

Diffusion Coefficients of Polychlorinated Biphenyls and Polycyclic Aromatic Hydrocarbons in Polydimethylsiloxane and Low-Density Polyethylene Polymers

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Received 20 March 2009; accepted 31 October 2009

DOI 10.1002/app.31704

Published online 5 January 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Diffusion coefficients (D) of polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) were determined by film-stacking technique in low-density polyethylene (LDPE) and two types of polydimethylsiloxane (PDMS) (also known as silicone rubber, SR) with the trade names AlteSilTM and Silastic[®]. The estimated values of D for PCBs and PAHs over a wide range of hydrophobicity were 2–2.5 orders of magnitude lower in LDPE than in SR polymers. Log D ($\text{m}^2 \text{s}^{-1}$) of PCBs ranged from -10.1 to -10.9 for SRs and from -12.4 to -13.7 for LDPE. For PAHs these ranges were -9.8 to -11.4 for SRs and -11.9 to -13.7 for LDPE. Compared with the D values calculated in water, D were 1–2 and 3–4 orders of magnitude lower in

SR and LDPE, respectively. For PAH molecules, D was lower than for PCBs with a similar molecular weight, probably because of their more rigid structure. The range of log D for PCBs in SR was only 0.5 log units (factor of 3.2) versus 1.2 log units (factor of 16) in LDPE. Although compound classes showed different relations, a linear relation of D with total surface area was the most universal. This relation may be used for prediction of D values in SR and LDPE polymers for other organic compounds. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 1803–1810, 2010

Key words: diffusion; molecular weight; passive sampling; silicone rubber; low-density polyethylene

INTRODUCTION

Properties of several polymers have allowed their successful application as a passive sampling material for uptake of organic environmental micropollutants. Passive sampling, involving the exposure of an organic polymer to water, sediment, soil, air, or other media has become a powerful tool for detecting environmental contaminants.¹ The driving force for the uptake of the analyte by the polymer sampler is the chemical activity gradient between the polymer and the sampled medium. During continued exposure, the analyte concentration increases in the sampler until equilibrium is reached. The application of polymers as passive sampling devices for monitoring the concentrations of hydrophobic organic contaminants (HOCs) requires data on diffusion coefficients (D) for the estimation of uptake rates. The D in polymers are directly proportional to the mass transfer coefficients and consequently to the sampling rates.² A low value of D in a polymer

tends to reduce the uptake rate, and therefore, the sampling rates. Diffusion in the polymer sampler should, preferably, not be a limiting factor in equilibrium passive sampling.

Transport of substances inside polymers depends on a number of factors, including the free volume within the polymer and the segmental mobility of the polymer chains. The glass transition temperature (T_g) of a polymer characterizes these properties. Polymers of low T_g have higher diffusivity. For instance, it is known that silicon rubber polymers have the lowest T_g and the highest permeability for gases and organic compounds in comparison with other polymers.^{3,4} The nature of the diffusant affects the rate of transport within a polymer. A decrease of diffusion coefficient with increasing molecular weight (M) and molecular size has been reported by several researchers. In general, linear, flexible, and symmetrical molecules have higher mobility than rigid molecules and penetrate polymers more quickly.^{5–9}

Various free volume theories are proposed to predict diffusion behavior of substances in polymers over wide ranges of temperature and concentration.^{10,11} However, they require accurate estimates of the free volume parameters of both the polymer and the substance. Data of these parameters are available

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for a limited amount of substances and often cannot be determined with sufficient accuracy. Some of the problems associated with the determination of these parameters have been discussed by Kreituss and Frisch.¹²

Direct methods to measure D were applied by Dubini et al.¹³ and Cicchetti et al.¹⁴ A compound was allowed to diffuse in a thick polymer sample, which after a set time was cut into thin slices. The measured concentration profile of diffusing molecules was used to calculate D . Roe et al.¹⁵ applied a similar method, called "film-staking method" determining D of antioxidants (M 220–1180) in low-density polyethylene (LDPE). A stack of LDPE films was positioned between two thicker LDPE films, containing an excess amount of antioxidant. After a certain contact time, each individual film was analyzed by the thermogravimetric method and D was calculated from the concentration profile.

The target compounds in this work are polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) for which the free volume parameters are not available or not simple to determine because of their toxic character. Therefore, in this study, a modified film-stacking method¹⁵ is applied to measure D in LDPE and two different types of polydimethylsiloxane (PDMS) or silicone rubber (SR) polymers with trade names AlteSilTM and Silastic[®]. These polymers are widely used in passive sampling.^{16,17} The specific effect of compound properties on D was assessed using two sets of chemicals, PCBs and PAHs, which cover wide range of hydrophobicity. The aim of the study was determination of D in the polymers to support the study of the uptake processes in passive sampling. The other target was to establish a relation of D with the compound properties to allow prediction of D values for compounds not covered in this study.

EXPERIMENTAL

Materials

Standards of 16 PAHs and a number of their deuterated analogues ($d10$ -acenaphthene, $d10$ -anthracene, $d12$ -benzo(e)pyrene, $d12$ -chrysene, $d12$ -coronene, $d10$ -phenanthrene, $d10$ -fluorene, $d10$ -fluoranthene, $d8$ -naphthalene, $d12$ -perylene, and $d10$ -pyrene) were obtained from Boom BV, Meppel, The Netherlands. The industrial PCB Clophen A50 mixture was purchased from Dr. Ehrenstorfer, Augsburg, Germany and individual PCB congeners (PCB 4, PCB 14, PCB 29, PCB 30, PCB 50, PCB 104, PCB 143, PCB 145, PCB 155, and PCB 204) were obtained from Boom BV, Meppel, The Netherlands. PCB 143 served as an internal standard for the quantitative analysis. All solvents were pesticide grade or equivalent (Boom BV, Meppel, The Netherlands). Silicone rubber sheets (AlteSilTM translucent material) with 0.5 mm thickness were purchased from Altec, UK. Silastic[®] Medical Adhesive Silicone (Dow Corning, USA) was used to make the polymerized SR sheet material of 0.3-mm thickness. LDPE of 0.07 mm thickness was obtained from Brentwood Plastics, Brentwood, MO. Some properties and the structures of used polymers are collected in Table I.

Methods

The Silastic[®] Medical Adhesive Silicone, referred to below as Silastic, was supplied as a paste, and was used to prepare sheets by spreading the paste on 0.12-mm thick polyethylene sheet between two spacers of 0.25 mm. Then, the rubber was covered with a second layer of polyethylene and using a metal roller, it was spread to form a layer limited by the spacer. It was covered with a wet tissue and a glass plate, and allowed to cure for a week. Before experiments, polymers were cut into sheets of $6.2 \times 1.5 \text{ cm}^2$ for Altesil, $3.3 \times 2.9 \text{ cm}^2$ for Silastic, and

TABLE I
Polymer Properties

Polymer	Thickness (mm)	Density (g cm ⁻³)	T_g (°C)	Melting point (°C)	Structure	Supplier
AlteSil TM translucent SR	0.5 ± 0.05	1.15 ± 0.03	~ -125	>230	$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{---}[\text{O}-\text{Si}-\text{O}-\text{Si}-\text{O}]_n\text{---} \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$	Altecweb, UK
Silastic [®] SR	0.3 ± 0.05	1.06 ± 0.03	~ -125	>230	$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{---}[\text{O}-\text{Si}-\text{O}-\text{Si}-\text{O}]_n\text{---} \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$	Dow Corning, USA
LDPE	0.07 ± 0.005	0.91 ± 0.03	~ -120	120	$\text{---}[\text{CH}_2\text{---CH}_2]_n\text{---}$	Brentwood Plastics, Brentwood, MO

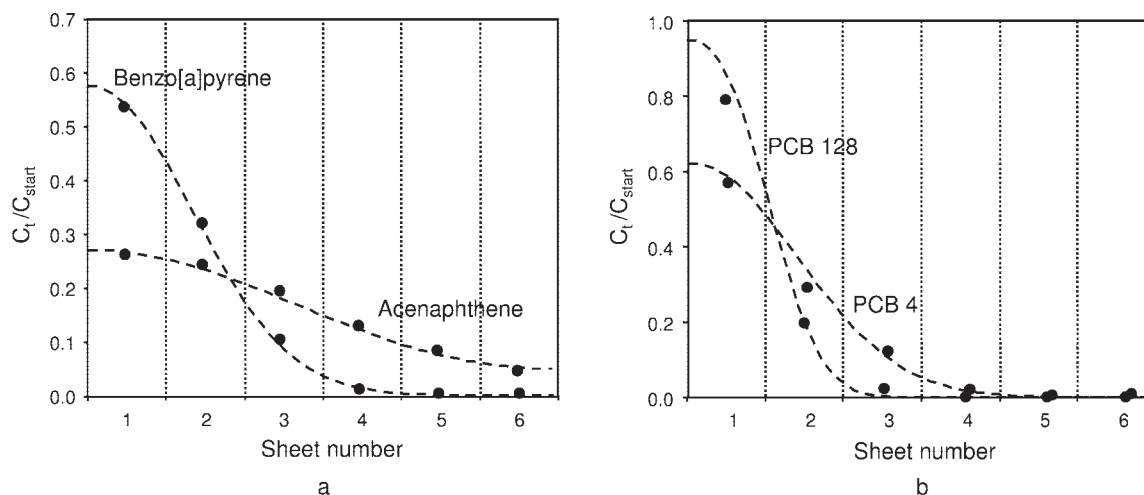


Figure 1 Measured (●) and fitted (---) concentration profile for acenaphthene, benzo[a]pyrene in Altesil polymer (a) and for PCB 4, PCB 128 in LDPE (b). Concentration at time t is plotted relative to start concentration at time zero.

$13.5 \times 2.6 \text{ cm}^2$ for LDPE. Altesil and Silastic were pre-extracted in Soxhlet apparatus for 3 days using ethyl acetate, and further shaken in methanol for 1 day to remove oligomers and other impurities.⁴ The procedure was identical for LDPE except that the extraction was performed at room temperature to avoid decomposition of the polymer. Two or three sheets of each material were spiked with the PCB and PAH standard mixtures. The spiking was done as described by Booij et al.,¹⁸ with a final concentration of 30% (v/v) methanol in the methanol-water mixture.

Five unspiked pre-extracted sheets were stacked with one spiked sheet on top, and positioned between two wooden boards covered with aluminum foil tape. The stack was compressed with a clamp, resulting in a pressure of $0.5\text{--}1 \text{ kg cm}^{-2}$. The stacks of sheets were wrapped in aluminum foil to prevent evaporation of the compounds. Contact periods for Altesil and Silastic were 3.83 and 2.92 h, respectively. Two exposure experiments were carried out with LDPE: 3.08 h (short) and 37.75 h (long). The contact time was selected based on the thickness of the sheets and previous measurements of diffusion coefficients.⁴ After the selected contact period, the sheets were separated and individually Soxhlet extracted in methanol. The extracts were Kuderna-Danish concentrated to 1 mL and solvent exchanged to hexane (15 mL of hexane was added and the solution was concentrated in a Kuderna-Danish apparatus to $\sim 1.5\text{--}2 \text{ mL}$). The final extract in hexane was reduced to 1 mL under gentle stream of N_2 . Afterward, 200 ng of the internal standard PCB143 was added to the concentrated extracts. Analysis was performed using a gas chromatograph coupled to a mass spectrometer (GC/MS: HP 6890-

HP 5972) in selective ion mode using electron impact ionization. The GC was equipped with a fused silica column (60 m, 0.25 mm i.d.) coated with 0.25- μm film of a stationary phase (5% phenyl, 95% methylpolysiloxane, J&W Scientific, Folsom, CA), using He as a carrier gas. Samples (1 μL) were injected in a splitless mode with the injector temperature set to 250°C . The temperature program started at 80°C , held for 1 min, raised to 180°C at $15^\circ\text{C min}^{-1}$, and to 300°C at 5°C min^{-1} , with a final hold of 20 min at 300°C .

The diffusion coefficient of a penetrant in a polymer was calculated using Fick's second law.

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (1)$$

where D is the diffusion coefficient inside the polymer, C is the concentration of diffusing substance at distance x from the reference point, and t is the diffusion time. The equation was solved by numerical integration using the Schmidt approximation method with the appropriate boundary condition ($dC/dx = 0$) at the two impermeable walls on both sides of polymer stacks.¹⁹ To increase the precision of estimation of D each polymer sheet was subdivided into 10 slices. D was estimated by locating the minimum in the sum-squared residual differences between measured and modeled concentrations. A few examples of the fitting of modeled to experimental values for Altesil and LDPE is shown in Figure 1.

The short and long exposure experiments for LDPE were chosen for more accurate determination of high and low D . For compounds of intermediate D , the results were compared for repeatability and averaged. The repeatability estimated from these

TABLE II
Physicochemical Properties and Measured Diffusion Coefficients

No.	Compound	CI No.	M (g mol ⁻¹)	V_{Lebas} (cm ³ mol ⁻¹)	TSA ^{a,b} (Å)	log D (m ² s ⁻¹ at 20°C)		
						Altesil	Silastic	LDPE
1	HCB	6	284.8			-10.12	^c	-12.68
2	PCB4	2	223.1	226.4	200.80	-10.27	-10.53	-12.53
3	PCB14	2	223.1	226.4	219.47	^c		-12.42
4	PCB18	3	257.5	247.3	218.32	-10.24	^d	-12.68
5	PCB28	3	257.5	247.3	230.83	-10.13	^d	-12.51
6	PCB29	3	257.5	247.3	228.74	^c	^c	-12.56
7	PCB30	3	257.5	247.3	224.16	^c	^c	-12.64
8	PCB31	3	257.5	247.3	230.66	-10.22	^d	-12.57
9	PCB44	4	292.0	268.2	233.21	-10.48	-10.66	-12.86
10	PCB47	4	292.0	268.2	236.19	-10.37	-10.32	-12.84
11	PCB49	4	292.0	268.2	236.01	-10.42	-10.57	-12.85
12	PCB50	4	292.0	268.2	229.51	^c	^c	-12.91
13	PCB52	4	292.0	268.2	235.84	-10.44	-10.66	-12.88
14	PCB56	4	292.0	268.2	243.63	-10.48	-10.51	-12.81
15	PCB66	4	292.0	268.2	246.44	-10.46	-10.48	-12.75
16	PCB74	4	292.0	268.2	246.43	-10.40	-10.49	-12.91
17	PCB85	5	326.4	289.1	249.16	-10.51	-10.74	-12.99
18	PCB87	5	326.4	289.1	248.99	-10.55	-10.77	-13.03
19	PCB97	5	326.4	289.1	248.99	-10.53	-10.76	-13.02
20	PCB99	5	326.4	289.1	251.79	-10.49	-10.71	-13.03
21	PCB101	5	326.4	289.1	251.62	-10.52	-10.68	-13.06
22	PCB104	5	326.4	289.1	234.87	^c	^c	-13.04
23	PCB105	5	326.4	289.1	259.41	-10.50	-10.74	-13.02
24	PCB110	5	326.4	289.1	254.65	-10.51	-10.74	-13.04
25	PCB118	5	326.4	289.1	262.04	-10.55	-10.73	-13.05
26	PCB128	6	360.9	310.0	262.13	-10.64	-10.87	-13.25
27	PCB137	6	360.9	310.0	264.76	-10.58	-10.77	-13.28
28	PCB138	6	360.9	310.0	264.76	-10.59	-10.77	-13.28
29	PCB141	6	360.9	310.0	264.59	-10.61	-10.72	-13.29
30	PCB145	6	360.9	310.0	247.84	^c	^c	-13.22
31	PCB149	6	360.9	310.0	260.00	-10.53	-10.71	-13.25
32	PCB151	6	360.9	310.0	259.12	-10.51	-10.64	-13.26
33	PCB153	6	360.9	310.0	267.39	-10.57	-10.71	-13.28
34	PCB155	6	360.9	310.0	252.56	-10.45	-10.72	-13.24
35	PCB156	6	360.9	310.0	275.01	-10.60	-10.78	-13.34
36	PCB170	7	395.3	330.9	277.74	-10.64	-10.87	-13.56
37	PCB180	7	395.3	330.9	280.37	-10.62	-10.76	-13.57
38	PCB187	7	395.3	330.9	274.89	-10.57	-10.73	-13.50
39	PCB194	8	429.8	351.8	293.34	-10.73	^c	-13.71
40	PCB204	8	429.8	351.8	278.50	-10.52	-10.78	-13.68
41	Acenaphthene		154.2	173	180.80	-10.04	-10.26	-12.36
42	<i>d</i> 10-Acenaphthene		164.2			-10.05	-10.29	-12.34
43	Acenaphthylene		152.2	165.7	193.60	-10.07	-10.29	-12.26
44	Anthracene		178.2	197	202.20	-10.18	-10.43	-12.36
45	<i>d</i> 10-Anthracene		188.2			-10.24	-10.44	-12.37
46	Benz[a]anthracene		228.3	248	244.30	-10.61	-10.88	-13.28
47	Benzo[a]pyrene		252.3	263	256.00	-10.77	-11.07	-13.72
48	Benzo[b]fluoranthene + benzo[k]fluoranthene		252.3	268.9	266.00	-10.79	-11.07	-13.70
49	<i>d</i> 12-Benzo[e]pyrene		264.3			^c	^c	-13.69
50	Benzo[ghi]perylene		276.3	277.5	266.90	-10.92	-11.18	-13.75
51	Chrysene		228.3	251	241.00	-10.61	-10.84	-13.28
52	<i>d</i> 12-Chrysene		240.3			-10.60	-10.88	-13.30
53	<i>d</i> 12-Coronene		312.3			-11.03	-11.44	^f
54	Dibenz[a,h]anthracene		278.3	300	286.50	-10.98	-11.37	-13.69
55	Phenanthrene		178.2	199	198.00	-10.18	-10.37	-12.45
56	<i>d</i> 10-Phenanthrene		188.2			-10.24	-10.45	-12.38
57	Fluorene		166.2	188	194.00	-10.06	-10.28	-12.29
58	<i>d</i> 10-Fluorene		176.2			^c	^c	-12.09
59	Fluoranthene		202.3	217	218.00	-10.40	-10.62	-12.70
60	<i>d</i> 10-Fluoranthene		212.3			^c	^c	-12.75

TABLE II. Continued

No.	Compound	Cl No.	M (g mol ⁻¹)	V_{Lebas} (cm ³ mol ⁻¹)	TSA ^{a,b} (Å)	log D (m ² s ⁻¹ at 20°C)		
						Altesil	Silastic	LDPE
61	Indeno[1,2,3-cd]pyrene		276.3	283.5		-10.94	-11.29	-13.70
62	Naphthalene		128.2	147.6	155.80	^d	^d	-11.88
63	<i>d</i> 8-Naphthalene		136.2			-9.82	^d	-11.90
64	<i>d</i> 12-Perylene		264.3			-10.73	-10.90	-13.74
65	Pyrene		202.3	214	213.00	-10.40	-10.62	-12.82
66	<i>d</i> 10-Pyrene		212.3	173		-10.44	-10.68	-12.85

^a TSA values and chemical structures for PAHs from Dabestani and Ivanov.²¹

^b TSA values for PCBs from Hawker and Connell²⁵ and chemical structures from Jäntschi et al.²²

^c Compound not included in spike mixture.

^d Insufficient concentration gradient between sheets for accurate estimation of D value.

experiments was within 0.1 log units. The criteria for including the value in the final result was the ratio between the concentration in the second (C_2) and the first sheet (C_1). For fast diffusion, where the ratio C_2/C_1 was higher than 0.8, i.e., the concentrations in sheets were close to equal, the concentration gradient was not large enough for accurate estimation of the D . In case of slow diffusion where the ratio C_2/C_1 was less than 0.2, i.e., insufficient amount of analyte has diffused in the second sheet, it was not possible to estimate D accurately. In such situations, correlation coefficients (R^2) between measured and predicted values were generally low ($R^2 < 0.5$). Therefore, the results of short exposure were used for high-diffusive substances and the results of long exposure for substances with low D , and data were accepted where $R^2 > 0.9$.

RESULTS AND DISCUSSION

Relation of molecular weights with diffusion coefficients

Estimated diffusion coefficients for PCBs and PAHs in three polymers are presented in Table II, together with some of their physicochemical properties. log D decreases with increasing M (Fig. 2), which is not unexpected as larger molecules tend to diffuse more slowly than small molecules. Significant log D - M correlations were found for all the tested polymers (Table III). Compared with D values in water calculated from M following Schwarzenbach et al.²⁰ relation (upper-dotted line in Fig. 2), D values were only factor 10–100 lower in SR, but factor 1000–10,000 lower in LDPE. Since the D values in LDPE were generally 2–2.5 orders of magnitude lower, the slopes were steeper than for SR polymer.

For all the tested polymers, the slope for PAH molecules was three to four times steeper than for PCBs, indicating that D is affected by compound structure (chemical structures for PAHs are available

from Dabestani and Ivanov,²¹ and for PCBs from Jäntschi et al.²²). PAH molecules having fused adjacent rings are compounds of rigid planar structure. Therefore, they diffuse more slowly than more elongated diffusants of the same M with greater conformational freedom.^{5,6,23} The limited effect of M of PCBs on diffusion resulted in the very low slopes, which were three times lower for Altesil and Silastic polymers than for LDPE. Strong relations of log D with M were found for all polymers however they were very different for PCBs and PAHs confirming that the different nature of organic compounds affects the diffusion in the polymers. Therefore, prediction of D within a single group is very well possible with high precision (Table III). However, no meaningful common relation with M can be derived that would allow reliable prediction for D values of

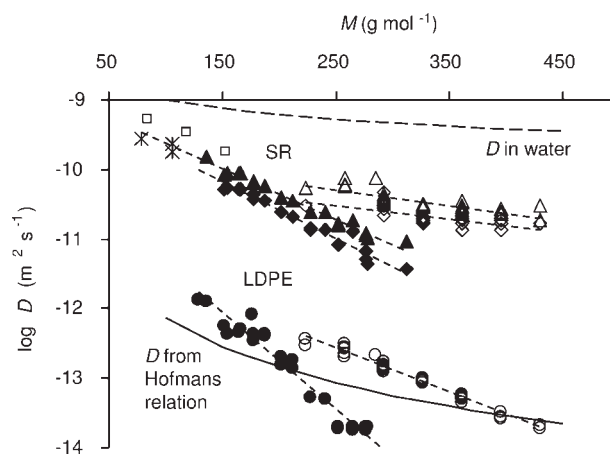


Figure 2 Plot of log D versus M for Altesil, Silastic, and LDPE polymers. Open symbols stand for PCBs, filled symbols for PAHs; \triangle , \blacktriangle , Altesil; \diamond , \blacklozenge , Silastic; \circ , \bullet , LDPE. Asterisks represent the D values measured in SR by Guo et al.²⁶ for benzene, *p*-xylene, and *o*-xylene and open squares represent chlorinated methanes. The upper dashed line represents D values in water calculated by the relation proposed by Schwarzenbach et al.²⁰ The solid curved line represents D values using Hofmans²⁴ relation.

TABLE III
Regression Parameters of log D - M Relations

Polymer	a^a	b^a	R^2	s_e	n
Altesil					
PCB	-0.0022 (± 0.0003)	-9.77 (± 0.09)	0.70	0.07	33
PAH	-0.0072 (± 0.0003)	-8.90 (± 0.06)	0.98	0.06	22
Silastic					
PCB	-0.0020 (± 0.0004)	-10.02 (± 0.13)	0.49	0.09	29
PAH	-0.0080 (± 0.0004)	-8.99 (± 0.08)	0.96	0.07	21
LDPE					
PCB	-0.0063 (± 0.0002)	-11.00 (± 0.05)	0.98	0.05	39
PAH	-0.0137 (± 0.0007)	-10.01 (± 0.15)	0.95	0.16	25

^a The standard error is given between brackets.

compounds not belonging to either group. An attempt for such a relation for LDPE was derived by Hofmans²⁴ from different classes of organic compounds and M ranging from 55 to 655.

$$\log D_{LDPE} = -2.33 \log M - 7.47 \quad (2)$$

$$n = 42, s_e = 0.44$$

The relation of Hofmans, plotted versus M in Figure 2, intercepts with relations for both PAHs and PCBs. Taking into account rather large standard error (0.44) of the Hofmans relation, all the experimental data from this work fall inside the confidence range ($2s_e$). It should be noted that the relation of Hofmans has a form of $\log D$ - $\log M$. For all three polymers tested, our data demonstrated better correlations using a $\log D$ - M instead of a $\log D$ - $\log M$ relation.

For a few compounds, diffusion coefficients in SR were found in the literature. Guo et al.²⁶ published D values for two different classes of organic solvents: Chlorinated methanes and one-ring aromatic compounds. Taking M into account the rate of diffusion was found to be higher for chlorinated methanes compared with aromatic compounds (Fig. 2). One-ring aromatic compounds including benzene, *p*-xylene, and *o*-xylene fall close to the extrapolated $\log D$ - M relation of PAHs in this study.

Concerning the different slopes for PCBs and PAHs, it can be noted that both predict the same D value for biphenyl (a compound that belongs to both homologue groups) as the lines for PCBs and PAHs intersect around the M of biphenyl (154.2).

Relation of total surface area with diffusion coefficients

The relations between $\log D$ and M above show that M is not a universal parameter to predict the diffusion over different compound classes. Alternatively, the Lebas molar volume could be used but within one compound group this parameter is proportional

to M . Plotting Lebas volume versus D values (not shown) also gave a compound specific relation. Instead another measure of molecular size, the total surface areas (TSA) of PAHs²¹ and PCBs²⁵ were related to $\log D$. The $\log D$ -TSA relations shown in Figure 3 are less compound specific than the $\log D$ - M relations. In LDPE, the slopes and intercepts for PCBs and PAHs are not significantly different (Table IV). Thus, they were averaged and a mutual $\log D$ -TSA relation was derived:

$$\log D_{LDPE} = -0.016 \text{ TSA} - 9.19 \quad (3)$$

$$s_e = 0.20, R^2 = 0.84, n = 53$$

The diffusion behavior of PCBs and PAHs in the two SR polymers is similar. Nevertheless, the slopes and intercepts for these two classes of organic compounds are significantly different from each other (Table IV). However, ignoring the significant difference and combining PCB and PAH data for Altesil

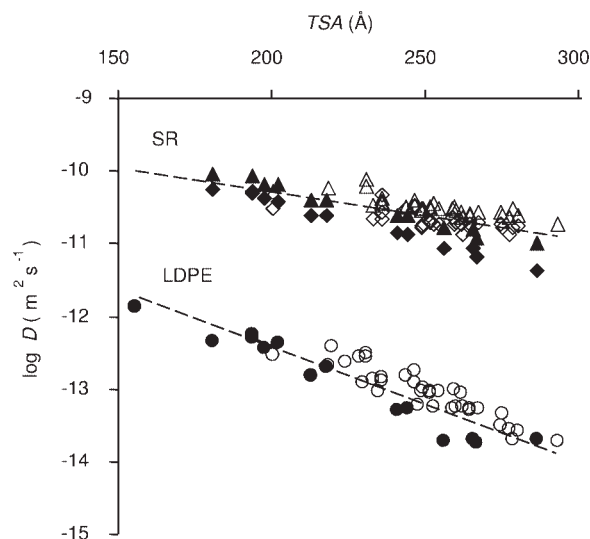


Figure 3 Log D plotted versus TSA for Altesil, Silastic, and LDPE polymers. Open symbols stand for PCBs, filled symbols for PAHs; \triangle , \blacktriangle , Altesil; \diamond , \blacklozenge , Silastic; \circ , \bullet , LDPE.

TABLE IV
Regression Parameters of log *D*–TSA Relations

Polymer	<i>a</i> ^a	<i>b</i> ^a	<i>R</i> ²	<i>s</i> _e	<i>n</i>
Altesil					
PCB	−0.0057 (±0.0006)	−9.05 (±0.16)	0.72	0.07	33
PAH	−0.0098 (±0.0004)	−8.22 (±0.10)	0.98	0.05	14
Silastic					
PCB	−0.0048 (±0.0011)	−9.47 (±0.27)	0.43	0.10	29
PAH	−0.0110 (±0.0004)	−8.21 (±0.09)	0.99	0.05	14
LDPE					
PCB	−0.0154 (±0.0010)	−9.21 (±0.26)	0.85	0.13	39
PAH	−0.0168 (±0.0012)	−9.16 (±0.26)	0.95	0.16	14

^a The standard error is given between brackets.

and Silastic polymers the following relation is obtained for SR:

$$\log D_{\text{SR}} = -0.0066 \text{ TSA} - 8.96 \quad (4)$$

$$s_e = 0.17, R^2 = 0.52, n = 90$$

This relation has even a slightly lower standard error (0.17) than obtained for LDPE (0.20), where compound classes did not show significantly different regression parameters. For both polymer relations, eqs. (3) and (4) have a quite acceptable standard error for prediction of log *D* values over different classes of organic compounds.

Effect of position of chlorine atoms on diffusion coefficients

In addition to finding general relations from which to predict values of *D*, it is also interesting to see if observed differences in *D* can be explained by structural differences within one compound class. The effect on log *D* of chlorine atoms in PCB congeners was determined separately for the ortho, meta, and para positions by multiple regression of the form:

$$\log D = a_1 n \text{Cl}_{\text{ortho}} + a_2 n \text{Cl}_{\text{meta}} + a_3 n \text{Cl}_{\text{para}} + b \quad (5)$$

in which the intercept *b* is essentially the log *D* of the biphenyl molecule.

The results of multiple regression are presented in Figure 4 as an average decrease in log *D*, starting from biphenyl molecule, per chlorine atom in ortho, meta, or para positions, respectively. Chlorine substitution in ortho and para positions had lower effect on log *D* values than chlorine atoms substituted in meta position. The latter had the largest effect on reduction of log *D* values for all the tested polymers. Chlorine atoms in the meta positions increase the di-

ameter of a molecule, and thereby may reduce the rate of diffusion inside the polymer.

CONCLUSIONS

The estimated *D* values for PCBs and PAHs in LDPE and SR were related to compound properties and structure. For both polymer types, the log *D*–*M* relation was compound specific. The downward linear log *D*–TSA relations were more universal and may allow prediction of log *D* values for other classes of compounds in SR and LDPE with a predictive capability (standard error) of 0.17 and 0.2, respectively. The *D* decreases in the following order: water > SR > LDPE and the slopes log *D*–*M* were steeper in the same order. Concerning molecular structure molecules with larger size and less flexible diffused slower in the polymers.

Finally, it can be concluded that maximum *D* values were observed for SR polymers making it an optimal polymer for fast uptake of HOCs in equilibrium passive sampling. The available *D* values will support evaluation of uptake process in passive sampling and allow to estimate in which

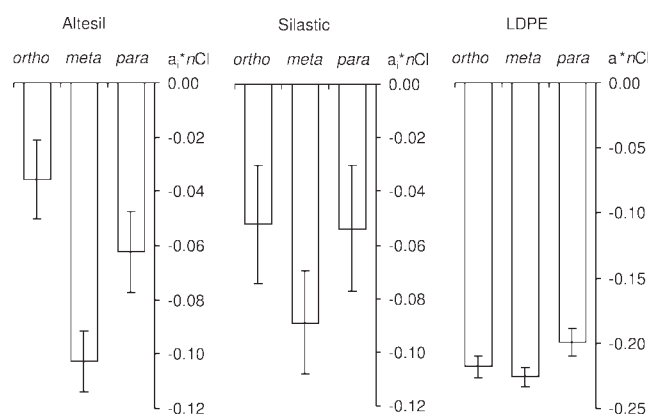


Figure 4 Contribution of chlorine atoms in ortho, meta, and para positions to the decrease of log *D*. Error bars indicate the standard deviation of estimated values.

cases the transport in the polymer will control the uptake.

The authors thank Ton van der Zande for contribution in practical work.

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