

Robert J. Schreiber

Missouri Department of Natural Resources  
Director - Division of Environmental Quality  
P.O.B. 1368 2010 Missouri Blvd.  
Jefferson City Mo 65102

TIMES BEACH DIOXIN RESEARCH FACILITY

ABSTRACT: This paper describes two successful experiments for destroying dioxin at the Times Beach Dioxin Research Facility in Missouri and explains the analytical results obtained as of October 1985.

Missouri's experience with dioxin has been characterized by a unique set of circumstances and events that affected a large number of our citizens. This environmental dilemma posed a technical and waste management challenge of unprecedented magnitude. The Missouri Department of Natural Resources faced this challenge at a time when there were few answers. Questions concerning possible health effects from exposure to various levels of dioxin; questions about removing the contaminant from soils, rocks, and brush; questions concerning the destruction of dioxin - all remained unanswered. In many cases we were faced with theories, assumptions, and inconclusive data.

A unique opportunity to fill the knowledge gap was created when our department established the Times Beach Dioxin Research Facility. This facility offers scientists and engineers a chance to stand on the frontier of science by filling in this gap.

Historically, the contamination of Missouri's 44 confirmed sites has been traced to improper disposal of chemical waste from a now-defunct firm, the Northeastern Pharmaceutical and Chemical Co. This company manufactured hexachlorophene and created dioxin as a waste byproduct. The dioxin contaminated the company's thousands of gallons of waste still bottoms, industrial sewage, and sludge.

A used-oil transportation firm, the Bliss Waste Oil Co., contracted to remove much of the still bottoms. After mixing the chemical waste with other salvaged oil, this transportation firm sold the waste as fuel oil or sprayed it to control dust on dirt roads, parking lots, and horse arenas.

Other dioxin-contaminated waste from Northeastern Pharmaceutical was buried on farms or sent to a wastewater treatment school - sites where they remained untreated. These disposal sites, plus the sprayed oil

sites, make up the 44 dioxin-contaminated sites in Missouri identified as of October 1, 1985. The greatest health hazard occurred at the sites where the dioxin-tainted oil was sprayed for dust control. This practice escalated the dioxin problem by introducing the chemical to areas where thousands of citizens resided. In these areas, dioxin levels ranged from less than one part per billion to as high as 1,800 parts per billion.

In December 1982, Missouri's dioxin problem gained world attention when more than 800 families were warned to stay out of their homes in the eastern Missouri town of Times Beach.

The dioxin problem prompted Missouri's Governor to create a Dioxin Task Force that was charged with finding technologies for destroying dioxin. In October 1983 the task force concluded that no technologies were available and that it would be several years before suitable technologies were developed.

So the major goal of the task force and the department became, and still is, to find ways to destroy the dioxin contamination.

The company that inherited the problem from Northeastern Pharmaceutical, Syntex Agribusiness, also worked to achieve this goal. Syntex developed a photolysis process that destroyed much of the dioxin in the contaminated waste. In this process, hexane was used as a solvent to absorb the dioxin from the waste oil. The hexane solution was then exposed to high-intensity ultraviolet light to destroy the dioxin molecule. Although this photolysis process worked well on the waste oil, it was not considered an appropriate technology for contaminated soil.

In an attempt to find a temporary solution to the problem of contaminated soil at Times Beach, the United States Environmental Protection Agency and the state of Missouri proposed a plan to contain and secure the contaminated soil until a method of destruction could be found. But, during the public-hearing process, many concerned citizens urged us to find a technology for dioxin decontamination other than containment and urged us to explore in-situ treatment. The extreme variability of soil contamination at the various sites, the types of soil,

and many other factors made this task a difficult one.

To address this challenge of finding a suitable dioxin-destroying technology, the Missouri Department of Natural Resources created the Times Beach Dioxin Research Facility to provide a set of controlled conditions. This facility serves as an available site for researchers to test and compare their technologies.

A committee formulated a plan and established guidelines for the use of the research facility, which is located in the portion of Times Beach that had the highest level of contamination. The asphalt cover was removed from the roadway, and the contaminated soil was excavated and then processed to assure a uniform sample. The processing consisted of screening the material to one-half inch; transferring it to a 10-cubic-yard cement truck; operating the cement mixer for six to eight hours during the filling process; recompacting the 10 cubic yards into three identical stainless-steel bins, six by eight by two feet; and then compacting to 80 percent of the nominal density.

The resulting construction project yielded 61 research units that consisted of 20 sets of three identical units and one control unit.

The research facility is supported by the addition of water and electricity at each of the soil bins. An observation trailer, from which the state can observe all research activities, and a decontamination trailer, from which researchers can change from their street clothes into protective clothing and equipment, are part of the facility along with on-site storage and showers. There also is a soils laboratory for the preparation of samples. An off-road vehicle and trailer are available for transportation of equipment, and a high-pressure steam cleaner is available for the decontamination of equipment.

This unique research facility was opened July 30, 1984, and has been used by a number of scientific companies in the quest for a dioxin-destroying technology.

Two technologies already have proven successful on a small scale. They are the J. M. Huber and Shirco processes.

In November 1984, J. M. Huber brought in an advanced electric reactor for testing. And on November 13, Huber demonstrated that its high-temperature thermal treatment device was capable of destroying dioxin in contaminated soil.

The Huber process utilizes a theory of raising the temperature of the finely ground contaminated soil to approximately 4,500 degrees Fahrenheit in a non-oxidizing environment. The advanced electric reactor consisted of a three-inch graphite tube that was heated externally by electrodes radiating at temperatures of 5,000 degrees Fahrenheit; the graphite tube subsequently reached temperatures of approximately 4,800 degrees Fahrenheit. A nitrogen blanket kept the falling soil from impacting the side of the graphite tube and the organic material in that soil broke down into its molecular constituents in the process of heating up. The soil formed into a liquid and then reconverted to a solid as it went through a cooling chamber. The solid material was tested after it was thermally treated. There was no detectable dioxin in the treated soil. The unit that was tested at the Times Beach facility treated approximately 100 pounds of soil in one day.

The exhaust gases from the Huber reactor went to a bag-type dust collector and also to a carbon absorption unit where any material that theoretically could escape was finally collected before gases went into the atmosphere.

The second process to prove successful was conducted on July 10, 1985, by Shirco, Inc. The company brought in a portable infrared heating system that demonstrated the capability of reducing the dioxin levels in the soil below one part per billion.

This particular system consisted of a moving metal belt where the soil, approximately two inches deep and three feet wide, was placed. The soil passed underneath electric infrared heating electrodes that raised the temperature of the soil to approximately 1,600 degrees Fahrenheit. The dioxin and organic molecules were driven off the soil in a vapor phase, and the exhaust gases were then collected and sent to an

afterburner where the temperature was raised to greater than 2,200 degrees Fahrenheit for longer than a two-second residence time. The gases then went to a high-efficiency Venturi scrubber where any particulate and chlorine gases were absorbed into the water before being exhausted to the atmosphere.

On the same day as the test, the Shirco unit demonstrated its capability of reducing dioxin to below one part per billion. In addition, no contamination was detected in the exhaust gases or in the dust from the air pollution control device.

Other technologies also are being tested at the Times Beach Dioxin Research Facility. One is a vaporization process by Monsanto Chemical Co. that involves the natural transfer of dioxin from the soil. Monsanto has demonstrated, by computer modeling and laboratory testing, that the dioxin molecule exhibits a low-vapor pressure. The company believes that vaporization may be the primary mode of environmental movement. Monsanto further believes that natural evaporation will cause the dioxin concentrations in the upper two-and-one-half inches of soil to decrease over a period of time. Once the dioxin molecule is in the atmosphere, ultraviolet light then will destroy it.

A hydrazine process is being tested by the RMC Corp. in cooperation with Agro-K Co. This test will determine whether the treatment of contaminated soil with hydrazine will destroy the dioxin molecule. Initial results have indicated no decontamination.

Another test activity currently going on is an enzyme degradation process that is being tried by Agro-K Co. This process provides an enzyme media to the research plots so natural bacteria can break down dioxin molecules. By enhancing the process with a growth media, the natural biological process may cause degradation of the dioxin molecule over time.

After four months, samples from these early experiments by Monsanto and Agro-K were analyzed without significant results.

Another company is trying two dioxin-destroying technologies. One of the technologies being tried by the Parts Per Million Co. is similar to Agro-K's enzyme degradation process. In addition, the Parts Per Million Co. is trying a process that treats contaminated soil with organic solvents. The company wants to determine if the dioxin molecule will be transported to the solvent, where it can more easily be destroyed.

All these experiments are unique in the world. They have been developed under a concept of providing a controlled site, the Times Beach Dioxin Research Facility, at which researchers can develop methods for successfully destroying dioxin.

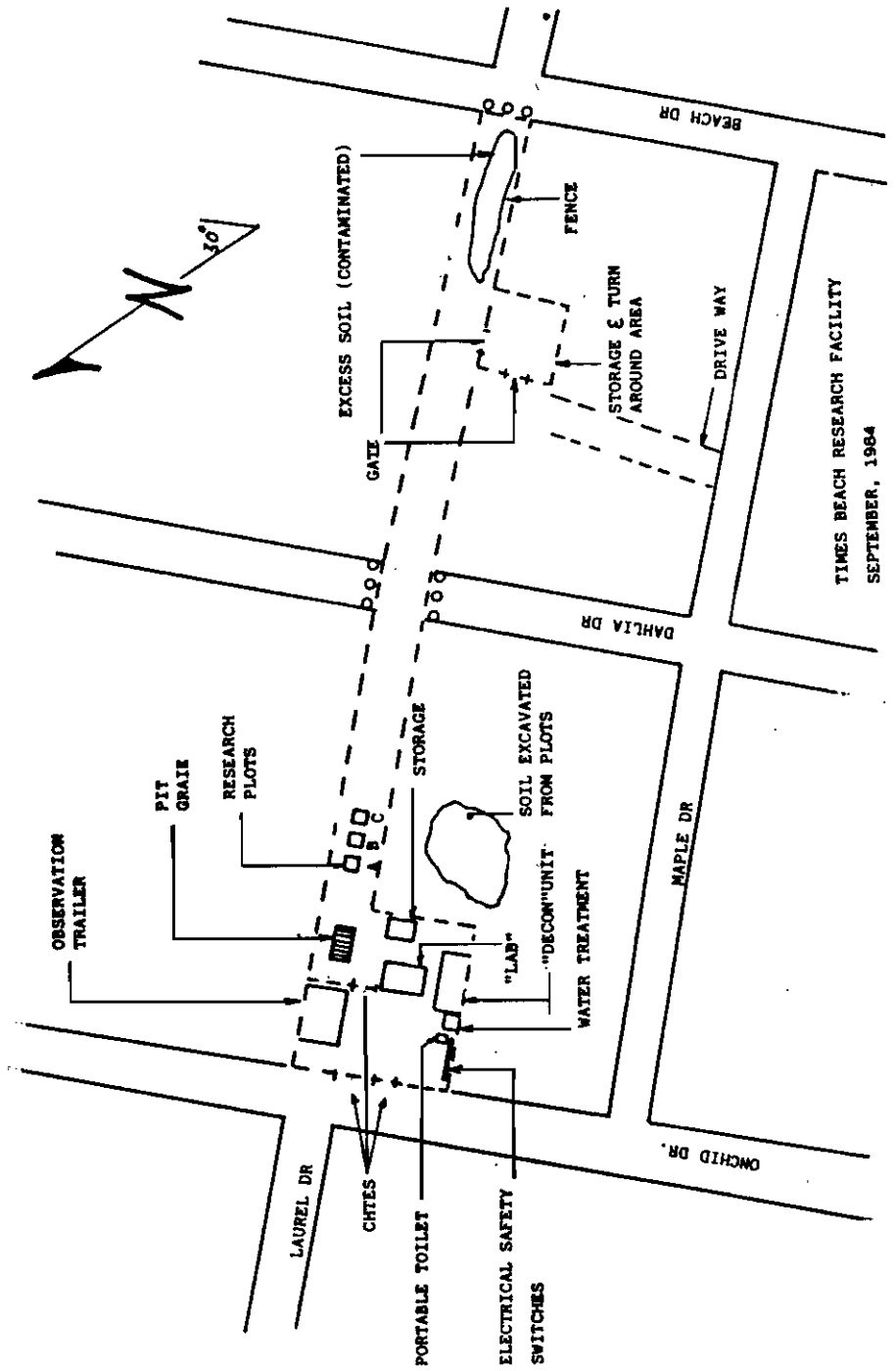
We sincerely hope that a suitable dioxin-destroying technology will result from Missouri's dioxin experience...a technology that will help all of us who must deal with dioxin contamination and its effects.

I invite all of you to come to Missouri to see our Times Beach Dioxin Research Facility and, perhaps, to use the facility to conduct research that might solve the dioxin problem.

Thank you.

SUMMARY OF TEST RESULTS

COMPANY	TECHNOLOGY	UNIT NUMBER	PRETEST CONCEN. 2,3,7,8 TCDD (PPB)	POST TEST CONCEN. 2,3,7,8 TCDD (PPB)	DATE OF POST TEST
Agro-K	Enzyme enhancement	1(a)control	260	217	10/31/84
		1(b)	220	159	10/31/84
		1(c)	220	314	10/31/84
PPM	Enzyme enhancement	3(a)control	120	NA	NA
		3(b)	120	NA	NA
		3(c)	110	NA	NA
Monsanto	Vaporization	4(a)control	110	NA	NA
		4(b)	110	NA	NA
		4(c)	110	122	10/31/84
		5(a)control	180	122	10/31/84
		5(b)	180	184	10/31/84
		5(c)	170	121	10/31/84
JM Huber	Advanced electric reactor	Batch	120	<1	11/13/84
Shirco	Infrared incineration	Batch	306	<1	7/10/85
		Batch	156	<1	7/11/85
Agro-K/ RMC	Hydrazine treatment (Lab)	Batch A	52	42	NA
		Batch B	63	33	NA
		Batch C	48.5	61	NA



TIMES BEACH RESEARCH FACILITY  
 SEPTEMBER, 1984

