J. Mater. Environ. Sci. 6 (9) (2015) 2386-2391
ISSN : 2028-2508
CODEN: JMESCN

Photolysis of herbicide safener Mefenpyrdiethyl under sunlight irradiation: an analytical and GC/MS investigation

A. El Boukili[1], A. El Bazaoui[2], A. Soulaymani[2], R. Soulaymani-Bencheikh[3,4], M. Taibi[5*], A. EL Hourch[1]

[1]*Faculty of sciences, University Mohammed V, Av. Ibn Battouta, BP 1014, Rabat, Morocco*
[2]*Faculty of Sciences, University Ibn Tofail, LGB, BP, 133, 14000 Kenitra, Morocco*
[3]*Moroccan Poison Control and pharmacovigilance Center, Rabat, Morocco*
[4]*Faculty of Medicine and Pharmacy, University Mohammed V, Rabat, Morocco*
[5]*University Mohammed V, LPCMIO, ENS, Rabat, Morocco*

Received 5 May 2015, Revised 11 Sept 2015, Accepted 11 sept 2015
[*]*Corresponding Author E-mail: taibiens@yahoo.fr*

Abstract
Photolysis of the herbicide safener Mefenpyer-diethyl by sunlight irradiation in aqueous buffer solution (pH 6.9) was investigated byGaz Chromatography /Mass Spectra (GC/MS).Notable photodegradation of mefenpyrdiethyl was observed at investigated pH. Photodegradation rate followed first-order kinetics with significant correlation coefficient. The $t_{1/2}$ value was 1.20h. Four metabolites were detected and identified according to GC-MS spectral data. Photoproducts PP1 and PP2 show their maximum intensities after 3 h of irradiation after which they also began to degrade into metabolites PP3 and PP4. To our knowledge, the photoproducts PP2 and PP4 were detected previously in mefenpyrdiethyl hydrolysis process.

Keywords: Mefenpyrdiethyl; Photolysis; GC/MS; Sunlight; kinetics.

1. Introduction
Mefenpyr-diethyl, also known as “antidote”, is usually used as an herbicide safener in combination with other herbicides over cereal grain crops to improve herbicide selectivity between crops and weed species [1-3].Pesticides in contaminated natural water can undergo transformation by different degradation processes such as microbial, and photochemical processes [4-6] the formed metabolites were sometimes more toxic than the parent compound [7]. Photochemical transformation is one of the main abiotic degradation pathways occurring in natural waters and one of the factors controlling the fate of pesticides in the environment [6-9]. Phototransformation of pesticides proceeds with different pathways through direct and indirect photolysis. Direct photolysis can occur if the concerned pesticide absorbs UV-Visible light, while indirect photolysis of the pesticide compound can be induced by chemical components in the aquatic environment such as dissolved organic matter, nitrate, hydrogen peroxide and iron species [10-12]. The time and type of degradation of pesticides (direct and indirect) are two important factors that govern the efficiencyand safety of these xenobiotics [13]. There is, however, no data available on the photodegradation of this herbicide under natural sunlight irradiation. This paper presents the rate of photolysis and nature of photoproducts of mefenpyrdiethyl formed in aqueous buffer solution (pH 6.9) under natural sunlight conditions.

2. Materials and methods
2.1 Chemicals
Mefenpyr-diethyl (**Figure1**) with their characteristics (**Table.1**) was supplied by Sigma–Aldrich (Germany) as analytical standards with purity>97%. Stock solution of mefenpyrdiethyl dissolved in methanol was established

at a concentration of 100 mg/L. Solvents were high-performance liquid chromatography (HPLC) grade (methanol, dichloromethane). Anhydrous sodium sulfate was analysis grade. Phosphate buffers (KH_2PO_4 and K_2HPO_4) were also purchased from Aldrich. Milli-Q quality water (Millipore, Bedford, MA) was used to prepare the buffer solution. All stock solutions were stored in a refrigerator at 4°C.

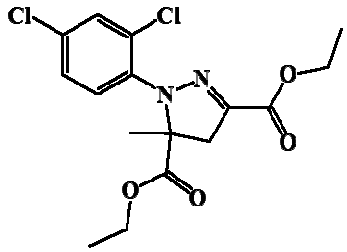

Figure 1: Chemical structure of MFD (Mefenpyr-diethyl)

Table 1: Some important physicochemical properties of Mefenpyrdiethyl

IUPAC: diethyl (RS)-1-(2,4-dichlorophenyl)-5-methyl-2-pyrazoline-3,5-dicarboxylate	
Molecular Weight	373.23
Molecular formula	$C_{16}H_{18}Cl_2N_2O_4$
purity	99.2%
Solubility in water(pH= 6,1; 25°C)	20mg/L
Solubility in dichloromethane	500 g/L
Solubility in methanol	400 g/L
UV/visible (nm)	Primary Amax = <200 Secondary Amax = 305

2.2 Photolysis experiment

Mefenpyr-diethyl photolysis experiment under sunlight was conducted in open air on June 16, 2014 in ENS institute, Rabat, Morocco (latitude 34.1 °N) from the time period between 9.00 a.m. and 6.00 p.m, at temperature 32°C. The kinetic experiment was performed by following the disappearance of mefenpyr-diethyl as well as the formation of its degradation products using GC-MS. The buffer solution at pH 6.9 was prepared by dissolving KH_2PO_4 and K_2HPO_4 in Milli-Q quality water. Mefenpyr-diethyl (stock solution) was added into buffer solution to achieve an initial concentration at 2 mg/L. The aqueous buffer solutions (100 mL) were transferred into six 10 mL glass tubes. All six tubes were immediately sealed and then placed under the irradiation of sunlight in open air. Irradiation times were 0.17, 1, 3, 6 and 9h. 2 mL aqueous buffer solution sample were removed at intervals and extracted with dichloromethane for three times (3×5 mL). The combined extracts were dehydrated on anhydrous sodium sulfate Na_2SO_4 and then evaporated to dryness and redissolved in 100 µl of methanol for GC/MS analysis. The experiment was performed in duplicate.

2.3 GC/MS analysis

The GC/MS analysis was carried out on Perkin Elmer Clarus Autosystem Gas Chromatograph/Turbomass Mass Spectrometer instrument operating in electron impact (EI) ionisation mode at 70 eV, with MS transfer line temperature: 280 °C, ion source temperature: 230 °C, quadrupole temperature: 150 °C. In the full-scan mode, the scanned mass range was 50–400 amu with a scan rate of 1.56 scans /s. Solvent delay was set to 5 min. An HP-5MS column (Hewlett Packard, Palo Alto, CA, USA) (30 m×0.25 mm×0.25 µm) was used. The flow rate of the carrier gas (He) was 1 mL/min. The temperature program was 100 (1 min isotherm) to 260 °C, ramped at 15 °C/min and hold at the final temperature for 3 min. Injector temperature was 210 °C. The mode of inlet was split 1/20 and the injected volume was 1µL. The total time of analysis was 14.65 min. The identification of the different photolysis products were confirmed by comparing the measured mass spectral data with those obtained from the library Nist, as well as literature data [2,3,14].

3. Results and discussion

3.1 Identification the metabolites of mefenpyerdiethyl

In the present study a GC-MS procedure was applied to identify the four photolysis products of irradiated herbicide mefenpyrdiethyl in buffer solutions at pH 6.9. Five compounds showed the characteristic mass spectral fragmentation of the pesticide mefenpyerdiethyl and their metabolites (**Figure 2**).

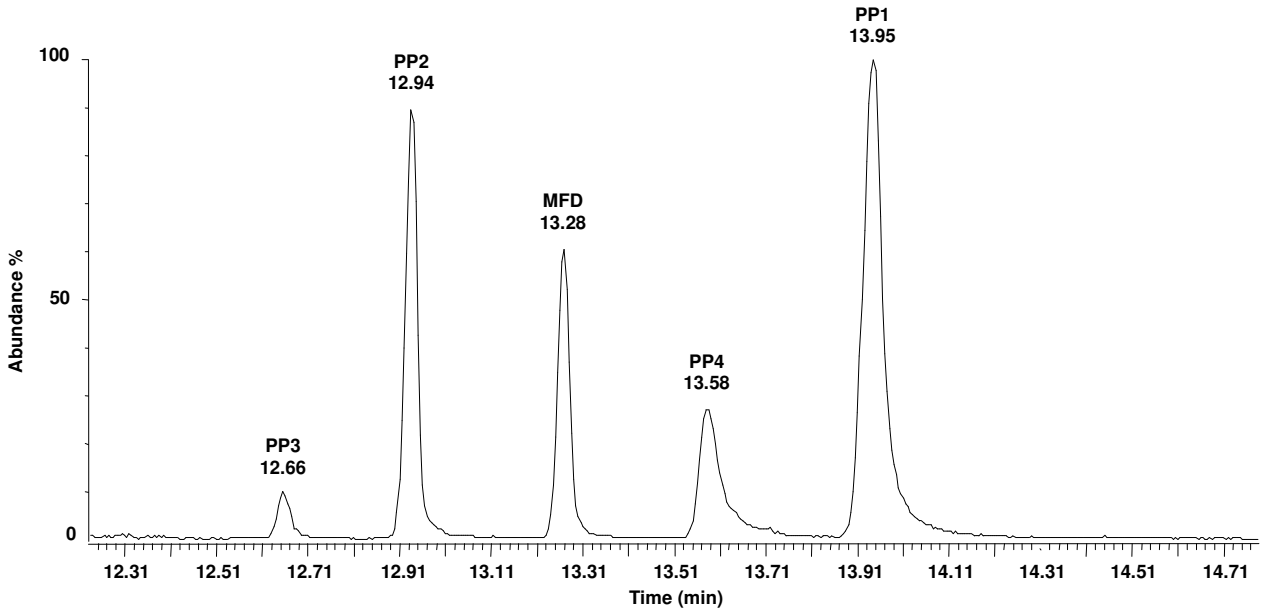

Figure 2: Analyticalchromatogramofmefenpyr-diethyl and these photoproducts

The parent compound mefenpyrdiethyl appeared at retention time 13.28 min and identified according its mass spectral data with a molecular ion peak at *m/z* 372 and a base peak at *m/z* 253. The first photoproduct (PP_1) appeared at 12.95 min was tentatively assigned as O_5-ethyl O_3-methyl 1-(2,4-dichlorophenyl)-5-methyl-4H-pyrazole-3,5-dicarboxylate or O_3-ethyl O_5-methyl 1-(2,4-dichlorophenyl)-5-methyl-4H-pyrazole-3,5-dicarboxylate with a molecular ion peak at *m/z* 358 and a base peak at *m/z* 253. The second photoproduct (PP_2) had a retention time at 13.95 min was identified as mefenpyrethyl (1-(2,4-dichlorophenyl)-5-ethoxycarbonyl-5-methyl-4H-pyrazole-3-carboxylic acid) with a molecular ion peak at *m/z* 344 ($C_{14}H_{14}Cl_2N_2O_4$) and a base peak at *m/z* 253. The third photoproduct (PP_3) appeared at 13.60 min was 2-(2,4-dichlorophenyl)-5-methoxycarbonyl-3-methyl-4H-pyrazole-3-carboxylic acid or 1-(2,4-dichlorophenyl)-5-methoxycarbonyl-5-methyl-4H-pyrazole-3-carboxylic acid with the molecular ion peak at *m/z* 330 ($C_{13}H_{12}Cl_2N_2O_4$) and a base peak at *m/z* 253. The fourth photoproduct (PP_4) had a retention time at 12.67 min was tentatively assigned as mefenpyr (1-(2,4-dichlorophenyl)-5-methyl-4H-pyrazole-3,5-dicarboxylic acid) with a molecular ion peak at *m/z* 316 and a base peak at *m/z* 253. The results are summarized in (**Table 2**). The (**Figure 3**) showed the chemical structures of the four photoproducts of mefenpyr-diethyl.

3.2 Kinetic photolysis of mefenpyrdiethyl

Mefenpyrdiethyl has strong absorbance at 200–400 nm [2,3], making it susceptible to sunlight irradiation. The photolysis experiment of mefenpyrdiethyl was carried out in aqueous buffer solution at pH 6.9 since the hydrolysis of mefenpyrdiethyl take place at pH≥7 [3]. Notable photolysis of mefenpyrdiethyl was observed under sunlight irradiation at investigated pH. The degradation of mefenpyrdiethyl was 8.80, 52.31 and 82.83 % of herbicide disappeared after 0.17, 1 and 3h, respectively. A linear correlation between ln C_t and t was obtained with a regression coefficient r^2greater than 0.99 (**Figure 4**), demonstrating that the first-order kinetics was followed. The half-life value was calculated from the regression equation. The rate constants (k), half-life ($t_{1/2}$) values and $r^2$of mefenpyrdiethyl in buffer solution are given in (**Table 3**).

Table 2: GC-MS analysis of metabolites of MFD in aqueous buffer solution pH 6.9 under sunlight (Base peaks are printed in bold). RT: Retention time; PP= photoproduct

Compound		RT [min]	$[M]^+$/base peak (*m/z*)	Characteristic ions
Mefenpyrdiethyl (MFD)		13.28	372/**253**	327, 301, 299, 257, 255, 253, 229, 227, 188, 186, 165,145, 124, 75.
PP_1	O5-ethyl O3-methyl 1-(2,4 dichlorophenyl) 5-methyl-4H-pyrazole-3,5-dicarboxylate	12.95	358/**253**	327, 289, 287, 285, 257, 255, 253, 241, 186, 165,145, 124, 109, 75.
	O_3-ethyl O_5-methyl 1-(2,4-dichlorophenyl)-5-methyl-4H-pyrazole-3,5-dicarboxylate			
PP_2	Mefenpyrethyl (1-(2,4-dichlorophenyl)-5-ethoxycarbonyl-5-methyl-4H-pyrazole-3-carboxylic acid)	13.95	344/**253**	327, 274, 272, 270, 257, 255, 253, 227, 188, 186, 145, 124, 109, 57.
PP3	2-(2,4-dichlorophenyl)-5-methoxycarbonyl-3-methyl-4H-pyrazole-3-carboxylic acid	13.60	330/**253**	313, 296, 274, 272, 270, 257, 255, 253, 227, 188, 186, 145, 124, 57.
	1-(2,4-dichlorophenyl)-5-methoxycarbonyl-5-methyl-4H-pyrazole-3-carboxylic acid			
PP4	Mefenpyr (1-(2,4-dichlorophenyl)-5-methyl-4H-pyrazole-3,5-dicarboxylic acid)	12.67	316/**253**	313, 287, 285, 281, 262, 255, 253, 227, 188, 186, 145, 124, 109, 57.

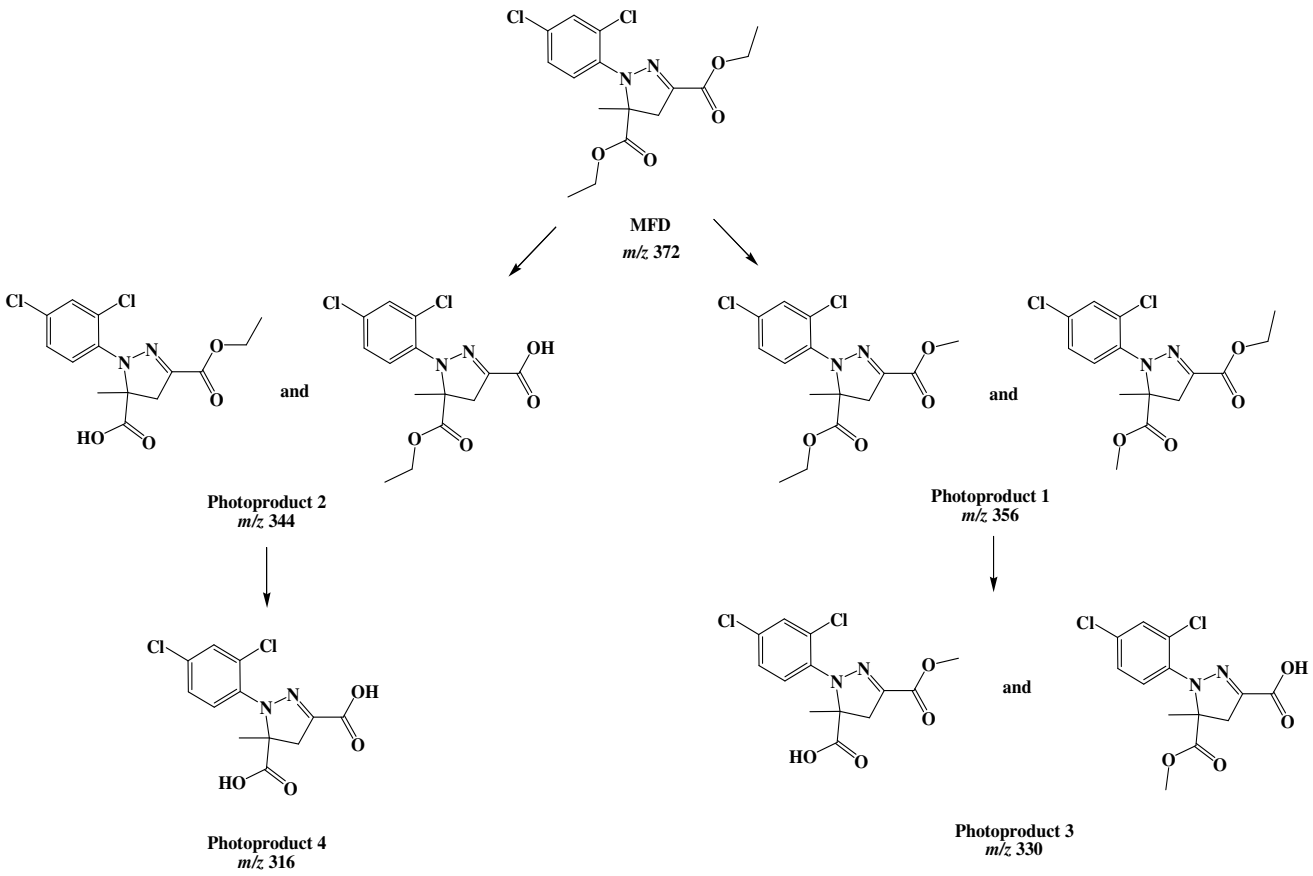

Figure 3: The possible photolysis pathway of mefenpyrdiethyl in aqueous buffer solution (pH 6.9) under sunlight

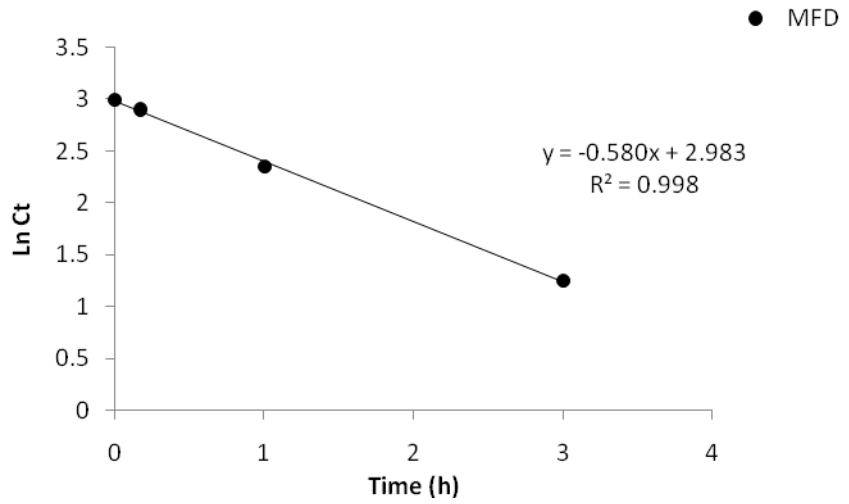

Figure 4: Linear correlation between ln C_t and t for mefenpyrdiethyl photolysis at pH 6.9. Points are the means of experiment data. Line is linear regression result.

Table 3: Rate constant, half-life and r^2 values for mefenpyrdiethyl in buffer solution

		Rate constant, k (h^{-1})	Half-life, $t_{1/2}$ (h)	Regression coefficient, r^2
Buffer solution Under sunlight	pH 6.9	0.580	1.20	0.998

The photodegradation of mefenpyrdiethyl in buffer solution pH 6.9 is presented in (**Figure 5**) with the evolution of four different photoproducts. We estimated the change in the amount by analysis of the area of every product.

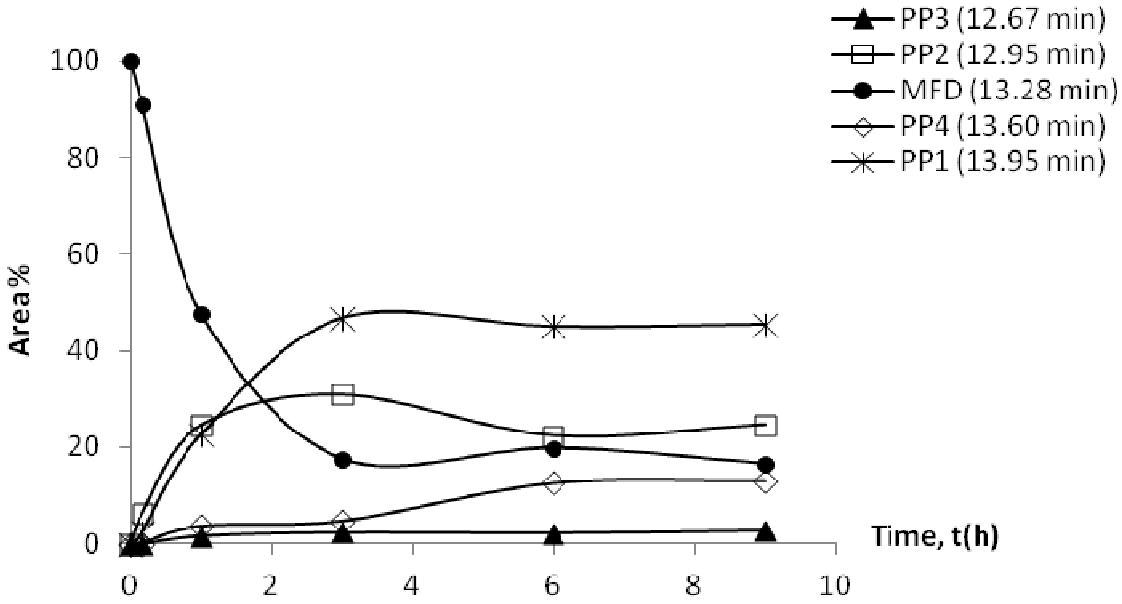

Figure 5: Change in amounts of parent and degradation products as a function of time under photolysis at pH 6.9

Studies on the kinetics of these photoproducts showed that the decrease in amount of the parent compound MFD was related to the simultaneous appearance of two photoproducts PP1 at m/z 356 (two possible forms) and PP2 at m/z 344 (two possible forms) at irradiation time 0.17h. The two photoproducts PP1 and PP2 show their maximum intensities on after 3h of irradiation after which they also began to degrade into metabolites PP3 at m/z 330 (two possible structures) and PP4 at m/z 316, respectively. The structures of the four photometabolites were all derived from the parent compound mefenpyrdiethyl. These structures indicate that the photoproducts (PP_3) and (PP_4) are formed by the loss of one terminal ethyl groups (mono-deesterification) of photoproducts (PP_1) and (PP_2) which are obtained from compound parent by dealkylation (concerted attacks of H and OH radicals on one of the terminal methyl groups) and mono-deesterification (of the free ester attached to the pyrazole ring), respectively. It is interesting to note that the both chemicals forms of photoproduct PP1, PP2 and PP3 have the same retention time and mass spectrum. Your separation is not possible by our analytical conditions.
These data confirm the result of Chnirheb *et al.* [2,3]. We can thus clearly see that the photolysis products M_1 and M_2 are a transient species which are not stable during the photolysis experiment, confirm the result of Chnirheb *et al.* [2,3].

Conclusion

Under sunlight, notable photodegradation of mefenpyrdiethyl was observed at pH 6.9. The kinetics of photolysis was determined to be first-order. From the GC/MS study on the photolysis, four photoproducts were identified. PP_1 and PP_2have been identified as the major products of the photolysis of mefenpyrdiethyl. The mechanism of photodegradation under sunlight of this pesticide included alkylation and mono-desertification. From this study, products PP_1 and PP_2 are a transient species, which are not stable during the photolysis experiment and are transformed into PP_3 and PP_4. Because of their current usage in many crops, photolysis will be important factors in determining its environmental fate in aquatic systems or in soil environment.

Acknowledgements - Authors of this study tank technicians GC/MS of the Anti-Poison Centre and Pharmacovigilance of Morocco for technical assistance.

References

1. Hacker E., Bieringer H., Willms L., Rosch W., Kocher H. Wolf R., *Pflanzen* 17 (2000) 493.
2. Chnirheb A., Harir M., Kanawati B., Fekete A., El Azzouzi M., Hertkorn N., Schmitt-Kopplin P., *Anal. Bioanal. Chem.* 398(5) (2010) 2325.
3. Chnirheb A., Harir M., Kanawatil B., El Azzouzi M., Gebefűgil I., Chmitt-Kopplin P., *J. Environ. Sci.* 24(9) (2012) 1686.
4. Durand G., Mansour M., Barcelo D. *Anal. Chem. Acta* 262 (1992) 167.
5. EL-Dib AA.,Abou-Wally HF. *Water Res.* 32 (1998) 1881.
6. Mansour, M., Feicht EA., Behechti A., Schramm KW., Kettrup A., *Chemos*. 39 (1999) 575.
7. Amoros I., Connon R., Garelick H., Alonso JL., Carrasco JM., *Water Sci. Technol.* 42 (2000) 19.
8. Durand G., Barcelo D., Albaiges J., Mansour M., *Toxicol. Environ. Chem*. (1991) 31.
9. Castillo M., DominguesR. , Alphenduarda MF., Barcelo D., *Anal. Chim. Acta* 353 (1997) 133.
10. Torrents A., Anderson BG., Bilboulian S., Johnson WE., Hapeman C., *J. Environ. Sci. Technol*. 31 (1997) 1476.
11. Vialation D., Richard C., *Aquatic Sci*. 64 (2002) 207.
12. Southworth BA, Voelker BM., *J. Environ. Sci. Technol*. 37 (2003) 1130.
13. Roy S., Singh SB., *J. Environ. Sci. Health Part B* 40 (2000) 525.
14. Alder L., Greulich K., Kempe G., Vieth B., *Mass Spectr. Rev*. 5 (2006) 838.