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Original Research

Assessment of Spatial and Temporal Variations in Chemical Parameters of Rainwater in Sivas City Center with Multivariate Statistical Approaches

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Abstract

This study was conducted between September 2023 and August 2024 in order to evaluate the spatial and temporal changes in the chemical parameters of rainwater in Sivas City Center using multivariate statistical approaches. It was determined that the rainwater quality in Sivas City Center was not acidic. In the study conducted, no statistically significant difference was found in terms of stations ($P>0.05$), while statistically significant differences were found in terms of seasons ($P<0.05$). Therefore, it is important to take into account seasonal changes in chemical parameters when determining and implementing managerial strategies for rainwater in Sivas City Center. As a result of examining the principal components and eigenvalues, two factors were formed in the data, and these two factors together explained approximately 70.43% of the total variance. While hierarchical cluster analysis revealed that the winter season differed from the other seasons, it also showed that station-4 was distinct from the other stations. The rainwater parameters analyzed in Sivas City Center exhibited changes at both temporal and spatial scales, and the results of this study can be used to provide important data and information support for sustainable and effective rainwater management, especially for Sivas City Center.

Keywords: rainwater, chemical parameters, multivariate statistical approaches

Introduction

Water is the main source of life, with all its physical and chemical properties. This vital water is delivered to the earth by rain, a form of precipitation. The amount of water on Earth is fixed and circulates with the water cycle [1]. Rain is necessary for agriculture, drinking water, and energy production in many parts of the world. Rain helps plants grow, renew water resources, and increase groundwater levels [2]. In addition to releasing water, which is an indispensable need for living things, rain also has a fertilizing effect [3]. Numerous mineral salts and elements that seeds and plants on earth need to grow reach them with this rainwater. These salts and elements that come down to the soil with rain are examples of traditional fertilizers used to increase productivity. Without rain, very few plants or animals can survive. A long drought without rain causes great damage to crops and animals [4]. In places where rain

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only falls in certain seasons, the absence of rain means hunger and even death.

Today, population growth, unplanned urbanization, and industrial and urban waste make it difficult to reach clean water. In addition, the global precipitation balance is disrupted due to global warming and climate change. While a severe drought occurs in a certain region of the world, floods may follow severe hurricanes and storms in another region, and extreme temperatures and fires may occur in another. This situation explains the disruption in natural water cycles. It is estimated that with the change of ecosystems, biodiversity will face the danger of extinction, and more poverty and disease will occur as a result of global problems in food production [5]. In recent years, with the increase in industrialization and human activities, various pollutants have occurred in the environment, and many harmful substances have entered the atmosphere. Toxic gases and other pollutants released from fuels used for heating and motor vehicles reach the atmosphere and fall to the earth with rain. Some of the water that forms oceans, seas, lakes, streams, snow covers, glaciers, and swamps evaporates and mixes into the atmosphere in the form of water vapor and, under certain conditions, condenses and returns to the surface as precipitation. Some of the precipitation that falls to the surface in the form of rain and the water formed by the melting of snow covers and glaciers accumulate in hollow places on the land or flow along the slope of the topographic surface, forming surface waters. The rest of this water seeps underground under suitable conditions and forms groundwater. With this cycle of water, pollutants in the atmosphere are transferred into the soil, plants, and water, posing a threat to life [6]. Rainwater content is a very variable water source. The main pollutants are considered to be organic matter and suspended solids. Factors like the location where rainwater is collected, the season, and the time between two rainfalls affect the quality of rainwater [7]. Factors affecting rainwater quality include air pollution, atmospheric conditions, and the structure of the water retention surface. With the increase in air pollution in areas where industry, urban areas, and transportation activities are intense, pure rainwater is exposed to a variety of pollutants. Rainfalls with a pH lower than 5.6 are called acid rain [8]. In regions with an arid climate, dust and particulate matter in the atmosphere containing alkaline cations increase the pH of rainwater, causing it to move away from its acidic character [9]. Based on this, the geographical location, topographic structures, and seasonal periods of the regions also affect rainwater quality [10]. Rainwater generally attracts attention due to its low pollutant levels [11].

Air pollution occurs when gases or aerosol particles released into the air reach a concentration sufficient to directly or indirectly harm humans, plants, animals, other life forms, ecosystems, structures, or works of art. Gaseous and vaporous pollutants in the air mix with rainwater and soil and water on Earth over time [12]. Pollutants released into the atmosphere by natural or anthropogenic means return to the planet via wet or dry deposition as a result of long-range or short-range transport. Wet deposition mechanisms play a more important role than dry deposition in the transport of many pollutants from the atmosphere to the earth. From this perspective, it is possible to obtain important information about the degree of air pollution in the local atmosphere through chemical analysis of pollutant parameters in wet deposition samples [13]. Therefore, rainwater helps determine the relative contributions of many pollutant parameters in the atmosphere. Rainwater has a very important function in atmospheric cleaning by removing atmospheric gases and aerosols. This important function can also cause pollutants and nutrients to reach terrestrial and aquatic ecosystems from the atmosphere. Pollutants and nutrients in rainwater can be dangerous for both aquatic and terrestrial ecosystems [8].

Contrary to popular belief, Turkey's freshwater resources are limited. The annual precipitation average calculated over many years in Turkey is 622.7 mm [14]. Turkey's annual precipitation average over many years is below the world's annual precipitation average of 800 mm [15]. It is not just that freshwater is scarce in Turkey; the amount of precipitation is lower than the world average. However, Turkey is experiencing a rapidly increasing population, industrialization, and pollution. Additionally, due to Turkey's location and geographical features, approximately one-fourth of Anatolia has an arid or semi-arid climate. This situation also brings with it an increase in the need for water and food. For these reasons, Turkey is among the countries at risk that will feel the most severe effects of global climate change [16]. Turkey is located in a climate zone with mild and extreme temperatures. The average altitude of Turkey is around 1200 m, and topographic differences lead to significant climatic variations. While the average altitude is higher in the eastern and central regions, it is lower in the western regions. For this reason, there is more snowfall in the Eastern Anatolia and Central Anatolia regions, where mountain ranges and high plateaus are located. The Mediterranean climate is seen in coastal areas, with hot, dry, and long summers, and rainy, short, and mild winters. Summers are extremely hot and winters are cold in the central Anatolia region, with precipitation levels being relatively low. There are major regional changes in rainfall, with precipitation exceeding 3000 mm on the Black Sea coast and around 250 mm in the southeastern region [15].

Rain is essential for life, and it also has a significant impact because it recharges both groundwater and surface water. Therefore, determining the chemical composition of rainwater is extremely important for protecting the health of both humans and other living things. Various emissions are released into the atmosphere from various activities, including industry, agriculture, combustion for domestic heating, and improper waste treatment. Some of these emissions return to the earth with precipitation. Monitoring the chemical composition of rainwater serves as an important tool for policymakers in controlling pollutant emissions [17]. Rainwater cannot complete its natural cycle due to the increasing number of impermeable surfaces and decreasing vegetation resulting from unplanned urbanization. This situation, which endangers water availability, also causes floods, inundations, and pollution in cities. As a result, sustainable rainwater management is necessary in countries around the world [2]. Rain is a natural event that is of vital importance for the world. Rain ensures that the water necessary for life's maintenance reaches the Earth's surface. However, it also brings some risks. Therefore, the chemical composition, effects, and management of rainwater should be carefully monitored by people. The number of scientific literature on the chemical composition of rainwater in Sivas City is relatively limited [18, 19], and only these two studies have been found on this subject. This study was carried out to address this deficiency or limitation. Scientific studies on the chemical composition of rainwater in Sivas City need to be increased. This study, which was carried out between September 2023 and August 2024, will make significant contributions to the scientific literature in eliminating this deficiency or limitation. The main purpose of this study is to reveal the spatial and temporal changes in the chemical parameters of rainwater in Sivas City Center using multivariate statistical approaches. Thus, this study will provide some theoretical and practical foundations for the development and implementation of chemical composition management of rainwater in Sivas City Center.

Materials and Methods

Study Area and Climate

The study area is Sivas City Center, located in the Central Anatolia region of Turkey. Sivas City Center is located at 39°44′50.5932" latitude and 37°0′42.4224" longitude. The surface area of Sivas City Center is 3336 square kilometers. The altitude of Sivas City Center is 1285 m above sea level. Consumption-oriented trade and agriculture are the primary economic activities in the city. There are medium and large-scale industrial enterprises in Sivas, mainly in the fields of iron-metal products, furniture, textiles, marble, cement, food, agricultural products, energy, the defense industry, and cosmetics. According to the results of the address-based population registration system, the population of Sivas City Center, which was 389,719 in 2023, increased to 392,711 in 2024 [20]. While the population is increasing in Sivas City Center, it is decreasing in other districts. Sivas City Center is more developed than other districts. The population of other districts is much lower than that of Sivas City Center. The population in the districts and rural areas has decreased over time due to migration to Sivas City Center and other district cities. This situation causes population growth and rapid urbanization problems in the Sivas City Center.

Sivas City Center exhibits the characteristics of a continental climate. Sivas is the coldest city of the Central Anatolia region and has a unique continental climate characteristic compared to the surrounding cities. This climate characteristic is generally characterized by noticeable temperature differences between seasons and during the day. While summer is very hot, dry, and relatively short, winter is freezing cold, snowy, and long. The average temperature in winter is around 0ºC, and it has been observed that the temperature drops to -36.4ºC. The average temperature in summer is usually above 19ºC. However, it is also seen that the temperature exceeds 38ºC. Rainfall is relatively low in summer. Since the humidity is low, hot and dry weather feels less oppressive. Spring and autumn seasons are experienced as short-term and transitional periods. In spring, March and April are usually rainy. This precipitation typically falls in the form of rain and can occasionally appear as sleet. The autumn months of September and October are generally mild, and precipitation is also seen during these periods. The annual average areal precipitation is 420 mm [21]. Sivas' climate has a significant impact on the city's living conditions. While harsh and prolonged winter conditions increase the need for heating, they also offer potential opportunities for winter tourism due to snowfall. Rainfall during the transition periods between seasons is vital for agriculture.

Sampling and Chemical Analyses

Rainwater samples were obtained from the Meydan (Station-1), Millet Garden (Station-2), Paşabahçe Picnic Area (Station-3), and Sivas Cumhuriyet University Campus (Station-4) shuttles located in Sivas City Center between September 2023 and August 2024 (Fig. 1). Rainwater samples were collected from Sivas City Center with a simple sampling system. In this system, the rainwater collection container consists of a five-liter polyethylene terephthalate plastic bottle and a funnel section. The funnel was obtained by cutting the upper 10 cm of the bottle and turning it upside down, with a diameter of around 16 cm. After the rain event, approximately 0.25 liters of rainwater samples were taken from the rainwater collection containers.

Rainwater samples were taken monthly from four selected stations in Sivas City Center. A total of 48 rainwater samples were obtained as part of the monthly sampling during the study period. Accordingly, sampling was carried out 3 times, once a month for each season. A total of 10 chemical parameters were analyzed in the rainwater samples obtained. The pH concentration of rainwater samples was measured in situ at the sampling site with Aquamerck water analysis equipment numbered 1.08027.0001, while ammonium nitrogen, nitrite nitrogen, nitrate nitrogen, chloride, total hardness, carbonate hardness,

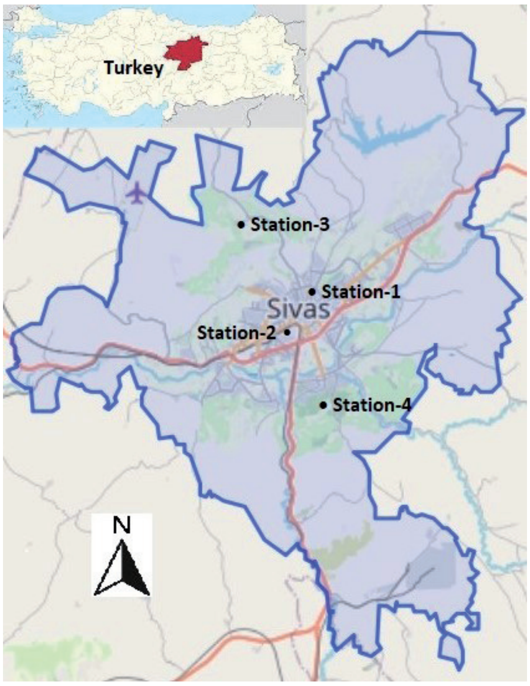

Fig. 1. Rainwater sampling stations in Sivas City Center.

and acid-binding capacity concentrations were analyzed within 24 hours. Ammonium nitrogen, nitrite nitrogen, and nitrate nitrogen concentrations were measured chlorimetrically using Aquamerck water analysis equipment numbers 1.08024.0001, 1.08025.0001, and 1.11170.0001, respectively. The pH, ammonium nitrogen, nitrite nitrogen, and nitrate nitrogen concentrations were determined semi-quantitatively by visually comparing the color of the measurement solutions with the color areas of a color card. Chloride, total hardness, carbonate hardness, and acid-binding capacity concentrations were analyzed using titrimetric methods with Aquamerck water analysis equipment numbered 1.11106.0001, 1.08039.0001, and 1.08048.0001, respectively. Chloride, total hardness, carbonate hardness, and acid-binding capacity concentrations were determined from the consumption of titration solutions with the help of a titration pipette. The calcium and magnesium concentrations of rainwater samples were determined separately using the total hardness change formulas and a calculation method [19]. Analyses and calculations were carried out in accordance with the procedures with Aquamerck analysis test equipment. Ammonium nitrogen, nitrite nitrogen, nitrate nitrogen, chloride nitrogen, calcium, and magnesium concentrations were determined in mg/L units. Carbonate and total hardness concentrations were determined in German hardness units (^{0}d). Acid-binding capacity was analyzed in mmol/L units.

Statistical Analysis of Data

Microsoft Excel 2016 and the SPSS Statistics version 26.0 package computer programs were used in the assessment of rainwater data collected in Sivas City Center and in finding the calculated values. The Kolmogorov-Smirnov test was used to analyze whether the data showed normal distribution. Since the data were not normally distributed, nonparametric tests were employed. The obtained data were summarized using descriptive statistics, normal distribution analysis, principal component analysis, factor analysis, correlation analysis, and cluster analysis. The Kruskal-Wallis H test was used for comparisons involving more than two groups according to stations and seasons, and the Mann-Whitney U test was used for comparisons involving two groups. In this study, the Kaiser-Meyer-Olkin (KMO) and Bartlett tests were used to assess the suitability of the data for factor analysis. In addition, Spearman's rho coefficient was used as the correlation coefficient. Significance was accepted as $P<0.05$ in statistical analyses.

Results and Discussion

Descriptive statistics and Kolmogorov-Smirnov test results of chemical parameters analyzed in Sivas City Center rainwater samples are presented in Table 1. In Table 1, it was seen that the data were not normally distributed according to the Kolmogorov-Smirnov normality test ($P<0.05$). The rainwater samples collected from Sivas City Center were found to have average concentrations of pH 6.90±0.266, ammonium 0.351±0.270 mg/L, nitrite 0.007±0.005 mg/L, nitrate 3.008±1.446 mg/L, chloride 9.290±2.202 mg/L, carbonate hardness 0.958±0.197^{0}d, acid-binding capacity 0.388±0.100 mmol/L, total hardness 1.704±0.324^{0}d, calcium 12.165±2.319 mg/L, and magnesium 7.321±1.454 mg/L (Table 1).

In the statistical analyses conducted in this study, it was observed that rainwater samples presented different characteristics. The average concentrations of the parameters analyzed in rainwater collected from 4 sampling points in Sivas City Center were listed from highest to lowest as calcium>chloride>magnesium> pH>nitrate>total hardness>carbonate hardness> acid-binding capacity>ammonium>nitrite (Table 1). In line with this study, Yatkin et al. [22] determined that the ion with the highest contribution to the total ion mass among the anions analyzed in rainwater samples collected from İzmir City, Turkey, was chloride, while the highest concentration among cations was determined for calcium.

The changes in the values obtained by analyzing rainwater samples taken monthly from four stations in Sivas City Center for a year are given in Table 2. In the study conducted, no statistically significant difference was found in terms of stations ($P>0.05$).

The results of the seasonal comparison of rainwater samples taken from the stations determined in Sivas City Center are presented in Table 3. In this study, the statistical differences in chemical parameters

Table 1. Descriptive statistics and Kolmogorov-Smirnov test results of chemical parameters.

Parameters	N	K-S	P-value	Min	Max	Average	±SD	Median
pH	48	0.388	0.000	6.50	7.50	6.90	0.266	7.000
Ammonium	48	0.329	0.000	0.16	0.80	0.351	0.270	0.160
Nitrite	48	0.222	0.000	0.00	0.015	0.007	0.005	0.007
Nitrate	48	0.459	0.000	1.15	5.60	3.008	1.446	2.300
Chloride	48	0.284	0.000	4.00	14.00	9.290	2.202	8.000
Carbonate Hardness	48	0.208	0.000	0.60	1.40	0.958	0.197	1.000
Acid-binding Capacity	48	0.195	0.000	0.20	0.60	0.388	0.100	0.400
Total Hardness	48	0.155	0.006	1.20	2.40	1.704	0.324	1.700
Calcium	48	0.155	0.006	8.57	17.13	12.165	2.319	12.135
Magnesium	48	0.168	0.002	5.14	10.72	7.321	1.454	7.275

N: Number of Observations, K-S: Kolmogorov-Smirnov test results, Min: Minimum, Max: Maximum, SD: Standard Deviation in the table.

Table 2. Comparison results of rainwater samples according to stations (*P<0.05).

Stations	Station-1 (N = 12)	Station-2 (N = 12)	Station-3 (N = 12)	Station-4 (N = 12)	P-value
pH	7.0 (6.5-7.5)	7.0 (6.5-7.0)	7.0 (6.5-7.5)	7.0 (6.5-7.5)	0.847
Ammonium	0.23 (0.16-0.8)	0.16 (0.16-0.8)	0.16 (0.16-0.8)	0.16 (0.16-0.8)	0.915
Nitrite	0.007 (0.007-0.015)	0.007 (0-0.15)	0.003 (0-0.015)	0.003 (0-0.015)	0.095
Nitrate	2.3 (1.15-5.6)	2,3 (2.3-5.6)	2.3 (2.3-5.6)	2.3 (1.15-5.6)	0.150
Chloride	9.0 (4.0-12.0)	9.0 (6.0-12.0)	8.0 (6.0-12.0)	9.0 (8.0-14.0)	0.468
Carbonate Hardness	1.0 (0.8-1.2)	1.0 (0.8-1.4)	0.9 (0.6-1.2)	0.9 (0.6-1.2)	0.462
Acid-binding Capacity	0.4 (0.3-0.5)	0.4 (0.3-0.6)	0.35 (0.2-0.6)	0.35 (0.2-0.5)	0.498
Total Hardness	1.8 (1.2-2.4)	1.7 (1.2-2.4)	1.7 (1.2-2.4)	1.6 (1.2-1.8)	0.405
Calcium	12.85 (8.57-17.13)	12.13 (8.57-17.13)	12.13 (8.57-17.13)	22.42 (8.57-12.85)	0.405
Magnesium	7.70 (5.14-10.72)	7.27 (5.14-10.72)	7.27 (5.14-10.7)	6.85 (5.14-7.7)	0.405

according to seasons were examined using the Kruskal-Wallis H test, and statistically significant differences were found (P>0.05). These significant differences are observed in Table 3. The pH level was found to be lower in winter than in other seasons (P>0.05). The average pH level changes in rainwater in Sivas City Center were determined to be 6.5 in the winter and 7.0 in the spring, summer, and autumn seasons (Table 3). As shown in Table 3, the average pH level was neutral during the spring, summer, and autumn seasons, while it was slightly below neutral in winter. It is thought that the pH level, which is slightly below neutral in winter, is due to the fuels used for heating. In Sivas City Center, the winter season, which is more intense from December to February, is likely the reason for the slightly below neutral value, as more fuel is consumed for heating during this period compared to other seasons. Fertelli [23] reported that the heating need is highest between October 1 and March 31 in Sivas City and that this is the period when the most fuel is used. Rainwater is very important for removing pollutants from the atmosphere, and it also provides valuable information about

Table 3. Comparison results of rainwater samples according to seasons (*P<0.05).

Parameters	Winter	Spring	Summer	Autumn	P-value
pH	6.5 (6.5-7.5)	7.0 (7.0-7.5)	7.0 (7.0-7.0)	7.0 (6.5-7.5)	0.000*
Ammonium	0.55 (0.16-0.8)	0.31 (0.31-0.8)	0.16 (0.16-0.16)	0.16 (0.16-0.8)	0.000*
Nitrite	0.015 (0-0.015)	0.007 (0-0.15)	0.000 (0-0.007)	0.007 (0-0.015)	0.002*
Nitrate	3.95 (1.15-5.6)	2.3 (2.3-5.6)	2.3 (2.3-2.3)	2.3 (2.3-2.3)	0.040*
Chloride	12.0 (8.0-14.0)	9.0 (8.0-12.0)	8.0 (8.0-10.0)	8.0 (4.0-12.0)	0.000*
Carbonate Hardness	1.1 (0.8-1.4)	0.8 (0.6-1.2)	1.0 (0.8-1.0)	1.0 (0.6-1.2)	0.002*
Acid-binding Capacity	0.45 (0.3-0.6)	0.3 (0.2-0.5)	0.4 (0.3-0.4)	0.4 (0.2-0.6)	0.009*
Total Hardness	2.0 (1.8-2.4)	1.4 (1.2-1.8)	1.6 (1.2-1.8)	1.8 (1.2-2.4)	0.000*
Calcium	14.28 (12.85-17.13)	9.99 (8.57-12.85)	11.42 (8.57-12.85)	12.85 (8.57-17.13)	0.000*
Magnesium	8.56 (7.70-10.72)	5.99 (5.14-7.7)	6.85 (5.14-7.7)	7.7 (5.14-10.72)	0.000*

the structure of the atmosphere it falls upon [24]. Kavak [21] in the measurements made to reveal the heating-related pollution for the city of Sivas; it was reported that the monthly average values of the particulate matter parameter smaller than 10 micrometers in the autumn and winter months exceeded the European member states and national limit values, while the measurement values of the particulate matter parameter smaller than 10 micrometers for the determination of pollution originating from transportation exceeded the national limit value in the spring, autumn, and winter months. However, it was recorded that the sulfate, nitrite, and carbon monoxide values in the city of Sivas remained below the relevant regulatory parameter limit values from 2016-2019. For the years 2016-2019, the average recent air quality index values for the spring months varied between approximately 30 and 60, the recent air quality index values for the summer months varied between 30 and 55, the recent air quality index values for the autumn months varied between 40 and 70, and the recent air quality index values for the winter months varied between 35 and 70. Following this, according to the national air quality index created based on the EPA air quality index classification, the air quality index of Sivas city is in the "good" and "moderate" categories.

The pH level of rainwater samples should be around 5.6 when rainwater is in equilibrium with atmospheric carbon dioxide in an unpolluted environment [8, 25]. In this context, rainwater with a pH level lower than 5.6 is considered acidic, or acid rain. The lowest and highest measured pH levels of rainwater samples collected in Sivas City Center were measured as 6.5-7.5 (Tables 1, 2, and 3). These pH level results indicate that the rainwater collected from Sivas City Center was not polluted during the study period, i.e., it did not exhibit the characteristics of acid rain (pH<5.6).

In a study conducted by Beyazit and Peker [18] on rainwater in Sivas City Center, the average pH level was reported as 6.78. Again, in the study conducted by Dirican [19] in the Suşehri District of Sivas City, the average pH level was recorded as 7.06. In this study, the average pH value obtained from all rainwater samples was found to be 6.90, which is in accordance with the average pH values reported by Beyazit and Peker [18] and Dirican [19]. Similar to this study, the average pH levels of rainwater were reported as 6.81 in Trabzon City, Turkey [13]; 6.38 in Erbil City, Iraq [24]; 6.90 in Rize City, Turkey [26]; 6.90 in Muğla City, Turkey [27]; 6.6 in Antalya City, Turkey [28]; and 6.42 in Villavicencio City, Colombia [29]. In contrast, the pH levels of rainwater were reported to be lower than the average values in this study, as 6.0 in Kırklareli City, Turkey [30]; 4.19-5.82 in European Union countries [31]; 4.56 in Chizhou City, China; and 4.85 in Beijing, China [32].

In this study, higher concentrations of ammonium, nitrite, nitrate, chloride, carbonate hardness, acid-binding capacity, total hardness, calcium, and magnesium were detected in winter compared to spring, summer, and autumn (P>0.05) (Table 3). Ammonium plays an active role in determining the final pH concentration and converting it to nitrate [33]. Ammonium nitrogen was measured at its highest in winter (average 0.55 mg/L) and at its lowest in summer and autumn (average 0.16 mg/L). The Kruskal-Wallis H test showed that there was a significant difference between ammonium concentrations and seasons (P>0.05) (Table 3). The average ammonium concentrations in Sivas City Center rainwater were found to be above the EPA [34] maximum drinking water contaminant limit of 0.30 mg/L in winter and spring. It can be said that agricultural and industrial activities are effective in this.

Nitrite and nitrate found in rainwater are products of fossil fuel combustion [35]. Nitrite was measured at its highest in winter (average 0.015 mg/L) and at its lowest in summer (average 0 mg/L). In Sivas City Center, nitrate was measured at its highest in winter (average 3.95 mg/L) and at its lowest in spring, summer, and autumn (average 2.3 mg/L). The Kruskal-Wallis H test (P>0.05) showed that there was a significant difference between nitrite and nitrate concentrations and seasons (Table 3). The average nitrite and nitrate concentrations in Sivas City Center rainwater were determined to be below 0.50 mg/L and 50 mg/L, respectively, which are the EPA [34] maximum contaminant limits for drinking water in all seasons.

The highest chloride concentration was measured in winter (average 12.0 mg/L), and the lowest in summer and autumn (average 8.0 mg/L). The Kruskal-Wallis H test showed that there was a significant difference between chloride concentrations and seasons (P>0.05) (Table 3). The average chloride concentrations in rainwater in Sivas City Center were found to be below the 250 mg/L value recommended as the maximum contaminant limit for drinking water by the EPA [34] and the WHO [36] in all seasons.

Total hardness concentration did not show much fluctuation throughout the year, but it was highest in winter (average 2.0^{0}d) and lowest in spring (average 1.4^{0}d). The Kruskal-Wallis H test showed that there was a significant difference between total hardness concentrations and seasons (P>0.05) (Table 3). When the total hardness levels of rainwater analyzed according to seasons in Sivas City Center were classified according to Klee [37], all samples were found in the "Very Soft Water" class.

Calcium and magnesium concentrations in rainwater in Sivas City Center are parallel to each other, and differences were detected between seasons. Calcium was measured at its highest in winter (average 14.28 mg/L) and lowest in spring (average 9.99 mg/L). Similarly, magnesium was measured at its highest in winter (average 8.56 mg/L) and lowest in spring (average 5.99 mg/L). The Kruskal-Wallis H test showed that there was a significant difference between calcium and magnesium concentrations between seasons (P>0.05) (Table 3). Normally, calcium is higher than magnesium in water. In polluted waters, not only do increases in water hardness occur, but at the same time, there are deteriorations in the calcium and magnesium ratio. The ratio of calcium to magnesium is approximately 4-5:1 in unpolluted waters [38]. As a result of the calculations made in this study, it was found that the calcium ratio was higher than the magnesium ratio (Tables 1, 2, and 3). It was observed that the calcium-to-magnesium ratio mentioned by Dirican and Barlas [38] for unpolluted waters was not disrupted in the rainwater of Sivas City Center.

Multivariate statistical approaches are a set of methods developed to examine complex relationships between variables and reach solutions, taking into account the subject under investigation and the variables it is related to. They have an important place in data analysis. Although multivariate statistical approaches require more complex operations, they are widely and effectively used today [39]. In order to evaluate the suitability of indicator data used in assessing rainwater parameters in Sivas City Center for multivariate statistical analysis, the Kaiser-Meyer-Olkin (KMO) and Bartlett tests were first applied. The results of the Kaiser-Meyer-Olkin and Bartlett tests are presented in Table 4. According to the analysis presented in Table 4, the Bartlett test yielded a Chi-Square value of approximately 1037.930. As a result of these analyses, the KMO value was found to be 0.712>0.5, and the significance level was determined to be 0.000<0.001. This shows that the data set for this study is suitable for conducting principal components and factor analysis.

Principal component analysis was performed on 10 chemical parameters affecting rainwater quality. The representation graph of the eigenvalues of the principal components is given in Fig. 2. The vertical axis of Fig. 2 symbolizes the factors, while the horizontal axis shows the principal components. The sharp decreases in Fig. 2 indicate a number of important factors. The horizontal lines indicate that the individual contributions of the additional changes brought by the factors are close to each other. The eigenvalue indicates the importance of the factor, and its importance increases as the value of the eigenvalue increases. Eigenvalues with a numerical value greater than 1.0 are considered important. Accordingly, the results obtained indicate that the eigenvalues for the first 2 axes are important. It was observed that the slope in Fig. 2 did not change much after accounting for these two main components and that it could be explained in a two-factor structure by overlapping with the results of the principal component analysis.

In determining the number of factors, factors with eigenvalue statistics greater than 1.0 were considered significant, and 2 factors were identified. The first factor

Table 4. Assessment of the suitability of data for principal component analysis.

Kaiser-Meyer-Olkin Measure of Sampling Adequacy		0.712
Bartlett's Test of Sphericity	Approximately Chi-Square	1037.930
	Df	45.000
	Sig.	0.000

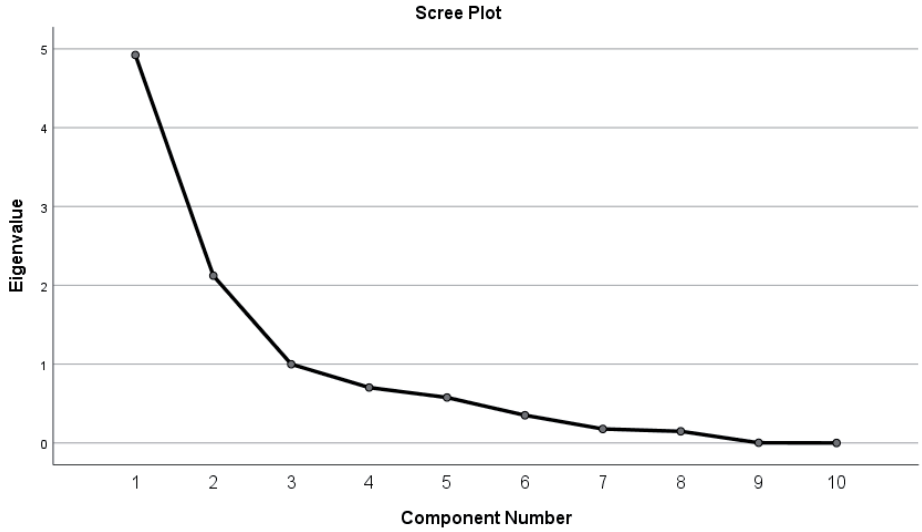

Fig. 2. Eigenvalues of principal components.

accounts for approximately 49.21% of the total variance, while the second factor accounts for approximately 21.22% of the total variance. These two factors together explain approximately 70.43% of the total variance (Table 5).

Factor analysis shows the common variance among variables and allows the investigation of mutual correlations between variables. Factor loadings represent the correlation coefficients between variables and factors. Factor loadings are considered high if they are >0.75, medium if they are between 0.75-0.50, and low if they are between 0.50-0.30 [40]. Rotation solution results, factor names, and factor loadings are given in Table 5. Using Kaiser varimax normalization, two factors were extracted and rotated in this study. These factors explain 70.43% of the total variance, which is sufficient to explain the sources of hydrochemical variation quite well. Factor-1 explains approximately 49.21% of the total variance and has positive loadings for ammonium, nitrite, nitrate, chloride, carbonate hardness, acid-binding capacity, total hardness, calcium, and magnesium. On the other hand, pH has a negative load. In factor-1, the highest and positive loadings were found in magnesium (0.940*), calcium (0.940*), total hardness (0.940*), and carbonate hardness (0.848*) parameters. Following these, nitrite was found to have a moderate positive effect, while pH was found to have a moderate negative effect (Table 6). The hardness caused by calcium and magnesium, which are the most common in natural waters, is accepted as total hardness with very little error. Cations other than calcium and magnesium contribute little to hardness in natural

Table 5. Number of factors formed based on eigenvalue statistics and total variance explained.

C	Initial Eigenvalues Range			Extraction Sums of Squared Loadings			Rotation Sums of Squared Loadings		
	T	%V	C%	T	%V	C%	T	%V	C%
1	4.922	49.217	49.217	4.922	49.217	49.217	4.518	45.183	45.183
2	2.122	21.220	70.437	2.122	21.220	70.437	2.525	25.254	70.437
3	0.999	9.988	80.425	-	-	-	-	-	-
4	0.703	7.034	87.460	-	-	-	-	-	-
5	0.576	5.764	93.223	-	-	-	-	-	-
6	0.351	3.509	96.733	-	-	-	-	-	-
7	0.177	1.773	98.506	-	-	-	-	-	-
8	0.148	1.475	99.981	-	-	-	-	-	-
9	0.002	0.019	100.000	-	-	-	-	-	-
10	4.056E-7	4.056E-6	100.000	-	-	-	-	-	-

C: Component, T: Total, %V: % of Variance, C%: Cumulative % in the table.

Table 6. Rotated component matrix.

Parameters	Factor-1	Factor-2
pH	-0.510**	-0.519**
Ammonium	0.088	0.856
Nitrite	0.572^{**}	0.386^{***}
Nitrate	0.000	0.873^{*}
Chloride	0.067	0.742^{**}
Carbonate Hardness	0.848^{*}	0.025
Acid-binding Capacity	0.739^{**}	-0.055
Total Hardness	0.940^{*}	0.147
Calcium	0.940^{*}	0.147
Magnesium	0.940^{*}	0.123

*: High ($F>0.75$); **: Middle ($0.50<F<0.75$); ***: Low ($0.30<F<0.50$) in the table.

waters. Therefore, hardness is expressed by measuring the amount of calcium oxide or carbonate in water [41]. Calcium and magnesium are accepted as parameters that help neutralize the acidity in rainwater [42]. Calcium and magnesium are soil-based parameters and are included in the aerosol structure, especially when dry soil is transported into the atmosphere. A large part of the soils in the Central Anatolia region, which includes the Sivas City Center, are sufficient in terms of available calcium (99.2%) and magnesium (93.4%). This is due to the region's hot and dry climate conditions, as well as the lack of leaching resulting from low rainfall in the region [43]. Calcium and magnesium in the soil structure play an important role in neutralizing the acidity of rainwater. Since there is no leaching in the soils of arid and semi-arid regions, such as the region where Sivas is located, the alkali saturation rate is high. Among the alkaline parameters found in the soil, calcium comes first. In arid region soils formed on calcareous parent material, magnesium is also found together with calcium. The high levels of calcium, magnesium, total hardness, and moderate levels of nitrite and pH loads found in the first factor may be attributed to the regions' soil structure and many human-induced activities.

Factor-2 represents approximately 21.22% of the total variance and has a negative load for pH, while it has positive loads for nitrite, nitrate, and chloride. In factor-2, nitrate (0.873^{*}) has the highest and positive load. This is followed by chloride (0.742^{**}), which has a medium and positive load. Chloride is followed by pH (-0.519^{**}), which has a medium and negative load. Nitrite (0.386^{***}) was found to be the parameter with a low and positive load in factor-2 (Table 6). The situation observed in factor-2 is likely a result of rainwater interactions in Sivas City Center. Nitrate, chloride, pH, and nitrite variables contributed significantly to factor-2, explaining 21.22% of the total variance, and are likely related to anthropogenic activities such as warming activities and agricultural practices.

In Thrace City, Greece, high concentrations of nitrate and nitrite have been linked to the use of fossil fuels for heating, traffic, and industrial activities, while high alkalinity, calcium, and magnesium have been associated with urban development [44]. Similarly, Cerqueira et al. [45] showed anthropogenic sources as the primary sources of ammonium and nitrate ions in rainwater samples collected in Juiz de Fora City, Brazil.

Correlation analysis was applied to the chemical analysis results of rainwater samples collected from Sivas City Center, and the results are presented in Table 7. Spearman's rank difference correlation coefficient was applied in accordance with normality calculations in the correlation coefficient. Significance levels between the data were determined in two different ways. The relationship levels between them were extracted as positive and negative. Significance levels for the correlations were set at 0.01 and 0.05. According to Spearman's rank difference correlation coefficient relationship, an excellent, that is, very strong positive correlation was determined between magnesium and calcium ($r = 1.000^{**}$), magnesium and total hardness ($r = 1.000^{**}$), and calcium and total hardness ($r = 1.000^{**}$) in Sivas City Center (Table 7). In other words, the highest correlations were determined between calcium, magnesium, and total hardness parameters ($P<0.01$). The reason for the high and very strong positive correlation between calcium, magnesium, and total hardness is attributed to the common behavior of these parameters and their shared origin.

These highest correlations were followed by strong positive correlations between acid-binding capacity and carbonate hardness ($r = 0.851^{**}$), carbonate hardness and total hardness ($r = 0.701^{**}$), carbonate hardness and calcium ($r = 0.701^{**}$), and carbonate hardness and magnesium ($r = 0.701^{**}$) (Table 7). Moderate positive correlations were found between ammonium and nitrate ($r = 0.683^{**}$), acid-binding capacity and total hardness ($r = 0.558^{**}$), acid-binding capacity and calcium ($r = 0.558^{**}$), acid-binding capacity and magnesium ($r = 0.558^{**}$), nitrite and total hardness ($r = 0.529^{**}$), nitrite and calcium ($r = 0.529^{**}$), and nitrite and magnesium ($r = 0.529^{**}$). On the other hand, moderate negative correlations were found between pH and total hardness ($r = -0.573^{**}$), pH and calcium ($r = -0.573^{**}$), pH and magnesium ($r = -0.573^{**}$), and pH and chloride ($r = -0.510^{**}$) (Table 7). It can be concluded that these parameters, which show a moderate negative correlation, behave differently from one another and originate from different environments. Similarly, moderate negative correlations have been observed between pH and total hardness, pH and calcium, pH and magnesium, and pH and chloride in other studies [19, 32]. Beyatiz and Peker [18] reported that the pH and sulfate levels, as well as their conductivity values in rainwater in Sivas City Center, changed inversely

Table 7. Results of Spearman correlation analysis of chemical parameters.

Parameters	pH	Ammonium	Nitrite	Nitrate	Chloride	Carbonate Hardness	Acid-binding Capacity	Total Hardness	Calcium	Magnesium
pH	1.000	-	-	-	-	-	-	-	-	-
Ammonium	-0.200	1.000	-	-	-	-	-	-	-	-
Nitrite	-0.425**	0.271	1.000	-	-	-	-	-	-	-
Nitrate	-0.224	0.683**	0.284	1.000	-	-	-	-	-	-
Chloride	-0.510**	0.393**	0.244	0.388**	1.000	-	-	-	-	-
Carbonate Hardness	-0.364*	-0.007	0.463**	0.053	0.052	1.000	-	-	-	-
Acid-binding Capacity	-0.335*	-0.066	0.398**	0.023	-0.034	0.851**	1.000	-	-	-
Total Hardness	-0.573**	0.130	0.529**	0.067	0.231	0.701**	0.558**	1.000	-	-
Calcium	-0.573**	0.130	0.529**	0.067	0.231	0.701**	0.558**	1.000**	1.000	-
Magnesium	-0.573**	0.130	0.529**	0.067	0.231	0.701**	0.558**	1.000**	1.000**	1.000

*: Correlation is significant at the 0.05 level (2-tailed), **: Correlation is significant at the 0.01 level (2-tailed).

and separately. Only the relationship between pH and conductivity is strong.

Hierarchical cluster analysis is widely used, especially in hydrochemistry studies, to classify collected water samples based on their similarities [46]. Hierarchical cluster analysis was applied to understand the similarities and differences in the temporal and spatial changes of chemical parameters in Sivas City Center. In this study, conducted in Sivas City Center, the results of the hierarchical cluster analysis between the seasons are presented in Fig. 3. Accordingly, two statistically significant clusters were determined between the seasons. The first cluster consists of the spring, summer, and autumn seasons. Since the similarities between the spring and summer seasons in the first cluster are very high, these profiles form a group at a distance of one unit. The autumn season is included in the spring and summer seasons at a distance of 9 units. Relatively low parameter concentrations were found in these spring, summer, and autumn seasons.

The second cluster includes only the winter season (Fig. 3). The winter season is included in the other seasons at a distance of 25 units. In the winter season, all parameters showed relatively higher concentrations (Table 3). The winter season is quite different in clustering. This situation may have occurred due to anthropogenic, that is, human-created activities, which are not present in the spring, summer, and autumn seasons.

The results of the hierarchical cluster analysis, according to the stations, are shown in Fig. 4. According to the results of the hierarchical cluster analysis in Fig. 4, the parameters are generally divided into two main clusters. The first cluster includes station-1, station-2, and station-3. The first group in the first cluster is formed by station-1 and station-2. Since the similarities between station-1 and station-2 are very high, these profiles formed the first group at a distance of one unit. Station-3 was included in the group, where stations 1 and 2 are located at a distance of 10 units. Therefore, it is concluded that station-1, station-2, and station-3 have similar or very close characteristics in terms of rainwater chemical parameters.

The second cluster is formed only by station-4 (Fig. 4). Station-4 is located 25 units away from the other stations. Therefore, station-4 has different chemical properties than stations 1, 2, and 3 in terms of measured rainwater chemical parameters. In this context, the hierarchical cluster analysis of the stations shows that they are similar in terms of chemical structure. However, station-4 is quite different from station-1, station-2, and station-3 in clustering. Station-4 is located a little further from the city center than the other stations. This situation may be due to the presence of more intense anthropogenic activities in station-1, station-2, and station-3.

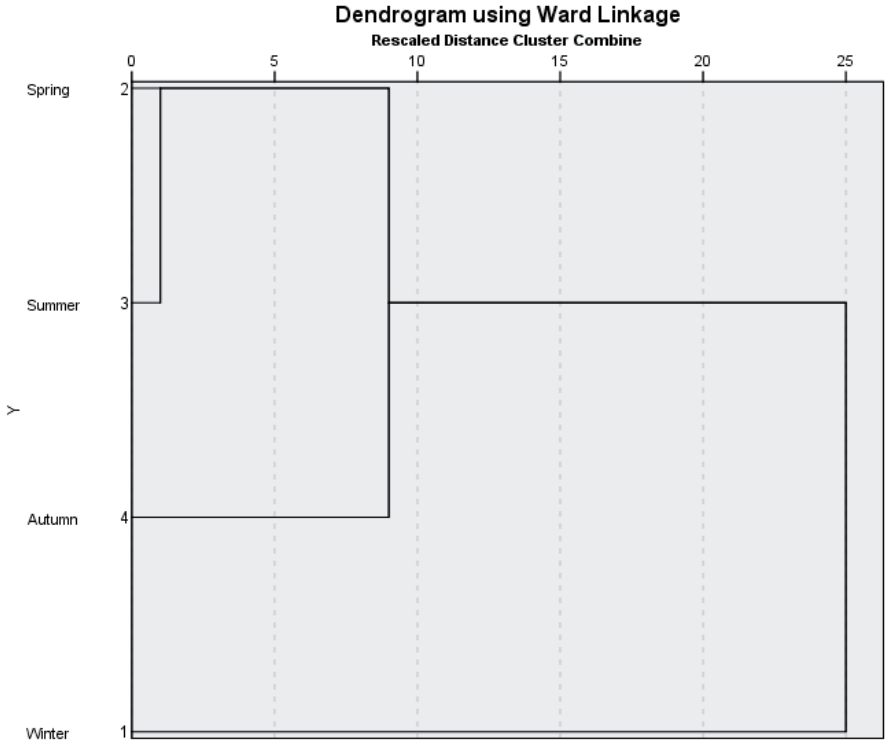

Fig. 3. Clustering for seasons.

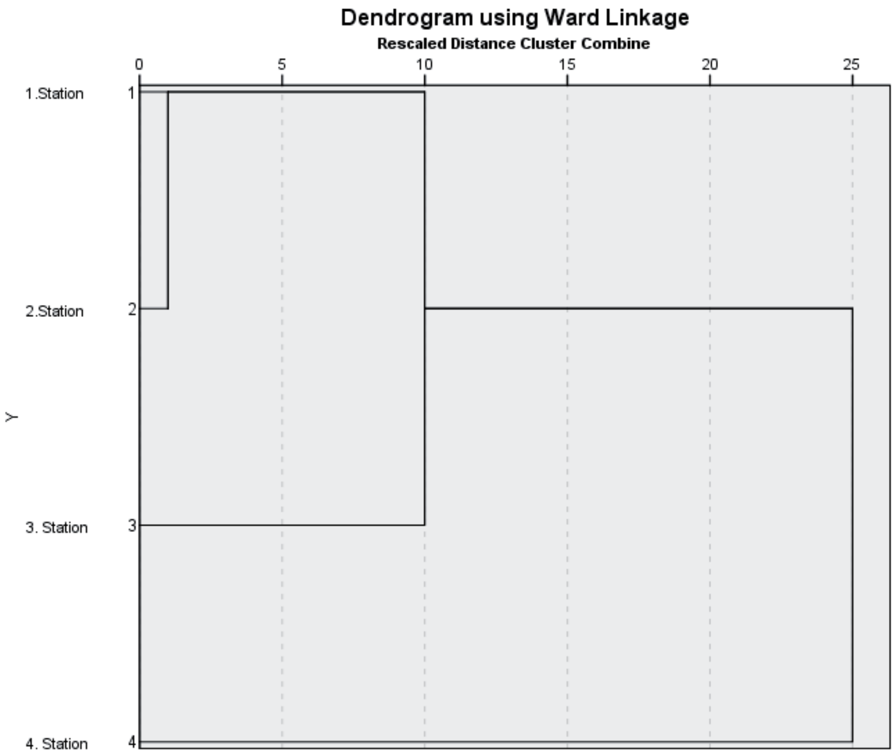

Fig. 4. Clustering for stations.

Conclusions

The chemical parameters of rainwater are constantly changing in Sivas City Center. This change can sometimes be fast or slow, depending on the structure of the environment and the sources of pollutants. Therefore, it is necessary to determine and monitor the chemical parameters of rainwater in Sivas City Center at certain intervals. This study was carried out between September 2023 and August 2024. The obtained data reflect the status of rainwater in Sivas City Center between the specified dates. Monthly rainfall data obtained from 4 different sampling points representing the entire research area for 12 months in Sivas City Center were first analyzed and evaluated in this study. Therefore, various multivariate statistical approaches were successfully employed in this study to evaluate the temporal and spatial changes in the chemical parameters of rainwater in Sivas City Center and to determine the main pollutants and their sources at the sampling points within the study area. According to the results of the Spearman correlation analysis conducted with the data obtained from this study, statistically significant and very high positive correlations were observed between magnesium, calcium, and total hardness parameters. The temporal and spatial variability of rainwater quality was determined by using hierarchical cluster analysis. According to these test results, it was determined that the winter season differed from other seasons, while station-4 differed from other stations. Multivariate statistical approaches are applicable in Sivas City Center to interpret complex datasets of rainwater chemical parameters, understand temporal/spatial changes in rainwater quality, and identify hidden pollution sources. The results show that there are temporal and spatial changes in the chemical parameters analyzed in Sivas City Center. Based on the obtained data and the applied multivariate statistical analyses, it was determined that there was no sign of acid rain in Sivas City Center. The importance of rainwater is increasing day by day. The natural rainwater balance needs to be protected, its deterioration minimized, and it must be managed sustainably and effectively. In Sivas City Center, where the effects of rapid urbanization and climate change are intensified, sustainable and effective rainwater management is crucial for the future. For future rainwater studies, the assessments in this study can serve as a tool to help managers identify pollution sources in different regions and set priorities for improving rainwater quality through chemical parameter monitoring plans.

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Conflict of Interest

The author declares no conflict of interest.

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