Emerging Contaminant PFOA Has Emerged

Perflurooctanoic Acid: the contaminant du jour

ALPHA GEOSCIENCE

Outline

- Chemical overview
- Sampling and lab analysis
- Water treatment by GAC
- Hoosick Falls and regulatory concerns
- Geologic and hydrogeologic considerations
- Info sources: USEPA, CDC, NIH, USGS, NYS

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

Perfluoronated Compounds (PFCs)

- Synthetic, saturated fluorinated carbons
- Used in manufacturing fluoro-polymers
- Products resist heat and chemical reactions
- Lipid- and water-repellent; oil, stains, grease, water

- Industrial and commercial use since 1950:

  surface coatings, textiles, leather, packaging, additives, cleaning, pesticides, personal care, cooking, metal plating, surfactants

PFCs

Categorized by properties, uses, chemical functional groups

- **Perfluorooctanoic Acid (PFOA)**
  other common: perfluorononanoic acid (PFNA)
- **Perfluorooctane Sulfonic Acid (PFOS)**
  other: perfluorohexane sulfonic acid (PFHxS)
- **Aqueous Film Forming Foam (AFFF)**
  fluorocarbon & hydrocarbon surfactants, and solvents

USEPA: Per- and Poly-fluoroalkyl Substances (PFASs) under TSCA

Long-chains comprise two sub-categories

- Perfluoroalkyl Carboxylic Acids (PFCA),
  8 or more carbons, including **PFOA**

- Perfluoroalkane Sulfonates (PFSAs),
  6 or more carbons, including **PFOS**

PFOA molecular formula $C_8HF_{15}O_2$

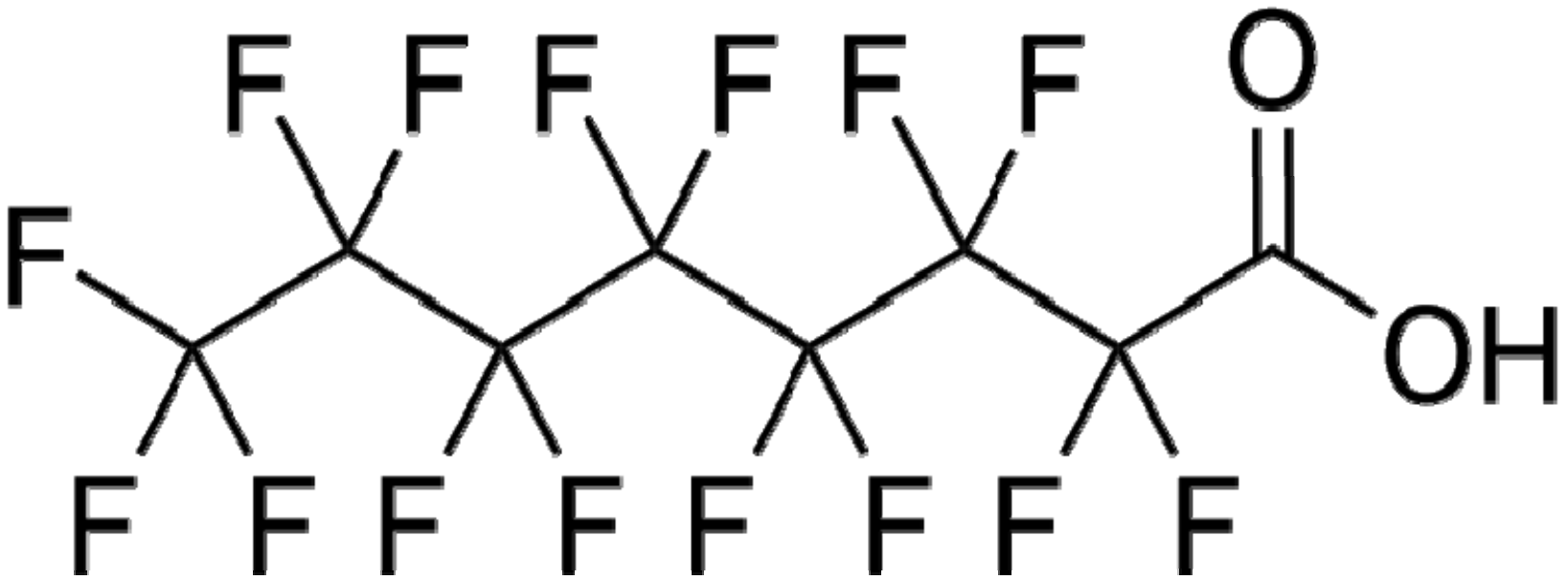
Pentadecafluorooctanoic acid (IUPAC)

2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-Pentadecafluorooctanoic acid

AKA: C8; hexanoyl fluoride; PFOA; octanoic acid; 3,3,4,4,5,5,6,6-nonafluoro-2-oxo; pentadecafluoro-; pentadecafluoro-1-octanoic acid; pentadecafluro-n-octanoic acid; pentadecafluorooctanoic acid; perfluorocaprylic acid; perfluoroheptanecarboxylic acid

… Let's just call it PFOA

PFOA Chemical Structure



PFOA molecular formula $C_8HF_{15}O_2$

Use & Occurrence of PFOA

- Aqueous dispersing agent (fluoropolymers)
- Aerospace, automotive, semiconductors, construction, chemical processing, electronics, photographic, paper, and textile industries
- Breakdown from some fluorinated telomers
- Consumer items such as Teflon™, GoreTex™, Scotchgard™ and other trademark products are **NOT PFOA**, but PFCs used in process.

EPA Concern with Long-chain PFAS

- Persistent, bioaccumulates, toxic
- Causes developmental and other adverse effects in laboratory animals
- Remains in people for a very long time
- Found world-wide in the environment, wildlife, and humans (bloodstream)

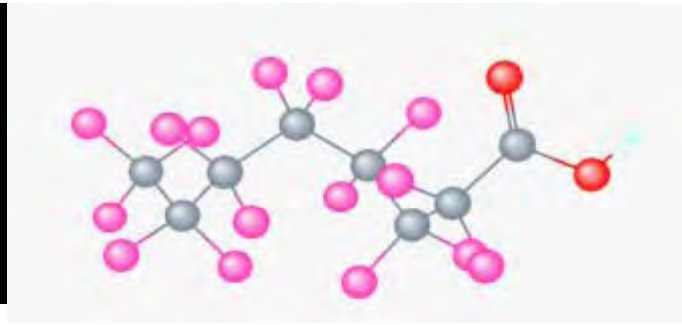
Two Exposure Concerns

- General low-level exposure from everyday contact and consumer products
  (cooking tools, packaging, personal care products, clothing, textiles, treated surfaces, cleaners, pesticides)

- Environmental exposure from various media at contaminated sites
  - drinking water, ground water, soil, air, and dust
  - primary (industrial) and secondary/satellite (dump) sites

Hazards: **Corrosive, Irritant, Toxic, Highly Flammable**

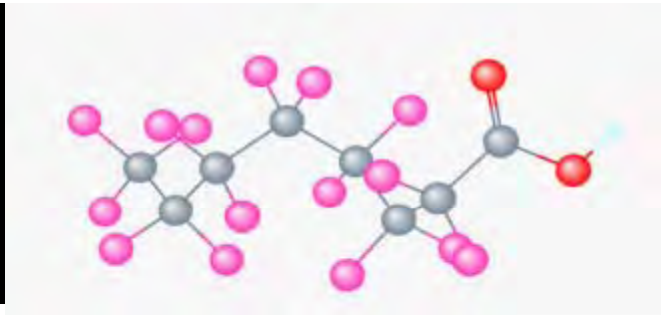
PFOA



White to off-white powder; waxy; pungent odor

- **Vapor pressure** 1.33 kPa @ 25°C (low volatility)
- **Est. Solubility in Water** 9500 mg/L at 25 °C (benzene = 1780 mg/L, TCE = 1100 mg/L at 20 °C)
- **Strong C-F bonds**
- **Doesn’t hydrolyze, photolyze, or biodegrade**

PFOA



- Half-life in water > 90 years
- High absorption, binds to substrate
- Decomposes above 300°C, toxic fluorine vapor
- Reacts with bases, oxidants, and reducing agents
- Attacks some metals, form flammable/explosive gas

Soluble, Mobile, Persistent, and Recalcitrant

Soil: Landfill, Isolate, or Incinerate

Water: Carbon Filtering; Developing Potential for Biological and Enzyme Treatment.

United States Environmental Protection Agency

Searching for Emerging Contaminants in Drinking Water

What is the Unregulated Contaminant Monitoring Rule?

The 1996 amendments to the Safe Drinking Water Act (SDWA) require that once every five years, the U.S. Environmental Protection Agency (EPA) issue a new list of no more than 30 unregulated contaminants to be monitored by public water systems (PWSs). The Unregulated Contaminant Monitoring Rule (UCMR) provides EPA and other interested parties with scientifically valid data on the occurrence of contaminants in drinking water. These data serve as a primary source of occurrence and exposure information that the agency uses to develop regulatory decisions.

The final rule "Revisions to the Unregulated Contaminant Monitoring Rule (UCMR 3) for Public Water Systems" was published in the *Federal Register* on May 2, 2012 (77 FR 26072). UCMR 3 monitoring will take place from 2013-2015, and includes monitoring for 28 chemicals and two viruses.

What contaminants are systems looking for as part of UCMR 3?

Under UCMR 3, public water systems or EPA will conduct sampling and analysis for Assessment Monitoring (List 1), Screening Survey (List 2), and Pre-Screen Testing (List 3) contaminants, as follows:

UCMR 3 Contaminant List			
Assessment Monitoring (List 1 Contaminants)			
1,2,3-trichloropropane	bromomethane (methyl bromide)	chloromethane (methyl chloride)	bromochloromethane (Halon 1011)
chlorodifluoromethane (HCFC-22)	1,3-butadiene	1,1-dichloroethane	1,4-dioxane
vanadium	molybdenum	cobalt	strontium
chromium[1]	chromium-6[2]	chlorate	perfluorooctanesulfonic acid (PFOS)
perfluorooctanoic acid (PFOA)	perfluorobutanesulfonic acid (PFBS)	perfluorohexanesulfonic acid (PFHxS)	perfluoroheptanoic acid (PFHpA)
perfluorononanoic acid (PFNA)			
Screening Survey (List 2 Contaminants)			
17-ß-estradiol	estriol	estrone	4-androstene-3,17-dione
17-a-ethynylestradiol	equilin	testosterone	
Pre-Screen Testing[3] (List 3 Contaminants)			
enteroviruses	noroviruses		

1. Monitoring for total chromium, in conjunction with UCMR 3 Assessment Monitoring, is required under the authority provided in Section 1445(a)(1)(A) of SDWA.
2. Chromium-6 will be measured as soluble chromate (ion).
3. Monitoring for microbial indicators, in conjunction with Pre-Screen Testing, will be conducted, including: total coliforms, *E.coli*, bacteriophage, *Enterococci* and aerobic spores. EPA will pay for all sampling and analysis costs for the small systems selected for this monitoring.

EPA PFOA Goals

- **2010: 95% reduction (relative to 2000) in PFOA emissions, precursor and related chemicals, and product content levels**

- **2015: Eliminate from emissions and products**

Participating Companies: Arkema, Asahi, Clariant, BASF Corporation (successor to Ciba), Daikin, 3M/Dyneon, DuPont, Solvay Solexis

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

Sampling Protocol

- No available field-screening test (yet)
- Collect 250-mL in HDPE containers
- No preservative (method 537); or,
- Trizma™ preservative, if chlorinated
- Preserve at 4 °C; use ice (avoid blue packs)
- 7-day holding time for water; 14 days for soil

Sampling

Potential contamination or false lab dectection

- Water-proof field books, footwear, clothing, Tyvek®
- Teflon® (bailers, septum or liners, well materials)
- Food packaging, coated cups and bags, Al foil
- Personal products (waterproof sunscreen, insect repellent, makeup)
- Certain decontamination solutions
- Pump parts (hoses, O-rings), tape, wire coatings

USEPA METHOD 537

DETERMINATION OF SELECTED PERFLUORINATED ALKYL ACIDS IN DRINKING WATER BY SOLID PHASE EXTRACTION AND LIQUID CHROMATOGRAPHY/ TANDEM MASS SPECTROMETRY (LC/MS/MS)

Document #: EPA/600/R-08/092
Version 1.1, September 2009

Method 537 Analyte	Acronym	Chemical Abstract Services Registry Number (CASRN)
N-ethyl perfluorooctanesulfonamidoacetic acid	NEtFOSAA	ņ
N-methyl perfluorooctanesulfonamidoacetic acid	NMeFOSAA	ņ
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
Perfluoroundecanoic acid	PFUnA	2058-94-8

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

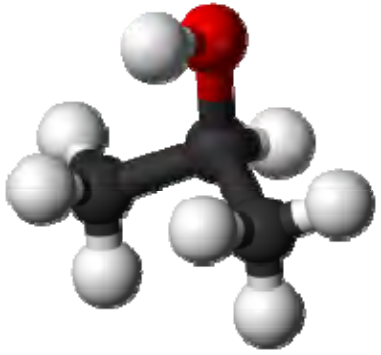
- Multiple sources, multiple media
- Large, relatively diffuse plumes, can be low-level concentrations (ID source?)
- Co-mingled and multiple contaminants (petroleum, chlorinated solvents, others)
- Chemical properties (solubility, non-volatile, strong C-F bonds
- Removal vs. destruction

Granular Activated Carbon

Readily Adsorbed Organics

- Aromatic solvents - benzene, toluene
- VOCs - TCE, PCE
- High MW HydroC - gasoline
- Chlorinated aromatics - PCBs
- PNAs - acenaphthene
- Phenols and chlorophenols
- Pesticides and herbicides
- Chlorinated non-aromatics - CCl4
- **PFOA**

BENZENE



ISOPROPYL ALCOHOL

Poorly Adsorbed

Alcohols, Low MW ketones, Acids, Aldehydes, Colloidal organics

Courtesy of Calgon Carbon

Starting Materials

- Raw material dictates performance
- Many combinations possible
- Most utilize thermal process

Courtesy of CalgonCarbon

Activated Carbon Works in Various Ways

Physical Adsorption

- adsorbs and removes
- coal, wood, coconut-based
- applicable to PFOA

Reaction - Dechlorination

Physical/Chemical Adsorption

Catalytic reaction

Courtesy of Calgon Carbon

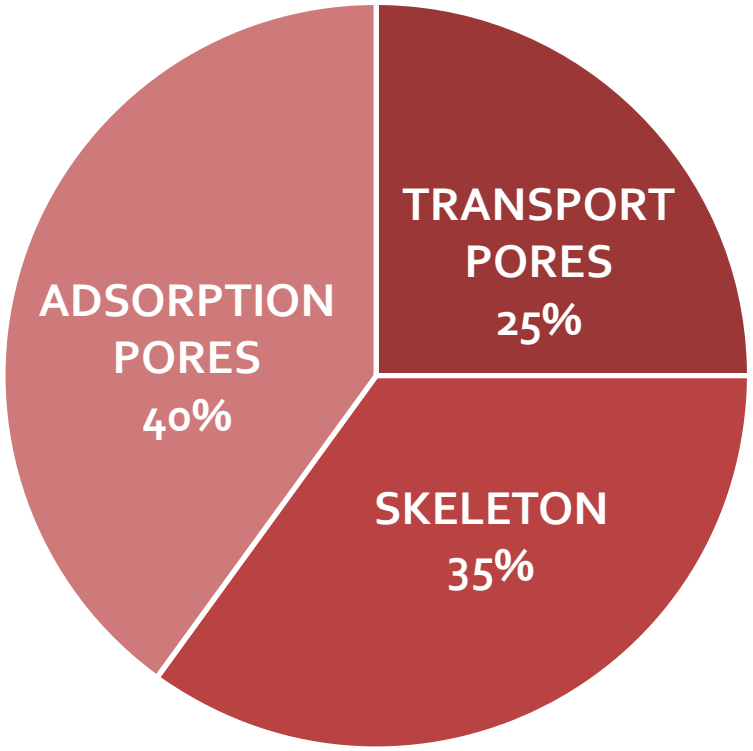
Granular Activated Carbon

Adsorption Pores

- Finest pores
- Adsorption capability

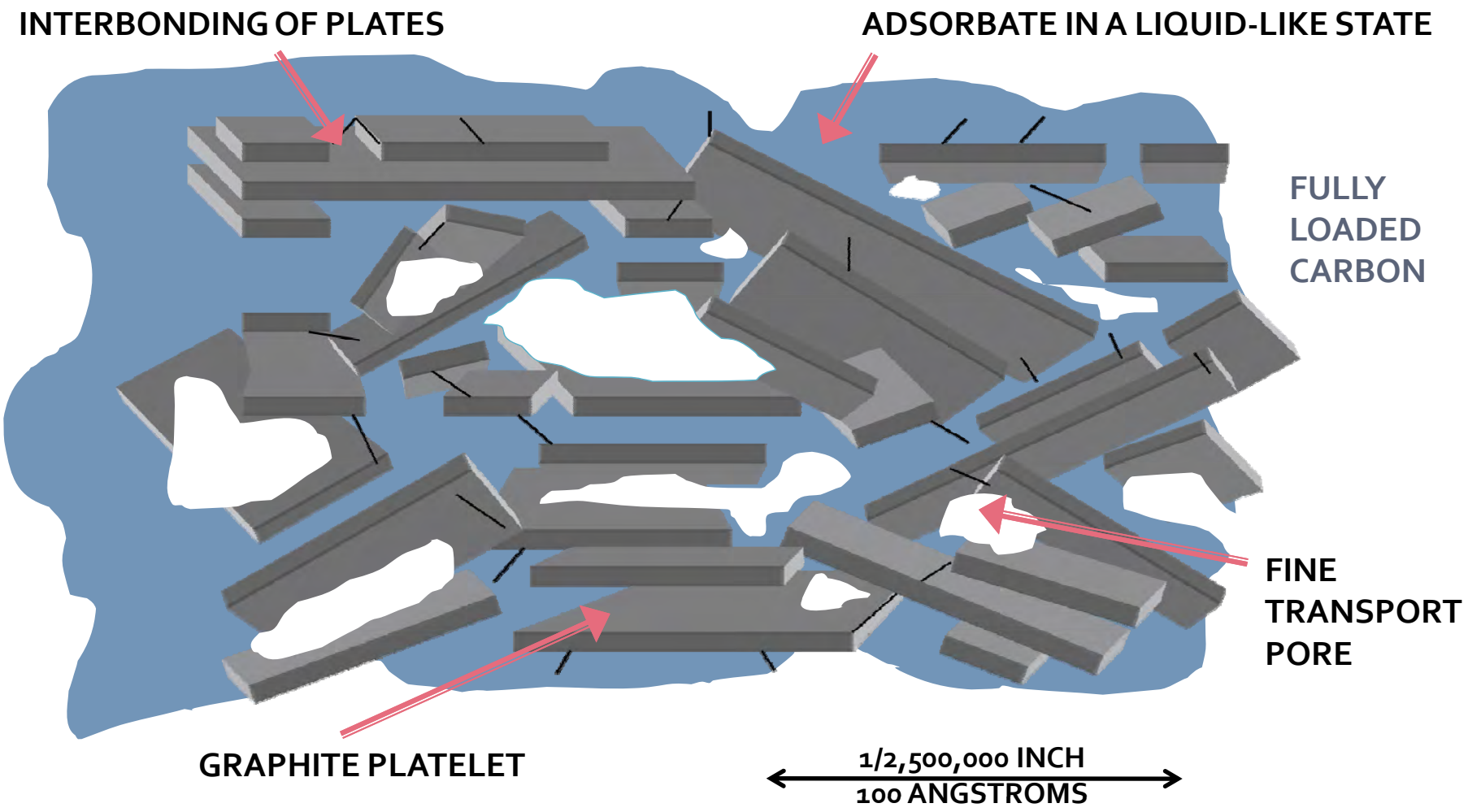
Transport Pores

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



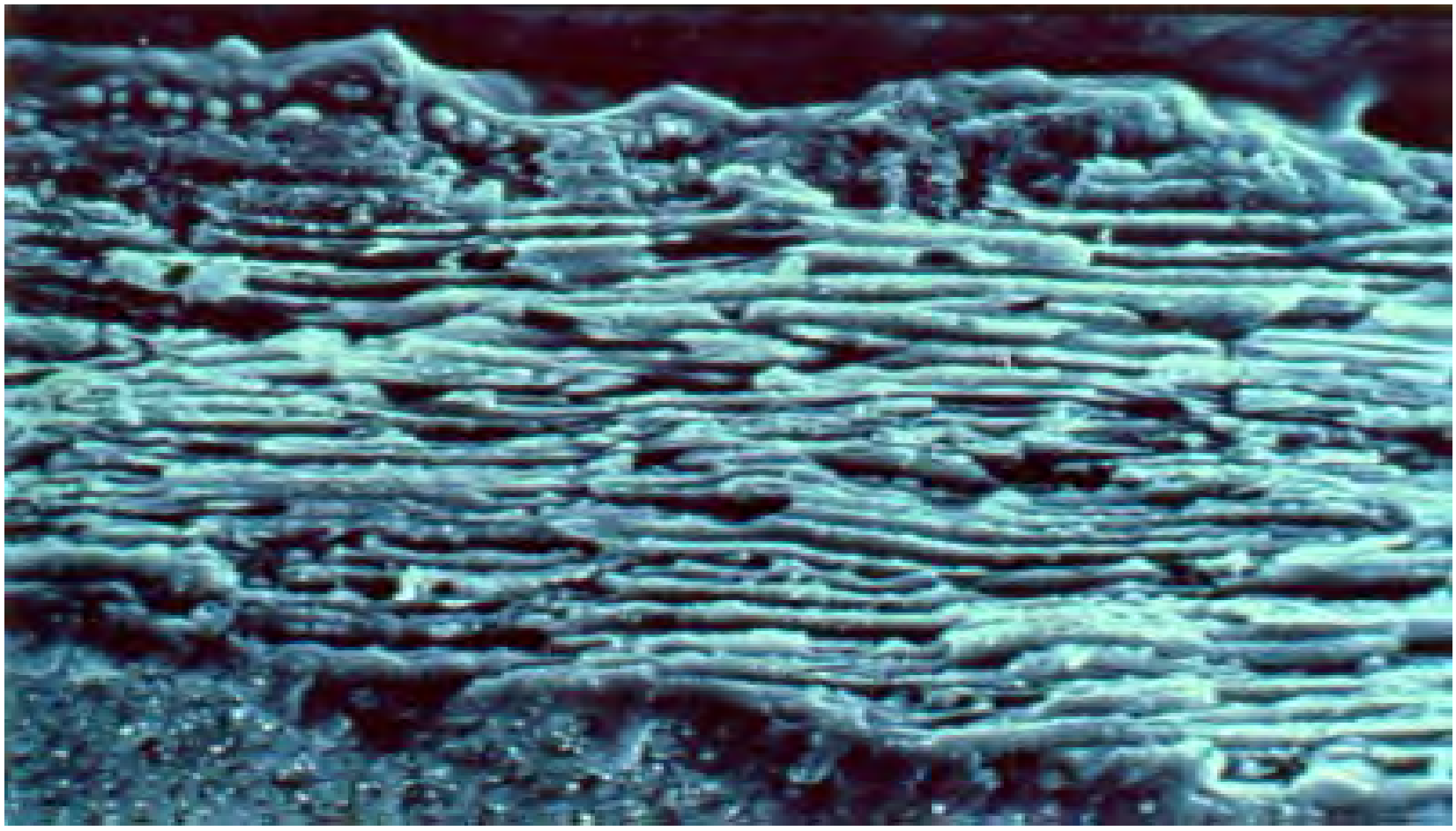
Courtesy of Calgon Carbon

The Structure of Activated Carbon



Courtesy of CalgonCarbon

Photomicrograph — 1,000,000X Magnification



Courtesy of Calgon Carbon

Carbon Specifications

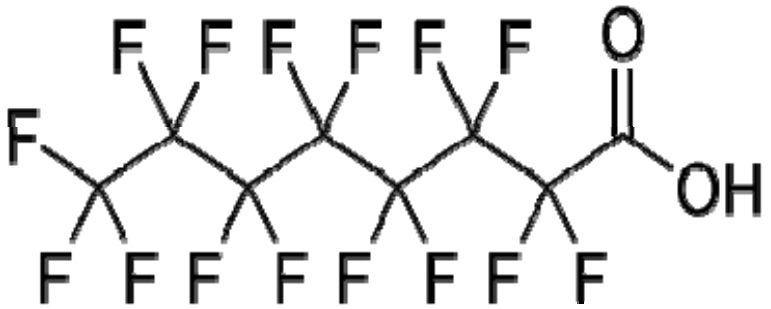
Specification	Property
Iodine/butane number	Indicator of total surface area or pore volume
Hardness/abrasion number	Mechanical strength or attrition resistance
Screen or mesh size	Size distribution of media
Moisture	Water content
Apparent density	Mass carbon per unit volume (g/cc)
Ash	Inorganic matter/non-adsorptive

Courtesy of CalgonCarbon

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

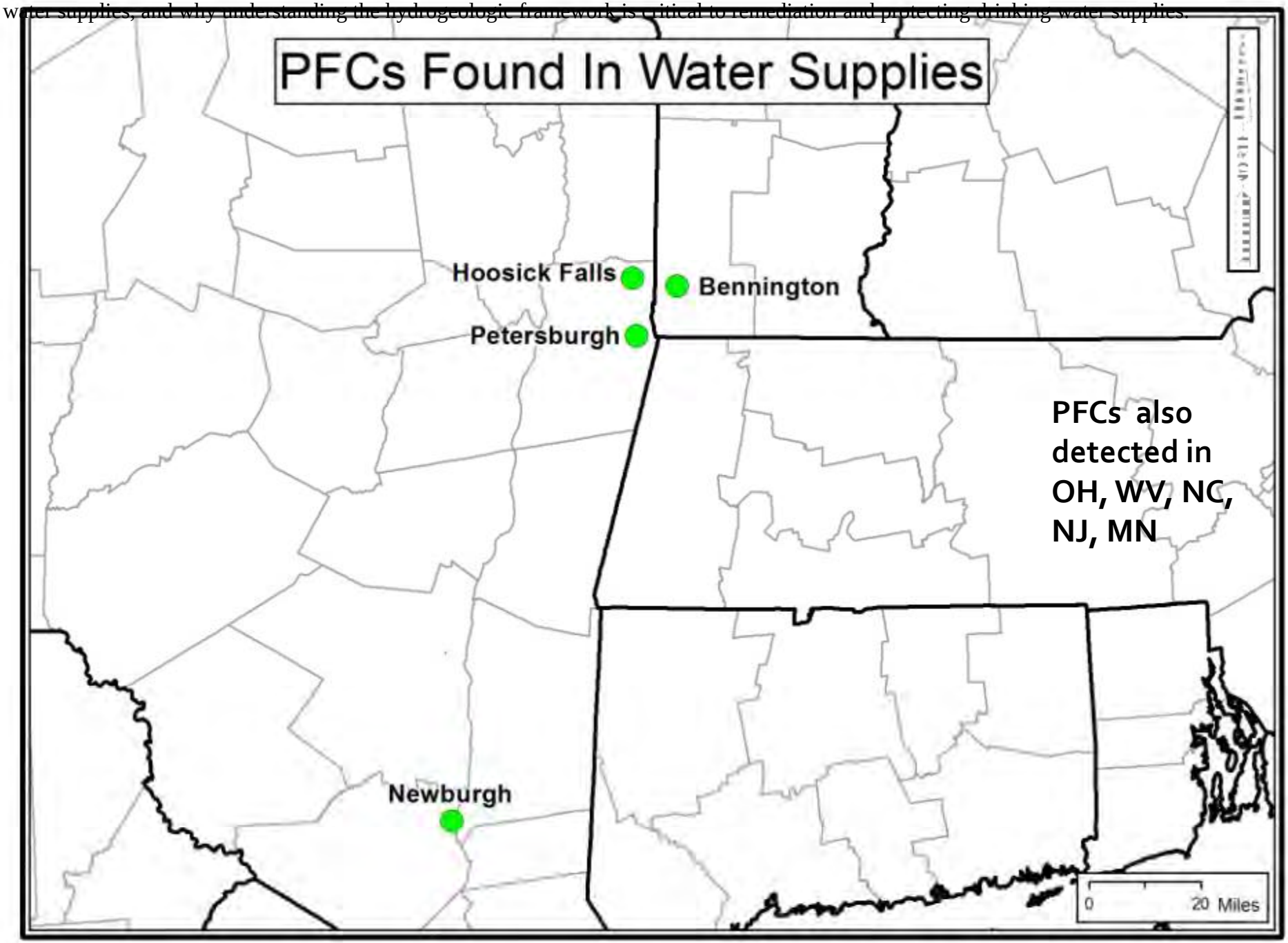
The higher the molecular weight, the better adsorbed

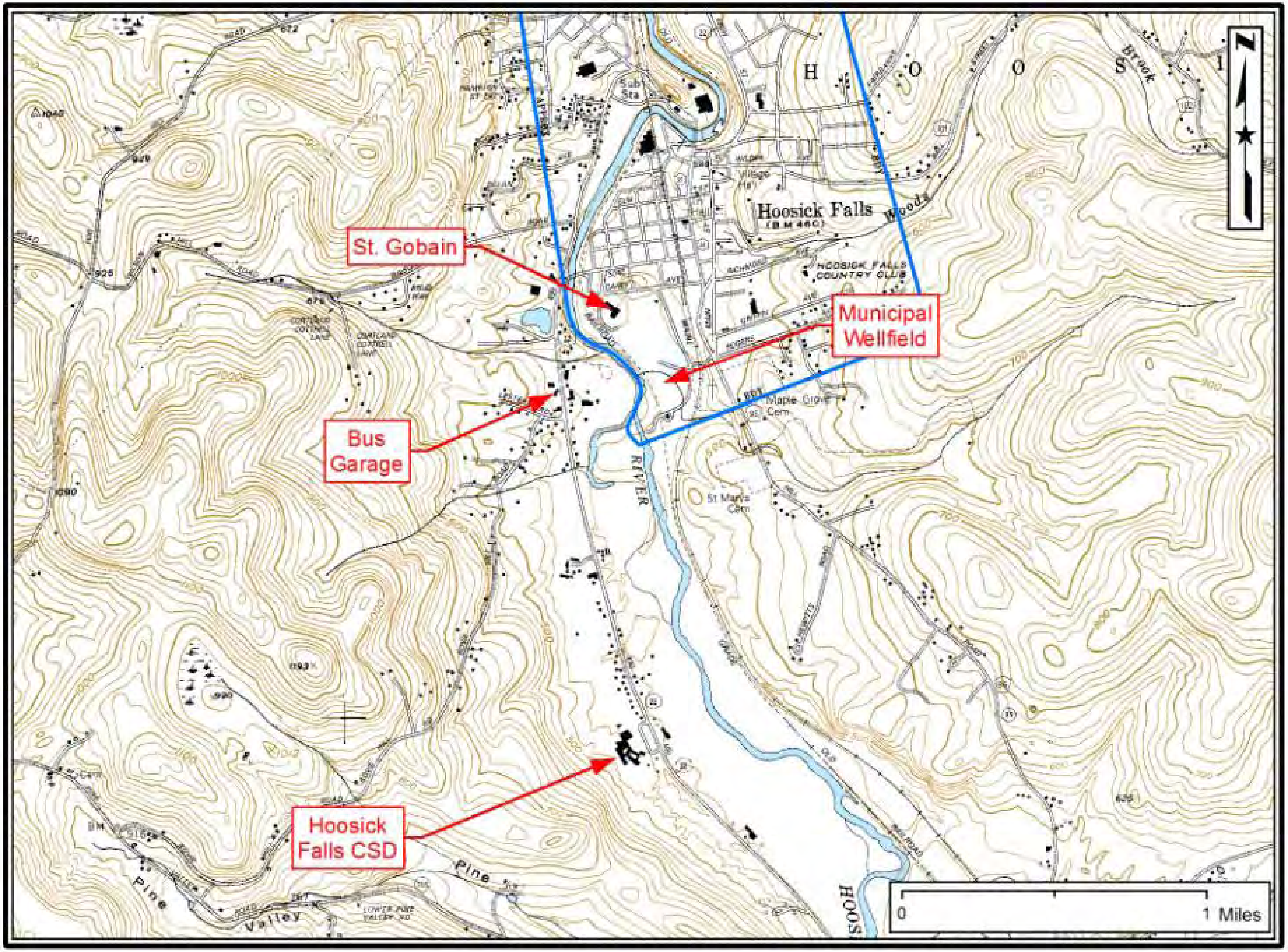
Functional groups

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
HOOSICK FALLS COUNTRY CLUB
RIVER
Maple Grove Cem
St Marys Cem
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

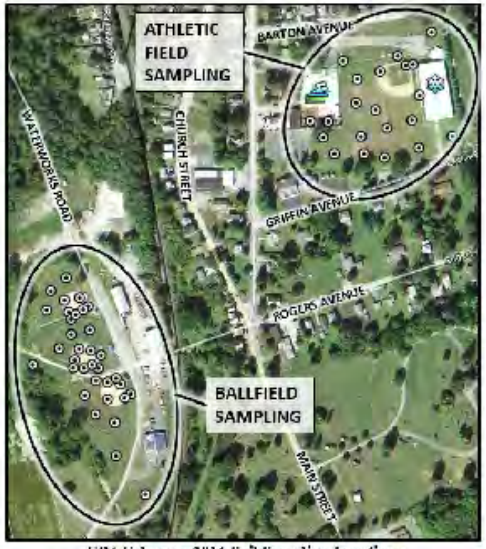
Introduction

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.

Hoosick Falls Update: EPA Results Show Ballfields & Athletic Field OK to Use

Community Update No. 3 **Spring 2016**



EPA February 2016 Soil Sampling Locations

WHAT IS PFOA?
Perfluorooctanoic acid (PFOA) belongs to a group of chemicals used to make household and commercial products that resist heat and chemical reactions and repel oil, stains, grease and water. PFOA was widely found in non-stick pots and pans, carpets and fire-fighting foam.

WHY IS PFOA A PROBLEM?
PFOA does not break down easily and therefore is very persistent in the environment. Its toxicity and persistence in the environment pose potential adverse effects to human health and the environment.

The U.S. Environmental Protection Agency (EPA) has been investigating the Hoosick Falls perfluorooctanoic acid (PFOA) contamination in conjunction with the Village of Hoosick Falls, the county health department and the New York State Department of Health (NYSDOH) and Department of Environmental Conservation (NYSDEC).

In February 2016, EPA sampled soil at the ballfields and park areas along Waterworks Road as well as throughout the Athletic Field to determine if past releases from local manufacturing facilities had contaminated the fields. Samples of soil were collected in the upper three inches and at a depth from three to twelve inches below the ground surface at 55 locations. Several samples were also collected from depths between 1.5 and 20 feet below the ground surface. Samples were analyzed for a wide range of contaminants, including PFOA and related compounds, volatile and semi-volatile organic compounds, polychlorinated biphenyls (PCBs) and metals.

WHAT DID THE RESULTS SHOW?

Levels of PFOA and related compounds ranged from non-detect to 0.021 parts per million (ppm), as compared with the EPA's action level for PFOA in soil, which is currently 15.6 ppm. These levels will not necessitate any need for cleanup work in any of the areas sampled. The highest concentrations of PFOA and related compounds were generally found deeper than three inches under the surface.

From HF Schools FaceBook Page January 22, 2016

Transportation Department Water Tests Positive for PFOA

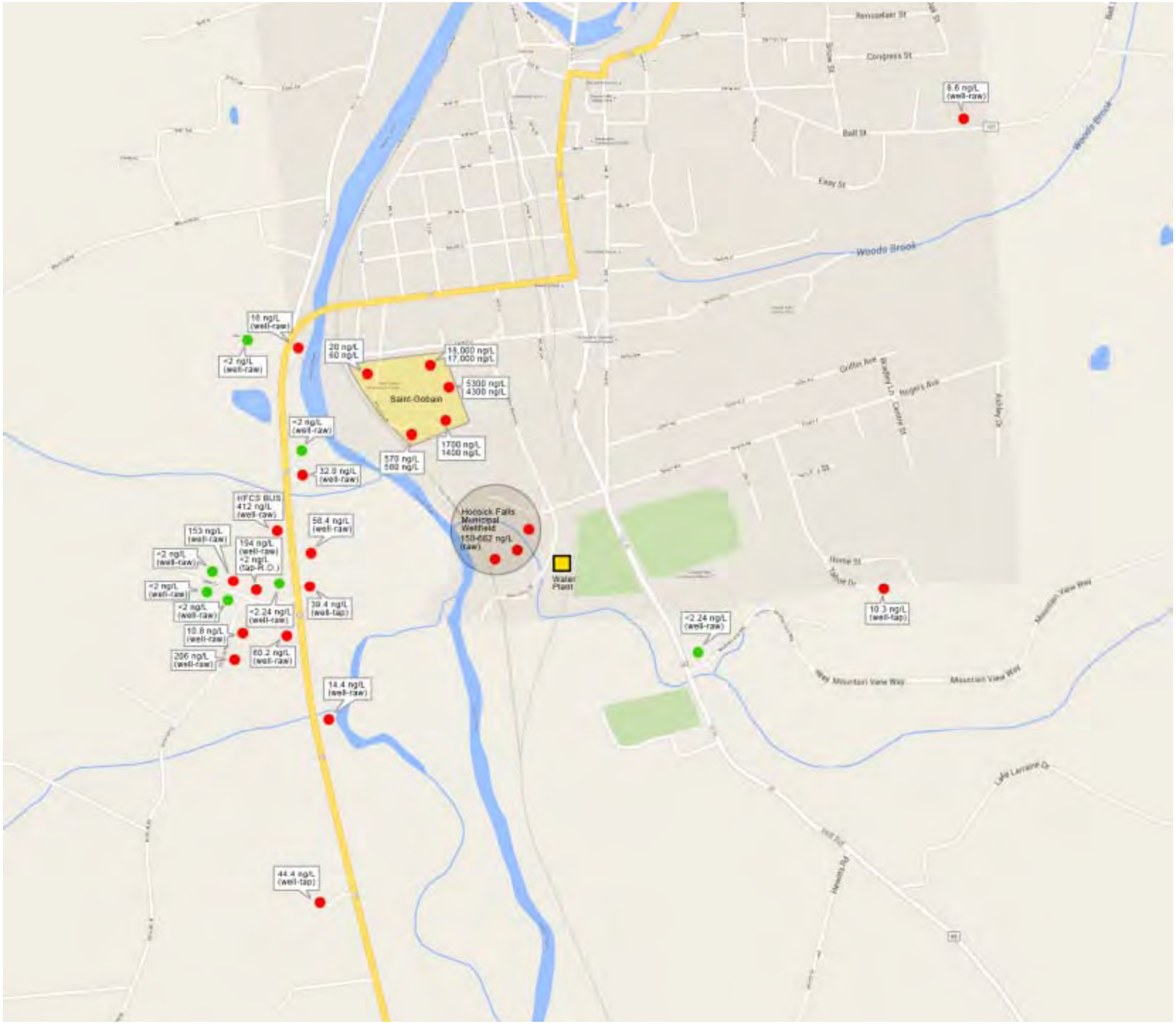
January 22, 2016 in Uncategorized

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.

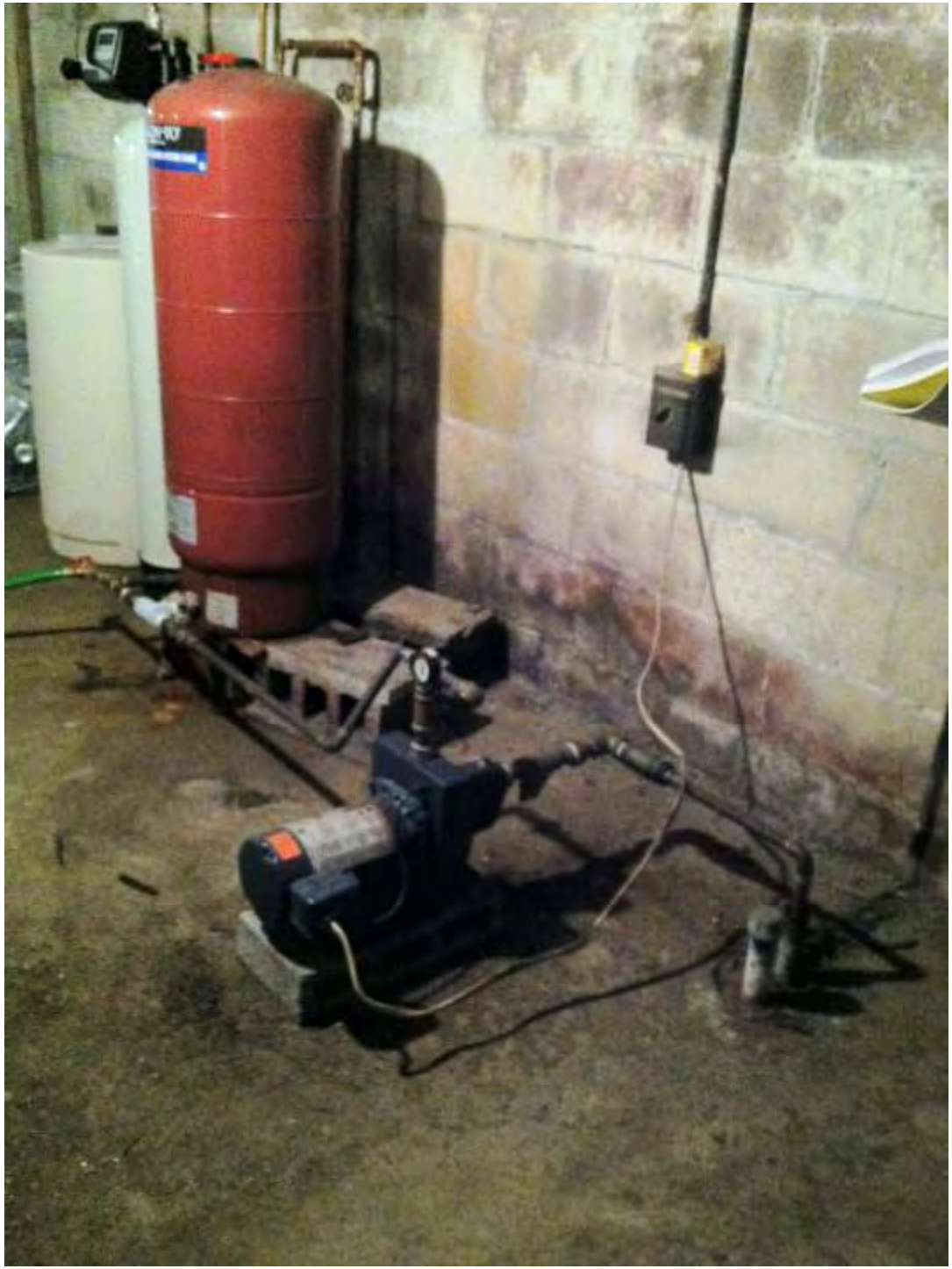
Drinking Water Sampling

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 Detections	**175**


Rensselaer St
Congress St
Ball St
Easy St
Woods Brook
Griffin Ave
Bradley Ln
Wright's Ave
Centre St
Ashley Dr
Howe St
Taylor Dr
Mountain View Way
Lake Lorraine Dr
Hill Rd
Howells Rd
8.6 ng/L (well-raw)
10 ng/L (well-raw)
<2 ng/L (well-raw)
20 ng/L
60 ng/L
15,000 ng/L
17,000 ng/L
5300 ng/L
4300 ng/L
Saint-Gobain
1700 ng/L
1400 ng/L
570 ng/L
560 ng/L
<2 ng/L (well-raw)
32.8 ng/L (well-raw)
HFCS BUS
412 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)
10.8 ng/L (well-raw)
206 ng/L (well-raw)
60.2 ng/L (well-raw)
58.4 ng/L (well-raw)
39.4 ng/L (well-tap)
Hocock Falls Municipal Wellfield
159-662 ng/L (raw)
Water Plant
14.4 ng/L (well-raw)
44.4 ng/L (well-tap)
<2.24 ng/L (well-raw)
10.3 ng/L (well-tap)


*PLEASE USE
ONLY CRYSTAL
ROCK WATER WHEN

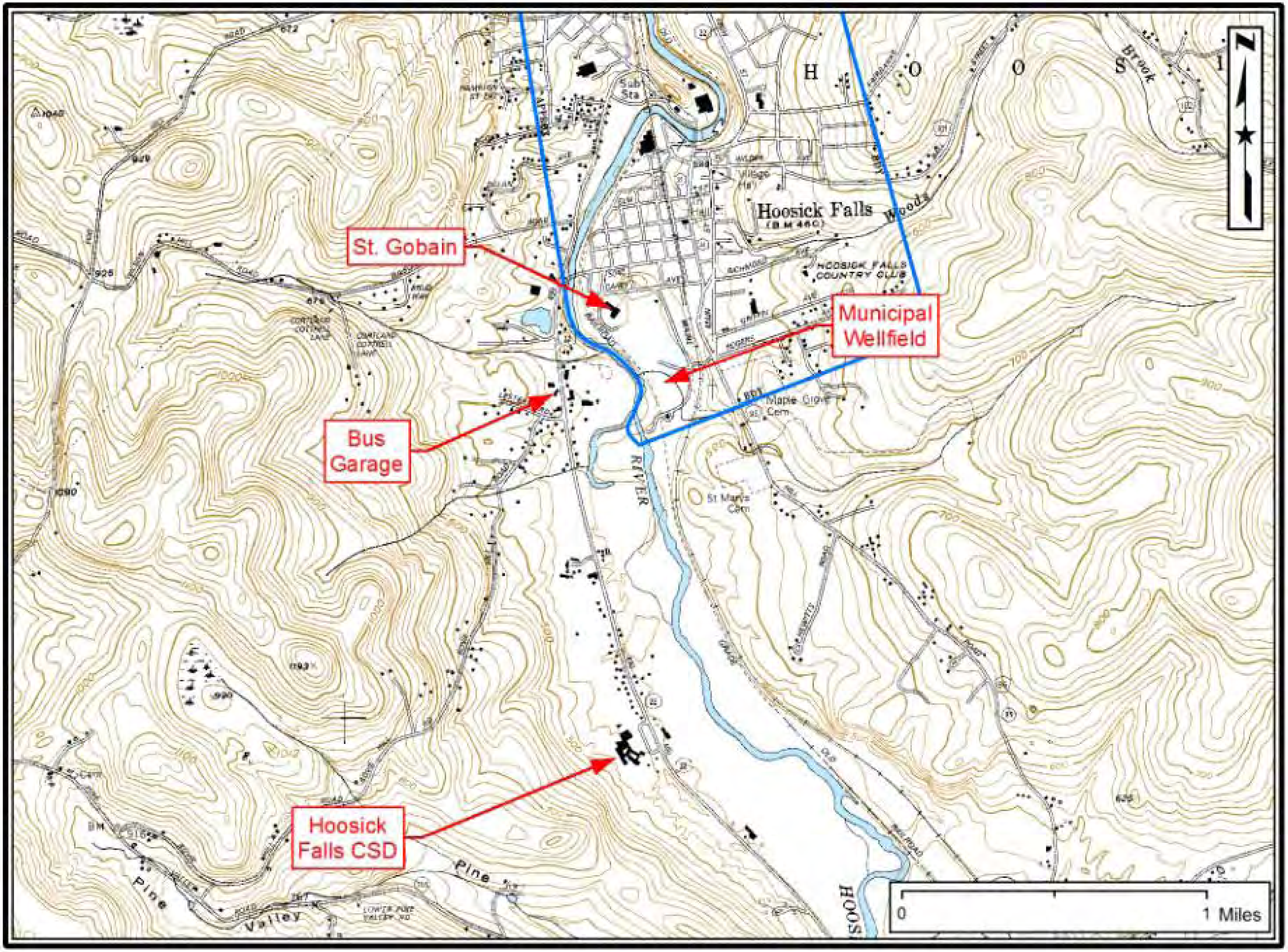


Geology and Hydrogeology

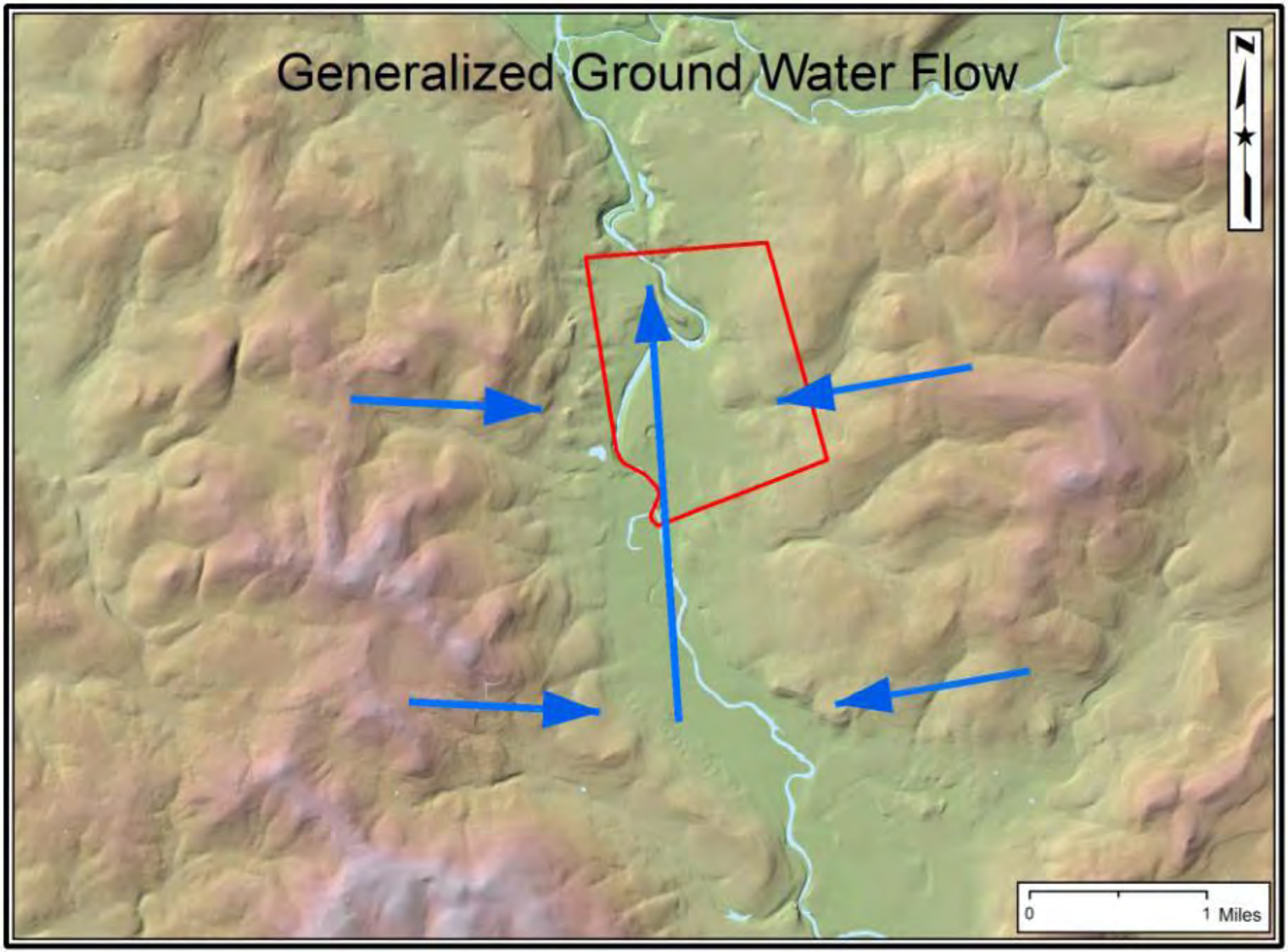
1. Sampling drinking water supplies:
   Assess exposure or quality at well or POU

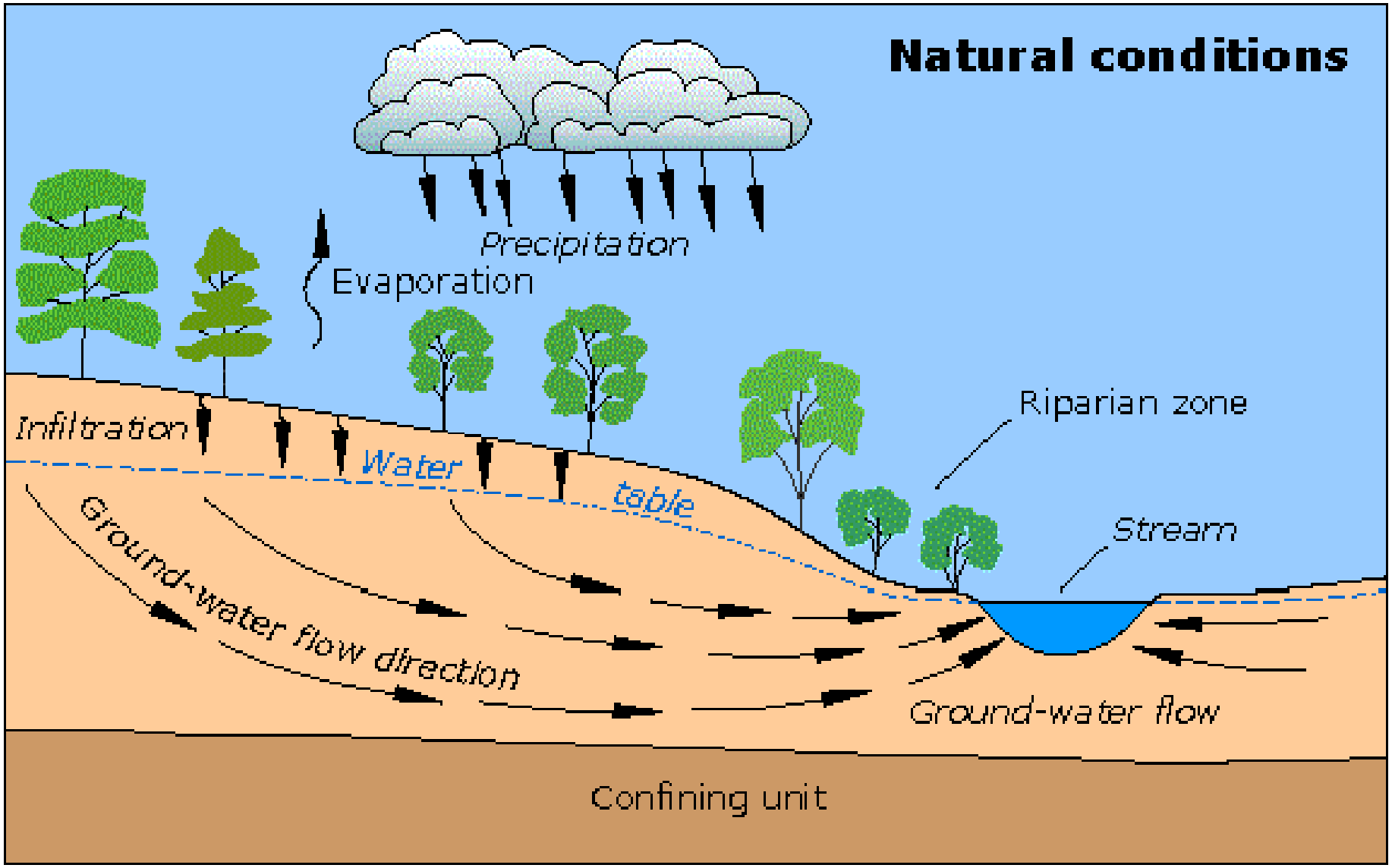
2. Sampling discreet zones:
   Investigate sources and migration pathways, assess remedial options

3. Geologic considerations:
   Locate and protect new water supplies

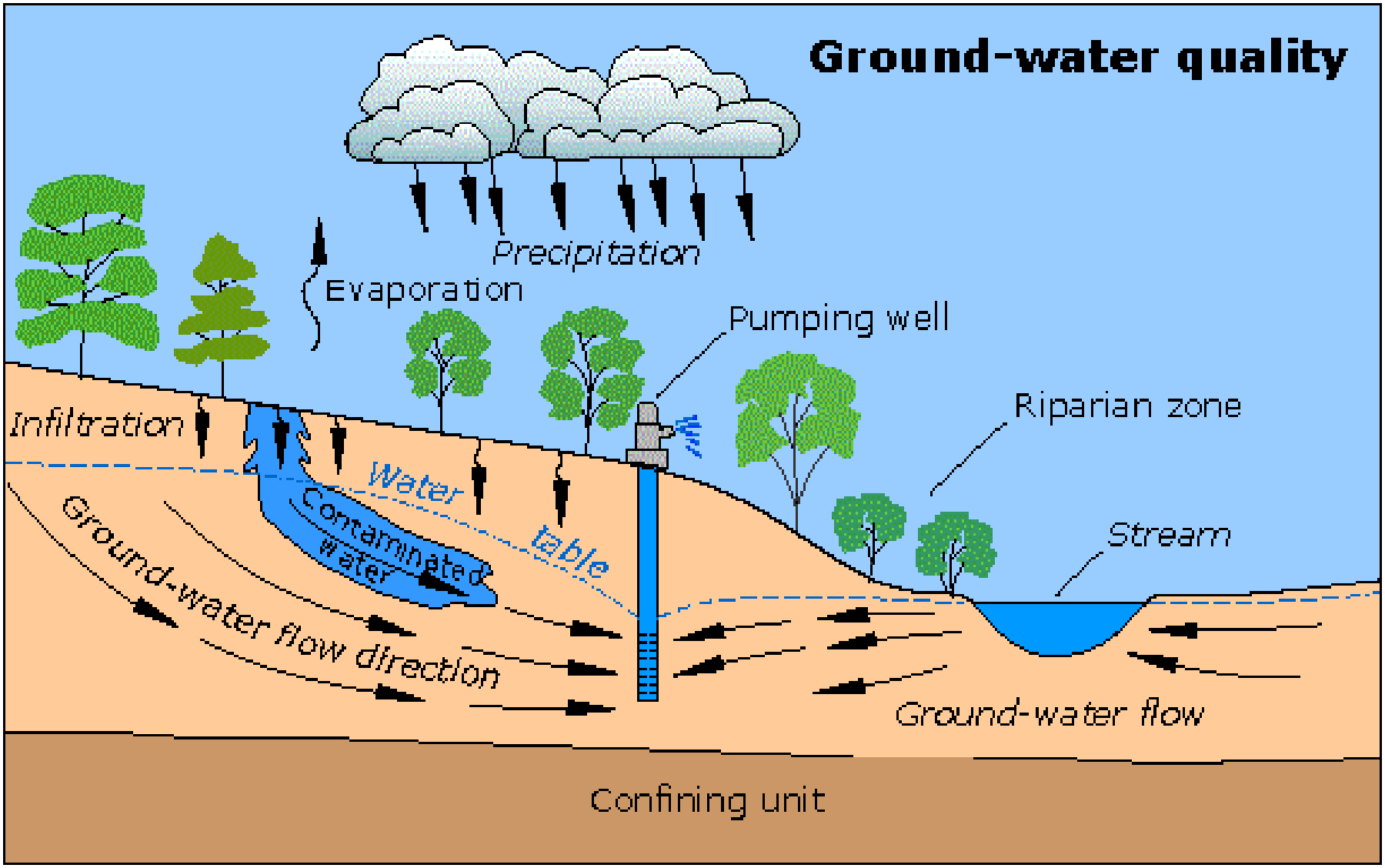


St. Gobain
Municipal
Wellfield
Bus
Garage
Hoosick
Falls CSD
Hoosick Falls
HOOSICK FALLS
COUNTRY CLUB
Maple Grove
Cem
St Marys
Cem
RIVER
Pine
Valley
0
1 Miles


Generalized Ground Water Flow
N
0
1 Miles

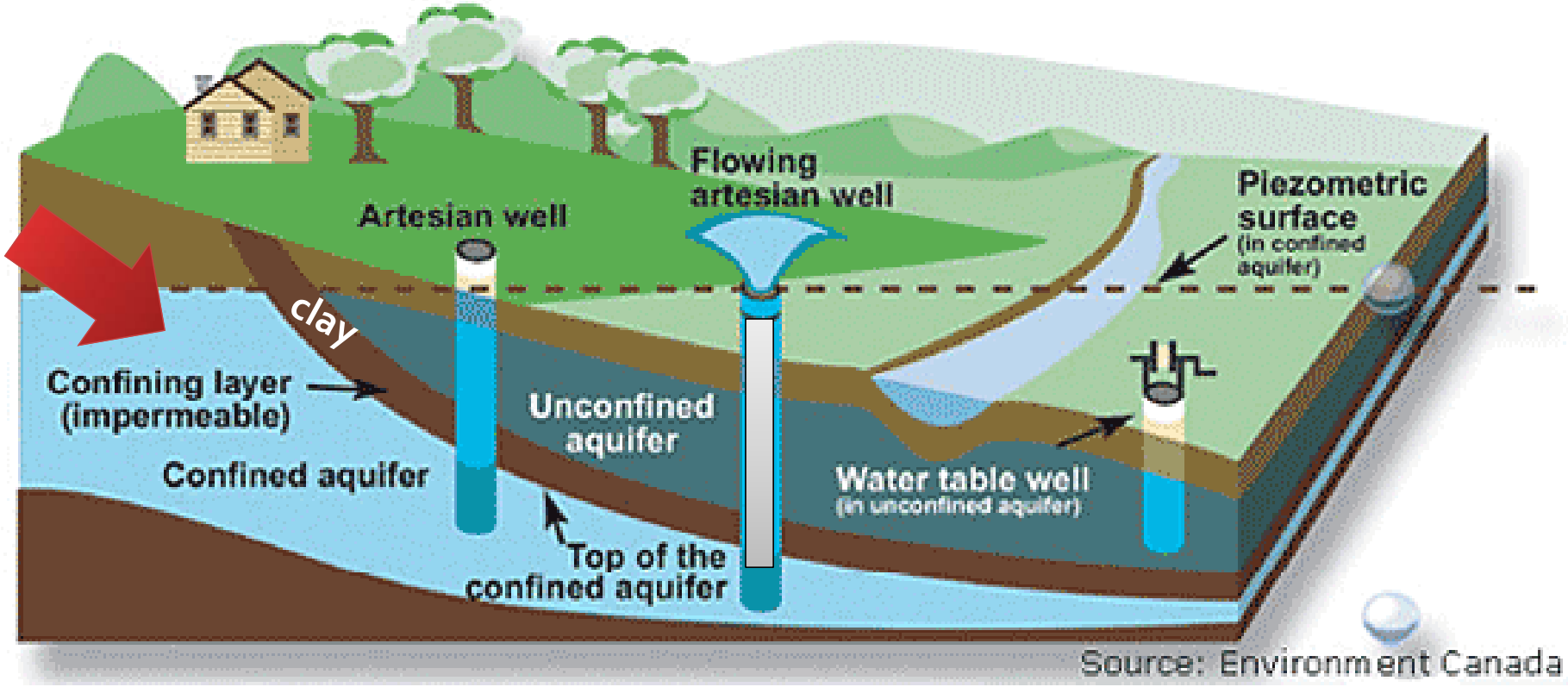

Natural conditions
Precipitation
Evaporation
Infiltration
Water table
Riparian zone
Stream
Ground-water flow direction
Ground-water flow
Confining unit

Source USGS

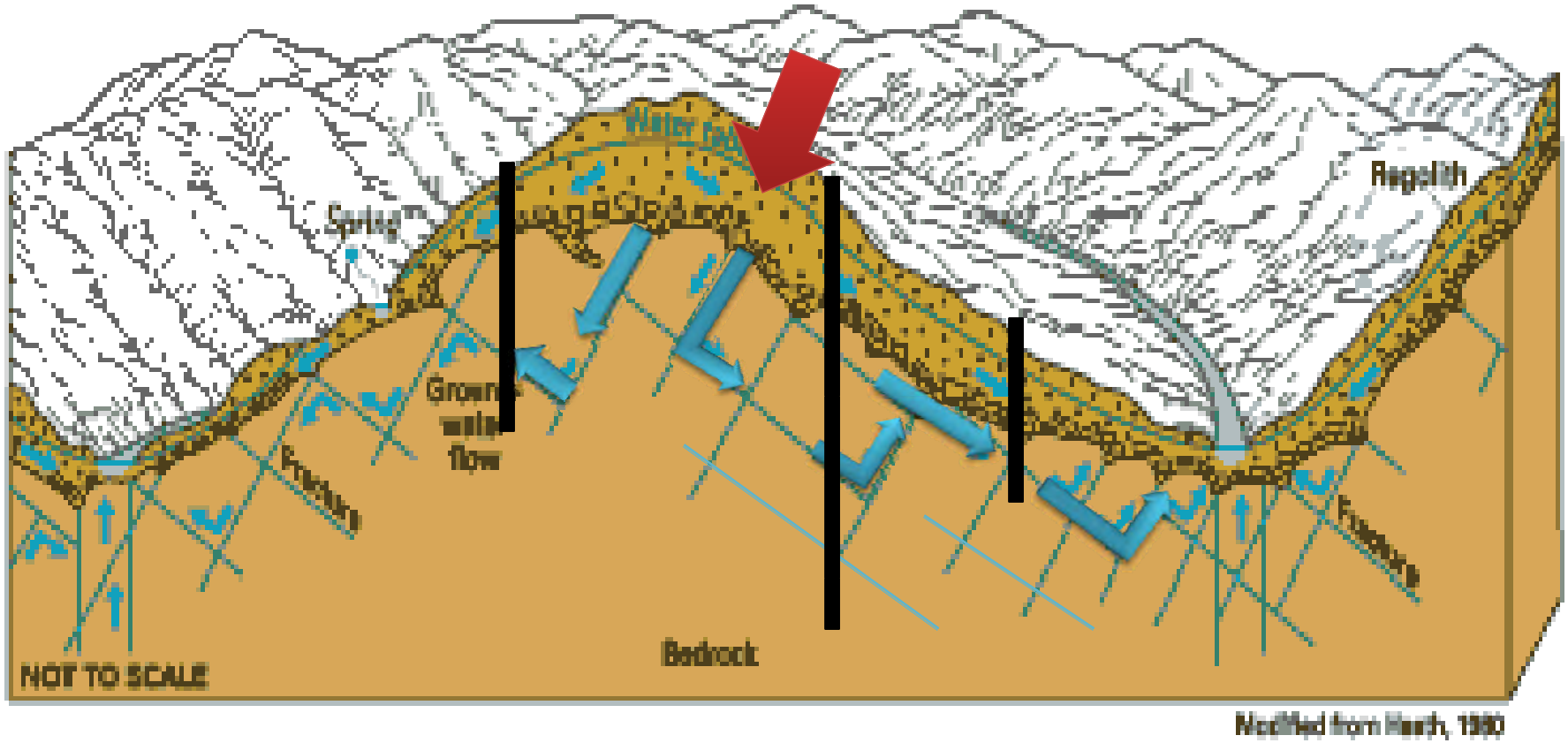


Induced infiltration and flow from pumping

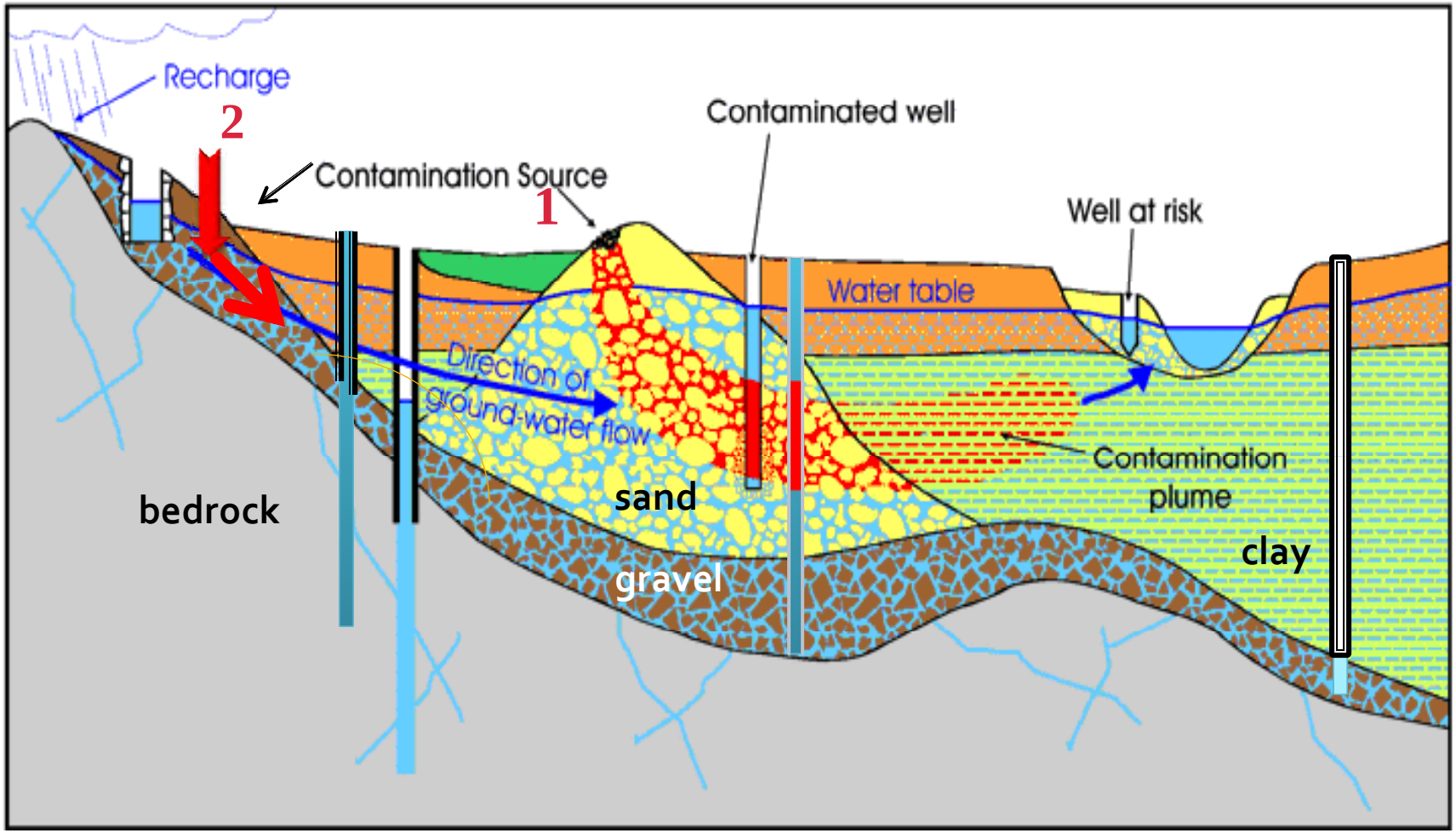
Source USGS



Water table and confined aquifer in unconsolidated material

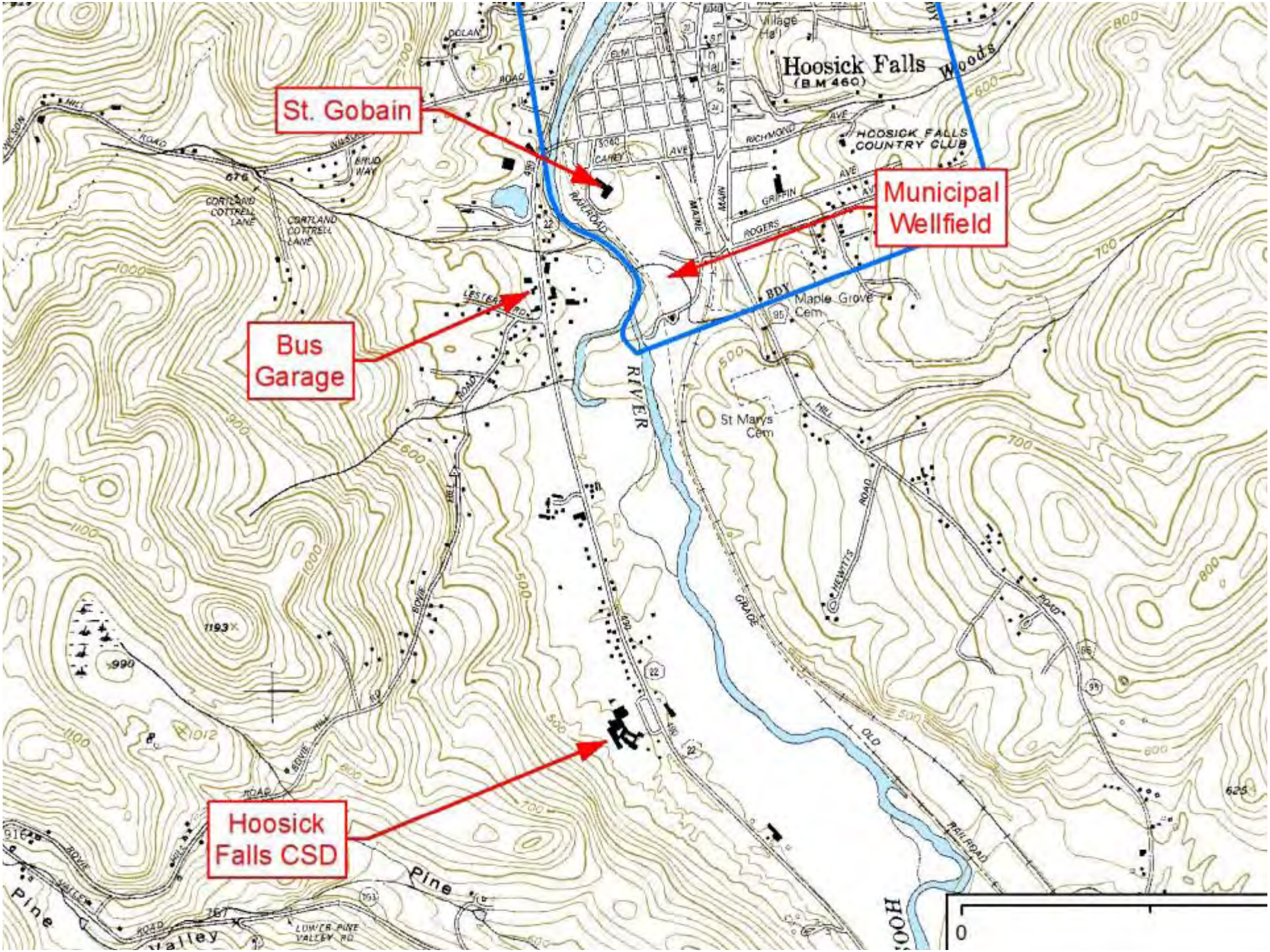


Consider other confounding factors:
multiple layers; differing lithologies; orientation; folds; faults

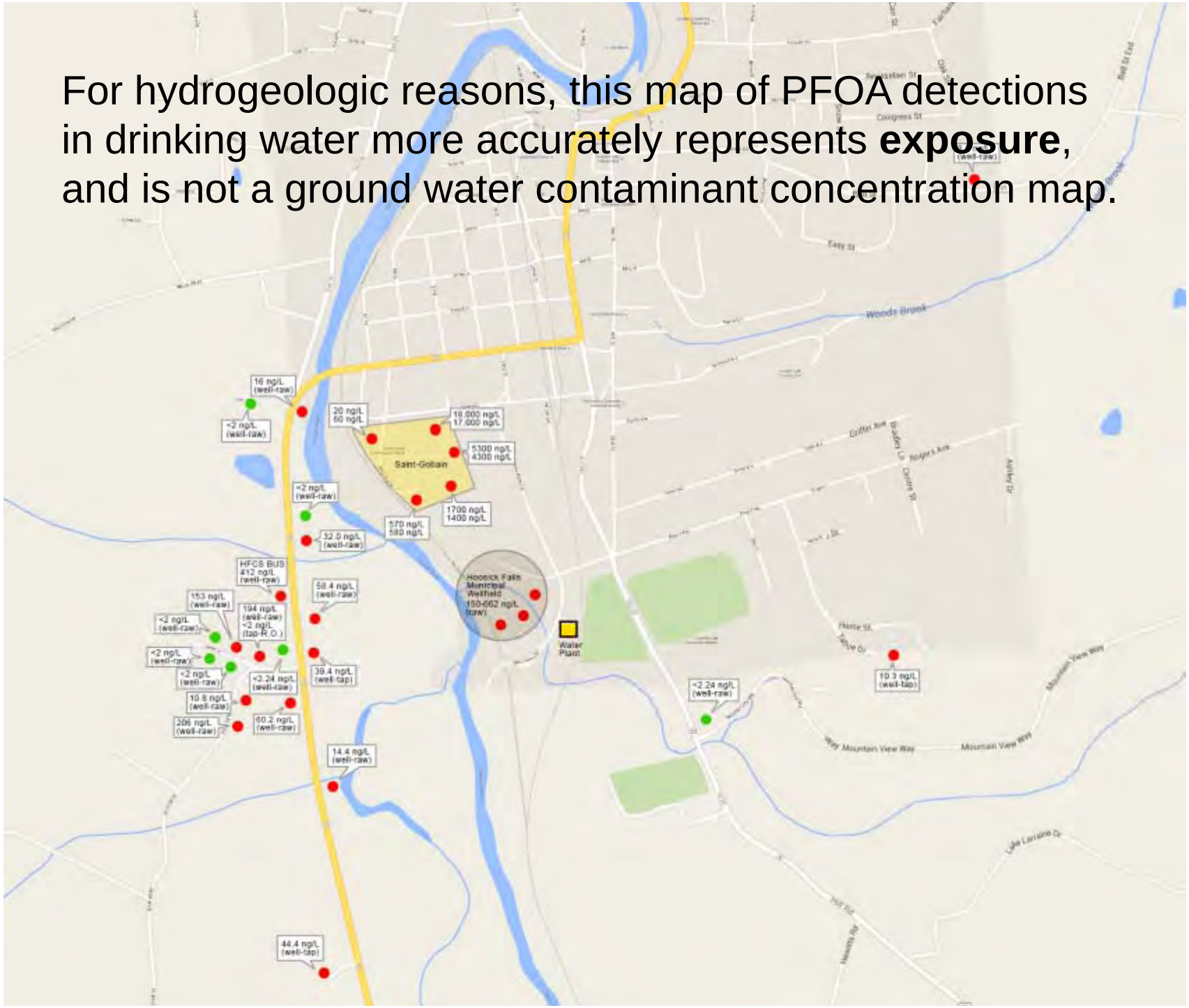


Maine Geological Survey

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
Pine Valley
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!**