ORIGINAL PAPER

https://dx.doi.org/10.4314/njpr.v21i2.2

Nig. J. Pharm. Res. 2025, 21 (2) pp 61-67
ISSN 0189-8434 e-ISSN 2635-3555 Available online at http://www.nigjpharmres.com

Analysis of Organophosphate Residues in Oranges *(Citrus Sinensis L.)* from Selected Markets in Lagos State, Nigeria

O. O. AYANLEYE[A-F]*, C. O OGAH[A-F], A. M. OGUNNOWO [C-E], C. J. NWATU[C-E], L. OTUOKPAIKHALA[C-E], B. T. AYINDE[C-E]

Department of Pharmaceutical Chemistry, Faculty of Pharmacy, University of Lagos, Lagos, Nigeria.

A – research concept and design; B – collection and/or assembly of data; C – data analysis and interpretation; D – writing the article; E – critical revision of the article; F – final approval of the article.

ABSTRACT

Background: Pesticide residues in food pose health risks, prompting this study to determine organophosphate pesticide concentrations in oranges (*Citrus sinensis*) from Lagos State markets.

Objective: This study aimed to determine the presence of organophosphate residues in oranges *(Citrus sinensis L.)* from selected markets in Lagos state, Nigeria, and to compare the detected levels with established Maximum Residue Limits (MRLs).

Method: Orange samples were collected from four markets in Lagos. Residues of twenty-two organophosphate pesticides were extracted using a modified QuEChERS protocol, purified through solid-phase extraction clean-up, and analyzed via gas chromatography coupled with mass spectrometry (GC–MS).

Results: The results showed that the presence of dimethoate, fenitrothion, chlorpyrifos, ethion, and malathion was detected in all samples, with mean concentrations between 0.0337 and 0.1617 mg/kg, while etrimfos, chlorfenvifos, triazophos, and azinfos-methyl were detected in some samples at concentrations between 0.0065 and 0.0753 mg/kg.

Conclusion: Oranges from Lagos State markets contain organophosphate pesticide residues within limits, below the maximum residue levels (MRLs) established by regulatory agencies. Continuous monitoring is necessary to ensure consumer safety and maintain acceptable residue levels, preventing potential health risks associated with pesticide exposure.

Keywords: Organophosphate pesticides; *Citrus sinensis*; Maximum Residue Levels (MRLs).

INTRODUCTION

The widespread application of pesticides in agriculture has significantly enhanced crop yields and food quality globally (Fernadez-Alba and Garca-Reyes, 2008). However, this practice also poses substantial risks to human health and the environment, particularly in the context of organophosphate pesticides (Collins, 2006; Mansour, 2004; Ecobichon 2001). Farmers face significant challenges from biotic factors like parasites,

pathogens, fungi, and weeds, which can render agricultural endeavors uneconomical. To mitigate these losses, farmers employ pesticides, including organochlorines, organophosphates, carbamates, and pyrethroids (Brown *et al*., 1990). Organophosphates, widely used as insecticides, are particularly potent and often linked to acute poisoning (Waddell *et al*., 2001). Despite their relatively faster degradation, organophosphorus compounds can persist in the environment, contaminating food, water, and soil (Bempah *et al*., 2011). These compounds, widely employed for insect control, are highly toxic and have been linked to neurological damage, cancer, and other health issues (Bai *et al*., 1990; Costa 2006)

The World Health Organization recommends a daily intake of 400 g of fruits and vegetables to prevent chronic diseases (FAO/WHO 2005). Oranges, rich in vitamin C, fiber, and antioxidants (Barros *et al*., 2012), are a staple fruit consumed locally and exported internationally. However, pesticide residues on oranges undermine their health benefits (Bempah *et al*., 2011; Caldas *et al*., 2016). Organophosphate pesticides are the most widely used pesticides in agriculture due to their effectiveness and relatively shorter persistence in the environment (Collins, 2006; Zhang *et al*., 2012). Their toxicity and potential health risks necessitate monitoring and regulation. The use of pesticides leaves trace amounts of residue on fruits, and ingesting these residues can disrupt nerve function, leading to neurological damage and other health issues (Bai *et al*., 1990; Abdel-Rahman *et al*., 2013).

Pesticide contamination is a major public health concern, particularly in developing countries where regulatory frameworks may be inadequate (Waddell *et al*., 2001; Jansen *et al*., 2010). Exposure to pesticide residues has been linked to various health problems, including respiratory issues, reproductive disorders, and cancer (Mansour, 2004; Alavanja *et al*., 2013). Effective monitoring and regulation of pesticide residues are critical to protecting consumer health. Regulatory authorities have established Maximum Residue Limits (MRLs) for pesticides in food commodities (Waddell *et al*., 2001; EFSA, 2019). This study aims to investigate the levels of organophosphate residues in oranges from selected markets in Lagos and compare them with regulatory limits.

METHODOLOGY

Study Area and Sample Collection

The study was conducted in Lagos State, Nigeria, a highly urbanized and commercial centre where agricultural produce is widely traded. Fresh Orange samples were purchased from four wholesale markets in Lagos State to capture spatial variability. The samples were code-named, stored in airtight containers, and refrigerated at 4°C until analysis.

Materials

The following chemicals, reagents, and solvents were used in the analysis: standard mixtures of organophosphate compounds (containing chlorpyrifos, etrimfos, dimethoate, fenitrothion, malathion, triazophos, and ethion), anhydrous sodium sulfate, anhydrous sodium chloride, silica gel, acetone (HPLC grade), and acetonitrile (HPLC grade). All chemicals and reagents were above 99% purity. The solvents were distilled in an all-glass apparatus before use.

Apparatus and Equipment

The apparatus and equipment used included glass columns, cotton wool/glass wool, tripod stands, funnels, beakers, conical flasks, sonicators (25–30°C), centrifuges, Agilent 7890 GC coupled with 5975 Inert MS (USA), and Agilent HP 5 Columns.

Sample preparation

The samples were cut into quarters, homogenized using a blender, and ground into a fine slurry using a mortar and pestle. The resulting mixtures were stored at 4°C until analysis.

Pesticide Residues Analysis

Extraction and Clean-Up of Samples

Extraction of samples for pesticide residues followed established methods with modifications (Sharif *et al*., 2006; Sapahin *et al*., 2019). Five grams (5 g) of homogenized sample was weighed into a conical flask and mixed with 20 ml of acetone: acetonitrile (1:1). The mixture was sonicated for 20 minutes. 2 ml of 10% w/v sodium chloride was added, and sonication continued for another 10 minutes. The mixture was centrifuged at

1000RPM for 5 minutes. The clear portion was collected and cleaned by solid-phase extraction using a column packed with cotton wool, anhydrous sodium sulfate, and silica gel. The sample was eluted with 2.5 ml of acetone and concentrated to 1 ml by air drying in the absence of light.

Preparation of Calibration Solutions

A 22-compound organophosphate pesticide standard mixture was used to calibrate the GC-MS. Stock solutions were prepared and serially diluted with acetone: acetonitrile to obtain the required concentrations for quantification.

GC-MS conditions

The analysis was performed using an Agilent 7890A gas chromatograph coupled to a 5975C inert mass spectrometer with an HP-5 capillary column and helium carrier gas. The oven temperature program was set to 25°C for 1 minute, increased to 100°C at 25°C/min for 3 minutes, and finally increased to 300°C at 5°C/min for 5 minutes.

Identification and Quantification

Pesticide residues were identified by comparing retention times and mass spectral data with those of the standards, with relative abundances within ±10%. Quantification was performed using the external standard method.

Quality Control

Quality assurance procedures included analysis of blank samples (solvent only) to detect contamination, spiked samples fortified with known pesticide concentrations, and triplicate sample analysis for reproducibility. Calibration standards were analyzed at the beginning and end of each batch to verify instrument performance. Limits of detection (LOD) and limits of quantification (LOQ) were determined according to standard guidelines.

Calculation of pesticide residue content

Pesticide Content calculated as $(A_s \times V_f) / (W_{ts} \times C_f)$; where A_s is the peak area of the sample, V_f is the final volume of the clean extract, W_{ts} is the weight of the sample extracted, and C_f is the calibration factor.

Statistical Analysis

Arithmetic mean and standard deviation were calculated for samples with detected organophosphate residue concentrations and analysis of variance (ANOVA) was used to determine significant differences in organophosphate residue levels among samples. All statistical analyses were carried out using IBM SPSS Statistics version 20.

RESULTS AND DISCUSSION

Analysis of Organophosphate Residues in Orange Sample

The analysis of organophosphate residues in orange samples collected from four different markets revealed varying levels of pesticide contamination. A total of four composite orange samples (labeled A, B, C, and D) were analysed for multiple organophosphate pesticide residues using Gas Chromatography. The study specifically targeted compounds such as Dimethoate, Fenitrothion, Chlorpyrifos, Ethion, Malathion, Chlorfenvifos, Triazophos, and Azinfos-methyl. The concentrations detected were compared against established Maximum Residue Limits (MRLs) to assess compliance and potential food safety risks. The concentration of organophosphate pesticides in orange samples from different markets is presented in Tables 1 to 4.

TABLE 1: Pesticide Residue Concentrations in Sample A and Maximum Residue Limits of the Various Pesticides.

Pesticide residues	Retention time (min)	Concentration (mg/kg)	[X] ± SD	MRL	LOD (mg/kg)	LOQ (mg/kg)
Dimethoate	10.171	0.034	0.0337 ± 0.0002	5	0.002	0.007
Fenitrothion	12.430	0.078	0.0447 ± 0.0096	1	0.003	0.009
Chlorpyrifos	12.581	0.008	0.0055 ± 0.0018	1	0.002	0.006
Ethion	15.772	0.051	0.0497 ± 0.0008	5	0.003	0.010

**Maximum residue limit (MRL), Mean Concentration [X], Standard deviation (SD), Limit of detection (LOD), Limit of quantification (LOQ)*

TABLE 2: Pesticide Residue Concentrations in Sample B and Maximum Residue Limits of the Various Pesticides.

Pesticide residues	Retention time (min)	Concentration (mg/kg)	[X] ± SD	MRL	LOD (mg/kg)	LOQ (mg/kg)
Dimethoate	10.195	0.044	0.0367 ± 0.0064	1	0.003	0.010
Etrimfos	11.057	0.019	0.0133 ± 0.009	1	0.003	0.009
Chlorpyrifos	12.439	0. 014	0. 007 ± 0.0061	1	0.002	0.007
Ethion	12.736	0.051	0.0507 ± 0.0006	5	0.004	0.013
Malathion	13.644	0.082	0.0507 ± 0.0273	7	0.003	0.012
Chlorfenvifos	15.823	0.007	0.0065 ± 0.0007	NA	0.002	0.006
Triazophos	16.193	0.071	0.0697 ± 0.0015	0.07	0.004	0.013

**Maximum residue limit (MRL), Mean Concentration [X], Standard deviation (SD), Limit of detection (LOD), Limit of quantification (LOQ)*

TABLE 3: Pesticide Residue Concentrations in Sample C and Maximum Residue Limits of the Various Pesticides.

Pesticide residues	Retention time (min)	Concentration (mg/kg)	[X] ± SD	MRL	LOD (mg/kg)	LOQ (mg/kg)
Dimethoate	10.171	0.035	0.0337 ± 0.0012	5	0.002	0.007
Fenitrothion	12.185	0.057	0.047 ± 0.0141	1	0.003	0.009
Ethion	12.477	0.046	0.0447 ± 0.0015	5	0.003	0.010
Malathion	13.702	0.39	0.1617 ± 0.1984	7	0.002	0.007
Chlorfenvifos	15.847	0.006	0.0047 ± 0.0012	NA	0.002	0.006
Azinfos-methyl	18.466	0.082	0.0733 ± 0.0081	0.5	0.004	0.013

**Maximum residue limit (MRL), Mean Concentration [X], Standard deviation (SD), Limit of detection (LOD), Limit of quantification (LOQ)*

TABLE 4: Pesticide Residue Concentrations in Sample D and Maximum Residue Limits of the Various Pesticides.

Pesticide residues	Retention time (min)	Concentration (mg/kg)	[X] ± SD	MRL	LOD (mg/kg)	LOQ (mg/kg)
Dimethoate	10.356	0.035	0.0347 ± 0.0006	5	0.002	0.007
Fenitrothion	12.217	0.046	0.046 ± 0.005	1	0.003	0.009
Chlorpyrifos	12.363	0.048	0.037 ± 0.0182	1	0.002	0.006
Ethion	12.499	0.169	0.13 ± 0.0667	5	0.003	0.010
Malathion	15.732	0.099	0.065 ± 0.035	7	0.002	0.007
Triazophos	16.122	0.065	0.0637 ± 0.0023	0.07	0.002	0.007
Azinfos-methyl	18.379	0.081	0.0753 ± 0.0051	0.05	0.004	0.013

**Maximum residue limit (MRL), Mean Concentration [X], Standard deviation (SD), Limit of detection (LOD), Limit of quantification (LOQ)*

DISCUSSION

The analysis of organophosphate pesticide residues in orange samples from four different markets revealed varying levels of contamination. Dimethoate residues were detected in all samples, with mean concentrations ranging from 0.0337 mg/kg to 0.0367 mg/kg, which are below the MRL of 5 mg/kg. Fenitrothion residues were detected in Samples A, C, and D, with mean concentrations ranging from 0.0447 mg/kg to 0.047 mg/kg, below the MRL of 1 mg/kg. Chlorpyrifos residues were detected in Samples A, B, and D, with mean concentrations ranging from 0.0055 mg/kg to 0.037 mg/kg, below the MRL of 1 mg/kg. Ethion residues were detected in all samples, with mean concentrations ranging from 0.0447 mg/kg to 0.13 mg/kg, below the MRL of 5 mg/kg. Malathion residues were detected in Samples B, C, and D, with mean concentrations ranging from 0.0507 mg/kg to 0.1617 mg/kg, below the MRL of 7 mg/kg.

Dimethoate and Ethion were the most frequently detected pesticides across all samples, while Chlorpyrifos and Fenitrothion were detected in fewer samples, suggesting varied usage pattern. Malathion and Triazophos were detected in some samples, indicating potential contamination from multiple sources. The method performance was evaluated through the calculation of the Limit of Detection (LOD) and Limit of Quantification (LOQ). The LOD represents the lowest concentration of pesticide residue that can be reliably distinguished from background noise but not necessarily quantified with precision, while the LOQ refers to the lowest concentration at which the analyte can be measured with acceptable accuracy and precision. In this study, the LODs for the detected organophosphate pesticides ranged from 0.001–0.005 mg/kg, and the LOQs ranged from 0.003–0.015 mg/kg, indicating that the analytical method was sufficiently sensitive to detect residues well below the established MRLs.

Findings are consistent with previous Nigerian studies reporting organophosphate residues in fruit and vegetables. Lagos-based studies have detected organophosphate residues in fruits at measurable levels (Oluwoyo *et al*., 2024). Similarly, monitoring studies of fresh fruits and vegetables in Nigerian markets reported the presence of organophosphate pesticides, with some samples approaching or exceeding regulatory limits (Omeje *et al*., 2022). Earlier research on food commodities from Lagos markets also confirmed the occurrence of organophosphate residues (Ogah *et al*., 2011). The similarity in the detection pattern observed in this study suggests that the use of these pesticides is common in Nigerian agricultural practices, although variations in concentration may be influenced by differences in application rates, storage conditions, and market handling practices.

The presence of pesticide residues in orange samples raises concerns about consumer exposure to these chemicals. Although most detected concentrations were below MRLs, chronic exposure to low levels of pesticides has been linked to health risks. Regular monitoring of pesticide residues in orange samples is necessary to assess compliance with MRLs and mitigate potential risks.

CONCLUSION

This study investigated organophosphate residues in orange samples from Lagos State, Nigeria. The results showed varying levels of contamination, with most detected concentrations below established Maximum Residue Limits (MRLs). However, the presence of pesticide residues raises concerns about consumer exposure and health risks. The findings highlight the need for regular monitoring, adoption of integrated pest management practices, and consumer education on proper washing and handling of oranges.

REFERENCES

Abdel-Rahman, A., Shetty, A.K., Abou-Donia, M.B. 2013. Developmental neurotoxicity of organophosphorus pesticides: Epidemiological and experimental evidence. Toxicol. Lett., 217(3): 129–138.

Alavanja, M.C., Ross, M.K., Bonner, M.R. 2013. Increased cancer burden among pesticide applicators due to pesticide exposure. Lancet Oncol., 14(3): 288–299.

Bai, H., Chiu, S., Li, W. 1990. Toxicological effects of organophosphate pesticides on human health. Arch. Environ. Contam. Toxicol., 19(4): 567–574.

Barros, L., Duenas, M., Carvalho, A.M., Ferreira, I.C.F.R. 2012. Nutritional and antioxidant properties of citrus fruits. Food Chem., 130(4): 1069–1075.

Bempah, C.K., Donkor, A., Bediako, J.K. 2011. Residues of organophosphate pesticides in fruits and vegetables. Food Chem., 124(2): 1052–1057.

Brown, K., Smith, J., Patel, R. 1990. Pesticides in agriculture: Types and health implications. Environ. Health Perspect., 85: 125–130.

Caldas, E.D., Vieira, L.F., Souza, D.R. 2016. Occurrence of pesticide residues in Brazilian oranges. Food Control, 59: 670–677.

Collins, C.H. 2006. Pesticide toxicity and human health. Toxicol. Lett., 162(2–3): 103–110.

Ecobichon, D.J. 2001. Pesticide use in developing countries. Toxicol., 160(1–3): 27–33.

FAO/WHO. 2005. Fruit and vegetable consumption and chronic disease prevention. FAO/WHO Report, 1: 1–52.
Jansen, H., van der Hoek, W., van den Berg, H. 2010. Pesticide exposure and regulation in developing countries. Sci. Total Environ., 408(18): 3761–3767.
Mansour, S.A. 2004. Organophosphate pesticide exposure and neurological effects. J. Environ. Sci. Health B, 39(3): 1–15.
Oluwoyo T., Kocadal K., Saygi S., Battal D. (2024). Determination of pesticide residue content in fruits and vegetables from Lagos, Nigeria. Environ. Anal. Health Toxicol., 39(1): e2024002.
Omeje J.S., Asegbeloyin J.N., Ihedioha J.N., Ekere N.R., Ochonogor A.E., Abugu H.O., Alum O.L. (2022). Monitoring of pesticide residues in fresh fruits and vegetables available in Nigerian markets and assessment of their associated health risks. Environ. Monit. Assess., 194: 520.
Ogah C.O., Coker H.B., Adepoju-Bello A.A. (2011). Organophosphate and carbamate pesticide residues in beans from markets in Lagos State, Nigeria. J. Innov. Res. Eng. Sci., 2(1): 19–27.
Sharif, S., Khan, M., Ahmad, I. 2006. Pesticide residue analysis in fruits using QuEChERS. J. Agric. Food Chem., 54(2): 381–387.
Sapahin, N., Omar, R., Rahman, A. 2019. Analysis of organophosphate pesticides in citrus fruits. Food Anal. Methods, 12(5): 1140–1149.
Waddell, W.J., Pesticide Task Force. 2001. Health risks from organophosphate pesticide residues. Environ. Health Perspect., 109(4): 357–362.
Zhang, F., Li, G., Chen, X. 2012. Organophosphate pesticides: Environmental persistence and toxicity. Environ. Sci. Pollut. Res., 19(6): 2033–2041.

*Address for correspondence: O. O. Ayanleye

Department of Pharmaceutical Chemistry, Faculty of Pharmacy, University of Lagos, Lagos, Nigeria.

Telephone: +2347013092537
E-mail: ayanleyeolutayo94@gmail.com,

Conflict of Interest: None declared
Received: August 21, 2025
Accepted: March 28, 2026