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Determination of Pesticide Residues in Water Using Extraction Method

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Abstract

In this work organochlorine pesticides were first extracted from water using a solvent mixture (hexane:dichloromethane) and the quantities were then determined using a GC-MS fitted with an Electron Ionization (EI) and Selective Ion Monitoring (SIM) method. At the same time changes in the recovery ratios of spike levels were seen ranging from 73.6% to 96.1% (*Chlorfenapyr*). The recovery values that we found to be the lowest and greatest were 0.100 µg L⁻¹ and 1.600 µg L⁻¹ respectively. We also noticed that the *Bromophos-ethyl*, *Bromophos-methyl* and *Chlorfenapyr* pesticides had the lowest recovery efficiency. Additionally, the important values of pesticides with double benzene rings were detected in the following decreasing order: 4.4'-DDE > 4.4'-DDD > o.p'-DDE > *Chlorfenapyr* > 2.4'-DDD.

Keywords: Residue, analysis, pesticide

1. INTRODUCTION

In recent years with the increase in birth rates in many countries and continents, there have been significant increases in population rates. While there is not much increase in food production, the food produced is insufficient because the population growth increases exponentially. According to the researches, the gap between population growth, which reduced the amount of agricultural land per capita from 0.33 hectares to 0.19 hectares between 1969 and 2015, and food production is gradually widening [1]. Efforts are being made to increase productivity in existing agricultural areas. These investigations can be divided into three categories: pest control,

yield-enhancing chemical (fertilizer, plant hormones) and genetic modification [2].

Since the middle of the 20th century, pesticides have been widely utilized in pest control efforts around the globe. However, in some residue studies conducted by Turkish and other researchers, it is seen that pesticide use may adversely affect human health [3], and create health risks [4-5-6]. In addition, it was predicted that the ecological balance was disturbed by the pollution of soil and water [7], among Turkish [8-9] and foreign researchers. The World Health Organization (WHO) has been estimated that pesticide poisoning causes 346.000 deaths annually [10-11]. Pesticide residue analyzes should be

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performed in order to determine the risks arising from pesticide use.

Depending on the chemical structure of the pesticides, several instrumental device and techniques must be used to determine the residues. The primary determinants of analytic procedures are physical characteristics (volatility, solubility, molecular size), as well as chemical characteristics (acidic/basic, neutral, and heat stability). For an understandable analysis of their non-volatile, non-thermally stable, and large molecule structure, the researchers have preferred the use of liquid chromatography in combination with Ultra/Violet [12], conductivity, mass spectrometry (MS) [13], and tandem mass spectrometry (MS-MS) [14-15-16] detectors for comprehensive.

For the residue analysis of volatile, thermally stable, and small molecule structure, gas chromatography (GC) in combination with electron capture detector (ECD) [17], nitrogen phosphorus detector (NPD) [18], flame photometric detector (FPD) [19], MS, GC was frequently employed in conjunction with ECD, NPD, or FPD to assess the trace level residue of pesticides in diverse matrices. However, the GC results were unable to provide the required qualification. In light of this, MS [20] and MS-MS have been employed in GC since GC-MS offer a lot of advantages over GC detectors for residue as well as confirmation difficulties and lowering the Maximum Residue Limits (MRL) to by many nations [15-21-22]. Additionally, the researchers can check the findings and prevent drawing erroneous conclusions thanks to the ion monitoring approach. Additionally, it was capable of analyzing many pesticides with the same retention time. A user-friendly guidebook for the definition and application of GC-MS analysis methods was created by Thier et al. in 1992 [23].

The extraction process is crucial for the pesticide analysis. Depending on the type of pesticides and the extraction matrix, a broad variety of organic solvents have been utilized.

An analytical technique known as QuEChERS (Quick, Easy, Cheap, Effective, Rugged, and Safe) has become popular in recent years for determining the quantities of pesticide residue on matrices [14-20]. Despite being a practical method, the detection limit of the method is insufficient for the MRL values of some pesticides; hence, different extraction methods are pertinently applied for the pesticides. According to [24], pesticide was extracted from fruit-based soft drinks using the solid-phase extraction (SPE) [22-25] method. Additionally, some studies prefer to utilize acetone to remove pesticides from fruits [26] while others use ethyl acetate as a solvent for the extraction of pesticides from vegetables [27].

The QuEChers method to determine pesticide residues in water samples [28], a rapid and multiple analysis method that can be used to determine pesticide residue levels in water samples [29], the QuEChERS method to determine herbicide residues in sediment and water samples [30], QuEChERS and solid phase extraction (SPE) methods for the analysis of pesticide residues in water and sediment [31], the residues of commonly used pesticides in soil, surface and ground water sources using QuEChERS and solid phase extraction (SPE) methods [32], organochlorine pesticide residues in sediment and water samples using liquid extraction and solid phase extraction methods [33], conventionally, several techniques have been performed for the extraction and analysis of OCPs in environmental matrices.

For OCPs, the most commonly used extraction methods are Soxhlet pressurized liquid extraction and Soxhlet extraction despite of some disadvantages such as over solvent depletion and extraction time or cost [33] and pesticides residues in drinking-use water, drinking water, natural spring water and natural mineral waters using analysis method [34], fast, easy, cheap, effective, robust and safe (QuEChERS) method for extraction and cleanup of pesticide residues in a wide variety of matrices [35] have been used

because of their speed, simplicity and low solvent depletion.

In this study, it was aimed to successfully extract organochlorine pesticides from water using a solvent mixture (hexane: dichloromethane). GC-MS equipped with Electron Ionization (EI) and Selective Ion Monitoring (SIM) method was used to detect pesticide residues in the extracted water samples.

2. MATERIAL AND METHODS

2.1. Material

All of the organochlorine pesticides (OCPs) utilized in this study were purchased from Sigma-Aldrich [35-36]. All chemicals and solvents used were analytical grade. Sodium sulfate (Na_2SO_4), sodium chloride (NaCl), sodium hydroxide (NaOH), sulfuric acid (H_2SO_4), dichloromethane and hexane were purchased from Merck (Darmstadt, Germany) Using a Brand Mark micro pipette (0-100 L), the spikes were injected into organic-free water. For the pesticide tests, a Gas Chromatography-Mass-Mass Spectrometry (GC/MSD 5977B, Agilent) with an HP 5MS capillary column (30 mx0.25 mm, Agilent) was used. For the concentration of pesticide residue extracts, a rotary evaporator was used at 40 °C and 150 rpm. until the desired volume was reached [2-19-36].

2.2. Method

The chosen pesticides were extracted and cleaned up from water samples using the QuEChERS extraction method developed [8-19-27-37-38]. A separatory funnel was filled with 0.5 L of organic-free water before stock standard pesticide solutions were added. The separating funnel was violently shaken after the spikes were vigorously shaken into it in a volume ranging from 0 μL to 100 μL until they reached the desired concentration levels. With the help of 1.0 M H_2SO_4 and 1.0 M NaOH , the pH was brought roughly to a neutral value, and the contents were violently

agitated once again. Then, 1 mL of saturated NaCl solution was poured into the separatory funnel prior to the pesticides being extracted three times with 60 mL of a hexan-dichloromethane solvent mixture (1:1, volume:volume). The pesticide residue-containing extract was dried with anhydrous Na_2SO_4 and concentrated to 10 mL at 150 rpm at 40°C. Six spike levels were recreated seven times after repeating the aforementioned technique. 1 μL of the 10 mL extract was injected into the GC-MS using the GC-MS-ChemStation Software to determine the pesticide concentrations.

3.3. Analysis of Pesticides

The GC oven was kept at 110 °C for 2 minutes before being elevated to 280 °C at a rate of 8 °C/min and kept there for 1 minute. The temperatures of the ion source, interface, and injection port were 280, 280, and 230 °C, respectively.

Table 1 Amount of pesticides according to quantification-retention time

Pesticide	t_r	Q_1	Concentration (μgL^{-1})
Bromophos-methyl	15.55	331	0.410
Bromophos-ethyl	16.82	97	0.268
o.p'-DDE	16.84	246	0.552
4.4'-DDE	17.92	246	0.333
2.4'-DDD	18.20	235	0.288
Chlorfenapyr	18.90	59	0.074
4.4'-DDD	19.35	235	0.239

The quantification of pesticides was performed using the Electron Ionization (EI) and Selected Ion Monitoring (SIM) mode. Each pesticide (1 μgL^{-1}) was injected into the GC-MS before SIM mode was used, and their fragmentation and quantation ions were determined (Table 1) [37-39-40]. The amounts of pesticides in SIM mode were calculated using Q_1 ions. As confirmation ions, the additional ions from each pesticide were used. When concentration of pesticides was normalized based on $S/N=6$, for pesticides the following operation was used.

Table 2 Amount of pesticides according to signal-noise

Pesticide	S/N	Concentration Normalized (μgL^{-1})
Bromophos-methyl	10.2	0.241
Bromophos-ethyl	6.1	0.264
o.p'-DDE	9.4	0.352
4.4'-DDE	6.9	0.290
2.4'-DDD	6.2	0.279
Chlorfenapyr	6.0	0.074
4.4'-DDD	7.2	0.199

$$\frac{C}{S/N} \times 6 = C_N \quad (1)$$

C: Concentration

C_N : Concentration normalized

S/N: Signal / Noise

and normalized concentration was obtained and given Table 2.

For the quantitative assessments of pesticides, a standard solution of each pesticide was made in a hexane-dichloromethane mixture at a concentration range of 39-5000 $\mu\text{g L}^{-1}$ and examined three times using GC-MS. The calibration graph of each pesticide plotted against pesticide concentration using GC-MS response was provided in Table 3, along with each pesticide's regression coefficients. Equations from these graphs were used to compute the amounts of pesticides (Table 4) [39-40].

Table 3 Standard ranges and regression coefficients of pesticides

Pesticide	Standard Range μgL^{-1}	r^2
Bromophos-methyl	5000-39	0.989
Bromophos-ethyl	5000-39	0.997
o.p'-DDE	5000-39	0.999
4.4'-DDE	5000-39	0.994
2.4'-DDD	5000-39	0.997
Chlorfenapyr	5000-39	0.994
4.4'-DDD	5000-39	0.996

Table 4 For pesticides equations of calibrations

Pesticide	Equation
Bromophos-methyl	$C = 0.962 \times 10^{-3} A + 10.130$
Bromophos-ethyl	$C = 6.224 \times 10^{-3} A + 9.209$
o.p'-DDE	$C = 1.675 \times 10^{-3} A + 1.436$
4.4'-DDE	$C = 2.973 \times 10^{-3} A + 1.315$
2.4'-DDD	$C = 1.732 \times 10^{-3} A + 4.605$
Chlorfenapyr	$C = 2.383 \times 10^{-3} A + 3.082$
4.4'-DDD	$C = 1.862 \times 10^{-3} A + 7.212$

4. RESULT AND DISCUSSION

Using the previously described GC-MS software, a sufficient differentiation was made in 19 minutes in the total ion chromatogram of the organochlorine pesticides. All information was collected by this analysis procedure. The findings of seven separate investigations and their average recoveries are shown in Table 5 for the six distinct pesticide concentrations dependent on water spike levels. According to Table 5, the recovery ratios of spike levels range from 73.6%, the lowest, to 89.1%, the greatest. *Chlorfenapyr* concentrations of 0.100 μgL^{-1} and 1.600 μgL^{-1} , respectively, yielded the lowest and maximum recovery values. In terms of *2,4'-DDD*, *4,4'-DDE*, *bromophos-ethyl*, and *bromophos-methyl*, the recoveries of the four pesticides spiked at the same lowest concentration level, 0.300 μgL^{-1} , were reported to be 0.261, 0.270, 0.244, and 0.246 μgL^{-1} , respectively. The relevant recovery at the same highest concentration level, 9.600 μgL^{-1} , for the same four pesticides was reported as 8.270, 8.407, 9.038 and 8.311 μgL^{-1} for the same order. The recoveries for *chlorfenapyr* and *4.4'-DDD* were calculated to be 0.074 and 0.159 μgL^{-1} at the lowest spike levels of 0.100 μgL^{-1} and 0.200 μgL^{-1} , respectively, while they were noted to be 2.757 and 2.647 μgL^{-1} at the highest spike levels for these pesticides, 3.200 μgL^{-1} . When the other spike levels were looked at, *4.4'-DDD*'s recovery was found to be 0.159 μgL^{-1} at 0.200 μgL^{-1} . *O.p'-DDE* recovery at 0.400 μgL^{-1} was measured at 0.368 μgL^{-1} .

One quantity ion was used in this investigation since the quantitative analysis of each pesticide was dependent on the ratio of Signal to Noise (S/N) ≥ 6 . S/N related to pesticide concentration and quantity ions are shown in Table 2 for each pesticide (Q_1). Normalized concentration values of pesticides were obtained and Table 2 is given.

On the other hand, organic free water was supplemented by adding pesticides before being extracted in order to determine the LOD values [36]. The limits of detection (LOD) for each analyte were calculated based on statistical analysis of the calibration curves using equations (2) and (3). The average recoveries with standard deviations from seven separate investigations utilizing the same amount of continuous enrichment for each pesticide are shown in Table 5. $LOD_{Exp.}$ can be determined using the standard deviations (σ) of the lowest concentration of pesticides, as indicated in Table 5., if the concentration of pesticide ($C_{Normalized}$) corresponding with S/N , 6 is considered as the detectable lowest concentration.

$$LOD_{Exp.} = C_{Normalized} + 3\sigma \quad (2)$$

σ : The Std of replicates of recovery repeats of each pesticide at LOD level spike (7 repeats) can be calculated.

Using the standard deviation of the responses (S_y) of the curve and the slope of the calibration curve (S) $LOD_{Cal.}$ can also be measured using the equations given below.

$$LOD_{Cal.} = 3.3 \left(\frac{S_y}{S} \right) \quad (3)$$

S_y : standard deviation of the responses (S_y) of the curve for each pesticides

S : slope of the calibration curve for each pesticides Finally, all results were given in Table 5.

Table 5 Liquid-liquid extraction process

Pesticide	Spike μgL^{-1}	R_{Aver} μgL^{-1}	R_{Aver} %
Bromophos-methyl	0.300	0.246	82.1
	0.600	0.496	82.7
	1.200	1.082	90.1
	2.400	2.105	87.7
	4.800	4.375	91.1
	9.600	8.311	86.6
Bromophos-ethyl	0.300	0.244	81.2
	0.600	0.556	92.7
	1.200	1.054	87.9
	2.400	2.225	92.7
	4.800	4.121	85.9
	9.600	9.038	94.1
o.p'-DDE	0.400	0.368	91.9
	0.800	0.739	92.4
	1.600	1.483	92.7
	3.200	2.647	82.7
	6.400	5.605	87.6
	12.800	11.87	92.7
4.4'-DDE	0.300	0.270	90.1
	0.600	0.496	82.7
	1.200	1.082	90.1
	2.400	2.105	87.7
	4.800	4.121	85.9
	9.600	8.407	87.6
2.4'-DDD	0.300	0.261	87.1
	0.600	0.543	90.6
	1.200	1.070	89.1
	2.400	2.071	86.3
	4.800	4.450	92.7
	9.600	8.270	86.1
Chlorfenapyr	0.100	0.074	73.6
	0.200	0.192	96.1
	0.400	0.350	87.6
	0.800	0.693	86.6
	1.600	1.426	89.1
	3.200	2.757	86.1
4.4'-DDD	0.200	0.159	79.6
	0.400	0.370	92.4
	0.800	0.769	96.1
	1.600	1.378	86.1
	3.200	2.647	82.7
	6.400	5.705	89.1

Table 5 Liquid-Liquid extraction process
(Continue)

Pesticide	STD %	LOD _{Cal} µg L ⁻¹	LOD _{Exp} µg L ⁻¹
Bromophos-methyl	7.1	0.441	0.299
	3.9		
	8.5		
	7.7		
	8.9		
	10.9		
Bromophos-ethyl	9.8	0.339	0.315
	9.2		
	6.6		
	9.2		
	12.0		
	11.5		
o.p'-DDE	4.0	0.170	0.412
	5.1		
	9.2		
	3.9		
	11.6		
	9.2		
4.4'-DDE	4.8	0.180	0.309
	3.9		
	8.5		
	7.7		
	12.0		
	11.6		
2.4'-DDD	7.7	0.259	0.322
	6.9		
	9.7		
	12.2		
	9.2		
	7.4		
Chlorfenapyr	13.7	0.238	0.104
	7.9		
	11.6		
	10.9		
	9.9		
	7.4		
4.4'-DDD	10.2	0.340	0.208
	5.1		
	7.9		
	7.4		
	3.9		
	9.7		

Table.3 displays the significant differences between LOD_{Exp.} and LOD_{Cal} when they were compared proportionally, varying from 0.3 to 3.2. While the LOD_{Exp.} / LOD_{Cal} ratios for a

group of pesticides that included *Bromophos-ethyl* and *2.4'-DDD* were calculated to be around 1 ± 0.2 , the ratios shifted from 0.3 to 0.7 for *4.4'-DDD*, *Chlorfenapyr* and *Bromophos-methyl*. For the pesticides *4.4'-DDE* and *o.p'-DDE*, on the other hand, it was seen that the relevant ratio altered from 1.7 to 3.2.

The calculated LOD_{exp} and LOD_{cal} were tested experimentally. Table 2 showed that LOD_{exp} and LOD_{cal} varied correspondingly from 0.104 to 0.412 µg L⁻¹ and from 0.170 to 0.441 µg L⁻¹ for all the analyzed analyte or compounds. These values are either in the same order, Tankiewicz et al., (2013) (0.015-0.13 for LOD [41], or better than those obtained by other researchers such as Filho et al., (2010) (0.02-0.3 µg L⁻¹ for LOD) [42], Lafuente et al., (2016) (0.05-1 µg L⁻¹ for LOD) [43].

The linearity of extraction methods on recovery value corresponding to each pesticide spike level was also investigated. The slope of the line in the graph for each pesticide plotted either as a percentage of recovery or as a level of spike pesticides represents the average recovery (*Rave*) in the range of spike levels (Table 5) [39-40]. Table 5 shows that with *2.4'-DDD* and *Bromophos-methyl*, *Rave* values increased from 0.785 (78.5%) to 1.056 (105.6%). According to Table.5, the extraction method recoveries for *Bromophos-ethyl* were approximately 100%, while the other recoveries were approximately 80%.

For the relative recoveries, known concentrations of the pesticides studied were added to ultrapure water and the results were compared and evaluated. Approximately the same recoveries were obtained at the same concentrations. The recoveries ranged from 82.1 % to 90.1% at 0.300 µg L⁻¹ and from 86.1% to 94.1% at 9.600 µg L⁻¹ demonstrating the suitability of the method used [44].

By using various extraction techniques, several researchers have extracted pesticides

from diverse matrixes, such as vegetables [27-45]. When their recovery results were compared to ours, which involved recovering pesticides from vegetables using water, it was discovered that some pesticides recovered from water were more effective than those recovered from vegetables. According to research done with the same matrix and a variety of pesticide solvent combinations, the results were nearly identical.

Using quadrupole mass spectrometry (qMS) and high resolution time-of-flight mass spectrometry, Hayward et al. [46] reported recovering certain pesticides from *Ginseng Root* for three concentration levels in 2009 (TOF). For each pesticide, the average recovery results indicated by slope could be derived when their results were plotted as recovery values vs spike levels. Due to their

hydrophobic nature, pesticides are more appealing to plants or other matrixes than water. As a result, these pesticides typically have better recovery values from water than they did in their original formulations.

This section compares the recovery levels of pesticides at the lowest and greatest spike levels. Figure 1 shows the graphs of pesticides. While certain chemicals showed no improvement, the spike levels changed from the lowest to the highest and the recovery % of the pesticides improved. The improvement values for the pesticides of *Bromophos-ethyl*, *chlorfenapyr* and *4,4'-DDD*, respectively, were 12.9%, 12.5%, and 9.5%, while the improvement values for the other pesticides examined were smaller.

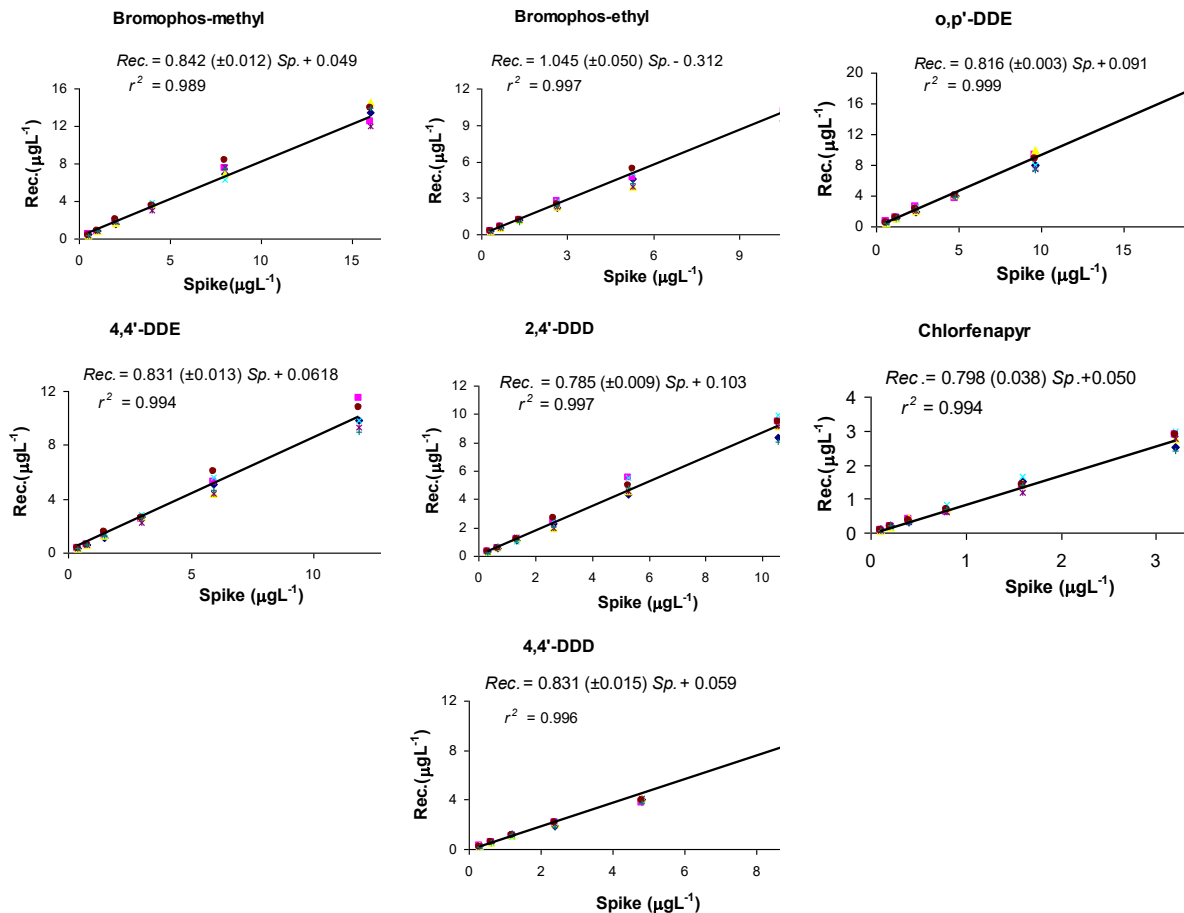


Figure 1 Graphical representation of linearity for pesticides

5. CONCLUSION

This study's objective was to extract organochlorinated pesticides from water using a solvent mixture (hexane: dichloromethane) and determine how much of them were present by utilizing a GC-MS system with the Electron Ionization (EI) and Selective Ion Monitoring (SIM) methods. Seven pesticides were successfully analyzed in 20 minutes, according to the results. The recovery ratios of the spike levels were seen to alter by 73.6% and 96.1%, respectively. For *Chlorfenapyr*, the lowest recovery value was found to be 73.6% at 0.100 µg/L. For the same insecticide, the greatest recovery value was recorded at 114.0% at 1.600 µg/L. When the recovery rates of pesticides with just a benzene ring were evaluated, it was found that *bromophos-ethyl* was followed by *bromophos-methyl* and then *chlorfenapyr*. On the other hand, the sequence 4.4'-DDE > 4.4'-DDD > *o.p'*-DDE > *Chlorfenapyr* > 2.4'-DDD was observed when the recovery efficiencies of pesticides containing double benzene rings were compared.

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Authors' Contribution

The authors contributed equally to the study.

The Declaration of Conflict of Interest/ Common Interest

No conflict of interest or common interest has been declared by the authors.

The Declaration of Ethics Committee Approval

This study does not require ethics committee permission or any special permission.

The Declaration of Research and Publication Ethics

The authors of the paper declare that they comply with the scientific, ethical and quotation rules of SAUJS in all processes of

the paper and that they do not make any falsification on the data collected. In addition, they declare that Sakarya University Journal of Science and its editorial board have no responsibility for any ethical violations that may be encountered, and that this study has not been evaluated in any academic publication environment other than Sakarya University Journal of Science.

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