Chlorinated Hydrocarbons in Heterogeneous Subsurface Environments

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Chlorinated Solvents

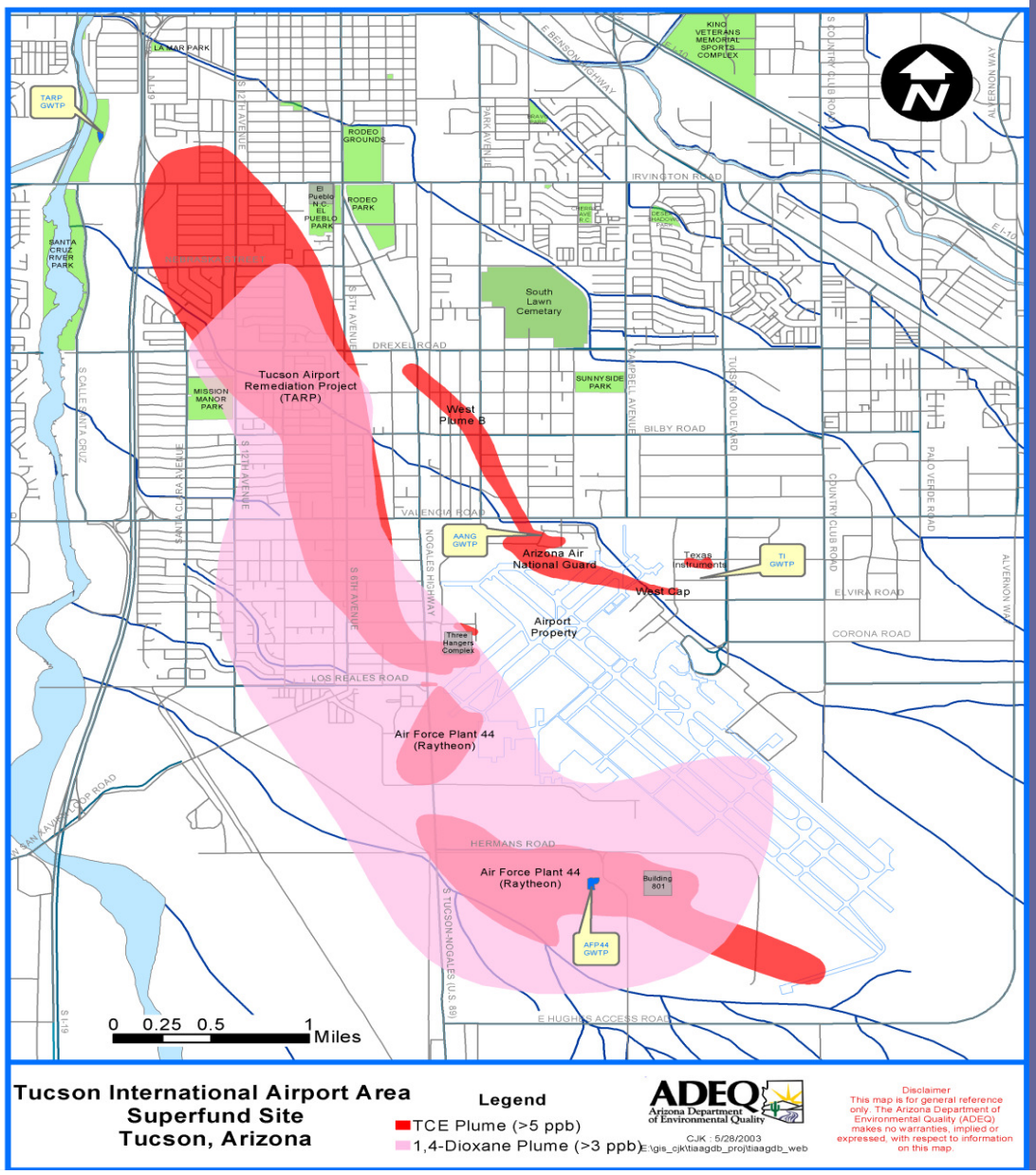
- Trichloroethene, Tetrachloroethene, Trichloroethane, Carbon Tetrachloride, etc
- Ubiquitous Contaminants in Groundwater
  - Present at 80% of Superfund Sites Nationwide
  - Primary COC for 44/48 state and federal sites in AZ
- Several Toxicological Effects
- Significant Impact on Sustainability of Water Resources

Evolution of GW Remediation

*Disclaimer: this is simplified

- Initial Approach (1970's to early 1990's)-
  - Pump-and Treat is king
  - Became evident that P&T not effective for complete site cleanup
  - Need to address the source zones
- First Paradigm Shift (mid 1990's to mid 2000's)-
  - Source-zone Remediation will solve problem
  - Became evident that can not remove all contaminant mass
- Alternate Paradigm Shift (2000's)-
  - Monitored Natural Attenuation (MNA)
  - Became evident that MNA often not successful without source-zone treatment
- What Next???

TIAA Superfund Site



- NPL Listing in 1983
- Multiple installations
- Extensive groundwater contamination
- Impact on City Well Field

Impact on Human Health, and Toxic-Tort Lawsuits

February 17, 1991

Hughes offers $85 million to TCE plaintiffs

By Chris Limberis
The Arizona Daily Star

More than 1,000 southside residents who joined in a lawsuit against Hughes Aircraft Co. and others over TCE contamination of water heard yesterday that Hughes is offering nearly $85 million to settle the 5-year-old case.

If accepted by 95 percent of the plaintiffs in the next 90 days, the settlement would be the largest of its kind in U.S. history, lawyers said.

Awards would vary for the 1,600 plaintiffs in the class-action suit, depending upon the extent of their diseases or illnesses they say were caused by Hughes' dumping of TCE, or trichloroethylene, an industrial solvent and probable human carcinogen.

The settlement money has been placed in escrow and plaintiffs would be paid around June 1 if they accept the offer, lawyer Frederick M. Baron said.

Recipients will receive itemized statements, detailing their cash award as well as the portion taken out by lawyers — roughly 30 percent

Tucson, Sunday, February 17, 1991 The Arizon

Hughes

Continued from Page 1A

of the total — and court costs, up to 3 percent of the total.

Plaintiffs streamed into the Sunnyside High School gymnasium to hear Baron explain the settlement proposal.

The assembly of more than 1,000 was closed to reporters and even family members who were not officially listed as plaintiffs. Admission was granted only when plaintiffs showed a letter, sent by lawyers last week notifying them of the meeting, and identification.

Baron, of the Dallas firm of Baron & Budd, one of three firms representing the plaintiffs, spoke for about an hour as the plaintiffs sat in grandstands normally used for crowds at Sunnyside wrestling matches and basketball games.

Bolstered by public address speakers, Baron's voice, regularly interrupted by applause, could be heard with mixed clarity outside the gymnasium.

Baron told the plaintiffs to be wary once they receive payment.

"What we don't want to have happen is your money to go from your pocket to another pocket," Baron said.

To prevent that, Baron said the lawyers could help plaintiffs meet with financial advisers.

During the meeting and later in a press conference, Baron called the $84.47 million settlement offer by Hughes, the principal defendant, "fair."

"Settlements are always a compromise," Baron said.

He emphasized that no amount of money could ameliorate the loss of a loved one or the illness suffered by plaintiffs.

One of his admonitions seemed to take effect. Baron cautioned the plaintiffs against discussing their offers with the media. Many people, including those who have long served as spokespeople, declined to discuss the settlement in any detail.

It was clear that the proposal did not answer all questions.

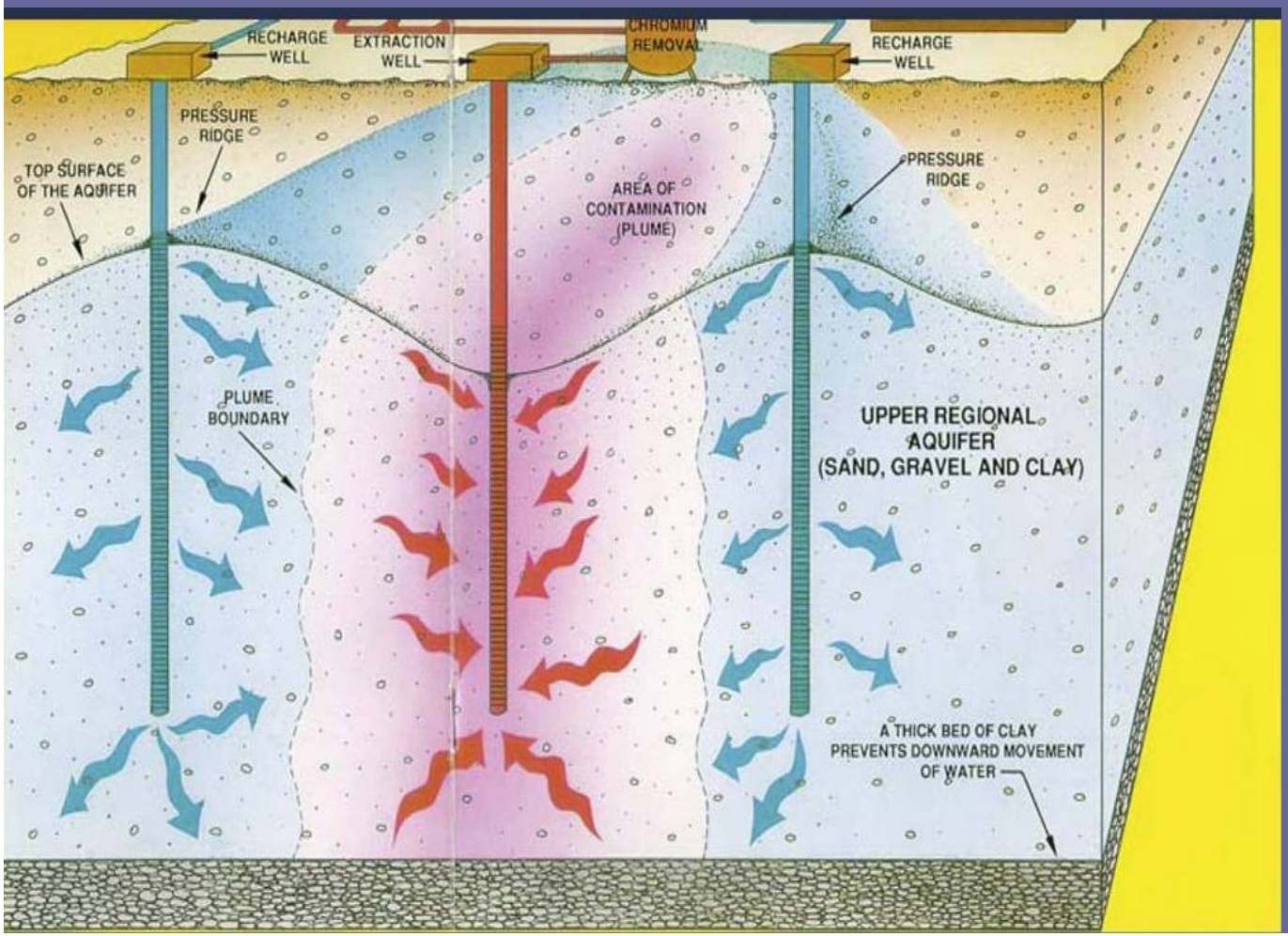
"It still concerns me that no money is being put aside for future medical problems and future medical bills," said Cora Esquibel, a long-

LAST TWO DAYS! SALE ENDS MONDAY!

Multiple Lawsuits have been settled for combined several $100's millions

Pump and Treat

- Five Systems in Operation
- South Plume- 1987
- Others- Early 1990's

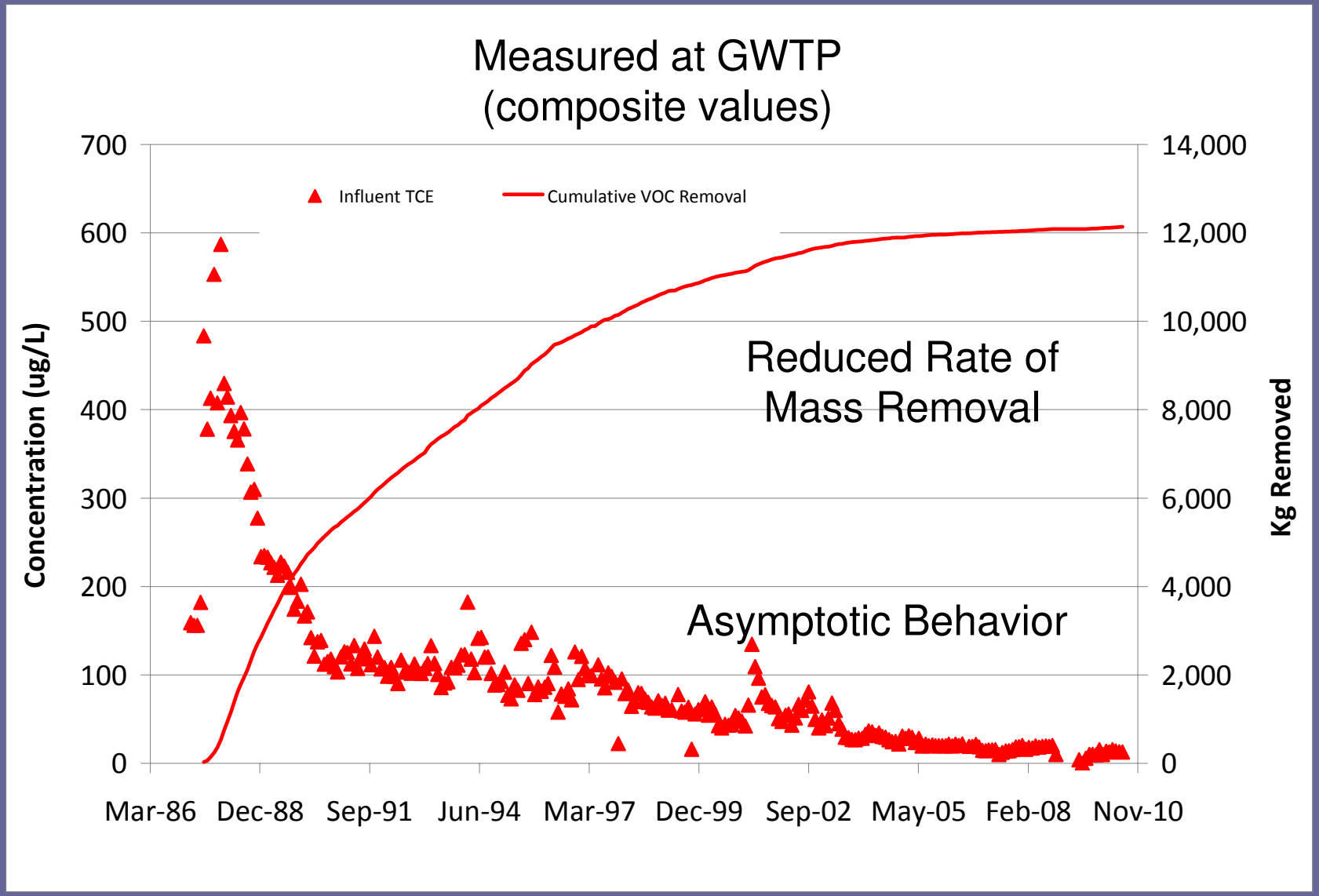


Removal

Groundwater = 235 Billion Liters

Solvent Mass = 15, 600 Kgs

TCE Removal


Measured at GWTP
(composite values)
Influent TCE
Cumulative VOC Removal
Reduced Rate of
Mass Removal
Asymptotic Behavior
Concentration (ug/L)
Kg Removed
700
600
500
400
300
200
100
0
14,000
12,000
10,000
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Mar-86
Dec-88
Sep-91
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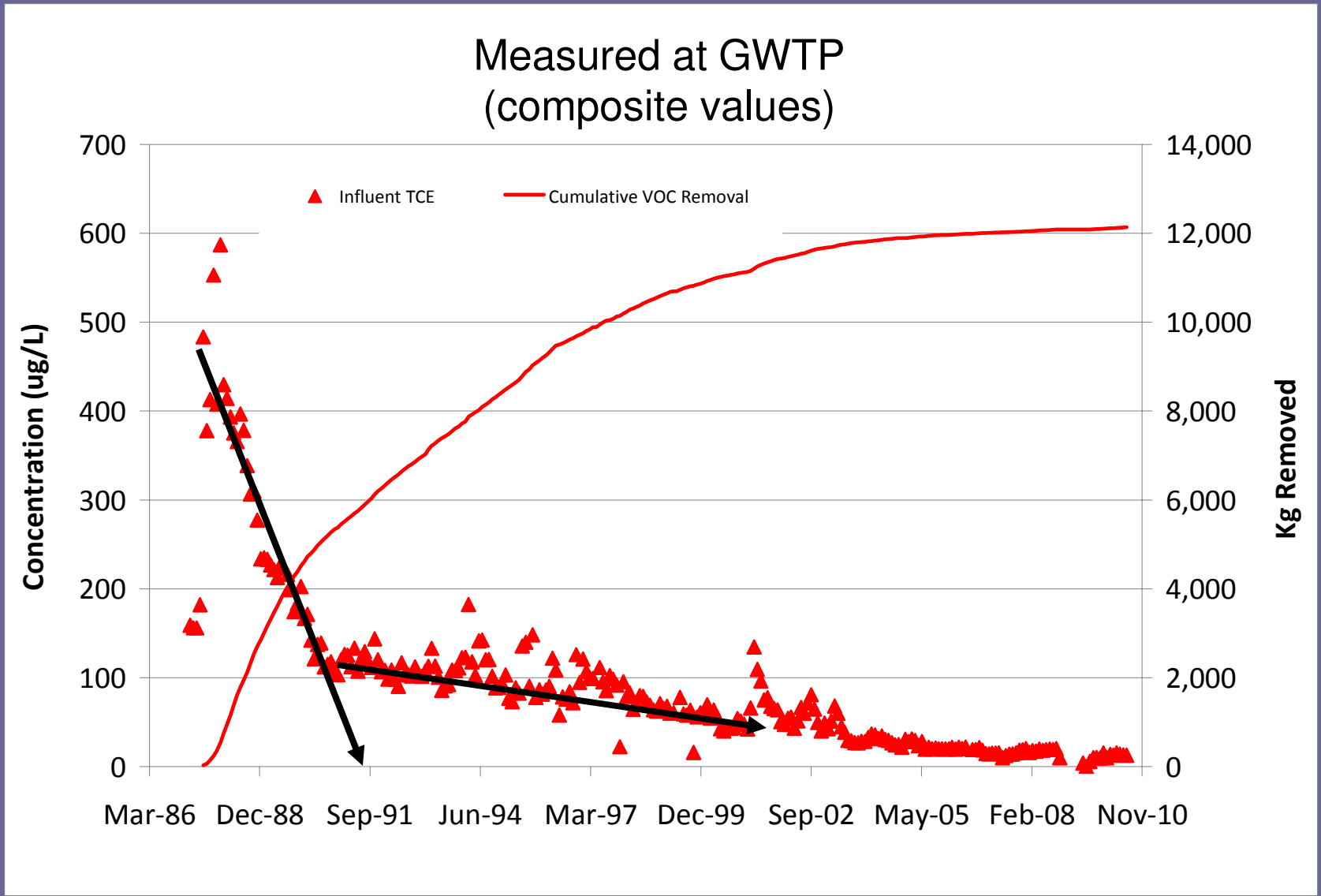
Nov-10

TCE Removal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Mar-86
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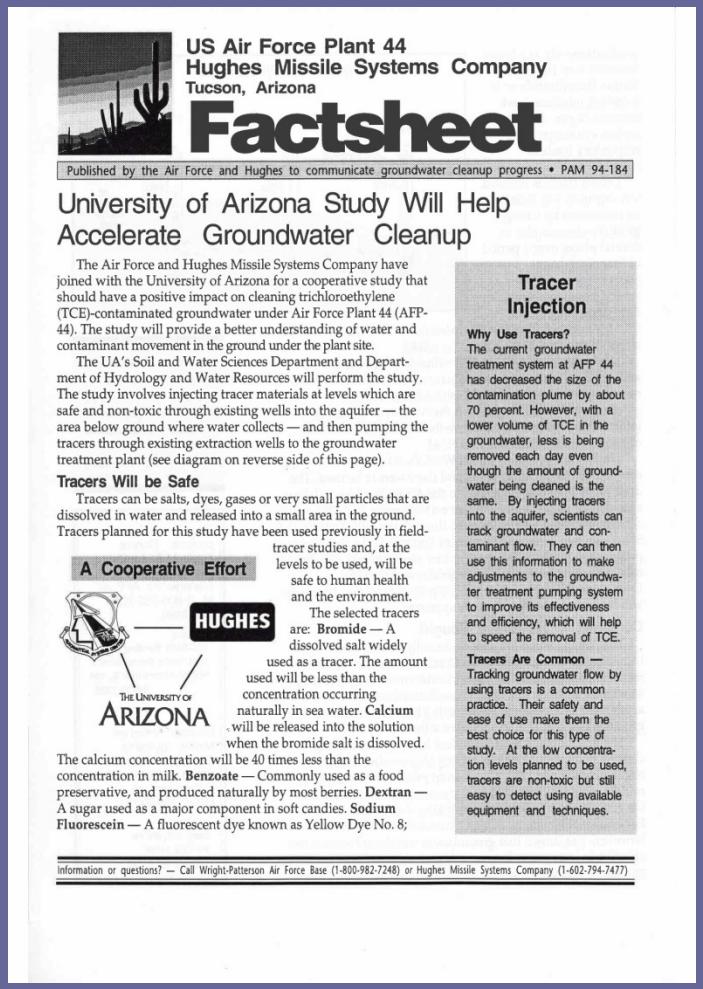
UA TIAA Study

- 1991/1992
  - Initial Meetings with Hughes Personnel
- 1993
  - Meet with Air Force Personnel
  - Submit Initial Proposal to Hughes/USAF
- 1994
  - Funding Approved
  - Meet with Regulators (EPA, ADEQ, ADWR)
  - Press Release
  - Present Plan at TIAA UCAB (community committee)
  - Fact Sheet for Project Released to Public
  - Work Plan submitted for Review (Regulators, USGS, Public)
- 1995
  - Field Work Initiated



US Air Force Plant 44
Hughes Missile Systems Company
Tucson, Arizona

Factsheet

Published by the Air Force and Hughes to communicate groundwater cleanup progress • PAM 94-184

University of Arizona Study Will Help Accelerate Groundwater Cleanup

The Air Force and Hughes Missile Systems Company have joined with the University of Arizona for a cooperative study that should have a positive impact on cleaning trichloroethylene (TCE)-contaminated groundwater under Air Force Plant 44 (AFP-44). The study will provide a better understanding of water and contaminant movement in the ground under the plant site.

The UA's Soil and Water Sciences Department and Department of Hydrology and Water Resources will perform the study. The study involves injecting tracer materials at levels which are safe and non-toxic through existing wells into the aquifer — the area below ground where water collects — and then pumping the tracers through existing extraction wells to the groundwater treatment plant (see diagram on reverse side of this page).

Tracers Will be Safe

Tracers can be salts, dyes, gases or very small particles that are dissolved in water and released into a small area in the ground. Tracers planned for this study have been used previously in field-tracer studies and, at the levels to be used, will be safe to human health and the environment.

The selected tracers are: **Bromide** — A dissolved salt widely used as a tracer. The amount used will be less than the concentration occurring naturally in sea water. **Calcium** will be released into the solution when the bromide salt is dissolved. The calcium concentration will be 40 times less than the concentration in milk. **Benzoate** — Commonly used as a food preservative, and produced naturally by most berries. **Dextran** — A sugar used as a major component in soft candies. **Sodium Fluorescein** — A fluorescent dye known as Yellow Dye No. 8;

A Cooperative Effort

HUGHES

THE UNIVERSITY OF ARIZONA

Tracer Injection

Why Use Tracers?
The current groundwater treatment system at AFP 44 has decreased the size of the contamination plume by about 70 percent. However, with a lower volume of TCE in the groundwater, less is being removed each day even though the amount of groundwater being cleaned is the same. By injecting tracers into the aquifer, scientists can track groundwater and contaminant flow. They can then use this information to make adjustments to the groundwater treatment pumping system to improve its effectiveness and efficiency, which will help to speed the removal of TCE.

Tracers Are Common — Tracking groundwater flow by using tracers is a common practice. Their safety and ease of use make them the best choice for this type of study. At the low concentration levels planned to be used, tracers are non-toxic but still easy to detect using available equipment and techniques.

Information or questions? — Call Wright-Patterson Air Force Base (1-800-982-7248) or Hughes Missile Systems Company (1-602-794-7477)

UA TIAA Study

- Site Characterization
  - Source-Zone TCE Mass Flux
  - TCE Spatial Distribution (areal, vertical)
  - DNAPL presence
  - Advective, Diffusive, Dispersive Transport
- Laboratory Experiments--- Mass Transfer Processes
- Mathematical Modeling--- Plume Behavior, S-Z Flux
- Pilot Source-zone Remediation Projects

Project Highlights

Intersection with SRP Strategic Plan

- Advances in Understanding DNAPL Behavior
  - integration of laboratory-based basic research with solution-based applied research conducted at an actual hazardous waste site
- Development and Testing of Innovative Methods
  - NAPL Partitioning Tracer Test
  - Diffusive Tracer Test
  - Contaminant Mass Discharge Test
  - Vertical Enhanced-Solubilization
  - In-situ Chemical Oxidation (permanganate)
- Student and Post-Doc Training
- Leveraging of Multiple Funding Sources
  - USAF, SERDP, ESTCP, Tucson Airport Authority, EPA
  - NIEHS SRP…. invaluable base and bridge support

Project Highlights

Research Translation

- Technology Transfer
  - Participate in Annual Technical Exchange Meeting
  - Study Results Used for Site Remediation
    - Revised Site Conceptual Model
    - *Pilot Test for ISCO-- used for full-scale operations at AFP44 and also used at other source-zone locations of TIAA*

- Information Transfer
  - Development of Print Media

¿Que es el TCE?

El tricloroetileno (TCE) es un solvente líquido usado para disolver sustancias aceitosas o grasosas.

El TCE ha sido introducido al medio ambiente por que la gente lo usa para limpiar la grasa de los metales, especialmente para limpiar partes de aviones. También las tintorerías usaban un solvente relativamente similar conocido como PCE para remover la mugre de la ropa sucia. El TCE puede formarse a través de la conversión del PCE cuando se introduce al medio ambiente.

Antes, no se savia que el TCE podia afectar negativamente a los humanos y al medio ambiente. Por esta falta de conocimiento, no se dispuso del TCE de forma adecuada. Además también se puede fugar al medio ambiente si no es almacenado adecuadamente. Ahora, se dispone del TCE quemándolo en incineradores de alta temperatura especialmente diseñados.

1,4-Dioxane and our Health

What is 1,4-Dioxane?

1,4-Dioxane is a synthetic organic chemical compound. It is a colorless, clear, flammable liquid and has a mild ether-like odor. Often referred to as just dioxane, it dissolves in water at all concentrations. 1,4-Dioxane is used as a:

Solvent – a liquid that can dissolve oily and greasy substances and is used in vapor degreasers.

Stabilizer for other solvents – 1,4-Dioxane prevents other solvents from degrading. Dioxane is used primarily as a stabilizer for chlorinated solvents like trichloroethylene (TCE). About 90% of the dioxane produced is used to stabilize TCE.

1,4-Dioxane is also produced (by-product) during the manufacturing of some chemicals used in cosmetics, detergents, and shampoos. The following ingredients PEG, polyethylene, polyethylene glycol or polyoxyethylene, listed on the product label, may also contain 1,4-Dioxane. 1,4-Dioxane may be present in food packaged in materials that contain this chemical, or in food from crops treated with pesticide chemicals that also contain 1,4-dioxane.

How is 1,4-Dioxane present in our environment?

1,4-Dioxane can be released into the air, water and soil at places it is produced, or used as a solvent or stabilizer. 1,4-Dioxane has similar evaporation properties to water. Therefore, it can be present in air as a vapor or mist. 1,4-Dioxane does not sorb to soil and can move from soil to groundwater and contaminate it. Mixed in water, 1,4-Dioxane does not readily decompose or degrade.

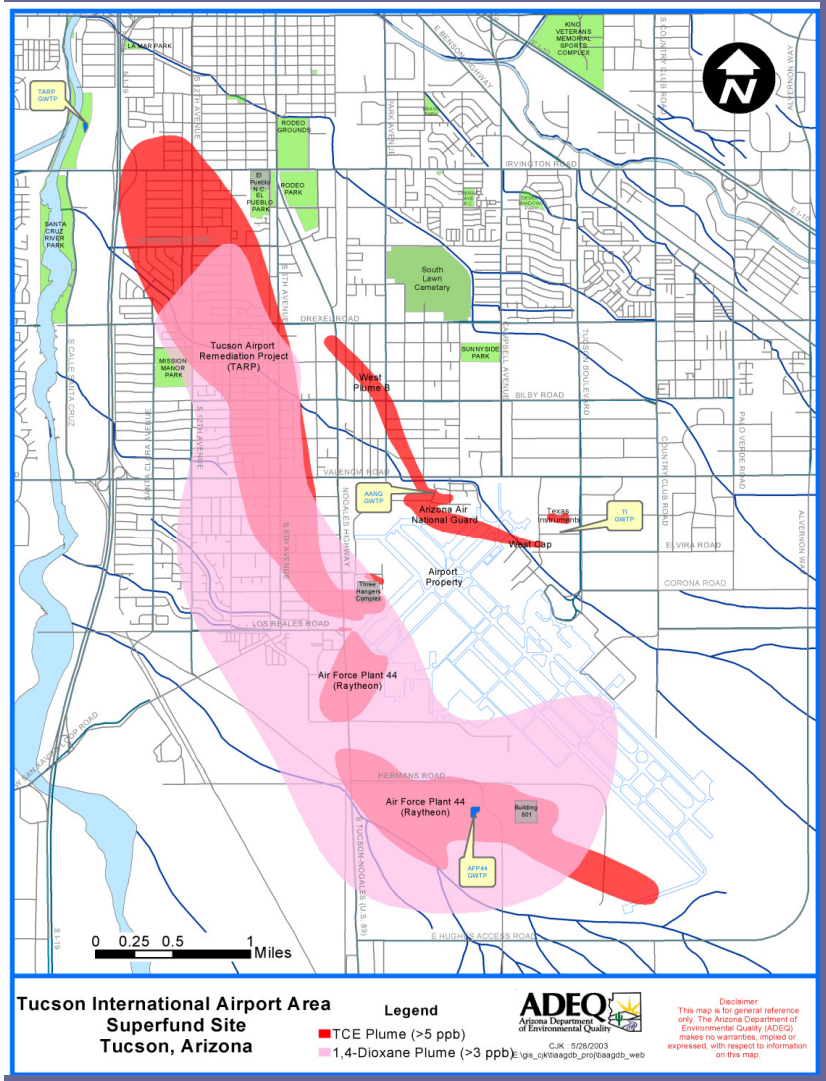
Translation & Outreach Coor's

Monica Ramirez

Denise Moreno

- Community Involvement
  - Participant in Community Advisory Board meetings and Community organized events

Case Study: ISCO at AFP44 Site



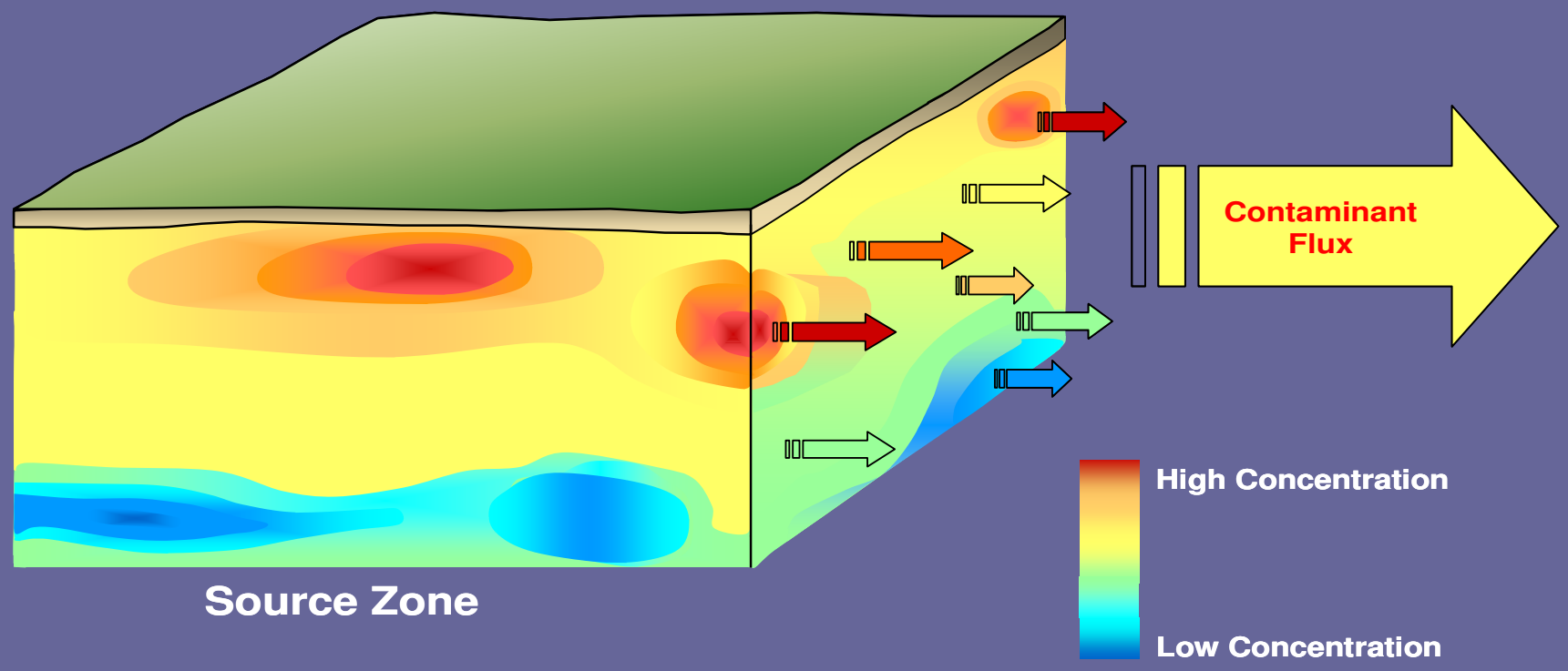
- In-situ Chemical Oxidation
  - Permanganate [MnO4-]
  - Abiotic Transformation of TCE, etc
  - Injected 37,500 Kg in two primary source zones

- Remediation Effectiveness Metric
  - Mass Flux Reduction

Source-zone Mass Flux

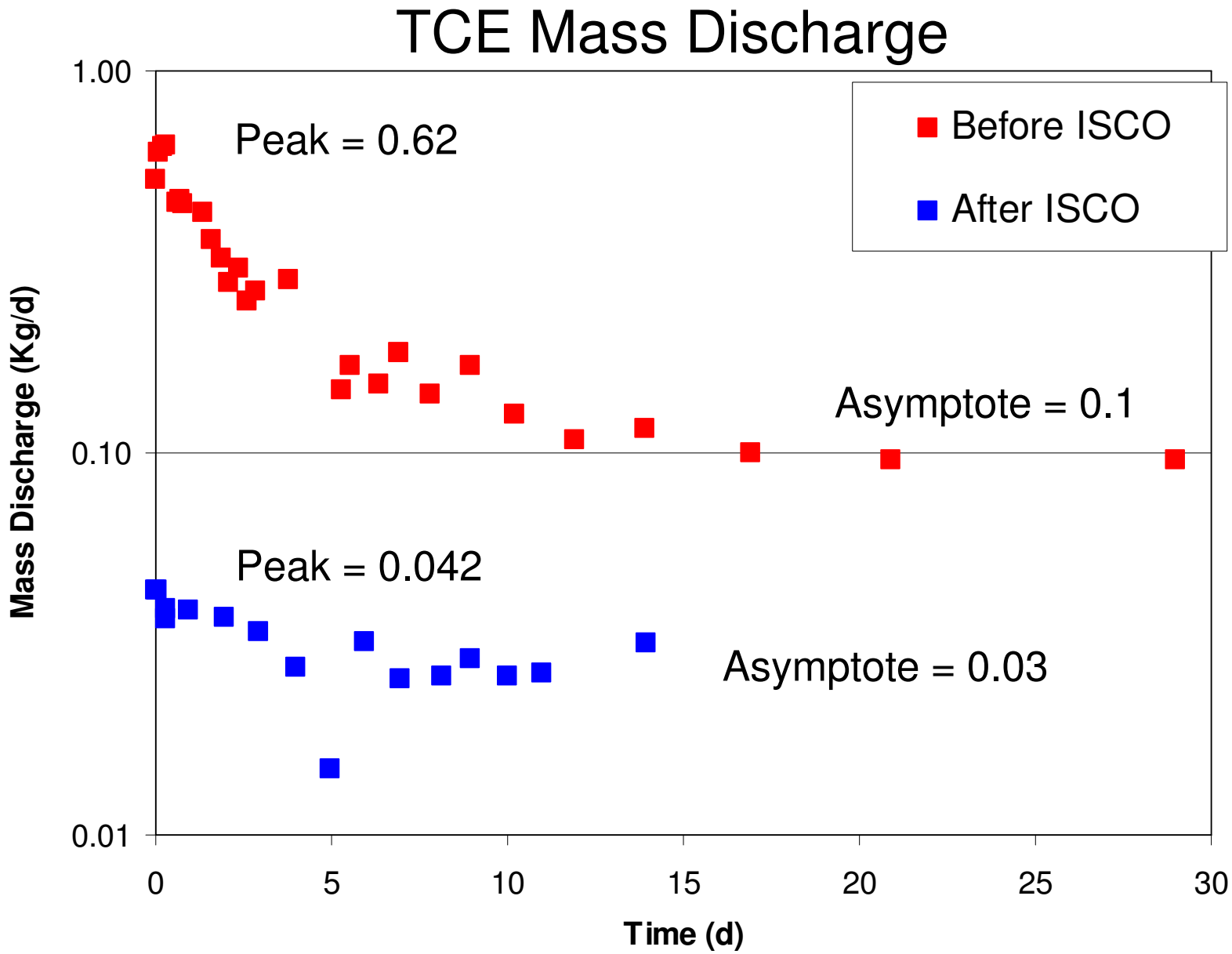
Input for dissolved-phase groundwater plume

(Function of Source-zone Architecture and Flow Field)



(Figure adapted from EPA)

Impact of ISCO: Single Source Zone



Summary

- MFR-MR Relationship Useful for Evaluating Behavior
- NAPL Distribution and Flow-field Dynamics are Key
  - Accessibility of NAPL
- Source-zone Remediation Can Not Remove all Mass
- Long-term Management of Sites

Acknowledgements

- NIEHS SBRP, DOD SERDP, US Air Force, DOD ESTCP, Tucson Airport Authority, US EPA

- UA CTG Students and Post-Docs