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December 12, 1985

Project No. 850037

Dr. Michael Champion
Riverdale Chemical Company
220 East 17th Street
Chicago Heights, Illinois 60411

Report
Sampling and Analysis
Sanitary Sewer Effluent
Riverdale Chemical Company

Dear Dr. Champion:

This report summarizes the findings of analytical testing conducted on the sanitary sewer effluent at the Riverdale plant.

## Background

Riverdale Chemical Company (Riverdale) operates a pesticide formulation facility in Chicago Heights, Illinois. Non-contact cooling water from its formulation processes are discharged directly to the sanitary sewer which is owned and maintained by the Thorn Creek Sewerage District.

Due to the recent controversy over the presence of dioxin on Riverdale's property, it was decided that the effluent discharging from the Riverdale plant be sampled for 2,3,7,8-TCDD. Riverdale voluntarily took the lead on this effort, and requested IT Corporation (IT) to carry out the sampling and analysis.

## Sampling and Analysis

On November 20, 1985, an IT representative collected an effluent sample from a manhole located on the east side of the main manufacturing building. Dr. Michael Champion and a representative of Thorn Creek Sewerage District were present to observe the sampling effort.

The discharge in the sewer was observed to be approximately four inches deep. The sample was collected with a stainless steel beaker attached to the end of a wooden pole. The beaker was previously cleaned with a solution containing trisodium phosphate, and rinsed in pesticide-grade methanol, followed by purified water, and allowed to air dry. The beaker was placed in a sealed plastic bag and transported to the site.

The sample was transferred directly to two, one-gallon, amber glass bottles with teflon-lined lids. Equal volumes of sample were split between each

container to ensure collection of a representative sample. The sample was given the code RIV-EF-01-1. The containers were decontaminated, packed in an iced cooler and shipped to IT's Analytical Laboratory in Knoxville, Tennessee. The laboratory was requested to analyze for 2,3,7,8-TCDD and to obtain the lowest possible detection limit. U.S. EPA contract lab protocols were requested.

## Results

The results of analysis of the effluent indicate the presence of 2,3,7,8-TCDD at a concentration of 2.1 parts per trillion (ppt). This value was obtained from analyzing approximately 4000 ml of sample. The instrument detection limit was 0.31 ppt. An additional analysis conducted on the second gallon of the sample (3855 ml) showed a concentration of 2.4 ppt with a detection limit of 0.84 ppt. The precision of the two results is within 13%, well within the EPA required range of 50%.

Because of the unexpected presence of 2,3,7,8-TCDD and the ultra-low detection limits required, I requested an internal QA review of the procedures by Dr. Paul Mills of our Knoxville office as an additional check on the accuracy of these values. Dr. Mills is considered to be an expert in QA review procedures. Dr. Mills assured me that proper protocols and procedures were followed and that he is confident of the results obtained.

Along with this report, I am including copies of the reports submitted by our lab.

## Discussion

Due to its hydrophobic nature, 2,3,7,8-TCDD has a very low solubility in water. Because it has been some years since Riverdale has used dioxin contaminated products (2,4,5-T) in its formulations, it comes as something of a surprise to detect 2,3,7,8-TCDD in the plant effluent. The most plausible explanations are residual contamination in the sewer line from past discharges. This would most likely be present in sediments in traps within the sewer itself. The 2,3,7,8-TCDD is probably adsorbed onto particulates in these sediments. The sediments may be acting as a continuing source of dioxin contamination even though dioxin contaminated products have not been used for a number of years.

## Recommendations

IT Corporation recommends additional sampling to determine the possible sources of the contamination, and that consideration be given to cleaning the sewer line. We are prepared to assist Riverdale in this endeavor, having had considerable experience in similar problems.

I hope this report meets your needs at this time. If you have any questions regarding this report or require further documentation of the analytical results, please do not hesitate to contact me.

Sincerely,

Mark L. Hinchey
Project Manager

MLH/re

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Enclosures

TABLE 1
INITIAL CALIBRATION SUMMARY

| Date | Instr. ID | Sol. ID | Measured RF Native | Measured RF Surrogate | Mean RF Used Native | Mean RF Used Surrogate |
|---|---|---|---|---|---|---|
| 8/29/85 | 4500 | CC1 | 0.494 | 0.868 | 0.483 | 0.810 |
| 8/29/85 | 4500 | CC1 | 0.505 | 0.844 | 0.483 | 0.810 |
| 8/29/85 | 4500 | CC1 | 0.507 | 0.778 | 0.483 | 0.810 |
| 8/29/85 | 4500 | CC2 | 0.482 | 0.803 | 0.483 | 0.810 |
| 8/29/85 | 4500 | CC2 | 0.469 | 0.807 | 0.483 | 0.810 |
| 8/29/85 | 4500 | CC2 | 0.477 | 0.813 | 0.483 | 0.810 |
| /29/85 | 4500 | CC3 | 0.446 | 0.774 | 0.483 | 0.810 |
| 8/29/85 | 4500 | CC3 | 0.476 | 0.807 | 0.483 | 0.810 |
| 8/29/85 | 4500 | CC3 | 0.482 | 0.798 | 0.483 | 0.810 |
| 8/29/85 | 4500 | CC4 | 0.482 | -- | 0.483 | 0.810 |
| 8/29/85 | 4500 | CC4 | 0.495 | -- | 0.483 | 0.810 |
| 8/29/85 | 4500 | CC4 | 0.495 | -- | 0.483 | 0.810 |
| 8/29/85 | 4500 | CC5 | 0.474 | -- | 0.483 | 0.810 |
| 8/29/85 | 4500 | CC5 | 0.469 | -- | 0.483 | 0.810 |
| 29/85 | 4500 | CC5 | 0.478 | -- | 0.483 | 0.810 |
| | | | $\bar{x}$ = 0.483 | 0.810 | | |
| | | | %RSD = 2.7% | 3.7% | | |

Solution ID Codes:

CC1 = Concentration calibration solution #1 = 0.2 ng/µl
CC2 = Concentration calibration solution #2 = 1.0 ng/µl
CC3 = Concentration calibration solution #3 = 5.0 ng/µl
CC4 = Concentration calibration solution #4 = 20.0 ng/µl
CC5 = Concentration calibration solution #5 = 40.0 ng/µl

TABLE 2

CONTINUING CALIBRATION SUMMARY

| Date | Instr. ID | Sol. ID | Measured RF | | Mean RF Used | | TCDD Isomer Resolution Percent Valley (Applies for PC only) |
|---|---|---|---|---|---|---|---|
| | | | Native | Surrogate | Native | Surrogate | |
| 11/22/85 | 4500 | PC | -- | -- | -- | -- | 8% |
| 11/22/85 | 4500 | CC2 | 0.486 | 0.774 | 0.483 | 0.810 | -- |
| 11/22/85 | 4500 | PC | -- | -- | -- | -- | 6% |

Solution ID Codes:

PC = Performance check solution
CC1 = Concentration calibration solution #1 = 0.2 ng/µl
CC2 = Concentration calibration solution #2 = 1.0 ng/µl
CC3 = Concnetration calibration solution #3 = 5.0 ng/µl
CC4 = Concentration calibration solution #4 = 20.0 ng/µl
CC5 = Concentration calibration solution #5 = 40.0 ng/µl

Lab: IIAS-Knoxville
Case No.: Riverdale Chemical
Batch/Shipment No.: 85 003/.12.2

# TABLE 3

Report Date: 12/03/85
Column: SP2331

| Sample Number | Extra Cleanup | Aliquot Wet Wt. (ml) | PPT TCDD Meas. | PPT TCDD DL | GC/MS Analysis Instr. ID | GC/MS Analysis Date | GC/MS Analysis Time | Rel. Ion Abund. 320/322 | Rel. Ion Abund. 332/334 | PPB *Surrogate Meas. | PPB *Surrogate % Acc'y | Relative Ion Abundance 320 | 322 | 257 | 328[a] | 332 | 334 | (IS % Rec Comment |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| RIV-EF-01-1 | No | 3860 | 2.1 | | 4500 | 11/22/85 | 14:46 | 0.80 | 0.83 | 159 | 80 | 120625 | 188307 | 89888 | 501846 | 1762780 | 2129590 | 72 |
| RB | No | 2000 | ND | 0.31 | 4500 | 11/22/85 | 13:55 | | 0.82 | 163 | 82 | | | | 495287 | 1699470 | 2042630 | 66 |

[a]Corrected for contribution by native TCDD; 0.91 of m/z 322 subtracted.

RB - Reagent Blank
P - Partial Scan/Confirmatory Analysis
N - Native TCDD Spike
D - Duplicate/Fortified Field Blank
FB - Field Blank
ND - Not Detected
DL - Detection Limited

*pg/µl final extract (200 pg/µl X 50 µl extract = 10 ng spike on 10g soil or 1 ppb spike)

D3H6:DC-1-H5

RIVERDALE CHEMICAL
CONFIRMATION REPORT FOR WATER SAMPLE

## Summary of Method

One water sample was received on 11/21/85 for the analysis of 2,3,7,8-TCDD. The sample and a blank were spiked prior to extraction with an internal standard/surrogate solution containing 50 ng $^{13}C$-2,3,7,8-TCDD and 10 ng $^{37}Cl$-2,3,7,8-TCDD. The samples were extracted and cleaned up using the EPA reference method 613. Extracts were analyzed by GC/MS operating in the selected ion monitoring mode for enhanced sensitivity.

## Sample Preparation

Approximately 3855 ml of the sample and 1000 ml distilled water (the blank) were transferred into individual separatory funnels. The samples were spiked with the internal standard/surrogate mixture, and then triple-extracted with $CH_2Cl_2$. The resulting extracts were filtered into a KD flask and the volume reduced to approximately 10 ml.

## Sample Cleanup

To aid in the removal of chemical interferences, the sample and blank were first treated using separatory funnel techniques found in Option C of "The Determination of 2,3,7,8-TCDD in Soil and Sediment," September 1983 revision. Extracts were washed with 20% KOH and distilled water followed by three concentrated $H_2SO_4$ washes. Further cleanup consisted of two steps of column chromatography. The first step involved a neutral alumina column while the second was a dual column system utilizing acid-modified silica gel followed by neutral alumina. Final extracts were concentrated to near dryness and raised to 50 µl with a solution containing 11 ng $^{13}C$-2,3,7,8-TCDF.

## GC/MS Analysis

The sample extracts were analyzed using HRGC/LRMS scanning in the selected ion monitoring mode for enhanced sensitivity. The column used for this isomer specific analysis was a 60 m SP2331 fused silica column. Before acquisition of the samples, a seven isomer performance mixture

containing the six most closely eluting TCDD isomers was run. In addition, a five point calibration plot was run in triplicate. The shift standard, analyzed on the same day as the samples, produced a response factor within 10% of the fifteen point. Percent recovery is reported by comparing $^{13}C$-TCDD to $^{13}C$-TCDF. Accuracy of the method is obtained by the recovery of $^{37}Cl$-TCDD versus $^{13}C$-TCDD.

GC/MS Results

The results, shown in Table 1, are reported in ppt. A detection limit is calculated from 2.5 times the signal in the area of the elution of $^{13}C$-TCDD whenever a sample contains no detectable TCDD.

Table 2 lists the results of the QA/QC samples. In all cases, precision and accuracy are within the limits established for acceptance of dioxin/debenzofuran data.

TABLE 1. RIVERDALE CHEMICAL -- 2,3,7,8-TCDD RESULTS

| Sample ID Client # | IT # | Date | Time | 2,3,7,8-TCDD (ppt) | Surrogate (% Accuracy) | Internal Standard (% Recovery) |
|---|---|---|---|---|---|---|
| RIV-EF-01-1 | J2990R | 12/06/85 | 19:04 | 2.4 | 80% | 73% |
| RB | TBlk 520 | 12/09/85 | 16:26 | ND(0.84) | 76% | 85% |

## TABLE 2. QA/QC REPORT

Surrogate Percent Accuracy

Number of Data Points = 4

Mean Percent Accuracy = 80

Range = 76-82%

EPA Range = 60-140%

Precision of Duplicates

Orig. Value (b) = 2.1

Dup. Value (a) = 2.4

$$\text{Precision} = \frac{a-b}{\frac{a+b}{2}} \times 100\% = 13\%$$

EPA Range = $\pm$ 50%