Combined statistical analysis of water quality for determination of relationships between parameters: case study of Akköprü Stream, Van/Turkey

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ABSTRACT
Today, water is affected negatively in terms of its characteristics and quality due to many factors. Necessary measures should be taken to control environmental pollution by analyzing the conditions and parameters that cause pollution and monitoring the water quality in water bodies such as lakes, streams, rivers and ponds. Akköprü Stream is one of the rivers flowing into Lake Van and it has great importance within the borders of Van/Turkey. The data in this study were used to perform water quality analysis based on the physicochemical parameters obtained from Akköprü Stream. A total of 22 water quality parameters were used to determine water quality at the discharge into Lake Van. Evaluation of these parameters was made according to the regulation about water pollution control (Turkey). As a result, Akköprü Stream has Class I water quality in terms of seasonal conditions and water parameters. Among the parametric analysis methods, trend distribution, normality, correlation, matrix table, regression and normal distribution of the data set were examined and the relationships between parameters were interpreted statistically. According to the results, most of the parameters were within the normal range, solid matter and hardness effects were correlated, and matrix relations and regression equations were related to other parameters.

Keywords: Akköprü Stream; Water quality; Statistical analysis; Correlation; Regression

1. Introduction

Water quality has become an increasingly important issue in the developing world with the impact of pollution. As a result of water quality analysis, the reasons for low or poor quality of waters are mostly increasing pollution problems and water may even become unusable by disruption of its quality [1,2]. Water pollution occurs due to changes that restrict the use of water due to human effects or deterioration of the ecological balance. This phenomenon occurs especially in waters such as streams, mostly under the influence of anthropogenic effects (organic matter and nutrients), mineral dissolution and physicochemical parameters [3–5]. In other words, domestic and industrial wastes being discharged into water bodies without treatment or with insufficient treatment, as well as the transport of chemical fertilizers and pesticides used in agricultural activities into the aquatic environment cause harm to water systems [6–9]. Increases in the amount of nutrients such as nitrogen, potassium and phosphate in detergents released into fresh waters due to domestic wastewater and municipal sewage cause algal blooms with the increase of algae in these waters. All living organisms in the food chain are severely affected by water quality [10,11]. Also, industrial

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wastes are known to affect water quality, especially in areas close to streams. To minimize or eliminate these increasing water pollution problems, water quality inspection is required [12–14].

Water quality is expressed by identifying the seasonal and local variables that affect the inorganic–organic matter content of the water, the concentrations of various physical, chemical and biological parameters, the environment and the diversity of the creatures living in the water system [15]. Although this statement is valid for some water sources, it is only possible to analyze the general water quality for water bodies such as rivers, lakes, ponds and streams, and sea coasts; in other words, for smaller scale surface waters that can be controlled. For this reason, a water source is defined according to whether the water is included in a closed or open system, whether it is fresh or saltwater, the purpose of usage and the area it affects. Situations such as over use of freshwater resources and the discharge of large amounts of pollutants into lakes adversely affect water quality temporarily and spatially [16–18]. After determining the water source, for example, freshwater sources such as lakes, streams, rivers and creeks, etc., related analyses can be applied. According to the data obtained, it is necessary to classify the water quality by comparing the values with the relevant regulations, monitoring amounts, taking account of the protection use balance for areas of use of these waters with sustainable targets, and researching the measures to be taken to ensure good quality water [10].

Analyzing such a large data set is very difficult and complex, as a large number of samples are required to determine water quality [19,20]. Collected data can provide important information about water characteristics and quality [21,22]. Therefore, information should be supported by modeling and statistical analysis when conducting water quality analysis [23–26]. Parametric analyses can be used for normally distributed parameter data or an entire data set. Among these analyses, basic statistical analyses such as descriptive parameters (mean, standard deviation, skewness, kurtosis, etc.), normality and correlation should be performed with high priority. Statistical analysis of the data is significant for making quick and logical decisions about determining the factors that cause pollution and should be avoided. In addition, data analysis contributes to the determination of the relationship between the change in water quality parameters and the pollutants that cause this change [27].

The aim of this study was to determine the water quality of the stream according to water parameters obtained at the discharge of the Akköprü Stream as it flows into Lake Van and to perform statistical analysis of the physicochemical parameters affecting water quality. In addition, some parametric analyses were completed by examining factors about preventing water pollution.

2. Materials and methods

2.1. Akköprü Stream and Its importance for Lake Van

Turkey’s largest natural lake of Lake Van is found in Van province, and the system encompasses lakes, ponds, rivers and streams in a closed basin with water from many different sources [28,29]. Akköprü Stream, one of the most important water sources which is located in Van, is a surface water body with seasonal changes in flow rate. The stream carries excess water from the reservoir of Sıhke Lake which is another water resource. Akköprü Stream is a water source connecting to Lake Van with a transition/protection line usage mechanism as a precaution against possible seasonal flow increase and floods from Sıhke Lake. The geological setting of the area consists of metamorphic rocks, ophiolite and turbidity deposits. Neotectonic and metamorphic movements affected the geomorphological evolution of the area together with fluvial processes. The basin of the stream contains Quaternary volcanic rocks. In meteorological and hydrogeological terms, there are simple sand, silt, gravel and limestone aquifers in the basin.

Akköprü Stream has a length of approximately 14 km. Although the flow rate varies seasonally, the water level decreases as a result of the decrease in precipitation especially in the summer months and the use of water for irrigation. Due to low rainfall, the water level has lowest in late September–October. Starting from Sıhke Lake, Akköprü Stream travels in a south-southeast direction, then turns west and flows into Lake Van. While the stream surroundings were empty until recently, with the increase in urbanization, a settlement area has grown around the stream at present. Şamran Canal joins Akköprü Stream west of the intercity road to Van city center, in a north-south direction and increases the flow rate of Akköprü Stream. Approximately 4 km later, Kirman Creek, which comes from the north, joins the stream which reaches its highest flow rate, continues on its way to the west and discharges into Lake Van. In Fig. 1, the route followed by Akköprü Stream starting from Sıhke Lake, the discharge point into Lake Van, and the confluences with Kirman Creek and the Şamran Canal are shown on Google Earth.

Although Akköprü Stream passed through mostly agricultural areas and gardens in the past, currently it is a water source where settlements are densely located around the stream and the stream is polluted. The physical appearance of the stream changes seasonally. In the spring, the water has a cloudy appearance due to colloidal substances carried by the water in parallel with the melting of snow and the increase in rainfall. The stream color is often observed to be dark brown or grayish. In parallel with the relative decrease of precipitation in the summer and autumn months, the turbidity decreases and the water in the stream is observed to become clearer. In autumn, especially in September and October, the flow is minimal and the water is clear. In the winter period, rain and snowfall increase the flow rate and the water becomes turbid again. The stream water color changes at the points where other tributaries join. At the points where Şamran Canal joins the stream and then Kirman Creek, a generally opaque appearance develops.

The analysis results for different water resources distributed to networks as drinking water in Van city and the large town of Erığ generally abide by the drinking water standards of Turkey [30,31]. However, in recent years, the pollution of waters has increased compared to the past with the population increase. It is thought that discharge of used drinking water indirectly to the sewers and discharge of sewage water to the stream beds or lakes causes pollution in Lake Van in particular. Again, as drought events
experienced in the past years decreased the flow of water resources in the province of Van, the density of pollution is further observed due to low flow [32]. In addition, considering the effects of volcanism on the river systems around Lake Van, changing water quality parameters may adversely affect the water characteristics and the ecosystem [33]. Regardless of whether natural or artificial, lakes are places where many different waters such as streams and rivers discharge, so they are also the end receivers of various pollutants carried by water bodies. Therefore, the discharge of waters such as Akköprü Stream is likely to cause significant environmental and organism problems and decrease fish species in the lake, especially if water reaches the lake without being treated for pollution first.

2.2. Determination of water quality parameters

Monitoring sampling and analysis of Akköprü Stream were carried out by the Regional Directorate of State Hydraulic Works (Turkey). The reason for analyzing the stream with parameters was to determine the seasonal variation in water quality, including the color of the water and the factors that cause pollution, as can be seen in Fig. 2. The samples taken at the water discharge point of Akköprü Stream into Lake Van were analyzed from a single point in 2018. The statistical analysis in this study was carried out with 22 water quality parameters for Akköprü Stream flowing within the provincial borders of Van and discharging into Lake Van. The water quality classes were evaluated according to the Regulation about Water Pollution Control (Turkey, 2015). Water quality parameters in the data set included nitrite (NO$_2^-$), nitrate (NO$_3^-$), ammonium (NH$_4^+$), sulfate (SO$_4^{2-}$), phosphate (PO$_4^{3-}$), chloride (Cl$^-$), fluoride (F$^-$), sodium (Na$^+$), potassium (K$^+$), calcium (Ca$^{2+}$), magnesium (Mg$^{2+}$), total hardness (TH), pH, turbidity (Turb), electrical conductivity (EC), total dissolved solids (TDS), suspended solids (SS), dissolved oxygen (DO), oxygen saturation (SaO$_2$), chemical oxygen demand (COD), color and permanganate index (PI) values. The Regional Directorate of State Hydraulic Works of Turkey (DSİ) performed instantaneous measurements and analyzed the samples taken at the Iskele shore discharge of the Akköprü Stream into Lake Van. The abbreviation, unit and measurement methods for water quality parameters used in this study are given in Fig. 3.

2.3. Combined statistical analysis for determination of relationship between water parameters

The examination and methodology used in this study are listed as follows;

- Since the measurements of the parameters in the data set were taken seasonal and statistical analyses were begun, after determining the water quality class of the stream according to the Regulation of Water Pollution Control data.
- For statistical analyses conducted in similar studies, it is necessary to select an appropriate program that can perform the necessary analysis, especially to explain the mutual relationship between water quality parameters.
Statistical analyses in this study were carried out with the Minitab and Microsoft Excel programs.

• Parametric and nonparametric data set distributions were examined, which is one of the first and most important checks required for data sets.

• The normal distribution of the data set was examined with p values for normality and probability graphs. While parametric analyses are used for data with normal distribution, analyses based on nonparametric modeling are performed for non-normal distributions. For this reason, parametric tests were applied to the data set in the study, as the data had normal distribution.

• In order to determine the water quality at the discharge point of the stream with basic statistical techniques, 22 different parameters (Fig. 3) data were provided by the relevant institution and analyzed by descriptive statistical analysis (mean, standard deviation, skewness, kurtosis, etc.).

• The variations of parameters in the data set were observed on figures with trend analysis.

• Relationships between the water quality parameters were examined with correlations of regression equations and matrix tables.

3. Results and discussion

The evaluations were made according to the Regulation about Water Pollution Control (Turkey, 2015) by looking at the average values for parameters in the data set. According to the general conditions and parameters, Akköprü Stream was determined to have water quality in classes II, III and IV mostly, with a few parameters in class I. As a result, it is understood that Akköprü Stream has class I water quality. Although the Şamran Canal, which is a tributary of the creek, is known to be a clean water source, it is thought that the other tributary of Kirman Creek is close to the industrial zone and is polluted along the route to Akköprü Stream.

Statistical analyses were performed with the Minitab program to determine the common values representing the parameters that make up the data set, and the results are shown in Table 1. The average values obtained were compared with the values in the Regulation about Water Pollution Control (Turkey, 2015) and standard deviation and variance values were calculated to determine how far the data diverged from the average values. Additionally, skewness, kurtosis and mean squares of consecutive differences (MSSD) values were calculated as variance estimates.
to determine the degree to which the data peaked compared to a normal curve and identify whether the data were symmetrical or not.

The descriptive statistical values for water parameters are given in Table 1 according to Regulation about Water Pollution Control (Turkey, 2015) and the water quality of the Akköprü Stream is class I for most of the parameters. When a detailed examination is made, values were ranked Class I (nitrate, ammonium, sulfate, chloride, fluoride, sodium, pH, conductivity, oxygen saturation, COD), Class II (permanganate index, phosphate, DO), Class III (color) and Class IV (nitrite) [35]. According to Turkish Standards (TS266), European Communities and World Health Organization (WHO) water standards, the stream water is appropriate in terms of pH, nitrate, nitrite and also sulfate limit values [36–38]. Considering EECCA standards, Akköprü Stream water is class I type which means good water quality [39]. Thus, the discharge of Akköprü Stream to Lake Van was determined to be appropriate in terms of water quality and the ecosystem. The analysis results show that the turbidity value is higher than the standard limit value in seasonal transitions, as in the study [40,41]. If TDS, DO, COD, pH and turbidity values are above the limits, these parameters appear to be important environmental pollutants. Since the values measured in this study are not critically high, it is thought that the contaminating effect is low and the negative effect of these parameters on aqueous organisms such as fish is negligible, if any [42,43]. As in previous studies, good results were obtained as a water source for drinking water, irrigation, etc. However, if it is not used as an alternative, it can be used for different purposes such as pools, factories, for cleaning of roads and irrigation [44,45]. As a result of statistical calculations, the stream has good (class I) water quality without any serious pollution problems.

Multivariate statistical analyses were used to assess the environmental status of physicochemical, nutrients, and trace metal parameters [46]. When examining the water quality assessment for Akköprü Stream, parameters such as dissolved oxygen, color, nitrite, nitrate, ammonium, sulfate, chloride, sodium, pH, COD, total dissolved and suspended solids were found to be of great importance. As is known, the water of Lake Sıhke, Şamran Canal and Kirman Creek determine the water characteristics and quality in Akköprü Stream. From this discharge point where the stream flows into Lake Van, the results of water measurement and analysis can be used to determine the water quality [47]. The pH value exhibited weak basic/alkaline characteristics with value around 8 on average. Calcium and magnesium average values had characteristics of hard water which is higher than other regions in Turkey. It is thought that the rock type of the riverbed, geographical location, climate, natural disasters, volcanic activity and seasonal conditions are effective on basic and hard water
characteristics [48,49]. Mean values for other water quality parameters (mg/L) were determined as TDS 505, DO 6.8, SS 90.5, COD 3.3, Mg 30, nitrite 0.155 and Ca 66.

When the average values are examined, according to Regulation about Water Pollution Control, the color is Class III, conductivity is Class I with 70.57, dissolved oxygen 6.81 in Class II, oxygen saturation 97.60 in Class I, COD 4.67 in Class I, ammonium 0.059 in Class I, nitrate 4.953 in Class I, nitrite 0.155 in Class III, and phosphate 0.17 in Class II. The classifications mostly indicate Class I. According to the eutrophication level, when the CHIN (nitrate + nitrite + ammonium)-Nitrogen (N) and total phosphate are calculated, it is at the eutrophic (i.e., the 3rd largest trophic) level with 1095.5 and 55.43 mcg/L.

The means for other values in the stream water throughout the year were calculated as sulfate 35.35, chloride 28.83, fluorine 0.192, sodium 48.74, potassium 3.925, Ca 66.13, Mg 30.31, TH 297.2, pH 7.926, turbidity 41.30, Conductivity 70.57, Total dissolved solids (mg/L) 505.0, SS 90.50 and PI 1.302. When the statistics for pH, Ca, Mg and total hardness, which are the most important parameters among these values, are examined, the pH did not change much throughout the year, and had its highest value in August as seen in Fig. 4. The stream was characterized by the lowest alkaline or alkaline water close to the neutral level. A standard deviation value of 0.3 for pH indicates that the data is distributed 30% from the mean, with higher standard deviation indicating more spread in the data. The water quality values are similar to the average, and there are not very large differences between them. Again, in parallel, the variance value is quite low (0.09), which indicates that the spread is narrow. Large variance represents a large spread in the data. The skewness value of 0.13 is the degree of non-symmetry of the data, and kurtosis of 0.67 indicates how different the tails of a distribution are from normal distribution. A kurtosis value of 0 represents perfectly normal distribution and the data show that it follows normal distribution perfectly. The 0.67 value has a slight positive suppression; that is, the values reached the highest single value without being too far from each other throughout the year. The MSSD value tests whether a set of observations is random. The pH MSSD value is distant from 0.08 to 1.0. Since this value is far from 1.0, it shows that there are data with similar values throughout the year with a sudden change or very low margin of error.

As seen in Fig. 4, Ca and Mg did not change much but they had high values in the year. The stream is characterized by lowest alkaline or alkaline water close to the neutral level. According to these two levels, the rock erosion effect involving enrichment in Mg and Ca was reflected in the river. The 12.69 and 2.902 standard deviation values for Mg and Ca respectively show that the data is spread around 120% and 29%, and higher standard deviation indicates more spread in the data. Therefore, while the values are similar to the mean Mg values, the differences between the data are noticeable with a higher spread of Ca values. Again in parallel, the variance values were 161.14 and 8.420, respectively. The fact that the Ca data is large compared to the variance value indicates a wide and large spread in the data, while the Mg data

<table>
<thead>
<tr>
<th>Variable</th>
<th>Mean</th>
<th>Standard deviation</th>
<th>Variance</th>
<th>Skewness</th>
<th>Kurtosis</th>
<th>MSSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrite (mg/L)</td>
<td>0.155</td>
<td>0.164</td>
<td>0.0271</td>
<td>1.19</td>
<td>0.29</td>
<td>0.0215</td>
</tr>
<tr>
<td>Nitrate (mg/L)</td>
<td>4.953</td>
<td>3.427</td>
<td>11.747</td>
<td>-0.25</td>
<td>-0.97</td>
<td>8.768</td>
</tr>
<tr>
<td>Ammonium (mg/L)</td>
<td>0.059</td>
<td>0.062</td>
<td>0.0039</td>
<td>1.67</td>
<td>3.06</td>
<td>0.0054</td>
</tr>
<tr>
<td>Sulfate (mg/L)</td>
<td>35.35</td>
<td>17.07</td>
<td>291.34</td>
<td>1.66</td>
<td>1.75</td>
<td>266.4</td>
</tr>
<tr>
<td>Phosphate (mg/L)</td>
<td>0.170</td>
<td>0.214</td>
<td>0.0458</td>
<td>0.87</td>
<td>-0.83</td>
<td>0.0502</td>
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<tr>
<td>Chloride (mg/L)</td>
<td>28.83</td>
<td>8.820</td>
<td>77.79</td>
<td>0.60</td>
<td>0.15</td>
<td>58.34</td>
</tr>
<tr>
<td>Fluoride (mg/L)</td>
<td>0.192</td>
<td>0.145</td>
<td>0.0211</td>
<td>-0.65</td>
<td>-1.57</td>
<td>0.0250</td>
</tr>
<tr>
<td>Sodium (mg/L)</td>
<td>48.74</td>
<td>19.60</td>
<td>384.04</td>
<td>1.58</td>
<td>1.28</td>
<td>440.95</td>
</tr>
<tr>
<td>Potassium (mg/L)</td>
<td>3.925</td>
<td>0.899</td>
<td>0.808</td>
<td>0.54</td>
<td>0.09</td>
<td>0.662</td>
</tr>
<tr>
<td>Calcium (mg/L)</td>
<td>66.13</td>
<td>12.69</td>
<td>161.14</td>
<td>1.51</td>
<td>2.55</td>
<td>169.43</td>
</tr>
<tr>
<td>Magnesium (mg/L)</td>
<td>30.31</td>
<td>2.902</td>
<td>8.420</td>
<td>0.61</td>
<td>-0.31</td>
<td>9.610</td>
</tr>
<tr>
<td>Total hardness (mg/L)</td>
<td>297.2</td>
<td>44.10</td>
<td>1,943.4</td>
<td>1.10</td>
<td>0.23</td>
<td>2,274.4</td>
</tr>
<tr>
<td>pH</td>
<td>7.926</td>
<td>0.305</td>
<td>0.0932</td>
<td>0.13</td>
<td>0.67</td>
<td>0.0824</td>
</tr>
<tr>
<td>Turbidity (NTU)</td>
<td>41.30</td>
<td>46.10</td>
<td>2,121.7</td>
<td>0.79</td>
<td>-1.41</td>
<td>2,104.9</td>
</tr>
<tr>
<td>Conductivity (mS/m)</td>
<td>70.57</td>
<td>7.740</td>
<td>59.96</td>
<td>0.82</td>
<td>0.41</td>
<td>67.12</td>
</tr>
<tr>
<td>Total dissolved solids (mg/L)</td>
<td>505.0</td>
<td>53.40</td>
<td>2,851.4</td>
<td>0.78</td>
<td>-0.42</td>
<td>4,356.6</td>
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<tr>
<td>Suspended solids (mg/L)</td>
<td>90.50</td>
<td>204.1</td>
<td>41,655.2</td>
<td>3.20</td>
<td>10.62</td>
<td>46,382.7</td>
</tr>
<tr>
<td>Dissolved oxygen (mg/L)</td>
<td>6.810</td>
<td>2.656</td>
<td>7.056</td>
<td>0.29</td>
<td>-1.13</td>
<td>2.850</td>
</tr>
<tr>
<td>Oxygen saturation (%)</td>
<td>97.60</td>
<td>35.70</td>
<td>1,275.4</td>
<td>-0.04</td>
<td>-1.29</td>
<td>396.5</td>
</tr>
<tr>
<td>Chemical oxygen demand (mg/L)</td>
<td>4.667</td>
<td>1.614</td>
<td>2.606</td>
<td>-0.59</td>
<td>-0.59</td>
<td>3.045</td>
</tr>
<tr>
<td>Color</td>
<td>3.250</td>
<td>2.768</td>
<td>7.659</td>
<td>-0.00</td>
<td>-1.57</td>
<td>8.364</td>
</tr>
<tr>
<td>Permanganate index (mg O2/L)</td>
<td>1.302</td>
<td>1.376</td>
<td>1.895</td>
<td>2.19</td>
<td>5.67</td>
<td>1.958</td>
</tr>
</tbody>
</table>
followed a close course with smaller and narrower spread. Ca fluctuations are larger. The skewness values were 1.51 and 0.61, respectively. Since Mg values are closer to 0 for these statistical values, the distribution of the data is more symmetrical compared to Ca. Ca skewness values were higher and there is a right-based effect. Kurtosis was 2.55 and –0.31, respectively. Mg values have a more normal distribution throughout the year compared to Ca, but it does not have a sharp jump throughout the year without being too far from each other, as it had slight negative suppression. Mg occurs due to the rock structure rather than seasonal changes and periodic anthropogenic pollution. The fact that the Ca value is 2.55 and very close to 3, which is considered the highest peak value, shows that it has a sudden peak value during the year (at the beginning and at the end of the year). MSSD values of 169.43 and 9.610 for Ca and Mg, respectively, indicate higher levels of Ca and Mg. The fact that these values are high may indicate that the difference between the data for these parameters and other values is high in some months during the year. Therefore, there are very high and low values among these values throughout the year. It is understood that the variability in Ca amounts over time, that is, during the year, is more than Mg. TH and TDS have the highest course throughout the year and they varied especially according to the Mg and Ca years, and had different values throughout the year. Therefore, the stream characteristics differ throughout the year.

Trend analysis is a type of analysis that shows the distribution of each parameter in the data set based on annual/seasonal time as shown in Fig. 4. The use of this statistical analysis method is important for interpreting water quality data sets, understanding time-related changes in water quality, and identifying hidden sources of pollution. The time dependent distribution of the parameters is given in Fig. 4. There are high distribution and changes in TDS and TH values, while other parameters do not change much during the year in this figure. Therefore, the results show that seasonal variations greatly affect the TH and TDS concentrations for the water in this study. Looking at the time-dependent parameters, while the TDS concentration decreases due to precipitation in the winter season, in June 2018, there is an increase in TH; there is a decrease in TH and TDS in the spring, TH and TDS constantly decrease in the summer, and TDS and TH decreased in October 2018. When analyzing the water quality parameters with trend changes, starting with a single observation point on the stream, as in this study, and measuring at several different stations along the riverbed will contribute to the determination of the region where the highest pollution is located, and therefore, water quality should be monitored in the future [50]. Also, it is noteworthy that the oxygen solubility in the dry season is always low, with the permanganate index having the same average values as the year’s highest average concentration [51]. In other previous studies, the eutrophication limit values for waters were evaluated and their effect on living organisms was evaluated [52,53]. Also, EC values were stable during the year.

When the summary reports for TDS and TH are examined as the two parameters with the most obvious changes as a result of trend analysis, it is possible to support the data with distribution histogram, box and whisker plot, Anderson-Darling normality calculation and p-values together with the normal distribution curve in Fig. 5. According to the figure, the concentrations of these two parameters are high, but in the histogram for all data, the
values are not far from each other and the parameters have normal distribution. The outlier test was performed by examining the summary report, normality and probability distribution charts among other parameters. Most of the data were found to have normal distribution after the outlier test. Parametric analysis should be done based on this information. The analysis was continued by removing the outlier values found in the outlier test from the data set. This test needs to be done to extract values due to any errors linked to sampling, experimental or instrumental errors. Seasonal and climatic changes will provide more normal or less erroneous results in subsequent analysis. In the linear regression analysis performed after this, the outlier values were removed from the data set and the parameters with normal distribution were used to ensure the reliability of this analysis.

According to the normality graphs given in Fig. 6, pH is a class I water quality value and its distribution is normal, while magnesium is a parameter that affects hardness and turbidity with abnormal distribution. The process of determining normality can take two forms. In the analysis in this study, the measurement distribution was examined with the normal curve on the graph and by looking at the p values. Therefore, parameters with p-value < 0.005 are non-normal and others are normal. The hardness concentrations in the waters of Akköprü Stream and the region are generally high. When the magnesium parameter is examined in this study, it shows a good normal distribution; that is the amount of magnesium throughout the year has a fairly regular distribution. As can be understood from this graph, there were sudden changes due to precipitation during seasonal transitions. Due to the proximity of Akköprü Stream to open spaces and residential areas, it is estimated that many substances enter the stream and affect the turbidity. Outlier values were determined according to boxplot, normal and probability graphs, and the plan was to reduce the errors in the rest of the analysis by eliminating them from the data set. Since abnormal parameters will not give healthy results, they should not be used in regression analysis. Phosphate, sulfate, sodium, fluoride, turbidity, and SS parameters are non-normal and the other parameters are normally distributed.

Pearson correlation analysis was performed to determine the relationships between water quality and variables such as environmental factors [54,55]. High positive and negative correlations (values between 0.60–1.00) were determined with correlation analysis performed in Minitab and Excel programs. The correlation data in these two programs were the same, and a more precise calculation was made with Minitab since it is a specialized statistics program. Correlation values of parameters with high correlation values from these analysis results are given in Fig. 7. Pearson’s correlation coefficient (r) was calculated as stated in Eq. (1) to examine the relationship between pollutant parameters and water quality analysis [56];

$$\text{Pearson correlation coefficient } r_{xy} = \frac{n(\sum xy) - (\sum x)(\sum y)}{\sqrt{[n\sum x^2 - (\sum x)^2][n\sum y^2 - (\sum y)^2]}}$$

where n is sample size, and x and y values are the individual sample points. When we look at the results in Fig. 7, positive correlations were in the range of 0.7–1.0, and the parameters with the highest correlation were chloride–sulfate $r = 0.89$, sodium–sulfate $r = 0.87$, total hardness–magnesium $r = 0.89$, total dissolved solid–conductivity $r = 0.86$ and dissolved oxygen–oxygen saturation $r = 0.98$. The relationship between hardness and magnesium is quite high at $r = 0.89$ for this surface water body. Likewise, Mg and Ca had a correlation of 0.72. Although both Mg and Ca directly affect hardness, the correlation between Ca and hardness is lower than 0.70. The fact that the Mg ratio in the water is higher than that of Ca is due to the irregular aquifer flow regime of the stream, eroding different rock types and coming with meteoric water characteristics. When the geological map of the hydrological basin is examined, it is estimated that rocks such as volcanic, tectonic, magmatic
Chloride-sulfate, $r = 0.89$
Sodium-sulfate, $r = 0.87$
Sodium-chloride, $r = 0.70$
Potassium-sulfate, $r = 0.70$
Potassium-sodium, $r = 0.82$
Magnesium-calcium, $r = 0.72$
Total hardness-magnesium, $r = 0.89$
Turbidity-phosphate, $r = 0.81$
Electrical conductivity-sulfate, $r = 0.84$
electrical conductivity-sodium, $r = 0.84$
Electrical conductivity-potassium, $r = 0.81$
Electrical conductivity-turbidity, $r = 0.73$
Total sol. solid-sodium, $r = 0.71$
Total sol. solid-turbidity, $r = 0.80$
Total sol. solid-conductivity, $r = 0.86$
Dissolved oxygen-oxygen saturation, $r = 0.98$

Nitrite-color, $r = -0.72$
Ammonium-potassium, $r = -0.60$
Ammonium-total sol. solid, $r = -0.63$
$pH$-phosphate, $r = -0.61$
Dissolved oxygen- phosphate, $r = -0.69$
Dissolved oxygen-potassium, $r = -0.65$
Oxygen saturation-potassium, $r = -0.74$
Turbidity-dissolved oxygen, $r = -0.61$
Turbidity-oxygen saturation, $r = -0.66$
E. conductivity-dissolved oxygen, $r = -0.65$
E. conductivity-oxygen saturation, $r = -0.68$
and metamorphic exist in the river bed and polluting elements mix with the water. Also, the geology of the river bed is affected by the lake sediments consisting of loose, moderately-compacted gravel, aggregate, sand, silt, mud and clay/amorphous clay. One of the reasons why Mg is high is that the water analysis includes Mg from the sanitary pond outlet. Young sediments and young volcanic rock types are seen along the bed of Akköprü Stream. Limestone, sandstone, alluvium, pumice, basalt, and lake sediments from these rocks reach the lake. Since these rock sources are rich in Mg and Ca, the Mg-Ca values are reflected in the water quality in parallel with the total hardness. It is also known that the Ca parameter has the same effect as Mg and the effect of these minerals on human health is observed with the occurrence of diseases such as calcification. In addition, Ca and Mg hardness causes blockages due to limescale forming in the pipes in the discharge or transmission lines. From the results obtained, the dissolved oxygen relationship has a high correlation with altitude-induced oxygen saturation. The highest negative correlations were between 0.6–1.0 for nitrite-color, \( r = -0.72 \) and oxygen saturation–potassium, \( r = -0.74 \) parameters. The negative relationship of potassium with oxygen is predicted to be caused by chemical reactions of minerals. As a result of correlation analysis, parameters with strong relationships were selected and used for regression and other analyses. Kirman Stream, which is an important tributary of Akköprü Stream, reaches the creek along a bed affected by pollution coming from small scale industrial areas. In addition, Mg and Ca intensity with the effect of rocks, the effect of the feed factory and the effect of the rock types along the bed. Therefore, when Şamran and Kirman waters join the surface flow, the total hardness value increases to the maximum at the point of discharge into the lake. The water quality parameters in Akköprü Stream generally concentrate in the basins in the western region, where population and industrial production increases and therefore pollution is more intense.

In addition to these, a matrix table was created using the Microsoft Excel program and the \( R \) squared \( (R^2) \) value was calculated. The interactive relationships between water quality parameters according to high \( R^2 \) values (between 0.7–1.0) are given in Fig. 8. The formula for \( R^2 \) is given in Equation (2), which demonstrates the square of the Pearson product moment correlation coefficient for known \( y \) and known \( x \)-values. The \( R^2 \) value can be interpreted as the deviation rate in \( y \) regarding the deviation \( x \). Therefore, while these values help explain the relationships between parameters, they also support the correlation results. The equation also states that the value of the dependent variable affects the independent variable.

\[
R^2 = \left( \frac{r_{xy}}{\sqrt{n} \left( \frac{\sum x^2 - (\sum x)^2}{n} \right)} \right)^2
\]

(2)

The highest data obtained as a result of this matrix table were for chloride–sulfate \( R^2 = 0.79 \), magnesium–total hardness \( R^2 = 0.79 \) and dissolved oxygen–oxygen saturation \( R^2 = 0.96 \). It is understood from the results of the analysis of \( R^2 \) values that chloride–sulfate and magnesium–total hardness correlations decrease-increase in direct proportion. These results are directly related to the correlation and support the results in Fig. 7. It is known that the chloride and phosphate relationship may be similar for different types of minerals, but more detailed chemical analyses are required in this regard. Considering the statistical analyses in this study, while human activities are the main effective factor, seasonal transitions and climate change also affect Akköprü Stream [57,58]. These effects disrupt the chemical balance of the stream established by the relationship between cations and anions; the hydrological regimes with the effect of increased drought; and consequently threaten the natural structure of the water [59,60]. When looking at the relationship between the tributaries of the stream and their qualities, while the environmental features of the Şamran Canal generally improve the water quality, the water quality is negatively affected by the increase in pollution after the Kirman Creek enters the stream. The parameters responsible for water quality changes are mainly related to TDS and SS, soluble salts and nutrients, and organic substances with natural and anthropogenic sources. In addition, fertilizers and pesticides used in agricultural activities and household wastes also affect water pollution [61,62]. Furthermore, it clearly seen that EC has correlation with TDS at 74%, as shown in Fig. 8.

In the final statistical analysis in this study, regression was performed with the Minitab program between the relevant parameters in order to determine the relationships between parameters. Regression analysis mainly examines linear or complex/indirect relationships between variables. In its simplest form, there are coefficient and slope values \( (b_1, b_2, \ldots) \) that intersect with the dependent variable and independent variables \( (x_1, x_2, \ldots) \) in a regression equation which has answer \( (y) \) as stated in Eq. (3).

Basic linear regression equation,

\[
y = a + b_1 x_1 + b_2 x_2 + \ldots
\]

(3)

In this study, regression equations for water quality allow better estimations of a response parameter associated with two or more parameters as variables. For the first equation created \( p, R^2 \) and adjusted \( R^2 \) values were checked. Since \( p \) value less than 0.05 and \( R^2 \) values close to 1.00% will give the most reliable result with the least error, the parameters with higher \( p \) values were regressed and equation analysis was performed. The equation that best fits the assessment was selected. This process is a method that expresses the water quality concentrations of the other parameters, apart from the response parameter, in terms of physical and chemical properties in an equation [63]. The linear equations determined as a result of the regression analysis and the \( R^2 \) and \( R^2 \) (adj) values for these equations are given in Table 2. The fact that these values are close to 100 percent indicates that the equation is healthy and reliable. Equations with more than 90% for \( R^2 \) values are given in Table 2. Accordingly, it shows that calcium and total hardness are parameters that affect each other, as is known from the literature [64]. For the regression analysis, the equation supports the result that magnesium affects the hardness together with calcium. In this study, it
was possible to represent pH with sodium, potassium, conductivity, oxygen saturation and COD. The pH parameter is affected by variations in many parameters as shown in the equation [65–67]. When the equation for the COD independent variable was examined, the parameters were related to the permanganate index, especially ammonium, and magnesium. In the equation created for the total dissolved solids variable, it is affected by high ammonium and sulfate parameters found in Akköprü Stream. In addition, the chloride effect is clearly seen in the conductivity equation, as in other equations [68,69]. Along with the positive correlation between turbidity and conductivity, the highest dependent variable in the turbidity equation in Table 2 is conductivity. It considered the reason for the turbidity increase is mostly due to sediment [70]. According to the results of regression analysis, the total hardness is related to sodium, magnesium, calcium, fluoride, oxygen saturation and sulfate; COD is related to potassium, permanganate

Table 2
Some important regression results with linear equations and $R$ values ($R^2 \geq 90\%$)

<table>
<thead>
<tr>
<th>Linear equations</th>
<th>$R^2$</th>
<th>$R^2$ (adj)</th>
<th>$R^2$ (pred)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrite = $0.258 + 0.0065$ oxygen saturation – $0.068$ color + $0.212$ potassium + $0.006$ sodium + $0.049$ magnesium – $0.26$ pH + $0.045$ COD – $0.018$ conductivity</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Sulfate = $-15.73 + 1.052$ chloride + $0.426$ sodium</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium = $-94.9 + 14.64$ potassium + $0.0502$ suspended solid – $2.331$ magnesium + $19.22$ pH</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calcium = $-785.1 – 1.805$ magnesium + $0.4885$ total hardness + $69.13$ pH – $0.4508$ turbidity + $2.983$ dissolved oxygen + $103.1$ phosphate + $0.42$ total dissolved solid + $7.21$ permanganate index – $5.985$ COD</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Magnesium = $50.17 – 0.804$ permanganate index – $0.521$ dissolved oxygen – $1.94$ pH – $0.124$ sodium + $0.093$ calcium</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH = $11.649 + 0.023$ sodium – $0.0114$ oxygen saturation – $0.008$ suspended solid – $0.20$ electrical conductivity – $0.56$ potassium – $0.061$ COD + $0.0703$ chloride – $0.043$ sulfate – $0.207$ permanganate index</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Turbidity = $43.7 – 7.92$ electrical conductivity + $1.112$ total dissolved solid – $1.014$ oxygen saturation + $3.257$ chloride</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electrical conductivity = $28.67 + 0.079$ total res. solid + $0.321$ chloride – $0.998$ dissolved oxygen</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Suspended solids = $4085 – 14.16$ sulfate + $5.45$ oxygen saturation + $17.73$ sodium + $6.87$ turbidity + $55.1$ electrical conductivity – $6.67$ total sol. solid – $544.1$ pH – $10.87$ chloride – $271.2$ potassium</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dissolved oxygen = $3.10 + 0.0276$ sodium + $0.516$ potassium + $2.19$ nitrite – $0.0986$ electrical conductivity + $0.0712$ oxygen saturation</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxygen saturation = $60.05 – 8.34$ potassium + $11.003$ dissolved oxygen – $3.568$ permanganate index</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: The units for all parameters are shown in Fig. 3.
index, ammonium and magnesium; color is related to nitrite and nitrate; and calcium is associated with magnesium, pH and turbidity parameters. According to Table 2, 99.99% $R^2$ correlation coefficient was determined for the Ca regression equation with Mg and TH. Mg equation had 93.60% $R^2$ value together with Ca and the total hardness regression equation with Ca had 87.24% correlation. Ca is an effective parameter on the total hardness and the Mg value is higher in the stream water due to rocks and other effects.

4. Conclusion

Akköprü Stream is a river that starts from Lake Sıhke and flows into Lake Van within the borders of Van province. This stream passes through residential areas and neighborhoods, where agriculture, animal husbandry, small industrial and factory activities are carried out. In this study, after determining the water quality with 22 physicochemical parameters and data determined seasonally from a single station at the point where Akköprü Stream discharges into Lake Van, the relationships between these parameters were analyzed using basic and parametric statistical methods. As a result of the analysis, it was determined that Akköprü Stream generally has Class I water and some other parameters indicate Class II, III and IV water quality. Our results were compared to the other standards (EC, WHO, TS 266 and EECCA), and the water quality values for the data set in this study did not exceed the limits and were good. Individual-annual fluctuations in physicochemical parameters were examined by trend analysis and it was understood from the data graphs that the two parameters with the biggest fluctuation are TDS and TH. When the pH and magnesium values are examined, they have normal distribution; that is, these parameters have a regular distribution throughout the year. Turbidity had abnormal distribution with sudden changes due to precipitation during seasonal transitions. It is estimated that the area surrounding Akköprü Stream is open and includes residential areas, so different substances mix into the stream and affect the turbidity. It was determined from normality graphs that phosphate, sulfate, sodium, fluoride, turbidity, and SS parameters have abnormal distribution and other parameters have normal distribution. The nitrite-color correlation was negative, with an increase in one parameter causing a decrease in the other parameter. Considering the regression results, it is understood that sodium, potassium, conductivity, oxygen and TDS in the pH equation are due to high ammonium and sulfate parameters in Akköprü Stream. In addition, turbidity, chloride and conductivity associations were seen in regression equations as in other studies. In conclusion, it was determined that the water quality of Akköprü Stream, which flows into Lake Van, is influenced by anthropogenic pollutants with slight effects. These generally consist of agricultural and livestock activities in settlements, and a small amount of small industrial and factory activity.

As a result of the statistical analyses, Akköprü Stream has Class I water quality but pollution is observed in the stream water with some parameters. The water quality of Akköprü Stream is affected by water from the Şaman river, which enters the stream after being affected by the regions/mountains/rocks, and Kirman Stream, influenced by the industrial zones and the surface flows as anthropogenic factors. It was observed that Akköprü Stream passes through areas in which domestic wastes play a large role in pollution as a result of the increase in population close to the stream.

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