"Forgotten Science – Forgotten History"

As of March 9, 2005, Dow posted the following information on www.dow.com :

"History of Dioxins and Furans in the Tittabawassee River"

More than 95 percent of the "dioxin" measured by MDEQ (on a "toxicity equivalents" or TEQ basis) in the 116 samples are actually various types of furans (called congeners). Less than 2 percent are actually dioxin in the form of 2,3,7,8-TCDD.

The congener pattern with the very high percentage of furans is unlike any Dow production waste produced in the years since manufacturing process wastes have been monitored and treated. In fact, Dow's original manufacturing processes, which were used between 1897 and 1915, could be the source of a high volume and high concentration chlorinated furan waste stream.

The original chlorine cells were used to produce chlorine in long shallow troughs made of local lumber that had been tarred. Workers used carbon sticks as both cathode and anodes. These carbon sticks were impregnated with paraffin. The use of petroleum products (e.g. tar and paraffin) would have provided a source of naturally occurring furans that could have been chlorinated during the manufacturing process. (Production information summarized from Campbell & Hatton, Herbert H. Dow – Pioneer in Creative Chemistry (1951)).

When I first read these paragraphs, I felt that The Dow Chemical Company was using "industrial-strength spin" to mislead web site visitors. However, after further reflection, I now believe that neither the webmasters nor their "technical experts" have the depth of knowledge of dioxin science or dioxin history at the Midland plant to be believable advocates for the company.

The statements are all "true" but there is an inherent lack of understanding of the science that is associated with dioxin and furan contamination of the river, the company's chemical processes and the chemical waste ponds that were in operation for approximately 70 years at the Midland plant.

Dow was a recognized leader in many aspects of dioxin contamination of the environment, including dioxin/furan formation chemistries, analytical technology and environmental contamination. It is a sad commentary that the company seems to have "lost" much of the science and much of the history that formed the basis for its past expertise. Work force attrition seems to have taken a heavy toll and corporate credibility has suffered.

1.   What's True:

The general description of the early chlorine cells is accurate.

1. What's been forgotten:

The original Dow chlorine cells used carbon electrodes originally intended for use in the electric arc lamps of the day. HH Dow bought "out-of-specification" electrodes at a very low price. With time, the carbon electrodes became porous and began to leak hydrogen that led to small explosions in the cell house. The electrodes were treated with paraffin, hydrogen leakage was reduced and electrode operating life increased.

In the early years of chlorine production, prior to use in the chlorine cells, brine was first de-brominated, with bromine being removed for sale. Some, but not all, of the chlorine was removed from the de-brominated brine. The spent brine and the wastes formed in the bromine and chlorine cells were discharged to the river. In later years, the company would reclaim most of the chemicals still remaining in the spent brine. Sludge's formed in the very early chlorine cells were low in volume and only drained from the cells on a periodic basis.

In 1945, the company began to use a relatively pure layer of sodium chloride as feedstock for the chlorine cells. Hot water was pumped into the deep formation (~5,000 ft below the surface) and the dissolved salt solution was stored and then pumped into the cell houses as needed. The use of this formation significantly reduced the volume of sludge's that formed in the chlorine cells.

In time, modern construction materials replaced tarred wood and mercury cell and diaphragm cell technology replaced paraffin coated electrodes. It is believed that Midland stopped using graphite electrode technology just before World War I. The overwhelming majority of Midland chlorine production was <u>not</u> made via graphite electrodes.

In December, 1970, a new chlorine plant was started up and, in 1973, a new caustic plant. Both plants were on the west side of the river and the plants were totally self-contained with no direct discharges to the river. As the new plants started up, the old chlorine and caustic plants on the east side of the river were shutdown.

Yes, the spent brine discharged to the river was a high volume flow. However, very little of the total spent brine came from the chlorine cells. The vast majority of the spent brines were from the calcium chloride, mag-hydrate and the epsom salt plants.

In the 1920's, the company built No. 6 Brine pond to store the spent brine in order to delay river discharges until there was high river flow. No. 6 Brine pond had a working capacity of approximately 830 million gallons of brine. On average, the pond was filled six months out of the year and drained three to four months out of the year. Spent brine flowing <u>into</u> No. 6 pond averaged 3,200 gallons per minute. The pond was drained to the river at a much higher flowrate since there was no guarantee that the river would continue to flow at high flow rates over much of the year.

A number of years later, the company began the re-injection of spent brines into the underground formations from where they had been removed. After this time, No. 6 Brine pond was no longer drained to the river.

Campbell and Hatton did write the referenced book. The two commercial writers were hired by the company to compile a biography of HH Dow. It is not known if either of the co-authors had a scientific background. A much better book that provides more details on the company's chemical processes is E.N Brandt, *Growth Company: Dow Chemical's First Century,* (1997). Ned Brandt was a long time Dow employee and served for many years as Director of Dow's Public Relations Department.

The *EPA Re-assessment on TCDD (2003)* provided some information on the levels of chlorinated dioxins and furans found in Graphite Electrode Sludge from Chlorine Production (Part 1, Chapter 8). It is believed that Dow used this information as a basis for its www.dow.com report.

2. What's true:

"The use of petroleum products (e.g. tar and paraffin) would have provided a source of naturally occurring furans that could have been chlorinated during the [chlorine] manufacturing process."

2. What's Been Forgotten:

Based on EPA 2003 data, the sludge's from the chlorine cells were probably not a "high concentration" furan waste stream, at least not in comparison to the waste streams from the chlorophenol plants. The following table provides some information on typical dioxin and furan levels found in products similar to those made by Dow. The levels are parts-per-million (ppm).

Table A
Chlorinated Dioxin and Furan Levels
(ppm)

	Chlorine Sludge	**Tech. Penta**(a)	**Na Salt Penta**(b)	**Na Salt 245-TCP**(c)	**Na Salt 2,3,4,6-TeCP**(d)	**HxBz**(e)
Total 2,3,7,8-CDD	0.002	2,813	1,059	0.28	21.7	212
Total 2,3,7,8-CDF	0.34	262	126	59.8	160.5	58.3

(a) Pentachlorophenol, Technical Grade
(b) Pentachlorophenol, Sodium Salt
(c) 2,4,5-Trichlorophenol, Sodium Salt
(d) 2,3,4,6-Tetrachlorophenol, Sodium Salt
(e) Hexachlorobenzene

2,3,7,8-CDD = All chlorinated dioxins with chlorine in 2,3,7,8 positions

2,3,7,8-CDF = All chlorinated furans with chlorine in 2,3,7,8 positions

The CDD/CDF levels may not be typical of the levels found in Dow products or waste streams. However, as can be seen, in comparison to levels found in other products similar to those manufactured at the Midland plant, the CDD/CDF levels found in chlorine cell sludge are very low. Process wastes generally have a much higher levels of dioxins/furans than do saleable products. Since the sludge's were only removed from the chlorine cells on a periodic basis, annual volumes of sludge's were probably low.

The 2,3,7,8-CDD/CDF dioxins and furans include all of the 17 most toxic dioxins and furans typically measured and reported by Dow, the DEQ and other regulatory agencies.

3. What's True:

"More than 95 percent of the "dioxin" measured by MDEQ (on a "toxicity equivalents" or TEQ basis) in the 116 [Tittabawassee River] samples are actually various types of furans (called congeners)."

3. What's Been Forgotten:

It is incorrect to try to use TEQ as a basis for a "link" between the dioxins/furans found in the river to those found in chlorine cell sludge. TEQ is a methodology to compare dioxin/furan **toxicity** between environmental samples and should not be used to compare the types of dioxins/furan produced by different chemical processes

Any comparison made between environmental samples (such as the river) and dioxins/furans from a chemical process should be based on **total dioxin and furans**.

Table B is a **TEQ comparison** between dioxin/furan levels found in the river during the DEQ 2002 sampling program and the EPA 2003 data on chlorine cell sludge's. This comparison may be the basis for Dow's statement.

Table B
TEQ COMPARISON
(ppt-TEQ)

	River Sampling (ppt-TEQ)	Pct.	Chlorine Cell Sludge (ppt-TEQ	Pct.
Total 2,3,7,8-CDD	115.6	5%	26.7	0.10%
Total 2,3,7,8-CDF	2199.9	95%	30,407.60	99.90%

As can be seen, on a **TEQ Basis**, the chlorinated furans are 95% or more of both the 2002 river samples and the chlorine cell sludge (Dow's true statement). However, without a depth of dioxin science and plant history, someone might conclude that chlorine sludge is a primary source of river dioxins/furans.

However, when the more appropriate **Total Dioxin and Furan Levels** are used as a comparison basis, a much different conclusion is reached:

Table C
Total Dioxin/Furan Comparison
(ppt-total)

	2002 River Sampling (ppt-total)	Pct.	Chlorine Cell Sludge (ppt-total)	Pct.
Total 2,3,7,8-CDD	29,691	52.4%	2,210	0.6%
Total 2,3,7,8-CDF	26,952	47.6%	341,700	99.4%

On a **total dioxin and furan basis**, the DEQ sampling indicated that the levels of dioxins and levels of furans in the river are approximately the same, with slightly more dioxins (52.4%) than furans (47.6%). On this basis, there is no correlation between furan levels in the river and furan levels in chlorine cell sludge.

4. What's True:

"The [chlorine cell sludge's] congener patterns... is unlike any Dow production waste produced in the years since manufacturing process wastes have been monitored and treated."

4. What's Been Forgotten :

a. All production wastes had unique congener profiles.

b. The identification of TCDD as a chlorangenic agent occurred in 1957. Monitoring of dioxins/furans levels in production wastes began in the mid-1960's with the development of isomer-specific test methods. Prior to that time, "rabbit-ear" tests were used to detect the presence of TCDD and other dioxins. The company has no information on the levels of dioxins/furans in production wastes before the late 1950's.

c. The 17 toxic dioxins and furans are chemically based on three (3) chlorinated phenols that have reacted with themselves or with other chlorinated phenols and chlorinated benzenes.

- 2,3,4 – trichlorophenol
- 2,3,4,6 – tetrachlorophenol
- pentachlorophenol

These three chlorinated phenols were all produced at one time or another at the Midland plant. The products were first produced in the 1910's to 1920's by the direct chlorination of molten phenol. As the demand for 2,4,5-T herbicide increased, trichlorophenol began to be produced by the high temperature hydrolysis of tetrachlorobenzene using methanol and caustic. After 1964, the quantities of TCDD produced by the Midland plant increased dramatically. Prior to 1964, the majority of the dioxins and furans produced at the site were mainly the higher (more than four chlorine atoms) chlorinated dioxins/furans.

Prior to 1937, all of the waste streams from these processes were released to the river after being settled in the chemical waste ponds at the site. It is not known what percentage of the dioxins/furans were retained in the ponds and what percentage flowed into the river. It should also be noted that the rapid draining of the high concentration organic chemical waste ponds in the summer may have re-suspended some of the heavier-than-water dioxins/furans that had settled to the bottoms of the ponds. Since dioxins/furans from <u>every source</u> at the plant site were mixed in the chemical waste ponds prior to discharge to the river and further mixing and settling occurred in the river, it is impossible to identify which dioxins and which furans came from which source. The only exception being that computer modeling of current dioxin/furan levels has shown that a large portion of earlier dioxins/furans may have come from the pentachlorophenol process.

d. There is some information that dioxins and furans may have been created by the action of sunlight on the chemicals dumped into the chemical waste ponds. As a result, some of the dioxins released into the river may not have been associated with any production plant wastes.

In 1980, Dow conducted laboratory experiments on the effects of simulated sunlight on dioxin formation in pentachlorophenol treated wood. With 5% penta in the wood, OCDD (octa-chlorinated dioxin) levels increased by a factor of 3,000. HpCDD (hepta) and HxCDD (hexa) were formed by the dechlorination of OCDD. HxCDD levels increased by a factor of 760.

Experiments by other researchers has shown that photolysis of OCDD resulted in the loss of chlorine in the 1,4, 6 and 9 positions resulting in the production of 2,3,7,8-TCDD.

e. Some of the plant's various waste incinerators and tar burners had coarse water spray nozzles to reduce flyash emissions. The heated scrubber water that was returned to the general water treatment plant contained the dioxins/furans that were partially removed from the incinerator's emissions. In addition, the spray water was general waste water plant effluent that contained measurable levels of chlorinated and non-chlorinated organic compounds. In all likelihood, some of these recycled chemicals were converted into additional dioxins in the high temperature water scrubber chambers. No information has been published on levels of dioxins that were formed and removed from the plant's waste incinerators. The current hazardous waste license for the Midland plant prohibits use of treated effluent as scrubber water.

5. What's Been Forgotten: Environmental Degradation of Dioxins

It is incorrect to compare dioxin/furan levels being found in 2002 (or in later years) with earlier historic chemical processes or waste streams <u>without acknowledging that dioxin levels degrade with time</u>. Since very little is known about the degradation of dioxins/furans in river sediments and in the floodplain, any comparison between 2002 dioxin levels and dioxin levels produced during 1897 to 1915 is probably suspect.

Based on estimates of the half-life of each dioxin and furan, it is possible to calculate the amounts of dioxins/furans that were present in the environment based on dioxin/furan levels still being found today in Midland and in the river. The estimate of dioxin/furan levels in Midland in earlier years is much more reliable than a similar estimate of dioxin/furan levels in the floodplain. The re-suspending, re-distribution and re-burying of dioxins by the springtime floods makes the half-life calculation extremely difficult and results may be invalid.

However, although difficult and unreliable, floodplain half-life calculations can be used to estimate the types of Dow processes that contributed to the current levels of dioxins/furans being found in the river in 2002.

Table D is a summary of some very preliminary calculations on dioxin and furan levels in the floodplain of the river from 2002, to 1942 to 1932.

Table D
Dioxin-Furan Levels : Tittabawassee River
(ppt-total)

	Avg. Half-life (yrs)(a)	**2002 Levels (ppt-total)**	**1952 Levels (ppt-total)**	**1932 Levels (ppt-total)**
2,4,5-trichlorphenol Based Dioxins and Furans	8.1	12,646	8,525,278	---
2,3,4,6-tetrachlorophenol Based Dioxins and Furans	10.6	1,398	305,749	4,055,868
Pentachlorophenol Based Dioxins and Furans	5.3	42,599	460,254,760	45,321,440,008 (45,421 ppm)

(a) Estimated half-life in Midland soils

Please remember that these of <u>very</u>, <u>very</u> preliminary calculations. However, the principle behind the calculations is sound – dioxin and furan levels were higher in earlier years. The question is “how much higher?”

Based on the information that is available, the dioxins/furans derived from pentachlorophenol have relatively short half-lives which indicates that these dioxins will degrade faster with time. As a result, levels of the “penta” dioxins/furans should have been much higher in prior years than the dioxins and furans with longer half-lives.

Based on incomplete information as to the products, the volumes and the time period that the Midland plant manufactured, I have assumed that, in 1932, the levels of the

2,4,5-trichlorophenol based dioxins/furans were low since the majority of the production in the 1920's was tetrachlorophenol and especially pentachlorophenol.

However, if these calculations are even remotely in the right ballpark, it is evident that a high percentage (~75%) of the dioxins/furans being found in 2002 could have been derived from waste streams from the Pentachlorophenol Production Plant. In 1932, the majority of the dioxins/furans that might be in the floodplain were probably the "penta" dioxin/furans and not those associated with the "historic chlorine cells" or later 2,4,5-T production.

6. What's Been Forgotten: Underground Leakage of Chemical Pond Dioxins

Until 1937, all of the chemical wastes that the Midland plant generated were "settled" in the more than 600 acres of waste ponds that the company had in operation in 1931. In the 1980's and into the 1990's, the company installed a collection system to collect and treat contaminated groundwater before it reached the river.

The DEQ requires periodic sampling and analysis of the groundwater prior to treatment. There is an underground sand layer that may result in more rapid leakage from three (3) of the historic waste ponds to the river. Lift Stations (LS) 4,5 and 6 have shown the highest levels of groundwater contamination and it is believed that they are located in the connecting sand layer.

Two of the ponds (No. 1 and No. 8) were primarily used to settle precipitates and suspended solids. Dioxin/furan levels may not have been extremely high in these two ponds.

No. 2 Strong Phenol pond, based on the types of wastes that it handled, should have the highest levels of dioxin/furans out of all the chemical waste ponds at the site. If dioxin/furan levels do increase as the result of photochemical reaction, No. 2 pond would be expected to have the highest rates of dioxin/furan formation.

It must be remembered that the three ponds were drained of liquids and sealed with clay to prevent rainwater and snow melt from entering the ponds a number of year ago. Any analysis of groundwater after the ponds were sealed may not be a true indication of the levels of dioxins and furans that were present in the ponds in earlier years. The DEQ has never required the company to report the composition of the organic chemicals that settled to the bottom of the three ponds.

Unfortunately, I do not have the total analysis, merely a summary, which shows the levels of all the 17 most toxic dioxins and furans. OCDD (a pentachlorophenol derived dioxins) constitutes a high percentage of the dioxins/furans. Table E is a summary of some of the 1998 Lift Station data.

It should also be remembered that a great many factors will influence the levels of dioxins/furans being found in contaminated ground water – the most important two being the solubility of each dioxin/furan in water and the solubility effects of 119 ppm of other organic compounds in the collected groundwater.

Table E
Dioxin Analysis of Groundwater Collected by LS 3,4,5
(1Q, 2Q – 1998)(ppt-total)

	LS-#5 1Q98 (ppt-total)	LS #4,5,6 2Q98 (ppt-total)	Avg. (ppt-total)	Pct.
2,3,7,8-CDD's	819	430	625	36%
2,3,7,8-CDF's	918	1,278	1,098	64%

Bottom Line Conclusions:

It is doubtful if the dioxins/furans generated in the early chlorine cells from 1897 to 1915 are a significant factor in the amounts and levels of dioxins and furans currently being found in the river sediments and floodplain soils of the Tittabawassee River.

Based on:

- how the chemical ponds were operated,
- whether dioxins and furans may have formed in the ponds,
- how many and what types of dioxins/furans were formed and removed from the incinerators,
- the dioxin/furan removal efficiencies of the phenolic and general waste water treatment plants (with and without the "T" pond),
- how the composition and levels of the dioxins and furans may have changed as the dioxins/furans leaked from the ponds into the river,
- how each dioxin and furan degraded after reaching the river and
- how the composition and levels of dioxins changed due to river flooding,

It will be extremely difficult to identify those chemical processes that most affected the current levels of dioxins and furans that are still being found in the river.

To even try to do so, shows a lack of knowledge of dioxin-related science and Midland plant history.

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