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PFASs distribution in Wisconsin

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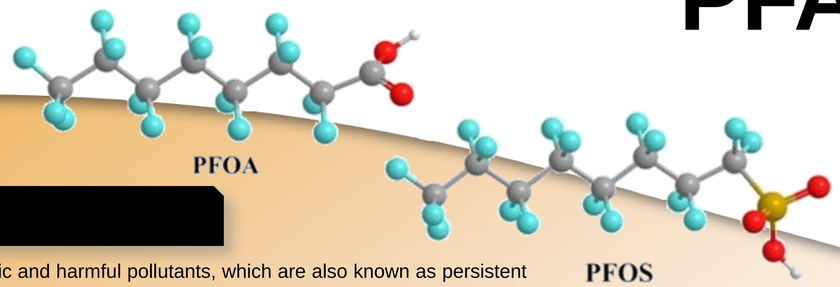

Abstract

PFASs are man-made toxic and harmful pollutants, which are also known as persistent organic pollutants. PFASs is widely distributed in the world because it is easy to migrate and difficult to degrade. Our study focused on the distribution of PFAS in Wisconsin, US. PFASs contamination have been reported in ten counties of Wisconsin, and the most reported contamination are in drinking water and groundwater. In most contaminated sites, concentrations of PFAS are higher than 20 ppt (Wisconsin's standard). A total of 13 PFASs have been detected in Wisconsin. Among them, long-chain PFASs, especially PFOA and PFOS, were the most frequently reported. Based on the data investigation, the most likely cause of pollution is firefighting foam and industrial manufacturing.
To investigate the distribution of PFAS in aquatic system, sediments from Madison and Holmen were selected for extraction and analysis. Results showed that sediment samples from Madison and Holmen do have a variety of PFASs, and the sediment adsorption capacity of PFASs is low. Compared with the sample from Holmen, the content of PFAS in Madison sample is relatively high.

Introduction

Perfluoroalkyl and polyfluoroalkyl substances (PFAS) are a large group of human-made chemicals that have been used in industry and consumer products worldwide since the 1950s.

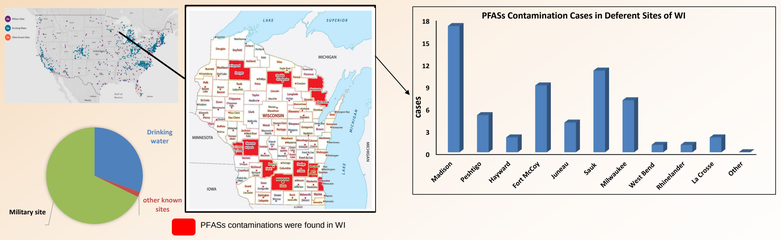

Fig.1 PFASs Distribution in Wisconsin

According to public health experts, people can come into contact with PFAS by eating food, like fish, drinking water and breathing air that contains PFAS. Most non-worker exposures occur through eating food that contains PFAS or drinking contaminated water. According to the data from EPA and EWG, we can get the picture of PFASs distribution in Wisconsin as shown in Fig. 1.
a) The PFASs contaminant sites are mainly distributed in 10 counties of WI;
b) PFASs contamination sites distributed unevenly;
c) The mainly contaminant sites are drinking water system and military sites.

In 2016, the U.S. EPA established cumulative-lifetime health advisories for PFOA and PFOS at 70 parts per trillion (ppt). Wisconsin Department of Health Services (DHS) recommended groundwater enforcement standards of 20 ppt for PFOA and PFOS individually and combined in the spring of 2019.

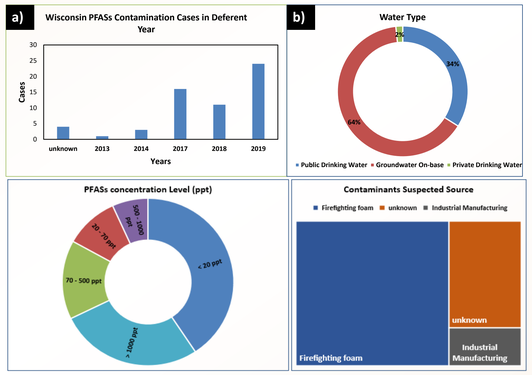

Fig.2 Analysis of PFASs Cases in Wisconsin

From Fig.2 we can get the conclusion that:
a) The PFASs contamination cases in WI increased from 2017, as the increasing attention of PFASs from 2016.
b) In WI the mainly contaminant water are drinking water and ground water.
c) The PFASs concentration in water of Wisconsin are higher than EPA advisories and DHS standards;
d) The mainly contaminants suspected source of PFASs in Wisconsin are firefighting foam and industrial manufacturing.

There are 13 kinds of PFASs found in Wisconsin contaminant sites. As shown in Fig. 3, PFOA and PFOS are the most outstanding contaminations.

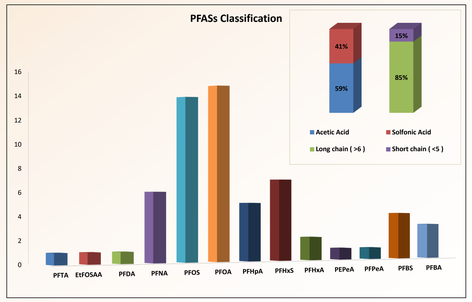

Fig.3 Classification of PFASs Found in Wisconsin

PFASs can be divided into long-chain PFASs and short-chain PFASs. In our research, most PFASs found in WI are long-chain PFASs (there are more than 6 carbons in their molecule), and the short-chain PFASs(there are less than 5 carbons in their molecule) only occupy 15%. It is due to the short-chain PFASs have better mobility than long-chain PFASs.
According to their group, PFASs can also be divided into sulfonic acid and acetic acid. From Fig.3, we can get the information that the presence of sulfonic acid PFASs and acetic acid PFASs in WI are closely.

Method

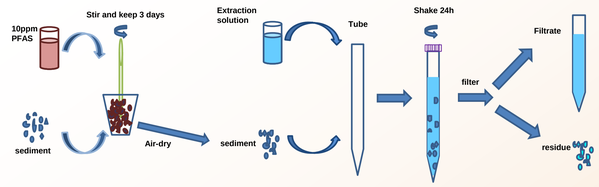

Fig. 4 Experimental process

A) Sediment loading: **10 g/L**;
B) Extraction solution: **H_2O+MeOH (V/V= 1:1)**
C) Contact time: **24 hours**.

When we added PFAS and stir the sediment, we also added ultrapure water every 12 hours to make sure that PFAS is uniformly attached on sediment.

Acknowledgement

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- Wisconsin Department of Natural Resources (DNR)
- College of Engineering & Applied Science

Results

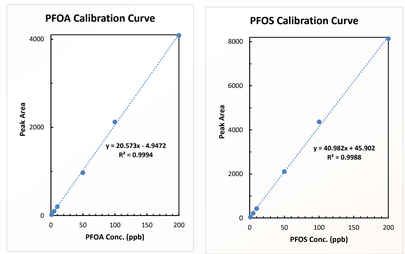

Fig. 5 Calibration Curve for PFAS

The recovery of PFOA and PFOS are between 90%-110%, that means the extraction solution we used works well and the PFAS in sediment is low.

Table. 1 PFAS concentration in different filtrates

PFOA								
Sediment	Initial (ppb)	Loading (mg)	Volume (mL)	Final concentration (ppb)	Recovery	Average R.E.	Std.	Qe(μg/g)
Madison	9.82	304.000	30	10.16	103.46%	105.74%	0.074509	0.03
		299.000	30	11.37	115.78%			0.16
		302.000	30	9.62	97.96%			-0.02
Holmen	9.82	301.000	30	11.03	112.32%	102.41%	0.077225	0.12
		302.000	30	9.18	93.48%			-0.06
		303.000	30	9.96	101.43%			0.01

PFOS								
Sediment	Initial (ppb)	Loading (mg)	Volume (mL)	Final concentration (ppb)	Recovery	Average R.E.	Std.	Qe(μg/g)
Madison	8.87	300.000	30	8.81	99.32%	94.10%	0.043764	-0.01
		301.000	30	8.37	94.36%			-0.05
		294.000	30	7.86	88.61%			-0.10
Holmen	8.87	302.000	30	8.96	101.01%	93.57%	0.058588	0.01
		297.000	30	8.25	93.01%			-0.06
		296.000	30	7.69	86.70%			-0.12

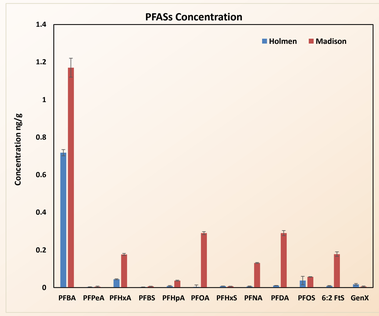

Fig.6 PFASs in Sediment of Holmen and Madison

Sediments from Madison and Holmen were selected for extraction and LC-MS analysis. Results showed that there are at least 12 types of PFASs in sediment from Madison and Holmen. Although the sediment adsorption capacity of PFASs is low, we can still get the conclusion that the content of PFAS in Madison sample is obviously higher than that of sediment in Holmen sample. PFBA, PFHXA, PFOA, PFNA, PFDA and 6:2 FTS were the most significant. In particular, the content of PFBA is the most prominent in sediment in two regions, which is significantly higher than that of other PFASs.

Conclusion

- PFASs contamination have been reported in ten counties of Wisconsin. The most reported contamination are in drinking water and groundwater.
- A total of 13 PFASs have been found in Wisconsin and PFOA and PFOS were the most frequently reported. In most contaminated sites, concentrations of PFAS are higher than 20ppt (Wisconsin's standard).
- The most likely cause of pollution is firefighting foam and industrial manufacturing.
- There are at least 12 types of PFASs in sediment from Madison and Holmen. PFBA, PFHXA, PFOA, PFNA, PFDA and 6:2 FTS were the most significant .In particular, the content of PFBA is significantly higher than that of other PFASs.