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Modeling Stormwater Loads of Contaminants of Emerging Concern: Literature Review and Recommendations

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Executive Summary

The Regional Monitoring Program for Water Quality in San Francisco Bay (RMP) has been expanding the use of modeling to address questions related to the management of contaminants of emerging concern (CECs). CECs – a diverse group of substances with different sources, chemical properties, and fate – wash into stormwater from a variety of ongoing sources. CECs vary widely in terms of their sources, how frequently they are detected, and the potential risks they pose. They also vary in terms of the properties that affect their fate and transport in aquatic environments.

The purpose of this report is to review literature on the modeling needs and available options for early estimation of annual stormwater CEC loads. Ideal modeling options should be inexpensive and usable with the limited monitoring data available in the near term. Numerical models for the simulation of CEC loads can be grouped into three general categories: spatially distributed models, fugacity models, and data-driven approaches. The Regional Watershed Spreadsheet Model (RWSM) and the Watershed Dynamic Model (WDM) are spatially distributed models developed by the RMP. For example, the RMP has used the RWSM to simulate annual PCB loads at a regional scale and the model can be extended to CECs if stormwater pollutant concentrations are provided for a group of land features. The WDM currently estimates flows and sediment, and is being further developed to estimate PCB and mercury loads for watersheds that drain to the Bay. Although the WDM can estimate pollutant loads at a daily time step, the model requires a large number of calibration parameters. Fugacity models are powerful tools used to estimate the fate and transport of chemicals in various environmental compartments, including air, water, sediment, and soil. Fugacity models require input data related to chemical properties (e.g., partition coefficients, degradation rates), emission rates, and environmental concentrations for specific contaminants, which may not always be readily available, especially for CECs. Data-driven approaches, for example statistical techniques and machine learning, can learn from historical data to establish relationships between input variables (e.g., land use, flow, weather pattern) and contaminant loads. However, data-driven approaches require substantial amounts of training data to derive such relationships.

The recommendations of this review are: 1) approach CEC load modeling based on specific CEC groups where possible, or on an individual chemical basis where necessary; 2) develop conceptual models to understand key factors influencing the loads of CECs in stormwater before initiating CEC load modeling; 3) use a hybrid data-driven and spatially distributed approach for regional stormwater CEC load estimation; 4) for those CECs for which the RMP intends to develop improved load estimates, implement long-term monitoring designed to inform load modeling. The hydrologic outputs from the RWSM (or WDM) can be used in concert with statistical manipulations of available CEC data to provide estimates of CEC loads in stormwater given the characteristics of Bay Area watersheds and the limited monitoring data available in the near term. When more site characterization data become available alongside better GIS data, and data at fixed stations with flows have been used to generate load estimates, it should be possible to build out a calibrated RWSM for individual CECs or CEC groups.

1. Introduction

Contaminants of emerging concern (CECs) – a diverse group of substances with different sources, chemical properties, and fate – wash into stormwater from a variety of ongoing sources. Previous CECs stormwater monitoring studies provided evidence that stormwater is a major pathway for CECs to enter receiving waters like San Francisco Bay (Gasperi et al., 2014; Masoner et al., 2019; Saifur & Gardner, 2021). To compare CEC loads from the stormwater pathway with loads from other pathways (e.g., wastewater, atmospheric deposition), both relative magnitude and the level of uncertainty are necessary information. Comparing loads of individual CECs from the stormwater pathway to loads from other pathways is a high priority near-term question for the Regional Monitoring Program for Water Quality in San Francisco Bay (RMP). Table 1 identifies how this modeling is being designed to respond to management questions identified by two RMP workgroups: Sources, Pathways, and Loadings (SPL) and Emerging Contaminants (EC).

This report focuses on the modeling needs and available options that can be used to provide stormwater CEC load estimates at the screening level and includes the following components:

1. review of existing modeling options and approaches for estimating annual stormwater CEC loads;
2. examination of the suitability of modeling options for early and inexpensive estimation of annual stormwater CEC loads given the characteristics of the Bay watersheds and the relatively limited monitoring data available in the near term; and
3. recommendations for modeling capacity development and monitoring design to support screening-level stormwater CEC load estimation in the near term.

Table 1. Study objectives and questions relevant to RMP SPL and EC workgroup management questions.

SPLWG Management Question	ECWG Management Question	Study Objective	Example Information Application
MQ1. What are the loads or concentrations of pollutants of concern from small tributaries to the Bay?	MQ2: What are the sources, pathways, and loads leading to the presence of individual CECs or groups of CECs in the Bay?	Examine the suitability of different modeling options. Select inexpensive, early model options given available data.	Provide a suitable list of model options and approaches for early stormwater load estimation. Provide the appropriate model options with consideration of data availability in near future.

In embarking on this effort, it is crucial to remember that, in some cases, CECs – and even CEC classes like PFAS – cannot be monitored and modeled as if they were a homogeneous group.

Because CECs are a large and diverse group of chemicals, we will not be able to model all of them. CECs vary widely in terms of their sources, how frequently they are detected, and the potential risks they pose. They also vary in terms of the properties that affect their fate and transport in aquatic environments, for example volatility, reactivity, solubility, and adsorption. However, it is possible to group CECs into classes with similar characteristics, and model these classes as if they were one constituent, and then make deductions about individual chemicals. Further, the modeling may require a “read across” approach, where information from a known substance (similar in structure or properties) is used to predict the properties or potential effects of another substance for which there is limited data. In terms of modeling CECs, this allows us to leverage existing knowledge to fill gaps in our understanding.

In this report we review the different modeling strategies and options that could be employed for different CECs and provide recommendations for estimating stormwater CEC loads. Our review of the literature provided few examples of urban stormwater CEC load estimates, suggesting that these applications are relatively novel. We examined the suitability of different models for Bay Area stormwater given limited data availability in the near term and the requirement to answer the specific question: ‘How does the local watershed runoff load to San Francisco Bay compare to loads from other pathways (for example inflows from the Delta and wastewater discharges)?’ Finally, we provide recommendations for model selection and monitoring to support early, inexpensive order-of-magnitude load estimates for stormwater for comparison to other CECs pathways.

This is an initial step of the CECs modeling element that will inform the stormwater CECs integrated monitoring and modeling approach that is under development by the RMP.

2. Load Modeling Methods

Modeling of watershed contaminant loading to receiving water bodies is an important tool for effective water quality management. This section provides a general introduction to different types of methods used for watershed contaminant load modeling. These fall into three general categories: spatially distributed models, fugacity models, and data-driven approaches. Most load modeling methods also rely on underlying conceptual models that address both the watershed and contaminant-specific sources and characteristics.

This section begins with brief summaries of models that are the core of SFEI’s current watershed modeling program. It then moves on to describe other types of models and tools that can also be used to estimate contaminant loads.

2.1 Spatially Distributed Models

The RMP's watershed contaminant modeling program has focused on spatially distributed models. These models capture the interactions between various hydrological and environmental factors, such as precipitation, evaporation, infiltration, runoff, streamflow, as well as erosion, sediment deposition, contaminant build-up, wash-off, and transport. These models provide a comprehensive assessment of contaminant loading mechanisms and can be calibrated and validated using field measurements. However, good calibration of spatially-distributed models can require large amounts of data, which makes modeling CECs challenging.

Two main types of hydrological models commonly employed are semi-distributed and distributed models. Two semi-distributed models, the RWSM and WDM (described below), have been developed by the RMP to simulate the hydrology and contaminant loads of Bay Area watersheds. Below, we describe four well-known models that have been widely used in the United States for TMDL development and water quality investigations. Other models exist, but are not mentioned here. Most of these are limited to use in research or have a much smaller user base.

Semi-distributed Models

Semi-distributed models discretize a watershed into small homogeneous spatial units defined as Hydrologic Response Units (HRUs). HRUs are areas with similar land features, slope, and soil characteristics. HRUs are an effective approach for simulating and analyzing water quality within a watershed. Each HRU is treated as an individual unit within the model, allowing for a more detailed representation of spatial variations in water quality processes. The models simulate various water quality parameters, including contaminant concentrations and sediment transport, by considering the unique characteristics of each HRU. By accounting for factors such as land features, hydrological connectivity, and contaminant sources, these models can provide insights into the transport of contaminants within a watershed.

Regional Watershed Spreadsheet Model

The San Francisco Bay regional watershed spreadsheet model (RWSM) was developed within the RMP to estimate Bay-wide local watershed pollutant of concern (POC) loads of copper, polychlorinated biphenyls (PCBs), and mercury. The RWSM provides estimates of relative load contributions from individual watersheds around the Bay to help identify high load-generating watersheds (Jing Wu et al., 2017). The model was also envisioned to provide information for prioritizing high-leverage watershed areas for management.

The RWSM is structured with two stand-alone empirical models; the hydrology model and the pollutant model. The hydrology model uses runoff coefficients based on land feature, soil, and slope combinations to estimate annual runoff from a watershed and can serve as the basis for any pollutant model . The pollutant model is essentially a “concentration map” that is driven by the hydrology model. Pollutant loads are estimated as a function of runoff volume and a stormwater pollutant concentration for a group of land features that are unique to each pollutant. The RWSM can provide an estimate of flow, concentration, and load for any area of interest as long as the user can provide a GIS boundary for that area. The hydrology model provides an accurate estimate of annual average flow and estimates of loads with uncertainty bounds but there is no provision inside the model for estimating flow or loads for any other time period (daily or hourly for example).

The RWSM has been calibrated to eight (PCBs) and six (mercury) well-sampled watersheds of the San Francisco Bay Area. One challenge of the application of the model is the selection and grouping of land features. The selection of land features may have a large influence on the resulting regional loads. To extend the application of the model for CECs, monitoring data for well-sampled watersheds in the region would be required to derive stormwater pollutant concentrations for a group of land features. There are plans for the model to be recalibrated for flow using a new calibration period (1991-2020) based on the most recent PRISM data release.

The Watershed Dynamic Model (In Development)

A new dynamic regional watershed model, the watershed dynamic model (WDM), currently focused on PCBs and mercury loads, is being developed by SFEI (Zi, McKee, et al., 2021; Zi et al., 2022). This regional model effort currently estimates flows and sediment, and is currently being updated to estimate PCBs and mercury concentrations and loads for watersheds that drain to the Bay. The WDM is based on the LSPC (Loading Simulation Program in C++) modeling platform (Tetra Tech, 2017). LSPC has also been used by the San Mateo and Santa Clara countywide water programs to simulate mercury and PCB loads (Paradigm Environmental, 2019).

LSPC simulates watershed hydrology and water quality, and allows the integrated simulation of land and soil contaminant runoff processes with in-stream hydraulic and sediment-chemical interactions. Each sub-watershed of a LSPC model consists of a combination of different HRUs. The hydrologic, sediment transport, and contaminant accumulation and wash-off processes are simulated at the HRU level and then aggregated at the sub-watershed scale. Data for a simulation include land features, topography, geology, hydrologic soil groups.

For hydrophilic contaminants with an affinity for sediment or particulate matter, LSPC can simulate contaminant export from land surfaces in proportional to sediment flux. Here, we must provide a potency factor in mg/kg. Emerging contaminants with an affinity for sediment, and which have been detected at levels in Bay sediments that trigger concern include indole, 4-methylphenol, and 4-n-Nonylphenol (Heberger et al., 2020). Other CECs are hydrophilic, i.e., have an affinity for water, so a potency factor approach may not accurately represent their transport. Dissolved pollutants can be simulated using a land-use-based runoff concentration, similar to an Event Mean Concentration (EMC).

The WDM dynamically simulates rainfall-runoff and sediment generation processes for three sediment classes (sand, silt, and clay) at a daily time scale for the water years 1995-2020 (Zi, McKee, et al., 2021; Zi et al., 2022) . As PCBs and mercury are mainly sediment-associated, they will be simulated in the model based on a sediment potency factor (e.g., mass of PCBs [ng] per gram of sediment). Therefore, the quality of the simulations is dependent on the quality of the estimates of the sediment transport parameters and the potency factors associated with a contaminant. Currently, potency factors are being estimated by using PCB concentrations of 1,361 sediment and soil samples taken between 1996-2016 around the Bay Area.

The hydrological models and numerical tools described in the following sections are additional available options but have not been used by the RMP to simulate water quantity and quality at a regional scale.

The Stormwater Management Model

The Stormwater Management Model (SWMM) is a computational tool used for simulating runoff quantity and quality in both single events and continuous scenarios (Rossman & Huber, 2016). It operates on a discrete time basis and divides a watershed's domain into sub-catchments. These sub-catchments have a maximum storage capacity defined by the maximum depression storage for both pervious and impervious areas. Surface runoff is generated when the water depth within a reservoir exceeds the depression storage capacity, and the outflows are estimated using Manning's equation. To facilitate the movement of excess surface runoff, SWMM incorporates a comprehensive network of pipes, culverts, channels, pumps, and treatment devices. Precipitation, air temperature, evaporation, and wind speed are the meteorological data required for a simulation. The data are represented by records at a sub-daily or daily time step. SWMM is best suited for urban hydrology and surface runoff collection networks.

In the context of continuous simulation, SWMM considers changes in surface runoff quality by accounting for contaminant buildup and washoff processes. For instance, the model can estimate the accumulation of contaminants on impervious areas during dry weather preceding a storm. Contaminant buildup is modeled to accumulate on predefined land features, following an exponential growth curve that asymptotically approaches a maximum limit. During wet weather periods, SWMM accounts for contaminant washoff from specific land features. The wash-off process can be described using different approaches, such as an exponential function, a rating curve, or an event-mean concentration.

As with other semi-distributed models, the data and computational demands for a SWMM model can be substantial. The pollutant build-up and wash-off functions can be very useful when seeking to model contaminants coming from products in the outdoor urban environment. SWMM has been used in the Bay Area by SFEI to simulate baseline flow and PCB loads and to estimate load reductions associated with green infrastructure implementation (https://greenplanit.sfei.org/) (Wu et al., 2018; Zi, Kauhanen, et al., 2021). In these applications, local-scale calibrations were done but SWMM has not been used for regional-scale load estimation.

The Soil and Water Assessment Tool (SWAT)

The Soil and Water Assessment Tool (SWAT) is a computational model that uses soils, climate, and land use data to simulate the movement of water, sediment, nutrients, and pesticides within a watershed (Arnold et al., 2012). SWAT divides a watershed into different sub-basins, each having a unique stream or channel segment. SWAT generates surface runoff when the amount of water that enters an HRU exceeds the rate of infiltration. Then, it routes surface runoff through the channel network using a variable storage routing method. Sediment yield is computed from a Modified Universal Soil Loss Equation, which is a function of the runoff volume, the peak runoff rate, HRU area, soil erosion factors, slope, vegetation cover, and land management factors. SWAT has predicted annual and monthly sediment yields relatively well across several studies (Gassman et al., 2007); however, model performance decreases at the daily time scale. SWAT has been applied to urban environments and can consider directly connected impervious areas (Her et al., 2017), but it lacks routines to simulate surface drainage systems (e.g., pipes, culverts). SWAT is more appropriately suited for simulating sediment transport in large, rural agricultural watersheds.

For water quality applications, SWAT is commonly used to simulate the transport of nitrogen, phosphorus, and agricultural pesticides. The pesticide module can be adapted to simulate a wide range of contaminants. When a pesticide is applied to an HRU, some fraction may be intercepted by the plant foliage while the remaining fraction reaches the soil. During a precipitation event on a given day, SWAT computes the amount of agricultural pesticide washing off plant foliage and onto the soil surface. In the soil, the agricultural pesticide degradation is calculated by a first-order kinetic process that is a function of the initial amount of agricultural pesticide and a degradation coefficient in the soil. An agricultural pesticide may enter the stream network through inflow and resuspension and diffusion of particles from the sediment layer. SWAT partitions a pesticide into particulate and dissolved phases as a function of the pesticide’s partition coefficient and the suspended solid concentration.

Distributed Models

A distributed hydrological model explicitly considers the spatial heterogeneity within a watershed by discretizing the watershed into smaller computational units, such as grid cells or segments. It enables the assignment of specific water quality parameters to individual grid cells or segments, facilitating assessment of contaminant transport, transformation, and fate within the watershed. Distributed models are particularly useful for examining the impacts of point source discharges or other localized pollution sources on water quality at different locations within the watershed. However, it is worth noting that the increased spatial resolution and complexity of a distributed hydrological model come at the cost of computational requirements. Running a distributed model requires more extensive data inputs, including detailed topographic information, land cover data, and spatially distributed meteorological data. Additionally, the increased number of computational units and the incorporation of more intricate water quality processes can result in longer simulation times and higher computational demands.

VELMA is an example of a distributed model that integrates a surface hydrology model with a terrestrial biochemistry model (McKane et al., 2022). VELMA spatially distributed modeling framework that integrates hydrological processes, nutrient cycling, vegetation dynamics, and land management practices. It simulates the interactions between climate, topography, land cover, soil properties, and management practices to estimate water quantity, water quality, and ecosystem responses within a watershed. It captures the complex interactions among hydrological processes, nutrient cycling, and vegetation dynamics, providing a more realistic representation of watershed functioning. The model provides spatially explicit outputs, enabling the identification of sensitive areas, hotspots, and vulnerable ecosystems within a watershed. It requires detailed and site-specific input data, which may be challenging to obtain, especially for regional load estimation. This spatially distributed hydrological model works well in rural watersheds, but has challenges in urban settings due to the spatial discontinuity caused by impervious surface and storm drain network (e.g., pipe diameters, pipe lengths).

MIKE SHE (DHI 2024) is another well-known distributed watershed model and is capable of simulating pollutants and chemistry. It is based on the *Système Hydrologique Européen*, originally developed by French researchers in the 1980s, and is now a commercial product of the for-profit Danish Hydraulic Institute (DHI), and subscription costs are several hundred dollars per month. It is capable of 1D, 2D, and 3D modeling, and has been used in a variety of applications on every continent, including in the US for development of TMDLs for mercury and nutrients.

Distributed hydrological models provide a detailed understanding of the hydrological response and contaminant loading patterns within a watershed. However, their computational demands, data requirements, and calibration difficulties can be substantial, requiring extensive input data and expertise. Representing contaminant transport processes in the highly urbanized Bay Area is also a challenge for spatially distributed models.

2.2 Fugacity Models

Fugacity models are powerful tools used to estimate the fate and transport of chemicals in various environmental compartments, including air, water, sediment, and soil. Fugacity models have been crucial to understand the transport and distribution of persistent organic pollutants at steady state conditions (Rodgers et al., 2023). Examples include QWASI (Quantitative Water, Air, Sediment Interaction) (Mackay & Diamond, 1989) and MUM (Multimedia Urban Model) (Rodgers et al., 2023).

Fugacity models are based on the principle of fugacity, which is the tendency of a chemical to move from one environmental compartment to another. Fugacity models use mathematical equations and algorithms to simulate the dynamic exchange of chemicals considering factors such as chemical properties, environmental conditions, and compartment characteristics. These models estimate the distribution and fluxes of chemicals over time among environmental media such as air, soil, and water.

One limitation of fugacity models is simplified assumptions about chemical behavior and contaminant transport processes. The results from fugacity models provide an average estimation of contaminant behavior within compartments (steady state assumption) and may not capture spatial and temporal variations at finer scales. Steady state (equilibrium) conditions are generally not present in dynamic stormwater systems. Fugacity models require input data related to chemical properties (e.g., partition coefficients, degradation rates), emission rates, and environmental concentrations for specific contaminants, which may not always be readily available, especially for CECs.

Fugacity models provide a simplified yet valuable approach to estimate the fate and transport of chemicals in different environmental compartments. While they offer versatility and chemical-specific estimations, they also come with limitations regarding assumptions, input data requirements, spatial and temporal resolution, and addressing the dynamic processes in stormwater transport. The lack of detailed hydrological processes limits the application of fugacity models in large and heterogeneous watersheds.

2.3 Data-Driven Approaches

Data-driven approaches, including statistical techniques and machine learning approaches, have been widely used in recent years for estimating contaminant loading in watersheds.

Statistical Techniques

Statistical techniques rely on statistical relationships between contaminant loads and easily measurable parameters, such as land use, population density, or impervious surface area. These models often utilize regression analysis to establish relationships between contaminant loads and the explanatory variables. Traditional regression techniques, such as linear regression or multiple linear regression, are commonly used for contaminant loading estimation.

One example of a statistical technique is the USGS SPARROW model (Schwarz et al., 2006). It combines regression analysis and hydrological principles to estimate nutrient and suspended-sediment loads and identify their spatial distribution at a regional watershed scale. It incorporates spatially explicit information on various watershed attributes, such as land use, hydrology, topography, soil properties, and contaminant sources. The model uses regression equations to relate these attributes to measured water quality data and flow data, allowing for the estimation of contaminant loads across the entire watershed. SPARROW uses simplified assumptions to represent complex watershed processes. For example, it assumes that contaminant sources and transport processes are constant over time and that relationships between explanatory variables and contaminant loads are also constant. These assumptions may not hold true in dynamic and changing watersheds, leading to potential inaccuracies in load estimates. It focuses on statistically relating watershed attributes to monitored water quality data. Calibrating the SPARROW model requires extensive datasets. The availability and quality of calibration/validation data greatly influence the accuracy of model results.

LOADEST is another widely used model to estimate contaminant loads in rivers and streams (Runkel et al., 2004). It combines statistical analysis with empirical relationships to estimate contaminant loads in large, non-urban watersheds. By employing a range of statistical techniques, including regression analysis, flow-weighted approaches, and seasonal adjustments, contaminant loads at specific monitoring sites can be estimated. LOADEST relies on historical water quality and flow data, making it suitable for situations where detailed process-based information is lacking. The model utilizes rigorous statistical techniques to establish relationships between contaminant concentrations and streamflow, improving the reliability of load estimates. The accuracy of load estimation heavily relies on the availability and quality of historical water quality and flow data. LOADEST assumes stationarity in contaminant concentration-flow relationships, which may not capture temporal variation or spatial heterogeneity within a watershed, and it is a purely empirical model that does not explicitly consider the underlying physical and chemical processes involved in contaminant transport.

Regression models are relatively simple to interpret and computationally efficient. These approaches learn from historical data to establish relationships between input variables and contaminant loads. The accuracy of regression models depends heavily on monitoring data quality, representativeness, and abundance. The relationships derived from statistical methods may not reflect the physical or chemical processes of the transport and fate of contaminants, and the interpretation of those derived relationships should be guided by conceptual models. Statistical methods lack accuracy in capturing complex contaminant transport processes and can be limited in their applicability to diverse watershed conditions.

Machine Learning Approaches

Machine learning approaches to predict watershed contaminant loads involve using computational models to learn patterns and relationships in data. These purely data-driven approaches have become more popular in watershed load estimation in recent years. Several machine learning approaches have been applied to estimate watershed contaminant load, such as Artificial Neural Networks (ANNs), Random Forest (RF), and Support Vector Machines (SVM).

Machine learning approaches for contaminant loading estimation require comprehensive and accurate input data, including contaminant measurements, hydrological data, land use and /land cover data, soil data, and climate data. They are particularly effective when sufficient data are available. Insufficient or poor-quality data can impact the performance and reliability of the models. Machine learning approaches are often considered as black box models since they lack interpretability compared to simpler models. It can be difficult to understand how the method arrives at its predictions and extract meaningful insights in terms of understanding of the contaminant transport processes from the modeling process.

Artificial Neural Networks (ANNs)

ANNs are used in contaminant loading estimation due to their ability to capture complex nonlinear relationships between input variables and contaminant loads (Kim et al., 2012; Lee et al., 2010). ANNs can learn from historical data and generalize the learned patterns to predict contaminant loads in unmeasured conditions. In ANNs, artificial neurons receive inputs (e.g., rainfall, land use, and soil data) and process them to produce an output (e.g., predicted load or concentration). These neurons are organized into layers, with each layer performing a specific task. By repeatedly comparing its predictions to the actual pollution levels in the training data, the ANN adjusts the weights to minimize the errors and make better predictions over time.

Once the ANN is trained, it can take new input data (e.g., rainfall, land use) and use the learned weights to produce a prediction for pollutant loads in the watershed. ANNs can find complex relationships and make predictions even when the exact rules behind them are unknown. However, ANNs can be data-intensive, requiring substantial amounts of training data, and may suffer from overfitting. Highly complex ANNs with numerous layers and parameters can be prone to instability and sensitivity to small changes in the data or network configuration.

Random Forest (RF) Models

RF modeling is an ensemble learning method that combines multiple decision trees to make predictions. It has been used to predict contaminant concentrations and load for various watershed conditions (Basu et al., 2023; Behrouz et al., 2022; Jimeno-Sáez et al., 2022). The Random Forest algorithm takes a random subset of the training data and creates a decision tree. The decision trees are built by repeatedly dividing the data based on the values of the input variables (e.g., land use, flow, weather pattern), trying to find patterns that can predict the contaminant load (high concentration, low concentration). Each tree in the Random Forest independently predicts the load based on its set of rules. The Random Forest combines the predictions of all the decision trees to average or take a majority vote of the predictions from all the decision trees. It can handle a large number of input variables and capture variable interactions effectively.

RF models are relatively robust to outliers and noise in the data. However, the results from RF models can be challenging to interpret compared to simpler models like linear regression. The ensemble nature of RF makes it difficult to understand the exact relationships between the input variables and the predicted load. RF models are sensitive to several parameters, such as the number of trees, number of decision nodes, and the number of features considered at each split. Choosing the optimal parameter values requires careful experimentation and can be difficult. If the dataset used for training the RF model is imbalanced, meaning it contains a significant imbalance between the contaminant load levels, the model may have a bias towards the majority class. RF models may struggle with making load predictions outside the range of the observed data. The model may not perform well in predicting load values that are significantly different from those present in the training data.

Support Vector Machine (SVM)

An SVM is a supervised learning algorithm that finds an optimal hyperplane to separate data points of different classes. SVM has been used successfully in contaminant loading estimation, particularly for classification tasks (Bhattarai et al., 2021; Meshram et al., 2020; Samantaray et al., 2020). SVMs consider which input variables (e.g., rainfall and land use) are most important in predicting the load levels and maps those data points into a higher dimensional space. It finds an optimal hyperplane to separate the load levels in the higher dimension space. By using an SVM, we can find the best way to separate the different load levels in the watershed based on the input variables. It can be used to predict watershed load level with new input variables after training. A SVM can handle both simple and complex relationships between the input variables and the load levels. SVMs are sensitive to the scale of input variables. If the features have different scales, SVM might prioritize variables with larger values, leading to biased predictions. The performance of SVM heavily relies on the selection of an appropriate kernel function. Different kernels (e.g., linear, polynomial, radial basis function) have different properties and work well for different types of data. Choosing the right kernel requires domain knowledge and experimentation, which is challenging with contaminants that lack monitoring data. In cases where the data are noisy or there is overlap between load levels, SVM may struggle to achieve optimal performance and may misclassify certain data points.

3. CECs Load Modeling Applications

This section provides a summary of a few model applications of CECs transport in urbanized watersheds via surface water, groundwater, and streamflow. The summary includes a brief overview of the data requirements, how different models were coupled, and overview of the main results. Overall, we identified few modeling studies specific to CECs loads, indicating a need for more work in this field. These studies are provided as examples, selected to cover contaminant fate and transport at a watershed scales and to focus on urban areas.

3.1 Spatially Distributed Models

A Semi-distributed Model

The Soil & Water Assessment Tool (SWAT) has been used to simulate per- and polyfluoroalkyl substances (PFAS) in the Huron River watershed (Michigan), a region known for its high PFAS levels due to many industrial sites, landfills, and an airport (Raschke et al., 2022). The integrated approach accounted for three transport paths: surface runoff (SWAT), groundwater (MODFLOW), and streamflow water quality (WASP). The SWAT model was based on a 10-m resolution digital elevation model, information on 16 reservoirs along the Huron River, land use data at a 30-m resolution, and soils and slope classes from various GIS sources. The input information consisted of precipitation and temperature records from 1999 to 2020 and streamflow was simulated on a daily time step. For the MODFLOW model, the domain was divided into three different layers with unique hydraulic parameters such as hydraulic conductivity, specific yield, and specific storage. An internal mapping was developed to exchange output from the SWAT HRUs and river network to MODFLOW grid cells and vice versa. Selected sub-basin features from the SWAT and MODFLOW models were used to configure a one-dimensional river network in WASP.

Monitoring data consisted of soil, stormwater, groundwater, and fish tissue samples for 24 different PFAS. For WASP, physicochemical properties (e.g., solubility, vapor pressure, partitions coefficients to sediment) were adopted from the literature. While the literature provided valuable insights for determining model parameters, model performance was not evaluated due to the lack of monitoring data at the required temporal frequency and spatial resolution. A significant modeling challenge arose from simulating multiple PFAS simultaneously, as the lack of understanding regarding their interactions presented a major obstacle. Other limitations to the modeling approach included: lack of source data, poor representation of sorption coefficients; inability of the model to simulate the interaction between groundwater and wetlands, ponds, and reservoirs; and lack of a conceptual model to simulate competitive sorption of PFAS to sediment particles.

A Distributed Model

The VELMA hydrologic model was utilized to assess the reduction in stormwater contaminant loads in the Longfellow Creek Watershed, located in West Seattle, WA (Halama et al., 2022). Salmon in the Longfellow Creek face significant mortality rates attributed to lethal levels of 6PPD-quinone, the transformation product of an antiozonant preservative (6PPD) commonly found in vehicle tires. The VELMA model was calibrated for streamflow but was solely verified using a limited dataset for 6PPD-Q concentrations. 6PPD-Q model parameters were established using chemical data sourced from the CompTox Chemical Dashboard, a database maintained by the US-EPA containing information on the chemistry of numerous chemicals. Preliminary findings from the study indicated that 6PPD-quinone demonstrated "first flush" hydrograph behavior, with the highest simulated concentrations occurring after periods of dry weather.

3.2 Fugacity Models

Organophosphate esters (OPEs) are used as flame retardants, lubricants, and plastic additives, and are found in a wide range of commercial products such as vehicles, textiles, and electronics. Some OPEs have been associated with high aquatic toxicity, endocrine disruption, and neurotoxicity (Gu et al., 2023; Yao et al., 2021). The Multimedia Urban Model (MUM), a multimedia fugacity modeling tool, was combined with a dataset from the Global Atmospheric Passive Sampling Megacities Network to elucidate the fate and transport of OPEs in 19 mega cities (i.e., Cairo, Kolkata, Bogota) around the world (T. F. M. Rodgers et al., 2023). The following seven compartments where considered to assess the movement of OPEs through the environment: upper air, lower air, urban areas, vegetation, soil, water, and sediment. Results showed that on a compound basis, tris (1-chloro-2-propyl) phosphate (TCIPP) and tris (2-chloroethyl) phosphate (TCEP) had the largest air emissions, accounting for about 48-91% of emissions in each of the mega cities. Emissions from building materials (i.e., insulation) seems to be a major source of TCIPP, which may be transported from the atmosphere to the land via precipitation.

Using MUM, a study in Toronto, Canada, found that OPEs stream concentrations originated from emissions to urban air transferred to water mostly via precipitation (Rodgers et al., 2018). Emissions from sources such as indoor air or traffic were sufficient to account for the high OPEs concentrations in streams. Wet deposition accounted for about 75% of TCiPP and 93% of TBOEP. Although these results offer an understanding of how OPEs move through different interconnected compartments (same seven compartments described in Rodgers et al. (2023)), the findings may not readily apply to watershed scales.

3.3 Data-Driven Approaches

Mean annual contaminant loads from the City of Toronto to Lake Ontario have been quantified using the LOADEST statistical model (Melymuk et al., 2014). This modeling effort included: polybrominated diphenyl ethers (PBDEs), which were once widely used as flame retardants; polycyclic musks (PCMs), commonly used fragrance ingredients; polychlorinated biphenyls (PCBs); and polycyclic aromatic hydrocarbons (PAHs). These contaminants are hydrophobic, meaning that they lack affinity for water and adhere to sediment particles. For stormwater runoff, the loads were calculated from stormwater concentrations and streamflow data from the Water Survey of Canada. Total loads to Lake Ontario were estimated by aggregating loads from atmospheric processes, tributary runoff, and effluent discharges from wastewater treatment plants. Water samples were collected at six downstream locations with a range of 19 to 30 samples per site. (For context, San Francisco Bay includes numerous creeks and streams that drain into the Bay: the Watershed Dynamic Model identifies 240 sub-watersheds). The data were adjusted using three statistical estimation methods: adjusted maximum likelihood estimation (AMLE), maximum likelihood estimation (MLE), and least absolute deviation (LAD) (Runkel et al., 2004).

PAH loads from surface runoff represented about 71% of the total load to Lake Ontario (i.e., air emissions, surface runoff, and discharges from wastewater treatment plants). Sources of PAHs were primarily from industrial and transportation activities. Also, coal tar sealants applied to impervious surfaces could be a potential source of PAHs. PAH loads were dominated by phenanthrene, fluoranthene and pyrene. PBDEs and PCBs found in surface runoff accounted for about ~45% and ~30%, respectively, of the total load to Lake Ontario. Most of the PCMs loads (~83%) were associated with wastewater treatment plant discharges.

4. Data and Knowledge Gaps

Due to their emerging status, data and knowledge gaps abound for CECs. This section summarizes gaps particularly relevant for development and application of models to estimate CECs loads from local tributaries. This section draws heavily from a thorough summary by Raschke et al. (2022) of the data and knowledge gaps for PFAS transport and fate modeling. Their conclusions apply to other CEC classes as well. In general, the data and knowledge gaps can be grouped into five categories.

4.1 Lack of Monitoring Data on Many Individual Chemicals

CECs encompass a wide range of compounds, used in plastic additives, personal care products, pesticides, and other industrial uses. Their various chemical structures and transport mechanisms pose challenges in both monitoring design and modeling studies. Different chemicals require different sampling and chemical analysis methods, which are often expensive and time-consuming. For watershed models, stormwater sampling data from source areas and the receiving waters is needed to estimate various model parameters. For example, monitoring data is required to estimate land-used-based event mean concentrations or grab sampling to enable setting of buildup and washoff parameters. Consequently, monitoring efforts have focused on a limited set of well-known CECs, leaving a significant knowledge gap regarding the occurrence and concentrations of many other emerging contaminants (Muir et al., 2023).

Some studies have investigated groups of CECs in stormwater and rivers, focusing on presence or absence of individual compounds (e.g., Jin & Zhu, 2016; Peter et al., 2022), or spatial distribution of CECs concentrations (e.g., Lian et al., 2022), and were not specifically designed for estimation of stormwater loads. The lack of data inhibits the development of accurate stormwater load models for individual CECs or the full spectrum of CEC classes.

4.2 Lack of Information on CEC Sources

A significant challenge in using numerical models to simulate CECs is the scarcity of information regarding the composition of CECs in products within the urban outdoor environment, where these products likely serve as the primary origin of CEC release. For example, PFAS are known to be used in many types of building products, such as roofing materials, concrete sealers, and glass and ceramic surfaces (Blumenthal et al., 2022), yet data characterizing the PFAS content of these and other outdoor products are not publicly available. Very few data exist to characterize other CEC sources, such as past use of these chemicals (e.g., PFAS-containing aqueous film- forming foam for firefighting), or indirect transport from products used indoors (e.g., transfer of OPEs from indoor air).

The challenge extends beyond the scarcity of information about the products themselves. It also encompasses the limited data available concerning the fate of CECs in outdoor products and the rate and efficiency of CEC transfer from these products into the stormwater runoff.

4.3 Limited Data and Study of CEC Transport in Different Media and Pathways

Once released into the environment, CECs can travel through the surface water (overland flow and streamflow), the vadose zone, and groundwater. Transport of CECs can occur through release from point sources and nonpoint sources, including volatilization into the atmosphere and deposition during rain events. In urban areas with extensive directly-connected impervious areas, surface runoff can effectively carry CECs from the source areas to creeks and stormwater infrastructure. For example, PFAS are added to materials to provide corrosion prevention and waterproofing (Blumenthal et al., 2022; Janousek et al., 2019). Rainfall can cause the building materials to erode and carry these chemicals directly to the drainage network (Janousek et al., 2019). Most watershed models do not capture these pathways as the landscape is only characterized by different land uses.

4.4 Limited Understanding of the Fate and Transport Processes

The fate and transport processes governing CEC movement in stormwater systems and on land prior to being washed into stormwater systems are complex and multifaceted. Factors such as partitioning, particle settling, sediment resuspension, volatilization, photodegradation, biodegradation, and transformation can influence the fate and transport of CECs. However, our understanding of these processes and their interactions is limited, and the influence of climate, land use, and stormwater management on CEC transport remains poorly understood (Harbourt et al., 2014).

Knowledge gaps exist regarding the rate of degradation of CECs in stormwater pathways, their interactions with sediments, partitioning between dissolved and particulate phases (Kalmykova et al., 2013), and potential transformations during transport. Accurate modeling of CEC loads requires us to identify and quantify the contributions of different stormwater pathways, such as industrial discharges, urban runoff, and agricultural activities. It is also important to understand the kinetics and mechanisms of degradation, as well as the formation of transformation products.

4.5 Lack of Data on Spatial and Temporal Variation of CECs in Stormwater

Understanding the spatial and temporal variation and patterns in contaminant loading rates is essential for understanding and improving modeling accuracy. The scarcity of stormwater data also hinders the estimation of uncertainty. The majority of CEC stormwater studies (Masoner et al., 2019) have been based on a limited number of storms at one location, lacking samples from multiple storm events at a sampling location to better understand temporal variation. This data gap hinders our ability to understand trends and patterns of CEC concentrations in stormwater runoff over extended periods, and adds considerable uncertainty to CECs stormwater loading estimation. Temporal variations, such as seasonal patterns and trends over time, are crucial for understanding the dynamics of CECs in stormwater systems. Comprehensive long-term data are needed to characterize and model temporal variation accurately. Loads will vary within a storm, between storms within a wet season, and across wet seasons.

Storm events can exhibit rapid and significant changes in pollutant concentrations due to high-intensity runoff and localized pollution sources. Detailed data on storm event characteristics, such as antecedent dry days, rainfall intensity, duration, and frequency, are necessary for modeling CEC transport during different storm events. However, capturing short-term variability in CEC concentrations requires high-frequency monitoring, which is usually lacking. CEC concentrations can also vary spatially due to different land use and land feature patterns, and hydrological characteristics (Masoner et al., 2019; Peter et al., 2022). Where possible, it is important to consider the spatial variability of CECs and incorporate it into the modeling approach.

5. Recommendations

We provide the following recommendations for estimating stormwater CEC loads based on the characteristics of Bay Area watersheds and the limited monitoring data available in the near term. We also recommend that the stormwater CECs monitoring strategy be adapted to contribute to this modeling effort. An appropriate monitoring design will allow for better uncertainty quantification of load estimation with the model.

1. <u>Approach CEC load modeling based on specific CEC groups where possible, or on an individual chemical basis where necessary.</u> CECs — and even CECs classes like PFAS and OPEs — cannot be monitored or modeled as if they were a homogeneous group of chemicals. When approaching CECs, the RMP and others generally group them by chemical class (e.g., OPEs, PFAS) or by sources (e.g., tire chemicals, pet parasiticides). Due to the diversity of chemicals in these classes, in many instances, it will be necessary to approach modeling on an individual chemical basis, or perhaps in small groups, where chemicals have similar chemical properties, fate, transport, and sources. We recommend focusing on obtaining data on *individual* CECs that are of particular concern or high priority.

2. <u>Develop conceptual models to understand key factors influencing the loads of CECs in stormwater before initiating CEC load modeling</u>. The conceptual models should outline sources and pathways by which pollutants enter stormwater and reach the Bay and are informed by chemical uses, distribution, and properties. The conceptual models will guide the data-driven aspect of load estimation, provide a framework for understanding the dominant processes and variables driving CEC transport, and guide future monitoring and modeling efforts.

   As an example, a conceptual model may include a linkage with land use. Some CECs may exhibit an association to a specific land feature. For instance, PFOS (perfluorooctane sulfonic acid) concentrations are expected to be higher around PFOS-using industrial facilities (e.g., airports, military bases) than residential/commercial areas (Raschke et al., 2022; Xiao et al., 2012). A conceptual model can help in identifying appropriate land features for estimating stormwater CEC loads.

3. <u>Use a hybrid data-driven and spatially distributed approach for regional stormwater load estimation</u>.

   We recommend using a data-driven method to investigate the relationship between CEC concentrations in stormwater runoff and various factors (e.g., landscape features, rainfall characteristics, and discharge rates), then extrapolating this relationship to the entire Bay Area utilizing the surface runoff outputs from a spatially distributed model, the RWSM or output from the WDM. This can be an efficient approach to obtain preliminary estimates of stormwater CEC loads, considering the limitations in available data and knowledge. With this hybrid approach, the RWSM can initially be used to provide an approximation for CEC load estimation in stormwater given the existing constraints. The current contaminant model of RWSM is based on land use groups and a stormwater contaminant concentration for each group. This structure can be adapted for CECs and incorporate land features beyond a specific land use (not necessarily linking a land use to a specific CEC). For example, the unit-area based land use output from the WDM could be used to provide surface runoff volumes. For a new land feature, a contaminant load could be determined by using the area of the new land feature, its unit-area surface runoff volume, and a specific contaminant concentration associated with this new feature. The use of a land feature approach is dependent on having suitable land feature data. However, further refinement and validation of the RWSM may be necessary as more data and knowledge become available to improve the accuracy of the estimates.

4. For those CECs for which the RMP intends to develop improved load estimates, implement long-term monitoring designed to inform load modeling. Such monitoring programs should capture the spatio-temporal variation and patterns of CECs in stormwater and provide data for model calibration. For an individual site, the variation in event mean concentrations may be due to different antecedent dry periods and rainfall intensities. Often, contaminants have higher concentrations in runoff at the beginning of the wet season. This is due to the prolonged accumulation period, allowing for a greater mass of contaminants to accumulate over time. In other cases, contaminant concentration may be related to rainfall intensity. A heavier storm can erode more CECs from building materials (e.g., paints, coatings, roofing membranes) than a low intensity storm. Interannual variation in loading will also occur due to variation in climate and sources. Repeated sampling over time is key to understanding potential relationships between event mean concentrations and storm characteristics and to characterizing these different components of temporal variation. Stormwater loads will also vary spatially, and spatial variation and patterns should also be characterized. Sampling during dry weather conditions can inform the relative contribution of dry-weather flow to the annual load. We recommend identifying the minimum amount of CEC observations needed to make first order load estimates, using a set of monitoring locations for repeated sampling and various locations around the Bay area.

A summary of the numerical models available for CECs load estimation is displayed in Table 2. The table rows list the features of different models. In each table cell, we show a checkmark ✓ where we judge the model to be suitable according to this criteria, or an ✗ where the model is unsuitable.

Table 2. Summary of models available to support stormwater CECs load estimate development. ✓: model meets the criteria. ✗: model does not meet the criteria.

Feature	RWSM	WDM	SWMM	SWAT	QWASI, MUM	LOADEST	Data-driven approaches
Watersheds are discretized into small homogeneous spatial units (HRU)	✓ Loads can be estimated for any area of interest	✓ Loads can be estimated for 240 sub-watersheds	✗ Best suited for urban areas with complex drainage networks	✓ Complex model based on hydrologic response units	✗ Low spatial resolution	✗	✗
Flexible structure based on land features (or land uses)	✓ Flexible	✓ Land uses	✓ Land uses	✓ Land uses	✗	✗	✗
Temporal resolution	✓ Annual	✓ Dynamic model: daily and hourly output	✗ Dynamic model: overly fine resolution (minutes)	✓ Dynamic model: daily and hourly output	✓ Steady-state conditions	✓ Daily and hourly datasets	✓ Daily and hourly datasets
Complexity of data inputs for parameterization	✓ Relatively few data input requirements	✗ Requires large datasets to represent the landscape	✗ Requires large datasets to represent the landscape	✗ Requires large datasets to represent the landscape	✓ Relatively few data input requirements	✗	✗
Hydrology and contaminant modules	✓ Loads can be estimated based on event-mean concentration (EMC) data	✓ Methods for sediment-associated contaminants	✓ Exponential functions, EMC for a land use	✗ Sediments, nutrients, phosphorus, pesticides only	✗ Basic hydrology, complex chemical module	✗	✗
Calibration and validation process	✓ Less complex than dynamic models	✗ Large number of calibration parameters	✗ Large number of calibration parameters	✗ Large number of calibration parameters	✗ Data for different compartments	✗ Requires large datasets	✗ Requires large datasets

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