TALLINN UNIVERSITY OF TECHNOLOGY
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MULTIVARIATE ANALYSIS OF ELEMENTAL COMPOSITION AND TEMPORAL DYNAMICS IN ESTONIAN RIVERS (1994-2021): IMPLICATIONS FOR WATER QUALITY AND ECOSYSTEM HEALTH

EESTI JÕGEDE VEE KEEMILISE KOOSTISE JA SELLE AJALISE DÜNAAMIKA MITMEMÕÕTMELINE ANALÜÜS (1994-2021): SEOSED VEE KVALITEEDI JA ÖKOSÜSTEEMI TERVISEGA

MASTER THESIS

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THESIS TASK

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Thesis topic:

(in English) *This thesis investigates the dispersion, patterns, and factors that impact the water quality parameters in Estonian rivers between 1994 and 2021 by employing multivariate statistical methods*

(in Estonian) ……*Käesolevas lõputöös uuritakse mitme muutujaga statistiliste meetodite abil Eesti jõgede veekvaliteedi parameetreid aastatel 1994–2021 mõjutavaid dispersioone, mustreid ja tegureid*

Thesis main objectives:

1. Analyzing the selected parameters
2. Defining the changes over the selected years
3. Determining reasons for these changes and impacts

Thesis tasks and time schedule:

No	Task description	Deadline
1.	To define and study the research area and collect data	15.10.2022
2.	To examine various methods to determining water quality	10.12.2022
3.	To assess the water quality index through methods	22.03.2023

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Table of Contents

LIST OF FIGURES

LIST OF TABLES

ABSTRACT

This thesis examines the distribution, trends, and influencing factors of water quality parameters in Estonian rivers from 1994 to 2021 using multivariate statistical techniques. The Q-Q plot analysis revealed non-normal distribution patterns for sulphate (SO4), pH, and magnesium (Mg), suggesting that these parameters might be influenced by environmental factors affecting their distribution in the water. Principal component analysis (PCA) identified key factors influencing water quality, including pollution-related factors (Cl, SO4, Mg, Na+K) and water hardness/pH factors (Mg, Na+K, pH), as well as cation presence and distribution (Ca, K, Na, Mg) related to both natural and anthropogenic influences. Trend analysis indicated variable changes in water quality parameters across different watercourses, highlighting the influence of multiple factors such as land use, agricultural practices, and geological features. Time series analysis of monthly variations in water quality parameters showed seasonal fluctuations for some parameters (e.g., Ca, K, Mn, temperature) and relatively stable concentrations for others (e.g., Cl, Na), with sulfate concentrations exhibiting some variability and pH values remaining consistently within acceptable ranges for most aquatic organisms. The study concluded that the overall water quality in Estonian rivers was of medium quality, with the primary sources of impact being agricultural activities in the Northeast, industrial activities in the Northern region, and mining activities throughout the country. To reduce the negative impact of human factors on rivers, the study recommends implementing further rules and regulations targeting the environmental impact of each industry. This comprehensive analysis underscores the need for a multi-pronged approach addressing both pollution-related and natural factors influencing water chemistry in Estonian rivers.

1. INTRODUCTION

Freshwater is, regardless, the most significant part of sustaining life on our Earth. It's an important part of the living organism and supports the livelihoods of human populations. Additionally, it serves as a critical factor for the productivity and financial growth of different industries, making it an indispensable resource for human societies [1].

Estonia is a Northern European nation, situated along the Baltic Sea to the west and the Gulf of Finland to the north. Its allure lies in the breathtaking and varied terrain featuring forests, hills, and waterways. A significant part of the country's natural beauty is its network of rivers that contribute to Estonia's ecology and economy. Rivers serve as critical links between human communities, natural habitats, plant and animal life, and other living entities. The concept of environmental life provides a framework to deepen our understanding of the relationships between river flows and human populations, and offers valuable insights to those who rely on it for their well-being [2]**.** These rivers, shaped by geological events like glaciers and their location between the Baltic Sea and the East European Plain, sustain a thriving plant and animal life and cater to the needs of agriculture and industry as well as offer opportunities for recreational activities like fishing, boating, and swimming.

In the past decade, there have been many programs, funding, and volunteering made in order to increase awareness, and concern about water pollution, and climate change all over the world, to achieve that Researchers, scientists, and entrepreneurs are creating new innovations to achieve sustainable approaches for water resources. The new environmental innovations, tools, technologies, techniques, and methods enable the analysis of water samples. The usage of multi-Criteria decision-making (MCDM) methods for developing the Water quality index is quite recent. One of the recent methods WQI based on the Analytic Hierarchy Process (AHP) was suggested for analyzing ecosystems in different fields. [3].

Despite their beauty and significance, the rivers in Estonia are facing a fresh challenge due to climate change. This has a profound impact on the Estonian rivers and their supported ecosystems, altering water quality, flow patterns, and the distribution of aquatic species. Climate change has the ability to significantly impact the hydrology, ecology, and biodiversity of these rivers, making it essential to comprehend the potential impacts and take steps to address them. Some of the keyways that climate change is affecting Estonian rivers include.

Rising Temperatures, the average temperature in Estonia has risen by 1.6-2.0 °C from 1966 to 2010, with the largest increases being seen in winter and spring. This warming trend is having a considerable impact on the duration and timing of the growing season for species that inhabit rivers, as well as altering migration and breeding patterns for aquatic animals. It's estimated that globally, the main factor impacting ice melting is the rate of temperature fluctuations, in case if the temperature rises 0.5 °C each decade the majority of ice and glaciers could be diminished by the year 2100. If this increase happens at 0.1 °C per decade it would be slower than expected [4].

Alterations in Precipitation Patterns: Changes in precipitation patterns in Estonia have not been as noticeable or consistent as the changes in temperature, however, there has been a general increase in winter rainfall due to the intensification of westerly winds from the North Atlantic during the winter. The enhanced rainfall results in higher water levels in Estonian rivers, which can change riverbank stability and flood patterns. It's noticeable to observe that in Estonia yearly maximum rainfall intensity has risen by an average of 4% per decade because of different climate changes [5]. Besides changes in precipitation, climate change is also impacting the timing and magnitude of snowmelt, which is crucial in replenishing Estonian rivers. As temperatures continue to rise, the amount of snow accumulation during winter is expected to decrease, leading to a reduction in water availability for rivers in spring and summer. This could greatly affect agriculture and local industries such as fishing and tourism that rely on healthy and functioning rivers.

Reduced Snow Cover: Due to the warming trend, the length of snow cover in Estonia has shortened by over three weeks, with the average thickness in February and March decreasing by 10-20 cm and the average snowmelt in these months reducing by 20-40 mm [6]. Overall, this observed trend affected almost all seasons, especially during spring and winter times, to take this data in Estonia snow cover duration has been shortened by 3-4 days per decade [7]. This is impacting the timing and volume of spring runoff and changing the flow patterns in Estonian rivers.

Decreased Ice Presence: The extent of ice coverage on Estonian rivers has diminished, with ice forming later and melting sooner due to the warming trend. This is influencing the timing and extent of winter fishing, as well as modifying the environment for aquatic plants and animals. Taking into consideration, it can be observed that the rate of increase in the Earth's temperature has been greater since 1970 than during any other 50-year period in the past 2000 years. Nevertheless, it is even more significant to note that the temperature measurements taken during the most recent decade, between 2011 and 2020, greatly surpass those of the warmest multi-century period [8]. The rise in global temperatures and escalating water usage have led to a reduction in the size of lakes and river streams worldwide. In response to this water scarcity, one of the prevailing solutions is to transfer water directly from freshwater sources such as rivers and lakes [9].

Earlier research has demonstrated that a link exists between river runoff and the time period between spring and summer, and this correlation is regarded as robust. To properly analyze the runoff period, it is essential to conduct long-term analyses that take into account seasonal variations and levels of snow cover [10]**.** Anthropogenic activities caused by climate change variability, the river runoff of most rivers in Estonia as well as on Earth, forced great changes and importantly the state of resources and mineral changes in water.

Due to climate changes and other natural effects, researchers have shifted their attention to analyzing trends in river runoff over extended periods. Traditional tendency analysis and identification methods, like time series and Principal component analysis (PCA) methods, as well as linear regression trend tests, are commonly used. For analyzing changes in water quality and levels of lakes and rivers, the Taylor and Loftis method can be applied. These techniques enable the analysis of trends in a single variable over a specified period.

This paper assesses the long-term changes in Estonian rivers and their environmental impacts. It provides a comprehensive understanding of the factors contributing to these changes and sources.

1.1 Aim of the study

Until now not so many studies have been carried out analyzing river water quality and lake ecosystem of the reservoirs as well as groundwater charges of the water retention landscape in Estonia. Generally, researchers talk about soil contamination, and the surrounding environment, with very few specific parameters, etc.

This research aims to evaluate the water quality data, as well as to analyze the changes and trends of rivers over an extended period of time, including the environmental effects of these changes. The objective is to gain a comprehensive understanding of these changes to ensure the sustainability of water resources and to propose more effective water quality management strategies for rivers. To determine water quality, the study uses trend analysis and the analysis of ion concentrations in river water. The data for this analysis was collected from the Ministry of Environment's website (ENVIR) for the period between 1994 and 2021. During the research, parameters for Calcium (Ca), Chlorine (Cl), Potassium (K), Magnesium (Mg), Manganese (Mn), Sodium (Na), pH, Sulfate (SO4), and Temperature. of river water in the study were measured and analyzed.

The findings of this study can aid authorities, researchers, and decision-makers in creating sustainable solutions for the local community and preserving the environment. This knowledge can be applied to initiatives such as the LIFE IP CleanEST project, a collaboration between the Estonian Ministry of the Environment and the European Commission aimed at improving river basin management in Estonia (2018-2028) as well as other local projects.

1.2 Statistical and Spatial Analysis

The spatial geolocation of the sampling points and geological background was located using Google Earth software. For the data cleaning, sorting, and other functional measures done with Microsoft Excel 2019. The IBM SPSS Statistics 26 software was employed to perform descriptive statistics, correlation, and Principal Component Analysis (PCA). Time series and trend analysis was conducted using PowerBI data visualization software.

1.3 Study area

Estonia covers an area of 45,227 km2, of which 43,200 km2 is considered land. According to spatial statistics, the topography is largely flat, with more than 40% of the territory with elevations generally ranging from 30 to 100m above sea level, although in the Haanja Upland area, it can reach a maximum of 317m. In general, the surface is flat, highlands and plateaus alternate with lowlands, but the height differences usually do not exceed 20m, 50 m, or greater differences are very rare. The average height of the ground above sea level is 50m [11].

The average temperature in January on the seacoast is -4.5C, while in all of Estonia, it is around -5 C. The isotherm of the winter months runs north-south in the western part of Estonia, while in northern Estonian their direction runs parallel to the coast. There is a difference of 4-5 C between the isotherm of Eastern and Western Estonia, in March and the temperature difference between Eastern and Western Estonian is only 2C. Taking overall in Estonia indicates that past 50 years the air temperature has risen by 2 C [12].

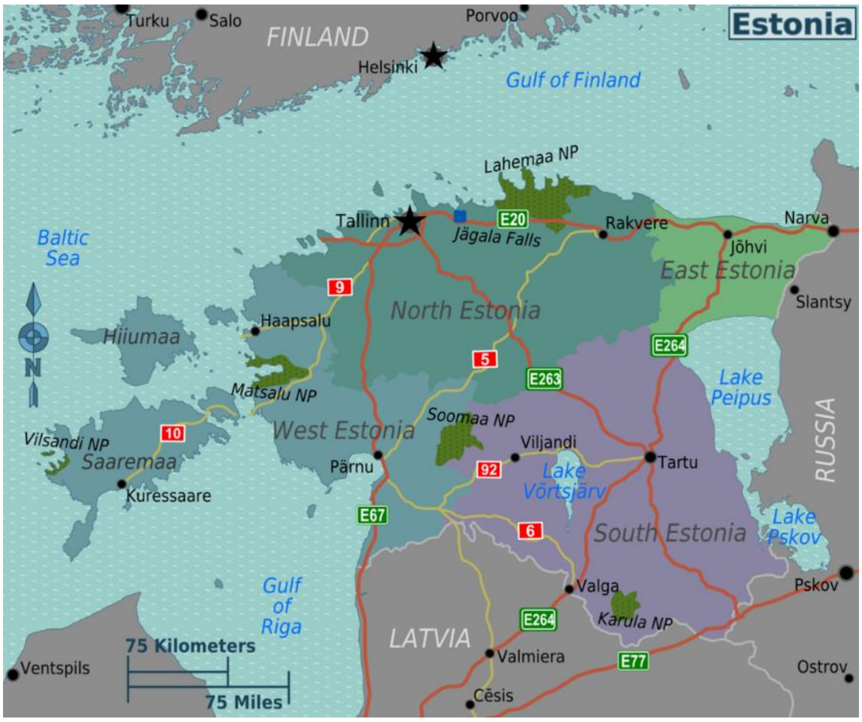


Figure 1.1: Map of Estonia (Source: WikiMedia)

In Estonia (Figure 1.1), there are 7,000 rivers, canals, and streams. Although the river network is dense, many of these rivers are short with small drainage areas and low flow rates. The majority of rivers, 90%, are less than 10 km in length, with only a small percentage exceeding 50 km in length. The longest river in Estonia is the 162 km Võhandu river, followed by the 144 km Pärnu river. Other significant rivers include the Põltsamaa, Pedja, Kasari, Keila, and Jägala rivers shown in Table 1.1 [13].

Table 1.1: 20 Longest rivers in Estonia

River	**Length (km)**	**Catchment area (km²)**	**Watercourses (m)**		**Decline (m)**	**Lang (m/km)**	**Flow rate at mouth (m³/s)**
			overall length (km)	**density (km/km²)**			
Võhandu	162	1420	599	0,42	86	0,55	10,2
Pärnu	144	6920	3367	0,49	78	0,54	65
Põltsama	135	1310	557	0,42	72	0,53	12
Pedja	122	2710	1195	0,44	67	0,55	10,9
Keila	116	682	282	0,41	75	0,65	6,4
Kasari	112	3210	1324	0,41	62	0,55	30
Piusa	109	796	240	0,3	212	1,94	5,8
Pirita	105	799	352	0,44	75	0,71	6

Table 2.1: 20 Longest rivers in Estonia (continued)

Emajõgi	101	9740	2739	0,28	4	0,04	70
Navesti	100	3000	1456	0,49	57	0,57	26,9
Jägala	97	1573	665	0,42	82	0,85	12,9
Vigala	95	1580	657	0,42	61	0,64	14,1
Ahja	95	1070	442	0,41	87	0,92	6,9
Õhne	94	573	267	0,47	62	0,66	4,8
Halliste	86	1900	917	0,48	76	0,88	17,1
Valgejõgi	85	453	155	0,34	107	1,26	3,9
Mustjõgi	84	1823	519	0,28	29	0,35	13,4
Emajõgi	83	1380	576	0,42	81	0,98	10,7
Narva	77	814	388	0,48	30	0,39	378
Reiu	73	917	443	0,48	49	0,67	7,9

1.4 Land

The main trends in Estonian land-use dynamics have been a decrease in agricultural land from 65% in 1918 to 30% in 1994 and an increase in forested areas from 21% to 43%, respectively. According to Estonian government data, climate change from agricultural activities is increasing steadily and data shows that emissions from these activities are increased by 25% compared to 2005 and 4.5% compared to 2019 predictions from data show that this stable increase will continue by 2030 (Figure 1.2). After the early years of becoming independent, the number of small farms in Estonia has grown from 1993 to 2001 sharply [14]**.** The share of agricultural land was the largest prior to the first land reform, as agriculture was the main branch of the economy then. In different counties, this number varied largely. It was the highest in Saaremaa, reaching an unbelievable 88%, and even in Virumaa, the least agricultural county, it exceeded 60% [15]. Since the start of the 1990s, there has been a five-fold reduction in the quantity of industrial water, which can be attributed to the implementation of sustainable production techniques and water recycling. There has been a decrease in the quantity of agricultural water, which can be attributed primarily to a reduction in agricultural practices. Specifically, the amount of agricultural water has decreased by around 7.5 times. [16]**.**

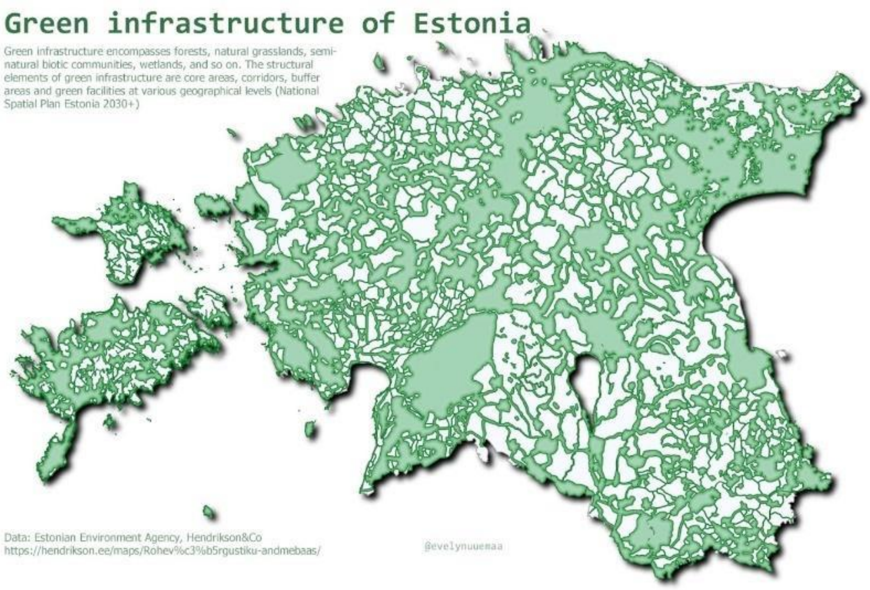


Figure 1.2: Green infrastructure refers to various natural features such as forests, natural grasslands, semi-natural biotic communities, and wetlands [17]

Water designated for human consumption has experienced the least significant alteration in terms of quantity, staying consistently below 50 million cubic meters per year over the past decade [18].

1.5 Water resources

In the way of natural river basin districts, Estonia has four natural districts: Narva-Peipsi, The Gulf of Finland, The Gulf of Riga, and the other islands. The majority of rivers in the mainland are situated on the Pandivere upland, which is an extensive kart area with sloping terrain. According to the data, the general health of Estonia's rivers is deemed satisfactory. In 2014, assessments of surface water quality revealed that merely 8% of the samples were in "excellent" condition, while 60% were classified as "good" and the remaining 30% as "moderate" [19].

Estonian rivers are typically small in size and, as a result, have limited water capacity. Moreover, the enhancement of water resources is constrained due to their division into small streams and parts, which also hinders economic growth by restricting the development of water transportation, hydro dams, and industrial infrastructure. Despite the need for distributed water supply in the Northern regions of Estonia, where most of the industrial areas are located, the surface water supply remains insufficient. Considering these facts in total industry water usage has increased by 3% in recent years (2019, 2020) [20].

From availability to resourcing, Estonia usually has enough and sufficient need to answer human needs, agricultural activities as well as industrial usages. Taking into consideration that Northern areas of Estonia have more industrial areas compared to

other parts of it, which means distribution and access to surface water are limited. The annual water usage for Estonia reached 704.28 thousand m3 in 2020, compared with 2019 it decreased -by 15.5% respectively.
Estonia is considered to have abundant groundwater resources, with approximately 4,000 million m3/year of internal groundwater resources. The primary collection area for groundwater is situated in the Pandivere uplands, an area dominated by limestone formations and locally significant gravel ridges.
A portion of the groundwater flows into the sea, while another portion is returned to the surface water system. This flow into the surface water system has caused an overlap or runoff of about 3,000 million m3/year over the years. As a result, the total renewable water resources of Estonia reach approximately 12,808 million m3/year.

1.6 Measured parameters

1.6.1 pH

The carbon dioxide-bicarbonate-carbonate equilibrium system regulates the pH of most naturally occurring fluids, which is a measurement of the acid-base equilibrium.
The process of environmental acidification that occurs naturally due to geological activities is recognized for its ability to decrease the pH level of natural water bodies to a point of acidity that is unsuitable for numerous aquatic life forms [21].
Lower pH can be affected by increased carbon dioxide, and oppositely decreased carbon dioxide can increase the level of the pH. One strong correlation with pH is temperature. Temperature can affect the equilibria and the pH. The connection between water pH levels and various water quality parameters can vary across distinct aquatic systems and may be impacted by the presence of other parameters.[22].
pH also measures how acidic or base the quality of water is. The pH scale can be measured from 0 (acidic) to 14 (alkaline). A neutral level of pH in the water is scaled with 7, while below it is accepted as acidic water, and above 7 is alkaline or basic. The pH in most of the drinking water stands on a scale between 6.5 to 8.5.

1.6.2 Sodium

The presence of sodium in natural water sources is the result of the erosion of rocks and minerals. The level of sodium usually depends on many conditions and the surrounding environment. In the water, sodium has no smell but it's possible to taste it if it's over 200 mg/L or above. Sodium in the water can range from 1-100 mg/L [23]. This level of sodium can be dependent on many factors as well, such as pollution from sewage effluent, industrial areas, infiltration of leachate from landfills, etc. Almost many waters contain sodium naturally because the rocks, minerals, and soils contain sodium as well, and it easily dissolves. The concentration of sodium in water can differ depending on the many conditions. Typically, sodium concentration in rivers ranges from a few milligrams per liter to less than 100 milligrams per liter. When it comes to precise amounts of sodium, often these results are inadequate. In the aftermath of the monsoon season, there is a noticeable increase in sodium levels, which suggests the contribution of sodium from the catchment area into the river [24].

1.6.3 Potassium

Potassium is an essential element for humans and is usually present in natural waters at safe levels for human consumption, with a recommended daily intake of over 3000 mg. Potassium in the river waters can vary from 2-3 ppm (parts per million) potassium [25]. Potassium can be also found in drinking water as well, because of the usage of potassium permanganate in water treatment. Potassium can be found in many minerals, passing through weathering processes, for instance from orthoclase, and microcline, which do not contain high levels of potassium but can be used at the production level. Some of the potassium materials, for example, potassium nitrate is used for synthetic fertilizers 95% are used for adding to synthetic fertilizers [26].

1.6.4 Magnesium

Magnesium is naturally found in minerals that can be found in lake and river waters as well. It's one of the essential parameters for the growth and life of aquatic organisms, for the flora and fauna. It's possible to find magnesium in different formations, for instance, soluble and insoluble, but the level of magnesium in waters, especially river waters, depend on many factors such as human factors, the geologic surface of the area, seasons, and weather as well.

The concentration of magnesium ranges from 1 mg/L to 40 mg/L in many water bodies [27]. Based on WHO guidelines for drinking water, there were levels of magnesium considered as 30 mg/L. It's also known that there is a strong correlation between calcium and magnesium in natural waters. The level of magnesium has a great impact on river water, especially high levels of magnesium with a mix of calcium can result in the formation of hard water and this can result in a negative impact on aquatic organisms, nutrients, and minerals in the water. Additionally, human factors can lead to rapid changes in the level of magnesium, such as industrial activities, and agricultural runoff, which can lead to great pollution and impact on environmental surroundings.

1.6.5 Manganese

Manganese is a silvery-gray metal that naturally occurs in river water. It is commonly found in waters, soils, and rocks. Manganese can also be present in drinking water, and European Regulations have established a limit of 50 µg/l to ensure safety [28]. Exceeding this limit can impact the water's color, odor, appearance, and taste, and pose risks to both humans and aquatic life. Generally, manganese concentrations in rivers and lakes can range from 0.01 mg/L to 1 mg/L. However, human factors, such as proximity to industrial areas, can lead to higher levels of manganese in the water.

1.6.6 Calcium

Calcium is one of the unique minerals found in freshwater bodies in all types of water. Calcium concentration can vary from 4-100 mg/L, and it depends on many factors. The biggest source of calcium for freshwaters is leaching from rocks, limestone, dolomite, gypsum, and other calcium contained rocks and minerals. There are many reasons why Calcium is important, but one of them is, it's important for freshwater flora and fauna. Although this is important, the level of calcium is also an essential factor for the well-being of the environment. This means the level of calcium can have significant changes and impacts on the health of the water. According to studies, water hardness (measured as an equivalent of $CaCO_3$) exceeding 200 mg/L can cause incrustations, which may vary depending on the interaction with other factors such as pH and alkalinity [29].

Low levels of calcium in river water are usually found in oligotrophic environments. These are called low nutrient levels and give life only to flora and fauna. But this low level of calcium can impact negatively the fish.

High levels of calcium can support many types of plant and animal life in its surroundings. But very high levels of calcium have a negative effect on the freshwater environment, for example, calcium can connect with phosphorus, and it would lead to the evolving of compounds that can settle down in the river and can limit the growth of organisms.

1.6.7 Chlorine

Because of high reactivity, chlorine is usually not present in high levels in natural river waters. Although, low levels of chlorine can be found in the river waters because of the erosion of rocks and minerals which contain some amount of chlorine. Human activities can also affect the level of chlorine in river waters such as the use of chlorine as a disinfectant in water treatment plans and discharge of the sewage effluent. As a chemical form of chlorine usually used to sanitize drinking water by dismissing the harmful bacteria’s and preventing growth in the distribution system [30]. Additionally, agricultural activity has an impact on rising levels of chlorine. Chlorine has several effects, including the elimination of organic compounds and the transformation of soluble metallic compounds into insoluble solids. The impact of chlorine depends on its form and the pH of its surroundings. Sunlight can also catalyze the effects of chlorine, and the resulting radiation can have significant consequences. Chlorine can react with ammonia values to produce various forms of hypochlorite, which also contain radiation. This is an important effect of chlorine.

1.6.8 Sulphate

Sulfate is a chemical compound that is formed from sulfuric acid that reacts with it as a base. Sulfate plays an important role in water as well as has many uses and properties, but with positive sides, sulfate also has negative effects on the environment and human health as well. It's important to note that it's observed that the level of Sulfate in freshwater bodies has been increased not locally but also globally. The trend has been connected to a significant decrease in atmospheric sulfur deposition in many regions including Europe and America. The issue of sulfate contamination in freshwater ecosystems is a worldwide concern that continues to persist [31]. This increase in sulfur can be connected to wetland drainage and nitrate pollution in water bodies.

One of the significant impacts of sulfate is on water quality changes. The concentration of sulfate changes in freshwaters can range from 0 to 250 mg/L in lakes, for river waters it can vary from 0-250 mg/L [32].

High levels of sulfate in water bodies can lead to different formations of sulfate and it will result in being highly acidic and can be harmful to flora and fauna nearby water bodies. Additionally, high levels of sulfate in drinking water can cause a negative impact on human health as well, and it will cause critical health issues.

2. METHODOLOGY

2.1 Data collection and analysis

This study analyzed annual and monthly time series data from 33 rivers and streams in Estonia. All the water quality data were taken by the Estonian Ministry of Environment website KESE (Environmental Monitoring Information system). KESE is a collection of data on the state of the environment collected within the framework of the national environmental monitoring program and related environmental research projects. All the data was examined for monthly and yearly trends from per river names and parameters. The seasonal and annual trends were also taken into account. The water quality data was collected for 33 rivers around Estonia and analyzed from 1994 to 2021. The complete data sets are divided into a couple of parts, seasonal, monthly, and cardinal directions in order to get accurate analyzing results. The spring season includes March, April, and May. Summer seasons include months of June, July, and August. Autumn seasons include September, October, and November. The winter includes December, January, and February. Table 2.1 shows nine chemical and physical water quality parameters are selected for all the analyzing processes. These parameters are Calcium (Ca), Chlorine (Cl), Potassium (K), Magnesium (Mg), Manganese (Mn), Sodium (Na), Sodium and Potassium (Na+K), pH, Sulfate (SO4), and Temperature.

Table 2.1: List of analyzed rivers and parameters

Name of Rivers	**Measured parameters for all rivers**		
Ahja jõgi	**Parameters**	**Abbreviation**	**Unit**
Alajõgi	Calcium	Ca	mg/L
Avijõgi	Chlorine	Cl	mg/L
Emajõgi	Potassium	K	mg/L
Jänijõgi	Magnesium	Mg	mg/L
Keila jõgi	Manganese	Mn	µg/l
Kullavere jõgi	Natrium	Na	mg/L
Kunda jõgi	Sodium and Potassium	Na+K	mg/L
Linnussaare oja	pH	pH	
Mustjõgi	Sulphate	SO4	mg/L
Narva jõgi	Temperature	T	°C
Navesti jõgi			
Õhne jõgi			
Oostriku jõgi			
Pärnu jõgi			
Pedja jõgi			
Piusa jõgi			
Põltsamaa jõgi			

Table 2.1: List of analyzed rivers and parameters (continued)

Porijõgi / Reola jõgi	
Preedi jõgi	
Rannapungerja jõgi	
Reiu jõgi	
Saarjõgi	
Taebla jõgi	
Tagajõgi	
Tänassilma jõgi	
Väike Emajõgi	
Valgejõgi	
Velise jõgi	
Vigala jõgi	
Vodja jõgi	
Võhandu jõgi	
Võisiku peakraav	

2.2 Statistical data analysis

In this study the following statistical and visual analysis performed by using the following methods:

1. Descriptive statistics
2. Q-Q plots
3. Time series visual and statistical analysis
4. Trend analysis
5. Principal component analysis

2.3 Quantile- Quantile (Q-Q) plots

The visual tool known as the Quantile-Quantile (Q-Q) plot is utilized to assess whether a dataset is normally distributed. Q-Q plots were developed to enable a visual comparison between the residuals of each distribution and a corresponding normal distribution with identical mean and standard deviation values [33]. The Q-Q plots can illustrate the parametric rating curve and quantile mapping function approaches and its capable of replicating the same distribution observed in the measured values [34]. This involves comparing the values of the dataset to the median normal order statistics presented on a horizontal straight line. The plot has two axes, with the vertical axis representing the ordered values and the horizontal axis representing the median normal order data. If the points on the plot are near the straight line, then the data can be deemed normally distributed. Conversely, if the points are far from the line, then the data contains outliers and cannot be considered normally distributed.

2.4 Time series visual and statistical analysis

The method of time series analysis is recommended for assessing the proportion, velocity, and modifications of data over a specified period. Time series analysis is a crucial tool employed to comprehend the variations in the physical and chemical attributes of rivers with time. This approach is widely utilized in environmental management, water resource management, and other fields to monitor the state of rivers and make informed decisions regarding their administration and conservation. Monitoring changes in water quality is a significant aspect of trend analysis for rivers, which involves measuring factors such as pH, temperature, levels of dissolved oxygen, nutrient levels, and the presence of pollutants like heavy metals, pesticides, and other chemicals. These measurements help to understand how the water quality of rivers is evolving over time and detect any potential threats to aquatic life and human health.

Time series techniques have the capability to identify deficiencies in water monitoring over an extended duration, and with the aid of predictive technologies like ARIMA, it is feasible to generate water quality projections for virtually all rivers. Research indicates that by establishing values for each water quality parameter, it is possible to forecast future water quality trends and take appropriate measures in response to changes in these trends [35].

The Autoregressive Integrated Moving Average (ARIMA) is a forecasting, predictions model that has been used among many researchers. It's a method that was invented by Box and Jenkins in 1970. There are great advantages of using ARIMA by the simplicity of setting up a data set to get an accurate prediction with a high significance. It's advised that, in order to get high accuracy and linear connection, it's better to use normal time series in the forecasting method.

Research indicates that the implementation of ARIMA models can forecast water quality over prolonged periods ranging from six months to several years. In one study, a 97.4% accuracy rate was achieved in predicting Phosphorus and Nitrogen water quality parameters [36]. Furthermore, according to another research, ARIMA methods are suggested as they inherently capture the seasonal fluctuations in the forecasted water quality parameters [37]. Aside from monitoring water quality, trend analysis and forecasting for rivers also entails monitoring changes in the physical characteristics of rivers such as flow rate, sediment load, and channel morphology. Another recent study for trend forecasting from 2020-2024 has carried out to determine river water pollution at India, measuring 12 water quality parameters as well as pollution parameters [38]. These alterations may be caused by various factors, including natural processes like erosion and sedimentation, and human activities like dam construction, land use changes, and urbanization. By monitoring these physical changes, trend analysis can detect potential issues like decreased river flow and increased sedimentation and inform management decisions aimed at preserving the health of rivers.

2.5 Principal component analysis

PCA and PCF techniques have been increasingly used in various environmental applications in recent years, such as assessing groundwater monitoring wells, interpreting groundwater hydrographs, analyzing temporal and spatial patterns of heavy metal contamination, and identifying herbicide species associated with hydrological conditions. Principal component analysis (PCA) is a statistical method used to analyze a dataset that contains multiple correlated variables [39]. Numerous investigations have been conducted utilizing the PCA approach, wherein contemporary scholars have applied it to various environmental issues, including the analysis of hydrographs, the measurement of long-term pollution patterns, and the study of hydrological conditions [40]. Through the utilization of PCA methods, it is feasible to identify crucial water quality constituents that have a significant influence on environmental pollution caused by nutrient and organic contaminants [41].

The goal of PCA is to extract important information from the data and transform it into a set of new independent variables called principal components. These components can then be used to visualize similar patterns among the variables and observations on maps. The usefulness of the PCA model can be measured with cross-validation approaches.

To determine if a dataset is suitable for factor analysis, the Kaiser-Meyer-Okin (KMO) and Bartlett tests can be used to evaluate all available data. A KMO value over 0.5 and a significance level below 0.05 for the Bartlett test indicates there is an appropriate correlation in the dataset [42]. To be considered appropriate, the KMO value should be above 0.4 and calculated for each variable. Values between 0.00 to 0.49 in the dataset indicate a weak correlation between the data variables.

3. RESULTS AND DISCUSSION

3.1 Descriptive statistics

The statistical parameters of the time series of yearly values of water quality parameters of the 33 Estonian rivers from 1994- 2021 are summarized in Table 3.1.

Tabel 3.1: Descriptive statistics of measured parameters

						Variance		Skewness		Kurtosis	
	N	Range	Minimum	Maximum	Mean	Std. Deviation		Std. Error		Statistic	Std. Error
Ca (mg/L)	2231	159	1	160	66.8	20.707	428.773	-0.24	0.052	0.288	0.104
Cl (mg/L)	6914	123	0.37	124	8.178	25.531	651.81	79.653	0.029	6522	0.059
K (mg/L)	1370	17.96	0.04	18	2.292	1.172	1.373	2.918	0.066	24.83	0.132
Mg (mg/L)	2231	108.9	0.1	109	17.2	10.11	102.229	3.024	0.052	14.41	0.104
Mn (µg/L)	127	257.96	0.04	258	70.02	51.88	2691.13	1.342	0.215	1.94	0.427
Na (mg/L)	1364	17.8	0.2	18	4.1	1.79	3.212	1.428	0.066	7.62	0.132
Na+K (mg/L)	649	68.8774	0	68.88	4.95	8.379	70.207	3.13	0.096	12.49	0.192
Ph	8814	6.9	2.6	9.5	7.8406	0.484	0.234	-4.55	0.026	34.41	0.052
SO4 (mg/L)	6920	242.9	0.1	243	21.8822	19.131	366.009	4.609	0.029	32.41	0.059
T (°C)	6941	27.3	-0.1	27.2	8.098	6.902	47.633	0.463	0.029	-1.006	0.059

The statistical summary (mean, standard error of the mean, std deviation, etc.) of selected samples presented and total 10 physicochemical parameters were analyzed for all the rivers.

Table 3.2: Statistical features of discriminant analysis compared to Tallinna Vesi for drinking water qualities

Tallinna Vesi					
Parameters	**Abbreviation**	**Unit**	**Min**	**Max**	**Avg**
Calcium	Ca (mg/L)	mg/L	59.8	78	67.6
Chlorine	Cl (mg/L)	mg/L	33	37	34
Hydrocarbonate	HCO3	mg/L	170	186	178
Potassium	K	mg/L	2.15	2.87	2.47
Magnesium	Mg	mg/L	7.75	8.91	8.25
Manganese	Mn	µg/l	0.73	20.4	5.4
Sodium	Na	mg/L	7.85	9.92	8.77
Sodium and Potassium	Na+K	mg/L	-	-	-
pH	pH		7.09	7.42	7.25
Sulphate	SO4	mg/L	19	27	23
Temperature	T	°C	2	25	10.5

The given data in Table 3.2 represents water quality parameters for the initial dataset and Tallinna Vesi drinking water. Here is the comparison of the two datasets:

For calcium (Ca) concentration, there were 2,231 samples taken. The concentration ranged from 1 mg/L to 160 mg/L. The average calcium (Ca) concentration is 66.816

mg/L, while Tallinna Vesi exhibits a marginally higher mean concentration of 67.6 mg/L. The calcium concentrations in both datasets are quite similar, with Tallinna Vesi demonstrating a slightly smaller range.

Chloride (Cl) concentrations were analyzed in 6,914 samples. The values ranged from 0.37 mg/L to 124 mg/L, with an average concentration of 8.178 mg/L. This suggests that the chloride levels in the water samples are relatively low on average.

Potassium (K) levels were studied in 1,370 samples. The concentration ranged from 0.04 mg/L to 18 mg/L, with a mean value of 2.292 mg/L, indicating a low potassium content in the samples.

Magnesium (Mg) concentrations were assessed in 2,231 samples, with values ranging from 0.1 mg/L to 109 mg/L. The comparing dataset presents a higher average magnesium (Mg) concentration of 17.230 mg/L, as opposed to Tallinna Vesi's mean concentration of 8.25 mg/L, indicating a significant difference in magnesium content between the two datasets.

A substantial difference exists in manganese (Mn) concentrations between the two datasets. The initial dataset has a much higher average concentration of 70.018 mg/L (converted to µg/l: 70,018 µg/l), while Tallinna Vesi has a lower mean concentration of 5.4 µg/l.

Sodium (Na) levels were studied in 1,364 samples. The concentration ranged from 0.2 mg/L to 18 mg/L, with a mean value of 4.1039 mg/L, indicating a low sodium content in the samples.

The sum of sodium and potassium (Na+K) concentrations in the given dataset was measured in 649 samples, with values ranging from 0 mg/L to 68.877 mg/L and a mean value of 4.9474 mg/L, indicating a low combined sodium and potassium content in the samples.

A minor difference in pH levels exists between the two datasets. The dataset has a higher mean pH of 7.84, suggesting slightly alkaline water, while Tallinna Vesi's average pH is lower at 7.25, which is nearer to neutral.

Sulfate (SO4) concentrations were analyzed in 6,920 samples. The values ranged from 0.1 mg/L to 243 mg/L, with an average concentration of 21.8822 mg/L. This suggests that the sulfate levels in the water samples are relatively low on average.

Temperature (T) was measured in 6,941 samples. The values ranged from -0.1°C to 27.2°C, with a mean value of 8.098°C, indicating that the water samples have a low average temperature.

3.2 Q-Q Plots

Before conducting the Principal Factor Analysis (PCA), it was necessary to check the normality of the 11 parameters at 33 rivers that were analyzed in the Figure 3.1 and Figure 3.2.

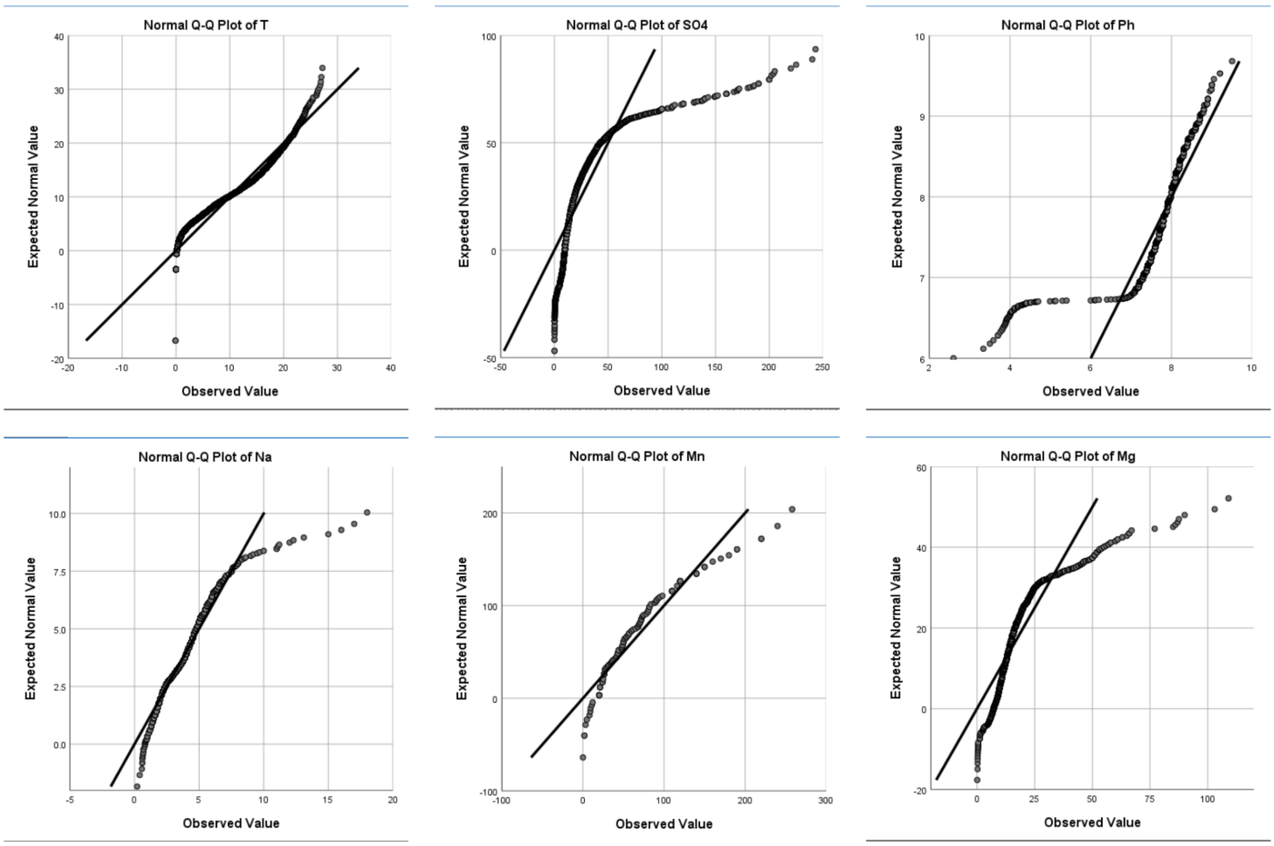


Figure 3.1: Q-Q plot 1 for measured parameters

The accuracy of the results obtained from the PCA analysis depends on the normal distribution of the dataset. To test the normality, a Quantile-Quantile (Q-Q) plot analysis was performed which provided a graphical representation of the distribution of data and showed that the data were normally distributed in most of the parameters.

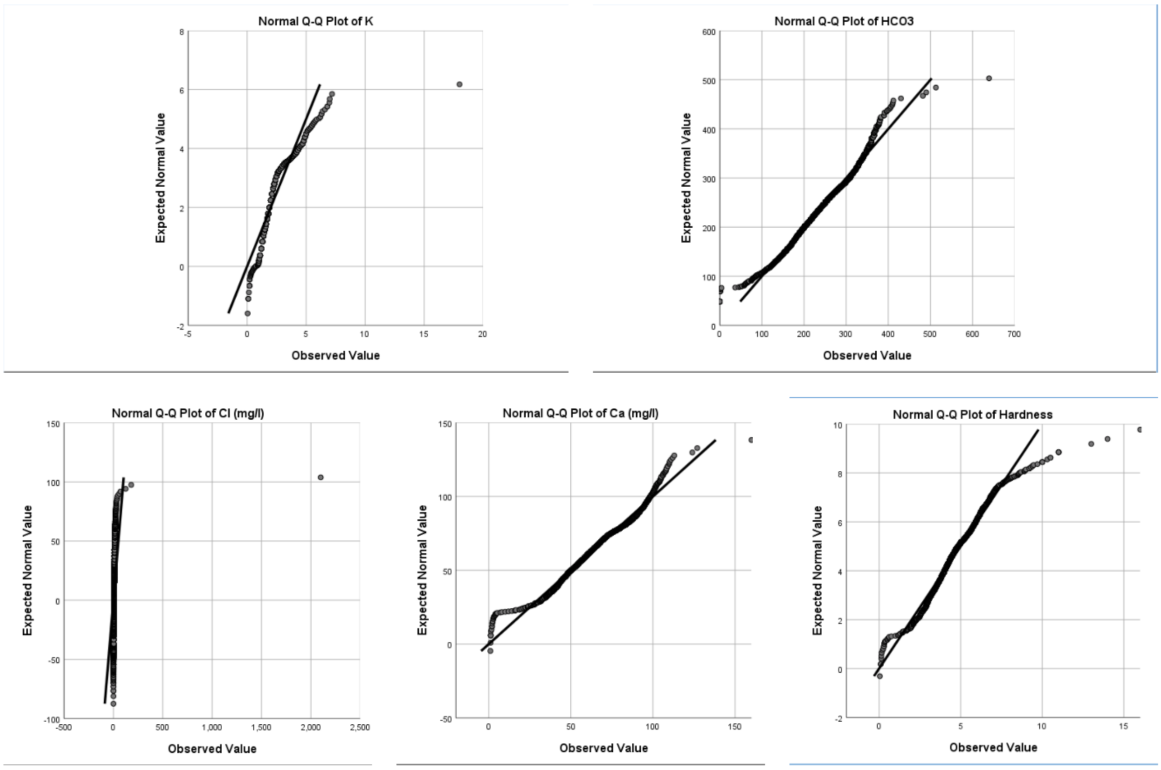


Figure 3.2: Q-Q plot 2 for measured parameters

Among these parameters, the Q-Q plot analysis answered that the value for Sulphur (SO4), pH, and magnesium (Mg) in river waters was not normally distributed based on the curve pattern or dots which is not parallel with the straight line shown in Figure 3.1 and Figure 3.2. Taking overall results, Q-Q plot analysis found that the data transformation was appropriate to ensure that data were normally distributed.

3.3 Principal factor analysis (PCA)

Principal factor analysis helps to classify the similarity of the parameters that are analyzed during the research.

Before starting factor analysis, it advised Kaiser-Meyer-Olkin (KMO) and Bartlett's Test, to evaluate the strength of the correlation factors in the dataset and between variables. By applying the KMO test, a value of 0.5692 was found in Table 3.3 which is the lowest acceptable range for the KMO test. KMO values closer to 1.0 are the ideal ones to interpret but the ones equal to 0.5 are also acceptable.

Table 3.3: Result of KMO and Bartlett's Test

KMO and Bartlett's Test		
Kaiser-Meyer-Olkin Measure of Sampling Adequacy.		0.5692
Bartlett's Test of Sphericity	Approx. Chi-Square	264.78
	df	66
	Sig.	0.000

In Figure 3.3 the scree plot is used to illustrate how much variation each principal factor captures from the dataset. In a scree plot the further away the vectors are from the first sample (dot), the less influence they have on it. But also, each plot shows how variables are correlated with one another.

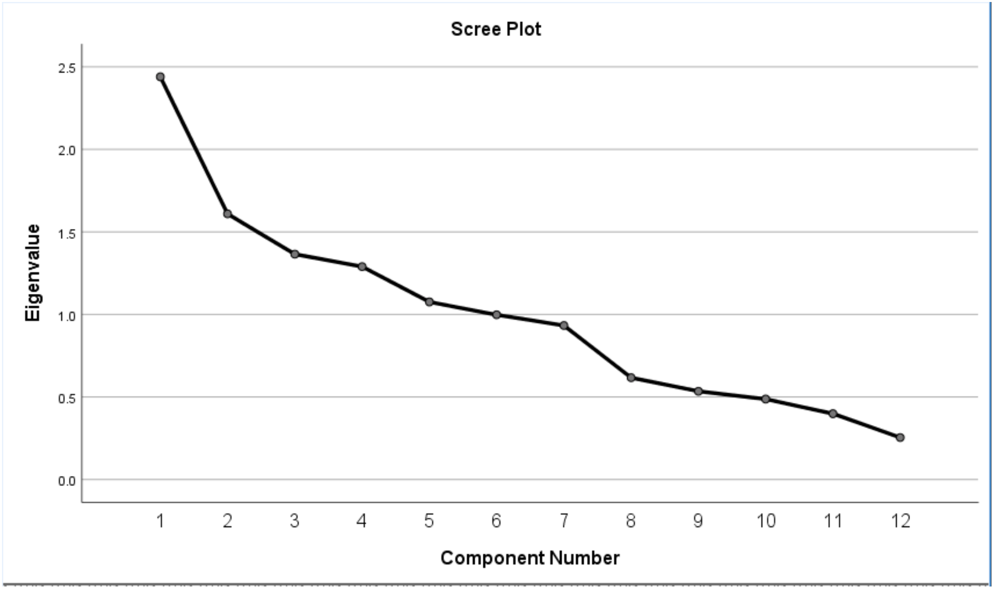


Figure 3.3: Scree Plot for PCA analysis

Shown in Table 3.4 are the initial Eigenvalues variance and Cumulative variance of PC1 20.32% and 20.33% respectively, for PC2 its 13.40% and 33.73%, for PC3 its 11.37% and 45.11%, for PC4 its 10.74% and 55.85%. In this study, four principal components were obtained from the analyses. In the Table 5 the factor loadings are divided into 3 different parts “strong” if the value is >0.75, “moderate” if the value is between 0.75-0.50, and “weak” if the value is between 0.50-0.30. Table 3.5 shows, result from statistical results of Component matrix for PCA.

Table 3.4: Initial Eigenvalues variance and Cumulative variance of PCA

Total Variance Explained						
Component	**Initial Eigenvalues**			**Extraction Sums of Squared Loadings**		
	Total	**% Of Variance**	**Cumulative %**	**Total**	**% Of Variance**	**Cumulative %**
1	2.439	20.329	20.329	2.44	20.33	20.33
2	1.609	13.407	33.736	1.61	13.41	33.74
3	1.365	11.374	45.110	1.36	11.37	45.11
4	1.290	10.746	55.856	1.29	10.75	55.86
5	1.076	8.965	64.821	1.08	8.96	64.82
6	0.998	8.314	73.135			
7	0.933	7.773	80.908			
8	0.617	5.139	86.047			
9	0.534	4.453	90.500			
10	0.487	4.059	94.560			
11	0.399	3.321	97.881			
12	0.254	2.119	100			

The first principal component (PC1) (Table 3.4 and Table 3.5), which is 20.33% of the total variance, it's a strong positive loading of Chloride (Cl) and Sulfate (SO4), and strong negative on Potassium (K). But at the same time, it's observed that there are more negative strong and weak loadings on the dataset. Negative loadings are located especially on Calcium (Ca) (-0.360) and Temperature (-0.485).

Table 3.5: Component Matrix from PCA

Component Matrix				
	Component			
	1	**2**	**3**	**4**
Ca	-0.360	0.052	0.659	-0.478
Cl	0.863	0.018	0.109	-0.007
HCO3	-0.212	-0.259	0.125	0.039
K	-0.290	0.047	0.633	0.504
Mg	0.012	0.670	0.298	-0.501
Mn	0.340	0.126	-0.055	-0.255
Na	0.162	0.155	0.240	0.492
Na+K	0.447	0.668	-0.184	-0.011
Ph	-0.111	0.603	0.074	0.454
SO4	0.846	-0.104	0.192	0.107
T	-0.485	0.417	-0.475	0.088

Although there are strong loadings on Chloride for PC1 (0.863), its observed weak positive (0.108) loadings were in the principal factor 2 (PC2), which is the same for Sulfate (SO4) with weak negative (-0.104) loadings. While analyzing the data in the second principal factor (PC2) with a total 33.73% total variance it observed that there are moderate positive loadings for only Magnesium (Mg) (0.670) and Na+K (0.668) parameters, but in essence parameters for PC2 are shown as weak positive.

For the principal factor 3 (PC3) with the total 11.37% variance, its characterized by a moderate positive on Calcium (Ca) (0.659) and Potassium (K) (0.633) and weak negative observed for Manganese (Mn) (-0.055) and Na+K (-0.184). Finally, the last principal factor 4 (PC4), resulted in mostly negative loadings moderate and weak negative loadings. Only positive moderate loadings were observed for the Potassium (K) (0.504) and the Sodium (Na) (0.492).

3.4 Time series

3.4.1 Monthly time series

Monthly time series data is data that is gathered and documented monthly for a defined period. Its purpose is to monitor the progress and patterns of a specific variable or group of variables over time. By analyzing this data, one can identify trends and patterns which can be helpful in making informed decisions based on historical performance and predicting future trends. Table 3.6 presents a monthly time series of measured water quality parameters, including major ions (Ca, Cl, K, Mg, Mn, Na, and SO4), pH, and temperature (T), which can offer insights into overall water quality and potential environmental consequences.

Table 3.6: Average monthly data of each parameter

Parameters	January	February	March	April	May	June	July	August	Septembe	October	November	December
Ca (mg/L)	63.65	73.90	61.22	58.69	62.67	68.66	66.75	67.22	64.03	70.14	61.17	74.47
Cl (mg/L)	8.35	7.84	8.20	6.25	7.44	7.45	8.20	8.38	8.61	10.98	8.30	7.83
K (mg/L)	2.41	2.22	2.88	1.93	2.62	2.21	2.59	2.18	2.74	2.60	2.92	2.45
Mg (mg/L)	20.64	15.34	22.36	12.14	22.48	17.78	23.50	16.83	23.00	16.57	19.00	15.83
Mn (µg/L)	49.00	100.83	50.00	60.15	52.47	74.01	21.00	62.97	21.00	54.63	11.00	96.21
Na (mg/L)	3.95	4.48	3.91	3.47	3.41	3.91	3.51	4.59	3.99	4.30	3.74	4.12
Ph	7.74	7.65	7.75	7.75	7.93	7.98	7.94	7.92	7.97	7.87	7.83	7.81
SO4 (mg/L)	23.96	22.55	22.84	19.19	21.52	20.19	21.68	20.17	22.63	22.49	24.59	24.07
T (°C)	0.91	0.96	1.05	3.80	10.41	15.46	17.51	17.25	13.93	8.91	4.26	1.78

Calcium (Ca): Throughout the year, calcium concentrations experience fluctuations, with peak values observed in February (73.90 mg/L) and December (74.47 mg/L), and the lowest value in April (58.69 mg/L).

Chloride (Cl): Chloride concentrations vary within a limited range, with the highest value in October (10.98 mg/L) and the lowest in April (6.25 mg/L). This indicates that the source of chloride ions in the water is relatively consistent throughout the year.

Potassium (K): The potassium level changes throughout the year, with the highest value in November (2.92 mg/L) and the lowest in April (1.93 mg/L). These fluctuations could be related to the varying input of potassium-rich sources or the potential biological uptake of potassium by aquatic organisms.

Manganese (Mn): Manganese concentrations exhibit a significant decrease over the year, with the highest value in February (100.83 µg/L) and the lowest in November (11.00 µg/L). Factors such as seasonal variations in water flow, changes in redox conditions, or differences in the input of manganese-rich sources could influence these changes.

Sodium (Na): Sodium concentrations show relatively minor changes, with the highest value in August (4.59 mg/L) and the lowest in May (3.41 mg/L). This suggests that the source of sodium ions in the water is stable, with only slight seasonal variations.

pH: pH values remain fairly consistent throughout the year, ranging from 7.65 to 7.98, which indicates a mildly alkaline aquatic environment. This is within the acceptable range for most aquatic organisms and does not pose immediate water quality concerns.

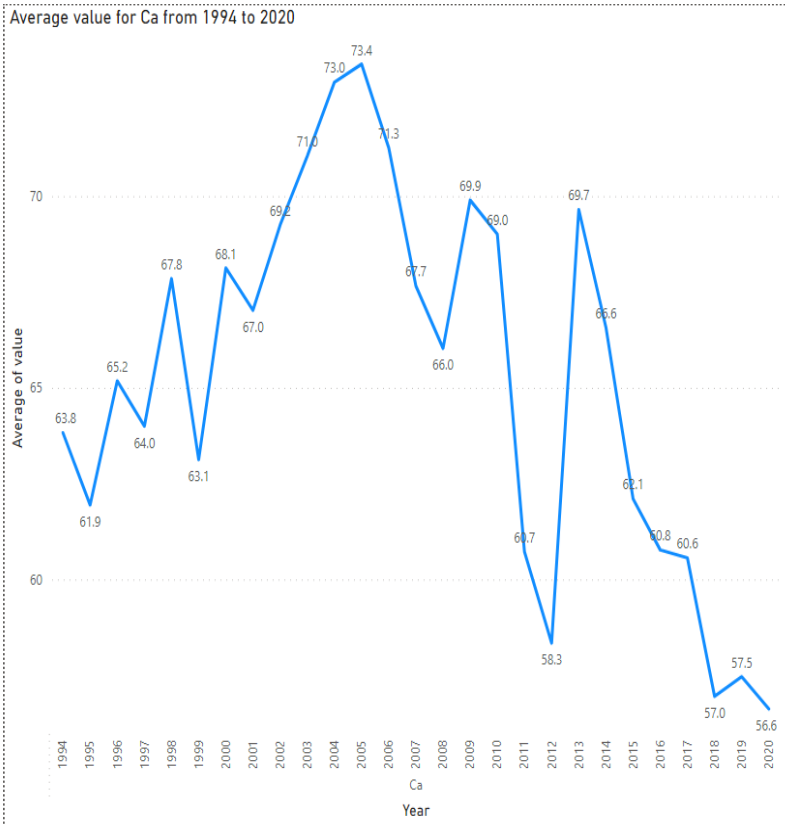
Sulfate (SO4): Sulfate concentrations show some variability throughout the year, with the highest value in November (24.59 mg/L) and the lowest in April (19.19 mg/L). This may be due to variations in the input of sulfate-rich sources or potential biological processes.

Temperature (T): As anticipated, water temperature follows a seasonal pattern, with the highest values in July (17.51°C) and August (17.25°C), and the lowest values in January (0.91°C) and December (1.78°C). The temperature trend demonstrates the typical influence of seasonal weather patterns on water temperature. Warmer temperatures during summer months may result in increased biological activity and growth of aquatic organisms, while colder temperatures in winter months can lead to reduced biological activity.

3.5 Yearly time series

3.5.1 Calcium

Calcium is one of the many abundant parameters in river water and groundwater and it exists in the water naturally as bicarbonates and to a lesser extent in the form of sulfate and chloride. In this time series analysis, the calcium concentration varies from a minimum of 1 mg/L to a maximum of 160 mg/L in all river waters. Figure 3.4 shows the data from 1994 to 2020 the changes in Calcium in the Estonian rivers and maximum, average, and minimum values for some of the rivers by name. The concentration of Calcium starts to increase from the year 1999 to 63.1 mg/L. There is an increased trend in the data from 1999 to 2005 from 63.1 mg/L to 73.4 mg/L. It's observed that in the next year, 2013 sharp increase was observed from 58.3 mg/L to 69.7 mg/L, continuing the previous years the concentration of Calcium sharply dropped from 69.7 mg/L to 57 mg/L till 2018.



param	Rivers name	Max of value	Average of value	Min of value
Ca	Ahja jõgi	81.00	62.93	1.10
Ca	Emajõgi	80.60	57.64	22.50
Ca	Keila jõgi	113.00	87.00	56.00
Ca	Kullavere jõgi	92.00	83.14	65.00
Ca	Kunda jõgi	99.40	82.06	29.20
Ca	Linnussaare oja	12.02	3.36	1.00
Ca	Mustjõgi	68.00	57.40	30.00
Ca	Narva jõgi	51.10	41.05	10.00
Ca	Navesti jõgi	100.00	64.61	31.00
Ca	Õhne jõgi	77.80	57.01	20.00
Ca	Oostriku jõgi	109.90	93.67	53.70
Ca	Pärnu jõgi	60.00	60.00	60.00
Ca	Pedja jõgi	108.30	78.64	28.06
Ca	Piusa jõgi	64.13	58.01	44.00
Ca	Põltsamaa jõgi	110.30	84.85	40.08
Ca	Porijõgi / Reola jõgi	84.17	64.93	32.06
Ca	Preedi jõgi	111.00	90.47	47.30
Ca	Rannapungerja jõgi	124.00	104.47	89.60
Ca	Reiu jõgi	63.00	43.43	20.00
Ca	Saarjõgi	99.00	59.09	33.00
Ca	Tagajõgi	160.00	48.72	1.20
Ca	Tänassilma jõgi	88.18	82.16	76.15
Ca	Valgejõgi	100.00	78.48	45.00
Ca	Velise jõgi	100.00	63.81	30.00
Ca	Vodja jõgi	127.00	85.19	14.00
Ca	Võhandu jõgi	75.40	60.24	34.00
Total		**160.00**	**66.82**	**1.00**

Figure 3.4: Average yearly time series of Calcium from 1994 to 2021

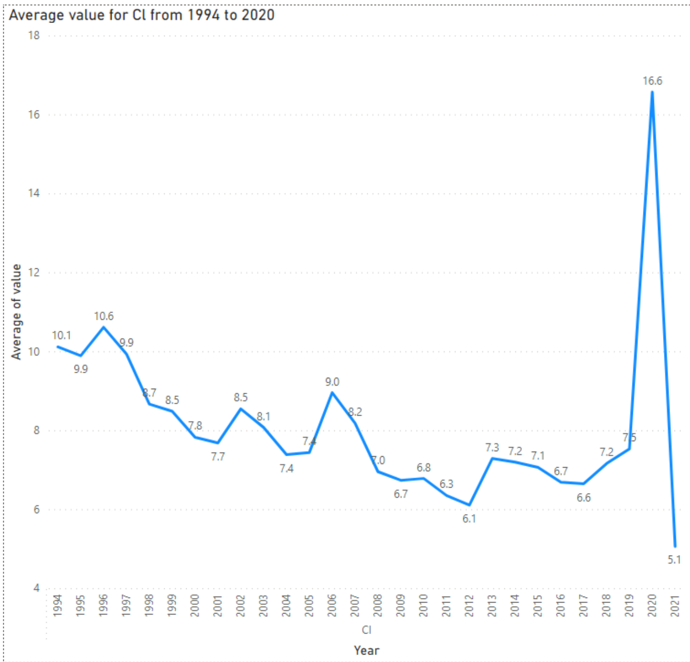
The calcium concentration in river water is strongly and partially linked to carbonate alkalinity. Both are higher in water with a pH between 7.5 and 8 and decrease as pH decreases. However, there is often a disconnection between calcium and carbonate alkalinity concentrations due to anthropogenic acid deposition. This deposition has been reduced, resulting in an increase or stable concentration of carbonate alkalinity in many freshwaters sources, while calcium concentrations have decreased rapidly (from 2005 to 2012) due to the recovery from anthropogenic acidification, approaching industrial conditions. Consequently, the decline in freshwater calcium concentration due to acid deposition has been widespread throughout the country for several years. [43].

It's also noticed that emissions of acidifying pollutants in Estonia dropped over 2.5 times from 1990 to 1999, and emissions of solids particles have decreased 74%, from 2005 to 2012 the value for this dropped 1.5 times [44].

The moderate to high levels of Calcium found in rivers as compared to lakes can be attributed to the fact that many rivers are located in colder geological regions with limited weathering effects. Additionally, river waters are typically more evenly distributed across latitudes, which may also contribute to higher Calcium concentrations in river water compared to lake water.

3.5.2 Chlorine

The following Figure 3.5 provides data on the levels of chlorine found in river waters between 1994 and 2021 with their maximum and minimum values by river name. During this time, the levels of chlorine in river waters increased from 10.1 mg/L to 10.6 mg/L between 1994 and 1996. This could be attributed to various factors such as an upsurge in industrial activity or increased use of cleaning products containing



Parameter	River	Max of value	Average of value	Min of value
Cl	Võisiku peakraav (Riivli oja)	46.00	11.49	3.70
Cl	Võhandu jõgi	14.00	7.69	3.30
Cl	Vodja jõgi	27.40	10.06	2.90
Cl	Vigala jõgi	8.70	7.14	5.90
Cl	Velise jõgi	21.00	6.08	1.00
Cl	Valgejõgi	16.00	9.00	1.00
Cl	Väike Emajõgi	14.00	7.67	3.40
Cl	Tänassilma jõgi	25.00	9.60	2.30
Cl	Tagajõgi	28.00	6.72	2.00
Cl	Taebla jõgi	17.00	10.58	5.80
Cl	Saarjõgi	25.40	6.68	0.75
Cl	Reiu jõgi	21.40	7.02	0.75
Cl	Rannapungerja jõgi	10.00	5.16	2.50
Cl	Preedi jõgi	13.00	5.94	3.20
Cl	Porijõgi / Reola jõgi	24.00	8.88	3.90
Cl	Põltsamaa jõgi	13.00	6.65	3.00
Cl	Piusa jõgi	12.00	5.80	2.70
Cl	Pedja jõgi	16.00	7.81	2.60
Cl	Oostriku jõgi	27.00	9.19	3.70
Cl	Õhne jõgi	18.00	5.60	1.60
Cl	Navesti jõgi	28.60	10.69	1.60
Cl	Narva jõgi	124.00	9.77	1.00
Cl	Mustjõgi	8.00	4.77	1.90
Cl	Linnussaare oja	11.00	1.47	0.37
Cl	Kunda jõgi	38.00	8.25	1.00
Cl	Kullavere jõgi	26.00	9.10	3.50
Cl	Keila jõgi	39.00	9.62	3.45
Cl	Jänijõgi	16.50	9.84	4.36
Cl	Emajõgi	23.00	8.06	3.00
Cl	Avijõgi	30.00	9.27	2.00
Cl	Alajõgi	59.00	6.72	1.00
Cl	Ahja jõgi	34.00	8.14	0.81
Total		**124.00**	**7.84**	**0.37**

Figure 3.5: Average yearly time series of Chlroine from 1994 to 2021

chlorine. In 1997, there was a decrease in the level of chlorine in river waters to 9.9 mg/L, which remained relatively stable until 1999 when it further decreased to 8.5 mg/L. This could have been due to efforts to reduce the use of chlorine in industries and households, or to the enforcement of stricter regulations concerning the discharge of chlorine-containing waste.

The River Basin Management Plans (RBMPs) had identified the impact of discharges from two sources, namely urban wastewater and wastewater from unconnected dwellings, on water quality in different water bodies. The latest RBMPs indicate that discharges of urban wastewater contribute significantly to the deterioration of water quality in 6.5% of river water bodies, 5.6% of lake water bodies, 68.8% of coastal water bodies, and 2.6% of the groundwater area [45]. This means that the water quality in these bodies does not meet the required standards due to the discharge of urban wastewater.

In addition, discharges of wastewater from unconnected dwellings also have a significant impact on the water quality of certain water bodies. According to the RBMPs, these discharges contribute to less than good water quality in 3.7% of river water bodies and 3.4% of lake water bodies. This implies that the discharge of wastewater from unconnected dwellings also adversely affects the quality of water in these water bodies. Overall, the RBMPs provide crucial information on the impact of various discharges on water quality and serve as a tool for managing and improving water quality in different water bodies. [46].

Between 2000 and 2002, the levels of chlorine in river waters continued to decrease, hitting a low of 7.7 mg/L in 2001. This suggests that the measures implemented to control chlorine usage and discharge of waste may have been effective during this time.

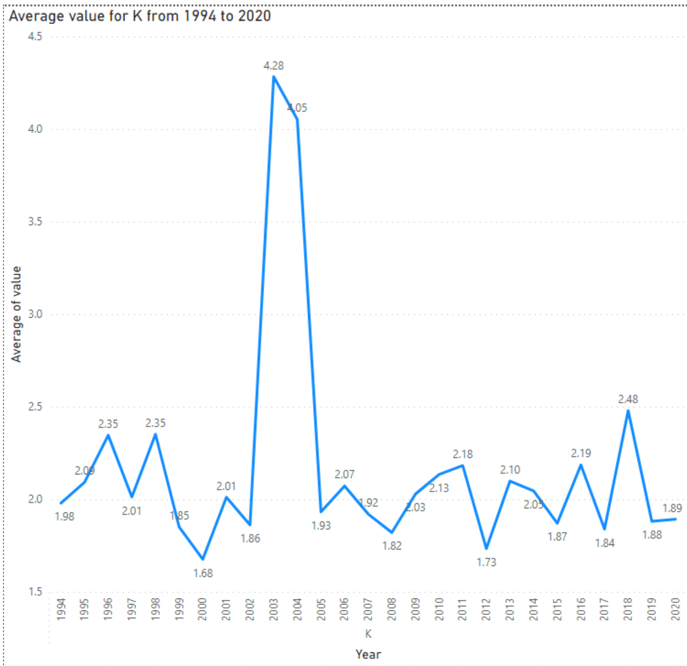
From 2003 to 2009, the level of chlorine in river waters remained fairly stable, with some fluctuations between 8.1 mg/L and 6.7 mg/L. In 2010, there was a slight increase in the level of chlorine to 6.8 mg/L, followed by a decrease to 6.1 mg/L in 2012. The level of chlorine in river waters then increased to 7.3 mg/L in 2013 and remained steady until 2019, with levels ranging from 7.5 mg/L to 6.6 mg/L.

However, there was a significant spike in the level of chlorine in river waters in 2020, reaching 16.6 mg/L, which may have been due to a major discharge of chlorine-containing waste or an industrial accident or amount of usage. This spike is alarming and demands further investigation and action to prevent similar occurrences in the future. It's important to mention that, from the table, the mention of Narva River and its highest level of chlorine at 124 mg/L, can be due to the number of industrial areas in that region. Considering the significant number of industrial zones in the Narva region, there is a considerable influence on both environmental pollution and chlorine levels. Furthermore, there is a noteworthy association between textile production and chlorine contamination in freshwater bodies. Research indicates that approximately 40% of global dyes consist of organically bonded chlorine, a known carcinogen frequently utilized in textile manufacturing [47].

Finally, in 2021, the level of chlorine in river waters dropped significantly to 5.1 mg/L, which is the lowest level recorded during the period under consideration.

3.5.3 Potassium

The data in Figure 3.6, gives a record of the levels of potassium in Estonian rivers from 1994 to 2020 with their maximum and minimum values by river name. The units used to measure the levels of potassium are milligrams per liter (mg/L). Upon analyzing the data, there are fluctuations in the potassium levels over the years. In 1994, the level was measured at 1.98 mg/L, and it increased to 2.09 mg/L in 1995. The level of potassium then rose again to 2.35 mg/L in 1996, but decreased to 2.01 mg/L in 1997, before increasing again to 2.35 mg/L in 1998. From 1999 to 2000, there was a significant decrease in the level of potassium from 1.85 mg/L to 1.68 mg/L. The levels of potassium remained relatively stable until 2003 when there was a sudden increase



Parameter	River	Max of value	Average of value	Min of value
K	Võhandu jõgi	18.00	3.01	1.20
K	Vigala jõgi	2.20	2.20	2.20
K	Väike Emajõgi	2.60	2.60	2.60
K	Tänassilma jõgi	2.80	2.65	2.50
K	Tagajõgi	6.80	2.12	1.00
K	Saarjõgi	1.90	1.23	0.75
K	Reiu jõgi	3.40	1.65	0.87
K	Rannapungerja jõgi	7.20	5.83	4.70
K	Preedi jõgi	4.50	2.39	1.40
K	Porijõgi / Reola jõgi	3.30	2.53	2.00
K	Põltsamaa jõgi	4.70	2.03	1.10
K	Piusa jõgi	2.40	2.40	2.40
K	Pedja jõgi	6.40	2.20	0.67
K	Oostriku jõgi	5.80	2.81	1.30
K	Õhne jõgi	4.30	1.68	0.59
K	Navesti jõgi	2.20	1.75	1.30
K	Narva jõgi	2.40	2.18	1.70
K	Mustjõgi	2.40	1.98	1.50
K	Linnussaare oja	1.00	0.38	0.10
K	Kunda jõgi	2.29	0.99	0.04
K	Kullavere jõgi	2.50	2.39	2.10
K	Keila jõgi	4.80	3.10	1.80
K	Emajõgi	6.20	2.61	1.10
K	Ahja jõgi	6.30	2.07	0.50
Total		**18.00**	**2.29**	**0.04**

Figure 3.6: Average yearly time series of Potassium from 1994 to 2021

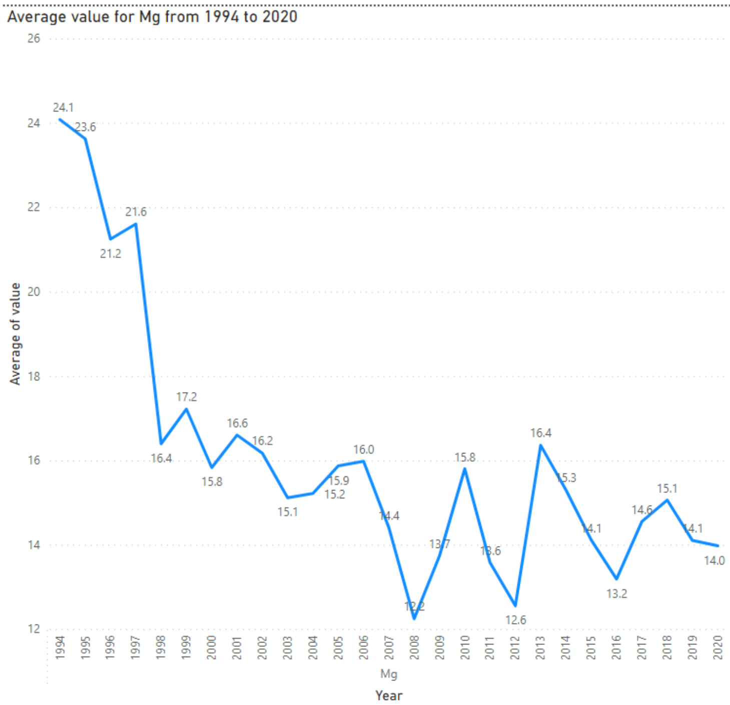
to 4.28 mg/L, which is more than twice the level in the previous year.

This sharp increase could be caused by various factors, including natural causes, human activities, or weather conditions. Existence of potassium can indicate contamination sources from agricultural usage and disposal of treated wastewater and industrial sewage discharges, from plants [48]. The levels then decreased in 2004 and remained stable until 2009, when there was a slight increase to 2.03 mg/L. Between 2010 and 2012, the levels of potassium remained relatively stable, but there was a sharp decrease to 1.73 mg/L in 2012. Studies indicate that the most significant parameters responsible for seasonal fluctuations in water quality are potassium, temperature, and turbidity. In 2013, the levels of potassium increased to 2.10 mg/L and remained relatively stable until 2018, where there was a sudden increase to 2.48 mg/L. This could be due to changes in agricultural practices, natural causes, or weather conditions. In 2019, the levels of potassium decreased to 1.88 mg/L and remained stable at 1.89 mg/L in 2020.

3.5.4 Magnesium

The information provided in Figure 3.7 is about the levels of magnesium in Estonian rivers from 1994 to 2020 and their maximum and minimum values by river name. Magnesium is an essential mineral for many biological processes in both humans and animals, and it also plays a critical role in the aquatic ecosystem. The concentration of magnesium in river water can have significant effects on the health of aquatic organisms and the overall ecosystem.

From the data, it's possible to see that the level of Magnesium in river waters has varied considerably over the years. The magnesium level in 1994 was 24 mg/L, which was nearly consistent in 1995 at 24.1 mg/L. Although in 1997 this level of magnesium decreased rapidly to 21.2 mg/L. In 1998, there was a small increase of around 0.4 mg/L such as from 21.2 mg/L to 21.6 mg/L. From the years 1999 to 2008, there was found a general decline in magnesium levels. The lowest level of magnesium was recorded in 2008 at 12.2 mg/L. This decline can relate to many factors such as agricultural activities, industrial pollution, and climate change. From the year 2008 to 2013, this level slightly increased with the highest level recorded in 2013 at 16.4 mg/L/.



Parameter	River	Max of value	Average of value	Min of value
Mg	Võhandu jõgi	24.32	12.77	6.80
Mg	Vodja jõgi	87.50	34.05	14.00
Mg	Velise jõgi	25.00	14.75	5.50
Mg	Valgejõgi	23.00	18.67	3.00
Mg	Tänassilma jõgi	26.75	25.54	24.32
Mg	Tagajõgi	30.00	13.68	0.50
Mg	Saarjõgi	103.00	29.82	4.90
Mg	Reiu jõgi	87.00	21.96	2.70
Mg	Rannapungerja jõgi	41.00	36.27	31.20
Mg	Preedi jõgi	27.20	16.09	9.20
Mg	Porijõgi / Reola jõgi	29.18	21.40	12.16
Mg	Põltsamaa jõgi	45.40	17.68	9.73
Mg	Piusa jõgi	16.00	13.03	7.30
Mg	Pedja jõgi	39.60	13.68	6.10
Mg	Pärnu jõgi	18.00	18.00	18.00
Mg	Oostriku jõgi	45.20	24.24	18.00
Mg	Õhne jõgi	24.32	11.29	3.60
Mg	Navesti jõgi	109.00	29.17	5.20
Mg	Narva jõgi	37.10	11.73	5.00
Mg	Mustjõgi	17.00	12.93	7.00
Mg	Linnussaare oja	22.60	2.22	0.10
Mg	Kunda jõgi	46.10	17.87	2.80
Mg	Kullavere jõgi	22.00	18.43	13.00
Mg	Keila jõgi	19.50	12.82	7.10
Mg	Emajõgi	36.00	14.94	6.80
Mg	Ahja jõgi	26.75	14.07	0.28
Total		**109.00**	**17.23**	**0.10**

Figure 3.7: Average yearly time series of Magnesium from 1994 to 2021

From 2014 to 2020 the level of magnesium stays slightly stable with a very low change from 15.3 mg/L to 14 mg/L, between these years.

As it is known, a large number of minerals contain calcium and magnesium, for instance, dolomite and magnesite. Magnesium usually enters the waters mainly from the leaching of rocks, it comes from streams flowing over magnesite, dolomite and carnallite, seawater, and lake brines. Magnesium is generally washed from rocks and as a result of it, it ends up in river and lake waters. Its also important to note that changes in magnesium are also connected with indirect effects on aquatic environments as well [49]. Tests from toxicity, shows that magnesium toxicity could develop at level nearing background level, especially soft freshwaters, although particular level of calcium can help reduce these effects.
Possible reasons for magnesium changes in river water can be related to industrial, agricultural water usage and mining water usage and extraction in nearby lakes and rivers.

3.5.5 Manganese

The following Figure 3.8 illustrates the average levels of Manganese (Mn) in Estonian rivers from 2007 to 2021, measured quarterly and yearly.

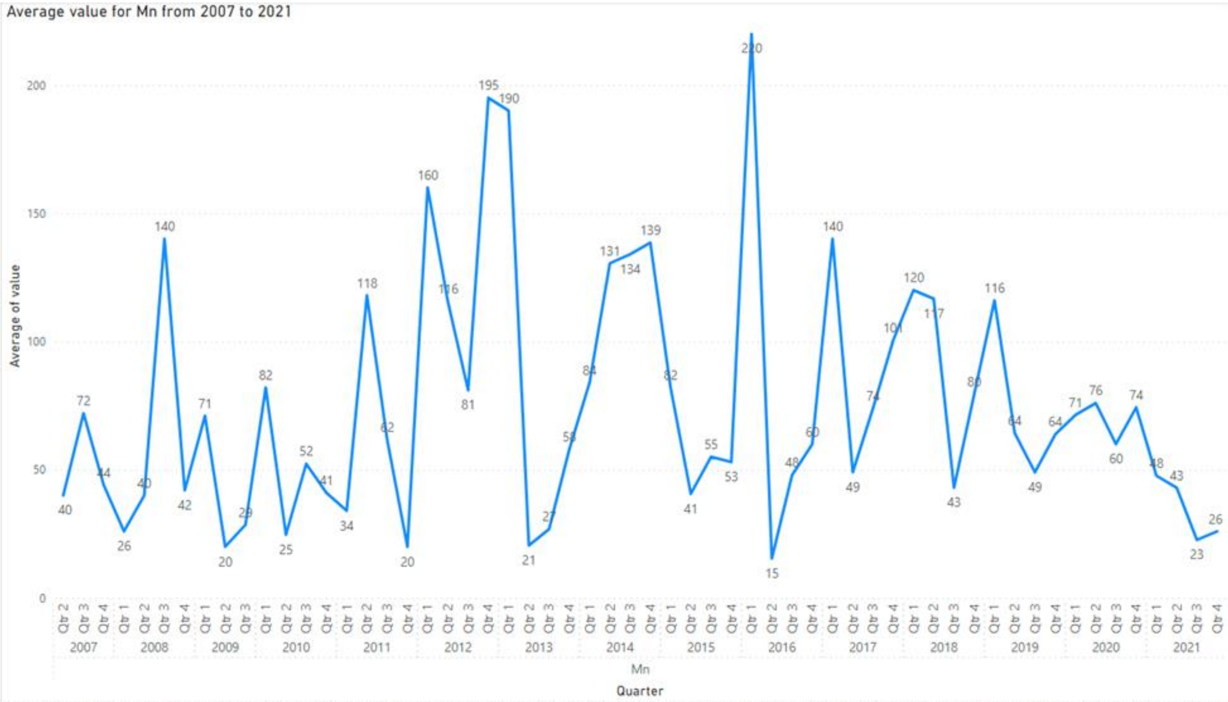


Figure 3.8: Average yearly and quarterly time series of Magnesium from 2007 to 2021

The values are given in micrograms per liter (µg/l). In 2007, the average Mn levels ranged from 40 µg/l in the second quarter to 72 µg/l in the third quarter. The following year, in 2008, the average Mn levels had a noticeable peak of 140 µg/l in the third quarter, which was the highest level in that year.

In 2009, the levels were generally lower, with the lowest average value of 20 µg/l in the second quarter. During 2010, the Mn levels fluctuated, with the highest average of 82 µg/l in the first quarter and the lowest of 24.7 µg/l in the second quarter. For the year 2011, the highest average Mn level was 118 µg/l in the second quarter, with a low of 20 µg/l in the fourth quarter.

In 2012, Mn concentrations rose, reaching a peak of 195 µg/l in Q4, which marked the dataset's highest level. The following year, 2013, saw significant fluctuations in Mn levels, with a low of 20.5 µg/l in Q2 and a high of 190 µg/l in Q1. Throughout 2014, Mn concentrations were generally elevated, with the lowest at 84 µg/l in Q1 and the highest at 138.5 µg/l in Q4. Mn levels in 2015 ranged from 40.6 µg/l in Q2 to 82 µg/l in Q1. Looking at 2016, Mn concentrations reached their peak at 220 µg/l in Q1, with the lowest average value of 15.4 µg/l in Q2. Mn levels fluctuated in 2017, with a high of 140 µg/l in Q1 and a low of 49.05 µg/l in Q2. The following year, Mn levels varied between 43 µg/l in Q3 and 120 µg/l in Q1. In 2019, Mn concentrations ranged from 49 µg/l in Q3 to 116 µg/l in Q1.

During 2020, Mn levels remained relatively stable, from 60 µg/l in Q3 to 76 µg/l in Q2. Lastly, in 2021, Mn concentrations were lower, with the highest average value of 47.67 µg/l in Q1 and the lowest at 22.67 µg/l in Q3.

Over these years, it was observed that manganese levels in Estonian rivers experienced highs and lows, with significant variations. The highest recorded value was 220 µg/l in Q1 of 2016, while the lowest was 15.4 µg/l in Q2 of 2016.

3.5.6 Sodium

Figure 3.9 below displays the yearly average variations in sodium concentrations, as well as the maximum and minimum levels for each river in Estonia from 1994 to 2021. In 1994, the sodium concentration in Estonian rivers was at 5.1 mg/L, representing one of the highest levels seen over the years. Sodium concentrations remained fairly constant at approximately 4.9 mg/L from 1995 to 1997. A substantial decrease to 3.6 mg/L occurred in 1998, followed by a slight increase to 4.2 mg/L in 1999 and stabilization at 4.1 mg/L in 2000. In 2001, sodium levels rose to 4.4 mg/L and further increased to 4.5 mg/L in 2002. However, a significant decline took place in 2003, with levels dropping to 2.1 mg/L.

In 2004, sodium concentrations reached their lowest level at 1.9 mg/L. Sodium levels then recovered and remained stable at 4.1 mg/L from 2005 to 2007. In 2008, levels dipped to 3.6 mg/L but rebounded to 4.1 mg/L in 2009. Sodium concentrations peaked at 4.3 mg/L in 2010 before slightly decreasing to 4.0 mg/L in 2011. Levels again dropped

Parameter	River	Max of value	Average of value	Min of value
Na	Võhandu jõgi	18.00	5.57	2.20
Na	Vigala jõgi	5.20	5.20	5.20
Na	Väike Emajõgi	7.30	7.30	7.30
Na	Tänassilma jõgi	11.00	8.85	6.70
Na	Tagajõgi	11.10	4.94	1.40
Na	Saarjõgi	6.20	3.10	1.70
Na	Reiu jõgi	6.00	3.71	1.70
Na	Rannapungerja jõgi	13.10	10.07	7.50
Na	Preedi jõgi	9.00	3.95	1.70
Na	Porijõgi / Reola jõgi	9.50	6.50	2.50
Na	Põltsamaa jõgi	6.50	3.54	1.60
Na	Piusa jõgi	5.10	5.10	5.10
Na	Pedja jõgi	8.60	3.91	0.70
Na	Oostriku jõgi	7.50	4.29	1.80
Na	Õhne jõgi	5.50	2.60	0.93
Na	Navesti jõgi	6.60	5.26	3.20
Na	Narva jõgi	6.20	5.06	4.20
Na	Mustjõgi	6.40	4.60	1.80
Na	Linnussaare oja	1.50	0.90	0.20
Na	Kullavere jõgi	6.00	5.20	3.80
Na	Keila jõgi	7.80	5.78	3.20
Na	Emajõgi	17.00	4.50	1.70
Na	Ahja jõgi	6.00	3.97	0.60
Total		**18.00**	**4.10**	**0.20**

Figure 3.9: Average yearly time series of Sodium from 1994 to 2021

to 3.6 mg/L in 2012, followed by an increase to 4.8 mg/L in 2013. In 2014, sodium concentrations reached 4.9 mg/L, similar to levels observed in the mid-1990s. Levels slightly decreased to 4.3 mg/L in both 2015 and 2016, then rose to 4.6 mg/L in 2017. The highest sodium levels were recorded in 2018 and 2019 at 5.2 mg/L. Lastly, in 2020, sodium levels declined to 4.6 mg/L.

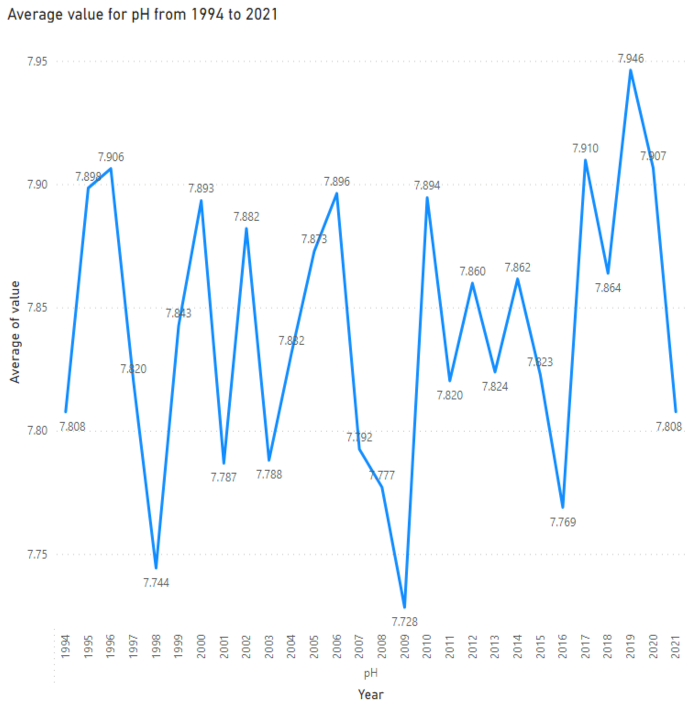
Observing these trends and irregularities, it can be concluded that sodium concentrations have experienced both dips and peaks over the years, but overall, they have not undergone significant changes when compared to international sources. Elevated sodium levels can also impact the water's soil content, with excessive concentrations potentially causing significant chemical issues related to river water, making it challenging for plant life to obtain adequate hydration. Additionally, sodium toxicity can be attributed to the presence of leaves from certain plants [50].

It is known that sodium can be found in most freshwater sources, originating from various natural and human-induced factors. Analyzing the results, it can be inferred that sodium fluctuations may be associated with leachate from industrial zones and landfills, precipitation leaching from soils with high sodium content into water bodies, and saline water from wells, among other sources.

3.5.7 pH

Figure 3.10 illustrates the yearly changes in pH level in Estonian rivers from 1994 to 2021. pH is crucial for assessing water quality, as it influences chemical constituent solubility and toxicity, as well as affecting aquatic life. An analysis of the data shows that the pH levels have been stable over the years, with fluctuations between 7.7 and 7.9, indicating consistent water quality in terms of pH. There were periods of stability at 7.9 in 1995-1996, 2005-2006, and 2010, and 2017-2020, as well as at 7.8 in 1997, 2001, 2003-2004, 2007-2008, 2011, 2013, 2015-2016, and 2021.

These stable periods suggest that factors influencing pH levels remained relatively constant during those years. Minor fluctuations were observed, with the lowest average pH of 7.7 recorded in 1998 and 2009, and the highest average pH of 7.9 recorded in multiple years. These fluctuations could result from natural environmental variations or seasonal influences. No significant anomalies were found in the dataset, as pH levels stayed within the narrow range of 7.7 to 7.9 throughout the years.



Parameter	River	Max of value	Average of value	Min of value
pH	Võisiku peakraav (Riivli oja)	8.38	7.81	7.00
pH	Võhandu jõgi	8.54	7.81	7.00
pH	Vodja jõgi	8.90	7.79	7.20
pH	Vigala jõgi	8.30	7.97	7.20
pH	Velise jõgi	8.70	7.98	7.20
pH	Valgejõgi	8.40	7.88	7.10
pH	Väike Emajõgi	9.00	7.85	7.28
pH	Tänassilma jõgi	9.20	7.86	6.95
pH	Tagajõgi	8.90	7.71	7.00
pH	Taebla jõgi	8.10	7.70	6.90
pH	Saarjõgi	8.90	7.95	7.24
pH	Reiu jõgi	8.80	7.83	7.10
pH	Rannapungerja jõgi	8.50	7.76	6.10
pH	Preedi jõgi	8.60	7.67	6.80
pH	Porijõgi / Reola jõgi	8.70	7.93	7.09
pH	Põltsamaa jõgi	8.70	7.94	7.20
pH	Piusa jõgi	8.80	7.86	7.10
pH	Pedja jõgi	8.78	7.92	7.06
pH	Pärnu jõgi	8.10	7.95	7.80
pH	Oostriku jõgi	8.60	7.53	6.90
pH	Õhne jõgi	8.60	7.90	7.17
pH	Navesti jõgi	8.90	7.95	7.22
pH	Narva jõgi	8.95	8.11	2.60
pH	Mustjõgi	8.40	7.92	7.50
pH	Linnussaare oja	7.80	4.33	3.34
pH	Kunda jõgi	8.45	7.59	7.10
pH	Kullavere jõgi	8.40	8.00	7.30
pH	Keila jõgi	8.60	8.01	7.19
pH	Jänijõgi	8.25	7.90	7.10
pH	Emajõgi	9.50	8.06	6.12
pH	Avijõgi	9.05	7.96	7.15
pH	Alajõgi	8.80	7.48	6.61
pH	Ahja jõgi	8.60	7.86	3.70
Total		**9.50**	**7.84**	**2.60**

Figure 3.10: Average yearly time series of pH from 1994 to 2021

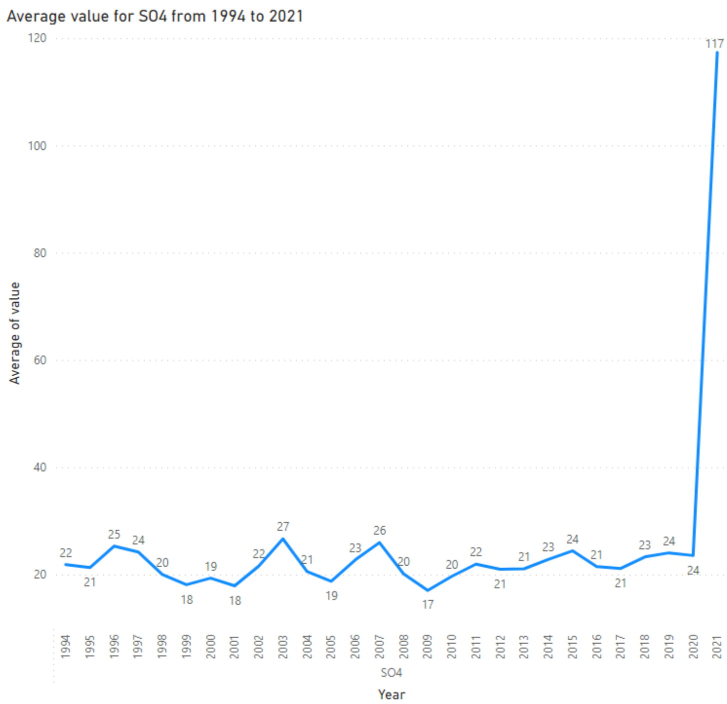
Following the table next to Figure 14, levels of pH per river name are listed. The pH levels of these rivers appear to fall within a neutral range, with the majority having average values between 7.5 and 8.1. The highest pH values vary from 7.8 to 9.5, while the lowest pH values vary from 2.6 to 7.8. "Linnussaare oja" shows the lowest average pH at 4.3, and Narva River has the lowest minimum pH at 2.6. Meanwhile, "Emajõgi" possesses the highest maximum pH, recorded at 9.5.

3.5.8 Sulfate

The following Figure 3.11 illustrates the average value for the level of sulfate concentration from 1994 to 2021. It's possible to see that the average value for the Sulfate ranged between 20 mg/L to 24 mg/L for the years from 1994 to 2020. In 2021 the concentration of sulfate increased rapidly to 117 mg/L. This could be due to external and also natural factors.

It's important to measure that there is a great difference found in analyzing the data between the Maximum value and the Average value for the sulfate concentration. The average value for sulfate varies around 23 mg/L, but meanwhile, the maximum value for this ranges around from 40 mg/L to 243 mg/L.

It is known that the concentration of sulfate usually varies from 0- 630 mg/L, comparing with the data for the Estonian rivers, it's possible to interpret that, the maximum level of sulfate in rivers is slightly below the average value.



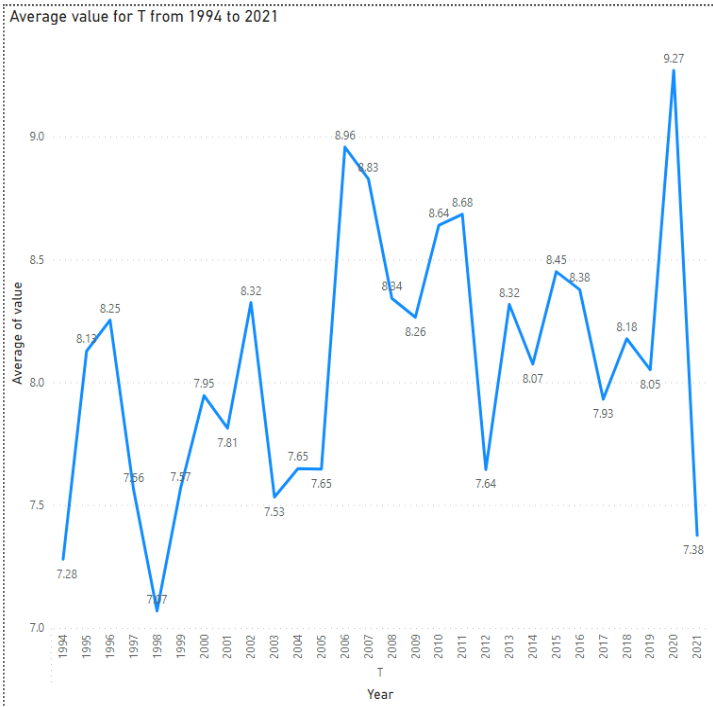
Parameter	River	Max of value	Average of value	Min of value
SO4	Ahja jõgi	26.00	14.07	0.86
SO4	Alajõgi	190.00	19.29	2.00
SO4	Avijõgi	80.00	21.83	3.00
SO4	Emajõgi	42.00	18.43	6.40
SO4	Jänijõgi	167.00	40.42	16.50
SO4	Keila jõgi	61.00	29.90	10.40
SO4	Kullavere jõgi	61.00	31.26	12.00
SO4	Kunda jõgi	140.00	38.42	8.00
SO4	Linnussaare oja	21.00	1.39	0.10
SO4	Mustjõgi	16.00	9.31	4.60
SO4	Narva jõgi	51.00	15.71	5.00
SO4	Navesti jõgi	56.00	30.10	4.30
SO4	Õhne jõgi	32.00	12.15	3.20
SO4	Oostriku jõgi	56.00	31.19	3.00
SO4	Pärnu jõgi	243.00	79.50	14.00
SO4	Pedja jõgi	54.00	23.37	8.00
SO4	Piusa jõgi	19.00	9.99	4.70
SO4	Põltsamaa jõgi	41.00	24.15	12.00
SO4	Porijõgi / Reola jõgi	37.00	15.65	6.50
SO4	Preedi jõgi	39.00	20.62	12.00
SO4	Rannapungerja jõgi	240.00	104.09	5.00
SO4	Reiu jõgi	38.00	9.77	1.00
SO4	Saarjõgi	45.00	18.86	1.30
SO4	Taebla jõgi	64.00	40.56	23.00
SO4	Tagajõgi	112.00	17.18	4.00
SO4	Tänassilma jõgi	99.00	20.82	4.00
SO4	Väike Emajõgi	36.00	14.47	6.10
SO4	Valgejõgi	32.00	16.90	8.60
SO4	Velise jõgi	59.00	20.07	0.70
SO4	Vigala jõgi	29.00	25.38	20.00
SO4	Vodja jõgi	73.00	38.49	16.00
SO4	Võhandu jõgi	26.00	12.49	2.00
SO4	Võisiku peakraav (Riivli oja)	120.00	58.31	11.00
Total		**243.00**	**21.88**	**0.10**

Figure 3.11: Average yearly time series of Sulfate from 1994 to 2021

The main sources of sulfate can be divided into two parts, natural and human factors. Natural sources of sulfate usually come from minerals and rocks such as gypsum, pyrite, etc. including precipitation and other natural activities. An human factors have a significant role in the sulfate level and also as a source, such as fertilizers, synthetics, discharges from industrial plants, mining drainage, and coal. High levels of sulfate may not have a direct impact on freshwaters but in different transformed toxic after different circumstances, it will result in changes in water formation and have an impact on flora and fauna. The issue of sulfate contamination in freshwater ecosystems is a worldwide concern that continues to persist. The significant amount of sulfate, if reached, in aquatic habitats has an impact on both human and aquatic life existence and creates limitations on the use of water for both living conditions. High levels of sulfate can also come from sulfate-containing fertilizers, and this can cause aerobic oxidation or nitrate leaching.

3.5.9 Temperature

Figure 3.12 shows an analysis of the average temperature levels in Estonian rivers between 1994 and 2021 uncovers multiple trends and irregularities.



Parameter	River	Max of value	Average of value	Min of value
T	Ahja jõgi	22.50	7.90	0.00
T	Alajõgi	22.70	7.82	0.00
T	Avijõgi	26.10	8.06	0.00
T	Emajõgi	26.40	8.97	0.00
T	Jänijõgi	18.30	7.50	0.40
T	Keila jõgi	25.00	8.01	0.00
T	Kullavere jõgi	20.30	7.58	0.00
T	Kunda jõgi	20.30	6.76	0.00
T	Linnussaare oja	21.10	7.16	0.00
T	Mustjõgi	20.60	8.01	0.00
T	Narva jõgi	24.20	8.38	-0.10
T	Navesti jõgi	26.60	9.41	0.00
T	Õhne jõgi	22.90	7.61	0.00
T	Oostriku jõgi	14.50	6.40	0.60
T	Pärnu jõgi	24.00	11.43	2.00
T	Pedja jõgi	24.20	8.08	0.00
T	Piusa jõgi	18.70	7.37	0.00
T	Põltsamaa jõgi	19.00	7.24	0.00
T	Porijõgi / Reola jõgi	19.90	7.09	0.00
T	Preedi jõgi	14.60	6.86	0.00
T	Rannapungerja jõgi	26.80	8.46	0.10
T	Reiu jõgi	27.20	9.68	0.00
T	Saarjõgi	23.70	8.58	-0.10
T	Taebla jõgi	22.00	9.72	1.00
T	Tagajõgi	26.90	7.67	0.00
T	Tänassilma jõgi	26.30	8.79	0.00
T	Väike Emajõgi	25.00	8.86	0.00
T	Valgejõgi	22.90	8.79	1.00
T	Velise jõgi	27.00	7.75	0.00
T	Vigala jõgi	18.00	10.71	2.00
T	Vodja jõgi	17.80	8.24	0.40
T	Võhandu jõgi	24.00	8.85	0.00
T	Võisiku peakraav (Riivli oja)	20.90	7.01	0.00
Total		**27.20**	**8.10**	**-0.10**

Figure 3.12: Average yearly time series of Temperature from 1994 to 2021

To begin with, a consistent increase in temperature can be observed over the years, as the average temperature climbed from 7.28°C in 1994 to 7.38°C in 2021. The peak temperature, which reached 9.27°C, was documented in 2020. Despite this overall trend, the data highlights noticeable variations in river temperatures over time, including a rise from 7.28°C in 1994 to 8.25°C in 1996, followed by a decline to 7.07°C in 1998.

In relation to anomalies, 1998 is particularly noteworthy due to its low average river temperature of 7.07°C, a value that is substantially lower than the temperatures recorded in adjacent years (7.56°C in 1997 and 7.57°C in 1999). Moreover, a remarkable increase in average river temperatures is evident in 2006 and 2007, surging from 7.65°C in 2005 to 8.96°C in 2006 before slightly dropping to 8.83°C in 2007. This surge is regarded as an anomaly since it is significantly higher than the temperatures observed in neighboring years. Furthermore, the year 2020 stands out as an exceptional case, exhibiting the highest average river temperature within the dataset at 9.27°C, a value that surpasses the temperatures noted in the years immediately preceding and succeeding it (8.05°C in 2019 and 7.38°C in 2021).

The following illustration in Figure 3.12 it's the visible temperature levels in Estonian rivers as per the name, including the maximum, average, and minimum temperatures recorded. The average temperature of each river demonstrates variation, with the Pärnu River exhibiting the highest average temperature at 11.42°C and the Oostriku River presenting the lowest at 6.4°C. The maximum temperatures span from 14.5°C in the

Oostriku River to 27.2°C in the Reiu River, whereas the minimum temperatures extend from -0.1°C in the Narva River and Saarjõgi to 2°C in both the Pärnu and Vigala Rivers.

The follwing data set in Figure 3.7 represents monthly median temperatures in Estonian rivers between 1994 and 2021.

Table 3.7: Median temperature of Estonian rivers by years and months

Years	January	February	March	April	May	June	July	August	Sept.	October	November	December
1994	0.40	0.00	0.35	1.60	10.20	14.00	19.00	19.20	12.50	7.00	3.85	0.65
1995	0.00	0.20	1.20	2.90	7.40	18.85	17.00	16.80	16.85	9.40	0.65	0.10
1996	0.00	0.00	0.30	6.00	14.50	15.75	16.65	18.10	11.20	8.50	6.50	2.60
1997	0.50	0.20	0.60	3.60	9.00	15.10	21.00	18.20	15.20	7.20	2.50	0.00
1998	0.70	0.00	0.40	2.60	13.30	15.65	16.00	15.70	11.50	5.55	4.10	0.10
1999	0.20	0.00	0.10	1.20	6.40	15.40	22.20	18.90	14.00	9.10	5.50	0.85
2000	0.00	0.00	0.30	3.65	10.40	14.50	17.10	15.55	12.00	9.90	6.40	4.45
2001	0.00	0.00	0.00	3.05	12.70	15.00	20.80	16.90	14.50	8.90	4.65	0.00
2002	0.00	0.25	0.50	4.90	13.00	18.00	16.25	18.20	17.65	8.15	1.45	0.00
2003	0.00	0.00	0.00	0.50	9.35	13.55	15.90	18.00	12.05	9.00	5.10	3.10
2004	0.00	0.00	0.80	4.60	12.05	14.10	15.10	17.50	14.65	6.30	5.10	0.00
2005	0.40	0.10	0.00	2.60	7.80	14.15	18.75	16.10	13.20	10.40	2.25	0.50
2006	0.10	0.00	0.20	1.65	10.30	14.10	22.50	17.70	15.20	12.05	4.20	5.55
2007	1.80	0.10	0.20	6.10	7.95	18.10	18.05	21.30	13.35	11.20	3.25	0.80
2008	0.30	1.00	1.60	4.90	12.50	16.95	15.70	15.40	11.90	9.00	5.85	2.85
2009	0.20	0.20	0.90	3.70	12.10	15.70	19.00	16.90	13.20	7.45	2.00	4.50
2010	0.20	0.10	0.90	3.50	9.70	14.40	21.30	18.45	13.15	6.00	5.60	0.30
2011	0.80	0.20	1.00	1.25	7.65	18.00	20.95	19.20	15.95	11.35	7.40	2.90
2012	0.70	0.05	0.80	1.50	10.70	12.50	17.50	17.70	14.70	10.60	4.20	0.30
2013	0.20	0.20	0.20	0.70	11.20	19.15	19.10	19.30	15.20	7.45	7.50	1.05
2014	1.80	0.25	1.20	3.60	8.70	14.40	13.95	21.65	14.05	9.00	4.20	0.40
2015	0.45	0.65	1.75	4.35	10.20	15.90	19.30	17.00	15.20	8.80	5.50	2.40
2016	0.40	0.70	1.60	5.00	10.50	18.70	16.30	17.00	13.50	9.30	3.35	0.65
2017	0.85	1.00	1.10	5.30	7.60	12.80	15.05	18.00	13.30	8.65	2.65	1.60
2018	1.55	0.50	0.40	1.90	11.80	14.75	15.15	20.90	17.90	8.70	5.15	0.60
2019	0.60	0.30	0.70	4.85	9.15	14.60	18.30	15.85	16.40	9.10	4.55	1.05
2020	1.70	2.40	1.80	6.30	11.20	15.50	17.85	16.40	15.00	12.50	7.00	2.60
2021	1.20	0.45	1.60	3.20	6.60	14.60	20.20	17.50	14.50	8.70	6.60	0.30

Over this 28-year period, the general trend shows seasonal fluctuations in temperature, with the highest temperatures typically occurring during the summer months (June to August) and the lowest during winter months (December to February). There is considerable interannual variability in the temperature data, with some years experiencing particularly warm or cool periods. For example, the warmest July on record was in 2006 with an average temperature of 22.5°C, while the coolest July was in 2014 with an average temperature of 14.0°C. Similarly, the warmest January on record was in 2020 with an average temperature of 1.7°C, while the coolest January was recorded in multiple years, with an average temperature of 0.0°C.

3.6 Trend analysis

Table 3.8 depicts a trend analysis of 33 Estonian rivers over the period of 1994 to 2021, taking into account various measured parameters. The p-value is a measure of the strength of evidence against the null hypothesis. It quantifies the probability of observing the data, or more extreme data, assuming that the null hypothesis is true. In simpler terms, it explains how likely the observed trend is due to chance. The t-value, also known as the test statistic, is a measure of the difference between the observed data and the expected data under the null hypothesis, standardized by the standard error. It is used in hypothesis testing to calculate the p-value If the p-value is low (less than 0.05 or 0.01), it suggests that the observed trend is unlikely to occur by chance alone. In this case, the results are considered statistically significant, and we reject the null hypothesis. The magnitude of the t-value is usually compared to critical values from the t-distribution to determine the p-value. The colors illustrated in the Table 3.8 is the distribution of t and p values from lowest to hight values. Blue color indicates lowest while red color indicated highest value for trend analysis.

Table 3.8: Trend analysis of Estonian rivers from 1994 to 2021 for each parameter

Rivers	Years	Calcium		Chlorine		Potassium		Magnesium		Na		pH		SO4		T	
		t-value	p-value	t-value	p-value	t-value	p-value	t-value	p-value	t-value	p-value	t-value	p-value	t-value	p-value	t-value	p-value
Ahja jõgi	1994-2021	1.351	0.189	-0.316	0.755	-0.371	0.714	-0.254	0.801	0.270	0.790	2.166	0.040	0.328	0.745	1.823	0.080
Alajõgi	1994-2021	-	-	-5.587	< 0.0001	-	-	-	-	-	-	0.311	0.758	0.188	0.852	1.097	0.283
Avijõgi	1994-2021	-	-	-8.224	< 0.0001	-	-	-	-	-	-	2.063	0.050	-1.990	0.058	1.248	0.224
Emajõgi	1994-2021	1.239	0.227	-1.242	0.226	-0.814	0.424	-0.334	0.741	1.494	0.148	2.746	0.011	-4.408	0.000	2.158	0.041
Jänijõgi	1994-2021	-	-	0.378	0.710	-	-	-	-	-	-	-2.742	0.014	-0.395	0.698	0.951	0.355
Keila jõgi	1994-2021	-2.116	0.047	-3.488	0.002	-	-	-1.340	0.195	-	-	1.349	0.189	-6.329	< 0.0001	1.455	0.158
Kullavere jõgi	1994-2021	0.180	0.864	-1.388	0.198	1.387	0.224	-1.302	0.250	-0.847	0.436	0.000	1.000	0.121	0.906	-0.406	0.694
Kunda jõgi	1994-2021	-0.789	0.449	-5.797	< 0.0001	-	-	-0.331	0.747	-	-	-1.919	0.066	-4.493	0.000	1.519	0.141
Linnussaare oja	1994-2021	-2.899	0.027	-3.003	0.007	1.649	0.150	-1.980	0.095	-1.599	0.161	1.604	0.125	-5.504	< 0.0001	0.179	0.860
Mustjõgi	1994-2021	0.202	0.845	-0.292	0.777	-1.800	0.105	-0.091	0.929	0.579	0.577	-0.770	0.461	-0.684	0.511	1.689	0.125
Narva jõgi	1994-2021	3.166	0.007	-7.848	< 0.0001	0.720	0.490	-1.292	0.219	-1.206	0.258	4.054	0.000	-2.967	0.007	1.513	0.143
Navesti jõgi	1994-2021	0.743	0.466	-4.041	0.001	-0.577	0.667	-6.028	< 0.0001	-1.865	0.313	-1.536	0.139	-3.250	0.004	1.218	0.236
Õhne jõgi	1994-2021	-1.528	0.141	-3.818	0.001	-1.301	0.208	-2.617	0.016	-2.583	0.017	0.830	0.414	-4.995	< 0.0001	0.144	0.886
Oostriku jõgi	1994-2021	1.998	0.069	-10.148	< 0.0001	1.143	0.275	-3.463	0.005	-2.837	0.015	1.221	0.233	-6.957	< 0.0001	-0.551	0.587
Pärnu jõgi	1994-2021	-	-	-	-	-	-	-1.882	0.074	-	-	-	-	-	-	-	-
Pedja jõgi	1994-2021	-1.177	0.253	-0.001	0.999	-0.674	0.508	-	-	-2.045	0.054	2.015	0.055	-4.198	0.000	1.760	0.091
Piusa jõgi	1994-2021	-5.087	0.037	-2.996	0.006	-	-	2.272	0.151	-	-	-0.504	0.619	-3.613	0.001	2.315	0.029
Põltsamaa jõgi	1994-2021	-1.850	0.079	-5.335	< 0.0001	-1.142	0.266	-2.953	0.008	-4.763	0.000	0.712	0.483	-6.735	< 0.0001	1.350	0.189
Porijõgi / Reola	1994-2021	-	-	-2.161	0.040	-	-	-	-	-	-	0.892	0.381	-4.247	0.000	2.661	0.013
Preedi jõgi	1994-2021	-0.478	0.641	-4.758	< 0.0001	1.098	0.294	-2.542	0.026	-4.436	0.001	-2.215	0.036	-5.662	< 0.0001	2.348	0.027
Rannapungerja	1994-2021	-4.243	0.008	-1.547	0.153	-0.490	0.641	-0.965	0.379	-0.278	0.791	1.285	0.228	0.927	0.376	0.037	0.971
Reiu jõgi	1994-2021	-2.148	0.042	-4.020	0.001	-1.523	0.202	-5.035	< 0.0001	-2.053	0.109	0.258	0.799	-0.884	0.386	0.475	0.639
Saarjõgi	1994-2021	0.428	0.675	-4.469	0.000	0.051	0.964	-3.492	0.003	-0.693	0.560	-1.376	0.181	-1.691	0.103	1.085	0.288
Taebla jõgi	1994-2021	-	-	-6.433	0.023	-	-	-	-	-	-	4.601	0.010	-0.291	0.798	-2.840	0.047
Tagajõgi	1994-2021	-0.440	0.664	-7.232	< 0.0001	-2.012	0.084	-0.479	0.637	-1.339	0.222	-0.444	0.661	-1.459	0.157	-1.928	0.065
Tänassilma jõgi	1994-2021	-	-	2.664	0.013	-	-	-	-	-	-	1.722	0.098	-3.771	0.001	0.718	0.480
Väike Emajõgi	1994-2021	-	-	0.526	0.603	-	-	-	-	-	-	3.161	0.004	-5.922	< 0.0001	0.658	0.517
Valgejõgi	1994-2021	3.919	0.001	-4.449	0.000	-	-	-1.234	0.236	-	-	-2.126	0.044	-6.581	< 0.0001	0.647	0.524
Velise jõgi	1994-2021	0.747	0.466	-2.481	0.020	-	-	-0.060	0.953	-	-	3.110	0.005	-4.535	0.000	1.932	0.065
Vigala jõgi	1994-2021	-	-	-	-	-	-	-	-	-	-	0.693	0.614	-	-	-12.124	0.052
Vodja jõgi	1994-2021	1.572	0.138	-4.483	0.000	-	-	-7.500	< 0.0001	-	-	-3.482	0.002	-2.350	0.027	0.983	0.335
Võhandu jõgi	1994-2021	-1.365	0.187	-0.510	0.615	-1.145	0.265	-1.979	0.061	-1.313	0.203	-0.307	0.762	-6.941	< 0.0001	2.606	0.015
Võisiku peakraa	1994-2021	-	-	-0.337	0.740	-	-	-	-			1.644	0.119	-3.348	0.004	-0.587	0.565

Calcium: The fluctuations in Calcium concentrations differ among various watercourses. Notably, a considerable decline in Calcium is observed in rivers such as Alajõgi, Kunda jõgi, Linnussaare oja, Navesti jõgi, Põltsamaa jõgi, and Preedi jõgi (with negative t-values and p-values < 0.05). In contrast, Piusa jõgi and Vodja jõgi exhibit a notable increase (with positive t-values and p-values < 0.05). Many other rivers display no discernable trends in Calcium concentrations. One potential cause for these changes may be differences in land use and geological features across the regions.

Chloride: A widespread decline in Chloride concentrations characterizes the majority of rivers, including Alajõgi, Avijõgi, Keila jõgi, Kunda jõgi, Linnussaare oja, Navesti jõgi, Õhne jõgi, Oostriku jõgi, Põltsamaa jõgi, Preedi jõgi, Reiu jõgi, Saarjõgi, Tagajõgi, and Vodja jõgi (with negative t-values). Many of these rivers display p-values < 0.0001, indicating a statistically significant decrease in Chloride concentrations. This decrease might be attributed to improved wastewater treatment processes and reduced industrial discharges.

Potassium: The tendencies in Potassium concentrations are variable. For instance, Kullavere jõgi and Piusa jõgi exhibit a significant rise (with positive t-values and p-values < 0.05), whereas Mustjõgi and Õhne jõgi display a notable reduction (with negative t-values and p-values < 0.05). No significant trends are observed in many other rivers. Changes in agricultural practices, such as the application of fertilizers, could be a contributing factor to these fluctuations.

Magnesium: A limited number of rivers, such as Õhne jõgi, Navesti jõgi, and Reiu jõgi, show a significant reduction in Magnesium concentrations (with negative t-values and p-values < 0.05), while a few rivers like Piusa jõgi exhibit an increase (with positive t-values and p-values < 0.05). No significant trends are observed in many other rivers. This variation might result from regional differences in water chemistry and geological composition.

Sodium: The trends in Sodium concentrations are inconsistent. For example, Linnussaare oja and Rannapungerja jõgi experience an increase (with positive t-values and p-values < 0.05), while Velise jõgi and Vodja jõgi exhibit a decrease (with negative t-values and p-values < 0.05). No significant trends are observed in many other rivers. Changes in Sodium levels could be influenced by human activities such as road salt application or natural processes like weathering.

pH: A select few rivers, including Ahja jõgi, Avijõgi, Emajõgi, Keila jõgi, and Pedja jõgi, display a significant rise in pH levels (with positive t-values and p-values < 0.05), whereas Jänijõgi and Valgejõgi exhibit a notable decline (with negative t-values and p-values < 0.05). No significant trends are observed in many other rivers. Changes in pH could be driven by factors such as acid rain or alterations in biological processes within the water bodies and human factors can also impact these changes.

Sulfate: The majority of rivers, such as Emajõgi, Keila jõgi, Kunda jõgi, Linnussaare oja, Narva jõgi, Õhne jõgi, Oostriku jõgi, Pedja jõgi, Piusa jõgi, Põltsamaa jõgi, Porijõgi/Reola jõgi, Preedi jõgi, Tänassilma jõgi, Väike Emajõgi, Valgejõgi, Velise jõgi, and Võhandu jõgi, display a significant decrease in Sulfate concentrations (with negative t-values and p-values < 0.05). This decline in Sulfate levels could be attributed to the implementation of stricter regulations on sulfur dioxide emissions from industrial processes and fossil fuel combustion.

Temperature: The analysis reveals notable temperature fluctuations in specific rivers. For instance, Ahja jõgi, Emajõgi, Piusa jõgi, and Võhandu jõgi exhibit a significant temperature increase (with positive t-values and p-values < 0.05). Conversely, Taebla jõgi and Vigala jõgi demonstrate a significant temperature decrease (with negative t-values and p-values < 0.05). In several other rivers, no significant trends are observed in temperature changes. These variations in temperature could be influenced by factors such as climate change, local weather patterns, or alterations in river morphology and water flow.

4. SUMMARY

This research focuses on evaluating water quality data and studying the changes and trends in rivers over a long period of time. It aims to understand the environmental effects of these changes and ensure the sustainability of water resources. The research also aims to propose more effective strategies for managing water quality in rivers. To assess water quality, the study utilizes trend analysis and analyzes the concentrations of ions in river water. The data for the analysis was collected from the Ministry of Environment's website (ENVIR) and covers the years 1994 to 2021.

The Q-Q plot analysis indicates that the distribution of Sulphur (SO_4), pH, and magnesium (Mg) in river waters is not normal, as evidenced by the curve pattern or dots that are not parallel with the straight line. This suggests that these parameters may be influenced by environmental factors that affect their distribution in the water. To improve this situation, it would be beneficial to identify and mitigate the sources of pollution that may be contributing to these variations.

The results of the principal component analysis (PCA) indicate that water quality parameters in the study area are influenced by several key environmental factors. The first two principal components are mainly driven by pollution-related factors (Cl, SO_4, Mg, Na+K) and water hardness/pH factors (Mg, Na+K, pH), while the third and fourth components are more related to the presence and distribution of specific cations (Ca, K, Na, Mg) that could be linked to both natural and anthropogenic factors.

The trend analysis reveals that changes in water quality parameters are variable across different watercourses in the study area. For example, Calcium concentrations show a considerable decline in some rivers but a notable increase in others, while Chlorine concentrations have decreased significantly across many rivers, possibly due to improved wastewater treatment processes and reduced industrial discharges. Potassium concentrations also show a variable trend, with some rivers exhibiting a significant rise and others a notable reduction. The fluctuation in Magnesium concentrations is limited to a few rivers, while Sodium concentrations show inconsistent trends. These variations suggest that the changes in water quality parameters are influenced by multiple factors, including differences in land use, agricultural practices, and geological features across the regions.

The time series analysis of the monthly variations in water quality parameters indicates seasonal fluctuations in some of the parameters, while others show relatively stable concentrations throughout the year. Calcium, potassium, manganese, and temperature all exhibit significant fluctuations, which may be attributed to changes in input sources, redox conditions, or biological processes. Chloride and sodium concentrations show relatively stable levels, indicating consistent sources throughout the year. Sulfate concentrations exhibit some variability, which may be due to variations in input sources or biological processes. pH values remain fairly consistent, indicating a mildly alkaline aquatic environment, and within the acceptable range for most aquatic organisms. The temperature trend follows the typical seasonal pattern, with warmer temperatures during summer months and colder temperatures during winter months.

The findings presented in this conclusion provided a comprehensive analysis of the changes in water quality parameters in Estonian rivers from 1994 to 2021. The study highlights the need for a multi-pronged approach that addresses both pollution-related and natural factors that influence water chemistry. Finally in the result it concluded that river quality in Estonia over these years measured as medium quality. Taking into account the measured parameters, its assumed that most of the sources of impact come from agricultural activity in the Northeast area of Estonia, industrial activities in the Northern area and number of mining activities and areas all around Estonia. Further rules and regulation can be done towards reduction of environmental impact of each industry in order to reduce negative impact of human factors to rivers.

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