



ChemFate: A fate and transport modeling framework for evaluating radically different chemicals under comparable conditions

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HIGHLIGHTS

- ChemFate is a multi-media dynamic chemical fate and transport tool.
- ChemFate includes four models: organoFate, ionOFate, metalFate, nanoFate.
- ChemFate predicts daily chemical environmental concentrations.
- ChemFate considers daily meteorology, chemical release, and region characteristics.

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ABSTRACT

With the ever-increasing development on novel chemicals and materials, with radically different properties and environmental behavior, it is challenging to compare their environmental behavior under similar conditions. For example, pesticides may be non-ionizable organics, ionizable organics, metal ion-based, or nanomaterials. These very different chemicals behave very differently. To date, no single modeling platform can handle all adequately, in a dynamic framework that accounts for actual variability in meteorology, rates of release to the environment, and the actual characteristics of the region of interest. Here we present ChemFate, a framework to address this challenge, by incorporating four different fate and transport models, each to address these four classes of chemicals (non-ionizable organics, ionizable organics, metal ion-based, or nanomaterials). We build upon established models, but have incorporated a number of additional processes. After demonstrating that the individual models comparable favorably with observed data and the previous models, under similar conditions, we conducted a case study with four radically different fungicides, used in the Central Valley, California. We found that although the concentrations of the non-ionizable and ionizable organic fungicide spike after application and temporarily may exceed toxicity thresholds for *Daphnia Magna*, they do not accumulate over time, while the metal ion and metallic nanoparticle result in increasing accumulation of Cu^{2+} , eventually exceeding the toxicity threshold during runoff events. This case study demonstrates the value of a framework that allows the comparison of different classes of chemicals under the same conditions.

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1. Introduction

开篇就提出科学问题及挑战

A major challenge in comparing the risk of chemicals from radically different classes is that their behavior in the environment requires taking into consideration their particular properties and processes. For example, how should we compare a novel nanopesticide to existing ionizable or non-ionizable organic chemicals,

or a pesticide based on metal salts, all used as fungicides? Or a sunscreen that may contain nano titanium dioxide or organic UV blockers/quenchers? While the characteristics of the geographical region of interest are the same, a correct assessment needs to consider the radically different properties of each one of these classes of chemicals. Multimedia fate and transport models are widely used in chemical risk assessment, chemical ranking and management support (Su et al., 2019; Zhu et al., 2016). They are designed to understand chemical transport behavior and fate in the environment and predict the concentrations in different environmental compartments. However, most multimedia fate and transport models are specific to a particular class of chemicals. This

under similar conditions

2019年的综述

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makes a proper comparison of different classes of chemicals challenging, **because** different models are built under different modeling formulations and are comprised of different sets of environmental compartments and assumptions.

A widely adopted multimedia fate and transport model is Equilibrium Criterion (EQC), a fugacity-based model developed by Mackay et al. (1996) and recently updated (Hughes et al., 2012). However, it only applies to non-ionizable organic chemicals and considers only four environmental compartments (air, water, sediment, and soil). Another prevalent model, called Multimedia Activity Model for Ionics (MAMI), is an activity-based model that considers chemical speciation in the environment and applies to both non-ionizable and ionizable (e.g. acids and bases) organics (Franco and Trapp, 2010; Trapp et al., 2010). MAMI is able to model seven environmental compartments, including air, freshwater, freshwater sediment, marine, marine sediment, and three soil types (urban, agriculture, and other), but it is not applicable to metals or nanomaterials. **TRANSPICII** is a coupled metal speciation-fate model that is specific for metals, and it only considers water, sediment (surficial and deep), and one type of soil (surficial and deep) (Bhavsar et al., 2008). TRANSPICII tracks metal distribution among three phases: dissolved, colloidal, and particulate. SimpleBox is a concentration-based nested multimedia fate model that is able to model non-ionizable organics, ionizable organics, and metals, and it contains the same seven environmental compartments as MAMI (Hollander et al., 2016). However, SimpleBox only models two phases for metals (particulate and dissolved), and ambient chemistry parameters are not considered in metal distributions. A version of SimpleBox adapted for nanomaterials was developed (Meesters et al., 2014), which takes into consideration the significant differences in processes and properties of metallic nanomaterials relative to metals. **Table S1** shows a more detailed comparison of these models including model capabilities and environmental compartment specificity.

EQC and TRANSPICII are **steady-state** (level III in Mackay's terminology) models with the assumption of **constant environmental conditions and emissions** (Bhavsar et al., 2008; Mackay et al., 1996). MAMI and SimpleBox have a **quasi-dynamic feature** that incorporates the **variability in emissions** (Franco and Trapp, 2010; Hollander et al., 2016). A dynamic pattern of chemical emissions is able to capture the temporal concentration changes in the past and provides more realistic predictions for the future (Ao et al., 2009; Di Guardo et al., 2006; Luo and Yang, 2007; Su et al., 2018; Sweetman et al., 2002). However, without considering the **dynamic nature of important environmental conditions** (e.g., temperature, precipitation, hydrologic flow), these models may underestimate or overestimate chemical concentrations and exposures (Ghirardello et al., 2010; Morselli et al., 2018; Parker and Keller, 2019; Su et al., 2019).

Here we present ChemFate, a framework that predicts chemical environmental concentrations for four classes of chemicals and incorporates both dynamic emissions and environmental conditions. ChemFate comprises four different models: (1) organoFate, a model specific for modeling the fate and transport of non-ionizable organic chemicals; (2) ionoFate, a model for ionizable organic chemicals; (3) metalFate, a model for metal ions; and (4) nanoFate, a model for nanomaterials (Garner et al., 2017). These models can be run with the **same environmental characteristics for particular geographical regions** (e.g. San Francisco, New York City, London, Des Moines), including the local temporal meteorological data. The models provide **predicted environmental concentrations (PECs)**, which can be compared to toxicity thresholds specific to each chemical to determine risk (e.g. Parker and Keller, 2019). This allows the direct evaluation of chemicals of radically different classes under comparable environmental conditions, to determine which one possess the most or least risk, while taking into account the

differences in behavior for each chemical.

ChemFate predicts chemical concentrations in nine compartments: atmosphere (including air and aerosols), **four types of soils** (including urban, natural, agriculture with and without applied biosolids) divided into surface soil solids, soil air, soil pore water, and deep soil compartments, two types of water (including freshwater, estuarine or coastal seawater, and suspended sediment in both), and freshwater and estuarine or coastal sediments. ChemFate **uses well-established equations** that take into account physicochemical properties of each type of chemical, reactivity and climatic variability. For example, **ChemFate uses Stokes' law to calculate the deposition rates by considering particle (e.g. aerosols, suspended sediments, nanoparticles) density, fluid (air or water) density, and fluid dynamic viscosity, which has been used extensively for modeling particle transport and deposition** (Nho-Kim et al., 2004; Tsuda et al., 2013). Moreover, soil runoff, soil erosion, and infiltration processes are modeled dynamically by considering daily precipitation intensity, regional slope and soil erodibility. ChemFate considers a wide range of processes, several of which are not modeled in previous models mentioned in **Table S1**, including aerosol resuspension from coastal splash and soils by wind that results in transfer back to the aerosol compartment (Gillette and Passi, 1988; Qureshi et al., 2009).

While ChemFate considers advective transport of air and aerosols, water and suspended sediments, and even the freshwater sediment bed, into and out of the various compartments, **it does not discretize the landscape into catchments, or the river into reaches, as would be done in river network models such as Soil and Water Assessment Tool (SWAT) (Arnold and Fohrer, 2005), Hydrological Simulation Program-Fortran (HSPF) (Singh, 2012), or Watershed Analysis Risk Management Framework (WARMF) (Keller et al., 2014)**. River network models assume that the concentration of a chemical in a given reach is homogeneous, which is the same assumption used in ChemFate. However, to model the flow from catchment to catchment, river network models require a more complex mathematical description of the hydrologic processes, which **requires considerable calibration**. Instead, in ChemFate we have opted for incorporating **measured river flow based on gauges**, which simplifies the use of ChemFate while retaining realistic daily flowrates. This is in contrast to the other multimedia models presented in **Table S1**, which consider a constant (steady-state) flowrate. A series of ChemFate models can be implemented in a given watershed to simulate the transport down several reaches.

ChemFate is novel and unique because the framework (i) considers fate and transport properties and processes that are specific to each class of chemicals (i.e. nano, metals, ionic and non-ionic organics) within the same tool; (ii) includes a higher level of structural and process detail for the compartments included, and the possibility to tailor them to specific regions and conditions, therefore considering realistic environmental parameter values and meteorological conditions (iii) can use dynamic inputs (e.g. actual daily meteorology and river hydrology); to generate time-dependent outputs; and (iv) works across these four radically different classes of chemicals under comparable environmental conditions. ChemFate also capitalizes on the use of common processes (e.g. runoff, erosion, infiltration, deposition, resuspension, etc.), which serve to transport the chemicals, minimizing differences in the comparison. **ChemFate was also developed with the ability to add environmental compartments (e.g. additional freshwater, or an estuary between the freshwater and marine environments) and additional transport processes if they are later deemed to be relevant for a class of chemicals**. In the following sections, we present the general conceptual framework of ChemFate and the key processes considered in all models, then we evaluate each model in ChemFate against other models and observational data available,

第四段描述了整体的设计和构想。

没有有机膜和植被

地面灰尘的泥沙动力学?

颜小曼做出来了

第二段开始
拿别人的
模型出来
抨击

主要针对
化学品类型
和环境相

第三段
开始讨论
时间的
变异性
(steady
state, quasi-
dynamic
pattern)

dynamic feature

and finally compare the fate of four radically different pesticides under the same dynamic environmental conditions.

2. Materials and methods

2.1. ChemFate framework

Fig. 1 show the conceptual diagram of ChemFate with model input and output information. Since nanoFate has been already extensively described in a previous publication (Garner et al., 2017), here we focus on the other three models and the overall framework. Four major model inputs are chemical-specific parameters, region-specific parameters, chemical release information, and chemical background concentrations. ChemFate considers different chemical parameters for different types of chemicals, for example, chemical half-life in various environmental compartments are needed for non-ionizable and ionizable organic chemicals, but not for metals which are assumed to be speciated in a particular water chemistry (e.g. freshwater, seawater, groundwater specific to a given land use/soil type) and do not transform further (Bhavsar et al., 2004). Region specificity is reflected in the consideration of compartment dimensions and characteristics (e.g., soil properties, water chemistry, aerosol concentration) and in the incorporation of local observed daily temperature, precipitation, wind speed, and river flow. ChemFate is able to handle various types of chemical release scenarios (at a daily time step), including constant, increasing, decreasing (e.g. phaseout), seasonal and accidental spills. Furthermore, for chemicals with known or estimated background concentrations in the different environmental compartments, ChemFate can incorporate the background concentrations into the model initial conditions; performing an initial equilibrium distribution in the sub-compartments (e.g. pore water, air and solids) in the corresponding compartment (e.g. groundwater in urban soil).

To provide a rapid evaluation of chemical fate in various regions, we have developed fourteen specific environments to represent a wide range of distinct climate conditions and land use types, and a global environment (Table S2). We also documented the detailed procedures for developing a customized region (Supporting Information User Guide (SIUG), Section 5).

2.2. ChemFate methodology

ChemFate uses the fugacity concept for non-ionizable organic chemicals and the equivalence concept for ionizable organic

chemicals and metals. The concept of fugacity was first applied by Mackay and Paterson based on the behavior of ideal gases to model the chemical fate of non-ionizable organics in the environment (Mackay and Paterson, 1981). However, fugacity is not suitable for ionizable chemicals given their low volatility, such as ionized organics or metals (Mackay et al., 2003). Thus, the approach of equivalence was developed as an equilibrium criterion for ionizable chemicals, along with a pseudo single species mass balance modeling technique for multi-species chemicals (Diamond et al., 1992). Both fugacity and equivalence are linearly related to concentration through the fugacity and equivalence capacity Z values, and D values are used to quantify transport and transformation rates for all chemicals (Csiszar et al., 2011; Diamond et al., 1992). The concentration C (mol m^{-3}) of a chemical species is calculated via the fugacity (Pa) and fugacity capacity Z_f ($\text{mol m}^{-3} \text{Pa}^{-1}$) for non-ionizable organic chemicals, and equivalence Q (mol m^{-3}) and equivalence capacity Z_Q (dimensionless) for ionizable organic chemicals and metals, $C = fZ_f = QZ_Q$. Z values are generated by phase partition coefficients and Z_Q values are species-specific for each phase and compartment. The detailed calculations of Z values and partition coefficients are described in SIUG, Section 3.1.

ChemFate simulates chemical transformations and transfers between compartments (Fig. 2), tracking the neutral species for non-ionizable organic chemicals and both neutral and primary ionic species for ionizable organic chemicals. The primary ionic species is the dissociated state of an ionizable chemical in water. For chemicals with multiple pK_a values, the primary ionic species would be the species with a pK_a value closest to the pH value. For metal ions, ChemFate tracks chemical concentrations in three phases: particulate, colloidal, and dissolved phases. Metal ions in the particulate phase refers to metal ions sorbed to aerosol or suspended solids, metal ions in the colloidal phase are ions bound to dissolved organic matter, and metal ions in dissolved phase include free metal ions and inorganic metal complexes (Bhavsar et al., 2004).

For ionizable organic chemicals, species fractions of neutral and ionic forms are calculated using the Henderson-Hasselbalch equations (Equations (1) and (2)), which considers the specific pK_a of a chemical and the water pH in each compartment:

$$Q_n = \frac{1}{1 + 10^{\alpha(\text{pH} - \text{pK}_a)}} \quad (1)$$

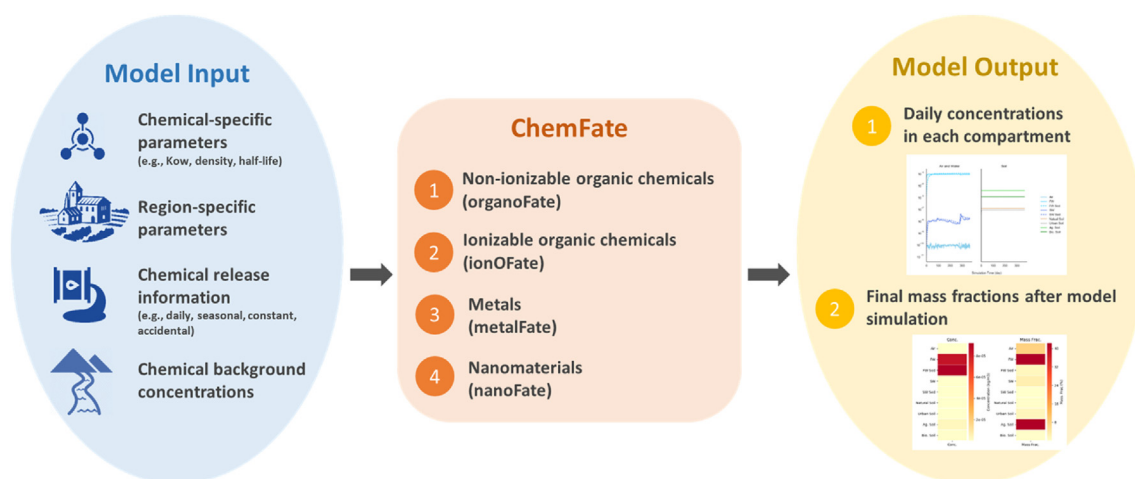


Fig. 1. ChemFate framework with model inputs and outputs information.

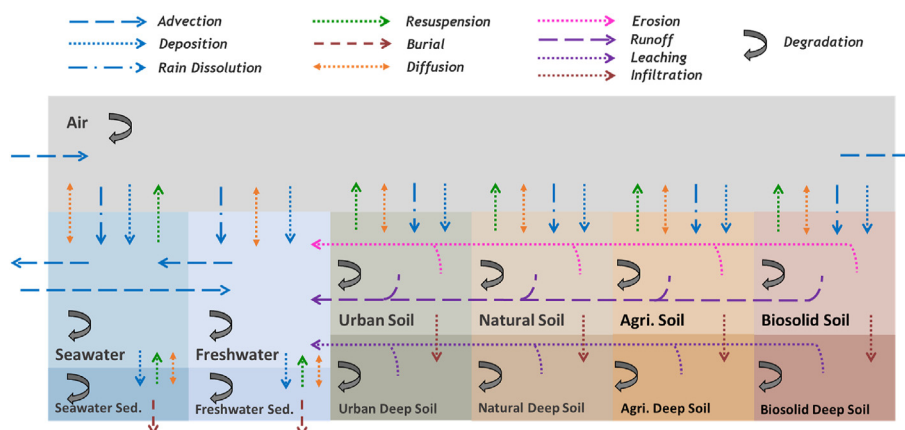


Fig. 2. Environmental compartments and major transport and transformation processes considered in ChemFate.

$$Q_i = 1 - Q_n \quad (2)$$

Where α is 1 for acids and -1 for bases. Q_n indicates the fraction of neutral molecules and Q_i indicates the ionized fraction. For metals, the speciation and partitioning in the water system depends largely on the water characteristics (e.g., pH, temperature, organic matter content, concentration of major ions such as Ca^{2+} , Mg^{2+} , Na^+ , Cl^- , SO_4^{2-} , HS^- or S^{2-}); the species fraction values can be generated from geochemical models such as Visual MINTEQ (Gustafsson, 2017) and WHAM (Centre for Ecology and Hydrology, 2014), for each water compartment within metalFate.

Following the simplicity tradition of multimedia fate models, we assume an instantaneous and homogenous distribution of species within an environmental compartment (Bhavsar et al., 2008; 2004; Csiszar et al., 2011; Franco and Trapp, 2008; Mackay, 2001; Trapp et al., 2010). Furthermore, we also consider that the overall reaction/transformation processes follow first order reaction rates, and convert measured or estimated chemical half-lives in different media (air, water, soil) into reaction rate constants in each sub-compartment (Mackay, 2001). ChemFate accounts for inter-compartmental transport through intermedia diffusion-limited transfer and advective processes. Diffusion-limited exchange is considered between air-water, air-soil, and sediment-water for non-ionizable organic and ionizable organic chemicals. For metals, only diffusion-limited transfer between sediment-water is included as other diffusion-limited exchanges are not generally applicable to metal ions (Bhavsar et al., 2008, 2004). A suite of advective transports are considered in ChemFate, including advection in and out of the system by wind in air; by water flow in freshwater, which then flows to a second water compartment (e.g. a broader freshwater body, an estuary or coastal seawater) with their associated suspended sediments; via dry and wet deposition from air and in aerosols; sediment resuspension and burial; aerosol resuspension from coastal seawater; wind erosion from surface soil; soil water runoff and soil erosion during precipitation events; infiltration from surface soil to deep soil; and horizontal ground-water transport (leaching) from soil to freshwater. These transport processes are described in detail in the SIUG, Section 3.4 with their mathematical representation, and the mass balance equations for organoFate, ionOFate, and metalFate. A summary table with all of the modeled transport processes, along with the chemical forms and phases that are tracked in ChemFate, is presented in Table S3.

2.3. Model evaluation

We selected three chemicals 2,4-dichlorophenoxyacetic acid

(known as 2,4-D), nickel (Ni), and benzene, to evaluate the different models (ionOFate, metalFate, organoFate). 2,4-D was chosen as an ionizable organic acid to evaluate ionOFate, Ni was chosen as a metal to evaluate metalFate, and benzene was chosen as a non-ionizable organic chemicals to evaluate organoFate. To determine whether the predicted environmental concentrations (PECs) estimated by the ChemFate models are reasonable, we first performed a comparison of model results to other widely used models, specifically, EQC (Hughes et al., 2012), MAMI (Franco and Trapp, 2010; Trapp et al., 2010), SimpleBox (Hollander et al., 2016), and TRANSPEC (Bhavsar et al., 2008, 2004). Since ChemFate is a fully dynamic level multimedia model that includes a broader range of processes compared to the other models, to make a valid comparison we had to consider constant climate, emissions and a long-term simulation time to reach steady-state. Observed data from case studies used to evaluate MAMI (Franco and Trapp, 2010) and TRANSPEC (Bhavsar et al., 2008, 2004) were used for the comparisons of ionOFate and metalFate, respectively. Because EQC, MAMI and SimpleBox are widely used and validated models that can be used for non-ionizable organics, organoFate is compared to these models directly.

To evaluate ionOFate, all the environmental parameters were parameterized as described in Franco and Trapp (2010) as well as their emission scenario for 2,4-D, so that the model outputs would be comparable to the monitoring data collected from the Canadian prairie provinces (Franco and Trapp, 2010). Physicochemical data (Table S4), environmental parameters (Table S5), and rate constants for major transport processes (Table S6) were gathered from Franco and Trapp (2010). Based on that study, an emission scenario for 2,4-D was implemented, with 21.22 kg d⁻¹ released to air and 509.28 kg d⁻¹ released to agricultural soil (Franco and Trapp, 2010). For model comparison purposes, although organoFate considers four soil types, to make the results comparable to MAMI and SimpleBox, we set the area of the fourth soil type, agricultural soil with biosolids, to be zero in ionOFate.

Ni was selected as a metal for the evaluation of metalFate and comparison with TRANSPECII. The models were applied to the Kelly Lake watershed described by Pearson et al. (1999) and Bhavsar et al. (2008). Kelly Lake watershed is located in the Greater City of Sudbury, Ontario, Canada, and the soils surrounding Sudbury contain Ni due to local geology and atmospheric releases from mining operations (Bhavsar et al., 2008). Therefore, Ni has been transported to nearby water bodies through direct atmospheric deposition and soil runoff. The chemical input data are displayed in Table S7 and the environmental parameters are gathered from Bhavsar et al. (2008) and displayed in Table S8. TRANSPECII considers three compartments: water, sediment and soil. The sediment

compartment comprises surficial (0–5 cm) and deeper (5–20 cm) sediment, and the soil compartment comprises surficial (0–5 cm) and lower (5–20 cm) soil layers. For a direct model comparison, the metalFate compartment depths were adjusted accordingly. The emission scenario selected from Bhavsar et al. (2008) was 0.01 kg d⁻¹ released to water, and 1.4 kg d⁻¹ released to surface soil. In addition, TRANSPECII considers the background concentrations in surficial sediment to be 17.5 g L⁻¹, in surficial soil to be 0.5 g L⁻¹, and in lower soil to be 0.75 g L⁻¹.

Benzene was selected as a non-ionizable organic chemical to compare organoFate to well-established models such as EQC, MAMI, and SimpleBox. The chemical input data for benzene were gathered from the EQC substance database (Table S9), and the environmental parameters (Table S5) were chosen from a Canada region described in MAMI (Franco and Trapp, 2010). EQC only considers four environmental compartments, air, one general water compartment with water and sediment, and one general soil compartment. For model comparison purposes, we parameterized the water compartment in EQC as a freshwater compartment and the volume to be the sum of freshwater and seawater volumes as other models. A similar approach was also applied to EQC's single soil compartment, which was assumed to have the same total volume as the sum of natural soil, agricultural soil, and other soil described in MAMI. Again, to make the results comparable to MAMI and SimpleBox, we set the area of "agricultural soil with biosolids" to be zero in organoFate. In addition, rate constants in major transport processes in all models were also parameterized to be the same as described in MAMI (Table S6). The emission scenario for benzene was set to be 120,000 kg d⁻¹ to air so that the mean ambient air concentrations of benzene would fall into the range of 5.0E-9 to 2.0E-8 g L⁻¹ (Europe, 2000).

Finally, we compared the fate of four radically different pesticides, including chlorothalonil (non-ionizable organic acid), cyprodinil (ionizable organic), copper sulfate (metal), and nano copper oxide (nanomaterial), under the same dynamic environmental conditions, to demonstrate the value of the ChemFate framework. For the comparison of the four radically different pesticides, Visalia in California was selected as a case study region because it is a productive agricultural location, all four pesticides are used in this region, and locally specific pesticide application information was available. The region consists of 22,300 km², with 0.43% freshwater, 48.95% natural soil, 6.56% urban soil, 44% agricultural soil, and 0.06% agricultural soil that receive biosolids (Fig. S1). Table S10 displays the list of regional parameters for Visalia, along with estimated uncertainty for each parameter. To demonstrate the model's sensitivity to input parameters, we conducted a simple sensitivity analysis of the agricultural soil curve number (which influences surface runoff) and the freshwater sediment resuspension rate values. The pesticides application dates and rates to agricultural soil were collected from the California Pesticide Information Portal for the year 2014 (California Department of Pesticide Regulation, 2019) (Table S11), and we extended the same amounts over ten years from 2005 to 2014. Pesticides are typically applied during specific times to the crops, and for simplicity we have selected the most common application dates for the various crops. The amounts of pesticides applied to biosolids agricultural soil were calculated based on the area ratio between agricultural soil and biosolids agricultural soil. Since no data were available for copper oxide (nano), we assumed the same amount of copper to be applied for both copper sulfate and copper oxide. Tables S12–S15 presents chemical parameters for each pesticide.

Model and Data Availability. ChemFate is coded in Python and the code, executables and a graphical user interface (GUI) are publicly available at <https://github.com/klaris-ak/ChemFate>. The

detailed data input for the parameterization of the third-party models are presented in the Supporting Information.

3. Results

3.1. Predicted exposure concentrations using ionOFate

The ionizable organic pesticide 2,4-D was selected for the evaluation of ionOFate and comparison with MAMI and SimpleBox, since observed data for air and freshwater compartments from field studies was available (Franco and Trapp, 2010).

3.1.1. Model with default rate constants

Even though ionOFate is able to model dynamic deposition rates for aerosol dry deposition and suspended sediment deposition, first we used a constant climate and deposition rate, as per Franco and Trapp (2010), for direct comparison. The same approach was also applied to soil erosion and soil runoff processes. Aerosol resuspension from coastal areas and soil erosion by wind were set to zero, as they were not modeled in MAMI or SimpleBox. Fig. S2 shows the predicted chemical concentrations estimated by ionOFate at the end of 10-year simulation time, along with the results obtained from MAMI, SimpleBox and observed data for air and freshwater. The steady state of 2,4-D in ionOFate is reached within the first year (Fig. S3). The major loss processes are advection from air and biodegradation in compartments. After the release of 2,4-D to air, it is rapidly removed from air to other compartments by rain dissolution and wet deposition. The concentration in agricultural soil decreases gradually via soil runoff and erosion processes, transporting 2,4-D to freshwater. Gradually, 2,4-D is transported via freshwater flow to the marine environment. 2,4-D is accumulated in freshwater and marine sediments, given its relatively low degradation rate. The three models predict the observed concentrations in freshwater within $\pm 30\%$, with MAMI slightly under-predicting and SimpleBox slightly over-predicting. The observed concentrations in air are five orders of magnitude smaller than in freshwater; ionOFate and MAMI predict the concentrations within the same order of magnitude, under-predicting the observed value by factor of around 2. However, under the same conditions, SimpleBox underestimates the concentration in air by two orders of magnitude, compared with the median measured concentration (Fig. S2).

3.1.2. ionOFate model with dynamic processes

To demonstrate the value of ionOFate's dynamic capabilities, we then considered a dynamic climate and compared the results to the range of observed data for air and freshwater. However, since the observed data were collected from the Canadian Prairie Provinces that covered many large areas in Saskatchewan, Manitoba, British Columbia, Quebec, and Ontario over the time period 1989–2005 (Franco and Trapp, 2010), instead of building a climatic dataset that is specific to this region, we selected the New York daily climatic data during 2005–2014 as a proxy to run ionOFate (Table S16). The goal of the comparison was to demonstrate ionOFate's dynamic simulation capabilities with dynamic climatic data. The daily distributions of climatic data (i.e., temperature, wind speed, precipitation, and water flow) over the 10-year simulation time from 2005 to 2014 are displayed in Fig. S4.

The boxplots in Fig. 3 display the overall daily concentration distributions over the 10-year simulation using ionOFate, along with the range of concentrations from various field studies over the 10 years as reported by Franco and Trapp (2010). The orange and purple dots show the single predicted values from MAMI and SimpleBox. While the range of air concentrations is under predicted by ionOFate, the range of freshwater concentrations is closely

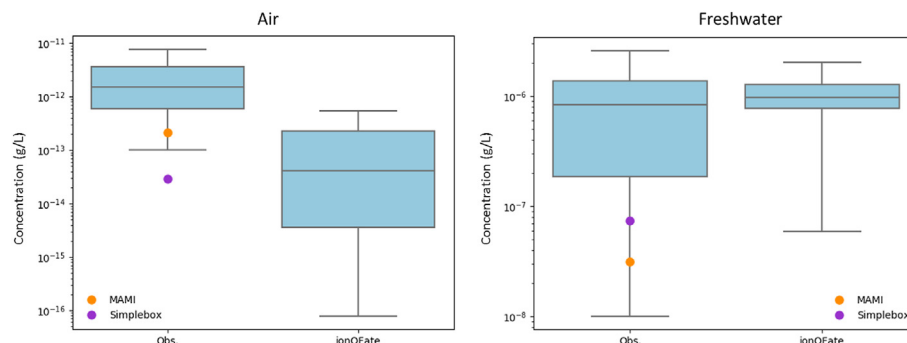


Fig. 3. Comparison of ionOFate model results to observed values in field studies (obs.) for air compartment (left) and freshwater compartment (right). The orange and purple dots indicate the steady-state results from MAMI and SimpleBox. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

matched, with a small difference in the median value.

Fig. S5 shows the predicted dynamic nature of the 2,4-D daily concentrations in the various environmental media, including their sub-compartments, over ten years of model simulation. The substantial variability of 2,4-D concentrations in air and soil is mainly caused by the large fluctuations of environmental processes influenced by wind speed and precipitation, such as air and aerosol advection, aerosol wet deposition, soil runoff and soil erosion. Thus, the comparison between a few observed data points and more than 3650 days of simulation (Fig. 3) needs to take into consideration the significant difference in the number of available data points. This natural variation in concentrations is important for risk assessment, since peaks in concentration could otherwise be missed. The highest concentrations can be found in aerosols, suspended particles in freshwater and agricultural soil solids. The concentrations in freshwater and marine sub-compartments exhibit significant accumulation over time. The dominant 2,4-D species is the anionic species, with over 99% in all compartments, except for air (Fig. S5). The mean predicted concentrations of 2,4-D are the highest in freshwater sediment, followed by freshwater and agricultural soil. In terms of mass fraction by the end of model simulation, the highest mass fractions are also associated with freshwater and agricultural soil (Fig. S6). There is some transport of 2,4-D from the agricultural soils where it was applied, to the surrounding natural and other soils.

3.2. Predicted exposure concentrations using metalFate

Fig. 4 shows the predicted concentrations (PECs) of Ni estimated by metalFate with 60 years of simulation and TRANSPECII,

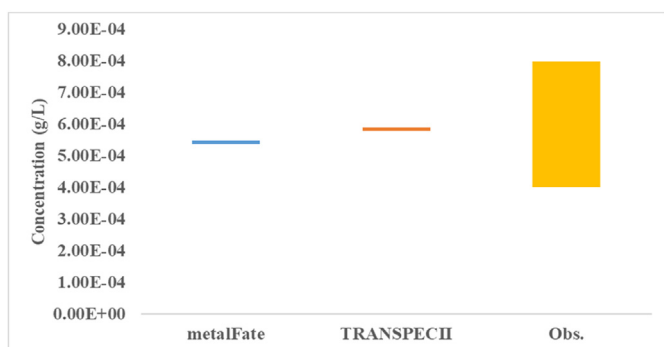


Fig. 4. Model results comparison among metalFate, TRANSPECII, and observational data (obs.) in water compartment.

compared with the observation data. The water compartment concentration is the target media for model results evaluation. There two models produce very similar results. metalFate predicted Ni concentration in freshwater to be $5.4\text{E-}4 \text{ g L}^{-1}$ and TRANSPECII predicted Ni to be $5.8\text{E-}4 \text{ g L}^{-1}$, indicating very good agreement between these two models under essentially the same scenario. Both of those predicted results are within the observational data range of $4.0\text{E-}4$ – $8.0\text{E-}4 \text{ g L}^{-1}$. Fig. S7 shows the predicted results by metalFate over the simulation time and Fig. S8 demonstrates the mean concentrations and mass fraction distributions for particulate, colloidal, and dissolved forms of Ni over the 60-year simulation in air, freshwater, freshwater sediment, and soil compartments. The mean predicted concentrations are the highest in the freshwater sediment, and the dominant species is the particulate form of Ni. The highest mass fraction is also associated with the particulate form of Ni in freshwater sediment, followed by soil compartment (Fig. S6).

3.3. Predicted exposure concentrations for organoFate

Fig. 5 displays the predicted chemical concentrations of benzene in eight environmental compartments estimated by organoFate at the end of a 10-year simulation, compared with the results obtained from MAMI, SimpleBox, and EQC. The steady state of benzene in organoFate is reached within the first year of simulation time (Fig. S9). PECs for air are very similar among the four models, and fall within the observed range. There is also very good agreement between the models for the water and sediment compartments, although SimpleBox estimates higher PECs in all cases, by between 30 and 50%. organoFate, MAMI and EQC also generate very similar PECs for soils, which are under predicted by SimpleBox. The dominant transport processes are aerosol dry deposition, aerosol wet deposition, and rain dissolution that transfer benzene from air to water and soils. Other diffusion-limited and advective processes (e.g., sedimentation, runoff, and erosion) were secondary for compartmental transfers under these conditions. Thus, under essentially the same environmental conditions, organoFate estimates PECs that are very similar to other proven models.

3.4. Comparison between four pesticides

PECs of the four different pesticides varied significantly, due in part to the differences in application rates, but also due to their very different physicochemical properties and reactivity (Fig. 6). Concentrations of chlorothalonil and cyprodinil in freshwater peak every year, as they are transported by winter storms to the receiving water body, but don't accumulate in soils, since they

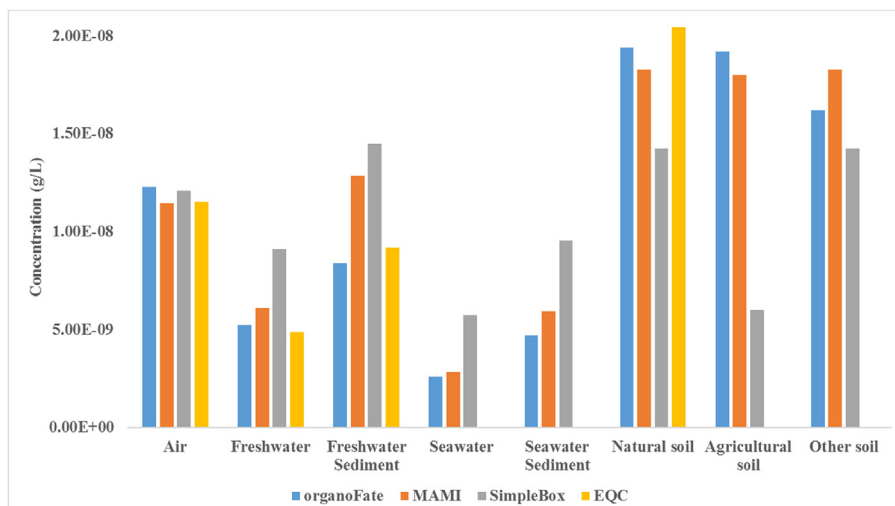


Fig. 5. Model results comparison for benzene. The simulation results from organoFate are at the end of a 10-year simulation.

degrade rapidly enough after every application. Since these organic pesticides have some volatility, they eventually transport to urban and natural soils, although their concentrations in those compartments are orders of magnitude lower than in agricultural soils. Also, there is minimal accumulation in freshwater sediments. In contrast, copper sulfate and nanocopper oxide result in the accumulation of copper in soils and sediments, with increasing concentrations in freshwater. There is no significant atmospheric transport of copper to other soils.

A comparison of long-term concentrations in freshwater with the EC50 toxicity endpoint for *daphnia magna* after 48hr (USEPA, 2019) indicates that (1) chlorothalonil exceeds its toxicity level of $3.0\text{E-}5\text{ g L}^{-1}$ over 60% of the simulated days; (2) cyprodinil exceeds its toxicity level of $3.3\text{E-}5\text{ g L}^{-1}$ almost half of the simulated days; (3)

copper sulfate is well below its toxicity level of $1.1\text{E-}1\text{ g L}^{-1}$; and (4) nano copper oxide exceeds its toxicity level of $2.7\text{E-}3\text{ g L}^{-1}$ around 10% of the simulated days (Fig. 6). Therefore, toxic effects may be observed in freshwater for cyprodinil and nano copper oxide. Freshwater oysters may be exposed to contaminated freshwater sediment. The EC50 toxicity of *Crassostrea virginica* (American oyster) after 96hr for chlorothalonil is $1.4\text{E-}5\text{ g L}^{-1}$ and for cyprodinil it is $4.3\text{E-}4\text{ g L}^{-1}$, and the toxicity level of copper sulfate for *Crassostrea gigas* (Pacific oyster) is $7.4\text{E-}6\text{ g L}^{-1}$, indicating that the toxic effects may be observed in freshwater sediment for cyprodinil and copper sulfate. In soil water, the toxicity endpoint of LC50 for *Hydroides elegans* (tubeworm) in 48hr is $1.2\text{E-}5\text{ g L}^{-1}$ for chlorothalonil; toxic effects may be observed for *Caenorhabditis elegans* (roundworm) after 96 h at $1.6\text{E-}2\text{ g L}^{-1}$ for copper sulfate and 3.9E-

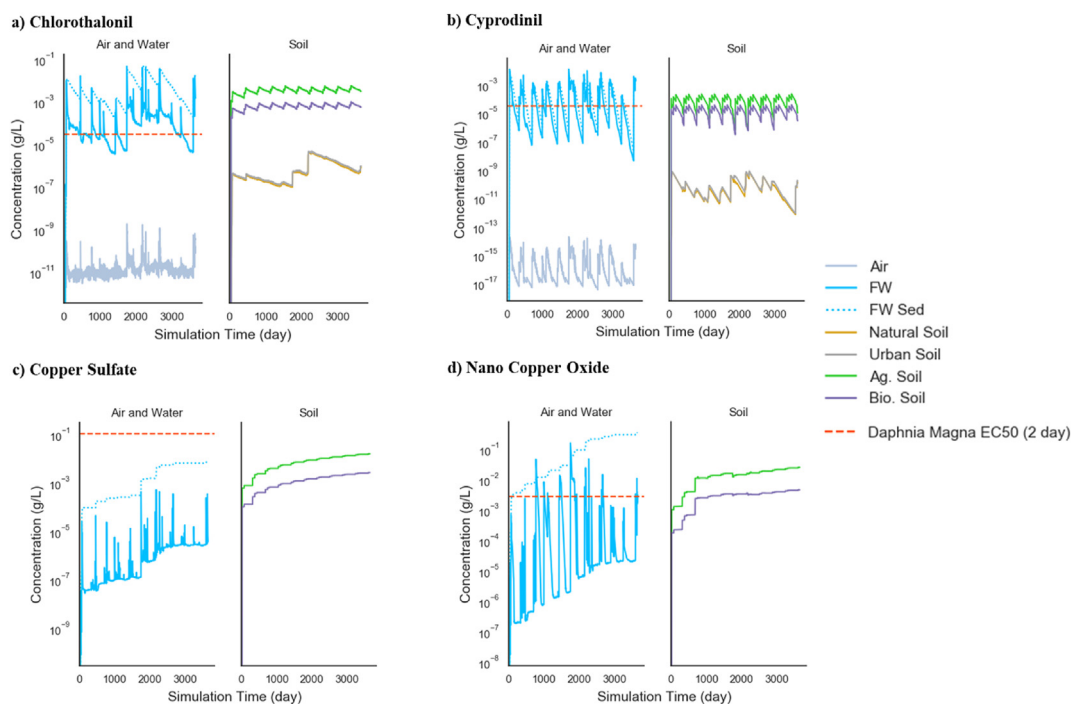


Fig. 6. Predicted daily concentrations in compartments and the toxicity endpoint EC50 of daphnia magna in freshwater.

3 g L⁻¹ for nano copper oxide (Mashock et al., 2016). Compared to soil bulk concentrations, it is likely that toxic effects may be observed in soil for chlorothalonil and nano copper oxide. For cyprodinil, the toxicity endpoint of LC50 for earthworms in 14 day in soil is 5.1E-1 g L⁻¹, indicating no toxic effect may be observed for this species at this toxicity level (EFSA, 2006).

While a more robust sensitivity analysis is planned for the future, the sensitivity of two parameters deemed to influence freshwater concentrations were evaluated, namely the agricultural soil curve number (CN) and the sediment resuspension rate in the freshwater compartment. The agricultural soil CN was modified by increasing or decreasing it by 2 units from its original value (CN = 83). A previous simulation with a change of 10 units resulted in very large changes in concentration (data not shown). With a change of 2 units, the concentrations of all pesticides change noticeably (Fig. S10). The change in concentration is better seen as a percent difference from the original simulation (Fig. S11). While there is some symmetry to the responses, there is a much greater increase in concentration when the CN is increased by 2 units, with concentration changes of more than 200%, while the concentration changes are less than 50% when the CN is decreased by 2 units. The two organic pesticides and the nanopesticide had the larger changes as CN was increased or decreased, although the response varied substantially for each pesticide, under the same conditions.

Similarly, when the freshwater sediment resuspension rate was increased by 50%, the freshwater PECs vary from -12 to +3% for chlorothalonil, -1 to 0.2% for cyprodinil, 0–5% for copper sulfate, and -99 to +347% for nano copper oxide (Figs. S12 and S13). The response in concentration changes for a decrease by 50% in the resuspension rate were very symmetrical, except for the nanopesticide. In the case of nano copper oxide, the decrease was noticeable less than the increase in concentrations when the resuspension rate was increased. All concentration changes displayed oscillatory patterns, in response to the input of surface runoff entering the freshwater compartment, and the degradation of the organic pesticides. These results serve to demonstrate the value of a framework that allows a direct comparison of behavior under the exact same environmental conditions, only changing the chemical properties accordingly for each type of chemical.

Copper from copper sulfate and nano copper oxide accumulated in freshwater sediments and soil compartments, but no substantial chemical accumulation was observed for the organic chemicals, chlorothalonil and cyprodinil (Fig. 7). This is mainly due to the degradation of the organic pesticide and naturally the lack of

degradation processes for copper. Due to accumulation of metal ions in freshwater sediments and soil compartments associated with particulates, the highest average long-term concentrations are observed in freshwater sediment for nano copper oxide, followed by nano copper oxide in agricultural soil and copper sulfate in agricultural soil (Fig. 7). Although the average long-term concentrations for chlorothalonil and cyprodinil are not high, they are still likely to pose a risk to water systems. For copper sulfate and nano copper oxide, the predicted concentrations in air, natural soil and urban soil compartments were nil for copper ion, because these pesticides were only released to agricultural soil with and without biosolids application, and copper was transferred to freshwater compartments through soil erosion, runoff, and horizontal leaching. Since the wind speed in Visalia region from 2005 to 2014 ranged from 0 to 6 m/s, considered light to moderate breeze, wind erosion was not significant, on average, to transfer copper attached to particulate from soil to air in a significant amount.

4. Discussion

4.1. Model application

The results from organoFate, ionOFate, and metalFate are comparable to other widely used models (i.e. EQC, MAMI, SimpleBox, and TRANSCII) under the same model parameterizations. ChemFate has several advantages over these previous models. First, ChemFate provides a consistent modeling framework that allows the direct comparison of chemicals of radically different types under the same environmental conditions. Second, the models in ChemFate are able to simulate time-dependent daily chemical concentrations with real regional daily climatic data that has daily fluctuations, as well as the actual daily river flow. Third, a fundamental determinant of concentrations is the emission rate (Sweetman et al., 2002), and ChemFate allows for more realistic dynamic emissions (e.g. pesticide application, variable release from a wastewater treatment plant or industrial facility). This is particularly important for chemicals that are used seasonally, episodically, or are released due to an accident spill. Environmental fluctuations and release fluctuations have the potential to cause short-term toxic effects (Garner et al., 2017), and ChemFate can capture the temporal risks of high contaminant concentrations, particularly to sensitive species in the environment (Parker and Keller, 2019). Due to its capability to handle realistic regional climatic data, hydrology and dynamic emissions, ChemFate is

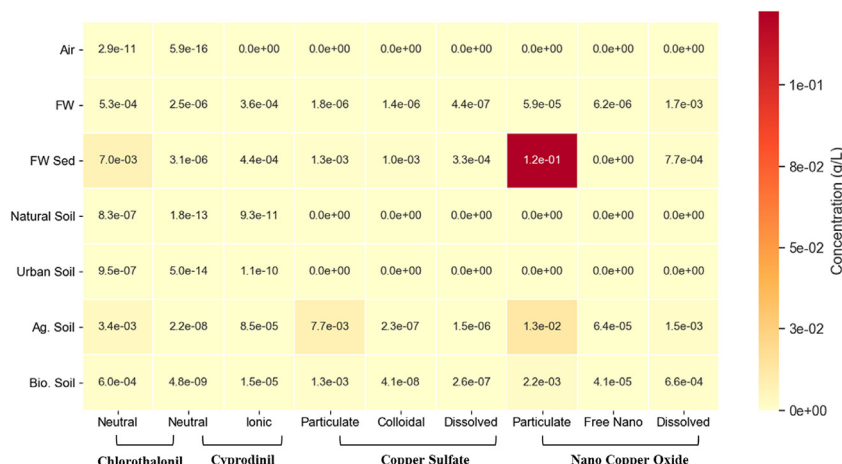


Fig. 7. Average long-term concentration of four pesticides (chlorothalonil, cyprodinil, copper sulfate, and nano copper oxide) by compartments and by species forms.

applicable to various spatial scales, although it would perform better in smaller, more homogenous regions. The time-dependent predicted concentrations also make it more useful to compare with monitoring data for validation purposes. Fourth, for ionizable organic chemicals and metals, ionOFate and metalFate not only generate predictions for total chemical concentrations in different compartment, but also generate predicted concentrations for the ionized and non-ionized forms. nanoFate tracks the additional nanoparticles and their aggregates. Fifth, ChemFate considers a wider range of processes than the previous models, such as aerosol resuspension and transformation for ionic species, and the transport processes consider the variations of climatic data instead of assuming constant rates, such as soil runoff and soil erosion. Finally, ChemFate is coded in Python and it can be easily extended to incorporate more environmental compartments and transport processes for future improvement. For general users, ChemFate has a user-friendly graphical user interface (GUI) to simplify running the models. Since all input data are in comma-separated (CSV) spreadsheets, it is readily viewable for the user, and can be easily adapted for new chemicals and regions.

4.2. Model limitations

In all multi-media fate and transport models, the general assumption of homogenous mixing is applied. In addition, ChemFate assumes an instantaneously homogenous distribution of various chemical species within the same environmental compartment. For example, in confined freshwater, metalFate assumes metals to be distributed among the dissolved, colloidal, and particulate phases immediately, based on their partitioning coefficients. This may not be valid for all chemicals, but we have made this assumption due to the lack of kinetics data to model the rate of distribution (Bhavsar et al., 2008).

ChemFate is designed to model regions with different combinations of environmental compartments, but it is not directly applicable to a river network that connects several sub-compartments to simulate river reaches. Some other models and tools are available to simulate soil-water interactions with more in-depth hydrological modeling of the connected watershed network, such as SWAT (Neitsch et al., 2011) and WARMF (Chen et al., 2001). One can consider the release to a particular river reach in the vicinity of a point source, and then model the far-field effects in a downstream freshwater, estuarine or coastal compartment (Parker and Keller, 2019). Furthermore, the advective transport out of air and coastal marine compartments are considered as losses from the modeled system. This is different from global or large regional scale fate models that simulate chemical transport from one grid to another (MacLeod et al., 2001; Su et al., 2018; Toose et al., 2004).

Observed concentrations are rarely available at the spatial and temporal frequency needed to validate these models. This was the case with the four pesticides, which are not monitored in the Visalia region. Typically, monitoring efforts are sporadic, and reflect point values, rather than averages for a region, making comparisons against model predictions difficult. The release scenarios we usually explore are at large scale, which makes it unfeasible to compare against small-scale field observations directly. Despite this challenge, models still need to be continuously improved and validated with monitoring data as close as possible to avoid systematic errors because of omitted or poorly described processes (Mackay et al., 2009).

Since models are simplifications of the real world, they always embed uncertainties in themselves. Two primary types of uncertainty exist in ChemFate, which are model uncertainty and parameter uncertainty (Dubus et al., 2003; Hertwich et al., 2000; MacLeod et al., 2002). In ChemFate, the model uncertainty includes

the transport and transformation processes involved in the model and the mathematical equations that are used to model each process. Even though state-of-art or widely used equations for major processes are incorporated in ChemFate, model uncertainty still exists and may be improved iteratively through constant model evaluation and calibration. The major source of parameter uncertainty in ChemFate come from the input parameters of physical-chemical properties and environmental parameters, which is usually addressed through Monte Carlo method (Hertwich et al., 2000; Luo and Yang, 2007).

5. Conclusions

Four multi-media fate and transport models were developed under the ChemFate framework to predict time-dependent daily chemical concentrations in various environmental media: (1) organoFate, a model for non-ionizable organic chemicals, (2) ionOFate, a model for ionizable organic chemicals, (3) metalFate, a model for metals, and (4) nanoFate, a model for nanomaterials. ChemFate aims to provide a consistent modeling framework that enables the direct comparisons of different classes of chemicals under the same environmental conditions. Model results from organoFate, ionOFate and metalFate are comparable with widely adopted models (i.e. EQC, MAMI, SimpleBox, and TRANSPECII) under the same model parameterizations. ChemFate presents the most comprehensive capabilities, providing predictions for four radically different types of chemicals, and also incorporating dynamic emissions and dynamic environmental conditions. The dynamic capabilities of ChemFate allow simulations with real regional meteorology and local release scenarios. ChemFate can be used to rapidly screen a wide range of chemicals in a region, providing information for risk and alternatives assessment.

Credit author statement

Dr. Mengya Tao was the major developer of ChemFate, the modeling framework, and was the lead author for the manuscript. She performed the simulations, created the figures and wrote the User Guide. She also participated in the revisions. Dr. Arturo A Keller was the lead in conceptualizing the ChemFate framework, guiding Dr. Tao through the development of the modeling framework, suggesting the simulations to be performed, the figures to be prepared, and the preparation of the manuscript. He also actively participated in the editing of the manuscript and all the documents associated with the model. He also obtained the funding needed to carry out the project.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2020.126897>.

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