PHYSICAL-CHEMICAL PROPERTIES OF THREE CONGENERIC SERIES OF CHLORINATED AROMATIC HYDROCARBONS

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ABSTRACT

It is suggested that when assessing the environmental fate or toxicity of organic chemicals, especially those of congeneric series, such as PCBs, it is useful to gather and critically review their basic properties including solubility, vapour pressure, octanol/water partition coefficient and Henry's law constant. This approach is illustrated for three series of chemicals, the chlorobenzenes, the polychlorinated biphenyls and the chlorinated dibenzo-p-dioxins.

KEYWORDS

Chlorinated aromatic hydrocarbons, congeneric series, chlorobenzenes (CBs), polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins (PCDDs), solubility, vapour pressure, octanol/water partition coefficient, Henry's law constants, correlations, chlorine number, molar volume.

INTRODUCTION

Accurate values of the physical-chemical properties of chemicals are essential for estimating environmental behaviour and for assembling quantitative structure-activity relationships (QSARs). Each chemical has a set of partitioning, reaction and transport properties controlling partitioning and migration between air, water, soils, sediments and biota, as well as within organisms, and between blood and various tissues, including, it can be presumed, the target tissue at which the toxic effect(s) are manifested. In view of the large number of organic chemicals released into the enviroment, it is essential to build up a predictive capability in which the behaviour and effects of one chemical can be deduced from those of structurally similar chemicals. These deductions are the subject of the chapters in this text.

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One often neglected aspect of this issue is the acquisition and treatment of the basic physical-chemical data. In this chapter we review the relationships between physical-chemical properties and suggest methods of treating data of congeneric series using as examples the chlorobenzenes (CBs), polychlorinated biphenyls (PCBs) and polychlorinated dibenzo-p-dioxins (PCDDs).

It transpires that chemicals partition between five basic media, and it is the relative extent of partitioning which controls environmental and pharmacokinetic fate. These media are as follows.

Air: Obviously, more volatile chemicals such as halo-methanes will partition primarily into air because of their high vapour pressure. Indeed, vapour pressure is really "solubility in air" in disguise. The common vapour pressure P^S (superscript S designating saturation or maximum value) being convertible into a concentration by dividing P^S by the gas constant temperature product RT.

Water: Water soluble chemicals such as phenols or linear alcohols tend to remain primarily in aqueous solution. In many cases they may dissociate to ionic forms thus further increasing their solubility.

Organic Media: Many hydrophobic, low vapour pressure chemicals (e.g., PCBs) partition primarily into organic media such as natural organic carbon of ligneous origin, lipids or fat. Such chemicals often display large bioconcentration factors and long retention in fatty tissues. Octanol is the most common surrogate phase for laboratory determinations of partitioning tendency into organic media. Rarely are solubilities in organic media measured; usually concentration ratios such as octanol/water partition coefficients (K_{OW}) are employed. There may not be a true solubility of, for example, benzene in octanol because the liquids are miscible, but a "pseudo-solubility" can be deduced if it is assumed that K_{OW} is the ratio of the pseudo-solubility in octanol Q to water solubility C^S. Q is thus the product $K_{OW}C^S$ and shows remarkable constancy at 200 to 3000 mol·m^{-3} (Miller et al. 1985).

Mineral Surfaces: These surfaces tend to be relatively unimportant for organic chemical sorption especially when competing organic media are also present. Indeed it is suspected that in many situations natural mineral surfaces become rapidly coated with organic matter. We ignore this medium.

Pure Phase: Some solid organic chemicals of very high molecular weight including polymers, certain hydrocarbons and some dyes have negligible solubilities in air, water and organic media and thus tend to remain in their pure phases as shown in FIGURE 1. As the amount of chemical is increased, the concentrations in each phase tend to increase linearly maintaining a constant ratio or partition coefficient to each other. At saturation, or the

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solubility limit, any extra chemical added forms a new pure phase. It is convenient to express these tendencies as solubilities in air, water and organic media, from which the various partition coefficients can be deduced. In principle "solubilities" can also be deduced for tissues such as muscle and liver. A chemical's three key environmental solubilities are those in air, in water and in octanol, i.e., the $K_{OW}C^S$ product.
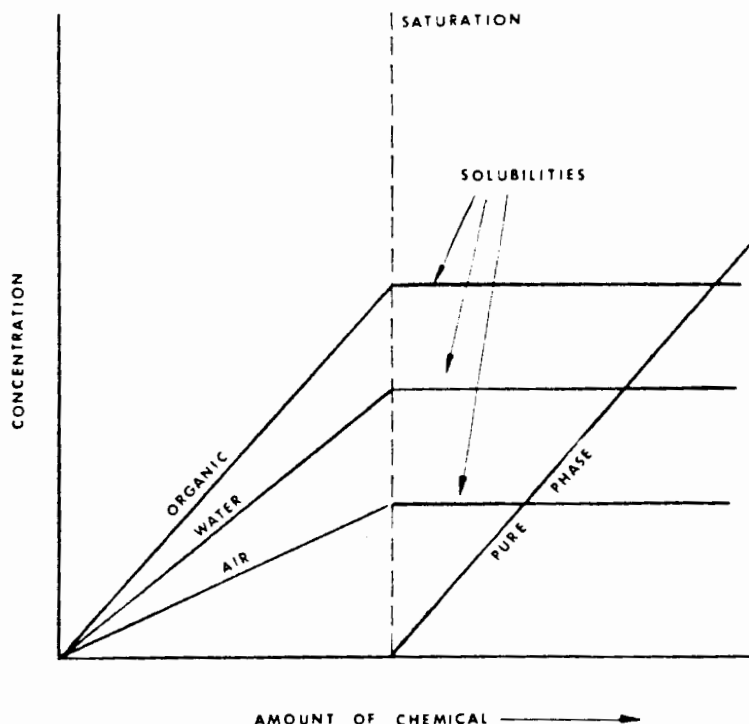

FIGURE 1: Generalized partitioning behaviour of chemicals in the environment.

THERMODYNAMIC BASIS

Solid and Liquid Solubilities: As has been discussed by several workers, including us in the previous text in this series (Mackay and Shiu 1984), it is essential to convert all solubilities and vapor pressures to the values for subcooled liquids, i.e., those solubilities which the solid chemical would have if it could exist at the desired temperature in the liquid state. The ratio of the solid to subcooled liquid solubility can be estimated by the approximate relationship (Prausnitz 1979)

$$F = C^S_S/C^S_L = \exp(-6.97(T_M/T - 1)) \tag{1}$$

where F is the fugacity ratio, T_M is the melting point and T is the system temperature, both in °K. The number 6.97 derives from Walden's rule and is the entropy of fusion at the melting point divided by the gas constant. Preferably it should be measured calorimetrically and a correction included for solid-liquid heat capacity differences, but for initial assessment purposes this expression is adequate.

Similarly, the ratio of the solid to subcooled liquid vapour pressure is

$$P^S_S = FP^S_L \tag{2}$$

The partitioning of organic chemical between air and water can be expressed by the Henry's law constant, H, [Pa·m³·mol⁻¹:

$$H = P^S_S C^S_S = P^S_L/C^S_L \tag{3}$$

and the dimensionless air/water partition coefficient is

$$H' = H/RT \tag{4}$$

The octanol/water partition coefficient is defined as

$$K_{OW} = C_{OW}/C_{WO} \tag{5}$$

where C_{OW} is the concentration of solute in octanol saturated with water and C_{WO} is the concentration of solute in water saturated with octanol.

The relation between aqueous solubility and octanol/water partition coefficient has been studied extensively. Mackay et al. (1980) and Banerjee et al. (1980) found their product Q to be relatively constant. However, recently, Miller et al. (1985) have analysed more accurate data for larger molecules (Miller et al. 1984) and shown that Q varies with molar volume or chlorine number in a homologous series,

$$\log Q = A - BV = A' - B'N \tag{6}$$

where A, A', B, B' are constants, V and N are molar volume and chlorine number, respectively. Since Q is $C^S_L K_{OW}$, it can be considered as an approximate "pseudo-solubility" of the chemical in octanol saturated with water.

We suggest that when considering the development of QSARs, some effort should be devoted to ensuring that the physical-chemical properties which are used to describe and correlate biological phenomena are consistent and sufficiently accurate. We illustrate this by considering three series of

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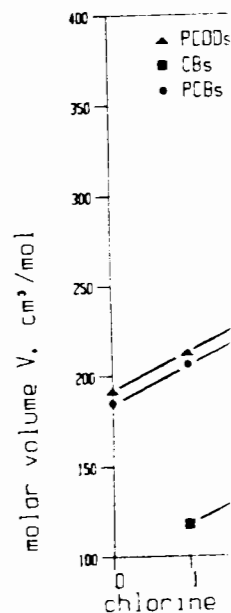ignored. A mor.   .gc
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chemicals; the well characterized chlorobenzenes, the polychlorinated biphenyls which are less well characterized and much greater in number, and the polychlorinated dibenzo-p-dioxins, which are still poorly characterized.

RESULTS AND DISCUSSION

TABLE 1 gives the reported values or ranges of the physical-chemical properties of chlorobenzenes (CBs), polychlorinated biphenyls (PCBs) and polychlorinated dibenzo-p-dioxins (PCDDs). Fugacity ratios were obtained from a single estimated entropy of fusion of 56 J·mol·°K (Yalkowsky 1979), molar volumes were calculated by the Le Bas method, an additive group contribution method (Reid et al. 1977). Total surface area (TSA) values were obtained from Yalkowsky et al. (1979 a,b). Solubilities, vapour pressures and octanol/water partition coefficients (Andren et al. 1986; Shiu and Mackay 1986; Bobra et al. 1985) are also tabulated. Henry's law constants were calculated as P^S_L/C^S_L and the octanol solubility Q as $C^S_L K_{OW}$.

A two-stage process is suggested for the analysis and correlation of the above environmentally relevant properties: C^S, K_{OW}, P^S and H. In the first stage, simple correlation equations can be derived by plotting the experimental data against chlorine number and molar volume. Isomer differences are thus ignored. A more rigorous second stage involves consideration of the difference between isomers using a more refined molecular descriptor, such as TSA.
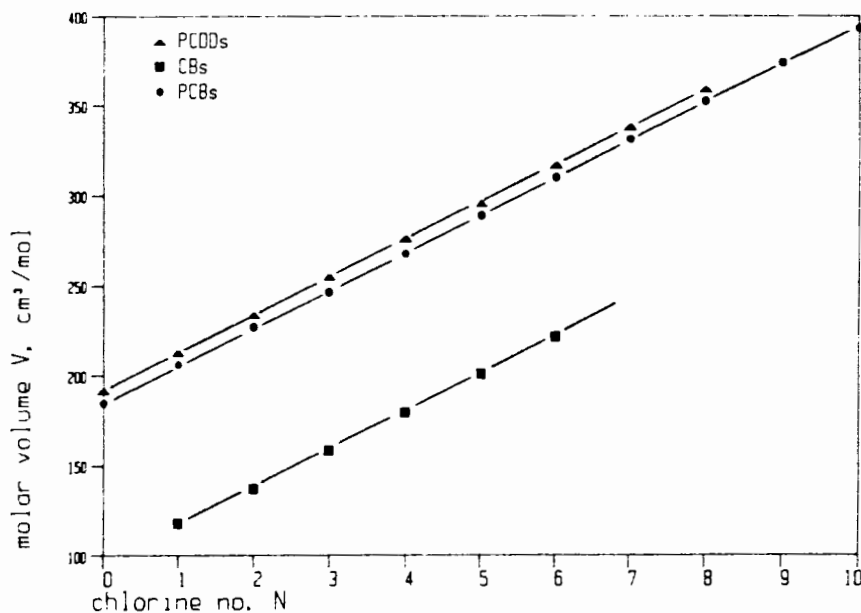

FIGURE 2:   Plot of molar volume (V) versus chlorine number (N) for three congeneric series.

TABLE 1: Selected physical-chemical properties of the chlorobenzenes, polychorobiphenyls, and polychlorodibenzo-p-dioxins, at 25°C. Given are molecular weight (MW) melting point (mp), fugicity ratio (F), total surface area, aqueous solubility of solid (C_S) and subcooled liquid (C_L), vapour pressure of solid (P_S) and subcooled liquid (P_L), Henry's law constant (H), log octanol/water partition coefficient (log K_{OW}), and the product Q = C_S•log K_{OW}.

Compound	Number of Chlorine Atoms per Molecule	MW	mp [K]	Fugacity Ratio F	Volume [cm³ mol⁻¹] (Le Bas)	Total Surface Area [Å²]	Aqueous Solubility [mmol m⁻³] of solid C_S	Aqueous Solubility [mmol m⁻³] of liquid C_L	Vapour Pressure [Pa] of solid P_S	Vapour Pressure [Pa] of liquid P_L	Henry's Law Constant H [Pa m³/mol]	log K_{OW}	Q
Chlorobenzenes													
mono	1	112.6	227.4	1.0	116.9	127.1	4.3	4.3	1580	1580	367	2.80	2713
di	2	147.01	256-326	0.53-1.0	137.8	142.7-144.7	0.53-0.83	0.8-1.0	90.2-307	172-307	171-370	3.4	2085-2512
tri	3	181.45	290-337	0.41-1.0	158.7	158.3-162.2	0.12-0.53	0.07-0.22	28-61	61-76	239-1100	4.10	881-2770
tetra	4	215.9	320-412	0.075-0.61	179.6	173.8-158.8	0.0059-0.36	0.03-0.08	0.72-9.8	5.6-10.8	122-590	4.50	949-2530
penta	5	250.3	357.7	0.258	200.5	189.4	0.0026	0.01	0.22	0.884	85	5.0	1000
hexa	6	284.8	501.1	0.0098	221.4	203.0	0.000017	0.0017	0.0023	0.245	139	5.50	537
Polychlorobiphenyls													
biphenyl	0	154.2	344	0.352	184.6	192.2	45.39	129.7	2.13	6.9	53.5	3.9	1030
mono	1	188.7	298.1-350.9	0.301-1.0	205.5	208.1-210	6.36-29.15	13.24-35.66	0.271-2.04	0.9-2.5	42.56-75.55	4.3-4.6	527-711.6
di	2	223.1	297.2-422	0.059-1.0	226.4	224.2-227.6	0.269-8.96	4.56-10.11	0.0018-0.279	0.008-0.60	17.0-92.21	4.9-5.30	550.8-1127
tri	3	257.5	317-360	0.241-0.651	247.3	241.6-243.6	0.0582-1.55	0.24-2.39	0.0136-0.143	0.003-0.022	24.29-92.21	5.5-5.9	189.2-949.8
tetra	4	292.0	320-453	0.0294-0.606	268.2	255.6-259.6	0.0147-0.342	0.133-1.30	0.000059-0.0054	0.002	1.72-47.59	5.6-6.5	249.4-914.2
penta	5	326.4	249.5-397	0.105-0.311	298.1	269.2-275.2	0.0123-0.0613	0.093-0.337	0.000304-0.0093	0.0023-0.051	24.8-151.4	6.2-6.5	247.8-639.3
hexa	6	360.9	358-433	0.0582-0.256	310	287.2-291.5	0.0011-0.0028	0.0061-0.0286	0.000020-0.00159	0.0007-0.012	11.9-81.8	6.7-7.3	80.7-285.5
hepta	7	395.3	395.4-472	0.0596-0.109	330.9	302.9	0.00114-0.0506	0.0191-0.046	0.0000273	0.00025	5.4	6.7-7.0	191.1-232.2
octa	8	429.8	432-435	0.0443-0.0474	351.8	317.9-318.7	0.00047-0.0007	0.0098-0.0158	0.0000266	0.0006	38.08	7.1	123.5-198.3
nona	9	464.2	455.8-479	0.0163-0.0276	372.7	331.9	0.000038-0.00024	0.00141-0.0146				7.2-8.16	207.1-230.9
deca	10	498.7	578.9	0.00167	393.6	345.9	0.0000024	0.0141	0.00000005	0.00003	20.84	8.26	262

TABLE 1: (cont'd).

tri-	3	257.5	[illegible]-360	0.244-0.651	24[illegible].3	241.6-243.6	0.0[illegible]82-1.55	0.24-2.39	0.0136-0.143	0.003-0.022	21.29-[illegible]	5.5-5.9	184-[illegible]
tetra-	4	292.0	320-453	0.0294-0.606	268.2	255.6-259.6	0.0147-0.342	[illegible]33-1.30	0.000059-0.0054	0.002	1.72-47.9	5.6-6.5	249.4-914.2
penta-	5	326.4	249.5-397	0.105-0.311	298.1	269.2-275.2	0.0123-0.0613	[illegible]33-0.337	0.000304-0.0093	0.0023-0.051	24.8-151.4	6.2-6.5	24[illegible]-[illegible]
hexa-	6	360.9	358-433	0.0582-0.256	310	287.2-291.5	0.0011-0.0028	[illegible]0061-0.0286	0.000020-0.00159	0.0007-0.012	11.9-818	6.[illegible]-7.3	80.7-[illegible]
hepta-	7	395.3	395.4-422	0.0596-0.109	330.9	302.9	0.00114-0.0506	0.0191-0.046	0.0000273	0.00025	5.4	6.7-7.0	191-[illegible]
octa-	8	429.8	43[illegible]-435	0.0443-0.0474	351.8	317.9-318.[illegible]	0.00047-0.0007	0.0098-0.0158	0.0000266	0.0006	38.08	7.1	12[illegible]5-198.[illegible]
nona-	9	464.2	455.8-479	0.0163-0.0276	372.7	331.9	0.000038-0.00024	0.00141-0.0146				7.2-8.16	202.1-230.9
deca-	10	498.7	578.9	0.00167	393.6	345.9	0.0000024	0.0144	0.00000005	0.00003	20.84	8.26	262

TABLE 1: (cont'd).

Compound	Number of Chlorine Atoms per Molecule	MW	mp [°K]	Fugacity Ratio F	Volume $[cm^3\ mol^{-1}]$ (Le Bas)	Total Surface Area $[Å^2]$	Aqueous Solubility $[mmol\ m^{-3}]$ of solid C_S	of liquid C_L	Vapour Pressure [Pa] of solid P_S	of liquid P_L	Henry's Law Constant H $[Pa\ m^3\ mol^{-1}]$	$\log K_{OW}$	Ω
Polychlorodibenzo-p-dioxins													
dibenzo-p-dioxin	0	184.0	397.6	0.105	192.0	4.58	43.62		0.055	0.514	12.39	4.20	691
mono-	1	218.5	367-367.9	0.203	212.9	1.27-1.91	6.27-9.4		0.012-0.02	0.086-0.1	8.38-14.82	4.75-5.08	352-1130
di-	2	253.0	410-473.7	0.0182-0.07	233.8	0.0148-0.066	0.814-1.09		0.00012-0.00039	0.0025-0.0093	2.13-8.11	5.75-5.8	475-688
tri-	3	287.5	396.7	0.105	254.7	0.0261	0.279		0.00010	0.00107	3.84	6.45	786
tetra-	4	322.0	439.9-578	0.0017-0.0396	275.6	0.00006-0.002	0.003-0.072		2.0E-8-5.8E-4	3.1E-5-0.014	0.71-10.3	6.64-7.2	13-1144
penta-	5	356.4	460.8	0.0244	296.5	0.000331	0.0136		8.8E-8	0.00000431	0.264	7.44	375
hexa-	6	391.0	533.2	0.00473	317.4	0.0000113	0.00239		5.1E-9	0.00000145	4.52	7.79	142
hepta-	7	425.2	533.2	0.00422	338.3	0.00000564	0.00134		7.5E-10	1.77E-7	0.133	8.20	712
octa	8	460.0	598.8	0.00107	359.2	0.00000016	0.000174		1.10E-10	1.19E-7	0.683	7.59-8.60	6.77-69.3

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FIGURE 2 shows the linear relationships between chlorine number N and molar volume V [$cm^3 \cdot mol^{-1}$]. The corresponding regressions are given in equations 7 to 9:

CBs: $V = 96 + 20.9\,N$ (7)
$r^2 = 1$

PCBs: $V = 184.6 + 20.9\,N$ (8)
$r^2 = 1$

PCDDs: $V = 192 + 20.9\,N$ (9)
$r^2 = 1$

where r^2 is the correlation coefficient which is unity for all three congeneric series because the Le Bas method (Reid et al. 1977) assumes an incremental molar volume increase of 20.9 $cm^3 \cdot mol^{-1}$ for each chlorine atom.
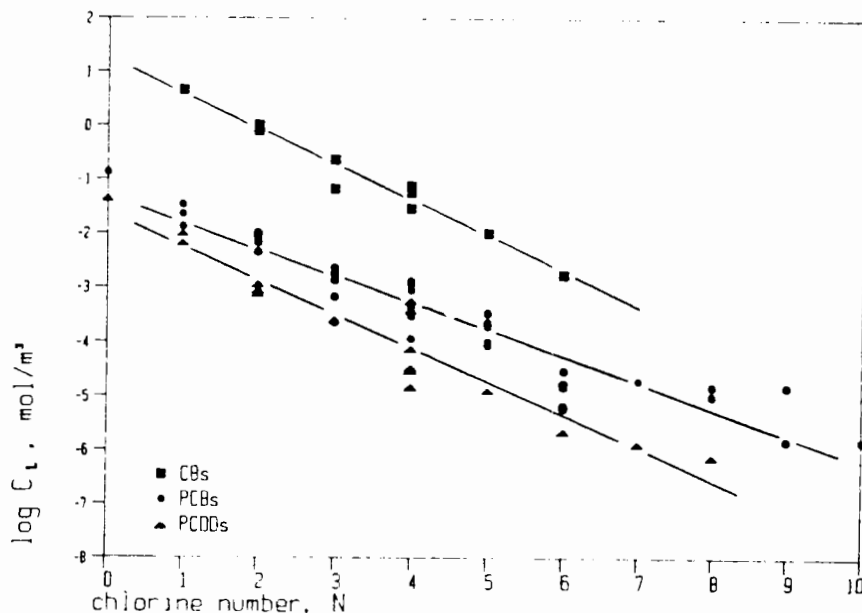
FIGURE 3: Plot of aqueous subcooled liquid solubility (C_L) versus chlorine number (N).

FIGURE 3 shows the new linear plots of log CL versus chlorine number and FIGURE 4 the same data as a function of molar volume. The slopes of the three group regressions are similar but not identical. It is possible to estimate solubility from molar volume from these plots with a probable accuracy of plus or minus a factor of 10 down to 10^{-3} $mol \cdot m^{-3}$ and a factor of 100 at 10^{-6} $mol \cdot m^{-3}$. Frequently, reported data contain considerable error. Plots such as FIGURE 4 help to identify such data.

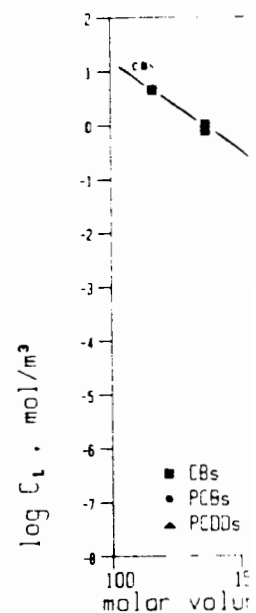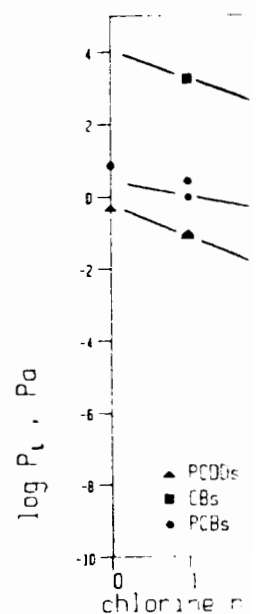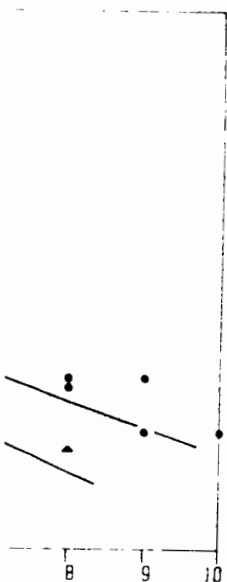**FIGURE 4:** Plot of the
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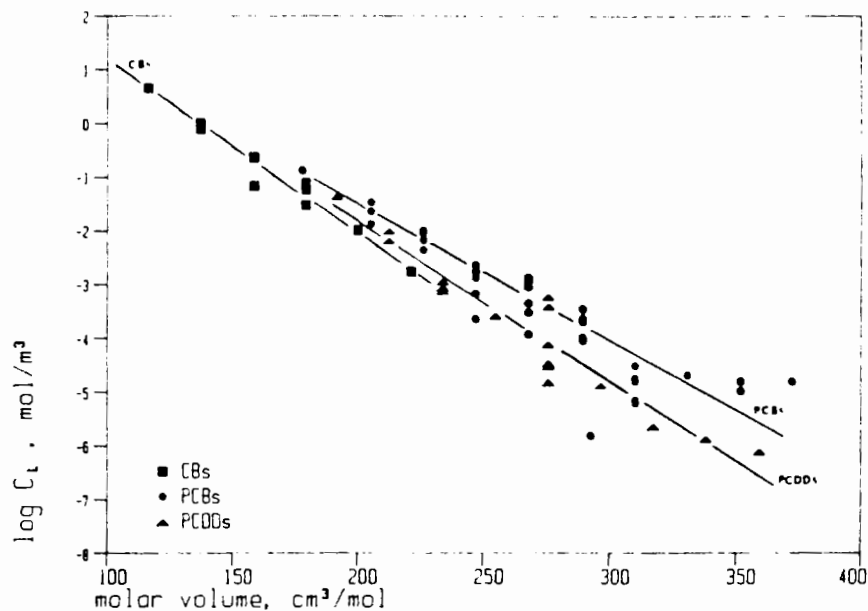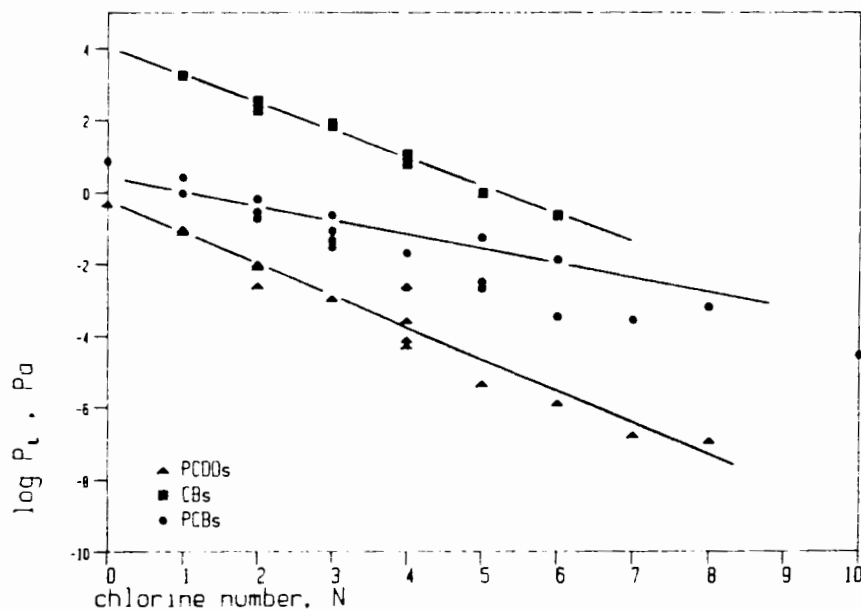factor of 100 at 10^{-6}
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FIGURE 5: Plot of the subcooled liquid vapour pressure (P_L) versus chlorine number (N).
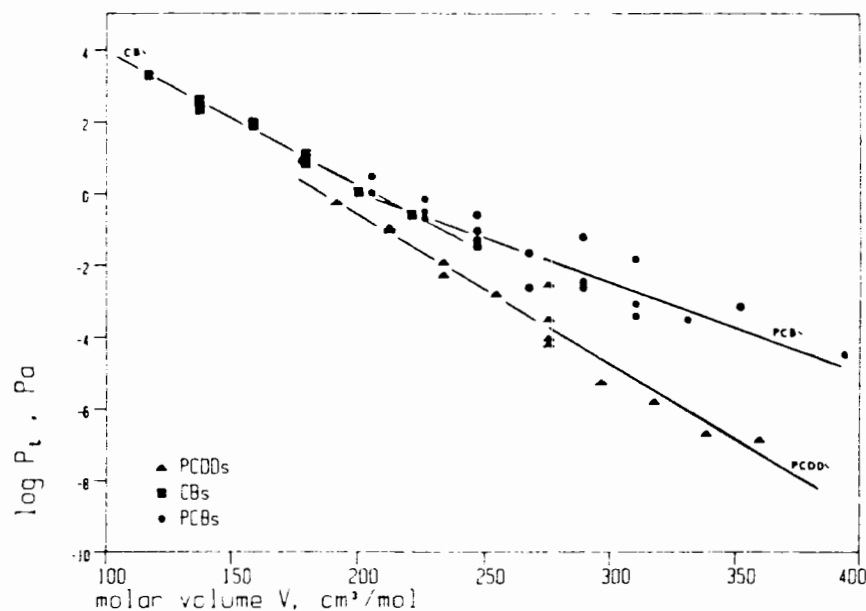
FIGURE 6: Plot of the subcooled liquid vapour pressure (P_L) versus molar volume (V).
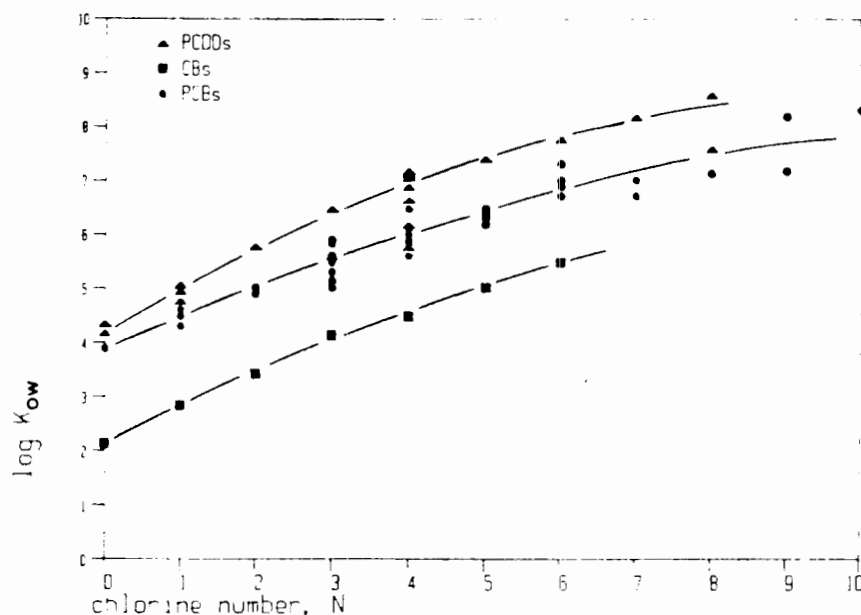

FIGURE 7: Plot of the logarithm of the octanol/water partition coefficient (log K_{ow}) versus chlorine number (N).
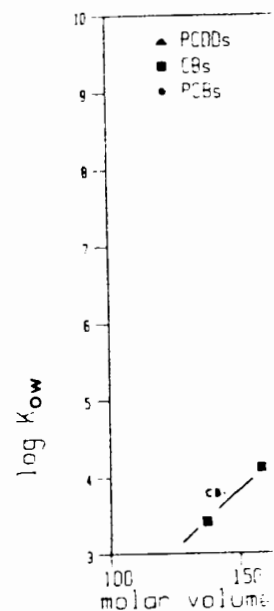

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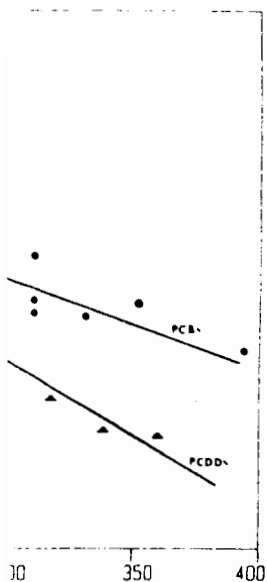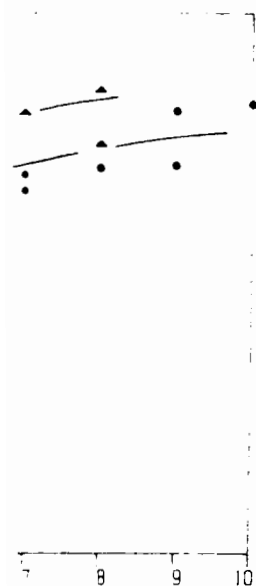
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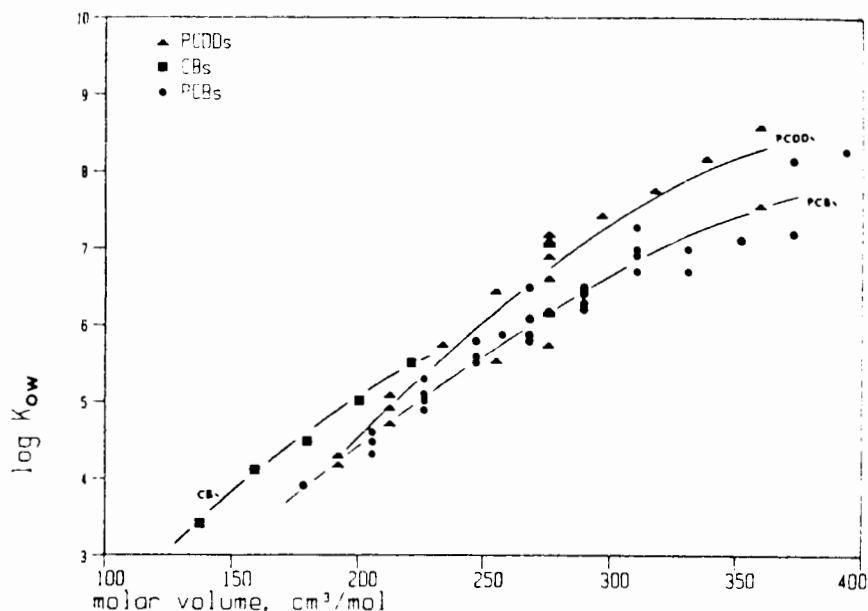

FIGURE 8: Plot of the logarithm of the octanol/water partition coefficient (log K_{OW}) versus molar volume (V).

FIGURE 5 and FIGURE 6 give the vapour pressure data in similar form, the linear behaviour being again evident. There is a greater spread in properties at a given molar volume than for solubility.

FIGURES 7 and 8 give the K_{OW} data. There is a distinct trend for nonlinear behaviour when log K_{OW} exceeds 6, thus extrapolation from low K_{OW} data using a consistent increment per chlorine added is inaccurate. The lines shown are quadratic regressions. This nonlinear progression is also illustrated in FIGURES 9 and 10 which give the plot for log Q. Log Q is fairly constant and in the range 2.5 to 3.5 for molar volumes up to $250 \, cm^{-3} mol^{-1}$ but it tends to fall at higher molar volumes and its behaviour is erratic. It is suspected that much of the variation is attributable to errors in K_{OW}. Few log Q values fall below 2, i.e., Q less than $100 \, mol \cdot m^{-3}$. FIGURES 11 and 12 give the Henry's law constants as a function of N and V. It is remarkable how constant the PCBs' Henry's law values are.

Finally, FIGURE 13 gives a plot of log K_{OW} versus log C_L showing the well established linear relationship with a slope of approximately -0.8 (Miller et al. 1985).
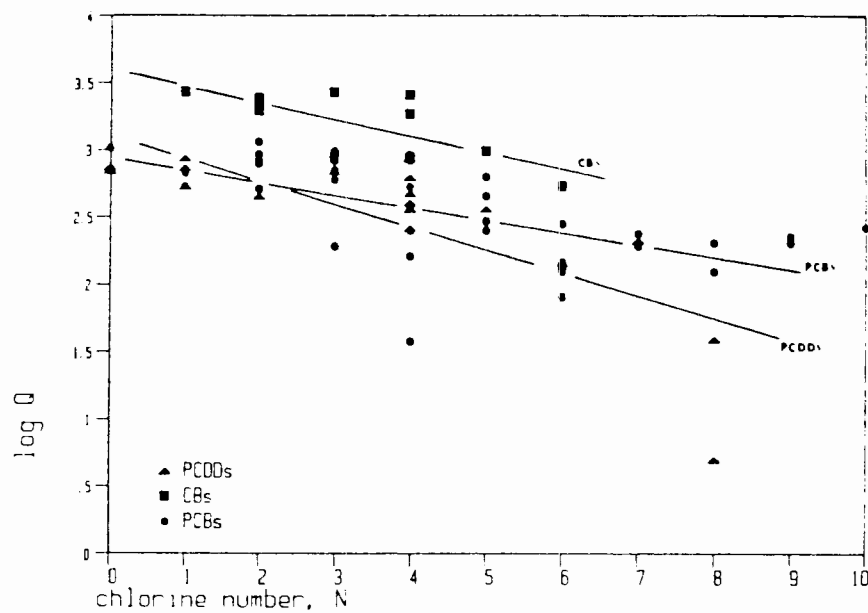
FIGURE 9: Plot of the derived parameter Q (see equation 6) versus chlorine number (N).

FIGURE 11: Plc   the

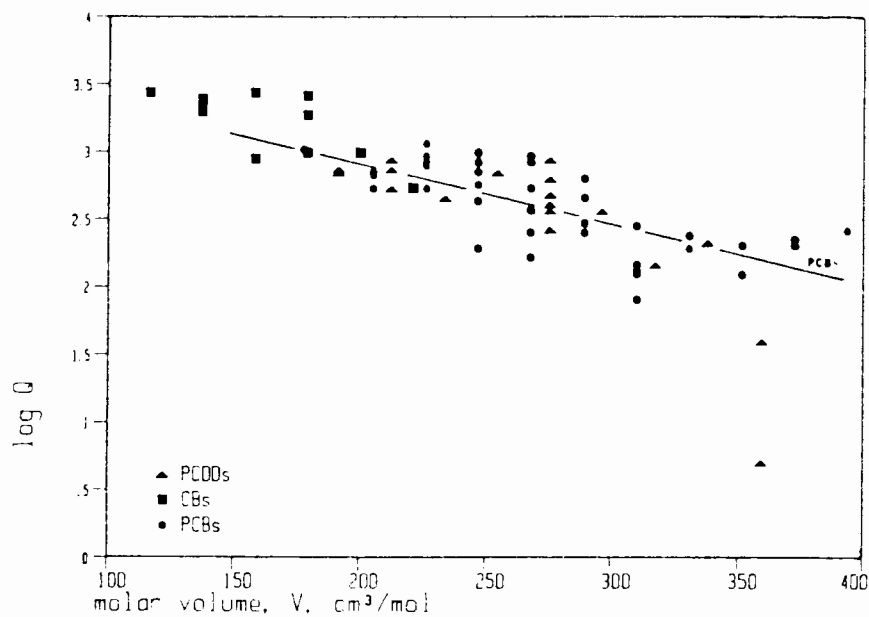**FIGURE 10:** Plot of the derived parameter Q (see equation 6) versus molar volume (V).
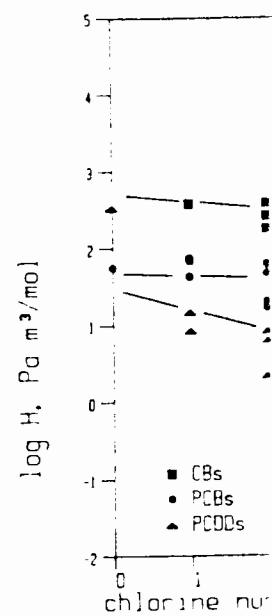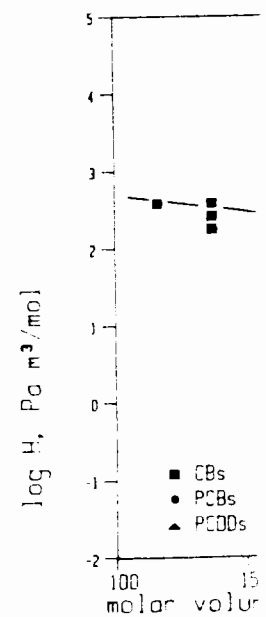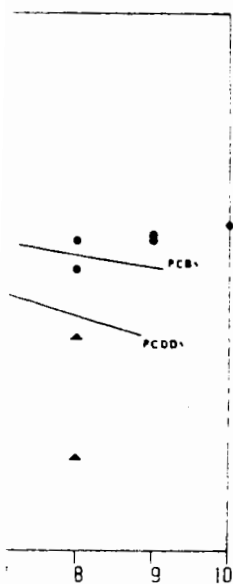

FIGURE 12: Plot of t
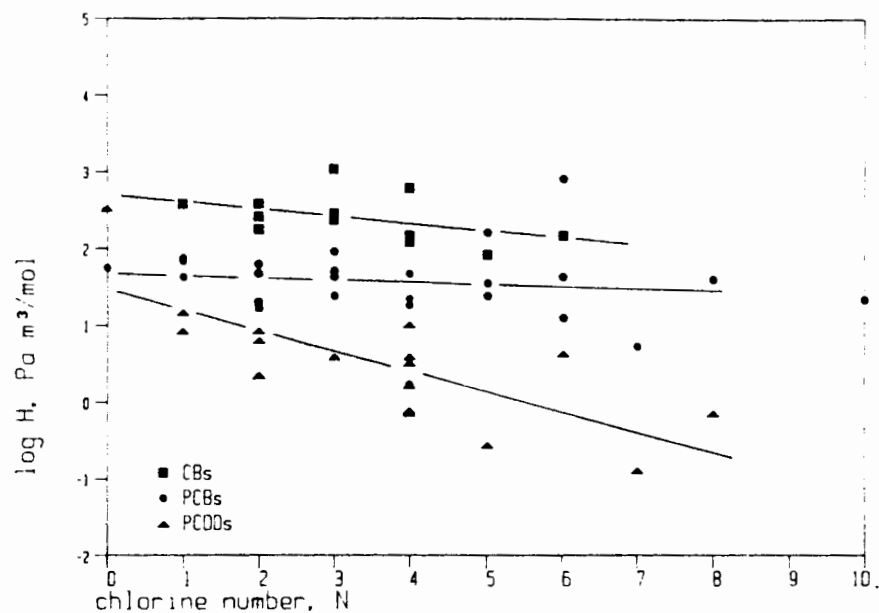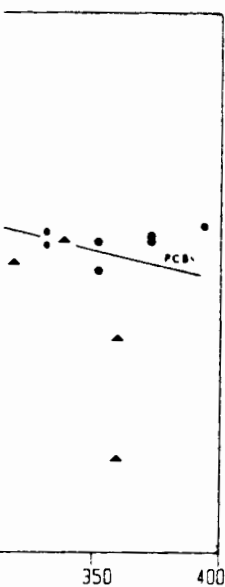
ion 6) versus chlorine

FIGURE 11:   Plot of the Henry's law constant (H) versus chlorine number (N).
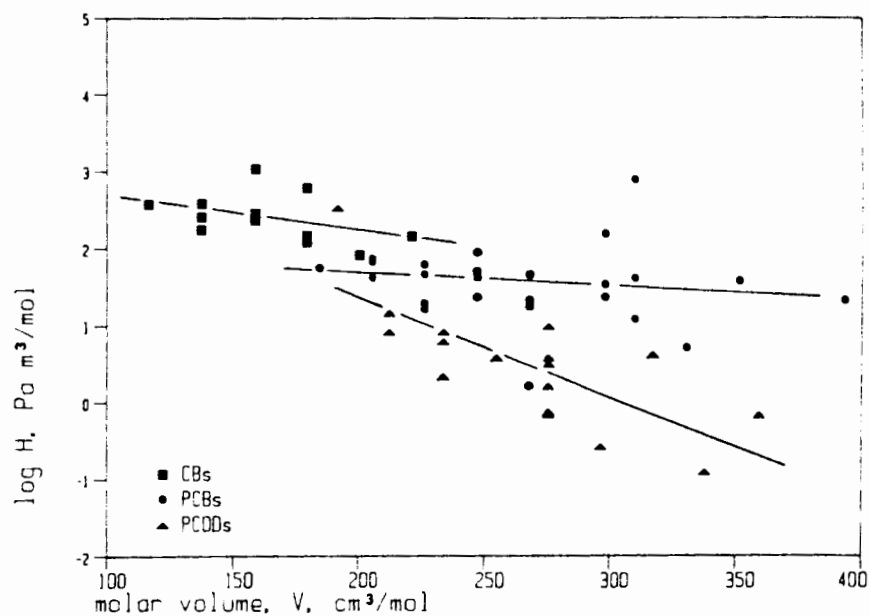

uation 6) versus molar

FIGURE 12:   Plot of the Henry's law constant (H) versus molar volume (V).
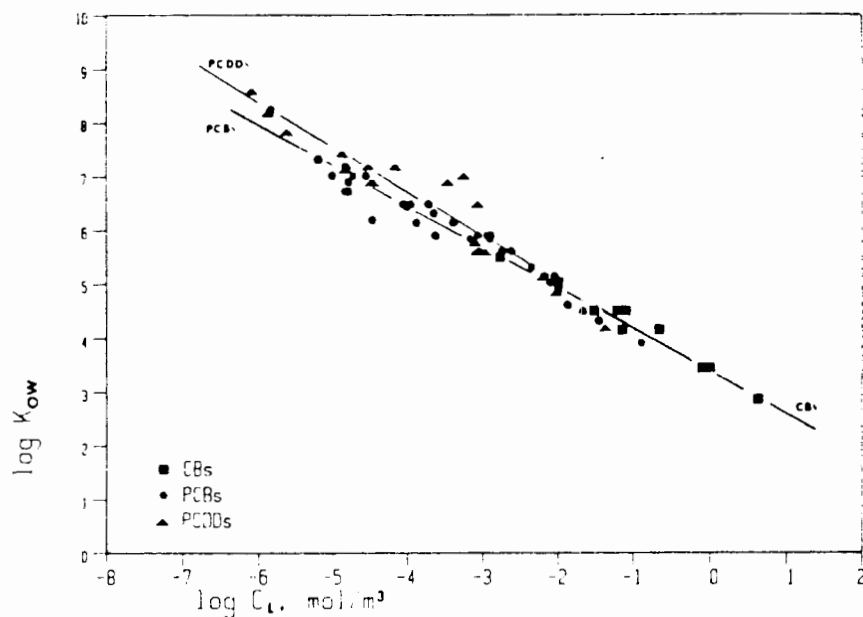
FIGURE 13: Plot of the logarithm of the octanol/water partition coefficient (log K_{OW}) versus the logarithm of the aqueous subcooled liquid solubility (log C_L).

We suggest that it is useful to prepare plots such as those presented here for a series of congeners. It appears that there are broad similarities in dependence of properties on N and V. Estimates can then be made of physical-chemical properties and "reasonableness" can be assessed. Erroneous data can be identified and discarded before they become too widely accepted.

These data enable assessments to be made of how chemicals in a series will differ in their environmental behaviour as they partition between air, water and organic phases. As is discussed by Gobas et al. (1987) elsewhere in this text, extreme caution must be used when calculating partitioning coefficients into organic media when log K_{OW} exceeds 5. It is suspected that octanol then ceases to be a satisfactory surrogate for lipids and probably also for organic matter sorption.

From these plots an impression can also be obtained of the relative partitioning behaviour, expressed as solubilities. For example, if we consider three hydrophobic organic chemicals typical of these series, we can estimate solubilities to be in the order of values given in TABLE 2, as follows (air solubility being P/RT as discussed earlier).

TABLE 2: Environmenta

Molar volume. $cm^3 \cdot mol$	
Solubility in air	
Solubility in water	
Solubility in octanol	
Typical log K_{OW}	
Typical K_{AW}	

The picture which emer
The result is a strong ter
air/water partition coef
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CONCLUSION

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Gobas. F A P C . Shiu W Y
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TABLE 2:   Environmental media solubilities $(mol \cdot m^{-3})$

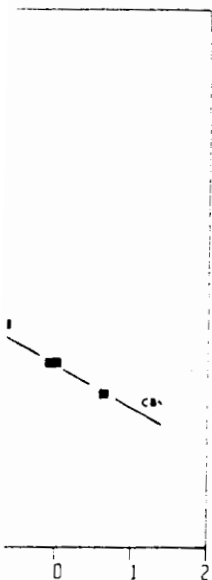|	Chemical A	Chemical B	Chemical C
Molar volume, $cm^3 \cdot mol^{-1}$	150	250	350
Solubility in air	$4 \cdot 10^{-2}$	$4 \cdot 10^{-6}$	$4 \cdot 10^{-10}$
Solubility in water	0.3	0.001	0.00001
Solubility in octanol	2000	300	100
Typical log K_{OW}	3.8	5.5	7.0
Typical K_{AW}	0.1	0.004	0.00004

The picture which emerges is of a fairly constant organic medium solubility. The result is a strong tendency to partition into biota and sediments. The low air/water partition coefficients are potentially misleading. Environmental volumes of air are larger than those of water by a factor of 10^3 to 10^5, thus K_{AW} values of 10^{-3} to 10^{-5} must be regarded as appreciable and values exceeding 10^{-3} are very large. Therefore a substantial fraction of chemicals A and B will tend to enter or remain in the atmosphere. But those of high molar volume and low vapour pressure will tend to partition on to atmospheric particulates and become subject to wet and dry deposition.

CONCLUSION

In conclusion, we suggest that when a new chemical or series of chemicals, such as the chlorinated dibenzofurans become the subject of environmental assessments it is important to obtain, correlate and interpret their physical-chemical property data using the approach suggested here. As more reliable experimental data become available, more refined property-structure relationships can be developed including isomer differences, but a necessary first stage is to establish reliable initial estimates of three key "solubilities". Much useful environmental fate information can be deduced from these data, indeed it is difficult to conceive how reliable environmental fate information can be obtained or interpreted without such data.

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INTRODUCTION

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