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Preventing **R**ecalcitrant **O**rganic **M**obile **I**ndustrial chemical**S** for **C**ircular **E**conomy in the soil-sediment-water **S**ystem

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D4.2 – Planning & design tool for drinking water treatment for PFAS & industrial chemicals

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Executive Summary

A planning and design tool for the removal of per- and polyfluoroalkyl substances (PFAS) and other industrial persistent, mobile and potentially toxic (iPMT) substances for drinking water treatment plants with source water with high dissolved organic matter (DOM) was developed.

Within PROMISCES, technologies to remediate PFAS and iPMT(s) in several environmental media have been studied. This deliverable reports on a tool developed to improve planning and design of drinking water treatment trains for PFAS and iPMT, especially focusing on the adsorption onto granular activated carbon (GAC), alternative adsorbents and removal using ion exchange (IX) resins. Despite several previous studies on PFAS and iPMT removal during drinking water treatment, informational gaps on how to best implement suitable treatment trains in practice remain. The design of a suitable treatment train will depend on the effectiveness of the adsorbent for the removal of various mixtures of chemicals, different background water qualities, and treatment goals. Modelling tools can be used to predict treatment performance under varying conditions and are especially helpful to improve the informative value of pilot tests. For example, potential changes in influent concentration, background water quality, flow rate, and adsorbent bed height not covered in pilot tests can be simulated using models. Whereas GAC adsorption of some organic micropollutants is already well studied, competitive adsorption of DOM and PFAS and iPMT in drinking water with elevated DOM-content is less understood, and design tools are lacking. The developed drinking water treatment and design tool (DWTDT) is applicable for fixed-bed adsorber design in water treatment trains. Using the tool, operational times until exhaustion of fixed-bed adsorbers using GAC or ion exchange resins can be predicted. This includes an estimation of ideal breakthrough using equilibrium isotherm data as main input data, as well as prediction of the dynamic breakthrough using additional input parameters describing internal and external mass transfer.

Dynamic breakthrough prediction is based on the pore surface diffusion model (PSDM) developed by the United States Environmental Protection Agency (EPA) and extended with the so-called tracer model (TRM), allowing the breakthrough of DOM and its competing effects on PFAS and iPMT removal to be mapped. Both the original model by the EPA as well as the DWTDT were developed using the programming language Python. A user interface was built for the DWTDT to make it more user friendly. The model was tested with experimental input data from the laboratory tests and validated with pilot plant data from the PROMISCES project. The DWTDT is publicly available on GitHub and Zenodo (https://doi.org/10.5281/zenodo.13982527). The tool allows users to simulate simultaneous DOM, PFAS and iPMT breakthrough in drinking water treatment trains using adsorbents or ion exchange resins, provided that the necessary input data including single solute isotherm data, external mass transfer coefficients, internal diffusion coefficients, and adsorption parameters for DOM background are known or can be estimated.

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List of abbreviations

ADSA Adsorption analysis

BTC Breakthrough curve

DOC Dissolved organic carbon

DOM Dissolved organic matter

DWTDT Drinking Water Treatment and Design Tool

EBCM Equivalent background compound model

EPA Environmental protection agency

GAC Granular activated carbon

GUI Graphical user interface

IAST Ideal adsorbed solution theory

iPMT Persistent, mobile and potentially toxic substances

IX Ion exchange resin

PFAS Per- and polyfluoroalkyl substances

PSDM Pore surface diffusion model

TRM Tracer model

1 Introduction

A new planning and design tool to assist drinking water treatment plant operators in the removal of per- and polyfluoroalkyl substances (PFAS) and other persistent, mobile, and potentially toxic (iPMT) substances from drinking water rich in dissolved organic matter (DOM) has been developed.

Within PROMISCES, technologies to remediate PFAS and iPMT(s) in several environmental media have been studied. This deliverable reports on a tool developed to improve planning and design of drinking water treatment trains for PFAS and iPMT, especially focusing on the adsorption onto granular activated carbon (GAC), alternative adsorbents and removal using ion exchange (IX) resins. Although previous research has addressed PFAS and iPMT removal in drinking water treatment, knowledge gaps regarding the optimal implementation of effective treatment trains remain. The design of a suitable treatment system relies on the adsorbent's efficiency in removing different chemical mixtures, varying water qualities, and specific treatment objectives. Modelling tools can forecast treatment performance under different conditions, which is particularly valuable for refining pilot tests. For instance, models can simulate potential variations in influent concentration, water quality, flow rate, and adsorbent bed height that are not captured in pilot studies. While GAC adsorption has been extensively researched, the competitive adsorption of DOM with PFAS and iPMT is less understood, and there is a lack of design tools in this area.

The newly developed drinking water treatment and design tool (DWTDT) is suitable for fixed-bed adsorber design in drinking water treatment systems. It enables predictions of operation times until the exhaustion of fixed-bed adsorbers using GAC or ion exchange resins. This tool incorporates rough estimates of ideal breakthrough based on equilibrium isotherm data and can also predict dynamic breakthrough using additional parameters that describe both internal and external mass transfer.

GAC adsorbers are commonly used in drinking water treatment to remove organic chemicals such as PFAS and iPMT. The capacity of a GAC fixed-bed adsorber is influenced by both adsorption equilibrium and kinetics, with mass transfer processes like film diffusion, pore diffusion, and surface diffusion affecting the adsorption rate. To accurately describe the breakthrough curve (BTC) for different adsorbates, a suitable model and knowledge of equilibrium and kinetic parameters are necessary. However, the complexity of BTC models increases the number of parameters needed, making model selection a balance between accuracy and parameter estimation effort (Burkhardt et al. 2022). Despite the development of various BTC models, their application in drinking water treatment design is limited due to challenges in parameter estimation, particularly because drinking water is a complex multi-component system (Worch 2012).

The ideal adsorbed solution theory (IAST) is currently the most important and most commonly used thermodynamic model to predict multi-solute adsorption equilibria. Initially developed for gas adsorption by Myers und Prausnitz in 1965, it was later applied to liquid-phase adsorption by Radke und Prausnitz in 1972 for the first time. The IAST in its original form requires single-solute isotherm data of all mixture components and performs the calculation with molar quantities. However, in addition to PFAS and iPMTs, concentrations of which can be precisely determined by target analysis, natural waters contain a certain amount of DOM with a complex and unknown composition. DOM is therefore usually quantified in the form of the dissolved organic carbon (DOC) as sum parameter. The presence of DOM complicates the application of the IAST in two ways: first, no individual single-solute isotherms can be determined for the large number of DOM components, and second, the sum parameter DOC cannot simply be converted into molar substance quantities.

There are two important model approaches to circumvent these methodological problems in the IAST: the equivalent background compound model (EBCM) and the tracer model (TRM) (Worch 2010). The EBCM utilizes multi-solute adsorption data along with single-solute Freundlich parameters for PFAS and iPMTs to model the concentration and Freundlich parameters of a hypothetical equivalent background compound, which accounts for the adsorption competition caused by DOM. However, since the equivalent background compound is a purely fictitious quantity, it is not possible to model the DOC concentration in the filter effluent. The TRM is based on an adsorption analysis (ADSA). The core idea of the ADSA involves formally transforming the unknown multi-component system (e.g. DOM), into a defined mixture of a limited number of fictive components. Each of these fictive components represents a fraction of the measured DOC with specific adsorption characteristics. After additional fitting of the Freundlich parameters of the organic chemical to isotherm data in presence of DOM, the TRM is able to calculate the removal of the organic chemical as well as to quantify the DOC breakthrough. In contrast to the EBCM, this enables characterisation of the inlet of a second, downstream adsorber stage. Therefore, the TRM was implemented in the DWTDT to model the removal of PFAS from DOC-rich groundwater and drinking water with GAC.

The developed DWTDT includes modules for ADSA and TRM which feed into the PSDM and allow simulation of PFAS and iPMT breakthrough in fixed-bed systems.

2 Modelling approach and theoretical background

2.1 Structure of the DWTDT and integration of the EPA PSDM

The DWTDT is based on the open-source pore surface diffusion model (PSDM) Python application developed and provided by the US EPA and under license of the Massachusetts Institute of Technology. The PSDM uses orthogonal collocation on finite elements to solve the underlying set of differential equations. Detailed information on the PSDM and the applied numerical methods are given elsewhere (Mertz et al. 1999; Crittenden et al. 1980; Burkhardt et al. 2022). The PSDM application of the EPA already includes simple empirical correction factors to account for capacity and kinetic reduction due to fouling of GAC as described by Jarvie et al. (2005). The Python PSDM model is available on Github (US EPA 2024).

This original PSDM was extended by an ADSA and TRM module and wrapped in a GUI for the DWTDT. Furthermore, minor adjustments to the PSDM were necessary to guarantee compatibility with the TRM. The results from the ADSA and TRM module serve as input to the PSDM module. All modules are accessible through the GUI and can also be used independently as Python scripts.
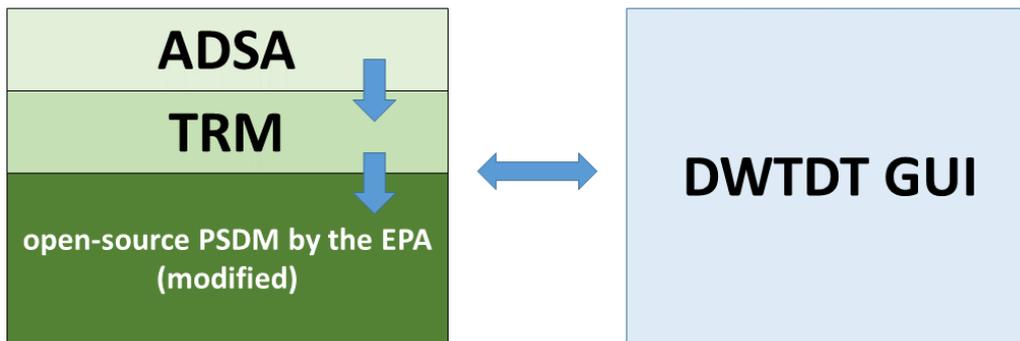

Figure 1 Structure of the DWTDT

2.2 Single-solute adsorption equilibrium

The adsorption equilibrium of one single-solute adsorbate is described with the empirical Freundlich isotherm equation (1):

$$q_i = K_i c_i^n \tag{1}$$

q_i: loading of adsorbate on the adsorbent in equilibrium

c_i: concentration of the adsorbate in the liquid phase in equilibrium

K_i and n: empirical Freundlich parameters

Isotherm data (c, q) needs to be determined with lab-scale batch experiments. Afterwards, a non-linear fitting approach (e.g. python *curve_fit* function) or linear fitting approach (after log transformation of c and q) can be applied to estimate K_i and n.

2.3 Modelling of multi-solute adsorption equilibrium with the IAST

The IAST is applied in the DWTDT to predict multi-solute adsorption equilibrium. To apply the IAST effectively, several conditions must be met. First, the model assumes that the adsorbed phase forms

a two-dimensional layer in equilibrium with the liquid phase, where all adsorbates have equal access across the entire surface of the adsorbent. Consequently, competitive factors like size exclusion or pore blockage are not considered. Additionally, the IAST operates under the assumption of ideal behaviour in both the liquid and adsorbed phases. This is generally valid for the liquid phase, as adsorbates are typically well-diluted. However, in the adsorbed phase, interactions between adsorbate molecules can be significant and may lead to unsatisfactory results at high loading levels or when specific interactions occur (Worch 2012). A modified version of the Gibbs fundamental equation, often called the spreading pressure integral, serves as the foundation for the IAST (equation (2)):

$$\varphi_i = \frac{\pi_i A_m}{RT} = \int_0^{c_i^0} \frac{q_i^0}{c_i^0} dc_i^0 \tag{2}$$

The spreading pressure π is defined as the difference between σ_{ws} (the surface tension at the water-solid interface) and σ_{ss} (the surface tension at the adsorbate solution-solid interface). This difference determines how adsorbate molecules are distributed between the liquid and the adsorbed phases. It is developed for a component i within an N-component mixture and connects the spreading pressure to its equilibrium loading q_i^0 and the associated concentration c_i^0. The spreading pressure term φ is included for simplification and is proportional to π, as the gas constant R, temperature T, and the adsorbent's surface area A_M can be considered constants. Similar to Raoult's law, the following equation (3) is applicable for multi-solute adsorption at a constant spreading pressure π or a fixed spreading pressure term φ, respectively:

$$c_i = c_i^0(\varphi) z_i \tag{3}$$

Equation (3) connects the concentration of a component c_i to the single-solute concentration $c_i^0(\varphi)$, which would generate the same spreading pressure as the mixture. Here, z_i represents the mole fraction of the component in the adsorbed phase. Therefore, it can be expressed with equation (4) as:

$$q_i = z_i q_T \tag{4}$$

With q_T being the total surface loading of all multi-solute components. The sum of the mole fractions follows per definition:

$$\sum_{i=1}^{N} z_i = 1 \tag{5}$$

q_T can as well be expressed as sum of the single-solute loadings $q_i^0(\varphi)$ and z_i at given φ, which results in equation (6):

$$q_T = \left[\sum_{i=1}^{N} \frac{z_i}{q_i^0(\varphi)} \right]^{-1} \tag{6}$$

A single-solute isotherm model (usually Freundlich, equation (1)) is employed to connect c_i^0 and q_i^0 and solve the the spreading pressure integral (equation (2)), resulting in equation (7):

$$\varphi_i = \frac{K_i}{n_i} (c_i^0)^{n_i} \tag{7}$$

Subsequently, solutions for q_i^0 (equation (8)) and c_i^0 (equation (9)) can be derived from equation (1) and (7):

$$q_i^0 = \varphi_i n_i \tag{8}$$

$$c_i^0 = \left(\frac{\varphi_i n_i}{K_i}\right)^{1/n_i} \tag{9}$$

A material balance (equation (10)) relates initial ($c_{0,i}$) and equilibrium concentration (c_i) with the adsorbent dose V_L/m_A.

$$q_i = \frac{V_L}{m_A}(c_{0,i} - c_i) \tag{10}$$

Inserting equation (9) in equation (3) and combining the results with equation (10) and (4) leads to equation (11):

$$z_i = \frac{c_{0,i}}{\frac{m_A}{V_L}q_T + \left(\frac{\varphi n_i}{K_i}\right)^{1/n_i}} \tag{11}$$

Following this, substituting equation (11) into equations (5) and (6) yields a set of equations (12 and 13) that can be solved numerically to determine the two unknowns q_T and φ.

$$\sum_{i=1}^{N} \frac{c_{0,i}}{\frac{m_A}{V_L}q_T + \left(\frac{\varphi n_i}{K_i}\right)^{1/n_i}} = 1 \tag{12}$$

$$\sum_{i=1}^{N} \frac{1}{\varphi n_i} \cdot \frac{c_{0,i}}{\frac{m_A}{V_L}q_T + \left(\frac{\varphi n_i}{K_i}\right)^{1/n_i}} = \frac{1}{q_T} \tag{13}$$

Finally, z_i, q_i and c_i can be calculated using equation (4), (10) and (11). The procedure of the IAST is summarized in Figure 2.
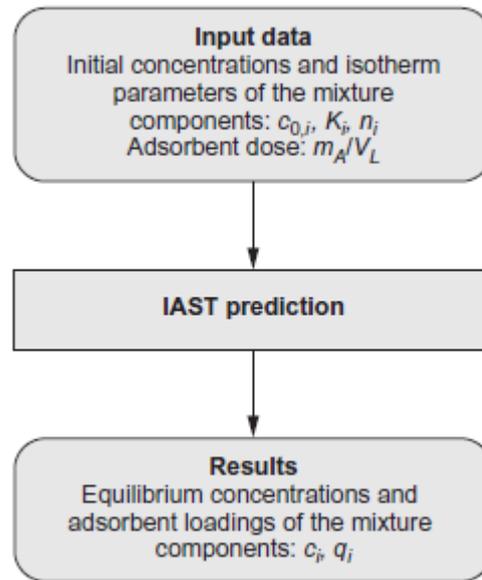
Figure 2 Calculation scheme of the IAST (Worch 2012). An IAST calculation in a defined mixture requires single-solute isotherm data for all adsorbates in the mixture.

2.4 Modelling of multi-solute adsorption equilibrium in presence of DOM: Adsorption analysis and Tracer model

The adsorption analysis (ADSA) is applied to model DOM breakthrough in the DWTDT. The fundamental concept of the ADSA involves transforming the unknown multi-component system of DOM into a defined mixture of a limited number of fictive components. The DOM is hereby quantified using the sum parameter DOC. Each of these fictive components represents a fraction of DOC with specific adsorption characteristics. During the adsorption analysis, the varying adsorption of the DOC fractions are defined by assigning them characteristic Freundlich isotherm parameters. To simplify the process, the exponent n is kept constant (e.g. n = 0.25), while different coefficients K_i can be employed to indicate the varying adsorption strengths. The non-adsorbable fraction is represented by setting K_i of one fraction to a very small value or to zero. Generally, selecting three to five fictive components is found to be effective for most practical scenarios. Once the number and isotherm parameters of the fictive components are defined, an IAST-based search routine is employed to determine the concentration distribution of the DOC fractions that best fits the measured DOC isotherm. The process of the ADSA is illustrated schematically in Figure 3. After completing the analysis, the DOC is characterized as a defined adsorbate mixture, meaning the isotherm parameters

and initial concentrations of the DOC fractions are known and can be utilized for further process modelling. The procedure of the ADSA is summarized in Figure 3.
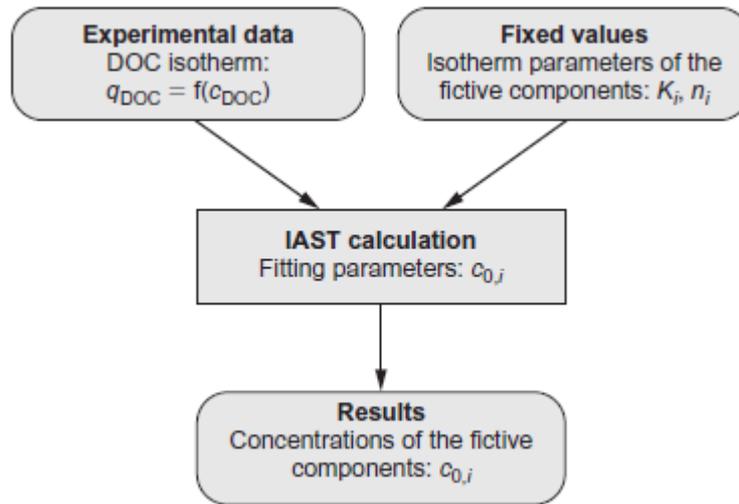

Figure 3 Calculation scheme of the adsorption analysis (Worch 2012).

The TRM relies on the findings from the ADSA, which are directly used as input data for calculating competitive adsorption between PFAS, iPMT, and DOM. To accurately represent this competitive adsorption with the IAST, adjustments are made to the single-solute isotherm parameters of the organic chemical. These corrected isotherm parameters are derived from experimental data on competitive adsorption (specifically, the organic chemical isotherm in the presence of DOM) through a fitting procedure based on the IAST. The outcome of this fitting process yields modified isotherm parameters for the organic chemical, enabling a more precise description of competitive adsorption when combined with the ADSA data. An overview of the TRM process is given in Figure 4.
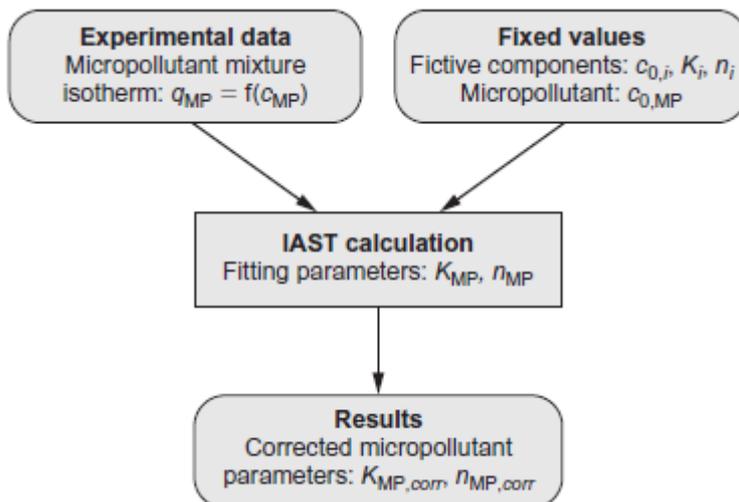

Figure 4 Calculation scheme of the tracer model (Worch 2012). A model run with DOM requires a DOC-isotherm as input for the ADSA as well as isotherm data of the adsorbate in the presence of DOM as input for the TRM.

2.5 Kinetic parameter estimation

2.5.1 Film diffusion

The film diffusion coefficient k_f is calculated using the Gnielski correlation (equation (14), Sontheimer at al 1988):

$$k_f = \frac{[1 + 1.5\,(1 - \varepsilon)]D}{d_p}\,[2 + 0.644\,Re^{1/2}Sc^{1/3}] \tag{14}$$

with d_p being the adsorbent particle diameter, D the adsorbate liquid phase diffusivity and ε the adsorber bed void fraction. The dimensionless numbers Re and Sc are determined by equation (15) and (16):

$$Re = \frac{\rho d_p v}{\mu} \tag{15}$$

$$Sc = \frac{\mu}{\rho D} \tag{16}$$

in which ρ is the liquid density, v the liquid phase interstitial velocity and μ the liquid phase viscosity. The adsorbate liquid phase diffusivity D is determined from a correlation by Hayduk and Laudie (1974) (equation (17)), with V_b being the molar volume of the chemical at the normal boiling point:

$$D = \frac{13.26\ 10^{-5}}{\mu^{1.14}V_b^{0.589}} \tag{17}$$

In case of a TRM run, the correlation by Worch (1993) (equation (18)) which uses the molar mass M of the adsorbate is employed:

$$D = \frac{3.595\ 10^{-14}T}{\mu M^{0.53}} \tag{18}$$

2.5.2 Surface diffusion

The surface diffusion coefficient D_s is determined by an empirical correlation (equation (19)) according to Sontheimer (1988), with ρ_a as apparent adsorbent density and SPDFR being the surface to pore diffusion flux ratio:

$$D_s = \frac{D\ \varepsilon\ c_{0,i}}{\tau\ \rho_a\ q_{0,i}} \cdot SPDFR \tag{19}$$

2.5.3 Pore diffusion

The pore diffusion coefficient D_p is related to the adsorbate liquid phase diffusivity D (equation (20)) and depends on the tortuosity τ of the adsorbent:

$$D_p = \frac{D}{\tau} \tag{20}$$

3 Introduction to the GUI and functionality of the DWTDT

3.1 Code availability

The DWTDT is published according to the FAIR principles, meaning that it will be findable, accessible, interoperable and reusable. In accordance with the PROMISCES data management plan, the code is available in a GitHub repository, which is linked to a Zenodo resource within the PROMISCES community page on Zenodo (https://doi.org/10.5281/zenodo.13982527).

3.2 Installation

The DWTDT requires the installation of Python (it was developed under Python 3.12.7, so python 3 is recommended). The user can check their python installation and version by entering the following command in the command window:

python –version

If Python is installed, the user will receive a notification with the version number. The next step is to download and save the 'Water_treatment_models' folder locally on the computer. The user should then navigate to the 'Water_treatment_models' folder using the following command in the command window:

cd <local path to 'Water_treatment_models' >

Following that, the user should enter the following command from the install.txt file:

pip install -r requirements.txt

This should automatically install all packages listed in the requirements.txt file.

3.3 Start

To start the model after installation from the 'Water_treatment_models' folder, the following command must be entered in the command window:

shiny run ShinyPy-GAC/app.py

A URL is displayed in the command window that can be opened in the browser. The user can now operate the model.

3.4 Input Data

3.4.1 Import and export of DWTDT projects

The DWTDT enables the user to save and reload projects as .json files. The tab of the GUI where the user can upload/ save project files is shown in Figure 5. All entries from 'Adsorbent Characteristics', 'Adsorber Specifications', 'Adsorbate Properties', 'Adsorption Properties' and 'Treatment Train' are saved in the .json file. The influent and effluent data from the 'Data'.xlsx file as well as the isotherms for the ADSA and TRM ('DOM' tab) are not saved and must be reuploaded. Under the 'Input Data' menu, users first enter all the information about the model input, while the 'Simulation' menu allows for the configuration of calculation settings.
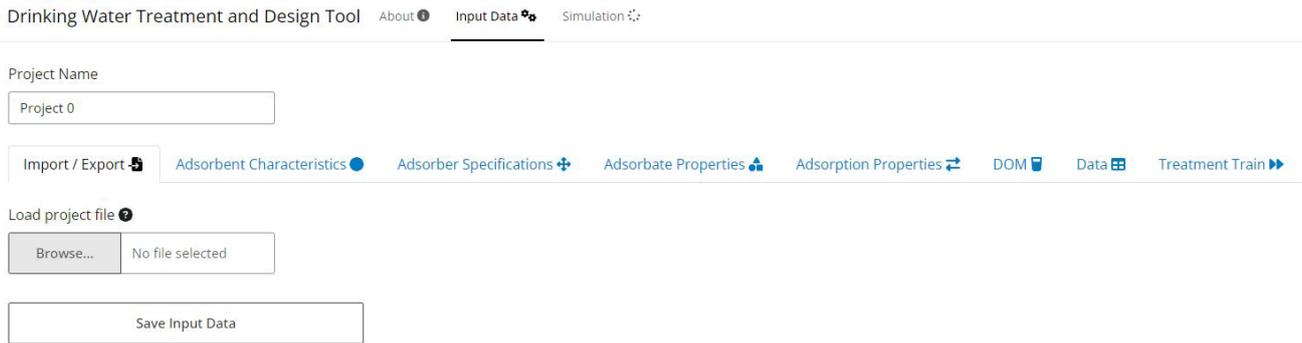
Figure 5 DWTDT menu with import/ export functionality

3.4.2 Adsorbent characteristics

Information on the adsorbent can be entered under 'Adsorbent Characteristics'. Each data entry must be confirmed using the 'add/update' button to be available for model runs. To revise the adsorber data, first select it from the right-hand menu ('Adsorbent Selection'), make modifications, and then confirm via 'add/ update'. The tab of the GUI that shows the settings for the adsorbent characteristics is shown in Figure 6.
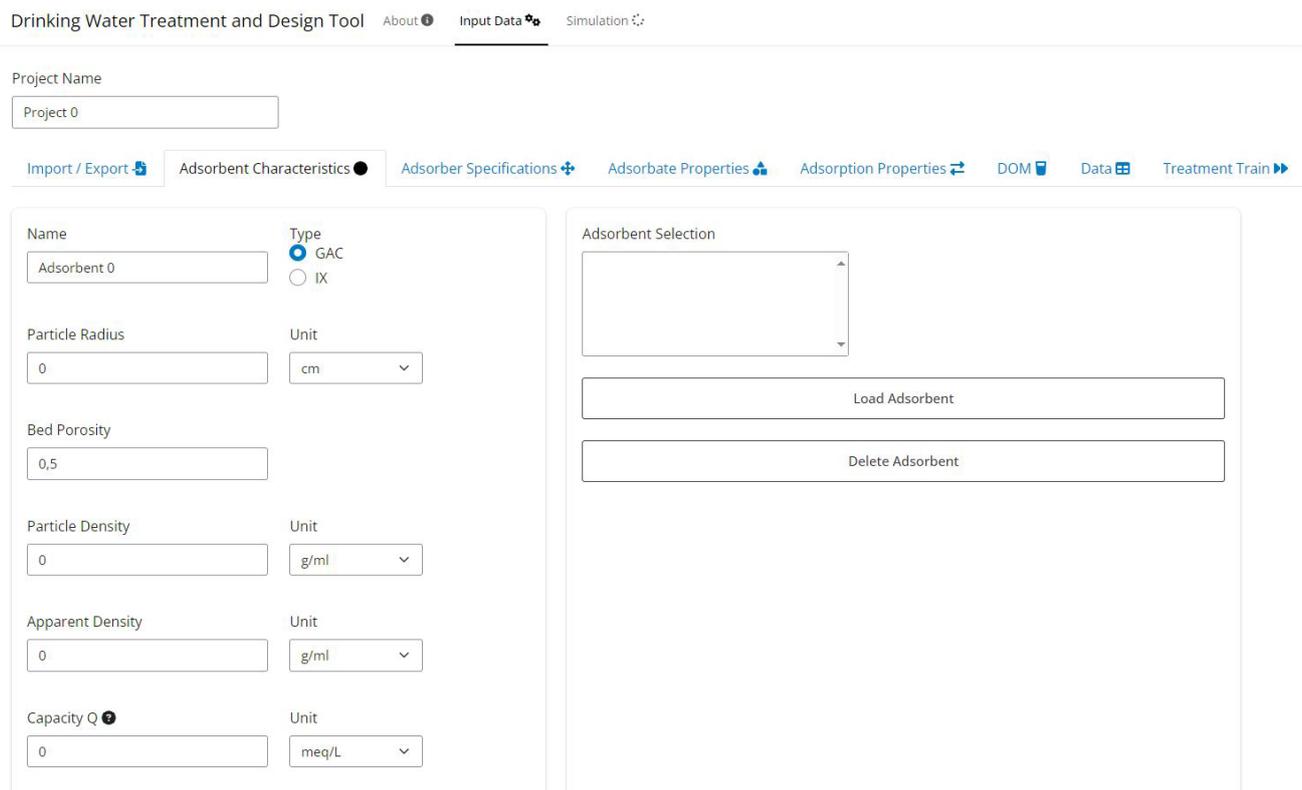

Figure 6 Adsorbent Characteristics menu of the DWTDT

3.4.3 Adsorber specifications

The data for the fixed-bed filter is stored under the 'Adsorber Specifications' tab (compare Figure 7). This includes, for example, the dimensions of the filter and the volume flow. This information is not adsorbent-specific and can be accessed for various adsorbents as part of a treatment train.

Figure 7 Adsorber specifications menu of the DWTDT

3.4.4 Adsorbate properties

All substance-specific data is stored under 'Adsorbate Properties' (compare Figure 8). The molar mass, the molar volume, and the density are used for the empirical correlations to calculate the diffusion coefficients. The sum formula is only required if calculating with the TRM, where the amount of substance is converted into mass of carbon (given as [mgC]). The valence is only needed if IX calculations are performed.

Figure 8 Adsorbate properties menu of the DWTDT

3.4.5 Adsorption properties

The actual isotherm data is entered under 'Adsorption properties', as shown in Figure 9. In the current version of the tool, only the Freundlich model can be used. When entering the K_i value, various units can be selected, while the Freundlich exponent n is dimensionless. The corresponding adsorbent and adsorbate must first be selected for input. To perform a calculation, it is essential that the adsorbent is stored under 'Adsorbent Characteristics' and the adsorbate is stored under 'Adsorbate Properties'. For the corresponding isotherm data to be accepted, it is necessary to confirm the entries using the 'Add/ Update Properties' button. Under the 'Advanced' settings, manual diffusion coefficients can be defined if these were determined using experimental data or are to be fitted to the breakthrough curve.

Figure 9 Adsorption properties menu of the DWTDT

3.4.6 DOM

If a calculation is to be carried out with the TRM, it is necessary to enter additional data under the 'DOM' menu item (compare Figure 10). To carry out an ADSA, a DOC isotherm (with DOC in mg/L as 'c' and adsorbent in g/L as 'm') must be entered. Only .xlsx file format is accepted. Any number of K_i values for the fictitious fractions can be specified in the 'Input K values' input field. Good results are usually achieved with 3-5 fractions. The Freundlich exponent n of the fractions and the mean molar weight can also be adjusted manually: the default values are '0.25' and '1000' in g/mol. After pressing 'Run ADSA', the calculation results are plotted and the IAST data is output in a table format. Following the ADSA, a TRM run can be carried out. This requires entering additional isotherm data of the organic chemical in the presence of DOM. The results of the ADSA are used as unmodified input to the TRM run. After the TRM calculation, it is possible to add the results of TRM and ADSA as inputs to the BTC simulation. It is important to know that this feature will overwrite any isotherm data of the modelled organic chemical inserted under 'Adsorption Properties'.

Figure 10 DOM input menu for ADSA and TRM

3.4.7   Data

Influent and effluent data is inserted under 'Data', as shown in Figure 11 The DWTDT accepts .xlsx file formats for this purpose. The specification of effluent data is optional, but the specification of influent data is essential. It is important to define the influent concentration at time 0. By default, the maximum simulation time is set to the last influent time. While influent data can be entered at any resolution, highly variable influents or very low concentrations can lead to long calculation times and numerical instability.

Figure 11 influent and effluent data

3.4.8   Treatment train

The 'Treatment train' menu enables the user to define different 'scenarios' for drinking water treatment trains (compare Figure 12). Within the DWTDT, the term 'Treatment Train' refers to one or a combination of fixed-bed adsorbers in series (with the same or different adsorbents equipped). The term 'scenario' describes the entire calculation example. This includes not only which adsorbents are used, but also which substances are modelled and at which influent concentrations. A 'Treatment train' can therefore be modelled in different 'scenarios'.

Each treatment step requires information about the adsorbent and the adsorber. The menu offers automatically all adsorber and adsorbent data entered in the previous menu steps. To guarantee compatibility, it is necessary that labelling of adsorbents is consistent within all menus of one project file. It is possible to add several adsorbers in series, although it should be mentioned that this option

can lead to long model runtimes. The menu options 'Water type' and 'Chemical type' refer to the empirical GAC-fouling correlations from the original EPA model (more information about these correlations can be found in (Mertz et al. 1999)). They can also be applied in the DWTDT for comparison purposes, or if no suitable isotherm data is available to carry out an ADSA and TRM run.

Figure 12 Treatment train menu of the DWTDT

3.5   List of input parameters

Abbreviation	Full name	Available units
D	diameter of adsorber	cm, mm, m
D	liquid phase diffusion coefficient	cm^2/s
D_P	pore diffusion coefficient	cm^2/s
D_S	surface diffusion coefficient	cm^2/s
K_i	Freundlich parameter	$(ug/g)/(ug/L)^n$, $(ug/mg)/(ug/L)^n$, $(mg/g)/(mg/L)^n$, $(mmol/mg)/(mmol/L)^n$
k_f	film diffusion coefficient	cm/s
L	length of adsorber	cm, mm, m
M	molar weight	g/mol
n	Freundlich parameter	
Q	capacity	meq/L
r	particle radius	cm, mm, m

T	temperature	C
T_b	boiling point	C
V	flow rate	L/h, L/min, m^3/h, m^3/min
V_b	molar volume	mol/L
e	bed porosity	
rho_a	adsorbate density	g/ml
rho_b	apparent density	g/ml, kg/L
rho_p	particle density	g/ml, kg/L

3.6 Simulation

The settings of the simulation are defined under 'Setup' (compare screenshot in Figure 13). The number of radial and axial collocation points can be defined here. The PSDM uses orthogonal collocation on finite elements as numerical solving method. Increasing the number of collocation points and/or finite elements increases the resolution of the calculation and can improve the accuracy of the model and prevent numerical instability. Numerical instability can be recognized, for example, by oscillation and extreme outliers. However, a high number of collocation points can also lead to very long calculation times (several hours). For practical applications, it is recommended to start with the default settings (or even a lower number) and to increase these gradually until the results look plausible or satisfactory.

The default for the number of finite elements is '1'. If numerical instability occurs, it can be helpful to minimize the axial collocation points and control collocation with the number of finite elements (e.g. 20-30 finite elements and low numbers (1-3) for axial and radial collocation) instead. This can be helpful for complex model runs in multi-solute systems. Clicking the 'Run Analyses' button will start the simulation. The user can view the results in a plot window and save as .png (example plot shown in Figure 14) and save all calculation results as .xlsx.
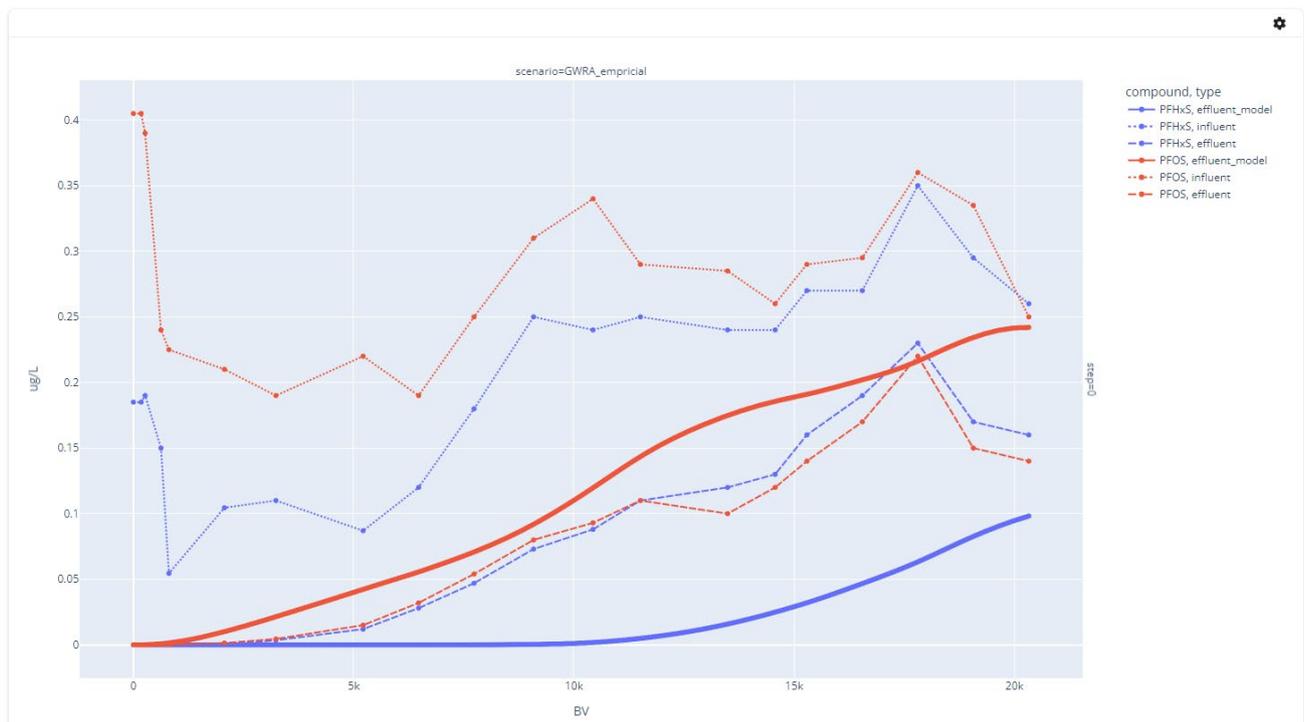
Figure 13 simulation setup

Figure 14: Example of a results output window. The user has the option to change the x-axis from bed volumes to time, deactivate or activate data series, and zoom in or out.

4 Calculation examples

4.1 Modeling example using the Tracer model

Figure 15 shows an example calculation (PFOS BTC in presence of DOM) for the first GAC adsorber at the pilot plant in Berlin-Tegel (DOC = 4.5 mg/L). The model was run using the TRM, building on an ADSA run with four fictive DOM fractions (TRM0-TRM3) with different K values (K = 1, 20, 40, 60 mg/g /(mg/L)^n and n = 0.25).

The TRM produces a realistic order of magnitude for the PFOS breakthrough behavior. Quantitatively, the model underestimates the time to 10 % breakthrough (t_{10}) by about 26 % (model: 48 days; measured: 65 days) and overestimates the time to 50 % breakthrough (t_{50}) by about 12 % (model: 170 days; measured: 190 days). These deviations are acceptable for a modeling approach without site-specific calibration, and they indicate that the TRM can reliably approximate adsorption dynamics in complex systems containing DOM.

Improvement of the model could be achieved by calibrating diffusion coefficients to the measured effluent data or incorporating experimentally derived kinetic parameters. However, such refinements require additional experimental or computational effort. For practical applications, the model already provides valuable preliminary insight into PFOS retention and expected breakthrough behavior.

To verify the robustness and transferability of the TRM, further validation studies should be conducted using different adsorbates (e.g., other PFAS or other iPMT) and water matrices with varying DOM concentrations and compositions. Such studies would help evaluate the sensitivity of the model to site-specific water chemistry and support its broader applicability for predictive modeling of GAC filter performance.
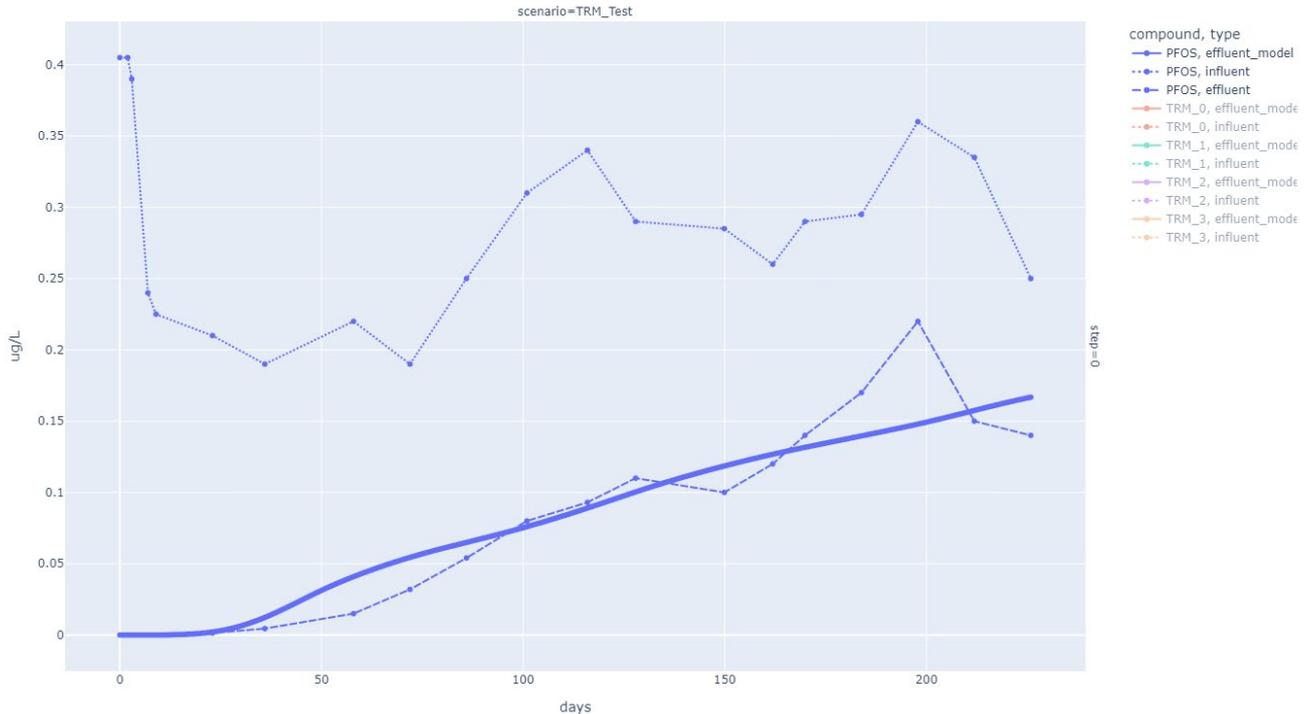
Figure 15 Removal of PFOS by GAC in the presence of DOM, modelled using the TRM. ADSA run with K = 1, 20, 40, 60 mg/g /(mg/L)^n and n = 0.25.

4.2 Modeling examples using the PSDM with a pseudo-single-solute equilibrium approach

In addition to the TRM described above, the DWTDT also allows modelling of BTCs using the PSDM and a simplified pseudo single-solute approach. This approach requires only the isotherm of the target PFAS or iPMT in the relevant water matrix, without separate DOC-isotherms or data on other competing adsorbates. In this method, competitive adsorption effects caused by DOM and co-occurring other adsorbates are implicitly represented in the empirical pseudo single-solute isotherm (Worch 2012).

In the simplest form, as demonstrated here, the calculation can even be performed using a single-point Freundlich isotherm. Figure 16 and Figure 17 show example model runs for the removal of short-chain PFAS—PFBS and PFBA—using the same GAC and water matrix as in the Berlin-Tegel pilot column. The single-point Freundlich isotherm constants applied were K_{PFBS} = 1.2242 (µg/g)/(L/µg)^n and K_{PFBA} = 0.2460 (µg/g)/(L/µg)^n with n = 0.45, following the recommendations of Burkhardt et al. (2022).

The model prediction for PFBS shows a steeper breakthrough curve compared to the measured data. This suggests that kinetic limitations or competitive effects not fully represented in the pseudo single-solute model may play a role. The model underestimates the t_{50} by approximately 20% (model: 60 days, data: 75 days) In contrast, PFBA, having a lower Freundlich constant, shows significantly earlier breakthrough, which is consistent with its lower hydrophobicity and weaker affinity for GAC.

While the slope of the model BTC for PFBA corresponds well with the measurement data, the BTC shows an overall earlier onset, which leads to an underestimation of the t_{50} by 38 % (model: 25 days, data: 40 days), indicating that adsorption capacity is underestimated by the input isotherm data. At

this point, an improvement could probably be achieved if the input isotherm were determined using more data points.

Overall, despite its simplicity, the pseudo single-solute approach provides reasonable first estimates of breakthrough behaviour and can be valuable in early-stage design or screening studies when limited data are available.
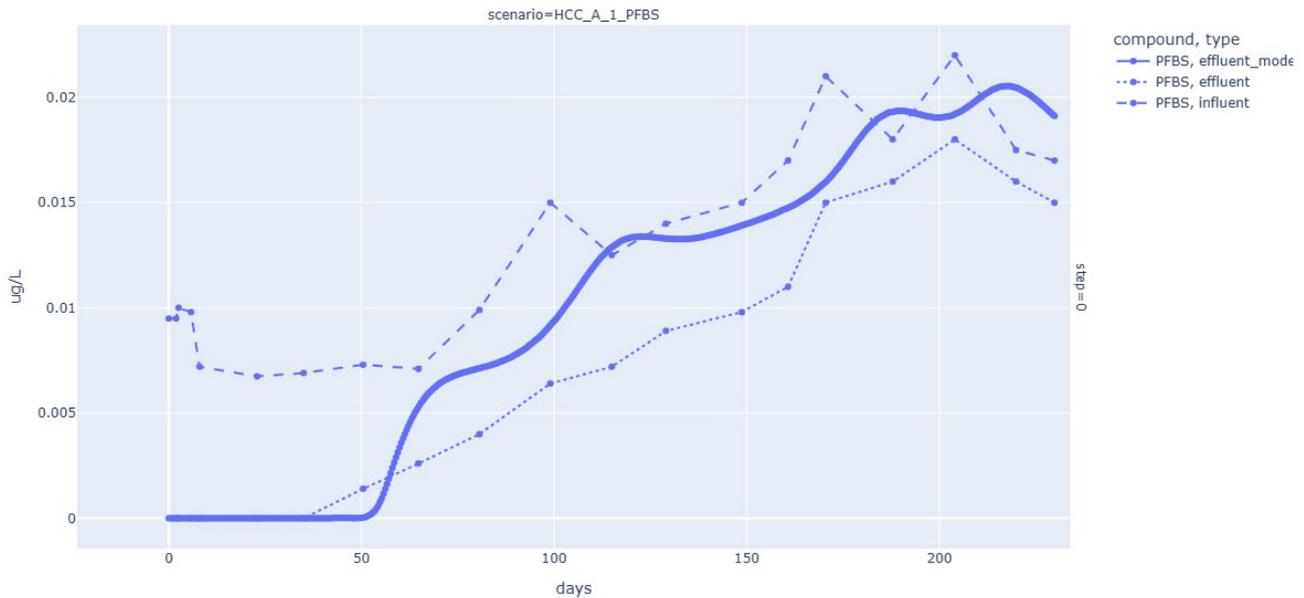

Figure 16 Removal of PFBS by GAC in presence of DOM, PSDM simualtions using a pseudo-single-solute equilibriumapproach (Freundlich isotherm (Equation (1)), K_{PFBS} = 1.2242 $(\mu g/g)/(L/\mu g)^n$, n = 0.45).
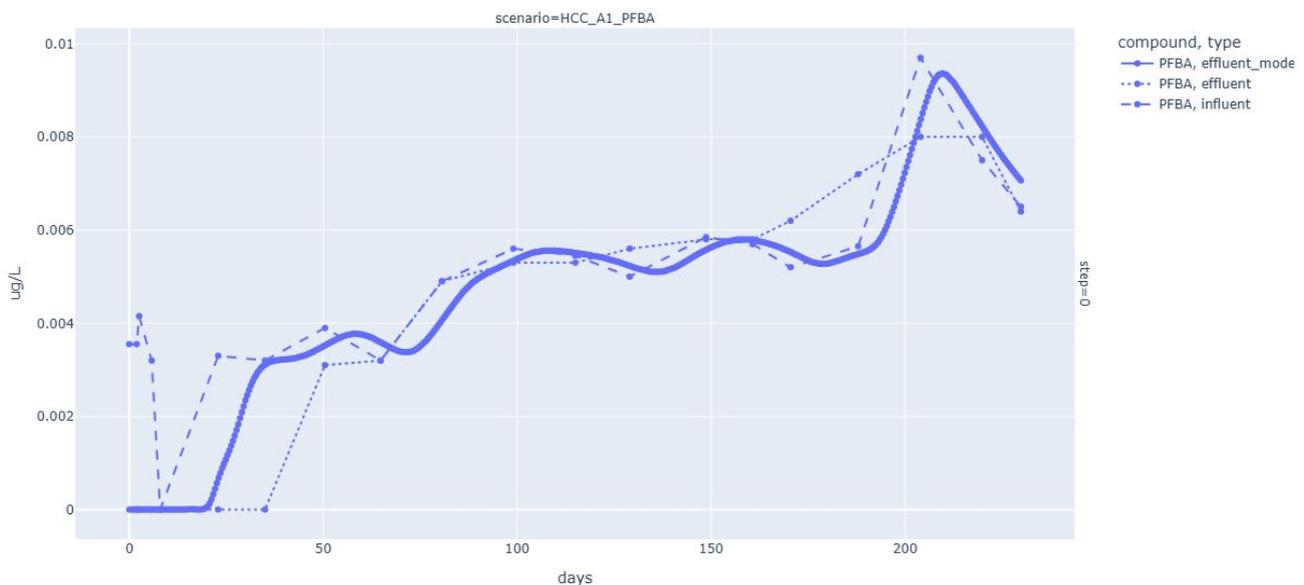

Figure 17 Removal of PFBA by GAC in presence of DOM, PSDM simulations using a pseudo-single-solute equilibrium approach (Freundlich isotherm (Equation (1)), K_{PFBA} = 0.2460 $(\mu g/g)/(L/\mu g)^n$, n = 0.45).

5 Conclusions

The calculation examples demonstrate that both the TRM and the pseudo single-solute approach can effectively describe the adsorption behavior and breakthrough of PFAS in the investigated full-scale GAC filters in Berlin-Tegel.

The TRM, which explicitly considers DOM fractionation and adsorptive competition, provides a more mechanistic and transferable framework for simulating adsorption in complex water matrices. While the TRM requires more input data and computational effort, it delivers good agreement with measured data and offers options for further refinement through site-specific calibration.

The PSDM using a pseudo single-solute equilibrium approach, on the other hand, offers a simplified and practical alternative when detailed adsorption data are not available. Although it cannot fully capture competitive effects or kinetic limitations, it produces reasonable approximations of breakthrough behavior and can be particularly useful for initial assessments or comparative studies. However, a mechanistic approach or even transferability to other locations is not given.

Together, these two modeling strategies complement each other within the DWTDT framework: the TRM supports detailed investigations and optimization, while the PSDM using a pseudo single-solute approach allows rapid evaluation with minimal data input.

To further enhance the predictive robustness of the DWTDT, additional validation across a broader range of PFAS (including short- and long-chain species) and other iPMT (e.g. non-anionic) as well as different GAC types and water chemistries is recommended. Such comprehensive testing would strengthen the applicability oft he DWTDT for both research and practical design of adsorption-based treatment systems.

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