



Chapter 4

PHYSICO-CHEMICAL PROPERTIES OF COAL TAR COMPONENTS

INTRODUCTION

Compound properties

The global fate of compounds depends on their transport and general distribution, as well as their enrichment and transformation in a specific environmental compartment²⁵⁻²⁷. The environment is usually divided into the major compartments air, water, soil/sediment, biota, plants and particles, as illustrated in **Figure 2.1**. The knowledge of the physico-chemical parameters is necessary to forecast partitioning into the environment and for modeling the multiphase distribution. Mackay²⁸ used the fugacity approach (relative escaping tendency) to determine the favorite compartment of a compound. The most important physico-chemical properties that are relevant for environmental behavior, are vapor pressure (P^0_L), water solubility (S_w), octanol-water partition coefficient (K_{ow}) and sorption coefficient on soil/sediment (K_{oc}). The K_{ow} is a useful index of compound hydrophobicity, and $\text{Log } K_{ow}$ of PAHs reported in literature²⁶ ranges from 3.36 (naphthalene) to 6.50 (benzo[a]pyrene). This implies that the heavier PAHs (high $\text{Log } K_{ow}$) will partition strongly from water onto soil/sediments due to their low solubility in pure water. The water solubility and volatility of PAH compounds generally decrease with an increase in the number of rings and degree of alkylation. The tendency of a chemical to transfer to and from gaseous environment phases (e.g.

the atmosphere) is determined to a large extent by its P^0 . This property is critical for prediction of either the equilibrium distribution or the rates of exchange to and from natural waters. Even compounds with very low ambient P^0 are of environmental importance, as these same chemicals have low solubilities in water (high aqueous phase fugacities), and partition appreciably into the atmosphere. The chemical and physical properties of target analytes were hence investigated. The compounds, which occur in coal tar, have a low volatility (boiling points ranges between 200 and 400 °C) and experimental data on vapor pressures of compounds such as the alkyl-PAHs is very scarce.

Knowledge of the physico-chemical properties of target analytes is also important for the development of analytical methods. It is, for example, necessary to identify those components with a sufficiently high vapor pressure to be analysed in the headspace mode. Headspace sampling at room temperature is limited to substances with sufficient vapor pressures. Information of P^0 is useful to understand the behaviour of a given organic compound during the headspace sampling process and to predict the equilibrium distribution between the soil, air and a SPME fiber. Vapor pressure governs the vaporisation of the analyte from soil, and consequently the amount adsorbed onto the SPME fiber. Capillary GC has been reported^{26,29} as a



practical method to at least get a good estimate of vapor pressures of low volatility compounds, assuming the subcooled liquid $[P^0(L)]$, since the molecules are *dissolved* in the stationary phase. The vapor pressures of selected target analytes were determined using capillary GC.

EXPERIMENTAL

Standards

Chromatograms were obtained using the following certified petrochemical and PAH mixtures:

- Diesel Range Organic Mix, C₁₀ - C₂₅, Chem Service Inc.
- Petrochemical Calibration Mix, C₆ - C₄₄ Chem Service Inc
- TLC mixture, 2000 ppm each PAH standard, Supelco
- Coal tar sample

GC/MS analytical conditions

The Varian Saturn model 2000 GC/MS was operated under the conditions listed in **Chapter 3**.

Determination of vapor pressures

The Petrochemical Calibration Mixtures obtained from Chem Service Inc., containing n-alkanes from n-hexane (C₆) to n-tetratetracontane (C₄₄) were used as reference compounds with known vapor pressures to calibrate the GC. A high-resolution gas chromatograph equipped with a DB-5 non-polar stationary phase was used under the conditions as stated above. Chromatograms were obtained for the target analytes and the n-alkanes respectively to determine the retention time of each individual component at standard instrumental conditions. These retention times were used to determine the Kovats³⁰

retention index for each component, using the following equation:

$$RI = 100.n + 100.[t_R(x) - t_R(n)]/[t_R(n+1) - t_R(n)] \dots\dots 4.1$$

where:

RI = temperature programmed retention index

n = carbon number of n-alkane eluting before substance x

n+1 = carbon number of n-alkane eluting after substance x

t_R = retention time

Using the assumption that vapor pressure is proportional to the retention index the vapor pressures for the target analytes were calculated at 298 K by linear regression²⁹:

$$\log P_L^0 = a.RI + b \dots\dots\dots 4.2$$

RESULTS AND DISCUSSION

The results are presented in **Figure 4.1**, showing the linear regression data. The saturated vapor pressure of the PAHs, their alkylated homologous series and heterocyclic compounds are determined using the values in **Figure 4.1**. The results for the determined vapor pressures and the water solubilities obtained from literature are presented in **Table 4.1** and graphically presented in **Figures 4.2** and **4.3**. The P_L^0 values obtained (298 K) range from 2.0×10^{-3} mm Hg for indene to 9.0×10^{-19} mm Hg for benzo[ghi]perylene. The observed rules for the vapor pressure of coal tar components are:

- There is roughly between 1 and 4 orders of magnitude difference between the P_L^0 of 2 and 3 ring structures, and between 2 and 10 orders of magnitude difference between 3 and 4 ring structures.
- There is a trend in decreasing P_L^0 for each methylene group added

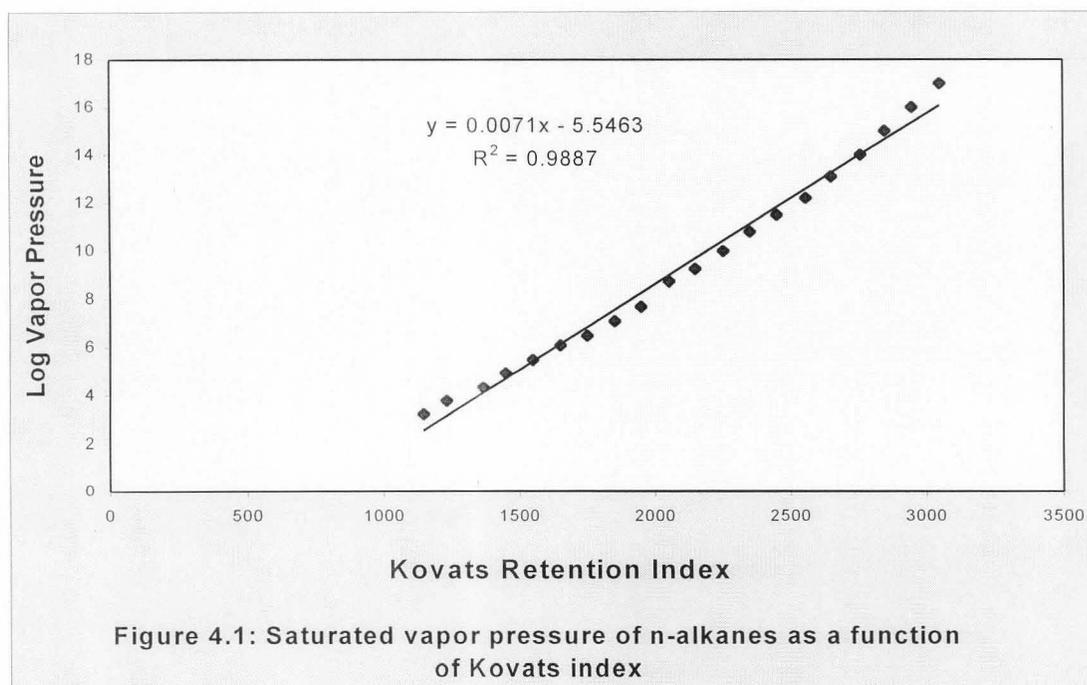


TABLE 4.1 : Physical-Chemical Properties of Selected Coal Tar Pollutants – P^0_L determined experimentally

No	COMPOUND	RINGS	KOVATS INDEX	Log P^0_L (mm Hg)	P^0_L (mm Hg)	Log Molar Solubilities ^a	S_w (mg/L)
1	Indene	1	1161	2.70	2.0E-03	-3.034	110
2	Naphthalene (N)	2	1255	3.36	4.3E-04	-3.606	32
3	2-Methyl naphthalene (C1-N)	2	1314	3.78	1.7E-04	-3.748	28
4	1-Methyl naphthalene (C1-N)	2	1330	3.90	1.3E-04	-3.705	25
5	Biphenyl (BP)	2	1397	4.38	4.2E-05	-4.345	6.6
6	1-ethyl-naphthalene (C2-N)	2	1413	4.49	3.3E-05	-4.162	10.7
7	1,3-dimethyl naphthalene (C2-N)	2	1458	4.81	1.6E-05	-4.292	8.0
8	1,5-dimethyl naphthalene (C2-N)	2	1425	4.57	2.7E-05	-4.679	3.3
9	2,3-dimethyl naphthalene (C2-N)	2	1438	4.66	2.2E-05	-4.716	3.0
10	2,6-dimethyl naphthalene (C2-N)	2	1443	4.70	2.0E-05	-4.888	2.0
11	1,2,5-trimethyl naphthalene (C3-N)	2	1556	5.50	3.2E-06	-4.923	2.0
12	Acenaphthylene (AC)	3	1470	4.89	1.3E-05	---	---
13	Acenaphthene (AE)	3	1503	5.13	7.5E-06	-4.594	3.9
14	Dibenzofuran (D1)	3	1537	5.37	4.3E-06	---	---
15	Fluorene (F)	3	1604	5.84	1.4E-06	-4.925	2.0
16	4-methyl dibenzofuran (C1-D1)	3	1639	6.09	8.1E-07	---	---
17	3,4-diethyl-1,1-biphenyl (C2-BP)	2	1692	6.47	3.4E-07	---	---
18	2-methyl fluorene (C1-F)	3	1720	6.67	2.2E-07	---	---
19	2-ethyl fluorene (C2-F)	3	1823	7.40	4.0E-08	---	---
20	Methyl-ethyl fluorene (C3-F)	3	1910	8.02	9.6E-09	---	---
21	Dibenzothiophene (D)	3	1775	7.06	8.7E-08	---	---
22	Phenanthrene (P)	3	1803	7.25	5.6E-08	-5.150	1.30
23	Anthracene (A)	3	1815	7.34	4.6E-08	-6.377	0.08
24	Fluoranthene (FL)	4	2084	9.25	5.7E-10	-5.898	0.26
25	Pyrene (PY)	4	2136	9.62	2.4E-10	-6.176	0.14
26	1,2-Benzanthracene (BA)	4	2476	12.03	9.3E-13	-7.214	0.017
27	Chrysene (C)	4	2486	12.10	7.9E-13	-8.057	0.002
28	3,4-Benzopyrene (BP)	5	2895	15.01	9.9E-16	-7.820	0.004
29	Benzo[k]fluoranthene (BK)	5	2780	14.19	6.4E-15	---	---
30	Dibenz[a,h]anthracene (DA)	5	3243	17.48	3.3E-18	---	---
31	Benzo[g,h,i]perylene (BP)	6	3323	18.05	9.0E-19	-9.018	0.0003
32	Indeno[1,2,3]perylene (IP)	6	3232	17.40	4.0E-18	---	---

^a - Data from Yalkowsky et. al.³¹

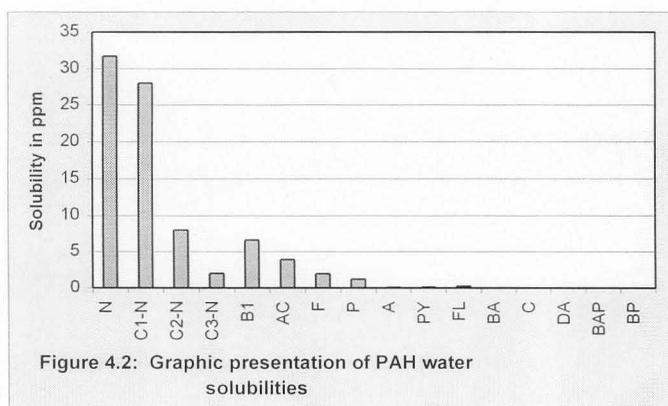


Figure 4.2: Graphic presentation of PAH water solubilities

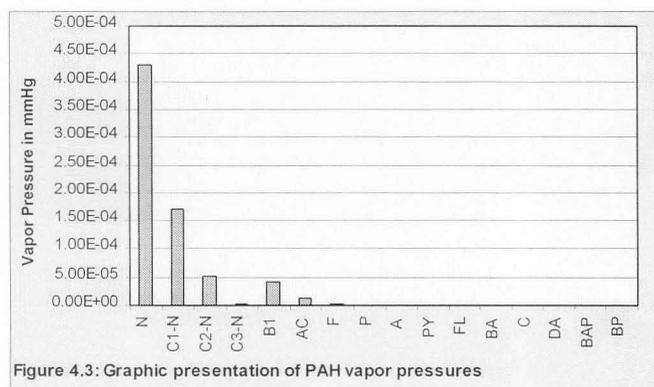


Figure 4.3: Graphic presentation of PAH vapor pressures

Compounds 1 - 25 have been identified as contaminants with sufficiently high vapor pressures to be analysed in the headspace mode using a SPME fiber. Of these compounds, pyrene has the lowest vapor pressure of 2.4×10^{-10} mm Hg, which also indicates a relatively low soil to air transfer potential. Compounds with a molecular weight lower than pyrene are of particular interest due to both their high groundwater and air transfer potentials. The conclusion was made that the SPME headspace technique is suitable for two- and three-ring, as well as selected four-ring polyaromatic and heterocyclic compounds.

The results in **Table 4.1** reveal that the 2-ring and some 3-ring PAHs have relatively

high solubilities in water ($\mu\text{g}/\text{cm}^3$ range). The solubilities dropped to the pg/cm^3 levels for 6-ring PAHs. A decrease in the solubility of alkylated compounds was also observed, which was proportional to the degree of alkylation. This is due to the fact that alkylated compounds are more hydrophobic than their corresponding parent compound. The occurrence of 5- to 6-ring PAHs in groundwater is, therefore, expected to be in the very low concentration range, especially those with a high degree of alkylation.

Environmental distribution and fate of PAHs

The environmental distribution and fate of PAHs depends on the physico-chemical properties as depicted in **Table 4.1**. Lower alkyl-PAHs possess greater P^0 (low fugacity in the gas phase) while those with a higher degree of alkylation are less soluble and more hydrophobic (high fugacity in aqueous solution). These differences will, therefore, govern the partitioning processes between soil, air and water. **Figure 4.4** is a diagram which tracks PAHs in the various compartments in the environment and their transfer between and dissipation within those compartments. This diagram shows that the PAHs can degrade (disappear) in many ways. During aerobic degradation bacteria break down PAHs while abiotic degradation involves the degradation without any contribution by animals, plants or microorganisms. Abiotic degradation includes photodegradation, oxidation, hydrolysis, evaporation or absorption.

Distribution and fate in soil/sediments

Due to their relative high water solubility, the lighter and lower alkyl-PAHs are expected to have a high convection into soils and sediments. The degree of transportation

will also depend on the presence of other organic matter or fluids, for example DNAPLs. The convection of PAHs will increase in the presence of co-contaminants with a higher solubility for PAHs than water, or with a high pH. Once dissolved into a DNAPL, the movement of the DNAPL will be mainly directed by gravity.

PAHs with a vapor pressure of $> 1E-10$ mm Hg.

PAHs normally dissolved in DNAPLs are in a relatively stable environment and may slowly decompose with photo chemical or biological processes or dissolve in surrounding groundwater. Larger PAHs and those with a higher degree of alkylation will have a lower rate of degradation. Photo oxidation will be restricted to the top layer of the soil, as sunlight cannot penetrate the deeper soil levels.

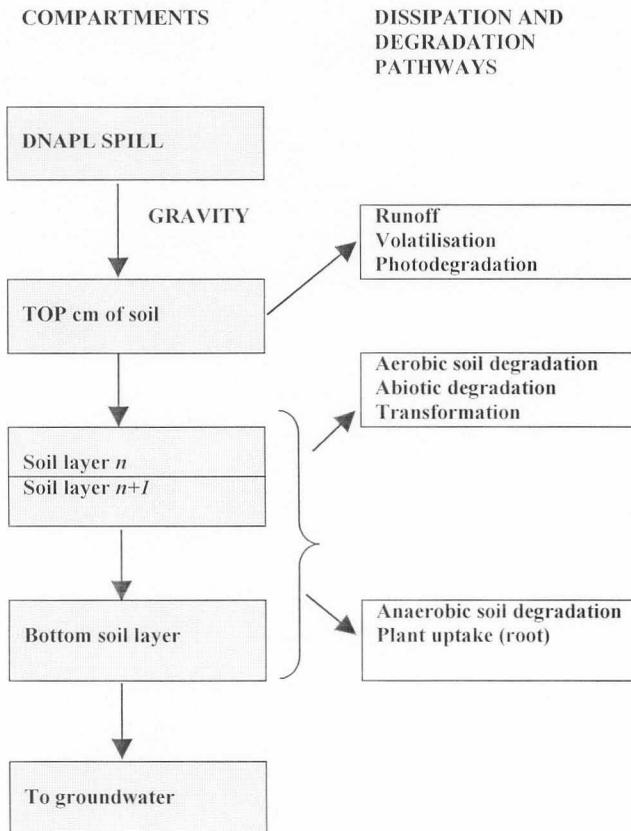


Figure 4.4: PAH environmental fate model

The heavier PAHs that are only sparingly soluble in water are expected to be more immobile, and will tend to remain on the surface, unless they move together with a DNAPL. Volatilisation from the soil surface may also occur, especially those

Distribution and fate in an aquatic environment

It is evident from **Table 4.1** that the heavy PAHs are highly insoluble in water. They will, however, dissolve into groundwater in sufficient proportions to pollute the groundwater beyond limits set by the USEPA. The solubility of benzo[a]pyrene (PAH reference compound) is 20 times the allowable concentration limit given by the USEPA. This indicates that even the smallest amount of DNAPL found in soils may contaminate the surrounding groundwater above the EPA standards. Due to the fact that the DNAPL density is greater than water, it will sink deep into the earth where it will deposit on an impermeable layer of soil or rock. Once dissolved, the most common mechanism for the removal of PAHs from water is the sorption to suspended matter or sediment. The concentration of the heavy PAHs are, therefore, normally higher in sediments than in the overlying water. Dissolved PAHs can also volatilise from surface water or decompose with photochemical reactions. They are, however, resistant towards chemical oxidation and hydrolysis.