Detecting PFAS Sources Location in Water Stream by Utilizing Flow Rate Changes Event for Inverse Modeling

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Abstract

The paper covers a method of detecting forever chemicals released in water stream sources by monitoring and detecting events of the rapid flow rate changes and analyzing the contaminant concentration signature triggered by flow changes to find distance from the point of collecting probes. The distance is computed with the inverse model of the contaminant transport using stochastic equations for the direct transport model. The solution of the inverse model is defined with the theory of hypernumber for solving non-linear operator equations.

It is shown that the proposed model can detect the source location when the existing fate transport model is not capable.

Keywords: PFAS, sources, location, stochastic, model, hypernumber

1. Introduction

The fundamental direction in preventing the risk of forever chemical exposure is detecting its sources and stopping releases into the environment (PFAS Fingerprinting and the Case for Source Control). The existing methods of PFAS source identifications (ITRC PFAS-1, 2020) are listed below.

- Chemicals fingerprinting
  The method provides the chemical formula and structure of the PFAS identification by using quadrupole time-of-flight mass spectrometry (qTOF/MS) with High-Resolution Mass Spectrometry (HRMS)
- Isotopic fingerprinting
  An isotopic signature (also isotopic fingerprint) is a ratio of non-radiogenic 'isotopes', stable radiogenic isotopes, or unstable radioactive isotopes of particular elements in an investigated PFAS. The ratios of isotopes in a sample material are measured by isotope-ratio mass spectrometry.
  molecular diagnostic ratios
- Molecular diagnostic ratios
  The method uses relative abundances of one or more PFAS
- Contaminant transport models

The method matches the distance from the monitoring point to the source by identifying the PFAS fate and using characteristics of the compound fate rate. (Charbonnet, J.A et al, 2021)

- Radionuclide dating
  PFAS is used in medical diagnostics, including imaging such as MRI, ultrasound, positron emission tomography (PET), and multi-modal contrast agents (Gaines, 2022). Some radionuclides are incorporated into PFAS for imaging applications. Detecting radionuclides in PFAS may allow locating the PFAS source.

Per paper (ITRC PFAS-1, 2020), the methods have limitations and are relatively new in application to PFAS, some of these tools have been used to identify regional and local PFAS sources.

The fingerprinting and existing contaminant transport methods have such limitations:

a) Determining PFAS release source based solely on its chemical signature is likely to be challenging for reasons including shifts in manufacturing, common manufacturing feedstocks, and an incomplete understanding of PFASs. (Charbonnet et al., 2021)

b) Stable isotope analysis is unsuitable because PFASs are highly stable in the environment, there is a single stable fluorine isotope, and the environmental concentrations of stable isotope detection limits. (Charbonnet et al., 2021)

c) Let's consider that there are multiple (m) PFAS compounds and each has fingerprint F_j. The combined fingerprint equals to $F_{comb} = \bigcup\limits_{j=1}^{m} F_j$. Detecting each fingerprint is a complex logical problem that may not provide unique results.

d) The defined fingerprint can not be associated with unique sources.

e) The transport and fate of Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS) is a rapidly evolving field of science, with many questions that are not yet resolved. (PFAS Transport and Fate – Enviro Wiki.). Such information is available for a few PFAS compounds. Because, PFAS compounds' chemical characteristics have a wide diapason, the known characteristics can not be used for PFAS with unknown properties.

Due to the low reliability in mapping PFAS sources using existing methods, developing new methods that would allow improved source identification is very important.

2. Related Works

The contaminant release in water streams can be detected by analyzing the signature of its transport in a transient regime (Dantsker et al, 2002, 2003, Burgin et al., 2023). The method is applied for detecting bacterial contamination and is an alternative to bacterial fingerprinting. The major advantage of this method in comparison with fingerprinting one (Claveau et al., 2024) that it does not require complex matching algorithms and does not provide low accuracy. The accuracy of the bacterial matching algorithm covered in (Moore D. F. et al., 2005):

44% for E. coli ARA, 69% for E. coli ribotyping.

Detecting PFAS sources of contaminant transport in a transient regime would require reading concentrations in real-time. However, such sensors do not exist. The problem can be solved by monitoring events of the rapid flow rate changes or artificial methods of changing water flow (Ashraf et al., 2018, 2022). The change in water flow rate causes transient contaminant transport with concentration signature corresponding to the dynamic of flow alternation, coefficient of diffusion, and distance from the source. For instance, n times reducing the flow rate results transient process with a final concentration n times higher than the initial. The methods of pursuing such a process are covered below.

3. Direct Model of the Contaminant Concentration at Monitoring Point per Changed the Water Stream Flow Rate

The chart in Figure 1 demonstrates monitoring water rapid changes in the flow rate events. The water samples are collected with period Δt to build a concentration time series by identifying PFAS concentration in each sample with a mass spectrometer. The sampling period should be defined by using the Dynamic Hypernumber theory covered in the publication (Burgin et al., 2023).
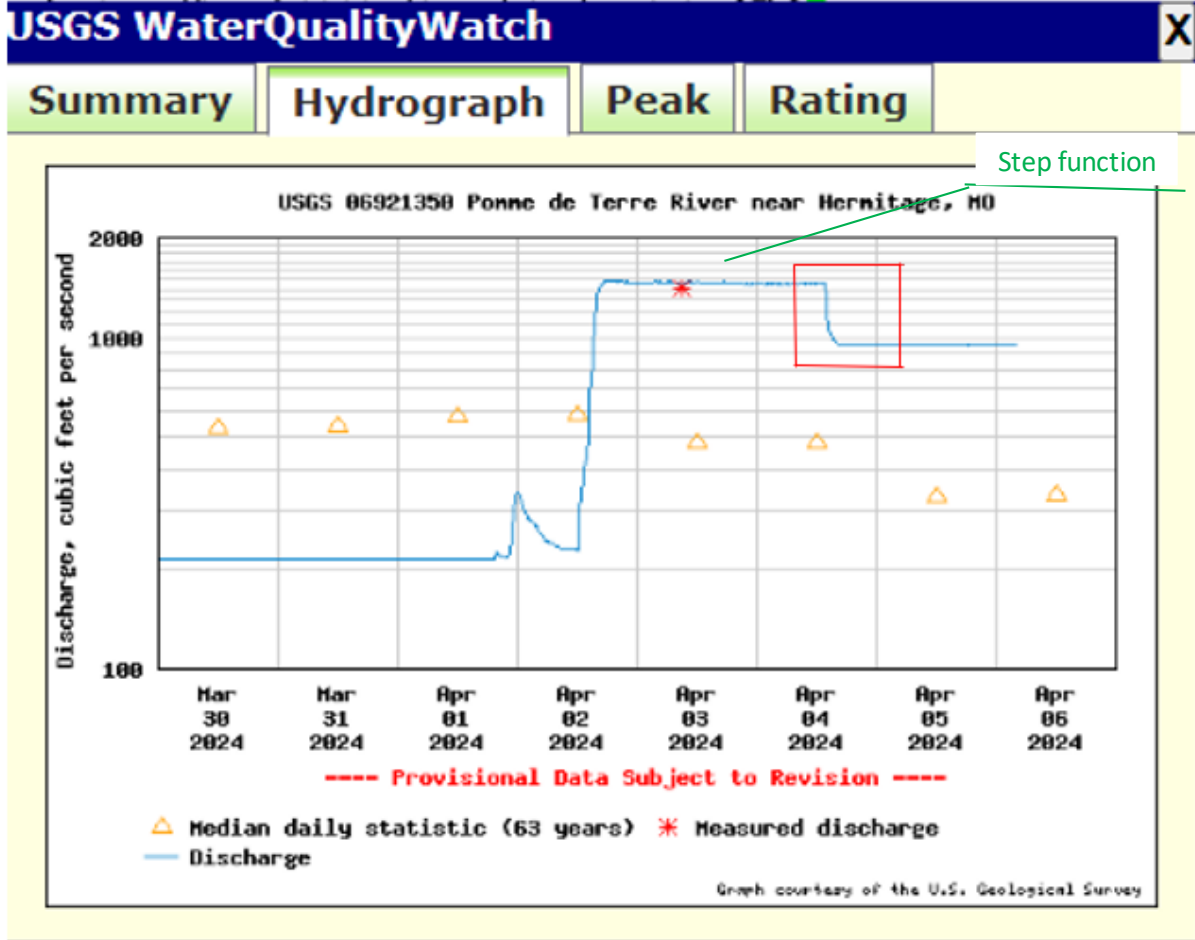
Figure 1. Water flow with step function flow rate event

The schema of collecting water samples, measuring water stream velocity, flow rate, and detecting source location is shown in Figure 2.
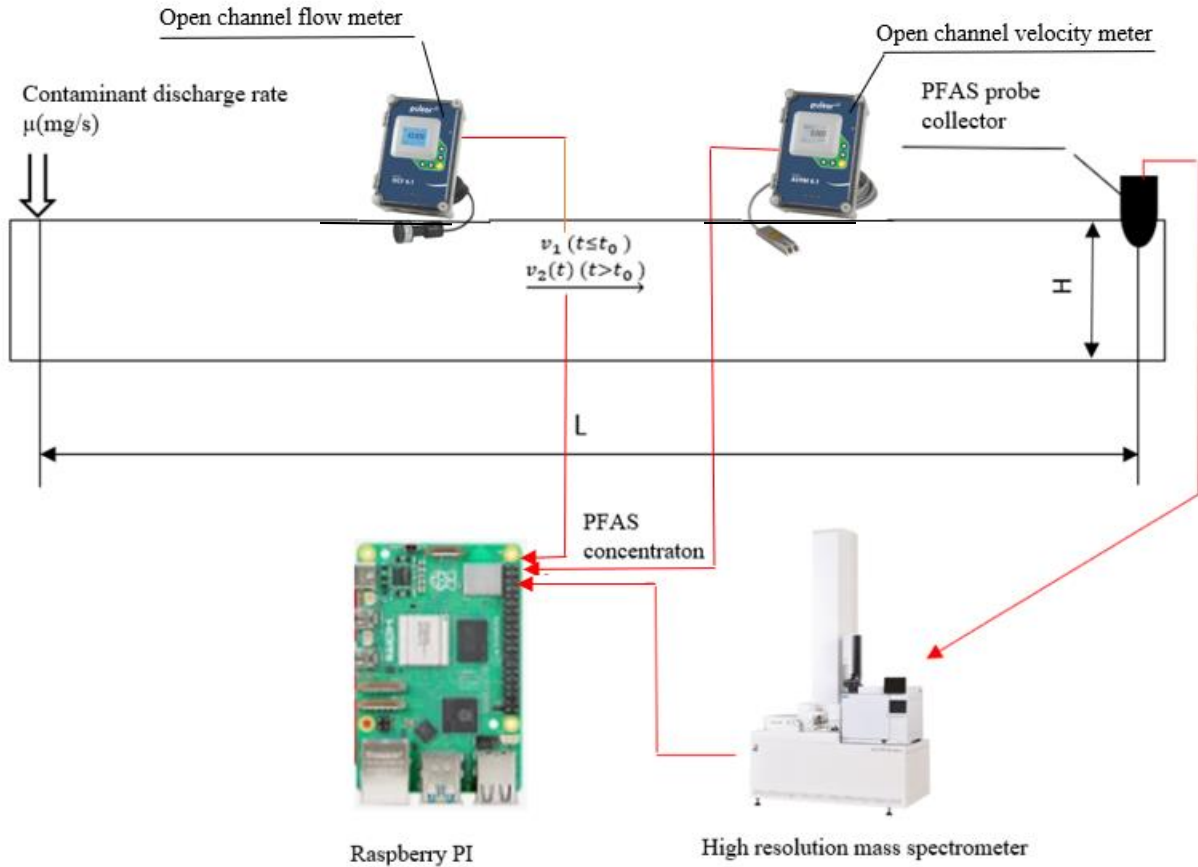
Figure 2 The schema of detecting PFAS source location by analyzing contaminant transport signature per rapid changes of water flow rate

The PFAS concentration can be defined with an expression below:

$$c(t,x) = c_d(\mu, t, v_2, L) + c_{st} \begin{cases} c_{be}(t < t_0), 0 < t < t_{bec} : \int_0^{t_{bec}} v_2(t)dt = L \\ \\ 0, \qquad t > t_{bec} : \int_0^{t_{bec}} v_2(t)dt = L: \end{cases}$$

(1),

where $c(t,x)$ - PFAS concentration after flow rate changes, $c_d(\mu, t, v_2, L)$ − the dynamic PFAS concentration contributed by the contaminant source from the moment of the flow rate changes, c_{st} - the static PFAS concentration before flow rate changes, v_2 − flow velocity after the event, μ − contaminant discharge rate.

The contaminant concentration in a water flow can be defined with a stochastic equation (Sveshnikov, 1966)

$$\frac{\partial c_d}{\partial t} + v_2(t)\frac{\partial c_d}{\partial x} + \frac{1}{2}D\frac{\partial^2 c_d}{\partial x^2} = 0,$$

(2)

Where D – is the coefficient of diffusion.

If the flow rate changes is a step function time of water before the flow rate changes event would pass the monitoring point equals to:

$$t_{bec} = \frac{L}{v_2}$$

(3)

The concentration equals to:

$$c_d = \int_0^t \frac{\mu e^{-\frac{(L-v_2\tau)^2}{2D\tau}}}{\sqrt{2\pi D\tau}\,A(\tau)}\,d\tau$$

(4),

Where $A(\tau)$ – is the cross area of the water stream at the sampling location.

4. Finding the PFAS Source Location with Inverse Model

The unknown parameters of the contaminant transport are defined as satisfying the best fit of the direct model concentration values to the monitoring PFAS concentration at the probe collection location:

$$\mathcal{L} = min \sum_{i=1}^{n} \left(c_d^{mon} - c_d^{th}\right)^2$$

(5)e

where c_d^{mon}, c_d^{th} - are correspondently dynamic monitoring and theoretical PFAS concentrations.

$$\mathcal{L} = min \sum_{i=1}^{n} \left(\left(c_{d,i}^{mon} - c_{st}\right) - c_d^{th}\right)^2$$

By plugging (4) into (6) the operator $\mathcal{L}$ is defined below:

$$\mathcal{L} = min \sum_{i=1}^{n} \left(\left(c_{d,i}^{mon} - c_{st}\right) - \int_{0}^{t} \frac{\mu e^{-\frac{(L-v_2\tau)^2}{2D\tau}}}{\sqrt{2\pi D\tau}\, A(\tau)} d\tau \right)^2$$

(7)

The source location distance and coefficient of diffusion can be found from the requirement (7)

$$\frac{\partial \mathcal{L}}{\partial D} = \sum_{i=1}^{n} \left(\left(c_{d,i}^{mon} - c_{st}\right) - \int_{0}^{t} \frac{\mu e^{-\frac{(L-v_2\tau)^2}{2D\tau}}}{\sqrt{2\pi D\tau}\, A(\tau)} d\tau \right) \int_{0}^{t} \frac{\mu e^{-\frac{(L-v_2\tau)^2}{2D\tau}} \left(4\pi D\tau \frac{(L-v_2\tau)^2}{2D^2\tau} - 1\right)}{2(2\pi D\tau)^{3/2}\, A(\tau)} d\tau = 0$$

(8)

$$\frac{\partial \mathcal{L}}{\partial L} = \sum_{i=1}^{n} \left(\left(c_{d,i}^{mon} - c_{st}\right) - \int_{0}^{t} \frac{\mu e^{-\frac{(L-v_2\tau)^2}{2D\tau}}}{\sqrt{2\pi D\tau}\, A(\tau)} d\tau \right) \int_{0}^{t} \frac{-\mu e^{-\frac{(L-v_2\tau)^2}{2D\tau}} \frac{L-v_2\tau}{D\tau}}{\sqrt{2\pi D\tau}\, A(\tau)} d\tau = 0$$

(9)

The solution of the (8, 9) equation is provided with the theory of the hypernumber for the distance from collecting probes to the PFAS release locations and coefficient of diffusion.

$$L_m = H_n (L_m)_{m\in\omega}$$

(10)

$$D_m = H_n (D_m)_{m\in\omega}$$

(11)

$$L_{m+1} = L_m + \delta(L_m)$$

(12)

$$D_{m+1} = D_m + \delta(D_m)$$

(13)

where $\delta(L_m), \delta(D_m)$ are the deviations of the distance from the water probes collection to the source of the PFAS release into water and coefficient of dispersion defined with hypernumbers L_m and D_m.

The hypernumber deviations are computed by solving the linear equation:

$$
\begin{cases}
\dfrac{\partial^2 \mathcal{L}}{(\partial D)^2}(D_m, L_m)\, \delta(D_m) + \dfrac{\partial^2 \mathcal{L}}{\partial D \partial L}(D_m, L_m)\, \delta(L_m) = -\varepsilon\, \dfrac{\partial \mathcal{L}}{\partial D}(D_m, L_m) \\[3mm]
\dfrac{\partial^2 \mathcal{L}}{\partial D \partial L}(D_m, L_m)\, \delta(D_m) + \dfrac{\partial^2 \mathcal{L}}{(\partial L)^2}(D_m, L_m)\, \delta(L_m) = -\varepsilon\, \dfrac{\partial \mathcal{L}}{\partial L}(D_m, L_m)
\end{cases}
$$

(14)

where coefficient $\varepsilon < 1$

Per solving operator equations with the theory of hypernumber (Burgin et al., 1995), there is always exists such ε, that provides the convergence of the operator equations solutions.

5. Conclusions

The new concept of detecting PFAS sources using concentration time series signature per water flow rate changes event does not require fate knowing the physical characteristics of each PFAS compound. Such knowledge is required for an existing source identification with the transport model and is a major problem in using the fate transport model. The method has the potential to provide better accuracy in comparison with chemical signature and isotropic fingerprinting methods. The objective of this statement is covered in the introduction. Per multiple PFAS sources, the method would require additional development when sources are close to one another and dynamic concentration would include significant ratios from both sources. However, the same approach can be used requiring operator minimization for each contamination source. The amount of the sources can be found by analyzing the shape of the concentration curve.

Per k amount of the PFAS sources the system (14) would have k equations for each soure s location $L_{s,m}$ as a hypernumber:

$$
\frac{\partial^2 \mathcal{L}}{\partial D \partial L_s}(D_m, L_{s,m})\, \delta(D_m) + \frac{\partial^2 \mathcal{L}}{(\partial L_s)^2}(D_m, L_m)\, \delta(L_{s,m}) = -\varepsilon\, \frac{\partial \mathcal{L}}{\partial L_s}(D_m, L_{s,m})\, t
$$

(15)

The water flow velocity in this research is considered to be constant. The solution of the stochastic equation when velocity is time-dependent will be covered in the next research paper.

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