Air & Waste Management Association

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Proudly Present

A Panel on PFOA in Regional Drinking Water, Including:

"Emerging Contaminant Update PFOA and PFASs" by Paul Dombrowski, AECOM

Mr. Dombrowski has 12 years of experience in the design, implementation, and oversight of groundwater and soil remediation projects. Paul serves on the Scientific Advisory Board for the AEHS International Conference on Soils, Sediments, Water, and Energy (UMASS Soils Conference) and earned bachelor's and master's degrees at Manhattan College in NYC.

"Overview of the Hydrogeologic Framework"
by Jean Neubeck, Alpha Geoscience

Ms. Neubeck has 32 years as a consulting geologist/hydrogeologist to commercial and industrial clients, government agencies, military clients, and attorneys. She is a certified professional geologist and a licensed Professional Geologist.

"PFOA in Hoosick Falls, New York" by Brian Moore, ARCADIS

Dr. Moore is a technical water and wastewater expert with global experience at automotive, chemical, pharmaceutical, aviation (commercial and military), healthcare and multinational conglomerate facilities. He has a BS, MS, and PhD from Penn State University.

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Part 1

"Emerging Contaminant Update PFOA and PFASs"

by Paul Dombrowski, AECOM

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What are PFAS Compounds?

– Synthetic chemicals used in manufacturing fluoro-polymers
  - PFOA – perfluorooctanoic acid and its principle salts, manufactured from 1947-present[1],
    8 manufacturers phased out production by 2010
  - PFOS – perfluorooctane sulfonate,
    manufactured from 1949-2002[2]

– Typically only a fraction of final product not an end product

– Used in making fire fighting foams

– Used in making surface treatments

– Used in making performance chemicals

[1] Prevedouros ES&T, 2006
[2] Paul et al. ES&T, 2009

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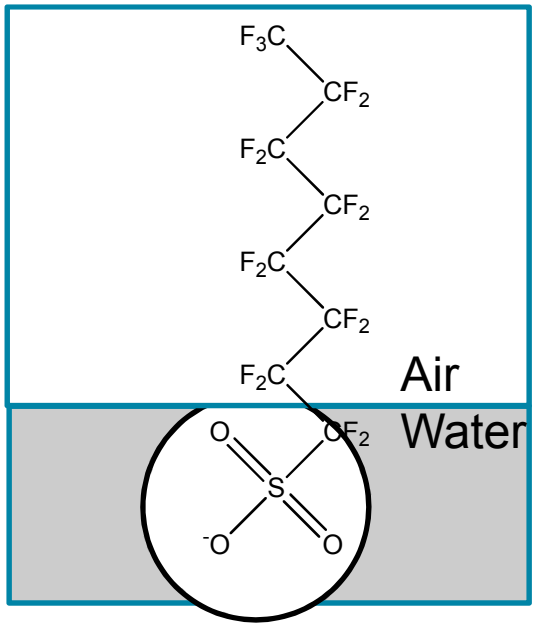
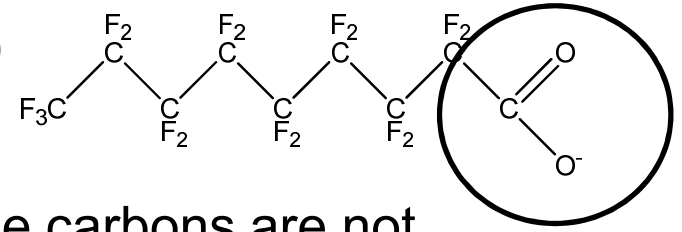
Unique Chemistry

- C-F bond is the shortest and strongest bond in nature
- Less tendency to associate with other phases (oil, water)
- Few degradation processes: too much energy to break bonds
  - stable in acids, bases, oxidants, heat
  - microorganisms cannot gain energy from breaking the bond



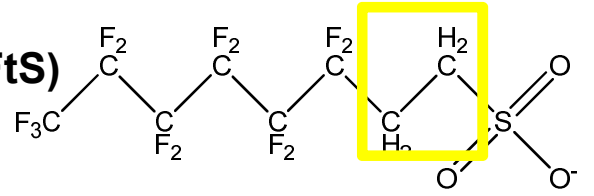
- Perfluorinated = all carbon atoms fully fluorinated (no hydrogen atoms)

PFOA (**per**fluorooctanoate)



- Polyfluorinated = some carbons are not fully fluorinated (have H)

(*Poly*)fluorotelomer sulfonate (FtS)



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Partial List of PFASs

Analyte	Acronym	Chemical Abstract Services Registry Number (CASRN)
N-ethyl perfluorooctanesulfonamidoacetic acid	NEtFOSAA	–
N-methyl perfluorooctanesulfonamidoacetic acid	NMeFOSAA	–
Perfluorobutanesulfonic acid	**PFBS**	**375-73-5**
Perfluorodecanoic acid	PFDA	335-76-2
Perfluorododecanoic acid	PFDoA	307-55-1
Perfluoroheptanoic acid	**PFHpA**	**375-85-9**
Perfluorohexanesulfonic acid	**PFHxS**	**355-46-4**
Perfluorohexanoic acid	PFHxA	307-24-4
Perfluorononanoic acid	**PFNA**	**375-95-1**
Perfluorooctanesulfonic acid	**PFOS**	**1763-23-1**
Perfluorooctanoic acid	**PFOA**	**335-67-1**
Perfluorotetradecanoic acid	PFTA	376-06-7
Perfluorotridecanoic acid	PFTrDA	72629-94-8
	PFUnA	2058-94-8

Bold = on Unregulated Contaminant Monitoring Rule (UCMR3) monitoring list

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PFAS Properties

Chemical Properties	PCB (Arochlor 1260)	PFOA	PFOS	TCE	Benzene
Molecular Weight	357.7	414.07	538	131.5	78.11
Solubility	0.0027 mg/L @24°C	3400–9500 mg/L @25°C	519 mg/L @20°C	1100 mg/L @ 20°C	1780 mg/L @20°C
Vapor Pressure (25°C)	4.05×10^{-5} mmHg	0.5-10 mmHg	2.48×10^{-6} mmHg	77.5 mmHg	97 mmHg
Organic Carbon Part. Coeff. (Log K_{oc})	4.8-6.8	2.06	2.57	2.42	2.15
Henry's Constant	4.6×10^{-3} atm-m^3/mol	0.0908 atm-m^3/mol	3.05×10^{-6} atm-m^3/mol	0.0103 atm-m^3/mol	0.0056 atm-m^3/mol

- High solubility, low volatility

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Environmental Impact and Transport

- Relevant properties of environmental significance
  - Soluble, non-volatile
  - Sorb to soil and sediments
  - Ubiquitous, persistent and very little degradation
  - Bioaccumulative, but do not bind to lipids, do not metabolize
  - Form separate layers in hydrocarbons and water so K_{ow} cannot be measured
- Groundwater
  - Wide range in PFAS concentrations (ng/L to mg/L)
  - Large dilute plumes
- Soil & Sediment
  - High detection frequency

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Where do we find PFASs?

- Aqueous film-forming foams (AFFF) for fire fighting
- Oil and water-repellent
- Stain-resistant upholstery, carpeting
- Non-stick coatings in cookware (Teflon®)
- Breathable, all weather clothing (Gore-tex®)
- Paper and packaging protectors (food packaging)
- Paints and adhesives
- Fluoro-elastomers (gaskets, O-rings, Hoses)
- Mining and oil surfactants
- Metal plating baths (chromium)
- Pesticides/Insecticides

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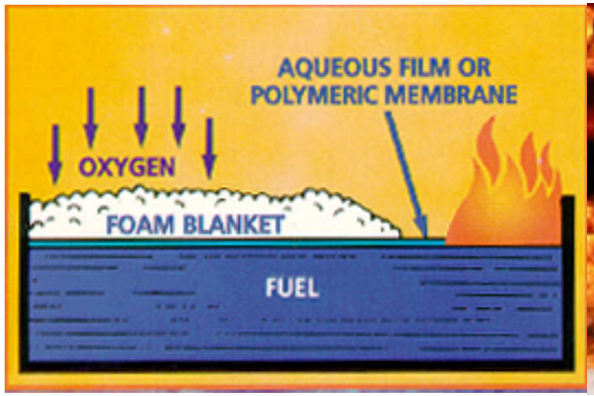
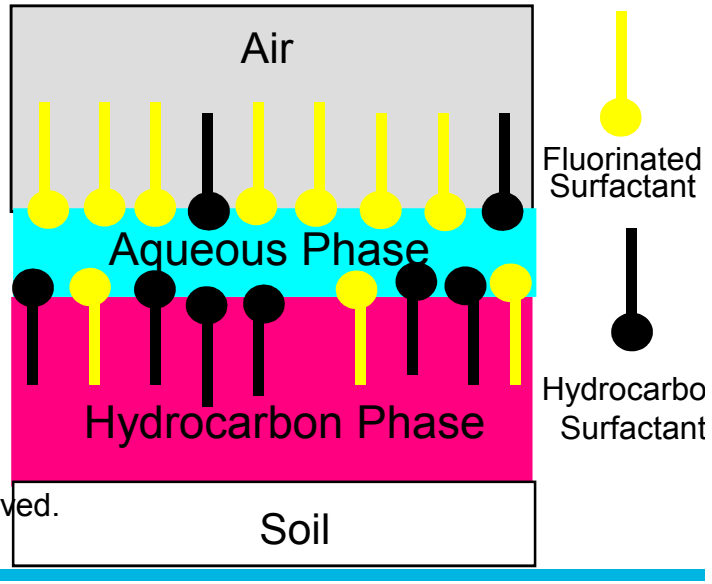
Aqueous Film Forming Foams (AFFF)

- PFASs are used in AFFFs that were routinely used for fire fighter training at municipal and military fire training areas
- Used for Class B fires (highly flammable or combustible liquid fires, including jet fuels, gas tankers & refineries)
- AFFFs have the ability to spread over the surface of hydrocarbon-based liquids (i.e., create a film)
- AFFF blankets fuel, cools the fuel surface, prevents re-ignition by suppressing release of flammable vapors
- Developed by the Navy in 1960s





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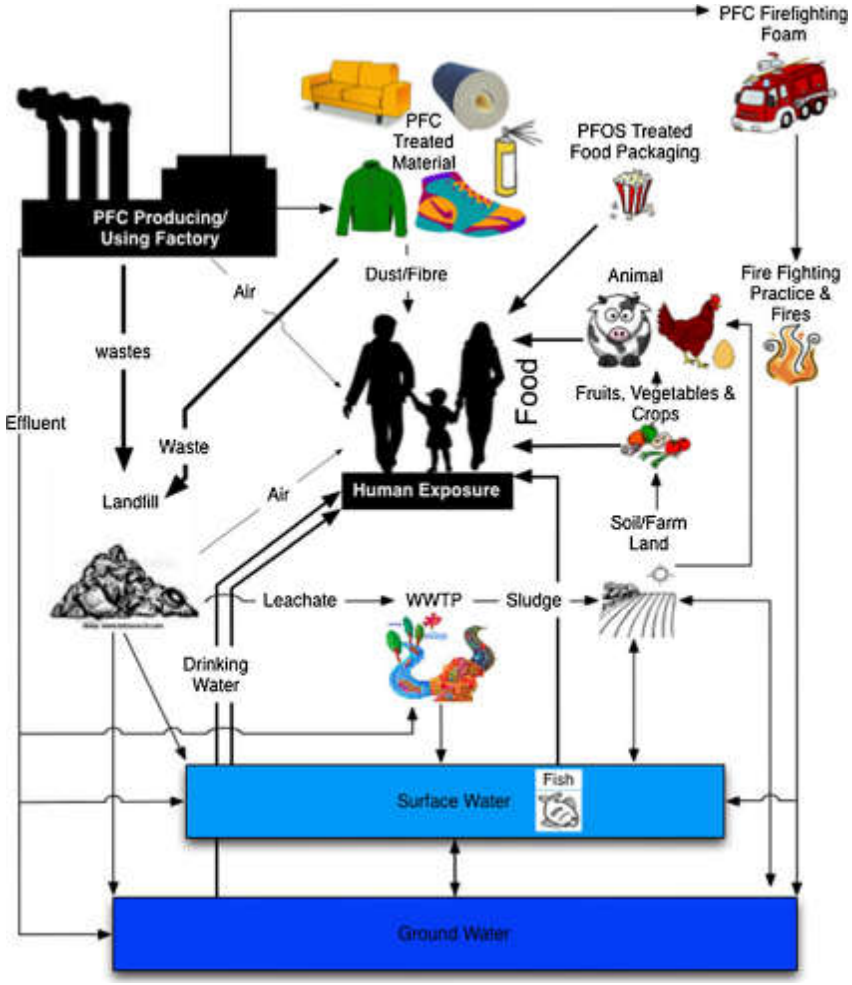
Sources and Exposure Pathways



- Food
  - Transfer to crops from water & soil
  - Biosolids and organic waste applied to soil
  - Fish
- Drinking water
- Indoor air and dust
  - from upholstery, fabrics, papers
- Human to human transfer
  - Transplacental exposure (comparable concentrations in material and cord blood)
  - Breast milk
- Cookware (not considered a significant source for humans)

From Oliaei 2013, Environ Pollut Res

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Toxicity and Toxicology

- Toxicology of PFASs, specifically PFOS and PFOA, highly studied (>10 years of research)
- Chemical mechanics are well documented
  - Absorption, Distribution, Metabolism and Excretion
- Lab animal studies conducted in multiple species (rat, mice, rabbits) with broad range of toxicity endpoints
- Humans studies of general population and workers
- C8 Science Panel
  - probable link between exposure and testicular cancer and kidney cancer
  - probable link between exposure and diagnosed high cholesterol
- Estimated half life of PFOS/ PFOA of 4 years in humans

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Regulatory History – Increasing Concerns

- Concerns originated in 1999
  - 3M submitted information to USEPA regarding potential risks
  - 3M phased out PFOS production in 2002
- 2002 market shift in focus to C4-C6 chain length sulfonates and fluorotelemer sulfonates (Fts)
- Several USEPA, OECD, and UK Environmental Hazard/Risk Assessments between 2002 and 2006
  - 2005 Stockholm Convention on Persistent Organic Pollutants listing
  - USEPA included several PFASs on Contaminant Candidate List-3 in 2009
  - USEPA included 6 PFASs in Unregulated Contaminant Monitoring Rule-3
- 2009 – USEPA OSWER established Health Advisory Levels
- 2015 – Texas TCEQ established Protective Concentration Limits (PCLs) for 16 PFASs
- May 19, 2016 – USEPA revised Health Advisory Levels for PFOS & PFOA

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Regulatory Values

State	PFOA (µg/L)	PFOS (µg/L)	Value
Alaska	0.4	0.2	(draft) Groundwater Cleanup Levels
Illinois	0.4	0.2	Class I Provisional Groundwater Remediation Objectives
Maine	0.06	0.1	Groundwater Remedial Action Guidelines (residential)
Michigan	0.42		Surface water quality standard (human noncancer value for water protected as source of drinking water)
Minnesota	0.3	0.3	Health Risk Limit (promulgated drinking water criteria)
New Jersey	0.04		Preliminary Health Based Guidance for Drinking Water
New York	0.1		
North Carolina	2		Interim Maximum Allowable Concentration in Groundwater
Texas	0.3	0.6	Protective Concentration Levels for screening residential groundwater.
USEPA	**0.07**	**0.07**	**Lifetime Health Advisory (sum of PFOS&PFOA = 0.07 ug/L)**

Texas has groundwater criteria for 16 different PFASs

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Characterization of PFASs

- Analytes ranged from:
  - PFOS/PFOA only
  - 6 UCMR-3 PFASs
  - Full commercial lab suite (12 to ~32 compounds)
  - Expanded University lab suite (200+ compounds)
- Significant potential for upgradient and non-point sources
- Form large dilute plumes without high concentration source area
  - Average source area soil concentration - ~3 to 5 ppm
  - Average source area groundwater concentration - ~1 to 2 ppm
  - Source area soil concentrations range from low ppb to >30 ppm
  - Source area groundwater concentrations range from low ppb to > 10 ppm
- Average plume length > 1 mile, but likely much longer
  - More than ¾ of the plume typically < 10 ppb
- Plume size and concentrations listed based on AECOM experience

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Site Characterization of PFASs

- Co-mingled plumes (e.g., petroleum HCs, CVOCs, & ethylene glycol)
  - Especially at fire training areas
- Existing remediation systems not likely addressing PFASs,
  - Could be exacerbating PFOS/PFOA concentrations
  - May be altering fate and transport
- PFOS/PFOA likely to be present at highest concentrations and at leading edge of plume
- Project size, complexity, and degree of characterization vary significantly
  - Largest AECOM site involved collection of >14,000 samples and sampling along 58 mile segment of a major river
  - Sampling can include groundwater, surface water, soil, sediment, air, human and livestock blood serum, crops/produce, fish tissue, site infrastructure/facilities (e.g. concrete, piping, etc.)

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Data Quality and Sampling Lessons Learned

– Data Quality Issues
  - Significant variability in results from lab to lab, especially for PFOS
  - Blanks and QA/QC samples very important

– Avoid cross contamination and false positives, sources include:
  - Water proof field notebooks / markers & Sharpies
  - Do not use Teflon lids (Teflon® Liner in bottles)
  - Teflon® pump o-rings, bailers or wells
  - Decon solutions
  - Avoid new and water-resistant clothing
  - Fast food wrappers/wash hands after handling food
  - Avoid blue ice (preserve on ice)
  - Fabric car seat coatings may contain PFASs
  - Sunscreen, insecticides, moisturizers, makeup

– Incomplete characterization

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Key Take Away Points

- PFASs are chemicals that are of great use to us but have resulted in high exposures
  - The health consequences are not known clearly
  - There is a global willingness to minimize usage and exposure
- Compounds are very soluble, recalcitrant and persistent
- Significant potential for background contamination/other sources
- Large dilute plumes represent potential financial & receptor risks
- PFASs appear to be unlike anything we've dealt with before and represent a significant challenge

Part 2

"Overview of the Hydrogeologic Framework"

by Jean Neubeck, Alpha Geoscience

Overview of the Hydrogeologic Framework

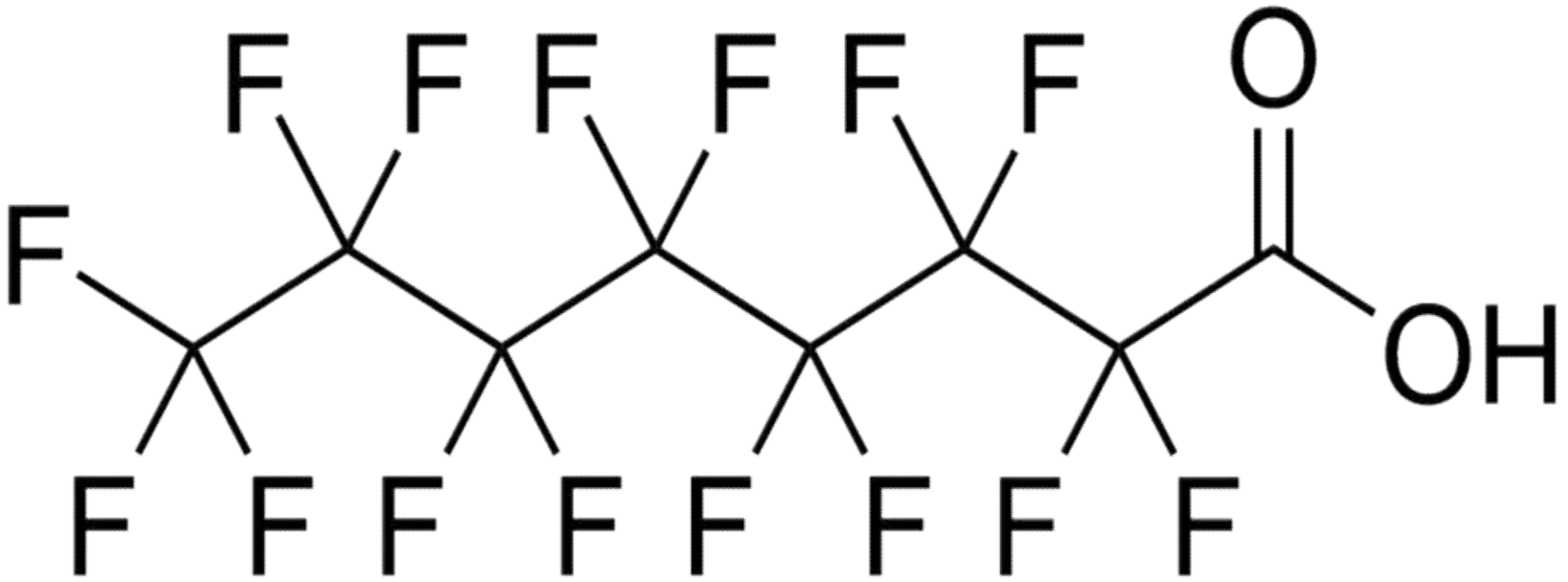
Why Geologic Conditions Are Critical to PFOA Source Identification and Interpreting Sampling Data

ALPHA GEOSCIENCE

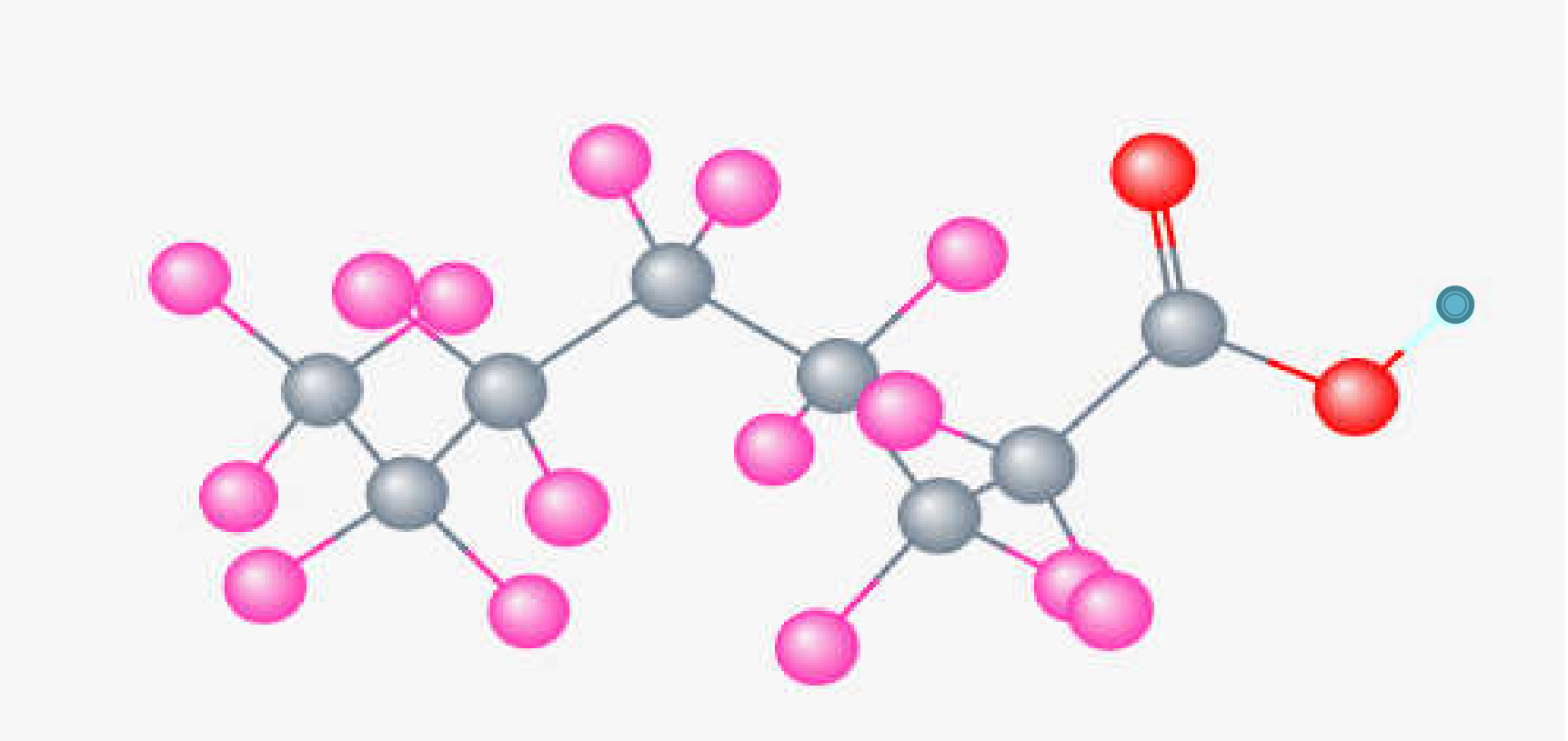
Emerging Contaminants

- Perceived, potential, or real threat to human health or the environment
- Lack of published health standards
- New source or new pathway is discovered
- New detection method or treatment technology is developed

PFOA Chemical Structure



PFOA molecular formula $C_8HF_{15}O_2$



Sampling and Laboratory Analysis

EPA Method 537 LC/MS/MS
Liquid Chromatography – Mass Spectrometry

PFOA Method Detection Limits:

Water: 0.010 to 0.004 ug/L (4 ppt)

Soil: 1.0 to 0.5 ug/kg (500 ppt)

Lab in-house MDLs can approach 0.1 ppt in water

SUMMARY OF METHOD 537

- Pass 250-mL water through an extraction cartridge
- Elute compounds using methanol
- Concentrate extract (dry in heated nitrogen bath)
- Bring it to known volume (10 µL)
- Inject into an LC with a C18 column that is interfaced to an MS/MS

LABORATORY INTERFERENCES

- Meticulously clean glassware; store inverted or capped
- No aluminum foil covers
- No glass contact with standards, extracts, and samples
- Contaminants in solvents, reagents, containers
- Analytes also found in many supplies and equipment
  (PTFE products, solvent lines, methanol, foil, transfer lines)

Remedial Challenges

- Multiple sources, multiple media
- Large, relatively diffuse plumes, can be low-level concentrations (ID source?)
- Co-mingled and multiple contaminants (petroleum, chlorinated solvents, others)
- Chemical properties (solubility, non-volatile, strong C-F bonds
- Removal vs. destruction

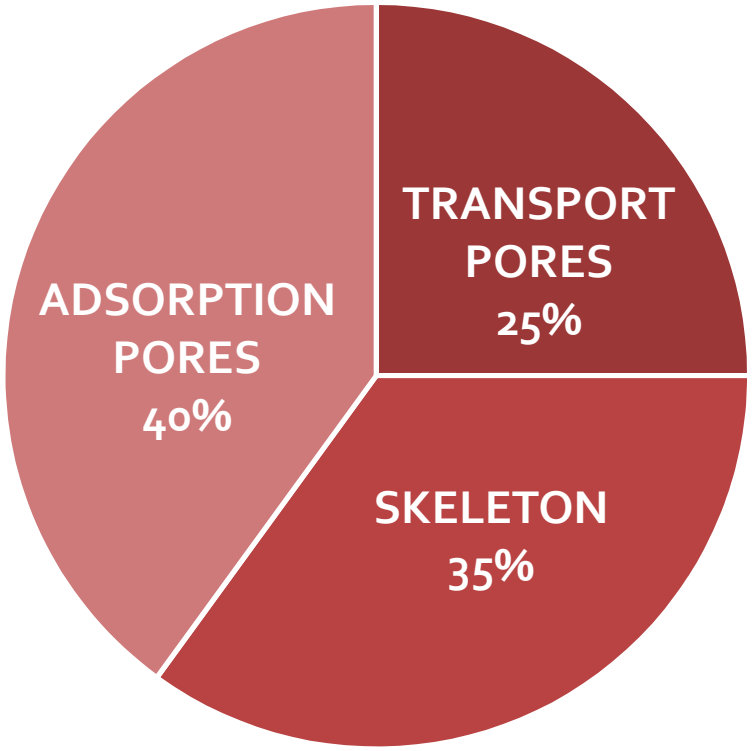
Granular Activated Carbon

Adsorption Pores

- Finest pores
- Adsorption capability

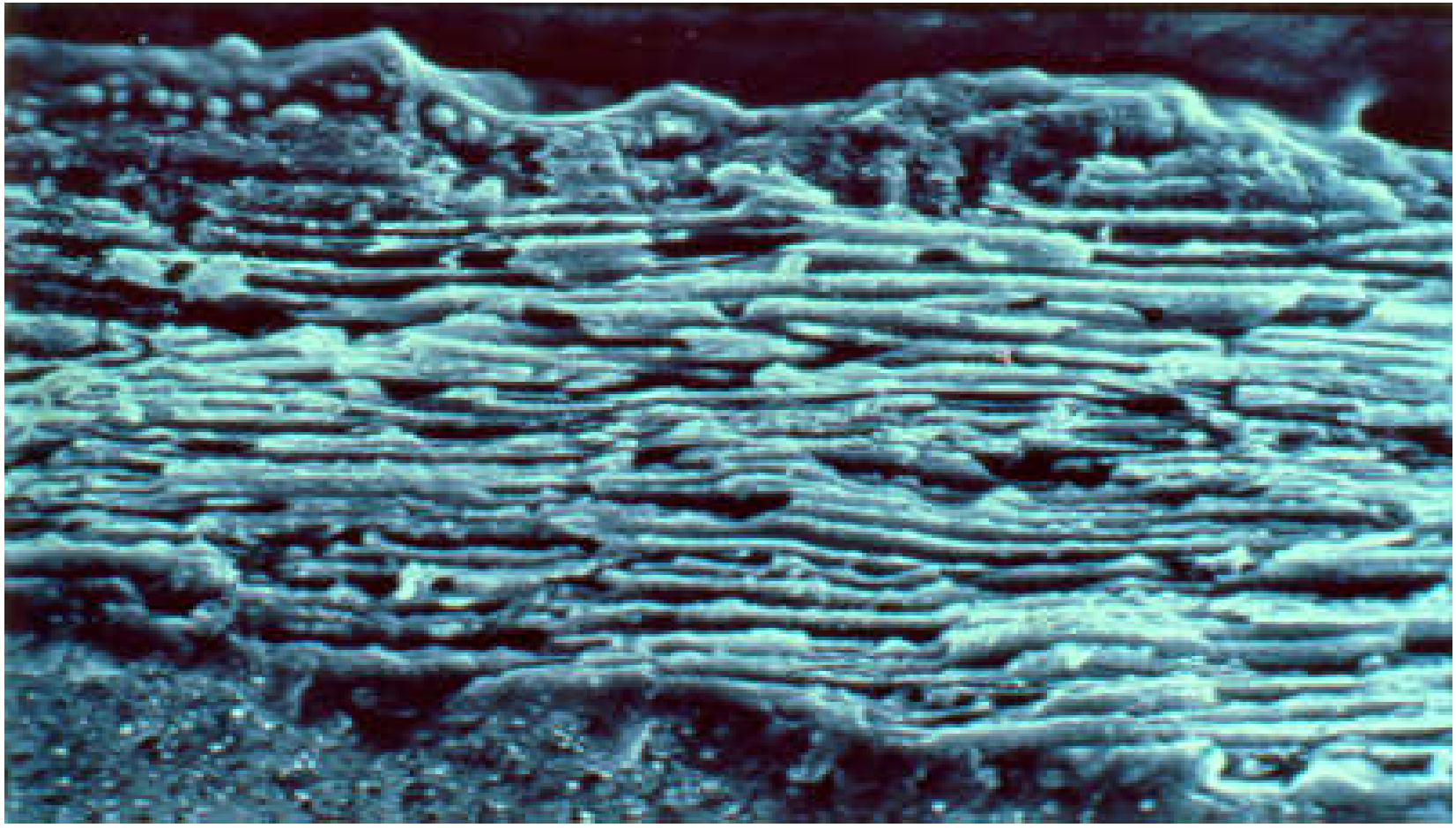
Transport Pores

- Larger than adsorption pores
- Function as diffusion paths
- Never adsorb, even near saturation



Courtesy of Calgon Carbon

Photomicrograph — 1,000,000X Magnification

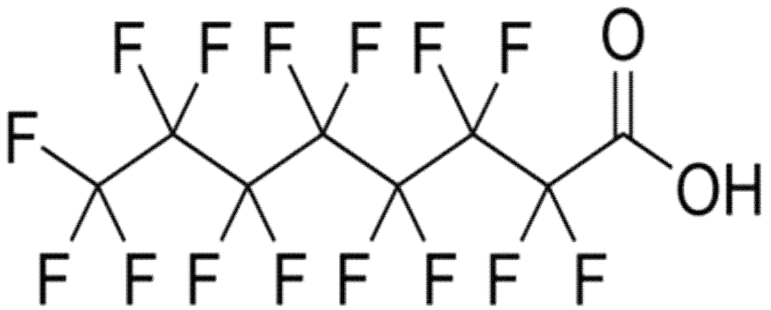


Courtesy of Calgon Carbon

Factors Affecting Liquid GAC Adsorption

Solubility

The higher the solubility, the more difficult to adsorb



Concentration

Wt% loading on carbon increases as influent species concentration increases

Molecular weight

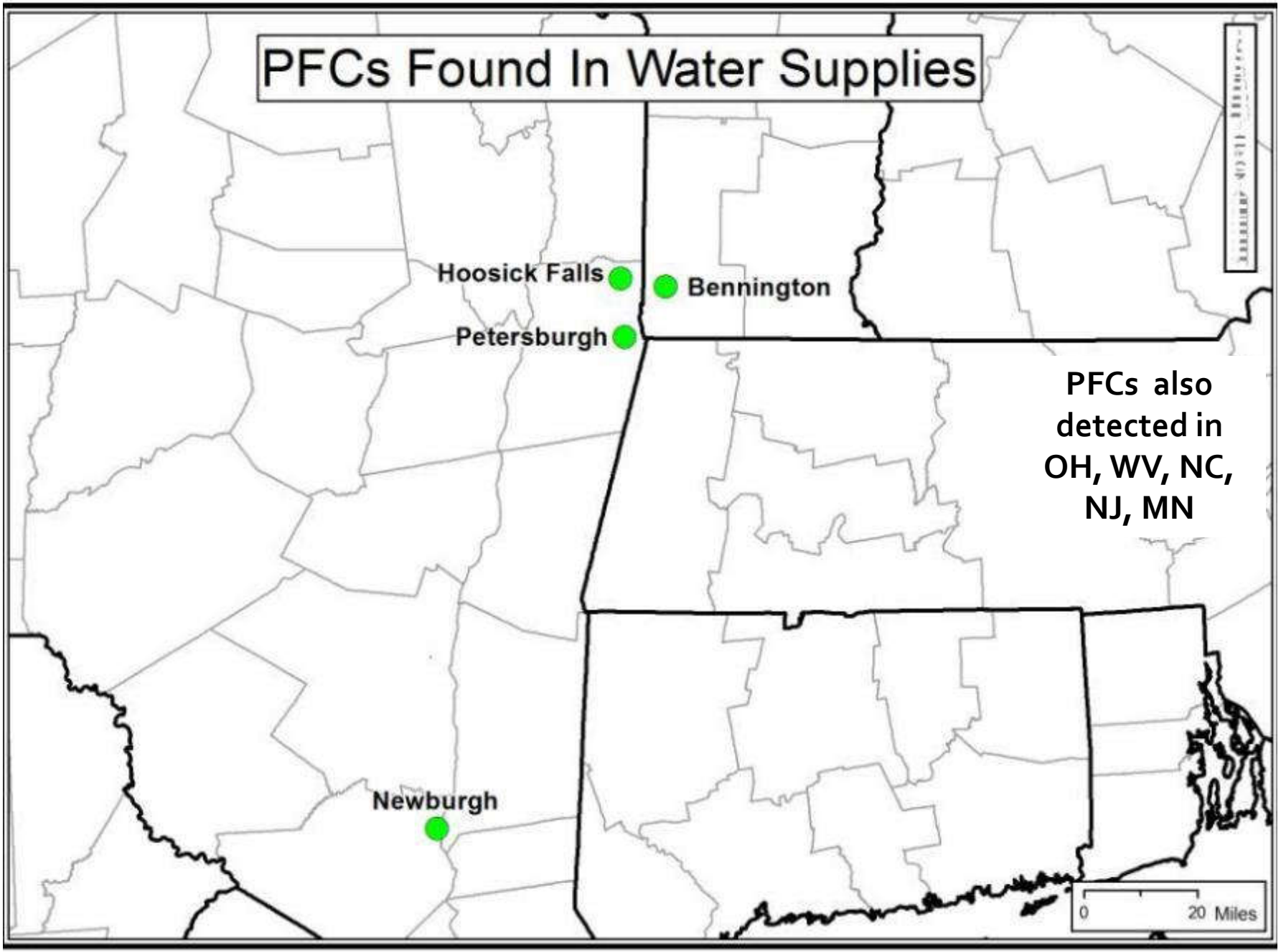
The higher the molecular weight, the better adsorbed

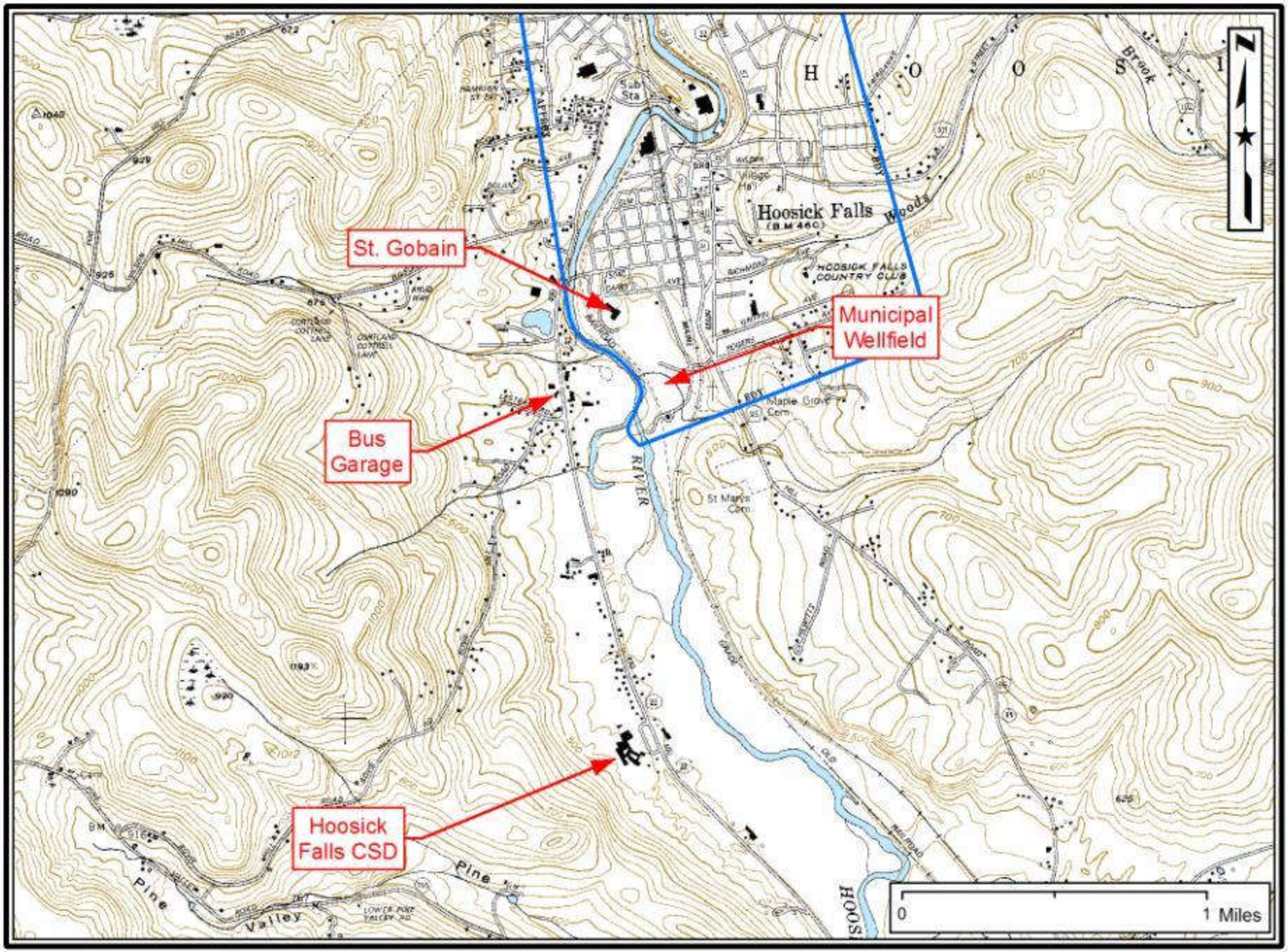
Functional groups

More complex structures adsorb more readily

Courtesy of CalgonCarbon

water supplies, and why understanding the hydrogeologic framework is critical to remediation and protecting drinking water supplies.




St. Gobain
Municipal Wellfield
Bus Garage
Hoosick Falls CSD
Hoosick Falls
(B.M. 460)
HOOSICK FALLS COUNTRY CLUB
Maple Grove Cem
St Mary's Cem
RIVER
Pine Valley
Pine
Brook
N
0
1 Miles

NYS Department of Environmental Conservation Police Statement on Search Warrant Activity in Hoosick

The New York State Department of Environmental Conservation sent this bulletin on 01/29/2016 01:53 PM EST

Re-sent: DEC Requires Companies to Fully Investigate and Clean Up Hoosick Falls PFOA Contamination

The New York State Department of Environmental Conservation sent this bulletin on 02/12/2016 11:30 AM EST

DEC and DOH Announce Commitment to Install Water Filtration System in Town of Petersburgh

The New York State Department of Environmental Conservation sent this bulletin on 03/09/2016 10:54 AM EST

EPA
United States
Environmental Protection
Agency

Emerging Contaminants – Perfluorooctane Sulfonate (PFOS) and Perfluorooctanoic Acid (PFOA)

March 2014

EMERGING CONTAMINANTS FACT SHEET – PFOS and PFOA

At a Glance

- Fully fluorinated compounds that are human-made substances and are not naturally found in the environment.
- Used as a surface-active agent and in a variety of products, such as firefighting foams, coating additives and cleaning products.
- Do not hydrolyze, photolyze or biodegrade under typical environmental conditions and are extremely persistent in the environment.
- Studies have shown they have the potential to bioaccumulate and biomagnify in wildlife.
- Readily absorbed after oral exposure and accumulate primarily in the serum, kidney and liver.

Introduction

An "emerging contaminant" is a chemical or material that is characterized by a perceived, potential, or real threat to human health or the environment or by a lack of published health standards. A contaminant may also be "emerging" because a new source or a new pathway to humans has been discovered or a new detection method or treatment technology has been developed (DoD 2011). This fact sheet, developed by the U.S. Environmental Protection Agency (EPA) Federal Facilities Restoration and Reuse Office (FFRRO), provides a summary of the emerging contaminants perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), including physical and chemical properties; environmental and health impacts; existing federal and state guidelines; detection and treatment methods; and additional sources of information. This fact sheet is intended for use by site managers who may address PFOS and PFOA at cleanup sites or in drinking water supplies and for those in a position to consider whether these chemicals should be added to the analytical suite for site investigations.

PFOS and PFOA are extremely persistent in the environment and resistant to typical environmental degradation processes. As a result, they are widely distributed across the higher trophic levels and are found in soil, air and groundwater at sites across the United States. The toxicity, mobility and bioaccumulation potential of PFOS and PFOA pose potential adverse effects for the environment and human health.

From HF Schools FaceBook Page January 22, 2016

Transportation Department Water Tests Positive for PFOA

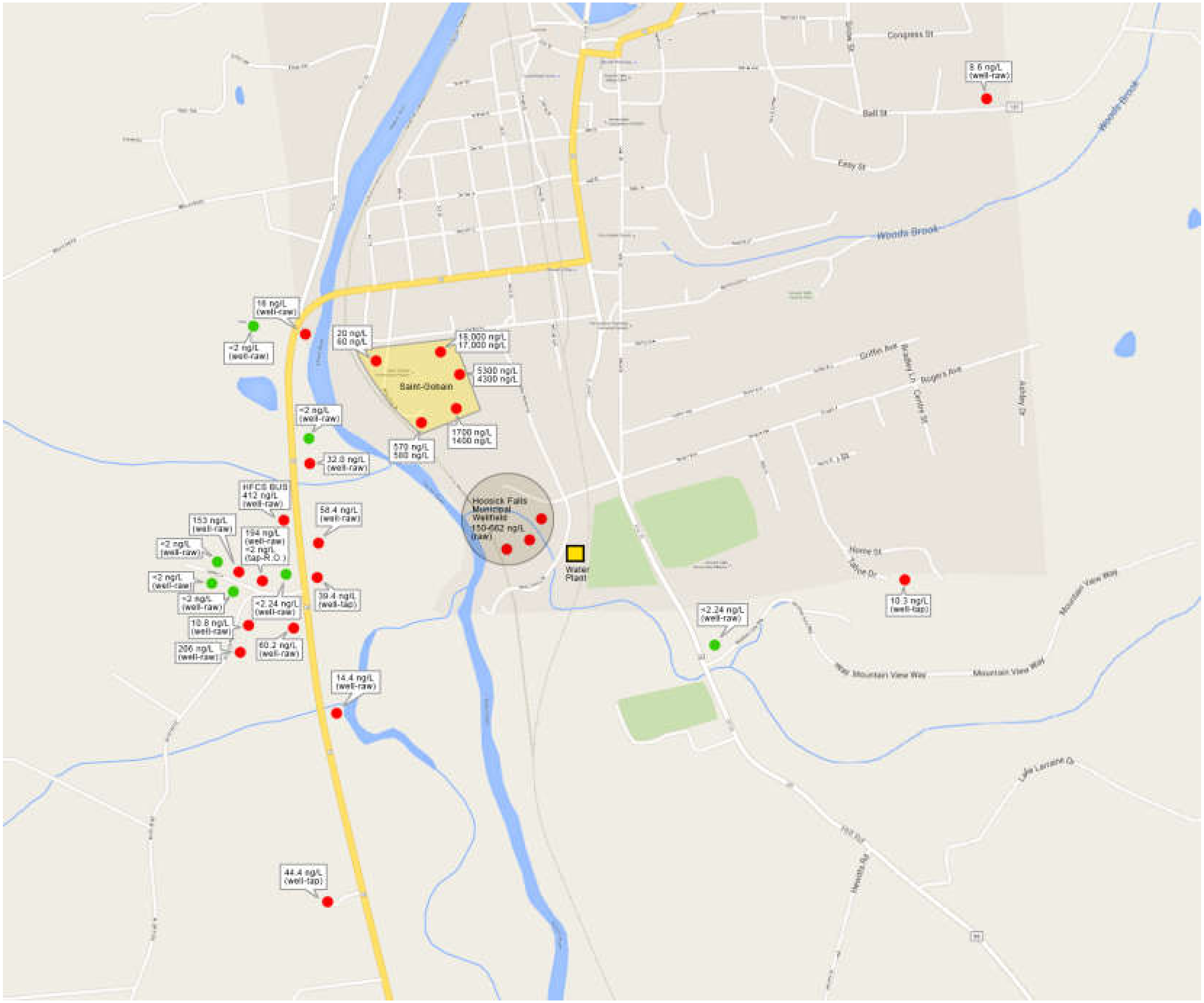
January 22, 2016 in Uncategorized

As part of our ongoing water testing, we have included our transportation department water supply, and the test came back positive for PFOA. It is important to note that our transportation department has tested positive, NOT the school campus. The bus garage location is 1.2 miles from our main campus. Our water at the school is safe, and we continue to test our school campus water to ensure that we are providing a safe water supply to our kids.

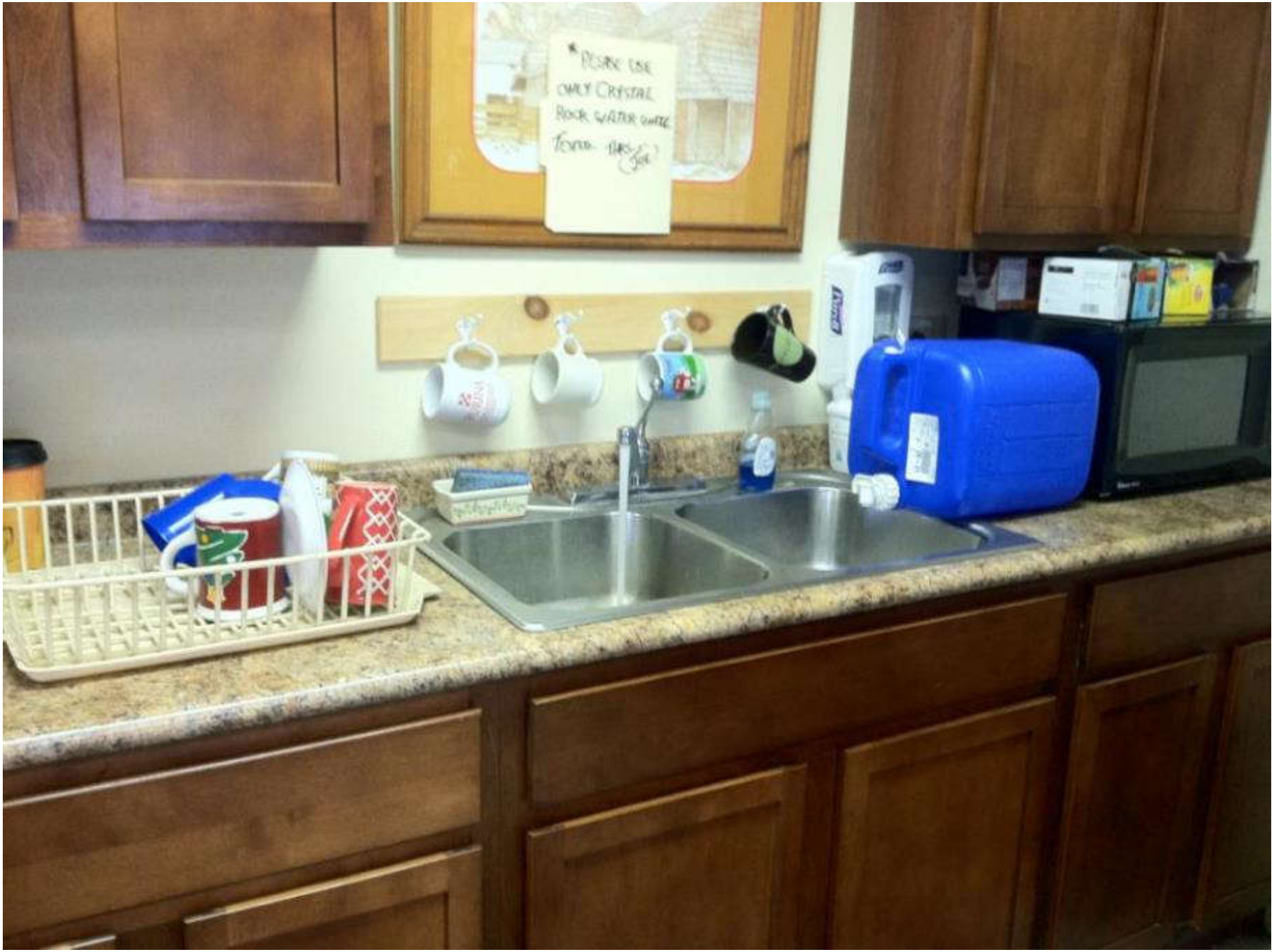
Drinking Water Sampling

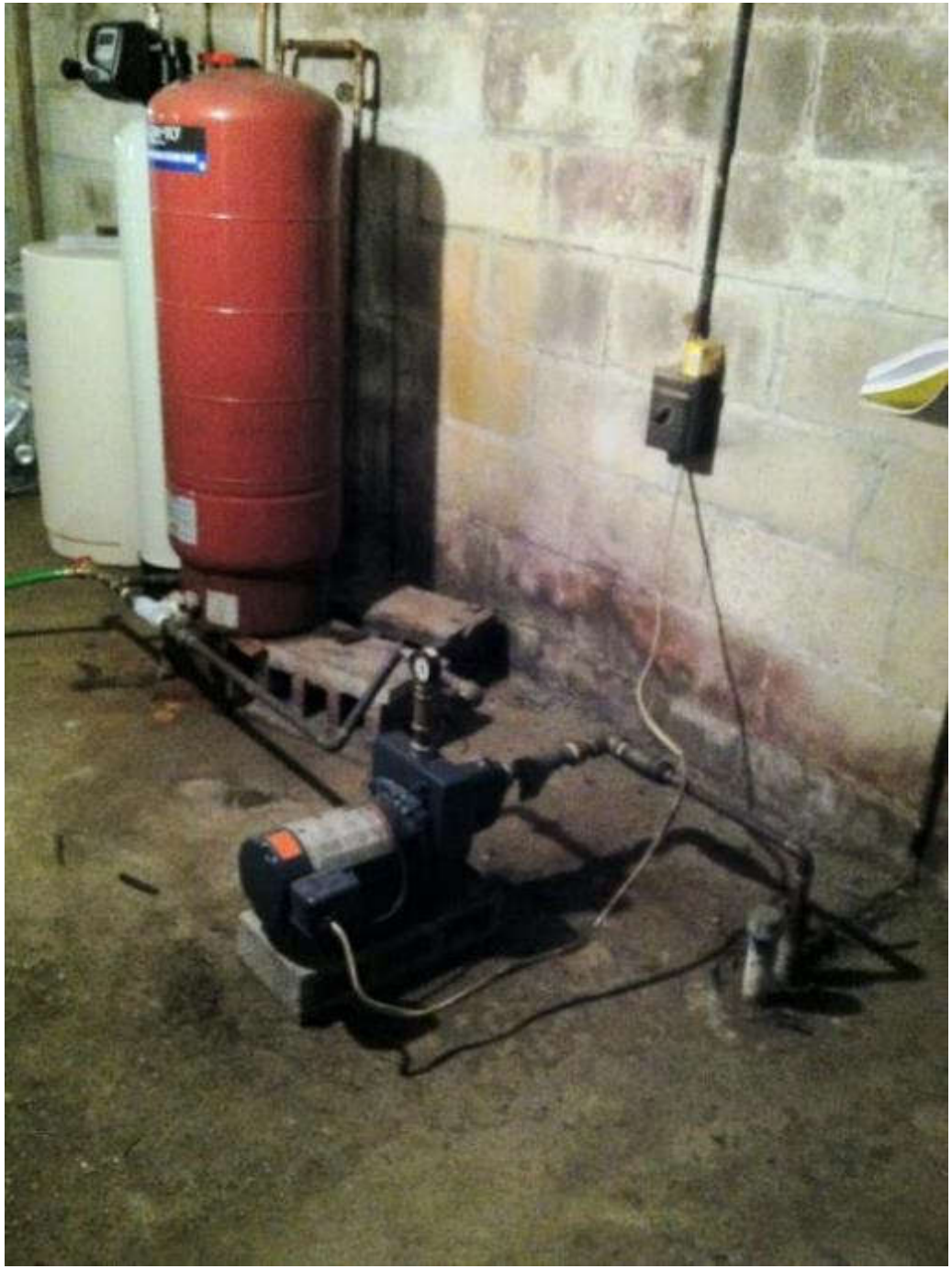
Public and Private Well Sampling in Hoosick Falls through March 4, 2016

Total Sampling Results	**298**
Results with PFOA below 2 ppt (i.e., ND)	**123**
Results with PFOA between 2 - 50 ppt	**105**
Results with PFOA between 50 - 100 ppt	**21**
Results with PFOA greater than 100 ppt	**49**
Total PFOA Dectections	**175**



Congress St
Ball St
Easy St
8.6 ng/L (well-raw)
Woods Brook
16 ng/L (well-raw)
<2 ng/L (well-raw)
20 ng/L 60 ng/L
18,000 ng/L 17,000 ng/L
5300 ng/L 4300 ng/L
Saint-Gobain
1700 ng/L 1400 ng/L
570 ng/L 580 ng/L
<2 ng/L (well-raw)
32.0 ng/L (well-raw)
Griffin Ave
Rogers Ave
HFCS BUS 412 ng/L (well-raw)
58.4 ng/L (well-raw)
153 ng/L (well-raw)
194 ng/L (well-raw) <2 ng/L (tap-R.O.)
<2 ng/L (well-raw)
<2 ng/L (well-raw)
<2 ng/L (well-raw)
<2.24 ng/L (well-raw)
39.4 ng/L (well-tap)
10.8 ng/L (well-raw)
60.2 ng/L (well-raw)
206 ng/L (well-raw)
Hoosick Falls Municipal Wellfield 150-662 ng/L (Raw)
Water Plant
Home St
10.3 ng/L (well-tap)
<2.24 ng/L (well-raw)
Mountain View Way
14.4 ng/L (well-raw)
Lake Lorraine Dr
44.4 ng/L (well-tap)


PLEASE USE
ONLY CRYSTAL
ROCK WATER

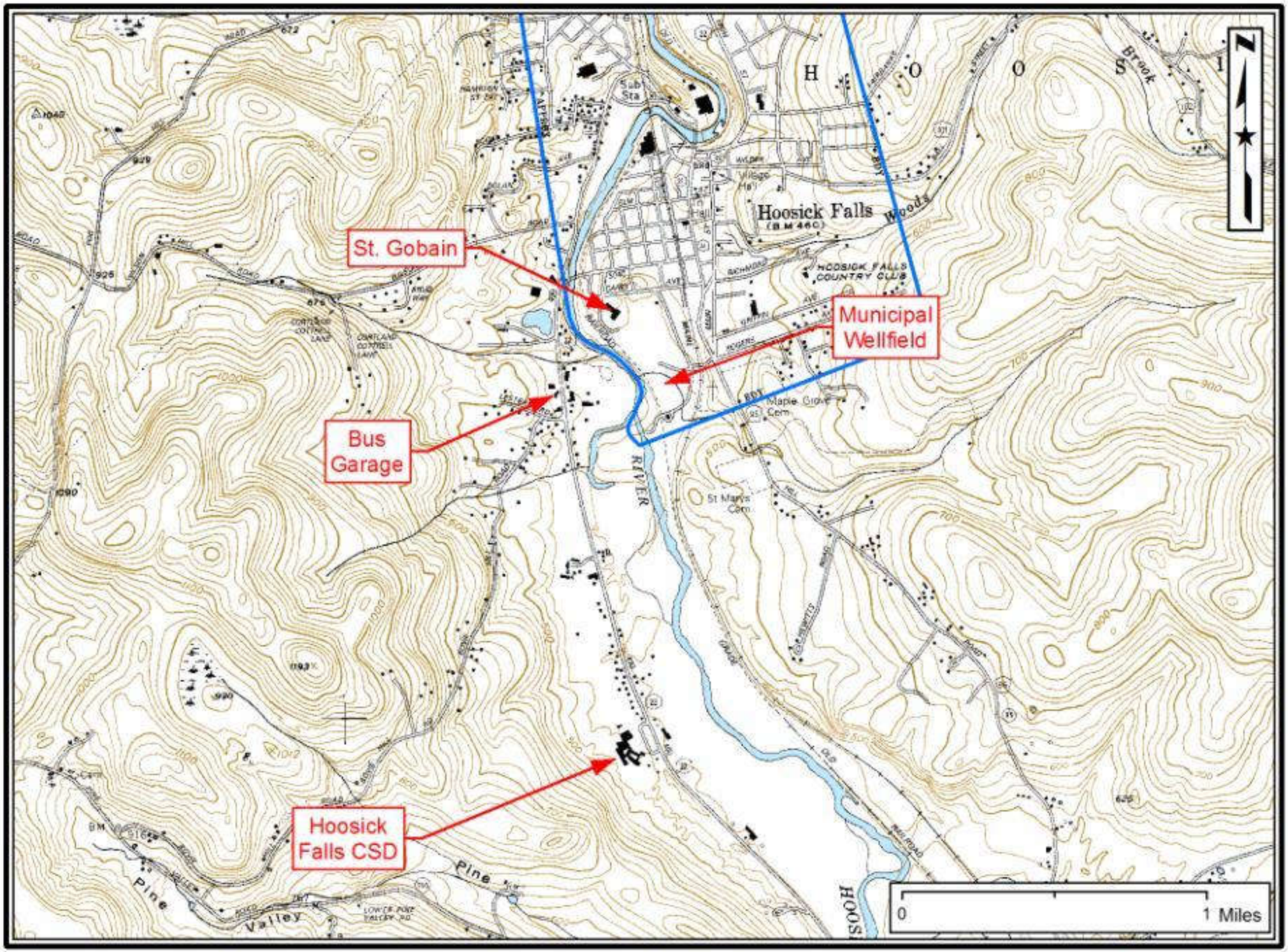


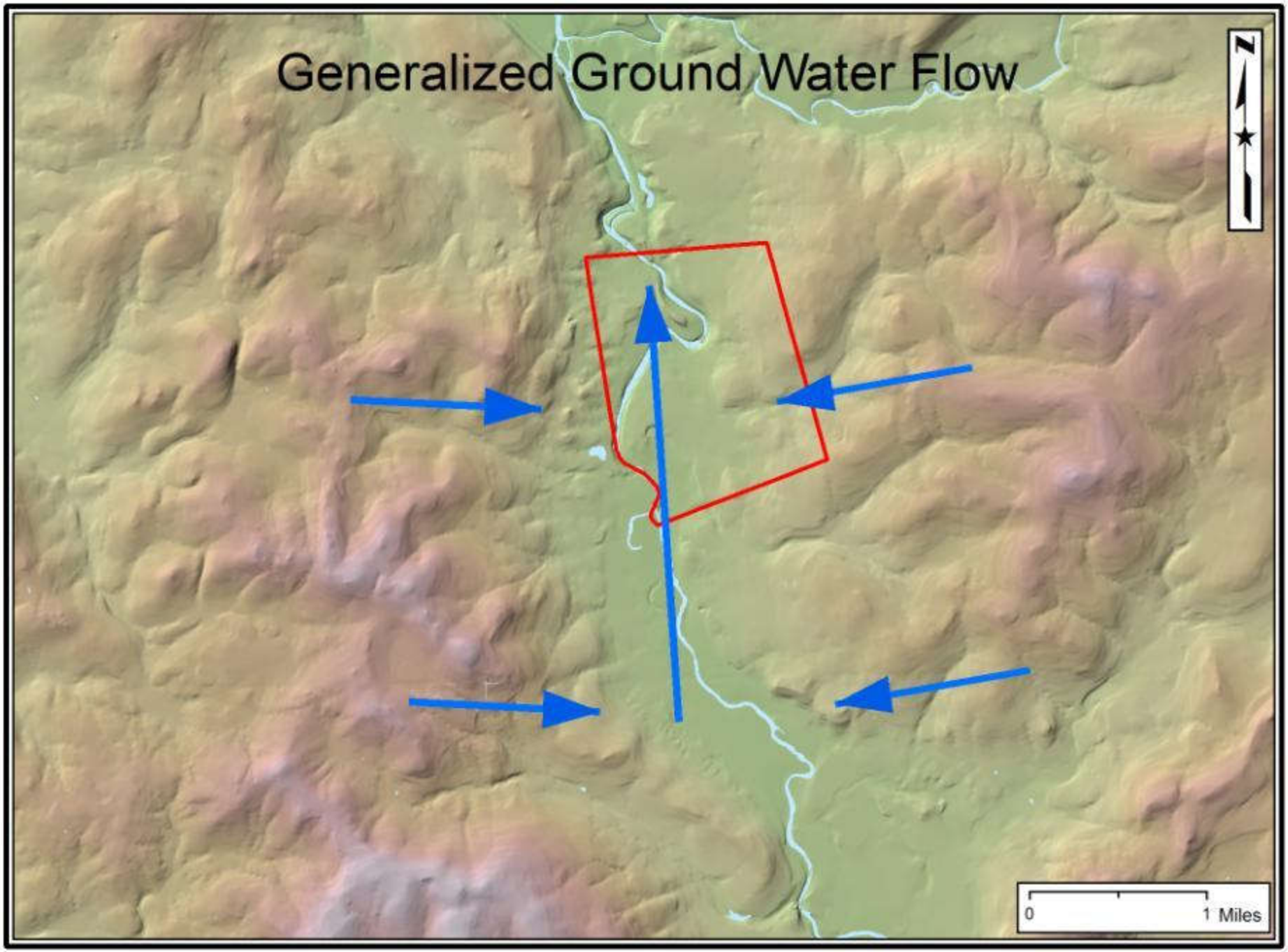
Geology and Hydrogeology

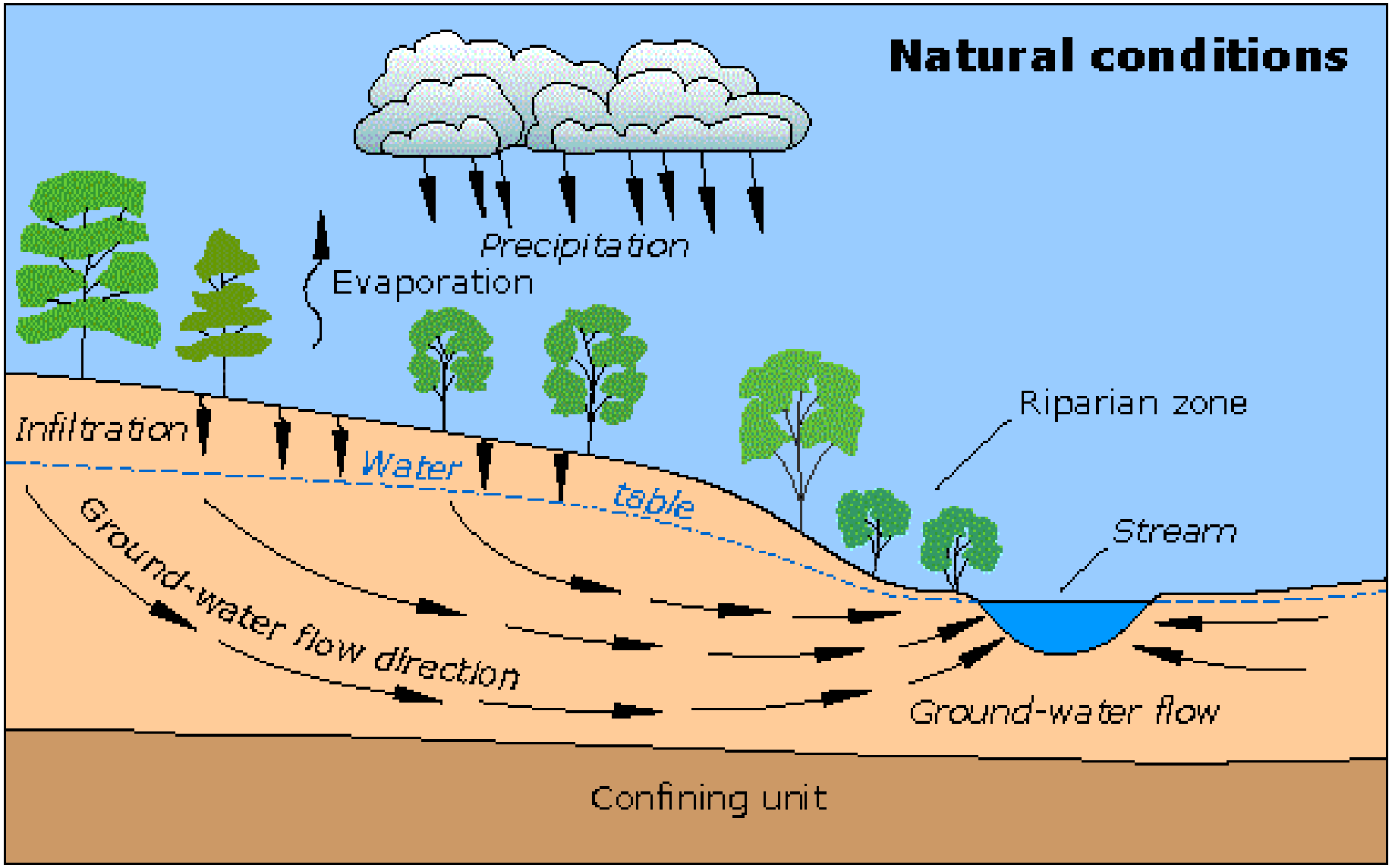
1. Sampling drinking water supplies:
   Assess exposure or quality at well or POU

2. Sampling discreet zones:
   Investigate sources and migration pathways, assess remedial options

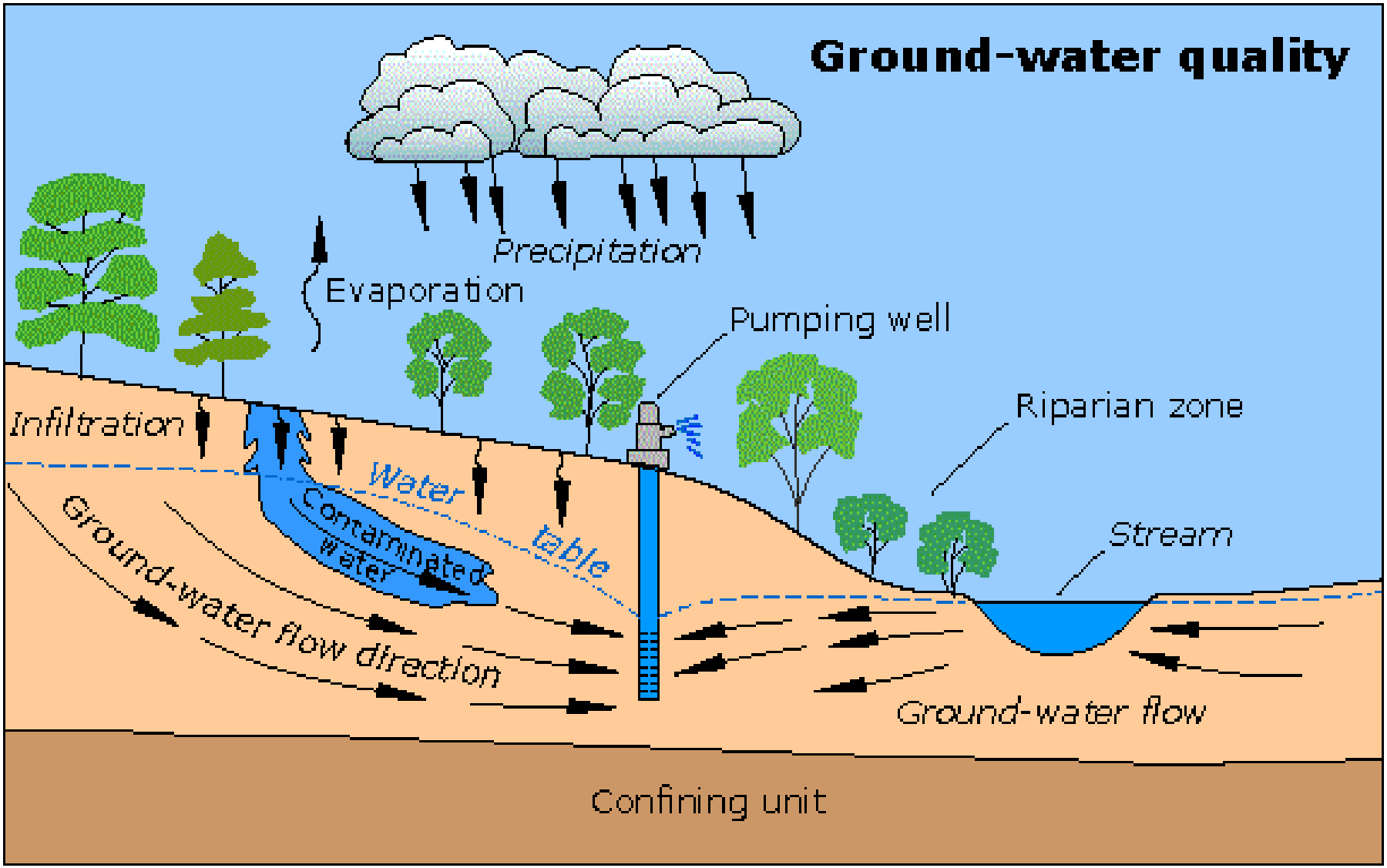
3. Geologic considerations:
   Locate and protect new water supplies


St. Gobain
Municipal Wellfield
Bus Garage
Hoosick Falls CSD
Hoosick Falls
(B.M. 460)
HOOSICK FALLS COUNTRY CLUB
Maple Grove Cem
St Mary's Cem
RIVER
Pine Valley
Pine
Brook
N
0
1 Miles


Generalized Ground Water Flow
N
0
1 Miles

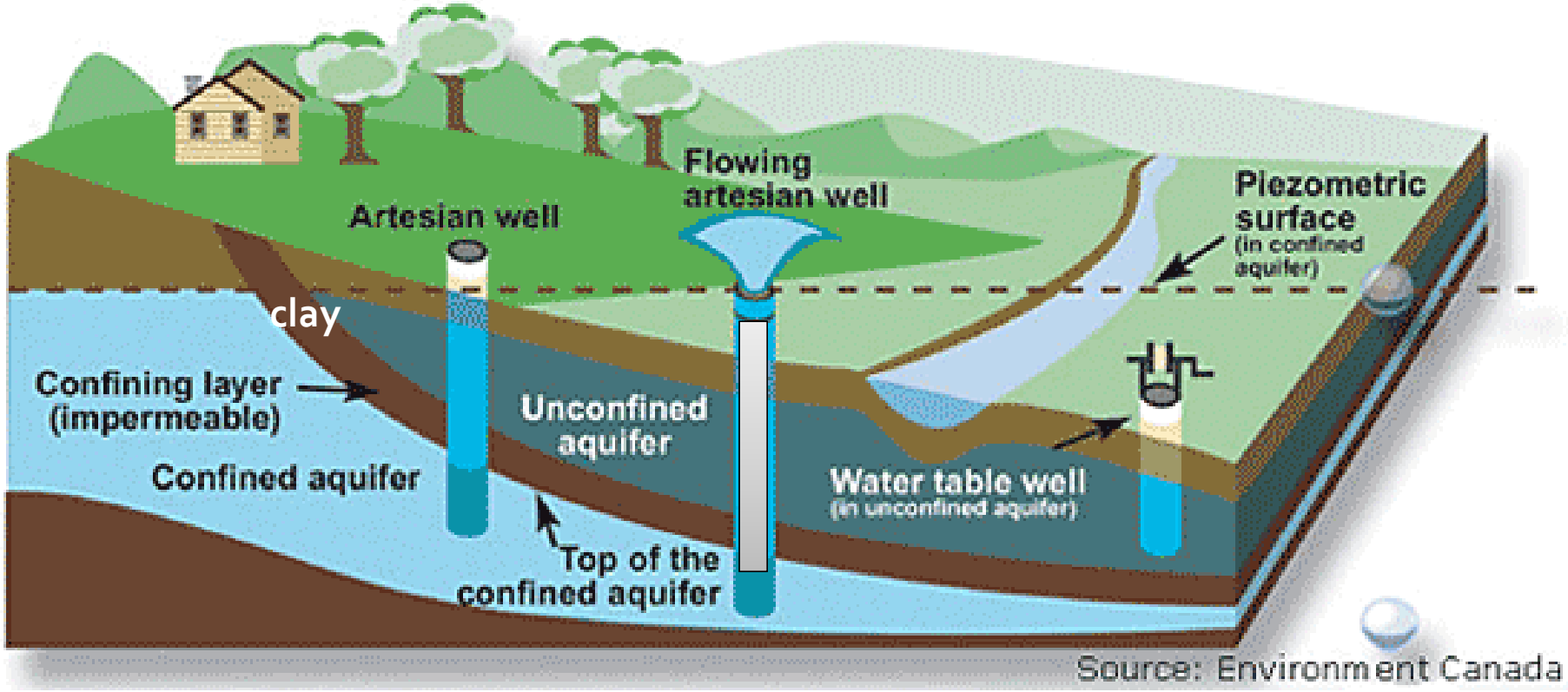

Natural conditions
Precipitation
Evaporation
Infiltration
Water
table
Riparian zone
Stream
Ground-water flow direction
Ground-water flow
Confining unit

Source USGS

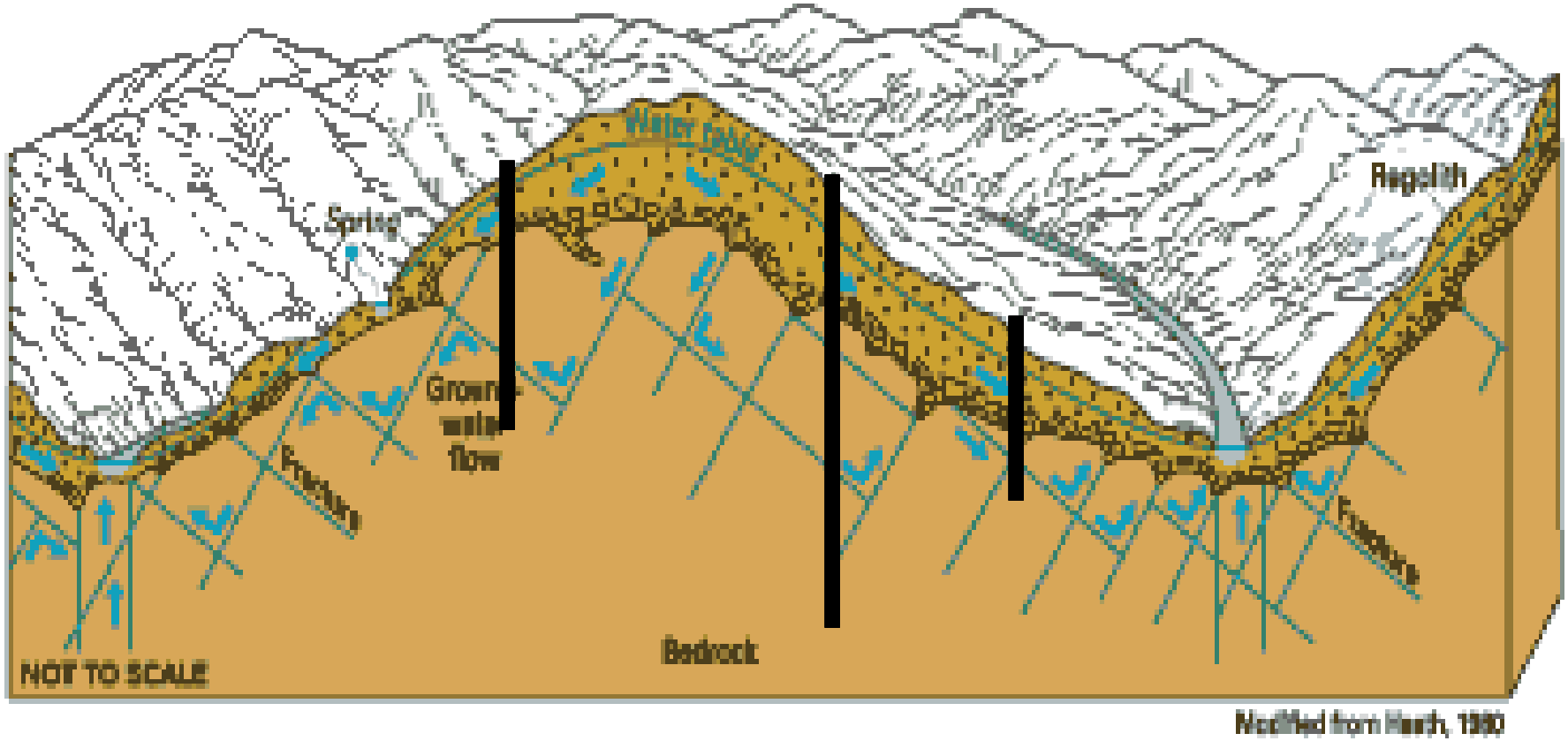


Induced infiltration and flow from pumping

Source USGS

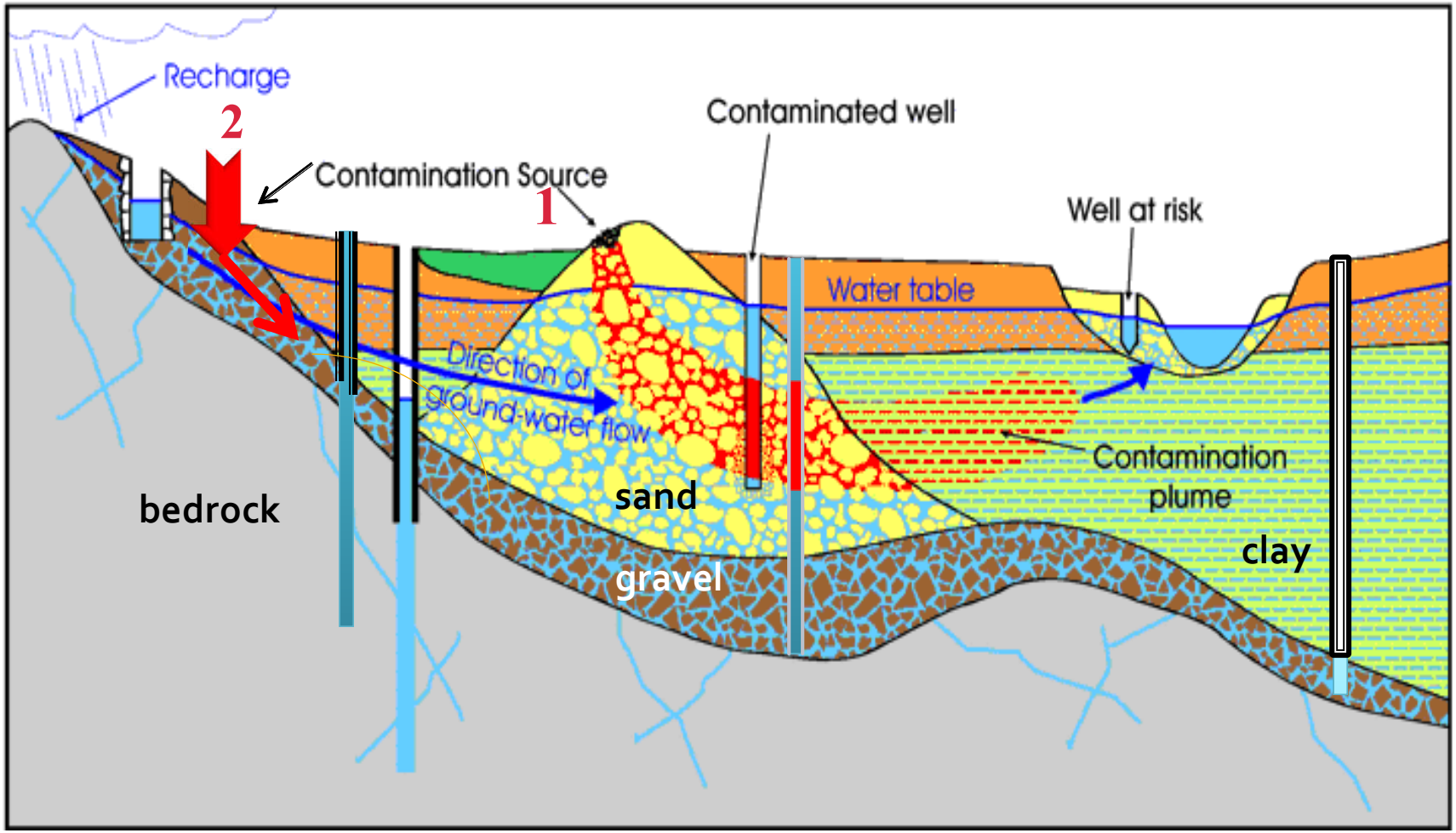


Water table and confined aquifer in unconsolidated material



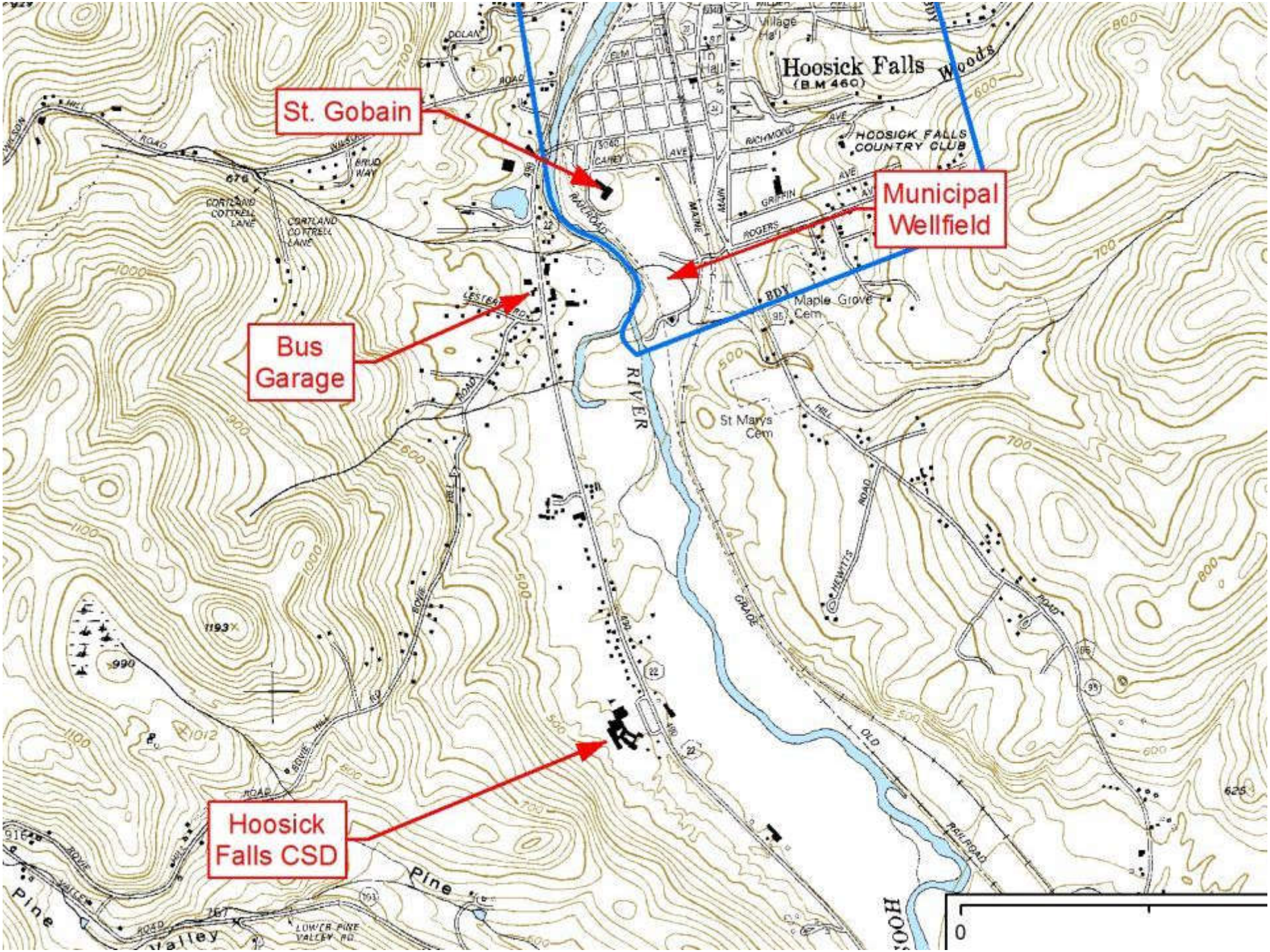
Modified from Heath, 1980

Consider other confounding factors:
multiple layers; differing lithologies; orientation; folds; faults

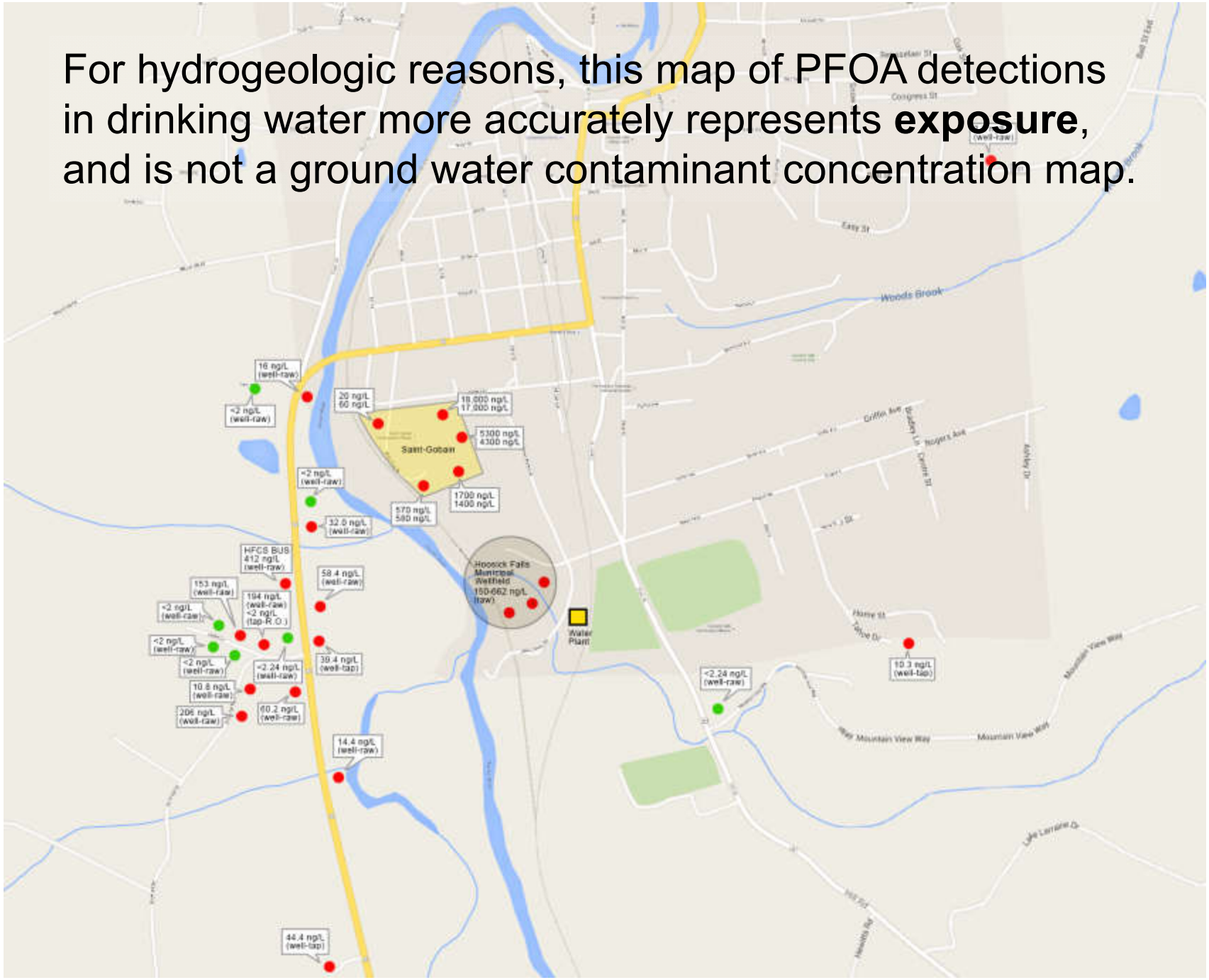


Maine Geological Survey

Typical stratigraphy in a glaciated valley


St. Gobain
Municipal Wellfield
Bus Garage
Hoosick Falls CSD
Hoosick Falls
(B.M 460)
Village Hall
HOOSICK FALLS COUNTRY CLUB
Maple Grove Cem
St Marys Cem
RIVER
RAILROAD
Woods
0

For hydrogeologic reasons, this map of PFOA detections in drinking water more accurately represents **exposure**, and is not a ground water contaminant concentration map.



Thank You

- PFOA and PFOS are PFCs
- Stable, persistent, saturated carbon chains, both hydrophobic and lipophobic
- Ubiquitous
- Limited treatment technologies
- Specialized sampling and lab analysis
- Geology and hydrogeology are critical
- Not going away anytime soon!

Part 3

“PFOA in Hoosick Falls, New York”

by Brian Moore, ARCADIS

ARCADIS Design & Consultancy for natural and built assets

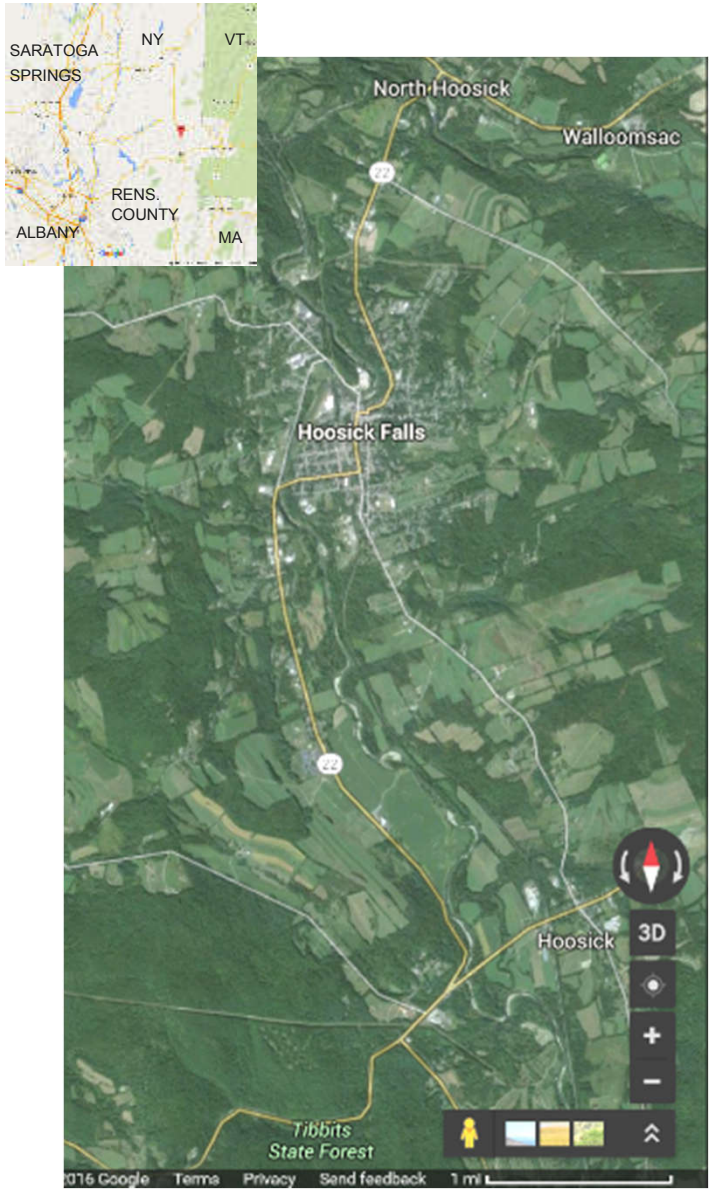
PFOA IN HOOSICK FALLS NY

NYS Department of Environmental Conservation

June 2016

Hoosick Falls, NY

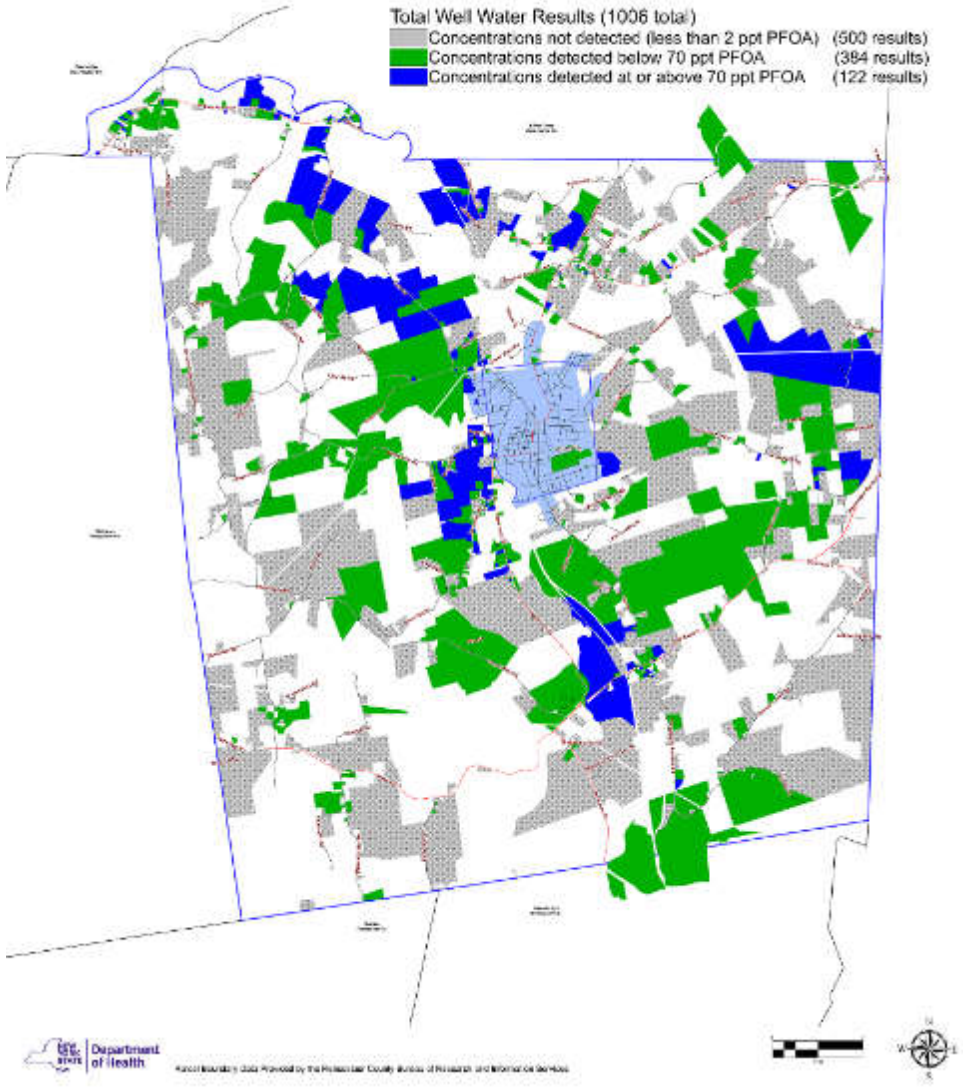
- Community of approximately 3,600 people located in northeastern Rensselaer County, New York – about 10 miles from New York-Vermont border.
- Situated along the Hoosic River – a 70-mile long tributary to the Hudson River with a 720 square-mile watershed in 3 states – Vermont, Massachusetts, and New York.
- Mix of residential, commercial and industrial zones.
- PFOA detected in Village water supply wells and other private wells.
- New York State responded by listing Saint-Gobain Performance Plastics on the State Superfund List.
- NYSDEC set up an Incident Command Center to respond to needs of residents, business owners and village officials.



ARCADIS Design & Consultancy for natural and built assets

Village of Hoosick Falls and Town of Hoosick Private Well Sampling

Perfluorooctanoic Acid (PFOA) Results Map - Updated May 18, 2016



Hoosick Falls - NYSDEC Work Assignments

- **Treatment System Design and Construction** - Granular Activated Carbon (GAC) treatment systems on water supply for schools and apartment complex
- **Point of Entry Treatment (POET) System: Bench-scale Testing**
- Small scale treatability testing (e.g. rapid small-scale column testing, RSSCT)
  - correctly design/size the treatment system
  - provides an estimate of expected service life to breakthrough.
  - performed within a much shorter time that a pilot or full-scale test.
- Because of the rapid response needed in this case, POET systems were being installed concurrently with design verification tests using via RSSCTs.

Hoosick Falls - NYSDEC Work Assignments (cont.)

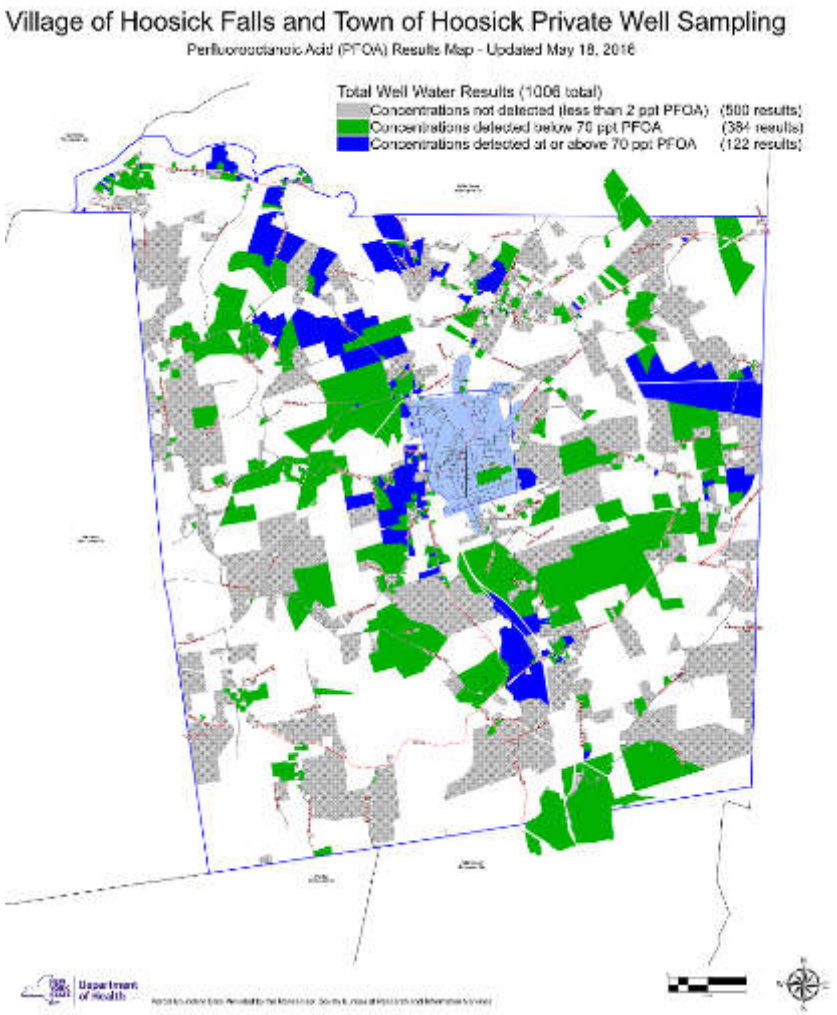
- **Engineering Oversight –** installing Point-of-Entry Treatment (POET) systems on approximately 900 residential and commercial water supply systems.

Hoosick Falls - NYSDEC Work Assignments

- **Incident Command Center -** Leading situational and planning tasks, operating call centers, scheduling field tasks, inventorying POET equipment, collecting and recording field and system data.
- **POET System Operation, Maintenance & Monitoring –** 20 months of PFOA water sampling and operations/maintenance of approximately 900 POET systems installed by NYSDEC contractors.

Hoosick Falls - NYSDEC Work Assignments (cont.)

- **Alternate Water Supply Evaluation –** Feasibility-style assessment evaluating options for an alternate water supply for the Village:
  - Upgrade the existing village well field
  - New surface water source
  - New groundwater source(s)
  - Tying into nearby municipal raw or treated water systems.



Thank You!

Questions?