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Research Article

TÜRKİYE EGİRDİR GÖLÜ'NDEKİ ELEMENT, PESTİSİT VE İYON KİRLETİCİLERİNİN TAYİNİ VE METOT VALİDASYONU

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Anahtar Kelimeler

Eğirdir Gölü,
Ağır metaller,
İyonlar,
Pestisitler,
Metot validasyonu.

Öz

Bu çalışmada Isparta/Eğirdir Gölü'nden alınan örneklerinde belirlenen element, iyon ve pestisit konsantrasyonları belirlenmiştir. İlk olarak, numunelerdeki klorpirifos, asetamiprid, methidathion, cyprodinil ve pyridaben pestisit kalıntıları (toplam 322 pestisit), iyonlar (toplam 12 anyon/katyon) ve elementlerin (toplam 17 element) tayini için analitik bir yöntem valide edilmiştir. Doğrusallık, tespit ve niceleme sınırı, seçicilik, geri kazanım (%) gibi çalışmanın validasyon parametreleri belirlendi. Metal miktarları, indüktif olarak eşleştirilmiş plazma kütle spektrometrisi (ICP-MS) ile tayin edildi. Arsenik, baryum, krom, bakır, demir, mangan, nikel, kurşun, stronsiyum, vanadyum ve çinko farklı konsantrasyonlarda belirlenmiş, ancak gümüş, berilyum, kadmiyum, kobalt, talyum ve antimon miktarları belirlenlenememiştir. İyon konsantrasyonları, iyon kromatografisi (IC) ile tayin edildi. Bu deneylerin sonuçlarına göre lityum, nitrat ve fosfat iyonlarının miktarları numunelerde tespit sınırının altındaydı. Aynı numunelerdeki pestisitlerin tayini, sıvı kromatografi-tandem kütle spektrometrisi'nde (LC-MS/MS) gerçekleştirilmiştir. Elde edilen sonuçlar tartışıldı.

ELEMENT, PESTICIDE AND ION POLLUTANTS DETERMINATION AND METHOD VALIDATION IN EGİRDİR LAKE/TURKEY

Keywords

Egirdir Lake,
Heavy metals,
Ions,
Pesticides,
Method validation.

Abstract

In this study, the concentrations of elements, ions and pesticides were determined in the samples collected from the Isparta/Egirdir Lake. Firstly, it was validated an analytical method for determination of chlorpyrifos, acetamiprid, methidathion, cyprodinil and pyridaben pesticide residues (total 322 pesticides), ions (total 12 anions/cations) and elements (total 17 elements) in samples. The validation parameters such as linearity, the limit of detection and quantification, selectivity, recovery (%) of the method were determined. The amounts of metal were determined by inductively coupled plasma mass spectrometry (ICP-MS). Arsenic, barium, chromium, copper, iron, manganese, nickel, lead, strontium, vanadium and zinc were determined in different concentrations, but silver, beryllium, cadmium, cobalt, thallium and antimony amounts were not determined. The concentrations of ions were assigned by the ion chromatography (IC). According to the results of these experiments the quantities of lithium, nitrate and phosphate ipns were below the limit of detections in samples. Determination of the pesticides in the same samples was performed on the liquid chromatography-tandem mass spectrometry (LC-MS/MS). The obtained results were discussed.

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ELEMENT, PESTICIDE AND ION POLLUTANTS DETERMINATION AND METHOD VALIDATION IN EGİRDİR LAKE/TURKEY

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Highlights

- With the use of an efficient sample preparation technique, it is possible to identify elements, ions, and pesticides that are present surface water in low amounts.
- Elements results can be determined by method validation studies using ICP-MS.
- Ion amounts can be determined by method validation studies using IC.
- Pesticites can be determined by method validation studies using LC-MS/MS.

Graphical Abstract

Figure. Pollution Sources

Purpose and Scope
In this study was aimed on the pretreatment methods used for the preparation of measurement samples of lake water containing the amounts of macro elements, pesticides and anion/cations for detection using ICP-MS, LC-MS/MS and IC instrumentations.

Design/methodology/approach
The possibility of traffic and human-induced pollution in Lake Eğirdir has been investigated. Element, ion and pesticide amounts in the water and sediment samples taken from the lake were determined by the validated analytical method.

Findings
In this study, an analytical method was validated to determine the pesticide residues, ions and elements of in the samples of Egirdir Lake. The linearity, limits of detection and quantification, recovery, trueness and precision were calculated.

Practical implications
The results obtained from this study show the analytical procedure will administer the validation parameters which need to be valued.

Social Implications
This study will highlight the importance of analytical methods.

Originality
With monitoring studies, heavy metals, ions and pesticides in water resources are the first step in determining how the pollution will be managed before it reaches the source to reveal the pollution and how to control this pollution.

1. Introduction

The need to prevent pollution of water resources comes to the fore more depending on the increasing water demand and the importance of water (Hussain et al., 2019). While the amount of heavy metals contained in surface waters was measured in previous years, compounds such as pesticides and other chemicals are being measured in today studies (Kümmerer et al., 2019; Li et al. 2019). As the lakes are more stable than rivers, pollution accumulation in the lake sediments is constantly increasing in studies (Pastorino et al., 2020). Especially the water management implemented by developed countries such as the European Union Water Framework Directive and Environmental Protection Agency has revealed a much more comprehensive application (Akinsete et al., 2019; Carvalho et al., 2019; Laskowski, 2019; Moustaka-Gouni et al., 2019). In this process, the steps of protecting, using and managing both surface and groundwater resources are examined and implemented in detail (Merga et al., 2020; Ondoo et al., 2019; Rowden et al., 2019; Şehnaz et al., 2019; Zhang et al. 2019). One of the most important steps of this water management is the continuous monitoring of the water content of the Target Lake or river (Ccanccapa-Cartagena et al., 2019; Dickens et al., 2019). One of these monitoring is chemical monitoring, and chemical parameters such as heavy metals, pesticides, and another pollution are measured at certain times (Altenburger et al., 2019; Christophoridis et al., 2020; Pastorino et al., 2020).

Contamination can become through atmospheric, geological, the discharge of agricultural, domestic, and industrial wastes in the environmental (Chowdhury et al., 2016; Sheikh et al., 2014; Sibal and Espino, 2018; Zhou et al., 2020). With atmospheric transport, rainwater can carry pollution. There may be pollution by local and remote transports (Berberler et al., 2022). An effective sample preparation step is required for compounds in water samples (Faraji et al., 2019; Hashemi et al., 2018). Therefore, analyzes of water require large sample volumes, which avoids selective removal of targets. As a result, chromatographic quantification may be inaccurate due to repression or amplification of the analyte signal in the chromatogram (Andrade-Eiroa et al., 2016; Faraji et al., 2019; Madikizela et al., 2019; Perin et al., 2021). In order to reach reliable results, validation studies have been carried out for all pre-preparation processes and method parameters. This issue is actually of great importance. Contamination in such matrices as sea, lake and rainwater is a frequently encountered situation especially in element determinations. All parameters should be supported by method validation studies to avoid such a situation in the study (Aceña et al., 2015; Bade et al., 2016).

To determine the risk that medications and pesticides represent to the environment and to human health, data collection and reporting on their presence are essential (Perin et al.,2021). According to several studies of the literature, the existence of micro pollutants as well as organic and chemical substances is quite concerning for the ecosystem. Personal care products, medications, illegal substances, microplastics, and pesticides have all been extensively studied (Fang et al., 2017; Lin et al., 2018; Niemeyer et al., 2017; Nurmi and Pellinen, 2011; Wöhler et al., 2020; Zhang et al., 2016).Since pharmaceuticals have been commonly found in surface water in amounts ranging from ng L1 to g L1 globally (Balakrishna et al., 2017; Bu et al., 2013; Sui et al., 2015), it is well acknowledged that urban effluents are contaminating the aquatic environment. Due to their potential toxicity and accumulation, elements (metals) at the trace-level analysis pose a problem in aquatic habitats (Kumar et al., 2019; Wallace and Buha Djordjevic, 2020).

Various heavy metals are reported to be mixed into the soil through sewage, irrigation, fertilizer application, and waste disposal as a result of increased industrial and urbanization activities (Guan et al. 2017). According to Yang et al. (2018), agricultural pollution is the main anthropogenic source of heavy metals in the soil. Cao et al. (2015) claim that contamination can pose serious dangers to human health due to its ability to bioaccumulate in animals and enrich the soil through the soil plant system.

This study aimes on the pretreatment methods used for the preparation of measurement samples of lake water containing the amounts of macro elements, pesticides and anion/cations for detection using ICP-MS, LC-MS/MS and IC instrumentations. For this purpose, it has been determination of chlorpyrifos, acetamiprid, methyladyon, cyprodinil and pyridaben pesticide residues, ions and elements with valitated analytical method in the Egirdir Lake samples. The analytical procedure objective should be clearly understood because this will administer the validation parameters which need to be valued. It is hoped that the findings obtained from the method validation studies obtained from this study will make various contributions to other literatures.

2. Material and Method

2.1. Chemicals and Equipments

Calibration standard (10 mg L^{-1}) of elements was purchased from Perkin Elmer (USA), the SPS-SW2 Surface Water reference material from LGC (Norway), respectively. Suprapur® 65% HNO_3 was supplied from Merck (Germany), filter paper (0.45 µm) from Sartorius (Germany). Sample collection bottles were obtained from Isolab (Turkey). Deionized water (Millipore® system, Bedford, USA)used to treated to remove all ions . Analytical standards were prepared from Dionex Seven Anion, Six Cation-I Cation standard (USA). As eluent, 35mM MSA (methanesulfonic acid, Sigma-Aldrich) and KOH (Sigma-Aldrich) were used for ion analysis. The pesticide standards were supplied by the purity approved from Dr. Ehrenstorfer (Germany). Mobil Phase A (1 mL formic acid + 4 mM ammonium formate in % 95-5 water-methanol) and Mobil Phase B (1 mL formic acid +4 mM ammonium formate in % 5-95 water-methanol) was used. Methanol (Merck), ammonium formate (Sigma-Aldrich), and formic acid (Sigma-Aldrich) were the organic solvents used in the study. Acetonitrile (Merck, HPLC grade), toluen (Merck, HPLC reagent grade), aceton (Merck, HPLC reagent grade), glacial acetic acid (Merck, HPLC reagent grade), $MgSO_4$ (Sigma-Aldrich, anhydrous, reagent grade >%97) were some solvents used throughout the research.

2.2. Study Area

The location of the sampling points of study area is in Egirdir Lake, Turkey (Figure 1). 5 water (W) and 4 sediment (S) samples were taken from 5 different sampling points from Lake. 1st 2nd and 3 th sampling points are especially selected to the study places where there are more residential areas, besides that agricultural pollution is very intense at 4th and 5th sampling points. Egirdir Lake is one of the most important water sources of Turkey both a source of drinking water and an agricultural applications and other purposes such as tourism. But domestic and agricultural pollution is another serious problem in that area. Egirdir Lake was preferred as study area. Because the presence of micro-pollutants and the increase of naturally occurring compounds is a major environmental problem.

2.3. Analytical Devices and Sample Preparation

2.3.1. ICP-MS

ICP-MS system (Perkin Elmer ELAN DRC-e) was used as simultaneous multi-element determined of ^{107}Ag,^{75}As, ^{137}Ba, ^{9}Be,^{111}Cd, ^{59}Co,^{52} Cr, ^{63}Cu, ^{57}Fe, ^{55}Mn, ^{60}Ni, ^{208}Pb, ^{121}Sb, ^{88}Sr, ^{205}Tl, ^{51}V and ^{66}Zn. The ICP-MS conditions are shown in Table 1 (Cengiz et al., 2017). Perkin Elmer Elan DRC-e model ICP-MS device was used to obtain fast and reliable results since the concentrations of the elements to be detected in drinking and utility water samples are considered in the low-high dynamic range. The Elan DRC-e model ICPMS (Perkin Elmer SCIEX, Norwalk, CT, ABD) equipment was utilized because of the low and high concentrations of the elements that needed to be detected in the lake water content. Because both concentration levels will yield quick and trustworthy findings (Alastuey et al., 1999; Norela et al., 2013; Pu et al., 2017). To measure the element concentrations in lake water samples, the EPA Method 6020-A analysis method was used.

Table 1. ICP-MS operating terms

Spectrometer	Elan DRC-e (Perkin Elmer SCIEX, Norwalk, CT, USA)
Sample Introduction	Scott Spray Chamber
RF Power	1000
Skimmer/Sampler Cone	Nickel
Gas flow rates (L min^{-1})	Nebulizer gas flow: 0.91, Auxillary gas flow:1.19, Plasma gas flow:18
Nebulizer	Meinhard TQ plus Quartz 0.5 ml
Scannig mode	Peak hopping
Analytical masses (amu)	Standart mode ^{107}Ag,^{75}As, ^{137}Ba, ^{9}Be,^{111}Cd, ^{59}Co,^{52} Cr, ^{63}Cu, ^{57}Fe, ^{55}Mn, ^{60}Ni, ^{208}Pb, ^{121}Sb, ^{88}Sr, ^{205}Tl, ^{51}V and ^{66}Zn
Number of sweeps/reading	20
Number of readings/replicate	1
Number of replicates	3
Auto sampler	CETAX ASX-520
Dwell time per AMU (ms)	50
Sample flush	Time (50), speed (+/- rpm)-48
Read delay	Time (15), speed (+/- rpm)-20

2.3.2. Sample preparation for elemental analysis

In this research, five different locations were collected from Egirdir Lake. Samples were sent to the laboratory by cold chain using 1000 mL sample collection bottle. For these, samples were collected in 1 liter bottles. Then 100 mL samples were filtered through 0.45 µm filters and they were acidified with 3 mL HNO_3 , 2 mL HCl, and 0.5 mL HF. As a result of acidification in water samples, pH < 2 was ensured. It was evaporated at a temperature of 70-80 degrees until 5-6 mL of solution remained in the water bath. The same acidification procedure was repeated a second time and evaporated until 5-6 mL of liquid remained. The final volume was brought to 15 mL with 18.2 mΩ distilled water. Concentration calculations were made by considering the initial sample volume (100 mL) and the final volume (15 mL) while making the calculation (Kılıç et al. 2015). Each sediment sample was collected approximately 15-20 cm below the surface using a shovel. The part in contact with the metal of the shovel used for sediment samples was removed. Weeds, gravel and other debris were removed from the sediment samples whenever possible. Each sample was used as approximately 100 g. It was then ground to pass through the sieve and stored for analysis. ETHOS One Microwave Digestion System (Milestone Inc. Italy) branded device was used for the sample digestions. The final volumes of the digested samples were completed to 15 mL with 18.2 mΩ pure water. Triplicate samples were collected from each sampling site, and elemental concentrations were determined for each sample in triplicate using the ICP-MS instrument. The average results were given by using the dilution coefficient of the obtained data. The microwave temperature program was linearly increased from room temperature to 180 °C in 5 minutes, and in the second step the temperature was increased to 220 °C linearly in 25 minutes (Kilic and Pamukoglu, 2023).

2.3.3. IC

Ion Chromatography (DIONEX ICS-5000 Anion-Cation System) is dual system that was used both anion (F^-, NO_2^-, Cl-, NO_3^-, SO_4^{-2}, PO_4^{-3}) and cation (Ca^{+2}, Na^+, Mg^{+2}, NH_4^+, K^+, Li^+) analysis. The ICS-5000 conditions were given Table 2.

Table 2. ICS-5000 operating terms

Anions		
Columns	Analytic, IonPac AS19 (250x2 mm); Guard, IonPac AG19 (50x2 mm)	
Column temperature	40 °C	
Flow	0.3 mL/min	
Injection volume	500 µL	
Detector	Suppressed Conductivity Anion Self-Regenerating Suppressor, ASRS 300(2-mm) AutoSuppression Recycle Mode Suppressor Current 34 mA	
Eluent	Potassium hydroxide	
Gradient Program	Time (min.)	KOH (mM)
	0	10
	10	10
	25	45
	26.1	10
	31.0	10
Cations		
Columns	Analytic, IonPac CS16 (250*3 mm); Guard, IonPac CG16 (50*3mm)	
Column temperature	40 °C	
Flow	0.4 mL/min.	
Injection volume	25 µL	
Detector	Suppressed Conductivity Cation Self-Regenerating Suppressor, CSRS 300(2-mm) Auto Suppression Recycle Mode Suppressor Current 41 mA	
Eluent	Methane Sulfonic Acid (MSA) Eluent Generator Concentration: 35 mM MSA (Isocratic)	

In containers that were tightly sealed, all solutions were stored at 4 °C. The eluent flowed at a rate of 1.0 mL/min. Thermo Scientific, Waltham, Massachusetts, USA) Dionex ICS-5000 ion chromatograph, which has a dual-piston pump, two valves (a six-port valve and a ten-port valve, of which I only utilized the six-port valve), and a 25 L sample loop, was used to do the cation separation. Under the working conditions, all anions and cations were entirely separated, and the entire analysis took 30 minutes. Anions and cations in samples were identified by comparing their retention times to those of commercially available standards.Calibration points prepared using redox 104 anion and 238 cation standards are shown in Tables 3 and 4 (Kilic and Pamukoğlu.2023).

Table 3. The calibration standards 1 (mg L^{-1})

PO$_4^{3-}$	**Cl$^-$**	**NO$_3^-$**	**NO$_2^-$**	**SO$_4^{2-}$**	**F$^-$**
200	100	100	100	100	20
PO$_4^{-3}$	**Cl$^-$**	**NO$_3^-$**	**NO$_2^-$**	**SO$_4^{2-}$**	**F$^-$**
0.2	0.1	0.1	0.1	0.1	0.02
0.4	0.2	0.2	0.2	0.2	0.04
0.8	0.4	0.4	0.4	0.4	0.08
2	1	1	1	1	0.2
4	2	2	2	2	0.4
10	5	5	5	5	1

Table 4. The calibration standards 2 (mg L^{-1})

Ca^{2+}	**K$^+$**	**NH$_4^+$**	**Mg^{2+}**	**Na$^+$**
500	500	250	250	200
Ca^{2+}	**K$^+$**	**NH$_4^+$**	**Mg^{2+}**	**Na$^+$**
0.5	0.5	0.25	0.25	0.2
1	1	0.5	0.5	0.4
2	2	1	1	0.8
5	5	2.5	2.5	2
10	10	5	5	4

2.3.4. Sample preparation for ion analysis

Transported to the lab and stored there in the refrigerator were the collected samples. Each lake water sample contained 100 mL, which was filtered using a 0.22 m cellulose acetate filter syringe. There was no preliminary work completed for sample preparation. Only samples were put into the vials for the ion chromatography. Utilizing a Dionex ICS 5000 model ion chromatography apparatus, the anion and cation were examined. Anions (F$^-$, Br$^-$, NO$_2^-$, Cl$^-$, NO$_3^-$, SO$_4^{2-}$, PO$_4^{3-}$) and cations (**Ca^{2+}**, Na$^+$, Mg^{2+}, NH$_4^+$, **K$^+$**) were measured in the samples. Ion Pac AS19 (250x2 mm) was the analytical column utilized for the anion measurements, while Ion Pac AG19 (50x2 mm) was the guard column. The matching columns for the cations were Ion Pac CS16 (250x3 mm) and Ion Pac CG16 (50x3 mm). Methane sulfonic acid and potassium hydroxide (KOH) were used as the eluents for the measurements of cations and anions, respectively. The instrumental conditions are listed in Table 2 (Perin et al., 2021; Kilic et al., 2023).

2.3.5. LC-MS/MS

A Thermo Scientific TSQ Fortis UHPLC-MS/MS system was used in research for pesticide analysis. Thermo Scientific Hypersil Gold RP C18 Column (100mm x 2.1mm, particle size: 1.9 micron) was used to remove other non-polar interferences. Mobil Phase A (1 mL Formic Acid + 4 mM Ammonium Formate in % 95-5 Water-Methanol) and Mobil Phase B (1 mL Formic acid +4 mM Ammonium formate in % 5-95 water-methanol) was used. Operating conditions were as follows: column oven temperature: 40 °C; capillary temperature: 270 °C; evaporation temperature: 50 °C; sheath gas pressure (Arb): 50; auxiliary gas pressure (Arb): 20; spray Voltage (V): ± 3500; injection: 10 µL. The LC-MS/MS status was given in Table 5 and instrument parameters of the detected pesticides was given in Table 6.

Table 5. The LC-MS/MS operating terms

Time	**Mobil Phase A%**	**Mobil Phase B%**	**Flow (µL min^{-1})**
0.00	90	10	600
0.30	85	15	600
2.20	80	20	600
3.00	70	30	200
4.00	50	50	250
8.00	40	60	300
11.00	35	65	300
12.00	25	75	300
13.00	15	85	300
14.50	0	100	300
15.80	90	10	300

Table 6. Instrument parameters of the detected pesticides

Pesticide	Polarity	Precursor ion	Product ions	Collision energies
Acetamiprid	Positive	223.2	126.1 / 99.1	-15 / -22
Chlorpyrifos	Positive	350.1	198.1 / 97.1	-15 / -25
Cyprodinil	Positive	226.1	209.1 / 133.1	-25 / -30
Methidathion	Positive	303.0	85.0 / 145.0	-10 / -18
Pyridaben	Positive	365.1	309.1 / 311.1	-12 / -20

2.3.6. Sample preparation for pesticide analysis

QuEChERS (Quick-Easy-Cheap-Effective-Rugged-Safe) extraction method was used for the determination of pesticide residues (Lehotay, 2007). Homogenized water samples were weighed as 15 gram in a 50 mL teflon (FEP) tube and homogenized soil sampleswere weighed also as 15 gram and added 12 mL water to soil samples for working of QuEChERS method. Onto 15 mL of 1% acetic acid containing acetonitrile (ACN) was added. After adding acetonitrile, 1.5 g anhydrous sodium acetate (NaAc) + 6 g anhydrous magnesium sulfate ($MgSO_4$) mixture and 300 µl standard were added. It could not be rinsed by hand for 1.5 minutes. It was centrifuged for 5 minutes at 4000 rpm. After the extract was transferred to the tubes, 200 mg of primary secondary amine (PSA) + 600 mg of anhydrous magnesium sulfate ($MgSO_4$) was added and mixed for the cleanup process. It was centrifuged again at 4000 rpm for 5 minutes. 1 mL extract was taken into vials and LC-MS/MS analysis was performed (Nagel, 2009; Ruiz-Gil et al., 2008; USEPA, 2007b).

2.3.7. Method validation studies

Experimental demonstration of the suitability of an analytical method is important in the practice of analytical measurement. These several analytical measurements parameters were evaluated for linear range, recovery, limit of detection (LOD), and limit of quantification (LOQ), accuracy, and precision. The quantification was done by using a calibration curve for each. This analytical method validation was made according to Eurachem guide (Eurachem, 2014).

3. Result and Discussion

3.1. Analytical Method Study Results

The coefficient (R^2) more than 0.9992 was obtained for all elements. LOD is the minimum concentration of analyte in a sample. LOQ is the minimum concentration that can be determined with an admissible level of repeatability and accuracy. The LOD, LOQ data for elements were shown in Table 7 (Kılıç et al., 2015).

Table 7. Analytical method results of the elements

Elements	Regressione equation	R^2	LOD (µg L^{-1})	LOQ (µg L^{-1})
Ag	y = 9228x + 2911	0.9996	0.2	0.6
As	y = 1672.9x + 113.01	0.9997	0.3	1.1
Ba	y = 17384x + 12917	0.9998	0.7	2.5
Be	y = 395.3x + 55.11	0.9995	0.2	0.7
Cd	y = 1927.6x + 295.63	0.9997	0.1	0.2
Co	y = 11598x + 4197.7	0.9993	0.1	0.3
Cr	y = 8786.3x + 1995	0.9994	0.1	0.3
Cu	y = 8829.3x + 4912.5	0.9992	0.1	0.4
Ni	y = 2676.3x + 603.46	0.9996	0.6	1.9
Fe	y = 271.18x + 292.86	0.9994	3.2	10.5
Mn	y = 12092x + 2596.3	0.9994	0.1	0.5
Pb	y = 11443x + 4007.9	0.9994	0.2	0.6
Sb	y = 5414.x + 1144	0.9997	0.1	0.4
Sr	y = 15783x - 6211.1	0.9996	0.7	2.3
Tl	y = 17025x - 6069.9	0.9998	0.1	0.2
V	y = 9966.9x + 2158.4	0.9993	0.1	0.4
Zn	y = 1731x - 2667.4	0.9998	0.6	1.9

The recovery was made using with SPS-SW2 Surface Water certified reference material for elements (Table 8). For recovery analysis were spiked (Lake water) with the minimum (4.0 µg L⁻¹), middle (40 µg L⁻¹), and maximum (80 µgL⁻¹) concentrations and then analyzed. The results were set between 99 and 107% for 4.0 µg L⁻¹, 99 and 103% for 40 µgL⁻¹, and 99 and 101% for 80 µgL⁻¹. The specificity/selectivity of the method was in an acceptable range of 80-120% (Millour et al. 2011). The average RSD % values was found between 0.1 and 2.3. The mean data was given in Table 9.

Table 8. The recovery values of elemental analysis

Elements	**(SPS-SW2 Surface Water) (N=7) Real Value (µg L−1±SD) (N=7)**	**(SPS-SW2 Surface Water) (N=7)Measured (µg L−1±SD) (N=7)**	**Recovery values (SPS-SW2 Surface Water) (N=7)**
Ag	Not available in CRM	-	-
As	50±0.3	50.88±0.11	102±0.2
Ba	250 ± 1	251.01± 0.25	100±0.1
Be	Not available in CRM	-	-
Cd	2.50 ± 0.02	2.52 ± 0.02	101±0.7
Co	10.0 ± 0.05	10.19 ± 0.03	102±0.3
Cr	10.0 ± 0.05	10.03 ± 0.03	101±0.3
Cu	100 ± 1	104.61 ± 0.34	104±0.3
Ni	50.0 ± 0.3	50.85 ± 0.19	102±0.4
Fe	100 ± 1	100.11± 1.05	100±1.0
Mn	50.0 ± 0.3	51.27± 0.05	103±0.1
Pb	25.0 ± 0.1	25.89 ± 0.06	103±0.2
Sb	Not available in CRM	-	-
Sr	250 ± 1	250.16 ± 0.23	100±0.1
Tl	2.50 ± 0.02	2.47± 0.02	99±0.9
V	50.0 ± 0.3	49.99 ± 0.04	100±0.1
Zn	100 ± 2	99.66 ± 0.19	99±0.2

Table 9. Recovery values (%) and average precision values (RSD %) of elements in spiked samples**.**

Elements	**Recovery values (4 µg L⁻¹) (N=7)**	**Recovery values (40µg L⁻¹) (N=7)**	**Recovery values (80 µg L⁻¹) (N=7)**	**Precision values (RSD)**
Ag	101±0.05	102±0.04	101±0.04	0.1
As	101±0.5	102±0.6	101±0.2	0.2
Ba	103±0.9	103±0.1	99.0±0.2	0.4
Be	99±1.8	101±1.7	100±0.7	0.6
Cd	102±0.5	100±0.5	100±0.3	0.2
Co	102±0.7	103±0.7	101±0.1	0.5
Cr	103±1.2	99.0±0.1	101±0.3	0.5
Cu	105±0.9	100±0.1	100±0.1	0.5
Ni	103±1.4	99.1±0.4	99.0±0.3	0.7
Fe	-	100±3.4	100±1.3	2.3
Mn	107±0.6	103±0.1	101±0.1	0.2
Pb	104±1.3	99.0±0.1	99.0±0.1	0.5
Sb	103±1.0	100±0.1	99.1±0.2	0.5
Sr	104±0.6	100±0.1	101±0.3	0.3
Tl	99±0.5	103±0.1	99.0±0.3	0.2
V	101±1.1	100±0.1	101±0.6	0.5
Zn	-	103±0.7	99.0±0.3	0.8

The LODs for the ions were from 0.01 to 0.3 mg L⁻¹. In the study, RSD values were in the acceptable limit of 5 %. The linearity was appraised in the range of 0–200 µg kg⁻¹. R^2 coefficient more than 0.996 were obtained for anion/cations (Table 10). Recovery studies with seven replicates were performed for each concentration and results shown in Table 11. The concentration ranges of all ions were similar to the literature values (Kilic and Pamukoğlu, 2023).

Table 10. Method validation results of the ions

Cation/anion	**%RSD**	**LOD** (mg L^{-1})	**LOQ** (mg L^{-1})
K^+	2.9	0.1	0.3
Ca^{2+}	3.3	0.3	1.0
NH_4^+	5.0	0.05	0.2
Mg^{2+}	2.7	0.3	1.0
Na^+	3.5	0.2	0.8
Li^+	1.4	0.01	0.03
F^-	3.0	0.01	0.03
Cl^-	2.0	0.3	1.0
NO_2^-	3.5	0.02	0.1
NO_3^-	2.5	0.2	1.0
SO_4^{2-}	2.0	0.08	0.3
PO_4^{3-}	2.0	0.06	0.2

Table 11. Recovery values for anion/cation

Anion/Cation	**Recovery**	**Recovery ±SD (N=7)**	**Recovery**	**Recovery ±SD (N=7)**
F^-	0.2 (mg L^{-1})	102.02±0.021	0.4 (mg L^{-1})	98.92±0.001
Cl^-	1.0 (mg L^{-1})	100.37±0.011	2.0 (mg L^{-1})	101.77±0.018
NO_2^-	1.0 (mg L^{-1})	101.08±0.019	2.0 (mg L^{-1})	98.36±0.015
NO_3^-	1.0 (mg L^{-1})	101.38±0.054	2.0 (mg L^{-1})	105.23±0.13
SO_4^{2-}	1.0 (mg L^{-1})	98.63±0.012	2.0 (mg L^{-1})	101.37±0.061
Li^+	0.8(mg L^{-1})	103.81±0.015	4.0 (mg L^{-1})	100.01±0.034
Na^+	0.8(mg L^{-1})	103.53±0.005	4.0 (mg L^{-1})	102.63±0.199
NH_4^+	1.0 (mg L^{-1})	103.35±0.023	5.0 (mg L^{-1})	103.73±0.215
K^+	2.0 (mg L^{-1})	100.33±0.06	5.0 (mg L^{-1})	102.42±0.14
Mg^{2+}	1.0 (mg L^{-1})	101.26±0.010	5.0 (mg L^{-1})	101.39±0.151
Ca^{2+}	2.0 (mg L^{-1})	102.68±0.004	5.0 (mg L^{-1})	98.45±0.083

The coefficient of determination, more than 0.996 was detected for pesticides. The LOD, LOQ and R^2 values were shown at Table 12 for all the pesticides. For recovery analysis were spiked with the 10 µg kg^{-1} and 100 µg kg-1 concentrations and analyzed. Recovery results were summarized in Table 13. The average recovery values were acceptable (USEPA, 2007b).

Table 12. Method validation results of the pesticides

Pesticides	**Regressione Equation**	**R^2**	**LOD** (µg kg^{-1})	**LOQ** µg kg^{-1})
Acetamiprid	y = 129219x + 629002	0.996	1.9	5.7
Chlorpyrifos	y = 173257x + 366804	0.998	2.6	7.7
Cyprodinil	y = 91154x + 136489	0.998	2.2	6.6
Methidathion	y = 260048x + 663273	0.998	2.3	6.8
Pyridaben	y = 378447x + 518431	0.999	2.2	6.5

Table 13. %Recovery values for pesticides

Pesticide	**Recovery**	**%Recovery ± %Uncertainty (N=6)**	**Recovery**	**%Recovery ± %Uncertainty (N=6)**
Acetamiprid	10 µg kg^{-1}	79.73±15.94	100 µg kg^{-1}	91.58±20.74
Chlorpyrifos	10 µg kg^{-1}	88.61±19.42	100 µg kg^{-1}	94.82±26,70
Cyprodinil	10 µg kg^{-1}	89.41±16.53	100 µg kg^{-1}	96.75±12.54
Methidathion	10 µg kg^{-1}	97.84±15.06	100 µg kg^{-1}	98.10±15.84
Pyridaben	10 µg kg^{-1}	95.96±15.84	100 µg kg^{-1}	96.13±15.40

3.2. Element Analysis Results

According to the results in Table 14, elements (Ag, Be, Cd, Sb) included those having values less than the limit of detection in water and sediment samples. The concentrations of heavy metals in river water samples were lower than those of the other river water samples (Tauraj , 2015). All Tl concentrations analyzed in the Egirdir Lake water samples are under the limit of detection value. Concentrations of Co were determined to be 943, 1175, 3901 and 6120 μg L^{-1} for sediment sampling points of 1st, 4th, 5th and 3th, respectively, and were found to be <LOD in the water samples. Toxic trace elements including As, and Pb are of great concern, their need careful monitoring. Pb collects in the bodies of water and soil organisms and affects health. However, all samples contained As and Pb at concentrations ranging from 10 to 8900 μg L^{-1}and 1- 5262 μg L^{-1}, respectively. While elemental results were low in samples taken from water sampling points in the lake (As and Pb, approximately 10 μg L^{-1} and 1 μg L^{-1}, respectively), it was observed that the elemental analysis results in sediment were quite high due to accumulation (As and Pb, approximately 8900 μg L^{-1} and 5262 μg L^{-1}, respectively). The results of minor elements were found as Ba (15-269697 μg L^{-1}), Cr (6-16792 μg L^{-1}), Cu (1-6290 μg L^{-1}), Fe (38-8066579 μg L^{-1}), Mn (0.3-174178 μg L^{-1}), Ni (1-26496 μg L^{-1}), Sr (63-42042 μg L^{-1}), V (2-23299 μg L^{-1}) and Zn (1-7040μg L^{-1}). Cr inserts the water, air and soil in the Cr (III) and Cr (VI) forms. The respiratory tract is also the major aim organ for Cr (III) toxicity, similar to Cr (VI). The amounts of Ni in the water of river and lake are very low. After Ni gets into our body, it can insert to all organs. Mn is toxic when high amounts are being found in human body. Fe is the most abundant (34.6%) element making up the Earth. Cu can be released into the environment by natural resources and human. Industrial waste involving metals are the main source of Zn contamination (Lenntech, 2018; Turhan et al., 2021).

Table 14. Composition of samples obtained by ICP-MS (μg L^{-1}±SD) (N=3)

S	Ag	As	Ba	Be	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Sb	Sr	Tl	V	Zn
W1	<LOD	11±0.005	16±0.001	<LOD	<LOD	<LOD	7±0.005	2±0.005	41±0.005	0.3±0.005	7±0.005	2±0.005	<LOD	64±0.001	<LOD	2±0.001	5±0.001
W2	<LOD	10±0.001	18±0.001	<LOD	<LOD	<LOD	7±0.001	3±0.02	66±0.005	1±0.001	3±0.005	4±0.002	<LOD	66±0.004	<LOD	2±0.002	5±0.002
W3	<LOD	10±0.002	86±0.05	<LOD	<LOD	<LOD	8±0.004	3±0.001	81±0.02	3±0.01	1±0.004	1±0.02	<LOD	98±0.003	<LOD	2±0.01	3±0.002
W4	<LOD	12±0.01	16±0.01	<LOD	<LOD	<LOD	7±0.03	3±0.04	46±0.06	1±0.01	2±0.002	1±0.002	<LOD	68±0.01	<LOD	2±0.01	9±0.003
W5	<LOD	12±0.01	15±0.01	<LOD	<LOD	<LOD	7±0.04	1±0.002	40±0.01	0.3±0.003	1±0.02	1±0.03	<LOD	69±0.1	<LOD	2±0.005	1±0.01
S1	<LOD	8900±11	28758±7	<LOD	<LOD	943±2	2597±1	701±1	225099±135	139286±16	3738±11	1772±2	<LOD	79173±14	<LOD	6530±26	1488±3
S2	<LOD	7470±31	12752±28	<LOD	<LOD	1175±1	2371±3	763±1	2611185±162	120049±5	2553±1	1635±1	<LOD	35558±5	<LOD	6775±19	1699±2
S3	<LOD	2268±1	269697±7	<LOD	<LOD	3901±1	9659±1	6552±2	6241772±47	127715±8	12942±5	5262±1	<LOD	71813±4	107±1	25062±4	6359±2
S5	<LOD	2456±1	18324±6	<LOD	<LOD	6120±2	16792±1	6290±3	8066579±34	174178±8	26496±4	2240±1	<LOD	42042±34	44±1	23299±4	7040±2

S4 sample could not be taken

3.3. Ion Analysis Results

According to the results in Table 15, Li^+, NO_3^-, PO_4^{3-} determined those having values less than the limit of detection in samples. K^+, Ca^{2+}, NH_4^+ , Mg^{2+} , Na^+, F^-, Cl^- , NO_2^-, SO_4^{2-} ions were detected in all samples. NH_4^+ is not significantly toxic to aquatic organisms. High Na^+amounts are seen in salty wastewater. The amount of K^+ is also a pollution parameter that can be evaluated in a similar to Na^+. The Cl^- and F^- ions are one of the ions that can be protected during the hydrological cycle in water (Tokalıoglu and Kartal, 2002).

Table 15. Ion amounts in water samples (mg L^{-1}±SD) (N=3)

Samples	K^+	Ca^{2+}	NH_4^+	Mg^{2+}	Na^+	Li^+	F^-	Cl^-	NO_2^-	NO_3^-	SO_4^{2-}	PO_4^{3-}
W1	3.6±0.01	12.8±0.02	0.9±0.02	38.4±0.02	11.7±0.02	<LOD	0.2±0.02	8.6±0.02	0.02±0.01	<LOD	9.9±0.02	<LOD
W2	3.2±0.01	15.9±0.02	0.8±0.02	36.9±0.02	11.3±0.01	<LOD	0.3±0.03	8.2±0.02	0.06±0.02	<LOD	9.5±0.02	<LOD
W3	3.8±0.02	20.9±0.03	0.8±0.02	38.3±0.02	11.8±0.02	<LOD	0.2±0.02	8.9±0.03	0.03±0.01	<LOD	9.4±0.02	<LOD
W4	3.5±0.02	13.5±0.01	0.8±0.02	38.4±0.02	12.2±0.01	<LOD	0.1±0.04	9.1±0.03	0.03±0.01	<LOD	10.2±0.01	<LOD
W5	3.4±0.01	12.8±0.01	0.8±0.02	38.4±0.03	12.8±0.01	<LOD	0.1±0.03	8.9±0.02	0.04±0.02	<LOD	9.9±0.01	<LOD

3.4. Pesticide Analysis Results

322 pesticides compatible with LC-MS/MS were screened. Because detected pesticides are compatible with this device. 322 pesticides were screened and 5 pesticides were detected as a result of this screening. In Table 15, acetamiprid, methidathion, cyprodinil and pyridaben pesticides were included those having values less than the limit of detection in water samples. Chlorpyrifos were measured between 0.01 and 0.06 mg kg^{-1} in all sediment

samples. Chlorpyrifos, acetamiprid, methidathion, cyprodinil, pyridaben pesticide species were detected in all sediment samples at the 5th sampling point where there is a lot of agricultural activity. The concentrations of pesticides in samples were similar than those of the other samples (Fang et al., 2017).

Pesticides with long half-lives reach water resources, harm aquatic creatures, and the use of these waters as a source of drinking water poses a danger to humans. Agriculture Pesticides applied in the fields reach water resources through mechanisms such as precipitation, wind, soil seepage, atmospheric transport.

Table 15. Pesticide residues in samples (mg kg^{-1})

Samples	Chlorpyrifos	Acetamiprid	Methidathion	Cyprodinil	Pyridaben
W1	<LOD	<LOD	<LOD	<LOD	<LOD
W2	<LOD	<LOD	<LOD	<LOD	<LOD
W3	<LOD	<LOD	<LOD	<LOD	<LOD
W4	<LOD	<LOD	<LOD	<LOD	<LOD
W5	<LOD	<LOD	<LOD	<LOD	<LOD
S1	0.06	<LOD	<LOD	<LOD	<LOD
S2	0.01	<LOD	<LOD	<LOD	<LOD
S3	0.04	0.01	0.03	0.01	0.02
S5	0.05	<LOD	0.02	0.01	<LOD

4. Conclusions

In this study, an analytical method was validated to determine the pesticide residues such as chlorpyrifos, acetamipride, methyladione, ciprodinil and pyridaben, ions and elements of in the samples of Egirdir Lake. The linearity, limits of detection and quantification, recovery, trueness and precision were calculated. The accuracy of the method and the spiked performance were considered satisfying. According to the elemental analysis results, Ag, Be, Cd, Tl, Sb was measured at values lower than the detection limit in all water samples. However, As and Pb were detected in all samples at concentrations. In pesticide analyses, acetamiprid, methidathion, cyprodinil and pyridaben pesticides included those with values lower than the detection limit in water samples. Chlorpyrifos were measured between 0.01 and 0.06 mg kg^{-1} in all sediment samples. Chlorpyrifos, acetamiprid, methydation, cyprodinil, pyridaben pesticide types were detected in all sediment samples due to agricultural activities. According to the ion analysis results, Li^+, NO_3^- and PO_4^{-3} were measured at values lower than the detection limit in all water samples. With monitoring studies, heavy metals, ions and pesticides in water resources are the first step in determining how the pollution will be managed before it reaches the source to reveal the pollution and how to control this pollution.

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Conflict of Interest

The authors have no conflicts of interest to declare.

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