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## Uncertainty and equifinality in environmental modelling of organic pollutants with specific focus on cyclic volatile methyl siloxanes†

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Multi-media fate and transport models (MFTMs) are invaluable tools in understanding and predicting the likely behaviour of organic pollutants in the environment. However, some parameters describing the properties of both the environmental system and the chemical pollutant under consideration are uncertain and or variable in space and time. Furthermore, model performance is often evaluated using sparse data sets on chemical concentrations in different media. This can result in equifinality – the phenomenon in which several different combinations of model parameters can result in similar predictions of environmental concentrations. We explore this idea for MFTMs for the first time using, as examples, three cyclic volatile methyl siloxanes (cVMS: D4, D5 and D6) and the QWASI lake model applied to Tokyo Bay. Monte Carlo simulation was employed with parameters selected from probability distributions representing estimated uncertainty in a large number of iterations. This generated distributions of predicted chemical concentrations in water ( $C_W$ ) and sediment ( $C_S$ ) which represent the aleatory uncertainty envelope but which also demonstrate significant equifinality. For all three compounds, the uncertainty implied in the  $C_W$  was lower (coefficient of variation, CV, of the order of 20%) than for  $C_S$  (CV ca. 45%), reflecting the propensity of cVMS compounds to sorb to sediment and the sensitivity of the model to  $K_{OC}$ . Confidence intervals were particularly high for the persistence of D5 and D6 in sediment which both ranged between approximately 1.7 years and approximately 26 years for Tokyo Bay. Predicted concentration distributions matched observations well for D5 and D6 not for D4. Equifinality could be reduced by better constraining acceptable parameter sets using additional measured data from different environmental compartments.

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### Environmental significance

Multi-media fate and transport models (MFTMs) are invaluable tools in understanding the likely behaviour of organic pollutants in the environment. In this paper we explore, for the first time, the concept of equifinality – the phenomenon in which several different combinations of model parameters can result in similar model predictions – for MFTMs. This is illustrated using the QWASI model applied to Tokyo Bay for three cyclic volatile methyl siloxanes. These compounds are currently under regulatory scrutiny in terms of their persistence and potential to bioaccumulate. As well as highlighting the idea of equifinality in MFTMs, the paper demonstrates the utility of calculating confidence intervals for predicted concentrations and persistence – which can help underpin our confidence in model-based regulatory decisions.

## 1. Introduction

Multi-media fate and transport models (MFTMs) are invaluable tools with which to explore the environmental behaviour of organic pollutants. They allow the integration of knowledge about chemical partitioning and degradation in different

environmental compartments with information about physical environmental characteristics (*e.g.* dimensions, composition, temperature, flow rates) to predict net outcomes such as concentrations in different compartments and chemical flux rates.<sup>1–3</sup>

Unlike models of some other types of environmental systems behaviour, such as in hydrology,<sup>4–6</sup> river water quality<sup>7</sup> and diffuse pollutant transfer,<sup>8</sup> MFTMs are rarely calibrated. Rather, their system-specific parameters (*e.g.* compartment dimensions, flow rates, organic carbon concentrations, temperatures, *etc.*) are often estimated from independent measurements reported in the literature. Model performance is usually evaluated in terms of the match between predicted concentrations and

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measured data. However, the spatial and/or temporal frequency of available samples is often low. This means that formal validation can be weak (in a statistical sense) and sometimes qualitative.<sup>9,10</sup> In addition, the possibility of “equifinality” (similar predictions of salient model outputs – such as predicted concentrations in various environmental compartments – resulting from very different combinations of model parameters<sup>11</sup>) is rarely, if ever, explored. For example, different values of sediment deposition rate, resuspension rate, burial rate and organic carbon mineralisation rate in a lake might lead to the same organic carbon content in sediment (*cf.* the derivation of the particulate organic carbon mass balance in CoZMo-POP<sup>12</sup>), but these combinations could have quite different implications for the predicted concentrations and residence times of organic contaminants in the sediment and water compartments. In some other fields, where measured data are more abundant (such as hydrology and diffuse pollution transfers<sup>13–17</sup>), equifinality is a widely recognised phenomenon and has been a major area of research over the last few decades. It sometimes occurs when models are poorly constrained (*e.g.* when measured data are available for only one predicted output variable, such as stream discharge, with other predicted internal state variables, such as soil water content or water table height, not measured and, hence, not used to constrain parameter choice or in validation). Equifinality can be important because it means that an “optimal” set of model parameters may appear to yield good predictions of the data available (in hydrology this is often the river discharge at the catchment outlet) but actually yield poor predictions for the variables which are not measured (*e.g.* soil water storage, groundwater levels or the specific contributions of different hydrological pathways). In other words, the model gives right results for the wrong reasons.<sup>18</sup> Other combinations of parameters may yield similarly good predictions of the available data but better (and unknown) predictions of the unmeasured state variables.<sup>19</sup>

MFTMs are often used to investigate the implications of different physico-chemical properties for the environmental fate and transport of organic pollutants<sup>20</sup> and in risk assessment to estimate levels of exposure in different environmental compartments resulting from a given emission scenario. However, significant uncertainties (and variability) exist in both chemical-specific parameters (such as partition coefficients and degradation rate constants) and in the parameters which are used to describe the characteristics of the receiving environment (such as inter-media mass transfer coefficients, advection rates, some system dimensions and organic carbon fluxes). Uncertainty in environmental parameters is sometimes unimportant if the aim of the modelling is to compare the relative behaviours, exposures and risks of different organic pollutants for the same environmental assumptions – as is the case in the adoption of “evaluative” unit world models.<sup>1,21</sup> However, it becomes more important if the aim is to predict (and explain) absolute exposure in specific environmental systems – where the accuracy of the model is judged on the basis of a comparison with (often sparse) measured concentrations. Similarly, if chemicals are evaluated in terms of their environmental persistence using absolute thresholds,<sup>22</sup> the uncertainty in both

chemical-specific and media-specific properties can be important. So-called benchmarking in which persistence is defined relative to other substances<sup>23</sup> can offer some advantages in this respect, although parameter uncertainties could potentially still impact outcomes.

The effects of uncertainty in model parameterisation can be assessed in a number of ways, including first order analysis and Monte Carlo Simulation.<sup>24</sup> The principles are identical to sensitivity analysis and uncertainties in parameters to which model outputs are most sensitive will make larger contributions to output uncertainty than those to which outputs are insensitive. Although it is often useful to quantify the propagation of uncertainty from parameters to outputs (*e.g.* to estimate the spread of output values resulting from *a priori* uncertainties in inputs), particularly when making comparisons with measured data, this is still not common practice in applications of MFTMs (although Buser *et al.* [2012]<sup>25</sup> suggest that it should be).

To illustrate and explore these ideas we adapted QWASI (Quantitative Water Air Sediment Interaction), a steady state non-equilibrium (Level III) MFTM, designed for lakes and applied it to three cyclic volatile methyl siloxanes (cVMS): octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5) and dodecamethylcyclohexasiloxane (D6). QWASI<sup>26,27</sup> has been previously applied to explore the fate of a range of different chemicals in different aquatic systems and its predictions have generally been shown to match observations adequately.<sup>28–32</sup> This model has also been used to explore the behaviour of cVMS compounds in various lakes including Lake Pepin and Lake Ontario<sup>3,9</sup> and is applied here to Tokyo Bay, Japan, where environmental monitoring for cVMS compounds has been conducted.<sup>33</sup> Importantly, we explicitly introduce the term equifinality to the applications of MFTMs and discuss the relevance of this concept for the interpretation of model outputs – particularly in comparison with measured environmental concentrations. A secondary aim of the paper is to use an MFTM as a framework for exploring aspects of cVMS behaviour in Tokyo Bay and to discuss levels of exposure and persistence for D4, D5 and D6.

## 2. Methods

The work described here was conducted using a modified version of QWASI v3.1 (<http://www.trentu.ca/academic/aminss/envmodel/models/models.html>) implemented in MS Visual BASIC for Applications, running behind Microsoft Excel.<sup>9</sup> As an example system, the model was applied to the Inner Tokyo Bay, Japan (Fig. 1), for which measured concentrations of cVMS have been determined in sediment.<sup>33</sup> Tokyo Bay is a large semi-enclosed marine environment with a surface area of approximately 992 km<sup>2</sup> and a mean depth of approximately 15–19 m.<sup>34,35</sup> It receives wastewater from a catchment inhabited by approximately 29 million people.<sup>36</sup> Approximately 8.7 million of these people live in Tokyo itself and the rest live in the surrounding area draining to the Bay. It is assumed that the entire population is served by good wastewater treatment.<sup>33,36</sup> It is also assumed that there is no degradation or volatilisation of cVMS compounds discharged to rivers before these rivers reach



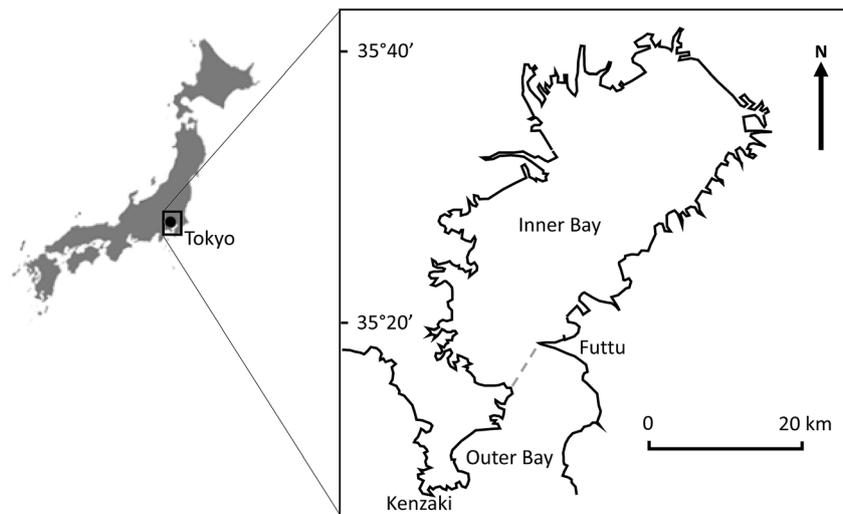


Fig. 1 Location map of Tokyo Bay showing the boundary between the Inner and Outer Bay. The dashed line marks the division between the Inner and Outer Bays (adapted from Okada *et al.*, 2011<sup>34</sup>).

the Bay (although we recognise that, in reality, there are likely to be losses of cVMS compounds from some discharge points where rivers are distant from the Bay). The dimensions and properties for Tokyo Bay adopted in the QWASI modelling described here are shown in Table S2.† In all cases, the concentrations of cVMS compounds were assumed to have a constant value of  $10 \text{ ng m}^{-3}$  in air which is consistent with measurements of D5 reported for rural Sweden.<sup>37</sup> Emissions of D4, D5 and D6 to Tokyo Bay were assumed to be 122, 3693 and  $426 \text{ kg year}^{-1}$ , respectively, based on the same *per capita* emission estimates to wastewater from “cosmetic” products (*i.e.* those products which are potentially washed off to wastewater) assumed by Brooke *et al.* (2008a, b, c)<sup>38–40</sup> and used by Whelan and Breivik (2013):<sup>10</sup> [*i.e.* 140, 4250 and  $490 \text{ mg cap}^{-1} \text{ year}^{-1}$ , respectively] but with an assumed removal in wastewater treatment of 97% for all three compounds. These *per capita* estimates are higher than unpublished estimates derived from average measured concentrations of D4, D5 and D6 in untreated wastewater by the Silicone Industry Association of Japan (SIAJ) *i.e.* 64, 1442 and  $90 \text{ mg cap}^{-1} \text{ year}^{-1}$ . However, given that the aim of this paper is to explore the concept of equifinality, the Brooke *et al.* (2008)<sup>38–40</sup> values have been retained.

## 2.1 Monte Carlo Simulation

In Monte Carlo Simulation (MCS), a deterministic model is run a large number of times (iterations). In each iteration, a different set of model parameter values is used with each parameter value selected randomly from pre-defined probability density functions (pdf's). A number of different pdf's can be used to describe the distribution of a parameter. If the parameter is well defined (*i.e.* if there are measured data on the parameter value) then it may be possible to fit a specific pdf to the measured data. More commonly, however, measured values are scarce and both the shape and the statistical parameters of the distribution must be estimated. Common pdf's employed to

represent uncertain distributions include the normal (Gaussian) distribution, the log-normal distribution and the triangular distribution.<sup>41</sup> Although many natural phenomena exhibit symmetrical (*e.g.* normal) distributions, it is more common for distributions to be positively skewed. The log-normal distribution is, therefore, often used.<sup>42</sup> One significant advantage of this distribution over the normal distribution is that it does not contain values less than or equal to zero. When used in MCS, therefore, negative values (which are not physically realistic for many model parameters) are not sampled, which means that models do not need to discard some iterations. Another advantage is that the width of the distribution can be described in relative terms *via* the coefficient of variation (CV) where:

$$CV = \frac{s}{m} \quad (1)$$

and where  $s$  is the standard deviation of the data and  $m$  is the arithmetic mean of the data.

The resulting log-normal distribution will have parameters  $\mu$  and  $\sigma$  given by:

$$\mu = \ln(m) - \frac{1}{2}\sigma^2 \quad (2)$$

$$\sigma = \sqrt{\left(\ln\left(1 + \frac{s^2}{m^2}\right)\right)} \quad (3)$$

In the code, exceedance quantiles (0–1) are generated from a random number generator. These quantiles are then converted to standard normal deviates  $N$  using an empirical formula.<sup>43</sup> For log-normally distributed parameters individual parameter values ( $G$ ) can then be generated from

$$G = \exp[(N \times \sigma) + \mu]$$



For normally distributed parameters with arithmetic mean,  $m$ , and standard deviation,  $s$ , values ( $G$ ) are simply:

$$G = (N \times s) + m$$

In all cases, simulated parameters were assumed to be uncorrelated<sup>41</sup> and 5000 iterations were performed.

## 2.2 Sensitivity versus uncertainty

MCS is used here explicitly to quantify the uncertainty in model predictions as a consequence of the combined realistic estimates of the uncertainty in model input parameters. Unlike in sensitivity analysis, where the distribution of the parameter is not important except for defining the extent of parameter space explored by the analysis, in uncertainty analysis the parameter distributions adopted could affect the uncertainty of the predicted variables (e.g. predicted concentrations in water and sediment) – particularly when the model is sensitive to the parameter in question. It should also be noted that the distributions assumed and, in particular, their parameter values are explicitly defined in terms of uncertainty rather than variability. This is an important distinction to make because we can be highly certain about a parameter (e.g. mean annual temperature) for which the variable upon which it is based varies significantly. This distinction is made clearer in the exploration of the effects of temperature on model performance.

## 2.3 Constructing probability distributions for key parameters

The following parameters were described using pdf's in MCS (grouped as either a chemical-specific or an environmental property). The chemical-specific properties considered were: the air water partition coefficient ( $K_{AW}$ ); the organic carbon to water partition coefficient ( $K_{OC}$ ); the chemical half life in water ( $HL_{water}$ ); the chemical half life in sediment ( $HL_{sed}$ ); the enthalpy of phase change between air and water ( $\Delta U_{AW}$ ); the enthalpy of phase change between organic carbon and water ( $\Delta U_{OC}$ ) which is assumed to be identical to that between octanol and water ( $\Delta U_{OW}$ ) and the Arrhenius activation energy ( $E_a$ ) for degradation by hydrolysis. The same  $E_a$  value is assumed for both water and sediment because degradation in both media is assumed to be controlled exclusively by hydrolysis in the dissolved phase. The environmental properties were the water inflow and outflow rates; the sediment deposition and resuspension rates; the sediment burial rate; the water surface area and volume; the “active” sediment depth (i.e. the sediment layer which can potentially be resuspended); suspended solids concentrations in the water column and in inflow water; the organic carbon concentration on suspended solids and on sediment particles; the concentration of aerosols in the air; the sediment porosity and particle density; the rainfall rate; the aerosol dry deposition rate; the aerosol scavenging ratio; partial mass transfer coefficients for the air and water sides of the air-water interface and for the sediment-water interface and the water temperature. With the exception of temperature, all

parameters were assumed to be log-normally distributed in accordance with similar work conducted on modelling cVMS compounds using QWASI.<sup>44</sup> In the absence of good empirical evidence, the pdf parameters ( $\mu$  and  $\sigma$ ) were derived, respectively, from  $m$  and  $s$  which, in turn were assumed to be the best estimate (base) and an expert estimation of the relative spread of the distribution (CV: eqn (1)). Model parameter CVs used here were based on the parameter “dispersion factors” estimated by Mackay *et al.* (2014)<sup>44</sup> who present detailed justification for their derivation. The method used for the conversion of dispersion factors to CVs is described in S1.† Details of the distributions used are given in S2.†

The case of temperature deserves special mention. QWASI is a steady state model and, therefore, does not represent the (potentially important) seasonal cycles in temperature and river flows. The inclusion of temperature in the uncertainty analysis is, therefore, interpreted here primarily in terms of the uncertainty in estimating the mean temperature of the system under consideration (i.e. the sampling error) which is assumed to be relatively small (CV 0.05). However, we also explored the implications of water temperature variability on cVMS behaviour in a separate set of iterations. In this case a normal distribution with an arbitrary CV of 0.5 was assumed. We do not have data on the CV for air or water temperature in Toyko but this value is approximately consistent with typical air temperature variability reported for the continental USA.<sup>45</sup>

In addition, emission is also known to be highly uncertain. The consequences of uncertainty in emission rate were, therefore, also examined by comparing the distribution in outputs obtained from the MCS where emission was assumed to be constant and a MCS where the emission was assumed to take a log-normal distribution with an arbitrary CV of 0.5. Note that uncertainty in the concentration of cVMS in air was not investigated because the model is very insensitive to the concentration assumed for cVMS in air.<sup>9,46</sup> This is because (i) the  $K_{AW}$  values for cVMS are so high that exchange is always in the direction water to air for water bodies exposed to waste water (i.e. the fugacity in water is always much greater than the fugacity in air which means that net air to water diffusion will not occur) and (ii) rate of exchange (which is described using the two film resistance model) is limited almost entirely by the partial mass transfer coefficient on the water side of the interface.<sup>9</sup>

# 3. Results and discussion

## 3.1 Uncertainty analysis using MCS

Example outputs from the MCS are shown in Fig. 2 for D5 (5000 iterations). Distributions for D4 and D6 are presented in the ESI (Fig. S1 and S2).† Pertinent statistics for the predicted distributions of  $C_w$  and  $C_s$  are given in Table 1. In all cases, the predicted concentrations in water are lower than the limits of detection (LOD) and limits of quantification (LOQ) typically reported for cVMS in water.<sup>47</sup> The distributions are slightly positively skewed (i.e. the mean is slightly greater than the median) with a relatively limited range (CVs of 18%, 21% and 22% for D4, D5 and D6 respectively). The predicted



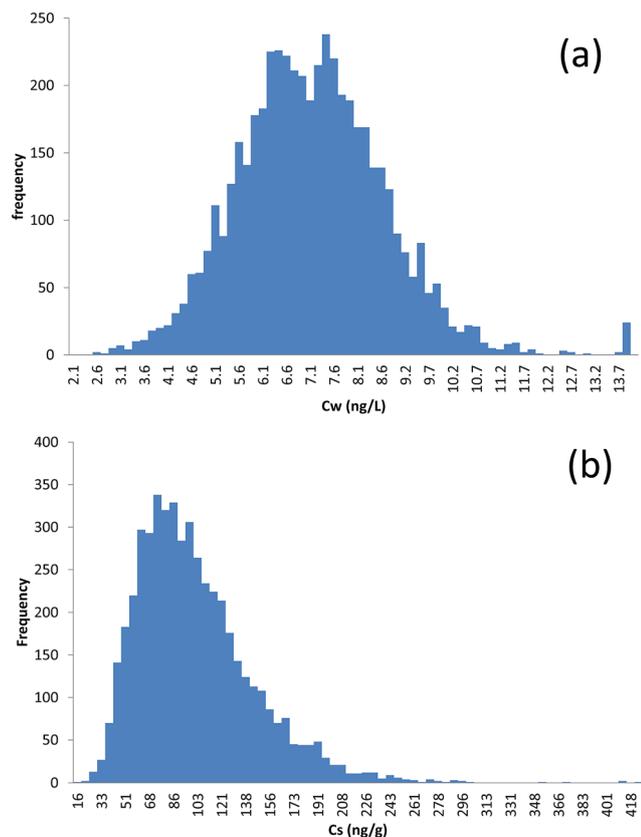


Fig. 2 Frequency distributions of (a) predicted concentration in the water column and (b) predicted concentration in sediment ( $\text{ng g}^{-1}$  dry weight) for D5 in Tokyo Bay.

Table 1 Descriptive statistics for the simulated distributions of  $C_W$  and  $C_S$  for D4, D5 and D6 (3SF)

		D4	D5	D6
$C_W$	Mean ( $\text{ng L}^{-1}$ )	0.032	7.24	0.864
	Median ( $\text{ng L}^{-1}$ )	0.032	7.22	0.848
	Skewness	0.681	0.201	0.539
	Kurtosis	1.35	0.151	0.374
	CV (%)	17.6	21.2	22.7
	2.5 percentile ( $\text{ng L}^{-1}$ )	0.023	4.37	0.526
$C_S$	97.5 percentile ( $\text{ng L}^{-1}$ )	0.044	10.3	1.31
	Mean ( $\text{ng g}^{-1}$ dw)	0.013	98.5	64.4
	Median ( $\text{ng g}^{-1}$ dw)	0.011	90.8	60.8
	Skewness	1.60	1.16	0.994
	Kurtosis	4.58	2.23	2.06
	CV (%)	55.1	43.3	37.6
	2.5 percentile ( $\text{ng g}^{-1}$ dw)	0.004	39.0	28.2
	97.5 percentile ( $\text{ng g}^{-1}$ dw)	0.030	199	122

concentrations in sediment, on the other hand, have a pronounced positive skew and a relatively wider range (CVs of 53%, 46% and 37% for D4, D5 and D6 respectively). With the exception of  $C_S$  for D4, all distributions are platykurtic (kurtosis < 3). Values between the 2.5<sup>th</sup> and 97.5<sup>th</sup> percentiles capture 95% of the distribution and can, thus, be interpreted as uncertainty confidence intervals (*i.e.* we are 95% confident that

predicted concentrations will be between these values, given the uncertainty distributions in the individual input parameters which were assumed in the simulation). In other words, as long as the “real” (but unknown) values for the input parameters used in QWASI for Tokyo Bay lie within the uncertainty bounds set by the input distributions, we can be 95% confident that the “real” model predictions will be captured by the distributions shown in Fig. 2 and in the ESI† (*i.e.* that the “real” predicted concentrations lie between the 2.5<sup>th</sup> and 97.5<sup>th</sup> percentiles shown in Table 1). Please note that these estimates refer only to the “aleatory” uncertainty in model predictions (*i.e.* the uncertainty in predicted concentrations resulting from given uncertainties in the input parameters). They do not refer to our degree of certainty in the ability of the model to represent processes in the actual system under consideration which can be considered “epistemic” and essentially unknown.<sup>48</sup>

The predicted concentration of D5 in water plotted against MCS-generated values of  $\log K_{AW}$ ,  $HL_{\text{water}}$ ,  $HL_{\text{sed}}$ ,  $E_a$ ,  $\log K_{OC}$  and sediment depth are displayed in Fig. 3. Although there appears to be little clear relationship between any of the parameter values and  $C_W$  in Fig. 3 (suggesting that each parameter, individually, exerts a relatively weak influence over  $C_W$ ), Spearman Rank correlations were significant ( $p \leq 0.05$ ) between  $C_W$  and (*inter alia*) the following parameters:  $K_{AW}$ ,  $HL_{\text{water}}$ ,  $HL_{\text{sed}}$ ,  $E_a$ ,  $Q_{\text{out}}$  (the advective outflow rate) and  $MTC_W$  (the water-side partial mass transfer coefficient for water–air exchange) for D4 and D5 and  $k_{\text{res}}$  (the sediment resuspension rate),  $Q_{\text{out}}$ ,  $D$  (the sediment deposition rate), SSC (the suspended sediment concentration) and  $MTC_W$  for D6 (see ESI Section S3†). There is also a moderate range of values for each parameter which predict (in various combinations with other parameters) the **same** value of  $C_W$ . For example, a  $C_W$  of  $8 \text{ ng L}^{-1}$  could be predicted with any value of  $\log K_{AW}$  between approximately 2.4 and 3.1 as long as other parameters were different. This is an example of equifinality.

The predicted concentration of D5 in sediment plotted against Monte-Carlo-generated values of  $\log K_{AW}$ ,  $HL_{\text{sed}}$ ,  $E_a$ ,  $\log K_{OC}$ , sediment deposition rate, sediment depth and sediment burial rate are displayed in Fig. 4. Here, the relationships between the parameter values and  $C_S$  appear a little stronger – particularly for the sediment deposition rate and, to a lesser extent,  $K_{OC}$ ,  $HL_{\text{sed}}$  and the depth of the active mixed sediment layer (all positive) suggesting that these parameters, individually, can exert significant influence over the predicted value of  $C_S$ . Spearman rank correlations between  $C_S$  and model input parameters are also shown in Table S4† (note the particularly strong control of  $D$ ). There is considerable equifinality here too but the extent of this (*i.e.* the range of parameter values which yield the same value of  $C_S$ ) varies, depending on  $C_S$ . For example, a  $C_S$  of  $100 \text{ ng g}^{-1}$  dw could arise from any value of the burial rate between 5 and  $15 \text{ g m}^{-2} \text{ d}^{-1}$ , provided other parameters are adjusted (from within their feasible distributions) to compensate.

### 3.2 Uncertainty in predicted environmental persistence

Frequency distributions (representing model uncertainty) of the predicted persistence of D5 in water ( $P_W$ ), sediment ( $P_S$ ) and



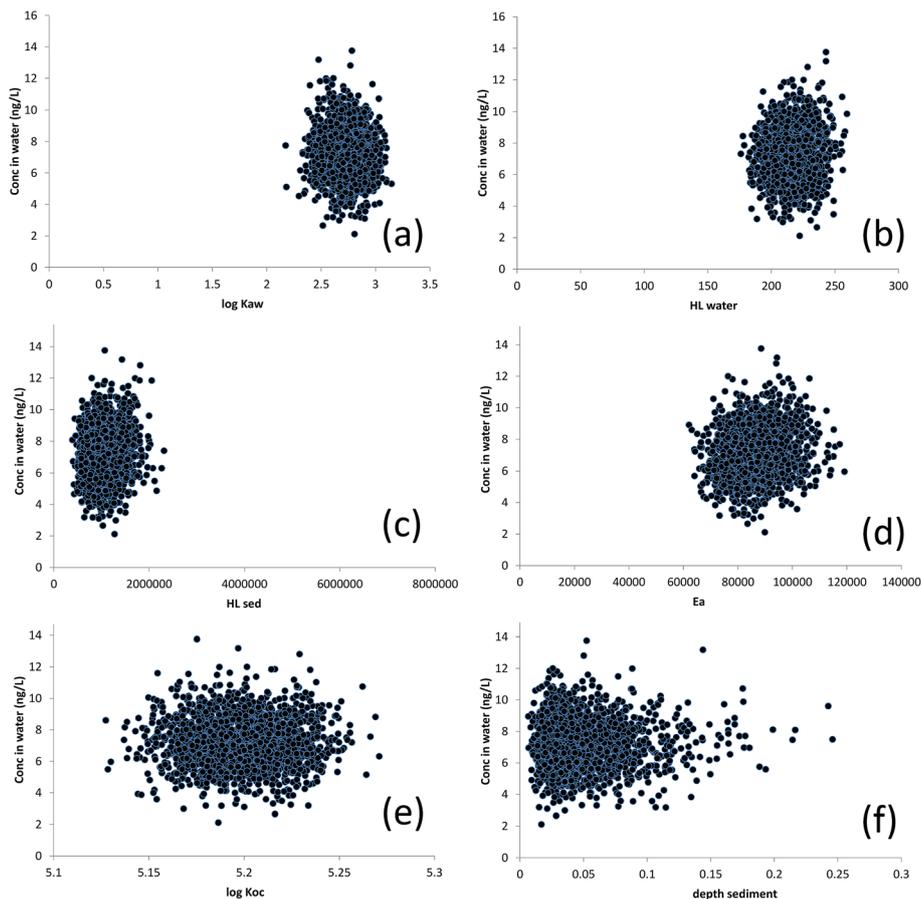


Fig. 3 Predicted concentrations of D5 in water in Tokyo Bay plotted against Monte-Carlo-generated values of (a)  $\log K_{AW}$ , (b)  $HL_{water}$  (hours), (c)  $HL_{sed}$  (hours), (d)  $E_a$ , (e)  $\log K_{OC}$  and (f) sediment depth (m).

overall ( $P_{OV}$ ) are shown, for illustrative purposes in Fig. 5. Descriptive statistics for the simulated distributions of  $P_W$ ,  $P_S$  and  $P_{OV}$  are shown in Table 2 for D4, D5 and D6. Although the spread in  $P_W$  is quite narrow (the 2.5<sup>th</sup> and 97.5<sup>th</sup> percentiles were 6.5 and 16.9 days, respectively, for D5), the spreads in  $P_S$  and  $P_{OV}$  are wider (the 2.5<sup>th</sup> and 97.5<sup>th</sup> percentiles for  $P_S$  range from 619 to 8275 days and for  $P_{OV}$  from 47 to 686 days for D5). As in the case of predicted concentrations, the distributions are all positively skewed, with higher skewness values for  $P_S$  than for  $P_W$  and with the highest values for  $P_{OV}$ . The distributions for  $P_W$  were all flat or platykurtic (kurtosis < 3) and were all peaky or leptokurtic (kurtosis > 3) for  $P_{OV}$ , with a mix of platykurtic and leptokurtic for the distributions of  $P_S$ , reflecting the distribution shapes shown in Fig. 5. The predicted persistence of all three compounds in water suggest that they do not fall into a regulatory persistence category. However, there is no doubt that the predicted persistence in sediment would meet regulatory criteria – even for D4 (e.g. chemicals with a half life of over 180 days would be classified as “vP” in the EU). This is, in part, due to the fact that fairly conservative assumptions have been made with respect to hydrolysis rates in sediment. The ranges of overall persistence predictions (spanning an order of magnitude) are, instead, open to different interpretations because  $P_{OV}$  is less well established as a regulatory threshold. It is worth re-emphasising

the fact that these distributions were generated using MCS employing input parameter distributions which represent feasible ranges and that the same predicted persistence could be predicted from several different combinations of parameters. For example over 300 different combinations of parameters predict a  $P_S$  value of about 2000 days. Whilst many of these combinations will be similar, some could be quite different.

### 3.3 Including the influence of temperature variability

In the MCS analysis conducted thus far, the uncertainty CV for the system temperature was assumed to be 5% (reflecting a relatively high certainty in the mean temperature of Tokyo Bay arising from the availability of measured data). However, if we consider the statistical distribution of system temperature – *i.e.* reflecting *variability* (CV assumed to be 50%), the results are quite different. Note that although the assumption of a Gaussian distribution for temperature is probably reasonable for the bulk of conditions experienced in Tokyo Bay, a small number of MCS samples will be selected which are outside the range of temperatures seen in this system using this assumption (e.g. some sub-zero temperatures may be simulated which are unrealistic). Results are shown in Fig. S3, S4 and S5.† The predicted mean concentrations in water and sediment are slightly lower (for D5



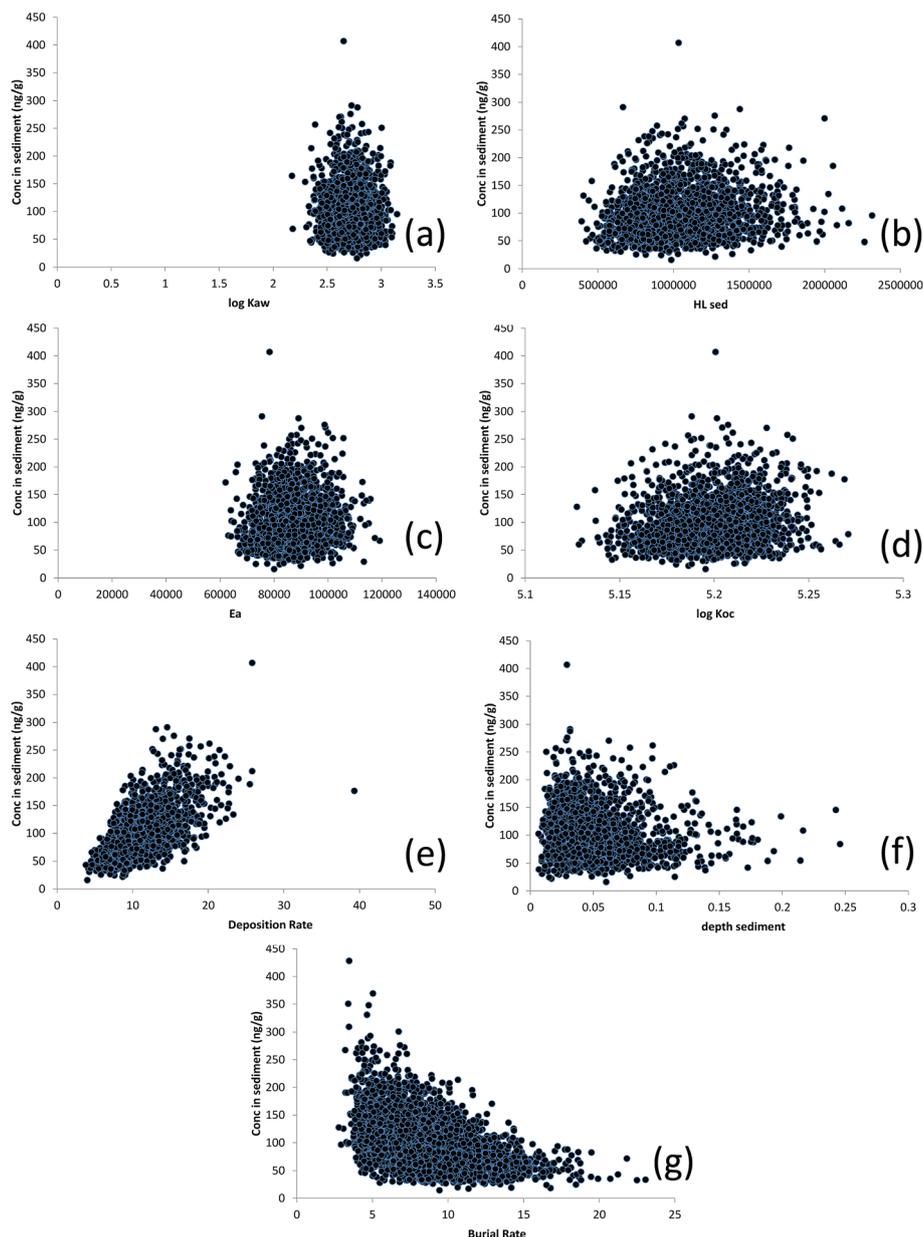


Fig. 4 Predicted concentrations of D5 in sediment ( $\text{ng g}^{-1} \text{ dw}$ ) in Tokyo Bay plotted against Monte-Carlo-generated values of (a)  $\log K_{AW}$ , (b)  $HL_{\text{sed}}$  (hours), (c)  $E_a$ , (d)  $\log K_{OC}$ , (e) sediment deposition rate ( $\text{g m}^{-2} \text{ d}^{-1}$ ), (f) sediment depth (m) and (g) sediment burial rate ( $\text{g m}^{-2} \text{ d}^{-1}$ ).

6.99  $\text{ng L}^{-1}$  and 88  $\text{ng g}^{-1} \text{ dw}$ , respectively) and the CV for predicted D5 concentration in sediment was similar (44%). However, the variability in the predicted concentrations in water was higher (CV = 39%). Although there is considerable scatter, there is a clear inverse relationship between temperature and  $C_W$  due to the effects of temperature on the hydrolysis rate constant, removal *via* sediment deposition (cVMS compounds are assumed here to become more hydrophobic with increasing temperatures on the basis of experimental data for  $K_{OW}$ :<sup>49</sup> see Table S3†) and (to a much lesser extent) on partitioning to air ( $K_{AW}$ ). For  $C_S$ , the relationship is less clear. There appears to be a temperature (near the mean) at which concentrations in sediment tend to be highest but this may simply reflect a higher frequency of

sampling at this temperature. The relationships between a number of other model parameters and  $C_W$  were also more apparent with a wider range of temperatures. Of particular note were the wider ranges of  $K_{AW}$  and  $K_{OC}$  which were predicted as a consequence of temperature-dependent partitioning along with a wider range in half lives in water and sediment. For sediment, clear relationships between predicted concentration and parameter values are less apparent. Examples of these scatter plots are given in the ESI (Fig. S4 and S5).†

### 3.4 Exploring the uncertainty in emission

As expected, the effect of emission uncertainty (log-normal distribution and a CV of 0.5) on  $C_W$  and  $C_S$  was directly



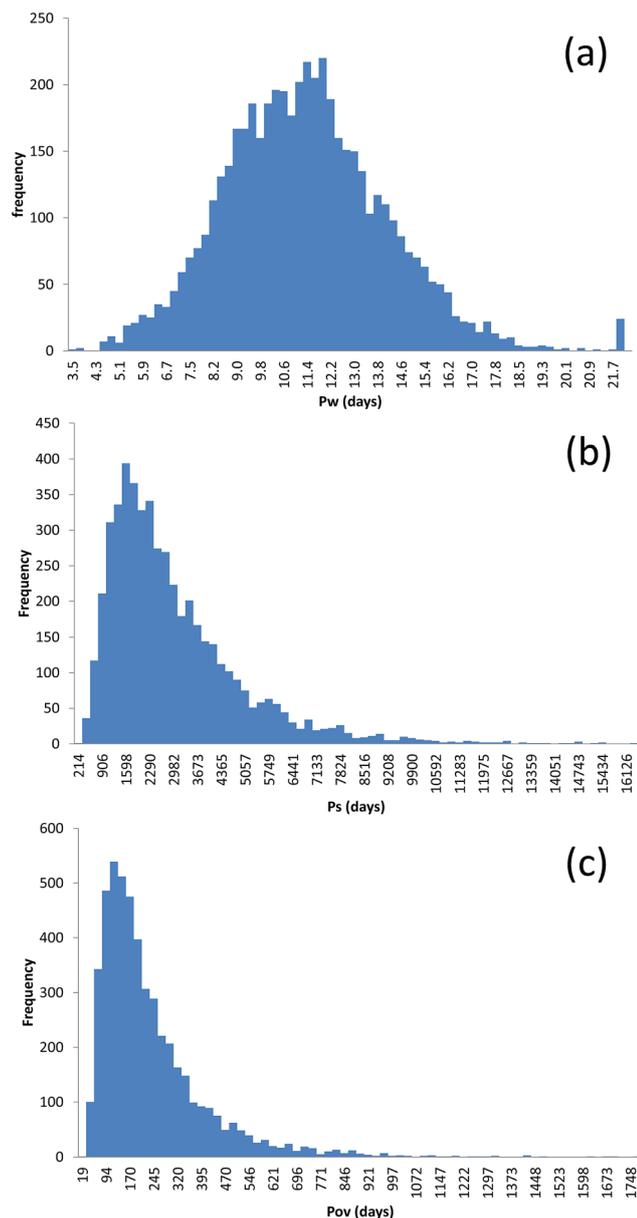


Fig. 5 Frequency distributions of (a) predicted persistence in the water column; (b) predicted persistence in sediment and (c) predicted overall persistence for D5 in Tokyo Bay.

proportional. Including an uncertainty in the emission value had little effect on the shape of the scatter plots generated, except to draw out the concentration scales (*i.e.* increasing the uncertainty in predicted concentrations). As an example, for D5, there was little effect on the mean value of  $C_w$  ( $7.42 \text{ ng L}^{-1}$ ), but there was an increase in the CV (58%) and the range between the 5<sup>th</sup> and 95<sup>th</sup> percentiles ( $2.7$  and  $15.4 \text{ ng L}^{-1}$ , respectively) was wider. The predicted mean concentration in sediment was also unaffected by introducing a distribution for emission (mean  $C_s$  was  $100 \text{ ng g}^{-1} \text{ dw}$ ). However, the CV increased to 68% and the 5<sup>th</sup> and 95<sup>th</sup> percentiles were 29 and  $227 \text{ ng g}^{-1} \text{ dw}$ , respectively (compare with data presented in Table 1 for the MCS scenario in which emission was kept constant).

Table 2 Descriptive statistics for the simulated distributions of  $P_w$ ,  $P_s$  and  $P_{ov}$  for D4, D5 and D6

		D4	D5	D6
$P_w$	Mean (d)	1.41	11.5	18.5
	Median (d)	1.39	11.4	18.1
	Skewness	0.750	0.233	0.528
	Kurtosis	1.70	0.059	0.371
	CV (%)	14.9	21.9	24.5
	2.5 percentile (d)	1.06	6.51	9.61
$P_s$	97.5 percentile (d)	1.87	16.9	30.4
	Mean (d)	312	2895	3102
	Median (d)	301	2374	2447
	Skewness	0.896	1.99	2.91
	Kurtosis	1.44	6.33	16.0
	CV (%)	27.8	71.5	78.9
$P_{ov}$	2.5 percentile (d)	174	619	643
	97.5 percentile (d)	525	8275	9456
	Mean (d)	2.08	222	1222
	Median (d)	1.99	172	940
	Skewness	1.45	2.59	3.06
	Kurtosis	5.29	11.7	18.7
	CV (%)	23.1	77.2	79.5
	2.5 percentile (d)	1.37	47.2	239
	97.5 percentile (d)	3.23	685	3883

### 3.5 Implications for interpretation of measured *versus* modelled comparisons

The analysis presented here has some important implications for the interpretation of predicted concentrations from QWASI (and other MFTMs, by extension), particularly with respect to discrepancies between predicted and measured concentrations of cVMS compounds in sediment. Predicted steady state values of  $C_w$  were  $0.034$ ,  $9.61$  and  $1.04 \text{ ng L}^{-1}$  for D4, D5 and D6, respectively, and values of  $C_s$  were  $0.011$ ,  $127$  and  $76.8 \text{ ng g}^{-1} \text{ dw}$  for D4, D5 and D6, respectively. The aleatory uncertainty confidence intervals for these concentrations were relatively narrow. Measured concentration data are only available for concentrations in sediment in Tokyo Bay.<sup>33</sup> Briefly, surface sediment samples were collected from 20 locations in the Bay in a systematic grid with a sampling interval of 5 km. They are, therefore, likely to be representative of the mean conditions in the Bay as a whole. Water depths at each location ranged from 10 to 35 m. Sediments were collected with a Birge-Eckman grab sampler and sub-samples representing the upper 1 cm were extruded into stainless steel storage containers (for further details see Supplementary Information in Powell *et al.*, 2017<sup>33</sup>). Mean measured dry weight concentrations for D4, D5 and D6 were  $5.9 \pm 6.4$ ,  $161 \pm 132$  and  $32 \pm 23 \text{ ng g}^{-1} \text{ dw}$ , respectively (where the error represents the standard deviation of 20 measurements). For reference with the model predictions of  $C_w$ , equivalent expected concentrations in water were derived from these dry weight sediment concentrations, assuming equilibrium partitioning with a sediment organic carbon content of  $0.05 \text{ g g}^{-1}$  and the log  $K_{oc}$  values reported in Table S3.† The calculated values were  $7.1$ ,  $20.3$  and  $0.6 \text{ ng L}^{-1}$  for D4, D5 and D6, respectively, which were below the LOD and LOQ typically reported for cVMS in water<sup>34</sup> for D4 and D6 but would



be detectable for D5. These values were less than a factor of  $\sim 2$  of the steady state values of  $C_w$  predicted by QWASI for D5 and D6 (9.61 and 1.04 ng L<sup>-1</sup>) but a long way from the predicted D4 value (0.034 ng L<sup>-1</sup>). Comparison with the range of MCS-predicted concentrations (e.g. Fig. 2, Table 1 and Fig. S1 and S2†) suggests that the mean measured  $C_s$  for D5 is close to the middle of the model envelope and that the mean measured  $C_s$  for D6 is also captured by the overall model envelope (see Fig. S2†), although it is only just above the 5<sup>th</sup> percentile prediction (i.e. 28.2 ng g<sup>-1</sup> dw), without accounting for uncertainty in emission. When uncertainty in emission is included (CV = 0.5), the 5<sup>th</sup> percentile predicted value of  $C_s$  for D6 becomes 21 ng g<sup>-1</sup> dw, which does capture the measured mean concentration of 32 ng g<sup>-1</sup> dw. For D4, the range of model predictions, even accounting for emission uncertainty (i.e. 5<sup>th</sup> and 95<sup>th</sup> percentile concentrations of 0.003 and 0.032 ng g<sup>-1</sup> dw, respectively) remains inconsistent with the mean measured  $C_s$  (5.9 ± 6.4 ng g<sup>-1</sup> dw  $n = 20$ ). There are a number of possible reasons for this including: (i) underestimation of emission; (ii) overestimation of losses due to volatilisation or hydrolysis in wastewater treatment, the water column or the sediment and (iii) underestimation of D4 sorption. In all cases, the error(s) in parameters extend beyond the uncertainty distributions considered in the analysis hitherto. Taking these in turn: it is unlikely that the current emission assumptions were underestimated in the model because independent estimates of *per capita* losses to wastewater (32–134, mean 64 mg cap<sup>-1</sup> year<sup>-1</sup>), based on measured concentrations of D4 in the influent of a wastewater treatment plant in Tokyo (unpublished industry data), were lower than the value assumed here (122 mg cap<sup>-1</sup> year<sup>-1</sup>). It is possible, however, that the removal rate assumed (97%) was too high. In addition, it is possible that measured D4 concentrations in sediment represent a legacy from previously high emissions (D5 has replaced D4 in many applications over the last 15 years) and this should be investigated further using dated sediment coring.

Losses of D4 in the water column due to volatilisation are controlled by the value assumed for the partial mass transfer coefficient on the water side of the air–water interface.<sup>9</sup> This affects all three compounds in a similar way and so is unlikely to explain the low D4 predictions. However, D4 is the most hydrolytically unstable of the cVMS compounds considered here, with an estimated half life in water of only 3.9 days at pH 7 and 25 °C which reduces to just 9.6 h at pH 8 and 25 °C (i.e. 2.9 days at pH 8 and 9 °C). Although hydrolysis in the model is adjusted for the fraction in the dissolved phase, rate of hydrolysis may still be overestimated – e.g. if sorption is elevated due to a higher concentration of suspended particles in the water column or if the real  $K_{OC}$  for D4 is higher than the value assumed here. We assumed a log  $K_{OC}$  value for D4 of 4.22 ( $K_{OC} = 16\,596\text{ L kg}^{-1}$ ) with a CV of 0.32 (i.e. a standard deviation = 5210 L kg<sup>-1</sup>). This equates to a 95<sup>th</sup> percentile value in a log-normal distribution of 26 412 L kg<sup>-1</sup> (equivalent to a log  $K_{OC}$  value of 4.42). This is still much lower than the log  $K_{OC}$  value reported by Panagopoulos *et al.* (2015)<sup>50</sup> of 5.06. This would suggest that the pdf for  $K_{OC}$  assumed here is too narrow (as was the case for D5). Furthermore, Panagopoulos *et al.* (2016)<sup>51</sup> have

suggested that  $K_{OC}$  increases with salinity due to the salting out effect<sup>52</sup> and that the slope of the relationship between  $K_{OC}$  and salinity is steeper for D4 than it is for D5 and D6. If we assume a salinity of 0.6 mol L<sup>-1</sup> (typical of seawater<sup>53</sup>), log  $K_{OC}$  could be as high as 5.45. The effects of assuming a mean log  $K_{OC}$  for D4 of 5.45 in the MCS resulted in a mean  $C_s$  of 0.87 ± 0.72 ng g<sup>-1</sup> dw (Fig. S7a†). However, this is still an order of magnitude lower than the measured data so other factors (e.g. the hydrolysis half life) may also be at play. Increasing the hydrolysis half life at 25 °C by a factor of 3 in the MCS resulted in a mean predicted  $C_s$  of 2.5 ± 1.9 ng g<sup>-1</sup> dw (Fig. S7b†).

### 3.6 General discussion

Although applied to specific chemicals in a specific environmental system, this paper is intended to illustrate some broader generic ideas about the role of uncertainty in assessing environmental exposure and persistence. We introduce, for the first time, the concept of equifinality to MFTMs – in which the same predictions of exposure and persistence can be derived using very different combinations of parameters. When model outputs are compared with measured data, “success” is often judged on the basis of the fidelity of the predictions compared with observations. However, it is important to recognise that model performance (good or poor) will, to some extent, be influenced by the parameter combinations selected. Although MFTMs are rarely calibrated in the same way as hydrological models (i.e. where some parameters are adjusted so as to optimise the model fit with observed data), a particular selection of parameters may yield apparent success in terms of the fidelity of predictions with one set of observations (e.g. measured concentrations in sediment) but may yield poor predictions of other (often unknown) end points (e.g. concentrations in water or biota). An alternative parameter set may yield good predictions for all end points and, hence, be a better description of system behaviour. In the work presented here, the Monte Carlo Simulation approach taken was similar to that employed elsewhere for sensitivity and uncertainty analysis<sup>54</sup> – essentially estimating the uncertainty distributions for each parameter and allowing these uncertainties to propagate forwards to yield uncertainty distributions in model predictions.

An alternative approach for exploring equifinality, and one frequently adopted in hydrology (e.g. in the Generalised Likelihood Uncertainty Estimation or GLUE<sup>54</sup>), is to make very few *a priori* assumptions about the nature of the distributions of the model parameters. In GLUE uniform distributions may be employed for all parameters, with minimum and maximum values set simply at feasible physically realistic limits. Those combinations of parameters which generate “successful” predictions of observed data (i.e. which meet certain threshold criterion or criteria) are considered to be equally plausible. However, this approach is not a particularly useful option when there is a paucity of observed data (as is often the case for environmental concentrations of organic pollutants) because the model will be poorly constrained and the number of “successful” combinations too high. One possible option for better constraining models (improving so-called model



identifiability and, potentially, reducing equifinality) would be to link the simulations for several different pollutants for which measured data are available in the same system of interest and to use the combined model performance to exclude system parameter combinations which fail to predict all the measured data adequately (*i.e.* parameter sets which successfully predict measured concentrations for one chemical would be rejected if they fail to match the observations for the other chemicals). Although this could be problematic where major (unexplained) discrepancies arise for some chemicals (as was the case here for D4) it should, nevertheless, be explored further for more data-rich systems, such as the Great Lakes.

Measured data on both chemical properties and system properties should also be used as much as possible to constrain parameter sets so that they are consistent. For example, in the case of chemical-specific properties, additional independent measurements of  $K_{OC}$  and its temperature dependence would be useful for better defining the parameters of the uncertainty distribution for  $K_{OC}$ . It is pertinent to note that the assumptions made for the uncertainty in  $K_{OC}$  (Table S3†) yield a distribution of  $\log K_{OC}$  values (Fig. 3e and 4d) which is relatively narrow compared with the wide range of  $\log K_{OC}$  values which have been reported for D5 in the literature from *ca.* 5.2 (ref. 55 and 56) to *ca.* 6.2.<sup>50,57</sup> Increasing the CV but maintaining a mean  $\log K_{OC}$  value of 5.2 results in a wider range of simulated  $K_{OC}$  values but too many of these values are unrealistically small. The effect of increasing the mean  $\log K_{OC}$  value to 5.7 and assuming a wider distribution (CV = 0.5) is illustrated in Fig. S6.† Unsurprisingly, high values of  $K_{OC}$  tend to result in higher predicted  $C_s$  concentrations – many of which are unrealistically high compared to the measured data for D5 in Tokyo Bay, although values of  $\log K_{OC} > 6$  can still generate a good match with the measured data in some parameter combinations. Additional data on the magnitude of  $K_{OC}$  for cVMS compounds would help to better-constrain this important parameter.

For system-specific properties, sediment deposition, resuspension and burial rates should be consistent with measured sediment accumulation rates, if available, and the organic carbon balance should close (*i.e.* carbon storage in the sediment should be consistent with POC input and output rates). In QWASI (like most MFTMs), both state variables (*e.g.* the pelagic suspended solids concentration or the organic carbon concentration of suspended or settled solids) and flux parameters (*e.g.* the rates of sediment deposition, resuspension and burial) are defined *a priori* by the user. However, since the concentrations and fluxes are not linked together, they may be inconsistent with one another. For example, the user could define a high rate of net sediment deposition even if the suspended solids concentration in the water column was low. Similarly, a high concentration of organic carbon in the active sediment layer may be defined, even if the rate of net carbon deposition is insufficient to maintain such a concentration. This issue was recognised in developing CoZMo-POP v2 (Coastal Zone Model for Persistent Organic Pollutants)<sup>12</sup> in which particulate organic carbon fluxes are defined by the user and state variables (such as the fraction of organic carbon in sediment) are calculated

from these fluxes. Although this requires the user to “fit” the state variables to sensible values (*e.g.* based on measured  $f_{OC}$  data) using manual trial and error iterations of the flux parameters, it does generate flux parameters and state variables which are internally consistent (although equifinality can, of course, be an issue here too). One approach for linking different observations in the model framework could be to employ some sort of recursive Bayesian estimation method in which new information results in a modification of existing beliefs (*e.g.* parameter combinations) and this should be explored further.

The lack of correlation in simulated parameters assumed in the work presented here is unlikely to be important for most parameters (where the uncertainty envelopes are independent) except in cases where parameters are physically connected (*e.g.*  $K_{OA} = K_{OW}/K_{AW}$  or  $\Delta U_{OW} = \Delta U_{OA} + \Delta U_{AW}$ ). In the latter case, even when the mean values are consistent, parameter combinations in individual MCS iterations may be selected which are beyond the range of statistical tolerance for consistency. The effect of this phenomenon on the output distributions is unknown but is probably not a major issue because the probabilities of selecting extreme values (which are more likely to be inconsistent) are low. Nevertheless, this could be investigated further in additional work.

## 4. Conclusions

This paper presents an uncertainty analysis of the QWASI model applied, as an example, to the fate of cVMS compounds in Tokyo Bay. Models like QWASI have historically been shown to generate reasonable predictions of chemical exposure and the relative importance of competing loss processes in lake.<sup>3,9,20,28–30</sup> The purpose here is not to undermine this successful approach. Rather, MCS provides a means of enhancing point estimates of exposure and persistence, with relatively modest additional computational effort (as long as the models are relatively simple).

The uncertainty in the predicted steady state values of  $C_w$  and  $C_s$  arising from uncertainty in the model parameters was fairly modest, even for those parameters to which the model is relatively sensitive. For all three compounds, the uncertainty implied in  $C_w$  is lower (CV of the order of 12–22%) than that in  $C_s$  (CV of the order of 38–55%), reflecting the propensity of cVMS compounds to sorb to sediment<sup>20,56,57</sup> and the sensitivity of the model to sediment deposition rate and  $K_{OC}$ .<sup>9,20,58</sup> Predicted concentrations in sediment were more sensitive than predicted concentrations in water for the same simulations (the relative range of outputs was wider). Uncertainty in the predicted persistence of all three cVMS compounds was lower in water than in sediment, both in relative and absolute terms. The confidence intervals were particularly high for the persistence of D5 and D6 in sediment which both ranged between approximately 1.7 years and approximately 26 years. Increasing the CV for water temperature from 5% to 50% had little effect on the predicted cVMS concentrations in sediment but increased the range of predicted concentrations in water. Higher temperatures tend to be associated with lower values of  $C_w$  due to an increase in the predicted hydrolysis rate and an assumed



increase in the hydrophobicity of cVMS compounds with increasing temperature. The latter assumption was based on three-phase experiments<sup>49,59</sup> in which simultaneous values for  $\Delta U_{OW}$ ,  $\Delta U_{AW}$  and  $\Delta U_{OA}$  were derived. Although the value for  $\Delta U_{OW}$  was based on just two temperatures, it was consistent with sum of  $\Delta U_{AW}$  and  $\Delta U_{OA}$ . In addition values of  $\Delta U_{OW}$  for other cVMS compounds were also positive. That said, this finding has been challenged by Panagopoulos *et al.* (2017)<sup>60</sup> who observed, *via* an indirect application of multi-media modelling to volatilisation experiments, that  $K_{OC}$  decreased with increasing temperature. Thus, the actual temperature dependence of cVMS partitioning may differ from that assumed here.

The distribution of model predictions generated by MCS to assess model uncertainty matched observations well for D5. However, the results demonstrate significant equifinality for both  $C_W$  and  $C_S$  (*i.e.* the same predicted concentrations can be generated by different combinations of parameter values). This suggests that a unique “optimal” parameter configuration does not exist. Additional observed data (*e.g.* measured  $C_W$  values > LOD and better emission estimates derived from measured concentrations in wastewater) could be used to constrain the possible parameter combinations which appear to yield “good” predictions (*i.e.* promoting the right results for the right reasons<sup>18</sup>). For D6, the measured concentrations are also captured by the uncertainty range of model predictions, particularly when uncertainty in emissions were accounted for. For D4, the range of model predictions was substantially lower than the measured concentration data. Including uncertainty in emissions (*via* the assumption of a log-normal distribution with a CV of 50%) and increasing the mean log  $K_{OC}$  value resulted in an increase in both the range and mean predicted concentrations in both water and sediment which were enough to capture the measured concentrations of D4 in sediment. In addition, it is possible that the measured D4 concentrations are, at least in part, a reflection of legacy emissions. Attention in monitoring efforts should be directed at better defining current emissions of D4 to Tokyo Bay and checking the real rate of hydrolysis.

Models can be seen as extended hypotheses which describe our current understanding of environmental system behaviour and which can be usefully employed to compare the expected behaviours and exposures of chemicals (*e.g.* in “evaluative” unit world models<sup>1,21</sup>). They can also be employed to make absolute predictions of exposure which can be compared to measurements. This comparison can test our understanding of chemical behaviour in environmental systems; increasing confidence in our understanding if model predictions agree with observations (*e.g.*, here, for D5) but challenging our assumptions when they do not adequately explain all the available observed data.<sup>61</sup> Disagreement (*e.g.*, here for D4) can result from gaps in our conceptual understanding and how this is translated into model code (epistemic uncertainty) and/or inappropriate parameterisation (aleatory uncertainty). Incorporating uncertainty into the modelling process (*e.g.* *via* MCS) can facilitate this comparison process because it provides confidence intervals for the predictions and, hence, an envelope within which discrepancies with measured data can be tolerated. It should also be remembered that there is also often considerable

uncertainty associated with measured data, which may not be representative of the system under consideration (*e.g.* due to low sample numbers in a variable system) or when our analytical methods are not sensitive enough to measure concentrations in some media sufficiently accurately (*i.e.* when concentrations are less than the limits of quantification). Explicit attempts to quantify uncertainty can also help to underpin our confidence in model-based regulatory decisions (*e.g.* in risk assessment and in the designation of persistence classes). For example, environmental persistence is both variable and uncertain, even for a specific environmental system. Whether a single estimate of persistence based on one set of parameters is above or below a regulatory threshold is, thus, uncertain. However, by quantifying the uncertainty distribution we can be more confident about the likelihood of exceeding this threshold. More (and better quality) data should help to reduce uncertainty (where needed) leading to increased confidence in our understanding and, thus, better-informed decision making.

An important consideration in this paper is the concept of equifinality and its use in MFTMs. Hitherto, equifinality has not been explicitly recognised by the MFTM community but it is relatively easy to identify using MCS. Does this matter? In most cases, probably not. Recognising that different combinations of parameters can generate the same predicted outcomes (or the failure to do so) will not change the utility of modelling as an extended hypothesis. However, it does add a layer of transparency to our predictions and to our understanding and interpretation of model outcomes. For example, it might be useful to be aware of the uncertainty in the relative contributions of different loss processes (*e.g.* volatilisation, reaction or advection) for a particular chemical and environmental system with the same predicted state (*e.g.* fugacity). Care may also need to be exercised when an apparently successful model for one chemical is employed to make predictions for other chemicals, if there are equifinality issues for the first chemical to which the outcome is insensitive but which are more important in the second. For example, the sediment deposition rate may not influence the predicted concentrations of a hydrophilic chemical but will be important for a hydrophobic one. Equifinality may also be a useful consideration in situations where models are used inversely to derive chemical properties<sup>50,56,57,60</sup> such as  $K_{OC}$  and its temperature-dependence. This should be investigated further.

## Conflicts of interest

There are no conflicts to declare.

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