Soil Adsorption Coefficients of *s*-Triazines Estimated with a New Gradient HPLC Method

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A high-performance liquid chromatography (HPLC) method employing gradient elution was developed to predict soil adsorption coefficients (K_{oc}) from HPLC capacity factors. The gradient method allows for the determination of K_{oc} values over a range of 4.4 orders of magnitude in a single experiment without adjustment of the solvent composition, as is required in isocratic HPLC measurements. The range of K_{oc} estimated can easily be extended by using reference compounds with lower or higher log K_{oc} values. Therefore, gradient HPLC is an appropriate screening method for K_{oc} and was used to investigate *s*-triazine herbicides and their degradation products. Log K_{oc} ranged from 0.8 for cyromazine to a maximum of 2.6 for anilazine and aziprotryne. HPLC-derived K_{oc} values of *s*-triazines containing an azido group were higher than and those of hydroxy-*s*-triazines were lower than K_{oc} values estimated according to the fragment contribution method of Meylan et al. (1992). According to this method, the log K_{oc} of the keto form of hydroxy-*s*-triazines was >1 log unit higher than that of the enol form.

INTRODUCTION

Symmetrical triazines (*s*-triazines) are among the most widely used pesticides. Their degradation in soil proceeds via N-dealkylation, deamination, and hydrolysis of the substituent on the C2 atom of the *s*-triazine ring, e.g. hydrolytic dechlorination of chloro-*s*-triazines. These reactions lead to cyanuric acid that is degraded by ring cleavage (Erickson and Lee, 1989). While N-dealkylation and deamination are known microbial reactions, dechlorination of chloro-*s*-triazines has mainly been attributed to abiotic processes, catalyzed by clay surfaces (Russel et al., 1968) and organic matter (Armstrong et al., 1967) and promoted by either acid or alkaline conditions (Armstrong et al., 1967). However, Mandelbaum et al. (1993) have reported a rapid transformation of atrazine to hydroxyatrazine by a soil bacterial culture. Furthermore, microorganisms are capable of dechlorinating dealkylated chloro-*s*-triazines (Ernst and Rehm, 1995). As a result, various *s*-triazine degradates are formed which have been detected in soils. Describing and modeling their behavior in soils and their eventual leaching to groundwater requires knowledge of their soil adsorption coefficient (K_{oc}).

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The soil adsorption coefficient (K_{oc}) of a chemical is defined as

$$K_{oc} = K_d/f_{oc} \tag{1}$$

where f_{oc} is the organic carbon fraction of the soil (expressed in grams per gram). The distribution coefficient K_d is given by

$$K_d = C_{soil}/C_{water}^n \tag{2}$$

where C_{soil} (micrograms per kilogram) is the concentration of the chemical adsorbed onto the soil, C_{water} (micrograms per liter) is the concentration in the soil solution, and n is a dimensionless exponent. If $n = 1$, K_d is the slope of a linear adsorption isotherm and is given in units of liters of water per kilogram of solid (soil or sediment). Sometimes, K_d is further multiplied with the density of water (1 kg L^{-1}), yielding a dimensionless quantity on a mass basis (kilograms per kilogram; this unit is then often omitted). If $n \neq 1$, eq 2 is known as the nonlinear Freundlich isotherm and n as the Freundlich exponent. In this case, the correct unit of K_d is μg kg^{-1} L^n μg^{-n} [cf. Mills and Thurman (1994)], but other units have also been used, e.g. m^{3n} kg^{-n} (Brouwer et al., 1990) or L kg^{-1} as for K_d of a linear adsorption isotherm (Singh et al., 1990). The latter unit is less awkward, but, strictly speaking, it does not match both the sides of eq 2 if $n \neq 1$. Similar considerations apply for K_{oc} if it is computed according to eq 1 from a nonlinear K_d. If the organic matter content of the soil is given, it is divided by 1.724 to yield the organic carbon content (Gerstl, 1990).

Several methods exist for the determination of K_{oc} (Green et al., 1980). One of the most commonly used

336 *J. Agric. Food Chem.,* Vol. 46, No. 1, 1998

Kaune et al.

techniques is the batch equilibrium method (OECD, 1981), in which an aqueous solution of the test compound is added to the soil. After adsorption equilibrium has been reached, the concentration of the chemical in the soil solution (C_{water}) is measured. The concentration in the adsorbed state is computed from the difference between C_{water} and the initial concentration of the chemical in the aqueous solution. However, more accurate results are obtained by analyzing both the soil solution and the sorbed phase (Singh et al., 1990). This procedure is known as the mass balance method.

The batch equilibrium and the mass balance methods are time-consuming and laborious. Therefore, they do not allow the routine investigation of many substances and are not suitable for screening purposes. Hence, many attempts have been made to estimate K_{oc}. It was estimated from water solubility and the octanol/water partition coefficient (Briggs, 1981; Karickhoff, 1981; Sabljic et al., 1995), quantum chemical descriptors (Reddy and Locke, 1994), and the first-order molecular connectivity index (MCI) to which polarity correction factors for 17 groups of polar compounds were added (Sabljic, 1987). The latter approach was extended by Meylan et al. (1992) by adding contribution factors of molecular fragments to the initial K_{oc} estimate, based solely on the first-order MCI. By doing so, fragment constants that have long been employed in the estimation of the octanol/water partition coefficient (Leo, 1993) were introduced in the K_{oc} prediction.

Experimental K_{oc} estimates can be made using high-performance liquid chromatography (HPLC) (Hodson and Williams, 1988). The HPLC method takes advantage of the fact that substances with high K_{oc} values elute later on some stationary phases than compounds with lower K_{oc} values. Stationary phases used were immobilized humic acid (Pussemier et al., 1994), silica–salicylic acid and silica–8-hydroxyquinoline (Szabó et al., 1995), trimethylammoniumpropyl and cyanopropyl (Kördel et al., 1993), and octadecyl (Kördel et al., 1993; Pussemier et al., 1994; Donati et al., 1994; Liu and Qian, 1995; Hong et al., 1996). The latter was also used in this study. One objection against the octadecyl column is that it does not permit the investigation of substances with very different log K_{oc} values at a certain mobile phase composition (Kördel et al., 1993). This objection led us to develop a gradient HPLC method instead of changing the stationary phase.

Till now, all HPLC experiments to estimate K_{oc} used isocratic elution, which was explicitly recommended by Kördel et al. (1995), who, however, did not give any reason for their recommendation. Indeed, there are some disadvantages of isocratic elution. For example, the solvent composition must be chosen in a way so that the compounds investigated have neither very short nor very long retention times. At a very short retention time, the capacity factor (K') and thus the predicted K_{oc} are sensitive to small changes in the retention time, producing a relatively large standard deviation of replicated measurements. A very long retention time is inconvenient and may produce broadened peaks or peaks of poor symmetry, both of which affect the accuracy of K' and K_{oc}. After selection of an eluent producing neither a very short nor a very long retention time of a test compound, reference compounds covering a slightly larger range of log K' values should be chosen so that no extrapolation of the log K_{oc} of the test compounds is required. Selecting an appropriate and

convenient eluent composition thus requires some effort and eventually a preliminary estimation of the expected K_{oc} by means of calculation. These difficulties encountered in isocratic elution experiments can be avoided by using gradient elution, which has not yet been applied to estimate K_{oc} by HPLC. The objectives of this paper were, therefore, (a) to develop a gradient HPLC method and (b) to apply it to the estimation of log K_{oc} of parent *s*-triazine herbicides and their degradates.

MATERIALS AND METHODS

HPLC experiments were conducted using a Gradient Former Model 250 B and a High Precision Pump Model 300 C (Gynkotek, Germering, Germany) or an L-6200A gradient pump (Merck, Darmstadt, Germany), a photodiode array detector DA320A, and a Gina 160 Autosampler (Gynkotek). The column was a LiChrospher 100 RP-18 endcapped (with methyl groups introduced in a second silanization step), particle size 5 μm, 250 mm × 4 mm (Merck). According to the manufacturer, this stationary phase is characterized by an average pore diameter of 10 nm, a pore volume of 1.25 mL g^{-1}, a specific surface area of 350 m^2 g^{-1}, a carbon content of 0.216 g g^{-1}, and a surface coverage [defined, for example, by Engelhardt and Ahr (1981)] of 4.09 μmol of functional groups m^{-2}. The analytical column was thermostated at 303 K. We used a flow rate of 1 mL min^{-1} and an injection volume of 20 μL. Absorption of the compounds was monitored at 210 nm except the absorption of 2-butanone, which was recorded at 270 nm. Spectral data were acquired between 200 and 356 nm to permit peak identification.

HPLC grade acetonitrile (Chromasolv) was purchased from Riedel-de Haën (Seelze, Germany) and methanol (LiChrosolv) from Merck. Demineralized water was passed through a Milli Q filtration system (Millipore, Eschborn, Germany). Eluents were degassed by sonication under reduced pressure. Commonly, methanol/water mixtures are used as the mobile phase, but acetonitrile/water mixtures are also feasible (Kördel et al., 1995). Due to its lower absorption compared to methanol, acetonitrile was employed in this study to elucidate the principal relation between log K_{oc} and log K' for different gradients. In an application of the gradient method for the K_{oc} determination of *s*-triazines, the more widely used methanol/water eluent was employed. The mobile phase was not buffered and its pH was 6.2. However, some substances, especially the hydroxy-*s*-triazines, which have pK_a values of ~5, were also chromatographed by employing a 10 mM KH$_2$-PO$_4$ mobile phase, buffered at pH 7.0. Log K_{oc} results obtained with both mobile phases did not show any systematic difference. The maximum difference was 0.15 and the mean difference 0.05 log unit. This indicates that the investigated compounds were in their nonionic form even in the unbuffered mobile phase.

Reference and test compounds were purchased from either Aldrich (Steinheim, Germany), Fluka (Buchs, Switzerland), Merck, Ehrenstorfer (Augsburg, Germany), or Riedel-de Haën and were of the highest purity available. Purities ranged from 99.9% to 96% (atrazine-deisopropyl) and to 93% (secbumeton). The latter two were certified reference materials and were not available at higher purity. Furthermore, impurities are chromatographically separated and, therefore, do not pose any problem in HPLC estimation of K_{oc}. Standard solutions of reference and test compounds were prepared in acetonitrile at concentrations ranging from 1 to 10 mg L^{-1}. Different reference compounds were used in the experiments performed to elucidate the log K_{oc} versus log K' relation in gradient HPLC (Table 1) and in the later experiments designed to estimate K_{oc} of *s*-triazines (Table 5).

The capacity factor (K') is defined as

$$K' = (t_R - t_0)/t_0 \qquad (3)$$

where t_R is the retention time of the substance investigated and t_0 is the retention time of a substance that is not retained

s-Triazine Soil Adsorption Coefficients

J. Agric. Food Chem., Vol. 46, No. 1, 1998 **337**

Table 1. Reference Compounds Used To Elucidate the Principal Relation between the Soil Adsorption Coefficient (K_{oc}) and the HPLC Capacity Factor

compound	log K_{oc}	s^a	n^b	reference
acetanilide	1.26			Müller and Kördel (1996)
phenol	1.32			Müller and Kördel (1996)
benzyl alcohol	1.43		1	Gerstl (1990)
benzene	1.90	0.19	7	Gerstl (1990)
toluene	2.06	0.34	7	Gerstl (1990)
trichloroethylene	2.28			Rippen (1987)
ethylbenzene	2.32			Müller and Kördel (1996)
chlorobenzene	2.34	0.22	11	Gerstl (1990)
bromobenzene	2.55	0.36	3	Gerstl (1990)
1,4-dichlorobenzene	2.80	0.21	9	Rippen (1987)
naphthalene	2.97	0.29	7	Gerstl (1990)
1,2,4-trichlorobenzene	3.35	0.19	7	Gerstl (1990)
phenanthrene	4.09			Müller and Kördel (1996)
p,p'-DDT	5.63	0.6	31	Müller and Kördel (1996)

^{a} Standard deviation. ^{b} Number of measurements.

Table 2. Calibration Curves for Different Gradient HPLC Experiments (According to Kaune, 1997)

type of experiment		calibration curve		
name	$\varphi_w =$	log $K_{oc} =$		eq
linear gradient	$a - kt$	$A \exp(-K \log k') + B$		
NLG60/0.1	$60 \exp(-0.1t)$	$A \exp(-K \log k') + B$		
NLG100/0.1 and NLG100/0.2	$100 \exp(-kt)$	$(-1/B) \log[D (\log k') + E]$		6

by the column (void time). t_0 was determined with thiourea and formamide using isocratic elution at water fractions of the mobile phase of $\leq 40\%$.

Linear Gradient Elution. In linear gradient elution runs, the water fraction of the mobile phase (φ_w, percent by volume) decreased linearly with time (t, min) according to

$$\varphi_w = a - kt \qquad (4)$$

where k is the rate constant (percent per minute). Gradients started at different initial water fractions (a) but always stopped at 0%. Then, initial conditions were re-established in 7.5 min and maintained for another 7.5 min to obtain equilibration.

Nonlinear Gradient Elution. In nonlinear gradient elution, φ_w decreased exponentially with time according to

$$\varphi_w = a \exp(-kt) \qquad (5)$$

where a is the initial volumetric water fraction (percent) and k is the rate constant (min^{-1}). It is possible to modify eq 5 by addition of a third parameter (b) so that the water fraction asymptotically approaches b. However, this was not done in this study. Three types of experiments were performed, which were characterized by $a = 100\%$, $k = 0.1$ min^{-1} (NLG100/0.1); $a = 100\%$, $k = 0.2$ min^{-1} (NLG100/0.2); and $a = 60\%$, $k = 0.1$ min^{-1} (NLG60/0.1). (Nonlinear gradients are abbreviated as NLG followed by their a and k values.) A maximum rate constant of 0.2 min^{-1} was used to avoid having the solvent composition change too rapidly, especially in the beginning of an experiment.

To approximate an exponentially shaped gradient with a two-pump solvent delivery system, experimental times required for a 5% change in the water fraction were programmed. Within each of these time steps, the gradient was linear. The gradient was reversed when φ_w was 5%. Thus, the time required for completion of the gradient was 30 min in experiment NLG100/0.1, 25 min in NLG60/0.1, and 15 min in NLG100/0.2. Total experimental time was 15 min longer since, as in linear gradient elution, the gradient was reversed within 7.5 min and the system was allowed to equilibrate for another 7.5 min.

Log K_{oc} values versus experimental log k' of the reference compounds were fitted to the equations given in Table 2, depending on the type of experiment performed. Curve fitting

was done by nonlinear regression analysis using the figure processor software (Biosoft, Cambridge, U.K.). Using the appropriate calibration curve, log K_{oc} values of test compounds were calculated from their experimental log k' values.

Furthermore, log K_{oc} was calculated according to the method of Meylan et al. (1992) using the software PCKOC (version 1.56, April 1995), which is commercially available from the Syracuse Research Corp., Chemical Hazard Assessment Division, Environmental Chemistry Center, Syracuse, NY 13210. For hydroxy-*s*-triazines, separate calculations were done for their enol and keto forms. When the Chemical Abstracts Service (CAS) Registry Number is fed into the PCKOC program, it should be noted that PCKOC inconsistently outputs the keto form of one polar triazine degradation product not investigated in this study [ammeline (2-hydroxy-4,6-diamino-*s*-triazine)] and the enol form of other hydroxy-*s*-triazines (hydroxy analogues of atrazine, simazine, and propazine).

Abbreviations of *s*-triazines explained in Tables 5 and 7 follow a four-letter nomenclature similar to those of Grossenbacher et al. (1984) and Erickson and Lee (1989) in which the fourth upper case letter denotes the triazine ring and the first three upper case letters represent the substituents on the ring. Anilazine was abbreviated by lower case letters because the substitution pattern of this compound differs from that of the other *s*-triazines and the four-letter nomenclature mentioned above is not applicable to this compound.

RESULTS AND DISCUSSION

Relation between Soil Adsorption Coefficient and HPLC Capacity Factor. The relationships between log K_{oc} and log k' in linear and nonlinear gradient HPLC experiments are shown in Figures 1 and 2, respectively, for different rate constants and different initial water fractions of the gradient.

The time required to complete a linear gradient decreased with increasing rate k (eq 4). Increasing k decreased log k' of a given compound and the range of log k' values (Figure 1a). This was accompanied by a decrease of the parameters A and K of the exponential calibration curve (Table 3). Decreasing the initial water fraction of the eluent (a in eq 4) decreased log k' of a given compound and increased the range of log k' values (Figure 1b). This was reflected in an increase of the parameters A and K of the exponential regression equation (Table 3). The accuracy of predicting the log K_{oc} of the reference compounds (i.e., the coefficient of determination, r^2) was very similar for all gradients, regardless of the rate k and the initial water fraction a (Table 3). Similar tendencies were also observed in nonlinear gradient experiments (Figure 2; Table 4). This investigation of the principal relation between log K_{oc} and log k' demonstrates that all of the different gradients employed are suitable to estimate log K_{oc}. The gradient HPLC method has the advantage of enabling the estimation of log K_{oc} over a range of more than 4 orders of magnitude in a single experiment. The nonlinear gradient NLG100/0.1 was selected to estimate log K_{oc} of *s*-triazines because it appeared to be the most suitable in terms of precision, range of K_{oc} covered, and experimental time and solvent required.

Soil Adsorption Coefficients of *s*-Triazines. Compared to the experiments described above, we used some *s*-triazines as reference compounds (Table 5). The use of structurally similar compounds as reference substances is recommended because it typically increases the accuracy of the estimated values (Liu and Qian, 1995). The calibration curve is depicted in Figure 3. Literature log K_{oc} values of the reference *s*-triazines
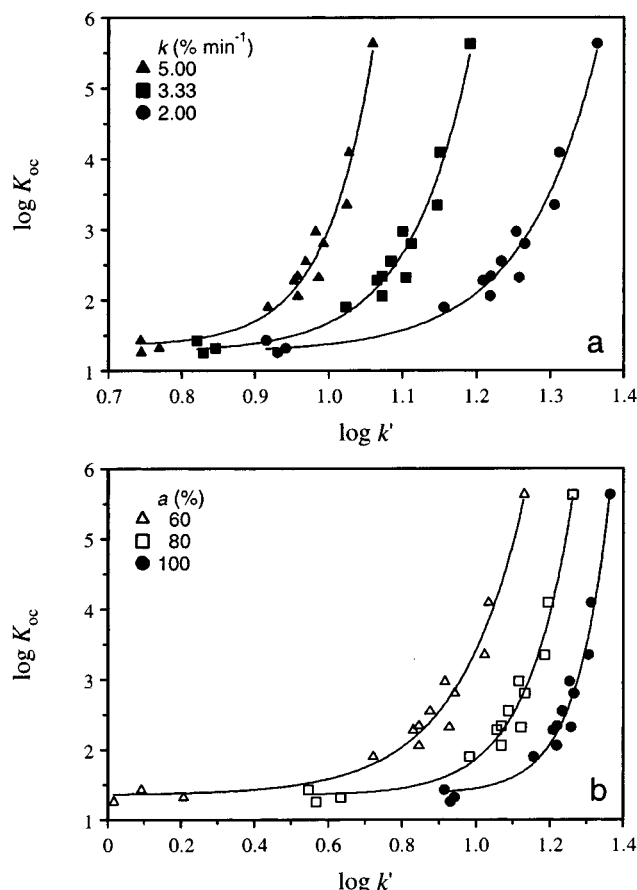
338 *J. Agric. Food Chem.,* Vol. 46, No. 1, 1998

Kaune et al.

Figure 1. Relation between the soil adsorption coefficient (K_{oc}) and the capacity factor (k') employing linear gradient elution according to eq 4: (a) the initial (a) and final water fractions of the eluent were 100% and 0%, respectively, and the rate (k) was varied; (b) k was held constant (2% min^{-1}), and a was changed. Solid lines were obtained by fitting data to an exponential equation, the parameters of which are given in Table 3. Note different scales on x-axes.

Figure 2. Relation between the soil adsorption coefficient (K_{oc}) and the capacity factor (k') employing nonlinear gradient elution according to eq 5: (a) the gradient started at 100% water ($a = 100\%$), and the rate constant (k) was varied; (b) k was held constant at 0.1 min^{-1}, and a was changed. The solid line is a fit to an exponential equation, and the dashed line is a fit to eq 6 (Table 2). The parameters of the regression equations are given in Table 4. Note different scales on x-axes.

differed from gradient HPLC estimates by a maximum of 0.24 (Table 5). The mean of the absolute deviations was 0.12 log unit. Similar results were obtained for another five s-triazines, which were excluded from the list of reference compounds and whose log K_{oc} was estimated with gradient HPLC. The maximum difference between literature and gradient HPLC-derived log K_{oc} was 0.37, and the mean of the absolute differences was 0.23 (Table 6). These data reflect a fairly good accuracy, considering the standard deviation of literature log K_{oc}, which may be as high as 0.55 log unit (secbumeton) (Table 5). The large standard deviation of log K_{oc} reported in the literature may result from different methods of determination (Singh et al., 1990), e.g. batch equilibrium versus mass balance method, and from differences in soil properties. As a conclusion, the gradient HPLC method and the calibration curve established (Figure 3) permit the precise estimation of presently unknown log K_{oc} values of s-triazines.

The precision, i.e., the reproducibility, of three replicated gradient HPLC measurements was 0.1 for cyromazine with log K_{oc} < 1 and ≤ 0.03 for all other substances. An error larger than that of replicated HPLC measurements is typically introduced by the choice of reference compounds and of reference log K_{oc} values. Therefore, log K_{oc} values are typically given with only two significant digits.
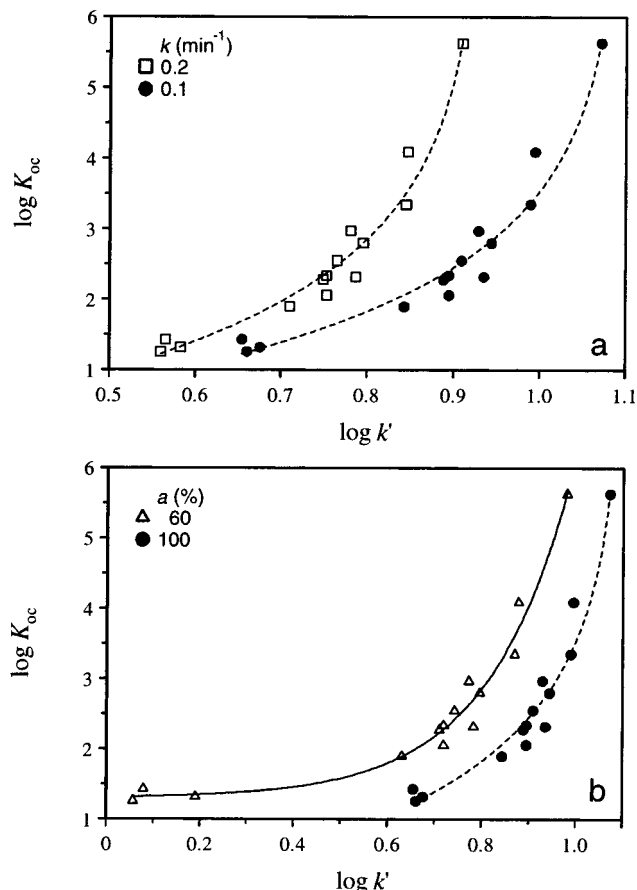
Table 3. Parameters of an Exponential Regression Equation Fitted to Results of Linear Gradient Elution Experiments (Figure 1)[a]

$\varphi_w = a - kt$		log $K_{ow} = A \exp(-K \log k') + B$			
a (%)	k (% min^{-1})	A	K	B	r^2
100	5.0	$(3.2 \pm 12.7) \times 10^{-7}$	-15.5 ± 3.7	1.35 ± 0.32	0.966
100	3.33	$(7.9 \pm 28.0) \times 10^{-6}$	-13.0 ± 3.0	1.33 ± 0.31	0.968
100	2.0	$(2.5 \pm 7.7) \times 10^{-6}$	-10.5 ± 2.3	1.32 ± 0.30	0.971
80	2.0	$(1.7 \pm 3.5) \times 10^{-4}$	-8.0 ± 1.7	1.35 ± 0.28	0.970
60	2.0	$(8.0 \pm 10.9) \times 10^{-3}$	-5.5 ± 1.2	1.36 ± 0.29	0.969

[a] Parameter estimates are given together with their 95% confidence intervals.

The results of the gradient HPLC method are collected in Table 7. The log K_{oc} of cyromazine (log K_{oc} = 0.8) was obtained by extrapolation due to lack of reference compounds with log K_{oc} < 1.17 (the reference log K_{oc} of aniline). However, we assume that the extrapolated value for cyromazine is fairly accurate because the range of extrapolation was small.

Effects of Chemical Structure. Given the same substituents in the fourth and sixth positions of the s-triazine ring, log K_{oc} estimated with HPLC decreased in the order of methylthio- > chloro- ≈ methoxy- > hydroxy-s-triazines. For log K_{oc} computed with PCKOC the order was methylthio- > chloro- = hydroxy- > methoxy-s-triazines, e.g. ametryn > atrazine = hy-

s-Triazine Soil Adsorption Coefficients

J. Agric. Food Chem., Vol. 46, No. 1, 1998   339

Table 4. Parameters (±95% Confidence Intervals) of the Regression Equations Fitted to the Results of Nonlinear Gradient Elution Experiments (Figure 2)

$\varphi_w =$ $a \exp(-kt)$ (eq 5)		log $K_{ow} =$ $(-1/B) \log[D (\log k') + E]$ (eq 6)			
a (%)	k (min^{-1})	B	D	E	r^2
100	0.1	0.29 ± 0.14	-1.00 ± 0.49	1.10 ± 0.60	0.951
100	0.2	0.28 ± 0.12	-1.23 ± 0.51	1.15 ± 0.53	0.959

$\varphi_w =$ $a \exp(-kt)$ (eq 5)		log $K_{ow} =$ $A \exp(-K \log k') + B$			
a (%)	k (min^{-1})	A	K	B	r^2
60	0.1	0.016 ± 0.019	-5.7 ± 1.2	1.3 ± 0.3	0.969

droxyatrazine > atraton (Tables 5 and 7). For comparison, the order found for adsorption to montmorillonite was slightly different: methylthio- > methoxy- > hydroxy- > chloro-s-triazines (Weber, 1970), but the methylthio-s-triazines are always most strongly adsorbed. Given the same substituent in the second position of the s-triazine ring, estimated and calculated log K_{oc} values decreased in the order of 4,6-bis(ethylamino) < 4-(ethylamino)-6-(isopropylamino) < 4-(ethylamino)-6-(tert-butylamino) $\approx$ 4,6-bis(isopropylamino), e.g. simetryne < ametryne < terbutryne = prometryne. A comparison of compounds that differ only in one of the three substituents (e.g. ethylamino versus amino) reveals that the effect of a single substituent is not purely additive but also depends on the other substituents present.

Comparison between Estimated and Calculated K_{oc} Values. Log K_{oc} values estimated with gradient HPLC and those calculated with the program PCKOC according to the method of Meylan et al. (1992) compare fairly well, except for s-triazines containing an azido or a hydroxyl group (Table 7). For aziprotryne (NSIT) and azidoatrazine (NEIT), which contain an azido group, the gradient HPLC estimate of log K_{oc} was much higher than the calculated value. Either the azido group is more polar than reflected by the retention behavior on an octadecyl column or the method of Meylan et al. (1992) overestimates the polar nature of the azido group.

The reverse is true for hydroxy-s-triazines, for which log K_{oc} values estimated with HPLC were lower than those of the PCKOC calculations. Furthermore, according to the HPLC measurements, log K_{oc} values of hydroxy-s-triazines were lower than those of the chloro analogues, but PCKOC calculations of the enol form produced identical results. For example, the calculated log K_{oc} of atrazine (Table 5) is identical with that of the enol form of hydroxyatrazine (Table 7). The reason is that the first-order molecular connectivity index and the fragment correction factors are identical, yielding identical K_{oc} values. (The fragment corrections of PCKOC account for nitrogen to nonfused aromatic ring, for an aliphatic nitrogen to carbon bond, and for the triazine ring but not for hydroxy.)

Comparison of the Enol and Keto Forms of Hydroxy-s-triazines. There are indications in the literature on keto−enol tautomerism of hydroxy-s-triazines and the predominance of the keto form. Without giving any proof, Weber (1966) stated that hydroxypropazine and hydroxyipazine "probably exist in the keto form rather than the enol form". The enol form of protonated hydroxyatrazine (OEIT) was found in the aqueous phase of a montmorillonite/water system, but the keto form was present when protonated OEIT was

adsorbed to the clay (Russel et al., 1968). Information is available on the keto−enol tautomerism of three hydroxy-s-triazines not included in our study. Wang et al. (1993) concluded from ab initio calculations that the enol form of ammeline should be the dominant tautomer in the gas phase. However, ammelide (2,4-dihydroxy-6-amino-s-triazine) exists in the keto form (Wang et al., 1993). Cyanuric acid also exists in the keto (triketo) form in aqueous solutions below pH 6.8, and the diketo (monoenol) form predominates between pH 6.8 and 10.5 (Smolin and Rapoport, 1959, pp 34 and 389).

Therefore, PCKOC calculations were also performed for the keto form of the hydroxy-s-triazines. The difference between log K_{oc} of both tautomers results from the fragment correction factors. The first-order molecular connectivity index (MCI) is identical for the enol and the keto form and so is the uncorrected log K_{oc}, which is only derived from MCI. In the enol form of hydroxy-s-triazines a correction is made for nitrogen to nonfused aromatic ring (fragment value of −0.7770), for the triazine ring (−0.7521), and (in the case of alkylated hydroxy-s-triazines) for a nitrogen to aliphatic carbon bond (−0.1242). The latter is the only correction made in the keto form. There are four nitrogen to aliphatic carbon bonds in monoalkylated (OEAT and OAIT) and five in dialkylated (e.g. OEET) keto hydroxy-s-triazines. As a result of the addition of correction factors, log K_{oc} of the keto form of all hydroxy-s-triazines investigated in this study is 1.157 log units higher than that of the enol form. The discrepancy from the HPLC-derived log K_{oc} increases by this value.

Literature Data on K_{oc} of Hydroxy-s-triazines. As stated above, log K_{oc} values of hydroxy-s-triazines were lower than those of their chloro analogues according to our HPLC measurements. However, according to the PCKOC calculations using the enol form, both values were identical, and according to the PCKOC calculations using the keto form, log K_{oc} values of the hydroxy-s-triazines were higher than those of the parent chloro compounds. Summarizing data reported by Brouwer et al. (1990), Chung et al. (1994), Mersie and Seybold (1996), and Solomon et al. (1996), log K_{oc} of hydroxyatrazine (OEIT) ranged from 2.25 to 4.1 and was 0.2−2.2 log units higher than that of atrazine (CEIT). K_d values of OEIT ranged from 1.98 to 389 L kg^{-1} (Solomon et al., 1996). A high K_d value of OEIT (K_d = 155 L kg^{-1}) was also reported by Clay et al. (1988). Weber (1966) studied the adsorption of s-triazines on montmorillonite. Adsorption maximum and adsorption at pH >3 were higher for hydroxypropazine compared to propazine and for hydroxyipazine compared to ipazine.

The mobility of s-triazines, which is inversely related to soil adsorption, was measured by soil thin-layer chromatography (Somasundaram et al., 1991; Kruger et al., 1996). OEIT was hardly mobile. It often remained at the start of the soil thin layer so that the retention factor R_f was 0.0. OEIT was always considerably less mobile than CEIT (Somasundaram et al., 1991; Kruger et al., 1996). Similarly, hydroxyprometryne was hardly mobile and always considerably less mobile than prometryne (Somasundaram et al., 1991). The mobility of ammeline was similar to that of hydroxyprometryne and hydroxyatrazine (Somasundaram et al., 1991; Kruger et al., 1996). For ammeline and ammelide, the adsorption to montmorillonite at pH 6.5 was in the same range

340 *J. Agric. Food Chem.,* Vol. 46, No. 1, 1998

Kaune et al.

Table 5. Reference Compounds Used in Gradient HPLC Experiments To Estimate the Soil Adsorption Coefficient of Parent *s*-Triazine Herbicides and Their Degradation Products

compound	abbrev	log K_{oc} (lit.)	s	n	ref	log k' gradient HPLC	log K_{oc} gradient HPLC	log K_{oc} PCKOC[f]
aniline		1.17			a	0.676	1.2	1.7
acetanilide		1.26			b	0.723	1.4	1.6
phenol		1.32			b	0.730	1.4	2.4
atrazine-deisopropyl	CEAT	1.45			c	0.697	1.3	1.7
atrazine-deethyl	CAIT	1.58			c	0.770	1.6	1.9
terbuthylazine-deethyl	CATT	1.84			c	0.854	2.0	2.1
simazine	CEET	2.02	0.35	240	d	0.844	1.9	2.2
monolinuron		2.16	0.40	44	d	0.872	2.1	2.3
atrazine	CEIT	2.19	0.34	217	d	0.894	2.2	2.4
prometon	XIIT	2.19	0.44	70	d	0.928	2.4	2.2
terbuthylazine	CETT	2.51	0.19	3	d	0.929	2.4	2.5
secbumeton	XEUT	2.64	0.55	12	d	0.924	2.4	2.3
prometryne	SIIT	2.66	0.38	125	d	0.974	2.7	2.8
trietazine	CDET	2.76	0.02	2	d	0.977	2.8	2.6
naphthalene		2.97	0.29	7	d	1.005	3.0	3.3
dimethametryne	SEJT	3.07			a	1.000	2.9	3.1
1,2,4-trichlorobenzene		3.35	0.19	7	d	1.063	3.5	2.9
dieldrin		3.84			e	1.092	3.8	4.0

[a] Sabljic (1987). [b] Müller and Kördel (1996). [c] Bottoni et al. (1996). [d] Gerstl (1990). [e] Rippen (1987). [f] PCKOC is the log K_{oc} calculated according to the method of Meylan et al. (1992).
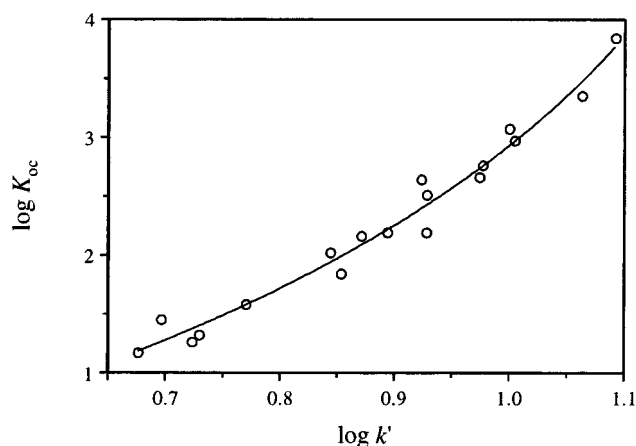

Figure 3. Calibration curve for the nonlinear gradient NLG100/0.1 in which the water fraction of the mobile phase decreased exponentially according to $\varphi_w = 100 \exp(-0.1 \text{ min}^{-1} t)$. The regression equation is given by log $K_{oc} = (-1/0.172)$ log$[-0.966 (\log k') + 1.28]$, $r^2 = 0.974$.

as that of the strongly sorbed methylthio-*s*-triazines and much higher than that of chloro-*s*-triazines (Weber, 1970).

To summarize this short review on the adsorption of hydroxy-*s*-triazines to soil and montmorillonite, soil adsorption coefficients of hydroxy-*s*-triazines may vary considerably between soils but seem to be generally higher than that of their parent compounds. This is correctly predicted if the keto form, but not if the enol form, is assumed in the PCKOC calculations. If one assumes that the calculational procedure is fairly accurate, this indicates the existence of the keto rather than the enol form of hydroxy-*s*-triazines in soils.

Furthermore, the gradient HPLC results underestimated log K_{oc} of the hydroxy-*s*-triazines compared to their parent herbicides. This conclusion, however, is not restricted to the gradient HPLC method but also applies for the well-established isocratic method (data not shown) and may depend on the type of stationary phase used. The substances are probably less retained on a nonpolar octadecyl column than they are adsorbed by the more polar organic carbon fraction of soils. This explanation can be verified by using a conventional

batch equilibrium method (OECD, 1981; Singh et al., 1990) or a different HPLC stationary phase, e.g. a humic acid or a cyanopropyl phase which has nonpolar as well as polar groups and may therefore simulate typical soil constituents better than the nonpolar octadecyl phase. Further experiments should, therefore, address the question of whether log K_{oc} of hydroxy-*s*-triazines can more accurately be estimated by a humic acid or a cyanopropyl phase.

Literature Data of Other Dealkylated *s*-Triazine Degradation Products. Log K_{oc} of atrazine (CEIT) was higher than that of the two monodealkylated degradation products, atrazine-deethyl (CAIT) and atrazine-deisopropyl (CEAT) (Table 5). A higher log K_{oc} of CEIT compared to CAIT was also reported by Mersie and Seybold (1996) and by Roy and Krapac (1994) for low organic carbon geologic materials. Furthermore, this ranking agrees with the mobility of CEIT, which was lower than that of CAIT (Bowman, 1991).

Experimental log K_{oc} values of CAIT and CEAT were 1.60 and 1.48 (Mills and Thurman, 1994) and (closely agreeing) 1.58 and 1.45, respectively (Bottoni et al., 1996). The same order of CAIT and CEAT was found in our HPLC measurements and the PCKOC calculations (Table 5). However, a different order was reported by Brouwer et al. (1990) and Mersie and Seybold (1996). In their soils, log K_{oc} of CEAT was higher than that of CAIT but still less than that of CEIT, implying a higher mobility of CEAT compared to CEIT. Conversely, CEAT was less mobile than CEIT according to Kruger et al. (1996). The mobility of CAAT ranged between that of CEAT and CEIT (Kruger et al., 1996).

Thus, there is no K_{oc} order of atrazine and its dealkylated degradation products that is generally valid for all soils studied. This may be due to different physicochemical properties of the compounds and due to the fact that different adsorption mechanisms predominate in the investigated soils. Therefore, it can also not be expected that any K_{oc} screening method as HPLC or the calculational method will rank chemicals accurately for all of the soils.

Literature Data of Cyromazine. Pote et al. (1994) quoted K_d values of cyromazine from the manufacturer's (Ciba-Geigy) *Summary of Field Dissipation Studies* and

s-Triazine Soil Adsorption Coefficients

J. Agric. Food Chem., Vol. 46, No. 1, 1998 341

Table 6. Comparison between Literature log K_{oc} Values of s-Triazines and Those Estimated with the HPLC Gradient Method

compound	abbrev	log K_{oc} (lit.)	s	n	ref	log K' gradient HPLC	log K_{oc} gradient HPLC	PCKOC
propazine	CIIT	2.14	0.21	81	a	0.942	2.5	2.6
cyanazine	CEYT	2.17	0.24	13	a	0.816	1.8	2.1
ametryne	SEIT	2.50	0.26	41	a	0.938	2.5	2.6
dipropetryne	VIIT	2.95	0.23	9	a	1.006	3.0	3.1
terbutryne	SETT	3.17	0.48	18	a	0.979	2.8	2.8

[a] Gerstl (1990).

Table 7. Soil Adsorption Coefficients (K_{oc}) of s-Triazines Estimated with the HPLC Gradient Method and Calculated with the Program PCKOC According to the Method of Meylan et al. (1992)

compound	abbrev	log K_{oc} gradient HPLC	PCKOC
chloro-s-triazines			
procyazine	CPYT	1.2	1.7
sebuthylazine-deethyl	CAUT	1.8	2.2
trietazine-deethyl	CDAT	2.1	2.1
sebuthylazine	CEUT	2.4	2.6
methoxy-s-triazines			
atraton-deisopropyl	XEAT	1.3	1.4
simeton	XEET	1.9	1.8
terbumeton-deethyl	XATT	2.0	1.7
atraton	XEIT	2.2	2.0
terbumeton	XETT	2.5	2.2
hydroxy-s-triazines			
atrazine-deethylhydroxy	OAIT	1.3	1.9[a]
terbuthylazine-deethylhydroxy	OATT	1.3	2.1[a]
simazine-hydroxy	OEET	1.4	2.2[a]
atrazine-hydroxy	OEIT	1.9	2.4[a]
terbuthylazine-hydroxy	OETT	2.0	2.5[a]
methylthio-s-triazines			
desmetryne	SIMT	2.2	2.4
simetryne	SEET	2.2	2.5
methoprotryne	SIKT	2.4	2.2
aziprotryne	NSIT	2.6	1.5
miscellaneous s-triazines			
cyromazine	AAPT	0.8	1.3
azidoatrazine	NEIT	2.4	1.6
anilazine	anil	2.6	3.2

[a] Value for the enol form; log K_{oc} of the keto form is 1.157 log units higher.

stated that "K_d values for cyromazine are less than 1.0 in some soils that are low in organic matter and clay, but are greater than 50 in some soils with high organic matter and clay content". Assuming organic carbon contents of 1% and 5%, respectively, for soils with low and high organic carbon contents, the resulting log K_{oc} values range between 2 and 3. This is surprisingly high compared to the high water solubility of cyromazine [11 g L^{-1} (Worthing, 1987) or 13.6 g L^{-1} at 22 °C (Pote et al., 1994) according to a Ciba-Geigy report]. The HPLC-derived log K_{oc} (= 0.8) is much lower and closer to the value one would expect from the high water solubility.

CONCLUSIONS

Gradient HPLC elution is especially suitable if an appropriate mobile phase composition for isocratic elution is not known or if substances with presumably very different K_{oc} values have to be investigated in a single series of experiments. The gradient method is more standardized than the isocratic method in which K_{oc} of some compounds may depend on the mobile phase composition. With gradient HPLC a large range of log K_{oc} values can be estimated in a single run. This range

was 4.4 orders of magnitude in this paper and depends primarily on the reference compounds used so that it can easily be extended.

The adsorption of s-triazines depends on the pH of the soil (Nearpass, 1965; Wang et al., 1992; Chung et al., 1994). Maximum adsorption is observed when the pH equals the pK_a of the s-triazine. This is also true for adsorption to the clay fraction of soils, e.g. montmorillonite (Weber, 1966). It remains an open question whether it is possible with HPLC experiments to account for the pH dependence of log K_{oc}. The need to consider the pH dependence particularly holds for the hydroxy-s-triazines with pK_a values ~5 so that a considerable portion of molecules is protonated at environmental pH. A quantitative consideration of pH and pK_a is currently also not possible in the PCKOC estimation program, which computes K_{oc} of the nonionized species (Meylan et al., 1992). At present, PCKOC addresses this problem by displaying a warning message whenever the program detects an aromatic hydroxyl group, an organic acid, or an aromatic nitrogen (as in all s-triazines except the keto form of the hydroxy derivates). Although the fraction of the ionized species at a given pH is described by the Henderson−Hasselbalch equation and the dependence of the octanol/water partition coefficient on pH can be modeled by knowing the pK_a and the octanol/water partition coefficient of the neutral and ionic forms (Roda et al., 1990), these methods may not be adequate to describe the pH dependence of the soil adsorption coefficient.

Future research is necessary to study keto−enol tautomerism of hydroxy-s-triazines and other tautomeric chemicals and the effect of tautomerism on adsorption behavior. Apart from hydroxy-s-triazines, tautomeric environmental chemicals include, e.g., phenylcarbamates, anilides, substituted ureas, and amides (Bailey et al., 1968) and degradation products of nonsymmetrical triazines such as deaminometribuzin (Dieckmann et al., 1994).

Both isocratic and gradient HPLC estimations of K_{oc} are affected by the type of stationary phase (Kördel et al., 1993) because the retention behavior of test compounds varies between stationary phases due to their different interactions with the solute. This can also be interpreted in such a way that different stationary phases simulate different adsorption mechanisms. Since no stationary HPLC phase is identical with a real-world soil, both the isocratic and the newly developed gradient HPLC techniques are considered as screening methods. Alternatively, the adsorption behavior of a naturally occurring soil may potentially be investigated by using a preparative HPLC column packed with this particular soil. This setup has already been used to study soil diffusion coefficients (Goss and Schramm, 1991). HPLC measurements using a soil-filled preparative column for determining K_{oc} may be advantageous as compared to

342 *J. Agric. Food Chem.,* Vol. 46, No. 1, 1998

Kaune et al.

the commercially available stationary HPLC phases. It may also be an alternative to the soil thin-layer chromatography method in which retention factors are measured (Somasundaram et al., 1991; Kruger et al., 1996) but no K_{oc} data are presently estimated.

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