Application of Standard Fate and Transport Modeling Approaches for Evaluating PFAS Compounds in Groundwater

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Introduction

- Per- and polyfluoroalkyl substances (PFAS) have numerous applications in consumer products and industry
- Because of their widespread use and persistence, they are commonly found in the environment
- PFAS have garnered attention from the public as well as regulatory agencies
  - Minnesota 3M PFAS settlement[1]
  - US Environmental Protection Agency (USEPA) PFAS Strategic Roadmap
- Currently no national regulations exist for PFAS in the USA
  - USEPA has set a health advisory limit of 70 ppt for PFOA and PFOS, but it is non-enforceable[2]
- More monitoring data and better modeling techniques are needed
- A modeling case study for the Monterey Regional Airport was completed and results were compared to monitoring data

State Level Regulations

Individual states are also taking initiative to monitor PFAS and set their own advisory limits. The most commonly monitored and regulated PFAS are perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS). State regulations take different forms including recommended concentration limits, notification requirements and maximum contaminant levels (MCL).

The EPA has set a health advisory level of 70 ppt for PFOA and PFOS. Several states have set MCLs more stringent than the EPA health advisory level. Michigan currently has the most stringent MCLs (Table 1).

*Sum of all PFAS

Table 1: State MCLs below 70 ppt

State	Contaminant	MCL (ppt)
MI[3]	PFNA	6
	PFOA	8
	PFOS	16
	PFHxS	51
NY[4]	PFOA	10
	PFOS	10
NH[5]	PFOA	12
	PFOS	15
	PFHxS	18
	PFNA	11
NJ[6]	PFOA	12
	PFNA	13
	PFOS	14
MA[7]	PFOS, PFOA, PFHxS, PFNA, PFHpA, PFDA	20*
VT[8]	PFHpA, PFHxS, PFNA, PFOS, PFOA	20*

Monitoring Data:

Table 2: UCMR 3 Data Summary

Contaminant	Min (ppt)	Avg (ppt)	Max (ppt)	Number of Detects
PFBS	90	184	370	19
PFOS	40	170	7000	292
PFHxS	30	139	1600	207
PFOA	20	41	349	379
PFNA	22	36	55	19
PFHpA	10	25	410	236

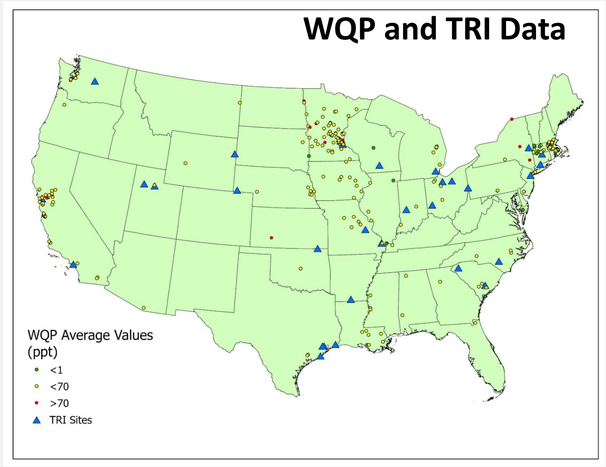


Figure 1. Measured PFAS concentrations were averaged for each site from surface water, groundwater, and stormwater samples.

Water Quality Portal (WQP):

The WQP[9] is one of the largest repositories for water quality monitoring data in the USA. It combines data from multiple sources including USEPA STOrage and RETrieval (STORET) Data Warehouse and the USGS National Water Information System (NWIS). PFAS monitoring data has begun to be added to the WQP and it currently represents the most comprehensive source of PFAS data at the national level (Figure 1). Currently there are 81,597 PFAS samples in the WQP (water, sediment, air, tissue) which represent more than 50 different PFAS.

Toxic Release Inventory (TRI)

The TRI[10] provides information on toxic chemicals released reported by industrial and federal facilities. Several PFAS were added to the list of chemicals covered by the TRI in 2020 and initial data were released mid-2021 and the full 2020 TRI National Analysis is expected in early 2022. Thirty-nine unique facilities reported information on 43 different PFAS (Figure 1).

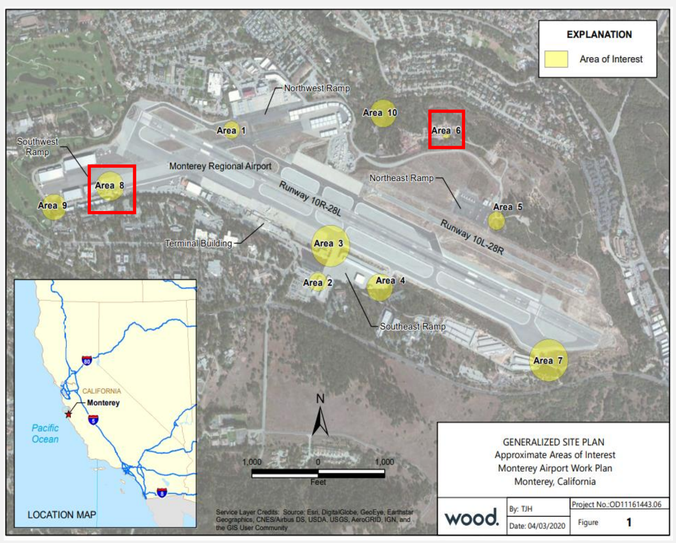
USEPA Unregulated Contaminant Monitoring Rule (UCMR)

The UCMR[11] is used to collect data for contaminants that are suspected to be present in drinking water, but do not have health-based standards set under the Safe Drinking Water Act (SDWA). Under UCMR-3, 6 PFAS (PFBS, PFOS, PFHxS, PFOA, PFNA, PFHpA) were monitored between 2013 and 2015 in public water systems. Similarly, UCMR-5 plans to measure 29 PFAS between 2023 and 2025. From the 221,831 samples taken, 1,152 are above the MDL (Table 2).

GW Modeling Site: Monterey Regional Airport

Aqueous film-forming foams (AFFF) contain PFAS and have been used in airports to suppress fires and during training activities. This increases the chance of groundwater contamination near airports. The State Water Resources Control Board of California has issued several orders to determine the presence of PFAS at airports throughout California. Because of this, the Monterey Regional Airport sampled for several PFAS in groundwater[12].

Figure 2 Sampling locations



Monterey Regional Airport PFAS Use

- Area 6: From the early 1940s through 1972, weekly fire fighting training, using AFFF, took place weekly
- Area 8: AFFF was accidently released from storage containers twice in 2007

Table 3: Monterey groundwater measured residues

Area	Sample Date	PFOA (ng/L)	PFOS (ng/L)	Depth (m)
6	2/14/2020	1,100	12.2	16.2
8	2/12/2020	0.634	<1.98	15.4

Modeling Inputs

Areas 6 and 8 from the Monterey Regional Airport study were chosen for modeling with GeoPEARL 4R. Soil profile information was retrieved from the SSURGO database and meteorological data (1994-2021) was retrieved from the nearest California Irrigation Management Information System (Salinas North) station. The chemical properties of PFOA and PFOS are summarized in Table 4.

Table 4. Chemical and environmental fate properties for PFAS

Chemical Property	PFOS	PFOA
Molar Mass (g.mol^{-1})	538	414
Partition Coefficient (Kom L kg^{-1})	4.43	3.55
Freundlich 1/n	0.93333	1
Vapor Pressure (Pa)	0.002	0.525
Water Solubility (mg L^{-1})	680	9500
Soil Half-life (d)	10000	10000
Plant Uptake Factor	0	0
Crop Half-life (d)	1000000	1000000
Crop Washoff Factor(-)	0.0001	0.0001

Using the GeoPEARL 4R model, the daily mass flux was calculated for PFOS and PFOA applied on April 1 at a rate of 2.45 kg/ha. Area 6, the training site received 50mm of water the day following the training. Area 8 received weekly sprinkler irrigation. A concentration in the saturated zone was calculated assuming instantaneous mixing in a volume of 1.5m^3, adjusted for the porosity of the soil.

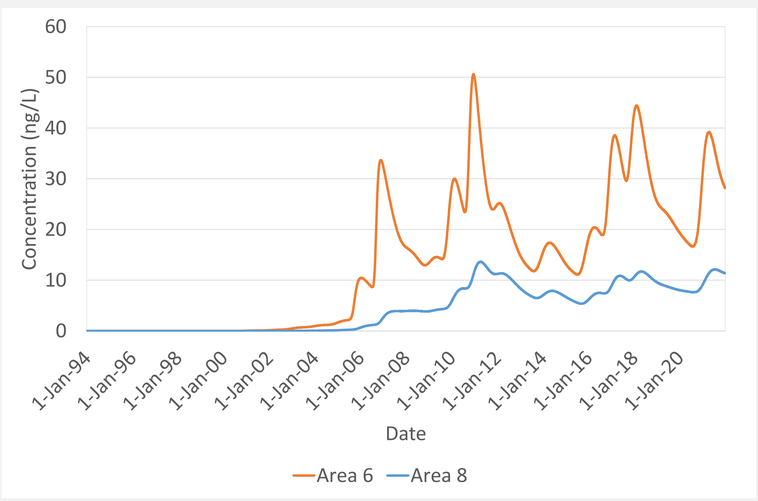


Figure 3. PFOA concentrations at sites 6 and 8

Modeling Results and Conclusions

Figures 3 and 4 show the leaching results for PFOA and PFOS for uncalibrated modeling runs. Results demonstrate that Area 6 has higher concentrations of PFOA and PFOS compared to Area 8.

Concentrations in the December 2020 period were 25.4 – 30.4 ng L^{-1} and 8.4 – 9.0 ng L-1 for PFOA at Area 6 and Area 8, respectively. PFOS, concentrations ranged between 100 – 120 ng L^{-1} and 60 - 65 ng L^{-1} at Area 6 and Area 8, respectively.

The current modelling scenarios over-estimate PFOS concentrations but underestimate the PFOA concentrations, especially at Area 6. However, only a single observation of PFAS at each site was available.

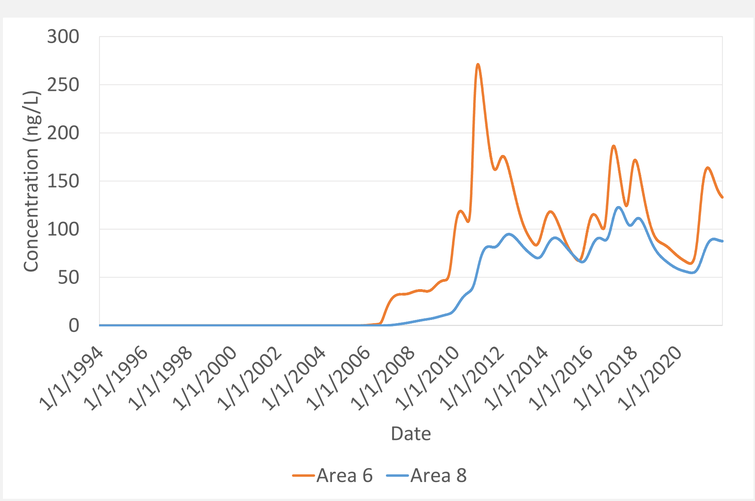


Figure 4. PFOS concentrations at sites 6 and 8

Differences between the modelling and monitoring data can be caused due to application timing, application rate, and formulation. Currently we do not have enough information on this. This will be the focus of future assessment refinements. Linking PEARL with a groundwater model such as ADAM will also be considered.

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