

Mapping Environmental Partitioning Properties of Nonpolar Complex Mixtures by Use of GC × GC

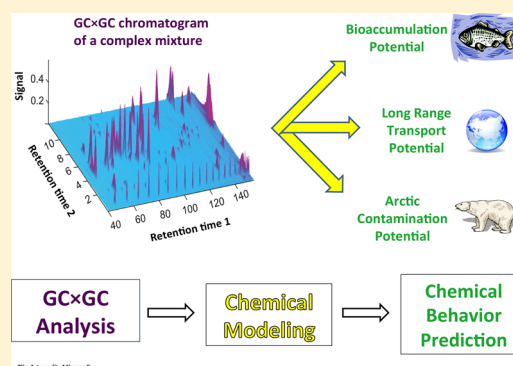
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Supporting Information

ABSTRACT: Comprehensive two-dimensional gas chromatography (GC × GC) is effective for separating and quantifying nonpolar organic chemicals in complex mixtures. Here we present a model to estimate 11 environmental partitioning properties for nonpolar analytes based on GC × GC chromatogram retention time information. The considered partitioning properties span several phases including pure liquid, air, water, octanol, hexadecane, particle natural organic matter, dissolved organic matter, and organism lipids. The model training set and test sets are based on a literature compilation of 648 individual experimental partitioning property data. For a test set of 50 nonpolar environmental contaminants, predicted partition coefficients exhibit root-mean-squared errors ranging from 0.19 to 0.48 log unit, outperforming Abraham-type solvation models for the same chemical set. The approach is applicable to nonpolar organic chemicals containing C, H, F, Cl, Br, and I, having boiling points ≤402 °C. The presented model is calibrated, easy to apply, and requires the user only to identify a small set of known analytes that adapt the model to the GC × GC instrument program. The analyst can thus map partitioning property estimates onto GC × GC chromatograms of complex mixtures. For example, analyzed nonpolar chemicals can be screened for long-range transport potential, aquatic bioaccumulation potential, arctic contamination potential, and other characteristic partitioning behaviors.



1. INTRODUCTION

Equilibrium partitioning properties of organic contaminants influence their transport and distribution among different environmental compartments, including air, water, natural organic matter, and other natural phases.^{1–3} In order to assess environmental behaviors and ecological impacts of hydrophobic contaminants, fate models usually employ equilibrium partitioning properties, defined as

$$P_{xy,i} = \left\{ \frac{C_{x,i}}{C_{y,i}} \right\}_{\text{equilibrium}} \quad (1)$$

where $P_{xy,i}$ is the partition coefficient between phases x and y , and $C_{x,i}$ and $C_{y,i}$ are the concentrations of contaminant i in those two phases when at partitioning equilibrium.

For many organic contaminants, partitioning property data have not been measured experimentally or have large uncertainties in their reported values.⁴ Relatively few partitioning property data exist for newly identified contaminants. Additionally, some commercial technical mixtures contain hundreds or thousands of distinct organic chemicals that may arise in environmental samples and that remain incompletely characterized.^{5,6} It remains unclear how to assess bioaccumulation potential or to parametrize transport models

describing inter-phase transfers for these mixtures. To address these challenges, the community would benefit from methods designed to estimate partitioning properties for the organic chemicals that are observed in analyzed mixtures.

For nonpolar complex mixtures, comprehensive two-dimensional gas chromatography (GC × GC) offers the opportunity to separate chemicals, quantify them, and simultaneously estimate their partitioning properties. GC × GC separates analytes by use of two columns that are interfaced by a cryogenic modulator.^{7,8} The resulting two-dimensional separation resolves an order of magnitude more analytes than conventional gas chromatography (GC).⁹ While studying petroleum complex mixtures from coastal oil spills, Arey et al.¹⁰ demonstrated that GC × GC chromatogram retention data could also be used to estimate several partitioning properties for diesel hydrocarbon analytes, via the two-parameter linear free energy relationship (LFER):

$$\log P_{xy,i} = aI_{1,i} + bI_{2,i} + c \quad (2)$$

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where $I_{1,i}$ and $I_{2,i}$ are the GC \times GC first and second column retention indices, respectively, for analyte i . Each retention index value is computed by converting the respective analyte retention time into an approximate scale of free energy of gas-stationary phase transfer at a reference temperature of 120 °C, normalized to the value for a hypothetical simultaneously eluting n -alkane. The constant coefficients a , b , and c are specific to each two-phase partitioning system, and these parameters were fitted to experimental partitioning data by multiple linear regression. Equation 2 successfully mapped several environmental partitioning properties ($P_{xy,i}$) directly onto GC \times GC chromatograms of diesel fuel hydrocarbons, including pure liquid vapor pressure, aqueous solubility, octanol-water and air-water partition coefficients, and pure-liquid enthalpy of vaporization.¹⁰

In subsequent work, eq 2 has dramatically accelerated advances in investigations of environmental behaviors and impacts of petroleum hydrocarbon complex mixtures. Several studies have used GC \times GC to parametrize partitioning properties of mass transfer models,^{11–13} to parametrize aquatic toxicity models,¹⁴ and to differentiate fractionation signatures of evaporation, dissolution, and biodegradation in GC \times GC chromatograms of weathered petroleum mixtures.^{15–20}

Recently, Tcaciuc et al.²¹ proposed an alternative approach for estimating partitioning properties from GC \times GC chromatogram retention data. They used the first dimension retention time ($t_{1,i}$) and second dimension retention time ($t_{2,i}$) to estimate phospholipid-water partition coefficients (K_{ph-w}) via multiple linear regression:

$$\log K_{ph-w,i} = at_{1,i} + bt_{2,i} + c \quad (3)$$

Tcaciuc et al.²¹ found good regression statistics for K_{ph-w} values of 38 nonpolar and polar aromatic chemicals using eq 3. The above studies^{10,21} propose apparently different methods for estimating partitioning properties by GC \times GC.

Here we present a generalized and easy-to-use approach for mapping environmental partitioning properties onto GC \times GC chromatograms. The method is validated for nonpolar organic analytes, defined here as those chemicals that experience limited or negligible hydrogen-bond donor or acceptor interactions with solvents. Specifically, (1) we develop and calibrate a generalized two-parameter LFER model for predicting partitioning properties of nonpolar chemicals and (2) we show that the two LFER solute parameters can be obtained by simple transformations of measured retention times of chemicals analyzed by GC \times GC. (3) This enables us to estimate 11 different environmental partitioning properties for nonpolar analytes on the GC \times GC chromatogram. (4) We compare the resulting predictions to a literature compilation of experimental partitioning data for two test sets of nonpolar chemicals. (5) We explain the domain and limits of the model. (6) We package the methodology into a user-friendly Matlab program that can be applied to user-defined GC \times GC instrument programs, requiring only simple and easily obtained input information. (7) Finally, we elaborate on potential applications of the resulting approach that can shed new light on phase-transfer fractionations and associated characteristic environmental behaviors of nonpolar complex mixtures containing fluorinated, chlorinated, brominated, iodinated, and nonhalogenated acyclic aliphatic, cyclic aliphatic, and aromatic hydrocarbon chemicals.

2. EXPERIMENTAL METHODS

2.1. Chemicals. **2.1.1. Nonpolar Contaminant Test Sets.** A mixture of standards comprising 79 nonpolar organic contaminants was analyzed by GC \times GC. These chemicals were divided into two test sets (I and II), explained further in section 3.2. The resulting chemical sets enabled validation tests of GC \times GC-estimated partitioning properties for nonpolar contaminants (section 4.4). Analyzed organic chemicals included the following:

1,2,3,4,5,5-hexachloro-1,3-cyclopentadiene
1,1,2,3,4,4-hexachloro-1,3-butadiene
11 polychlorinated n -alkane (PCA) individual standards
two toxaphenes (Parlar 11 and 32)
 α -hexachlorocyclohexane (α -HCH), γ -HCH, β -HCH, and δ -HCH
seven linear alkyl benzenes (LABs) (n -propyl to n -octyl plus n -decyl)
13 polycyclic aromatic hydrocarbons (PAHs)
five chlorinated benzenes (CBs)
4-chlorodiphenyl ether
11 polychlorinated biphenyls (PCB numbers 28, 52, 101, 105, 118, 128, 138, 153, 156, 170, and 180)
2-chloronaphthalene
heptachlor
aldrin
trans-chlordane and *cis*-chlordane
mirex
2,4,5,6-tetrachloro-*m*-xylene
p,p'-DDE, *p,p'*-DDD, and *p,p'*-DDT
two polybrominated diphenyl ethers (PBDE numbers 3 and 47)

In addition to these chemical sets, we also analyzed C₇–C₄₀ n -alkanes. Standards were obtained from Sigma–Aldrich Corp., Restek Corp., LGC UK, Cambridge Isotope Laboratories Inc., and AccuStandard Inc. PCA individual standards were kindly provided by Dr. Mehmet Coelhan of Technische Universität München. A complete listing of chemical names and retention time data is given in Supporting Information Tables S1, S2, and S3.

2.1.2. Polychlorinated Alkanes Technical Mixture. A technical-grade short-chain (C₁₀–C₁₃) PCA mixture having 51.5% degree of chlorination was analyzed with GC \times GC instrument program A (section 2.2). The PCA mixture was obtained from Dr. Ehrenstorfer GmbH.

2.2. Analysis by Comprehensive Two-Dimensional Gas Chromatography–Time of Flight Mass Spectrometry. A GC \times GC–time of flight mass spectrometer (TOF-MS) instrument (Zoex Corp.) was used to analyze the chemical mixtures described above. The first-dimension column was a nonpolar Rxi-1MS, and the second-dimension column was a semipolar BPX-50. Three different GC \times GC instrument programs were used, referred to here as instrument programs A, B, and C. This allowed us to verify that our results were not idiosyncratic outcomes of specially chosen instrument parameters. Instrument program A used a gradual temperature program having ramp rates of 0.75 and 1.5 °C·min^{–1} for the first- and second-dimension columns, respectively. Instrument program B used 2 \times faster temperature ramps for both columns and thus produced shorter analyte retention times than program A. Program C employed the fastest ramp rates, with 3 and 5 °C·min^{–1} for the first and second dimension, respectively. See section S1 in Supporting Information for

complete details of these instrument programs. These instrument programs are different from those used in ref 10.

3. PHYSICAL PROPERTY DATA COMPILATIONS FROM LITERATURE

3.1. Partitioning Model Training Set. We compiled Abraham solvation model (ASM) solute parameters and partitioning property data, where available, for a selected set of 79 nonpolar chemicals (Table S4, Supporting Information). This set was used to calibrate the coefficients of the partitioning property model described by eq 5, as explained in section 4.2. The model training set is formulated to span several nonpolar families in a balanced way, composed of chemicals for which ASM solute parameters were previously reported.^{22–39} These included *n*-alkanes, cycloalkanes, cycloalkenes, fluorinated alkanes, chlorinated alkanes, chlorinated alkenes, brominated alkanes, iodinated alkanes, benzene, linear alkylbenzenes, fluorinated benzenes, chlorinated benzenes, brominated benzenes, iodinated benzenes, PAHs, and PCBs. Further added to the set were γ -HCH (lindane), *p,p'*-DDE, enflurane, and sulfur hexafluoride. We preferentially selected chemicals having updated ASM parameters over chemicals coming from older ASM data sets. These updates included corrections to McGowan volumes of PCBs³⁵ and improved determinations of solute parameters *S*, *A*, and *B* for several chemicals.^{37,38} We also compiled previously established ASM regression coefficients for several partitioning systems (Table S5, Supporting Information).^{24,26,31,33–35,40–44} Taken together, this collection of ASM solute parameters and ASM system coefficients was intended to capture the solute–solvent interactions explored by nonpolar solute chemicals in several important environmental phases. Some overlap exists among the chemical sets: 34 chemicals are common to both the model training set and to either contaminant test set I or II.

3.2. Nonpolar Contaminant Test Sets I and II. The 79 nonpolar contaminants analyzed by GC \times GC (section 2.1.1) were divided into two sets: I and II. Set I comprised 50 contaminants for which replete sets of up-to-date ASM solute parameters were available (Table S1, Supporting Information),^{22–39} and these were analyzed by the three GC \times GC instrument programs A, B, and C. Set II comprised 29 contaminants for which complete sets of experimental ASM solute parameters were not available or possibly had not been consistently determined, and these chemicals were analyzed only by GC \times GC instrument program A. Experimental partitioning property data for both sets (I and II) were collected from several sources^{1,4,10,21–23,27,29,33–35,37,38,41,45–86} and include the following:

pure (subcooled) liquid vapor pressure (p_L)
 hexadecane–air partition coefficient (K_{h-a})
 octanol–air partition coefficient (K_{o-a})
 Leonardite humic acid–air partition coefficient (K_{OC-a})
 air–water partition coefficient (K_{a-w})
 pure (subcooled) liquid aqueous solubility (S_{wL})
 octanol–water partition coefficient (K_{o-w})
 amorphous organic carbon–water partition coefficient (K_{OC-w})
 dissolved organic carbon–water partition coefficient (K_{DOC-w})

(see Tables S7, S9–S13, S15–S17, S19, and S20, Supporting Information). We also considered the aquatic bioconcentration factor (BCF), which describes equilibrium partitioning between

water and the lipid pool (i.e., membrane plus storage lipid) of an organism,⁸⁷ reported for several species of fishes and worms (Table S18, Supporting Information) (ref 34 and references cited therein). We finally compiled enthalpy of vaporization (ΔH_{vap}), needed to account for liquid vapor pressure temperature dependence (Table S8, Supporting Information). Experimental K_{OC-a} data were reported at 15 °C and 98% relative humidity.⁴⁵ All other partitioning property data were reported at 25 °C. The source of dissolved organic matter for K_{DOC-w} data was commercial Aldrich humic acid.^{33,60,66} For chemicals occurring as pure phase solids at room temperature, the free energy of melting of the pure phase, $\Delta G_{s \rightarrow L}$, used to convert aqueous solubility and vapor pressure data from pure solid state to hypothetical pure subcooled liquid state, was estimated by different methods.^{1,47,69,71} For further details, see Supporting Information section S2 and Tables S6, S7, and S13.

Some experimental methods are considered more reliable than others for determining partitioning properties of hydrophobic chemicals.¹ Where available, we preferred measured S_{wL} and K_{o-w} data acquired through the generator column method,¹ which ensures stable aqueous concentrations. We preferred K_{OC-w} and K_{DOC-w} data that had been measured employing negligible-depletion solid-phase microextraction (nd-SPME), which enables sampling without phase separation, over traditional batch methods.⁸⁸ See Supporting Information Tables S7–S17 for further details.

4. RESULTS AND DISCUSSION

4.1. Dimensionality of Solute–Solvent Interactions for Nonpolar Chemicals. As a starting point for developing a model to estimate environmental partitioning properties from GC \times GC retention data, we propose that partitioning properties of nonpolar chemicals may be estimated by use of only two general solute parameters, corresponding to two dimensions of information. To explore this hypothesis, we analyzed the information content contained in published Abraham solute parameters of the partitioning model training set (section 3.1) and contaminant test set I (section 3.2).

According to the ASM^{89,90} and related expressions proposed by Goss,⁹¹ equilibrium partition coefficients for nonionic chemicals can be described by the following general expressions:

$$\log P_{xy,i} = c + eE_i + sS_i + aA_i + bB_i + vV_i \quad (4a)$$

$$\log P_{xy,i} = c + eE_i + sS_i + aA_i + bB_i + lL_i \quad (4b)$$

$$\log P_{xy,i} = c + sS_i + aA_i + bB_i + lL_i + vV_i \quad (4c)$$

where V_i is the McGowan molecular volume of solute *i*; L_i is the hexadecane–air partition coefficient of the solute at 25 °C; E_i describes the polarizability of the solute in excess of that of a comparably sized *n*-alkane; S_i describes a mixture of electrostatic polarity and polarizability of the solute;⁹² and A_i and B_i are hydrogen-bond donating and accepting capacities of the solute, respectively. To describe partitioning from a pure-phase system (S_{wL} or p_L), the term $-5.94X_i$ has also been added to eqs 4a–4c,³⁵ where X_i is defined as the product A_iB_i . Small letters *c*, *e*, *s*, *a*, *b*, *l*, and *v* are coefficients specific to each two-phase partitioning system *xy*. The wide success of eqs 4a–4c indicates that five dimensions of information are needed generally to explain phase partitioning of diverse neutral organic chemicals in a broad range of different media.^{90,91}

Table 1. Regression Coefficients^a of Equation 5a for 11 Partitioning Properties Based on Fits of the Model Training Set ($n = 79$)

property	λ_1	λ_2	λ_3	RMSE ^b	r^2
$\log p_L$ (Pa)	-1.87 ± 0.06	0.0 ^c	6.31 ± 0.17	0.30	0.986
ΔH_{vap} (kJ·mol ⁻¹)	16.0 ± 0.5	0.0	14.3 ± 1.2	3.0	0.98
$\log K_{h-a}$ (mol·L ⁻¹ ·mol ⁻¹ ·L)	1.926 ± 0.001	-0.869 ± 0.007	0.241 ± 0.004	0.0043	0.999 997
$\log K_{o-a}$ (mol·L ⁻¹ ·mol ⁻¹ ·L)	1.77 ± 0.07	0.0	0.51 ± 0.14	0.24	0.989
$\log K_{OC-a}$ (mol·kg ⁻¹ ·mol ⁻¹ ·L)	1.77 ± 0.04	1.65 ± 0.32	0.19 ± 0.12	0.23	0.992
$\log K_{a-w}$ (mol·L ⁻¹ ·mol ⁻¹ ·L)	-0.20 ± 0.12	-7.04 ± 0.69	-0.51 ± 0.33	0.51	0.87
$\log S_{wL}$ (mol·m ⁻³)	-1.61 ± 0.11	6.88 ± 0.75	3.36 ± 0.32	0.50	0.93
$\log K_{o-w}$ (mol·L ⁻¹ ·mol ⁻¹ ·L)	1.38 ± 0.08	-6.40 ± 0.61	0.34 ± 0.19	0.37	0.95
$\log K_{OC-w}$ (mol·kg ⁻¹ ·mol ⁻¹ ·L)	1.30 ± 0.06	-4.15 ± 0.45	-0.21 ± 0.14	0.32	0.96
$\log K_{DOC-w}$ (mol·kg ⁻¹ ·mol ⁻¹ ·L)	1.49 ± 0.07	-4.62 ± 0.50	-0.31 ± 0.19	0.39	0.95
$\log \text{BCF}$ (mol·kg ⁻¹ ·mol ⁻¹ ·L)	1.36 ± 0.06	-4.53 ± 0.52	0.66 ± 0.17	0.35	0.95

^aReported regression coefficient uncertainties correspond to a 95% confidence interval of the fitted values, estimated by the bootstrap method¹²⁹ with 1000 synthetic resamplings. ^bRMSE is the root-mean-squared error. ^cA reported value of 0.0 indicates that the fitted coefficient value was found to be statistically indistinguishable from zero; in these cases, the corresponding variable was removed and the regression was repeated.

However, for chemicals having limited or negligible hydrogen-bonding capacity, phase partitioning might be approximated from less information. Applying singular value decomposition^{93,94} to the 79×6 matrix, $[E \ S \ A \ B \ V \ L]$, of Abraham solute parameters of the model training set (Table S4, Supporting Information), we found that 99.9% of the total variance can be ascribed to the first two principal components. These two eigenvectors are found to be linear combinations of the solute parameters V , L , E , and S , with very small contributions from A and B . Similar results are found for contaminant test set I (Table S1, Supporting Information). Hence, for nonpolar chemicals, the six Abraham solute parameters might be effectively reduced to two independent dimensions of information, reflected in the ASM terms V , L , E , and S . Taken together, these ASM terms are considered to account for the cavitation energy of solvation of the solute, London dispersion forces, Debye dipole-induced dipole forces, and Keesom dipole-dipole forces, and these are the physical effects expected to control solute-solvent interactions for nonpolar solutes.^{1,95,96}

4.2. A Two-Parameter Linear Free Energy Relationship for Partitioning Properties of Nonpolar Chemicals. On the basis of the above findings, we propose the following generalized two-parameter LFER as a trial model for estimating partitioning properties of nonpolar chemicals:

$$\log P_{xy,i} = \lambda_1 u_{1,i} + \lambda_2 u_{2,i} + \lambda_3 \quad (5a)$$

with $u_{1,i}$ and $u_{2,i}$ defined as

$$u_{1,i} = \log L_{1,i} \quad (5b)$$

$$u_{2,i} = \log L_{2,i} - \beta_{\text{orth}} \log L_{1,i} \quad (5c)$$

where $\log L_{1,i}$ and $\log L_{2,i}$ are base-10 log-transformed gas-stationary phase partition coefficients (mol·L⁻¹·mol⁻¹·L) at 120 °C for chemical i on GC phases 1 and 2, and coefficients λ_1 , λ_2 , and λ_3 are specific to each partitioning system xy . The constant parameter β_{orth} is defined such that the vectors $u_{1,i}$ and $u_{2,i}$ are mutually orthogonal for a designated chemical calibration set. We assigned the stationary phase of L_1 as 100% methylpolysiloxane and that of L_2 as 50% phenyl methylpolysiloxane, since these same phases previously led to good results with eq 2 for diesel hydrocarbons.¹⁰

We calibrated eq 5 for 11 different environmental partitioning properties using the 79 chemicals of the model

training set (section 3.1), as follows. Solute $L_{1,i}$ and $L_{2,i}$ values were estimated with the ASM equation based on previously determined ASM coefficients for the equivalent stationary phases SE-30 and OV-17,⁹⁷ respectively, and the ASM solute parameters of the training set (Table S4, Supporting Information). The parameter β_{orth} was determined by Gram-Schmidt orthogonalization⁹³ of vectors $u_{1,i}$ and $u_{2,i}$ by use of ASM-predicted $\log L_{1,i}$ and $\log L_{2,i}$ values of the training set. This produced $\beta_{\text{orth}} = 1.1353$. Individual experimental $P_{xy,i}$ values for chemicals of the training set were obtained from the literature (Table S4, Supporting Information). In cases where experimental data were not available, we estimated $P_{xy,i}$ entries by use of eq 4a, 4b, or 4c, based on previously published ASM coefficients (Table S5, Supporting Information).^{24,26,31,33–35,40–44} Finally, the coefficients λ_1 , λ_2 , and λ_3 of eq 5a were determined by multiple linear regression for each partitioning system.

Regression of eq 5a coefficients gave reasonable fit statistics for all 11 partitioning properties that we considered, with squared correlation coefficient (r^2) values ranging from 0.87 to 0.999 97 for the training set (Table 1). Root-mean-squared error (RMSE) values ranged from 0.004 to 0.51 for $\log P_{xy}$ properties, and the RMSE was 3.0 kJ·mol⁻¹ for ΔH_{vap} . Regression fits gave the best results for gas phase-organic phase properties, and fit statistics were slightly less good for partitioning properties involving the water phase. For example, eq 5a regressions of $\log K_{a-w}$ and $\log S_{wL}$ exhibited RMSE values of 0.51 and 0.50, respectively. Equation 5a regressions of aqueous properties all had large λ_2 coefficient values (Table 1). This may have inflated the uncertainties of associated aqueous partitioning property estimates, since the chemical parameter $u_{2,i}$ which represents a difference between two similar $\log L$ values, likely has larger relative uncertainty than $u_{1,i}$. In other words, the GC organic stationary phases used here produce a good representation of gas phase-organic phase partitioning and a more approximate representation of partitioning into water phase. Equation 5 produces reliable results for ΔH_{vap} . The enthalpy of phase transfer is correlated with Gibbs free energy of phase transfer for a number of partitioning systems,^{98–100} attributed to entropy-enthalpy compensation.¹⁰¹

Both GC \times GC dimensions are important for partitioning property predictions. For 8 of the 11 properties, both $u_{1,i}$ and $u_{2,i}$ contributed to explaining variability in $\log P_{xy}$ data,

Table 2. Calibrated α Values^a for Equations 6 and 7 and Fit Statistics for $u_{1,i}$ and $u_{2,i}$ with Three Different GC \times GC Instrument Programs

	α_1	α_2	RMSE ($u_{1,i}$)	r^2 ($u_{1,i}$)	α_3	RMSE ($u_{2,i}$)	r^2 ($u_{2,i}$)	n
program A	0.237 \pm 0.007	-0.17 \pm 0.11	0.12	0.990	0.81 \pm 0.10	0.085	0.89	50
program B	0.229 \pm 0.002	0.0 ^b	0.13	0.988	0.61 \pm 0.17	0.091	0.89	50
program C	0.227 \pm 0.002	0.0	0.13	0.987	0.51 \pm 0.11	0.087	0.89	50

^aReported α value uncertainties correspond to a 95% confidence interval of the fitted values, estimated by the bootstrap method¹²⁹ with 1000 synthetic resamplings. ^bA reported value of 0.0 indicates that the fitted coefficient value was found to be statistically indistinguishable from zero; in these cases, the corresponding variable was removed and the regression was repeated.

Table 3. Prediction Statistics of Eqs 5, 6, and 7 for 11 Partitioning Properties of Nonpolar Contaminant Set I, for Three Different GC \times GC Instrument Programs

partitioning property	n^a	eqs 5, 6, and 7						Abraham solvation model (eqs 4a–4c)	
		GC \times GC program A		GC \times GC program B		GC \times GC program C		RMSE	r^2
		RMSE	r^2	RMSE	r^2	RMSE	r^2		
log p_L (Pa)	43	0.19	0.992	0.20	0.991	0.20	0.991	0.41	0.97
ΔH_{vap} (kJ·mol ⁻¹)	36	4.9	0.95	4.8	0.96	5.0	0.95	4.0	0.97
log K_{h-a} (mol·L ⁻¹ ·mol ⁻¹ ·L)	50	0.26	0.986	0.30	0.98	0.30	0.98	n.a.	n.a.
log K_{o-a} (mol·L ⁻¹ ·mol ⁻¹ ·L)	27	0.38	0.97	0.40	0.96	0.41	0.96	0.40	0.96
log K_{OC-a} (mol·kg ⁻¹ ·mol ⁻¹ ·L)	20	0.28	0.96	0.27	0.96	0.26	0.97	0.33	0.96
log K_{a-w} (mol·L ⁻¹ ·mol ⁻¹ ·L)	41	0.47	0.92	0.42	0.96	0.41	0.96	0.64	0.93
log S_{wL} (mol·m ⁻³)	36	0.44	0.92	0.43	0.92	0.37	0.94	0.46	0.93
log K_{o-w} (mol·L ⁻¹ ·mol ⁻¹ ·L)	44	0.33	0.93	0.36	0.93	0.30	0.95	0.27	0.96
log K_{OC-w} (mol·kg ⁻¹ ·mol ⁻¹ ·L)	27	0.34	0.92	0.32	0.93	0.30	0.94	0.45	0.87
log K_{DOC-w} (mol·kg ⁻¹ ·mol ⁻¹ ·L)	21	0.36	0.94	0.48	0.88	0.41	0.92	0.32	0.95
log BCF (mol·kg ⁻¹ ·mol ⁻¹ ·L)	24	0.31	0.94	0.34	0.95	0.30	0.96	0.24	0.97

^a n refers to the number of experimental data available for comparison to model predictions.

evidenced by the statistically nonzero values of λ_1 and λ_2 (Table 1). For example, using either $u_{1,i}$ or $u_{2,i}$ as a single regression variable for log K_{o-w} produced r^2 values of 0.65 and 0.001, respectively. However, for the properties p_L , K_{o-a} , and ΔH_{vap} , only first-dimension retention information, $u_{1,i}$, was needed. Taken together, the above results suggest that eq 5 is a robust, parsimonious, and quantitative model of solvation for nonpolar chemicals.

Finally, one could alternatively formulate eqs 5a–5c by choosing to assign $\beta_{\text{orth}} = 1$. This leads to $u_{1,i} = \log L_{1,i}$ and $u_{2,i} = \log K_{21,i}$ where $K_{21,i}$ is the partition coefficient of chemical i between stationary phases 2 and 1. This alternative approach produces $u_{1,i}$ and $u_{2,i}$ vectors that are nonorthogonal and correlated with each other for the training set ($r^2 = 0.79$), thus leading to inflated uncertainties in eq 5a regression coefficients. Instead, we assign $\beta_{\text{orth}} = 1.1353$, which produces $u_{1,i}$ and $u_{2,i}$ vectors that are mutually orthogonal and only weakly correlated ($r^2 = 0.29$). This leads to smaller and more stably determined eq 5a regression coefficients.

4.3. Mapping $u_{1,i}$ and $u_{2,i}$ Values onto the GC \times GC Chromatogram. Equations 5a–5c provide a practical basis for estimating partitioning properties from GC \times GC retention information, because $L_{1,i}$ and $L_{2,i}$ can be easily estimated from the two-dimensional retention times obtained in a single GC \times GC analysis. Here we summarize the final equations of the approach; a detailed derivation is given in Supporting Information section S3. In short, we simplified a previously developed model of GC \times GC gas–stationary phase partition coefficients¹⁰ to arrive at the expressions:

$$\log L_{1,i}(T_0) = \alpha_1 N_i^* + \alpha_2 \quad (6)$$

$$\log L_{2,i}(T_0) = 0.2613 N_i^* + \log \left(\frac{t_{2,i} - \alpha_3}{t_{2,i}^* - \alpha_3} \right) - 0.557 \quad (7)$$

where $t_{2,i}$ is the measured second-dimension retention time of the analyte and T_0 is a reference temperature assigned as 120 °C. The variable N_i^* is the number of carbon atoms of the hypothetical n -alkane that would elute with the same first-dimension retention time as analyte i , and $t_{2,i}^*$ is the second-dimension retention time of the hypothetical n -alkane that would elute with the same first-dimension retention time as the analyte. The N_i^* and $t_{2,i}^*$ values assigned to the analyte are computed by linear interpolations of the carbon number and recorded second-dimension retention times, respectively, of the nearest two eluting n -alkanes, based on the first-dimension retention times of the analyte and the two n -alkanes (eqs S7 and S17, Supporting Information). For analytes that elute outside the first-dimension elution window of the n -alkane set, N_i^* and $t_{2,i}^*$ values are determined by extrapolation from the values of the two nearest n -alkanes. In eq 7 the numerical constant 0.2613 has units of [carbon number⁻¹] and the constant 0.557 is dimensionless.

Equations 6 and 7 are adapted to a specific GC \times GC instrument program by calibrating the constant parameters α_1 , α_2 , and α_3 , based on the measured GC \times GC retention times of a set of chemicals selected by the analyst. This “instrument calibration set” should span the elution region of interest in both dimensions of the GC \times GC chromatogram. Additionally, the calibration set must include a homologous series, used to adjust $L_{1,i}$ and $L_{2,i}$ estimates in eqs 6 and 7 (section S3 in Supporting Information). Here we use the n -alkane homologous series, but the approach could be adapted to another

Table 4. Comparison of Experimental Values to Predictions by Equation 5 with GC × GC Instrument Program A and by Other Estimation Methods, for Selected Chemicals from Nonpolar Contaminant Set II

chemical	property	exptl ^a	eq 5	ASM	other models
<i>p,p'</i> -DDT	log p_L (Pa)	−3.25	−3.43	−4.62	−3.85 ^b
α -chlordane (<i>cis</i>)	ΔH_{vap} (kJ·mol ^{−1})	82.00	89.6	97.31 ^c	
PDBE 47	log K_{h-a} (mol·L ^{−1} ·mol ^{−1} ·L)	10.66	10.71		
γ -HCH	log K_{o-a} (mol·L ^{−1} ·mol ^{−1} ·L)	7.74	7.26	7.08	8.82 ^b
mirex	log K_{a-w} (mol·L ^{−1} ·mol ^{−1} ·L)	−1.74	−2.63	−5.75 ^c	−4.28 ^b
1,2,5,6-tetrachlorodecane B	log S_{wL} (mol·m ^{−3})	−2.60	−2.38	−3.65 ^c	−0.41 ^b
1,2,5,6,9,10- hexachlorodecane A	log K_{o-w} (mol·L ^{−1} ·mol ^{−1} ·L)	3.82	6.35	6.89 ^c	6.48, ^b 6.32 ^d
<i>p,p'</i> -DDT	log K_{OC-w} (mol·kg ^{−1} ·mol ^{−1} ·L)	5.24	6.02	6.51	5.23 ^b
aldrin	log K_{DOC-w} (mol·kg ^{−1} ·mol ^{−1} ·L)	5.14	6.10	6.38	
β -HCH	log BCF (mol·kg ^{−1} ·mol ^{−1} ·L)	3.90	4.03	3.86	2.40 ^b

^aSee Tables S19 and S20 in Supporting Information for a complete list of experimental and prediction data for contaminant test set II. ^bEstimated values from U.S. EPA Episuite. ^cAbraham solute descriptors were estimated by use of Absolv²⁷ (Table S2, Supporting Information); we expect large uncertainties in ASM-predicted values for these cases. ^dEstimated value from the relationship¹³⁰ $\log K_{o-w} = -0.386 + 0.600N_{\text{tot}} - 0.0113N_{\text{tot}}^2$ ($R^2 = 0.992$; $n = 35$), where N_{tot} = total number of Cl and carbon atoms in PCA congener.

homologous series, requiring only that the two numerical constants in eq 7, 0.2613 and −0.557, are rederived. Reference $L_{1,i}$ and $L_{2,i}$ values of the instrument calibration analytes are determined from the ASM model, based on the previously reported ASM coefficients for the stationary phases SE-30 and OV-17.⁹⁷ The parameters α_1 , α_2 , and α_3 are tuned such that fitted values of $u_{1,i}$ and $u_{2,i}$ produced by eqs 6 and 7 give the lowest sum of squared residuals with respect to ASM-predicted values.

We used the 50 chemicals in contaminant set I to calibrate the parameters α_1 , α_2 , and α_3 for each GC × GC instrument program. Nonlinear fits of eqs 6 and 7 produced good statistics for all three instrument programs that we applied (Table 2). For example, for GC × GC instrument program A, fitted $u_{1,i}$ and $u_{2,i}$ values compared favorably with ASM estimates, with r^2 values of 0.99 and 0.89 and RMSE values of 0.12 and 0.085, respectively. The fitted parameter α_3 , interpreted as the second-dimension column hold-up time, was found to have physically reasonable values that ranged from 0.5 to 0.8 s for the three instrument programs. Equation 7 also produced accurate log L_2 values, exhibiting $r^2 = 0.989$ and RMSE = 0.15 with respect to ASM estimates. However, log L_2 is strongly correlated with log L_1 . The solute parameters $u_{1,i}$ and $u_{2,i}$ are mutually uncorrelated, exhibiting $r^2 = 0.14$. Overall we concluded that eqs 6 and 7 provide usefully accurate estimates of $u_{1,i}$ and $u_{2,i}$ for contaminant set I.

4.4. Mapping Environmental Partitioning Properties onto the GC × GC Chromatogram for Nonpolar Analytes. Using the approaches outlined above, we projected $u_{1,i}$ and $u_{2,i}$ values onto the n -C₉ to n -C₂₅ elution range of the GC × GC chromatogram. This enabled us to map 11 different environmental partitioning properties onto the GC × GC chromatogram by use of the generalized equation 5 (Figure 1). Resulting GC × GC-predicted partitioning properties were compared to experimental values reported in the literature for both contaminant sets I and II.

For contaminant set I, eq 5 produced successful estimates of all partitioning properties that we considered (Table 3). For nonaqueous partitioning properties, relevant to contaminant modeling in terrestrial systems, eq 5 predictions had RMSE values ranging from 0.19 to 0.41 log unit with respect to experimental values. For partitioning properties involving the water phase, relevant to contaminant modeling in aquatic systems, RMSE values fall between 0.30 and 0.48 log unit.

Finally, for ΔH_{vap} , eq 5 exhibited RMSE values of 4.8–5.0 kJ·mol^{−1}. Equation 5 predictions exhibited little dependence on the choice of GC × GC instrument program (Table 3). Thus, the partitioning property model is robust across different instrument programs, as long as the α parameters are properly calibrated to the instrument program.

Equation 5 performed slightly better than the ASM-type models for predicting partitioning properties of contaminant set I, based on a comparison of RMSE values (Table 3). Equation 5 coefficients were determined by use of a nonpolar-only training set, whereas the ASM coefficients have been fitted with much broader data sets. However, it is challenging to assess partitioning models for hydrophobic chemicals, because measured environmental partitioning properties of these chemicals may exhibit uncertainties of a factor of 2 or more.^{1,102} For example, for DDE and DDD, the standard deviation in reported experimental log K_{o-w} values was 0.48 in our compiled database (see Table S14 in Supporting Information for other compounds). Error may also arise from the estimation of free energy of melting ($\Delta G_{S \rightarrow L}$), especially for chemicals with high melting points (Figure S1, Supporting Information). For example, for chrysene ($T_M = 529$ K), the estimated pure liquid vapor pressure differs by 0.8 log unit when the fugacity is estimated by Walden's rule compared to accounting correctly for the heat capacity effect. We observed that for both p_L and S_{wL} , eq 5 discrepancies were worst for chemicals expected to have high uncertainty in $\Delta G_{S \rightarrow L}$, consistent with the possibility that $\Delta G_{S \rightarrow L}$ may be in error.^{69,71}

For contaminant set II, eq 5 agrees with reported experimental data in most cases. However, a quantitative performance assessment of this chemical set is less clear, since some contradictory entries appear among the reported experimental property data. We compared eq 5 predictions to both reported experimental data and also to other estimation methods available (Tables S19 and S20, Supporting Information). Although we do not report statistics for contaminant set II, a few illustrative cases are shown in Table 4. For most property data, eq 5 predictions are in reasonable agreement with experiment. However, some discrepancies arise. For example, reported experimental K_{o-w} data for 1,2,5,6,9,10-hexachlorodecane A and other PCA compounds disagree with eq 5 predictions by >100× (Table 4). However, K_{o-w} estimates by other models are in agreement with eq 5. The experimental K_{o-w} values for PCAs were obtained by reverse-phase high-

performance liquid chromatography, employing reference compounds that were structurally different from PCAs.⁷² Equation 5 predictions of p_L , K_{a-w} , and S_{wL} are in reasonable agreement with experimental data for 1,2,5,6-tetrachlorodecane B (Tables S19 and S20, Supporting Information). For aldrin, the reported experimental K_{DOC-w} value differs from both eq 5 and ASM predictions by $\geq 10\times$ (Table 4). However, reported experimental values of the related properties K_{o-w} and K_{a-w} of aldrin agree satisfactorily with both eq 5 and the ASM (Tables S19 and S20, Supporting Information). In short, it is difficult to attribute such discrepancies clearly to shortcomings in eq 5 or the ASM or to uncertainties in experimental data.

On the basis of results found for the model training set and for contaminant test sets I and II, we conclude that eq 5 predictions are accurate enough to estimate partitioning property input parameters for many applications in transport modeling and chemical screening. Taken together, the above results validate the central hypothesis of the present work, which is that GC \times GC retention information can be employed to estimate a broad range of partitioning properties of nonpolar chemicals with useful quantitative accuracy.

Finally, correlations are known to exist among some of the partitioning properties investigated here.¹ Hence one may ask how one-parameter LFERs would compare to eq 5 for the estimation of some properties. We evaluated the RMSE values of fitted one-parameter LFERs for all possible 110 combinations of the 11 partitioning properties of the model training set ($n = 79$), using experimental data where available and using the ASM to estimate missing data entries (Table S22, Supporting Information). For all solvent–gas partitioning properties, none of the one-parameter LFERs surpassed eq 5 for the training set (compare Table 1 with Table S22, Supporting Information). However, for organic solvent–water and natural sorbent–water partitioning systems, some one-parameter LFERs exhibited better regression statistics than eq 5. Thus, individual one-parameter LFERs may serve as useful independent estimation methods for these properties, provided that appropriate proxy partitioning data are available. Equation 5 differs from one-parameter LFERs in that a single basis of two solute parameters, $u_{1,i}$ and $u_{2,p}$, is used to estimate all 11 properties considered in Table 1. These two parameters can be obtained with GC \times GC.

4.5. Valid Chemical Domain of the GC \times GC Partitioning Property Model. The partitioning property estimation model described by eqs 5, 6, and 7 is considered valid for any nonpolar chemical that elutes between n -C₉ and n -C₂₅ on the GC \times GC chromatogram. We recommend against application of the model to polar chemicals; chemicals eluting after n -C₂₅ (boiling point >402 °C); or n -alkanes of chain length >11 carbons for partitioning properties involving water solvent. These limitations and the validated model domain are explained further below.

Equation 5 is validated for chemicals that are nonpolar, defined here as those that undergo negligible or limited hydrogen-bond acceptor/donor interactions with their environment. One may alternatively consider the validated scope of eq 5 as strictly the chemical families encompassed by Tables S1, S2, and S4 (Supporting Information) and their structural analogues. This comprises acyclic aliphatic, fused and bridged cyclic aliphatic, aromatic, and double-bonded hydrocarbon chemicals that are unsubstituted or substituted with fluorine, chlorine, bromine, and/or iodine.

Our model training set and test sets both include some chemical families that engage in very weak hydrogen bonding, and we also consider these as “nonpolar”. For example, large PAHs have apparently significant Abraham B parameters (e.g., 0.33 for chrysene and benz[*a*]anthracene). These B values are comparable to those of formaldehyde (0.33), aliphatic formates (0.38–0.40), aliphatic nitriles (0.33–0.36), and water solute (0.35),¹⁰³ which are known hydrogen-bond acceptors. However, in their localized, specific interactions with surroundings, PAHs exhibit limited hydrogen-bonding character compared to the other chemical types listed above. The B value of benzene is only 0.14.¹⁰³ The increased B values of PAHs are attributable to summed contributions of several weak H-bond acceptor sites. For example, chrysene ($B = 0.33$) presumably has eight acceptor sites, each occurring along the axial center of each side of each six-membered ring. Recently published quantum chemical calculations support the interpretation that a phenyl ring is only a weak hydrogen-bond acceptor. The weakly interacting gas-phase water–benzene complex is bound chiefly by dispersion forces, having small contributions from electrostatics and orbital overlap,¹⁰⁴ suggesting limited hydrogen-bonding character. In contrast, the water–water dimer interaction energy is dominated by large electrostatic and electronic orbital overlap components,¹⁰⁴ indicative of more substantial hydrogen-bonding character. We extend these rationales to other entries in our chemical sets, some of which exhibit apparently large A and B parameters (e.g., isomers of hexachlorocyclohexane).³⁸ As discussed in section 4.1, very weak hydrogen bonding appears to be approximately captured in the information content of Abraham descriptors of nonspecific interactions (E , S , L , and V) for these solutes.

We recommend that eq 5 should not be applied to polar chemicals, defined here as those that participate in substantial hydrogen-bond donor or acceptor interactions. Extensive previous work has shown that five terms (eqs 4a–4c) are needed generally to describe the partitioning of chemicals exhibiting significant localized hydrogen-bond acceptor or donor capacity.^{90,97} We briefly attempted to calibrate eq 5 for K_{o-w} and K_{a-w} values of a test set of polar chemicals, finding larger errors than for the nonpolar set (data not shown). Hence we recommend against using GC \times GC retention data to estimate partitioning properties of chemicals exhibiting significant localized hydrogen-bonding donor or acceptor capacity.

Equations 5, 6, and 7 have not been validated for nonpolar chemicals having boiling point >402 °C. Our preliminary attempts to do so produced poor results (not shown), and we ascribe this outcome to different possible factors. For these very hydrophobic chemicals, partitioning property data are limited and often have large uncertainties, as discussed in section 4.4.^{4,63,102} Additionally, the Abraham solvation model itself gives poor predictions for many of these chemicals, plausibly due to poorly determined solute parameters,^{37,38,105,106} calibration of the ASM model that is conventionally based on smaller chemicals, or inadequacy of the ASM model for describing partitioning of large hydrophobic chemicals. Equation 5 represents a simplification of the Abraham model, and hence it may exhibit poor performance for chemicals where the Abraham model also fails. Finally, for chemicals having boiling point >402 °C, eqs 6 and 7 produce increased errors in estimated $L_{1,i}$ and $L_{2,i}$ values, as discussed in section 4.6 below. For all of these reasons, we presently recommend against application of eqs 5, 6, and 7 to chemicals eluting after n -C₂₅.

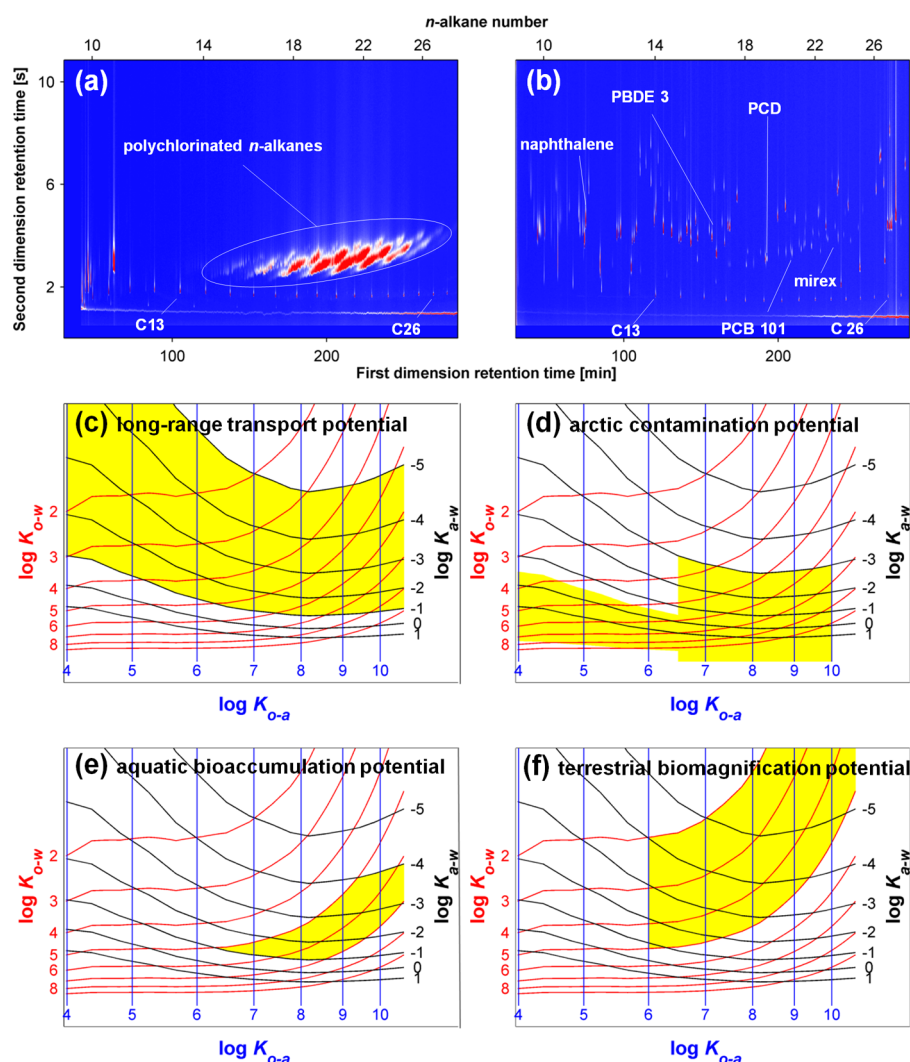


Figure 1. Mapping environmental behaviors of nonpolar contaminants onto a GC \times GC chromatogram. Top panels show GC \times GC chromatograms of (a) the short-chain polychlorinated alkanes technical mixture and (b) a mixture of injected standards. Lower panels (c–f) show maps of $\log K_{o-w}$ (black contours), $\log K_{o-a}$ (blue contours), and $\log K_{o-w}$ (red contours) overlaid onto the GC \times GC retention time space. Shaded yellow regions would contain analytes having (c) long-range transport potential (L RTP), (d) arctic contamination potential (ACP), (e) aquatic bioaccumulation potential (ABP), and (f) terrestrial biomagnification potential (TBP). In panel B, the acronyms PCD and PBDE 3 refer to 1,2,5,6,9-pentachlorodecane A and 4-bromodiphenyl ether, respectively.

Finally, straight-chained alkanes having chain length >11 carbons constitute a special family where application of eq 5 may lead to errors for properties involving aqueous solvent, due to their possible folding in aqueous solvent.¹⁰⁷ However, recent simulation results have challenged this interpretation.¹⁰⁸

4.6. Role of the GC \times GC Instrument Program and Column Configuration for Partitioning Property Predictions. How many calibration analytes are needed to robustly constrain the α parameters in eqs 6 and 7 for a given GC \times GC instrument program? Also, do eqs 5, 6, and 7 imply any limitations on the GC \times GC instrument program, elution range of modeled analytes, or column configuration? We address each of these issues briefly.

To determine the number of calibration analytes needed to estimate reliable α values, we conducted a bootstrap sensitivity analysis of eqs 6 and 7. Synthetic subsets of analytes were repeatedly selected randomly from contaminant set I, and resulting apparent α parameters were fitted for each subset. We evaluated the errors thus propagated into property predictions of eq 5. With synthetic samples containing 15 calibration

analytes plus the n -alkanes homologous series, eq 5 RMSE values typically fell within 0.1 log unit of eq 5 RMSE values obtained for the full contaminant set I (50 calibration analytes plus n -alkanes). We thus recommend the use of ≥ 15 calibration analytes that are well-distributed in the GC \times GC chromatogram, plus the n -alkanes (or other homologous) series, for fitting the α values of eqs 6 and 7.

What flexibility is allowed with the GC \times GC instrument program? The trained coefficients of eq 5 are independent of the instrument program. We evaluated three simple, representative GC \times GC temperature ramp programs for calibration of the α parameters. Resulting $L_{1,i}$, $L_{2,i}$, and partitioning property estimates were comparable for all three programs (Tables 2 and 3). However, the expression used to describe $L_{1,i}$ (eq 6) may worsen with higher temperature ramp rates.^{109,110}

Equations 6 and 7 were successfully validated for chemicals eluting between n -C₉ and n -C₂₅ on the GC \times GC chromatogram. We did not consider chemicals having volatility exceeding n -C₉. However, in additional experiments (not shown), we

attempted to apply eqs 6 and 7 to nonpolar chemicals eluting between n -C₂₅ and n -C₃₁, and this produced inflated deviations for $L_{2,i}$ estimates. These discrepancies may be expected: the approximations in eq 7 progressively degrade with increasing distance from the reference temperature of $T_0 = 120\text{ }^\circ\text{C}$, due to differences in heat capacity of vaporization between the modeled analytes and that of the simultaneously eluting hypothetical n -alkane.^{10,11,112} Hence we presently recommend against applying eqs 6 and 7 to compounds eluting after n -C₂₅ (boiling point $>402\text{ }^\circ\text{C}$).

Finally, the GC \times GC column types used here must also be used in future applications of the model. Coefficients of eqs 5, 6, and 7 were optimized with the assumption of 100% methylpolysiloxane stationary phase and 50% phenyl methylpolysiloxane stationary phase for columns 1 and 2, respectively. Other column sets may also be appropriate for partitioning property estimation via eqs 5, 6, and 7, and this would require that the coefficients and numerical constants of these equations be recalibrated and revalidated (sections 4.2 and 4.3).

4.7. How to Estimate Partitioning Properties of Nonpolar GC \times GC Analytes. We briefly summarize the practical steps needed for the reader to estimate partitioning properties of GC \times GC-analyzed nonpolar analytes, using a Matlab software program that can be accessed from the authors.

(1) Optimize the GC \times GC instrument program to achieve desired separation of the sample(s) of interest, using the same GC column stationary phases employed here.

(2) Identify 15 or more nonpolar calibration analytes, plus an n -alkane series, that span the elution region of interest of the GC \times GC chromatogram. Calibration analytes may include chemicals occurring in the sample(s) of interest or they may be injected separately as standards.

(3) Input to the software the first- and second-dimension retention times and ASM solute parameters of the calibration analytes. These data are used to optimize the α values of eqs 6 and 7, adapting the algorithm to the GC \times GC instrument program.

(4) Query the software to (a) estimate 11 partitioning properties for nonpolar analytes, on the basis of their GC \times GC retention times (by use of eq 5); (b) map partitioning property estimates directly onto the GC \times GC chromatogram; or (c) project the sample signal information onto a plot of partitioning property space, with the sample chromatogram itself as input.

4.8. Partitioning Property Estimates Using GC \times GC Raw Retention Times (eq 3). We briefly evaluated the model of Tcaciuc et al.²¹ by performing regression fits of eq 3 to nonpolar contaminant test set I. Equation 3 regressions produced fit statistics (Table S21, Supporting Information) that were reasonable but inferior to predictions provided by eqs 5, 6, and 7 (Table 3) in most cases. The differences in success of these two models can be rationalized. The variables $\log L_{1,i}$ and $\log L_{2,i}$ represent scales of phase-transfer free energy, and their use in linear free energy relationship correlations is appropriate. By contrast, the GC \times GC retention times, $t_{1,i}$ and $t_{2,i}$, are not free energies and are not expected to be reliable for predicting partition coefficients. By correspondence, the Abraham solvation model predicts partitioning properties accurately⁹⁰ but predicts retention times inaccurately.⁹⁵ We recommend application of eqs 5, 6, and 7 rather than eq 3 for prediction of GC \times GC analyte partitioning properties.

5. APPLICATIONS OF GC \times GC TO CHEMICAL SCREENING AND MULTIMEDIA MODELING FOR NONPOLAR COMPLEX MIXTURES

When its combined capabilities to separate nonpolar analytes, quantify them, and estimate their partitioning properties are considered, GC \times GC is a powerful tool for performing chemical screening or multimedia transport modeling of both legacy and emerging environmental contaminants. In Figure 1a we present the GC \times GC chromatogram of technical mixture short-chain (C₁₀–C₁₃) polychlorinated n -alkanes estimated to theoretically contain 7820 structurally distinct congeners.¹¹³ Initially eluting PCA congeners are well-resolved, but the separation is less good for later bands of coeluting PCA groups. Despite the complexity of this sample, different regions of the GC \times GC chromatogram can be classified into categories of distinct environmental behavior. By use of eq 5, we mapped contours of K_{o-w} , K_{o-a} , and K_{a-w} onto the GC \times GC chromatogram. PCA congeners are flagged as having high long-range transport potential (LRTP) if they fall in the range $-5 \leq \log K_{a-w} \leq -1$ (Figure 1c).¹¹⁴ Highly persistent contaminants are considered to have arctic contamination potential (ACP) if they fall in the region $4 > \log K_{a-w} > -0.5$ and $\log K_{o-a} < 9$ or alternatively if they exhibit $\log K_{a-w} > -3$ and $6.5 < \log K_{o-a} < 10$ (Figure 1d).¹¹⁵ Analytes having suspected aquatic bioaccumulation potential (ABP) are those with $5 < \log K_{o-w} < 7$ and $-4 < \log K_{a-w} < -1$ (Figure 1e).¹¹⁶ For air-breathing organisms (including those living in water), chemicals with $2 < \log K_{o-w} < 5$ and $\log K_{o-a} \geq 6$ are considered to have terrestrial biomagnification potential (TBP) (Figure 1f).¹¹⁷ These and other classifications might be further tuned by considering compartment-specific coefficients such as K_{OC-w} , K_{DOC-w} , and BCF instead of the proxy property, K_{o-w} . For nonpolar chemicals arising in technical mixtures and environmental samples, all of these properties may be estimated by use of GC \times GC. This may aid regulatory instruments such as REACH¹¹⁸ that employ categories of environmental behaviors as screening criteria to prioritize individual chemicals for potential hazard to the environment.

GC \times GC compositional information also can be used to interpret or diagnose compositional changes of complex mixtures arising due to mass transfers in the environment. With appropriate hypotheses about the physical processes involved, analysts can simulate compositional alterations to GC \times GC chromatograms of samples that represent the prefractionated state in the environment and then compare these predictions to observed chromatograms of actual samples. For example, previous studies have reported simulations of the compositional changes of spilled oils resulting from evaporation and dissolution of oil hydrocarbons in coastal environments; resulting simulated GC \times GC chromatograms were successfully compared to weathered field samples collected after the 2003 Bouchard 120 oil spill and the 2007 Cosco Busan oil spill.^{11,13,15}

When investigating environmental samples, GC \times GC practitioners should ensure that studied analytes are indeed nonpolar before applying eqs 5, 6, and 7. Several strategies exist to handle this requirement. Target analyte chemical structures may be confirmed by use of injected standards with matching retention times and matching TOF-MS spectra.^{119–121} Recent studies show that GC \times GC coupled with high-resolution TOF-MS can be used to determine molecular structure and elemental formula information on nontarget analytes.^{122–127} Additionally, selective extraction methods can effectively obtain

only the nonpolar fraction of an environmental sample.¹²⁸ Thus, strategies exist to confirm that GC \times GC analytes are nonpolar, either by selective extraction or by chemical structure identification.

By use of the methods developed here, partitioning property estimates are made immediately available for the hundreds or thousands of nonpolar chemicals that are measured by GC \times GC in an environmental sample or technical mixture. This approach can leverage applications in the screening and fate modeling of complex mixtures containing legacy and emerging nonpolar contaminants.

■ ASSOCIATED CONTENT

■ Supporting Information

Three sections with additional text and equations describing GC \times GC–TOF-MS instrument programs, calculation of solid–liquid fugacity ratios, and derivations of eqs 6 and 7 and one figure showing deviation in vapor pressure resulting from using different methods for estimation of solid–liquid fugacity ratio (pdf); 22 tables listing nonpolar contaminant test set I and II retention time data and Abraham parameters, retention time data for *n*-alkanes, partitioning model training set list of Abraham parameters and experimental partitioning property data, literature-reported ASM coefficients for 11 partitioning systems, estimated solid–liquid fugacity ratios by different methods, contaminant set I and II experimental values and eq 5 predictions for various parameters, variability in $\log K_{ow}$ values reported in literature, eq 3 prediction statistics for 11 partitioning properties of contaminant set I, and r^2 and RMSE values for one-parameter LFERs of 11 properties of 79 chemicals in the model training set (xls). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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