

The Dow Chemical Company – Flawed Science

Volume 3 Tittabawassee River Sediment : Dioxin/Furan Concentration Variability Study

On April 13, 2005, employees of the DEQ and EPA observed a Dow contractor sampling portions of the Tittabawassee River in possible violation of Dow's Operating License for the hazardous waste facilities at the company's Midland plant.

The DEQ indicated that the Operating License required that the company notify the DEQ and obtain prior approval of all environmental testing carried out beyond the facility boundary of the Midland plant. It was determined that the company had conducted similar unapproved testing in 2003 and 2004. The company does not agree with the DEQ's interpretation of the conditions of the Operating License.

The DEQ requested copies of all testing data and the company provided written copies of six (6) studies plus additional information.

One of the unapproved studies was Tittabawassee River Sediment : Dioxin/Furan Concentration Variability, March 2005.

The study has several defects that significantly limit the value of the study in defining the extent of dioxin contamination in the sediments and flood plain of the river. Defects are as follows:

1. Neither the DEQ nor the EPA were provided with advance notification of the sampling and were not present to verify that sampling was carried out according to specified protocols.
2. Neither the DEQ nor the EPA were provided with "split" samples and the accuracy of the analytical testing can not be verified.
3. The study was designed to determine the concentrations of dioxins in the uppermost 4 inches of underwater river sediments in the Tittabawassee River from Saginaw to below Dow's Midland plant. The 0.0 to 4 inch portion of the sediment core was too small to collect field duplicates and to carry out dioxin "spiking" to verify analytical protocol requirements.
4. The Nov/Dec 2003 sampling failed to obtain "equipment blanks" required to verify that sampling equipment was not contaminated with dioxins.
5. Sample THT-02245 was obtained through the use of a sample tube that was different than all other sample tubes used in the 2003/2004 sampling.
6. Sample THT-02244 (water depth = 4.0 ft) taken to replace incorrectly obtained sample THT-02245 (water depth = 5.5 ft) was taken at a different location as shown by reported water depth information.

A significant portion of the study was related to determining the variability of dioxin levels in the river location associated with sample THT-02245 (9,312 ppt-TEQ) taken in Nov. 2003 and sample THT-02244 (265 ppt-TEQ) taken in one month later in Dec 2003. The variability portion of the study was defective in the following areas:

- a. The study continually referred to the samples taken in 2004 as the “Summer 2004 sampling event”. The 2004 samples were actually taken in March, 2004 when the river was swollen with springtime flooding.
- b. The study failed to address the impact that repeated increases in river flows that occurred between the Nov. 2003 and Dec. 2003 sampling may have had in decreasing dioxin levels in the topmost sediments. Dioxin analysis in this study was limited to the top 4 inches of river sediment that could have been significantly disturbed by the river flooding that occurred between the November and December 2003 sample dates.
- c. The study failed to report that river flows (and water heights) between the Nov/Dec 2003 sampling and the March 2004 sampling were significantly different as shown in the table below. During the March 2004 time period, the river was at flood and the height of the river was approximately 10 feet higher than the Nov/Dec 2003 time period.

Table A
Tittabawassee River Flow Conditions

<u>Sample Period</u>	<u>River Flow</u> (a)	<u>River Height</u> (b)
Nov 2003	1120	~10.7 ft
Dec 2003	1170	~10.7 ft
March 2004	10,700	~21.0 ft

(a) cu.ft/sec
(b) Midland USGS station

- d. Based on the water depth information provided in the study, it is believed that 9 out of the 10 samples taken in the vicinity of THT-02244/02245 during the March 2004 sampling were taken in locations that could have been dry riverbank in the Nov/Dec 2003 time period.

The chart on the last page shows the depth of the March 2004 sampling adjusted to the depth of the river at the time of the 2003 sampling. Sampling was taken at a bend in the river that apparently was associated with a wide flat area that was exposed and dry when the river is low and flooded when the river is high.

A similar problem with sampling locations and varying water depths may be present in the samples taken in the Shields portion of the river during March 2004.

- e. The study reported that sample THT-02244 (265 ppt-TEQ) was taken on 12/04/2003 to correct a sampling error associated with THT-02245 (9,312 ppt-TEQ) taken on 11/12/2003. The study reported that these two samples became the basis for the expanded 2004 testing to better define dioxin variability.

The exact date in which THT-02244 was obtained is in question. Table B.1-1 of the study reports that the sample was actually taken on 11/12/2003. An examination of the actual sample log sheets may be able to resolve this discrepancy.

- f. One of the samples taken in Mar 2004 to verify dioxin levels in the river location associated with THT-02245 (9,312 ppt) and THT-02244 (265 ppt) is **sample THT-02781**. Neither the study nor any data table provides any information on this sample. The study does not indicate that this particular sample was discarded.

Since THT-02781 may have been taken in the vicinity of the highest levels of dioxins found in the Nov/Dec 2003 sampling, it may have provided valuable information and the reasons for its loss should be determined to improve the credibility of the study.

- g. A number of 2003 and 2004 samples were analyzed to determine vertical dioxin distribution. Table B shows the vertical dioxin analysis for samples with the highest dioxin levels at the top and bottom of the sediment core.

Table B
Vertical Dioxin Distribution

<u>Sample ID</u>	<u>Location</u>	<u>Water Depth</u>	<u>Shallow Sediment</u>		<u>Deepest Sediment</u>	
			<u>Core Segment (Ft)</u>	<u>ppt-TEQ</u>	<u>Core Segment (Ft)</u>	<u>ppt-TEQ</u>
THT-02245	(a)	5.5 ft	0 - 0.3	9,312	(1)	NA
SHL-02233	(b)	7.0 ft	0 - 0.3	18	2.9 - 3.9	19,000

(a) Vicinity Imerman Park; (b) Shields, M-46 Bridge
(1) Insufficient Sediment Core; NA = Not Analyzed

The sediment core associated with THT-02245 was only 0.83 ft (~10 inches) in total length. It is unfortunate that the Dow contractor did not obtain a sufficient sediment core that would have allowed dioxin analysis of other sediment levels at this location.

Based on the information collected during this study, approximately 68% of dioxin levels found in the first 0 to 0.3 ft. of sediments are less than 100 ppt-TEQ. Expanded dioxin analysis of the THT-02245 location may have provided dioxin contamination data that would have improved understanding of how dioxin distributes throughout the river – both horizontally and vertically. Without this additional information, it can not be determined if

dioxins levels in the Imerman Park area are greater than the 19,000 ppt-TEQ found at deeper depths in the Shields area.

The study did not provide any information as to why a substandard THT-02245 sediment core was obtained. The river flow was low. Sieve analysis of a sample taken in the immediate area of THT-02245 indicates that the 2.8 to 3.8 ft. sediments were 9% gravel and 89% sand. This sediment composition should have allowed easy penetration of the sampling tube needed to obtain a deeper sediment core.

- h. The Dow contractor that carried out the Nov/Dec 2004 sampling (THT-02245 location included) also failed to record the depth of sediment penetrated for several samples and, as a result, a percent sediment recovery could not be calculated.

Summary:

The study contains a number of significant defects, which if remain unexplained, may seriously damage the validity of the data, the study and its conclusions.

Sampling and procedural errors made by the Dow contractor during the Nov/Dec 2003 sampling event appear to be significant. The loss of additional dioxin contamination data at the location with the highest level of dioxins at a shallow sediment depth is particularly severe and troublesome.

Dow is to be commended for improving compliance with sampling procedures and record keeping during the March 2004 sampling event. The issue of sediment sampling during 2004 while the river height was 10 feet above the Nov/Dec 2003 level is unresolved.

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DOW CHEMICAL DIOXIN/FURAN TITTABAWASSEE RIVER STUDY

WATER LEVEL - MAR 2004 SAMPLING

