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The Prediction of Soil Sorption Coefficients of Heterocyclic Nitrogen Compounds by Octanol/Water Partition Coefficient, Water Solubility, and by Molecular Connectivity Indices

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Quantitative structure-property relationships researches(QSPRs) concerning environmental distribution, persistence, and effects is necessary for hazard assessment of pesticides, particularly for those massively used in agriculture and industry. The derivatives of 1,3,5-triazines are one of the most important herbicides known today. Pyrimidines are also used as pesticides. The extensive application of these chemicals has raised the problem of their distribution to soil, plants and animals(Lee,H.B 1986, Thurman,E.M. 1992)

Soil sorption coefficient, expressed on an organic matter (Kom) or an organic carbon basis(Koc), is one of the key parameters used to estimate the mobility and fate of the contaminants. Because the experimental determination of Kom is difficult and expensive, estimated values are often used. A number of studies dealing with the prediction of the soil sorption coefficients of organic chemicals are available in the literature. These empirical predicting models depended highly on the chemicals used to create them. Unfortunately, Quantitative study on the prediction of the soil sorption coefficient of heterocyclic nitrogen compounds such as triazines and pyrimidines are rather scare. As a contribution of filling this information gap, the soil sorption coefficient of 12 hetrocyclic nitrogen compounds has been measured. Tested compounds were 7 1,3,5-triazines, 4 pyrimidines and 1 pyridazine. The triazines and pyrimidines differed with respect to the substituent groups at the carbon atoms in the heteroaromatic ring. The homogeneous data on the set of heterocyclic nitrogen structure permitted the attempt of developing QSPR models to prediction the soil sorption coefficient of these chemicals.

MATERIALS AND METHODS

The chemicals were synthesized by college of chemistry and chemical engineering of Nanjing University. Purity was checked by Mass spectrometry. The chemicals were listed in table 1 .

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The soil was of silt loam texture, which was collected from the top 20cm layer of agriculture of field plots in northeast of P.R.China. The soil was air-dried, grounded to pass 60 mesh sieve, and stored in the laboratory in a dry place at ambient temperature. Organic carbon was 3.51 percent, which was determined by the Walkley-Black method using a correction factor of 1.3. Organic matter was converted by multiplying by 1.724. The pH of the soil was 5.8

Table 1. The Chemicals tested in the experiment

chemicals	
1	2,6-dichloro-4-mopholino-1,3,5-triazine
2	3,6-dichloro-pyridazine
3	2,4-dichloro-pyrimidine
4	2,6-dichloro-4-dimethylamino-1,3,5--triazine
5	2,6-dichloro-4-N-phenylamino-1,3,5-triazine
6	2,6-dichloro-4-N-methyl-phenylamino-1,3,5-triazine
7	4,6-dichloro-5-nitro-pyrimidine
8	4,6-dihydroxyl-5-nitro-pyrimidine
9	4,6-dihydroxyl-pyrimidine
10	2,6-dihydrazino-4-dimethylamino-triazine
11	2,6-dihydrazino-4-phenylamino-1,3,5-triazine
12	2,6-dihydrazino-4-morpholino-1,3,5-triazine

The soil sorption coefficients of chemicals were determinated experimentally according to methods described by Briggs G.G. (1981). For the adsorption tests, 7 concentrations of the test substance in 0.01 $CaCl_2$ were used, ranging from 1-10ppm for lower solubility chemicals or 10-100ppm for higher solubility chemicals. After centrifugation for 10min, the concentrations of adsorption solution were measured at an appropriate wave length by uv absorption against a soil blank. Concentrations in soil were calculated from the concentration decrease in the aqueous phase. To minimize loss by volatilization, adsorption tests were carried out in stoppered centrifuge tube. The adsorption isotherms gave a good fit to Freundlich isotherm. K_f and l/n were determinate by linear regression. The sorption coefficient K_f was converted to Kom by the organic contents.

The Octanol/water partition coefficients were determined by shakeflask method at 25 °C (OECD guideline, 1981). The solubility of the compounds was determinated by generator column method and shake-flask method respectively as described by OECD guideline (1981). The concentrations of the chemicals were measured with UV- spectrophotometer.

RESULTS AND DISCUSSION

Table 2 summarizes the soil sorption coefficients, water solubility, octanol/water partition coefficients and other molecular descriptor for the tested compounds. There were enormous reports correlating the soil sorption coefficients to water solubility or Octanol /water partition coefficients (Lambert,1965.1968;

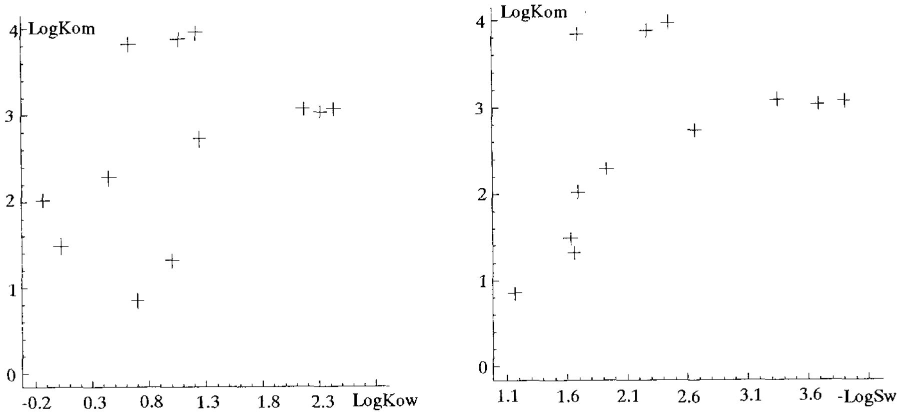

Figure 1. The Scatter of LogKom vs LogKow and LogKom vs LogSw

Hamaker, 1972; Karickhoff, 1979;Schwartzhenbach,1981). For nonpolar chemicals, sorption to the organic matter of the soil could be regarded as a distribution process between a polar aqueous phase and a nonpolar organic phase (Briggs, 1991). However, the soil sorption coefficients correlated to LogSw and LogKow poorly for heterocyclic nitrogen compounds tested. Scatter plots of LogKom vs LogKow and LogKom vs LogSw for all tested compounds are shown in Figure 1.

Table 2. The soil sorption coefficients(LogKom), solubility(Sol,M/L) octanol/water partition coefficients(LogKow), non-disperse force (Δ^1X^v) and first order molecular connectivity indices (^1X) of tested compounds

NO.	LogKow	Sol	Logkom	Δ^1X^v	^1X
1	2.73	2.67	1.25	1.12	6.98
2	0.84	1.17	0.70	0.27	3.79
3	1.32	1.66	1.00	0.59	3.79
4	3.08	3.35	2.17	0.64	6.17
5	3.03	3.69	2.32	0.61	7.24
6	3.07	3.91	2.43	0.65	7.66
7	2.29	1.93	0.45	0.62	5.13
8	2.02	1.69	-0.13	1.16	5.13
9	1.49	1.63	0.03	0.84	3.79
10	3.97	2.45	1.22	1.68	7.24
11	3.88	2.27	1.07	1.64	8.31
12	3.84	1.69	0.62	2.11	7.83

Regression analysis of these data yielded the following equations:

$$\text{LogKom} = -0.62\ \text{LogSw} + 1.17 \qquad (1)$$

$r=0.44$ $s=0.95$ $n=12$ $F=3.70$ $P=0.083$

$$\text{LogKom} = 0.53\ \text{LogKow} + 2.04 \qquad (2)$$

$r=0.31$ $s=1.01$ $n=12$ $F=2.165$ $P=0.172$

Statistical test revealed that LogKom did not significantly correlate to LogSw and

LogKow (P>0.005). The correlation between the soil sorption coefficient and Water solubility, octanol/water partition coefficient significantly depended on the homogeneity of the chemicals used to create them. For these chemicals, LogKow range from -0.13 to 2.43, LogSw range from 1.17 to 3.91. There are three kinds of heterocyclic nitrogen rings, seven kinds of substituent group(chloro-, phenylamina-, N-methyl-phenylamino-, methyl-, hydrazino-, nitro-, hydroxyl-) in these chemicals. The insignificant correlation is therefor due to the heterogeneity of the 12 heterocyclic nitrogen compounds.

Non-disperse force factor is a topological indice calculated from molecular connectivity indices (Bahnich, 1988). It reflects the ability of the non-disperse force of the molecular. We found the non-disperse force factor improved greatly the correlation of LogKom vs LogSw or LogKom vs LogKow:

$$\mathrm{LogKom} = -0.76\ (0.11)\ \mathrm{LogSw} + 1.56\ (0.1S)\Delta\,{}^{1}\chi^{v} - 0.71\ (0.35) \qquad (3)$$

$r^{2}=0.91$ $s=0.32$ $n=12$ $F=53.51$ $P<0.005$

$$\mathrm{LogKom}=0.79(0.14)\mathrm{LogKow} + 1.66(0.21)\Delta^{1}\chi^{v} + 0.11(0.31) \qquad (4)$$

$r^{2}=0.87$ $s=0.38$ $n=12$ $F=38.34$ $P<0.005$

As shown in the equation above, the soil sorption coefficients of the heterocyclic nitrogen compounds were not only influenced by the partition effection induced by lipophility(or water solubility) of the chemicals, but also by the non-disperse force between the compound molecule and the soil particle. The QSPR researches concerning the correlation between the lipophlicily (water solubility) and the soil sorption coefficients were on a set of homogeneous chemical compounds in the past literature, their non-disperse force was near and could be combined to the constant part of the correlation equation. Therefore, LogKom correlated to LogKow or LogSw significantly. As for the heterocyclic nitrogen compounds with very different no-disperse force factor, their no-disperse force factor could not be combine to constant parts. Thus, LogKow or LogSw alone correlated to LogKow poorly.

Molecular topology has long been shown to be a useful structural parameter for describing and predicting the soil sorption coefficients (Sabljic 1982 1984,Koch1983; Govers 1984). The first order molecular connectivity index (${}^{1}X$) was demonstrated to correlated well with soil sorption coefficients of chemicals(Sabljic 1987). ${}^{1}X$ can be viewed as a quantitative measure of the area occupied by the prediction of the non-hydrogen skeleton of molecular(Sabljic 1984). The regression of the LogKom of the 12 heterocyclic nitrogen compound vs the first order molecular connectivity indice (${}^{1}X$) yielded the following result:

$$LogKom = 0.59\,{}^{1}\chi - 0.97 \qquad (5)$$

$r=0.94$ $s=0.38$ $n=12$ $F=74.19$ $P<0.005$

${}^{1}X$ could explain 88 percent of the variance in this prediction model. Sabljic(1984) has established a linear relationship between LogKom and ${}^{1}X$ for polycyclic aromatic hydrocarbons (PAHs) and halogenated hydrocarbons:

$$LogKom = 0.55\,^1\chi + 0.45 \qquad (6)$$

$r=0.97 \quad n=37 \quad s=0.338$

Comparing the equation(5) and equation(6), the regression coefficients for ^1X were found to be almost equal (0.55, 0.58 respectively), while the intercept of the equations was very different(0.45, -0.91 respectively). This observation suggested that the soil sorption coefficient were proportional to ^1X (reflecting the molecular surface area) at same scale, for hydrophobic PAHs, halogenated hydrocarbons, or for hydrophilic heterocyclic nitrogen compounds. The difference in hydrophilic character only affect the intercept of equations. For hydrophobic compounds, intercepts were positive, for hydrophilic compounds, negative.

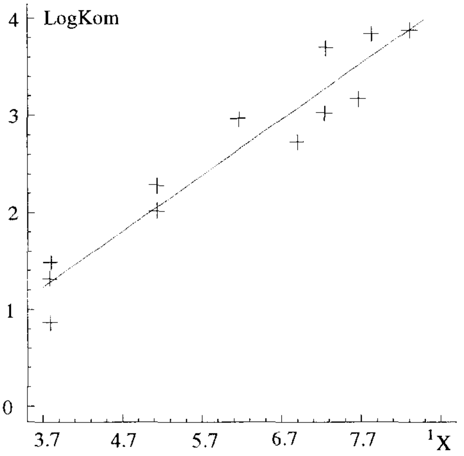

Figure 2. Regression of LogKom vs ^1X

The present study showed that soil sorption coefficients of 12 heterocyclic nitrogen compounds(7 triazines, 4 pyrimidines and 1 pyridazine) correlated poorly to the lipophilicity or water solubility. Non-disperse factor could improve the prediction of LogKow(or LogSw)-dependent model greatly, which suggested that the soil sorption coefficients of the heterocyclic nitrogen compounds were not only determined by the partition effection induced by lipophility(or water solubility) of the chemicals, but also by the non-disperse force between the compound molecule and the soil particle. Nevertheless, the first order molecular connectivity indice could explain 88 percent of the variance. This result demonstrated that first order molecular connectivity indice was a better molecular descriptor than lipophilicy or solubility character of the molecules for predicting the soil sorption coefficient of hetercocylic nitrogen compound.

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REFERENCES

Bahnich AA, Doucetle WJ(1988) Use of molecular connectivity indices to estimate soil sorpiton coefficients for organic chemicals. Chemosphere 17:1703-1715

Briggs GG(1981) Theoretical and experimental relationships between soil adsorption, octanol-water partition coefficients, water solubility, bioconcentration factors, and the parachor. J Agric Food Chem 29: 1050-1059

Govers H, Ruepert C, Ailcing A(1984) Quantitative structure-activity relationships for polycyclic aromatic hydrocarbons:Correlation between molecular connectivity physio-chemical properties,bioconcentration and toxicity in Daphnia Pulex. Chemsphere 13:227-236

Hamaker JW,Thompson JM(1972) Adsorption . In:C.A.I. goring and J.W. Hamaker(eds). Organic Chemicals in the Soil Environment. Vol. 1 . Marcel Dekker Inc.New York.pp51-143

Karickhoff WW, Brown DS, Scott TA (1979) Sorption of hydrophobic pollutants on natural sediments . Water Res 13: 241-248

Koch R (1983) Molecular connectivity index for assessing ecotoxicological behavior of organic compounds. Toxicol Ecviron Chem 6: 87-96

Lambert SM, Omwega A(1968) Useful index of soil sorption equilibria. J Agric food Chem 16: 340-343

Lambert SM ,Porter E ,Schieferstein H(1965) Movement and sorption of chemicals applied to soils. Weeds 13:185-190

Lee HB, Stokker YD (1986) Analysis of eleven triazines in natural waters. J Assoc off Anal Chem 69: 586-572

OECD Guideline for testing of chemicals, The Organization for Economic Cooperation and Development(OECD), Paris, 1981

Sabljic A, Protic M(1982) Relationship between molecular connectivity indices and soil sorption coefficients of polycyclic aromatic hydrocarbons. Bull Environ Contam Toxicol 28: 162-165

Sabljic A (1987) On the prediction of soil sorption coefficients of organic polutants from molecular structure: Applicaton of molecular topology model. Environ Sci Technol 21: 356-366

Sabljic A(1984) Prediction of the nature and strength of soil sorption of organic pollutants by molecular topology. J Agric Food Chem 32:243-246

Schwartzenbach RP, Westall J(1981) Transport of nonpolar organic compounds form surface water to groundwater, laboratory sorption studies. Environ Sci Technol 15: 1360-1367

Thurman EM, Goolshy A (1992) A reconnaissance study of herbicides and their metabolites in surface water of midwestern united states using immunoassay and gas chromatography/mass spectrometry. Environ Sci Technol 26: 2440-2447