Monsanto

APR 19 1982

COST REDUCTION

FROM (NAME—LOCATION—PHONE) R. T. Parker - Nitro Plant - #507

DATE : April 13, 1982

cc. H. S. Scott - E2ND
T. M. Bistline - E2NJ
H. M. Galloway

SUBJECT : TCDD ANALYSES

REFERENCE :

TO : A. M. Ford
A2SA

ATTORNEY WORK PRODUCT
ATTORNEY-CLIENT PRIVILEGE

Regarding your inquiry about the TCDD levels reported in the 1969 Nitro TSD Annual Summary, we have no documents that can verify or determine the source of these numbers. The TSD summary reports that TCDD levels averaged 40-50 ppm during 1968. The Nitro research notebooks of Phil Balderson and Marty Wilson contain no analytical data on TCDD levels during this time period. Balderson stated that if any TCDD analyses were run at Nitro, the results would be recorded either in his notebook or Marty Wilson's notebook. Balderson and Wilson were apparently the only Nitro chemists to run analyses for TCDD. Rick Atkinson, the only other Nitro chemist working with 2,4,5-T during 1968, stated he does not recall having run an analysis for TCDD in 2,4,5-T. These facts suggest that no TCDD determinations were made at Nitro during 1968.

Nitro measurements of TCDD levels in 2,4,5-T were carried out in both the years before and after 1968. These measurements suggest that the 40 to 50 ppm figures cited in the TSD summary are not realistic (assuming the Nitro analytical method is reasonably accurate). Nitro measurements never exceeded 28 ppm, and TCDD values typically averaged 12 ppm or less. The attached notebook pages comprise all of the Nitro analytical data I could find on TCDD analyses. I have included some comments on these copies in parenthesis. In particular, I suspect the numbers reported in Marty Wilson's notebook may be questionable. The numbers are quite low and certain samples run by both St. Louis and Marty do not agree. The St. Louis numbers cited in Marty's notebook were probably generated by Bill Udell (currently with Monsanto Agricultural Division). It should be noted that Phil Balderson employed a slightly different method from Marty Wilson for TCDD analyses, and Balderson's method was based on a method obtained from Dow.

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022902

Another possible source of TCDD analytical data would be Bill Udell. Apparently, he ran TCDD analyses for Corporate Research around the time period in question. The TSD summary might be based on numbers generated by Udell. It should be noted that lots of 2,4,5-T produced in 1968 should begin with the code letters "NK" and this can be used to determine if analytical results correspond to material made in 1968.

Finally, the report in the 1969 TSD summary was probably generated by R. L. Dillon, Jr. and/or J. C. Strum. These engineers were handling process changes, etc. at that time. I questioned Dillon (currently superintendent of MHA operations at Nitro) and he said he did not recall the source of the numbers. Strum is no longer working for Monsanto. It is quite possible the numbers they reported are erroneous.

Terry Parker

R. T. Parker

sa

Attachment

(Bolderson NO 6)

'48)

DIOXANE IN T

7/18/66

PRODUCTION REQUESTED THAT WE RUN SAMPLES OF FINISHED T FROM DECEMBER '65 THROUGH PRESENT PRODUCTION TO DETERMINE IF THIS MATERIAL IS BUILDING UP.

RUN ON F&M 720 @ 250°C, INJECTOR 330°C, BLOCK 320°C, 2 METER 3% QF-1 ON AW-HMDS CHROMOSORB G

DIOXANE @ 2.6 min RETENTION

WEIGH OUT 10 grams 2,4,5-T ADD 10 ml $CHCl_3$ + SHAKE 10 MINUTES. FILTER AND WASH THE FILTER CAKE WITH 5 ml. $CHCl_3$. TRANSFER FILTRATE TO A VIAL AND ADD 5 ml 2 M NaOH. SHAKE 10 min. DILUTE TO 25 ml WITH WATER AND CENTRIFUGE. SEPARATE OFF THE ORGANIC LAYER AND EVAPORATE DOWN TO 2 ml. INJECT 40 µl INTO THE INSTRUMENT @ AN ATTENUATION OF X1.

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C22904

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Note: This is the first Nitro attempt to run TCDD analyses per Bolderson.

RAP 4/12/82

NE 12 - 026	12 ppm	
NH 01 - 024	6 ppm	
NH 02 - 036	10 ppm	
NH 03 - 054	7.5 ppm	
NH 04 - 004	8 ppm	
NH 04 - 028	3.5 ppm	
NH 05 - 029	12 ppm	
NH 05 - 033	11 ppm	
NH 06 - 020	13 ppm	
NH 06 - 067	17 ppm	
NH 07 - 016	21 ppm	
NH 07 - 038	28 ppm	
NH 07 - 052	21 ppm.	
NH 08 - 016	5 ppm	8/12/66
NH 08 - 024	11 ppm	8/12/66

7/21/66

7/21/66

177

T.O.D. IN 2,4,5-T

1/23/67

PROCEDURE SAME AS ON PAGES 78 - 79.

BATCH	R.P.M.	T.O.D.
NH09-011	3	
NH09-051	4	
NH10-022	12.5	
NH10-082	18	
NH-11-010	5	
NH11-060	3	
NH12-009	5	
NH12-051	7	
NI01-004	4	
NI01-021	3	

(Calderon NB 6)

100

TOO IN T ANALYSES

2/17/67

PROCEDURE SAME AS ON PAGES 78-79. CALCULATION

$$\frac{\text{PEAK HEIGHT SAMPLE} \times 15 \times 2 \times 1000}{\text{PEAK HT. ST.}} = \text{ppm}$$

NH09-085	8 ppm
NH09-100	12
NI02-001	nil
NI02-010	nil
NI02-020	trace
NI02-030	9
NI02-040	1
TCP ~~B#4~~ 2/16/67	5

TCP — T — TDD ANALYSES

NEED METHODS TO RUN ALL THESE MATERIALS ON ONE INSTRUMENT. QF-1 ON CHROMOSORB G WORKS WELL WITH PROGRAMMING FOR 2,4,5-T ALID. THE SAME COLUMN WORKS WELL FOR TDD @ 250° ISO. TCP HOWEVER TAILS AND AS THE COLUMN AGES IT TAILS BADLY.

SILYLATION OF THE TCP WAS TRIED BUT ANISOLE IS ONLY SLIGHTLY SEPARATED FROM THE TCP.

(Balderson NB # 7)

4/3/67

41

TDD IN 245-T

10 GRAM SAMPLE ADD 10 ml $CHCl_3$, SHAKE 15 min. FILTER + WASH 5 ml $CHCl_3$. ADD 5 ml 2 M NaOH TO FILTRATE + SHAKE 10 min. CENTRIFUGE WITHDRAW BOTTOM LAYER. EVAPORATE DOWN TO 2 ml. RUN ON 2 METER SF-1 @ 250°C + 120 ml/min He. 40 µl ON NX FILAMENTS

LOT	TDD
03 -001	1 ppm
010	3
020	14
030	1
040	7
045	8
050	15
060	15

$$\frac{\text{PK. HEIGHT SAMPLE} \times 15 \times 2}{\text{PK. HT. STD}} = \text{ppm TDD}$$

C32909

4

(Goldberson NB # 7)

2,4,5-T - ANALYTICAL METHODS

4/17/67

ATTEMPTING TO FIND V.P.C COLUMNS SO AS TO RUN 2,4,5-T ACID, TLP & TDD ON ONE INSTRUMENT.

FFAP ON AW-DMCS CHROMOSORB G TRIED APPEARED TO WORK WELL AT FIRST BUT AFTER SEVERAL SAMPLES COULD NO LONGER OBTAIN T-ESTER PEAK. HMDS HELPED SOMEWHAT FOR ONE SAMPLE BUT DID NOT LAST.

4/20/67

3% SE-54 ON AW-DMCS CHROMOSORB G. WORKS OR SEPARATES WELL BUT THE PHENOLS TAIL TOO BADLY FOR A GOOD ANALYSIS.

PROGRAMMED 100° → 240°C @ 7.5°/min

THEN TRIED ADDING B.S.A. TO ACIDIFIED EXTRACTED N2 TCP. GOOD CURVES & GOOD SEPARATIONS OBTAINED UNDER THE SAME CONDITIONS.

TCB DCP TCA TCP METHOXY DCP.

THE BSA WAS THEN TRIED WITH T & BIS ACIDS. THE T ACID IS SILYLATED EASILY BUT THE BIS DID NOT SILYLATE IN SHF EVEN AFTER HEATING AT. 70°C FOR ½ HOUR. ALSO THERE WERE NOT APPARENT PEAKS FOR THE METHOXY DICHLORO PHENOXY ACETIC ACIDS.

TRIED THIS PROCEDURE AGAIN LATER AFTER MANY OTHER TYPES OF SAMPLES HAD BEEN RUN THROUGH. TCB & DCP PEAKS APPARENTLY HAVE GONE TOGETHER.

(Peterson NB # 7) 17

4/27/67

TDO LEVELS

RAW ON 720 WX @ 250° ON

IF-1

LOT	TDO
HJ04-001	10 ppm
4-005	10
4-010	15
4-015	8
4-020	7
4-030	18
4-040	20
4-050	12

(Balderson NB # 8)

56/

TDD IN N2TCP

1/31/69 OBJECTIVE: DETERMINE THE TDD LEVEL IN N2TCP FROM THE PLANT 2/4/69

EQUIPMENT: F&M 720 W-2
FILAMENTS 2 METER QF-1-6500
ON GAS CHROM Z RUN @ 220°C

PROCEDURE: WEIGH ~~OUT~~ 10 GRAMS
OF N2TCP INTO A 2 OZ BOTTLE.
ADD 10 m/ $CHCl_3$ AND 2-3
m/s. H_2O. ACIDIFY SLOWLY AND
WITH SHAKING TO. a pH OF 1-2
SHAKE FOR 5-10 MINUTES.
ADD 5 m/ 2N (OR 25%) NaOH
AND AGAIN SHAKE FOR 5-10 MIN.
LET STAND UNTIL FULLY SEPARATED.
WITHDRAW THE BOTTOM $CHCl_3$ LAYER
AND PLACE IN A 4 DRAM VIAL
EVAPORATE DOWN TO 2 MILLILITERS.
WITHDRAW 40 µl AND INJECT
MEASURE PEAK HEIGHT AND CALCULATE
PPM TDD.

STD. TK HTS. 57 mm, 60 mm, & 66 mm (3 RUNS)
B# 149 NIL
B# 154 NIL

M. Wilson
2-21-69

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C32913

27)

(Balderson NB #10)

TDD STANDARD

3/2/70 OBJECTIVE: PREPARE A TDD STANDARD IN CHLOROFORM FROM PURE SOLID SUPPLIED BY DOW THROUGH Ag RESEARCH

6.60 mg

6.26 mg

0.34 mg. DILUTED TO 25 ml

0.0136 mg/ml

OR 13.6 µg/ml

STD APPEARS CONTAMINATED

7.17

6.35

82 mg DIL TO 25 ml

0.0328 mg/ml

2.38

6.96

0.42 mg dil TO 25 ml

0.0168 mg/ml

Patty Wilson

540

C22914

TOD ANALYSES

UOHRD 3/6/70

LID

EXTRACTION DONE BY SHAKING 10 GRAMS T WITH 20 ml $CHCl_3$ FOR 1 HOUR. THE SAMPLE IS THEN CENTRIFUGED AND THE CHLOROFORM WITHDRAWN. 25 ml 1 N NaOH ADDED AND THE SAMPLE IS SHAKEN FOR 15 MINUTES. CENTRIFUGED AND THE BOTTOM $CHCl_3$ LAYER WITHDRAWN NOTING VOLUME. THE $CHCl_3$ LAYER IS EVAPORATED TO DRYNESS AND 5% OF THE AMOUNT OF $CHCl_3$ LAYER ADDED BACK RUN ON 9FT OV-1 ON 6 @ 190°C FLAME. 1 µl X20. ALL STEPS RUN IN GLASS NO PLASTIC SHAKING DONE IN GLASS STOPPERED BOTTLE. GLASS INJECTION INSERT

		USING BENZENE
NL07-024	12 ppm	1.6 ppm
NL07-028	1.7 ppm	1.5 ppm
NL07-031	1.3 ppm	
NL08-003	1.4 ppm	1.7 ppm
NL08-004	1.8 ppm	
NL08-006	1.4 ppm	1.6 ppm
NL08-012	1.0 ppm	
NL08-018	3.0 ppm	
NL07-018	2.7 ppm	
NL07-020	1.6 ppm	

Marty Wilson
5470

C02915

291

(Balderson NB #10)

NL08-020	2.7-2.5 ppm	
NL08-023	2.8 ppm	3.8% BIS
NL08-007	2.7 ppm	
NL08-026	1.0 ppm	
NL07-009	0.8 ✓	
NL07-011	0.9 ✓	
NL08-019	1.4	
NL08-025	2.2	
NL07-019	1.5	3.3% BIS
NL07-012	0.7-0.9-0.7 ✓	
NL06-026	1.2	
NL06-030	1.1	
NL06-012	1.6	
NL06-011	2.1	4.3% BIS
NL06-003	1.6	
NL06-007	1.8	
NL06-022	2.2	
NL-05-010	0.8	
NL-04-013	1.6	
NL-07-013 ✓	1.1	3.8% BIS
NL-06-020	0.8	
NL-04-019	1.4	
NL-05-005	1.8	
NL-08-023	2.9	
NL-08-027	1.6	
NL-08-007	2.0	
NL-07-013 ✓	0.9 ✓	3.8% BIS

Marty Wilson 5470

(Balderson NB #10) (3d

	NL07-023	0.7 ppm	10.6% Bis"
% Bis	NL07-016	9.7 ppm	~~CHECK 7 Bis~~
	NL07-015	APPROX 22.0 ppm	11.5% Bis
	NL08-028	1.7	
	~~NL06-020~~	~~0.1 ppm~~	
	NL06-015 ✓	1.1 ppm	3.9% Bis-T
	NL06-015	1.4 ppm	
	NL07-021	1.5 ppm	
315	NL08-021	1.4 ppm	
	NL06-013	.9 ppm	
	NL06-028	.3 ppm	
	NL05-009	1.0 ppm	
	NL06-023	.7 ppm	
	NL05-032	.5 ppm	
	NL08-033	1.3 ppm	
	NL08-030	1.1 ppm	
	NL08-031	1.3 ppm	
	NL06-038	0.5 ppm	
	NL08-029	1.1 ppm	
	NL03-007	4.4 ppm	
	NL04-024	.6 ppm	
	NL05-013	1.0 ppm	
	NL05-014	0.7 ppm	
	NL05-036	0.8 ppm	
	NL06-006	0.5 ppm	
	NL06-034	0.9 ppm	
70	NL06-020	0.8 ppm	

Marty Wilson 5-4-10

31

(Balderson NB # 10)

NL06-024	0.8 ppm
NL07-~~027~~-029 (CURT)	1.2 ppm
NL05-003	0.9 ppm
DOW	0.5 ppm
NL01-005	10 ppm
NL01-006	@ 90 ppm
NL08-022	2.6 ppm
mm-120639	0.5 ppm
NL07-010	1.1 ppm
NL08-034	38 ppm
mm-120619	0.6 ppm
NL07-030	2.8 ppm
NL06-014	2.1 ppm
NL08-005	2.4 ppm

Marty Wilson
5470

C22918

(Balderson NB 70-1 T) 13

TDD

10/30/70

INSTRUMENT 5754A FLAME. 2 FT 3% OV-1 ON ABW - DMCS CHROMOSORB G COLUMNS. COLUMN TEMPERATURE 200°C, INJ 260°C, FLAME DETECTO 265°C. AIR FLOW ROTAMETER 3.5 -4.0, HELIUM ROTAMETER 2.9 TOP OF BALL, HYDROGEN FOR MAXIMUM SENSITIVITY @ 2.4 ROTAMETER (TOP OF BALL, RANGE 10 ATTEN X2 PEAK HT. 5 μl OF 16.8 μg/m TDD IN $CHCl_3$ GIVES PK HT OF ~ 25 CHART DIVISIO (2.5 INCHES)

C22919

(Balderson NB 70-1T) [illegible]

TDD CONTAMINATION LEVEL IN BLDG

11/4/70

OBJECTIVE: DETERMINE AS WELL AS POSSIBLE THE TDD LEVEL ON VARIOUS PIECES OF EQUIPMENT + IN THE BUILDING ITSELF IN BLDG 92. PROCEDURE USED WAS TO MARK OFF AN AREA GENERALLY 1 SQ FOOT IN AREA AND WIPE WITH BENZENE SOAKED "KIM-WIPES" 10 TIMES. THE "KIM WIPES" THEN EXTRACTED WITH ∅ IN THE LAB TO RUN FOR TDD LEVELS. THE BENZENE EXTRACTED WAS WASHED WITH DILUTE NaOH, ~~AND~~ SEPARATE[D] + FILTERED. BENZENE EVAPORATED OFF

#1 EMICO DOOR — 40 μg/sq ft max (TOO MUCH MAT'L TO POS[ITIVELY] I[D])

#2 2nd LEVEL GRATING 0.5 (1.5) μg/sq ft max (NO DETECT[ABLE] @ LOWER TEMP)

#3 TCP W/T EXT 14 μg/sq ft max (NO DE[TECTABLE] LOWER [TEMP])

#4 ACIDIFIER INT 13 μg/sq ft max (9 μg/[sq ft] at LOWER TE[MP])

#5 3d LEVEL STEEL (VENT) 11 μg/sq ft max

RUN @ lower temp to give maximum separation

#6 PAN FILTER (2 LEAVES) TRACE

#7 PAN FILTER HOPPER (DIRTY WITH T) 34 μg/sq ft

#8 AUTOCLAVE HORIZ TC NOT DETECTABLE

#9 STILL VERT SIDE NONE DETECTABLE

#10 1st LEVEL VERT STEEL TOO MUCH CONTAMINATION CAN NOT TELL WHAT IS PRES[ENT]

C22920

6/

TDD FROM PLANT.

11/20/70 THESE SAMPLES TAKEN AFTER CLEANING IS ESSENTIALLY COMPLETE. THESE WILL BE RUN BY A MODIFIED PROCEDURE TO REMOVE MOST OF THE IMPURITIES AWAY FROM THE TDD. THE KIM-WIPES ARE PLACED IN A FLAT BOTTOM FLASK. 20 ml IN H2SO4 AND 30 ml H_2O ADDED. AN AIR CONDENSER IS ATTACHED AND THE SAMPLE HEATED TO REFLUX FOR ~2 1/2 HOURS. 20 ml TOULENE ADDED & REFLUXED FOR ANOTHER HOUR. THE MIXTURE IS THEN TRANSFERRED HOT TO A SEP FUNNEL AND THE WATER LAYER DRAWN OFF & DISCARDED. THE TOULENE LAYER IS THEN WASHED TWICE WITH 25 ml H_2O & IT WITH 10 ml CONC H_2SO_4. THE TOULENE IS THEN EVAP TO DRYNESS SAMPLE DISSOLVED IN 10 ml PET ETHER (HEAT) & TRANSFERRED TO A VIAL. EVAP DOWN TO 1 ml & RUN

(Balderson NB 70-1T) 17

SAMPLE No	POINT	TDD
1	BRICK FLOOR GROUND LEVEL	NIL
2	PAN VERT. SIDE 2nd EXTR.	NIL
3.	EMICO FILTER DOOR	NIL
4	HORIZ TOP CARRIER SCREW FEED	NIL
5	PAN VERTICAL SIDE 1st EXTR	0.1 - 0.2 μg
6	TOP #1 REACTOR	NIL
7	SIDE OF ELEVATOR REWORK CHUTE	NIL
8	GRATING 3rd LEVEL	2.5 μg/sq ft
9	VERT STEEL EXTR FEED TANK	0.7 μg
10	VERT STEEL EXTR FILTER FD TK	< 1.0 μg

(Marty Wilson Notebook)

2-24-69
2-25-69

TDD Analysis

Object: To analyze T samples for percent TDD. Samples had been analyzed in St. Louis and TDD reported in the following samples:

#	149	TDD 4.3	Total Phenols 20.9	
	150	14.	21.5	A
	151	11.5	20.64	B
	152	3.1	22.3	B
	154	2.6	30.7	A
	155	2.3	30.5	A
	157	6.5	26.2	B

Procedure:

(1) Five gram sample was weighed into small vial. H_2O added until sample was dissolved (all samples were liquid) One ml of C_6H_6 was added and mix two was shaken for 10 min. The same sample was duplicated except one ml of $CHCl_3$ was used.

(2) Step one was repeated with a one hour hold on automatic shaker.

(3) Step one repeated with testing of sample.

P Bellerjeau
3/11/69

C22923

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Note - this may be 1968 product ? due to early run date in 69. Bill Udell & Pinkable - Ran St Louis samples RPP 4/12/82

Instrument Settings:

F+M 720
Column Temp 250°C
Inj. Temp. 250°C
Det. Temp. 300°C
Flow 75 ml/min
Vacuum on exit port
175 ma
att. 1X
40 μl size sample

Sample	Solvent	Shake Time	TDD
# 148	C_6H_6	10 min	Nil
# 148	$CHCl_3$	10 min.	Nil
# 149	C_6H_6	10 min	Nil
# 149	$CHCl_3$	10 min	Nil
# 151	C_6H_6	1 Hour	Nil
# 151	$CHCl_3$	1 Hour	Nil
# 151	C_6H_6	10 MIN	Nil
# 151	$CHCl_3$	30 min	Nil

Standard solution produced a TDD peak.

Possible problem in extraction

↑

Marty's Method May Be No Good ?

R Balfersen
3/11/69

C22924

(Marty Wilson Notebook

3-18-19-69 TDD Analysis

Instrument Conditions
5750 A
Flame
265°C column
Flame Det. 295°C
Inj Port 310°C
X1 10^2

Settings
Air # 4 B #
H_2 A # 3½ B #
Helium A # 3½ B #
OV-17 column

Procedure #1
(1) 5 gram sample; 3-4 ml H_2O
Shake, add 1 ml $CHCl_3$
Shake 10 min.
(2) Inject sol from bottom layer

Sample	p.p.m.
293	~~#1~~ 0.5 ppm
240	~~#1~~ 0.6 ppm
239	0.6 ppm
248	0.5 ppm
296	0.3 ppm
300	0.4 ppm
303	0.5 ppm

Std peak height = 14

Published
4/21/69

Procedure #11

Take a 10 gram sample, add water to dissolve then add 5 ml CCl_4 and shake 15 - 20 min Put CCl_4 layer in small vial via a hypodermic, then evaporate to 1 ml. Do not go to dryness and add back. Inject 5ul size sample into Chromatograph. Measure peak height and calculate ppm.

3-21-69

Instrument Conditions the same as on page 6.

Sample	TDD
#1	0.4 ppm
264	0.6 ppm
281	0.4 ppm
283	0.4 ppm
264	0.8 ppm
247	1.1 ppm

4-16-69

TOD Analysis

Instrument conditions: Refer to page 6 and procedure Book #2

Std peak height = 151.5 mm. Std = 1 µl

Calculations:

$$\text{ppm TOD} = \frac{(\text{peak height} - \text{peak base})(\text{mg TOD/ml std})(1\text{ml})(10^6)}{(\mu\text{l of std.})(\text{sample wt in g})(3)}$$

$$\text{Factor} = (0.0652)(\text{peak height of unknown})$$

Sample	Height	ppm TOD
341	3.5	0.2
276	1	0.1
342	2.75	0.2
272	3.0	0.2
394	3	0.2
252	1.75	0.1
261	1.75	0.1
395	3.5	0.2
396	3	0.2
242	3.15	0.3
250	4	0.3

(Marty Wil's Notebook

Analysis of Solvent TCE for TDD

Objective: To analyze TCE for % TDD to confirm low level TDD. Question was raised when contract lab reported 8 ppm TDD in TCE acid.

Procedure

① Five gram sample in small vial; add H_2O (several ml to dissolve sample) shake well.

② Add 1 ml $CHCl_3$ and shake for 10 mins. Let separate and inject Gel from $CHCl_3$ layer.

③ Standard solution - Gel size sample for CC

Sample	TDD in PPM
477	0.6
479	ND
439	0.2
490	0.5
495	0.5
510	0.5
517	0.2

6/13/67