KARST INFLUENCE IN THE CREATION OF A PFC MEGAPLUME

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Abstract

Perfluorochemicals (PFCs) are fully-fluorinated organic chemicals used to produce a wide range of industrial and commercial products. Their extreme persistence and mobility in the environment and nearly ubiquitous presence in humans and wildlife has raised serious concerns regarding their environmental and human health effects. In the 1940s to 1970s, PFC-bearing wastes were disposed of in three unlined landfills in Washington County, Minnesota. The resulting co-mingled PFC plumes created a "megaplume" that contaminated over 250 km^2 of groundwater and four major drinking water aquifers; affecting eight municipal water supply systems and thousands of private wells. Site investigations revealed that karst features, particularly in the Prairie du Chien Group (OPDC), and groundwater-surface water interactions played a critical role in contaminant migration.

Introduction

Perfluorochemicals (PFCs) are a class of fully-fluorinated organic chemicals that have been used to produce a wide range of industrial and commercial products. Their extreme persistence and mobility in the environment and nearly ubiquitous presence in humans and wildlife has raised serious concerns regarding their environmental and health effects (Giesy and Kannan, 2002; Olsen, et al., 2003; ATSDR, 2009). As a result, in 2006, the EPA announced it would seek the phasing out of production and most uses of two PFCs, perfluoro-octane sulfonate (PFOS) and perfluorooctanoic acid (PFOA).

3M Corporation (3M) researched and produced PFCs in Cottage Grove, MN since the 1940s. From the 1940s to 1970s, PFC-bearing wastes were disposed of at the 3M Cottage Grove facility and in three unlined landfills in Washington County, MN (ATSDR, 2008). All of these sites were investigated for industrial solvent contamination in the 1980s and had active groundwater extraction systems operating. In 2003, 3M notified the Minnesota Pollution Control Agency (MPCA) that PFCs had been detected in the drinking and production water at the Cottage Grove plant.

The MPCA and Minnesota Department of Health (MDH) began testing Washington County public and private wells for PFCs in 2003. This work eventually delineated three major co-mingled PFC plumes that contaminated over 250 km^2 of groundwater in four major drinking-water aquifers; affecting eight municipal-water supply systems and thousands of private wells (Yingling, et al., 2014).

Initial groundwater flow modeling predicted more limited, discreet PFC plumes (Barr Engineering, 2005). It was also assumed that a north-south trending groundwater divide that bisects the county would largely limit PFC contamination to the west of the divide. However, further investigation revealed groundwater-surface water interactions and the influence of karst features in a key bedrock aquifer created unanticipated pathways for contaminant migration.

Hydrogeology of Southern Washington County

Southern Washington County is located on the eastern edge of the Twin Cities Basin and is underlain by the lower Paleozoic sedimentary sequence typical of the Hollandale Embayment, covered by 3 – 30 m of unconsolidated glacial drift and alluvium (Figure 1). Reactivation of Proterozoic faults sometime after the Middle Ordovician resulted in large-scale, northeast-southwest trending block faults with vertical displacement of up to 45 m and associated subperpendicular and subparallel jointing (Figure 2; Mossler and Bloomgren, 1990; Mossler and Tipping, 2004).

Four major aquifers provide the majority of drinking water for community and private wells in the area: St. Peter Sandstone (OSTP), Prairie du Chien Group (OPDC), Jordan Sandstone (CJDN), and Tunnel City Group (CTCG; formerly the Franconia). Although separated by lower permeability layers or "leaky" aquitards (as in the case of the St. Lawrence [CSTL], between the CJDN and CTCG), bedrock faults and vertical joints have compromised the integrity of these layers, particularly in the southern- and eastern-most portions of the county. This, in part, accounts for hydraulic communication between the aquifers.

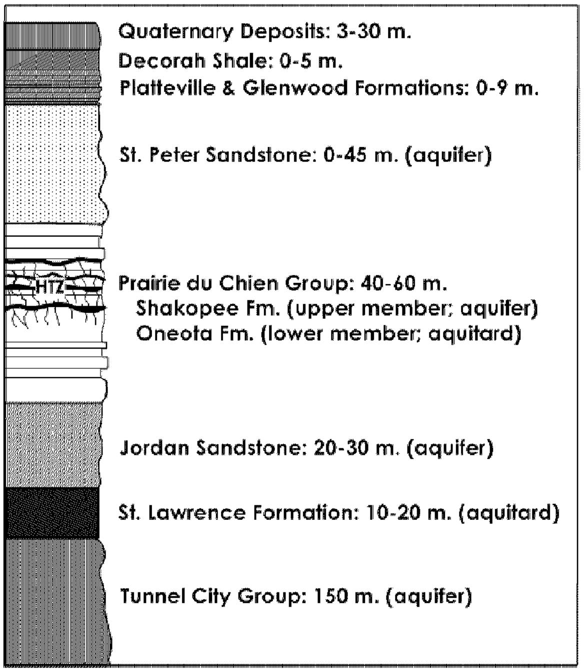

Figure 1. *Generalized stratigraphic column for Washington County, Minnesota.*

A network of deeply incised bedrock valleys, which are eroded down to the CJDN and possibly even the CSTL in some places, provide another route of hydraulic communication between the upper aquifers (OSTP, OPDC, and CJDN). The valleys were once tributaries to the Mississippi River, which bounds the county to the south and southwest, and the St. Croix River, which bounds it to the east. The two rivers are the major groundwater discharge points for southern Washington County and create a north-south groundwater divide that roughly bisects the county (Figure 2, Kanivetsky and Cleland, 1990).

Karst features, particularly in the OPDC, further facilitate groundwater and contaminant movement. Alexander et al. (2013) report the Oneota Formation, the lower member of the OPDC, underwent karstification during the 4 to 5 million year depositional hiatuses that preceeded deposition of the overlying Shakopee Formation. Karstification of the Shakopee also occurred during a 15 million year hiatus prior to deposition of the overlying OSTP (Mossler, 2008). As a result of both karstification events, a dense network of solution-enhanced conduits parallel and perpendicular to bedding near the contact of the Shakopee and Oneota members of the OPDC appears to provide much of the hydraulic conductivity for this otherwise dense, low-permeability dolomite.

This portion of the OPDC is sometimes referred to as the "high transmissivity zone" (HTZ), as much of the groundwater flow within the OPDC occurs at this horizon. Runkel et al. (2007) reported horizontal hydraulic conductivities up to 0.3 km/day in some domestic wells in the city of Lake Elmo that intersect solution-enlarged bedding-plane fractures in the OPDC. Wheeler (1993) reported dye trace flow velocities up to 10 km/day for the OPDC in southeastern Minnesota. Tipping et al. (2006) reported borehole observations elsewhere in Minnesota of vertical flow upward from the CJDN and downward flow from the upper Shakopee Formation toward the HTZ, with outward flow into the aquifer at that horizon. Upward flow from the CJDN also was documented, under pumping conditions, in monitoring wells at one of the PFC disposal sites in Washington County (Weston Solutions, Inc., 2007).

Tipping, et al. (2006) reported increased aperture size and density of solution-enlarged fractures where the Shakopee Formation is buried less than 60 meters, relative to those in more deeply buried areas. It is also expected that solution-enlarged features (bedding plane partings, systematic and non-systematic fractures, etc.) would be larger and more abundant near the erosional surfaces of the now buried bedrock valleys (Runkel et al., 2003).

PFC Plume Delineation

Nearly 2,000 public, private, and monitoring wells in southern Washington County have been sampled since 2003, providing detailed spatial and temporal delineation of the PFC plumes. The most widespread of the PFCs detected is perfluorobutanoic acid, PFBA (Figure 2). PFBA is one of the most mobile PFCs due to its extremely low soil/water adsorption coefficient value (Kd<0.01). The extent of the PFBA plume far exceeds early modeling predictions of the plumes (Barr Engineering, 2005), including transport across the groundwater divide. This was also observed in the distribution of other PFCs (ATSDR, 2008).

While most of the PFCs mapped generally appear to follow fairly typical concentration trends - highest at the source areas and decreasing with distance downgradient - PFOS in the Oakdale-Lake Elmo area does not (Figure 3). Low concentrations of PFOS are detected in the Washington County Landfill monitoring wells and the PFOS plume dissipates to below detectable levels (<0.05 µg/L) a short distance downgradient. However, further

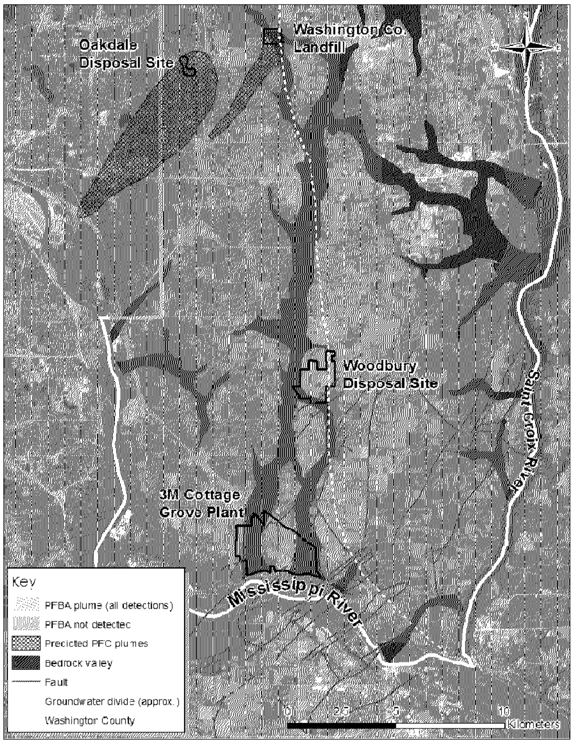

Figure 2. *Bedrock and hydrologic features and extent of PFBA contamination in southern Washington County. Areas without shading indicate no PFC samples have been collected.*

south and southwest (i.e. downgradient) of the site, "hot spots" of elevated PFOS concentrations (>2 µg/L) in private wells were identified. Also, the plume southwest of these "hot spots" has a distinctive "fingering" pattern (Figure 3). This suggested that other factors besides simple contaminant transport by regional groundwater flow were at work.

Groundwater-Surface Water Interactions

Review of the groundwater sampling data revealed that all PFOS detections in Lake Elmo private wells were located south and west of Raleigh Creek (Figure 3). This intermittent stream emerges from a series of wetlands near the 3M-Oakdale Disposal Site, where high levels of PFOS (>45,000 µg/L) have been detected in the water-table aquifer. Sampling of Raleigh Creek in 2006 detected concentrations of PFOS, PFOA, and PFBA up to 8 µg/L near the disposal site and up to 3 µg/L near the "hot spot" in Lake Elmo (ATSDR, 2008). The surface water concentrations correlated closely to PFC levels detected in the nearby private wells completed in the OSTP and OPDC up to 55 m below ground surface.

Between 1988 and 1995, groundwater extracted from the Washington County Landfill as part of the industrial solvent remediation was discharged to a nearby storm sewer. This sewer ultimately discharges to Raleigh Creek, approximately 2 km north of Eagle Point Lake (Figure 4). MDH estimates more than 450 kg PFBA and 35 kg PFOA were discharged to the creek during this time (ATSDR, 2008).

Eagle Point Lake and Lake Elmo are classified as "flow through" lakes, where groundwater recharge and discharge occur in different parts of the lakes (Washington County, 2014). Groundwater discharges to Eagle Point Lake from the north and recharges back to the groundwater near the south and west shoreline. Groundwater also discharges to Lake Elmo from the north and recharges back to the groundwater near the east and southeast shoreline.

Historically, during flood state, Eagle Point Lake overflowed through a series of wetlands to Lake Elmo, on the east side of the groundwater divide. To control flooding of Lake Elmo, a pipeline was constructed from Eagle Point Lake to Horseshoe Lake.

PFCs were detected in the surface water of Eagle Point Lake and Lake Elmo. As with Raleigh Creek, the lake water PFC concentrations correlated closely to groundwater samples from nearby OPDC wells (Figure 3, Table 1). PFCs have also been detected in OPDC wells downgradient (east-southeast) of Horseshoe Lake at concentrations similar to those detected in Lake Elmo (samples GW-4a and SW-4).

The PFC data illustrate the intimate groundwater-surface water interactions which help explain, in part, how PFCs spread further than modeling predicted. For example, PFCs discharge from the groundwater at the Oakdale Disposal Site into Raleigh Creek. Then, as the creek flows toward the city of Lake Elmo, it transitions from a gaining to a losing stream (just east of I-694), acting as a linear source of PFCs recharging to the groundwater and co-mingling with the PFC groundwater plume sourced from the Washington County Landfill (Figure 4). At Eagle Point Lake, PFCs from Raleigh Creek are added to those discharging to the lake from the groundwater. From Eagle Point Lake, some PFCs recharge to the ground-water, resulting in the area of contaminated wells south and southwest of the lake. However, some

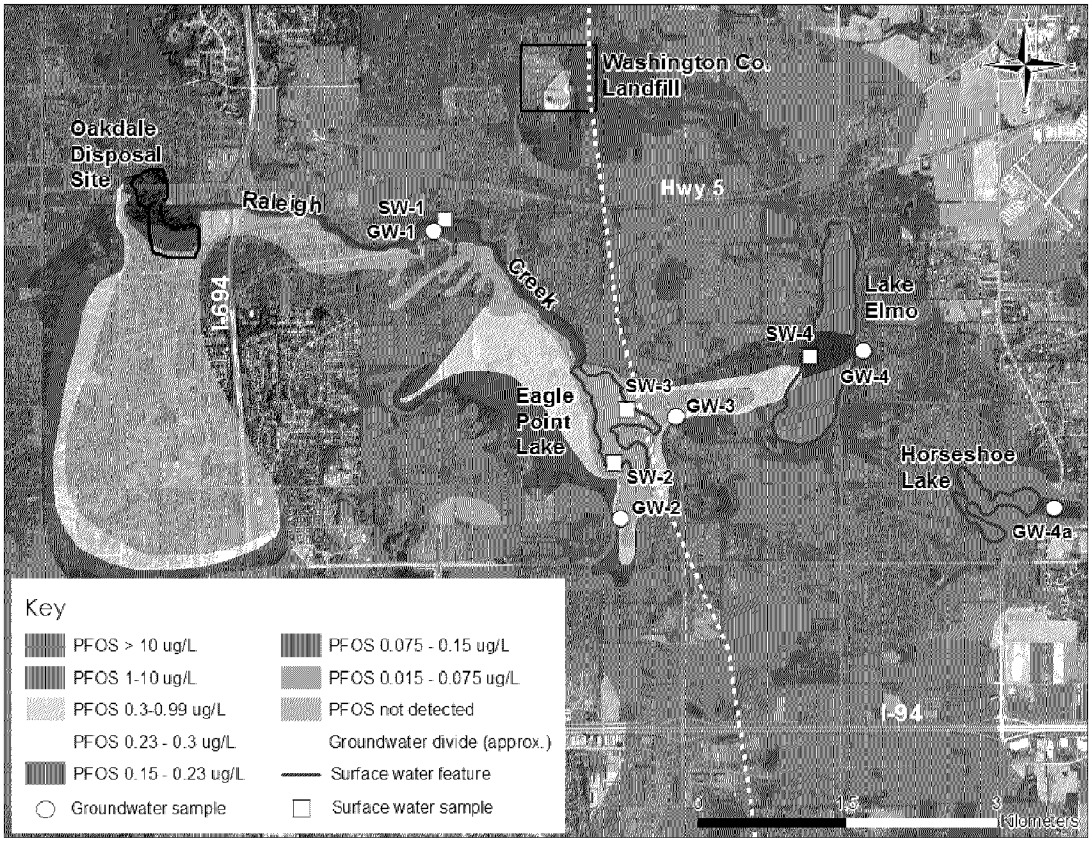

Figure 3. Anomalous distribution of PFOS in the Oakdale-Lake Elmo area. Data shown is a compilation of PFOS results for all aquifers. Where lakes are shaded, color indicates concentrations detected in surface water. Areas without shading indicate no PFC samples have been collected. Numbered, co-located surface and groundwater results are presented in Table 1.

Table 1. Co-located Groundwater (GW) and Surface Water (SW) Samples (in µg/L). Sample locations shown on Figure 3

Sample No.	PFOS	PFOA	PFBA
SW-1	5.2	1.9	1.4
GW-1	3.3	3.0	3.4
SW-2	0.3	0.3	0.3
GW-2	0.2	0.4	1.5
SW-3	0.6	0.4	0.3
GW-3	0.6	0.5	1.1
SW-4	0.26	0.08	0.4
GW-4	0.07	0.06	0.4
GW-4a	0.058	0.067	0.29

of the Eagle Point Lake water (and PFCs) recharge to the groundwater on the east side of the lake and then discharge into Lake Elmo while some is piped directly to Horseshoe Lake. In Lake Elmo, PFCs from Eagle Point Lake combine with PFBA discharging with the groundwater into the north end of the lake. The PFCs then recharge into the groundwater on the east side of the lake. Similarly, PFCs discharge from Horseshoe Lake to the groundwater to the east and southeast.

The Role of Karst in PFC Migration

Groundwater-surface water interactions alone cannot account for the anomalous distribution of PFCs entirely. For example, PFCs were unexpectedly detected in private wells east of the Washington County Landfill, across the assumed groundwater divide, even though groundwater flow at the landfill is to the south-southwest (Figure 4). Similarly, movement of PFCs through the groundwater between Eagle Point Lake and Lake Elmo is unexpected, given the location of the groundwater divide between these two lakes.

The places where the PFC plume crosses the groundwater divide appear to coincide with buried bedrock valleys, along the walls of which the HTZ within the OPDC subcrops below the Quaternary deposits. As noted above,

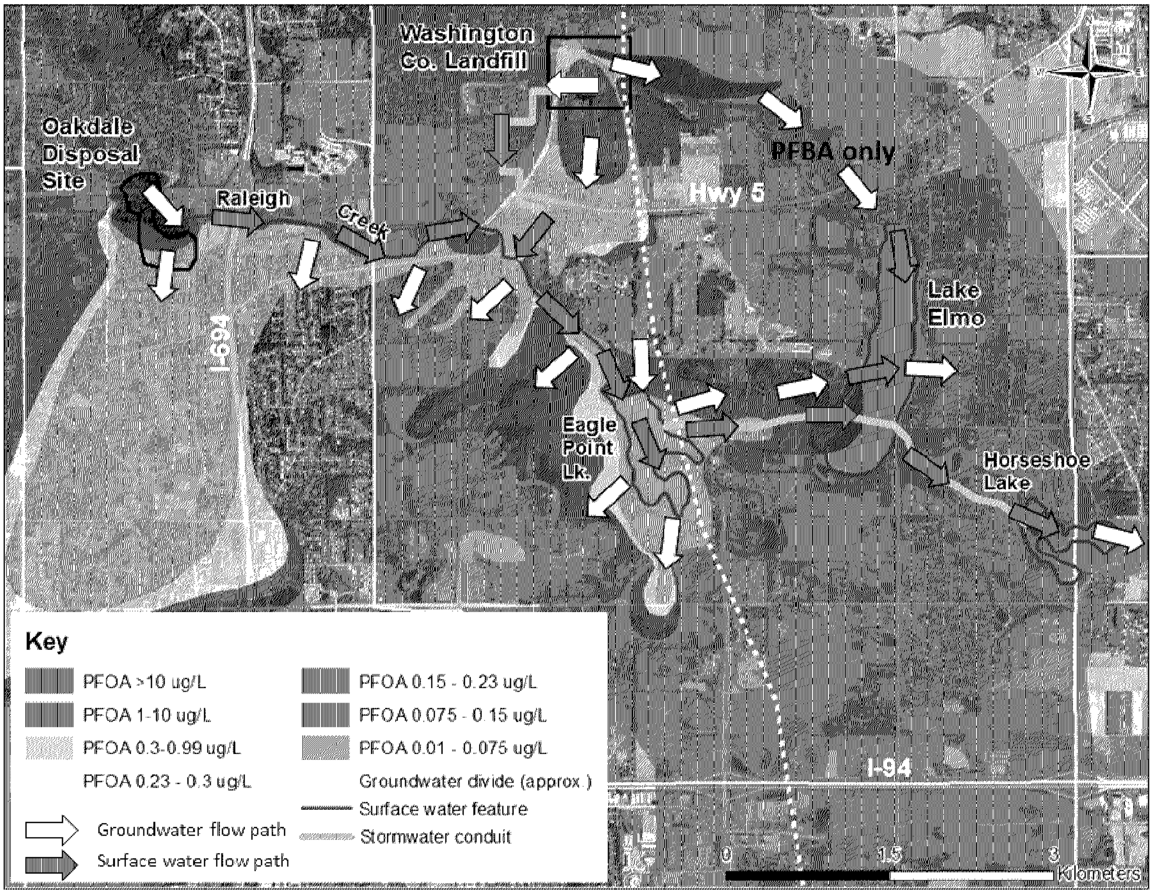

Figure 4. *Anomalous PFOA distribution illustrates complex PFC transport pathways. Data shown is a compilation of PFOA results for all aquifers. Where lakes are shaded, color indicates concentrations detected in surface water. Areas without shading indicate no PFC samples have been collected.*

where the Shakopee Formation is buried less than 60 m, the density and aperture of solution-enlarged features increase creating high flow velocity groundwater conduits. Mapping of where the HTZ subcrops below the Quaternary deposits (Olsen, 2008) yields nearly perfect correlation to the areas where the PFC plume crosses the groundwater divide (Figure 5).

As observed in aquifer tests and flow metering in area wells, the high hydraulic conductivities measured in the HTZ create significant potentiometric head differences that can draw water from both overlying and underlying aquifers where they are hydraulically connected by a borehole or fractures. The same phenomenon appears to occur along the bedrock valleys, which provide large scale hydraulic connections between the aquifers above and below the Oneota Formation. This allows for rapid migration of PFCs into the OPDC via the HTZ. In places, the head differences are apparently great enough to locally displace the groundwater divide from its assumed location, allowing the PFCs to appear to cross the divide as they migrate through the HTZ and are then transported east-southeast with the regional groundwater flow. Another explanation may be the strong anisotropy in karst, which can allow for flow directions that differ from the gradient (Tipping, personal communication). This may also account for the apparent "upgradient" migration of PFCs (relative to regional groundwater flow) along some branches of the bedrock valley, as seen immediately east of the Washington County Landfill (Figure 5). Although regional groundwater flow in this area is to the east-southeast, PFCs are detected in wells 600 m north of the bedrock valley.

The southwest-trending finger-like lobes of the PFC plumes (Figures 3, 4, and 5) may also be an indication of karst influence on contaminant transport. The "fingers" are oriented roughly 240 degrees. This is consistent with lineament orientations reported by Mossler and Tipping (2004). It seems reasonable to suspect that higher flow rates in solution-enlarged, subparallel joint sets in this area provide preferential pathways for PFC migration.

Summary

The PFC investigations in southern Washington County illustrate the potential for highly complex contaminant migration pathways in karsted aquifers, particularly for highly persistent chemicals. While groundwater modeling provided initial direction for groundwater sampling, a thorough understanding of the underlying bedrock features, groundwater-surface water interactions, and the distribution and orientation of karst features, was critical to accurately delineating the PFC plumes. This had significant implications for public health, as many of the drinking water wells located in the PFC "hot spots" - that were not predicted by modeling - exceeded Minnesota drinking water standards and required treatment to remove the PFCs.

Disclaimer

This publication was supported by the Grant or Cooperative Agreement Number, TS14-1403, funded by the Centers for Disease Control and Prevention (CDC). Its contents are solely the responsibility of the author and do not necessarily represent the official views of the CDC or the Department of Health and Human Services.

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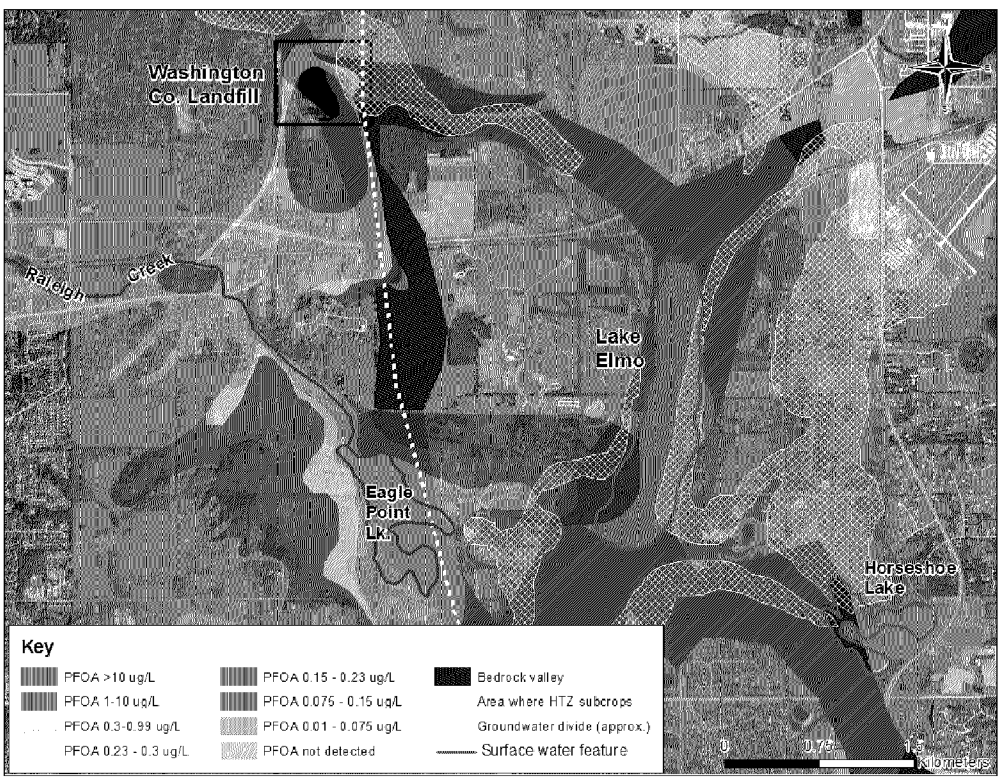

Figure 5. *Correlation of areas where high transmissivity zone (HTZ) subcrops and PFCs cross groundwater divide. The white arrows indicate areas where HTZ subcrop (shown in yellow hatching) correlates with PFC migration across the groundwater divide. Note that PFCs are detected at significant distance "upgradient" of the buried valley. Data is a compilation of PFOA results for all aquifers.*

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