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Review of Available Software for PFAS Modeling Within the Vadose Zone

Michigan Department of Environment, Great Lakes, and Energy (EGLE)

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1. Introduction

AECOM Technical Services Inc. (AECOM) has been contracted by the Michigan Department of Environment, Great Lakes, and Energy (EGLE) to complete a review and identify the most suitable numerical modeling platform to simulate the transport of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) from municipal biosolid-amended soils through the unsaturated zone to the underlying groundwater (saturated zone).

2. Project Understanding and Background

Per- and polyfluoroalkyl substances (PFAS) are an emerging contaminant class of human-made chemicals that were first developed in the late 1930s and started to be used in commercial products in the late 1940s. The term PFAS is attributed to a large class of chemicals composed of many families that have vastly different physical and chemical properties (Buck et al., 2011). A recent survey reported more than 4,000 PFAS had been identified (OECD, 2018). Due to their unique chemical properties, PFAS production increased as these chemicals were incorporated into components of inks, varnishes, waxes, firefighting foams, metal plating, cleaning solutions, coating formulations, lubricants, water and oil repellents, paper, and textiles (Paul et al., 2009). Examples of industries using PFAS include automotive, aviation, aerospace and defense, biocides, cable and wiring, construction, electronics, energy, firefighting, food processing, household products, oil, and mining production, metal plating, medical, paper and packaging, semiconductors, textiles, leather goods, and apparel (OECD, 2013; UNEP, 2013). The Interstate Technology Regulatory Council (ITRC) has identified four primary sources of PFAS: fire training/fire response sites, industrial sites, landfills, and wastewater treatment plants/biosolids. Other point and diffuse sources of PFAS exist and may be significant locally, but generally, are expected to be small by comparison to these primary sources (ITRC, 2017).

PFAS have been classified by the United States Environmental Protection Agency (USEPA) as an emerging contaminant, that is regulated by EGLE under Part 201 of the Natural Resources and Environmental Protection Act, Act 451 of 1994, as amended and Rule 323.1057 (Rule 57) (Toxic Substances) of the Michigan Administrative Code. Michigan's Rule 57 values or Water Quality Standards (WQS) were developed to protect humans, wildlife, and aquatic life. The applicable (most stringent) WQS for PFOS and PFOA are noncancer human values, as follows:

- **PFOS**: 12 ng/L (nanograms per liter or parts per trillion) for surface waters that are not used for drinking water and 11 ng/L for those used as a drinking water source.
- **PFOA**: 12,000 ng/L for surface waters that are not used for drinking water and 420 ng/L for those used as a drinking water source.

Widespread use of fluorinated chemistry at various manufacturing and industrial facilities in conjunction with extreme resistance to degradation have resulted in the presence of PFAS in the environment, as well as wastewater treatment plants. Effluents discharged from wastewater treatment plants and their biosolids have been identified as one of the main known PFAS sources by ITRC (ITRC, 2017); however, wastewater treatment plants are not the sources of PFAS. Discharges from industrial facilities can also contaminate groundwater and surface water, effluents from wastewater treatment plants treating domestic or industrial waste, and storm water runoff, as well as air deposition from manufacturing sites.

Leachate of PFAS from biosolid-amended soils applied to agricultural lands and their transport through the unsaturated zone can lead to contamination of downgradient groundwater and surface water resources. PFOS and PFOA mass flows in municipal wastewater treatment facilities, as well as their fate and transport in the subsurface have been areas of active academic research in recent years.

Vadose zone numerical modelling provides a tool to simulate complex physical and chemical processes controlling the fate and transport of PFAS compounds (e.g., PFOA and PFOS) from the biosolid-treated soil to the water table and to predict the relative importance of various parameters governing PFAS fate and transport in the unsaturated zone. When properly utilized, numerical models can be used to guide laboratory investigations, field investigations, monitoring network design, and development of regulations that govern the use and management of PFOA and PFOS. Numerical modelling can also be used as a tool to assist with identifying potential relations between concentrations of PFOA and PFOS in municipal biosolids that could potentially be land applied to agricultural fields and the resulting PFOA and PFOS concentrations that will leach out from the soils and impact the groundwater and surface water.

3. Objectives

The objectives of this literature review and model evaluation study are as follows:

- To identify available vadose zone contaminant transport numerical modelling tools (hereafter referred to as VZMs) capable of simulating the fate and transport of PFOA and PFOS from ground surface to the underlying water table.
- To evaluate and summarize the capabilities and limitations of each VZM in a tabular format.
- Provide recommendations for the selection of one or more VZMs that are suitable for simulation of the critical processes governing fate and transport of PFOS and PFOA in the subsurface.

4. Physical and Chemical Properties

The general properties of the PFOA and PFOS compounds include limited sorption to soil and sediments, high water solubility, non-volatile, high mobility in water, exceptional stability and persistent with minimal attenuation; and bioaccumulative. The physical and chemical properties of PFOS and PFOA are the subject of ongoing research, and as shown in **Table 1**, there is a wide range of reported physicochemical properties in the literature (Concawe, 2016).

The low polarity of the fluorocarbon chain makes PFOA and PFOS hydrophobic and lipophobic, giving fluorocarbons even stronger surfactant properties than hydrocarbons. The carboxylate (in PFOA) or sulfonate (in PFOS) heads of these molecules are slightly polar, which gives this end of the molecule hydrophilic properties. These properties are believed to result with PFOA and PFOS to concentrate at the air-water interface, which may, in turn, affect the fate and transport of these compounds in the subsurface

A summary of physical and chemical properties from a limited literature review is provided in **Table 1**.

Table 1. Summary of Physical and Chemical Properties

PFAS Compounds	Molecular Weight (g/mol)	Dissociation Constant (pKa)[b]	Solubility (g/L)[b] (20-25^{0}C)	Log K_{ow}[a]	Log K_{oc} (L/kg)[b]	K_{ai}[c] *(cm)*	Freundlich Power Term
PFOS	500	-6.0 to -2.6	0.52 -0.57	2.45[e], 6.43	2.5 - 3.1	0.0755[d]	0.8
PFOA	414	-0.16 to 3.8	3.4 - 9.5	1.92[e], 5.30	1.31 - 2.35	0.0234[d]	0.8

[a]Wang et al. 2011; [b]Concawe, 2016; [c]Brusseau et al., 2019, calculated from data in Vecitis et al., 2008.; [d]Calculated for an aqueous PFAS concentration of 0.1 mg/L; [e]Jing et al., 2009

Based on the physical and chemical properties of PFOS and PFOA, and considering the objectives of this evaluation, the following physical and chemical processes have been identified as the key processes to be considered when modelling fate and transport of PFOS and PFOA in the subsurface:

- Transient analysis of groundwater flow through the unsaturated (vadose) zone using the Richards Equation. This is the fundamental equation governing vertically downward groundwater flow from the surface to the water table. Alternative approaches ignore the fundamental processes governing groundwater flow in the unsaturated zone.
- Nonequilibrium sorption. Sorption is the process that governs the portioning of contaminants from the mobile aqueous phase to the relatively immobile (sorbed) solid phase. Nonequilibrium sorption allows for kinetically controlled sorption whereby equilibrium conditions are not achieved instantaneously at every time step. This process is especially important in highly dynamic transient systems.

- Partitioning to the air-water interface. This refers to the distribution of contaminants within the variably saturated capillary fringe and other residual water above the water table. This process must be considered due to the chemical properties of PFOA and PFOS. The hydrophobic tail is expected to preferentially partitions to the gas phase, while the hydrophilic head partitions to the aqueous phase thereby affecting contaminant distribution and mobility. Recent academic research (Brusseau et al., 2019) found that approximately 50% of the retardation of PFOA and PFOS between the surface and the water table was due to partitioning to the air-water interface. Based on this research, any numerical modelling investigation must consider the importance of this process to produce technically valid outcomes.

Although the following mechanisms are likely to play a role in the fate and migration of PFASs, they are presently considered to be of less importance than the mechanisms described above, or beyond the scope of the current scope of the investigation:

- Plant uptake and accumulation. This refers to the uptake of water and/or solutes by plant roots, which can lead to the accumulation of solutes in plant biomass and shallow soils if the plant is allowed to decay in place.
- Farming practices. This refers to the process of ploughing, seeding, the reworking of fields, and the addition of agricultural amendments (e.g., biosolids) during farming. These processes can result in the redistribution of solutes (upward or downward) within the soil profile.
- pH and Redox Influences. This refers to the chemical conditions (i.e., acidic/basic, oxidizing/reducing, etc.) within the soil profile that may affect the fate and transport of solutes. Academic research indicates the sorption of PFOA and PFOS is sensitive to pH and redox conditions. This is especially relevant to systems containing ferrous compounds. Although possibly important, it is thought to be secondary to other mechanisms.

5. A Critical Review of Existing Vadose Zone Models (VZMs)

Several VZMs have been used to simulate fate and transport of a wide variety of contaminants through the unsaturated zone. The most common groups of contaminants analyzed are petroleum hydrocarbons and pesticides. PFOA and PFOS have significantly different chemical and physical properties than petroleum hydrocarbons and pesticides, requiring an in-depth evaluation of the suitability of existing VZMs for simulation of the fate and transport of these compounds in the subsurface.

A literature review was conducted to identify vadose zone numerical modelling tools and determine the most suitable VZMs for modelling PFOA and PFOS. The following VZMs were identified and compared in this study:

- CTRAN/W (GeoStudio)
- HYDRUS (PC-Progress)
- PEARL (Collaboration by three Dutch universities: WENR, PBL, and RIVM)
- PELMO (Frauhofer Institute for Molecular Biology and Applied Ecology)
- PRZM (US EPA)
- RZWQM2 (USDA Agricultural Research Service)
- SESOIL (ESCI)
- SVENVIRO (Soil Vision)
- VLEACH (US EPA)

Each of the VZMs listed above incorporates different key processes governing groundwater flow in the unsaturated zone and contaminant fate and transport. The simpler models simulate downward migration of groundwater using a water balance approach, while more rigorous VSMs simulate vertically downward groundwater flow through the vadose zone by solving Richards Equation. Richards Equation incorporates the effects of variable moisture contents and pressure heads on the unsaturated hydraulic conductivity.

The suitability of any of these modelling software options for achieving the defined objectives was evaluated based on the fundamental physical and chemical processes that are considered most relevant to the downward mobility of PFOS and PFOA, and how those processes have been implemented in each VZM. Secondary considerations include the availability of the software for commercial application, access to technical support and data requirements. All of the VZMs considered during this review are well established, having been applied to real world problems and validated against standardized case studies.

5.1 CTRAN/W with SEEP/W

CTRAN/W is an integrated modelling suite that uses one code to solve groundwater flow that is coupled to a separate code that solves contaminant transport. CTRAN/W is capable of modeling both the vadose zone and the saturated zone.

CTRAN/W is a finite-element model that solves groundwater flow using Darcy's Law equation in one, two, or three dimensions. CTRAN/W simulates multiphase, multicomponent reactive transport with linear and non-linear equilibrium sorption, sequential decay chain reactions, transient climate conditions, and plant root uptake.

5.2 HYDRUS

HYDRUS is capable of modelling groundwater flow and contaminant transport in both the vadose zone and the saturated zone.

HYDRUS is a finite-element numerical model that solves groundwater flow using Richards' Equation in one, two, or three dimensions. HYDRUS can model a variety of different contaminant transport mechanisms. The base version of HYDRUS allows for multiphase, multicomponent reactive transport with linear and non-linear, equilibrium or non-equilibrium sorption, sequential decay chain reactions with the individual parameterization of daughter products, transient climate conditions, and plant root uptake. Add-on modules allow for partitioning to the air-water interface, colloid-facilitated transport mechanisms, reaction and transport of major ions, and coupling with PHREEQC to simulate geochemical reactions in one or two-dimensions.

5.3 PEARL

Pesticide Emission Assessment at Regional and Local scales (PEARL) is intended for numerical modelling of pesticide behavior in the soil-plant system.

PEARL is a finite-difference model that solves groundwater flow using Richards' Equation in one dimension. PEARL allows for multiphase, multicomponent reactive transport with linear and non-linear, equilibrium or non-equilibrium sorption, sequential decay chain reactions with the individual parameterization of daughter products, transient climate conditions, and plant root uptake.

5.4 PELMO

Pesticide Leaching Model (PELMO) is a VZM that is based on PRZM (another VZM) and used to simulate the vertical movement of pesticides in soil due to leaching processes.

PELMO is a finite-difference model that solves groundwater flow using a specific capacity 'tipping bucket' approach in one-dimension. PELMO can simulate multiphase, multicomponent reactive transport of a parent compound as well as two-daughter products, and it can solve linear and non-linear equilibrium sorption as well as root uptake.

5.5 PRZM

The US EPA originally developed PRZM, but it is no longer supported. However, PRZM forms the basis for another VZM (PELMO) that is still supported by its developers in the European Union.

PRZM is a finite-difference model that solves groundwater flow using a specific capacity 'tipping bucket' approach in one-dimension. PRZM is capable of simulating the transport of a given parent compound as well as two-daughter products, and it can solve linear equilibrium sorption as well as root uptake of solutes.

5.6 RZWQM2

The Root Zone Water Quality Model 2 (RZWQM2) is a process-based model that simulates the growth of the plant and the movement of water, nutrients, and pesticides over, within and below the crop root zone of a unit area. RZWQM2 offers the capability for incorporating farming practices and processes, such as snow accumulation.

RZWQM2 is a finite-difference model that solves groundwater flow using Richards' Equation in one-dimension. RZWQM2 simulates major physical, chemical, and biological processes in an agricultural crop production system. Unfortunately, RZWQM2 is a tailored solution for agricultural users and does not give the user access to some of the parameters relevant for contaminant transport modelling (such as solubility). Available information suggests sorption processes can only be simulated as equilibrium processes.

5.7 SESOIL

Seasonal Soil compartment model (SESOIL) is a screening level tool capable of simulating contaminant transport, soil water movement, and soil erosion.

SESOIL is a finite difference model that approximates groundwater flow through the vadose zone using an infiltration-based mass balance approach in one dimension. SESOIL can simulate multiphase reactive transport and can model linear and non-linear equilibrium sorption.

5.8 SVENVIRO

Soil Vision Enviro (SVENVIRO) is an integrated modelling suite that uses one code to solve groundwater flow that is coupled to a separate code that solves contaminant transport. SVENVIRO is capable of modeling both the vadose zone and the saturated zone.

SVENVIRO is a finite-element model that solves groundwater flow using Richards' Equation in one, two, or three dimensions. SVENVIRO simulates multiphase, multicomponent reactive transport with linear and non-linear equilibrium sorption, sequential decay chain reactions, transient climate conditions and plant root uptake.

5.9 VLEACH

Vadose Zone Leaching (VLEACH) is used to make preliminary assessments of the effects of the leaching of volatile and sorbed contaminants through the vadose zone on groundwater.

VLEACH is a finite difference screening level model that approximates groundwater flow through the vadose zone using Darcy's Law in one dimension. VLEACH can simulate multiphase reactive transport and can model linear equilibrium sorption.

5.10 Discontinued Vadose Zone Models

Several additional VZMs have historically been used for modeling contaminant transport in the vadose zone. Although many of the discontinued VZMs are highly capable and have been applied to solving a wide variety of environmental problems, they were not included in this review because the developers no longer support them. Discontinued VZMs identified during this review include Leaching Estimation and Chemistry for Management of Pesticides Model (LEACHMP), Vadose Zone Flow and Transport Model (VADOFT), and PESTicide Leaching and Accumulation (PESTLA).

6. Model Comparison

A summary of the capabilities of each of the VZMs to meet the defined objectives is provided in **Table 2**, with VZMs ranked from most suitable to least suitable.

Table 2. Summary of Model Capabilities and Limitations for PFAS Modeling within Vadose Zone[1]

Vadose Zone Modelling Code	Method of Solving Groundwater Flow	Non Equilibrium Sorption	Freundlich (non linear) Sorption	Partitioning to the Air Water Interface	Root Uptake Function	Dual Permeability	Advanced Geochemical Modeling Capabilities	1D, 2D or 3D	Surfactant Induced Flow	Availability
HYDRUS	Richards Equation	Yes	Yes	Yes	Yes	Yes	PHREEQC Coupling, Colloid Transport	1D, 2D, and 3D	Customized Code	Free (1D), Commercial (2D &3D)
PEARL	Richards Equation	Yes	Yes	No	Yes	Yes	pH Dependence, User-Defined Functions	1D	No	Free (current)
RZWQM	Richards Equation	Yes (limited)	No	No	Nitrogen Only	Yes	Limited Solute Transport, Cation Exchange, pH Considerations	1D	No	Free (current)
SVENVIRO	Richards Equation	No	Yes	No	Yes	No	No	2D and 3D	No	Commercial
CTRAN/W with SEEP/W	Darcy's Law	No	User-Defined Function	No	Yes	No	No	1D and 2D	No	Commercial
PELMO	Capacity-based Approach	No	Yes	No	Yes	No	2 Sorption Sites	1D	No	Free (current)
SESOIL	Infiltration-based Approach	No	Yes	No	No	No	No	1D	No	Commercial
PRZM	Darcy's Law	No	No (Nitrogen only)	No	Solute Only	No	No	1D	No	Free (not current)
VLEACH	Darcy's Law	No	No	No	No	No	No	1D	No	Free (not current)

[1]**Green** = Ideal; **Yellow** = Less than ideal; **Red** = Least suitable / not recommended.

7. Conclusions and Recommendations

Based on our review of VZM capabilities against the stated objectives, we conclude the following:

1. The physical and chemical characteristics of PFOA and PFOS are unique in that they are highly stable and do not readily degrade over time. Furthermore, they are comprised of a hydrophilic head and hydrophobic tail that impart surfactant properties at elevated concentrations and drive accumulation at the air-water interface. These physical and chemical properties should be considered when selecting a VZM to simulate the fate and migration of PFOA and PFOS.
2. The current understanding of the physical and chemical processes governing the fate and migration of PFOA and PFOS is an emerging field of academic research. The relative importance of various processes is not well understood. Further exploration using highly capable VZMs that accurately incorporate key fate and transport processes will help resolve outstanding questions about their relative importance. Simplified approaches are unlikely to produce definitive answers.
3. Groundwater flow through the unsaturated zone is highly complex, with frequent changes in moisture content, hydraulic conductivity, and groundwater flow impacting the rate of groundwater migration from the surface to the water table. Of the nine (9) VZMs reviewed herein, only four (4) VZMs (HYRRUS, PEARL, RZWQM and SVENVIRO) implement Richards Equation, which is the most rigorous approach to solving groundwater flow in the unsaturated zone. HYDRUS, PEARL and RZWQM are able to simulate dual permeability systems, but only HYDRUS is able to simulate flow in the unsaturated zone in two or three dimensions. The remaining five (5) VZMs (CTRAN/W, PELMO, PRZM, SESOIL, and VLEACH) adopt simplified groundwater flow equations that are not considered to be sufficient to meet the study objectives.
4. Transport of PFOA and PFOS in the unsaturated zone is also highly complex. While the persistence of the fluorinated compounds diminishes the importance of degradation, the chemical properties result in the partitioning of the compounds to the air-water interface. Partitioning to the air-water interface may have significant implications for PFOS and PFOA retardation as found in recent research (Brusseau, 2019). Sorption reactions may take some time to reach equilibrium after each application of municipal biosolids or infiltration events. Further, the surfactant properties of the compounds may become important at elevated aqueous concentrations.
5. The importance of geochemical conditions to sorption processes can be evaluated with several models, but HYDRUS allows for more rigorous evaluation. Given the complexity of the system, a highly capable VZM must be utilized to explore the fate and migration of PFOA and PFOS in the unsaturated zone. Of the models reviewed, HYDRUS was identified to have the most exceptional capabilities for simulation of contaminant fate and transport in the unsaturated zone. The difficulty of understanding the fate and transport PFOA and PFOS, as well as high costs associated with its remediation, makes it imperative to consider key governing physical and chemical processes during the assessments transport in the unsaturated subsurface.

AECOM recommends using HYDRUS to carry out vadose zone modelling of PFOA and PFOS. HYDRUS implements scientifically rigorous equations governing unsaturated flow and contaminant transport in one, two, and three dimensions. It is well supported and has been applied to solve a wide variety of environmental problems. The numerical solutions have been vetted by academic researchers and independently validated. The graphical user interface offers the modeler flexibility to incorporate additional processes governing contaminant fate and transport if warranted. Further, HYDRUS utilizes the Richards Equation to simulate groundwater flow and has been used to simulate non-equilibrium sorption and partitioning to the air-water interface. Utilization of other VZMs would come at the expense of technical rigor and the ability to investigate the importance of fundamental processes individually rather than through a “lumped parameter” approach.

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