, suggested by M. Lorber to model a "worst case" sand, would not change the results significantly.

In response, the PESTANS model was run in-house to check this assertion. These PESTANS runs are included as Tables 1, 2, and 3. Table 1 shows the results with all the initial parameters assumed, and Table 2 shows the results with the parameters changed as suggested by M. Lorber. The results confirm what FMC said: no more leaching was implied, as the plume appeared to concentrate in the profile at 10-12 cm with the revised parameters (Table 2) rather than leach further in the profile. However, in reality, when the water content of the soil decreases (see "Projected Water Content" parameter on Tables 1 and 2), recharge will also increase. Table 3 shows a PESTANS run with the recharge rate increased from $0.035 \text{ cm}^{-1}/\text{hr}$ to $0.045 \text{ cm}^{-1}/\text{hr}$. As can be seen, the depth of penetration increased from 15 (Table 2) to 22 cm (Table 3) with the higher recharge."

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"However, this reviewer is not comfortable that PESTANS is accurately portraying the effect of a reduced water content, based on the following experience. For a different chemical from a different registrant, a PESTANS study showed that 1% of applied would leach below 1 meter. This reviewer then set up an identical steady-state scenario with PRZM and confirmed that 1 % of applied would also leach according to PRZM simulations. He then lowered the soil water content from the PESTANS assumption of 24 % to 9 % for further PRZM simulations. This is a more appropriate assumption for a "worst case" sand soil scenario. In that case, PRZM simulated that 8 % of applied would leach below one meter. This increase in pesticide leaching resulted from the change in water content alone; recharge was not changed. Then the reviewer substituted an actual weather record in PRZM simulations in place of the steady-state rainfall record. The annual recharge in that case, 60 cm/yr, was still equivalent to the steady state recharge, .007 cm/hr (.007 cm/hr * 24 hr/day * 365 day/yr = 60 cm/yr). However, most of the water recharge occurred near the time of pesticide application. As a result, between 17 and 29 % of applied leached below 1 meter, depending on date of application. Therefore, predictions increased from 1% to 17-29% simply by a change in soil characterization and inhomogeneous weather assumptions.

The implication here is not that a similar difference would result if the same exercise were done with PRZM instead of PESTANS on FMC 57020." "The recommendation is made that FMC obtain a copy of the PRZM model and use it for further simulation work. PRZM is a little more difficult to use than PESTANS, mainly because of actual weather data input requirements," but it is more realistic.

10.5 A. Study Identification

Field Dissipation (FMC Report No. P-0896), Section 3.14 of EAB review of 11/23/84.

B. EPA Comments and Conclusion

1. Explain the mathematical equation in terms of log time and concentration.
2. For the half-life calculations, FMC 57020 levels in soils deeper than 6 inches should also be considered.
3. Soil sampling should have been done at depths deeper than 12 inches.

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C. FMC's Response

1. Half-life estimation

Utilizing the best fit "power rate law", second-order or 1.5-order rate law was chosen.

In response to the requests to replot the half-lives including the deeper soil layer, the FMC 57020 soil residue values (ppm) of 0-6 inches and 6-12 inches were added together. The added data were replotted based on the "best fit" principle. Table 3 (p. 22 of the attachment) presents the half-lives (HL) resulting from the 0-6 inches plus 6-12 inches residues. Graphs derived from these plots are presented in figures 9-16 (pp. 23-26 of the attachment).

2. Soil sampling depth

This study was designed for soil dissipation. The soil dissipation protocol only required sampling down to a 12-inch depth. Field mobility study was specifically designed to address the leaching question.

D. Reviewer's Comments

The data points used for plotting figures 9-16 need to be provided in tables. To incorporate the residues in the 6-12 inch soil increment for the calculation of half-lives, the registrant explained that the concentration (ppm) in 0-6 inches and in 6-12 inches were added together. How can concentrations be added?

Also, it is not true that the soil dissipation protocol only requires sampling down to a 12-inch depth. The protocol states that sampling need to be done to a 15 cm depth only if laboratory leaching studies indicate no leaching potential of the compound. If data on leaching indicate that the compound is likely to leach into soil to a depth greater than 15 cm, or if the pesticide is incorporated into soil, then samples should be taken to a depth sufficient to define the extent of leaching. However, since a separate field mobility study was done and it showed that FMC 57020 will not leach below 1 foot (although laboratory leaching studies indicated a high leaching potential), there is no concern about the residues leaching below 12-inch depth.

It is recommended that soil concentrations in 0-12 inch depth be recalculated and dissipation rate be recalculated.

The field dissipation data requirement has not yet been satisfied.

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10.6 A. Study Identification

Fish accumulation (FMC Report Nos. PC-0018 and P-0889),
Section 3.17 of EAB review of 11/23/84.

B. EPA Cited Deficiency

Labeling position of FMC 57020 used in the fish accumulation
study (methylene- ^{14}C vs. phenyl ring).

C. FMC's Response

The use of methylene- ^{14}C FMC 57020 should be adequate for
fish accumulation studies based on its observed stability
in other animal (rat) metabolism studies as demonstrated
by an adequate material balance recovery (no loss due to
 $^{14}\text{CO}_2$) and formation of metabolites containing the radio-
labeled methylene carbon intact. Also, analysis of meta-
bolites in the rat studies revealed that the major routes
of metabolism were hydroxylation for aromatic ring, 5-
position of heterocyclic ring and gem-dimethyl groups at
the 5-position of the heterocyclic ring, and cleavage of
the N-O bond of the heterocyclic ring. No C-C cleavage
of the methylene-aromatic ring was observed. This is also
true for FMC 57020 residues taken up by fish.

D. Reviewer's Comments

EAB accepts FMC's explanation. The fish accumulation
data requirement is satisfied.

11. ONE-LINER: A one-liner has been initiated.

12. CBI:

A copy of the FMC's response (EPA Acc. No. 256508) is attached
to this review, and it is regarded as CBI.

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FMC 57020/Validation/

Model: PESTAN

Date: June 3, 1985

Solubility = 1100 ppm

Recharge Rate = .035 cm/hr

Sorption Constant = 1.65

Degr. Rate Coeff. = .004458 /hr

Bulk Density = 1.5 gms/cc

Soil Porosity = .41 cc/hr

Char. Curve Coeff. = 4.328

Sat. Hydraul. Cond. = 59 cm/hr

Dispersion Coeff. = .060cm²/hr

Proj. Water Content = 0.22

Pore Water Velocity = .161cm/hr

Pollutant Velocity = .013cm/hr

Length of Slug = .008cm

Equivalent to 2.24 kg a.i./Ha

SOLUTION CONCENTRATIONS in PPM [ppB]

At Day...	0	3	6	9	12	15	18	21	24	27	30
0 cm	4.69	1.78	0.56	0.20	.079	.031	.013	[5.3]	[2.2]	[.92]	[.39]
1 cm	0.49	2.64	1.87	0.89	0.39	0.17	.073	.031	.013	[5.8]	[2.5]
3 cm	[.56]	0.15	1.24	1.33	0.88	0.49	0.25	0.12	.055	.025	.012
4 cm		[.36]	0.16	0.68	0.88	0.72	0.48	0.28	0.15	.078	.039
6 cm			[4.3]	0.12	0.39	0.57	0.55	0.42	0.28	0.17	.094
7 cm			[.023]	[6.8]	.077	0.23	0.36	0.39	0.34	0.25	0.16
9 cm				[.13]	[6.8]	.050	0.14	0.23	0.27	0.26	0.21
10 cm					[.27]	[5.6]	.032	.087	0.15	0.19	0.19
12 cm					[.21]	[.32]	[4.2]	.020	.054	.095	0.13
13 cm						[.013]	[.33]	[3.0]	.013	.034	.061
15 cm							[.022]	[.28]	[2.1]	[8.4]	.021
16 cm									[.23]	[1.4]	[5.4]
18 cm									[.016]	[.18]	[.98]
19 cm										[.013]	[.13]
21 cm											[.016]
22 cm											
24 cm											
25 cm											
27 cm											
28 cm											
30 cm											

[] = VALUES LESS THAN OR EQUAL TO 0.01 ppB

Table I

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FMC 57020

Model: PESTAN

Date: JUNE 5, 1985

Solubility = 1100 ppm

Recharge Rate = .035 cm/hr

Sorption Constant = 1.65

Degr. Rate Coeff. = .004458 /hr

Bulk Density = 1.5 gms/cc

Soil Porosity = .38 cc/hr

Char. Curve Coeff. = .5

Sat. Hydraul. Cond. = 59 cm/hr

Dispersion Coeff. = .060 cm²/hr

Proj. Water Content = 0.06

Pore Water Velocity = .590 cm/hr

Pollutant Velocity = .014 cm/hr

Length of Slug = .008 cm

Equivalent to 2.24 kg a.i./Ha

SOLUTION CONCENTRATIONS in PPM [ppB]

At Day...	0	3	6	9	12	15	18	21	24	27	30
0 cm	4.99	0.57	.029	[1.7]	[.092]						
1 cm	0.52	3.41	2.84	0.42	.042	[3.5]	[.27]	[.026]			
3 cm	[.59]	[.30]	1.06	2.56	1.02	0.20	.028	[3.1]	[.31]	[.030]	
4 cm			[1.5]	0.38	1.54	1.22	0.42	.093	.015	[2.1]	[.25]
6 cm				[1.4]	0.14	0.80	1.02	.057	.019	.044	[8.0]
7 cm					[.83]	.057	0.39	0.71	0.57	0.27	.085
9 cm						[.44]	.023	0.18	0.43	0.47	0.30
10 cm							[.21]	[9.3]	.081	.024	0.34
12 cm								[.10]	[3.8]	.036	0.13
13 cm									[.043]	[1.6]	.016
15 cm										[.018]	[.66]
16 cm											
18 cm											
19 cm											
21 cm											
22 cm											
24 cm											
25 cm											
27 cm											
28 cm											
30 cm											

| = VALUES LESS THAN OR EQUAL TO 0.01 ppB

Table II

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FMC/57020 VALIDATION

Model: PESTAN

Date: JUNE 5, 1985

Solubility = 1100 ppm

Recharge Rate = .045 cm/hr

Sorption Constant = 1.65

Degr. Rate Coeff. = .004458 /hr

Bulk Density = 1.5 gms/cc

Soil Porosity = .38 cc/hr

Char. Curve Coeff. = .5

Sat. Hydraul. Cond. = 59 cm/hr

Dispersion Coeff. = .060 cm²/hr

Proj. Water Content = 0.18

Pore Water Velocity = .257 cm/hr

Pollutant Velocity = .017 cm/hr

Length of Slug = .008 cm

Equivalent to 2.24 kg a.i./Ha

SOLUTION CONCENTRATIONS in PPM [ppB]

At Day...	0	3	6	9	12	15	18	21	24	27	30
0 cm	4.77	1.01	0.16	.030	[5.8]	[1.2]	[.24]	[.046]			
1 cm	0.50	3.47	1.49	0.38	.087	.019	[4.3]	[.93]	[.21]	[.045]	[.011]
3 cm	[.59]	0.23	1.91	1.31	0.49	0.15	.040	[9.9]	[2.4]	[.57]	[.13]
4 cm		[.30]	0.34	1.22	1.04	0.51	0.19	.060	.017	[4.7]	[1.2]
6 cm			[8.5]	0.30	0.82	0.80	0.47	0.21	.077	.025	[7.7]
7 cm			[.023]	.020	0.24	0.57	0.61	0.41	0.21	.088	.033
9 cm				[.36]	.027	0.19	0.41	0.46	0.35	0.20	.092
10 cm					[1.1]	.027	0.14	0.29	0.35	0.28	0.18
12 cm					[.016]	[1.9]	.025	0.11	0.21	0.26	0.23
13 cm						[.066]	[2.4]	.022	.081	0.16	0.20
15 cm							[.12]	[2.6]	.019	.061	0.12
16 cm								[.17]	[2.6]	.015	.046
18 cm									[.22]	[2.5]	.012
19 cm									[.015]	[.26]	[2.2]
21 cm										[.019]	[.27]
22 cm											[.021]
24 cm											
25 cm											
27 cm											
28 cm											
30 cm											

| = VALUES LESS THAN OR EQUAL TO 0.01 ppB

Tabl. III

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