Bioavailability of polycyclic aromatic hydrocarbons in sediments : experiments and modelling

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Supercooled liquid vapour pressures and related thermodynamic properties of polycyclic aromatic hydrocarbons determined by gas chromatography

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Abstract

A gas chromatographic method using Kováts retention indices has been applied to determine the liquid vapour pressure (P_i), enthalpy of vaporization (ΔH_i) and difference in heat capacity between gas and liquid phase (ΔC_i) for a group of polycyclic aromatic hydrocarbons (PAHs). This group consists of 19 unsubstituted, methylated and sulphur containing PAHs. Differences in log P_i of –0.04 to +0.99 log units at 298.15 K were observed between experimental values and data from effusion and gas saturation studies. These differences in log P_i have been fitted with multilinear regression resulting in a compound and temperature dependent correction. Over a temperature range from 273.15 to 423.15 K, differences in corrected log P_i of a training set (–0.07 to +0.03 log units) and a validation set (–0.17 to 0.19 log units) were within calculated error ranges. The corrected vapour pressures also showed a good agreement with other GC determined vapour pressures (average –0.09 log units).

Introduction

Many hydrophobic organic chemicals of environmental interest are solid compounds at ambient temperatures. The vapour pressure that a solid compound would have if it were liquid at environmental temperatures, *i.e.* the supercooled liquid vapour pressure, is often estimated. It is necessary to estimate this vapour pressure when predicting or relating properties in solution such as solubility in water, Henry's law constants, sorption to organic matter and aerosols [1]. Therefore, it is frequently used as an input parameter in fate models. Vapour pressure, P_i, enthalpy of vaporization, ΔH_i, and the difference between the heat capacity of the gas and that of the liquid ($\Delta C_i = C_{P,G} - C_{P,L}$) are linked by exact thermodynamic relationships [2].

Among the direct experimental methods available to determine low vapour pressures (~1 Pa) of organic chemicals, effusion and gas saturation are generally considered the most accurate. Effusion methods allow accurate measurements in the range between 10^{-1} and 10^{-5} Pa with a reproducibility of ±1 to ±10% at 2 to 2.10^{-3} Pa. Gas saturation methods normally show relative standard deviations between ±0.5% and ±18% in the range between 10^{-8} and 10^4 Pa [3]. Indirect experimental methods that require the use of one or several reference compounds whose vapour pressures are accurately known are based on measuring either evaporation rates or gas chromatographic (GC) retention times [4]. Methods using relative evaporation rates showed very good agreement with direct methods in the range between 10^{-5} and 10^{-1} Pa [3]. GC methods relying on retention times are based on the partitioning behaviour of test compounds between the gas (or mobile) phase and an organic (or stationary) phase at different, isothermal or programmed, temperatures [5]. Methods using GC retention times have several advantages over other methods in that they are fast, easy to perform and relatively insensitive to impurities.

The retention time of a solute is directly related to both its volatility or vapour pressure in the pure liquid phase and its activity in the column stationary phase [6]. The method depends on the selection of appropriate reference compounds for which accurate vapour pressure data are available as well as on the choice of an appropriate stationary phase in which both test and reference compounds exhibit similar activity coefficients. Note that for solid compounds, the solutes are *dissolved* in the liquid stationary phase and as a consequence, GC methods yield directly the vapour pressure of the supercooled liquid [5]. Vapour pressures are generally reported at room temperature while the GC measurements are made at much higher temperatures resulting in possible extrapolation errors.

Earlier GC methods, based on the Hamilton method [7] make use of linear relationships of GC derived and supercooled liquid vapour pressures by calibrating against structurally similar reference compounds. It is assumed in this method that the enthalpy of vaporization is constant and the activity coefficients of test and reference compounds are similar in the range of temperature taken into consideration [8, 9]. According to a recently published review, errors as high as threefold could arise if the differences in the activity coefficient at infinite dilution are neglected [10].

In a method using isothermal Kováts retention indices (GCVAP), a constant and temperature independent ratio of activity coefficients at 393.15 K of the test compound and the nearest eluting *n*-alkane was incorporated by an expression based on McReynolds constants of model compounds [6, 11, 12]. However, the limited group of model compounds available and the constant temperature reported for these activity coefficient ratios restricts the use of this method. This called for a compound and temperature dependent correction in a study concerning structurally diverse, polar compounds [13]. The method of GCVAP has been applied before to determine the supercooled liquid vapour pressures of chlorobenzenes [11], tetrachlorobenzyltoluenes [12], N-PAHs [14], fatty acid esters [6] and terpenoids [13]. An additional advantage of the GCVAP method over other GC methods is the temperature dependent determination of the enthalpy of vaporization and the difference in heat capacity.

In this study, the vapour pressure of polycyclic aromatic hydrocarbons (PAHs) has been measured with the GCVAP method including a compound and temperature dependent correction based on literature data of liquid vapour pressures of a number of PAHs determined by effusion and gas saturation measurements. In this way, a next step is made to improve the GCVAP method specifically for the temperature dependence of compounds with very low vapour pressures. The method is tested for 19 PAHs with a large range in hydrophobicity. Among the test compounds are 14 PAHs, 3 methylated PAHs and 2 sulphur containing PAHs. Diphenylmethane, *p,p*'-DDT and methylbehenate were included to make a comparison with previous GCVAP studies.

Method

The procedure of determining the liquid vapour pressure of a test compound (denoted as *i*) by using linear *n*-alkanes as reference standards through the determination of Kováts retention indices has been published before [6, 11, 13]. The relationship between the ratio of the mole fractions in the carrier gas (y_i) and stationary phase (x_i), respectively, vapour pressure of the compound (P_i) and activity coefficient at infinite dilution (γ_i) can be derived from the fugacity model of equilibrium partitioning between carrier gas and liquid phase:

$$\frac{y_i}{x_i} = \gamma_i \frac{P_i}{P_t} \tag{1}$$

in which P_t is the mean carrier gas pressure and $\gamma_i = 1$ for pure liquids and ideal solutions. It is assumed that the pure vapour and the vapour-carrier gas mixture both exhibit ideal behaviour (or similar non-ideal behaviour). The determination of vapour pressure is based on the assumption that the capacity factor at infinite dilution is inversely proportional to the ratio y_i/x_i (or volatility). The same reasoning applies for the *n*-alkanes with *z* and *z*+1 carbon atoms just

eluting before and after *i* [11]. Substitution of these relations into the definition of the Kováts index yields the following expression:

$$I_i = 100.z + \frac{100[\log(t'_{R,i}) - \log(t'_{R,z})]}{[\log(t'_{R,z+1}) - \log(t'_{R,z})]} = 100.z + \frac{100[\log(\gamma_i P_i) - \log(\gamma_z P_z)]}{[\log(\gamma_{z+1} P_{z+1}) - \log(\gamma_z P_z)]} \tag{2}$$

The retention times of the compounds studied are adjusted here with the hold-up time of the unretarded component ($t'_{R,i} = t_i - t_0$). This equation thus incorporates the differences in vapour pressure and activity in the stationary phase between the unknown compound and those of the nearest eluting *n*-alkanes. In order to calculate the vapour pressure of compound *i*, Eq. (2) is rearranged to:

$$\log P_i = \log P_z + \frac{(100.z - I_i)(\log P_z - \log P_{z+1})}{100} + \log \frac{\gamma_z}{\gamma_i} \tag{3}$$

The ratio of the activity coefficients of *n*-alkanes (γ_z/γ_{z+1}) is equated to 1 as this has been shown not to influence the results to a large extent (maximum correction of -0.05 log units) [13]. The correction factor of log (γ_z/γ_i) has been tabulated at 393.15 K and varies for an SE-30 column (equivalent to DB-1) from -0.245 to +0.236 for nine selected model compounds based on the McReynolds number [11]. This correction factor is considered to be temperature independent. It will be shown later that the value of log (γ_z/γ_i) depends on both temperature and type of compound.

The enthalpy of vaporization and difference in heat capacity can be derived by taking the first and second order derivatives of the vapour pressure according to the thermodynamic functions: $\Delta H_i = RT^2 \, d\ln P_i/dT$ and $\Delta C_i = d\Delta H_i/dT$:

$$\Delta H_i(T) = \Delta H_z + \frac{(100.z - I_i)(\Delta H_z - \Delta H_{z+1})}{100} - \frac{2.303 RT^2(\log P_z - \log P_{z+1})(dI_i/dT)}{100}$$

$$+ 2.303 RT^2 \frac{d\log(\gamma_z/\gamma_i)}{dT} \tag{4}$$

and,

$$\Delta C_i(T) = \Delta C_z + \frac{(100.z - I_i)(\Delta C_z - \Delta C_{z+1})}{100} - \frac{RT(\log P_z - \log P_{z+1})(dI_i/dT)}{50}$$

$$- \frac{(\Delta H_z - \Delta H_{z+1})(dI_i/dT)}{100} - \frac{RT^2(\log P_z - \log P_{z+1})(d^2 I_i/dT^2)}{100} \tag{5}$$

A quadratic relationship was used to calculate the first and second order derivatives of the Kováts index of a compound *i* as a function of temperature with the following expression:

$$I_i(T) = I_0 + I_1.T^2 \tag{6}$$

where I_0 and I_1 are empirical regression constants and are determined by linear regression. Next, the value for log P_z in Eq. (3) is calculated by fitting T and z to experimental values of vapour pressure, heat of vaporization and heat capacity differences of *n*-alkanes:

$$\log P_z = A_z + \frac{B_z}{T} + \frac{C_z}{T^2} \tag{7}$$

with A_z = 4.877735 (± 0.014939) + 0.303157 (± 0.00222).z – 0.007281 (± 0.00007).z^2,
B_z = 485.6891 (± 5.613) – 261.5436 (± 0.47628).z + 5.8678 (± 0.005539).z^2 and
C_z = -86487.5 (± 55.09) + 344.999 (± 14.2985).z – 874.879 (± 0.8257).z^2.

The corresponding equations for the heat of vaporization and heat capacity difference are found by using the thermodynamic functions mentioned above. The empirical regression parameters of A_z have been derived from 297 experimental P_z values of *n*-alkanes (range of z = 3–35), determined at 150–763 K (log P_z values between –4.56 and +3.31). The parameters of B_z have been derived from calorimetric determination of the heats of vaporization of *n*-alkanes at 298.15 K (range of z = 6–17) and heat capacity differences of *n*-alkanes at 298.15 K (range of z = 3–14) have been used to calculate the C_z parameters (no experimental values were omitted in the regression) [6].

In order to make a comparison with effusion and gas saturation literature data selected from a review [3], solid vapour pressures ($P_{S,lit}$) were converted to supercooled liquid vapour pressures ($P_{L,lit}$), using melting point temperatures (T_{mp}) and entropy of fusion data (ΔS_{fus}), through the equation:

$$\ln \frac{P_{L,lit}}{P_{S,lit}} = -\frac{\Delta S_{fus}}{R}\left(1 - \frac{T_{mp}}{T}\right) \tag{8}$$

where R is the gas constant and T is the temperature of measurement. Using the converted liquid vapour pressures, Clausius-Clapeyron equations (log P_i = A_i/T + B_i) for a number of PAHs were derived from the separate equations for the temperature ranges reported in the selected literature studies.

Subsequently, average differences were calculated between experimentally determined vapour pressures and liquid vapour pressures from the individual literature studies in order to determine a temperature and compound dependent correction factor. These differences were plotted as a function of temperature and number of carbon atoms (n_i) and fitted with multilinear regression (see Eq. 9). In this way, an average correction factor dependent on the number of carbon atoms and temperature will be used to correct the vapour pressures of all other PAHs.

This temperature and compound dependent correction factor is in this way similar to the logarithm of the activity coefficient ratio from Eq. (3):

$$\Delta \log P_{n,i} = \log \frac{\gamma_z}{\gamma_i} = \log P_{n,\text{lit}} - \log P_z - \frac{(100.z - I_i)(\log P_z - \log P_{z+1})}{100} =$$

$$(E_0 + E_1.n_i) + \frac{(F_0 + F_1.n_i)}{T} \tag{9}$$

The first derivative of this factor also gives a (constant) correction for the enthalpy of vaporization according to Eq. (4) with the last term calculated as follows:

$$\Delta\Delta H_i = RT^2 \frac{\mathrm{d}(E_i + F_i/T)}{\mathrm{d}T} = -2.303RT^2 \frac{F_i}{T^2} = -2.303R(F_0 + F_1.n_i) \tag{10}$$

All linear and nonlinear regression calculations were performed with the statistical program S-Plus 6.0 (Insightful Corporation, Seattle, Washington, USA) and graphic outputs were prepared with Prism 3.02 (Graphpad Software Inc., San Diego, CA, USA).

Experimental

Chemicals and standards
The unsubstituted PAHs were obtained in a purity higher than 98% from Dr. Ehrenstorfer (Augsburg, Germany), except for benzo[*e*]pyrene (purity 99.4%) which was obtained from Accustandard (New Haven, CT, USA). The methylated PAHs, 1-methylnaphthalene, 2-methylanthracene and 1-methylpyrene were obtained from Accustandard (purity higher than 97.9%) and the sulphur-containing compounds, dibenzothiophene and benzo[*b*]naphto(2,3-D)thiophene (both in a purity of 99.2%) were purchased from Chem Service (West Chester, PA, USA) and Chiron A.S. (Trondheim, Norway), respectively. The compounds used for comparison with previous studies, diphenylmethane, *p,p*'-DDT and methylbehenate ($C_{23}H_{46}O_2$) originated from Merck-Schuchardt (Hohenbrunn, Germany), Analabs (North Haven, CT, USA) and Sigma-Aldrich (Steinheim, Germany). The C_{10}-C_{19} *n*-alkane reference standards (purity >99%) were purchased from Polyscience (Niles, IL, USA) and the even, C_{20}-C_{32}, *n*-alkane standards were from Sigma-Aldrich (purity >97%). The compounds were split into three standard mixtures depending on their volatility. This ensured that the total retention time of the last eluting compound at the lowest temperature used did not exceed 90 minutes.

Instrumentation
The retention times of the studied compounds were determined with a HP5890 series II gas chromatograph equipped with a flame ionisation detector (FID) and a split/splitless injection port. The analyses were performed using a 30 m DB-1 column from J&W (Folsom, CA, USA) with an internal diameter of 0.32 mm and a film thickness of 0.25 μm operating in the split mode with a split ratio of 1:20 (split flow 27.5 ml/min., septum flow 1 ml/min. and column flow of 1.45 ml/min.). Injector and detector temperatures were 250 and 275 °C, respectively. Helium was used as a carrier gas at a constant pressure of 61.5 kPa. The gas chromatograph was run isothermally in a temperature range of 60-260 °C with 5 to 8 intervals of 10 °C. The Kováts indices of the component mixtures were determined by injecting 1 μl manually in quadruplicate. The retention time of the unretarded compound was measured by injecting methane in between samples.

Results and discussion

Kováts index

The calculated quadratic relationship of the retention index with temperature (see Eq. 6) provides good results with squared correlation coefficients generally higher than 0.9997 (see Table 1). Methylbehenate is an exception ($r^2 = 0.9940$) as the temperature effect of the Kováts index (I_1) is small indicating that the alkane chain of this compound is very similar to the *n*-alkanes used as reference compounds. Results earlier reported for methylbehenate [6] also show a similar weak relationship with temperature. The regression parameters for diphenylmethane obtained in this study agree very well with results from a previous GCVAP study [13]. In another GCVAP study [12], lower slopes of the temperature dependence were found for diphenylmethane and *p,p*'-DDT. For some compounds, not every temperature interval of 10 K was used in the regression, because of co-elution with the nearest eluting *n*-alkane or a large scatter in the retention time at high oven temperatures due to short residence times in the column.

Table 1. CAS numbers, regression parameters (±SE), squared correlation coefficients of the regression, temperature range (in K) and standard error of the regression for the test compounds.

Compound	CAS no.	I_1*1000	I_0	r^2	T range	SER
Naphthalene	91-20-3	1.038±0.002	1039.4±0.2	0.9999	333.15 – 403.15	0.1445
1-Methylnaphthalene	90-12-0	1.152±0.002	1138.6±0.3	0.9999	343.15 – 423.15	0.2114
Acenaphthylene	208-96-8	1.408±0.003	1224.1±0.5	0.9999	363.15 – 423.15	0.2599
Acenaphthene	83-32-9	1.413±0.002	1253.0±0.3	0.9999	363.15 – 423.15	0.1653
Fluorene	86-73-7	1.474±0.002	1332.2±0.4	0.9999	373.15 – 423.15	0.1552
Dibenzothiophene	132-65-0	1.864±0.005	1412.2±1.0	0.9998	413.15 – 473.15	0.4815
Phenanthrene	85-01-8	1.896±0.006	1431.2±1.1	0.9998	413.15 – 483.15	0.6447
Anthracene	120-12-7	1.890±0.005	1440.0±0.9	0.9998	413.15 – 473.15	0.4484
2-Methylanthracene	613-12-7	1.915±0.005	1540.6±1.0	0.9998	413.15 – 473.15	0.4758
Fluoranthene	206-44-0	2.305±0.006	1594.8±1.2	0.9998	423.15 – 493.15	0.6766
Pyrene	129-00-0	2.489±0.005	1601.0±1.2	0.9999	423.15 – 493.15	0.6484
1-Methylpyrene	2381-21-7	2.610±0.006	1707.1±1.3	0.9998	423.15 – 493.15	0.7235
Benzo[b]naphto(2,3-D)thiophene	243-46-9	2.937±0.010	1766.1±2.4	0.9998	473.15 – 523.15	0.7552
Benzo[a]anthracene	56-55-3	2.891±0.009	1798.3±2.1	0.9998	463.15 – 523.15	0.8972
Chrysene	218-01-9	2.911±0.008	1802.3±2.0	0.9998	463.15 – 513.15	0.6902
Benzo[b]fluoranthene	205-99-2	3.305±0.013	1968.5±3.0	0.9997	463.15 – 513.15	0.9431
Benzo[k]fluoranthene	207-08-9	3.289±0.010	1978.2±2.5	0.9998	463.15 – 513.15	0.8388
Benzo[e]pyrene	192-97-2	3.558±0.013	1969.9±3.3	0.9997	463.15 – 523.15	1.3729
Benzo[a]pyrene	50-32-8	3.591±0.013	1971.4±3.2	0.9997	463.15 – 523.15	1.3697
Diphenylmethane	101-81-5	0.935±0.002	1281.1±0.4	0.9998	363.15 – 423.15	0.2022
Diphenylmethane[a]		0.905±0.003	1293.1±0.4	0.9997	343.15 – 393.15	0.19
Diphenylmethane[b]		0.777±0.017	1276.9±3.6	0.998	433.15 – 493.15	0.7363
p,p'-DDT	50-29-3	1.809±0.005	1949.8±1.0	0.9998	433.15 – 493.15	0.4509
p,p'-DDT[b]		1.316±0.006	1994.6±1.2	0.9999	433.15 – 493.15	0.2816
Methylbehenate	929-77-1	0.108±0.002	2502.0±0.4	0.9940	463.15 – 513.15	0.1459
Methylbehenate[c]		0.032	2504.4	0.93	463.15 – 523.15	0.190

[a] Ref. [13]; [b] Ref. [12]; [c] Ref. [6].

Comparison with literature data from effusion and gas saturation studies

The regression parameters and statistics of the Clausius-Clapeyron equations mentioned in the method section are shown in Table 2 along with their entropies of fusion and melting point temperatures.

Comparison of the experimentally determined vapour pressures (calculated with Eq. 3 and $\log(\gamma_z/\gamma_i)=0$) and literature data at 298.15 K shows that there is a discrepancy in the vapour pressure between this value and literature (see Table 3). The deviation from literature data amounts to –0.04 and +0.99 log units for naphthalene and benzo[*a*]pyrene, respectively. This deviation from literature data is not only dependent on the type of compound considered but also on temperature in a nonlinear way. A correction with a selected value of $\log(\gamma_z/\gamma_i) = +0.236$ for benzene from [11] in Eq. (3) did not improve the experimental values as the data became even more positive compared to literature values.

Differences between literature data and experimental vapour pressures were determined for a selection of PAHs, acenaphthene, phenanthrene, pyrene and benzo[*a*]anthracene, that served as a training set and covered a range in n_i of 12 to 18 carbon atoms. The other PAHs in Table 2 were used as validation set from which the endmembers (naphthalene and benzo[*a*]pyrene) were not included in the training set due to a high variability in $\log(\gamma_z/\gamma_i)$ values close to zero for naphthalene and a low amount of data available for benzo[*a*]pyrene. The differences in vapour pressure for the selected PAHs were fitted with Eq. (9) resulting in the following parameters (*n* = 293; SER = 0.0223):

$$E_0 = 2.685 \pm 0.1389; \; E_1 = -0.1227 \pm 0.0085;$$
$$F_0 = -464.94 \pm 46.184; \; F_1 = 5.789 \pm 2.885 \tag{11}$$

Applying these parameters to both naphthalene (*n* = 10) and benzo[*a*]pyrene (*n* = 20) resulted into a correction of +0.09 and –0.94 at 298.15 K. At a higher temperature (498.15 K), these corrections are +0.64 and –0.47 for the same compounds showing the temperature dependence of the deviation.

Table 2. Selected values of entropies of fusion (in J/K.mol) and melting point temperature (in K), parameters of Clausius-Clapeyron equation (±SE), temperature range of measurements reported in literature (number of selected studies are shown in parentheses), squared correlation coefficients and standard error of regression.

Compound	ΔS_{fus}	$T_{mp}{}^f$	$A_i{}^g$	$B_i{}^g$	T range	r^2	SER
Naphthalene[a]	53.94[c]	353.4	-2797 ± 6.889	10.95 ± 0.02264	271-354 (9)	0.9986	0.0216
Acenaphthene[b]	58.55[d]	366.6	-3442 ± 31.66	11.73 ± 0.1042	283-323 (2)	0.9939	0.0330
Fluorene[a]	50.48[d]	387.9	-3566 ± 9.612	11.66 ± 0.03143	283-323 (2)	0.9996	0.0093
Phenanthrene[b]	44.83[d]	372.4	-4037 ± 17.56	12.41 ± 0.05608	273-363 (5)	0.9965	0.0501
Anthracene[a]	60.08[d]	488.9	-3639 ± 20.34	11.21 ± 0.05917	301-393 (6)	0.9927	0.0540
Fluoranthene[a]	48.85[d]	383.33	-3863 ± 44.63	10.70 ± 0.1412	298-358 (2)	0.9988	0.0278
Pyrene[b]	40.97[d]	423.81	-4100 ± 9.957	11.50 ± 0.02694	320-423 (4)	0.9988	0.0278
Benzo[a]anthracene[b]	49.23[e]	434.4	-4624 ± 31.98	11.88 ± 0.0858	330-426 (4)	0.9908	0.0767
Benzo[a]pyrene[a]	38.14[e]	454.15	-5273 ± 2.213	12.61 ± 0.0056	358-431 (1)	1.0000	0.0026

[a] PAHs selected as validation set;
[b] PAHs selected as training set for multilinear regression of compound and temperature dependent correction;
[c] Ref. [15];
[d] Ref. [16];
[e] Ref. [17];
[f] Melting point temperatures originate from same references as ΔS_{fus} data;
[g] Calculated regression parameters of Clausius-Clapeyron equations from [3]. Original references for Naphthalene: Ref.[18], [19], [20], [21], [22], [23], [24], [25], [26]; Acenaphthene: Ref. [27], [26]; Fluorene: Ref. [18], [26]; Phenanthrene: Ref. [18], [19], [28], [24], [26]; Anthracene: Ref. [29], [30], [28], [23], [24], [31]; Fluoranthene: Ref. [27,32]; Pyrene: Ref. [18], [33], [34], [28]; Benzo[a]anthracene: Ref. [35], [32], [29], [36] and Benzo[a]pyrene: Ref. [34].

Table 3. Comparison of experimentally determined vapour pressures with calculated literature data (references shown in Table 2) at 298.15 K (log P_i in Pa; ±SE).

Compound	log P_i		log γ_z/γ_i
	Lit.	This study	
Naphthalene	1.57 ± 0.03	1.53 ± 0.04	-0.04
Acenaphthene	0.19 ± 0.15	0.28 ± 0.05	+0.10
Fluorene	-0.30 ± 0.05	-0.14 ± 0.05	+0.16
Phenanthrene	-1.13 ± 0.08	-0.81 ± 0.05	+0.32
Anthracene	-1.00 ± 0.09	-0.86 ± 0.05	+0.14
Fluoranthene	-2.26 ± 0.21	-1.79 ± 0.06	+0.47
Pyrene	-2.25 ± 0.04	-1.89 ± 0.06	+0.36
Benzo[*a*]anthracene	-3.63 ± 0.14	-3.00 ± 0.07	+0.63
Benzo[*a*]pyrene	-5.08 ± 0.01	-4.09 ± 0.07	+0.99

Liquid vapour pressures in the reported temperature range from literature and this study including the corrections at different temperatures (273.15 – 423.15 K) are shown in Table 4. In this temperature range, the corrected vapour pressures show a good agreement within the calculated error ranges with the literature values of PAHs included in the training set (–0.07 to +0.03 log units difference) as well as with the literature values that were not used in the derivation of the parameters of Eq. (9) (–0.17 to +0.19 log units difference). The correction factor has not been applied to the compounds that were used to compare with previous GCVAP studies as these compounds are structurally different from the PAHs studied. A very close agreement is found for the determined vapour pressure of *p*,*p*'-DDT (log P_i = -3.24 ± 0.06) compared to averaged data from a number of effusion and gas saturation studies (log $P_{L,lit}$ = -3.24 ± 0.03) [37-40]. Conversion of solid to liquid vapour pressures of *p*,*p*'-DDT was performed by applying Eq. (8) with ΔS_{fus} = 68.78 J/mol.K and T_{mp} = 382.1 K [17].

At 298.15 K, linear regression of liquid vapour pressures from literature (N = 9; SER = 0.0884) and this study with and without log(γ_z/γ_i) correction (both N = 17; SER = 0.0695) as a function of the number of carbon atoms, n_i, resulted in the following Eqs:

$$\log P_{L,lit} = -0.6556 \, (\pm 0.0102).n_i + 8.145 \, (\pm 0.153) \tag{12}$$
$$r^2 = 0.9983$$
$$\log P_{L,exp.} = -0.5533 \, (\pm 0.0051).n_i + 7.000 \, (\pm 0.082) \tag{13}$$
$$r^2 = 0.9987$$
$$\log P_{L,corr.} = -0.6566 \, (\pm 0.0052).n_i + 8.126 \, (\pm 0.082) \tag{14}$$
$$r^2 = 0.9991$$

Table 4. Calculated vapour pressures from literature (references shown in table 2) and corrected vapour pressures at different temperatures ($\log P_i$ in Pa; ±SE).

Compound	$\log P_i$						
	$T=273.15$	$T=298.15$	$T=323.15$	$T=348.15$	$T=373.15$	$T=398.15$	$T=423.15$
Naphthalene[a], lit.	0.71 ± 0.03	1.57 ± 0.03	2.30 ± 0.03	2.92 ± 0.03			
This study, corr.	0.64 ± 0.26	1.63 ± 0.25	2.43 ± 0.24	3.10 ± 0.23			
Acenaphthene[b], lit.		0.19 ± 0.15	1.08 ± 0.14				
This study, corr.		0.17 ± 0.26	1.11 ± 0.25				
Fluorene[a], lit.		-0.30 ± 0.05	0.63 ± 0.04				
This study, corr.		-0.36 ± 0.27	0.64 ± 0.26				
Phenanthrene[b], lit.	-2.37 ± 0.09	-1.13 ± 0.08	-0.08 ± 0.08	0.81 ± 0.08			
This study, corr.	-2.42 ± 0.30	-1.13 ± 0.28	-0.08 ± 0.27	0.80 ± 0.26			
Anthracene[a], lit.			-0.05 ± 0.09	0.76 ± 0.08	1.46 ± 0.08		
This study, corr.			-0.12 ± 0.27	0.76 ± 0.26	1.50 ± 0.25		
Fluoranthene[a], lit.		-2.26 ± 0.21	-1.25 ± 0.20	-0.40 ± 0.19			
This study, corr.		-2.32 ± 0.30	-1.16 ± 0.29	-0.20 ± 0.28			
Pyrene[b], lit.			-1.19 ± 0.04	-0.28 ± 0.04	0.51 ± 0.04	1.20 ± 0.04	1.81 ± 0.04
This study, corr.			-1.26 ± 0.29	-0.30 ± 0.28	0.51 ± 0.27	1.20 ± 0.26	1.79 ± 0.26
Benzo[*a*]anthracene[b], lit.				-1.40 ± 0.13	-0.51 ± 0.12	0.27 ± 0.12	0.95 ± 0.11
This study, corr.				-1.39 ± 0.30	-0.50 ± 0.29	0.25 ± 0.28	0.90 ± 0.27
Benzo[*a*]pyrene[a], lit.					-1.52 ± 0.01	-0.63 ± 0.01	0.15 ± 0.01
This study, corr.					-1.53 ± 0.30	-0.72 ± 0.30	-0.02 ± 0.29

[a] PAHs selected as validation set;
[b] PAHs selected as training set.

The slope and intercept of the obtained log $P_{corr.,liq}$ vs n_i relationship (Eq. 14) have become very similar to the regression parameters of literature data (Eq. 12).

As can also be seen from Fig. 1, the slope of the (corrected) log P_i vs n_i relationship is very different from the slope of the vapour pressures of *n*-alkanes (calculated with Eq. 7). This is caused by activity coefficient differences of PAHs and *n*-alkanes in the stationary phase of the column. The compound and temperature dependent correction has also been applied to the sulphur containing PAHs, dibenzothiophene and benzo[*b*]naphto(2,3-D)thiophene, which fall below the linear relationship of the PAHs. The other compounds shown in Fig. 1 are diphenylmethane, *p,p*'-DDT and methylbehenate.
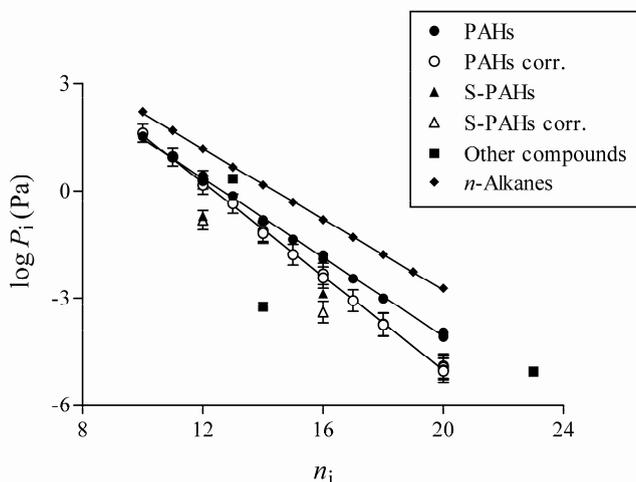

Figure 1. Calculated liquid vapour pressures with and without correction (with Eqs 3 and 9) for PAHs including alkylated PAHs, S-PAHs as well as obtained values for diphenylmethane, *p,p*'-DDT and methylbehenate (other compounds) compared to calculated liquid vapour pressures of *n*-alkanes (with Eq. 7) at 298.15 K as a function of the number of carbon atoms (n_i).

Comparison with GC determined literature values

The vapour pressures with and without correction at 298.15 K are shown in Table 5 and a comparison is made with literature data from other GC studies. In the first GC study from Lei *et al.* [9], the liquid vapour pressure of 35 unsubstituted and alkylated PAHs was determined using GC retention times. In this method, the Hamilton approach was followed by calculating GC vapour pressures (P_{GC}) using pyrene and benzo[*a*]anthracene as standard reference compounds. The enthalpies of vaporization were assumed to be constant over the temperature range from the measurement temperatures to 298.15 K. The GC determined vapour pressures were subsequently calibrated with nine PAHs resulting in liquid vapour pressures of all studied PAHs [9]. The data agree reasonably well with the data obtained in this study (within -0.15 and +0.15

log units), except for benzo[*a*]anthracene, benzo[*b*]fluoranthene and benzo[*a*]pyrene that deviate -0.28 to +0.23 log units.

Table 5. Number of carbon atoms (n_i) and liquid vapour pressures with and without correction compared to GC determined literature values at 298.15 K (log P_i in Pa; ±SE).

Compound	n_i	log P_i			
		This study	This study corr.	Lit. values	
Naphthalene	10	1.53 ± 0.04	1.63 ± 0.25	1.57[a]	
1-Methylnaphthalene	11	0.98 ± 0.04	0.97 ± 0.26	0.82[a]	
Acenaphthylene	12	0.43 ± 0.04	0.32 ± 0.26		
Acenaphthene	12	0.28 ± 0.05	0.17 ± 0.26	0.18[a]	
Fluorene	13	-0.14 ± 0.05	-0.36 ± 0.27	-0.28[a]	
Dibenzothiophene	12	-0.70 ± 0.05	-0.82 ± 0.26	-0.94[b]	
Phenanthrene	14	-0.81 ± 0.05	-1.13 ± 0.28	-1.10[a]	-1.00[e]
Anthracene	14	-0.86 ± 0.05	-1.18 ± 0.28	-1.14[a]	-0.97[e]
2-Methylanthracene	15	-1.35 ± 0.05	-1.78 ± 0.29	-1.68[a]	-1.92[e]
Fluoranthene	16	-1.79 ± 0.06	-2.32 ± 0.30	-2.22[a]	
Pyrene	16	-1.89 ± 0.06	-2.42 ± 0.30	-2.27[a]	-2.06[e]
1-Methylpyrene	17	-2.44 ± 0.06	-3.07 ± 0.31		
Benzo[*b*]naphto(2,3-D)thiophene	16	-2.87 ± 0.07	-3.39 ± 0.30		
Benzo[*a*]anthracene	18	-3.00 ± ±0.07	-3.73 ± 0.32	-3.45[a]	-3.42[e]
Chrysene	18	-3.02 ± 0.06	-3.75 ± 0.32	-3.77[a]	
Benzo[*b*]fluoranthene	20	-3.95 ± 0.07	-4.89 ± 0.34	-5.12[a]	
Benzo[*k*]fluoranthene	20	-3.99 ± 0.07	-4.93 ± 0.34	-5.05[a]	
Benzo[*e*]pyrene	20	-4.07 ± 0.07	-5.01 ± 0.34		
Benzo[*a*]pyrene	20	-4.09 ± 0.07	-5.03 ± 0.34	-5.23[a]	-4.34[e]
Diphenylmethane	13	0.35 ± 0.04		0.56[c]	0.30 ± 0.04[f]
p,p'-DDT	14	-3.24 ± 0.06		-3.21[c]	
Methylbehenate	23	-5.05 ± 0.07		-5.05 ± 0.08[d]	

[a] Ref. [9], GC study using pyrene and benzo(*a*)anthracene as reference compounds; [b] Ref. [2] recommended value of $P_{S,lit}$ converted to $P_{L,lit}$ with ΔS_{fus} 58.17 J/mol.K and T_{mp} 371.0 K from ref. [17]; [c] Ref. [12], GCVAP study of tetrachlorobenzyltoluenes; [d] Ref. [6], GCVAP study of fatty acid esters; [e] Ref. [8], GC study using eicosane and *p,p'*-DDT as reference compounds; [f] Ref. [13], GCVAP study of terpenoids.

In a second GC study from Hinckley *et al.* [8], a similar procedure was followed by using eicosane (n-C_{20}) and p,p'-DDT as standard reference compounds and calibrating the P_{GC} data with a large range in semivolatile compounds. As is explained in [8], the discrepancy between P_{GC} and P_L is caused by activity coefficient differences between the standard reference and calibration compounds. In both GC studies, the infinite dilution activity coefficients in the stationary phase were assumed to be equal for both the analyte and the standard reference compound making calibration with closely related compounds necessary [9]. A number of calibration equations were presented in [8] using different reference compounds (n-C_{20} or p,p'-DDT) and measured or constant values of ΔS_{fus} were used to convert solid to liquid vapour pressures (with Eq. 8). A comparison is made with the calculated average of the vapour pressures obtained by using both reference compounds and measured entropies of fusion. The values determined in this study are -0.13 to -0.69 log units lower than the values reported in Hinckley *et al.* [8]. The average difference between the corrected and the GC determined vapour pressures from [8] is –0.09 log units.

For one of the sulphur containing PAHs, dibenzothiophene, a recommended value for the vapour pressure is only 0.12 log units lower [2]. Finally, the vapour pressures obtained for diphenylmethane, p,p'-DDT and methylbehenate compare favourably with data previously reported in other GCVAP studies [13], except for the published value for diphenylmethane in [12]. By comparing the experimentally determined vapour pressures with literature data of liquid vapour pressures, uncertainties in the values of the used entropies of fusion and melting point temperatures are also introduced.

Related thermodynamic properties

The first and second order derivatives of the vapour pressure (see Eqs 4 and 5 and Table 6 and 7) yield the enthalpy of vaporization (ΔH_i) and difference in heat capacity (ΔC_i), respectively. The ΔH_i values were corrected with a constant factor (see Eq. 10) that resulted from the compound dependence of the vapour pressure correction.

Again, a comparison with literature data from the GC studies from [8, 9] was performed (see Table 6). Both studies assumed a constant enthalpy of vaporization for the standard reference compounds that were used to estimate the vaporization enthalpy for the studied PAHs. In an extensive review by Chickos and Acree [44], vaporization enthalpies were derived from the slopes of the Clausius-Clapeyron equations ($\Delta H_i = -2.303RA_i$) and reported at the mean temperature (T_m) at which the GC measurements were carried out.

Table 6. Experimental and literature values for the enthalpy of vaporization (ΔH_i, in kJ/mol) at 298.15 K (standard errors shown).

Compound	ΔH_i			
	This study corr.	Lit. values		Estimated[h]
Naphthalene	60.32 ± 1.05	62.00[a]	55.65 ± 2.8[f]	54.24
1-Methylnaphthalene	65.10 ± 1.09	69.01[a]		58.81
Acenaphtylene	69.11 ± 1.11			66.81
Acenaphthene	70.54 ± 1.12	71.42[a]		66.05
T = 366.535 K	65.35 ± 1.12	61.09[b]		
Fluorene	74.39 ± 1.16	75.05[a]		72.82
Dibenzothiophene	78.31 ± 1.13			78.61
T = 371.796 K	71.82 ± 1.13	69.91[b]		
Phenanthrene	79.01 ± 1.20	81.38[a]	80.38[g]	74.26
T = 372.360 K	72.36 ± 1.20	71.10[b]		
Anthracene	79.50 ± 1.19	81.70[a]	79.06[g]	74.26
2-Methylanthracene	84.42 ± 1.23	86.40[a]		79.75
Fluoranthene	86.78 ± 1.28	90.23[a]	88.29[g]	88.83
Pyrene	87.15 ± 1.28	90.97[a]	89.82[g]	86.91
T = 423.775 K	75.56 ± 1.29	76.77[b]		
1-Methylpyrene	92.33 ± 1.32			90.74
Benzo[*b*]naphto(2,3-D)thiophene	95.22 ± 1.29			98.02
Benzo[*a*]anthracene	96.62 ± 1.37	95.25[a]	104.30[g]	94.28
Chrysene	96.96 ± 1.37	103.32[a]		94.28
Benzo[*b*]fluoranthene	104.00 ± 1.47	105.57[a]		108.23
Benzo[*k*]fluoranthene	105.48 ± 1.46	104.54[a]		108.23
Benzo[*e*]pyrene	104.97 ± 1.48		108.11[g]	106.32
Benzo[*a*]pyrene	105.03 ± 1.48	107.22[a]	111.69[g]	106.32
T = 449.600 K	86.03 ± 1.54	97.10[b]		
Diphenylmethane	64.71 ± 0.17	65.72[c]		66.20
p,*p*'-DDT	97.92 ± 0.26	105.10[d]	107.78[g]	97.23
Methylbehenate	125.98 ± 0.28	126.09[e]		124.98

[a] Ref. [9], extrapolated value calculated with integrated heat capacity difference;
[b] Ref. [2], recommended values at the triple point temperature;
[c] Ref. [13], GCVAP study of terpenoids;
[d] Ref. [12], GCVAP study of tetrachlorobenzyltoluenes;
[e] Ref. [6], GCVAP study of fatty acid esters;
[f] Ref. [15], recommended value;
[g] Ref. [8], extrapolated value calculated with integrated heat capacity difference;
[h] Ref. [41], estimated with a group contribution method of Kolská *et al.*

Table 7. Experimental and estimated heat capacity differences (ΔC_i, in J/mol.K) at 298.15 K (standard errors shown).

Compound	ΔC_i	
	This study	Estimated[a]
Naphthalene	-76.72 ± 0.04	-68.69
1-Methylnaphthalene	-85.26 ± 0.04	-73.57
Acenaphtylene	-93.51 ± 0.05	-67.43
Acenaphthene	-96.20 ± 0.05	-64.09
Fluorene	-104.50 ± 0.05	-87.19
Dibenzothiophene	-114.03 ± 0.06	-112.58
Phenanthrene	-116.14 ± 0.06	-87.91
Anthracene	-117.19 ± 0.06	-87.91
2-Methylanthracene	-129.14 ± 0.07	-92.79
Fluoranthene	-136.33 ± 0.07	-91.34
Pyrene	-138.72 ± 0.07	-92.04
1-Methylpyrene	-153.19 ± 0.08	-96.93
Benzo[*b*]naphto(2,3-D)thiophene	-161.97 ± 0.08	-131.81
Benzo[*a*]anthracene	-166.01 ± 0.09	-107.13
Chrysene	-167.91 ± 0.09	-107.13
Benzo[*b*]fluoranthene	-194.29 ± 0.10	-110.56
Benzo[*k*]fluoranthene	-195.63 ± 0.10	-110.56
Benzo[*e*]pyrene	-195.56 ± 0.10	-111.26
Benzo[*a*]pyrene	-195.91 ± 0.10	-111.26
Diphenylmethane	-98.27 ± 0.05	-106.95
p,*p*'-DDT	-185.30 ± 0.09	-149.59
Methylbehenate	-270.20 ± 0.12	-237.83

[a] ΔC_i values calculated from estimated values of $C_{P,G}$ by the method of Benson, Cruickshank *et al.* from ref. [42, 43] and $C_{P,L}$ by the method reported in ref. [44, 45].

The method suggested by Chickos and Acree assumed a linear temperature dependence by using constant and thus temperature independent heat capacity differences to extrapolate the values reported in [8, 9] from T_m = 398 K to 298.15 K (ΔH_i(298.15K) = ΔH_i(T_m) + ΔC_i[298.15-T_m]). Experimental heat capacities for liquids are available only for some compounds and gas phase heat capacities generally need to be estimated. A constant heat capacity (at 298.15 K) was estimated with group contribution methods from [42, 43] and [44, 45] for the gas and liquid phase, respectively. Shown in Table 7 are the experimental and estimated heat capacity differences for all compounds studied. Experimental heat capacity differences obtained in this study are however much lower than the estimated values (by −1.45 to –84.65 J/mol.K). The estimated heat capacity differences are probably more positive because gas phase heat capacities estimated for PAHs by the method of Benson *et al.* [43] are based on group contributions obtained from more volatile compounds (alkylated benzenes and biphenyl) compared to the

studied PAHs. Also, the group values used in the estimation of heat capacities for the liquid phase of PAHs for tertiary and (internal) quaternary aromatic sp^2 carbon atoms by the method of Chickos *et al.* [45] are based on mostly (alkylated) aromatic compounds with 6 to 14 carbon atoms or are based on tentative assignments only.

Therefore, the ΔH_i values determined in [8, 9] were extrapolated from 398 to 298.15 K with a temperature dependent heat capacity difference by adding the integral of the experimental ΔC_i values over this temperature range ($\Delta H_i(298.15K) = \Delta H_i(398K) + \int\Delta C_i dT$). Compared to values reported in [9], the ΔH_i values determined in this study are lower for nearly all compounds (by – 0.66 to –6.36 kJ/mol), except for benzo[*a*]anthracene and benzo[*k*]fluoranthene which are +1.37 and +0.94 kJ/mol higher. Comparison with ΔH_i values from Hinckley *et al.* [8] shows deviations of –3.14 to 0.44 kJ/mol, except for benzo[*a*]anthracene and benzo[*a*]pyrene which are 7.68 and 6.66 kJ/mol lower. A larger deviation exists for *p*,*p*'-DDT, which is 9.86 kJ/mol lower. Using a similar procedure for vaporization enthalpies obtained in this study by extrapolating from T = 398 K to 298.15 K resulted in increasingly higher ΔH_i values from naphthalene (+0.47 kJ/mol) to benzo[*a*]pyrene (+2.06 kJ/mol) compared to experimental ΔH_i values calculated at 298.15 K with Eqs (4) and (10) (data not shown). The ΔH_i values for two compounds, benzo[*a*]anthracene and *p*,*p*'-DDT, that showed the largest differences compared to values reported in [8] were additionally calculated by subtracting enthalpies of fusion (ΔH_{fus}) from enthalpies of sublimation (ΔH_{sub}). Literature values of ΔH_{sub} and ΔH_{fus} for benzo[*a*]anthracene (ΔH_{sub}, $n = 9$; ΔH_{fus}, $n = 1$) and *p*,*p*'-DDT (ΔH_{sub}, $n = 7$; ΔH_{fus}, $n = 1$) were taken from [16] and [46], respectively, and were adjusted to 298.15 K with equations (5) and (6) from [44] employing (constant) heat capacity corrections for the solid and liquid phase (estimated at 298.15 K). This resulted in ΔH_i values of 104.1 $\pm$ 7.9 and 97.4 $\pm$ 4.3 kJ/mol at 298.15 K for benzo[*a*]anthracene and *p*,*p*'-DDT, respectively, which showed a good agreement with the value determined in this study for *p*,*p*'- DDT. However, the uncertainties associated with these corrections by extrapolating from high temperatures to 298.15 K are still dependent on the use of constant heat capacities and the way they are derived as mentioned above.

A comparison with recommended values from literature was also performed (see Table 6). Naphthalene has been proposed as (secondary) reference material for thermochemical measurements based on various criteria in [15] and the recommended value for this compound is 4.67 kJ/mol lower than the experimentally determined value. Recommended values of ΔH_i for acenaphthene, dibenzothiophene, phenanthrene and pyrene from [2] at the triple point temperature deviate -1.21 to +4.26 kJ/mol from the experimental values at these temperatures. Only benzo[*a*]pyrene is 11.07 kJ/mol lower than the recommended value. Relatively small deviations in ΔH_i values of –1.01 and –0.11 kJ/mol were observed for diphenylmethane and methylbehenate compared to other GCVAP studies [6, 13]. The ΔH_i value of *p*,*p*'-DDT was 7.18 kJ/mol lower than the value reported in the GCVAP study of [12]. Also, ΔH_i values at 298.15 K for all compounds were estimated with a three-level calculation procedure from [41] that was based on a large database of 831 organic compounds (molecular mass range of 41 to 462 g/mol).

These values showed minimum and maximum deviations of –4.23 and +6.29 kJ/mol for benzo[*k*]fluoranthene and 1-methylnaphthalene, respectively (see Table 6). A reasonable good agreement was found with ΔH_i values determined for diphenylmethane (-1.49 kJ/mol), *p*,*p*'-DDT (+0.69 kJ/mol) and methylbehenate (+1.00 kJ/mol) compared to estimated values.

Conclusions

In this method, liquid vapour pressures have been determined for a large group of PAHs covering a wide range in hydrophobicity. A temperature and compound dependent correction was applied by calibrating the method to accurate literature values of effusion and gas saturation measurements. In previous GCVAP studies, differences in activity coefficients of test and reference compounds in the stationary phase were accounted for by including activity coefficient ratios of model compounds based on McReynold numbers [11]. These proposed activity coefficient ratios of a limited group of compounds introduces some uncertainties regarding the selection of the appropriate model compound and the temperature independence of the correction. The method used in this study has been improved compared to earlier studies by incorporating the logarithm of the activity coefficient ratio that is dependent on both temperature and number of carbon atoms. The obtained vapour pressures deviate –0.69 to 0.23 log units from other GC determined vapour pressures from literature [8, 9].

The first and second derivatives of the relationship of vapour pressure and temperature also results in temperature dependent values for the enthalpy of vaporization and the heat capacity difference between gas and liquid phase, that are not found in other methods employing GC retention times. Enthalpies of vaporization determined in this study deviate –7.68 to +1.37 kJ/mol from published values determined with GC [8, 9] that were extrapolated to 298.15 K by integrated experimental heat capacity differences. The heat capacity differences from this study are however much lower than estimated values as explained before.

Previously, improvements in GC measurements of vapour pressures of 32 plant volatiles including both terpenoids and more polar compounds were based on temperature dependent differences in ideal gas solubility of test and reference compounds that approximated the differences in the logarithm of activity coefficients at infinite dilution. These were calculated from normal boiling point data and values of the entropy of vaporization deduced from structural information such as the torsional bond number and number of polar groups capable of hydrogen bonding [47]. In a different approach, a temperature dependence of the logarithm of the activity coefficient ratio was derived from the Wilson mixing model in which temperature dependent molar volumes and vaporization enthalpies were included [48]. The determination of vapour pressure with GC based methods could be improved in this way by using temperature dependent structural information for other more structurally diverse compounds.

Acknowledgement

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