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High-performance liquid chromatographic measurement of the 1-octanol–water partition coefficient of *s*-triazine herbicides and some of their degradation products

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Abstract

1-Octanol–water partition coefficients (K_{ow}) of *s*-triazines and some of their degradation products were determined using two reversed-phase high-performance liquid chromatography (HPLC) methods. In the first method, an octadecyl column was coated with 1-octanol and eluted with 1-octanol–saturated water. Using this method, a maximum log K_{ow} of 2.86 could be determined. For higher values a recently developed gradient HPLC method was used. The determined 1-octanol–water partition coefficients are helpful for studies and mathematical models dealing with the fate of *s*-triazine herbicides and their degradation products in the environment. © 1998 Elsevier Science B.V.

Keywords: Octanol–water partition coefficients; Mobile phase composition; Pesticides; Triazines

1. Introduction

Symmetric triazines (*s*-triazines) are among the most widely used pesticides. In soils, many degradation products are formed as a result of *N*-dealkylation, deamination and hydrolysis of the substituent on the C2 atom of the *s*-triazine ring [1]. All metabolic pathways lead to cyanuric acid that is further degraded by ring cleavage. The same degradation products as formed in soils are also produced by photolytic reactions [2].

Some *s*-triazine degradation products bioaccumulate, they are persistent, phytotoxic, and ecotoxicologically relevant [3]. A mathematical model [4] revealed that uptake by plants and volatilization from leaves into the atmosphere was much higher for the medium polar degradation products of terbuthylazine than for the parent compound. Furthermore, the 1-octanol–water partition coefficient (K_{ow}) was one of the two most sensitive input parameters for the model. Thus, reliable K_{ow} data is required to model the environmental fate of *s*-triazines. Furthermore, K_{ow} values permit the estimation of other environmental fate and effect-relevant properties, like soil adsorption coefficients [5], bioaccumulation factors [6] and baseline toxicity. However, despite numerous publications and reviews (e.g., [7]) K_{ow} data are often not available for parent compounds and data

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availability is usually even worse for degradation products. For example, K_{ow} values are known for 23 out of the 27 parent *s*-triazines investigated by us and for 2 out of 17 *s*-triazine degradates. Therefore, the objective of this paper was to report K_{ow} values for *s*-triazine pesticides and their major degradation products. To achieve this aim, two methods were used which complement each other. First, a coated-column method was employed. It is suitable for low but not for high $\log K_{ow}$ values because retention times become extremely long. Therefore, a gradient HPLC method was employed for the determination of higher $\log K_{ow}$ values. Advantages of the gradient method are that it allows for the determination of K_{ow} values over a range of many orders of magnitude in a single experiment without adjustment of the solvent composition as is required in isocratic HPLC measurements. The range of K_{ow} estimated can easily be extended by using reference compounds with lower or higher $\log K_{ow}$. Therefore, gradient elution is especially suitable if the K_{ow} of a compound cannot preliminarily be estimated, or if an appropriate eluent composition for isocratic elution is not a priori known, or if substances of presumably very different K_{ow} values are to be investigated in a single series of experiments.

2. Experimental

Experiments were performed using an eluent vacuum degasser, a Gina 160 autosampler (Gynkotek, Germering, Germany), a gradient HPLC pump (L6200A, Merck, Darmstadt, Germany) and a photodiode array detector DA320A (Gynkotek). Photodiode array data were acquired at 210, 230, 250 and 270 nm. These wavelengths allowed detection of all reference and test compounds at or close to their absorption maxima. However, absorption was usually high enough to permit peak detection at 210 nm only, except for 2-butanone that was recorded at 270 nm. Spectral data was acquired between 200 and 356 nm to permit peak identification.

Reference compounds (Table 1) and test compounds were purchased from Aldrich (Steinheim, Germany), Fluka (Buchs, Switzerland), Merck, Ehrenstorfer (Augsburg, Germany), Riedel-de Haën (Seelze, Germany) and Wacker (Burghausen, Germany). The substances were of the highest purity available. Purities ranged from 99.9% to a minimum of 96% (atrazine-desisopropyl) and 93% (sec-bumeton). The latter two were certified reference materials from Ehrenstorfer and were not available at higher purity. Furthermore, impurities are chromatographically separated and therefore do not pose any problem in HPLC estimations of K_{ow}. This is one of the advantages of the HPLC methods over the conventional slow-stirring and shake-flask techniques in which impurities may cause large errors. Methanol (LiChrosolv) and 1-octanol (extra pure) were from Merck. Water was prepared by passing demineralized water through a Milli-Q filtration system (Millipore, Eschborn, Germany).

Abbreviations of *s*-triazines explained in Table 2 follow a four-letter nomenclature [1] in which the 4th letter (''T'') denotes the *s*-triazine ring and the first three letters represent the substituents on the ring. The three substituents on the carbon atoms of the *s*-triazine ring are abbreviated as follows: chloro (C), methoxy (X), methylthio (S), ethylthio (V), azido (N), ethylamino (E), diethylamino (D), isopropylamino (I), *tert*.-butylamino (T), *sec*.-butylamino (U), cyanoisopropylamino (Y), 1,2-dimethylpropylamino (J), cyclopropylamino (P), 3-methoxypropylamino (K), methylamino (M), amino (A), hydroxy or keto (O). For example, CEIT denotes 2-chloro-4-(ethylamino)-6-(isopropylamino)-*s*-triazine (atrazine). The four-letter nomenclature is not applicable to metamitron (because it is a nonsymmetric triazine) and to anilazine because the substitution pattern of this compound differs from that of the other *s*-triazines. Therefore, metamitron and anilazine were abbreviated by lower case letters (meta and anil, respectively).

2.1. 1-Octanol-coated column method

The stationary phase was LiChrospher 100, RP-18 (17 mm×4 mm, particle size 5 μm, Merck) thermostated at 298 K. The mobile phase was water, buffered with 10 m*M* KH_2PO_4 (suprapur, Merck), adjusted to pH 7.5 by addition of NaOH (analytical-reagent grade, Merck) and saturated with 1-octanol (0.6 g 1-octanol in 1 l water [11]). The pH value of 7.5 was chosen because at this pH the *s*-triazines are in their nonionized form. The pK_{a1} values describing

Table 1
Capacity factors (k') and 1-octanol–water partition coefficients (K_{ow}) of reference compounds

Compound	Log k'			Log K_{ow}	Refs.
	1-Octanol-coated column method at a flow-rate of		Gradient method		
	2 ml min^{-1}	4 ml min^{-1}			
2-Butanone	0.152		0.604	0.3	[8]
Ethyl acetate	0.348		0.696	0.71	[9]
1,2-Dihydroxybenzene	0.443			0.88	[10]
Aniline	0.556		0.676	0.9	[8]
Acetanilide	0.707		0.723	0.95	[8]
Benzyl alcohol	0.624			1.1	[8]
Phenol	1.027	1.050		1.50	[8]
Benzonitrile	1.251	1.271	0.796	1.55	[8]
Nitrobenzene	1.523	1.533	0.850	1.85	[8]
Benzene		1.829	0.902	2.13	[8]
Atrazine		2.198		2.47	[5]
Trichloroethylene			0.951	2.42	[8]
Chlorobenzene			0.962	2.84	[8]
Toluene		2.357	0.965	2.69	[8]
1-Naphthol		2.558		2.71	[8]
Bromobenzene			0.978	2.99	[8]
Naphthalene			1.005	3.59	[8]
Ethylbenzene			1.010	3.15	[8]
1,4-Dichlorobenzene			1.018	3.38	[8]
Biphenyl			1.045	3.95	[8]
1,2,4-Trichlorobenzene			1.063	4.18	[8]
Phenanthrene			1.082	4.5	[8]
Fluoranthene			1.116	4.7	[8]
Benzanthracene			1.162	5.73	[9]
Benz[*a*]pyrene			1.218	6.02	[9]
Dibenz[*a*,*h*]anthracene			1.239	6.39	[9]

the relation between the neutral and the positively charged species range from 1.0 to 2.0 for chloro-*s*-triazines (including the dealkylated chloro-*s*-triazines CEAT and CAIT [12]). The pK_{a1} values range from 4.2 to 4.8 for methoxy-*s*-triazines, 4.0 to 4.4 for methylthio-*s*-triazines, and 4.7 to 5.2 for hydroxy-*s*-triazines and melamine [13–16]. The second ionization constant (pK_{a2}) of the hydroxy-*s*-triazines describing the relation between the neutral and the negatively charged molecule (in which the hydroxy group is deprotonated) is about 11 [13]. Therefore, the *s*-triazines studied are predominantly in their neutral form at the chosen pH=7.5 because (pK_{a2}−2)≥pH 7.5≥(pK_{a1}+2) [12].

We found it useful to disconnect all the capillary tubes from the column before starting the coating process because the capillary tubes can then be filled with water-saturated 1-octanol (30.6 g water in 1 l 1-octanol [11]) at a much higher flow-rate when compared to if the column was connected and the column pressure would have been relatively high. After filling the capillary tubes with water-saturated 1-octanol they were connected to the column again. Water-saturated 1-octanol was then passed through the column at a flow-rate of 0.5 ml min^{-1} resulting in a column pressure of about 7.5 MPa. When a stable baseline was obtained (i.e. after approximately 90 min), the column was eluted with the mobile phase at a flow-rate of 1 ml min^{-1} until the baseline was stable again. This took approximately 3.5 h. At this time, the column pressure was about 4.5 MPa.

A flow-rate of 2 ml min^{-1} was used for compounds with log K_{ow}≤1.85, and 4 ml min^{-1} for substances with higher log K_{ow}. Test and reference compounds were dissolved in the mobile phase at a maximum concentration of 10 mg l^{-1}. The injection

Table 2
1-Octanol–water partition coefficients measured with a 1-octanol-coated column and the gradient HPLC method

Compound		Log K_{ow}					
Name	Abbreviation	1-Octanol-coated column method			Gradient method	Literature value	
		Mean	S.D.[a]	n[b]			
Ametryne	SEIT	2.86	0.01	3	2.67	2.83	[19]
Anilazine	anil				2.87	3.02	[20]
Atraton	XEIT	2.26		1	2.21	2.69	[21]
Atraton-desisopropyl	XEAT	0.89	0.02	5	0.77		
Atrazine	CEIT	2.46	0.006	4	2.28	2.47	[5]
Atrazine-desethyl	CAIT	1.39	0.03	4	1.30	1.51	[21]
Atrazine-desethyl-hydroxy	OAIT	−0.08	0.05	5			
Atrazine-desethyl-desisopropyl	CAAT	0.11	0.03	6			
Atrazine-desalkyl-hydroxy[e]	OAAT	−0.46	0.09	5			
Atrazine-desisopropyl	CEAT	1.01	0.008	5	0.78	1.15	[21]
Atrazine-desisopropyl-hydroxy	OEAT	−0.3	0.1	5			
Atrazine-hydroxy	OEIT	0.76	0.001	4			
Azidoatrazine	NEIT				2.57		
Aziprotryne	NSIT				2.88	3.00	[5]
Cyanazine	CEYT	2.01	0.02	4	1.64	2.24	[5]
Cyanuric acid	OOOT	−0.47	0.05	5			
Cyromazine	AAPT	0.16	0.06	4	−0.05		
Desmetryne	IMST	2.41	0.005	2	2.30	2.38	[20]
Dimethametryne	SEJT				3.29	3.37	[22]
Dipropetryne	VIIT				3.36	3.81	[19]
IMMT[c]	IMMT	1.87	0.02	4			
Melamine[d]	AAAT	−0.4	0.1	5			
Metamitron	meta	0.82	0.006	5	1.05	0.83	[20]
Methoprotryne	SIKT	2.70	0.003	2	2.61	2.81	[19]
Procyazine	CPYT				0.69	1.99	[22]
Prometon	XIIT	2.61	0.0005	2	2.59	2.55	[22]
Prometryne	SIIT				3.03	2.99	[5]
Propazine	CIIT				2.72	2.89	[22]
Sebuthylazine	CEUT	2.10	0.002	2	2.61		
Sebuthylazine-desethyl	CAUT	1.86	0.04	5	1.70		
Secbumeton	XEUT	2.64		1	2.55	2.85	[20]
Simazine	CEET	2.11		1	1.86	2.03	[5]
Simazine-hydroxy	OEET	0.35	0.03	5			
Simeton	XEET	1.90	0.01	4	1.79	1.82	[23]
Simetryne	SEET	2.47		1	2.30	2.41	[24]
Terbumeton	XETT				2.71	3.04	[20]
Terbumeton-desethyl	XATT	1.93	0.04	5	1.94		
Terbuthylazine	CETT	2.59		1	2.59	3.04	[20]
Terbuthylazine-desethyl	CATT	2.19		1	1.94		
Terbuthylazine-desethyl-hydroxy	OATT	0.43	0.01	5			
Terbuthylazine-hydroxy	OETT	1.50	0.01	3			
Terbutryne	SETT				3.08	3.48	[20]
Trietazine	CDET				3.05	3.35	[5]
Trietazine-desethyl	CDAT	2.14	0.007	3	2.11		

[a] Standard deviation.
[b] Number of measurements.
[c] 4,6-Bis(methylamino)-2-isopropylamino-*s*-triazine.
[d] Degradate of cyromazine.
[e] Ammeline.

volume was 20 μl but was increased to a maximum of 200 μl when investigating substances with high K_{ow}.

The hold-up time of the uncoated column (t_0= 0.130 min) was determined with formamide and with methanol–water (80:20, v/v) as eluent. The hold-up time of the 1-octanol-coated column was considerably shorter (t_0=0.074 min). It was also determined with formamide but with a mobile phase of 1-octanol–saturated water adjusted to pH 7.5 (see above). The difference between the hold-up times, multiplied by the flow-rate (2 ml min^{-1}), indicated that 1-octanol occupied 0.112 ml of the column volume. We previously found that formamide was retained on an uncoated RP-18 column and therefore did not provide estimates of the hold-up time at water fractions of the mobile phase >40% [17]. Similarly, formamide might have also been retained on the 1-octanol-coated column when a mobile phase of 1-octanol–saturated water was used. Consequently, the hold-up time would be overestimated. However, this could not be quantified because the 1-octanol-coated column can only be flushed with 1-octanol–saturated water and not with methanol since otherwise 1-octanol will be displaced from the column. However, the possible error is smaller than for the gradient HPLC method described below due to the shorter column length. A linear calibration curve of the reference compounds was established between their $\log K_{ow}$ taken from the literature and their measured $\log k'$. The calibration curves were $\log K_{ow}=1.04 \log k'+0.31$ ($r^2=0.95$) for a flow-rate of 2 ml min^{-1} and $\log K_{ow}=0.89 \log k'+0.50$ ($r^2=0.98$) for a flow-rate of 4 ml min^{-1}.

2.2. HPLC gradient method [17]

The column was LiChrospher 100 RP-18 endcapped (250 mm×4 mm, particle size 5 μm, Merck) thermostated at 303 K. A nonlinear water–methanol gradient was used in which the water fraction of the mobile phase (φ_w) decreased exponentially with time (t, min) according to $\varphi_w=a \exp(-kt)$, where a is the initial volumetric water fraction (%) and k the rate constant (min^{-1}). We used a=100% and k=0.1 min^{-1}. To approximate an exponentially shaped gradient, experimental times required for a 5% change in the water fraction were programmed. Within each of these time steps the gradient was linear. When φ_w was 5%, the gradient was reversed within 7.5 min and the system was equilibrated for another 7.5 min. This nonlinear gradient was used because it was superior over a linear gradient in terms of precision, range of K_{ow} covered, experimental times required and solvent consumed [17].

Standard solutions of reference and test compounds were prepared in methanol at concentrations ranging from 1 to 10 mg l^{-1}. Fifteen of the 21 reference compounds were included in a single standard mixture. The flow-rate was 1 ml min^{-1} and the injection volume 20 μl.

The capacity factor (k') was calculated according to

$$k' = (t_R - t_0)/t_0 \quad (1)$$

where t_R is the retention time of the substance investigated and t_0 is the hold-up time. The hold-up time was determined with formamide using isocratic elution with water–methanol at water fractions (v/v) <40%. The calibration curve of reference $\log K_{ow}$ versus measured $\log k'$ is depicted in Fig. 1. If the retention time rather than $\log k'$ is used, the calibration curve becomes linear. This is also true for linear gradient experiments used for the prediction of $\log K_{ow}$ (data not shown) or for the prediction of the chromatographic hydrophobicity index [18]. However, we used $\log k'$ because this is more common,

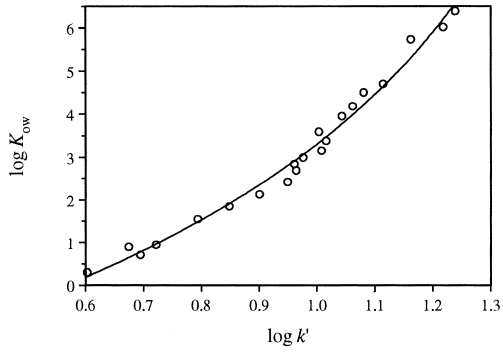

Fig. 1. Calibration curve for determining 1-octanol–water partition coefficients (K_{ow}) from capacity factors (k') determined on a LiChrospher 100 RP-18 endcapped column (250 mm×4 mm, particle size 5 μm) with an exponentially shaped gradient and a methanol–water eluent. The calibration curve is given by: $\log K_{ow}=(-1/0.0762) \log[-1.02(\log k')+1.58]$, $r^2=0.986$.

especially in isocratic experiments, e.g., the coated-column method described above.

No buffer was employed in the gradient HPLC experiments because no hydroxy-*s*-triazines were measured with this method and all other *s*-triazines (including the methylthio-*s*-triazines) are predominantly in their neutral form at the mobile phase of pH 6.2. However, some of the compounds were also chromatographed with a 10 m*M* KH_2PO_4 solution, buffered at pH 7.0. The results were nearly identical to those of the nonbuffered mobile phase.

3. Results and discussion

Using the coated-column method, baseline noise (± 1 mAU, sometimes up to ± 5 mAU) was higher than with an uncoated column. This was due to the displacement of small drops of 1-octanol from the column. However, displacement was small, hence the retention times of the reference compounds did not decrease significantly during a running time of 78 h. (The running time is defined as the time during which the coated column is flushed with the mobile phase at a flow-rate of either 2 or 4 ml min^{-1}.) This is in agreement with Ritter et al. [10] who used a coated column for 100 h before the retention times of the reference compounds decreased considerably and the column had to be recoated.

Long retention times of highly lipophilic compounds lead to broad peaks that may hardly be detected. This was particularly true because the noise was high and in some HPLC runs the baseline increased. These negative effects on the detectability could not be compensated by an increase in the injection volume. Thus, it was not possible to determine the $\log K_{ow}$ of anilazine, prometryne, propazine, aziprotryne and terbumeton although a number of experiments were performed. Similarly, a few compounds could only be measured once ($n=1$ in Table 2) so that no statement about the reproducibility of these measurements can be made. However, reproducibility was generally very good. The maximum standard deviation of replicated measurements was 0.04 for $\log K_{ow} > 0.3$. For compounds with $\log K_{ow} < 0.3$, the standard deviation was slightly higher (0.03 to 0.1) because the $\log K_{ow}$ had to be slightly extrapolated due to lack of appropriate reference compounds. A second reason is that the retention time of these compounds was close to the hold-up time so that relatively small errors of the hold-up time and of the retention time of the compound greatly influence the determined K_{ow}. The standard deviation of the HPLC gradient method was typically ≤ 0.03 for three replicated measurements.

Using a longer octanol-coated column than ours (30 mm compared to 17 mm), Ritter et al. [10] were able to determine a maximum $\log K_{ow}$ of 3.53 and applied a flow-rate of 4 ml min^{-1} only for $\log K_{ow} > 3$. Contrary to these results, our maximum $\log K_{ow}$ was 2.86 (ametryne). Furthermore, a flow-rate of 4 rather than 2 ml min^{-1} was necessary for $\log K_{ow}$ higher than about 2. At a flow-rate of 4 ml min^{-1} a substance with $\log K_{ow} = 3$ would have eluted after approximately 22 min, a substance with $\log K_{ow} = 3.5$ after approximately 80 min. At such a long retention time, substance peaks can hardly be detected.

Most of the $\log K_{ow}$ values obtained with the 1-octanol-coated column method were higher than those of the gradient method (Fig. 2). The largest difference was observed for cyanazine (CEYT) for which $\log K_{ow}$ of the coated column ($\log K_{ow} = 2.01$) was closer to the literature value of 2.24 [5] and the value obtained with the gradient method ($\log K_{ow} = 1.64$) was probably too low. Contrary to the tendency of higher values of the coated-column method,

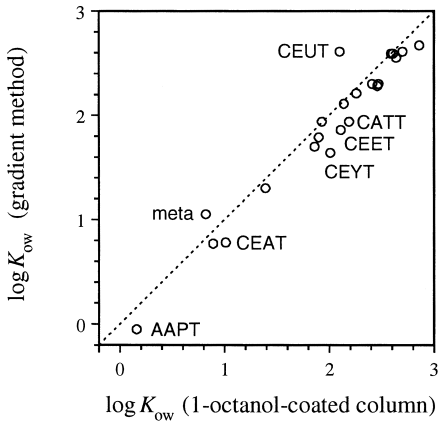

Fig. 2. Comparison of the gradient method and the 1-octanol-coated column method for the estimation of 1-octanol–water partition coefficients (K_{ow}). Substances are indicated for which the difference between both methods was ≥ 0.2 log unit.

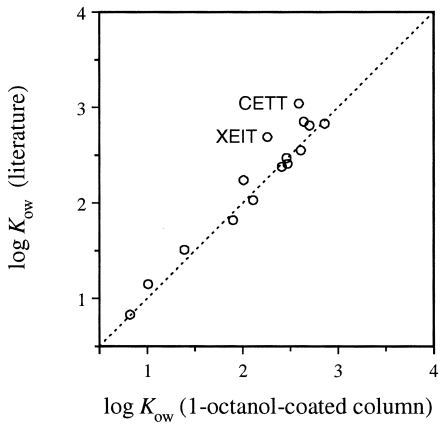

Fig. 3. Comparison between 1-octanol–water partition coefficients (K_{ow}) taken from the literature and those estimated by the 1-octanol-coated column method. The dotted line represents $x=y$.

the value of sebuthylazine (CEUT) obtained with this method was considerably lower ($\Delta\log K_{ow} = 0.51$) than that of the gradient method. This is also surprising because both methods yielded identical values for terbuthylazine which is very similar to sebuthylazine. The only structural difference is that terbuthylazine has a *tert.*-butyl group rather than sebuthylazine's *sec.*-butyl substituent.

Some of the $\log K_{ow}$ values determined in our study were lower than literature results. This also holds true compared to the results given by Finizio et al. [21]. However, their values seem to be too high compared to other sources. For example, $\log K_{ow}$ of

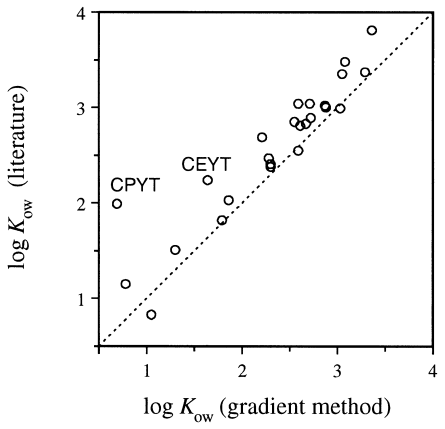

Fig. 4. Comparison between 1-octanol–water partition coefficients (K_{ow}) taken from the literature and those estimated by gradient HPLC. The dotted line represents $x=y$.

simetryne given by Finizio et al. is 2.80 [21] compared to 2.54 [23], 2.41 [24] and our value of 2.47. Except for procyacine (CPYT), there is a fairly good agreement between literature values and the data determined in this study, either by the coated-column method (Fig. 3) or the gradient HPLC method (Fig. 4). Thus, the $\log K_{ow}$ values of the 19 compounds for which no data were available so far, can be considered to be reliable.

4. Conclusions

The coated-column method is more difficult to perform than conventional HPLC methods for the determination of $\log K_{ow}$. Problems involved are peaktailing, higher noise and an eventual increase of the baseline during a HPLC run. However, the method closely simulates the 1-octanol–water system and is characterized by an excellent reproducibility, but it is restricted to $\log K_{ow}$ of about 3. For higher values, the gradient HPLC method is very convenient and reliable.

The reported $\log K_{ow}$ values are helpful in the physico–chemical characterization of *s*-triazines, in environmental fate studies, fate models, estimation of fate-relevant and effect-relevant properties (like soil adsorption coefficients, bioaccumulation factors and baseline toxicity) and quantitative structure–activity relationships [25].

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