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EXPLORING THE QuEChERS - GAS CHROMATOGRAPHY APPROACH FOR SEDIMENT PESTICIDE ANALYSIS

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Abstract

Pesticides have been classified as the most harmful substances in the world because of their extensive application, toxicity, and persistence. Hydrophobic chemicals, such as pesticides, have a considerable tendency to sorb to organic matter in sediment and soil. Measuring pesticides in sediment is crucial for monitoring their environmental fate and possible toxicity because they are typically found at higher concentrations in sediment. Since many hydrophobic substances do not break down easily, they remain in the environment for a very long time. This study aims to develop an integrated approach to extracting and quantifying pesticides from sediment samples using QuEChERS-gas chromatography techniques. The extraction of organochlorine and organophosphorus pesticides from the sediment sample was achieved by slightly modifying the QuEChERS method. The extracted compounds were identified and quantified by gas chromatography with a triple-quadrupole mass detector. Organochlorine pesticides or their degradation compounds provided the majority of the target substances. Monitoring pesticide content in sediments is essential for understanding bioaccumulation and long-term environmental effects, as well as for promoting sustainable agricultural practices.

Key words*: pesticides, sediments, chromatography, QuEChERS.*

INTRODUCTION

In present-day agriculture, pesticides are crucial for both ensuring global food security and protecting crops from pests (Khurshid et al., 2024). Even though these substances offer several advantages, using them might have major negative effects on the environment and human health. Pesticide residues in food and the environment cause chronic health hazards, such as cancer, endocrine disruption, and neurological diseases (Zhou et al., 2025). Their presence in water, accumulation in sediments and soils, and possible biomagnification in the food chain could harm non-target organisms due to their possible toxicity (Peris et al., 2022). Pesticides that are used carelessly find their way into bottom sediments, where sediment particles absorb them and might eventually constitute a major cause of contamination in aquatic environments (Shah & Parveen, 2023). According to their physicochemical characteristics, such as solubility and octanol-water partition coefficient, pesticides disperse throughout the several aquatic ecosystem compartments (water, suspended materials, and biota) after being released into the environment (Ijzerman et al., 2024). Additionally, entrapped contaminants can be released at any moment through resuspension by natural processes or human intervention (Peris et al., 2022). Some pesticides adsorb onto suspended particles and have stronger affinities for organic materials; these particles subsequently settle and

accumulate in the waterbed (Khurshid et al., 2024).

The presence of hydrophobic pollutants in a waterway may be effectively determined by analyzing contaminants in the sediment and aquatic biota. Hydrophobic compounds have limited solubility in water, but high solubility in lipids. They also tend to accumulate to organic material in soil and sediment and their resistance to degradation makes them very persistent (USGS Fact Sheet, 2000). Over the past 50 years, a large number of pesticides have been detected in sediments, most of them belonging to organochlorine insecticides and their breakdown products.

The most frequently detected pesticides in sediment were DDTs, dieldrin, and chlordane even though some of them had been banned since the 1970s and 1980s (Yang et al., 2015). Studies have shown that sediment pollution has been linked to negative impacts on aquatic life such as hepatic lesions or DNA adducts (Yang et al., 2015). Moreover, hazardous substances present in aquatic ecosystems can accumulate and pose toxic risks when transferred to humans through consumption (Bashir et al., 2020). Pesticide residues were first analyzed using acetonitrile and petroleum ether. Then, acetone was added to prevent partial loss of polar insecticides, whereas salt improved their recovery.

In order to achieve a lower limit of quantification, solid-phase extraction and many other methods (supercritical fluid extraction, accelerated solvent extraction, gel-permeation chromatography, or microwave-assisted extraction) were included (Afify et al., 2022). The introduction of the (QuEChERS) method (quick, easy, cheap, effective, rugged, and safe) was revolutionary, innovative, and applicable to most official analysis methods. The QuEChERS approach is faster, requires less solvents, and produces consistent results (Shendy et al., 2019). Moreover, the combination of gas chromatography and mass spectrometry has proven to be among the best methods for the examination of pesticides from different matrices (Tankiewicz & Berg, 2022). Therefore, the objective of this study is to provide an optimal approach for the simultaneous extraction, determination, and quantification of 27 pesticides from both organochlorine (OCP) and organophosphorus (OPP) categories in sediment samples.

MATERIALS AND METHODS

QuEChERS Extraction

Organochlorine and organophosphorus pesticides were extracted from all sediment samples using a modified QuEChERS (rapid, simple, cheap, effective, robust, and safe) approach. Therefore, the following protocol was carried out, after spiking with different concentrations of the standard mix and the addition of the internal standard mix: 5 g of the sample and 10 mL of ACN (acetic acid 1%) were well homogenized. To begin the extraction stage, 6 g of MgSO4 and 1.5 g NaOAc were added as QuEChERS salts. The final mixture was vigorously shaken for 5 minutes and then centrifuged. A volume of 5 mL from the supernatant was collected and cleaned with different one, or two units of clean-up consisting of 50 mg MgSO4, 25 mg PSA, 25 mg C18, and 5 mg GCB. After a second centrifugation, the liquid part was subjected to evaporation through a nitrogen system and reconstituted with 0.5 mL or 0.250 mL acetonitrile. Even though this extraction method has many advantages, sometimes certain steps need to be particularly optimized because there are also problematic pesticides. Such pesticides are sensitive to pH, which creates strong bonds with other substances, leading to their misquantification. For example, using PSA (Primary Secondary Amine) in the QuEChERS extraction method is not indicated in the case of acidic pesticides that can form acid-base interactions with the sorbent. This combination can lead to the loss of acidic pesticides during the clean-up phase (Musarurwa et al., 2019).

Instrument and Method Setup

A TSQ 9000 Triple quadrupole GC-MS/MS instrument coupled with a Thermo Scientific™ TRACE™ 1310 GC was used to analyze the samples (Figure 1). A Thermo Scientific™ TriPlus™ RSH autosampler was used to inject the sample, and a Thermo Scientific™ TraceGOLD TG-5MS 30 m × 0.25 mm I.D. × 0.25 µm film capillary column was used for chromatographic separation. The instrument

was operated in a splitless mode with a 2 µL injection volume. The GC oven program was set up as follows: initial temperature 80°C with a 0.5 min hold time, from 80°C to 190°C at a rate of 25°C/min, from 130°C to 300°C at a rate of 6°C/min, and the final step, 300°C with a hold time of 10 min. The total run time was about 33 minutes.

Three SRM transitions - two for further ion ratio confirmation and one for quantitation - were utilized to identify each targeted compound. The Chromeleon 7.3 software was used to process and report the data.

Figure 1. TSQ 9000 Evo triple quadrupole mass spectrometer coupled to a Thermo Scientific™ TRACE™ 1310 GC

Analytical standards

- EPA 625/CLP Pest. Mix, 1x1 mL, 2000 µg/mL in hexane:toluene (50:50) containing Aldrin, α-BHC, β-BHC, Lindane, δ-BHC, 4,4′-DDT, Dieldrin, α-Endosulfan, β-Endosulfan, Endosulfan sulfate, Endrin, Endrin aldehyde, Heptachlor, Heptachlor exo-epoxide
- EPA 8270 Organophosphorus Pesticides Mix 2, 1x1 mL, 2000 µg/mL in dichloromethane containing Dimethoate, Disulfoton, Famphur, Parathion, Parathion-methyl, Phorate, Sulfotep, Thionazin, Triethyl thiophosphate. A mixture containing two internal standards (ε-HCH and PCB-143) was used for the calibration curve.

RESULTS AND DISCUSSIONS

Five different samples were prepared to provide an optimal method for the extraction and detection of the target analytes. The first sample (A) is represented by sediment with internal standards. Sample B was obtained by spiking sample A with a standard solution in a concentration of 20 ng/mL. Samples coded C, D, and E represented sediment spiked with 100 ng/mL standard solution, cleaned up and redissolved differently after the concentration step. In this context, the evaluation of specific extraction steps was conducted to achieve the most precise, rapid, and efficient quantification of the compounds, while confirming their presence through three distinct transitions (Table 1).

Table 1. Pesticides retention time and product ions

Compounds	Retention Time	Quant. Ion	Conf. Ion #1	Conf. Ion #2
	min	m/z	m/z	m/z
O, O, O-Triethylphosphoro thioate	3.86	65	93.1	65
Thionazin	6.45	79.1	68	79
Sulfotep	7	202	174	174
Phorate	7.13	65	75	81
d-BHC	7.28	182.9	146.7	146.5
Dimethoate	7.44	42.1	63	79
g-BHC (Lindane)	7.72	145	109	183
a-BHC	7.82	183	146.6	146.2
Disulfoton	8.11	59,8	45	96.9
b-BHC	8.23	145	146.6	183
e-HCH	8.42	181	111	111
Methyl parathion	8.93	109	79	89
Heptachlor	9,.15	236.9	39	65
Aldrin	9.89	192,9	191	298.9
Parathion	9.94	96.9	65,1	81
Heptachlorepoxide Isomer B	10.76	262.9	192,9	264.9
Endosulfan I (a)	11.61	205.9	125	159.4
4,4`-DDE	12.14	176.1	246	248
Dieldrin	12.25	192.9	190.9	227.8
Endrin	12.79	192.9	173	245.3
Endosulfan II (b-Isomer)	13.02	159	205.8	123
PCB-143	13.19	290	325	290
4,4`-DDD	13.21	165.1	199	165
Endrin Aldehyde	13.49	215	317	142
Famphur	13.82	109	63	79
Endosulfan Sulfate	14.11	236.8	234.9	203.9
4,4`-DDT	14.17	165.1	199.5	165

Figure 2 displays the peaks corresponding to each investigated compound. In Figure 3, the final amount of each tested experimental variant is exposed.

As expected, similar values for most of the

organochlorine pesticides were obtained when variants E, D, and C were applied. The common aspect among these three samples is the spiking level, which is 100 ng/mL. The difference lies in the final step of the extraction. However, it is important to mention that variant E was distinguished by better and easier quantification during data processing. Therefore, in addition to a slightly higher final concentration, the peak intensities corresponding to each compound - including the internal standard - were significantly higher than those calculated in the other variants. Even though organochlorine chemicals are banned, their traces can still be found in food and the environment as contaminants (Zohair, 2001).

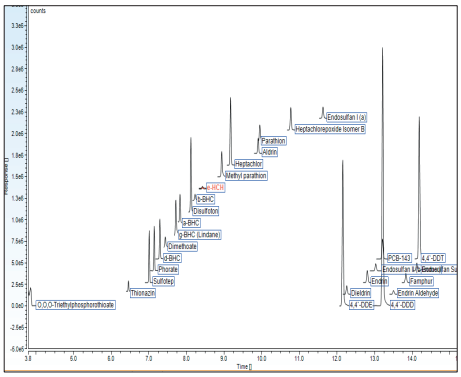


Figure 2. Standard solution (OCP and OPP) chromatogram in MS Quantitation

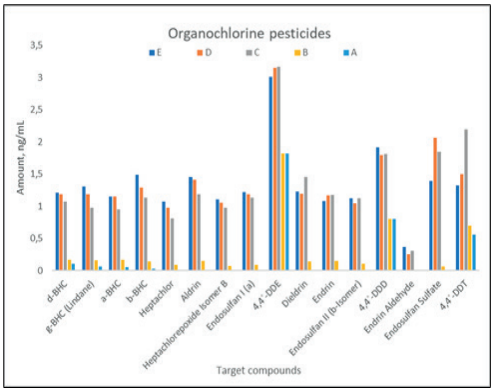


Figure 3. Organochlorine pesticides concentration in each experimental variant

A similar observation can be made for the organophosphorus pesticides in Figure 4. With a few exceptions, the best variant of the extraction is sample E. It seems that redissolving the final extract in a smaller volume of acetonitrile promotes the detection of the compounds. Of course, that in the case of sample B, where the spiking was made with a much lower concentration of pesticides, the final concentration is also much lower than the final amount detected in other samples.

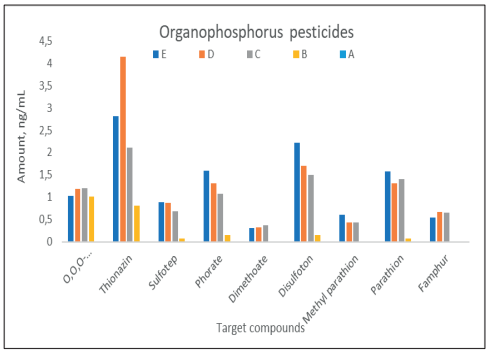


Figure 4. Organophosphorus pesticides concentration in each experimental variant

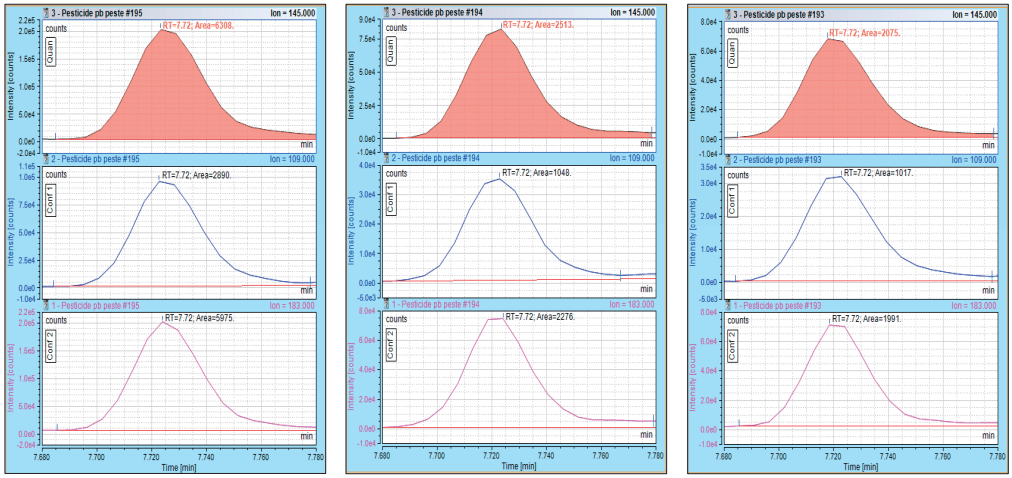
Compared to organochlorines, organophosphorus pesticides are more acutely hazardous, but they have the benefit of being quickly broken down in the environment (Zohair, 2001).

In a study conducted by Khurshid et al., 2024 on pesticide contamination in sediments of 38 water bodies, only one sample was 'pesticide-free' and 3 samples contained a single pesticide.

Figure 5 and Figure 6 confirm the abovementioned idea. As can be observed, an example of a well-known agricultural insecticide, γ-BHC is represented along with its representative ions (Figure 5). The higher intensity peak for this compound highlights variant E compared to Variants D and C. Moreover, an identical situation is valid for the internal standard PCB-143 represented in Figure 6. It is very important to improve the compounds' detection because in most cases they belong to complex matrices. Matrix effects are a major challenge for analyzing low levels of different contaminants using gas chromatography-triple quadrupole mass spectrometry. When examining complex matrices, a practical approach is required due to the complex nature of matrix effects, which can be influenced by various factors such as the

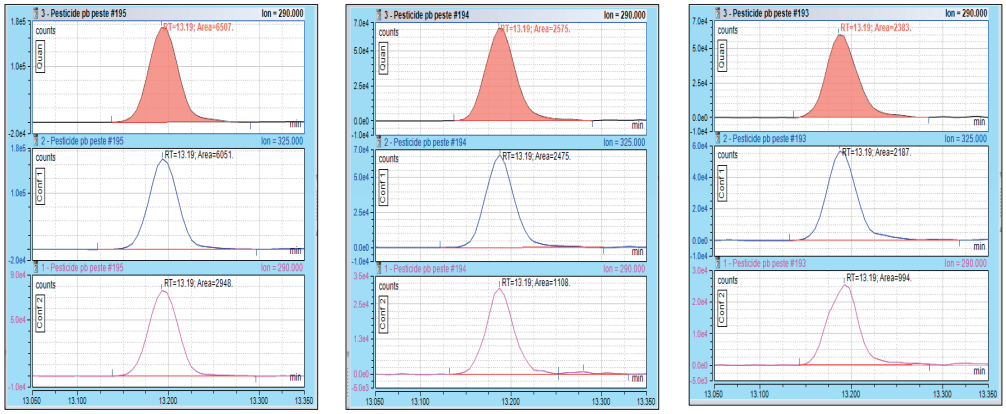
target analyte, sample preparation technique, composition, and instrument selection (Williams et al., 2023). Most often, salts and SPE sorbents are the key components in terms of removing water residues or other matrix interferences (QuEChERS Pesticides, 2011). However, PSA does not apply, for example, to non-polar pigments, and can be replaced or supplemented with GCB (graphitized carbon black). Florisil and low temperature can be used also when fatty matrices are analyzed (Musarurwa et al., 2019).

Moreover, studying residual pesticide compounds in sediments emphasizes the necessity of investigating the immediate and long-term impacts of pesticide use on aquatic systems and, eventually, the need for more ecologically friendly and sustainable farming methods (Khurshid et al., 2024).



a) Variant E b) Variant D c) Variant C

Figure 5. MS Components for g-BHC



a) Variant E b) Variant D c) Variant C

Figure 6. MS Components for PCB-143 (IS)

The screening of these contaminants in sediments is essential to understanding their dynamics and any possible hazards to aquatic life (Peris et al., 2022). Sediments may provide important details about the quality of water and vary considerably in composition, shape, and processes (Brondi et al., 2011).

CONCLUSIONS

The development of a method for determining pesticides in sediment is essential for many reasons, including pollution monitoring, ecosystem protection, identifying contamination sources, evaluating toxicity and bioaccumulation potential, establishing regulations in the field, and assessing the detrimental impact on human health.

QuEChERS approach' short operating time, ease of use, and affordability facilitate the simultaneous analysis of multiclass pesticide residues in sediment samples. Because the QuEChERS approach produces far less waste and requires less hazardous solvents and reagents, it is also consistent with green chemistry.

In the present study, the QuEChERS approach using the 1:5 ratio for the clean-up: liquid extract, as well as the re-dissolution after concentration in a smaller volume of solvent, resulted in better separation and identification of compounds.

There is an increasing demand for validated techniques capable of detecting pesticide residues in sediments, comparable to those used for water and vegetable samples. This is an area that is constantly evolving and demands ongoing research into better, more affordable, quicker, wider-ranging, and environmentally friendly methods.

Protecting and conserving aquatic ecosystems as well as achieving the European Union's goal of zero pollution in soil, air, and water by 2050 (European Commission. Directorate General for Environment. et al., 2021) depend on the understanding of the dynamics and effects of (mixtures of) pesticide residues.

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