STUDIA UBB. CHEMIA, LV, 3, 2010

THE LIPOPHILICITY DETERMINATION OF SOME PESTICIDES BY HIGH PERFORMANCE THIN-LAYER CHROMATOGRAPHY AND VARIOUS COMPUTING METHODS

RODICA DOMNICA NAŞCU-BRICIU[a],*, COSTEL SÂRBU[a]

ABSTRACT. The lipophilicity of some emerging pesticides is investigated by reversed-phase high performance thin-layer chromatography (RP-HPTLC) on RP-18, RP-8 and CN stationary phases. The mobile phases were mixtures of methanol-water in different proportions of volume. The lipophilicity indices taken in consideration during this study are: R_{M0}, mean of R_F and R_M, b, φ_0, scores corresponding to the first principal components of R_M and R_F. The obtained results are compared with the computed lipophilicity indices (Log P) in order to evaluate the suitability of the involved method in the lipophilicity estimation for the pesticides. The comparison is performed through correlation matrices and profiles. The obtained correlations are indicating a high statistical significance.

Keywords: *Pesticides, Lipophilicity, Log P, PCA*

INTRODUCTION

The pesticides are defined as being substance or mixture intended to prevent, destroy, repel or mitigate any pest including insects, rodents, and weeds [1]. The use of pesticides, in some crude forms has starting since early times but the modern use of synthetic pesticides began in the early to mid twentieth century. Nowadays the pesticides are accounting over 800 compounds that are formulated in an extremely large variety [2]. If comparing the newly synthetic pesticides with those used in 18th century, such as arsenic or mercury based pesticides, the health benefits are obvious [3]. However, even if the concern has been reduced it has been evidenced that the nowadays used pesticides have also a substantial negative impact on the environment and public health. The most significant effects are a consequence of their toxicity and endocrine activity [4]. One of the most remarkable pesticides that have illuminated the entire world regarding the negative effects was DDT, which is known as the most used insecticide of the nineteen century [5]. All the effects of pesticides, even if speaking of toxicity, is closely related to the chemical structure. These considerations were taken into account in the quantitative

[a] *Babeş-Bolyai University, Faculty of Chemistry and Chemical Engineering, 11, Arany Janos Str., RO-400028 Cluj-Napoca, Romania; * rodicab2003@yahoo.com*

structure –property/activity relationship experiments (QSPR/QSAR). Such studies were basically involved in the pharmaceutical development, but they have gained remarkable importance in toxicology [6].

One of the most important parameter taken in consideration in the QSAR/QSPR studies is the lipophilicity. It is defining the affinity of a molecule for a lipophilic environment. The lipophilicity is connected with an increased biologically activity, poorer aqueous solubility, faster metabolization and elimination, increased plasma protein binding, sometimes shorter duration of action. Recently, has been proved that it plays a significant role in the pharmacodynamic and toxicological profile of drugs and xenobiotics [7]. The lipophilicity is usually defined by the partition coefficient, denoted in few different ways, frequently depending by the determination method (log P, log k_w, log K_{ow}, log K_{oc}, R_{M0}).

According to Sangster [8] and Kaliszan [9], the lipophilicity determination methods are divided in direct and indirect methods. The most known and used direct method of determination is the “shake-flask” procedure, which is starting with the analyte repartition between two immiscible phases, usually octanol-water or hexanol-water, followed by the quantitative determination in one or both phases. Even if it is considered to be a reference method, it was almost totally replaced by the indirect methods, such as chromatographic ones, mainly because of the multiple drawbacks that characterize these methods, i.e. the analyte must have a very high purity, high consumption of solvents, involves a quantification step, and so on. On the other side, the chromatographic methods are more flexible and present some significant advantages: dynamic process, the consumption of the investigated compounds is minimal, high-purity chemicals and additional analytical quantification are not required. The lipophilicity indices are computed easily from the retention parameters (retention time, retention factor) [10]. Some previous studies have proved to be very efficient in the lipophilicity determination of pesticides [11, 12].

The purpose of this work was focused on the lipophilicity determination of some pesticides by high performance thin-layer chromatography (HPTLC). The accepted TLC lipophilicity indices (arithmetical mean of R_F: mR_F, arithmetical mean of R_M: mR_M, R_{M0}, the scores corresponding to the first principal components of R_F: $PC1/R_F$, and the scores corresponding to the first principal components of R_M: $PC1/R_M$), were analyzed and compared with the computed log P values. In addition, the scores obtained applying principal component analysis (PCA) offer the possibility to get a new lipophilcity scale, while the eigenvalues and eigenvectors (loadings) give new insights about the chromatographic mechanism and the chromatographic behaviour of the investigated compounds.

Methods. The thin layer chromatography is providing a series of lipophilicity indices starting from the retention parameter. The most popular and used lipophilicity parameter, namely retardation parameter, was defined by the Bate-Smith and Westall [13] through the following formula:

$$R_M = \log\left[\left(\frac{1}{R_F}\right) - 1\right] \quad (1)$$

Since within this studies the used mobile phase are usually hydro-alcoholic and the solvents fraction selection does not respect a strict rule, Soczewiński-Wachtmeister [14] have developed a new equation that takes into account the concentration of the organic modifier, as follows:

$$R_M = R_{M0} + b\varphi \quad (2)$$

where R_{M0} represents the extrapolated value to pure water as mobile phase, and the same time it is considered the most relevant lipophilicity descriptor provided by the TLC. The regression slope (b) is directly related to the specific surface area of the stationary phase and also it is considered to be an alternative descriptor of lipophilicity, while φ represents the volume fraction of the organic solvent in the mobile phase.

Furthermore, Valkó [15] has proved that the fraction of the organic modifier may be also used as lipophilicity descriptors for the situation when the amount of solute in the mobile phase is equal to that in the stationary phase i. e. the retention factor is 1 ($R_M = 0$). The new indices, called index of hydrophobicity (φ_0), derived from Eq. 2, is computed through the following formula:

$$\varphi_0 = \frac{R_{M0}}{b} \quad (3)$$

More recently, the scores corresponding to the first principal components of R_F and R_M have proved to have a very high lipophilicity descriptive capacity. Even more, PCA is providing significant information about the interactions that define the separation process, and also allows the obtaining of some lipophilicity maps, both for the compounds and chromatographic stationary phases. In addition, the mean values of R_F and R_M appeared also as an illuminating alternative for the lipophilicity scales estimation [16-18].

Log P. Log P represents the computed lipophilicity indices. Many values are computed according different algorithms involved in the computer software and internet module. For the present study the compounds structures were firstly preoptimized with the Molecular Mechanics Force Field procedure included in Hyperchem version 7.5 (HyperChem, release 7.5 for Windows, Molecular Modeling System; Hypercube), and the resulting geometries were further refined by means of the semi-empirical method Parametric Method-3 using the Fletcher–Reeves algorithm and a gradient norm limit of 0.009 kcal $Å^{-1}$. On the basis of obtained geometries, the software like Chem3D Ultra 8.0, and Dragon Plus version 5.4 calculate various lipophilicity descriptors. Three of the log P values were calculated by Chem3D Ultra 8.0 (CLOGP, logPC—Crippen

method, logPV—Viswanadhan method), while two are given by the Dragon 5.4 (MLOGP-Moriguchi method, ALOGP-Ghose–Crippen method). Another seven were offered by the internet module ALOGPS 2.1-vcclab (ALOGPs, AC logP, AB/LogP, miLogP, KOWWIN, XLOGP2, XLOGP3) [19]. The investigated compounds are presented in Figure 1. All the computed values are listed in Table 1.

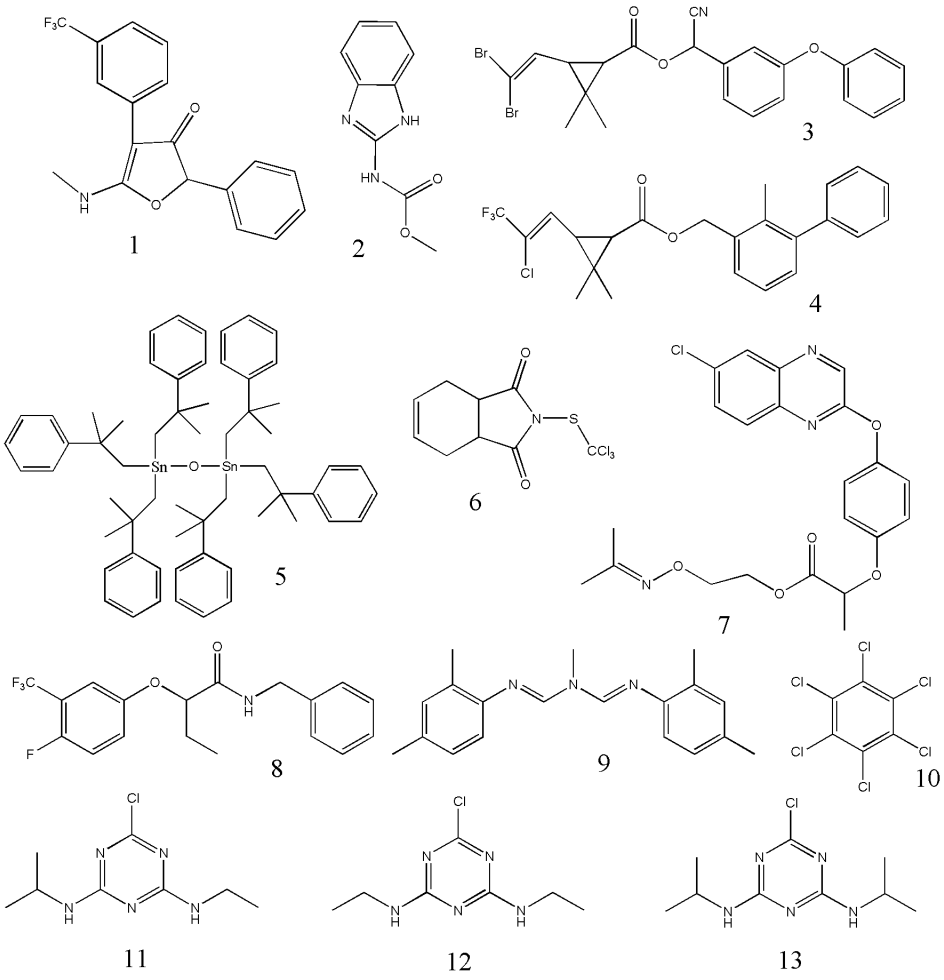

Figure 1. The chemical structure of the investigates pesticides: flurtamone (1), carbendazim (2), deltamethrin (3), bifethrin (4), fenbutatin oxide (5), captan (6), propaquizafop (7), beflubutamid (8), amitraz (9), hexachlorobenzene (10), atrazine (11), simazine (12), propazine (13).

RESULTS AND DISCUSSION

The chromatographic lipophilicity indices obtained for the investigated pesticides are presented in the Table 2 and 3. The results are indicating that the most lipophilic compound investigated in this experiment is the fenbutatin oxide. The abundance of phenyl groups founded in the molecule is favouring the lipophilic interactions. Deltamethrin, bifethrin and hexachlorobenzene are, also characterized by high lipophilicity. The group of triazine are distinguished with lower lipophilicity and within them the simazine is the most hydrophilic. Moreover, the lipophilicity level of carbendazin and amitraz is comparable to that corresponding to triazine group. The highest lipophilicity indices were obtained on the RP-8 stationary phase, closely followed by RP-18 and CN. However, all the lipophilicity indices are comparable and not very different from one stationary phase to another.

According to some authors a good correlation between slope and intercept of Eq. 2 is an indicative of a congeneric series [20, 21]. In this case the determination coefficients (R^2) were higher than 0.99 for RP-8 and CN and higher than 0.94 for RP-18. The group of investigated pesticides is not a homogeny one and as a consequence it may not be considered a congeneric group. These results, sustained by some previously presented data [17, 18] are indicating that the correlations are not necessarily related to the chemical reality.

The regression correlation coefficients are offering information about the chromatographic behaviour related to the methanol fraction from the mobile phases. Excepting few cases (carbendazin: $r_{CN} = 0.96$; bifethrin: $r_{CN} = 0.96$; fenbutatin oxide: $r_{RP-8} = 0.95$, $r_{CN} = 0.96$; captan: $r_{RP-18} = 0.97$; amitraz: $r_{RP-18} = 0.97$), the correlations obtained were higher than 0.98, which is indicating that the chromatographic behaviour of the compounds was a linear one. All these considerations may be observed in the Figure 2. The presented profiles allow appreciating that the interactions involved into the chromatographic process during the development with mobile phases consisting of different fraction of methanol are constant and they are not modifying while the solvents ration in the mobile phases has been changed. This aspect is strongly sustained by the fact that in all situations the mean value of the retardation parameter is overlapped with the median. In addition, the symmetry observed in the correlation profiles of the lipophilicity indices (Figure 3) is suggesting that the investigated stationary phases are inducing a very similar retention mechanism. The correlations between means and PCs are indicating that the CN results are more specific than those obtained on RP-18 and RP-8 when the diagrams are indicating very high correlations. The highest differences of chromatographic behaviour in the case of RP-18/RP-8 vs. CN are observed for the bifethrin, propaquizafop and beflubutamid. In the Figure 3 C the R_{M0} values were compared with the computed Log P values and there may be easily observed that the results obtained by chromatographic analysis are comparable with

those obtained by applying different theoretical algorithms. Even more, the diagrams trend is similar in all cases. The highest differences can be identified in the case of fenbutatim oxide, when because of the Sn presence some of the computing algorithms are failing.

Table 1. The computed lipophilicity indices

No	Compound	ALOGPs	AC logP	AB/LogP	mi LogP	ALOGP	MLOGP	KOWWIN	XLOGP2	XLOGP3	Log P^C	Log P^V	CLOGP
1	Flurtamone	4,83	3,81	4,40	3,95	4,24	3,20	3,82	5,27	5,25	3,67	3,73	3,91
2	Carbendazin	1,46	2,00	1,49	1,46	1,65	1,05	1,55	1,23	1,52	1,29	1,30	1,71
3	Deltamethrin	6,13	6,02	5,71	6,65	5,63	4,11	6,18	5,84	6,20	6,47	6,40	6,79
4	Bifethrin	5,71	6,50	6,93	7,36	6,37	5,40	8,15	7,19	6.00	6,52	6,30	7,36
5	Fenbutatim O.	10,63	15,57	10,00	9,90			13,63	16,70	19,85			11,33
6	Captan	3,00	1,97	2,29	2,84	4,02	1,82	2,74	2,27	2,35	3,51	3,24	2,35
7	Propaquizafop	4,41	4,96	4,39	5,10	4,21	3,11	4,59	5,23	4,60	4,52	4,62	4,74
8	Beflubutamid	4,10	4,00	4,52	4,35	4,72	4,25	4,81	4,79	4,65	4,55	4,52	4,86
9	Amitraz	4,42	3,52	5,23	5,09	5,41	4,90	5,55	4,57	5,50	5,63	5,53	5,50
10	Hexachloro-benzene	5,70	5,66	4,90	5,72	5,82	5,21	5,86	5,75	5,73	5,38	5,15	6,06
11	Atrazine	2,70	2,48	2,52	2,55	2,54	2,59	2,82	1,66	2,61	1,95	2,06	2,70
12	Simazine	2,48	2,08	2,27	2,25	2,16	2,27	2,40	1,20	2,18	1,63	1,65	2,39
13	Propazine	2,94	2,88	2,78	2,85	2,91	2,89	3,24	2,12	2,93	2,26	2,47	3,01

Table 2. The experimentally determined lipophilicity indices on RP-18 and RP-8 HPTLC plates

No	Compound	RP-18							RP-8						
		mR_F	mR_M	R_{M0}	b	φ_0	$PC1/R_F$	$PC1/R_M$	mR_F	mR_M	R_{M0}	b	φ_0	$PC1/R_F$	$PC1/R_M$
1	Flurtamone	0.633	-0.239	1.98	-0.026	-75.84	-0.496	1.184	0.645	-0.270	3.85	-0.048	-79.42	-0.384	0.859
2	Carbendazin	0.545	-0.081	3.28	-0.040	-82.96	-0.302	0.825	0.645	-0.263	2.24	-0.029	-76.05	-0.383	0.861
3	Deltamethrin	0.196	0.659	6.68	-0.071	-94.30	0.480	-0.843	0.285	0.439	7.36	-0.081	-90.39	0.420	-0.749
4	Bifethrin	0.099	1.033	7.94	-0.081	-97.71	0.697	-1.683	0.178	0.734	8.15	-0.087	-93.40	0.662	-1.408
5	Fenbutatim O.	0.023	1.645	4.65	-0.035	-131.49	0.869	-3.026	0.060	1.334	10.75	-0.111	-97.04	0.926	-2.773
6	Captan	0.590	-0.161	2.39	-0.030	-79.64	-0.401	1.007	0.649	-0.278	3.79	-0.048	-79.19	-0.393	0.876
7	Propaquizafop	0.291	0.403	4.83	-0.052	-92.74	0.266	-0.261	0.402	0.185	5.72	-0.065	-87.85	0.160	-0.171
8	Beflubutamid	0.548	-0.087	3.78	-0.045	-83.09	-0.309	0.836	0.545	-0.084	4.83	-0.058	-83.55	-0.161	0.434
9	Amitraz	0.656	-0.285	2.27	-0.030	-75.53	-0.549	1.283	0.710	-0.399	3.07	-0.041	-75.23	-0.528	1.149
10	Hexachloro-benzene	0.059	1.223	4.69	-0.041	-115.01	0.788	-2.085	0.173	0.718	6.28	-0.065	-95.98	0.672	-1.349
11	Atrazine	0.570	-0.123	0.87	-0.012	-74.44	-0.354	0.932	0.625	-0.230	3.84	-0.048	-80.20	-0.338	0.771
12	Simazine	0.613	-0.201	0.59	-0.009	-63.39	-0.451	1.107	0.674	-0.324	3.26	-0.042	-77.31	-0.448	0.982
13	Propazine	0.518	-0.031	1.44	-0.017	-83.21	-0.238	0.724	0.565	-0.118	4.35	-0.053	-82.75	-0.204	0.517

Table 3. The experimentally determined lipophilicity indices on CN HPTLC plates

	Compound	CN						
		mR_F	mR_M	R_{M0}	b	φ_0	PC1/R_F	PC1/R_M
1	Flurtamone	0.724	-0.427	2.49	-0.034	-72.56	-0.341	0.727
2	Carbendazin	0.544	-0.078	2.40	-0.029	-82.33	0.063	-0.041
3	Deltamethrin	0.449	0.094	5.15	-0.060	-86.58	0.279	-0.453
4	Bifethrin	0.528	-0.053	4.68	-0.056	-84.06	0.102	-0.123
5	Fenbutatim O.	0.087	1.088	7.71	-0.078	-98.97	1.081	-2.682
6	Captan	0.602	-0.182	2.23	-0.028	-78.60	-0.067	0.191
7	Propaquizafop	0.641	-0.256	2.74	-0.035	-77.73	-0.153	0.347
8	Beflubutamid	0.685	-0.346	2.86	-0.038	-75.85	-0.253	0.544
9	Amitraz	0.759	-0.501	1.08	-0.019	-58.12	-0.421	0.908
10	Hexachlorobenzene	0.141	0.837	6.83	-0.071	-96.86	0.964	-2.114
11	Atrazine	0.756	-0.496	1.44	-0.023	-63.28	-0.414	0.891
12	Simazine	0.754	-0.489	1.40	-0.022	-62.97	-0.409	0.877
13	Propazine	0.763	-0.514	1.83	-0.028	-66.33	-0.429	0.928

Beside of the fact that PCA is providing very efficient lipophilicity descriptors, it is offering also very important information about the compounds characteristics through the generically named “lipophilicity maps”. They are in fact a 2D graphically representation of the scores corresponding to the first two principal components. The efficiency of these representations is sustained by the cumulative proportion and eigenvalues, which gave information about how the raw information of the initial data is adsorbed in the principal components. In the present case, by applying PCA on the R_F values the first principal component accounts more than 98.51%, while in the case of R_M the first principal component accounts more than 98.92%. Moreover, the first two principal components account more than 99.79% in all cases. These values are indicating that the first two principal components are retaining the majority of the variance and in the same time they are enough to be used for the compounds classification. In the Figure 4 are presented the lipophilicity maps obtained by applying PCA on the matrix of R_M values of the investigated pesticides. The triazine group is identified as linear cluster, while the rest of the compounds are more or less correlated. The hexachlorobenzene and fenbutatim oxide are distinguished as the most lipophilic compound and this may be remarked as well in the obtained lipophilicity maps.

The PCA is a very powerful tool in the chromatography, because it may be involved in the compounds and stationary phase classification, and it provides very successful lipophilicity indices. Even more, by graphical representation of PCA loadings as function of the methanol fraction used in the mobile phases, there may be obtained some pertinent information concerning the retention mechanism involved in the development process of each stationary phase. By carefully examining the patterns depicted in Figure 5, the similarity and differences between the bonded phases investigated can be clearly observed.

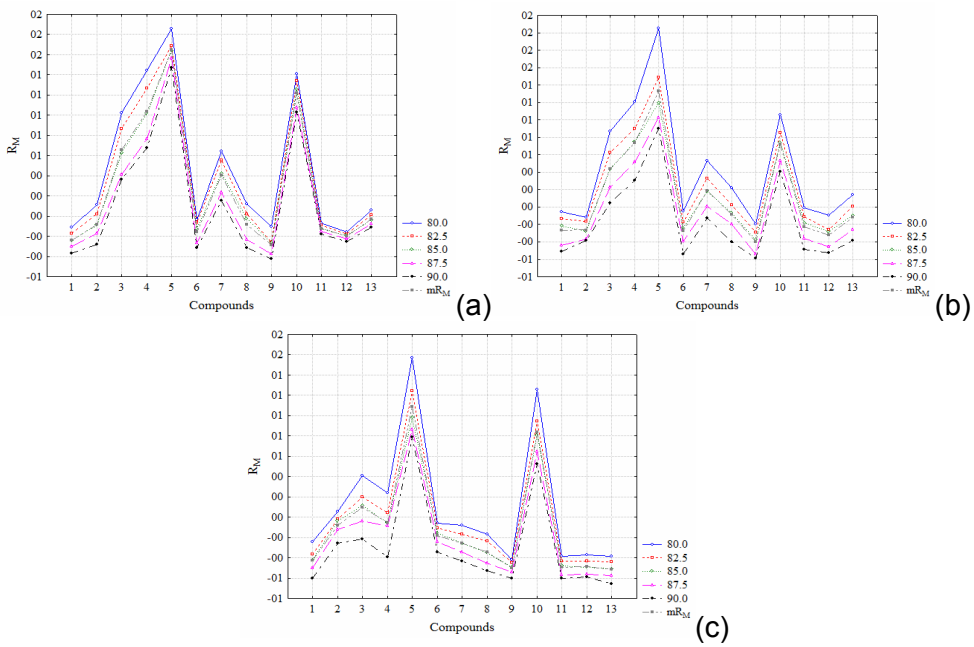

Figure 2. Profiles of R_M values for all fraction of methanol: (a) RP-18; (b) RP-8; (c)-CN.

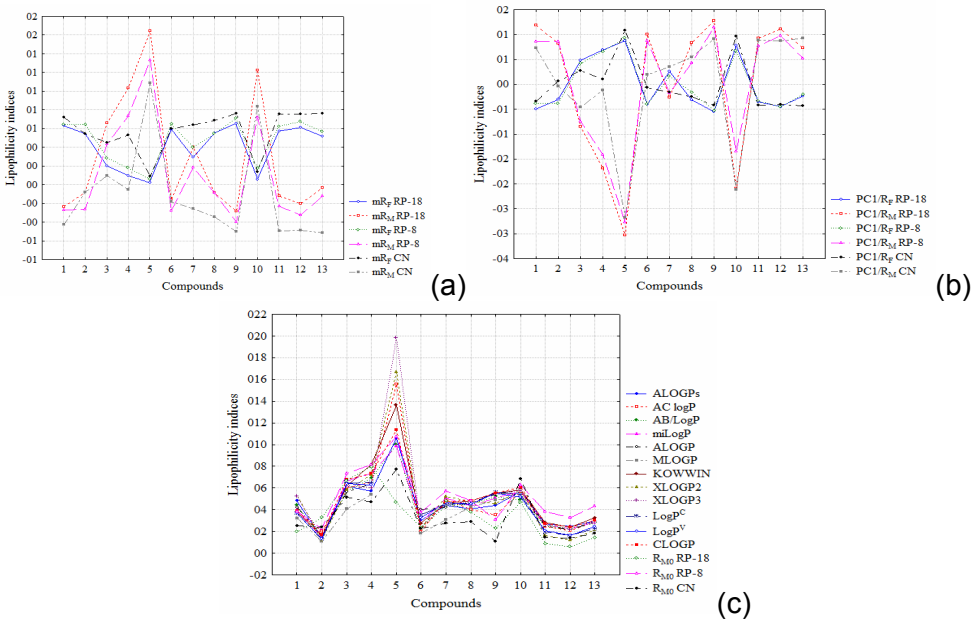

Figure 3. The correlation profiles of the lipophilicity indices: mR_F and mR_M (a), $PC1/R_F$ and $PC1/R_M$ (b), and R_{M0} and LogP (c).

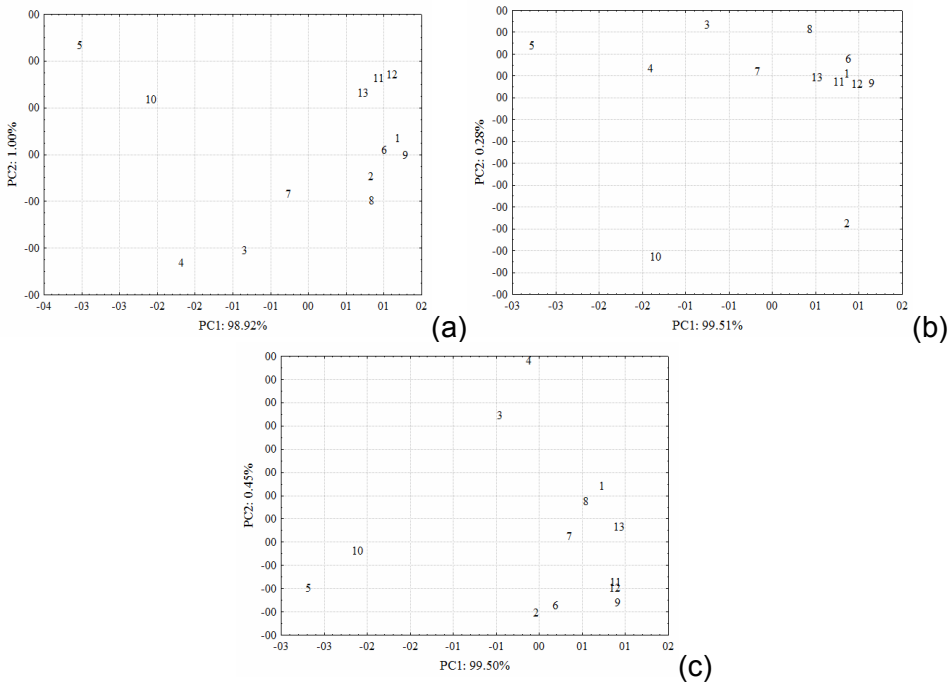

Figure 4. The lipophilicity maps of the investigated pesticides, obtained by applying PCA on the R_M values: RP-18 (a), RP-8 (b), and CN (c).

The strong lipophilic character of the RP-18 may be observed in diagrams corresponding to R_M, while the RP-8 and CN are leading to more or less similar interactions.

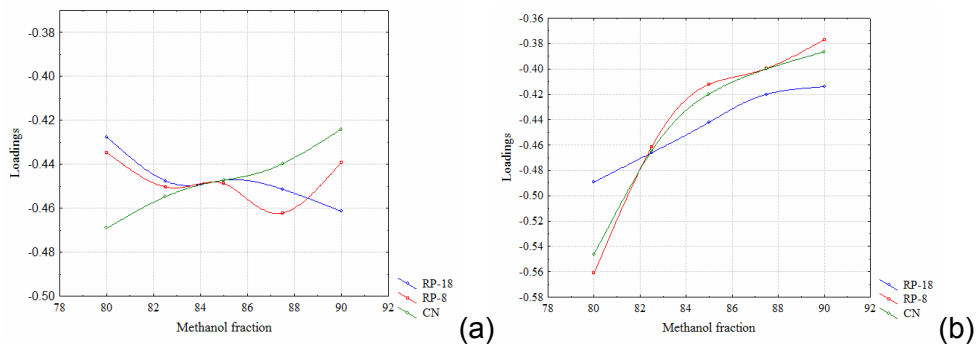

Figure 5. The loadings profiles: R_F (a), and R_M (b).

The similarities existed between the involved stationary phases are sustained by the correlation matrices (Table 4). The best correlations were obtained for the RP-8 lipophilicity indices versus those obtained on RP-18. The CN results are better correlated with the RP-8 lipophilicity indices. The highest correlation coefficients are of 0.99 and in some particular cases 1. The correlation matrix of the experimentally vs. computed lipophilicity indices may offer some information about the molecular particularities which are responsible for the chromatographic behaviour. In the Table 5 are listed the obtained correlations. The highest correlations are obtained for the $R_{M0,\ RP-8}$ vs. AC logP when the correlation coefficient is reaching 0.92. The AC logP index presents the highest correlations with all experimentally expressed indices. Significant correlations are obtained also, for the miLogP. Both lipophilicity indices are computed with ALOGPS 2.1 module. These significant correlations obtained ($r > 0.80$) are sustaining the experimentally obtained lipophilicity indices.

CONCLUSIONS

The lipophilicity of some emerging pesticides has been investigated on three reversed phase stationary phases using different mixtures of methanol-water as mobile phases. The most lipophilic compound has been founded to be the fenbutatim oxide, since the compound with the lowest lipophilicty is the simasine. The chromatographic behaviour of the compounds observed was constant while the mobile phase composition has been changed, for all the employed stationary phases. Once more, the PCA has been proved the power of compounds classification, as lipophilicity indices provider and the capacity if retention mechanism information support. The correlation matrices have been indicating that all the experimentally obtained lipophilicity indices are highly correlated, while the AC logP has been distinguished as the best computed descriptor.

Table 4. The correlation matrix of the experimentally obtained lipophilicity indices

Stationary phase	Index	RP-18							RP-8							CN						
		mR_F	mR_M	R_{M0}	b	φ_0	PC1/R_F	PC1/R_M	mR_F	mR_M	R_{M0}	b	φ_0	PC1/R_F	PC1/R_M	mR_F	mR_M	R_{M0}	b	φ_0	PC1/R_F	PC1/R_M
RP-18	mR_F	1.00	**-0.98**	**-0.81**	0.64	**0.91**	**-1.00**	**0.98**	**0.99**	**-0.96**	**-0.90**	**0.87**	**0.97**	**-0.99**	**0.96**	**0.85**	**-0.83**	**-0.92**	**0.93**	**0.85**	**-0.85**	**0.84**
	mR_M		1.00	0.72	-0.53	-0.95	**0.98**	**-1.00**	**-0.98**	**0.99**	**0.92**	**-0.89**	**-0.96**	**0.98**	**-0.99**	**-0.90**	**0.90**	**0.95**	**-0.95**	**-0.86**	**0.90**	**-0.90**
	R_{M0}			1.00	**-0.97**	-0.64	**0.81**	-0.73	-0.79	0.72	0.72	-0.71	-0.75	0.79	-0.72	-0.57	0.52	0.69	-0.73	-0.70	0.57	-0.52
	b				1.00	0.45	-0.64	0.54	0.62	-0.53	-0.56	0.55	0.58	-0.62	0.53	0.37	-0.32	-0.51	0.56	0.56	-0.38	0.32
	φ_0					1.00	**-0.91**	**0.95**	**0.92**	**-0.95**	**-0.87**	**0.83**	**0.90**	**-0.92**	**0.95**	**0.93**	**-0.94**	**-0.94**	**0.93**	**0.89**	**-0.93**	**0.94**
	PC1/R_F						1.00	**-0.98**	**-0.99**	**0.96**	**0.90**	**-0.87**	**-0.97**	**0.99**	**-0.96**	**-0.85**	**0.83**	**0.92**	**-0.93**	**-0.85**	**0.85**	**-0.84**
	PC1/R_M							1.00	**0.99**	**-0.99**	**-0.92**	**0.89**	**0.96**	**-0.99**	**0.99**	**0.90**	**-0.90**	**-0.95**	**0.95**	**0.86**	**-0.90**	**0.90**

Stationary phase	Index	RP-18							RP-8							CN						
		mR_F	mR_M	R_{M0}	b	φ_0	PC1/R_F	PC1/R_M	mR_F	mR_M	R_{M0}	b	φ_0	PC1/R_F	PC1/R_M	mR_F	mR_M	R_{M0}	b	φ_0	PC1/R_F	PC1/R_M
RP-8	mR_F								1.00	**-0.98**	**-0.94**	**0.92**	**0.99**	**-1.00**	**0.98**	**0.85**	**-0.84**	**-0.94**	**0.95**	**0.84**	**-0.85**	**0.84**
	mR_M									1.00	**0.96**	**-0.94**	**-0.96**	**0.98**	**-1.00**	**-0.87**	**0.88**	**0.95**	**-0.95**	**-0.84**	**0.88**	**-0.88**
	R_{M0}										1.00	**-1.00**	**-0.92**	**0.94**	**-0.96**	-0.75	0.75	**0.87**	**-0.89**	-0.74	0.75	-0.76
	b											1.00	**0.90**	**-0.92**	**0.94**	0.70	-0.71	**-0.84**	**0.86**	0.70	-0.70	0.71
	φ_0												1.00	**-0.99**	**0.96**	**0.81**	**-0.80**	**-0.92**	**0.94**	**0.82**	**-0.81**	**0.81**
	PC1/R_F													1.00	**-0.98**	**-0.85**	**0.84**	**0.94**	**-0.95**	**-0.84**	**0.85**	**-0.84**
	PC1/R_M														1.00	**0.87**	**-0.88**	**-0.95**	**0.95**	**0.84**	**-0.87**	**0.88**
CN	mR_F															1.00	**-1.00**	**-0.96**	**0.92**	**0.93**	**-1.00**	**1.00**
	mR_M																1.00	**0.95**	**-0.91**	**-0.91**	**1.00**	**-1.00**
	R_{M0}																	1.00	**-1.00**	**-0.93**	**0.96**	**-0.95**
	b																		1.00	**0.92**	**-0.92**	**0.92**
	φ_0																			1.00	**-0.93**	**0.92**
	PC1/R_F																				1.00	**-1.00**
	PC1/R_M																					1.00

Table 5. The correlation matrix of the experimentally vs. computed lipophilicity indices.

Stationary phase	Index	ALOGPs	AC logP	AB/ LogP	miLogP	ALOGP	MLOGP	KOWWIN	XLOGP2	XLOGP3	$LogP^C$	$LogP^V$	CLOGP
RP-18	mR_F	-0.70	**-0.86**	-0.63	-0.76	-0.63	-0.59	-0.72	-0.68	-0.60	-0.65	-0.64	-0.74
	mR_M	0.70	**0.85**	0.63	0.75	0.65	0.62	0.73	0.68	0.60	0.64	0.63	0.74
	R_{M0}	0.72	**0.88**	0.76	**0.84**	0.73	0.58	**0.81**	**0.80**	0.68	0.79	0.78	**0.81**
	b	-0.68	**-0.83**	-0.75	**-0.81**	-0.70	-0.53	-0.77	-0.78	-0.65	-0.78	-0.78	-0.78
	φ_0	-0.65	-0.78	-0.55	-0.67	-0.64	-0.57	-0.64	-0.66	-0.58	-0.62	-0.61	-0.66
	PC1/R_F	0.70	**0.86**	0.63	0.76	0.63	0.59	0.72	0.68	0.60	0.64	0.64	0.74
	PC1/R_M	-0.70	**-0.85**	-0.64	-0.75	-0.65	-0.62	-0.73	-0.68	-0.60	-0.64	-0.63	-0.74
RP-8	mR_F	-0.75	**-0.90**	-0.69	**-0.80**	-0.69	-0.65	-0.77	-0.73	-0.65	-0.69	-0.68	-0.78
	mR_M	0.75	**0.89**	0.69	**0.80**	0.69	0.66	0.78	0.73	0.65	0.68	0.68	0.78
	R_{M0}	**0.82**	**0.92**	**0.80**	**0.88**	0.76	0.69	**0.85**	**0.80**	0.73	0.78	0.78	0.85
	b	**-0.82**	**-0.91**	**-0.80**	**-0.88**	-0.76	-0.68	**-0.85**	**-0.80**	-0.73	-0.78	-0.79	-0.84
	φ_0	-0.76	**-0.88**	-0.67	-0.78	-0.68	-0.65	-0.74	-0.73	-0.65	-0.66	-0.66	-0.76
	PC1/R_F	0.75	**0.90**	0.69	**0.80**	0.69	0.65	0.77	0.73	0.65	0.69	0.68	0.78
	PC1/R_M	-0.75	**-0.90**	-0.70	**-0.80**	-0.69	-0.66	-0.78	-0.73	-0.65	-0.69	-0.68	-0.78
CN	mR_F	-0.51	-0.58	-0.34	-0.47	-0.49	-0.38	-0.43	-0.45	-0.40	-0.46	-0.43	-0.48
	mR_M	0.50	0.56	0.33	0.46	0.48	0.39	0.41	0.44	0.39	0.44	0.41	0.46
	R_{M0}	0.73	**0.80**	0.59	0.69	0.66	0.58	0.65	0.68	0.62	0.64	0.62	0.69
	b	-0.77	**-0.84**	-0.64	-0.74	-0.69	-0.61	-0.69	-0.72	-0.67	-0.67	-0.66	-0.74
	φ_0	-0.49	-0.60	-0.34	-0.47	-0.46	-0.26	-0.40	-0.50	-0.37	-0.44	-0.42	-0.44
	PC1/R_F	0.51	0.58	0.34	0.48	0.49	0.38	0.43	0.45	0.40	0.46	0.43	0.48
	PC1/R_M	-0.50	-0.57	-0.33	-0.46	-0.49	-0.39	-0.42	-0.45	-0.40	-0.45	-0.42	-0.47

EXPERIMENTAL SECTION

All the compounds and solvents were obtained from commercial source (Merck, Fluka, and Sigma) in analytical degree purity. The stationary phases were Merck products (Nordic Invest, Cluj Napoca, Romania). The standard solutions of pesticides were prepared in acetone (1 mg mL^{-1}). The spots (2 µL) were applied at 1.5 cm from bottom edge and at 0.7 cm from lateral edges using a Hamilton microsyringe of 10 µL. The distance between the spots was by 0.7 cm. The elution was performed on 8 cm, by ascendant development into a chromatographic chamber previously saturated for 10 min. The chemically bonded plates were by RP-18 and RP-8 silica gel 60 modified with aliphatic hydrocarbons of increasing hydrocarbon chain length resulting in increased hydrophobicity and the CN modified plate which are based on a silica gel 60 modified with cyanopropyl groups. Each stationary phase type has been developed with five mobile phases based on methanol and water. The methanol fractions used in the mobile phases were between 80 and 90% changed with 2.5% per each step. The visualization of the compounds has been realized under UV light at 254 nm.

ACKNOWLEDGEMENT

The financial support of the Ministry of Education Research, Youth and Sport of Romania (CNCSIS, IDEI 560/2007-2010) is gratefully acknowledged.

REFERENCES

1. E.R. Laws, W.J. Hayes, “Handbook of Pesticide Toxicology”, Academic Press, San Diego, **1991**.
2. D.B. Barr, L.L. Needham, *J. Chromatogr. B*, **2002**, *778*, 5.
3. P. Kaushik, G.J. Kaushik, *Haz. Mat.* **2007**, *143*, 102.
4. R. McKinlay, J.A. Plant, J.N.B. Bell, N. Voulvoulis, *Environ. Int.* **2008**, *34*, 168.
5. J. Beard, Australian Rural Health Research Collaboration, *Sci. Tot. Environ.* **2006**, *355*, 78.
6. P. Baur, H. Marzouk, J. Schonherr, B.T. Grayson, *J. Agric. Food Chem.* **1997**, *45*, 3659.
7. R. Kaliszan, *Chem. Rev*. **2007**, *107*, 3212.
8. J. Sangster, “Octanol–Water Partition Coefficients: Fundamentals and Physical Chemistry”, Wiley, West Sussex, **1997**.

9. R. Kaliszan, “Structure and Retention in Chromatography: A Chemometric Approach”, Harwood Academic Publishers, Amsterdam, **1997**.
10. R.D. Briciu, A. Kot-Wasik, A. Wasik, J. Namiesnik, C. Sârbu, *J. Chromatogr. A*, **2010**, *1217*, 3702.
11. C. Sârbu, B. Malawska, *J. Liq. Chromatogr. & Rel.Technol.* **2000**, *23*, 2143.
12. T. Djaković-Sekulić, N. Perišić Janjić, C. Sârbu, Z. Lozanov- Crvenković, *J. Planar Chromatogr.* **2007**, *20*, 251.
13. E.C. Bate-Smith, R.G. Westall, *Biochim. Biophys. Acta,* **1950**, *4*, 427.
14. E. Soczewiński, C.A. Wachtmeister, *J. Chromatogr. A*, **1962**, *7*, 311.
15. K. Valkó, *J. Liq. Chromatogr.* **1984**, *7*, 1405.
16. R.D. Briciu, A. Kot-Wasik, J. Namiesnik, C. Sârbu, *J. Sep. Sci.* **2009**, *32*, 2066.
17. R.D. Briciu, C. Sârbu, *Sep. Sci. Technol.,* **2010**, *45*, 1275.
18. C. Sârbu, R.D. Briciu, *J. Liq. Chromatogr. & Rel. Technol.* **2010**, *33*, 903.
19. I.V. Tetko, J. Gasteiger, R. Todeschini, A. Mauri, D. Livingstone, P. Ertl, V.A. Palyulin, E.V. Radchenko, N.S. Zefirov, A.S. Makarenko, V.Y. Tanchuk, V.V. Prokopenko, *J. Comput. Aid. Mol. Des.* **2005**, *19*, 453.
20. G.L. Biagi, A.M. Barbaro, M.C. Guerra, G. Gantelli-Forti, M.E. Fracasso, *J. Med. Chem*. **1974**, *17,* 28.
21. P.J. Schoenmakers, H.A.H. Billiet, L. de Galan, *J. Chromatogr.* **1979**, *185,* 179.