American Journal of Analytical Chemistry, 2011, 2, 63-68
doi:10.4236/ajac.2011.228125 Published Online December 2011 (http://www.SciRP.org/journal/ajac)

A New Approach for Atrazine Desorption, Extraction and Detection from a Clay-Silty Soil Sample

Rossy Feria-Reyes[1], Paola Medina-Armenta[2], M. Teutli-León[3], M. G. García-Jiménez[2], I. González[1*]
[1]*UAM-Iztapalapa*, *Chemistry Department*, *Autonomous Metropolitan University*, *Mexico City*, *Mexico*
[2]*Chemistry Department*, *University of Guanajuato*, *Guanajuato*, *Mexico*
[3]*Engineering Department*, *Distinguished Autonomous University of Puebla*, *Puebla*, *Mexico*
E-mail: *igm@xanum.uam.mx
Received November 12, 2011; *revised December* 13, 2011; *accepted December* 23, 2011

Abstract

This paper reports an alternative method for extraction, detection and quantification of atrazine from a clay-silty soil. Atrazine adsorption isotherm for this kind of soil fits to a Freundlich adsorption isotherm with a correlation coefficient of 0.994, sorption intensity 1/n = 0.718 and K_f = 1, with a maximum soil adsorbed atrazine concentration of 8 $mg \cdot g^{-1}$. Atrazine desorption was approached using several surfactants including non-ionic (Triton X-100, Triton X-114, and Triton X-405), anionic (SDS) and cationic (CTAB), these surfactants were used at critical micellar concentration (CMC) and higher concentrations. Atrazine quantification was done by high resolution liquid chromatography coupled to spectrophotometric detection (HPLC-UV), optimized conditions correspond to a flow rate of 1.0 $mL \cdot min^{-1}$, λ = 260 nm, a C_{18} PAH Agilent-Eclipse column with a mobile phase of CH_3OH/1 × 10^{-3}, a phosphate buffer, pH 3.2/CH_3CN 55:30:15 (v/v). At these conditions it can be obtained a good chromatographic separation of atrazine and soil organic matter. Atrazine desorption was aided by surfactants at CMC conditions, it can be claimed that atrazine desorption was enhanced by surfactants since desorption, from higher to lower, goes as follows: 98.5% with Triton X-114, 98% with SDS, 89.5% with Triton X-405, 86.5% with Triton X-100; and 45% with CTAB.

Keywords: Atrazine, Desorption, Soil, Surfactants

1. Introduction

In Mexico, it is estimated that annual pesticide application amounts 55,000 tons [1], from which 28.7% corresponds to herbicides, and in this class atrazine represents 12.8%, being the third most used herbicide. Atrazine (2-chloride-4-ethylamino-6-isopropylamino-1,3,5-triazine) belongs to the S-triazine herbicide group. This herbicide is practically non-volatile, at neutral state its average half-life is 200 days, but its active state ranges from 4 to 57 weeks, its persistence is affected by environmental factors such as pH, humidity, temperature and microbial activity [2-8]. Health concerns about atrazine are related to liver and heart, as well as endocrine and teratogenic alterations.

Atrazine has been mainly used for weeds control in corn, sorghum, pineapple and sugar cane farming. According to EPA, environmental concentration levels of herbicides and pesticides are very low, therefore in EPA 508.1 method [9] it is recommended to include a solvent aided extraction and pre-concentration stage so an increase on selectivity is favored.

In the last decades methods for pre-concentration have been studied in order to be implemented before analytical determination of compounds at trace level concentrations. This approach pursued a minimization/elimination of organic solvents of common use in liquid-liquid extraction; some of the reported methodologies are: extraction with membranes [10-12], solid phase extraction (SPE) [13,14], and solid phase micro-extraction (SPME). Use of micellar systems (surfactants) has become a common practice for either new analytical methods or modification of old ones. Aqueous surfactant solutions have been used in micellar extraction (ME) and cloud point extraction (CPE), in the first methodology selective extraction can be done because micellar aggregates have

a size which unable them to pass through ultrafiltration membranes, this fact, plus micelle solubilization capacity for a wide set of solutes, it is the basis of separation methods. Most applications of CPE for organic compounds extraction are usually complemented by HPLC, since the obtained surfactant rich extraction phase is totally compatible with the common hydro-organic phases used in this type of chromatography [15].

Non-ionic surfactants like Genapol X-080 and Triton X-114 have been used as extractive agents for organophosphorate compounds such as methyl and ethyl-parathion, paraoxon, and fenitrothion, when the CPE method is applied in their extraction, previously to HPLC determination [16,17].

Considering that in a soil sample, an analysis of herbicide and pesticide it is though a challenge because presence of them, plus organic matter creates a highly complex matrix. In this work it is presented evidence of a modified methodology in which surfactants inclusion allowed to get atrazine desorption and extraction from a clay-silty soil, and left an extract which provides a clear chromatographic separation signal between atrazine and organic matter.

2. Methodology

2.1. Reagents

All reagents used in this study were analytical grade. A 1000 $mg \cdot L^{-1}$ standard atrazine (Sigma Aldrich, 99%) solution was prepared with HPLC grade acetonitrile (Caledon, 99%); this was storaged at –10˚C, in darkness condition. One hour before experimentation reference solution was allowed to warm at room temperature. A 5 $mg \cdot L^{-1}$ humic acid (Sigma Aldrich, 98%) solution was prepared using 1×10^{-3} M NaOH. Additional reagents for the mobile phase are methanol (J.T. Baker, 99.9%), phosphoric acid (Sigma Aldrich, 98%), anhydrous monobasic sodium phosphate (Monterrey, 99.5%). Also, considered surfactants in the extraction stage were obtained from Sigma Aldrich, three types were used: a) anionic type: sodium dodecyl sulfate (SDS, 96%), b) cationic type: cetyl trimethyl ammonium bromide (CTAB, 95%); and c) non-ionic ones like octylphenol ethylene oxide condensate (Triton X-100, 99%), tert-octylphenoxypoly (ethoxyethanol) (Triton X-114, laboratory grade), Octylphenol ethoxylate (Triton X-405, 70% in water).

2.2. Soil Characterization

In order to assure that experiments will be run with a clean soil, the sample used in this study was collected at 50 cm depth in a clean site. Soil particle characterization was done following the ASTM-D2487 procedure, while density and texture were determined by the Bouyoucos hydrometer method [18]. Identification of soil mineralogical phases were done with a Siemens D-500 powder diffractometer, which has an X-ray tube, Cu cathode, using a CuKα wavelength of 1.5418 Å and Ni filter; for detection runs it was used 30 KV with 20 mA, the scanning rate was done at 2° min^{-1} [19]. Analytical samples were prepared by mixing soil with deionized Milli-Q water in a proportion of 1:2.5; this samples were used to measure pH and conductivity with a PC 45 conductivity meter coupled to an Orion 710 A instrument provided with a HI203 electrode, which is useful for in-situ soil pH measurements. Organic matter content was determined using the ASTM-D 2974 procedure [20].

2.3. Atrazine Adsorption/Desorption

This study considered preparing a synthetic polluted sample from clean soil (pesticide free), which was spiked with an acetonitrile dissolved atrazine solution. After adsorption, the extraction step was done using different solvents, this with the purpose of establishing which one provides the best characteristics for atrazine recovery and analysis.

Atrazine impregnation (adsorption step) was realized by a batch equilibrium method [22]. The sample is prepared into centrifuge tubes, placing 1 g soil sample which is mixed with atrazine solutions whose concentrations go from 5 - 100 $mg \cdot L^{-1}$, in 10 mL of 0.01 M $CaCl_2$, tubes were stirred for 3 hrs at 25˚C ± 1˚C, centrifugated at 3500 rpm during 30 min, the supernatant was decanted, and atrazine equilibrium concentration is determined.

Later on, for extraction (desorption step), polluted soil sample was added with 3 mL of extractant solution, being either acetonitrile or surfactants (SDS, CTAB, Triton X-100, Triton X-114, Triton X-405), these mixed with Milli-Q water at 1, 2 and 3 times critical micellar concentration (CMC).

Samples of soil plus extractant are placed in an ultrasound bath for 2 h, after doing that, a 1 mL aliquotat was taken and centrifuged at 14,000 rpm for 30 min; then, samples are filtered by a 0.2 mm Iso-Disc™ filters N25-2 (Supelco), this step allowed suspended particle separation. Afterwards, 20 µL of each filtered samples were injected in the CC5-BAS Liquid Chromatographic column coupled with an UV-116 BAS detector.

As a first step chromatographic separation was done by using Carabias *et al.* reported procedure [12], later on conditions were modified up to get the ones reported in this paper which are a mobile phase of CH_3OH: 1 mmol L^{-1} NaH_2PO_4 pH 3.2:CH_3CN (55:30:15), a flow rate of 0.4 $mL \cdot min^{-1}$, analysis performed in an Agilent Eclipse

C_{18} PAH reverse phase column (100 mm × 4.6 mm 3 μm particle size). Spectrophotometric detection was done at a 260 nm wavelength.

Soil adsorbed atrazine (C_s) is calculated from the difference between the initial concentration (C_i) and the equilibrium concentration (C_e). Adsorption isotherms were obtained by plotting the amount of adsorbed atrazine per unit soil weight at equilibrium conditions (C_s, $mg \cdot Kg^{-1}$), against the atrazine equilibrium concentration in solution (C_e, $mg \cdot L^{-1}$). It was considered to fit the experimental data to the linear adsorption isotherm:

$$C_s = K_d C_e \quad (1)$$

where K_d = linear adsorption constant. And to the Freundlich adsorption isotherm, which in linearized form can be expressed as:

$$\log C_s = \log K_F + \frac{1}{n} \log C_e \quad (2)$$

in this equation K_F is Freundlich adsorption constant, while 1/n is a measure of sorption intensity.

3. Results

3.1. Soil Characterization

The results of soil physical characterization, by the Bouyoucus and X-Ray Diffraction methods, are reported in **Table 1**. From these data it can be established that used soil corresponds to a clay-silty soil with high feldspar content.

Table 1. Physical and textural soil properties.

Mineralogical characteristics	
Feldspar	54.8%
Kaolinite	5.1%
Chlorite	8.3%
Carbonate	5.8%
Quartz	21.9%
Textural characteristics	
Sand	29.0%
Clay	45.8%
Silt	23.9%
pH	8.6
C. E.[a]	0.334 S m^{-1}
O. M.[b]	2.6%

a. Electrical conductivity; b. Organic matter.

3.2. Detection Method Calibration

In order to assess the precision of atrazine detection by HPLC technique, it was necessary to get the calibration curve, then a set of atrazine solutions, from 0.5 to 40 $mg \cdot L^{-1}$, was prepared using acetonitrile as a solvent. In this concentration range it was possible to get a 0.999 correlation coefficient for atrazine detection.

3.3. Atrazine Adsorption onto Soil

Experimental approach considered batch experiments as described in the methodology section. Considered concentrations were from 5 to 100 $mg \cdot L^{-1}$ of atrazine, results allowed to calculate C_e and C_s values which are plotted in **Figure 1**.

From the **Figure 1** it becomes evident that adsorption process is not a linear one, then experimental data was fitted to the linearized form of Freundlich isotherm, after doing the data conversion to get a log-log plot, and applying a linear regression the following data were obtained: a correlation coefficient of 0.994, 1/n = 0.718, K_f = 1. At this stage, it was determined that maximum atrazine adsorbed concentration corresponds to 8 mg g^{-1}, which it is in the range of 5 - 10 $mg \cdot g^{-1}$, values reported in published works [22,23].

In order to get the best chromatographic conditions to detect atrazine in obtained soil extracts, it was used HPLC grade acetonitrile as solvent.

In **Figure 2(a)** it is observed that the humic acid chromatogram presents an elution time of 1.9 min; while the one for the unpolluted soil-acetonitrile extract, **Figure 2(b)**, exhibits a signal at the same time, then this peak was assigned to the organic matter in soil. Although,

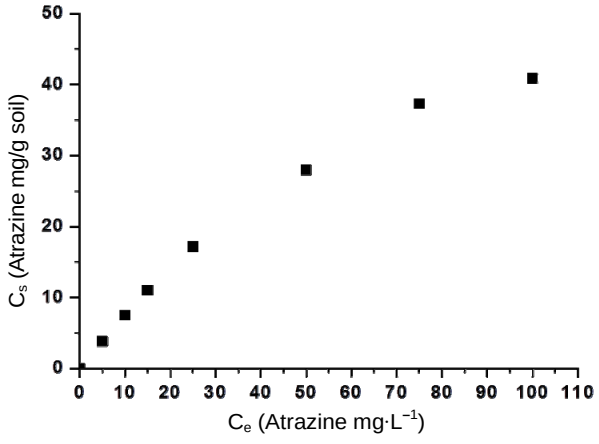


Figure 1. Results of equilibrium adsorbed atrazine per unit soil weight (C_s, $mg \cdot Kg^{-1}$) against liquid equilibrium atrazine (C_e, $mg \cdot L^{-1}$), all batch adsorption experiments used 1 g clean soil sample [22].

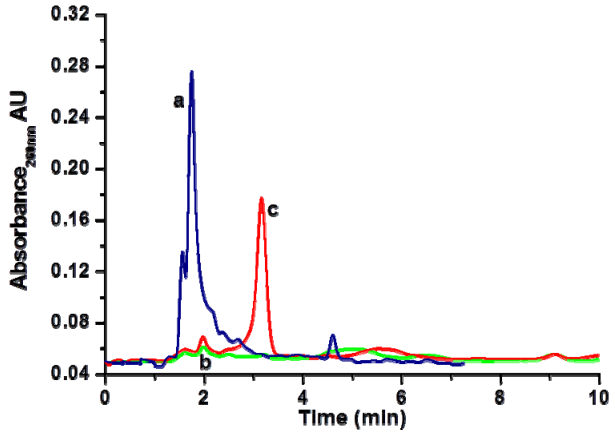


Figure 2. Chromatograms for extracts obtained from: (a) 5 mg·L^{-1} humic acid/CH_3CN; (b) 1.0 g clean soil/ CH_3CN; (c) 1.0 g soil previously contaminated with 10 mg·L^{-1} atrazine/CH_3CN, and experimental detection conditions: flow rate: 0.4 ml·min^{-1}, λ = 260 nm, agilent eclipse C_{18}PAH column. Mobile phase CH_3OH/1 × 10^{-3}, phosphate buffer, pH 3.2/CH_3CN 60:30:10 (v/v).

when atrazine is present in soil, **Figure 2(c)**, it is observed a slight increase of the signal for the same position; this phenomena can be attributed to the intermolecular bonds between organic matter and atrazine, so the last one enhances organic matter desorption, atrazine is eluted at 3.1 min. In **Table 2** it is shown the surfactant used for this study and the aqueous applied concentrations for atrazine desorption from soil. In the table are explicit those values of the Critical Micellar Concentration (CMC) equivalent to the 1 CMC, 2 CMC and 3 CMC.

A first approach to determine atrazine desorption by chromatographic analysis, was intended with the first 3 surfactants (SDS, CTAB, Tritón X-114), experimental conditions were those reported by Carabias *et al.* [12], results are shown in **Figure 3**.

As it can be observed in **Figures 3(b)** and **(c)**, obtained results with SDS and CTAB at CMC are quite imprecise, it is considered that the obtained signal is inadequate since the organic matter was eluted a very short times together with the atrazine; also, SDS and CTAB absorbance peaks exhibit a wide signal masking onto the required ones for organic matter and atrazine. An opposite behavior is observed when the used surfactant is non- ionic as Triton X-114, **Figure 3(a)**, for this one it is observed that the organic matter elutes at 3.1 min, while the one for atrazine appears at 4.1 min; but as it can be observed the signal for organic matter is broad and exhibits 2 peaks, phenomena which can be accounted such as a bad chromatographic separation.

Therefore, in order to improve the chromatographic separation, the next set of experiments considered to increase surfactant concentrations up to 2 and 3 times the CMC (results are not shown), for these it was observed that the complex signal prevails, additionally it happens that the absorbance peak increases as surfactant does it.

Table 2. Surfactants employed for atrazine desorption in aqueous media.

Surfactant	CMC (M)	2 CMC (M)	3 CMC (M)
SDS	8.1×10^{-3}	1.6×10^{-2}	0.0243
CTAB	9.2×10^{-4}	1.8×10^{-3}	0.00276
Triton X-100	2.5×10^{-4}	5.0×10^{-4}	0.00075
Triton X-114	3.5×10^{-4}	-----	------
Triton X-405	8.1×10^{-4}	-----	------

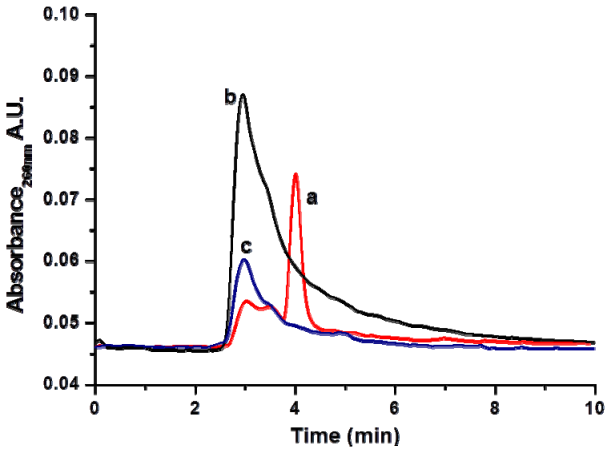


Figure 3. Chromatograms of 1.0 g of soil contaminated with an aqueous solution of 10 mg·L^{-1} atrazine, in its extraction it was used (a) Triton X-114, (b) SDS and (c) CTAB, all at CMC. Flow rate: 1.0 mL·min^{-1}, λ = 260 nm, in an agilent eclipse C_{18} PAH column. Mobile phase CH_3OH/ 1 × 10^{-3} phosphate buffer, pH 2.6/CH_3CN 60:30:10 (v/v).

These behaviors could indicate that there is a molecular interaction between soil and extractant. Desorption was estimated from the area under each peak, results are presented in **Table 3**, in which it is reported the surfactant, the concentration used and the attained desorption expressed in percentage.

It can be observed that a 100% desorption is estimated for Triton X-114 at 3 CMC (1.05×10^{-3} M). Also, 98% desorption is obtained with a 3 CMC (2.43×10^{-2} M) SDS, finally, 57% desorption is obtained with a 3CMC (2.76×10^{-3} M) CTAB. Although, again these values are not trustable because the poor chromatographic separation of the peaks, that is why it was decided to modify detection conditions. Optimized detection conditions correspond to: a mobile phase of methanol/1 × 10^{-3} M phosphate buffer, pH 3.2/acetonitrile, a volume relationship of 55:30:15.

Table 3. Atrazine desorption percentage for the different surfactants.

Surfactant		Desorption percentage
Triton X-114	CMC	96
	2 CMC	97
	3 CMC	100
SDS	CMC	91
	2 CMC	96
	3 CMC	98
CTAB	CMC	42
	2 CMC	55
	3 CMC	57

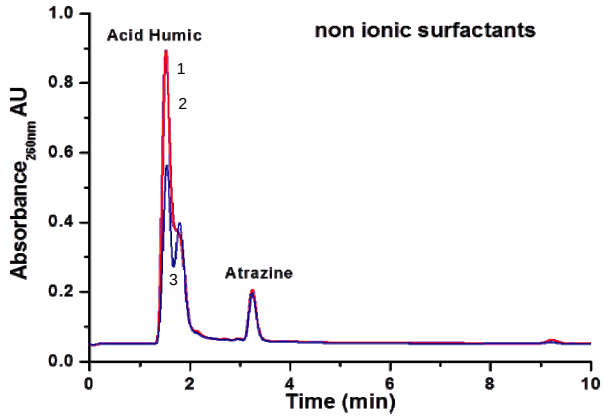
A new evaluation of atrazine desorption was done including three non-ionic surfactants from the octylphenol etholxilate group being: 1) Triton X-114; 2) Triton X-100; and 3) Triton X-405; also the anionic 4) SDS, and the cationic 5) CTAB; all of them were tried at the CMC, under the optimized conditions. Results are shown in **Figure 4(a)** for non-ionic surfactants, and in **Figure 4(b)** for the anionic and cationic surfactants.

In **Figure 4(a)** can be observed that extraction with the non-ionic surfactants allowed for organic matter signal occur at 1.7 min, and the one for atrazine at 3.2 min, both with well defined peaks, then it becomes evident that non-ionic surfactants allowed to realize atrazine extraction from soil. Obtained desorption percentage with Triton X-114 is 98.5%, Triton X-100 is 86.5%; and with Triton X-405 is 89.5%. Even though atrazine signal is similar for the three surfactants, it happens that Triton X-100 affects the organic matter signal; then, this surfactant should be discarded.

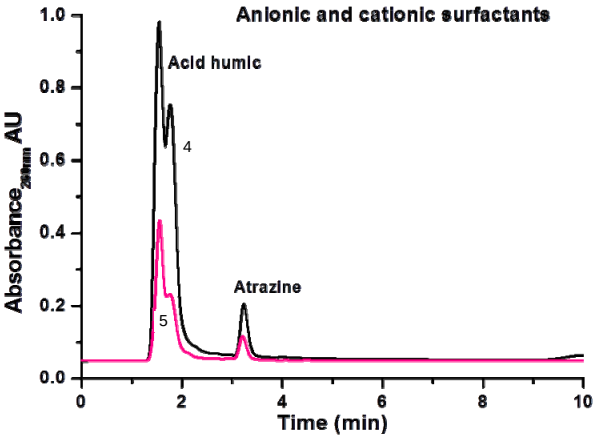
In **Figure 4(b)** are presented the chromatograms for the anionic surfactant (iv) SDS and the cationic one (v) CTAB, it can be observed that for both the organic matter signal elutes at 1.7 min, and atrazine at 3.1 min. Desorption of atrazine with SDS amounts 98% and with CTAB is only 54%. It is important to remark that, even though the CTAB allowed a chromatographic separation with clear peaks for the organic matter and atrazine the obtained desorption was very low, phenomena which can be attributed to a strong interaction between the hydrophobic part of CTAB with the laminar clay structures, as a result atrazine desorption is diminished.

4. Conclusions

It was possible to optimize the condition for detection and chromatographic separation of organic matter and atrazine by HPLC-UV, from a clay-silty soil matrix. Soil extracted atrazine determination and quantification was



(a)



(b)

Figure 4. Chromatograms of extraction from 1.0 g clean soil contaminated with 10 mg·L^{-1} atrazine by using 3 mL of aqueous extractant solution at CMC. (a) non ionic extraction: (1) X-114, (2) Triton X-100 and (3) TritonX-405; (b) ionic extraction: (4) anionic SDS, (5) cationic CTAB at CMC. Flow rate: 0.4 ml/min., λ = 260 nm, agilent eclipse C_{18} PAH column. Mobile phase CH_3OH/1 × 10^{-3} M. Phosphate buffer, pH 3.2/CH_3CN 55:30:15 (v/v).

extracted atrazine determination and quantification was done in aqueous samples containing surfactants, using a methanol mobile phase/1 × 10^{-3} M, phosphate buffer pH = 3.2/acetonitrile.

From desorption results it can be affirmed that use of non-ionic surfactant Triton X-114 favors desorption and extraction of atrazine from soil, being possible to attain up to 98.5% recovery; also, this surfactant is the one with lower affinity for soil organic matter, fact which provides an advantage in respect to the other surfactants applied in this study. One of the main advantages of this experimental approach is that samples are prepared and analyzed in a simpler way, since it is not required special conditions for extraction, cleaning or additional treat-

ments in order to determine atrazine in soil, which it can be a good option for extracting organic compounds.

5. Acknowledgements

Author Rossy Feria is very thankful to CONACyT in México, for sponsoring the post-doctoral fellowship under which this work has been.

6. References

[1] C. de Plaguicidas, "Comisión Intersecretarial para el Control del Proceso y Uso de Plaguicidas, Fertilizantes y Sustancias Toxicas," CICOPLAFEST, México, 2004. www.cofepris.gob.mx.

[2] S. Cohen, S. Creager, R. Carsel and C. Enfield, "Potential Pesticide Contamination of Ground Water from Agriculture Uses in Treatment and Disposal of Pesticide Waste," Ameican Chemical Society, Washington DC, 1984, pp. 297-325.

[3] L. L. Mc-Cormick and A. E. Hiltbold, "Microbiological Decomposition of Atrazine and Diuron in Soil," *Weeds*, Vol. 14, No. 1-2, 1966, pp. 77-82. doi:10.2307/4041129

[4] D. E. Armstrong, G. Chesters and R. F. Harris, "Atrazine Hydrolysis in Soil," Soil Science Society of America, Vol. 31, 1967, pp. 61-66. doi:10.2136/sssaj1967.03615995003100010019x

[5] D. D. Kaufman and P. C. Kearney, "Microbial Degradation of S-triazine Herbicides Residues," *Reviews*, Vol. 32, No. 2, 1970, pp. 235-266.

[6] R. Frank and R. G. Sirons, "Dissipation of Atrazine Residues from Soil," *Bulletin of Environmental Contamination and Toxicology*, Vol. 34, 1985, pp. 541-548. doi:10.1007/BF01609773

[7] P. Howard, "Handbook of Environmental Fate and Exposure Data for Organic Chemicals," *Pesticides*, Lewis Publishers, Chelsea, Vol. 3, 1991, pp. 345-360.

[8] D. R. Nair, J. G Burken, L. A. Licht and J. L. Schnoor, "Mineralization and Uptake of Triazine Pesticide in Soil-Plant Systems," *Journal Environmental Engineering*, Vol. 119, No. 5, 1993, pp. 842-854. doi:10.1061/(ASCE)0733-9372(1993)119:5(842)

[9] J. W. Munch, USEPA Method 508.1, "Determination of Chlorinated Pesticides Herbicides and Organ Halides by Liquid-Solid Extraction and Electron Capture Gas Chromatography," 1995. www.caslab.com/EPA-Methods/pdf/508_1.pdf

[10] N. C. Van de Marbel, J. J. Hageman and U. A. Th. Brinkman, "Membrane-Based Sample Preparation for Chromatography," *Journal of Chromatography*, Vol. 634, 1993, pp.1-29. doi:10.1016/0021-9673(93)80308-U

[11] M. E. Fernández Laespada, J. L. Pérez Pavón and B. Moreno Cordero, "Continuous Membrane Extraction Coupled with Chromatographic Analysis for the Determination of Phenols in Fuels," *Journal Chromatography*, Vol. 823, No. 1-2, 1998, pp. 537-548. doi:10.1016/S0021-9673(98)00297-0

[12] R. Carabias-Martínez, E. Rodríguez-Gonzalo, P. H. Paniagua-Marcos and J. Hernández-Méndez, "Analysis of Pesticide Pesidues in Matrices with High Lipid Contents by Membrane Separation Coupled On-Line to a High-Performance Liquid Chromatography System," *Journal of Chromatography A*, Vol. 869, No. 1-2, 2000, pp. 427-439. doi:10.1016/S0021-9673(99)01218-2

[13] M. C. Hennion, C. Cau-Dit-Coumes and V. Pichon, "Trace Analysis of Polar Organic Pollutants in Aqueous Samples Tools for the Rapid Prediction and Optimisation of the Solid-Phase Extraction Parameters," *Journal of Chromatography A*, Vol. 823, 1998, pp. 147-161. doi:10.1016/S0021-9673(98)00479-8

[14] E. R. Brouwer, S. Kofman and U. A. Th. Brinkman, "Selected Procedures for the Monitoring of Polar Pesticides and Related Microcontaminants in Aquatic Samples," *Journal of Chromatography A*, Vol. 703, 1995, pp. 167-190. doi:10.1016/0021-9673(94)01237-9

[15] R. Carabias Martínez, E. Rodríguez Gonzalo, B. Moreno Cordero, J. L. Pérez Pavón, C. García Pinto and E. Fernández Laespada, "Surfactants Cloud Point Extraction and Preconcentration of Organic Compounds Prior to Chromatography and Capillary Electrophoresis," *Journal of Chromatography A*, Vol. 902, No. 1, 2000, pp. 251-265. doi:10.1016/S0021-9673(00)00837-2

[16] R. P. Frankewich and W. L. Hinze, "Optimization of Solid-Phase Microextraction Conditions for Determination of Phenols," *Analytical Chemistry*, Vol. 66, 1994, pp. 160-167. doi:10.1021/ac00073a027

[17] G. Stangl, R. Niessner and J. Albaiges, "Micellar Extraction—A New Step for Enrichment in the Analysis of Napropamide," *International Journal Environmental Analytical Chemistry*, Vol. 58, No. 1-4, 1995, pp. 15-22. doi:10.1080/03067319508033108

[18] G. J. Bouyoucos, "Directions for Making Mechanical Analysis of Soils by the Hydrometer Method," *Soil Science*, Vol. 42, 1936, pp. 225-229. doi:10.1097/00010694-193609000-00007

[19] R. L. Snyder and D. L. Bish, "Quantitative Analysis," In: D. L. Bish and J. E. Post, Eds., *Modern Powder Diffraction, Mineralogical Society of America Reviews in Mineralogy*, Vol. 20, 1989, pp. 101-144.

[20] ASTMD-2974, "Standard Methods for Moisture, Ash, and Organic Matter of Peat and Organic Soils," *Soil and Rock* (I), 2011.

[21] OECD Guidelines for the Testing of Chemicals Adsorption/Desorption, Using a Batch Equilibrium Method, 2000. www.oecd.org/dataoecd/9/11/33663321.pdf

[22] M. M., Socias Viciana, M. Fernández Pérez, M. Villafranca Sánchez, E. González Pradas and F. Flores Céspedes, "Sorption and Leaching of Atrazine and MCPA in Natural and Peat Amended Calcareous Soils from Spain," *Journal of Agricultural and Food Chemistry*, Vol. 47, No. 3, 1999, pp. 1236-1241. doi:10.1021/jf980799m

[23] Y. Coquet, "Variation of Pesticides Sorption Isotherm in Soil at the Catchment Scale," *Pest Management Science*, Vol. 58, 2002, pp. 69-78.

