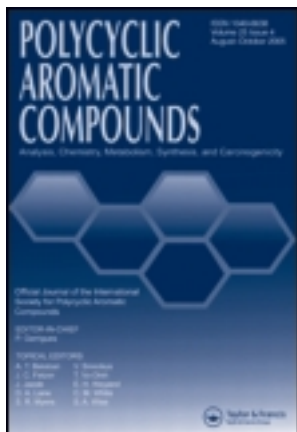


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Predicting Physico-Chemical Properties of Alkylated Naphthalenes with COSMO-RS

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COSMO-RS, the Conductor-like Screening Model for Real Solvents, has been used to predict a set of basic partition coefficients of 22 (alkylated) naphthalenes. To validate the approach, methyl-, dimethyl-, and ethylnaphthalenes have been chosen, according to the availability of experimental data. Then, predictions have been extended to diisopropylnaphthalenes. Given the model's expected uncertainty intervals, COSMO-RS predictions of aqueous solubilities, (subcooled) vapor pressures, Henry's law constants, as well as octanol-water partition coefficients, are in agreement with available literature data. Simultaneous overestimation of aqueous solubilities and vapor pressures of comparable magnitude leads to partial error cancellation in the Henry's law constants. Based on physico-chemical property data obtained with COSMO-RS, the Mackay Level III fugacity model, a steady-state, non equilibrium, and regional-scale model, has been applied to exemplarily evaluate the tendency of 2,6-diisopropylnaphthalene to migrate between media by modelling emissions to each individual medium and calculating the amount present at steady state.

Key Words: alkylated naphthalenes, aqueous solubilities, COSMO-RS, COSMOtherm, Henry's law constant, octanol-water partition coefficient, subcooled vapor pressures

INTRODUCTION

Environmental risk associated with oil extraction, transport, and processing is a legitimate concern, as can be seen in numerous examples of related accidents, with the Deepwater Horizon oil spill as the latest climax, for the time being. US-EPA priority pollutant list of 16 polycyclic aromatic hydrocarbons is largely

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Dedicated to Professor Lothar Beyer on the occasion of his 75th birthday.

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setting the frame for hydrocarbon monitoring. Taking the example of crude oil, alkyl derivatives are dominating the composition, with the implication of the possibility of underestimated environmental risks (1), since additional structural features control the physicochemical properties of the substances which are not covered in this list. For example, with naphthalene being the most volatile compound in the list, the introduction of alkyl substituents drastically diminishes the tendency of evaporation and aqueous solubility, while the relative contribution to toxic effects may greatly increase.

Alkylated naphthalenes are widely used as solvents, heat transfer fluids, insulating material, dye works auxiliary, and specialty lubricants. Due to a variety of novel applications, diisopropylnaphthalene isomers recently became of interest. They are used as a plant growth regulator (e.g., 2,6-diisopropylnaphthalene to prevent potato sprouting in storage facilities) and in the food packaging industry, and, in addition, have been introduced as PCB replacement fluids (2). Of special importance is the application of diisopropylnaphthalene isomer mixtures as solvent for carbonless copy paper, known as KMC (Kureha Micro Capsule Oil.) Furthermore, given the intended fade-out of production and use of perfluorooctane sulfonic acid (PFOS), its salts and perfluorooctane sulfonyl fluoride (PFOSF), diisopropylnaphthalenes are amongst the featured substances considered as substitutes. At the fourth Conference of the Parties (COP4) to the Stockholm Convention on Persistent Organic Pollutants (POPs), a moratorium concerning these fluorosurfactants was announced by all parties, except for some exemptions. The key to the performance of the aforementioned fluorinated substances is their extremely low surface tension, which currently cannot be matched with other surfactants. Up until now it has been difficult for something other than fluorinated alternatives to gain a foothold on the market. One alternative being discussed (3) is summarized as “propylated aromatics” with the trade name Ruetasolv[®]. These aromatic surfactants are based on propylated naphthalenes and biphenyls whose isomeric mixtures are used as water-repelling agents for a variety of applications, such as corrosion protections, marine paints, resins, inks, coatings, plasticizers, or electrical, electronically, and mechanical applications.

A set of some basic physicochemical properties is governing fate and transport of any given organic pollutant and hence may serve as input data in environmental models predicting the distribution in defined media in the environment as well as in remediation studies. While in the case of methylated naphthalenes, for example, a variety of data describing vapor pressures, aqueous solubilities, and octanol-water partition constants are available in the literature, at least for some of the isomers, the situation becomes less favorable when turning to higher alkylated derivatives. This might be attributed to two main reasons: (1) it becomes a challenging task to separate all present isomers in pure form; and (2) with a higher alkylation degree, measurements of

physicochemical property data become more challenging. Besides the difficulty in guaranteeing the required purity of substances for quality measurements, measured properties may converge towards the limit of an available measurement method. Information on environmental and toxicological effects are still scarce. The same holds true for accurate physico-chemical property data, most prominent vapor pressure, aqueous solubility, Henry constants, and octanol-water partition coefficients, which belong to the fundamental parameters for predicting transport, distribution, and fate of organic substances in the environment. Here, modern in-silico prediction methods may supply missing data with reasonable accuracy.

Traditional approaches for correlating or predicting thermodynamic properties are primarily based on dividing the molecules into various groups (GCMs). Quantitative Structure Property Relationships (QSPR) (or Linear Free Energy Relationships (LFER)) are frequently used successfully, as demonstrated for methylnaphthalenes (4). COSMO-RS, the Conductor-like Screening Model for Realistic Solvation (5), is a different approach which combines quantum chemistry, dielectric continuum models, electrostatics surface interactions, and statistical thermodynamics and which can predict thermodynamic properties of neutral and charged molecules in the liquid phase. The method is based on a very small number of adjustable parameters only, which are independent of any molecular or structural information (6).

In this article, vapor pressures, aqueous solubilities, Henry constants and octanol-water partition coefficients were calculated for a set of alkylated naphthalenes with COSMO-RS in its COSMOtherm implementation. On the basis of the obtained data, the predicted partitioning of 2,6-diisopropylnaphthalene in an evaluative environment is exemplarily discussed.

METHODS

COSMO-RS in its COSMOtherm Implementation

All statistical COSMO-RS thermodynamics calculations (7) have been performed with COSMOtherm Version C2.1 Revision 01.10 (8), using the parameter file BP_TZVP_C21_0110. Prior to this step, DFT/COSMO (density functional theory/conductor-like screening model) calculations were performed using Turbomole V6.2 (9), with the RI-DFT BP (resolution of identity standard density functional theory) level of theory, using the def-TZVP basis set.

In the course of COSMO-RS property predictions, only the most stable conformers with respect to the gaseous phase and COSMO state were considered. Due to the flexible side chains, isopropyl substituted naphthalenes occur in a variety of different conformations. Conformational analysis at the RI-DFT BP level with the def-TZVP basis set showed nearly identical energies, however;

furthermore, sigma profile-similarities and the chemical potentials of each conformer in different solvents support this approach.

Prediction of Partition Coefficients with COSMO-RS

In COSMO-RS, a variety of environmentally important partition coefficients can be predicted directly from a statistical thermodynamic treatment following quantum chemical COSMO calculations.

Aqueous Solubility

The ability of COSMO-RS to predict aqueous phase equilibria was successfully demonstrated, e.g., in the prediction of mutual solubilities of hydrocarbons and water (10) or in the prediction of solubility of water in fluorocarbons (11).

Predicting aqueous solubility of organic substances in COSMOtherm is a rather straightforward approach via the build-in automatic solubility calculation routine, as previously shown in a number of publications, as in the case of chlorobenzenes (12), carboxylic acids (13), PAHs (14), and fluorobenzenes (15).

The mole fractions of the solute were refined using the iterative automatic solubility calculation option of COSMOtherm:

$$\log_{10}(x_2^{SOL(i+1)}) = [\mu_2^{(P)} - \mu_2^{(1)}(x_2^{SOL(i)}) + \min(0, \Delta_{fus}G)] / (RT \ln 10) \quad (1)$$

where x_2^{SOL} is the mole fraction of solid 2 dissolved in the solvent phase 1 at saturation, $\mu_2^{(P)}$ is the chemical potential of pure compound 2, $\mu_2^{(1)}$ is the chemical potential of compound 2 at infinite dilution in the solvent compound 1, and i represents the iteration count. In this article, we are focused on the solubility of the substances in the subcooled state.

Vapor Pressure

In addition to the prediction of the chemical potential of liquids, COSMO-RS provides an empirical estimate of a pure compound's chemical potential in the gas phase, which is only valid for pure compounds. This includes all contributions to the free energy of phase transfer, as well as a non electrostatic contribution representing dispersive or van der Waals-interactions, a correction for ring shaped molecules, and a constant that connects the reference state in the ideal gas state with the reference state in the liquid state:

$$\mu_{Gas}^{X_i} = E_{Gas}^{X_i} - E_{COSMO}^{X_i} + c_{disp}(T) \sum_a A_a^{X_i} \tau_{el(a)} - \omega \eta_{Ring}^{X_i} + \eta_{Gas}(T). \quad (2)$$

The vapor pressure of compound X_i is predicted via

$$p^{X_i} = \exp[-(\mu_{Gas}^{X_i} - \mu_{X_i}^{X_i})/RT] \quad (3)$$

with $\mu_{Gas}^{X_i}$ as the chemical potential of the pure compound in the gas phase and $\mu_{X_i}^{X_i}$ as the chemical potential of the pure compound in itself.

Henry's Constant or Henry's Law Coefficient

The respective Henry's law coefficient of a solute 2 at infinite dilution in water, $k_{H,2}$, is obtained applying Henry's law:

$$k_{H,2} = \gamma_2^\infty(T, p, x_2) p_2(T) \quad (4)$$

with γ_2^∞ as the infinite dilution activity coefficient, x_2 the mole fraction, and p_2 the vapor pressure of the solute.

Other common representations of the Henry's law constant are depicted in Equations (5) and (6):

$$H/(\text{Pa} \cdot \text{m}^3 \cdot \text{mol}^{-1}) = \frac{p_2}{c_2} \quad (5)$$

with p_2 as the vapor pressure of the solute, c_2 as the molar concentration of the solute, and, furthermore, the air-water-partition partition coefficient defined accordingly to

$$\log K_{AW}/(\text{dimensionless}) = \log \left(\frac{H}{RT} \right) \quad (6)$$

Octanol-Water Partition Coefficient

In COSMO-RS, the partition coefficient, $\log K_{OW}(wet)$, is predicted via computation of the chemical potentials of substance x in the respective solvent, at infinite dilution:

$$\log K_{OW}(wet) = \log_{10} \left\{ \exp \left[(\mu_W^x - \mu_O^x) / RT \right] \frac{V_{W,m}}{V_{O,m}} \right\} \quad (7)$$

with μ_W^x as the chemical potential of pure compound x in water and μ_O^x as the chemical potential of pure compound x in 1-octanol. A quotient of molar volumes $V_{W,m}/V_{O,m}$, of 0.1141 has been used. Besides of the density difference of the solvents, their mutual solubility has to be taken into account. Furthermore, the current COSMOtherm release includes a number of QSPR property files holding QSPR coefficients for the five Abraham parameters, based on group contributions, and on the definition of thermodynamic partition properties via the six Abraham coefficients, for both computational COSMO levels BP-SVP-AM1 and BP-TZVP (16), which was used for deriving octanol-water partition coefficients (wet and dry), as well.

Octanol-Air and Soil Sorption Coefficients

The octanol-air coefficient is frequently used to describe partitioning of organic substances between air and organic phases in soils, plants and atmospheric aerosols. It has been obtained according Equation (8):

$$\log K_{OA} = \log K_{OW}(\text{dry}) - \log K_{AW} \quad (8)$$

The data for $\log K_{OW}(\text{dry})$ maybe generated in COSMO-RS using the pure quantum chemical approach, or alternatively, via QSPR. Furthermore, COSMOtherm is supplied with a soil-sorption partition coefficient (K_{OC}) property file parameterized on the Turbomole BP-SVP-AM1 COSMO level of theory. It has been shown that the σ -moment approach (7) is a robust tool in analysing partitioning of substances between very diverse phases—including chemically undefined phases, like those encountered in soils. The rms deviation of $\log K_{OC}$ from experimental data was given to be within 0.65 log units for the training set, and 0.72 log units for a demanding test set (17); a large portion of these deviations can be attributed to experimental errors. Considering that the experimental determination itself is difficult and rather often unsound, the prediction via COSMO-RS σ -moments provides an alternative which might meet valuable requirements in a number of occasions.

RESULTS AND DISCUSSION

At $T = 298.15$ K, 9 out of the 22 chosen compounds are in the liquid state. In the following, COSMO-RS results for the respective (subcooled) liquids are given. The (subcooled) literature aqueous solubilities as well vapor pressures, at $T = 298.15$ K, have been generated using fugacity ratios based on the assumption of ΔS_{fus} data as given in Appendix 1. It should be mentioned here that a principal difficulty in accurate physico-chemical property measurements inherent to, e.g., diisopropylnaphthalenes is the availability of pure isomers. The main components of diisopropylnaphthalene isomer mixtures are 2,6-diisopropylnaphthalene and 2,7-diisopropylnaphthalene, contributing each with ca. 40% to the mixture, while a few percent are made of the 1,3-, 1,6-, and 1,7-diisopropylnaphthalenes (19). Diisopropylnaphthalenes with isopropyl groups positioned in adjacent ring positions are usually not detected in the mixtures. Separating all the isomers or synthesizing them in pure form remains a challenging task.

Aqueous Solubility

Table 1 presents literature values as well as COSMO-RS results on (subcooled) aqueous solubilities, at $T = 298.15$ K, as well as the average absolute

Table 1: (Subcooled) aqueous solubilities, at $T = 298.15$ K. Values selected by Mackay (18), corrected for individual fugacity ratios, and COSMO-RS results

PAH	$\log S(\text{selected}) / \text{mol}\cdot\text{L}^{-1}$	$\log S(\text{COSMO-RS}) / \text{mol}\cdot\text{L}^{-1}$
Naphthalene	-3.09	-2.73
1-methylnaphthalene	-3.71	-3.18
2-methylnaphthalene	-3.72	-3.28
1-ethylnaphthalene	-4.19	-3.68
2-ethylnaphthalene	-4.29	-3.78
1,2-dimethylnaphthalene	—	-3.59
1,3-dimethylnaphthalene	-4.29	-3.73
1,6-dimethylnaphthalene	—	-3.69
1,4-dimethylnaphthalene	-4.14	-3.67
1,8-dimethylnaphthalene	—	-3.53
1,5-dimethylnaphthalene	-4.14	-3.66
2,7-dimethylnaphthalene	—	-3.81
2,3-dimethylnaphthalene	-4.14	-3.70
2,6-dimethylnaphthalene	-4.05	-3.84
1,4,5-trimethylnaphthalene	-4.54	-3.98
1-isopropylnaphthalene	—	-4.08
2-isopropylnaphthalene	—	-4.18
2,6-diisopropylnaphthalene	—	-5.81
1,3-diisopropylnaphthalene	—	-5.60
1,5-diisopropylnaphthalene	—	-5.52
2,7-diisopropylnaphthalene	—	-5.81
1,3,6-triisopropylnaphthalene	—	-7.22
AAD		0.46

deviation (AAD):

$$AAD = \sum |\log \Theta_{calc} - \log \Theta_{exp}| / n \quad (9)$$

where Θ is the thermodynamic property in question.

With increasing degree of alkylation, aqueous solubility drops—from naphthalene to 1,3,6-triisopropylnaphthalene about 4.5 $\log S$ units. COSMO-RS reproduces this trend reasonably well, while slightly overestimates aqueous solubilities. The root-mean-square (rms) deviation of 0.47 $\log S$ units corresponds to the reported COSMO-RS deviations (6) of the parameter optimization set given as 0.285 (rms) $\log S$ units and 0.451 (max) $\log S$ units, while for the validation set 0.47 (rms) $\log S$ units and 1.10 (max) $\log S$ units have been reported (6).

Vapor Pressure

Table 2 resumes literature data on (subcooled) liquid vapor pressures and the COSMO-RS results, as well as the average absolute deviation (AAD). For the compounds where literature data are available, it can be seen that COSMO-RS is overestimating the respective vapour pressures (0.50 (rms) $\log p$ units). Again, with increasing degree of alkylation, the measured property

Table 2: (Subcooled) vapor pressures, at $T = 298.15$ K. Overview of values selected by Mackay (18), corrected for individual fugacity ratios, as well as COSMO-RS results

PAH	$\log_{10}p_L/\text{Pa}$ (selected)	$\log_{10}p_L/\text{Pa}$ (COSMO-RS)
Naphthalene	1.54	1.84
1-methylnaphthalene	0.95	1.46
2-methylnaphthalene	0.88	1.37
1-ethylnaphthalene	0.40	1.03
2-ethylnaphthalene	0.60	0.94
1,2-dimethylnaphthalene	-0.06	0.78
1,3-dimethylnaphthalene	0.49 ^a	0.97
1,6-dimethylnaphthalene	—	0.74
1,4-dimethylnaphthalene	0.36	1.04
1,8-dimethylnaphthalene	—	1.05
1,5-dimethylnaphthalene	—	1.02
2,7-dimethylnaphthalene	0.49 ^b	0.86
2,3-dimethylnaphthalene	0.66	0.90
2,6-dimethylnaphthalene	0.50	0.87
1,4,5-trimethylnaphthalene	0.21	0.66
1-isopropylnaphthalene	—	0.40
2-isopropylnaphthalene	-0.16 ^a	0.34
2,6-diisopropylnaphthalene	—	-0.93
1,3-diisopropylnaphthalene	—	-0.80
1,5-diisopropylnaphthalene	—	-0.71
2,7-diisopropylnaphthalene	—	-0.93
1,3,6-triisopropylnaphthalene	—	-2.23
AAD		0.48

^aexperimental data as compiled in EPLsuite (US EPA's EPI Suite (Estimations Programs Interface for Windows, version v4.1)) (28)

^bderived from DIPPR database (30)

drops—from naphthalene to 1,3,6-triisopropylnaphthalene about 4 log p -units. With a difference of 0.84 log p -units, the highest deviation was obtained for 1,2-dimethylnaphthalene; this might indicate problems with the reported literature value, since the accuracy range expected for COSMO-RS calculations was reported (6) with 0.307 (rms) log p units and 0.566 (max) log p units, with regard to the parameter optimization set.

Henry's Law Constant

Table 3 gives an exemplary overview about the range of data encountered in the literature, and COSMO-RS results, at $T = 298.15$ K, as well as the average absolute deviation (AAD). The COSMO-RS results correspond to an air-water partition coefficient range of $-1.9 < \log K_{AW} < -1.4$.

Both the scarceness of available data as well as the distribution are indicative of the practical experimental problems encountered in the measurements. The calculated rms deviation (0.18 log K_{AW} units) corresponds to the deviation of a validation set of 150 Henry's law constants given (6) with 0.38 (rms) log

Table 3: Henry's Law constants, at infinite dilution in water, at $T = 298.15$ K. Overview of the spread of available literature data and data selected (calculated p/c) by Mackay (18), US EPA EPI suite 4.1 experimental data collection (28), as well as COSMO-RS results. Given AAD are related to $H(\text{selected})$ data.

PAH	H (lit) / Pa·m ³ /mole	H (selected) / Pa·m ³ /mole	H (EPIsuite-exp) / Pa·m ³ /mole	H (COSMO-RS) / Pa·m ³ /mole
Naphthalene	36.5 – 124	43.00	44.60	36.84
1-methylnaphthalene	26.3 – 62.5	44.89	52.10	43.88
2-methylnaphthalene	32.23 – 62.0	51.19	52.50	44.51
1-ethylnaphthalene	14.8 – 69.4	38.82	69.40	51.98
2-ethylnaphthalene	54.5 – 82.2	78.11	54.50	52.94
1,2-dimethylnaphthalene	—	—	—	23.59
1,3-dimethylnaphthalene	71.03	-	60.40	49.81
1,6-dimethylnaphthalene	—	—	—	26.56
1,4-dimethylnaphthalene	48.84	31.11	39.10	50.61
1,8-dimethylnaphthalene	—	—	35.50	38.34
1,5-dimethylnaphthalene	35.6 – 61.8	—	35.50	47.90
2,7-dimethylnaphthalene	—	—	—	47.40
2,3-dimethylnaphthalene	38.92 – 92.16	62.49	93.20	40.67
2,6-dimethylnaphthalene	121	128.7	—	51.04
1,4,5-trimethylnaphthalene	23.50	55.21	—	43.85
1-isopropylnaphthalene	—	—	—	30.25
2-isopropylnaphthalene	—	—	—	32.69
2,6-dilisopropylnaphthalene	—	—	—	75.86
1,3-dilisopropylnaphthalene	—	—	—	62.97
1,5-dilisopropylnaphthalene	—	—	—	63.58
2,7-dilisopropylnaphthalene	—	—	—	74.73
1,3,6-trisopropylnaphthalene	—	—	—	97.93
AAAD				20.28

K_{AW} units and 0.75 (max) $\log K_{AW}$ units. The good performance of COSMO-RS in the prediction of Henry's law constant of the title compounds is partially to be seen in the simultaneous overestimation of comparable magnitude of aqueous solubilities as well as vapor pressures, which are largely cancelled out in the Henry's law constant itself.

Octanol-Water Partition Coefficient

Table 4 summarizes $\log K_{OW}$ data (wet) as encountered in the literature, selected values, and COSMO-RS results, both as obtained from the pure quantum chemical approach as well as the incorporated QSPR, at $T = 298.15$ K, as well as the average absolute deviation (AAD). Again, experimental difficulties in determining the property become evident. The respective octanol-water partition coefficients (wet) are slightly underestimated, with 0.51 (rms) $\log K_{OW}$ units for the COSMO-RS results (with a reported deviation of 0.471 (rms) $\log K_{OW}$ units and 0.723 (max) $\log K_{OW}$ units in the parameter optimization (6)) and 0.29 (rms) $\log K_{OW}$ units for the QSPR approach. As to be expected, the $\log K_{OW}$ data increase with the degree of alkylation—from naphthalene to 1,3,6-triisopropylnaphthalene slightly more than 4 $\log K_{OW}$ units, while separate calculations of (subcooled) solubilities in pure octanol suggest that lipophilicity is not increasing with increasing alkyl chain length. Actually, octanol solubility is found to decrease slightly (from $\log (S/\text{mol}\cdot\text{L}^{-1}) = 0.3$ (naphthalene) to $\log (S/\text{mol}\cdot\text{L}^{-1}) = 0.2$ (1,3,6-triisopropylnaphthalene)). The increase in $\log K_{OW}$ is therefore mainly caused by the decrease in aqueous solubility.

Predictions of Environmental Fate of the Title Compounds

Given the growing economic importance of diisopropylnaphthalene isomer mixtures, surprisingly few accurate data can be found on physico-chemical data of their pure constituents in the open literature. Production capacities for these mixtures were reported with a total amount of 10,000 t/a each in Japan and Germany, while in comparison, the annual world production of 2-methylnaphthalene and 1-/2-methylnaphthalene mixtures was estimated at 1500 t each (20).

Meanwhile, diisopropylnaphthalenes are more commonly detected as environmental contaminants, mostly in rivers and aquatic sediments (21–22). When comparing laboratory mussels exposed to aromatic fractions of crude oil with wild mussels, a higher abundance of diisopropylnaphthalenes has been detected in the latter. The origin was hypothesized being nonpetrogenic, coming probably from sources related to paper manufacturing or recycling industries (23). Recently, diisopropylnaphthalenes were reported as environmental contaminants of increasing importance for organic geochemical studies (24).

The Mackay Level III fugacity model (EQC version 2.02) (25–27), a steady-state, non equilibrium, and regional-scale model, is frequently applied for predictions of how the medium of release affects environmental fate. The EQC

Table 4: 1-Octanol-water partition coefficients (wet), at $T = 298.15$ K. Overview of the spread of experimental literature data and selected values (18), and COSMOtherm results, both from partition coefficient calculations ($\log K_{OW}$ (COSMO-RS)) and from the QSPR-approach, using implemented Abraham's linear free energy relationships. Given AAD are related to $\log K_{OW}$ (selected) data.

PAH	$\log K_{OW}$ (exp)	$\log K_{OW}$ (selected)	$\log K_{OW}$ (COSMO-RS)	$\log K_{OW}$ (COSMO- Abraham)
Naphthalene	3.10–3.77	3.37	2.90	3.20
1-methylnaphthalene	3.87	3.87	3.35	3.60
2-methylnaphthalene	3.70 – 4.11	3.86	3.45	3.70
1-ethylnaphthalene	4.38 – 4.8016	4.40	3.84	4.08
2-ethylnaphthalene	4.00 – 4.43	4.38	3.94	4.18
1,2- dimethylnaphthalene	—	4.31	3.74	3.88
1,3- dimethylnaphthalene	4.42 – 4.421	4.42	3.88	4.10
1,6- dimethylnaphthalene	—	—	3.84	4.08
1,4- dimethylnaphthalene	4.37 – 4.372	4.37	3.82	4.04
1,8- dimet/hylnaphthalene	—	—	3.68	3.93
1,5- dimethylnaphthalene	4.38	4.38	3.81	4.02
2,7- dimethylnaphthalene	—	—	3.97	4.17
2,3- dimethylnaphthalene	4.396 – 4.40	4.40	3.85	4.09
2,6- dimethylnaphthalene	4.31 – 4.38	4.31	4.00	4.20
1,4,5- trimethylnaphthalene	—	—	4.12	4.33
1-isopropylnaphthalene	—	—	4.22	4.50
2-isopropylnaphthalene	—	—	4.32	4.64
2,6- diisopropylnaphthalene	—	—	5.88	6.07
1,3- diisopropylnaphthalene	—	—	5.68	5.85
1,5- diisopropylnaphthalene	—	—	5.60	5.77
2,7- diisopropylnaphthalene	—	—	5.88	6.06
1,3,6- triisopropylnaphthalene	—	—	7.21	7.34
AAD			0.50	0.27

evaluative environment spans an area of 100,000 km² (10% of which is covered by water). While illustrating transport and transformation, a chemical's tendency to migrate between media can be assessed by modelling emissions to each individual medium and calculating the amount present at steady state.

It was exemplarily applied on 2,6-diisopropylnaphthalene, assuming reaction half-lives in air (55 h), water (550 h), soil (5,500 h) and sediment (17,000 h), and using the predicted COSMO-RS physico-chemical properties as given in Tables 1–4 (aqueous solubility and (subcooled) liquid vapor pressure have been corrected for their systematic COSMO-RS overestimation (0.5 log units each), and $\log K_{OW}$ (COSMO-RS) (Table 4) has been used). As a first approximation, since the substance has been in use for many years, it can be assumed having reached a steady-state condition in the environment (that is, the change in concentration of the substance in each compartment with respect to time eventually approaches zero). Hence, in this case, the use of a steady-state model is justified for this type of regional mass balance calculations.

Appendix 2 shows the amount of 2,6-diisopropylnaphthalene predicted to be present in each medium of the EQC Level III model environment for “individual” emissions of $1000 \text{ kg}\cdot\text{h}^{-1}$ to the air, water, and soil compartments, as well as a “total” for simultaneous emissions of $1,000 \text{ kg}\cdot\text{h}^{-1}$ to each of the aforementioned compartments. The model outputs of “individual” and “total” emissions reflect the importance of each single emission into individual compartments to the occurring quantities in each compartment in the “total” emission scenario and provide estimates on residence time and steady-state build-up quantities. From the EQC Level III output of the “total” emission scenario, additional information may be obtained. The predisposition of 2,6-diisopropylnaphthalene to intermedia transport is presumably most pronounced in the net transfer from water to air and from water to sediment, while net transfer from air to soil and from soil to water remains negligible. As main removal mechanism, reaction in soil is suggested, with advection and reaction of similar order of magnitude in the other compartments.

Comparing with the use of uncorrected COSMO-RS physico-chemical property data, the change in the obtained output data gives an idea on how the uncertainty of predicted properties is projected to the uncertainty of the EQC model, for the compound in question. Amongst the different release scenarios, only the “air only” scenario shows some differences in the percentage which partitions to the respective environmental compartments (with the air-soil intermedia exchange as principally influenced exchange route comparing the two data sets; the simultaneous overestimation of vapour pressure and aqueous solubility which is cancelling out in the Henry constant): with the uncorrected COSMO-RS data set, in air, the substance is contributing with 10% more to the total amount, a decrease of 15% to the partition into the soil compartment, 4% increase in sediment, while all other emission scenarios yield a nearly identical output.

Additionally, biodegradation half-life has been estimated with the BioHCwin model v1.01 which was developed specifically for the biodegradation half-life prediction of petroleum hydrocarbons; it is part of US EPA’s EPISuite v4.1 (Estimations Programs Interface for Windows) (28). BioHCwin predicts

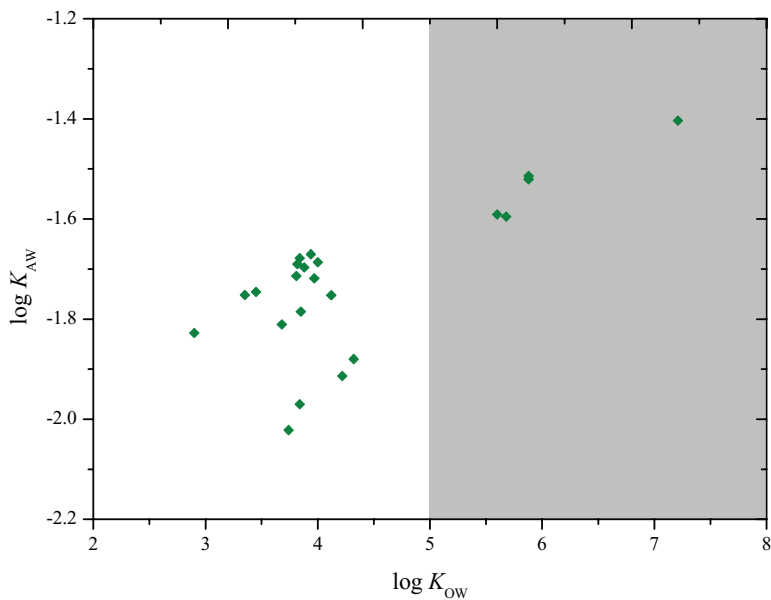


Figure 1: Chemical partitioning space for the studied alkylated naphthalenes: $\log K_{AW}$ vs. $\log K_{OW}$ (color figure available online)

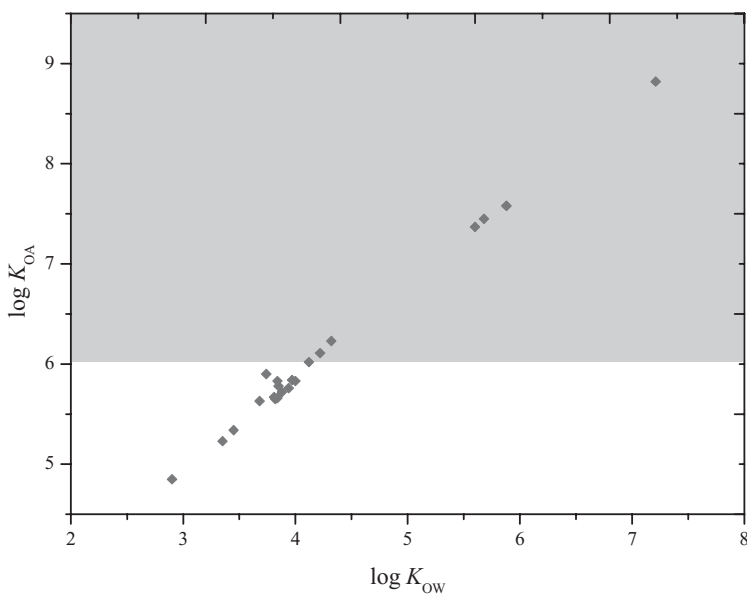


Figure 2: Chemical partitioning space for the studied alkylated naphthalenes: $\log K_{OA}$ vs. $\log K_{OW}$.

for naphthalene (5.6 d), methylnaphthalenes (8.9 d), ethylnaphthalenes (6.1 d), dimethylnaphthalenes (14.2 d), trimethylnaphthalenes (22.7 d), isopropyl-naphthalenes (13.0 d), diisopropyl-naphthalenes (30.5 d), and triisopropyl-naphthalenes (71.3 d), clearly indicating the increasing persistence with the introduction of longer or branched carbon chains.

In order to screen a compound's potential for bioaccumulation, a number of criteria based on chemical partitioning properties have been published (29, and references therein). In the case of lack of experimental bioconcentration/bioaccumulation factors, $\log K_{OW}$ is used to evaluate the bioaccumulation potential. As a rule of thumb, substances with $\log K_{OW} \geq 5$ are, in general, regarded as potentially bioaccumulative, while organic chemicals with $\log K_{OW} > 2$ and $\log K_{OA} > 6$ are likely to exhibit bioaccumulation in the terrestrial environment. Compounds with $-5 \leq \log K_{AW} \leq -1$ are considered having a high long range transport potential. Figures 1–2 illustrate the chemical partitioning space of the title compounds in this context, using partitioning data

Table 5: Derived 1-Octanol-air partition coefficients, at $T = 298.15$ K, as obtained with COSMO $therm$, both from partition coefficient calculations ($\log K_{OW}$ (COSMO-RS)) and from the QSPR-approach, using implemented Abraham's linear free energy relationships, as well as soil sorption coefficients, as obtained from QSPR.

PAH	$\log K_{OA}$ (COSMO-RS)	$\log K_{OA}$ (COSMO-Abraham)	$\log K_{OC}$ (QSPR)
Naphthalene	4.85	5.14	2.67
1-methylnaphthalene	5.23	5.58	2.84
2-methylnaphthalene	5.34	5.69	2.88
1-ethylnaphthalene	5.66	6.10	3.10
2-ethylnaphthalene	5.76	6.20	3.15
1,2-dimethylnaphthalene	5.90	6.01	2.97
1,3-dimethylnaphthalene	5.72	6.12	3.06
1,6-dimethylnaphthalene	5.83	6.10	3.01
1,4-dimethylnaphthalene	5.65	6.06	3.03
1,8-dimethylnaphthalene	5.63	5.93	2.99
1,5-dimethylnaphthalene	5.67	6.04	3.02
2,7-dimethylnaphthalene	5.84	6.20	3.10
2,3-dimethylnaphthalene	5.78	6.11	3.05
2,6-dimethylnaphthalene	5.83	6.24	3.10
1,4,5-trimethylnaphthalene	6.02	6.37	3.18
1-isopropyl-naphthalene	6.11	6.55	3.29
2-isopropyl-naphthalene	6.23	6.71	3.33
2,6-diisopropyl-naphthalene	7.58	8.26	4.10
1,3-diisopropyl-naphthalene	7.45	8.03	3.98
1,5-diisopropyl-naphthalene	7.37	7.93	3.93
2,7-diisopropyl-naphthalene	7.58	8.25	4.09
1,3,6-triisopropyl-naphthalene	8.82	9.65	4.73

obtained from COSMO-RS. This includes the data of Table 5, which summarizes the generated octanol-air partition coefficients and gives an idea about the expected magnitude of the soil sorption coefficients. As shown in Figure 1, all of the compounds are within the long range transport potential threshold, while the naphthalene congeners with $\log K_{OW} \geq 5$ (shaded area) simultaneously exhibit bioaccumulation potential in the aqueous environment. The shaded region in Figure 2 indicates bioaccumulation potential in the terrestrial environment. In the chosen scale, the compounds falling in this area also coincide with the requirements of having the potential for bioaccumulation in humans ($2 < \log K_{OW} < 11$ and $6 < \log K_{OA} < 12$, using a level I model for the physical environment). For the title substances with $\log K_{OA} \geq 6$, the criteria for posing arctic contamination and bioaccumulation potential are met, as well ($\log K_{OW} \geq 3.5$, $\log K_{OA} \geq 6$ and $\log K_{AW} \leq -1.78 \cdot \log K_{OA} + 14.56$).

A key question which remained out of the focus of this study are physical, chemical, and biological degradation processes which are likely to appear once the substances are released into environmental compartments.

CONCLUSIONS

Against the background of scarce and scattered literature data caused by known difficulties in experimental determinations, satisfactory results were obtained in the prediction of aqueous solubilities and vapor pressures of the subcooled liquid, as well as Henry's law constants and 1-octanol-water partition coefficients for alkylated naphthalenes. Where experimental data are not available, COSMO-RS represents an interesting alternative and possible auxiliary to existing prediction methods. While simulating various emission scenarios with the Mackay Level III fugacity model, a steady-state, non equilibrium, and regional-scale model, an affinity to soil and sediment compartments, has been exemplary shown for 2,6-diisopropylnaphthalene. To complete our full understanding of the behaviour of these substances when released into the environment, additional data on physical, chemical, and biological degradation processes are needed. To support and improve the methodology of a variety of approaches for the prediction of physico-chemical property data, more experimental work needs to be done on the highly accurate determination of basic partition coefficients of pure substances.

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APPENDIX 1 Parameter used to calculate subcooled liquid data (T_m – melting point, $\Delta S_{\text{fus}}(T_m)$ – molar entropy of fusion at melting point, $\Delta C_{p,\text{fus}}(T_m)$ – molar heat capacity change upon fusion (at melting point), ΔH_{trs} – molar enthalpy of solid-solid phase transition, and T_{trs} – solid-solid phase transition temperature, fugacity ratio at $T = 298.15 \text{ K}$)

	T_m/K	$\Delta S_{\text{fus}}(T_m)/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$\Delta C_{p,\text{fus}}(T_m)/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$\Delta H_{\text{trs}}/\text{kJ}\cdot\text{mol}^{-1}$	T_{trs}/K	Fugacity ratio at $T = 298.15 \text{ K}$
Naphthalene	353.434 ^a	53.90 ^b	20 ^a	—	—	0.3002 ^a
2-methylnaphthalene	307.73 ^b	39.40 ^b	26 ^a	5.606 ^b	288.5 ^b	0.9278 ^a
2,7-dimethylnaphthalene	368.812 ^a	63.32 ^a	36 ^a	—	—	0.1779 ^a
2,3-dimethylnaphthalene	378.4 ^b	51.27 ^b	35 ^c	—	—	0.2165 ^d
2,6-dimethylnaphthalene	383.32 ^b	65.37 ^b	32 ^a	—	—	0.1209 ^a

^aDIPPR data base (30)

^bNIST webbook (31)

^cassumed

^dbased on solid vapour pressure as selected by Mackay (18)

APPENDIX 2 EQC Level III output: chemical amounts in each medium based on single and multiple emissions of 2,6-dilisopropylnaphthalene.

Emission medium	Amount at steady state (kg) (% in brackets)			Residence time (d)	Time to 97% steady state/clearance (d)
	Air	Water	Soil Sediment		
Air	43850(41.1)	1250(1.2)	37560(35.2)	4.5	13.4
Water	11730(0.3)	214,000(4.9)	10050(0.2)	180.8	542.5
Soil	156(< 0.1)	230(< 0.1)	7,900,000(99.9)	329.5	988.4
"Total"	55740(0.5)	216,000(1.7)	7,950,000(64.4)	171.6	514.8