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Modeling Plant Uptake of Airborne Organic Chemicals. 1. Plant Cuticle/Water Partitioning and Molecular Connectivity

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■ Molecular connectivity indexes were tested with regard to their ability to describe the cuticle/water partitioning for a variety of organic chemicals. A model is derived that accounts for 99% of the variation in the published cuticle/water partition coefficients (K_{CW}), which cover the range of 8.5 orders of magnitude. It is shown that the molecular size is directly proportional to the cuticle/water partition coefficients. It is also the most important structural feature that accounts for 89% of the variation in the measured K_{CW} data. Moreover, the molecular connectivity model outperforms in accuracy and speed the traditional empirical models based on 1-octanol/water partition coefficients or water solubilities. Our results and their comparison with previously published models demonstrate that the molecular connectivity model is an accurate predictive tool for the cuticle/water partition coefficients of a wide range of commercial chemicals and that it can be confidently used to assess their potential to penetrate and to accumulate in aboveground vegetation.

1. Introduction

Plants may accumulate pollutants either by uptake from soil and water through the roots or from the atmosphere by their aboveground parts after wet or dry deposition. For apolar airborne compounds, the main route of uptake will be via the leaf surface (1) for three reasons: (i) the total leaf surface area may exceed by factors up to 20 the ground area on which a plant is growing, (ii) the mobility of apolar chemicals in the soil and in the transport system of plants is fairly low due to their low aqueous solubility and strong sorption by lipophilic compartments, and (iii) the permeability of plant surfaces is larger for apolar compounds (2). Thus, there is a high probability that the apolar airborne pollutants will be taken up by the foliage rather than by the root system of a plant.

Uptake of environmental chemicals by leaves or fruits may proceed via two independent pathways: (a) nonvolatile substances must penetrate the cuticle before they reach internal tissues, while (b) gases and volatile chemicals additionally can enter via open stomata. The transport of a nonelectrolyte across the cuticle is determined both by the solubility and by the mobility of the compound in the cuticle (2). The solubility in the cuticle is characterized by the cuticle/water partition coefficient (K_{CW}).

However, the plant cuticle is not only a route for the uptake of atmospheric pollutants into plants but it may also act as an accumulation compartment for persistent lipophilic chemicals. The total amount of cuticular material in temperate forests and agricultural plant communities may range from 180 to 1500 kg/ha (3). Nearly the whole content of persistent, highly nonpolar chemicals in

a given leaf or fruit will be found in the cuticle, which in turn makes up only a small fraction of their total mass or volume (4). The parameter describing the tendency of environmental chemicals to accumulate in the cuticle phase in an ecosystem as well as on a single leaf or fruit scale is again the cuticle/water partition coefficient.

For these reasons, cuticle/water partition of nonvolatile organic chemicals has been studied (2). At present, the cuticle/water partition coefficients are available for a total of 15 compounds, which differ greatly in their structural and physicochemical properties, and for the cuticle of the leaves and fruits of two species each. The values of K_{CW} cover the range of 8.5 orders of magnitude and were determined under controlled and uniform conditions, thus representing a data set with the highest degree of internal consistency and comparability. Consequently, this data set should be perfectly suited for modeling cuticle/water partitioning by use of topological indexes.

Our primary objective in this study is to examine the possibility to quantitatively model the cuticle/water partition coefficients by application of molecular connectivity indexes. The molecular connectivity indexes have been found to be very successful in modeling environmental parameters like soil sorption (5-9), association with dissolved humic substances (10), the Henry's law constants (11), bioconcentration (7, 12, 13), biodegradation (14-16), and aquatic toxicity (17-22) of major organic pollutants. It should be useful to have a quantitative model, based on the same concept, for cuticle/water partitioning. Our goal is to develop a quantitative model, based on molecular connectivity indexes, that will predict the cuticle/water partition coefficients of nonvolatile chemicals within their experimental errors. In addition, we hope to gain more information about structural features that are important in cuticle/water partitioning. Since molecular connectivity indexes describe and quantify the size, the shape, the degree of branching, and the cyclicity of molecules, this investigation will show whether and how these particular structural features influence the cuticle/water distribution.

The second objective of this study is to check the quality of such a quantitative structure-activity relationship (QSAR) model by comparing it with other models for predicting the cuticle/water partition coefficients. This comparison will provide important information about the performance and range of applicability of molecular connectivity indexes. Finally, those models will be critically evaluated with particular emphasis on their advantages and limitations.

2. Method of Calculation and Experimental Data

Several extensive reviews of the theory and method of calculation of molecular connectivity indexes have been published recently (23-27). Thus, only a brief description is given here of the calculation of the valence third-order

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Table I. Observed *Citrus*, *Ficus*, *Lycopersicon*, and *Capsicum* Cuticle/Water Partition Coefficients ($\log K_{CW}$) of 15 Organic Compounds in the Systems Cuticular Membrane (CM)/Water and Polymer Matrix Membrane (MX)/Water, plus Their Valence Third-Order Molecular Connectivity Indexes ($^3\chi^v$) and the Number of Aliphatic Hydroxy Substituents (no. OH_{aliph})

compound	$^3\chi^v$	(no. OH _{aliph})	$\log K_{CW}$							
			<i>Citrus</i>		<i>Ficus</i>		<i>Lycopersicon</i>		<i>Capsicum</i>	
			CM	MX	CM	MX	CM	MX	CM	MX
methanol	.000	1	-1.15							
phenol	.756	0			1.51	1.69	1.58	1.64	1.59	1.67
benzoic acid	.977	0								1.58
2-nitrophenol	1.045	0			1.84	1.99	1.83	1.99	1.92	2.04
4-nitrophenol	1.061	0	1.79	1.76	1.80	1.89	1.89	1.91	1.97	2.03
atrazine ^a	1.529	0	2.15	2.17	2.16	2.15	2.12	2.13	2.19	2.20
1-naphthaleneacetic acid	2.222	0	2.18	2.25			2.24	2.31	2.33	2.43
2,4-D ^b	1.774	0	2.47	2.48	2.50	2.69	2.63	2.79	2.76	2.89
triadimenol ^c	3.177	1	3.37		3.26		3.37		3.37	
2,4,5-T ^d	2.341	0	3.13	3.20	3.11	3.20	3.19	3.24	3.21	3.26
bitertanol ^e	4.073	1	3.77		3.95		3.91		3.85	
pentachlorophenol	3.437	0	4.42	4.46	4.55	4.60	4.57	4.70	4.66	4.72
hexachlorobenzene	3.996	0	5.70	5.79	5.74	6.01	5.83	5.85	5.80	5.82
perylene	4.390	0	6.45	6.59	6.20	6.58	6.50	6.49	6.55	6.58
bis(2-ethylhexyl) phthalate	5.354	0	7.22	7.38	7.28	7.58	7.32	7.33	7.48	7.66

^a Atrazine, 6-chloro-*N*-ethyl-*N'*-(1-methylethyl)-1,3,5-triazine-2,4-diamine. ^b 2,4-D, (2,4-dichlorophenoxy)acetic acid. ^c Triadimenol, β -(4-chlorophenoxy)- α -(1,1-dimethylethyl)-1*H*-1,2,4-triazole-1-ethanol. ^d 2,4,5-T, (2,4,5-trichlorophenoxy)acetic acid. ^e Bitertanol, β -[1,1-biphenyl]-4-yloxy]- α -(1,1-dimethylethyl)-1*H*-1,2,4-triazole-1-ethanol.

molecular connectivity index used in this study.

The valence third-order molecular connectivity indexes ($^3\chi^v$) are calculated from the non-hydrogen part of the molecule. Each non-hydrogen atom is described by its atomic δ^v value, which is calculated from the following equation:

$$\delta^v = (Z^v - h) / (Z - Z^v - 1) \quad (1)$$

where Z is its atomic number, Z^v is the number of valence electrons in the atom, and h is the number of hydrogen atoms bound to the same atom. The $^3\chi^v$ indexes are then calculated from the atomic δ^v values by eq 2, where $i, j,$

$$^3\chi^v = \sum (\delta^v_i \delta^v_j \delta^v_k)^{-0.5} \quad (2)$$

k , and l correspond to four consecutive non-hydrogen atoms and summation is over all sequences of three adjacent bonds between non-hydrogen atoms in a molecule.

Molecular connectivity indexes were calculated with the GRAPH III computer program on an Apple Macintosh SE personal computer (6, 23). The GRAPH III program can calculate the molecular connectivity indexes up to the tenth order for molecules with 36 non-hydrogen atoms or less. It is possible to extend the program to handle larger molecules if sufficient memory is available.

A regression analysis was carried out on an Apple Macintosh SE personal computer using the statistical analysis system (SYSTAT, version 3.2). To test the quality of generated regression equations, the following statistical parameters were used: the correlation coefficient (r), the standard error of the estimate (s), a test of the null hypothesis (F test), and the amount of explained variance (EV).

The cuticle/water distribution coefficients are taken from the studies of Schönherr and Riederer (2), Kerler and Schönherr (28), Shafer and Schönherr (29), Schönherr (30), Schönherr et al. (31), Shafer and Bukovac (32), and Shafer et al. (33). For chemicals with dissociable groups, the cuticle/water partition coefficients were calculated for the nondissociated species. Coefficients were measured for isolated cuticles from leaves of bitter orange (*Citrus aurantium* L.) and rubber plant (*Ficus elastica* Roxb. var. *decora*) and from fruits of tomato (*Lycopersicon esculentum* Mill.) and green pepper (*Capiscum annuum* L.). Cuticles from these species were selected since the chemical

composition of their cutins is representative for most plant species and because they cover the whole range of the interspecies variability of cuticle/water partition coefficients (3). Two types of cuticular material were used for each plant species: (a) enzymatically isolated cuticular membranes (CM) and (b) the solvent-extracted CM, which are called polymer matrix membranes (MX). The modeling process for eqs 3-5 is based on the logarithms of the CM/water partition coefficients ($\log K_{CW}$). For each compound, the $\log K_{CW}$ values from one to four plant species were entered into regression analysis (Table I). The average experimental error of $\log K_{CW}$ is $\sim 3\%$, which corresponds to a range of ± 0.15 in logarithmic units.

3. Results and Discussion

Molecular Connectivity Model for Estimating Cuticle/Water Partition Coefficients. The 15 organic chemicals examined in the present QSAR study are shown in Table I together with their cuticle/water partition coefficients and molecular connectivity indexes used as structural descriptors. Previous studies (6, 10, 13) have shown that the distribution coefficients of lipophilic organic chemicals in the environment correlate strongly with their molecular sizes. Thus, we have concentrated our initial search for structural descriptors on molecular connectivity indexes that describe primarily the size of molecules. The linear single-variable models were calculated for the simple and valence zero- to sixth-order molecular connectivity indexes (34). The best single-variable correlation was obtained between $\log K_{CW}$ and the valence third-order molecular connectivity index ($^3\chi^v$). The regression equation and statistical parameters describing this quantitative model are

$$\log K_{CW} = 0.17 (\pm 0.40) + 1.26 (\pm 0.13)^3\chi^v \quad (3)$$

$$N = 50 \quad r = 0.944 \quad s = 0.649 \quad F^{1,48} = 392 \\ EV = 88.9\%$$

The statistical parameters show that eq 3 is highly significant ($p < 0.00005$). It accounts for almost 90% of the variations in $\log K_{CW}$ data. The 95% confidence intervals are shown in parentheses in eq 3. Although a high correlation coefficient was obtained, this model was not able to account for all variations in the $\log K_{CW}$ data, whose

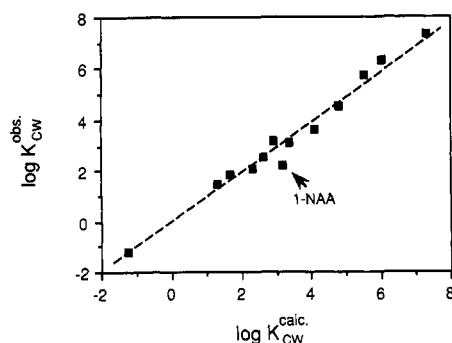


Figure 1. Plot of calculated (eq 4) vs observed cuticle/water partition coefficients ($\log K_{CW}$) for the chemicals listed in Table I. The average values of calculated and observed $\log K_{CW}$ data for CM membranes were used for the plotting procedure. The third square from the left represents 2- and 4-nitrophenol. 1-NAA, 1-naphthaleneacetic acid.

average experimental error is $\sim 3\%$. However, the residual analysis shows that methanol, triadimenol, and bitertanol are outliers that exert an undue influence on the regression model. Their calculated $\log K_{CW}$ data are approximately 1 log unit higher than the measured values. The only common structural feature that can explain such a systematic deviation is the presence of aliphatic hydroxy groups. Thus, an indicator variable, the number of aliphatic hydroxy groups, was tested in a multivariate regression analysis. The resulting two-variable regression model and its statistical parameters are

$$\log K_{CW} = 0.26 (\pm 0.21) + 1.32 (\pm 0.07)^3\chi^v - 1.43 (\pm 0.26)(\text{no. OH}_{\text{aliph}}) \quad (4)$$

$N = 50 \quad r = 0.985 \quad s = 0.345 \quad F^{2,47} = 754$
EV = 96.8%

The introduction of the second variable ($\text{no. OH}_{\text{aliph}}$) significantly improved the model and helped to explain all of the remaining variations in $\log K_{CW}$. In comparison to eq 3, its standard error is lower by 47%. Furthermore, the value of the F test clearly shows that improvements are real and are not caused by the fact that more variables are used. The level of cross-correlation ($r^2 = 0.03$) between the two independent variables is negligible, thus permitting their simultaneous use in the regression model. A comparison of the observed and predicted partition coefficients of compounds studied clearly demonstrates that the molecular connectivity model (eq 4) is very accurate in predicting their K_{CW} data. The average difference between predicted and observed values of $\log K_{CW}$ is only 0.26 (factor 1.8) and all but one compound are predicted within the 2 standard deviations. The high accuracy of the molecular connectivity model in predicting the cuticle/water distribution coefficients is shown in Figure 1, where the observed vs predicted (eq 4) $\log K_{CW}$ data are plotted. However, the analysis of residuals and visual inspection of the plot of observed vs predicted (eq 4) $\log K_{CW}$ data revealed that 1-naphthaleneacetic acid is a serious outlier (residuals from -0.86 to -1.01 log units), which exerts an undue influence on the regression model. Eliminating it from the regression analysis resulted in an improved correlation and also in a statistically more reasonable and meaningful quantitative model:

$$\log K_{CW} = 0.37 (\pm 0.16) + 1.31 (\pm 0.05)^3\chi^v - 1.49 (\pm 0.19)(\text{no. OH}_{\text{aliph}}) \quad (5)$$

$N = 47 \quad r = 0.992 \quad s = 0.250 \quad F^{2,44} = 1418$
EV = 98.4%

Equation 5 is highly significant ($p < 0.00005$) and accounts

for almost 99% of the variations in $\log K_{CW}$ data. The average difference between predicted and observed $\log K_{CW}$ values is only 0.21 (factor 1.6), and all compounds are predicted within 2 standard deviations. Equation 5 enables K_{CW} to be predicted within a factor of 3, the probability being $\sim 99\%$.

Structural Considerations of Cuticle/Water Partitioning. The present QSAR analysis shows that the cuticle/water partition coefficients are primarily influenced by the size of the molecule, which is described best by the $^3\chi^v$ index, i.e., larger molecules show a higher affinity for cuticles than smaller ones. However, not all parts of a molecule contribute equally to its affinity for plant cuticles. The major contribution is from chlorine substituents, hydrocarbon chains, and benzene rings. On the other hand, bonds that contain oxygen or nitrogen atoms contribute to a lesser extent both to the $^3\chi^v$ index and to the K_{CW} values. This is illustrated best by hexachlorobenzene, pentachlorophenol, perylene, and bis(2-ethylhexyl) phthalate, which contain either no or very small fractions of bonds with oxygen and/or nitrogen atoms and thus have the highest affinity for cuticles. However, it is difficult to imagine that the linear relationship between K_{CW} and $^3\chi^v$ will continue infinitely, and it is reasonable to expect that such a trend will level off at some limiting molecular size.

Now, the question arises why the $^1\chi^v$ index, which describes structural properties similar to those of the $^3\chi^v$ index, does not work satisfactory. The residual analysis of correlation between $\log K_{CW}$ data and $^1\chi^v$ indexes clearly shows that this index underestimates the partition coefficients of nonpolar compounds [hexachlorobenzene, pentachlorophenol, perylene, and bis(2-ethylhexyl) phthalate] and overestimates those of more polar compounds. The best examples of this inadequacy are atrazine and hexachlorobenzene, whose $^1\chi^v$ indexes are almost identical (4.912 and 4.897) while their partition coefficients differ by 3.6 orders of magnitude. On the other hand, their $^3\chi^v$ indexes are quite different and correlate nicely with the corresponding $\log K_{CW}$ data. Thus, it seems that the inability to adequately describe the presence of various polar groups accounts for the poor performance of the $^1\chi^v$ index in correlation with the cuticle/water partition coefficients.

Another factor controlling the magnitude of K_{CW} is the presence of aliphatic hydroxy groups. The negative regression coefficient of the ($\text{no. OH}_{\text{aliph}}$) variable shows that the association with cuticles decreases with the presence of aliphatic hydroxy groups. Compared with the main factor, the size of molecule, ($\text{no. OH}_{\text{aliph}}$) can be viewed only as a fine tuning element for the affinity of organic chemicals for plant cuticles. It must be noted that, like the molecular connectivity indexes, the ($\text{no. OH}_{\text{aliph}}$) variable is also a topological property. Thus, both independent variables in eqs 4 and 5 are based on the same theoretical concept. Finally, a warning should be added concerning the application of this model for predicting K_{CW} of organic acids. For the time being, it is not clear why the $\log K_{CW}$ calculated for the nondissociated species of 1-naphthaleneacetic acid is higher by 0.93 log unit than the measured value, while the respective coefficients for other organic acids (benzoic acid, 2,4-D, and 2,4,5-T) are very close to the observed values. It seems that more experimental work is necessary with organic acids.

Molecular Connectivity vs Traditional Empirical Models. As part of the validation process we will compare our model (eq 5) with the QSAR models based on 1-octanol/water partition coefficients (K_{ow}) and water solubility

Table II. Range of Reported Experimental 1-Octanol/Water Partition Coefficients ($\log K_{ow}$) and Water Solubilities (WS in mol/L) for Some Environmental Chemicals^a

compound	$\log K_{ow}$	$-\log WS$
benzene	1.56–2.15	1.64–1.98
nitrobenzene	1.79–2.93	1.51–2.07
2-nitrophenol	1.69–2.52 ^b	
4-nitrophenol	1.35–2.91	
hexachlorobenzene	4.13–7.42	6.78–7.78
pentachlorophenol	3.32–5.86	
naphthalene	3.01–4.70	3.52–4.01 ^c
perylene		8.70–9.38 ^c
2,4,5,2',4',5'-hexachlorobiphenyl	6.34–8.18	8.47–11.44
p,p'-DDT	3.98–6.36	7.95–11.65
aldrin	5.52–7.40	
lindane		4.50–6.29
bis(2-ethylhexyl) phthalate	4.20–7.68 ^d	5.79–10.60 ^e

^a Original literature is cited in ref 6 and 22. ^b References 29 and 38. ^c Reference 39. ^d References 40–42. ^e References 2 and 43.

(WS). These models are described by eqs 6 and 7, respectively (2):

$$\log K_{CW} = 0.057 + 0.970 \log K_{ow} \quad (6)$$

$$N = 13 \quad r = 0.987 \quad s = 0.339 \quad F^{1,11} = 383 \\ EV = 97.2\%$$

$$\log K_{CW} = 1.118 - 0.569 \log WS \quad (7)$$

$$N = 13 \quad r = -0.978 \quad s = 0.413 \quad F^{1,11} = 244 \\ EV = 95.3\%$$

Equations 6 and 7 were also derived for the compounds listed in Table I, but benzoic acid, 1-naphthaleneacetic acid, and methanol were omitted from the regression analysis. Although high correlation models were developed, their application and usefulness are limited since they suffer from two serious shortcomings: (a) the low precision of the K_{ow} and WS data and (b) the violation of statistical requirements for linear regression models due to great errors in the independent variables. The low precision of the K_{ow} and WS data is illustrated in Table II. A brief examination of Table II clearly shows a surprisingly high variability in the experimental K_{ow} and WS data even for compounds with a high solubility in water. Particularly disturbing are the wide ranges of reported experimental K_{ow} data for hexachlorobenzene, pentachlorophenol, and bis(2-ethylhexyl) phthalate, which are between 2.5 and 3.5 log units. Thus, the accuracy of the predicted cuticle/water partition coefficients cannot be better than the accuracy of the experimental K_{ow} and/or WS data. It should be noted that Table II contains only experimental K_{ow} and WS data and that all reports cited have been published within the last several years. A detailed discussion on that subject is presented elsewhere (6, 8).

In addition to their low accuracy, some basic statistical requirements have been violated when simple quantitative models based on K_{ow} and WS were developed. The most important assumption underlying every linear regression model is that the dependent variable contains all the errors in each data pair while the independent variable is essentially free of error (35, 36). It is obvious from an examination of Table II that the data for K_{ow} and WS do not conform with this assumption. It was demonstrated (37) that the fitted slopes may deviate by as much as 40% from the correct value when this basic assumption is violated. Thus, the validity and applicability of quantitative models describing the relationship between the K_{ow} or WS data and cuticle/water partition coefficients are limited. In the molecular connectivity model the requirement that the independent variable is error-free is completely fulfilled.

Notwithstanding these problems, inspection of eqs 6 and 7 and of their statistical parameters shows that the molecular connectivity model developed in this study (eq 5) is superior. Equation 5 enables the K_{CW} data to be predicted within a factor of 3, the probability being ~99%, while eq 6 and 7 will predict the same set of K_{CW} data within factors of 4.5 and 6.5, respectively, the probability being ~95%. It is fair to conclude that in general the performance and future applications of molecular connectivity models are superior to conventional QSAR models for cuticle/water partition coefficients using K_{ow} or WS data as predictor variables.

The nonempirical nature of molecular connectivity derived models makes it possible to estimate the plant uptake of organic pollutants only from information encoded in their structural formulas. Cuticular membrane/water partition coefficients have been determined for cuticles having cutin compositions representative of most plant species. Therefore, it can be expected that eq 5 will give valid estimates of K_{CW} for the majority of plant species. The molecular connectivity indexes can be calculated very fast and for large sets of compounds. Thus, modeling and estimations can be very fast and easily made even for compounds that have not yet been synthesized.

Plant and Cuticle Specific Affinity for Organic Chemicals. In this concluding section, we address the question of differences in cuticle/water partition coefficients between cuticles of the four plant species: leaves of bitter orange (*C. aurantium* L.) and rubber plant (*F. elastica* Roxb. var. *decora*) and fruits of tomato (*L. esculentum* Mill.) and green pepper (*C. annuum* L.). In addition, results on coefficients measured for the cuticular membranes as isolated from the plants (CM) and the coefficients obtained with the solvent-extracted cuticular membranes, polymer matrix membranes (MX), are subdivided. For comparability and uniformity reasons, alcohols (methanol, triadimenol, and bitertanol) and benzoic acid are omitted from this analysis. The individual models have been calculated for each plant species and membrane

Table III. The Single-Variable ($^3x^y$) Cuticle/Water Partition Coefficients Models for Various Plants^a

cuticle	CM				MX			
	N	a	b	r	N	a	b	r
<i>Citrus</i>	8	0.13	1.35	0.993	8	0.07	1.39	0.993
<i>Ficus</i>	10	0.33	1.30	0.996	10	0.38	1.35	0.993
<i>Lycopersicon</i>	10	0.36	1.32	0.994	10	0.46	1.30	0.994
<i>Capsicum</i>	10	0.41	1.32	0.995	10	0.48	1.33	0.994
leaf	10	0.32	1.30	0.995	10	0.37	1.33	0.992
fruit	10	0.39	1.32	0.995	10	0.47	1.32	0.995
all	10	0.36	1.31	0.995	10	0.42	1.32	0.994

^a CM are results for cuticular membrane and MX for polymer matrix membrane. N is the number of compounds in each model, a and b are the regression coefficients for equation $\log K_{CW} = a + b(^3x^y)$, while r is their correlation coefficient.

type and the respective results are presented in Table III. The analysis of regression coefficients for CM models from Table III shows that their slopes (b) are very similar. At the same time, their intercepts (a) are constantly increasing while going from *Citrus* to *Capsicum*. For some plant species the differences in the uptake of pollutants studied is not great, but the pairwise comparison on a compound by compound basis shows that these differences are real and not an artifact of the statistical procedure employed in the modeling process. Consequently, the fruits of green peppers have the highest affinity and the leaves of bitter orange have the lowest affinity for organic compounds among all plant species investigated. Furthermore, the fruits studied tend to accumulate more organic compounds than the leaves studied. It is interesting to note that the partition coefficients for each chemical investigated vary only by a factor of 2.4 for the four cuticular membranes tested (2). This fact let us speculate that the partition coefficients of organic chemicals can be predicted for all plant cuticles regardless of the plant species. Since there is very little enzymatic activity in the cuticle itself (44), it can be expected that equilibrium between the two phases will be reached even for hydrophilic organic compounds. Finally, the results above hold for both types of cuticular membrane, CM and MX.

We have also compared the partition coefficients obtained with cuticular membranes and polymer matrix membranes. Here, again, the differences are small but highly consistent. Partition coefficients in the system MX/water are in general higher than in the system CM/water. This tendency is nicely reflected by the individual plant species models as well as by the leaf, fruit, and global models for MX and CM membrane partition coefficients. This demonstrates that the organic pollutants prefer to be sorbed by cutin rather than by the soluble cuticular lipids, which are removed by solvent extraction. Furthermore, this result also demonstrates that, most probably, the cutin is the ultimate sink for lipophilic pollutants accumulated in plant leaves and fruits.

4. Summary and Conclusions

In this investigation we have demonstrated that a simple model, based on topological properties of organic molecules, can be used to accurately predict the cuticle/water partition coefficients for a variety of organic chemicals. In addition, the ability to accurately predict the cuticle/water partition coefficients of organic pollutants will also make it possible to estimate the rate-limiting step in their transport across the cuticle and to determine the accumulation potential of cuticular compartments for airborne pollutants in living or dead plant material. The accumulation potential of plant material, leaves and fruits, for airborne pollutants is also important as the first step in the terrestrial food web. Finally, such an accurate and fast nonempirical model is almost the ideal predictive tool for ranking potentially hazardous chemicals and for setting up priority lists for test compounds. It will enable the manufacturers of pesticides and other toxic substances to predict via the cuticle/water partition coefficients their affinity for plants and, consequently, the potential environmental hazards of their future products, even before such compounds are synthesized.

Another highly valuable outcome of this study is that two priority areas have been identified for future experimental investigations. As pointed out in the preceding chapter, it is unrealistic to expect that the linear upward trend in the cuticle/water partition coefficients of organic pollutants will continue forever. Thus, one area where

more experimental data are needed is for chemicals with 20 non-hydrogen atoms or more, the great majority of which should be halogen and/or carbon atoms. Such data will enable us to define the upper limit for validity of our model described by eq 5. The second research area where more experimental data are needed relates to various types of organic acids. The unusual behavior of 1-naphthaleneacetic acid indicates either its very specific nature or the possibility that our model is not valid for organic acids. At present, the limited number of log K_{CW} data for organic acids precludes a satisfactory solution to that dilemma.

Registry No. 2,4-D, 94-75-7; 2,4,5-T, 93-76-5; methanol, 67-56-1; phenol, 108-95-2; benzoic acid, 65-85-0; 2-nitrophenol, 88-75-5; 4-nitrophenol, 100-02-7; atrazine, 1912-24-9; 1-naphthaleneacetic acid, 86-87-3; triadimenol, 55219-65-3; bitertanol, 55179-31-2; pentachlorophenol, 87-86-5; hexachlorobenzene, 118-74-1; perylene, 198-55-0; bis(2-ethylhexyl) phthalate, 117-81-7; water, 7732-18-5.

Literature Cited

- (1) Buckley, E. H. *Science* **1982**, *216*, 520-522.
- (2) Schönherr, J.; Riederer, M. *Rev. Environ. Contam. Toxicol.* **1989**, *108*, 1-70.
- (3) Riederer, M.; Schönherr, J. *Ecotoxicol. Environ. Saf.* **1984**, *8*, 236-247.
- (4) Riederer, M. *Environ. Sci. Technol.* **1990**, *24*, 829-837.
- (5) Sabljic, A.; Protić, M. *Bull. Environ. Contam. Toxicol.* **1982**, *28*, 162-165.
- (6) Sabljic, A. *Environ. Sci. Technol.* **1987**, *21*, 358-366.
- (7) Sabljic, A. In *Physical Property Prediction in Organic Chemicals*; Jochum, C., Hicks, M. G., Sunkel, J., Eds.; Springer Verlag: Heidelberg, 1988; pp 335-348.
- (8) Sabljic, A. *Environ. Health Perspect.* **1989**, *83*, 179-190.
- (9) Bahnick, D. A.; Doucette, W. J. *Chemosphere* **1988**, *17*, 1703-1715.
- (10) Sabljic, A.; Lara, R.; Ernst, W. *Chemosphere* **1989**, *19*, 1665-1676.
- (11) Sabljic, A.; Güsten, H. *Chemosphere* **1989**, *19*, 1503-1511.
- (12) Sabljic, A.; Protić, M. *Chem.-Biol. Interact.* **1982**, *42*, 301-310.
- (13) Sabljic, A. *Z. Gesamte Hyg. Ihre Grenzgeb.* **1987**, *33*, 493-496.
- (14) Boethling, R. S. *Environ. Toxicol. Chem.* **1986**, *5*, 797-806.
- (15) Boethling, R. S.; Sabljic, A. *Environ. Sci. Technol.* **1989**, *23*, 672-679.
- (16) Boethling, R. S.; Gregg, B.; Frederick, R.; Gabel, N. W.; Campbell, S. E.; Sabljic, A. *Ecotoxicol. Environ. Saf.* **1989**, *18*, 252-267.
- (17) Kier, L. B.; Hall, L. H. *Bull. Environ. Contam. Toxicol.* **1982**, *29*, 121-126.
- (18) Schultz, T. W.; Kier, L. B.; Hall, L. H. *Bull. Environ. Contam. Toxicol.* **1982**, *28*, 373-378.
- (19) Sabljic, A. *Bull. Environ. Contam. Toxicol.* **1983**, *30*, 80-83.
- (20) Hall, L. H.; Kier, L. B. *Bull. Environ. Contam. Toxicol.* **1984**, *32*, 354-362.
- (21) Yoshioka, Y.; Mizuno, T.; Ose, Y.; Sato, T. *Chemosphere* **1986**, *15*, 195-203.
- (22) Protić, M.; Sabljic, A. *Aquat. Toxicol.* **1989**, *14*, 47-64.
- (23) Sabljic, A.; Trinajstić, N. *Acta Pharm. Jugosl.* **1981**, *31*, 189-214. Program GRAPH III, PC and Macintosh versions, are now fully operational and available for distribution. More details about this program and conditions for its distribution are available on request from A.S.
- (24) Balaban, A. T.; Motoc, I.; Bonchev, D.; Mekenyan, O. *Top. Curr. Chem.* **1983**, *114*, 21-55.
- (25) Trinajstić, N. *Chemical graph theory*; CRC Press: Boca Raton, FL, 1983.
- (26) Kier, L. B.; Hall, L. H. *Molecular connectivity in structure-activity analysis*; Research Studies Press: Chichester, England, 1986.
- (27) Seybold, P. G.; May, M.; Bagal, U. A. *J. Chem. Educ.* **1987**, *64*, 575-581.
- (28) Kerler, F.; Schönherr, J. *Arch. Environ. Contam. Toxicol.* **1988**, *17*, 1-6.

- (29) Shafer, W. E.; Schönherr, J. *Ecotoxicol. Environ. Saf.* **1985**, *10*, 239-252.
- (30) Schönherr, J. *Biochem. Physiol. Pflanz.* **1976**, *170*, 309-319.
- (31) Schönherr, J.; Kerler, F.; Riederer, M. *Dev. Plant Biol.* **1984**, *9*, 491-498.
- (32) Shafer, W. E.; Bukovac, M. J. *Plant Physiol.* **1987**, *83*, 652-656.
- (33) Shafer, W. E.; Morse, R. D.; Bukovac, M. J. *HortScience* **1988**, *23*, 204-206.
- (34) The large majority of the simple and valence zero- to six-order molecular connectivity indexes correlate far worse than the $^3\chi^v$ index. Their explained variances are between 50 and 70%. More specifically, the $^1\chi$ and $^1\chi^v$ indexes have explained variance of 54 and 66%, respectively. The only exception was the $^4\chi^v$ index with explained variance of 80%.
- (35) Irvin, J. A.; Quickenden, T. I. *J. Chem. Educ.* **1983**, *60*, 711-712.
- (36) Maes, F. W. *J. Theor. Biol.* **1984**, *111*, 817-819.
- (37) York, D. *Can. J. Phys.* **1966**, *44*, 1079-1086.
- (38) Tsantili-Kakoulidou, A.; El Tayar, N.; van de Waterbeemd, H.; Testa, B. *J. Chromatogr.* **1987**, *389*, 33-45.
- (39) Pearlman, R. S.; Yalkowsky, S. H.; Banerjee, S. *J. Phys. Chem. Ref. Data* **1984**, *13*, 555-562.
- (40) Mackay, D. *Environ. Sci. Technol.* **1982**, *168*, 274-278.
- (41) Davies, R. P.; Dobbs, A. J. *Water Res.* **1984**, *18*, 1253-1262.
- (42) Harnisch, M.; Möckel, H. J.; Schulze, G. *J. Chromatogr.* **1983**, *282*, 315-332.
- (43) Isnard, P.; Lambert, S. *Chemosphere* **1989**, *18*, 1837-1853.
- (44) Krell, H. W.; Sandermann, H., Jr. *Plant Sci.* **1985**, *40*, 87-93.

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Kinetics of the Atmospherically Important Reactions of Dimethyl Selenide

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■ The biomethylation of selenium into dimethyl selenide from soils, sediments, and plants is a major source of atmospheric selenium. The photolysis and kinetics of the gas-phase reactions of dimethyl selenide with OH and NO₃ radicals and O₃ were investigated at 296 ± 2 K and atmospheric pressure of air. No evidence for photolysis of dimethyl selenide was observed. Rate constants for reaction with the OH radical and O₃ of (6.78 ± 1.70) × 10⁻¹¹ and (6.80 ± 0.72) × 10⁻¹⁷ cm³ molecule⁻¹ s⁻¹, respectively, were obtained. The rate constant for reaction with the NO₃ radical was observed to increase with increasing NO₂ concentration, with an extrapolated value of 1.4 × 10⁻¹¹ cm³ molecule⁻¹ s⁻¹ at zero NO₂ concentration. Combining these rate constants with estimated ambient tropospheric concentrations of OH radicals (1.5 × 10⁶ molecule cm⁻³), NO₃ radicals (2.4 × 10⁸ molecule cm⁻³) and O₃ (7 × 10¹¹ molecule cm⁻³) leads to the following calculated lifetimes of dimethyl selenide due to reaction with these species: OH radicals, 2.7 h; NO₃ radicals, 5 min; and O₃, 5.8 h. The products of these reactions of dimethyl selenide are presently unknown but are likely to be involved in gas-to-particle conversions and aerosol scavenging during the global cycling of selenium.

Introduction

Volatile selenium compounds are released into the environment from both anthropogenic and natural sources (1, 2). Gaseous selenium species detected in the atmosphere include dimethyl selenide, dimethyl diselenide, dimethyl selenone, and methaneselenol (3, 4). Hydrogen selenide may also be released into the atmosphere under reduced conditions, but it is quickly oxidized into elemental selenium in the presence of air (5). One of the most important vapor-phase selenium species found in the atmosphere appears to be dimethyl selenide (1). Biomethylation is a major source for this metalloid-carbon bond formation in the natural environment (6). Although the biological methylation of Se has been poorly quantified in the past and was once considered to be less important than the generation of volatile selenium compounds from

the combustion of fossil fuels and refuse, biological transformations are now believed to constitute an important link in the global cycling of this element. Within the accuracy of current estimates, anthropogenic and natural source emissions are of the same order of magnitude, being approximately (1-10) × 10⁹ g of Se/year (1). Higher levels of selenium are detected in atmospheric and rainfall samples collected in Denmark, Scotland, and the United States during the warmer spring and summer months, when biological activity is at its peak, than in the winter months when combustion of fossil fuels is at its highest (7, 8).

Selenium is an element that is required in trace amounts by some microorganisms. It is considered to be an essential element for plants and animals, but is toxic at higher concentrations. Relatively high concentrations of selenium (>2 ppm) can occur in certain arid, saline, alkaline, and poorly drained soils including the west side of the San Joaquin Valley in California. Agricultural irrigation water percolates through these soils and displaces the shallow saline- and selenium-enriched groundwater. In this manner, soluble salts including toxic selenium ions are removed from the cropland via tile drains into drainwater evaporation ponds, and the evaporation of agricultural irrigation water in these ponds may lead to levels of selenium that are toxic to wildlife (9). Laboratory and field research has shown that microorganisms naturally present in the contaminated soil and water transform selenium compounds into dimethyl selenide, which is liberated into the atmosphere (10-20). Dimethyl selenide has been found to be nonhazardous to rats (21-23).

Characterization of this naturally occurring microbial selenium detoxification and removal process has led to the discovery that biomethylation can be accelerated to the point where there is a significant drop in the initial selenium inventory within a relatively short period of time (10-12, 16-20). Biomethylation could play a significant role in the bioremediation of selenium-contaminated sites in the California Central Valley and be used to prevent the harmful accumulation of selenium in agricultural areas