Genesis and Response to a Perfluorochemical (PFC) Megaplume – Washington County, Minnesota

Midwest Ground Water Association
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Acknowledgement & Disclaimer

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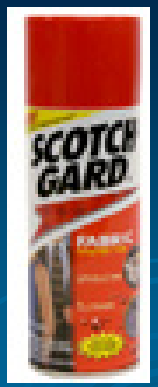
Perfluorochemicals (PFCs)

- Surfactants (surface active agents) with unique chemical properties
- Used for many years in products that resist heat, stains, water, oil and grease
- Many other specialized industrial and commercial uses (operative word: non-stick)

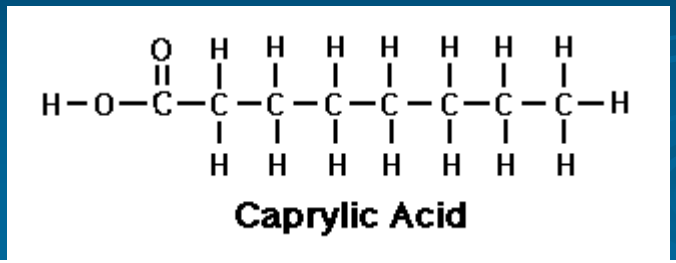


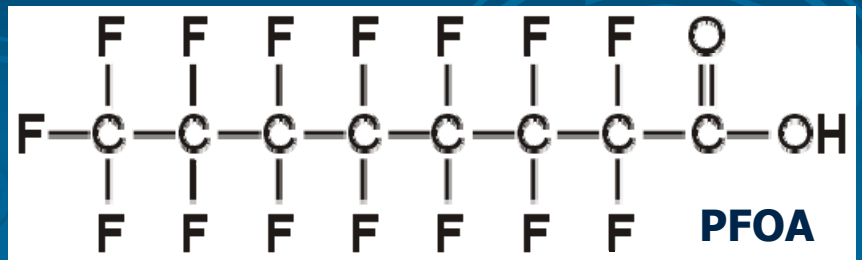





PFCs Behave in Unique Ways

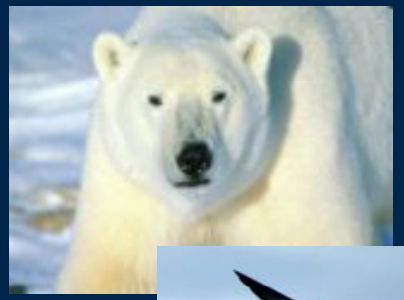
- Do not break down in the environment
  - C-F bond
- Do not adsorb readily to aquifer materials
  - Infiltrate rapidly to the groundwater
  - Little or no retardation
  - Travel long distances
- Chemical structure similar to fatty acids
  - Readily adsorbed into blood serum of living organisms
  - May, in part, explain long half-lives in the body



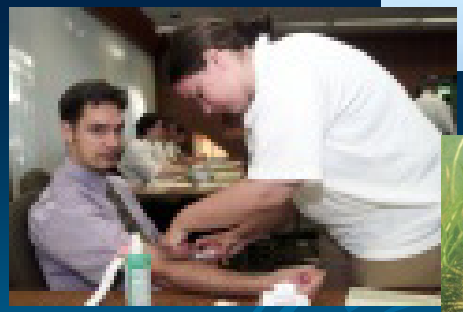


PFCs Are Globally Distributed

Numerous studies have documented PFOS, PFOA, and other PFCs (but not PFBA) in wildlife worldwide, including deep sea and arctic species.



Human blood samples from US, Europe, and Asia also detect PFCs – primarily PFOS and PFOA, rarely PFBA – concentrations higher in very young and the elderly

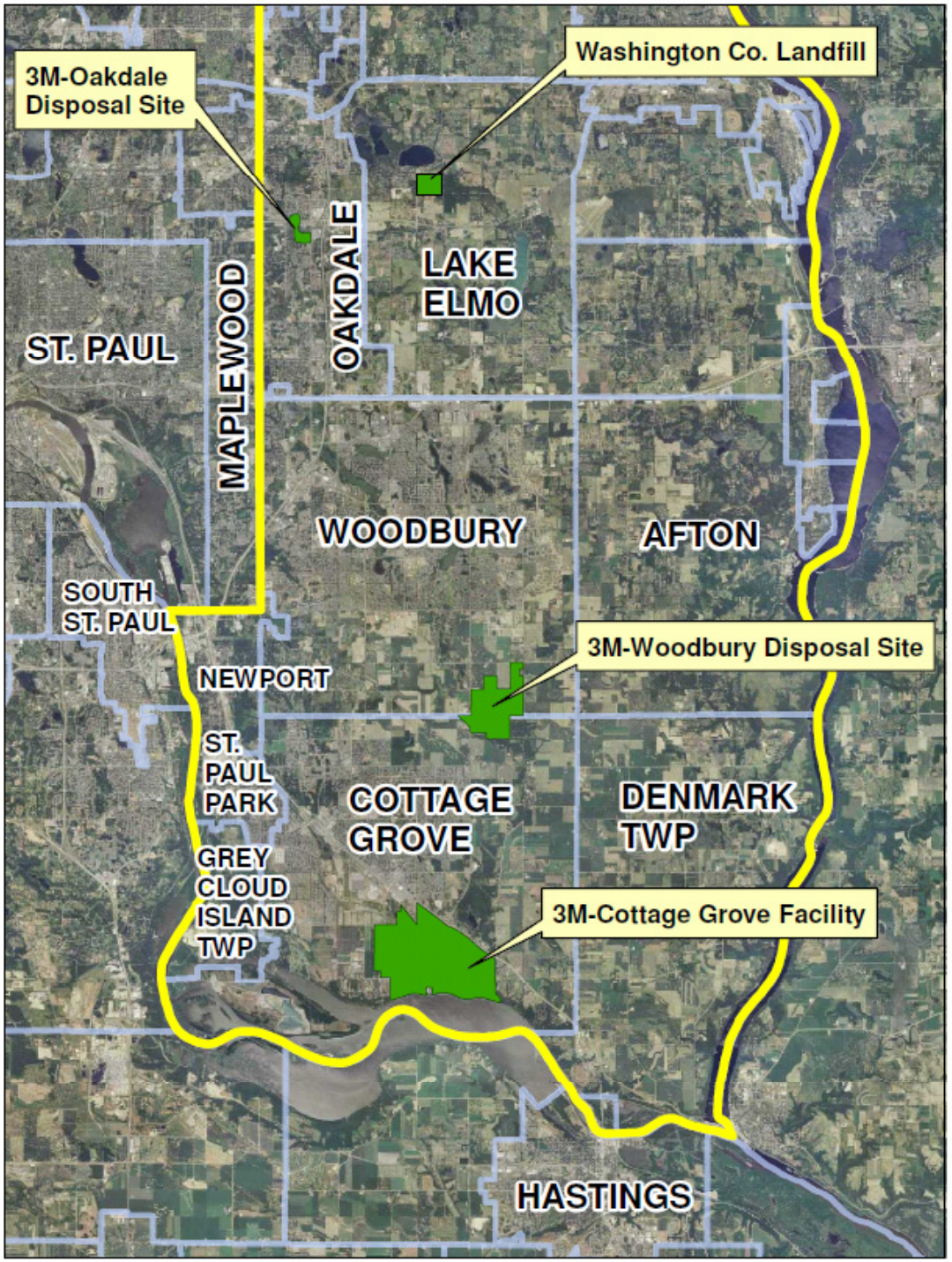


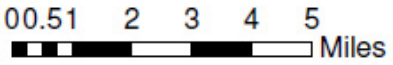
Atmospheric transport of PFC precursor chemicals is believed to be a major mechanism in the global distribution

Why Are PFCs An Issue in MN?

- 3M Corporation manufactured PFCs since 1940's
  - In 2000, announced phase-out of PFOA production by 2002
  - Also produced PFOS and PFBS
  - Other PFC research and development on-going, but no "large quantity" generation
- PFC wastes disposed of on-site and at 3 major off-site disposal areas

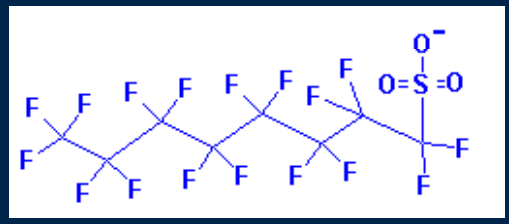
Location of 3M PFC Sites in Washington Co., Minnesota



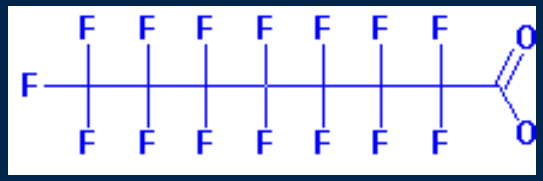


PFCs of Interest in Southeast Metro Area

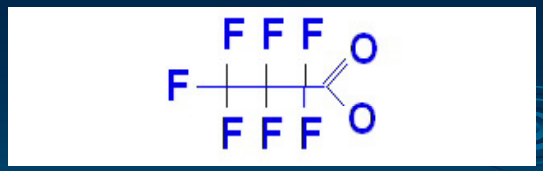
- **PFOS: $C_8F_{17}SO_3^-$**
  Perfluorooctane sulfonate and its salts



- **PFOA: $C_8F_{15}O_2^-$**
  Perfluorooctanoic acid and its salts



- **PFBA: $C_4F_7O_2^-$**
  Perfluorobutanoic acid and its salts



- Other PFCs detected: **PFPeA, PFHxA, PFHxS, PFBS**

MDH Drinking Water Guidelines

- **Health Risk Limits:**
  - **PFOS: 0.3 ppb**
  - **PFOA: 0.3 ppb**
  - **PFBA: 7.0 ppb**
  - **PFBS: 7.0 ppb**

- Protective for both long-term/lifetime and fetal exposures
- Based on slight liver and thyroid effects
- Waiting for more toxicology studies to set HRL for PFHxS

Bedrock Layers in South Washington Co.

Sedimentary Deposits: 0-100 ft. thick, sand and gravel with clay layers

Decorah Shale: 0-15 ft. thick

Platteville & Glenwood Formations: 0-30 ft. thick, thinly bedded limestone, dolomite, and shale

St. Peter Sandstone: 0-150 ft. thick; private well aquifer

Prairie du Chien Group: 130-200 ft. thick, heavily karsted dolomite with sandy and shaley layers – high transmissivity zone near Shakopee - Oneota contact; private well aquifer

Jordan Sandstone: 65-95 ft. thick; main aquifer used by city wells, also used by private wells

St. Lawrence Formation: 35-60 ft. thick, dolomitic sandy shale and siltstone - can help slow or stop downward movement of PFBA

Franconia Sandstone: 165 ft. thick, green glauconitic sandstone, private well aquifer near river

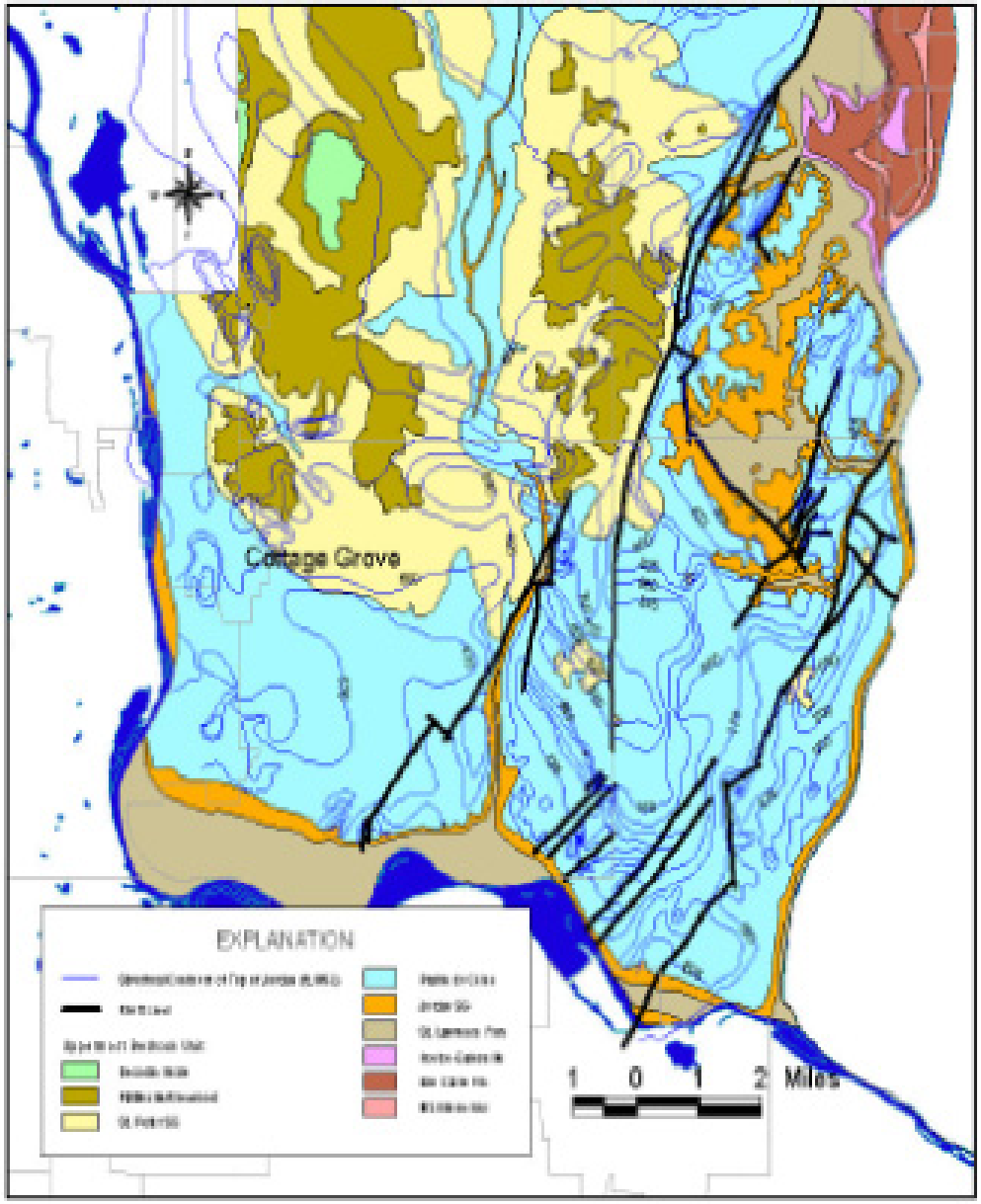
Bedrock Structure S. Washington Co.

Regional Scale (kms):
Bedrock Valleys – eroded as deep as the Jordan in some areas; associated karst

Faults – associated with St. Croix Anticline; up to 150 ft. displacement

Large Scale (10-100s m):
Joint Sets and associated karst in OPDC

Small Scale (cm-10s m):
Fractures – bedding plane and vertical; esp. in OPDC



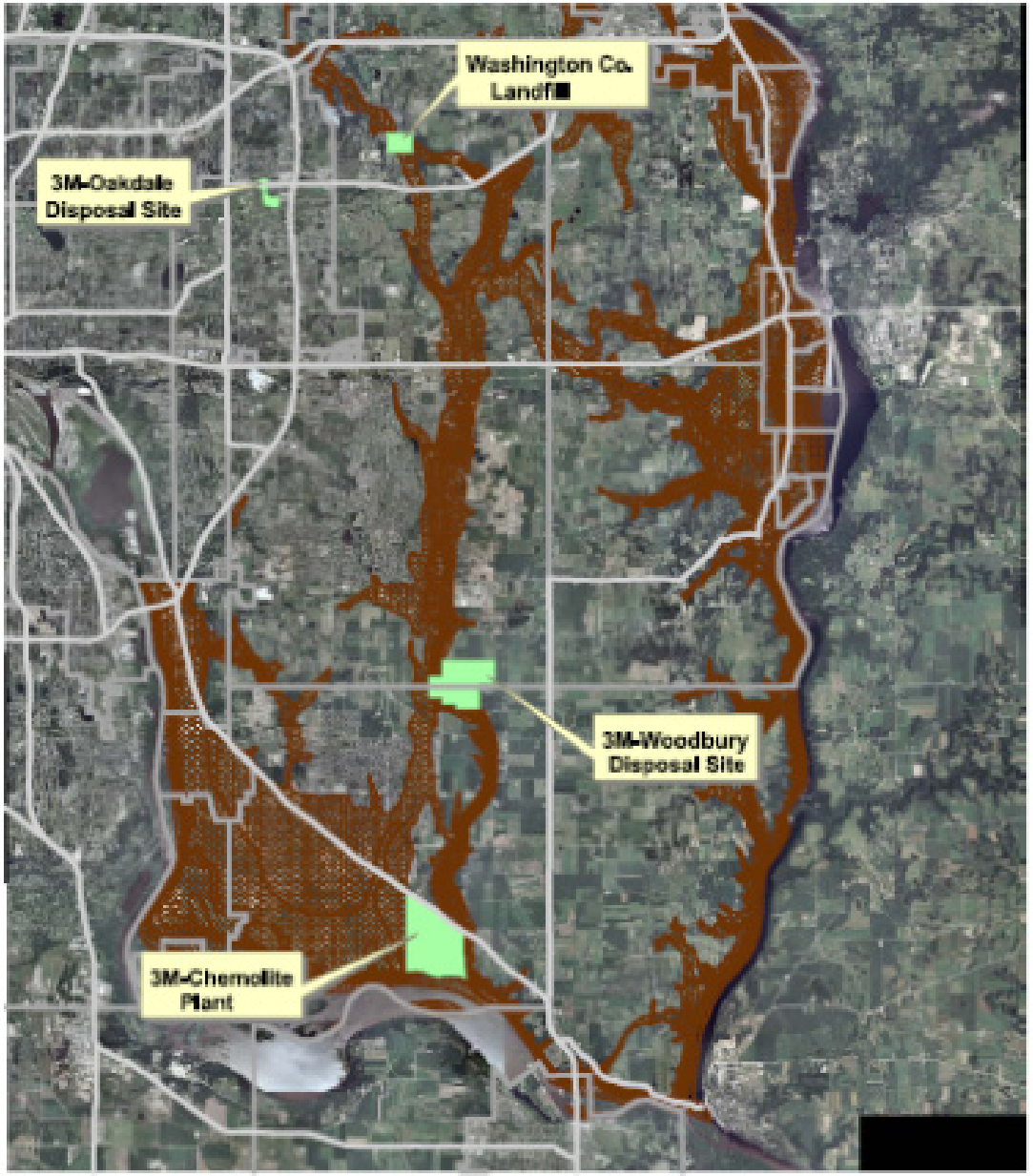
(adapted from Mossler, 2003)

Bedrock Valleys

Deep buried valleys provide conduits for groundwater and contaminant migration to Prairie du Chien & Jordan

Karst development in both the St. Peter and Prairie du Chien proximal to bedrock valleys provides rapid distribution pathways into these aquifers.

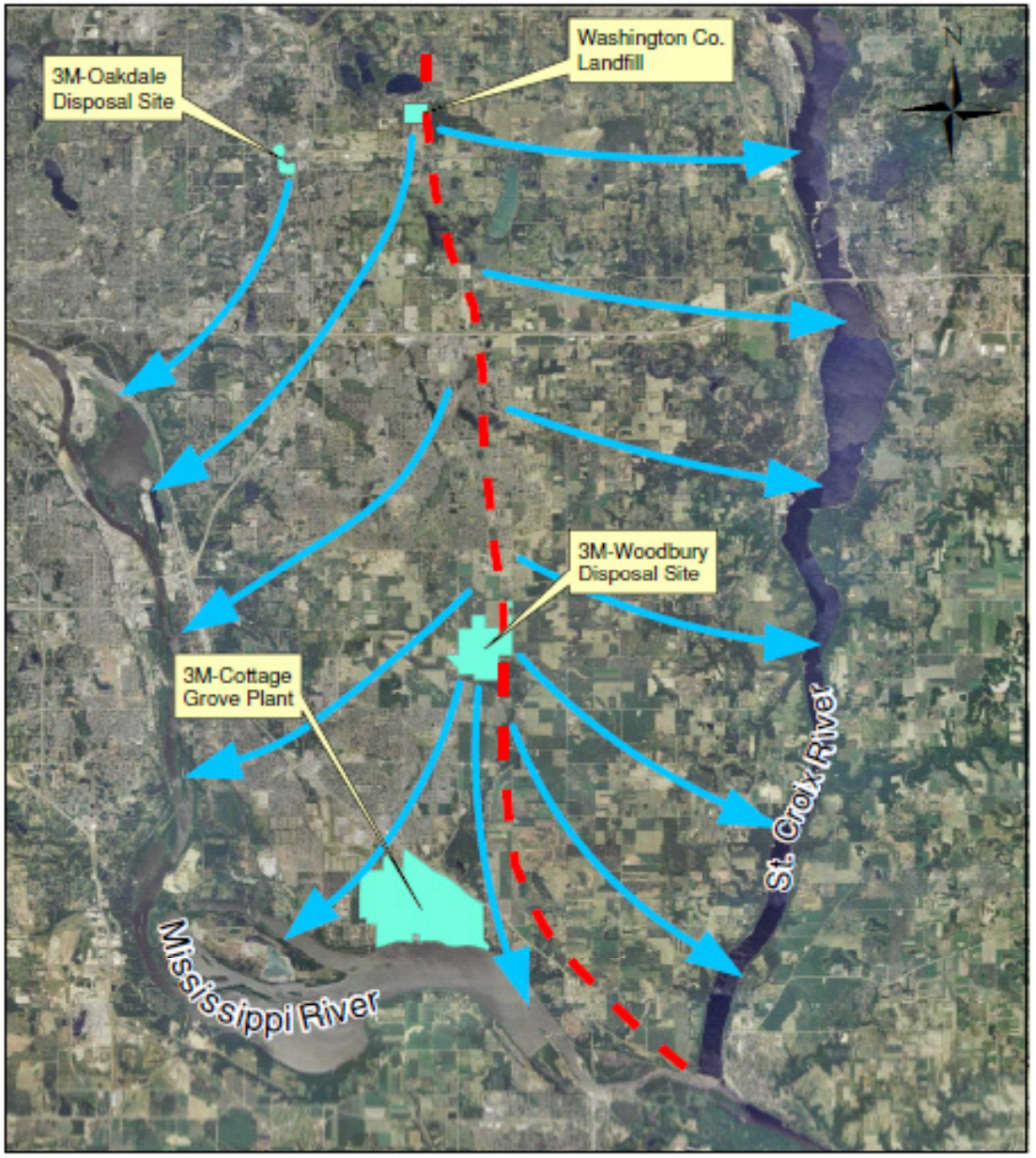
Note location of Wash. Co. landfill and 3M-Woodbury disposal site relative to bedrock valleys



Location of Buried Bedrock Valleys in South Washington County

Groundwater Flow

- A groundwater divide extends from north to south beneath the county
- East of the divide groundwater flows to the St. Croix River
- West of the divide groundwater flows to the Mississippi River
- Close to where the two rivers meet, the flow "fans out" toward either river
- Locally, groundwater flow may be influenced by pumping wells



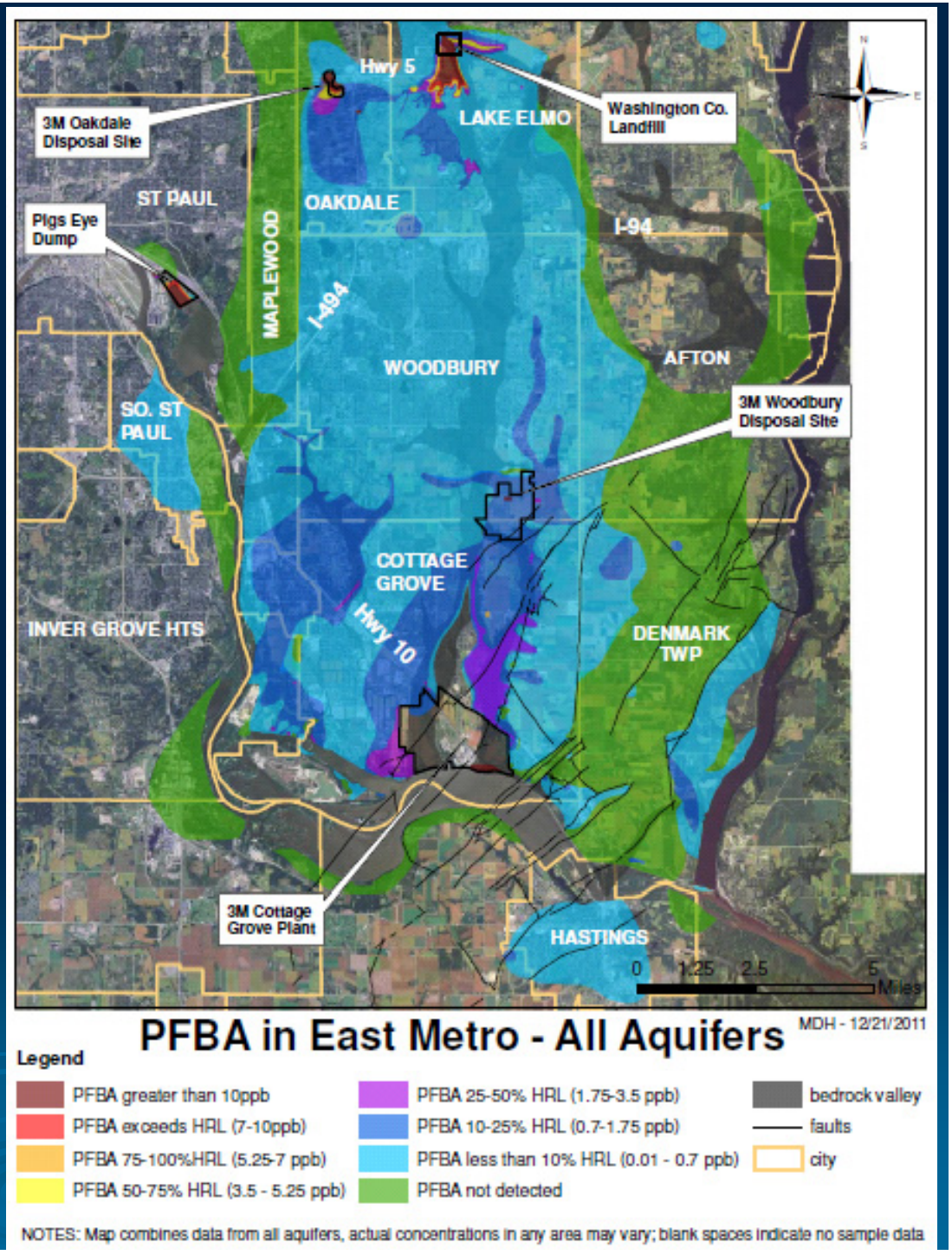
General Groundwater Flow - South Washington Co.

Approximate location of regional groundwater divide

General direction of regional groundwater flow

Result: Extremely Large Plumes

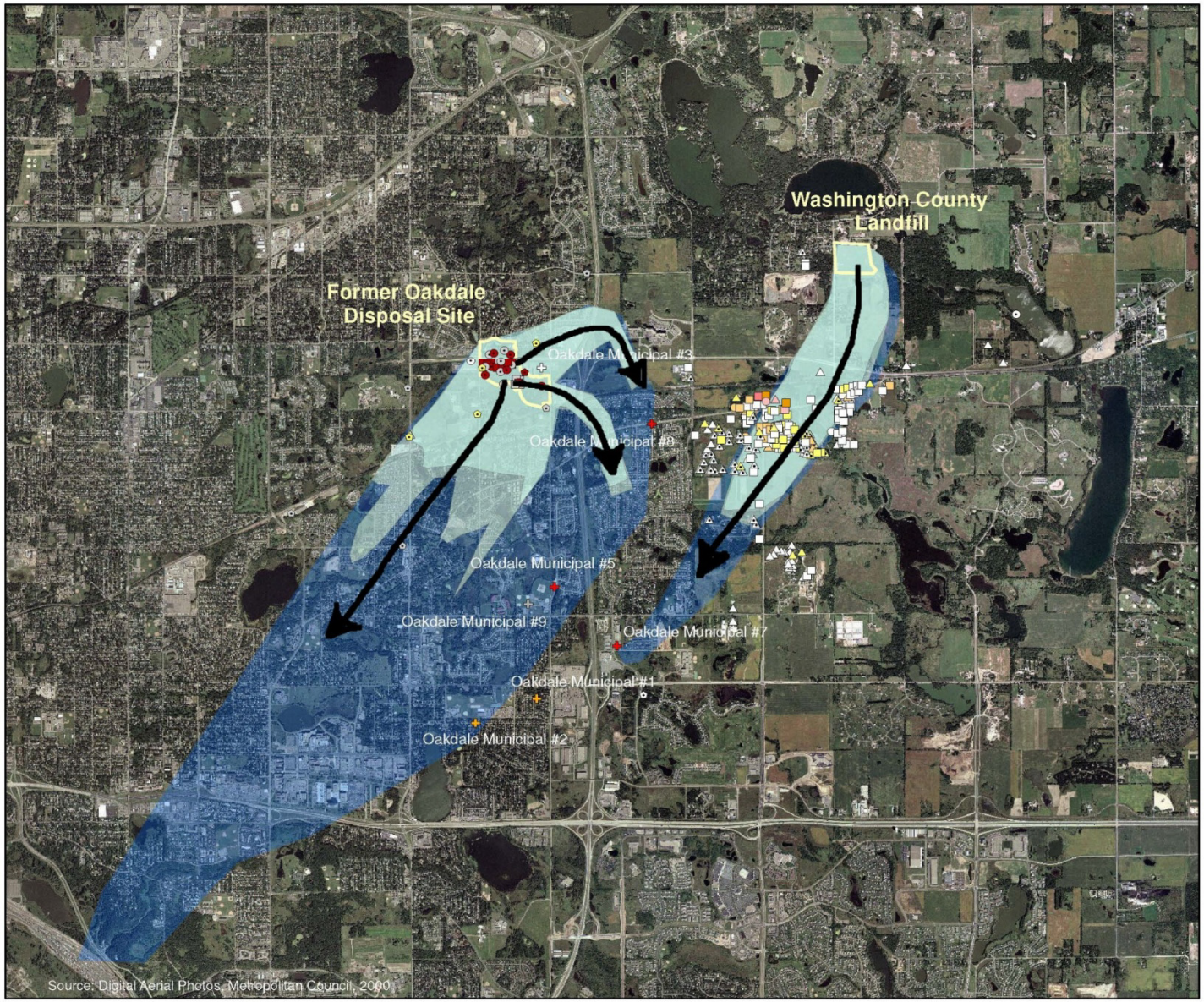
- **Over 100 sq. mi.**
  - 4 major aquifers
  - 8 municipal systems
  - >1,000 private wells
  - Much larger than predicted by models
- **PFBA most widespread**
  - More PFBA in source areas
  - More mobile
- **Distribution controlled by:**
  - Bedrock features
  - Groundwater - Surface water interactions
  - Groundwater pumping
- **Several "anomalous" areas**
  - PFOS in Lake Elmo
  - Crossing groundwater divide
  - Isolated patches of PFCs
  - PFBA across Mississippi R.



PFOS in the Lake Elmo Area

Groundwater–Surface Water Interactions and the Law of Unintended Consequences

Predicted PFC Plume



Legend

PFC - Oakdale Municipal Wells

- Non-detect
- <0.1 ppb PFOA/PFOS
- >0.5 ppb PFOA/PFOS
- Not Measured

- Plume Estimate 2005 (MODPATH)
- Plume Estimate 1984 (MODPATH)
- Plume Estimate 1982 (MODPATH)

Aquifer Symbol

- Multiple Aquifers
- Prairie du Chien
- Platteville Formation
- St. Peter Sandstone
- Quaternary Aquifer
- Unknown Aquifer

PFOA Detection Range Color Key

- Non-detect
- .01-.5 ug/L
- .51-1.0 ug/L
- 1.01-1.5 ug/L
- 1.51-2.0 ug/L
- 2.01-2.5 ug/L
- 2.51-3.0 ug/L
- >3 ug/L

Feet
5,000

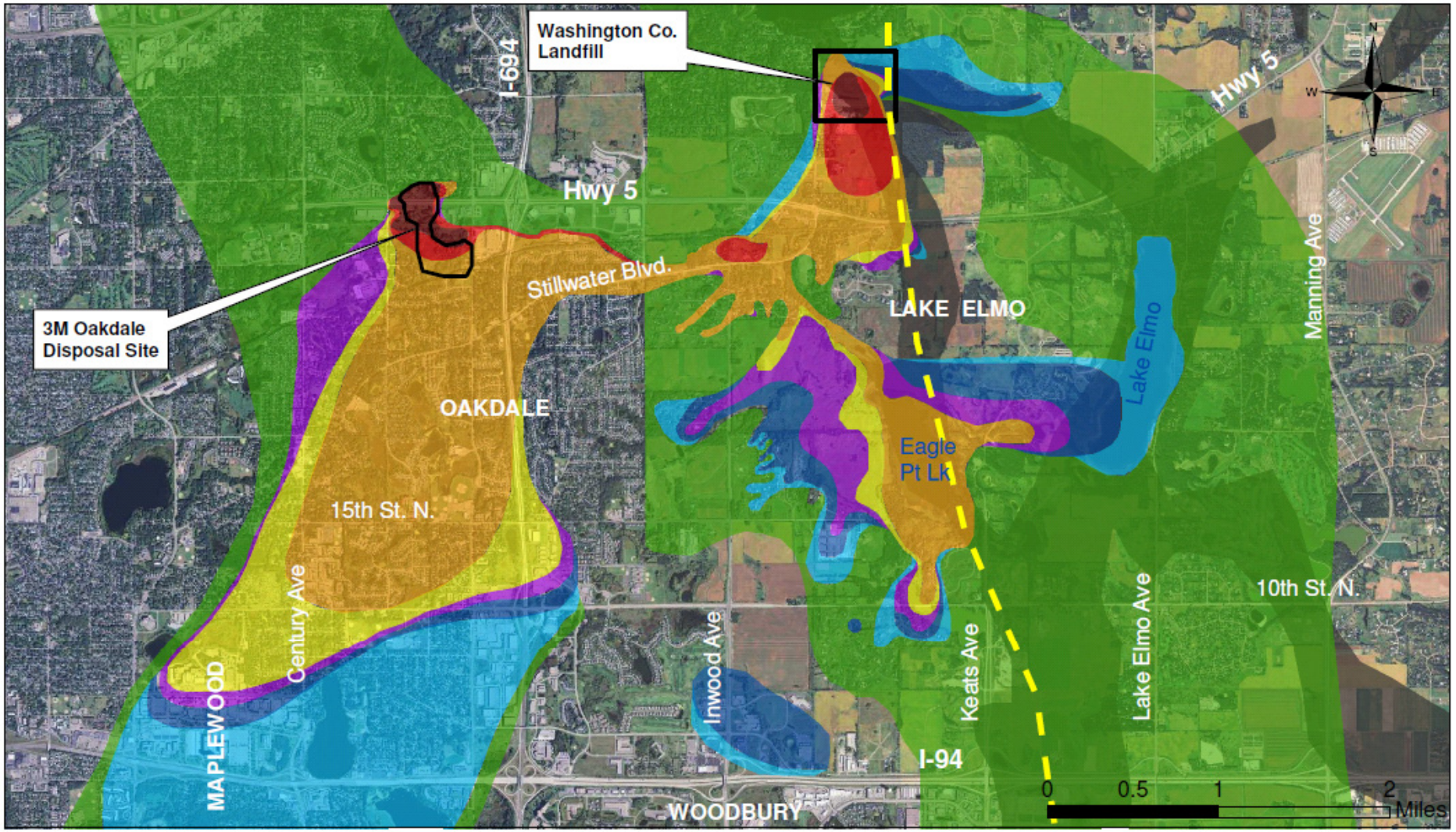
Meters
500 0 500 1,000 1,500 2,000

Figure 7

PREDICTED PFC PLUME LOCATIONS (MODPATH)

Former Oakdale Disposal Site/Washington County Landfill Groundwater Modeling

Minnesota Pollution Control Agency
Washington County, Minnesota



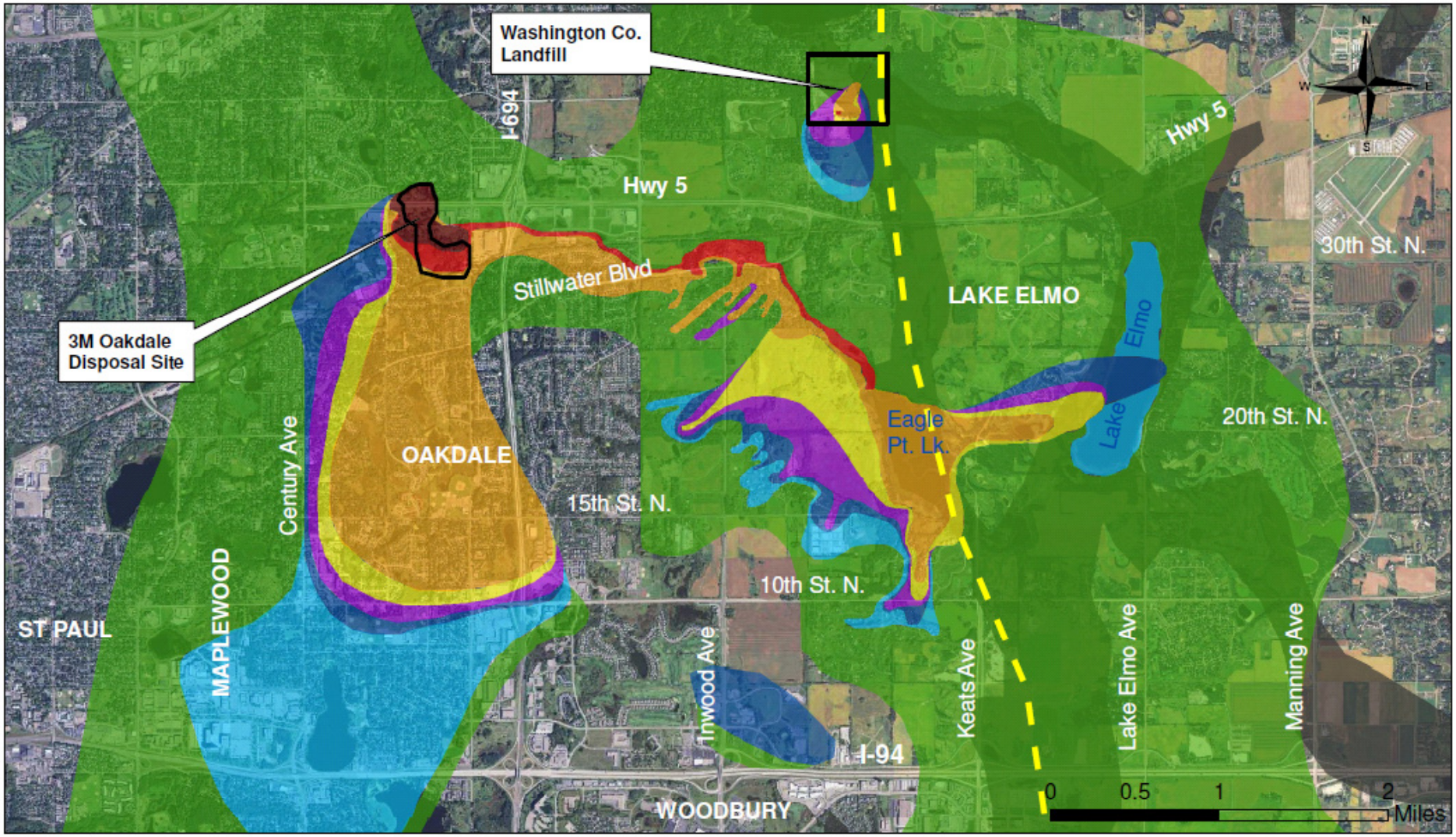
PFOA in Lake Elmo/Oakdale - All Aquifers

Legend

- PFOA exceeds HRL (>10 ppb)
- PFOA exceeds HRL (1-10 ppb)
- PFOA exceeds HRL (0.3-0.99 ppb)
- PFOA 75-100% HRL (0.23 - 0.3) ppb)
- PFOA 50-75% HRL (0.15 - 0.23 ppb)
- PFOA 25-50% HRL (0.075 - 0.15 ppb)
- PFOA less than 25% HRL (0.01 - 0.075 ppb)
- PFOA not detected
- Approx. location groundwater divide
- bedrock valley

NOTES: Map combines data from all aquifers, actual concentrations in any area may vary; blank spaces indicate no sample data

MDH - 9/25/2012



PFOS in Lake Elmo/Oakdale - All Aquifers

Legend

- PFOS exceeds HRL (> 10ppb)
- PFOS exceeds HRL (1-10 ppb)
- PFOS exceeds HRL (0.3-0.99 ppb)
- PFOS 75-100% HRL (0.23 - 0.3 ppb)
- PFOS 50-75% HRL (0.15 - 0.23 ppb)
- PFOS 25-50% HRL (0.075 - 0.15 ppb)
- PFOS less than 25% HRL (0.015 - 0.075 ppb)
- PFOS not detected
- Approx. location of groundwater divide
- bedrock valley

NOTES: Map combines data from all aquifers, actual concentrations in any area may vary; blank spaces indicate no sample data

MDH - 9/25/2012

Effect of Groundwater-Surface Water Interactions on PFC Migration

- Raleigh Creek identified as major factor in PFOS and other PFC migration into Eagle Pt. Lake and Lake Elmo
  - May account for PFOS in fish in Lake Elmo
- Wastewater discharge to Raleigh Creek from pump-out well at Washington Co. landfill (1988-1995)
  - Conservative estimate: 1,000+ lb PFBA, 75+ lb PFOA, 1.5+ lb PFOS

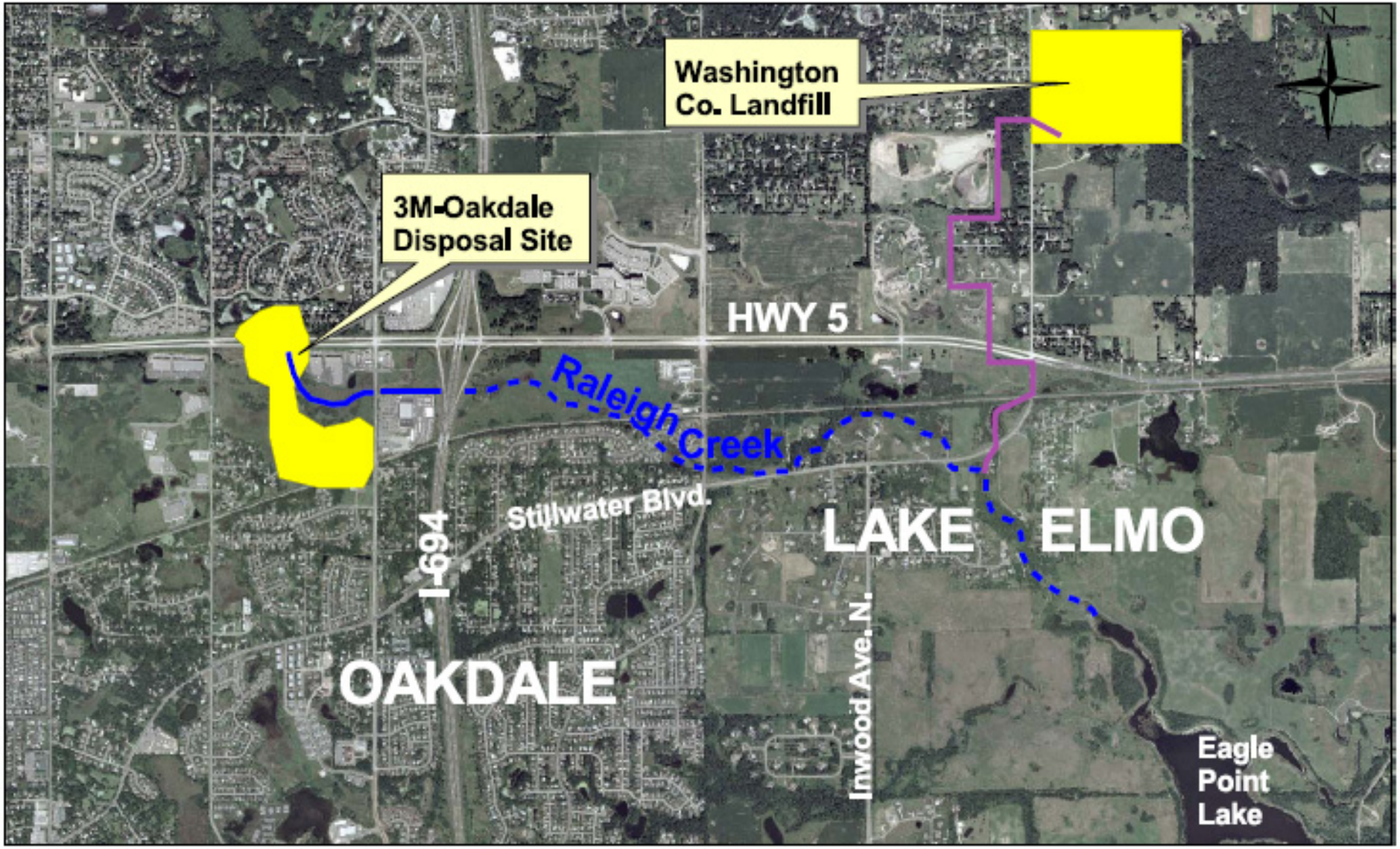


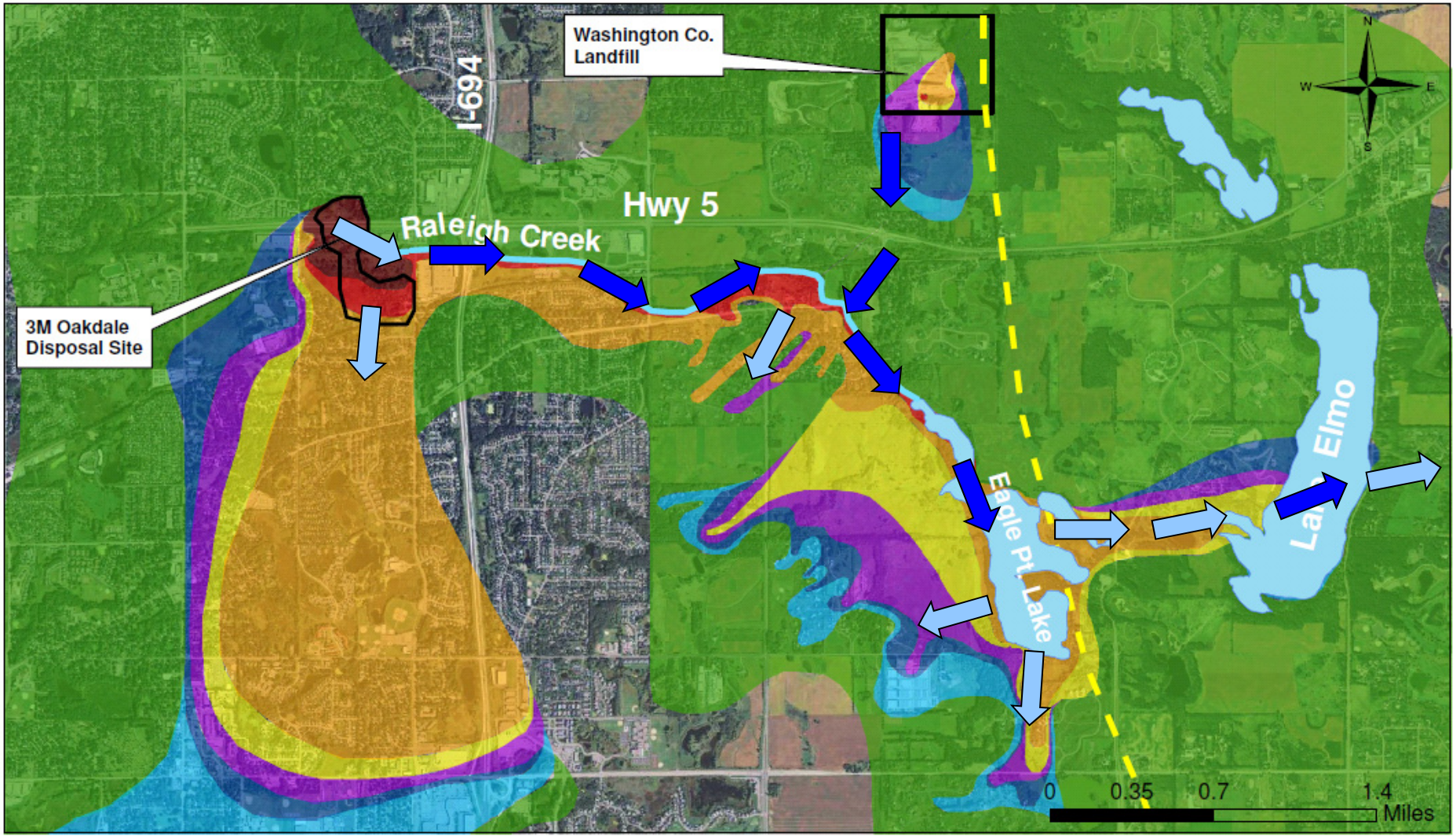
Figure 9: Raleigh Creek

"Gaining" stream section of creek*

"Losing" stream section of creek*

Route of 1988-1995 discharge from landfill to the creek

* see page 22 or glossary



PFOS in Lake Elmo/Oakdale - All Aquifers

Legend

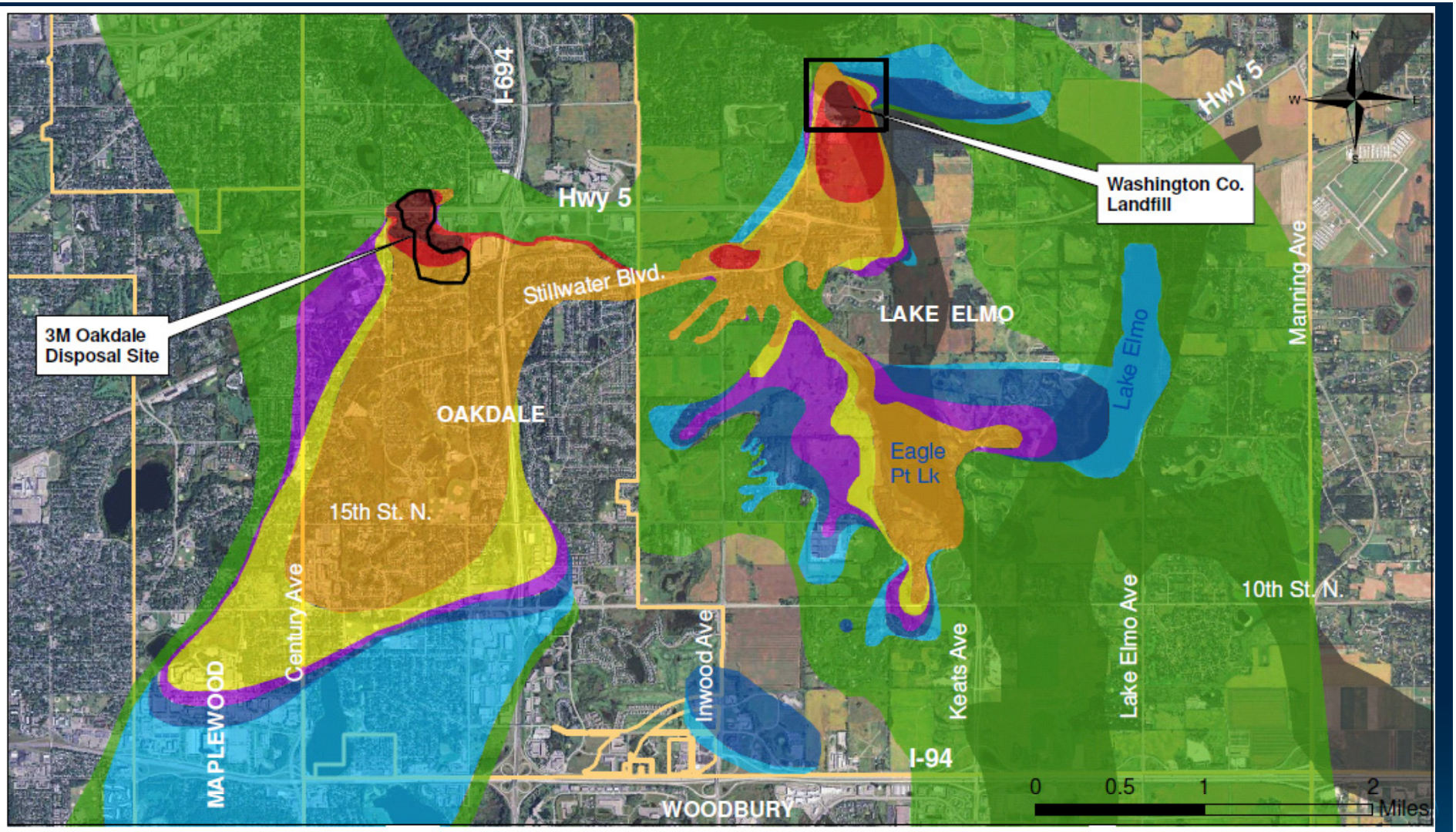
- PFOS exceeds HRL (> 10ppb)
- PFOS exceeds HRL (1-10 ppb)
- PFOS exceeds HRL (0.3-0.99 ppb)
- PFOS 75-100% HRL (0.23 - 0.3 ppb)
- PFOS 50-75% HRL (0.15 - 0.23 ppb)
- PFOS 25-50% HRL (0.075 - 0.15 ppb)
- PFOS less than 25% HRL (0.015 - 0.075 ppb)
- PFOS not detected
- Surface water
- Groundwater divide
- Surface water flow
- Groundwater flow

NOTES: Map combines data from all aquifers, actual concentrations in any area may vary; blank spaces indicate no sample data

MDH - 9/25/2012

Anomalous Areas

The Influence of Bedrock Structures



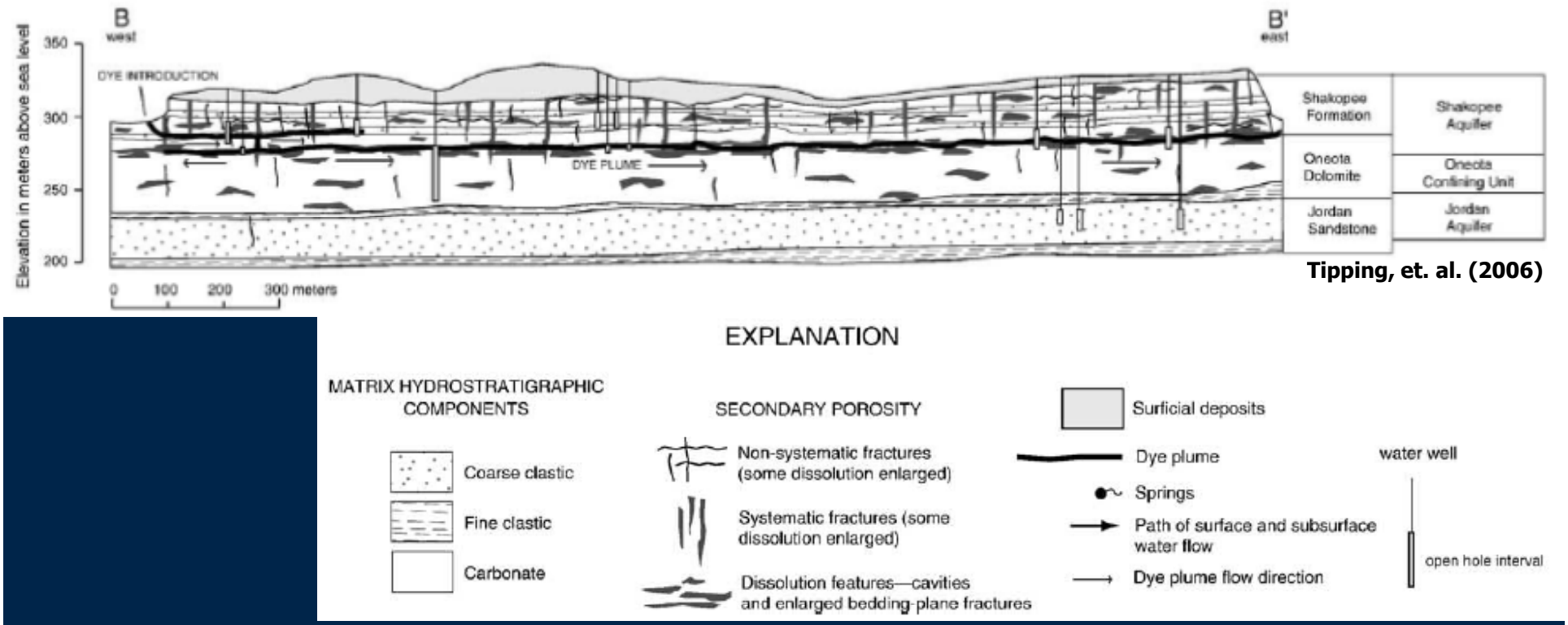
MDH - 12/23/2011

PFOA in Lake Elmo/Oakdale - All Aquifers

Legend

- PFOA exceeds HRL (>10 ppb)
- PFOA exceeds HRL (1-10 ppb)
- PFOA exceeds HRL (0.3-0.99 ppb)
- PFOA 75-100% HRL (0.23 - 0.3) ppb)
- PFOA 50-75% HRL (0.15 - 0.23 ppb)
- PFOA 25-50% HRL (0.075 - 0.15 ppb)
- PFOA less than 25% HRL (0.01 - 0.075 ppb)
- PFOA not detected
- bedrock valley
- faults
- city

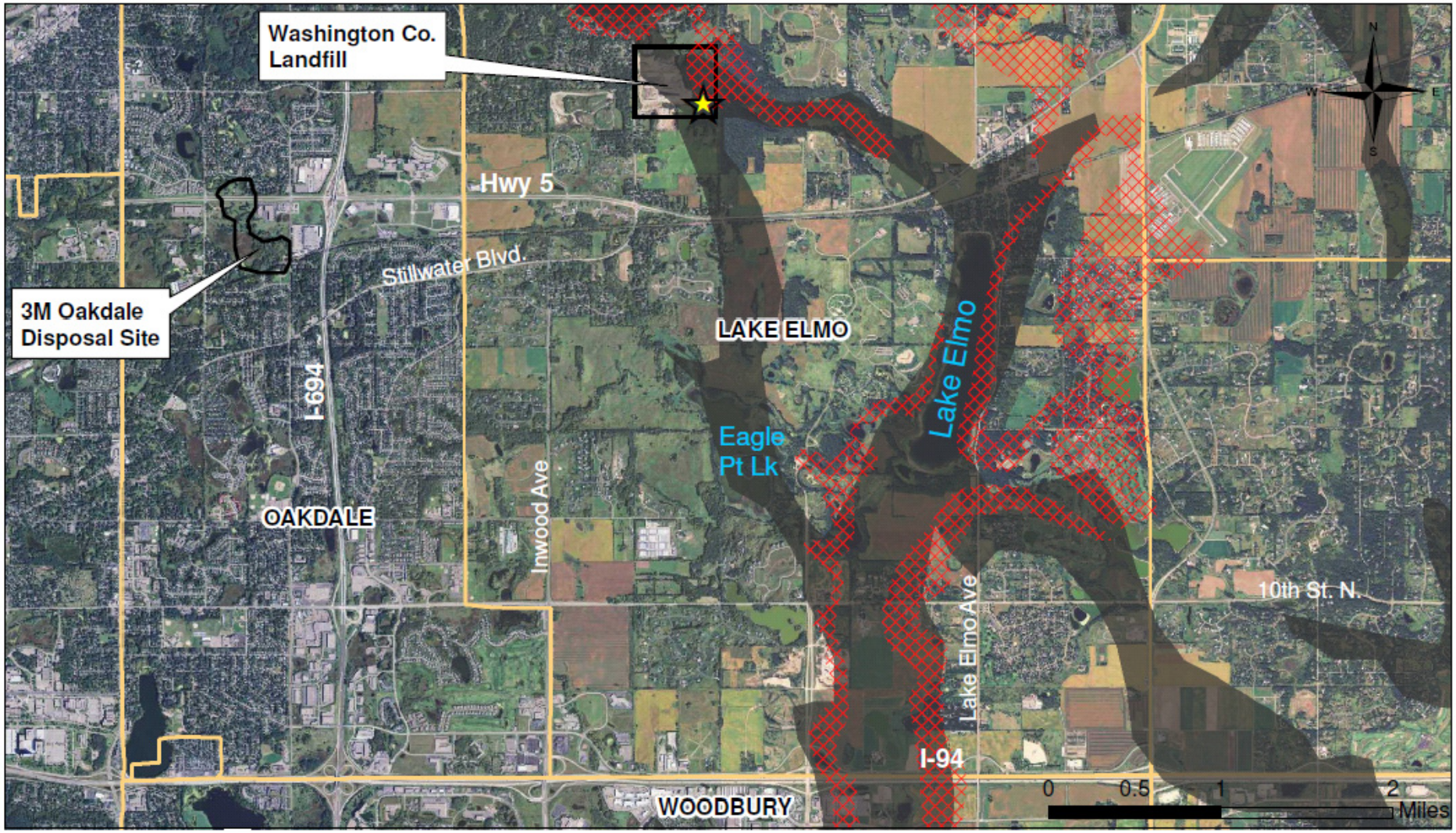
NOTES: Map combines data from all aquifers, actual concentrations in any area may vary; blank spaces indicate no sample data



Tipping, et. al. (2006)

High Transmissivity Zone – Prairie du Chien

Tipping, et al (2006) noted that the Shakopee and upper 1/3 of the Oneota has ubiquitous solution widened fractures. Fracture abundance increases as the depth to the Shakopee decreases.



High Transmissivity Zone Subcrops Quaternary - Lake Elmo

Legend

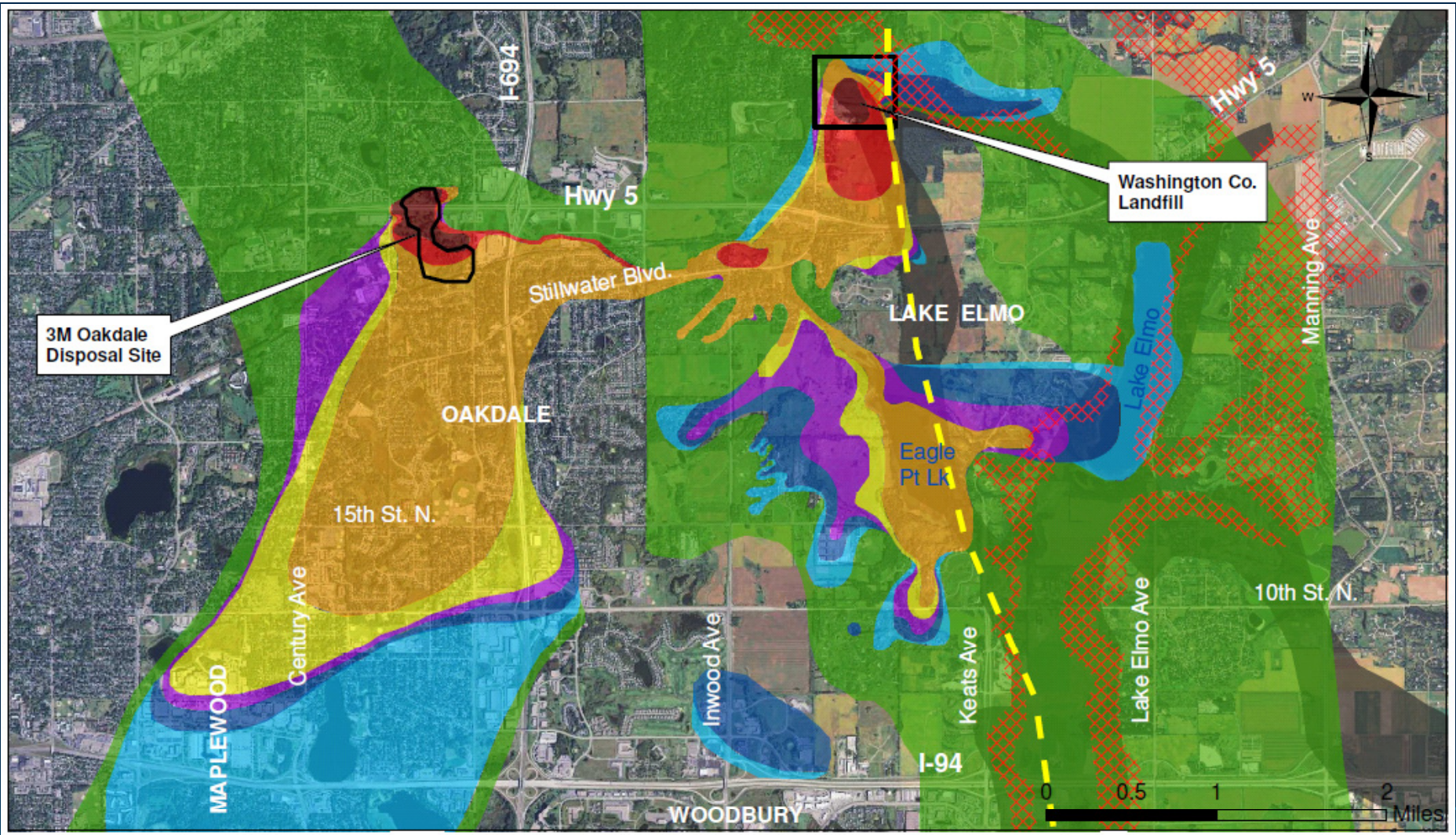
Area of HTZ Subcrop

bedrock valley

former spray irrigation/infiltration area

NOTES: Map combines data from all aquifers, actual concentrations in any area may vary; blank spaces indicate no sample data

MDH - 9/28/2012



PFOA and Subcropping of High Transmissivity Zone

Legend

- PFOA exceeds HRL (>10 ppb)
- PFOA exceeds HRL (1-10 ppb)
- PFOA exceeds HRL (0.3-0.99 ppb)
- PFOA 75-100% HRL (0.23 - 0.3) ppb)
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- PFOA less than 25% HRL (0.01 - 0.075 ppb)
- PFOA not detected
- Approx. location groundwater divide
- Area of HTZ Subcrop
- bedrock valley

NOTES: Map combines data from all aquifers, actual concentrations in any area may vary; blank spaces indicate no sample data

MDH - 9/25/2011

Bedrock Valleys & Faults

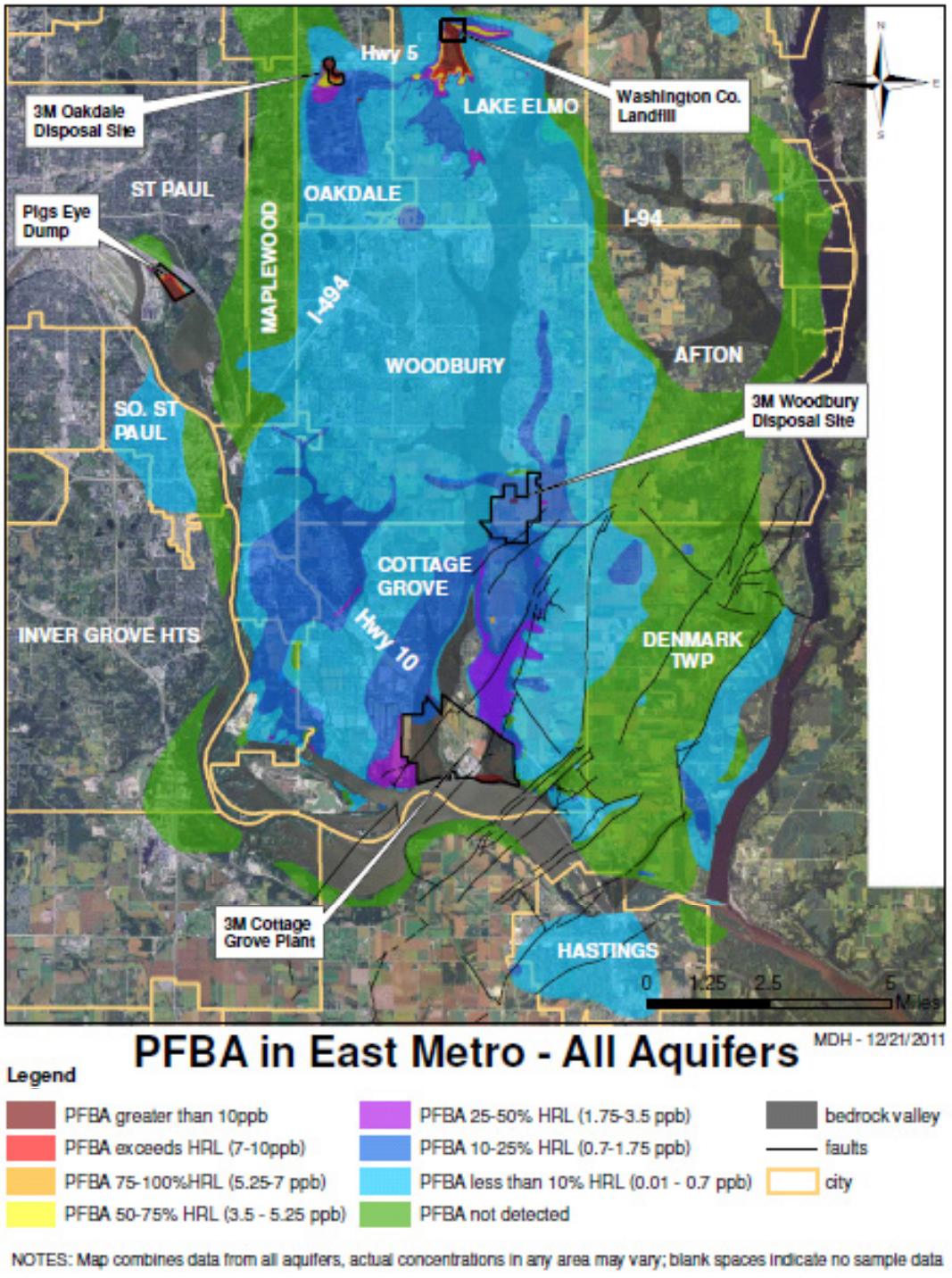
Higher PFBA levels coincide with major bedrock valley & faults

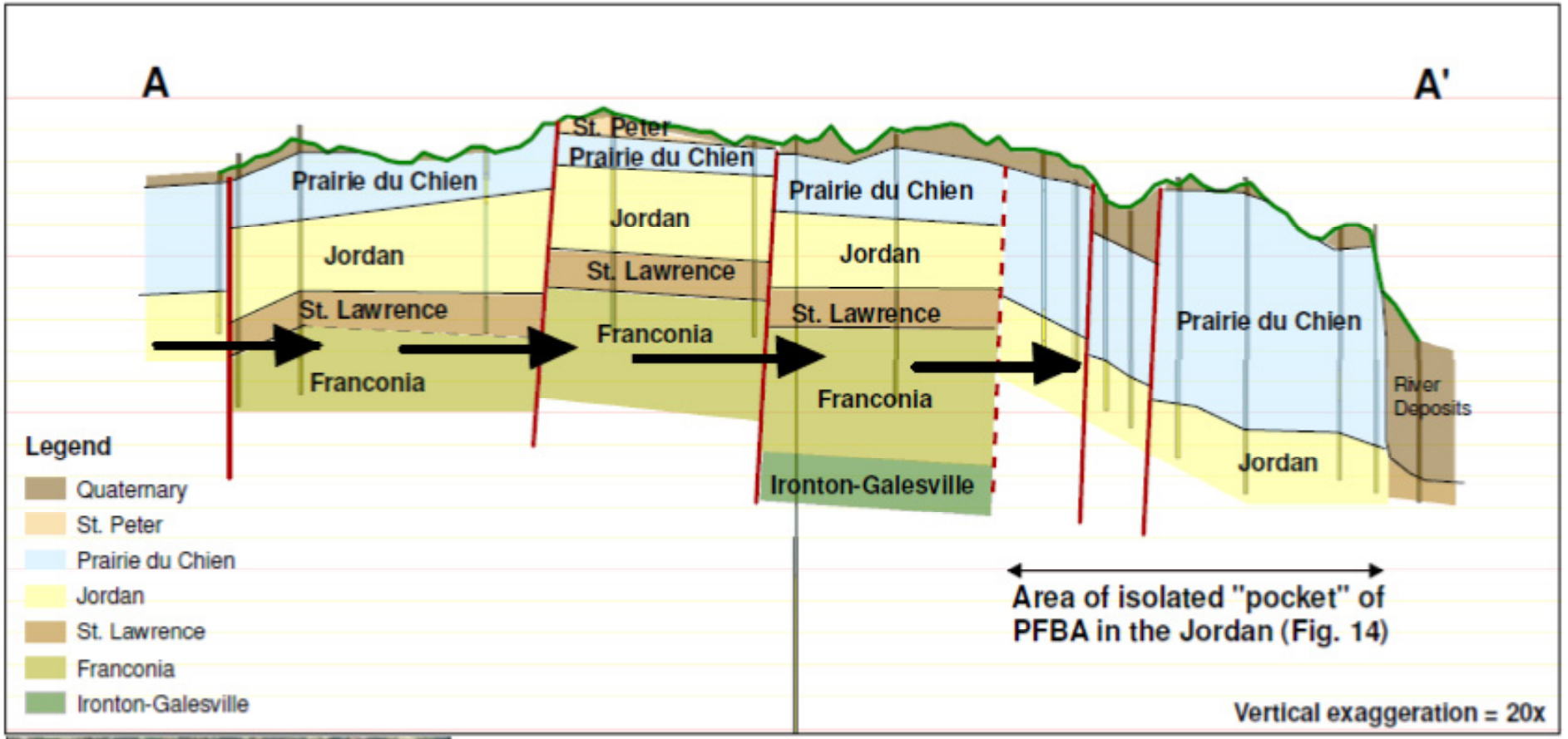
- Especially where HTZ subcrops

"Fingers" of plume subparallel with faults

Apparently isolated areas of PFBA a result of flow across major faults

- Along St. Croix River
- Hastings





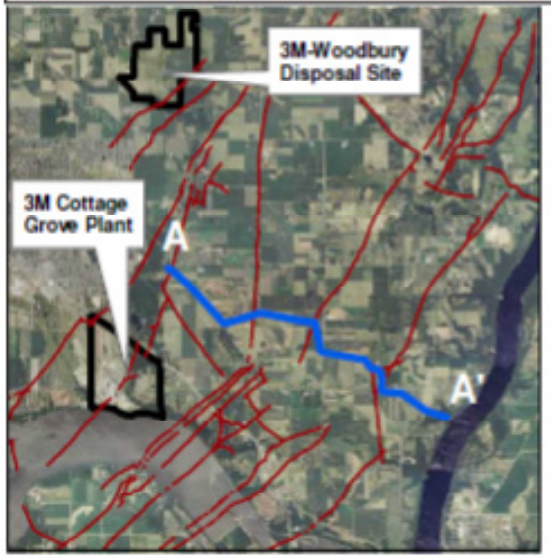


Figure 4 - Cross-Section Across Highly Faulted Zone

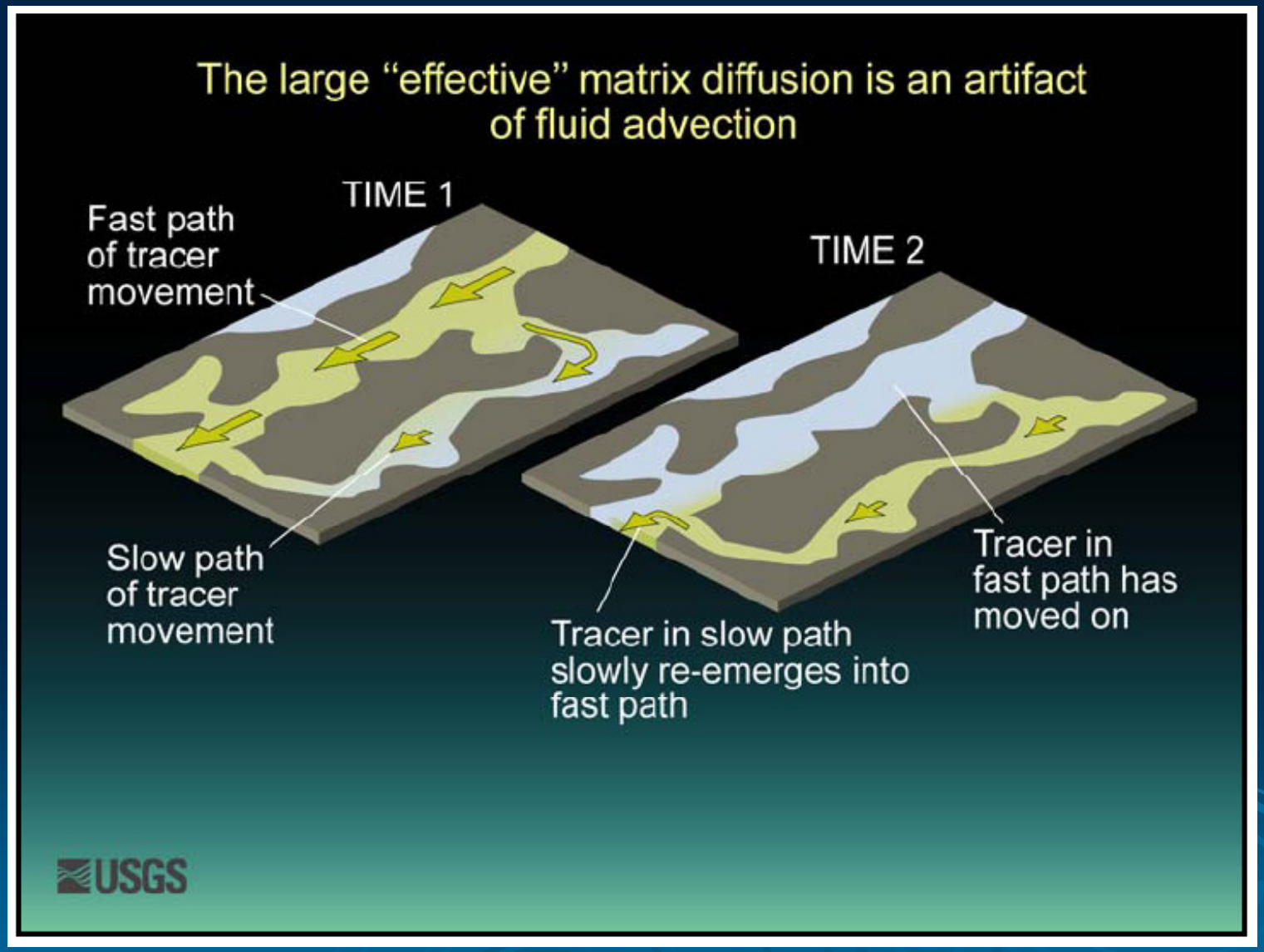
This figure shows a cross-sectional view of the bedrock along a transect (blue line in map) from Cottage Grove near Ravine Park and trending east-southeast to the St. Croix River. Many bedrock faults (shown in red) have disturbed the geology in this area, bringing different bedrock units into contact with one another. This may have allowed PFBA to move from one aquifer to another, creating what appear to be isolated "pockets" of contamination when viewed on a map (such as Fig. 9). The arrows on the cross-section view show a hypothetical pathway that PFBA may have followed that would allow the contaminant to migrate from the Jordan into the Franconia and back into the Jordan again.

Prepared by MDH - 8/26/09

Theory of Plume History

- PFCs escaped from disposal sites very soon after waste disposal began
- Very large, deep plumes established quickly:
  - Persistence and mobility of PFCs
  - High flow rates resulting from bedrock structures
  - Groundwater-surface water interactions
  - Human interventions
- Current plumes are remnants largely sustained by slower PFC release from secondary flow paths and matrix diffusion
  - Concentrations extremely stable

Secondary Flow Paths in Fractured Rock



From Shapiro, 2008

Response Actions – East Metro:

- **Water Treatment where HRLs Exceeded**
  - Granular Activated Carbon (GAC)
  - Oakdale city wells & 140 whole-house residential
  - Pilot study also found reverse osmosis effective

Response Actions – East Metro:

- **Additional Site Cleanup**
  - Waste, soil and sediment excavation (redisposed in triple-lined cells with leachate collection)
  - Enhanced groundwater gradient control
- **Biomonitoring**
  - 190 residents in areas with PFOS & PFOA
  - 2008 and 2010
- **Garden & House Dust Study**
  - Preliminary results indicate plant uptake of PFCs, but below levels of health concern

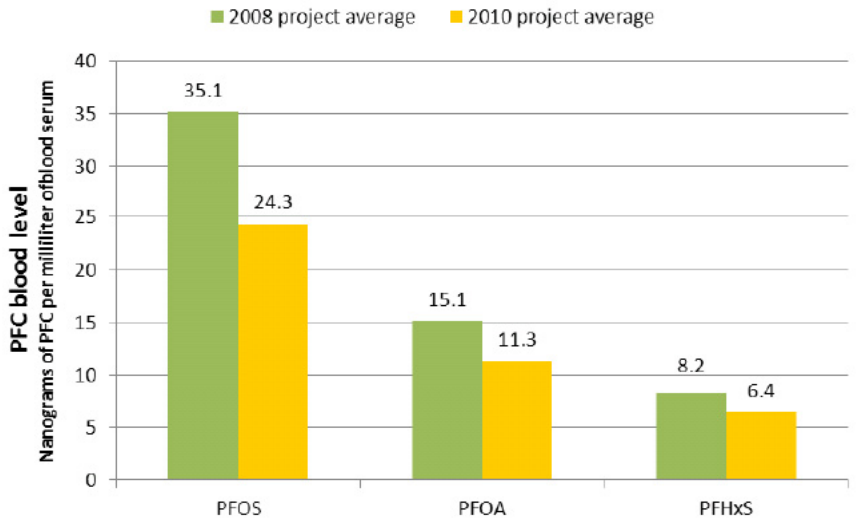
Health Implications

- Most private wells have only PFBA at levels below health concern
  - Doesn't accumulate in the body
- Areas with levels of PFCs above health concern have been identified and addressed
  - Clean city water
  - Carbon filter systems

Biomonitoring Shows Effectiveness of Response

Change since 2008

- PFOS ↓ 26%
- PFOA ↓ 21%
- PFHxS ↓ 13%



- Other PFCs less commonly detected; PFBA detected in 21% in 2010, 25% in 2008

MINNESOTA MDH DEPARTMENT OF HEALTH

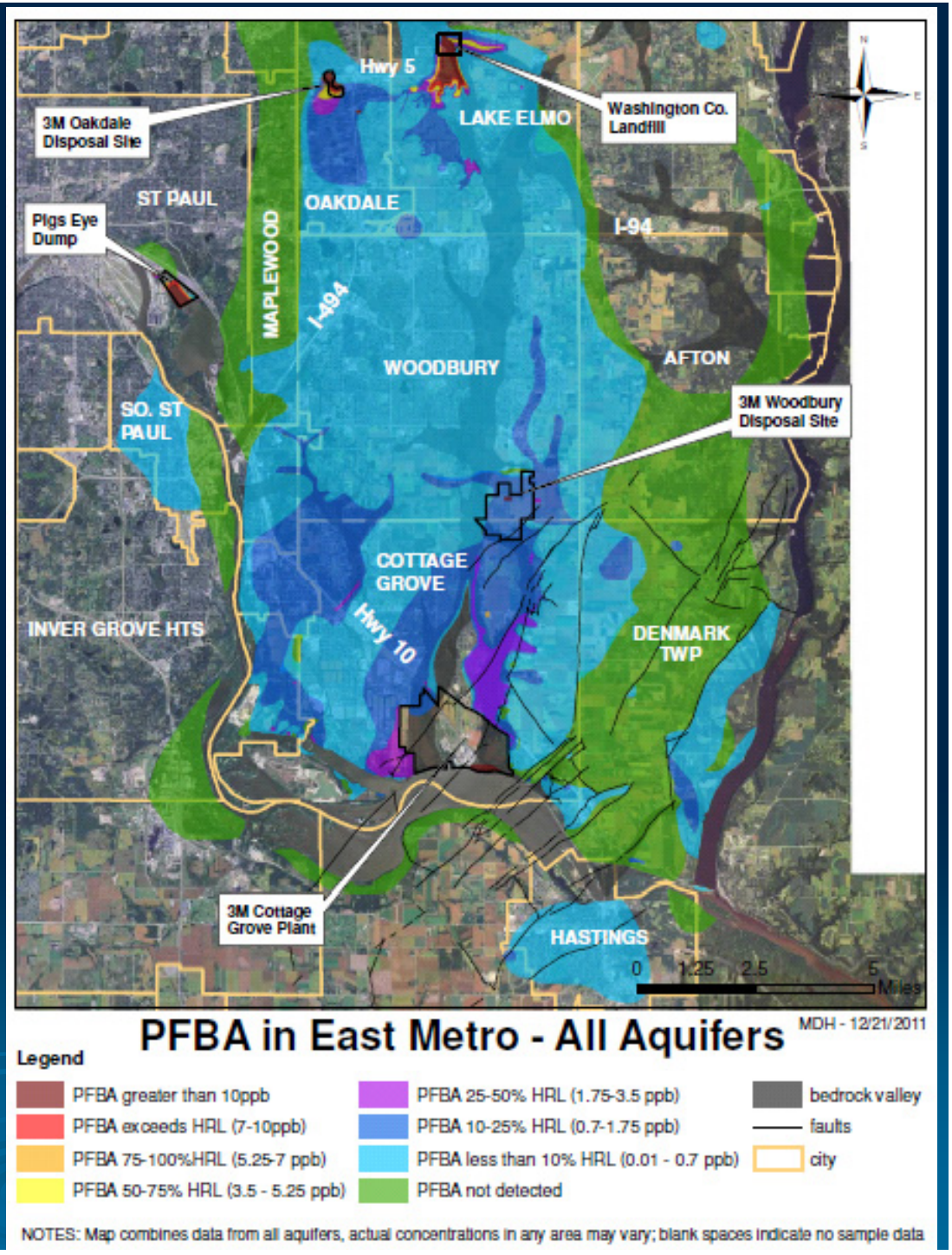
PFCs decreased in blood of people drinking treated water (but average concentrations still above national averages)

Response Actions – Statewide:

- Fish Studies & Consumption Advisories
- Ambient Groundwater Monitoring
- Fire Training Site Investigations
- Wastewater Treatment Plant Effluent
- Landfill Sampling (groundwater, leachate, condensate)
- Air & Precipitation Monitoring

Conclusions:

- PFCs are highly mobile and persistent in the environment
- This allows them to generate extremely large plumes
- Smaller chain PFCs, such as PFBA, move more rapidly and are more widespread, than longer-chain PFCs.
- You must consider unusual pathways and sources for PFCs – take nothing for granted and know the local geology
- Stable concentrations suggest plumes establish rapidly and then stabilize



Acknowledgements

- MDH - Environmental Health and Health Promotion & Chronic Disease Divisions
- MPCA – Closed Landfill & Superfund Programs
- Minnesota Geological Survey
- Washington County
- Valley Creek Watershed District
- University of Minnesota
- West Central Environmental Consultants, Delta Environmental Consultants, Barr Engineering & Interpoll Labs
- ATSDR
- USGS
- 3M Company

Questions?

More Information:

MDH general PFC Information:
http://www.health.state.mn.us/divs/eh/hazardous/topics/pfcs/index.html

MDH Reports:
http://www.health.state.mn.us/divs/eh/hazardous/topics/pfcs/reports.html

MDH Health Risk Limits:
http://www.health.state.mn.us/divs/eh/risk/guidance/gw/table.html

MPCA PFC Investigations:
http://www.pca.state.mn.us/index.php/waste/waste-and-cleanup/cleanup-programs-and-topics/topics/perfluorochemicals-pfc/perfluorochemicals-pfcs.html?menuid=&redirect=1