Comparison of the use of Activated Charcoal and C18 for Extracting Pesticide Residues from River Mada, Nasarawa State, Nigeria

Matthew, Motolani O., Eneji, Ishaq S., Ombugus, William M., and Ofeogbu, Obinna.

Joseph Sarwuan Tarka University, Makurdi, Benue State, Nigeria.

DOI: https://doi.org/10.51584/IJRIAS.2023.8902

Received: 26 July 2023; Accepted: 29 August 2023; Published: 28 September 2023

ABSTRACT

This study aimed to compare the efficiency of C18 and Activated Charcoal (AC) for extracting pesticide residues (glyphosate, butachlor, lambda-cyhalothrin, and paraquat dichloride) from river Mada in Nigeria during the rainy and dry seasons. Solid phase columns were packed with 0.1 g of each adsorbent material, and water samples were taken from five different points along the river during each season. Pesticide residues were extracted using the two adsorbents, and elution was done using n-hexane, acetonitrile, and acetone. The eluents were analyzed using UV-visible spectrometry. Glyphosate levels were found to be significantly higher (at $P<0.05$) during the rainy season than in the dry season for C18 with a residue level of 89.9 ppb and 51.8 ppb respectively. AC extractions followed the same pattern with 73.2 ppb during the rainy season and 26.6 ppb during the dry season. AC extractions for butachlor and lambda-cyhalothrin were higher for the dry season with residue concentrations of 250 ppb and 64.4 ppb respectively. Paraquat dichloride was only found with the C18 adsorbent during the dry season with a concentration of 25.8 ppb. The result showed that adsorbent efficiency was pesticide-dependent and that C18 performed better in most cases except for dry season lambda-cyhalothrin and butachlor. The study also found that the pseudo-control (water sample from a township stream) had significantly lower pesticide residue concentrations than the river Mada samples. It can be concluded that River Mada exhibits pesticide residue contamination, with C18 showing greater adsorption than AC but AC's affordability allows interchangeability with C18. Further study is needed on pesticide bio-concentration in river organisms and enhancing AC's pesticide adsorption. The treatment plant should adopt comprehensive purification before supplying Mada River water to Nasarawa state for improved health care.

Keywords: Activated charcoal, C18, solid phase extraction, pesticide residues, river water sample.

INTRODUCTION

When pesticides are applied, only a part of it falls exactly on the target and becomes degraded to harmless compounds, the rest drifts into the environment or gets accumulated along the food chain. Through various fate processes, the residue of pesticides has been found in surface water (Pereira and Hostettler, 1993; Thurman *et al.*, 2000). Degradation of water quality by pesticide residues has two principal human health impacts. The first is the consumption of fish and shellfish that are contaminated by pesticides. The second is the direct consumption of pesticide-contaminated water (Glaser, 2006).

In developing countries like Nigeria, India, Cameron, etc., effective curtailing in the trade of these harmful pesticides has not been achieved; instead, their use for agricultural purposes is on the increase (Racke*et al.*, 1997, Mazlan, *et al*., 2017).

Water is one of the primary pathways by which pesticides are transported from their application area to other parts of the environment (Majewski and Capel, 1995). When pesticides are applied on fields, gardens,

ISSN No. 2454-6194 | DOI: 10.51584/IJRIAS |Volume VIII Issue IX September 2023

parks, and other places, a percentage of the chemicals end up as runoff. This runoff moves into streams, rivers, and lakes. Similarly, when pesticides are applied on lawns and gardens in urban and suburban areas, rain washes some of the pesticides into street gutters, where the pesticide-contaminated water goes through drains and pipes and eventually flows into nearby streams and rivers. Some of the pesticides also end up in groundwater systems by leaching down through the soil (Gabriel *et al*., 2018). Small amounts also volatilize into the atmosphere, and then later falls back to land as precipitation (Pimentel, 1995). As a result of all these pathways, pesticides are widely found in rivers, streams, lakes, and even in drinking water.

In the Solid Phase Extraction procedure, the choice of the appropriate sorbent is a critical factor to obtaining a full recovery. Activated carbon (AC) is an old sorbent, likewise, C18 and they have been extensively used for pre-concentration and sample clean-ups. Sometimes it is necessary to consider the cost of adsorbent in addition to its analytical performance; this is of great importance especially when cheaper sorbent does the job with satisfactory analytical performance. This necessitates performing comparative studies among these sorbents and then deciding which sorbent is the cheapest with appropriate analytical performance. There are very few comparative studies in literature among various sorbents. For example, Zhou *et al*. (2006) conducted a comparison of the enrichment efficiency among MWCNTs, AC, and C18 silica as sorbents for SPE of Atrazine and Simazine in environmental waters. However, they did not specify the type, surface properties, and textural characteristics of the AC used in their study (Zhou *et al*., 2006). They proposed that AC did not give the expected extraction efficiency because of its large size, blank volum,e and less active sites for adsorption.

It is crucial to assess the level of pesticide residues in River Mada. This is because extensive farming activities are taking place along the length of the river, which may constitute run-offs of pesticides to the river. By examining the residual levels of pesticides in the river, appropriate actions can be taken to ensure the safety of the water and the surrounding ecosystem. The river supplies drinking water through the Mada Water Works to Akwanga, Keffi, and Kokona Local Government Areas of the State with a population of 172,800, 142,900, and 167,600 respectively (HTTP, Nasarawa State population) and several villagers drink directly from it also. The objective of this study is to determine the more efficient sorbent between C18 and Activated Charcoal for the extraction of the residues of some pesticides commonly used for agricultural purposes in River Mada during the rainy season and dry season.

MATERIALS AND METHODS

Study Area

River Mada is about 14 kilometres long, occupying Latitude 7^{o} 58? 00? N and Longitude 7^{o} 55? 00? E. The sun rises from the East at 06.22 hours and sets in the West at 18.06 hours local time. The river originates from Kaduna State, passes through Akwanga West Local Government Area of Nasarawa State, and empties its contents into River Niger. The river is at an elevation of 51 meters above sea level. The physical features of the river areas are rocky and undulating highlands of average heights. The climate of the area is quite pleasant with a maximum temperature of 35^{o}C and a minimum temperature of 10^{o}C. The climate is characterized by two distinct seasons: dry and rainy seasons. The dry season span from October to March, while the rainy season spans from April to September. The Mada and Eggon people, who are the predominant occupants of the Akwanga West LGA of Nasarawa State are mostly farmers, cultivating crops like Maize, Guinea corn, Millet, Soybeans, Cowpea, and Rice. They also rear animals like Cattle, Goats, poultry, pigs, and a few of the people are engaged in fishing. The total land area occupied by the Mada people is estimated as 235 square miles and has a population of over 100,000 (Mada Reference Ethnology, 2013).

Survey

The study area was surveyed to determine the type of pesticides mostly used for farming activities.

ISSN No. 2454-6194 | DOI: 10.51584/IJRIAS |Volume VIII Issue IX September 2023

Butachlor, glyphosate, lambda-cyhalothrin, and paraquat dichloride were mentioned by the farmers. Pesticide vendors also mentioned these pesticides. Hence, these are the pesticides investigated in this study.

Chemicals and Reagents

Analytical-grade chemicals and reagents including n-hexane, acetonitrile, and acetone were utilized in this study. C18 silica was procured from Alltech Associate Incorporated, while untreated granular activated charcoal (20-60 mesh) was obtained from Sigma. Distilled water was sourced from the Chemistry Department of the University of Agriculture in Makurdi, Benue State. To prepare standard solutions for calibration curves, four commonly used pesticides in the study area (41% Glyphosate, 50% Butachlor by Jubaili AGROTEC, 276G, Paraquat dichloride with 200G of paraquat ion by Naijing Red Sun Biochemistry Co. Limited, China, and 2.5% EC Lambda-cyhalothrin by Jubaili AGROTEC) were procured from Akwanga LGA due to the unavailability of pure samples. UV analysis was conducted using the Mini Sipper Compatible Ultraviolet Spectrometer by He?ioS ?.

Sample Collection

To conduct pesticide residue analyses, five different points along the length of the river Mada, separated by approximately 2 kilometres were sampled. Sampling was carried out during two different seasons: during the rainy season samples were taken in May, while in the Dry season samples were taken in November of the same year. These corresponded to the beginning and ending of planting seasons respectively. At each of the five sampling points, one litre of water was collected from the turbulent midstream position of the river. Additionally, a control sample (Pseudo control) was obtained by collecting one litre of water from a stream located within Akwanga town.

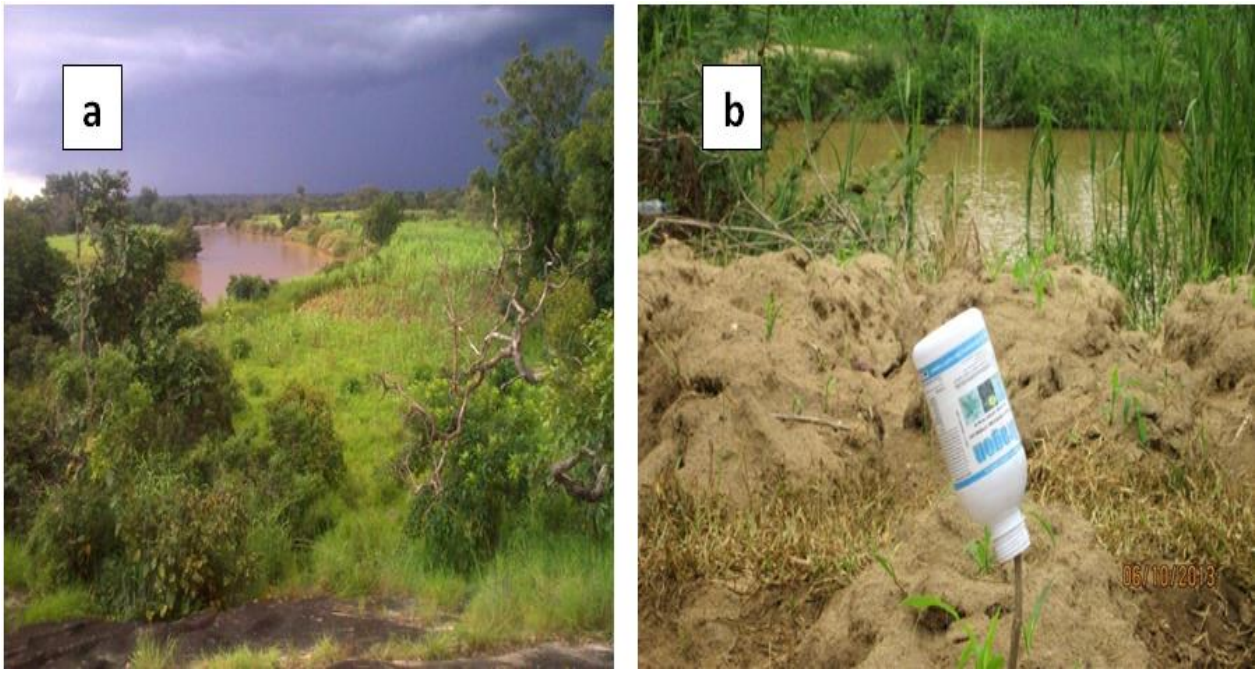

Plate 1: a). Maize farm along the length of the river. b). a pesticide bottle hanging on a stick after the content has been applied on the farm next to the river.

Sample Extraction

To prepare an Activated Charcoal (AC) packed column, an empty 10mL borosilicate SPE column was filled with 0.10g of adsorbent. Glass wool with a 20µm porosity, obtained from Supelco, was used to hold the

ISSN No. 2454-6194 | DOI: 10.51584/IJRIAS |Volume VIII Issue IX September 2023

adsorbent at the bottom and top of the column. The glass wool was pre-conditioned with 5mL of distilled water before the concentration procedure. The river Mada sample was passed through the column using a Knf Lab suction pump, with a flow rate of 20mL/min-1 of the water sample (Sandstrom, 2001). After passing 1.0 L of the River Mada samples through the column, the cartridge was eluted with 5mL of n-hexane, followed by acetonitrile and then acetone, in that order. Each eluting solvent was allowed to soak the packed column material for 5 minutes before flowing through (Schmidt *et al*., 1993). This process of passing 1.0 L of the River Mada sample through the column and eluting with the three different solvents was repeated for each of the rainy season and dry season samples using a C18 packed column.

Ultra-violet Spectrometer analysis

Stock solutions were prepared from the four pesticides selected which were commonly used in the study area. They were glyphosate, butachlor, lambda-cyhalothrin and paraquatdichloride.

From these, various concentrations in parts per billion (ppb) were prepared by appropriate dilution of the stock solutions. These were analyzed using the UV Visible Spectrophotometer to develop a calibration curve for each of the pesticides. The calibration curve was a plot of the concentration of each pesticide versus its absorbance.

Once the pesticide residues were extracted from the river samples using the mobile phase solvents, 2.0 millilitres of eluent for each solvent were added to a cuvette and then placed in a UV spectrometer. A blank of each solvent was used sequentially for each of the pesticide residues eluted by them. The UV spectrometer was set to a wavelength range of 190nm to 450nm, which covers the range displayed by UV for developing calibration curves for the four pesticides.

For each sample, the wavelength from the stock solutions earlier used to prepare the calibration curves was tracked to identify the types of pesticide residues present in each river sample. The absorbance from the sample eluents at these wavelengths of interest were then compared on the calibration curve to determine the concentration of the pesticide residue in each of them.

The total concentration of each pesticide residue extracted by each of the solvents was summed to obtain the total concentration extracted from the river sample. The statistical analysis for all the data collected for the pesticide residues was done using the general linear model of S.A.S (S.A.S, 1995). The differences between the means were separated using the Duncan Multiple Range Test.

Spike recovery

The spike recovery analyses were performed by passing a known concentration of each of the four pesticide solutions through C18 and AC-packed columns. The eluted concentrations were then analyzed using a UV-visible spectrophotometer in the same manner as the river samples. The eluting solvents used were n-hexane, acetonitrile, and acetone in that order.

RESULTS AND DISCUSSION

The results obtained for the different adsorbent materials for the rainy season and dry seasons are presented in Tables 1 and 2. The comparison of the mean concentration of each of the pesticides in the rainy and dry seasons is presentedin Figure 1.

Table 1: Mean Concentration of C18 Extractions for Rainy and Dry Seasons

Pesticide	Rainy Season(ppb)	Dry Season (ppb)
Glyphosate	89.8	73.2

ISSN No. 2454-6194 | DOI: 10.51584/IJRIAS |Volume VIII Issue IX September 2023

Butachlor	261.6	214.0
Lambda Cyhalothrin	27.0	Nil
Paraquat dichloride	Nil	25.8

Table 2: Mean Concentration of AC Extractions for Rainy and Dry Seasons

Pesticide	Rainy Season(ppb)	Dry Season (ppb)
Glyphosate	51.8	26.6
Butachlor	220.0	250.0
Lambda Cyhalothrin	16.0	64.4
Paraquat dichloride	Nil	Nil

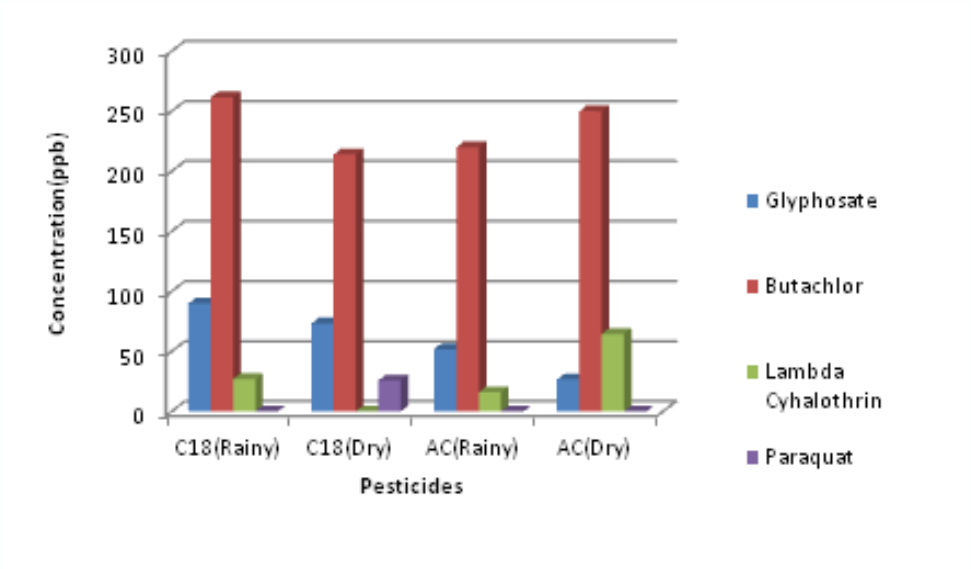

Figure 1: Comparison of C18 and AC extractions. Butachlor concentration was highest in the river sample for both C18 and AC adsorbents followed by glyphosate levels. Levels of lambda-cyhalothrin and paraquat dichloride were higher during the dry season extractions.

Table 3: Statistical differences between Rainy season, Dry season, and Control samples for the four pesticides.

Pesticides	C18 (Rainy) (ppb)	C18 (Dry) (ppb)	AC (Rainy) (ppb)	AC (Dry) (ppb)	Control (C18) (ppb)	Control (AC) (ppb)
Glyphosate	89.8^{a}	73.2^{b}	51.8^{c}	26.5^{e}	0.0^{f}	48.2^{d}
Butachlor	261.6^{a}	214.0^{d}	220.0^{b}	250.0^{c}	0.0^{e}	0.0^{e}
Lambda cyhalothrin	27.0^{b}	0.0^{d}	16.0^{c}	64.4^{a}	0.0^{d}	0.0^{d}
Paraquat dichloride	0.0^{b}	25.8^{a}	0.0^{b}	0.0^{b}	0.0^{b}	0.0^{b}

ISSN No. 2454-6194 | DOI: 10.51584/IJRIAS |Volume VIII Issue IX September 2023

a, b, c, d, e, and f on the same row means they differ significantly in that order (at $p<0.05$), 'a' being the highest and 'f' is the lowest. The same letter superscript means no statistical difference.

Table 4: Spike recovery analyses result

Pesticide	Adsorbent	n-hexane	Acetonitrile	Acetone
Glyphosate	C18	–	55	56
	AC	–	108	50
Butachlor	C18	33	35	–
	AC	33	93	–
Lambda-cyhalothrin	C18	35	–	74
	AC	46	–	54
Paraquat dichloride	C18	–	63	109
	AC	–	56	118

C18 extractions for glyphosate for both rainy and dry seasons were found to be statistically (at $P<0.05$) higher than the AC extractions for the seasons (Table 1,2, and Figure 1). These results can be explained by an earlier report that AC is a poor sorbent for organophosphate pesticides (LeDoux, 2011), hence the higher extraction obtained for C18.

C18 extractions for butachlor for the rainy season were statistically higher (at $P<0.05$) than the AC extractions. However, the C18 extractions for the dry season were found to be statistically lower (at $P< 0.05$) than the AC extractions. Butachlor is a relatively non-polar compound, hence, its attraction to more non-polar packing of C18. The disparity between the extracted concentrations by the sorbents might be random, but AC has also been found to be a good sorbent for other pesticides apart from organophosphates (LeDoux, 2010).

The concentration of paraquat dichloride residue was 25.8 ppb for C18 extraction and 0.00 ppb for that of activated charcoal. This study indicates that C18 is a better sorbent for Paraquat dichloride. C18 has been reported as a more efficient adsorbent than AC (El-Sheikh *et al*., 2008), and was able to adsorb the concentration obtained here, while AC did not.

Lambda-cyhalothrin was 27.0 ppb for C18 extractions for the rainy season and nil for the dry season, while AC extraction for the rainy season was 16.0 ppb and 64.4 ppb for the dry season. AC extraction was statistically (at $P<0.05$) higher for lambda-cyhalothrin than for C18 extraction.

Therefore, these results suggest that C18 extractions were better for two of the pesticides considered (glyphosate and paraquat dichloride), not distinctly for one (butachlor), and less for lambda-cyhalothrin. Spike Recovery results showed slightly higher recovery from AC than C18 (Table 3), favoring AC as an alternative for C18 (El-Sheikh *et al*., 2008). El-Sheikh's study contradicts the study conducted by Zhou *et al* ., 2006, which showed that C18 adsorbent was more effective than that of AC. However, due to the cost of AC, which is cheap, it can still be considered as the solid phase material for the extraction of pesticides from water samples. A higher mass of AC column material can be employed to achieve the same result as that of C18 (El-Sheikh *et al*., 2008).

CONCLUSION

River Mada exhibits pesticide residues. The comparison of the pesticide residue adsorption showed that C18 adsorbed higher residues than Activated Charcoal (AC). However, AC could be used interchangeably because of its cost-effectiveness. Higher pesticide concentrations detected during the rainy season when intensive farming activities took place suggest that pesticide contamination was from agricultural activities. It is recommended that farmers should seek alternative means of weed control such as the use of biopesticides or manual means of removal. Continuous use of pesticides without checks can result in a high health hazard for many people. Further studies on the bioaccumulation of these pesticides and deposits on river sediments are recommended.

REFERENCES

1. Antoniou, M. (2012). Teratogenic Effects of Glyphosate-Based Herbicides: Divergence of Regulatory Decisions from Scientific Evidence. *Journal of Environmental and Analytical Toxicology* S4:006. doi:10.4172/2161-0525.S4-006.
2. El-Sheikh, A. H., Sweileh, J. A., Al-Degs, Y. S., Insisi, A. A., and Al-Rabady, N. (2008). Critical evaluation and comparison of enrichment efficiency of multi-walled carbon nanotubes, C18 silica and activated carbon towards some pesticides from environmental waters. *Talanta*, 74(5): 1675-1680. ISSN 0039-9140, https:// doi.org/ 10.1016/j.talanta.2007.09.005.
3. Food and Agriculture Organization (2003). Pesticide residues in food. Agriculture and Consumer Protection, FAO Corporate Document Repository. www.fao.org/AG/AGP/AGPP/Pesticid/
4. Gabriel Pérez-Lucas, Nuria Vela, Abderrazak El Aatik. and Simón Navarro. (2018). Environmental Risk of Groundwater Pollution by Pesticide Leaching through the Soil Profile, Pesticides – Use and Misuse and Their Impact in the Environment, Marcelo Larramendy and Sonia Soloneski, Intech Open, DOI: 10.5772/ intechopen.82418.
5. Glaser, A. (2006). Threatened Waters: Turning the tide on pesticide contamination. [http://www. beyondpesticides.org /pesticidefreelawns/ resources/DWDangers_Pesticides_Wildlife.pdf] (Accessed 20/01/14).
6. Koivunen, M. E., Gee S. J., Park, E. K., Lee, K., Schenker, M. B. and Hammock, B. D. (2005). Application of an Enzyme-Linked Immunosorbent Assay for the Analysis of paraquat residues in milk, beef, and potatoes. *Analytical Chemistry* 58: pp1866-1873.
7. LeDoux M. (2011). Analytical methods applied to the determination of pesticide residues in foods of animal origin. A review of the past two decades. *Journal of chromatography*. A. 1218(8):1021-1036. DOI: 10.1016/j. chroma. 2010.12.097. PMID: 21236435.
8. Mada reference Ethnology, 17th edition (2013). 1993 Census.
9. Majewski, M.S. and Capel, P.D. (1995). Pesticides in the atmosphere-distribution, trends, and governing factors, Ann Arbor Press, Inc., Chelsea, Mich., P. 228.
10. Mazlan, N., Ahmed, M., I.; Muharam, F. M. and Alam, A. (2017). Status of persistent organic pesticide residues in water and food and their effects on environment and farmers: a comprehensive review in Nigeria. *Semina: Ciências Agrárias, Londrina,* 38(3): 2221-2236. DOI: 10.5433/1679-0359.2017v38n4p2221.
11. Nasarawa State population (2022). (https://www.citypopulation.de/en/nigeria/admin/NGA026_na sara wa/)
12. Pereira, W.E. and F.D. Hostettler (1993). Non-point source contamination of the Mississippi River and its tributaries by herbicides. *Environmental Science Technology,* 27: 1542- 1552.
13. Pimentel, D. (1995). Amounts of pesticides reaching target pests: Environmental impacts and ethics. *Journal of Agricultural Environmental Ethics,* 8**:**17–29. https://doi.org/10.1007/BF02286399.
14. Racke, K. D., Skidmore, M.W., Hamilton, D.J., Unsworth, J.B., Miyamoto, J. and Cohen, S.Z. (1997). Pesticides fate in the tropic soils (technical report). *Pure and Applied Chem*. 69:1349-1371.

15. Sandstrom, M. W. (2001). Methods of analysis by the US Geological Survey National Water-Quality Laboratory. Determination of Moderate-use Pesticides and Selected Degradates in Water by C-18 Solid Phase Extraction and Gas Chromatography/ Mass Spectrometry. Vol 4098(1): 70pp.
16. S. A. S. (1995). General Linear Model of S.A.S. https://pages.stat.wisc.edu/~yandell/software /sas/ linmod. html# anova
17. Schmidt, L., Sun, J. J., and Fritz, J. S. (1993). Solid-phase extraction of phenols using membranes loaded with modified polymeric resins. *Journal of Chromatography*, 641: 57 – 61.
18. Thurman, E. M., Bastian, K.C. and Mollhagen, T. (2000). Occurrence of cotton herbicides and insecticides in playa lakes of high plains of West Texas. *Science Total Environ*ment, 248: 189-200.
19. Wilson, A. G. E. and Takei, A. S. (1999). Summary of Toxicology Studies with Butachlor. Agro-Science Division, Mosanto Company, Japan.
20. World Health Organization (2003). WHO Specification and Evaluations for Public Health Pesticides-Lambda-Cyhalothrin. http://www.who.int/ctd/whopes.
21. World Health Organization (2006). Water Sanitation and Health, Guidelines for Drinking Water Quality, 3rd Edition, ISBN 92 4 154696 4, WHO http://www.who.int /water_ sanitation_health/ dwq/gdwq3rev/ en/index. html.
22. World Health Organization (2003). Sulphate in Drinking Water. Background document for development of Guidelines for drinking- water quality. Pp. 1-6.
23. Zhou, Q.X., Wang, W.D., Xiao, J.P., Wang, J.H., Liu, G.G., Shi, Q.Z. and Guo, G.L. (2006). Determination of atrazine and simazine in environmental water samples using multiwalled carbon nanotubes as the adsorbents for pre-concentration prior to HPLC with diode array detector. *Talanta*, 68, 1309-1315.