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Supplementary Information

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

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S1 Equivalency between the Dispersion Factor and CV as descriptors of distribution spread

Kim *et al*. (2013) define statistical distributions using a "dispersion factor", *k*, from which they approximate the 95% confidence intervals as follows:

$$C_{low} = \frac{M}{k} \qquad \text{(A1)}$$

$$C_{high} = M.k \qquad \text{(A2)}$$

where M is the best estimate value and where C_{low} and C_{high} are the lower and upper values of the parameter in question corresponding to 2.5 percentiles and 97.5 percentiles in a cumulative log-normal distribution.

In the work reported here we use the coefficient of variation (CV) to define the "spread" of the distribution where:

$$CV = \frac{s}{m} \qquad \text{(A3)}$$

in which m is the arithmetic mean value (best estimate) and s is the (arithmetic) standard deviation. It is useful to evaluate how these parameters compare. To do this we derive the value of CV required to generate equivalent 2.5 and 97.5 percentiles of a log-normal distribution. These percentiles can be calculated from

$$x_p = \exp(z_p.\sigma + \mu) \tag{A4}$$

where x_p is the value of x given percentile p, z_p is the z-score for percentile p and where σ and μ are the parameters of the log-normal distribution (see Equations 2 and 3 above). For the 95 percent confidence intervals we are interested in p=0.025 and p=0.975 which have z-scores of -1.96 and 1.96. Given that σ and μ can both be derived from m and s and knowing that s can be derived from m, given CV, we can, therefore, estimate by trial and error the value of CV required to generate $x_{2.5}$ and $x_{97.5}$ values equivaluent to C_{low} and C_{high}. Alternatively, the equation of Macleod *et al.* (2001) can be used to define k:

$$k = \exp(1.96 * \sqrt{\ln(CV^2 + 1})) \tag{A5}$$

which can be rearranged to give

$$CV = \sqrt{\exp\left(\frac{\ln(k)}{1.96}\right)^2 - 1} \tag{A6}$$

Table S1 shows the values of CV which generate the same outcomes as various values of k employed by Kim *et al.* (2013).

Table S1 Values of CV which generate the same confidence limit outcomes as various values of *k*.

k	CV
1.13	0.06
1.19	0.09
1.5	0.21
1.8	0.31
2.57	0.51
3.0	0.61

S2 Best estimate parameter values, distribution type and CV assumed in MCS

The best estimate parameter values, distribution types and CVs assumed in MCS are shown in Tables S2 and S3. Note that the best estimate value is assumed here to be the arithmetic mean of the distribution and not the geometric mean (equivalent to the median) which was adopted by Kim *et al.* (2013).

Table S2 Best estimate environmental parameter values (supplied by the Environmental Control Center Ltd, Japan), distribution type and CV assumed in MCS. NB recent monitoring data from Tokyo Bay measured mean f_{OC} value of 0.026 g g^{-1} (Silicone Industry Association of Japan: SIAJ). LN = Log-normal; N = normal. *considering variability rather than uncertainty in the mean. SS is suspended sediment.

Parameter	**Explanation**	**Assumed Value**	**Ref**	**Distribution and CV**
A	Bay Surface Area	9.22 x 10^{8} m^{2}	NITE (2009)	LN (0.1)
V	Bay Volume	1.48 x 10^{10} m^{3}	NITE (2009)	LN (0.1)
Z	Mean Depth	16 m	NITE (2009)	Calculated (V/A)
Q_{in}	Inflow Discharge	1.2 x 10^{6} m^{3} h^{-1}	NILIM (2006)	LN (0.5)
Q_{out}	Outflow Discharge	1.4 x 10^{7} m^{3} h^{-1}	NITE (2009)	LN (0.25)
P	Precipitation	1.46 m yr^{-1}	MSJ (2004)	LN (0.04)
C_{SSin}	Conc SS in inflow	120 mg L^{-1}	AIST (2008a)	LN (0.21)
C_{SS}	Conc SS in Bay	4.0 mg L^{-1}	TMA	LN (0.21)
f_{OC} *(susp)*	Organic C frac in solids (water coln.)	0.15	AIST (2008a)	LN (0.09)
f_{OC} *(sed)*	Organic C fraction in solids (sediment)	0.05	AIST (07, 08a,b)	LN (0.09)
D	Sediment deposition rate	11.1 g m^{-2} d^{-1}	AIST (2008a)	LN (0.31)
R	Sediment resuspension rate	2.8 g m^{-2} d^{-1}	AIST (2008a)	LN (0.31)
B	Sediment burial rate	8.4 g m^{-2} d^{-1}	AIST (2008a)	LN (0.31)
zsed	Mixed sediment layer depth	0.05 m	AIST (2008b)	LN (0.61)
ϕ	Porosity of Sediment	0.8	Default	LN (0.21)
ρ_{sed}	Density sediment particles	2400 kg m^{-3}	Default	LN (0.21)
ρ_{X}	Density aerosol particles	1400 kg m^{-3}	Default	LN (0.21)

C_X	Concentration of aerosols in air	53 μg m^{-3}	Default	LN (0.21)
D_X	Aerosol dry deposition rate (default)	7.2 m h^{-1}	Default	LN (0.51)
S_X	Scavenging Ratio	200000	Default	LN (0.1)
k_W, k_A	Partial MTCs at air water interface	0.03, 3 m h^{-1}	AIST (2008b)	LN (0.51)
k_{diff}	Sediment diffusion MTC	3 x 10^{-4} m h^{-1}	AIST (2008b)	LN (0.51)
T	Water Temperature	17 °C	AIST (2008b)	N (0.05)
T	Water Temperature	17 °C	AIST (2008b)	N (0.50)*

Table S3 Best estimate chemical parameter values, distribution type and CV assumed in MCS. LN = Log normal. *Arbitrary value (Not enough information to estimate reasonably). # CV for log K_{OC}. Note that ΔU_{OC} was assumed to equal to ΔU_{OW}.

	Best Estimates					**Reference**
Parameter and Units	**D4**	**D5**	**D6**	**Distribution**	**CV**	**For Best Estimates**
K_{AW}	490	1349	1023	LN	0.3	Xu et al., 2014
K_{OC} (L/kg)	16596	158489	1071519	LN	0.05#	Kozerski et al., 2014
HLWater (hours)	9.6	216	960	LN	0.06	Brooke et al. 2008a,b,c
HLSediment (hours)	20060	4248600	8760000	LN	0.51	Whelan & Breivik, 2013
ΔU_{OC} (kJ/mol)	7.9	29	33.6	LN	0.1*	Xu & Kozerski, 2007
ΔU_{AW} (kJ/mol)	51.9	80.4	92.1	LN	0.1*	Xu & Kozerski, 2007
Ea (kJ/mol)	87.6	87.2	93.5	LN	0.1*	Xu & Kozerski, 2007

S3 Spearman Rank Correlation Coefficients

The strength of relationships between randomly generated parameter values and the predicted concentrations in water and sediment can be usefully estimated using calculated statistics such as the Spearman Rank Correlation Coefficient between the parameter and the predicted concentration (C_W or C_S), together with its significance. The Spearman Rank Correlation (Table S4) is a non-parametric method and has the advantage over the Pearson Product Moment Correlation that it can detect non-linear (monotonic) associations.

Table S4. Spearman rank correlation coefficients between different parameters and the predicted concentrations of D4, D5 and D6 in water and sediment. *HLw* is half-life in water; *HLs* is half-life in sediment; *Qin* is the water flow into the Bay, *Qout* is the water flow out of the Bay; *Resusp* is the sediment resuspension rate; *Dep* is the sediment deposition rate; *Bur* is the sediment burial rate; *Zsed* is the sediment depth; *foc_w* and *foc_s* are the organic carbon contents of the water and sediment compartments; *SSC* is the suspended solids concentration in the water column; *MTCa* and *MTCw* are the partial mass transfer coefficients at the air and water side of the two-film air-water interface and *Diffn* is the diffusion coefficient across the sediment-water interface. Shaded cells indicate that the correlation was significant at $p < 0.05$.

	Kaw	*HLw*	*HLs*	*ΔUow*	*ΔUoa*	*ΔUaw*	*Ea*	*Koc*	*Qin*	*Resusp*	*Qout*	*Dep*	*Bur*	*Zsed*	*foc_w*	*foc_s*	*SSC*	*MTCa*	*MTCw*	*Diffn*
										Correlations with C_W										
D4	-0.126	0.307	0.439	-0.003	0.007	0.011	0.490	0.012	0.000	0.003	-0.045	-0.003	-0.010	-0.016	-0.007	-0.015	0.018	-0.005	-0.173	0.016
D5	-0.040	0.079	0.082	0.007	0.004	0.001	0.137	-0.037	-0.010	0.023	-0.259	-0.093	-0.036	0.028	0.011	-0.003	0.051	0.008	-0.868	0.025
D6	0.004	0.010	-0.056	0.017	0.017	0.010	0.014	-0.057	0.005	0.135	-0.237	-0.486	-0.130	-0.005	-0.052	-0.042	0.187	0.010	-0.648	0.005
										Ranks for correlations with C_W										
D4	7	5	3	24	20	15	2	14	29	26	8	25	16	11	19	13	10	21	6	12
D5	10	8	7	23	24	29	3	11	20	16	2	6	12	13	19	26	9	22	1	14
D6	26	21	8	16	15	19	18	7	25	5	3	2	6	23	9	13	4	20	1	24
										Correlations with C_S										
D4	-0.058	0.174	0.332	-0.034	-0.006	-0.010	0.262	0.154	0.005	-0.011	-0.015	0.408	-0.063	-0.663	0.119	0.139	-0.013	-0.004	-0.058	0.006
D5	0.020	0.054	0.168	-0.080	0.014	-0.004	0.073	0.109	-0.002	-0.130	-0.121	0.624	-0.434	-0.008	0.181	0.073	0.009	-0.016	-0.437	-0.136
D6	-0.001	0.007	0.102	-0.072	-0.017	0.026	0.017	0.077	-0.008	-0.108	-0.163	0.488	-0.653	0.004	0.121	0.032	-0.042	-0.011	-0.399	-0.021
										Ranks for correlations with C_S										
D4	13	7	3	15	25	22	4	9	28	21	18	2	12	1	11	10	20	29	14	26
D5	17	14	5	10	19	26	13	9	28	7	8	1	3	22	4	12	21	18	2	6
D6	29	25	7	10	20	16	21	9	24	6	4	2	1	27	5	14	11	23	3	17

S4 Predicted frequency distributions of C_W and C_S for D4 and D6

Predicted frequency distributions of C_W and C_S for D4 and D6 are shown in Figures S1 and S2, respectively.

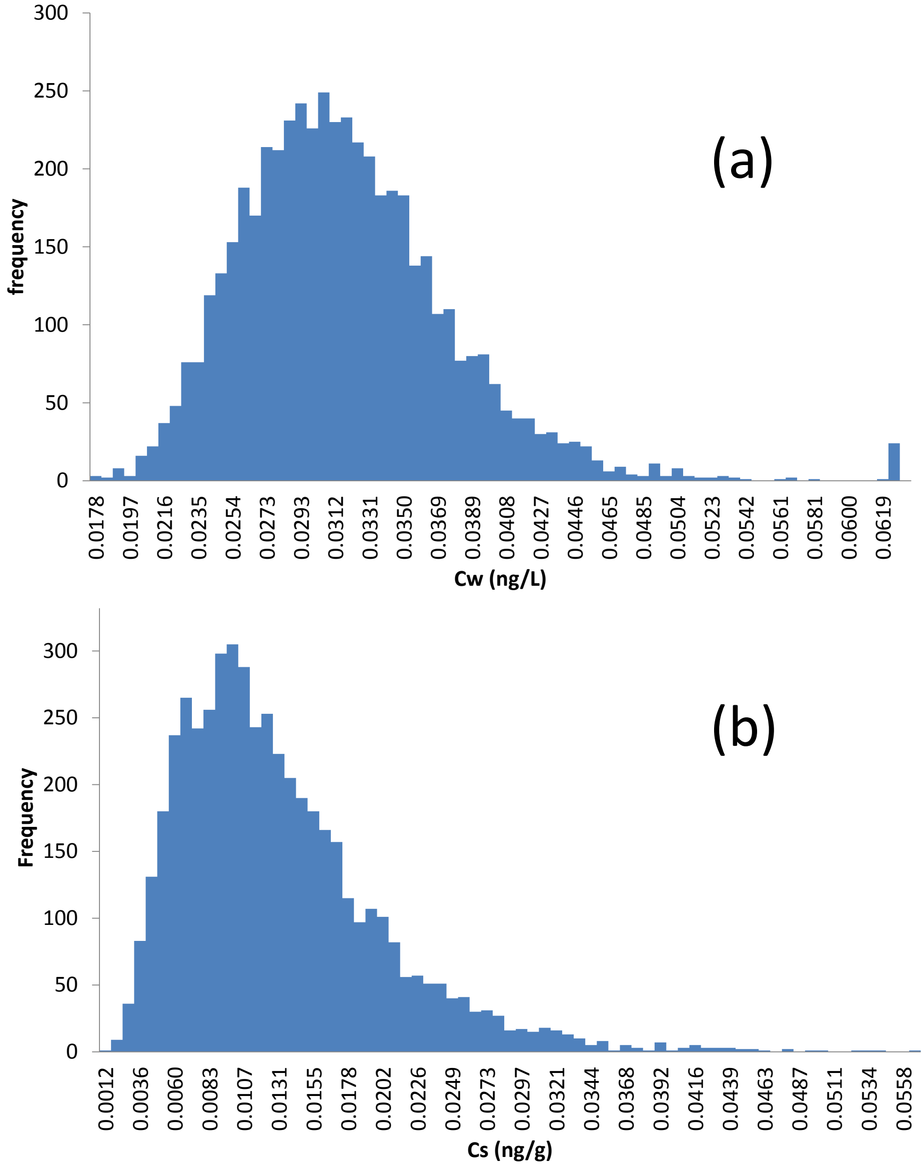

Figure S1 Predicted frequency distributions of (a) C_W and (b) C_S for D4 in Tokyo Bay

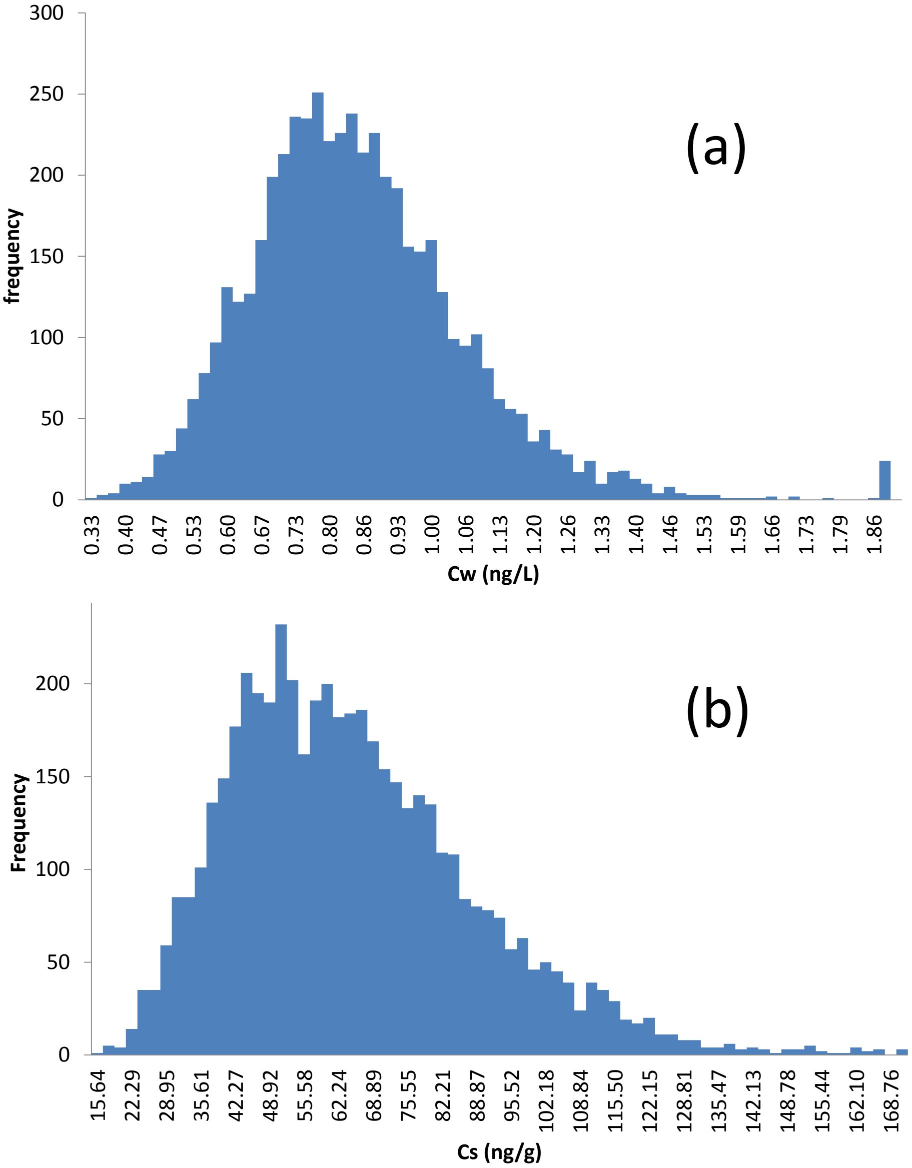

Figure S2 Predicted frequency distributions of (a) C_W and (b) C_S for D6 in Tokyo Bay.

S5 Predicted concentrations of C_W and C_S versus various parameters for the case in which temperature was selected from a wide distribution (CV 0.5).

Please note that the distributions of the sampled parameters do no always expand significantly when the CV for temperature is increased. This is because extreme parameter values (high and low) have a low probability and extreme values of temperature also have a low probability which means that the probability of getting a combined extreme value of the parameter and temperature is low. The CV assumed for K_{OC} and *HLwater* was particularly low so the distributions are very narrow in any case for these parameters. This is exacerbated for K_{OC} by the fact that the value of ΔU_{OC} assumed was low (just 29 kJ/mol) which means that the slope of the K_{OC} v temperature relationship is shallow.

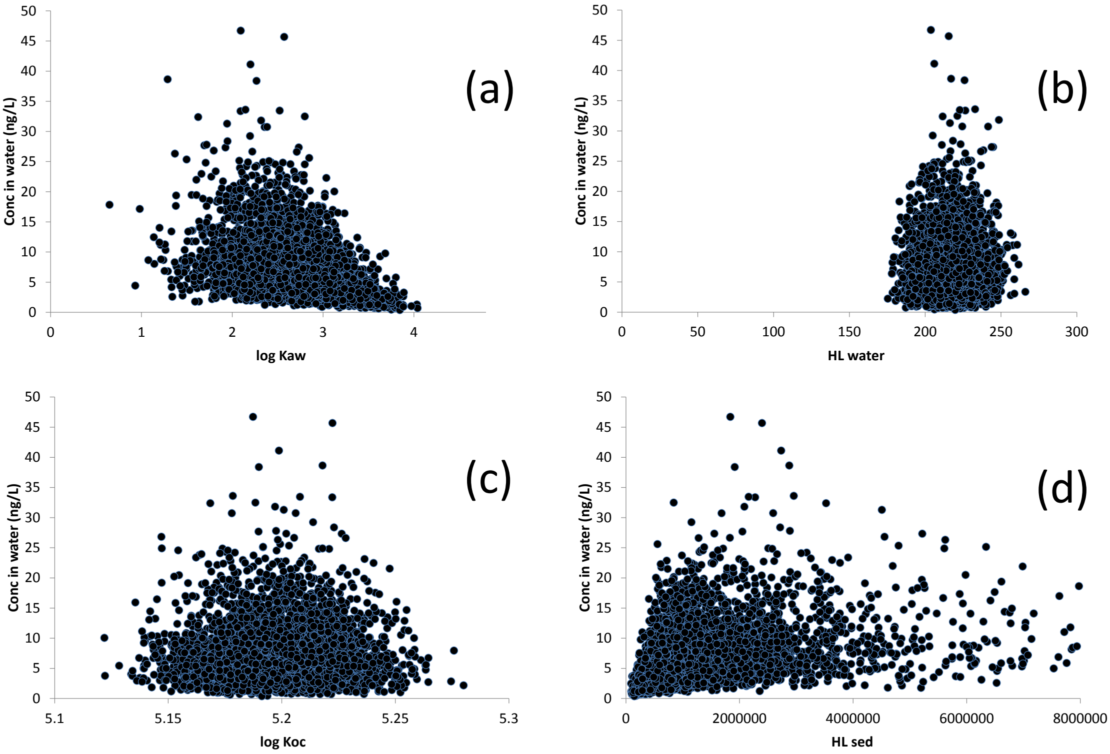

Figure S3 Predicted concentrations of D5 in <u>water</u> in Tokyo Bay plotted against Monte-Carlo-generated values of (a) log K_{AW}, (b) HL_{water} (hours), (c) log K_{OC} and (d) HL_{sed} (hours).

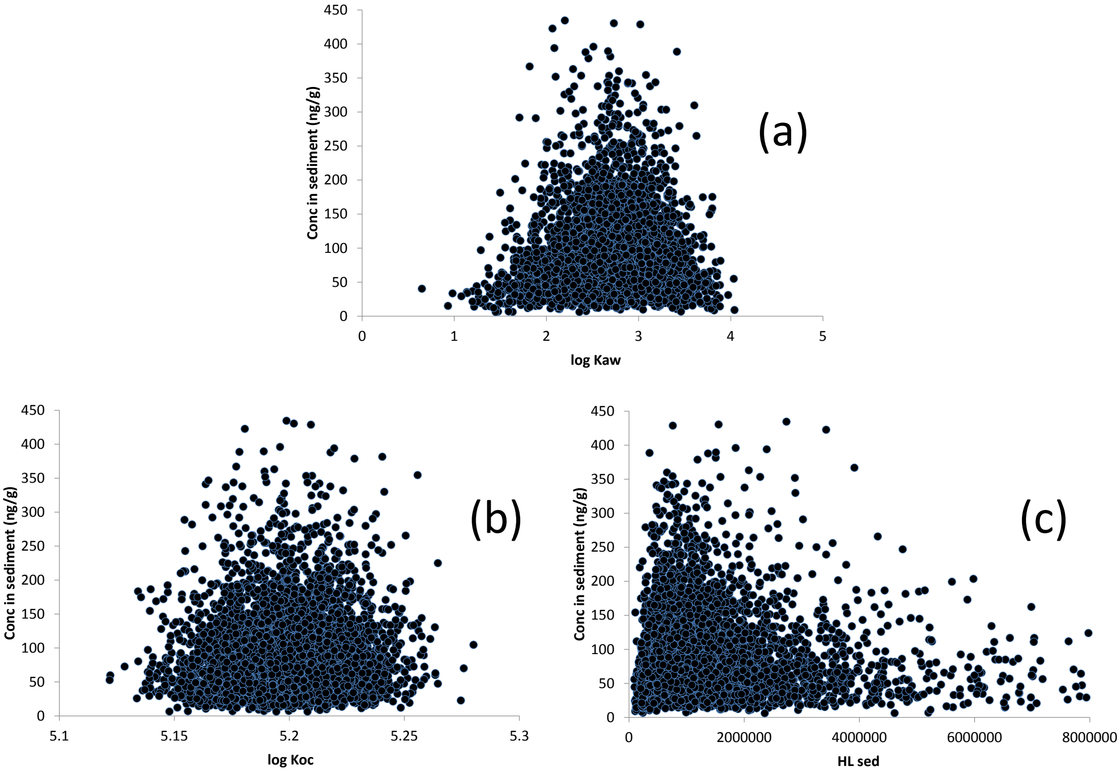

Figure S4 Predicted concentrations of D5 in *sediment* in Tokyo Bay plotted against Monte-Carlo-generated values of (a) log K_{AW}, (b) log K_{OC} and (c) HL_{sed} (hours).

Please note that by assuming a normal distribution for temperature, several values sampled at the very low end of the temperature range are less than zero. This does not reflect a realistic expectation that water temperatures fall below zero in Tokyo Bay and predictions for these temperatures should be ignored. It should be noted also that uncertainty in the relationships between temperature and hydrolysis rates and between temperature and partitioning will be more uncertain towards the tails of the assumed temperature distribution. Figure S5 should, therefore, be viewed as illustrative only.

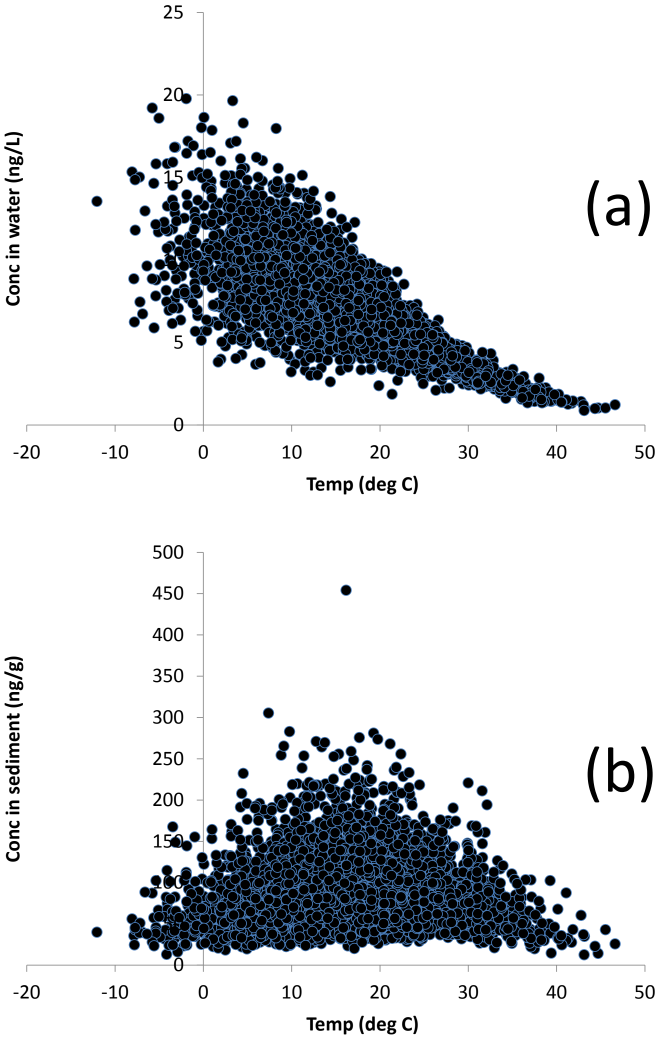

Figure S5 Predicted concentrations of D5 in (a) water and (b) sediment in Tokyo Bay plotted against Monte-Carlo-generated values of temperature.

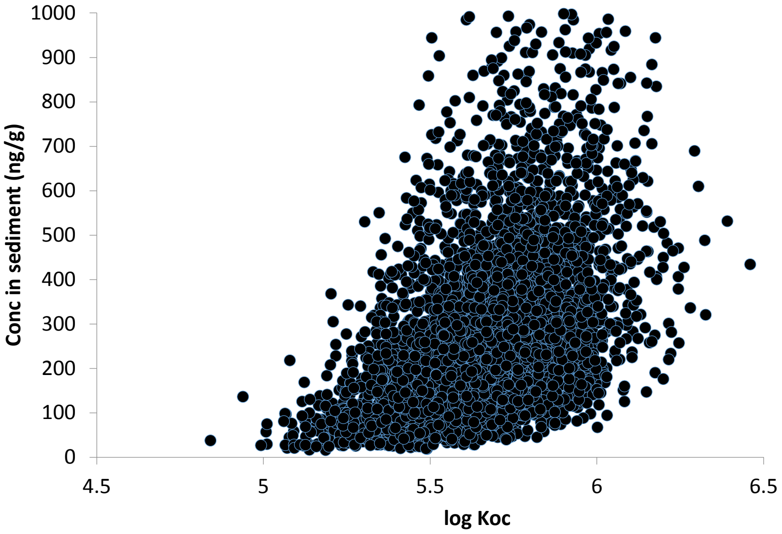

Figure S6 Predicted concentrations of D5 in sediment in Tokyo Bay plotted against Monte-Carlo-generated values of log KOC, assuming a mean log K_{OC} value of 5.7 and a CV for K_{OC} 0.5.

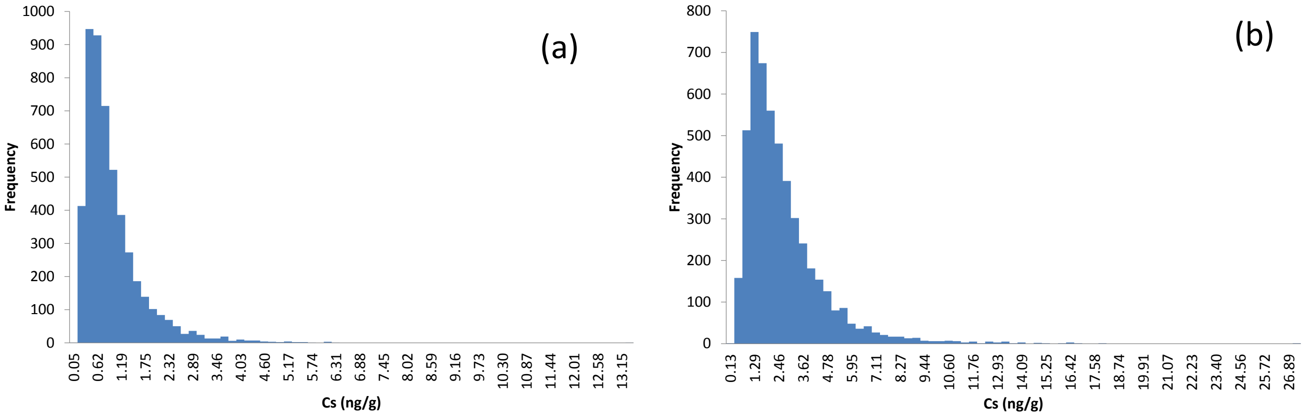

Figure S7 Predicted frequency distributions C_S for D4 in Tokyo Bay generated by Monte-Carlo simulations with a mean log K_{OC} increased to 5.45 and (a) HLwater = 9.6 h at 25 °C (default) and (b) HLwater = 3 x 9.6 h at 25 °C to illustrate the potential role of reduced hydrolysis in influencing C_S.

References

- Brooke D.N., Crookes M.J., Gray D. and Robertson S. (2008a) *Risk Assessment Report: Octamethylcyclotetrasiloxane*, Environment Agency of England and Wales, Bristol
- Brooke D.N., Crookes M.J., Gray D. and Robertson S. (2008b) *Risk Assessment Report: Decamethylcyclopentasiloxane*, Environment Agency of England and Wales, Bristol
- Brooke D.N., Crookes M.J., Gray D. and Robertson S. (2008c) *Risk Assessment Report: Dodecamethylcyclohexasiloxane,* Environment Agency of England and Wales, Bristol
- Kozerski, G. E., Xu, S., Miller, J., Durham, J. (2014) Determination of soil-water sorption coefficients of volatile methylsiloxanes *Environ. Toxicol. Chem.*, 33, 1937-1945.
- Whelan M.J. and Breivik K. (2013) Dynamic modelling of aquatic exposure and pelagic food chain transfer of cyclic volatile methyl siloxanes in the Inner Oslofjord *Chemosphere* 93, 794-804.
- Xu, S., Kozerski, G., Mackay, D. (2014) Critical review and interpretation of environmental data for volatile methylsiloxanes: partition properties. *Environ. Sci. Technol.*, 48, 11748-11759.
- Xu, S. H., Kozerski, G. E.(2007) *Assessment of the fundamental partitioning properties of permethylated cyclosiloxanes;* SETAC Europe, Porto, Portugal.