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# Evaluation of PFOS contamination in aquifers under single lined landfills

## Evaluation de contamination d'aquifères par PFOS sous dépotoirs à revêtement composite singulier

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**ABSTRACT**: Perfluorooctane sulfonic acid (PFOS) is among the most concerning types of a large group of compounds called per- and polyfluoroalkyl substances (PFAS). PFOS has captured significant attention due to its persistence in the environment and negative effects on human health. Landfills are a major source of PFOS to the surrounding aquifer and usually require composite liner systems for hydraulic and chemical containment. However, knowledge of the transport of PFOS through liner systems remains limited, and relevant numerical simulations are scarce. The paper reports an evaluation of PFOS contamination in the aquifer under a standard, single-liner, barrier system in a landfill, conducted using a 2D finite-element model of advective-diffusive PFOS transport. Three different levels of construction quality assurance (CQA) for the liner system are investigated. It's concluded that the advection process dominates PFOS transport through the liner system over molecular diffusion and mechanical dispersion. A considerable level of contamination for a scenario with excellent CQA indicates that a single composite liner may not be adequate to mitigate PFOS impact on an aquifer below or close to a municipal solid waste landfill.

**RÉSUMÉ**: Le perfluorooctane sulfonique (PFOS) est l'un des polluants les plus graves parmi le groupe des substances per- et polyfluoroalkyl (PFAS). Le PFOS a suscité l'intérêt en raison de sa persistance dans l'environnement et de ses effets néfastes sur la santé humaine. Les centres de décharge de déchets (dépotoirs) constituent une source majeure de PFOS pour les aquifères voisins et nécessitent un système de revêtement pour l'isolement hydraulique et chimique. Cependant, la connaissance de la migration du PFOS à travers les systèmes de revêtement des dépotoirs est limitée, et les simulations numériques du problème sont rares. Cette publication présente les résultats préliminaires d'une série de simulations en éléments finis en 2D du transport par diffusion-advection du PFOS à travers le dessous d'un dépotoir pourvu d'un revêtement composite singulier. Trois niveaux de qualité de construction de revêtement sont considérés. Les simulations tiennent compte des meilleures estimations de la distribution de probabilité des propriétés des matériaux, des variables environnementales et des taux de contaminants dans les déchets, afin de calculer des distributions de probabilité de la concentration maximale de PFOS dans l'aquifère. Les résultats des simulations révèlent que le processus d'advection est dominant par rapport à la diffusion moléculaire et à la dispersion mécanique. Le risque de contamination reste élevé, même dans un scénario de qualité de construction excellente, ce qui indique qu'un revêtement composite singulier n'est probablement pas suffisant pour protéger les aquifères situés sous les dépotoirs de déchets municipaux.

**Keywords:** PFOS; liner system; landfill; finite element method; construction quality assurance.

## 1 INTRODUCTION

Per- and polyfluoroalkyl substances (PFAS) are a diverse group of synthetic organic compounds with thermal stability, chemical inertness, and significant surfactant properties. They have been widely used since the 1950s in both consumer products and industrial applications (Renner, 2001), leading to their extensive detection in the environment, wildlife, and humans. Perfluorooctane sulfonic acid (PFOS, $C_8F_{17}$-$SO_3H$) is one of the most problematic PFAS compounds. Although the production of PFOS and its precursors ceased in the United States in 2002 (USEPA, 2000), PFOS remains notable in the environment due to its historical use (Paul et al., 2009), continued precursor presence (Rhoads et al., 2008), and identification as an end product in PFAS environmental transformations (Bouazza, 2021). As the destination for most consumer products and industrial wastes containing PFAS, landfills are a major source of PFAS, including PFOS, to the environment. PFOS is widely detected in landfill leachates at ng/L to μg/L levels (Zhang et al. 2023). Meanwhile, the health advisory standard for PFOS in drinking water varies by jurisdiction, such as 70 ng/L for Australia (NHMRC, 2022), 600 ng/L set by Health Canada (2018), 4 ng/L set by the US Environmental Protection Agency (USEPA, 2023), and 100 ng/L for Europe (EurEau, 2018).

Geosynthetic composite liner systems are widely used in landfills to mitigate contamination and protect surrounding groundwater (Giroud and Bonaparte, 1989; Rowe, 1998, 2005, 2012; Rowe et al., 2004; Bouazza, 2002). A single composite liner system typically comprises a geomembrane (GMB), a geosynthetic clay liner (GCL) or a compacted clay liner (CCL), and an underlying attenuation layer. Hence investigating PFOS interactions with liner components to determine relevant material properties is necessary for evaluating PFOS's environmental impact in landfills equipped with liner systems.

While some studies have estimated key transport properties of PFOS in lining systems (Di Battista et al., 2020; Rowe et al., 2023; Rowe and Jabin, 2021; Bouazza, 2021; Schaefer et al., 2019), there have been very few attempts to numerically simulate the migration of PFOS in a liner system, partly because of limited data.

Rowe and Barakat (2021) examined the transport of PFOS in a municipal solid waste landfill lined by a single composite liner, which was numerically analysed using a 1½-D model finite-layer method (Rowe and Booker, 1984, 1985; Rowe et al., 1997; Rowe and Booker, 2004; Rowe and Abdelrazak, 2019) which considered the downward advective-diffusive-dispersive migration through periodically spaced wrinkles to an aquifer that was modelled as a boundary condition with horizontal flow. It was concluded that the no-leakage, pure-diffusion case can in principle maintain acceptable concentrations in the aquifer. However, with leakage through a reasonable number of holes in the geomembrane for landfills with a single liner system containing significant concentrations of PFOS in the leachate, there was likely to be a significant impact on a shallow underlying aquifer.

The present study uses a 2D finite element method (FEM) model to simulate the leakage of leachate and the migration of PFOS through a typical single-liner system while considering the full 2D effects of a series of leaks in the lining system.

The primary advantage of a 2D model over the 1½-D model used by Rowe and Barakat (2021) is the ability of the 2D model to examine migration downgradient of the landfill and the impact of monitoring points away from the landfill.

# 2 METHOD

## 2.1 Problem description

The 2D model of a municipal solid waste (MSW) landfill simulated in the study is shown in Figure 1, where PFOS transport involving both advection and diffusion occurs. The landfill is 400 m long in the direction of flow in the underlying aquifer and 100 m wide in the direction normal to the plane of the diagram. The landfill base is equipped with a single composite liner which is comprised of a 1.5 mm-thick HDPE GMB, a 7 mm-thick GCL, above a 3.743 m-thick attenuation layer (AL) and a 3 m-thick aquifer (AQ). The combined thickness of the clay liner and attenuation layers is selected according to MoE (1998). If the unlikely condition of no defects on GMB is assumed, the advective PFOS transport is eliminated and the leakage rate $q_a$ is nil, giving a pure-diffusion problem. Selected input variables related to material properties, dimensions, and boundary conditions have been estimated, and are shown in Table 1.

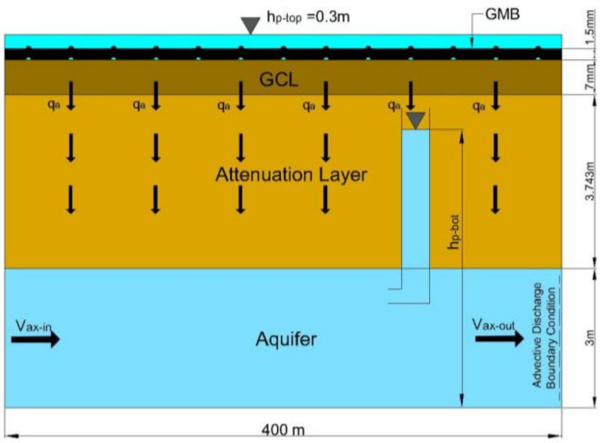


*Figure 1. Schematic of the liner-subsoil system for "good CQA and with ELLS": holed wrinkles of 325 m/ha, corresponding to 13 leaks per 400 m. Not to scale.*

Input parameters used in the simulations have been obtained based on an extensive review of the literature, data study and expert judgement. In addition, calibration on data from landfill cells where there is good construction quality assurance (CQA) and a dipole method electrical leak location survey (ELLS) gave an estimation of 325 m/ha for the holed wrinkle length per hectare (Rowe and Zhao, 2023). Two other levels of CQA are also investigated in this study, i.e., "good CQA and no ELLS" corresponding to 475 m/ha and "excellent CQA" corresponding to 75 m/ha.

*Table 1. Input parameters.*

| Parameters | Symbols | GM estimations |
|---|---|---|
| Total hydraulic head drop across the model | $\Delta H$ | 1.05 m |
| Length of holed wrinkle per hectare for "good CQA & no ELLS", "good CQA & with ELLS", and "excellent CQA" | $L_w$ | 475 m/ha, 325 m/ha, and 75 m/ha |
| Wrinkle width | $2b$ | 0.2 m |
| PFOS concentration in landfill leachate | $C_0$ | 900 ng/L |
| PFOS mass per unit waste mass | $p_0$ | 1800 ng/kg |
| Inward horizontal groundwater Darcy velocity in the aquifer | $V_{ax\text{-}in}$ | 0.95 m/a |
| Transmissivity | $\theta$ | $1.0315\times10^{-3}$ $m^2/a$ |
| Hydraulic conductivity of GCL in contact with GMB | $k_a$ | $9.4\times10^{-4}$ m/a |
| Hydraulic conductivity of GCL below holed wrinkles | $k_b$ | $7.52\times10^{-3}$ m/a |
| Hydraulic conductivity of AL | $K$(AL) | $1\times10^{-7}$ m/s |
| Dispersivity of AL | $\alpha$(AL) | 0.052 m |
| Transverse dispersivity of AQ | $\alpha_T$(AQ) | 0.1 m |
| Longitudinal dispersivity of AQ | $\alpha_L$(AQ) | 2 m |

## 2.2 Analysis method

The migration of PFOS within the investigated landfill model occurs in tandem with the flow of leachate, which is governed by the semi-coupled steady-state saturated water flow equation and time-dependent reactive diffusion-advection equation (RDAE) representing the transport of solutes. A specified mass of PFOS is applied at the top of the model's domain hence allowing for decline of PFOS concentration in the waste as is removed through leachate drainage and/or migration into the subsurface. The numerical simulations are conducted using the Soil Pollution Analysis System (SPAS), a multi-purpose finite-element method simulation software specifically tailored to lining systems (El-Zein, 2008; El-Zein and Balaam, 2012). Maximum concentration of PFOS anywhere in the aquifer, at any time, $C_{max}$, is computed by SPAS and used to characterise the level of contamination. The point in space and time at which maximum concentration is found is given by $x_{max}$ and $t_{max}$ (low transverse dispersivity in the aquifer leads to low dispersion of contaminants in the vertical direction and hence contaminants reaching the aquifer largely remain at the upper aquifer and reach their maximum concentrations at the top).

# 3 RESULTS AND DISCUSSION

Table 2 summarizes results of the simulations. $C_{max}$ for the pure-diffusion case is 0.55 ng/L (occurring at 580 years), which is around two to three orders of magnitude lower than those of the advection-diffusion cases and occurs at much later time (Table 2). Such a contrast suggests that advection is the dominant process in PFOS transport through the liner system and causes the vast majority of its impact in the aquifer, while diffusion has a much smaller effect. Meanwhile, comparing the $C_{max}$ value of 0.55 ng/L to four drinking water standards, namely 4 ng/L (USEPA), 70 ng/L (Australia), 100 ng/L (Europe), and 600 ng/L (Canada), indicates that a single-liner system with an intact GMB may serve as an effective barrier to PFOS.

*Table 2. Summary of leakage rate and PFOS contamination.*

| **Case** | $L_w$ (m/ha) | $q_a$ (Lphd) | $C_{max}$ (ng/L) | $t_{max}$ (yr) | $x_{max}$ (m) |
|---|---|---|---|---|---|
| Pure diffusion | 0 | 0 | 0.55 | 580 | 400 |
| Good CQA and no ELLS | 475 | 300 | 508 | 145 | 391 |
| Good CQA and with ELLS | 325 | 197 | 403 | 155 | 386 |
| Excellent CQA | 75 | 46 | 176 | 145 | 335 |

However, even with high-quality ELLS and an excellent CQA, holed wrinkles in the GMB are inevitable, hence generating both advection and diffusion. Some landfills are designed with the leachate level below the potentiometric surface in the underlying aquifer which induces a "hydraulic trap" (Rowe, 1988; Rowe et al., 2000, 2004). In these cases, the flow through the holes in the geomembrane will be inward. However, when the leachate level is above the potentiometric surface in the underlying aquifer, leakage through holes will be downward. It is this latter case that is examined in this paper.

Figure 2 shows the horizontal variation in concentration at the top of the aquifer at 150 years. The overall rising trend of concentration is mainly attributed to the PFOS transport caused by the horizontal groundwater flow. Meanwhile, the "waves" in curves reflect the effect of leakage spikes under GMB defects.

Figure 3 shows PFOS concentration versus time at the point of highest concentration in the aquifer below the landfill. Contamination levels in the aquifer first increase to a peak before gradually declining. Under the premise of good CQA, applying ELLS reduces the density of defects on the GMB, the leakage rate ($q_a$, reducing from 300 Lphd to 197 Lphd), and the peak PFOS concentration in the aquifer ($C_{max}$, declining from 508 ng/L to 403 ng/L). Under an excellent CQA, $q_a$ and $C_{max}$ will be reduced to 46 Lphd and 176 ng/L, respectively. This indicates that, as expected, a higher level of CQA can contribute to limiting PFOS contamination in the aquifer.

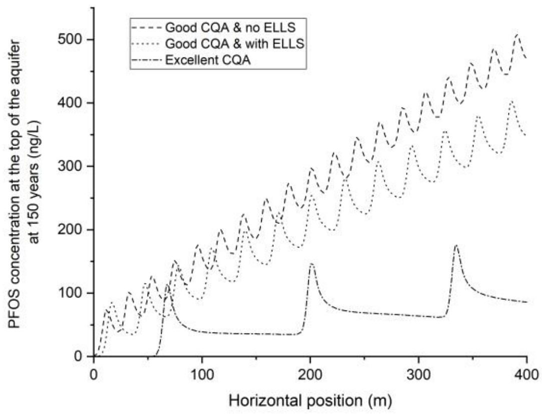


*Figure 2. Change in PFOS concentration at the top of the horizontal direction in the aquifer at 150 years.*

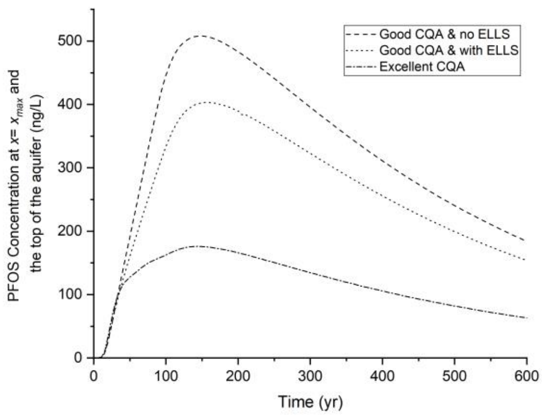


*Figure 3. PFOS concentration over time at x= $x_{max}$ and the top of the aquifer.*

However, in all 3 cases considered, $C_{max}$ remains higher than some of less stringent standards (i.e., 70 ng/L for Australia and 100 ng/L for Europe), and significantly higher than the strictest ones (4 ng/L for USEPA). Even the most lenient standard (600 ng/L for Canada), is approached by $C_{max}$ under a good CQA. This is consistent with and adds support to the findings of Rowe and Barakat (2021) and suggests that single lining systems, even under high quality construction, may not be sufficient to protect groundwater from PFOS contamination under landfills unless the PFOS concentration in the landfill is substantially lower than that assumed or there is a substantially higher level of natural attenuation than that considered in this study. However, the simulations presented here are based on deterministic analyses for a single representative case under various assumptions of construction quality. In reality, there is significant uncertainty in input data and a more thorough assessment of the adequacy of different lining systems needs to take these uncertainties into account.

## 4 CONCLUSIONS

This study is the first to conduct a 2D finite element simulation of PFOS migration through landfills with a single composite lining system into underlying aquifers. The study's findings must be qualified by a number of limitations. These include the assumption of steady-state flow and full saturation, no adsorption or biodegradation of PFOS, and input parameters obtained based on limited information.

Despite these limitations, the study's key finding is noteworthy, indicating that, while high construction quality reduces the contamination level, single lining systems in MSW landfills may not be sufficient to prevent PFOS contamination in aquifers. Further investigations are required to assess the necessity of double composite lining systems to mitigate PFOS contamination in similar contexts. In addition, it is important to take into account data uncertainty in future analyses by estimating probability distributions of key input variables and conducting probabilistic simulations of PFOS contamination.

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