A multimedia fate model to support chemical management in China: a case study for selected trace organics

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Abstract

SESAMe v3.3, a spatially explicit multimedia fate model for China, is a tool suggested to support quantitative risk assessment for national scale chemical management. Key advantages of the model include consideration of environmental pH for ionisation of chemicals and agricultural soil irrigation with surface water. We evaluate the model performance using estimates of total industry usage of three UV filters and three antimicrobials. The model generally performs well for the six case study chemicals as shown by the comparison between predictions and measurements. The importance of accounting for chemical ionisation is demonstrated with the fate and partitioning of both triclosan and climbazole sensitive to environmental pH. The model predicts ionisable chemicals (triclosan, climbazole, benzophenone-3) to primarily partition into soils at steady state, despite only being released to freshwaters as a result of agricultural irrigation. However, further model calibration is needed when more field data is available for soils and sediments for larger areas of water. As an example, accounting for the effect of pH in the environmental risk assessment of triclosan, limited freshwater areas (0.03% or ca. 55 km^2) in mainland China are modelled to exceed its conservative environmental no-effect threshold. SESAMe is a tool that can be used to support chemical risk assessment and the spatial aspect provides a guide to identify relatively regions of interest to focus monitoring campaigns.

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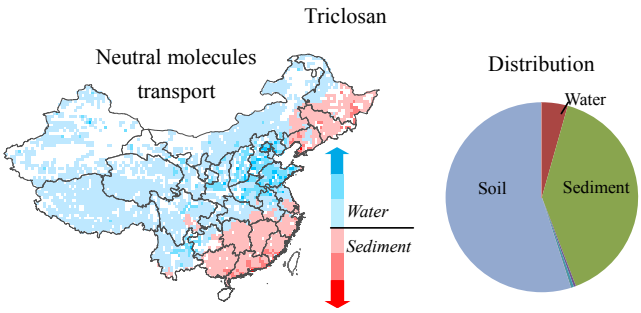

Introduction

Assessment of exposure pathways, relative risk, prioritization and risk management are key to better characterising chemicals and managing potential risks to humans and the environment.[1, 2] For chemical management in China, attention is often currently focussed on new chemicals (i.e. newly manufactured or imported) and trace organics (TO) that are used or can enter the environment as a common part of our daily life. Examples include pharmaceutically active compounds (PhACs), personal care product ingredients (PCPs), endocrine-disrupting chemicals, disinfection byproducts and some industrial chemicals etc.[3] Several categories of TO can be released directly with sewage effluent to aquatic environments or via wastewater treatment plants (WWTPs), and partially to soil (e.g. via the application of sludge). Some may be ionisable, which have different partitioning behaviour from neutral chemicals after being released.

For better chemical regulation and environmental and health protection, the European Union (EU) and the US have both introduced legal frameworks, EU REACH (2007, Registration, Evaluation, Authorisation and Restriction of Chemicals)[1] and US TSCA (1976, Toxic Substances Control Act).[4] Multimedia environmental fate models have been widely adopted by developed countries in frameworks for chemical management (e.g. EUSES, US PBT Profiler and OECD chemical screening tool etc.),[5-7] and have been demonstrated to be useful decision-support tools.[7, 8] China has so far lagged behind on chemical management. However, as a rapidly industrialising country with a large population, the increasing use and release of TO has raised questions as to their potential impacts or otherwise on the environment and human health. The Ministry of Environmental Protection (MEP) of China has published the Provisions on the Environmental Administration of New Chemical Substances in China (edition 2010)[9] to require the registration of new chemicals with relevant risk assessment information. There is therefore a research need to develop a multimedia fate model specifically for China to support regulation[2] and there is the opportunity for China to exert leadership in the use and adoption of state-of-the-art modelling approaches.

A further development of the SESAMe model,[10] SESAMe v3.3, is presented in this study to account for the spatially variable surface water and soil pH values and chemical ionisation, so that ionisable chemicals can be included in model predictions for aiding chemical management for China. Three antimicrobials agents and three UV filters (i.e. TCS, TCC, climbazole, benzophenone-3 (BP-3), octocrylene (OC) and octyl methoxycinnamate (OMC)), covering a range of physico-chemical properties were selected for a case study in China to: (1) predict spatially resolved exposure concentrations and partitioning in environmental media, (2) demonstrate the importance of accounting for ionisation and environmental pH in chemical risk assessments and (3) illustrate the application of SESAMe v3.3 for chemical management in China. These substances represent chemicals where there are common challenges for modellers and risk assessors, to estimate use and release to the environment from diffusive everyday activities.

Methods and materials

Chemicals selection and properties

Figure 1 shows a chemical space plot indicating the predicted compartment distribution (air, water or sediment) for chemicals with a range of LogD/Kow and LogKaw values. Chemical and environmental properties determine chemical fate.[11] Extreme chemicals with LogD/Kow around -12 and LogKaw < -20 Pa·m^3/mol almost entirely distribute into a single compartment; while moderate chemicals with LogD/Kow between 0 and 10 or LogKaw between -10 and 5 Pa·m^3/mol tend to distribute in multiple compartments. Example chemicals (142 antimicrobial agents and 19 UV filters) used in commerce are shown in Figure 1 (chemical properties predicted mostly by Pipeline Pilot[12]). Freshwater pH may affect ionisable chemicals partitioning between freshwater and sediment to a varied extent (shown as error bars). Other environmental parameters may also impact on this distribution (e.g. soil pH) but are not shown in Figure 1.

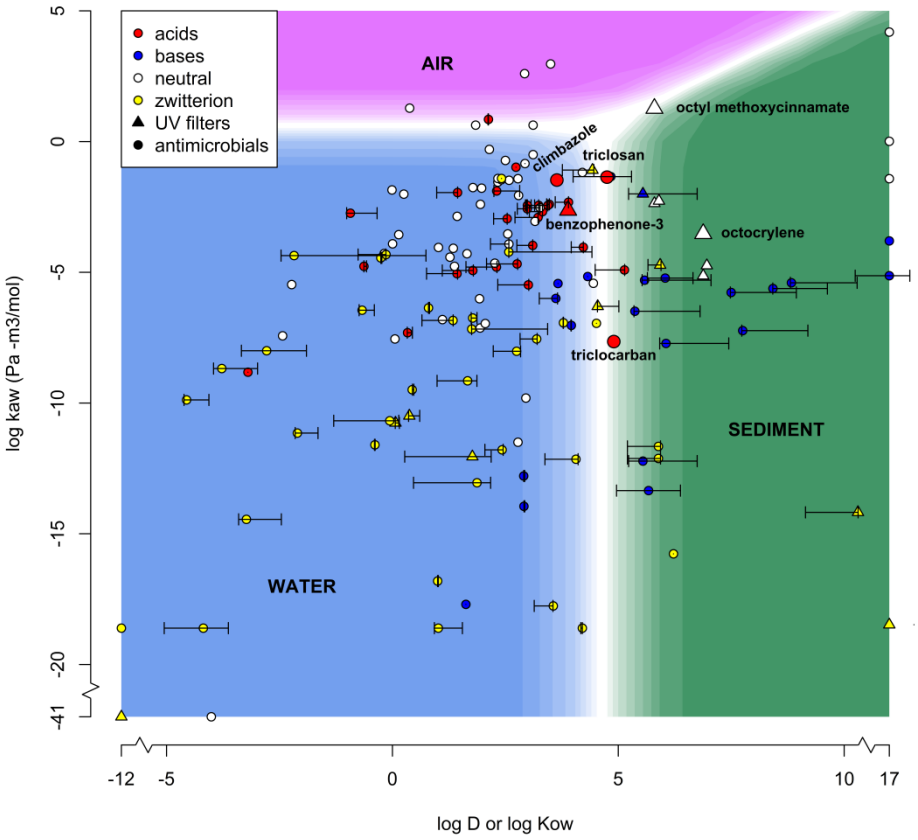

Figure 1 Chemical space indicating where chemicals with different log Kaw and log D/Kow will distribute in the environment; circles represent antimicrobial agents and triangles are UV filters; the middle of the white conjunction indicates the chemicals evenly distributing in multiple environmental media and the area away from the white indicates chemicals mostly distributing in a single environmental compartment. Error bars show the range of the log D of the ionisable chemicals with different environmental pH (5.7 – 10.5 with consideration of possible pollution), which could affect chemical partitioning between water and sediment.

The six case study chemicals (highlighted in Figure 1) were selected from a portfolio used by the PCPs industry covering neutral and ionisable chemicals. Antimicrobial agents and UV filters are two commonly used groups of PCPs. They have been detected in multiple media in different regions across China.[13] UV filters are ingredients used in sunscreen products or cosmetics for protection against the adverse effect of ultraviolet radiation;[14] antimicrobial agents can be used in consumer products to protect against certain types of bacterial or fungi. The lifetime exposure of aquatic organisms to these substances can be sustained regardless of their persistence, when they are continuously discharged into the aquatic environment. Although the ecotoxicity of these chemicals were studied and observed in acute or chronic exposure tests under high testing concentrations,[15] the environmental measurements or modelling results generally indicates concentrations below the level of concern.[16] However,

these chemicals have 'intermediate' physicochemical properties (Table S1) and can partition into multiple environmental compartments, which makes them ideal case study chemicals for this model application. TCS and climbazole are acids with pKa values of 7.9 and 7.5, which are in the range of pH for freshwaters and soils in China (stated below); and BP-3 and TCC are acids with high pKa of 9.54 and 12.7. BP-3 has a lower log Kow than TCC; and OC and OMC are hydrophobic neutral chemicals with relatively high log Kow values (6.9 and 5.8), which are more likely to be adsorbed to sediment.

Model configuration and evaluation

So far, multimedia chemical fate models used to simulate real environments have typically focussed on neutral organic chemicals. To account for the different partitioning behaviour of ions, it requires chemical ionisation to be considered in the model and the range and variability of pH in the Chinese environment. SESAMe v3.3 (with a 50×50 km^2 grid) was therefore developed and updated to incorporate spatial pH data for freshwater and sediment across China (model feature see Supporting Information). The spatial freshwater pH dataset was generated using weekly pH data from 99 gauging stations in China in 2012 (details see Supporting Information).[17] It ranged from 6.8 to 8.6 across China with a median of 7.8 (Figure S1). The pH of solid phases in sediments was assumed to be 0.6 lower than that in freshwater within the same grid cell.[18] Agricultural soil pH values ranged from 4.8 to 8.5 with a median of 6.5 (Figure S2). Agricultural soil irrigation by freshwater in the same grid cell was an important process for the transport of compounds from water to soil, during which ca. 370 billion m^3 water was assumed to be uniformly distributed to agricultural soil across mainland China, as described previously by Zhu et al.[10] Other environmental parameters have been introduced previously.[10]

Emissions were assumed to be all released to freshwater. The model was used to predict the spatial concentration of chemicals in environmental media, especially aquatic systems, total mass of chemicals in each environmental compartment and net fluxes between freshwater and sediment at steady state, to show the spatial variation in transport behaviour. The neutral TCS concentration was predicted for a pH adjusted environmental risk assessment for China. Measured data for freshwater and sediment in China were collated from peer-reviewed literature for the six chemicals to evaluate the model (Figure S5 and Table S5). No measured data of UV filters in freshwater sediment was found, however these chemicals are highly insoluble and sorbed to organic material on sediment solids which will likely result in low bioavailability and toxicity in the environment.[16] Statistical distributions of predicted and measured concentrations in freshwater and sediment for China were compared. For individual catchments, as literature on monitoring data was limited and measurements for individual

sampling sites was not normally provided, average measurement data were compared with average predicted concentrations of grid cells covering the catchment. Model uncertainty for each chemical was explored by Monte Carlo simulation by running the model 10,000 times with parameters randomly taken from the environmental parameter and the emission databases. Sensitivity analysis was implemented by adopting a variability-based sensitivity coefficient (SCV, see Supporting Information).

Emission inventory

Emissions are principle model inputs for predicting chemical concentrations. The six chemicals are frequently used formulation ingredients, but their emissions/discharges cannot be readily acquired directly. Therefore a spatially resolved emission inventory was developed, for which chemical specific inclusion levels in products and removal ratios in WWTPs were collected or estimated.

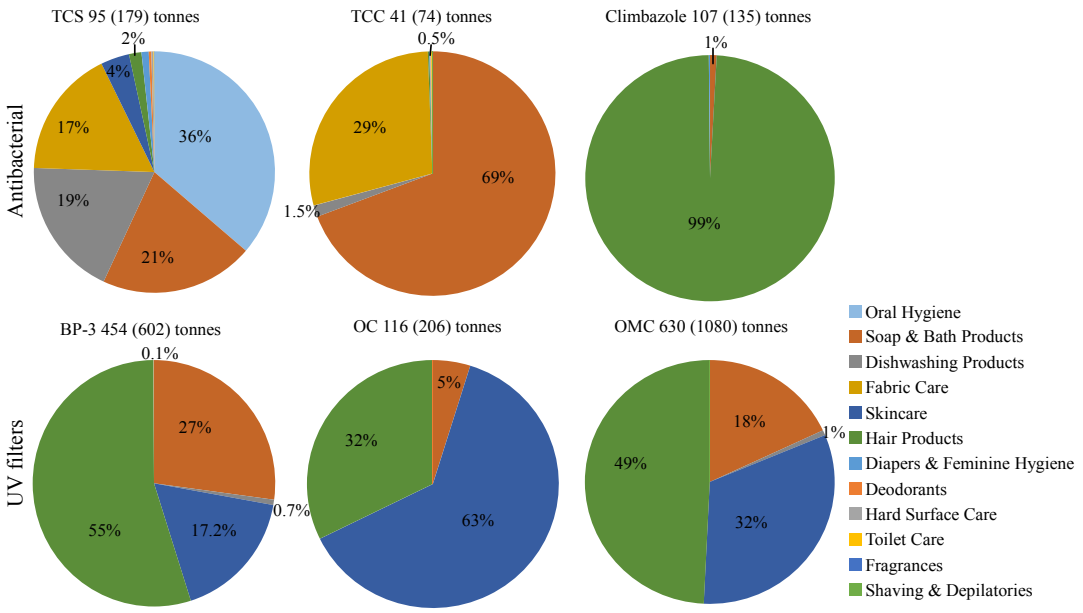

Figure 2 Estimated source composition and total emission (usage) of three antimicrobial agents (TCS, TCC and climbazole) and three UV filters (BP-3, OC and OMC) in China in 2012

Usage. The Mintel Global New Products database[19] provided i. the (sub-)categories of personal and home care products in the Chinese market; ii. the total number of variants released on to market under each sub-category; iii. the number of variants with each of the six chemicals under each sub-category. This provided the fraction of products containing specific chemicals. The tonnage of products sold in the Chinese market was exported from the Euromonitor database.[20] Figure 2 shows the categories of products which contain some or all the six chemicals, which will ultimately be released to the wastewater system. The inclusion

levels of chemicals for each sub-category were collected from the literature (Table S2). Combining the above information, the usage (tonnes) of individual chemicals in the Chinese market for 2012 was estimated. Subsequently, it was allocated to counties across China, by linking estimates of product usage at the population level (based on a population's ability to purchase individual products) with spatial distributions of GDP across China.[21]

Emissions. All products sold in the Chinese market in 2012 were assumed to be consumed and released with the domestic wastewater within the same year. Due to uneven socioeconomic development, the proportion of population connected to WWTPs for wastewater treatment varied between urban and rural areas and also between different counties. The proportion of population connections to WWTPs for urban and rural areas were estimated based on the per capita daily domestic water use, the domestic wastewater discharge and the rural and urban population data at the province level (details see Table S3 and Supporting Information). Owing to a lack of data, urban and rural per capita water use was assumed to be equal and the estimated proportions of population connections to WWTPs were assumed to be the percentage of wastewater processed by WWTPs and assigned to each county.

The measured removal ratios of the six chemicals in WWTPs taken from the peer reviewed literature ranged from 55->97% for TCS,[22, 23] 96-98% for TCC,[24] 18-67% for climbazole,[25, 26] 10-99% for BP-3,[27-29] 40-99% for OMC [28-30] and 36-99% for OC.[29-31] The variation of values for each chemical is due to different sampling seasons and methods or WWTP technologies in different studies. To aid the selection of a representative value for a secondary activated sludge plant (which are typical wastewater technologies in China), SimpleTreat 3.2 model,[32] which can model ionisable chemicals, was used. The predicted values were typically within the removal ratio ranges from the literature and were considered reasonable and thus used in the SESAMe model. The predicted removal ratios were 95% for TCS, 96% for TCC, 89% for OMC, 91% for OC and 49% for BP-3. For climbazole, the predicted value was 12% and beyond the measured range (reason see Supporting Information), so a measured value of 40% from a study in Beijing[26] was assumed.

The emissions of the six chemicals by county were calculated combining the usage, chemical removal ratio in WWTPs and the fraction of domestic wastewater treated by WWTPs. This estimation method is not limited to the six chemicals but can be used for most PCP chemicals. The emissions by county were allocated by population to the 50×50 km^2 grid using ArcGIS 10.2.2.

Correcting for pH dependent toxicity

For ionisable chemicals, toxicity has been demonstrated to be pH dependent.[33, 34] However, current toxicity data or standard guidelines on such chemicals are suggested without pH correction or pH conditions, which may cause high uncertainty for environmental risk assessments. For example, 100 ng/L of total TCS was the recommended standard by the UK Technical Advisory Group on the Water Framework Directive for long-term exposure in freshwater but without suggesting the applicable environmental pH;[35] the PNEC (predicted no effect concentration) of TCS has been reported to range from 26.2 to 1550 ng/L as total TCS concentration,[34, 36-38] probably due to uncertainties and variability in pH during toxicity studies, which typically increase (7.5/7.7 to 8.65/10.2) in the growth media during the algal test due to photosynthesis.[34, 39] This range of values may also have resulted from other factors such as the measurement system used or analytical measurement errors, etc. It has been demonstrated that where strictly controlled pH conditions are used, the effective component for toxicity (i.e. neutral TCS) has relatively constant concentration in toxicity test with daphnia[34] and algae[40] (Table S4).

Therefore, a pH corrected indicator of $PEC_n/PNEC_n$ (PEC, predicted environmental concentration; the subscript 'n' indicates the neutral concentration) was developed for ionisable chemicals to better account for toxicity in the environment and ultimately a more realistic environmental risk assessment. TCS was selected as an example, as it is well studied with a large toxicity dataset.[39] $PNEC_n$ in freshwater can be derived by the same method for PNEC - $NOEC_n/EC_{n,X}$ (x, 5-20%) of a most sensitive aquatic species to TCS (i.e. certain algae)[15, 38] divided by the assessment factor (AF).[41] $NOEC_n$ was calculated using NOEC at different pH levels reported by Roberts et al.,[40] as the pH in exposure growth media was well controlled in this study (Table S4). The lowest $NOEC_n$ (1.5 ug/L) was taken to calculate $PNEC_n$ for freshwater as a conservative estimation for environmental quality, by which $PNEC_n$ of 150 ng/L was estimated with an AF of 10. PEC_n across mainland China was predicted using SESAMe v3.3.

Results and discussion

Emission inventory

Figure 2 shows the total emissions (usage) (unit, tonnes) estimated to be 95 (179) for TCS, 41 (74) for TCS, 107 (135) for climbazole, 454 (602) for BP-3, 116 (206) for OC and 630 (1080) for OMC in mainland China for 2012. Oral hygiene (36%), soap & bath products (21%), dishwashing (19%) and fabric care products (17%) comprise the main sources of TCS; soap & bath products (69%) are the main sources of TCC; climbazole is mainly used in hair products (99%) as an anti-dandruff agent. OC is mostly used in skincare products (63%) including daily face care (usage 47 tonnes) and sun care products (usage 80 tonnes), as it is

more photo-stable than the other UV filters and can stabilize the other UV filters in the formula;[42] in contrast, hair products are the dominant category for BP-3 (55%) and OMC (49%); soap & bath products are an important source for BP-3 (27%) and fragrances are an important source for OMC (32%).

The emission and usage in this study for 2012 are ca. 1.5 and 1.8 times higher for TCS[43] but less than half for climbazole[44] of those estimated for 2011 by Zhang et al. Although product consumption will probably increase every year in China along with the economic growth, it is still unlikely that the usage/emission of TCS could increase significantly over a year. As an important category of products consumed in the Chinese market, the consumption of fabric care products (power/liquid detergents) is probably greatly underestimated (431 t/year)[43] by Zhang et al. For climbazole, the fraction of variants for shampoo that contain this chemical in our study (1.15%) is estimated to be lower than that by Zhang et al. Uncertainty may exist in usage and emission estimation for these chemicals, because (1) it remains challenging to obtain total industry usage and estimate an relatively accurate WWTPs connectivity in China; (2) the inclusion levels are assumed to be constant for all variants under the same category and (3) the removal ratio are assumed to be identical in all STPs across the country for individual chemical, which are probably not the reality.

Figure S3 shows total emissions by county across China (exclusive of Taiwan) in 2012 for the six selected chemicals. The ranges (5^{th}-95^{th} percentiles) plus median are 0.001-0.11 (median, 0.02) tonnes TCS, 0.0004-0.05 (0.01) TCC, 0.002-0.12 (0.03) climbazole, 0.007-0.5 (0.1) BP-3, 0.001-0.14 (0.02) OC and 0.01-0.75 (0.14) OMC. Generally, emissions of all six chemicals are similar and relatively high in highly populated regions in Liao River basin in Liaoning, North China Plain (NCP), Jiangsu, Shanghai, north Zhejiang, eastern Sichuan, coastal regions in Fujian and Guangdong. Several regions in Guangdong province (e.g. Dongguan, Guangzhou, Shenzhen and Foshan etc.) and Shanghai have the highest emission of all six chemicals, followed by the Beijing area. The lowest usage and emission for six chemicals is in Cuoqin in Tibet. Figure S4 shows the emissions allocated to 50 × 50 km^2 grid.

Model evaluation and spatial distribution of the six chemicals

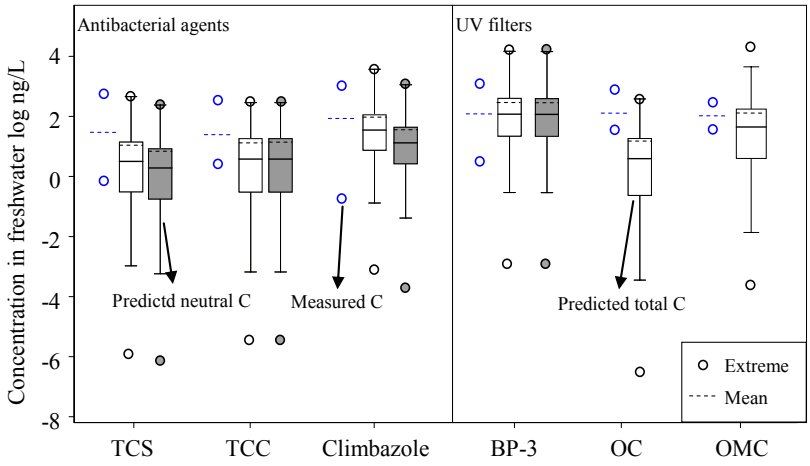

Figure 3 Boxplot of predicted total and neutral chemical concentrations, and measurements in freshwater; white-box group indicates predicted total chemical concentration (neutral plus ionic molecules); grey-box group indicates predicted neutral concentration; extreme circles are max/min values.

The model generally performs well for the six chemicals as shown by the comparison between predictions and measurements (Figure 3, S6-S7). Predictions cover a broader range of concentrations than measurements, especially for lower concentrations, as measured data are only available for several major catchments with higher emissions in more densely populated regions. In addition, in the Chinese aquatic environment, the four ionisable chemicals mostly exist in neutral form, although contents of neutral molecules are significantly less than total concentrations for TCS and climbazole with lower pKa values. Figure S7 shows the comparison between measurements and predictions for each catchment, with differences within 1-2 orders of magnitude, which is a reasonable agreement for these types of model predictions. The differences are probably a reflection of the model calculating the average concentration of the individual 50×50 km^2 grid cell in contrast to measurements representing an instant on-site level. Therefore, larger sample sizes relative to the catchment area which cover both mainstream and tributaries would probably ensure a better match with model predictions, e.g. TCS and TCC (Table S5). For climbazole in the Yangtze River, as the sample size (n=27) was relatively low compared to the large area of the river basin, greater difference is shown between measurements and predictions. Results of the sensitivity analysis are shown in Table S6. The distribution of chemical concentrations in freshwater and sediment using Monte Carlo simulation is lognormal and is shown in Figure S8, along with their interquartile range.

A range of concentrations (5^{th} - 95^{th}, plus mean) are predicted in freshwater and sediment as follows (Figure S9-S10): freshwater, 2.3 $\times 10^{-4}$ - 71 (15) ng/L for TCS, 4.0×10^{-4} - 57 (14) ng/L for TCC, 0.03 - 334 (86) ng/L for climbazole, 0.05 - 1209 (310) ng/L for BP-3, 7×10^{-5}-74 (17)

ng/L for OC and 0.004 - 634 (149) ng/L for OMC; freshwater sediment, 8×10^{-5} - 25 (5) ng/g for TCS, 1.5×10^{-3} – 183 (44) ng/g for TCC, 6×10^{-4} - 13 (3) ng/g for climbazole, 2×10^{-3} - 56 (15) ng/g for BP-3, 4×10^{-4} - 250 (57) ng/g for OC and 4×10^{-3} - 386 (89) ng/g for OMC. The chemicals in sediment are mostly predicted adsorbed on solids rather than in pore water especially for high logKow chemicals. As a result of the freshwater irrigation in agricultural production, predictions show mean concentrations in agricultural soil across mainland China as 0.04 ng/g for TCS, 0.03 ng/g for TCC, 0.2 ng/g for climbazole, 0.4 ng/g for BP-3, 0.01 ng/g for OC and 0.1 ng/g for OMC. This study predicts a broader concentration range for TCS than that by Zhang et al.,[43] as finer resolution of SESAMe v3.3 can identify extreme values better. Lower estimated emission in this study is the main reason that the concentration of climbazole is predicted lower in this study than that by Zhang et al.[44] However, the highest concentration of climbazole in this study is close to that by Zhang et al., which also proves the model can predict the extreme values better. Predictions also indicate the chemical input to coastal seawater system and the relevant concentrations are in Supplement Information.

Generally, the distribution pattern of the six chemicals is similar and the distribution pattern of predicted concentrations and emissions match at the national scale for each chemical. For all chemicals, regions in NCP, Liao River basin in Liaoning, Jiangsu and coastal area in Zhejiang, Fujian and Guangdong have higher concentrations than other regions, which also have higher emissions due to high population. Also the high concentration in NCP is probably related to the low river discharge there. Regional contrasts exist between emissions and concentrations mainly due to the discharge flow, e.g. regions that have the highest emissions in Guangdong and Shanghai do not have the highest concentrations in freshwater and sediment as a result of the dilution by large discharge flows; whilst western and northern Guizhou do not have very high emissions but have relatively high concentrations due to low discharge flow.

Chemical fate and partitioning among environmental media

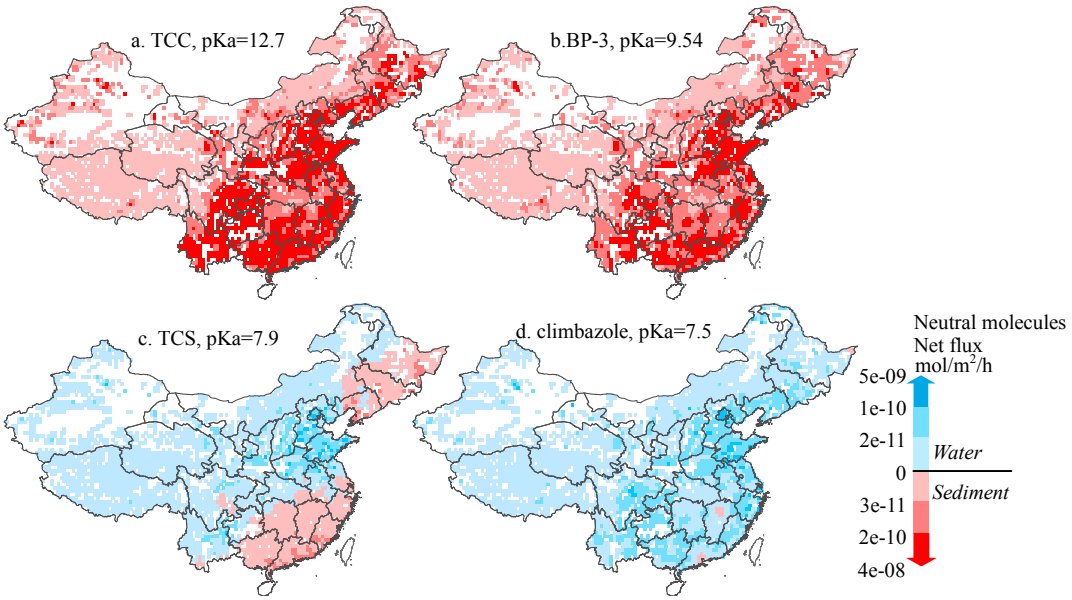

Figure 4 the net flux of neutral molecules of ionisable chemicals between freshwater and sediment compartments; blue indicates the net flux from sediment to freshwater and red is from water to sediment

As a result of constant emission to freshwater, the total molecules (neutral plus ionic forms) of all six chemicals and ionic molecules of the four ionisable chemicals are predicted to be transported from freshwater to sediment across China at steady state (Figure S13). However, the regionally varied main transport direction of neutral molecules of TCS and climbazole (Figure 4), which is the main toxic form, demonstrates that the fate of ionisable chemicals with pKa values within the range of environmental pH is sensitive to the small changes in pH. The neutral molecules of TCS and climbazole are mainly transported from freshwater to sediment in red areas but from sediment to freshwater in blue areas. In red areas (lower water pH), chemicals are mostly present in the neutral form in freshwater after being released and so are transported mainly from water to sediment. In blue areas (higher water pH), a high proportion of molecules are in the ionic form in freshwater but become neutral after partitioning to sediment (pH 0.6 lower than that in water), so neutral molecules partition back to freshwater. The water pH ranges of red areas are 6.8-7.8 for TCS and 6.8-7.2 for climbazole (Figure 4c-d). However the assumption on sediment pH is only one scenario, so there might be regional uncertainty due to the possible different sediment pH in real Chinese environment to that in the model. Sediment can therefore act as either a receiving compartment or a source for neutral/toxic molecules of ionisable chemicals. BP-3 and TCC are mainly present in their neutral form in the Chinese environment, unless the region is polluted resulting in an abnormally high pH, so neutral molecules are mainly transported from freshwater to sediment across China.

If considering all environmental compartments at the national scale, not all of these 'down-the-drain' chemicals emitted to water primarily remain or degrade in the aquatic environment. Agricultural soil is also modelled to be an important compartment at steady state for ionisable chemicals with relatively low pKa and logKow values, under the assumption that land application of sewage sludge or wastewater released directly to soil is not considered in the model. For example, TCS (54% in soil and 41% in freshwater sediment, respectively), climbazole (63% in soil, 13% in freshwater sediment and 18% in freshwater) and BP-3 (54% in soil, 21% in freshwater sediment and 19% in freshwater) (Figure S11) are all predicted to be mainly transported to soil due to the irrigation. These chemicals have either relatively low logKow (BP-3) or low pKa (TCS) or both (climbazole), so a higher proportion will be present in freshwaters rather than in sediments when continuously released compared to chemicals with high logKow and pKa (Figure 1). Then they could be transported to agricultural soil by freshwater irrigation and converted to neutral forms (BP-3 is already neutral) in most regions in China with ca. 85% regions of soil pH < 7.5. The neutral molecules tend to adhere to soils. Climbazole has both lower pKa and logKow, so it is modelled to have the highest proportion in soils among the three. However, it should be noted that despite representing an important environmental compartment, soil concentrations of these chemicals are low as stated above, which are far below the terrestrial toxicity threshold.[45, 46]

The other three neutral (TCC is almost neutral) hydrophobic chemicals are modelled to partition more to sediment after release, so only a limited proportion of chemicals will transport to soil by freshwater irrigation, i.e. TCC (85% in freshwater sediment, 8% in agricultural soil and 1.7% in freshwater), OC (91% in freshwater sediment, 3% in soil, 1.7% in freshwater) and OMC (77% in freshwater sediment, 12% in agricultural soil, 7% in freshwater) (Figure S11). The chemical distribution in different media can vary regionally, as shown in Figure S12. Regional uncertainty should be noted owing to the assumptions on agricultural irrigation with freshwater in this model. In reality, agricultural vegetation forms may vary in different regions, e.g. rice and wheat, which will require significantly different amount of irrigation water per area; and source of irrigation water may not only come from the local surface water in some regions but from other regions/grid cells. However, no monitoring data is available to explore the validity of this prediction.

This is a first study accounting for environmental fate of ionisable chemicals at the national scale for China. The findings contrast with conclusions in modelling studies by Zhang et al. that at steady state, the greatest amount of chemical is predicted to be in sediment for climbazole (83.7%)[47] and TCS (96.7%).[44] It is believed that conclusions on environmental fate of these chemicals are more refined in this study, because in Zhang's study (1) only sewage irrigation was considered (no freshwater used), which provides insufficient water

supply for agricultural irrigation requirements, so the chemical transfer to soil is likely to be underestimated; and (2) the two chemicals were modelled in their neutral form only, which would probably overestimate the ratio of chemicals in sediment to those in water, especially for TCS with a higher logKow than climbazole. So in this study, although sewage irrigation hasn't been considered, freshwater irrigation, albeit with diluted chemical concentrations compared to wastewater, is predicted to be an important source of the two chemicals to soil. This conclusion is probably applicable to many other down-the-drain chemicals with low pKa or logKow values.

Accounting for ionisable chemicals in environmental risk assessment

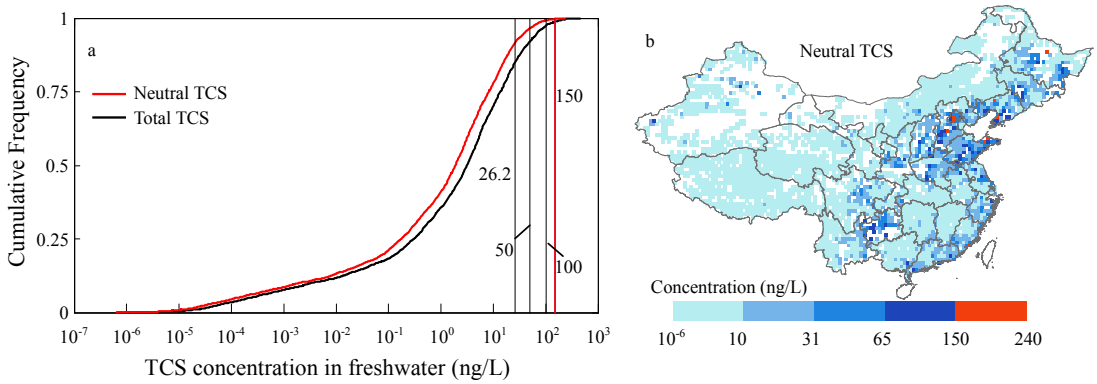

Figure 5 a, cumulative frequency of total and neutral TCS concentration in freshwater and the comparison with $PNEC_n$ for water; b, concentration of neutral TCS in freshwater across China.

An illustrative pH dependent environmental risk assessment was conducted on TCS by comparing its $PNEC_n$ (150 ng/L) with both the PEC and the PEC_n produced by this study (Figure 5a). It was estimated that limited freshwater areas (0.03%, 55 km^2) in mainland China have PEC_n values exceeding 150 ng/L. These areas are mainly in NCP, Liaodong Peninsula and Shandong Peninsula, as shown in red in Figure 5b, which probably need to be further investigated by researchers to ascertain actual environmental risks posed by TCS and its relative contribution versus other wastewater constituents (e.g. PhACs, substances released with industrial wastewater and pesticides etc.). The blue areas in Figure 5b are of relatively low risk. If comparing PEC values with the threshold, the areas with risk will probably be overestimated. In addition, other reported PNEC values or guideline values are shown in Figure 5a to indicate the significant deviation of environmental risk assessment if a different reported PNEC is used. The same method can be applied to sediments and soils for other ionisable chemicals.

Potential application of SESAMe v3.3 in chemical management in China

399 The use of these case study chemicals is illustrative and a previous model version has also
400 been successfully applied on benzo[a]pyrene, with a greater focus on atmospheric
401 emissions.[48] The illustrations show that SESAMe v3.3 can be a potential tool linking
402 emissions, exposure concentrations and toxicity data. This can provide chemical prioritization
403 and screening level assessment with spatial information, which could potentially resolve the
404 issues stated at the beginning in the introduction and provide a guide to identify relatively
405 high risk regions for monitoring campaigns and a refined risk assessment, which can support
406 chemical management in China. Further model calibration is needed when more field data is
407 available for soils, sediments or for larger areas of water.

408 **Why SESAMe v3.3** Firstly, as a multimedia fate model, the outputs can be easily interpreted
409 by decision makers, which has been previously argued to be an advantage compared to
410 chemical transport models.[49] Secondly, when a risk assessment is required for a broad range
411 of chemicals for developing an effective chemical management strategy, it surpasses models
412 which only predict concentrations within a single environmental compartment (e.g.
413 atmospheric models and water quality models etc.), because chemicals may partition into
414 multiple environmental compartments due to various chemical properties as shown in Figure
415 1 and may affect the environment or human health through different exposure pathways. Very
416 few national scale studies using multimedia models for China have been implemented or
417 published to date. As discussed above, the river basin based multimedia models used by
418 Zhang et al. for national modelling of PhACs and PCPs for China[43, 44, 47, 50] are fugacity
419 models, which have treated their targeted chemicals in their neutral form resulting in higher
420 uncertainty in chemical concentration and fate estimations. For example, if modelling TCS as
421 a neutral chemical by SESAMe v3.3, the predicted average concentration in sediment across
422 China is approximately twice that estimated by modelling it as an acid, with sediment
423 becoming the primary compartment that TCS distributes in at the steady state as suggested by
424 Zhang et al.[44]

425 **Role in national water quality management** Currently the approach to water quality
426 management in China is usually river basin or province based. National estimates of
427 chemicals in aquatic systems by SESAMe v3.3 could provide an overall perspective of the
428 residue levels at the national scale and guide monitoring campaigns and policy decision
429 making. Wu et al. (2010) has indicated that China should make its own national water quality
430 criteria (WQC) system, rather than take the WQC from developed countries directly, as China
431 has different eco-environmental systems/structures and priority pollutants as compared with
432 other countries[51]. Besides, the priority pollutants probably vary regionally, due to the diverse
433 climate and unbalanced economic development across the country. To achieve this, SESAMe
434 v3.3 can be supportive as it provides exposure concentrations in aquatic environments for risk

assessments, combining regionally different eco-environments and social economics to identify the priority pollutants for different areas within China.

Role in new chemical registration management Because quantitative risk assessment is required for new chemicals registration,[9] SESAMe v3.3 could also be used for preliminary risk estimation before a chemical is allowed to enter the Chinese market. For registration purposes and definitive risk assessments, data on the mass or volume of chemicals to be introduced to the market is required which can be used for the estimation of emissions, otherwise, OECD emission scenario documents[52] can be utilized to explore chemical emissions for a screening level assessment. To conduct environmental risk assessments in China, a national strategy for estimating chemical usage in the country is important and needs be established. Care should be taken when using predictive tools to estimate physico-chemical properties and toxicity data for all chemical registrations. In particular, the use of mathematical estimations by models such as EPI Suite should be carefully interpreted for ionisable chemicals[53] but has been widely used by researchers,[43] which may cause higher uncertainties. In particular, the pH conditions for toxicity data should be reported for ionisable chemicals to properly interpret study results for use in risk assessment.

Supporting information

Additional information on description of model features, methods, input parameters, the literature for measured data and output figures are in the Supporting Information. The Supporting Information is available free of charge on the ACS Publications website at http://pubs.acs.org/.

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