SITE INVESTIGATIONS OF PER- AND POLYFLUOROALKYL SUBSTANCES (PFAS) BY THE WI DEPARTMENT OF NATURAL RESOURCES (DNR)

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ABSTRACT

Per- and Polyfluoroalkyl Substances (PFAS) are anthropogenic organic compounds first manufactured in the 1940's. Due to their widespread use in industry, PFAS are now ubiquitous in the environment and at high concentrations have been associated with deleterious health effects. Wisconsin DNR has been collecting and analyzing samples in drinking water, ground water, surface water and wildlife (mainly fish) samples statewide to quantify their concentrations and investigate sites of potential contamination when higher concentrations are found. Since PFAS are found in all environmental matrixes, the WI DNR utilizes a cross-programmatic approach (in these examples, Drinking Water and Groundwater, Water Quality and Fisheries Management programs) to share results when a potential site is identified, and then implement follow-up sampling by collecting PFAS in the corresponding matrix (e.g., drinking water, surface water, fish tissue). Here we present WI sites from a surface water perspective that have been characterized. In some instances, PFAS remain confined to certain matrices or areas, in others, PFAS is pervasive. These results can then be used to quantify the risk to the environment or human health.

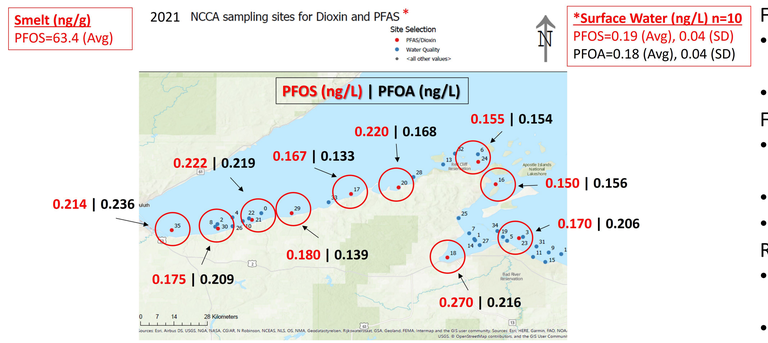
METHODS

This poster will not follow a strict scientific format but rather summarize site studies across WI where PFAS have been discovered and then follow-up sampling has been pursued to define the area and extent of contamination. Sometime high PFAS levels are confined to small areas and one type of matrix, whereas other times our investigations find high concentrations to be wide-spread and in groundwater, surface water and fishes.

Most results presented have been analyzed by the WI State Laboratory of Hygiene using their certified PFAS isotope dilution method via LC-MS/MS. Usually at least 33 different PFAS have been analyzed, but here only Perfluoro-n-octanesulfonic acid (PFOS) and Perfluoro-n-octanoic acid (PFOA) are shown for simplicity and the fact that WI has surface water (SW) standard for PFOS (8 ng/L, or ppt) and PFOA (95 ng/L or ppt for non-drinking water sources). Fish consumption advisories are issued when PFOS concentrations in fish reach the following levels: unrestricted (< 10 ng/g), 1 meal per week (10-50 ng/g), 1 meal per month (50-200 ng/g) and do not eat (>200 ng/g).

More frequently than investigative sampling, the WI DNR routinely monitors surface water state and fish statewide for "background" PFAS concentrations.

2021 Lake Superior Follow-up after Smelt Advisory



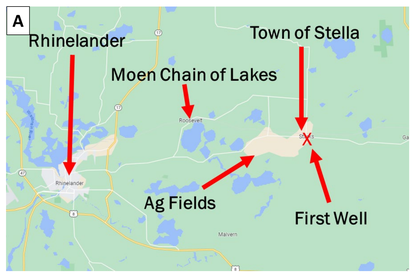
LAKE SUPERIOR (left)

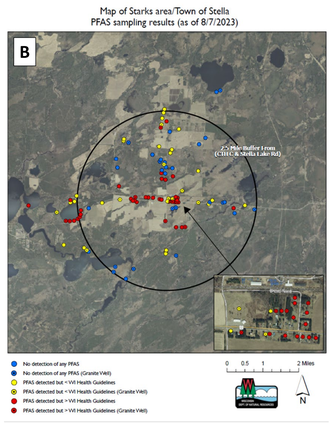
Findings:
- Smelt were found to have PFOS concentrations above the 1/meal per month category.
- A consumption advisory was issued for Lake Superior smelt.

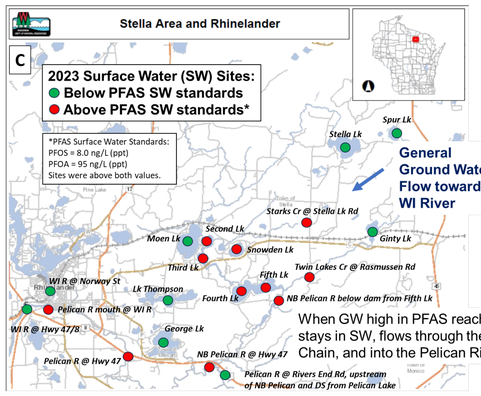
Follow-up investigations:
- SW PFAS samples were taken across the near-shore Superior coastline.
- PFAS concentrations were consistently very low across sites.
- No PFAS "hot spots" were discovered.

Results:
- Later analysis found possible false high PFAS in smelt from bile acid.
- More Lake Superior smelt from WI waters will be collected and analyzed for PFAS using revised methods.

The Town of Stella and Area East of Rhinelander, WI







When GW high in PFAS reaches SW, it stays in SW, flows through the Moen Chain, and into the Pelican River.

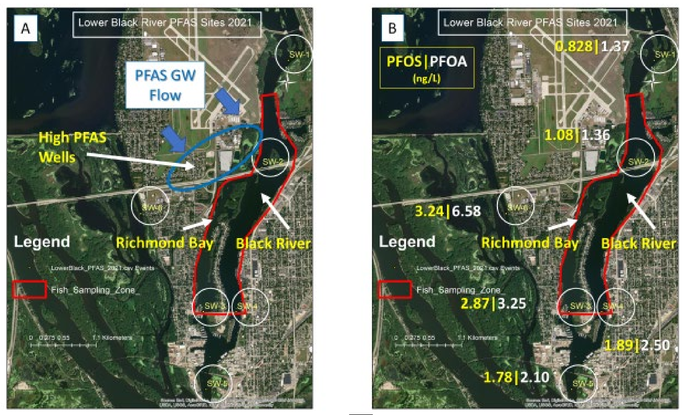
STELLA AREA (above)

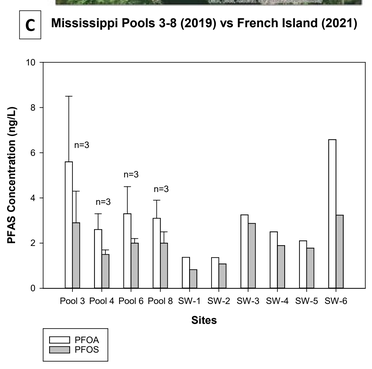
Findings:
- Stella is a town ~10 miles E of Rhinelander in an agricultural area and surrounded by forests and the Moen Chain of Lakes (Fig A).
- A 2022 Drinking and Groundwater (DG) Bureau private groundwater (GW) study discovered a well with very high PFAS (PFOA=9,030 ng/L, PFOS = 2,440 ng/L), which is above the WI Health Guidelines for drinking water.

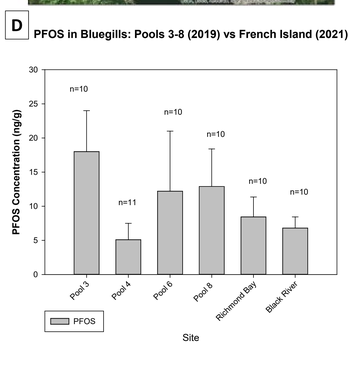
Follow-up investigations:
- Subsequent private wells were analyzed in a 2.5 radius out from the first well and discovered many more wells with high PFAS levels, with the highest being > 37,000 ng/L PFOA (Fig B).
- SW was collected from several waterbodies in the area. The highest values were in Snowden Lake (PFOS=71.5 ng/L, PFOA=1600 ng/L) and elevated levels in the Moen Chain, which continue down the Pelican River, to its confluence with the WI River (Mouth of Pelican: PFOS=22.8 ng/L, PFOA=96.6 ng/L, Fig C).
- Multiple fish species were collected from Fifth Lake.

Results:
- A fish consumption advisory was issued for all fish species in the Moen Chain (1 meal/month) due to levels > 50 ng/g PFOS.
- In 2024, more wells are being tested out to 3 miles. A successful protocol has been developed for drilling and casing new wells to provide safe drinking water. Replacement private wells have begun to be drilled.
- More sites are being sampled for SW and fish to define extent of SW contamination.

La Crosse: French Island and Black River







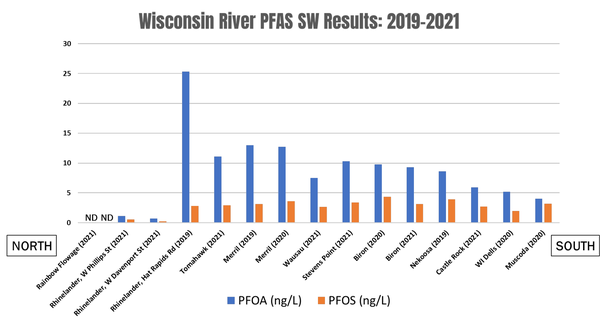
FRENCH ISLAND (left)

Initial Findings:
- PFAS contaminated groundwater flowing SE from the La Crosse airport (blue arrows) was found to be reaching private wells which were above safe drinking water limits (Fig A).

Follow-up Investigations:
- Was this reaching surface water (SW) and getting into fish tissue in the Black River and Richmond Bay?
- Six SW sites were chosen (SW1-SW6) and fish were sampled within the red highlighted areas (Fig A)
- SW PFAS samples were low across sites, not above SW standards, and increased only slightly downstream of airport (Fig B).
- SW concentrations around the island were similar to levels previously measured in the Mississippi River Pools (Fig C).
- Fish collected from Richmond Bay and the Black River were also at similar levels to Mississippi River fish (Fig D). Only Bluegills are shown in this figure.

Result:
- No new PFOS fish consumption advisories were issued since there already is an advisory for fish on the Mississippi River pools.

Wisconsin River



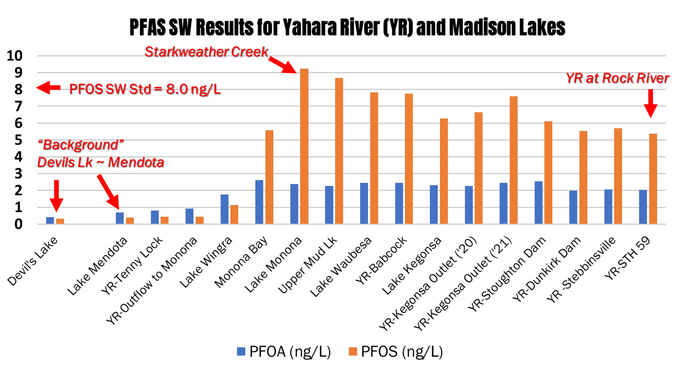
WISCONSIN RIVER (left)

Initial Findings:
- PFAS SW results showed non-detectable levels in the North, and then a jump in PFOA concentration at Hat Rapids Road, which is South of Rhinelander.
- PFOS concentrations were below the SW standards of 8.0 ng/L.

Follow-up investigation:
- SW samples from Stella investigation (above) showed Pelican R was source of PFAS between Rhinelander and Hat Rapids Road.
- Fisheries has collected fishes from major impoundments from Rhinelander to Castel Rock.

Result:
- Fisheries has issued consumption advisories for most impoundments in the WI R (see WDNR Choose Wisely publication for specifics) although PFOS is < 8.0 ng/L.
- Water Quality has been sampling major tributaries of WI River looking for localized sources of PFAS and reasons for high fish levels.

Madison Chain of Lakes (Yahara River) & Starkweather Creek



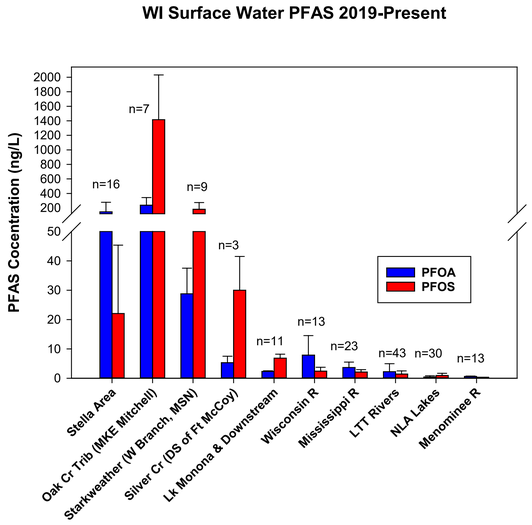
YAHARA RIVER WATERSHED (left)

Initial Findings:
- PFAS SW results in the western branch of Starkweather Cr, downstream of the Dane County Regional Airport were measured to be above SW standard for PFOS (see Summary to right).

Follow-up investigation:
- SW samples were taken from Lake Mendota down the Yahara River chain to the Rock River.
- Fisheries collected fishes from the Madison Lakes.
- SW samples from Lake Mendota had similar "background" concentrations as Devils Lake, which has no known sources of PFAS.
- SW PFAS (i.e., PFOS) does not increase downstream until Lake Monona, which is where Starkweather Cr enters the watershed and remain elevated downstream.

Result:
- Fish consumption advisories issued (1 meal/week or 1 meal/month) depending on fish species in the Madison Lakes, down to the Rock River.
- Water Quality has monitored the PFAS concentrations in Starkweather Cr and Lk Monona since these findings. Levels continue to be consistent with PFOS > 8 ng/L.

Surface Water Summary and Statewide Site Comparisons



SUMMARY AND STATEWIDE SITE COMPARISONS (left)

- For SW, the Stella Area has the highest concentration of PFOA, whereas the Oak Cr Tributary, Starkweather Cr and Silver Cr have the highest PFOS.
- Three of the four highest PFAS sites are associated with airports.
- The Stella Area has noticeable different ratio of PFOA/PFOS concentrations than the airport sites, which is further noticeable when looking at the relative ratios of all 33 PFAS (not shown). This suggests different sources for PFAS between the Stella Area and airport-associate sites.
- The LTT (Long Term Trends) Rivers and NLA (National Lakes Assessment) programs extensively sampled statewide rivers and lakes and consistently found very low levels of PFOS and PFOA.
- Although many private wells in Marinette, WI have PFAS contamination, the Menominee R has low levels of PFAS since GW does not flow towards the river (far right site).

Conclusion:
- Most waterbodies in WI have very low levels of PFAS concentrations and high PFAS concentrations have been found in only a few specific sites, which cause localize health concerns.