TALLINN UNIVERSITY OF TECHNOLOGY
SCHOOL OF ENGINEERING
Department of Civil Engineering and Architecture

ASSESSMENT OF THE WATER QUALITY INDEX FOR THE NARVA RIVER AND THE RIVERS OF THE LAKE PEIPSI BASIN, ESTONIA

VEEKVALITEEDI INDEKSI ARVUTAMINE NARVA JÕELE JA PEIPSI JÄRVE VESIKONNA EESTI POOLSETELE JÕGEDELE

MASTER THESIS

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Tallinn 2021

(*On the reverse side of title page*)

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THESIS TASK

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Thesis topic:

(in English) Assessment of the water quality index for the Narva river and the rivers of the Lake Peipsi basin, Estonia.

(in Estonian) Veekvaliteedi indeksi arvutamine Narva jõele ja Peipsi järve vesikonna Eesti poolsetele jõgedele.

Thesis main objectives:

1. To choose different water quality index models for assessing the water quality.
2. To calculate the water quality index of the Narva river and the rivers of the Lake Peipsi basin using different water quality index models.
3. To compare and interpret the results of the water quality index score.

Thesis tasks and time schedule:

No	Task description	Deadline
1.	To define study area and data gathering.	25.03.2021
2.	To review the different water quality index methods.	15.04.2021
3.	To calculate the water quality index by using different water quality index models and compare the results.	03.05.2021

Language: English **Deadline for submission of thesis:** 26.05.2021a

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PREFACE

The thesis topic was proposed by the supervisor Dr. Alvina Reihan, Senior Lecturer, and Co-supervisor Kati Roosalu, Junior Researcher, from Tallinn University of Technology. The author is highly thankful to his supervisor and Co-supervisor and appreciates practical and constructive suggestions during the calculations and development of this work. The study goes along with the NarvaWatMan project (www.narvawatman.com), which is conducted with the financial support of the Estonia – Russia Cross Border Cooperation Programme 2014-2020 (www.estoniarussia).

The main objective of this thesis is to determine and analyze the water quality index (WQI) of the Narva river and the major rivers of the Lake Peipsi basin in Estonia by using different water quality index methods. Moreover, this study compares the WQI methods for assessing the water quality status in different rivers.

This thesis work was performed in Tallinn, Estonia, and maximum permissible limit values of analysed parameters were received from the NarvaWatMan project and Estonian legislation Act No. 19. The studied parameters data was received from the Estonian Environment Agency (WWW.kaur.ee).

The author expresses gratitude to the Tallinn University of Technology for the perfect environment for studying and doing research work and all the lecturers and researcher for the cordial support the author has received.

Finally, I would like to thanks to my late father, who passed away in 2020, and could not witness my maters thesis, for supporting and encouraging me to keep on with my higher studies and fullfill not only my but also his dream.

Water quality index; parameter; CCME WQI; WA WQI; MCWQI; master thesis

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LIST OF ABBREVIATIONS AND SYMBOLS

BC - British Columbia;

BSAP - Baltic Sea Action Plan;

BOD - Biochemical Oxygen Demand;

CARTs - Country Allocated Reduction Targets;

CCME – Canadian Council of Ministers of the Environment;

COD - Chemical Oxygen Demand;

EC - Electrical Conductivity;

EST - Estonia

EU - European Union;

GOF – Gulf of Finland;

HELCOM – Helsinki Commission;

MAI - Maximum Allowable Inputs;

MCWQI - Modified Canadian Water Quality Index

NSF - the National Sanitation Foundation;

$\mathbf{N_{tot}}$ **-** Total Nitrogen;

$\mathbf{P_{tot}}$ - Total Phosphorous;

SRDD - Scottish Research Development Department;

WA – Weighted Arithmetic;

WFD - Water Framework Directive;

WHO - World Health Organization;

WQI – Water Quality Index;

1 INTRODUCTION

Water covers more than 70% of the earth's surface. The total volume of water on earth is about 1.386 billion cubic kilometers, which does not change, and about 96% of this water is saline, and the remaining 4% in glaciers, ice caps, groundwater, lakes, rivers, and aquifers. All human activities, like agriculture, drinking, irrigation, industry, and domestic work, depend on the river water. As a result, the rivers are considered to be vital sources of surface water on earth. Nevertheless, all these activities are responsible for deteriorating the quality of the river's water in the world, particularly in developing countries. [1, 6]

Eutrophication is one of the significant threats nowadays as it has long-term negative consequences on the biodiversity of the Baltic Sea due to the excessive amount of nutrients in nitrogen, and phosphorus input. The surplus amount of nutrients causes escalated levels of algal and plant growth, elevated turbidity leading to deplete light conditions in the water, reduce oxygen level due to the increased oxygen consumption at the seafloor, changes in species composition, and nuisance blooms of algae. The Baltic Sea is located in Northern Europe, which is most polluted seas on our planet [15, 16]. In 2013, the total number of nutrient inputs to the Baltic Sea was 910,343 tonnes of nitrogen and 36,893 tonnes of phosphorus [42]. During 2010, The Baltic Sea Proper accepted 53% of total nitrogen and 54% of total phosphorus input, followed by the Gulf of Finland, which was received 13% of total nitrogen and 17% of total phosphorus inputs. [20]

The Gulf of Finland (GOF) is heavily loaded sub-basins in the Baltic Sea by nutrient input, which significant portions come from riverine and rest of them from a direct point sources and atmospheric deposition. The total catchment area of the GOF is 423,000 km², of which 107,000 km² (25%) territory belongs to Finland, 286,000 km² (68%) to Russia, 26,400 km² (6%) to Estonia, and 3,600 km² (less than 1%) to Latvia. During 2009-2013, the average nitrogen input into the Gulf of Finland was 112,000 tons per year, and the primary sources of nutrients of nitrogen input are rivers (79%), direct point sources contribute for 10%, and deposition for 11% of the input. The phosphorus input was 4,270 tons per year for the period 2009-2013, with rivers were accounting for 88% and the rest of the 12% from point sources. The total annual nutrients of nitrogen and phosphorous input from the Estonian territory are 14,400 ton (13%) and 434 ton (10%) respectively in the period 2009-2013. The Narva River is one of the large transboundary rivers in the Baltic Sea catchment area, with some 63% of its catchment area located in Russia, 31% in Estonia, and 7% in

Latvia. Estonia contributes one-third of the nitrogen and phosphorous inputs into the Narva River and two-thirds come from the Russian side. [19]

The Baltic Sea Action Plan (BSAP) was first introduced and adopted in 2007 by HELCOM's (Baltic Marine Environment Protection Commission) contracting parties (i.e., countries and the EU) and its objectives are unaffected by eutrophication, the favorable status of Baltic Sea biodiversity etc. In 2013, HELCOM revised MAIs into the Baltic Sea were set at 21,716 ton per year for P and approximate 792,209 ton per year for N and Country Allocated Reduction Targets (CARTs) were set up for the different sea areas and countries of the Baltic Sea. The CARTs for Estonia are 1800 ton total nitrogen per year and 320 ton total phosphorous per year [31]. However, it estimated that nutrient inputs will reduce by 34 ton phosphorous per year and 942-ton nitrogen per year into the GOF within 2015. [19, 31, 32]

The Republic of Estonia joined the EU in 2004 and is one of the smallest countries in the EU. With the Water Framework Directive (WFD) 2000/60/EC of the European Parliament and a framework for Community action in the field of water policy and structure, a goal of accomplishing "good status" includes "good ecological" and "good chemical status for all waters. The main concern is the oil shale mining region in northeast Estonia, which produces many hazardous substances and contaminates Estonia's aquatic environment [33]. The water qualities in Estonian are affected by social, food, and light industry and nutrients. The lengths of the rivers in Estonia are short, with a small catchment area. There are four natural river basin districts for different Estonian rivers based on water drainage systems: Narva-Peipsi river basin, the Gulf of Finland river basin, the Gulf of Riga river basin, and the river basin district of islands. Agriculture leads to nutrients and eutrophication of the water bodies in Estonian rivers, and eutrophic signs in water bodies are easily visible due to the rapid growth of water plants and algae blooms. [23]

The Water Quality Index (WQI) is one of the most effective tools for assessing water quality for various uses such as drinking, irrigation, livestock, aquatic life, and recreation since Horton first developed it in 1965 to evaluate and communicate the suitability of water bodies [2, 6]. WQI is a mathematical tool used to convert extensive amounts of water quality data into a single numerical value that quickly explains the water quality [6]. This paper is focused on evaluating an appropriate WQI for the Narva River and the rivers of the Peipsi Lake Basin. The Canadian Council of Ministers of the Environment Water Quality Index (CCME WQI) method, MCWQI, and Weighted Arithmetic Water Quality Index (WA WQI) method are applied to assess the

WQI for the studied Estonian rivers and then make a comparison of the methods to ascertain the difference between them [6]

The objective of the Study

- To determine the physical and chemical parameters of the river water at several monitoring stations in Estonia.
- To analyze the CCME WQI method and modify to the new water quality index method is called Modified Canadian Water Quality Index (MCWQI).
- To calculate WQI using different methods (CCME WQI, MCWQI, and WA WQI) to evaluate the water quality of the studied rivers from different sampling sites.
- To interprete and compare the results of these methods and then evaluate the quality of water for the Narva river and the rivers of the Lake Peipsi Basin.

2 BACKGROUND

Nowadays, maintaining a good quality of water is a big challenge all over the world. As a result, water quality monitoring management requires using modern, practical water quality assessment tools and techniques [2]. Water quality protection is critical work to ensure the safe water supply for production, agriculture, drinking, recreation, and aquatic life. However, this job makes easier now by using various technological improvement, and developed countries are using these technological tools to make better water quality.

Eutrophication is the primary concern of the Baltic Sea; between the 1950s and the late 1980s, nitrogen and phosphorus inputs have been expanding for a long time in the Baltic Sea. The sea has limited water exchange with other seas, resulting in accumulating nutrients and pollutants and their very slow dilution [15, 16]. The Baltic Marine Environment Protection Commission, known as the "Helsinki Commission" or "HELCOM," was established in 1974. HELCOM consisted of the nine countries that border the Baltic Sea (Denmark, Germany, Poland, Lithuania, Latvia, Estonia, Russia, Finland, and Sweden) and the European Union (Baltic Marine Environment Protection Commission). Most of the nutrient input to the Baltic Sea is riverine. HELCOM set up a goal of reducing the inputs of nutrients into the Baltic Sea and Baltic Sea being unaffected by eutrophication [17]

The main reasons for the selection of the studied rivers (Narva, Emajõgi, Piusa, Võhandu, Avijõgi, Alajõgi, Kullavere, Rannapungerja, and Mustajõgi) are responsible for input nutrients of nitrogen and phosphorus to the Baltic Sea. Notably, the Lake Peipsi basin drains into the Gulf of Finland through the Narva river. All studied rivers, except Mustajõgi, discharge into the Lake Peipsi and then falls into the GOF through the Narva river. The Mustajõgi river directly drain into Narva river, and finally inflow into the Gulf of Finland of the Baltic Sea. The Narva river is flowing from Peipsi Lake into Narva Bay. The pollutants concentrations in the Narva river as the transboundary river, are of great interest itself and the contribution to the loading from the Peipsi Lake.

A water quality index is an effective tool that can convert large amounts of water quality data from a sampling site into a single value [39]. The most widely used water quality index model is CCME WQI, while in this work; we used the CCME WQI, MCWQI, and WA WQI method to evaluate the water quality status in the Narva river and the rivers of the Lake Peipsi basin. However, the water quality rank scale is reverse in the

WA WQI method compare to the CCME WQI and MCWQI methods. Furthermore, six constant parameters (pH, BOD_5, O_2%, NH_4^+, N_{tot}, P_{tot}) are selected to calculate the water quality index and then adding new parameters (EC, COD_{Mn}, NO_3^-, PO_4^{3-}) with constant variables to cross-check the index score variation.

3 WATER QUALITY INDEX METHODS

Water Quality Index (WQI) is one of the most efficient tools for assessing water quality in surface water and groundwater, which could be deal a stable and straightforward unit of measurement to communicate water quality and can be used as an essential parameter for the assessment and management of surface water [6, 7]. The quality of water for the use of various purposes is evaluated through different water quality indexes (WQI), which consider the rank of water quality in different sources of the water (lakes, streams, rivers, and reservoirs) [6]. The strong point of a water quality index as an overall quality indicator is affected by insensitivity to individual quality variables, and the weak point of WQI methods are subjectivity, obscurity, and eclipsing [40].

According to Abbasi, the concept of water quality index was first introduced in the mid-1800s in Germany [40]. Water Quality Index (WQI) models were introduced more than 50 years ago. In 1965, Horton developed the WQI model to give a single value and represent the water quality class, which was based on ten water quality parameters [5, 39, 40]. In 1972, Brown developed Horton's WQI model with the support of the National Sanitation Foundation (NSF) and with the help of 142 water quality experts who selected the particular parameter and weighting. In 1973, the Scottish Research Development Department (SRDD) developed SRDD-WQI to evaluate the river water quality, which is based on Brown's model. The later developed Bascaron Index (1979), House Index (1986), and Dalmatian Index model for assessing water quality. In 1982, Steinhart et al developed another Quality Index model for assessing water quality in the great lake's ecosystems. [5]

The most crucial water quality index development was the British Columbia WQI (BCWQI) by the British Columbia Ministry for Environment, Lands, and Parks in 1995, which model was used to assess the many water bodies quality in the province of British Columbia, Canada. In 2001, The Canadian Council of Ministers of the Environment developed the CCME WQI by update of the BCWQI model. Recently developed Liou Index, the Malaysian Index, and the Almeida Index models. Over 35 WQI models have been developed in many countries to assess surface water quality (Figure 3.1). However, WQI models are used to evaluate the quality of water bodies; 82% of applications have been to assess river water quality. [5]

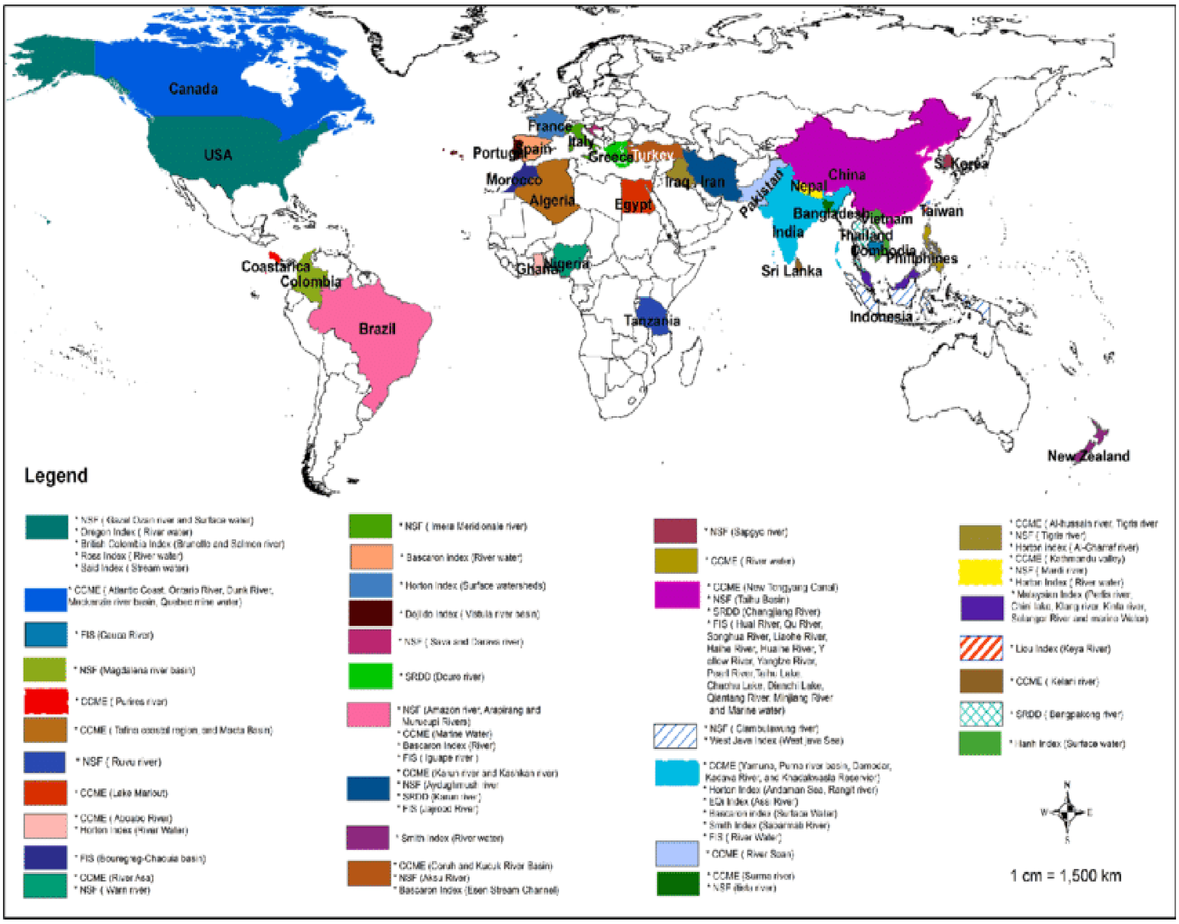

Figure 3.1: WQI used in different countries according to the Water types [5].

3.1 The Estonian Water Quality Index Method

Estonia has its own evaluation method to assess the water quality for surface water. The classification system of the Estonian rivers is based on the assessment of six physico-chemical indicators in accordance with Act No. 19 of the Ministry of the Environment. The parameters used for the quality assesement are pH, dissolved oxygen, biochemical oxygen demand (BOD_5), ammonium nitrogen (NH_4-N), total nitrogen (N_{tot}), and total phosphorus (P_{tot}).

According to the legislation Act No. 19 in Estonia, the limit value of the individual parameter depends on the types of the river. Rivers are classified into water body types according to their catchment area size and organic matter content. There are four types according to the size: I is 10-100 km^2, II is 100-1000 km^2, III is 1000–10 000 km^2, IV is 10 000 km^2. Types and they are further divided into dark (A) and light

(B) water rivers. Type's I-III are divided into dark (A) and light (B) water rivers according to the content of organic matter. Furthermore, type IV is a distinct type due to the large size of the river, in this group is only the Narva river, which catchment area is more than 10,000 km^2 and it is classified as light water river (B). Type A river water is dark, with high organic material content and higher water color, where 90% of COD_{Mn} value is higher than 25 mgO/l. Whereas type B river water is light-colored with lower humic substance content, where 90% of COD_{Mn} value is less than 25 mgO/l [47]. The limit values (table 3.1.1) of the individual parameter, according to the type of water bodies.

Table 3.1.1: Limits of ecological status classes of watercourses according to physico-chemical quality indicators according to the Estonian legislation [47].

Indicator		Type	Excellent 5 points	Good 4 points	Moderate 3 points	Poor 2 points	Bad 1 Point
DO (%)	10% value	A	>61	60–50	49–40	39–35	<34
		B	≥70	69-60	59–50	49–40	≤39
		IV (Narva)	≥70	69-60	59–50	49–40	≤39
BOD_5 (mg O_2/l)	Arithmetic mean	A	≤2.2	2.3-3.5	3.6-5.0	5.1-7.0	≥7.1
		B	≤1.8	1.9-3.0	>3.1-4.0	>4-5	≥5.1
		IV (Narva)	≤1.8	1.9-3.0	>3.1-4.0	>4.0-5.0	≥5.1
N_{tot} (mg N/l)	Arithmetic mean	A	≤1,5	1,6-3,0	3,1-6,0	6,1-8,0	≥8,1
		B	≤1,5	1,6-3,0	3,1-6,0	6,1-8,0	≥8,1
		IV (Narva)	≤0.5	0.6-0.7	0.8-1.0	1.1-1.5	≥1.6
P_{tot} (mg P/l)	Arithmetic mean	A	≤0.05	0.05-0.08	0.08-0.1	0.101-0.12	≥0.121
		B	≤0.05	0.05-0.08	0.081-0.1	0.101-0.12	≥0.121
		IV (Narva)	≤0.04	0.041-0.060	0.061-0.08	0.081-0.10	≥0.101
NH_4 (mg N/l)	90% Value	A	≤0.1	0,11-0,30	0,31-0,45	0,46-0,60	≥0.61
		B	≤0.1	0,11-0,30	0,31-0,45	0,46-0,60	≥0.61
		IV (Narva)	≤0.1	0,11-0,30	0,31-0,45	0,46-0,60	≥0.61

To assess the water quality class of rivers on annual basis according to the Estonian quality model, either the annual average value (N_{tot}, P_{tot}, BOD_5) or a certain percentile value of the quality indicator is found (NH_4 – 90^{th} percentile, DO – 10^{th} percentile, pH – 10^{th} percentile). If the pH value (10%) is higher than 9 or lower than 6, the overall water status is bad, regardless of the status classes assigned to the other quality indicators. If the pH value is between 6 and 9, the individual status class will be determined for each quality indicator, except pH, according to the limit values given in table 3.1.1, on a scale of 1 to 5 as follows: 5 - excellent; 4 - good; 3 - moderate; 2 - poor; 1 - bad. The general water quality class is the sum of the scores awarded to the individual quality indicators and the water quality class is determined from the final score according to the scale in Table 3.1.2. If the status class of at least one of the quality indicators, except pH, is poor or bad, the overall status class can not be more than poor regardless of the sum of points [47].

Table 3.1.2: The Estonian water quality points classification [47].

The Estonian Water Quality Scale with colours		
Excellent	23-25	
Good	18-22	
Moderate	13-17	
Poor	8-12	
Bad	<8	

3.2 The Canadian Council of Ministers of the Environment Water Quality Index (CCME WQI)

Index (CCME WQI) was founded in 1995 based on a water quality index developed by the British Columbia Ministry of Environment, Lands, and Parks and in 1999 includes modifications by the Alberta Agricultural Water Quality Index. Nowadays, the Canadians Water Quality Index (CWQI) is calculated using the Canadian Council of Ministers of the Environment Index method. Three factors are combined to calculate the CCME WQI based on these objectives [8, 9].

F_1 and F_2 are relatively straightforward to calculate, whereas the factor F_3 calculation requires some more steps. It has been determined that the first term (F_1) contribution to the final CCME WQI score is more significant than the contribution of the other two terms [8].

F_1 (Scope) - Scope represents the percentage of parameters that do not meet their objectives at least once during the period under consideration (failed parameters), relative to the total number of parameters measured [8, 9]:

$$F_1 = \left(\frac{\text{Number of failed parameters}}{\text{total number of parameters}}\right) \times 100$$

F_2 (Frequency) - Frequency represents the percentage of individual tests that do not meet guidelines (failed tests): [8]

$$F_2 = \left(\frac{\text{Number of failed tests}}{\text{total number of tests}}\right) \times 100$$

F_3 (Amplitude) - Amplitude represents the amount by which failed test values do not meet their objectives. F_3 is calculated in three steps. [8]

Step 1: Excursion calculation

The excursion is the number of times by which an individual concentration is more significant than (or less than, when the guideline is a minimum) the objective. When the test value must not exceed the guideline: [8, 10]

$$\text{Excursion} = \left(\frac{\text{Fail test value}}{\text{Objective}}\right) - 1$$

For the cases in which the test value must not fall below the guideline:

$$\text{Excursion} = \left(\frac{\text{Objective}}{\text{Fail test value}}\right) - 1$$

Step 2- Calculation of Normalized Sum of Excursions (nse)

The normalized sum of excursions or nse, is the collective amount by which individual tests are out of compliance, which is calculated by summing the excursions of individual tests from their objectives and dividing by the total number of tests (both those meeting guidelines and those not meeting guidelines) [8, 10]

$$\text{nse} = \frac{\sum_{i=1}^{n} \text{Excursion}}{\text{Number of tests}}$$

Step 3– F_3 Calculation

Amplitude (F_3) is calculated by an asymptotic function that scales the normalized sum of the excursions from objectives (nse) to yield a range between 0 and 100 [8, 9, 10].

$$F_3 = \frac{\text{nse}}{0.01\text{nse} + 0.01}$$

These are three factors (F_1, F_2, F_3), which are combined as the summation of the three vectors (scope, frequency and amplitude), and using the Pythagoras theorem to produce a single value between 0 and 100, which shows the quality of water (Table 3.2.1). The index is defined as a three-dimensional space by each factor along one axis (Figure 3.2.1). With this model, the index changes in direct proportion to changes in all three factors. [8]

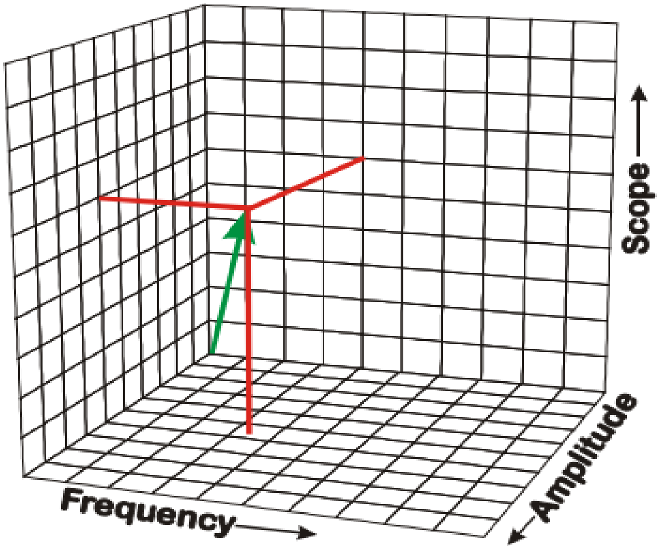

Figure 3.2.1: The conceptual model of the Index [8].

Water quality index (CCME WQI) is calculated by equation:

$$\text{CCME WQI} = 100 - \frac{\sqrt{F_1^2 + F_2^2 + F_3^2}}{1.732}$$

Where 1.732 is the scaling factor ($\sqrt{3}$), which normalizes the resultant values to a range between 0 and 100, where 0 depicts the "worst" water quality and 100 shows the "best" water quality [8, 40].

The CCME WQI values are then converted into rankings by using the water quality index categorization scheme, the range of modified Water quality index value according to the proposal from NarvaWatMan project and Original CCME WQI value (Table 3.2.1).

Table 3.2.1: The CCME WQI score classification [8, 9].

Rank	WQI Value (Original)	WQI Value (Modified)	Description
Excellent	95-100	90-100	Water quality is protected with a virtual absence of threat or impairment; conditions very close to natural or pristine levels
Good	80-94	80-89	Water quality is protected with only a minor degree of threat or impairment; conditions rarely depart from natural or desirable levels
Moderate	65-79	65-79	Water quality is frequently threatened or impaired; conditions often depart from natural or desirable levels.
Poor	45-64	55-64	Water quality is almost always threatened or impaired; conditions usually depart from natural or desirable levels
Bad	<45	<55	Water quality does not meet any criteria for use as a source.

The significant advantages of using the CCME WQI method are given in below:

1. CCME WQI can present measurements of a variety of variables in a single number.
2. The objectives and input parameters selection is flexible in the CCME WQI method.
3. Adaptability to different legal requirements and other water uses.
4. CCME WQI presents complex multivariate data in statistical simplification.
5. The diagnosis of water quality is clear and intelligible for the general public.
6. CCME WQI calculation formula is relatively easy.
7. This method has tolerance to missing data.
8. The upcoming data from automated sampling is possible to analyze.
9. To produce in a single unit by combining many measurements in various measurement units. [28]

The main disadvantages of the CCME WQI method are:

1. Lack of data on single variables.
2. Sensitivity of the results to the methodology of the water quality index.
3. Scarcity of information on interactions between different variables.
4. Inadequate portability of the index to different ecosystem types.
5. All variables are considered to be of the same importance.
6. Scope (F_1) cannot work perfectly during the number of variables considered very few or when too much covariance exists among them. [28]

3.3 The Weighted Arithmetic Water Quality Index (WA WQI)

The Weighted Arithmetic mean was introduced by Brown (1970) and Dinius (1987) to aggregate parameters [40]. The weighted arithmetic water quality index is a handy tool to evaluate the quality of the water. The most suitable water quality parameters are used and compared with the allowable values for the river water quality to calculate a water quality index given in the following steps[6].

Step 1: Calculate the unit weight (W_n) factors for each parameter by using this formula:

$$W_n = K/S_n$$

Where,

$$K = \frac{1}{\frac{1}{S_1}+\frac{1}{S_2}+\frac{1}{S_3}+\cdots+\frac{1}{S_n}} = \frac{1}{\sum\frac{1}{S_n}}$$

S_n = Standard desirable value of the n^{th} parameters.

K = proportionality constant

On summation of all selected parameters unit weight factors, $W_n = 1$

Step 2: Calculate the sub-index (Q_n) value by using this formula:

$$Q_n = \frac{[(V_n - V_0)]}{[(S_n - V_0)]} * 100$$

Where,

V_n = Mean concentration of the n^{th} parameters.

S_n = Recommended standard desirable value of the n^{th} parameters

V_o = Actual/Ideal values of the parameters in water (Generally, $V_o = 0$, for all parameters except pH= 7 and Dissolve Oxygen = 14.6)

$$Q_{pH} = \frac{[(V_{pH} - 7)]}{[(8.5-7)]} * 100$$

Step 3: Calculate the Weighted Arithmetic Water Quality Index (WA WQI) using the formula,

$$\text{Overall WA WQI} = \frac{\sum W_n Q_n}{\sum W_n}$$

Finally, the overall Weighted Arithmetic WQI derives as the weighted arithmetic mean of the individual sub-index values and ranges from 0 to 100 or above 100. As reported by Tyagi (2013) and Sutadian (2016), WA index is not a water quality index but a water pollution index. If the numerical index value rises, that indicates the quality of water is worse. It means WQI = 0 is indicate the excellent water quality [40]. According to this index score, the quality of the water body is categorized into five classes (Table 3.3.1), namely "excellent," "good," "moderate," "poor," and "bad" [30].

Table 3.3.1: The Weighted Arithmetic Water Quality Index (WA WQI) scale classification [6,30].

The Weighted Arithmetic Water Quality Scale with colours		
Excellent	0-25	(blue)
Good	26-50	(green)
Moderate	51-75	(yellow)
Poor	76-100	(orange)
Bad	>100	(red)

The advantages of the weighted arithmetic mean method are:

1. The WA WQI method incorporates data from multiple water quality parameters into a mathematical equation that rates the health of the water body with a number.
2. The small number of parameters required in comparison to all water quality parameters for specific use.
3. Effective for communication of general water quality information to the concerned citizens and policymakers.
4. Reflects the composite influence of different parameters, i.e., essential for assessing and managing water quality.
5. The WA WQI can illustrate the suitability of both surface and groundwater sources for human consumption [28, 29]

The disadvantages of the weighted arithmetic mean method are:

1. The WA WQI is not carried sufficient information about the actual quality situation of the water.
2. Different uses of water quality data are not capable to met an index.
3. Over-emphasizing a single wrong parameter value
4. The WA WQI based on some vital parameters can provide a simple indicator of water quality. [28]

3.4 Modified Canadian Water Quality Index (MCWQI)

The fundamental mathematical problems of the CCME WQI method illustrates for a different situations due to the pathological memory effect. The strange behavior of CCME WQI is quentionable regarding the factor F_1 in practical applications. As a result, The CCME (2006) called the consulting agency Gartner and Lee, to find the solution. Gartner Lee proposed two alternative formulations of F_1 according to the sensitivity analysis of the quantity of parameter, parameter selection, number of tests, and guidlines selection [40], which are more correlated with all three factors [35]. The first alternative of formulations of F_1 is;

$$F_1 = \frac{F_{1a} + F_{1b}}{2}$$

Where:

F_{1a} = (number of failed parameters/total number of parameters)*100

F_{1b} = (number of test that exceed objectives/total number of tests)*100

Second alternative of formulations of F_1 proposed by Gartner Lee limited is;

$$F_1 = F_{1a}, \text{ if } F_2 > 10$$

$$F_1 = (0.5 * F_{1a}), \text{ if } F_2 \leq 10$$

Where

F_{1a} = (number of failed parameters/total number of parameters)*100

F_2 = (total number of failed tests/total number of tests)*100.

According to Gartner and Lee, The first scenerio of formulation F_1 proposed produced the index value is correlated with all factors, whereas the second formulation of F_1 tended to provide the maximum WQI values and rankings, and occasional exceedances of objectives. If the frequency of exceedance of guidelines is less than or equal to 10%, then F_1 formulation is divided by 2. [35, 40]

In 2012, one expert group (Tim Hurley et al.) proposed a modified CCME WQI calculation procedure to accommodate parameters measured at different frequencies with considering factor weightings. Factor weightings (W_n) minimize the deviation between the mean expert score and the resulting weighted index score. [38]

$$\text{CCME WQI}_{\text{weighted}} = 100 - \frac{\sqrt{W_1 F_1^2 + W_2 F_2^2 + W_3 F_3^2}}{\sqrt{W_1 + W_2 + W_3}}$$

In 2019, Modher Hassan proposed another CCME WQI modification. This modified WQI is removing frequency and incorporates with scope and amplitude. [37]. Proposed modified WQI was:

$$\text{MCWQI}_1 = 100 - \frac{\sqrt{F_{ms}^2 + F_{ma}^2}}{1.414}$$

Where,

F_{ms} – Scope, F_{ma} – Amplitude,

In this work, author considered a modified version of the CCME WQI introduced by Van Dao et al. (2020). This expert team calculates WQI by using the multiplication and geometric mean, called the Modified Canadian Water Quality Index (MCWQI). According to the paper of Gallant (2020), the geometric mean provides more accurate measurement for data series cmpare to the arithmetic mean [35]. The idea of MCWQI is considering the analysis of factors (F_1, F_2, F_3) as different viewpoints of water quality. The MCWQI is determined by combining the three factors (F_1, F_2, F_3) using the geometric mean [35]. The MCWQI equation is expressed below.

$$MCWQI_2 = 100 - \sqrt[3]{F_1 * F_2 * F_3}$$

The $MCWQI_2$ produces different results compare to the CCME WQI. Therefore, the value classification for the MCWQI method of water quality index remains the same with the CCME WQI [35].

For completeness sake, it is stated that always CCME WQI ≤ $MCWQI_2$. It is well-known mathematically that the geometrical mean of three numbers is always less than or equal to the arithmetic mean of these numbers.

$$\sqrt[3]{F_1^2 * F_2^2 * F_3^2} \leq \frac{F_1^2 + F_2^2 + F_3^2}{3}$$

The square root on both sides leads to

$$\sqrt[3]{F_1 * F_2 * F_3} \leq \sqrt{\frac{F_1^2 + F_2^2 + F_3^2}{3}}$$

Hence,

$$100 - \sqrt{\frac{F_1^2 + F_2^2 + F_3^2}{3}} \leq 100 - \sqrt[3]{F_1 * F_2 * F_3}$$

4 STUDY AREA

In this thesis work, author studied nine rivers with ten chemical monitoring stations (Figure 4.1). Figure 4.1 depicts that the seven rivers drains into the Lake Peipsi basin, then discharge into the Baltic sea through the Narva river, and the Narva river flows into the Baltic Sea along with the water discharge from the Mustajõgi river.

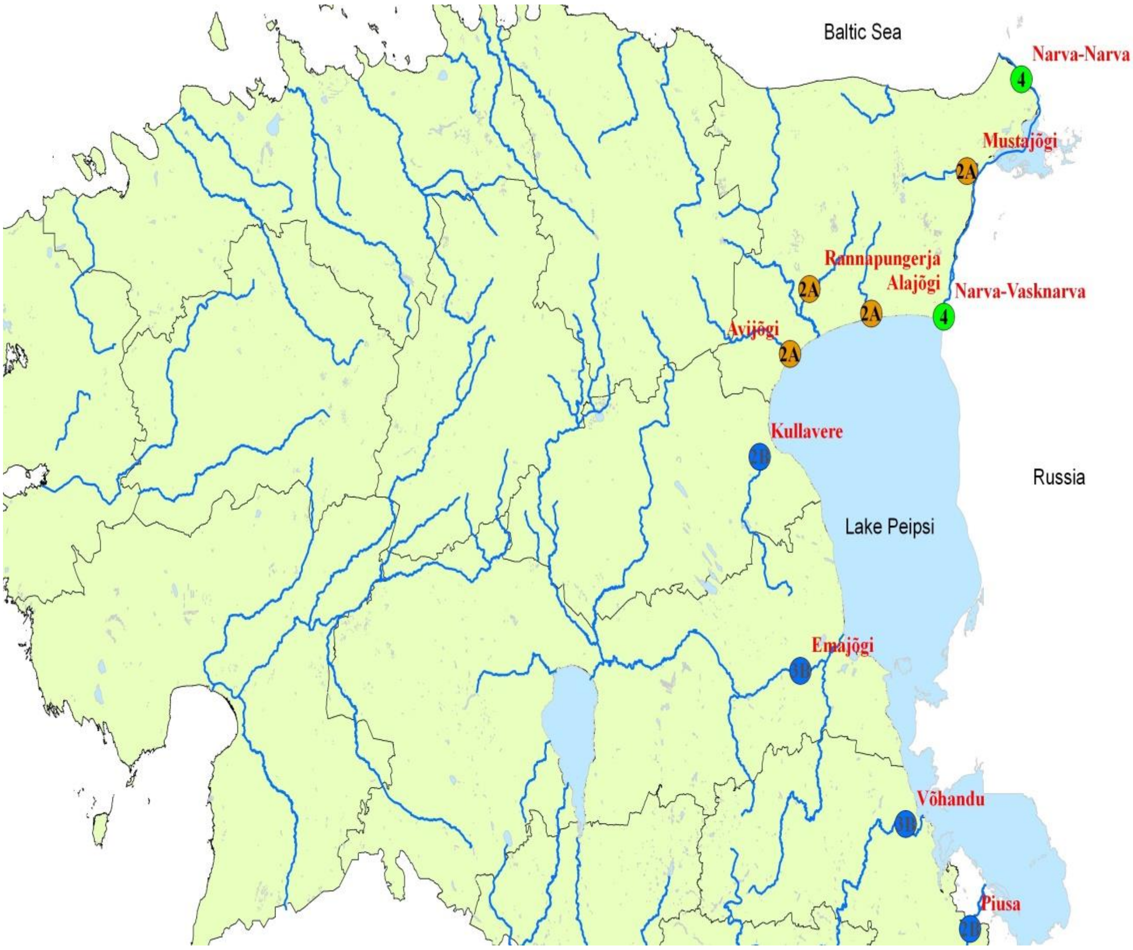

Figure 4.1: Geographical location of the studied rivers with monitoring stations.

4.1 Narva River

The Narva river, also known as Narova, is a river on the eastern border of Estonia and the largest Estonian river according to discharge, which its source at the North-eastern end of the Lake Peipsi near the Vasknarva village and flows into the Narva Bay in the Gulf of Finland (figure 4.1.1). On the Estonian side is the city of Narva; on the other side of the river is the Russian city Ivangorod [13].

The length of the Narva river is 77 km, which is the biggest river in Estonia in terms of annual flow (annual volume of 400 m^3/s) and the second-largest river after the Neva river entering the Gulf of Finland [12, 13, 25]. The total catchment area of the Narva river is 58,126 km^2, (30.2% of which located in Estonia, 6.3% in Latvia, 63.0% in Russian federation and 0.5% in Belarus) [12, 13, 21]

According to HELCOM classification, Narva is a border and a transboundary river between Estonia and Russia, which mouths to the Baltic Sea. The Baltic Marine Environment Protection Commission, 2019 declared that 1/3 of the total pollution load from the Narva river to the Baltic Sea comes from the Estonian side. As a transboundary river, Narva is the river that crosses at the political border and has its mouth to the Baltic Sea in one of the HELCOM Contracting Parties. [12, 14].

In Narva river, there are two hydro chemical stations and two hydrological stations in Estonia. One hydrometric station called Vasknarva is located near the Vasknarva village in Ida-Viru County, Estonia, which has been in operation since 1902 and was automated in 2010. The Vasknarva hydrometric station 76.4 km away from the river's mouth, and the catchment area is 47800 km^2. Narva city is another hydrometric station, which is situated in Narva city port, Ida-Viru County. The Narva city hydrometric station started its operation in 2000 and was automated in 2002, and this hydrometric station is 14.6 km distance from the river mouth, and the total catchment area is 56000 km2 [12, 21, 26, 27, 34]. On the Russian side, there is one chemical monitoring station, 12 km away from the river mouth, and one hydrological station 16 km from the river mouth [14, 21].

The Vasknarva and Narva City hydrometric station measure the water discharge [m^3/s] (2-3 times per month; 5-6 times per month during high water periods) and daily water level and water temperature at the bottom of the river; manually measured water temperature in surface water (0.10-0.50 m) during flow measurement. Observe the residual signs and aquatic vegetation if it is present during the flow measurement. In addition, the Vasknarva hydrometric station measures the air temperature. [26].

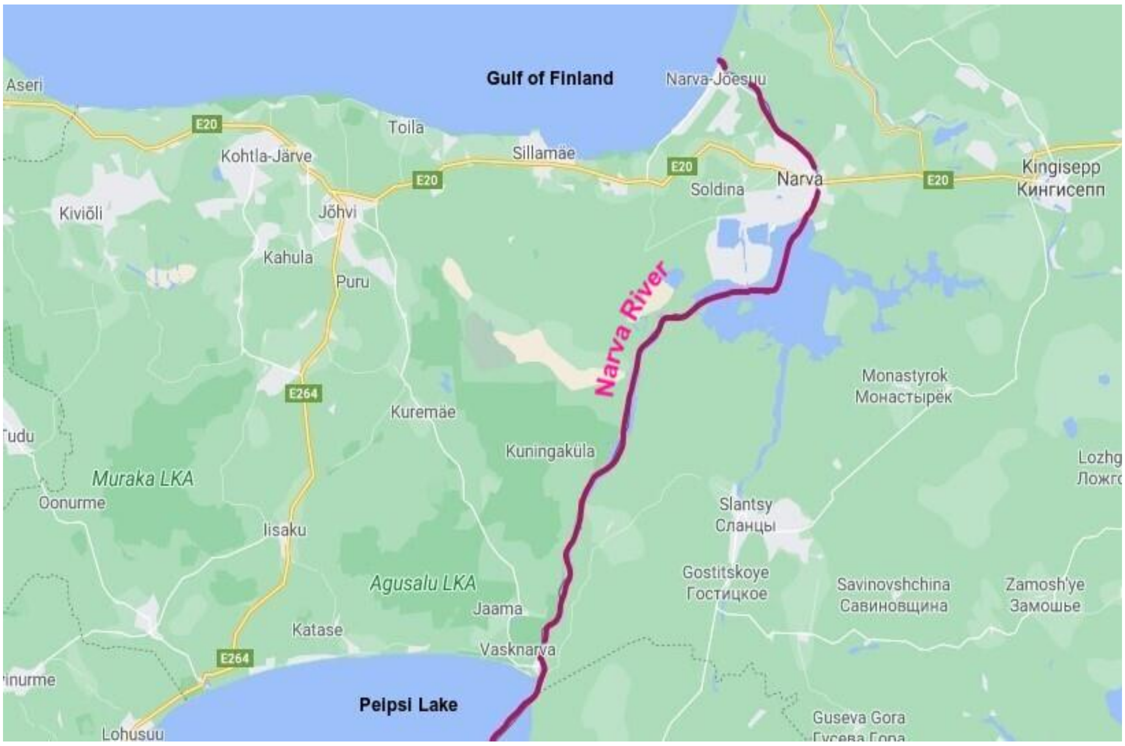

Figure 4.1.1: Narva River

4.2 Emajõgi River

Emajõgi river is called the "Suur Emajõgi," and Emajõgi is the second-largest river according to the annual water discharge and the only fully navigable river in Estonia. Also, the river's length is 100 km, which starts from the Võrtsjärv Lake at Rannu-Jõesuu and passes through Tartu City, flows into the Lake Peipsi, crossing the city of Tartu for 10 km (figure 4.2.1). The total catchment area of the river is 9745 km^2, and the average water discharge at the mouth is 72 m^3/s. [25]

The unique character of this river is that it can flow in both directions. Generally, the water flows from west to east, which is the Võrtsjärv Lake to the Peipsi Lake; also, it can flow east to west, i.e., Pepsi Lake to Võrtsjärv Lake when the water level of the Võrtsjärv Lake is lower. Hydrological observations on the Emajõgi river began in 1867. According to National observations of the water quantity, there are hydrometric stations in Emajõgi river, which is conducted annually in its headwaters in Rannu-Jõesuu, the middle course Tartu at Kvissentali, and lower course in Kavastu. The Kvissentali hydrometric station was opened in 1867 and automated in 2010, which is located at Emajõgi in Tartu city, Estonia and 42.6 km away from the mouth of the river and the total catchment area is 7840 km^2.[12, 26, 34]

The Rannu-Jõesuu hydrometric is located near the viable village in Viljandi County. The Rannu-Jõesuu station was opened in 1916 and automated in 2010. The Rannu-Jõesuu hydrometric is 101 km away from the mouth of the river and total catchment area of 3370 km^2 [26, 27]. This hydrometric station measures water level, the water temperature at the bottom of the river; manually measured water temperature in the surface water layer (0.1-0.5 m) 2-3 times a month during flow measurement. Measure the ice stars, the thickness of the ice and snow of the river every five days, and ice formation and decomposition daily. Moreover, calculation of the water flow rate [m^3/s] 2-3 times a month, in high water period 5-6 times a month and measure the air temperature, precipitation and observe the aquatic vegetation 2-3 times per month during flow measurement if it is available in the water. [26]

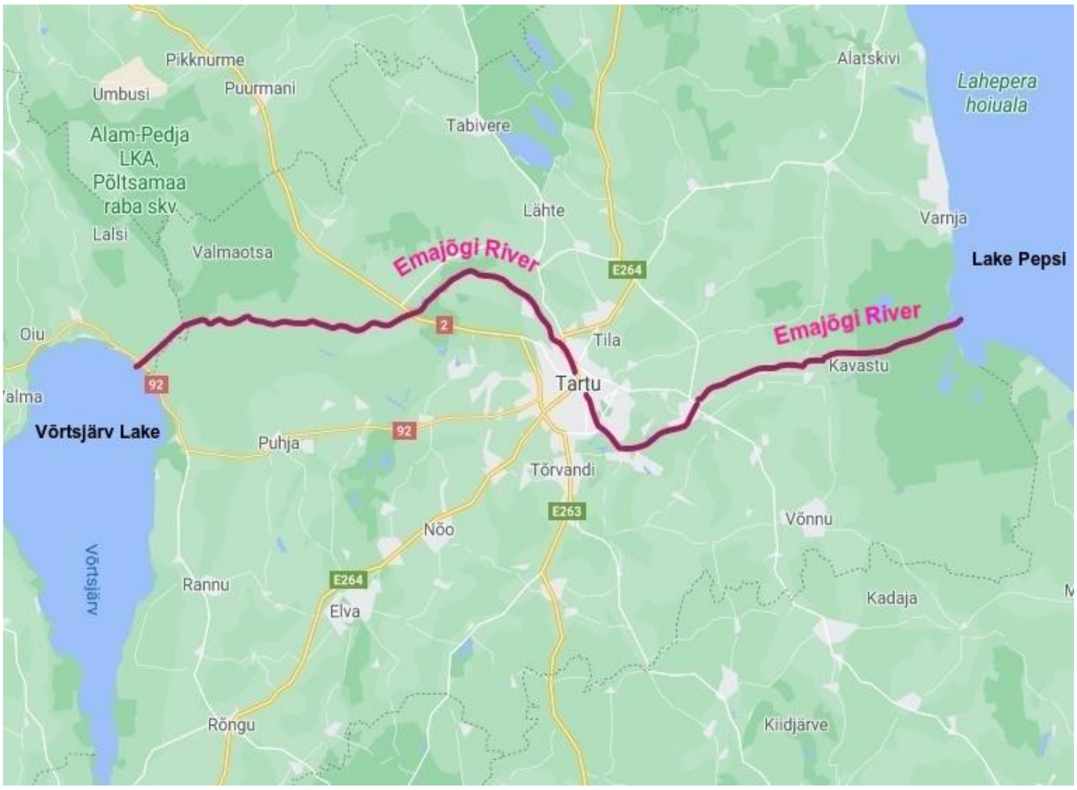

Figure 4.2.1: Emajõgi River

4.3 Piusa River

The Piusa is a river in South-Eastern Estonia and the Russian Pskov Oblast, 109 km in length. The total catchment area of Piusa river is 796 km^2 [25], of which 508 km² are on the Estonian side, and the annual average water discharge is 5.5-6-0 m^3/s, and the flows from Plaani Külajärv in Võru county into Lake Pihkva, in Pskov Oblast, Russia (figure 4.3.1). The Piusa is the border river between Estonia and the Russian

Federation near Pechory, a 17-km-long section. Also, The Piusa is the river with the most significant fall of all Estonian rivers, which is 208m altitude distance from source to mouth [23].

The Piusa river has one hydrometric station is Korela, which is located in Võru county. Korela hydrometric station was opened in 1961and automated in 2006. The distance from the Korela hydrometric station to the mouth of the river is 16.2 km, and the total catchment area 733 km^2 [26, 27, 34]. This hydrometric station measures water level, the water temperature at the bottom of the river; manually measured water temperature in the surface water layer (0.1-0.5 m) 2-3 times a month during flow measurement. Moreover, calculate the water flow rate [m^3/s] 2-3 times a month, and measure the air temperature, Precipitation, Snow cover thickness and coverage, atmospheric phenomena [26].

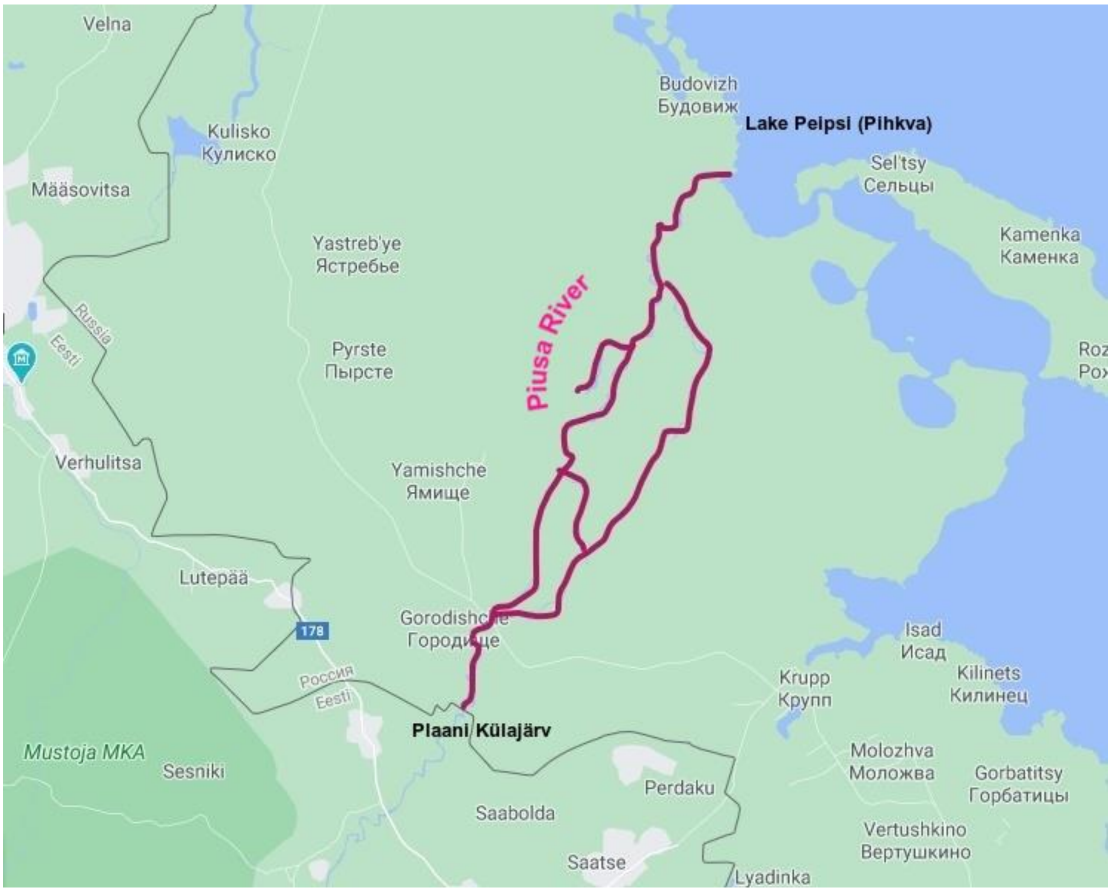

Figure 4.3.1: Piusa River

4.4 Võhandu River

The Võhandu river is the longest in Estonia, located in south-eastern Estonia and entirely in Estonian territory. The length of Võhandu river is 162 km, which starts from Lake Vagula near Saverna village, passes through lake jõksi Räpina and Võõpsu, and flows into Lämmijärv near Võõpsu in Lake Peipsi (figure 4.4.1). Võhandu river has different names such as Väike Võhandu in the upper course, Võhandu in the middle course, and Voo in the lower course. The total catchment area of the Võhandu river is 1420 km^2, and the annual average water discharge is 6m^3/s [25]. The wide Võhandu River downstream is over 60m and has a delta at its mouth with several river islands, and it is navigable from Lake Peipsi-Pskov to the port of Võõpsu. The main tributaries of the Võhandu river are the Mügra stream , Kokle river , Sillaotsa river (16 km), Kärgula stream , Jaska stream , Rõuge river (26 km), Koreli stream (21 km) , Iskna river (29 km) , Palumõisa stream , Pahtpää river , Mädajõgi (27 km), Varesmäe stream (9 km), Parisoo , Karioja stream (14 km) , Viluste stream (9 km), Toolamaa stream . The Leevaku (38 ha) and the Räpina (51 ha) are two largest dam lakes on the Võhandu river [24].

There are two hydrometric observation stations in the Võhandu river, one hydrometric station is Räpina, and another is Kirumpää. The Räpina hydrometric station is located at the Räpina city in Põlva country. The Räpina hydrometric station was opened in 1924 and automated in 2007. The Räpina hydrometric station distance from the river's mouth is 11.8 km, and the total catchment area 1130 km^2. The Kirumpää hydrometric station is located near the Kirumpää village in Võru County. The Kirumpää hydrometric station was opened in 2010 and automated in 2010. The Kirumpää hydrometric station distance from the river's mouth is 88.7 km, and the total catchment area 576 km^2. [26, 27, 34]

The Räpina and Kirumpää hydrometric station are measure water level and water temperature at the bottom of the river; manually measured water temperature in the surface water layer (0.10-0.5 m) 2-3 times a month during flow measurement. Measure the ice residues, the thickness of ice and snow on the river 2-3 times a month during flow measurement. Moreover, calculation of the water flow rate [m^3/s] 2-3 times a month. Measure the air temperature and observe the aquatic vegetation 2-3 times a month during flow measurement. [26]

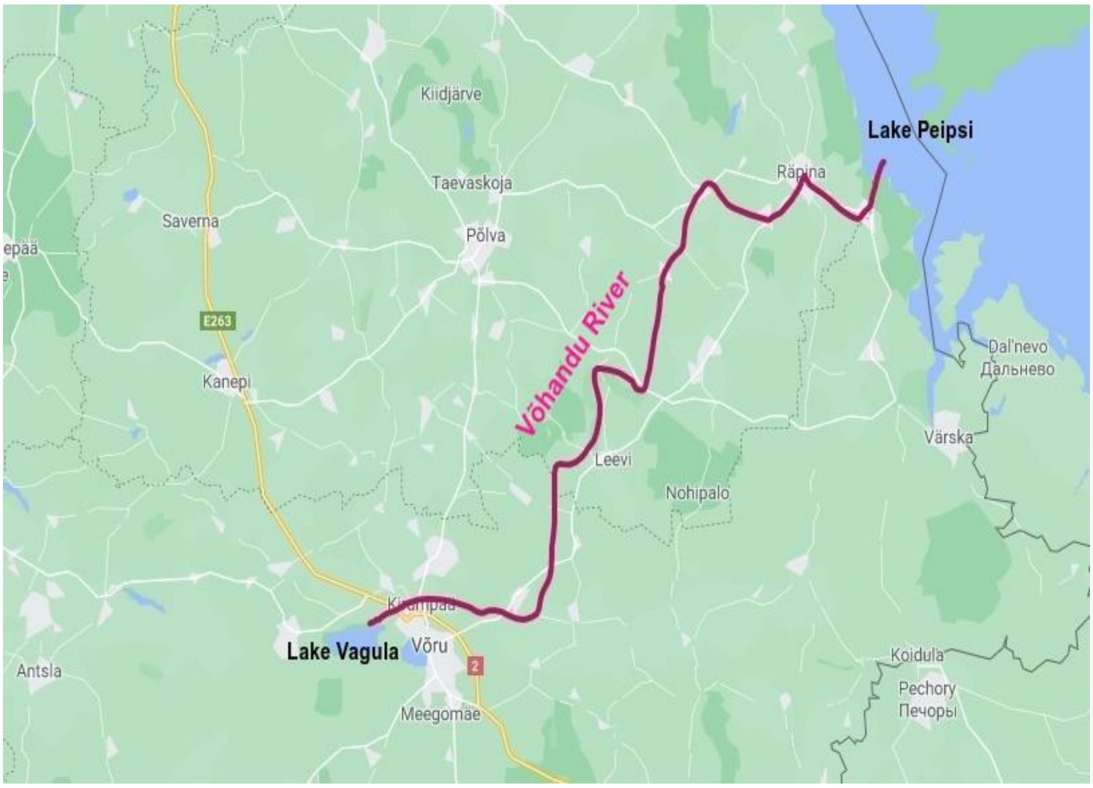

Figure 4.4.1: Võhandu River

4.5 Avijõgi River

The river Avijõgi is located in Jõgeva and Lääne-Viru County, Estonia, which starts from the Muuga Manor in Lääne-Virumaa and flows into Lake Peipsi in Ida-Virumaa (figure 4.5.1). The Avijõgi river is also called in different names, such as Paasvere, Venevere, Avinurme, and Lohusuu rivers. The river's total length is 55.7 km long, and the total catchment area is 391 km^2[25]. The fall height of the Avijõgi river is 64.4m, and the average depth of the river is 1-1.5m. The Trouts and Thymallus thymallus fish are live in the river. The river water flow speed in the upper course 0.3 m/s, and the lower course 0.2 m/s. The average water discharge speed in the lower course 2.5–3.0 m^3/s; however, the maximum water flow rate is up to 60 m^3/s in the lower course; [18].

The Muuga settlement and farms have polluted the upper course of the river Avijõgi, and the Pärniku village, the small town of Avinurme and timber industry are responsible for the pollution in the river middle courses, and in the lower course of the Avijõgi river has been polluted by the Maetsma farms and the small city of Lohusuu. [18].

The Separa hydrometric station is situated near the Separa village in Jõgeva County. The Separa hydrometric station was opened in 2010 and automated in 2010. The Separa hydrometric is 4.1 km distance from the mouth of the river and total catchment area 381 km^2 [26, 27, 34]. The Separa hydrometric station measures water level and water temperature at the bottom of the river; manually measured water temperature in the surface water layer (0.1-0.5 m) 2-3 times a month during flow measurement. Also, calculation of the water flow rate [m^3/s] 2-3 times a month, in high water period 5-6 times a month. Measure the air temperature, and observe the aquatic vegetation 2-3 times per month during flow measurement if it is present in the water. [26]

Figure 4.5.1: Avijõgi River

4.6 Alajõgi River

The river Alajõgi is located in the Ida-Viru country. The river's length is 29 km long, which starts from Kõnnu Pikkjärv, near the village of Ongassaare, and falls into the Lake Peipsi near the Alajõe village (figure 4.6.1). The total basin size of the river is 150 km^2. The elevation of the Alajõgi river is 36m [25].

The only hydrometric station is Alajõgi, which is located near the Alajõe village in Ida-Viru country. The Alajõgi hydrometric station was opened in 1955 and automated in

2010. The distance from the Alajõgi hydrometric station to the river's mouth is 3.7 km, and the total catchment area 140 km^2 [26, 27, 34]. This hydrometric station measures water level and water temperature at the bottom of the river; manually measured water temperature in the surface water layer (0.10-0.5 m) 2-3 times a month during flow measurement. Moreover, calculate the water flow rate [m^3/s] 2-3 times a month and 5-6 times a month in a high water period, and measure the air temperature, ice thickness, and ice phenomena. Besides, observe the aquatic vegetation at the time of flow measurement. [26]

Figure 4.6.1: Alajõgi River

4.7 Kullavere River

The Kullavere river is called Omedu River, which is located in Jõgeva County. The Kullavere river starts in Jõgeva and Tartu County near the village of Sadala, and the lower course of the Kullavere river mix-up with the Kääpa River flows into the Lake Peipsi, and this mix-up point is six kilometers distance from the lake Peipsi (figure 4.7.1). The river's length is 52.8 km long, and the total basin size is 629.3 km^2 [25]. The water flow rate of the river Kullavere is 4.3 m^3/s.

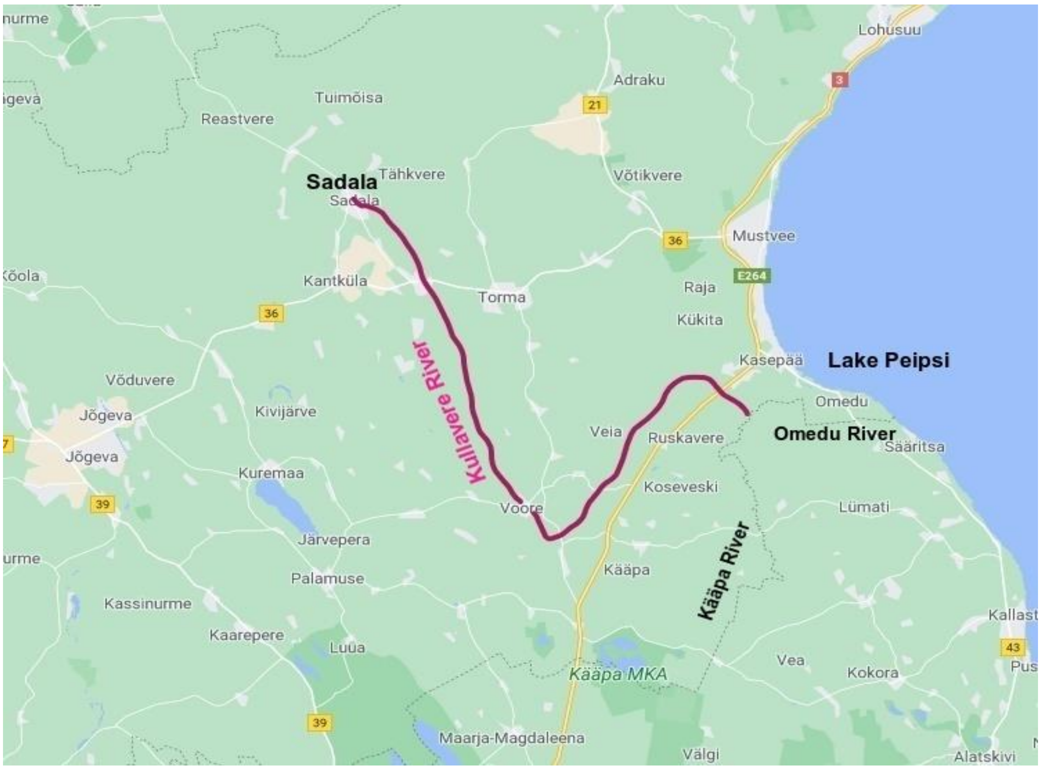

Figure 4.7.1: Kullavere River

4.8 Rannapungerja River

The Rannapungerja river is located in the Ida-Viru County, which starts near the Atsalama village and runs into Peipsi Lake (figure 4.8.1). The river's length is 63 km long, and the basin size is 594.6 km² [25]. The long term average water flow 3.16m^3/s, and the historical maximum water flow is 67.4m^3/s. The main tributaries of the Rannapungerja river are Tagajõgi, Kõveroja, Tudulinna oja, Saarevälja oja, and Härjaoja.

The river Rannapungerja, including its abovementioned tributaries, is the biggest river flowing from the Alutaguse Lowland to Peipsi Lake. In past days, the river Rannapungerja was used as an essential river for rafting logs from the Alutaguse forests to Peipsi Lake. At the end of 1988, The Rannapungerja river was polluted due to the fire-fighting works in the Estonia mine [18].

The Roostoja hydrometric station is situated near the Roostoja village in Ida-Viru County. The Roostoja hydrometric station was opened in 1955 and automated in 2006. The Roostoja hydrometric 13.4 km distance from the mouth of the river and total catchment area 313 km^2 [26, 27, 34]. This hydrometric station measures water level and water temperature at the bottom of the river; manually measured water temperature in the surface water layer (0.1-0.5 m) 2-3 times a month during flow measurement. Also, calculation of the water flow rate [m^3/s] 2-3 times a month, in high water period 5-6 times a month. Measure the air temperature, and observe the aquatic vegetation, ice phenomenon, and ice thickness at the time of flow measurement if it is present in the water. [26]

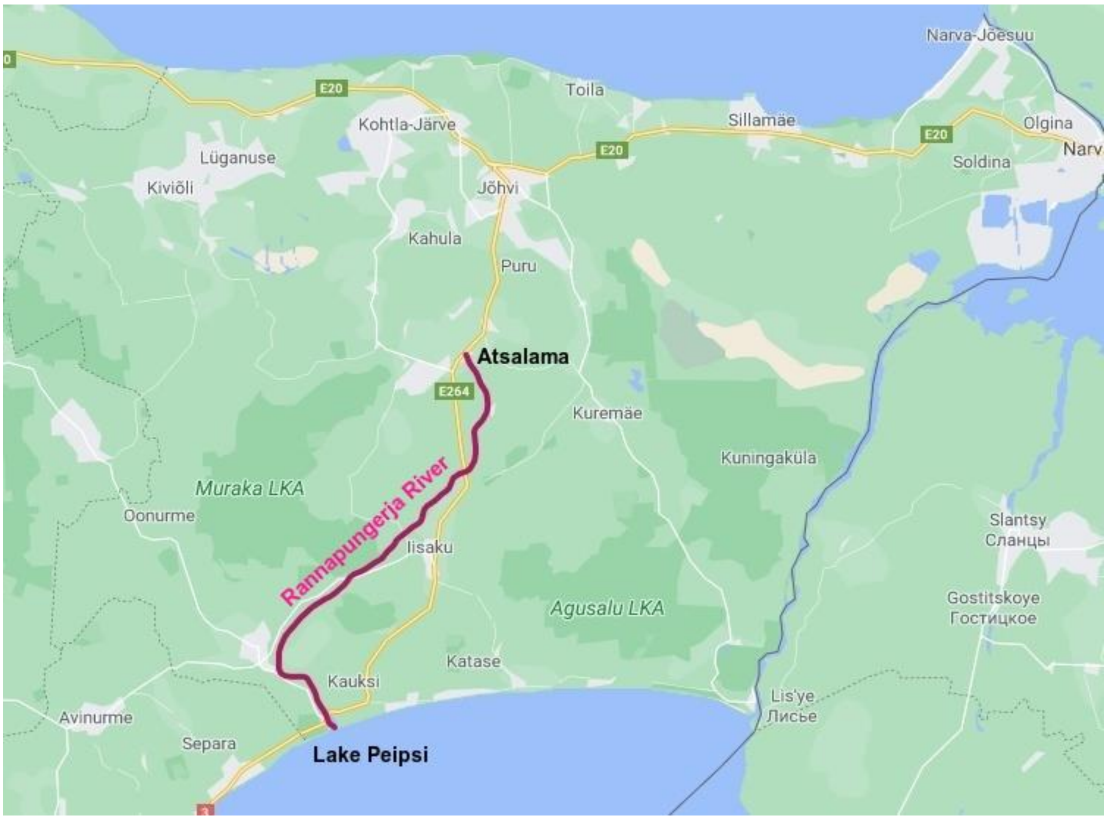

Figure 4.8.1: Rannapungerja River

4.9 Mustajõgi River

The Mustajõgi river is also called "Black River," located in Ida-Viru County in Narva-Jõesuu. The Mustajõgi river starts from Peen-kirikjärvi Lake in the Kurtna Lake District and drains into the Narva river (figure 4.9.1). The total length of the Mustajõgi river is 23 km, and the size of the river basin is 418 km², which is the largest on the left bank of the Narva river [25]. The main tributary of the Mustajõgi river is the Narva river. The Mustajõgi river is polluted by discharging white water from oil shale quarries, and industrial power is supplied to it by the Estonian Power plant.

The Narva Karjääri is the only hydrometric station in the Mustajõgi river, located in the Ida-Viru country. The Narva Karjääri hydrometric station was opened in 2002 and automated in 2006. The distance from the Narva Karjääri hydrometric station to the mouth of the river is 5.8 km and a total catchment area 317 km^2 [26, 27]. This hydrometric station is measures water level and water temperature at the bottom of the river; manually measured water temperature in the surface water layer (0.10-0.5 m) during flow measurement. Moreover, calculate the water flow rate [m^3/s] 2-3 times a month and 5-6 times a month in a high water period. Measure the air temperature, precipitation and observe the ice thickness, ice phenomena, and aquatic vegetation at the time of flow measurement. [26]

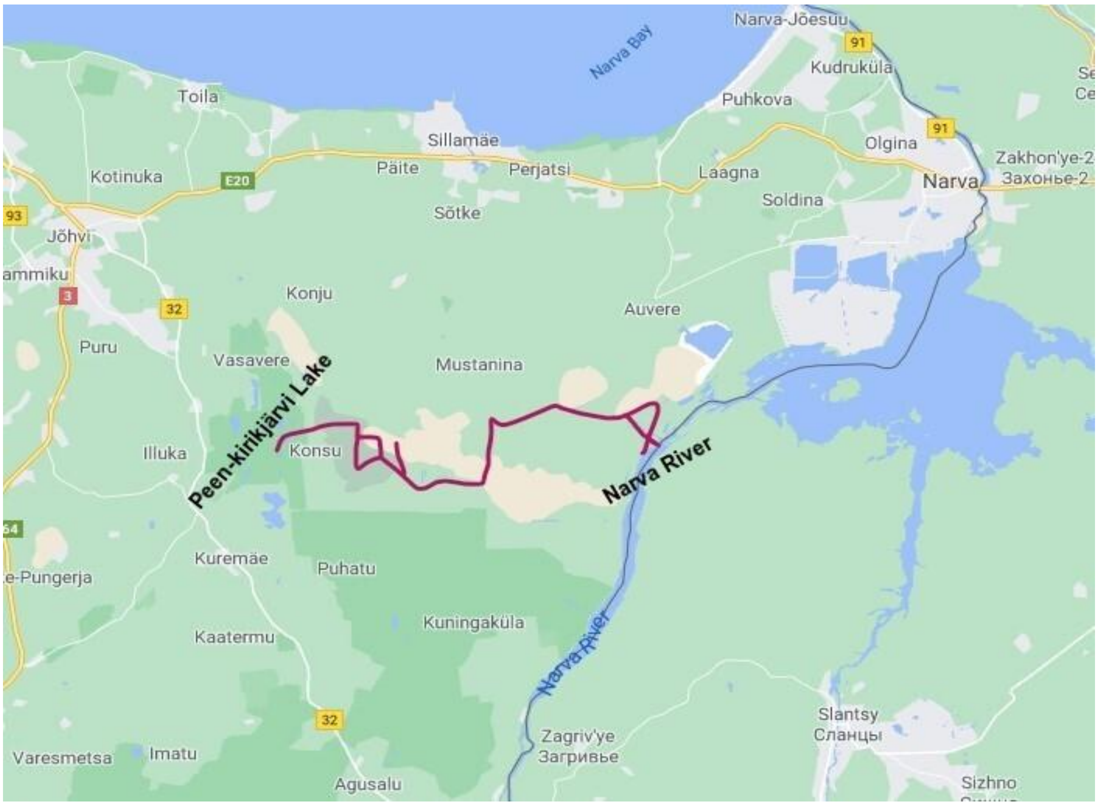

Figure 4.9.1: Mustajõgi River

5 DATA FOR WATER QUALITY INDEX

5.1 Data

To determine water quality index score ten different Physico-chemical water quality parameters from ten monitoring stations of the individual river between 2015-2019 were used. For instance, two monitoring stations at the Narva river (Vasknarva and Narva city), one station at the Emajõgi river (Kavastu), Värska-Saatse station at the Piusa river, Räpinast allavoolu station at the Vöhandu river, Mulgi station at the Avijögi river, Alajõe station at the Alajögi river, Tartu-Mustvee mnt station in the Kullavere river, Mustvee mnt station at the Rannapungerja river and Mustajõe station at the Mustajõgi river. The Estonian Environment Agency has provided physical-chemical parameter data to calculate the Water Quality Index (WQI). The studied rivers are three types according to the types of water, Type A (Avijögi, Alajögi, Rannapungerja and Mustajõgi rivers), Type B (Emajõgi, Piusa, Vöhandu, and Kullavere rivers) and Another type is IV (Narva river), which is particular type due to the size of this river. Type A means dark watered, with higher organic material content and higher color of water, where 90% of COD_{Mn} value higher than 25 mgO/l. Type B is light-colored waters with lower organic content, where 90% of COD_{Mn} value less than 25 mgO/l.

Table 5.1.1: Data used for WQI calculations

River	Monitoring stations	Types of River	Year	Parameter
Narva	Vasknarva	IV	2015-2019	O_2%, pH, EC, BOD_5, COD_{Mn} NH_4^+, N_{tot}, NO_3^-, PO_4^{3-}, P_{tot}
Narva	Narva city			
Emajõgi	Kavastu	B		
Piusa	Värska-Saatse			
Vöhandu	Räpinast allavoolu			
Kullavere	Tartu-Mustvee mnt			
Avijögi	Mulgi	A		
Alajögi	Alajõe			
Rannapungerja	Mustvee mnt			
Mustajõgi	Mustajõe		2015-2018	

The water quality parameters data were collected monthly from 2015 to 2019, except Mustajõe station of the river Mustajõgi. Mustajõgi the sampling frequency is 4 times a year from 2015 to 2018.

5.2 Parameters and Limit Values

The received limit values (Table 5.2.1) is based on the types of waterbody for the Estonian rivers. This study used two types of limit value; the first scenario of limit values are taking from Estonian legislation Act 19 for the river water, which was considered the arithmetic mean value of the individual parameters between the moderate and good class of the water bodies, except pH value. According to the legislation Act 19, if the pH value range is between 6 and 9, the individual Physico-chemical status class shall be determined for each quality indicator. If the 10% pH value is higher than 9 or lower than 6, then the overall determination of the general physico-chemical conditions is bad. The other types of limit values are receving from NarvaWatMan project according to the typification of the rivers.

Table 5.2.1: The limit value of physical-chemical parameters for the Estonian rivers.

Parameter	Estonian Legislation Act No. 19			NarvaWatMan Project		
	Type A River	Type B River	Narva River	Type A River	Type B River	Narva River
pH	6-9	6-9	6-9	6.5-8.5	6.5-8.5	6.5-8.5
O_2;%	50	60	60	60-70	70-80	70-80
BOD_5; mgO_2/l	3.5	3	2.5	2.3	2.3	2
NH_4^+; mgN/l	0.3	0.3	0.3	0.2	0.2	0.1
N_{tot}; mgN/l	3	3	0.7	1.6	1.6	1
P_{tot}; mgP/l	0.08	0.08	0.06	0.06	0.07	0.05
COD_{Mn}; mgO/l	N/A			40	19	22
EC; µS/cm				620	420	320
NO_3^-; mgN/l				1	1	0.3
PO_4^{3-} ; mgP/l				0.04	0.02	0.02

The standard value (Table 5.2.2) of each parameter is taking to calculate the weighted arithmetic water quality index (WA WQI). This standard values measured by the calculated mean value of each parameter value from the last 20 years data. Furthermore, to determine the standard limit value, the arithmetic mean of the average values of the river types calculated.

Table 5.2.2: Standard value of different parameters for the Estonian rivers.

Parameter	Type A River	Type B River	Narva River
pH	8	8	8
O_2;%	77	87	84
BOD_5; mgO_2/l	2	1.7	1.8
NH_4^+; mgN/l	0.05	0.08	0.03
N_{tot}; mgN/l	1.7	1.7	0.7
P_{tot}; mgP/l	0.04	0.06	0.04

The following water quality parameters are considered to calculate the Water Quality Index (WQI):

• DO (Dissolved Oxygen):

Dissolved oxygen (DO) measures the amount of oxygen present in the clean waters, which comes from the atmosphere and aquatic plants [41, 45]. The solubility of oxygen in water has a reverse relationship with temperature. When the water temperature is high, the dissolved-oxygen concentration is often lower, and DO concentration is higher during the lower temperature [45]. The DO concentration can be represented in two ways, mg/l or as a percent of saturation (%). The inorganic waste discharge into the water affects the DO level [40].

• pH (Potential Hydrogen);

pH is a significant parameter in assessing water quality, which measures the acidic and alkaline conditions in the water bodies [36, 40]. Water pH determines the solubility and biological availability of chemical components such as nutrients and heavy metals [44]. The higher concentration of the hydrogen ion in the water indicates the lower pH and lower concentration indicates the higher pH. In general, the range of pH scale in water is 0-14; in that case, water with a $pH < 7$ is considered acidic, and with a $pH > 7$ is considered basic, and 7 being neutral [40, 41]. However, acidic water will not impact the health of human beings, the dissolved minerals in the water may affect human health [40].

• BOD_5 (Biochemical Oxygen Demand);

Biochemical Oxygen Demand is the amount of oxygen consumed by micro-organisms needed to oxidize organic material. BOD_5 represent the amount of oxygen consumed during a five-day period of incubation. High BOD means the level of oxygen is depleted in water, which indicates organic pollution [12]. BOD concentration is directly connected with the dissolve oxygen in water bodies, high amount of BOD in water bodies indicates the low level of DO [36].

• COD (Chemical Oxygen Demand);

The chemical oxygen demand is the amount of oxygen equivalent to the amount of oxidizing agent (potassium dichromate or potassium permanganate) used in the acidic medium to chemically oxidize organic substance to inorganic end products in the water [12]. During COD reaction, all organic substance is oxidised to carbon dioxide. COD test is unable to determine the difference between the organic material and inorganic material. Moreover, the COD values are always higher than the BOD values [43].

• NH_4^+ (Ammonium Nitrogen);

Ammonium nitrogen (NH_4) is the first intermediate stage for converting organic nitrogen compounds into inorganic forms. When high levels of ammonium compound present in the water, which indicates recent pollution. Ammonia is an indicator for elevated pollution of water bodies from organic substances [7].

• N_{tot} (Total Nitrogen);

Total nitrogen is the sum of nitrate (NO_3), nitrite (NO_2), organic nitrogen and ammonia. Total nitrogen is a vital nutrient for plants and animals. Nevertheless, the higher amount of nitrogen in waterbodies may guide to low levels of dissolved oxygen and negatively change different plant life and organisms. The causes of nitrogen in water are wastewater treatment plants, drainage from fertilized lawns and animal manuare, and industrial effluent discharges into the water [46].

• NO_3^- (Nitrate);

Nitrate formes in the water bodies due to bacterial action on ammonia and organic nitrogen. The high concentration of nitrate in surface water and groundwater regarding the use of nitrogen fertilizers to grow plants, and the rest of the amount comes from infiltration with rainfall into water bodies. In decomposition, bacteria break down protein molecules into ammonia, ammonia oxidize to NO_2^- and then NO_3^- [40]. The high concentration of nitrate in drinking water may be harmful to health, such as methemoglobinemia (also known as a blue baby syndrome), cancer risks, increased starchy deposits, and hemorrhaging spleen [7,40].

• P_{tot} (Total Phosphorous):

The total phosphorus is the sum of all forms of phosphorus: mineral (ortho- and polyphosphate) and organic phosphorus. A high amount of phosphorus helps to enlarge the growth of algae and aquatic life. As a result, the levels of dissolved oxygen are reduced, which is called eutrophication. [12].

• EC (Electrical Conductivity);

The electrical conductivity (EC) value of water represents the concentration of soluble salts in water. Also, the conductivity of water measures the number of dissolved substances, chemicals, and minerals is present in the water. Higher conductivity shows due to the results of impurities rise in the water, which is harmful to aquatic life and humans. Therefore, a high concentration of dissolved solids in the water significantly affects the taste of the drinking water [7].

• PO_4^- (Phosphates);

The high amount of phosphate concentrations in the water indicates the pollution associated with a reduction in dissolved oxygen in water bodies due to the rise of mineral and organic nutrients (eutrophication) conditions. Furthermore, domestic effluents (detergents), fertilizer runoff, and industrial wastewater are the main reasons for increase phosphate levels in surface and ground waters. [36]

6 CALCULATION OF THE WATER QUALITY INDEX (WQI)

To calculate the water quality index (WQI) using the Microsoft excel, and the CCME WQI (Estonian legislation Act No. 19 and NarvaWatMan), MCWQI, and WA WQI methods described earlier. This study represents three scenarios to assess the water quality assessment in the different monitoring stations. In the first scenario, to involve six parameters (pH, BOD_5, O_2%, NH_4^+, N_{tot}, P_{tot}) to calculate water quality index score, and then make comparison between the methods. In the second scenario, to determine and compare water quality index score from 2015-2019 including more parameters to six constant parameters using the CCME WQI (NarvaWatMan) method. For example, six parameters (pH, BOD_5, O_2%, NH_4^+, N_{tot}, P_{tot}), seven parameters (adding EC), eight parameters (adding EC, COD_{Mn}), nine parameters (adding EC, COD_{Mn}, NO_3^-), and ten parameters (adding EC, COD_{Mn}, NO_3^-, PO_4^{3-}) using CCME WQI (NarvaWatMan) method. According to the third scenario, the water quality index is compared every year by allowing different sampling frequency and parameters (six, eight, and ten) were considered using the CCME WQI (NarvaWatMan) method at the Emajõgi Kavastu station and Narva city station on the Narva river.

The calculations of the Water Quality Index by using the CCME WQI, WA WQI, and MCWQI method are below:

The first step is to establish the limit values for different rivers to calculate the CCME WQI. Then the most crucial step is to check each parameter for analytical data that exceed the limit value one by one. Identify the analytical data that exceed the standard limit value. Then, calculate the F_1 value using the total number of parameters and number of failed parameters, calculate the F_2 value by the number of fail analytical test and a total number of tests. After that, calculate the excursion value for each failed analytical test using the fail analytical test value divided by the standard limit value of this test. Then normalized sum excursion (nse) by summation of excursion value divided by a total number of test and calculate F_3 using the formula. Finally, calculate CCME WQI for each sampling station by using the formula. The difference between the CCME WQI (EST Act No. 19) and the CCME WQI (NarvaWatMan) considers the different limit values for the studied parameters.

To start the WA WQI methods calculation process, identify the standard desirable value (S_n) for each parameter and calculate the unit weight (W_n) factors for individual parameters by using the $W_n = K/S_n$ formula. Where K is constant for each parameter, and the summation of all unit weight factors is 1. The ideal value (V_0) for every parameter is 0, except pH (7.0) and dissolved oxygen (14.6). Furthermore, calculate the mean concentration value (V_n) of the selected parameters for every year. Then subtract the mean value (V_n) by the standard value (S_n), and multiply the calculated value to get the sub-index value (Q_n). Finally, the sub-index value multiplies with unit weight factors for the selected parameters. Then the summation of this all calculates the value to get the final water quality index score.

For the MCWQI method, the calculation process of scope (F_1), frequency (F_2), and amplitude (F_3) are the same as in the CCME WQI method. Finally, multiply each factor, and then apply the cubic root of this multiplied value and subtraction this calculate the value from 100 to get the water quality index score.

Tables (6.1.1, 6.2.1, 6.3.1, 6.4.1, 6.5.1, 6.6.1, 6.7.1, 6.8.1, 6.9.1 and 6.10.1) show the annual water quality index score by using different WQI methods for the six parameters (pH, BOD_5, O_2%, NH_4^+, N_{tot}, P_{tot}) with every monitoring station from 2015 to 2019. Tables (6.1.2, 6.2.2, 6.3.2, 6.4.2, 6.5.2, 6.6.2, 6.7.2, 6.8.2, 6.9.2, and 6.10.2) represent the comparison of the CCME WQI (NarvaWatMan) score by adding more parameters between 2015 and 2019. Furthermore, each water quality index score is visualized using a different colour code, which indicates the water quality class. The colour scale classification is mentioned in table 3.2.1 and table 3.3.1. However, the water quality score classification is different in the WA WQI method, shown in table 3.3.1.

6.1 Narva River (Narva)

Table 6.1.1 showes that the index score comparison between CCME WQI (EST Act 19 and NarvaWatMan), WA WQI, and MCWQI methods using six parameters in the Narva river at the Narva city station. The MCWQI method provides a better score than other methods, and the quality grade was excellent for all studied periods. If we consider CCME WQI method based on the limit values of EST Act 19 and NarvaWatMan, then CCME WQI (EST Act No. 19) gives a significantly higher score than the CCME WQI (NarvaWatMan) index score. The WA WQI scale is reverse compare to the other index methods; it indicates the water quality calss is moderate, except in 2016 (Poor). Furthermore, the Estonian water quality evaluation method shows the water quality class in the Narva station is excellent.

Table 6.1.1: Comparison of WQI calculations results between different methods for the Narva city station of the Narva river.

Narva-Narva-CCME WQI -(pH, O_2%, BOD_5, NH_4^+, P_{tot}, N_{tot})					
Year	EST_WQI	CCME WQI_EST ACT	CCME WQI_ WatMan	MCWQI	WA WQI
2015	24	100.00	80.49	96.05	64.02
2016	23	80.60	70.57	90.59	85.95
2017	24	80.34	70.72	91.61	70.66
2018	24	90.34	61.20	91.32	64.62
2019	24	90.24	80.69	96.35	68.51

Table 6.1.2 shows that the CCME WQI (NarvaWatMan) index score was marginally decreasing by adding the EC from 2015-2019. After that, the 60% index score was slightly rising due to the add COD_{Mn}. Furthermore, the Water quality score increased with 9th parameter nitrates between 2015 and 2019, while the 40% index score was a tiny bit drop by including phosphates. The overall water quality class (moderate) remained unchanged in 2016. Whereas, the water quality status in 2015 and 2019 was good by using six parameters, and then one step drop the class by adding EC regarding the number of times exceeds the guidelines. Moreover, it observes that the water quality class (poor) was one step up due to the adding nitrates variable and remained the same class with 10th parameter in 2017 and 2018. The concentration of total BOD_5 and electrical conductivity affected the water quality class in the Narva station of the Narva river.

Table 6.1.2: Comparison of CCME WQI calculations results between number of parameters for the Narva city station of the Narva river

Narva-Narva-CCME WQI					
Number of Parameter	2015	2016	2017	2018	2019
6 (pH, O_2%, BOD_5, NH_4^+, P_{tot},N_{tot})	80.49	70.57	70.72	61.20	80.69
7 (Add EC)	75.02	66.14	66.14	58.39	75.10
8 (Add EC, COD_{Mn})	78.14	70.37	63.07	63.59	70.97
9 (Add EC, COD_{Mn}, NO_3^-)	80.57	73.66	67.17	67.64	74.20
10 (Add EC, COD_{Mn}, NO_3^-, PO_4^{3-})	76.72	76.30	64.70	70.87	76.78

6.2 Narva River (Vasknarva)

Table 6.2.1 depicts that the water quality index score comparing the CCME WQI (EST Act 19 and NarvaWatMan), WA WQI, and MCWQI methods by using six parameters in the Narva river at the Vasknarva station. The MCWQI and Estonian WQI method provide quality grade was excellent for all studied period. Then CCME WQI (EST Act 19) provides a higher score than the CCME WQI (NarvaWatMan) index score due to the different limit values. However, the WA WQI method shows the water quality status range in between moderate and poor.

Table 6.2.1: Comparison of WQI calculations results between different methods for Vasknarva station of the Narva river

Narva-Vasknarva-CCME WQI- (pH, O_2%, BOD_5, NH_4^+, P_{tot}, N_{tot})					
Year	EST_WQI	CCME WQI_EST ACT	CCME WQI_ WatMan	MCWQI	WA WQI
2015	24	100.00	91.64	98.69	61.24
2016	23	90.34	83.28	96.05	89.18
2017	24	70.84	74.65	92.23	70.74
2018	23	80.60	74.78	90.75	75.94
2019	24	100.00	83.00	95.71	62.63

Table 6.2.2 shows the CCME WQI (NarvaWatMan) index score, which has increased slightly by adding the EC, COD_{Mn}, NO_3^- from 2015-2019. There was no significant impact on the water quality class when adding more parameters were included. The water class was moderate class in 2017 and 2018. The major driving force to impact the water quality class is the higher concentration of BOD_5 and pH in the Vasknarva station. The most important feature is that NH_4^+, NO_3^-, and N_{tot} followed the Vasknarva station's goals. The overall water quality class moderate in 2017, and good in 2016 and 2019, while the water quality status changed in 2015 and 2018 by adding NO_3^-.

Table 6.2.2: Comparison of the CCME WQI calculations results between number of parameters for Vasknarva station of the Narva river

Narva-Vasknarva-CCME WQI					
Number of Parameter	2015	2016	2017	2018	2019
6 (pH, O_2%, BOD_5, NH_4^+, P_{tot}, N_{tot})	90.23	80.49	70.42	70.58	80.16
7 (Add EC)	91.64	83.28	74.65	74.78	83.00
8 (Add EC, COD_{Mn})	92.68	85.37	70.51	77.93	85.12
9 (Add EC, COD_{Mn}, NO_3^-)	93.50	86.99	73.78	80.38	86.77
10 (Add EC, COD_{Mn},NO_3^-, PO_4^{3-})	88.36	82.44	70.65	82.35	88.10

6.3 Emajõgi River (Kavastu)

Table 6.3.1 illustrates the index score comparison between different methods using six parameters. The Estonian WQI method provides a better score than other methods, and quality grade was good for all studied periods. According to the NarvaWatMan limit values, the MCWQI method give a significantly higher score than the CCME WQI (NarvaWatMan). Whereas the WA WQI method shows, the water quality class range was poor to bad.

Table 6.3.1: Comparison of WQI calculations results between different methods for Kavastu station of the Emajõgi river.

Emajõgi-Kavastu-WQI-(pH, O_2%, BOD_5, NH_4^+, P_{tot}, N_{tot})					
Year	EST_WQI	CWQI_EST ACT	CWQI_ WatMan	MCWQI	WA WQI
2015	21	70.33	67.35	74.86	80.07
2016	19	60.24	56.46	67.06	105.77
2017	22	90.34	68.95	80.54	76.90
2018	22	80.68	58.94	77.26	85.89
2019	21	70.70	58.88	74.18	107.32

Table 6.3.2 shows that the water quality class was moderate and poor by using six parameters for all studied years. Furthermore, the WQI index score was falling for 2015-2019, when the EC parameter added, and it continues to decrease with adding of COD_{Mn}, NO_3^-, and PO_4^{3-}, except in 2015, which is increase with COD_{Mn}.The CCME WQI (NarvaWatMan) index score was dropping by using a 10-parameter compare to 6-parameter. The overall water quality class was moderate (12%), poor (56%), and bad (32%) in Emajõgi river. The high concentration of total nitrogen, nitrates, ammonium nitrogen, BOD_5, and electrical conductivity affected the water quality, which exceeds the goals of the Emajõgi river.

Table 6.3.2: Comparison of the CCME WQI calculations results between number of parameters for Kavastu station of the Emajõgi river.

Emajõgi-Kavastu-CCME WQI					
Number of Parameter	2015	2016	2017	2018	2019
6 (pH, O_2%, BOD_5, NH_4^+, P_{tot}, N_{tot})	67.35	56.46	68.95	58.94	58.88
7 (Add EC)	62.03	53.29	63.44	55.64	55.13
8 (Add EC, COD_{Mn})	66.75	51.58	60.70	54.20	53.81
9 (Add EC, COD_{Mn}, NO_3^-)	62.22	48.44	57.25	51.81	51.51
10 (Add EC, COD_{Mn}, NO_3^-, PO_4^{3-})	60.51	47.76	56.07	56.63	56.34

6.4 Piusa River (Värska-Saatse)

Table 6.4.1 shows that the water quality comparison between different methods using six parameters. The MCWQI and CCME WQI (EST Act 19) methods provide a better score compare to CCME WQI (NarvaWatMan) method, and the quality grade was excellent, except in 2016, as like as Estonian water quality index status for all studied period. The quality range CCME WQI (NarvaWatMan) is good to moderate. The water quality status using in WA WQI is poor, except in 2016 (bad).

Table 6.4.1: Comparison of WQI calculations results between different methods for Värska-Saatse station of the Piusa river.

Piusa- Värska-Saatse –WQI-(pH, O_2%, BOD_5, NH_4^+, P_{tot}, N_{tot})					
Year	EST_WQI	CWQI_EST ACT	CWQI_ WatMan	MCWQI	WA WQI
2015	24	90.07	70.83	91.14	79.48
2016	23	80.24	70.07	84.85	112.95
2017	24	89.51	89.08	92.32	96.57
2018	23	100.00	80.16	93.96	96.28
2019	24	90.06	89.80	94.45	92.20

Table 6.4.2 displays that the index score was plummeting due to the addition of EC for all studied years, while the score escalates by the addition of COD_{Mn}, and then score are sink and soar by adding NO_3^-, PO_4^{3-} respectively. The moderate water quality class remained the same in 2016, while the water quality status in 2015 was modified, including 10th-parameter, and one step depreciates quality class in 2019 using EC parameters. In contrast, the water quality grade was undulating in 2017 and 2018 between 6-parameters and 10-parameters. The high concentration of phosphates (PO_4^{3-}), total phosphorous, and electrical conductivity impact the water quality to drop in the Piusa river.

Table 6.4.2: Comparison of the CCME WQI calculations results between number of parameters for Saatse Station of the Piusa river

Piusa- Värska-Saatse-CCME WQI					
Number of Parameter	2015	2016	2017	2018	2019
6 (pH, O_2%, BOD_5, NH_4^+, P_{tot}, N_{tot})	70.83	70.07	89.08	80.16	89.80
7 (Add EC)	66.64	66.18	82.70	74.60	82.30
8 (Add EC, COD_{Mn})	70.81	70.41	77.63	77.82	84.51
9 (Add EC, COD_{Mn}, NO_3^-)	67.63	73.70	80.12	80.28	86.23
10 (Add EC, COD_{Mn},NO_3^-, PO_4^{3-})	64.22	68.20	73.82	74.95	80.07

6.5 Võhandu River (Räpina)

Table 6.5.1 presents the Estonian WQI and CCME WQI (EST Act 19) methods that provide excellent quality grades, except in 2016. Then MCWQI gave good quality class, except in 2015, which was excellent. CCME WQI (NarvaWatMan) quality ranges from moderate to poor. However, the water quality status using WA WQI is poor, except in 2015 (moderate).

'Table 6.5.1: Comparison of WQI calculations results between different methods for Räpina station of the Võhandu river.

Võhandu-Räpina-WQI-(pH, O_2%, BOD_5, NH_4^+, P_{tot}, N_{tot})					
Year	EST_WQI	CWQI_EST ACT	CWQI_ WatMan	MCWQI	WA WQI
2015	23	100.00	70.58	90.70	73.39
2016	21	70.59	60.24	82.95	98.95
2017	23	90.34	60.82	88.37	81.56
2018	23	80.69	70.22	89.13	76.69
2019	24	90.08	70.40	89.38	79.66

Table 6.5.2 explains the water quality index score that was oscillating with the 7th and 8th parameters, while the score was a decline by using nitrates and phosphates from 2015-2019, and one step falls quality grade in 2016. However, the quality grade moderate was remained constant in 2015. The overall quality class range was moderate to bad in the Võhandu river. The high concentration of phosphates, total phosphorus, nitrates, and lack of oxygen saturation in water were the main reason to deteriorate the water quality in the Võhandu river.

Table 6.5.2: Comparison of the CCME WQI calculations results between number of parameters for Räpina station of the Võhandu river.

Võhandu-Räpina-CCME WQI					
Number of Parameter	2015	2016	2017	2018	2019
6 (pH, O_2%, BOD_5, NH_4^+, N_{tot}, P_{tot})	70.58	60.24	60.82	70.22	70.40
7 (Add EC)	74.78	57.74	66.42	66.28	66.28
8 (Add EC, COD_{Mn})	77.93	55.84	63.40	63.30	63.30
9 (Add EC, COD_{Mn}, NO_3^-)	73.76	54.13	61.05	60.97	60.96
10 (Add EC, COD_{Mn}, NO_3^-, PO_4^{3-})	69.18	51.32	57.81	57.97	58.23

6.6 Avijõgi River (Mulgi)

Table 6.6.1 shows that the Estonian WQI and CCME WQI (EST Act 19) methods also provide better-quality class than others. Then MCWQI gave a good index score compared to CCME WQI (NarvaWatMan), while that method indicates almost the same quality class. It is notable that WA WQI shows better quality status than the CCME WQI (NarvaWatMan) and MCWQI methods.

Table 6.6.1: Comparison of WQI calculations results between different methods for Mulgi station of the Avijõgi river.

Avijõgi-Mulgi-WQI-(pH, O_2%, BOD_5, NH_4^+, P_{tot}, N_{tot})					
Year	EST_WQI	CWQI_EST ACT	CWQI_ WatMan	MCWQI	WA WQI
2015	22	89.55	67.12	74.78	46.47
2016	22	79.34	56.30	66.33	69.15
2017	23	89.85	77.25	81.37	39.33
2018	23	87.80	76.03	78.33	53.16
2019	23	87.90	76.30	78.84	42.75

Table 6.6.2 shows that the index score increases due to the addition of EC, improving the grade in 2017 and 2019, and the rest of the year remaining the same class. However, the score marginally fell for all studied years by adding nitrates and impact to decline quality categories in 2018 and 2019. Phosphates addition helps to improve the index score without any effect on the water quality grade. It was notable that the water quality classification remains constant in 2015 and 2016 due to the add more parameters. The water quality status range in the Avijõgi river was good to poor in all studied years. The high concentration of total nitrogen and nitrates impact the water quality in the Avijõgi river.

Table 6.6.2: Comparison of the CCME WQI calculations results between number of parameters for Mulgi station of the Avijõgi river.

Avijõgi-Mulgi-CCME WQI					
Number of Parameter	2015	2016	2017	2018	2019
6 (pH, O_2%, BOD_5, NH_4^+, P_{tot}, N_{tot})	67.12	56.30	77.25	76.03	76.30
7 (Add EC)	71.79	62.48	80.48	72.10	79.62
8 (Add EC, COD_{Mn})	75.29	60.42	76.26	68.79	82.12
9 (Add EC, COD_{Mn}, NO_3^-)	67.43	55.08	70.20	61.56	72.59
10 (Add EC, COD_{Mn}, NO_3^-, PO_4^{3-})	70.59	59.48	73.15	65.25	75.14

6.7 Alajõgi River (Alajõe)

Table 6.7.1 shows that the MCWQI and CCME WQI (EST Act 19) method gives excellent water quality like the Estonian WQI, except in 2016, which was good. The CCME WQI (NarvaWatMan) quality range excellent to poor. However, the water quality range using in WA WQI was moderate to bad.

Table 6.7.1: Comparison of WQI calculations results between different methods for Alajõe station of the Alajõgi river.

Alajõgi-Alajõe-WQI-(pH, O_2%, BOD_5, NH_4^+, P_{tot}, N_{tot})					
Year	EST_WQI	CWQI_EST ACT	CWQI_ WatMan	MCWQI	WA WQI
2015	25	100.00	70.73	92.33	73.79
2016	23	80.66	60.56	82.89	128.71
2017	23	100.00	80.60	95.25	98.03
2018	23	100.00	90.06	95.75	118.51
2019	25	100.00	61.09	90.05	91.45

Table 6.7.2 illustrates that the index score fluctuates with the addition of separate parameters for all studied years. The addition of COD_{Mn} values impacts depreciating one step the water quality class between 2016 and 2018, while moderate water quality class remained the same in 2015. Moreover, in 2019 the quality status was improved by including the 10th-parameter. In comparison, the water quality grade was moving in 2016 and 2017 between 6-parameters and 10-parameters. The high concentration of BOD_5, COD_{Mn}, and oxygen deficit affect the water quality of the Alajõgi river.

Table 6.7.2: Comparison of the CCME WQI calculations results between number of parameters for Alajõe station of the Alajõgi river.

Alajõgi-Alajõe-CCME WQI					
Number of Parameter	2015	2016	2017	2018	2019
6 (pH, O_2%, BOD_5, NH_4^+, P_{tot}, N_{tot})	70.73	60.56	80.60	90.06	61.09
7 (Add EC)	74.91	66.19	83.37	91.48	58.38
8 (Add EC, COD_{Mn})	78.05	62.83	78.04	85.24	56.35
9 (Add EC, COD_{Mn}, NO_3^-)	74.06	66.96	80.48	86.88	61.20
10 (Add EC, COD_{Mn}, NO_3^-, PO_4^{3-})	76.66	64.53	82.44	88.19	65.08

6.8 Kullavere River (Tartu-Mustvee mnt)

Table 6.8.1 shows that the CCME WQI (EST Act 19) method gives a better index score than MCWQI compare to CCME WQI (NarvaWatMan). However, WA WQI index score was worse, and the water quality range was good to bad. Notably, the Estonian evaluation method indicates the excellent water quality in all studied years.

Table 6.8.1: Comparison of WQI calculations results between different method for Tartu-Mustvee mnt station of the Kullavere river.

Kullavere-Tartu-Mustvee mnt-WQI-(pH, O_2%, BOD_5, NH_4^+, P_{tot}, N_{tot})					
Year	EST_WQI	CWQI_EST ACT	CWQI_WatMan	MCWQI	WA WQI
2015	23	89.11	77.85	82.12	91.17
2016	23	69.81	66.58	72.30	146.91
2017	24	90.06	69.31	80.59	55.24
2018	24	90.34	88.20	89.71	28.19
2019	24	89.96	87.49	88.31	101.19

Table 6.8.2 explains that the water quality index score decreased from 2015-2018, whereas the index score oscillated in 2018 and 2019 by adding different parameters. Furthermore, the electrical conductivity affected fall one step of quality class in 2016, 2017, and 2019, and nitrates depreciate quality grade 2015 and 2019, and phosphates dropping into bad grade in 2017. The higher concentration of total nitrogen, electrical conductivity, nitrates, and phosphates decline the index score in the Kullavere river.

Table 6.8.2: Comparison of the CCME WQI calculations results between number of parameters for Tartu-Mustvee mnt station of the Kullavere river.

Kullavere-Tartu-Mustvee mnt-CCME WQI					
Number of Parameter	2015	2016	2017	2018	2019
6 (pH, O_2%, BOD_5, NH_4^+, P_{tot}, N_{tot})	77.85	66.58	69.31	88.20	87.49
7 (Add EC)	70.56	61.38	62.91	78.26	77.83
8 (Add EC, COD_{Mn})	67.59	58.99	60.75	80.96	80.57
9 (Add EC, COD_{Mn}, NO_3^-)	61.95	53.15	56.76	83.07	73.97
10 (Add EC, COD_{Mn}, NO_3^-, PO_4^{3-})	60.10	51.57	54.86	75.96	71.19

6.9 Rannapungerja River (Mustvee mnt)

Table 6.9.1 shows that the Estonian WQI, MCWQI, and CCME WQI (EST Act 19) method gives excellent water quality, except in 2016 for MCWQI, which was good. The CCME WQI (NarvaWatMan) quality range good to moderate like WA WQI.

Table 6.9.1: Comparison of WQI calculations results between different methods for Mustvee mnt station of the Rannapungerja river.

Rannapungerja-Mustvee mnt-WQI-(pH, O_2%, BOD_5, NH_4^+, P_{tot}, N_{tot})					
Year	EST_WQI	CWQI_EST ACT	CWQI_ WatMan	MCWQI	WA WQI
2015	25	100.00	70.73	92.16	41.73
2016	24	90.34	69.75	86.07	67.59
2017	25	100.00	70.72	91.90	46.66
2018	25	100.00	80.60	96.66	57.45
2019	25	100.00	80.60	95.91	49.84

Table 6.9.2 illustrates that the index score fluctuating by adding more parameters for all studied years. The addition of EC influence to decrease index score significantly, changing a quality class to depreciate one step in between 2018 and 2019, and COD_{Mn} steps down the class in 2016 and 2017. However, the moderate water quality class remained the same in 2015. The higher concentration of EC, BOD_5, and COD_{Mn} was affecting the water quality of the Rannapungerja river.

Table 6.9.2: Comparison of the CCME WQI calculations results between number of parameters for Mustvee mnt station of the Rannapungerja river.

Rannapungerja-Mustvee mnt-CCME WQI					
Number of Parameter	2015	2016	2017	2018	2019
6 (pH, O_2%, BOD_5, NH_4^+, P_{tot}, N_{tot})	70.73	69.75	70.72	80.60	80.60
7 (Add EC)	66.13	65.56	66.54	74.28	74.28
8 (Add EC, COD_{Mn})	70.36	62.25	63.30	70.21	70.35
9 (Add EC, COD_{Mn}, NO_3^-)	67.26	66.44	67.38	73.52	73.65
10 (Add EC, COD_{Mn}, NO_3^-, PO_4^{3-})	70.54	69.80	70.64	76.17	76.28

6.10 Mustajõgi River (Mustajõe)

Table 6.10.1 depicts that the Estonian method, MCWQI and CCME WQI (EST Act 19) method gives excellent water quality, except in 2016 for Estonian WQI and MCWQI, which was good. The CCME WQI (NarvaWatMan) quality range excellent to moderate. However, WA WQI depicts poor water quality, while it indicates bad in 2018.

Table 6.10.1: Comparison of WQI calculations results between different methods for Mustajõe station of the Mustajõgi river.

Mustajõgi-Mustajõe-WQI-(pH, O_2%, BOD_5, NH_4^+, P_{tot}, N_{tot})					
Year	EST_WQI	CWQI_EST ACT	CWQI_ WatMan	MCWQI	WA WQI
2015	24	100.00	90.08	97.96	76.01
2016	22	100.00	68.52	81.31	85.12
2017	23	100.00	80.16	94.21	86.24
2018	23	100.00	87.91	92.48	100.50

Table 6.10.2 explains that the index scores fluctuating with the addition of separate parameters for all studied years. The significant influence to decrease the index score was electrical conductivity and plummeting one step for all calculated years. However, others parameters changed the index score slightly, and the overall quality grade remains constant. The higher concentration of total nitrogen, nitrates, and EC affected the water quality class of the Mustajõgi river.

Table 6.10.2: Comparison of the CCME WQI calculations results between number of parameters for Mustajõe station of the Mustajõgi river.

Mustajõgi-Mustajõe-CCME WQI					
Number of Parameter	2015	2016	2017	2018	2019
6 (pH, O_2%, BOD_5, NH_4^+, P_{tot}, N_{tot})	90.08	68.52	80.16	87.91	No Data
7 (Add EC)	81.87	62.65	71.85	77.07	
8 (Add EC, COD_{Mn})	84.13	60.07	68.15	79.91	
9 (Add EC, COD_{Mn}, NO_3^-)	85.89	57.93	65.15	75.13	
10 (Add EC, COD_{Mn}, NO_3^-, PO_4^{3-})	87.29	62.13	68.63	77.60	

6.11 Comparison of the CCME WQI (NarvaWatMan) using different sampling frequencies in the Emajõgi and Narva River

Comparison of the water quality status under different sampling times in a year by using the CCME WQI (NarvaWatMan) method and observing the WQI scores impacts by adding parameters in the Emajõgi river was done and is shown in table 6.11.1. This analysis was performed six different sets of sampling frequency in a year, and the WQI score is gradually decreased by adding more parameters (table 6.11.1). Furthermore, the same analysis was performed for the Narva river at Narva city stations using six parameters (table 6.11.2)

The variation of the index score between different periods in a year for the Emajõgi river shows in table 6.11.1. Notably, the water quality index score for a year and season 1 (Jan/Mar/May/Jul/Sep/Nov) were very close to each other, and the quality grade was the same. However, the WQI index score significantly variated between season 1 and season 2 (Feb/Apr/Jun/Aug/Oct/Dec), and in most cases, the quality class was falling one step from 2015-2019. The calculated index score was more or less the same for season 2, season 3 (Jan/Apr/Jul/Oct), and season 4 (Feb/May/Au/Nov). However, season 5 (Mar/Jun/Sep/Dec) provided a better index score, and the quality of water class was slightly better to compare the other seasons. The main reason for the worse water quality in the Kavastu station was the high concentration of total nitrogen, nitrates, ammonium nitrogen, BOD_5, and electrical conductivity, which exceeded the goals of the Emajõgi river.

Table 6.11.1: Compare the CCME WQI with different sampling frequencies and parameters for Kavastu station of the Emajõgi river.

Emajõgi-Kavastu-CCME WQI-Different sampling frequencies and Parameters.							
Year	Number of Parameter	12 times (Year)	Season 1 (Jan/Mar/May/Jul/Sep/Nov)	Season 2 (Feb/Apr/Jun/Aug/Oct/Dec)	Season 3 (Jan/Apr/Jul/Oct)	Season 4 (Feb/May/Aug/Nov)	Season 5 (Mar/Jun/Sep/Dec)
2015	6*	67.35	67.42	76.86	77.24	76.16	76.06
	8**	66.75	67.18	73.47	74.51	73.30	73.23
	10***	60.51	59.95	71.76	65.09	71.41	71.40
2016	6*	56.46	56.58	66.02	63.77	65.42	75.83
	8**	51.58	51.35	59.22	64.90	58.15	65.40
	10**	47.76	47.18	54.16	58.12	52.79	63.83
2017	6*	68.95	68.57	78.76	88.56	77.68	76.91
	8**	60.7	60.88	67.52	75.58	68.07	65.75
	10***	56.1	55.72	67.24	73.42	61.14	65.79

2018	6*	58.94	58.67	78.04	77.94	76.89	68.50
	8**	54.2	53.81	75.49	68.22	74.66	68.30
	10**	56.6	56.06	73.77	67.71	72.33	68.11
2019	6*	58.88	58.06	68.48	68.98	57.66	67.52
	8**	53.8	59.87	60.81	61.43	59.40	66.90
	10***	56.3	61.09	62.17	62.78	60.77	66.07

* pH, BOD_5, O_2%, NH_4, N_{tot}, P_{tot},
** pH, BOD_5, O_2%, NH_4, N_{tot}, P_{tot}, EC, COD_{Mn}
*** pH, BOD_5, O_2%, NH_4, N_{tot}, P_{tot}, EC, COD_{Mn}, PO_4^{3-} , NO_3^-

Furthermore, check the WQI score in the separate time in a year with six parameters by the CCME WQI (NarvaWatMan) method for the Narva river at the Narva city station. Table 6.11.2 illustrates the overall index score fluctuation, where the January to June index score is higher than the July to December index score, while the water quality index score per year is lower than the calculated for two periods index score. If we consider the separate periods (Jan to Jun and Jul to Dec), then the water quality class remains the same, and the quality grade is raising compare to the whole year. The exception was in 2017 when WQI was dropped in Jul to Dec season. The concentration of total BOD_5 and electrical conductivity were the parameters that affected the water quality class at the Narva station of the Narva river.

Table 6.11.2: Compare the CCME WQI with different sampling frequencies and six parameters for the Narva City station of the Narva River.

Narva_Narva (pH, O_2%, BOD_5, NH_4^+, N_{tot}, P_{tot})					
Sampling frequency/Year	2015	2016	2017	2018	2019
12 times	80.49	70.57	70.72	61.20	80.69
6 times (JAN – JUN)	100.00	89.83	100.00	89.19	90.24
6 times (JUL – DEC)	90.24	79.67	79.09	80.49	90.24

7 INTERPRETATION OF RESULTS OF THE WATER QUALITY INDEX (WQI)

7.1 Comparison of the water quality index calculation results obtained by different methods

Comparison of the WQI results between the CCME WQI (EST Act 19 and NarvaWatMan), WA WQI, and MCWQI methods was done for six parameters (pH, BOD_5, O_2%, NH_4^+, N_{tot}, P_{tot}). In this chapter, the column charts are built to visualize the index score comparison among the methods, except for the WA WQI method, and monitoring stations. However, the WA WQI score in this column chart was done to show the graph and compare the score among the methods in 2015-2019. WA WQI index score classification is in reverse order compared to the CCME WQI and MCWQI methods. The WA WQI index score scale classification was shown in table 3.3.1.

Figure 7.1.1 shows the WQI score comparison between the CCME WQI (EST Act 19 and NarvaWatMan) and MCWQI methods using six parameters in the Narva river at the Narva city station. The figure shows that the MCWQI method provides a better score compare to CCME WQI. According to the limit values of EST Act 19 and NarvaWatMan, the CCME WQI (EST Act 19) gives a higher index score than the CCME WQI (NarvaWatMan). Water quality status estimated by the WA WQI method is moderate, except in 2016 (Poor).

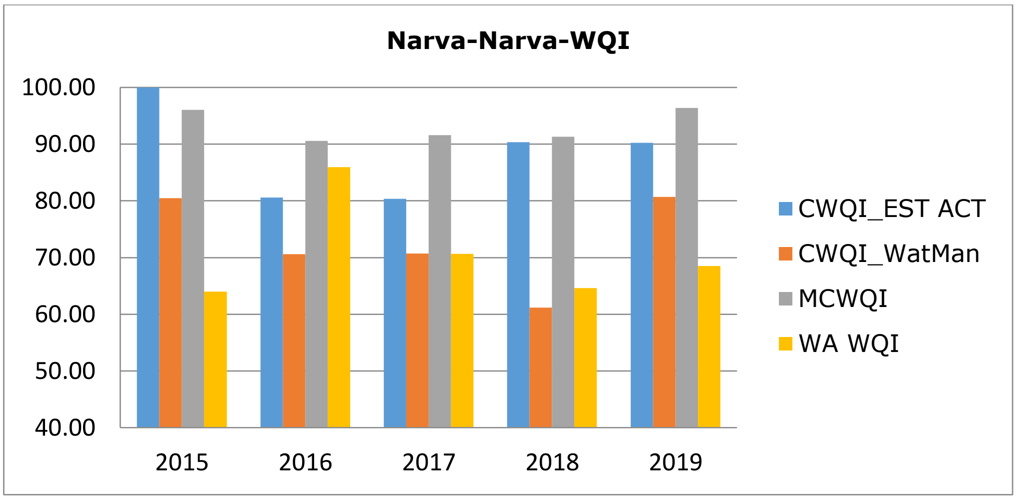

Figure 7.1.1: Comparison of WQI using different method in the Narva-Narva.

Figure 7.1.2 illustrates that the index score calculated by the MCWQI method gives a better score compared to all others in the Narva river at the Vasknarva station and provides excellent water quality classes for the study period of 2015-2019. The CCME

WQI presents a water quality range that changes from moderate in 2017 to excellent in 2015, 2016 and 2019. Estimated by the WA WQI method, the water quality status is changing from moderate to poor.

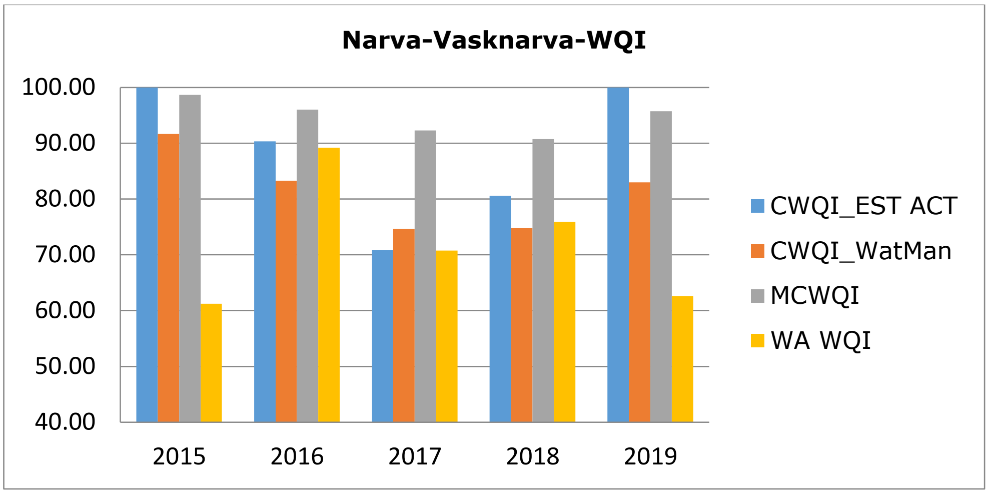

Figure 7.1.2: Comparison of WQI using different method in the Narva-Vasknarva.

Figure 7.1.3 shows that the index score of the MCWQI method gives a better result compared to all other methods in the Emajõgi river at the Kavastu station. Nevertheless, the water quality status estimated by different methods is mostly moderate and poor for this site. The WA WQI method gives even worse water quality as it varies from poor to bad in 2016 and 2019.

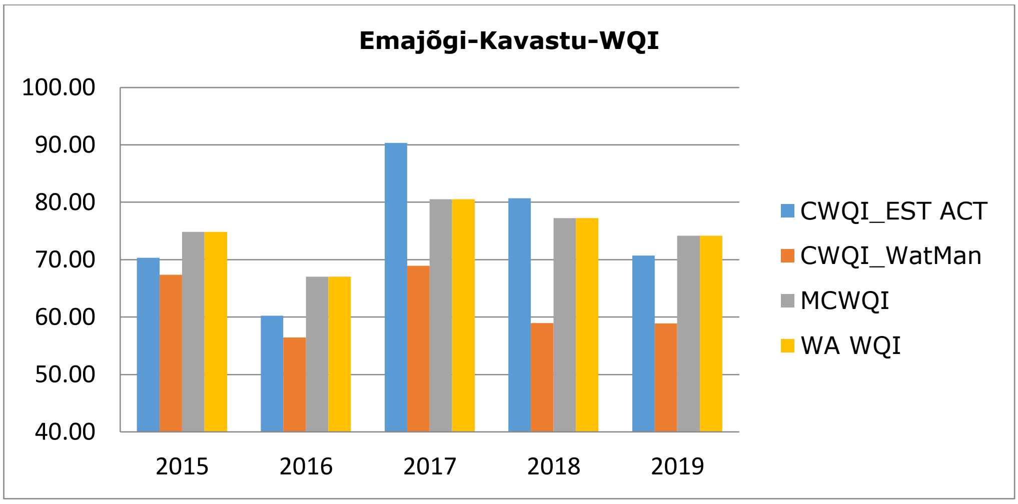

Figure 7.1.3: Comparison of WQI using different method in the Emajõgi-Kavastu.

Figure 7.1.4 depicts that the MCWQI and CCME WQI (EST Act 19) methods gave better water quality estimates, when the status changed from good to moderate. The water quality status calculated by WA WQI is poor, except in 2016 (bad) in the Piusa river.

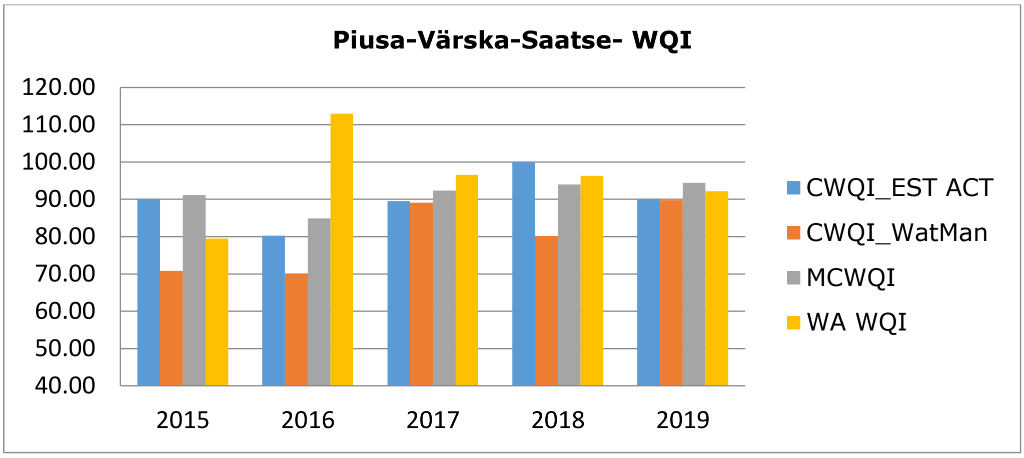

Figure 7.1.4: Comparison of WQI using different method in the Piusa-Värska-Saatse.

Figure 7.1.5 presents the WQI for Võhandu – Räpina. The CCME WQI (EST Act 19) method provides excellent quality grades, except in 2016. Then MCWQI gave good quality class, except in 2015, which was excellent. The CWQI (NarvaWatMan) estimates the quality range from moderate to poor. However, WQI is poor in water quality status in the WA WQI method, except in 2015 (moderate).

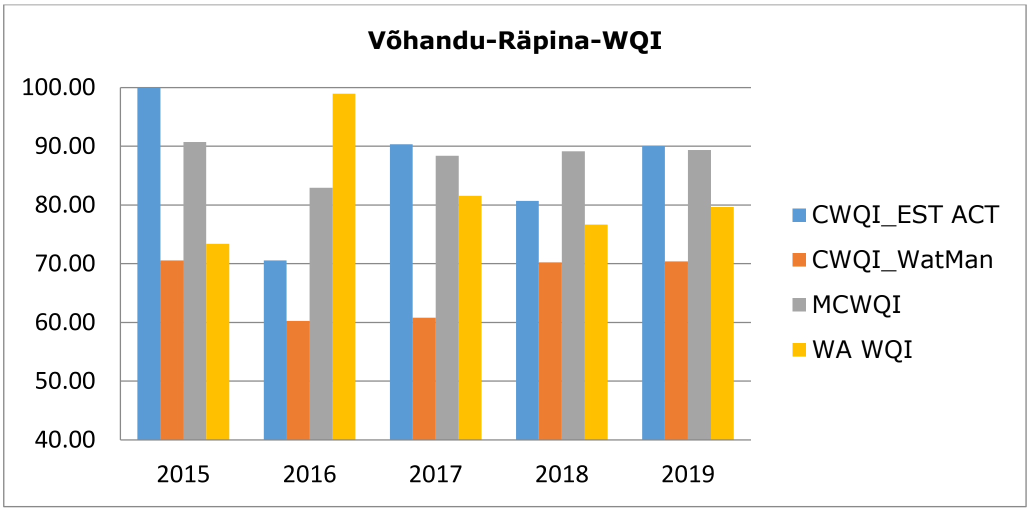

Figure 7.1.5: Comparison of WQI using different method in the Võhandu-Räpina.

Figure 7.1.6 depicts the WQI for the Avijõgi-Mulgi the CCME WQI (EST Act 19) method represents a better quality level. Then MCWQI gives a high index score compare to CCME WQI (NarvaWatMan), while that method provides almost the same quality class. Remarkably, the WA WQI shows better quality status than the CCME WQI (NarvaWatMan) and MCWQI methods.

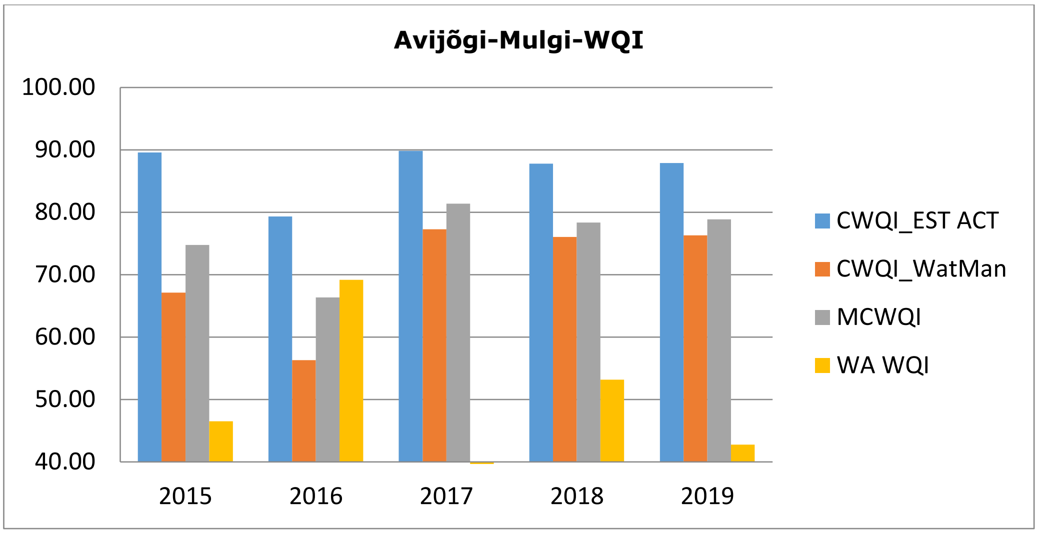

Figure 7.1.6: Comparison of WQI using different method in the Avijõgi-Mulgi

Results for WQI of Alajõgi-Alajõe illustrates that the MCWQI and CCME WQI (EST Act 19) method presents excellent water quality, except in 2016, which was good (figure 7.1.7). The CCME WQI (NarvaWatMan) quality range is excellent to poor. However, the range of water quality obtained by WA WQI is moderate to bad.

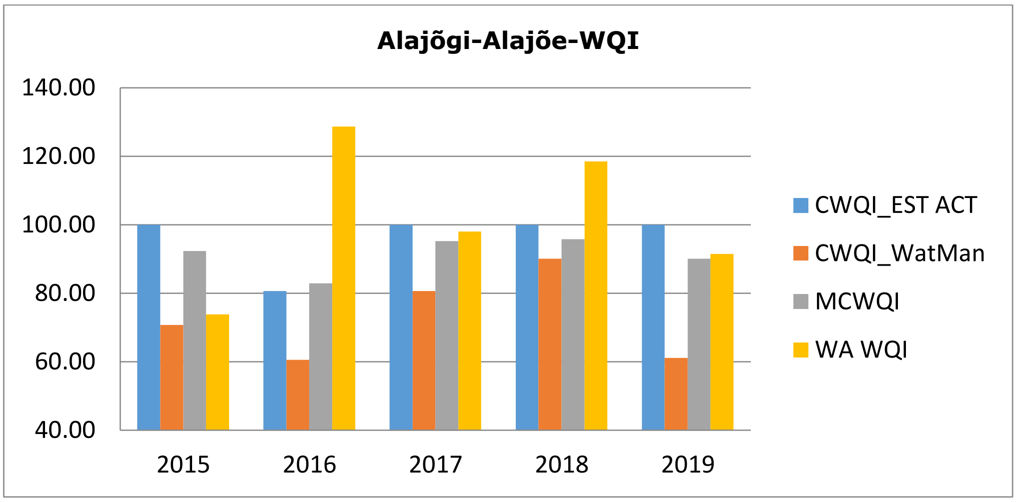

Figure 7.1.7: Comparison of WQI using different method in the Alajõgi-Alajõe.

Figure 7.1.8 shows that the CCME WQI (EST Act 19) method gives higher quality rank, then is following MCWQI and then CCME WQI (NarvaWatMan). The WA WQI index score was worse, and the water quality range is good to bad.

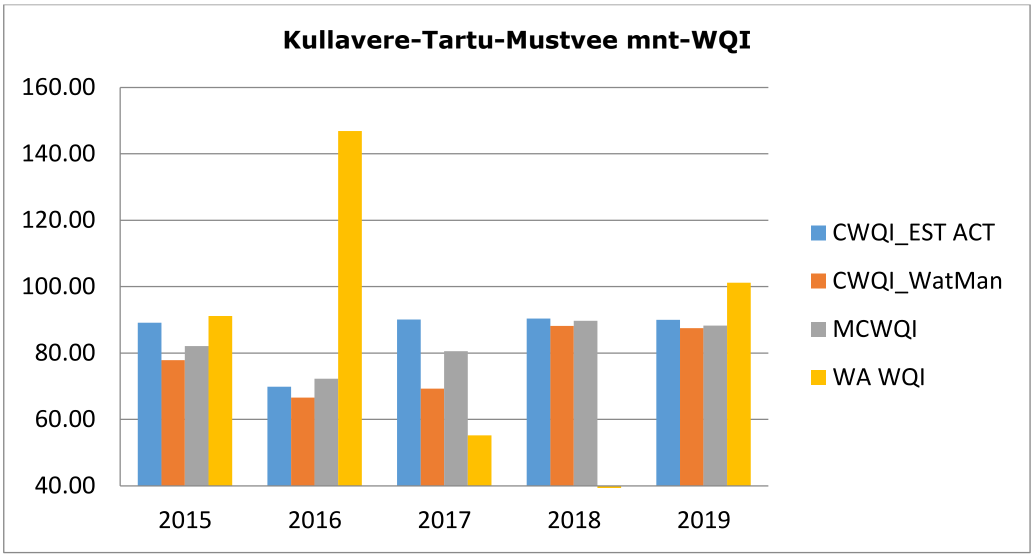

Figure 7.1.8: Comparison of WQI using different method in the Kullavere-Tartu-Mustvee mnt.

Figure 7.1.9 illustrates that the Rannapungerjia-Mustvee WQI, the MCWQI and CCME WQI (EST Act 19) method gives excellent water quality, except in 2016 for MCWQI, which was good. The CCME WQI (NarvaWatMan) quality range is from good to moderate like WA WQI.

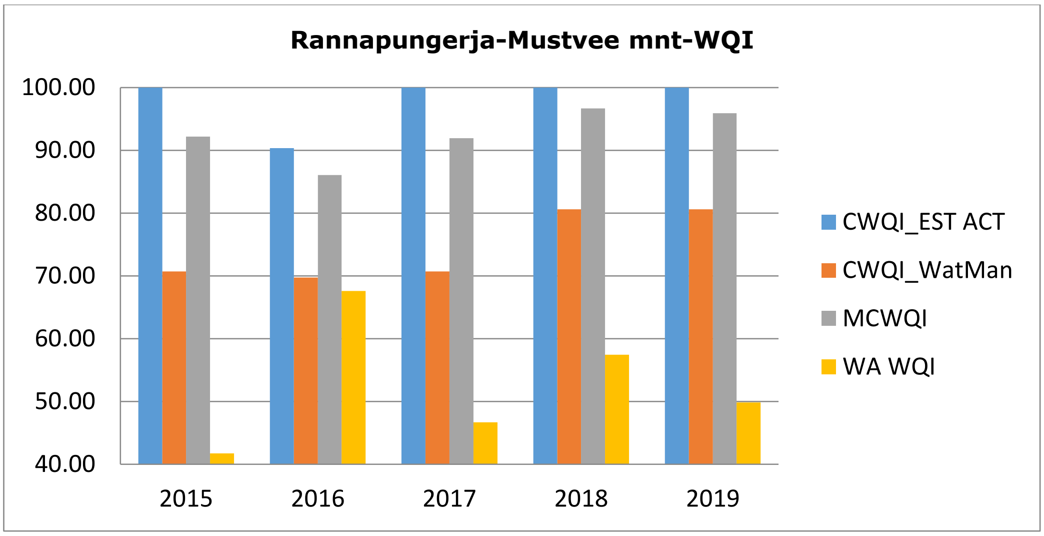

Figure 7.1.9: Comparison of WQI using different method in the Rannapungerja-Mustvee mnt.

Figure 7.1.10 explains that the WQI for Mustajõgi-Mustajõe estimated by the MCWQI and CCME WQI (EST Act 19) method gives excellent water quality, except in 2016 for MCWQI, which was good. The CCME WQI (NarvaWatMan) quality range good to moderate like in WA WQI.

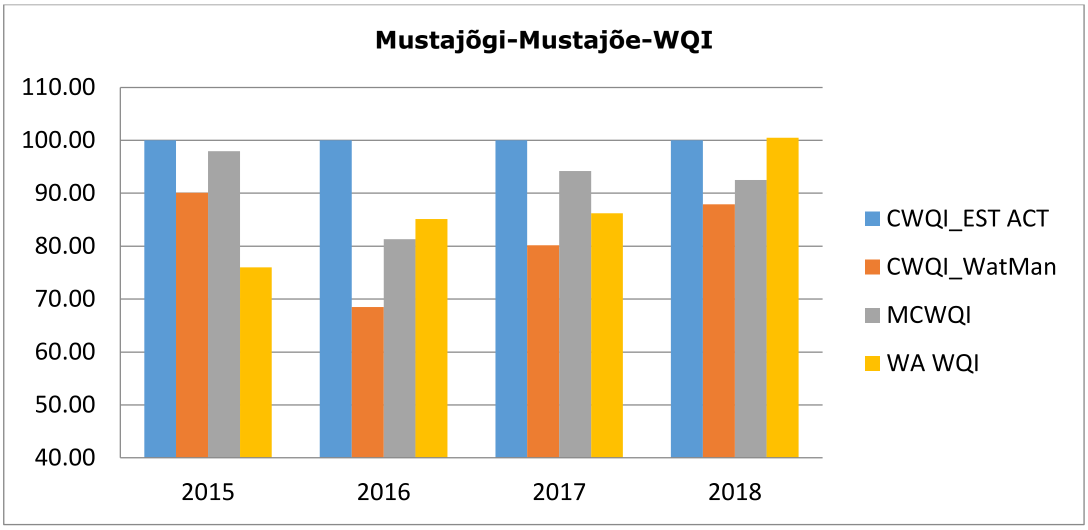

Figure 7.1.10: Comparison of WQI using different method in the Mustajõgi-Mustajõe.

7.2 Comparison of the CCME WQI (NarvaWatMan) calculation results by different parameters

The CCME WQI (NarvaWatMan) computed with the different parameters (six, seven, eight, nine, and ten parameters) was compared between these parameters to check the variation of the calculated index score by adding more parameters for all stations. The results on the CCME WQI (NarvaWatMan) score and corresponding water quality classes are shown in Figure 7.2.1-7.2.10. It is notable that the CCME WQI (NarvaWatMan) scores fluctuated by adding more parameters compared to six parameters for all the monitoring stations (pH, BOD_5, O_2%, NH_4^+, N_{tot}, P_{tot}). This change in the score fluctuates the water quality class by one step, while in most cases, the general class does not affect the oscillation of the index score. The major output from the CCME WQI (NarvaWatMan) illustrates that four are insignificant impairing in the water quality class if adding EC, COD_{Mn}, NO_3^-, PO_4^{3-}. The main drivers to impact the index score are pH, BOD_5, O_2%, NH_4^+, N_{tot}, P_{tot}.

Figure 7.2.1 illustrates that the CCME WQI (NarvaWatMan) index score is fluctuating between 6-parameters and 10-parameters. The overall 72% score is in the moderate water quality class, 16% is in poor class, and the rest are good quality class. It observed that the electrical conductivity (EC) is the main factor that impacts the water quality class of the Narva monitoring station in 2015-2019. Furthermore, BOD_5 is another variable in the Narva river, which leads the one-step drop down the water quality class. Whereas, 60% of the index score was slightly rising when adding COD_{Mn}, and continue increasing when 9th parameters nitrate was added in 2015 - 2019. The moderate class remains unchanged in 2016, while the water quality status in 2015 and 2019 was good with using only six parameters, and then reduced the class by one step when ECs were added because they exceeded the limit many times. Moreover, it observed that the water quality class (poor) was one step upward when nitrate variables were added and remained the same class with the 10^{th} parameter in 2019.

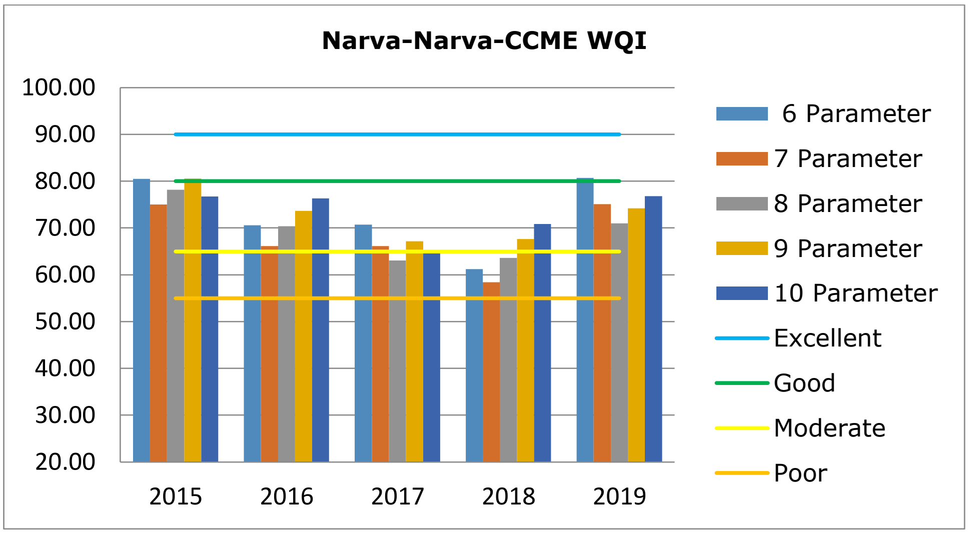

Figure 7.2.1: Comparison of the CCME WQI using different parameters in the Narva-Narva.

Figure 7.2.2 shows that the index score was slightly rising by adding EC, COD_{Mn}, NO_3^- in 2015-2019, while the water quality grade remains the same categories. Other parameters did not significantly affect the water quality class. Results show in the figure illustrate that the water quality class was moderate in 2017 and good in 2016-2019, and remained unchanged, while the status was the change in 2015 and 2018 by adding NO_3^-.

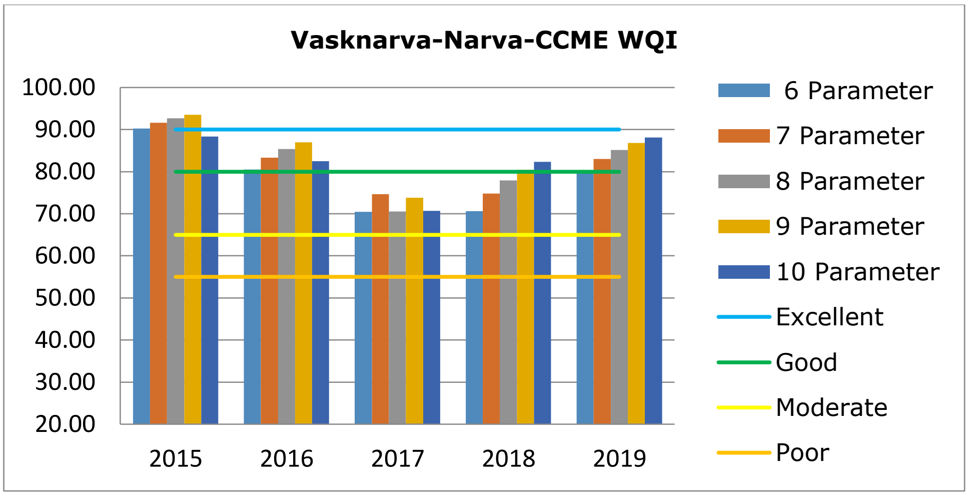

Figure 7.2.2:Comparison of the CCME WQI using different parameters in the Narva-Vasknarva.

Figure 7.2.3 shows that the CCME WQI (NarvaWatMan) index score was dropping by using 10-parameters versus 6-parameters. If we consider 6-parameters, then the water quality class is moderate in 2015 and 2017, and poor in the rest of the years. The index score decreases when adding EC variables in 2015-2019, and it continues to decline with the addition of COD_{Mn}, NO_3^-, and PO_4^{3-}, except in 2015, which increases with COD_{Mn}. The water quality grade was moderate in 12%, poor in 56%, and bad in 32% of cases. The high amount of total nitrogen, nitrates, ammonium nitrogen, BOD_5, and electrical conductivity are responsible for deteriorating the water quality in the Emajõgi river.

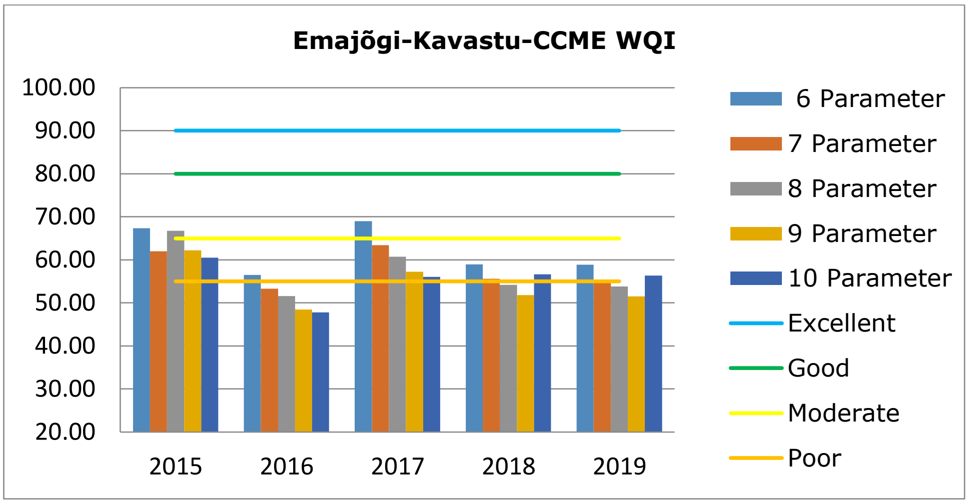

Figure 7.2.3: Comparison of the CCME WQI using different parameters in the Emajõgi-Kavastu

Figure 7.2.4 portrays that EC affects the index score fallen for all studied years, whereas the score increasing by adding COD_{Mn} and then score fluctuating by adding NO_3^- and PO_4^{3-}, respectively. However, there was no significant effect on the quality class, except in the 2015 moderate category, including the 10^{th}-parameter, and in 2019 depreciate quality class using EC parameters. In contrast, the quality grade was oscillating in 2017 and 2018 between 6-parameters and 10-parameters. The higher concentration of phosphates, total phosphorous, and electrical conductivity are responsible for affectinh the water quality in the Piusa river.

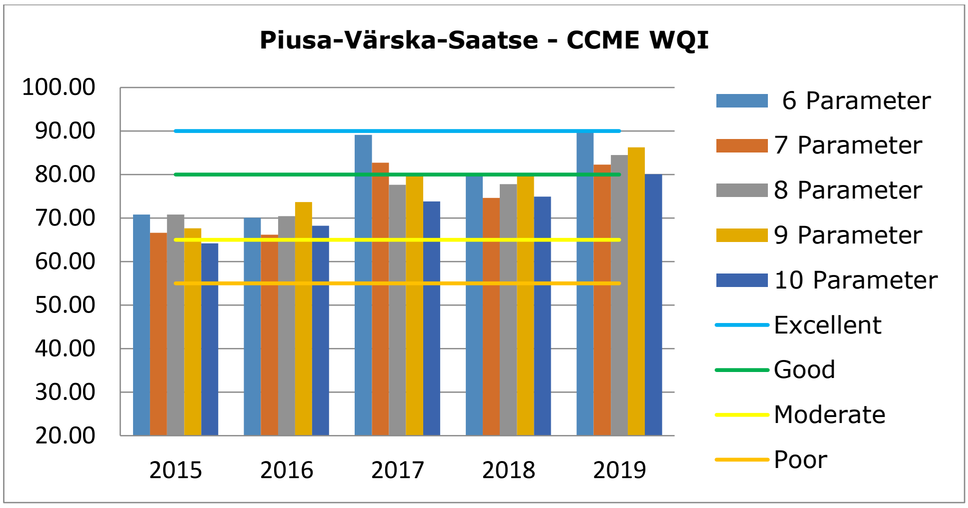

Figure 7.2.4: Comparison of the CCME WQI using different parameters in the Piusa-Värska-Saatse.

Figure 7.2.5 shows the constant of the water quality status in 2015 by adding different parameters. The grade was gradually decrased using COD_{Mn} in 2017-2019, and the quality class was one step fall in 2016 with adding nitrates. In most cases, the overall water quality class was poor in 52%, then moderate in 40%, and bad only in 8%. The high concentration of phosphates, total phosphorus, nitrates, and lack of oxygen saturation in the Võhandu river were the main reasons for deteriorating the water quality.

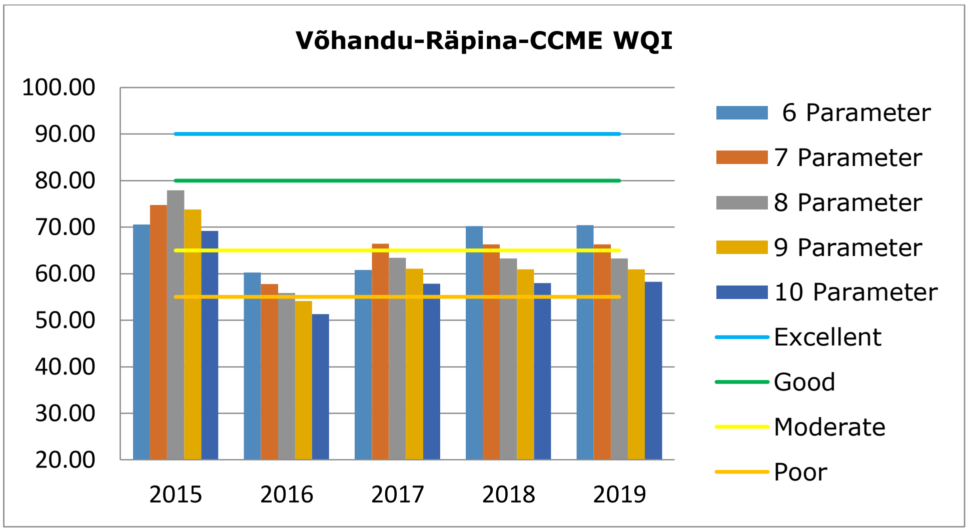

Figure 7.2.5: Comparison of the CCME WQI using different parameters in the Võhandu-Räpina.

Figure 7.2.6 represents that the index score fluctuated in all years studied. The addition of EC improves the grade in 2017 and 2019 with no changes in the rest of the years. At the same time, the score was significantly falling for all studied years by using nitrates, which impacted the declining one-step quality categories in 2018 and 2019. Phosphates addition helps to improve the index score without any impact on quality grade. Notably, the water quality classification remains constant between 2015 and 2016 with adding different parameters. The water quality status range in the Avijõgi river was good to poor in the studied years. The high concentration of total nitrogen and nitrates were the leading causes to impact the water quality in the Avijõgi river.

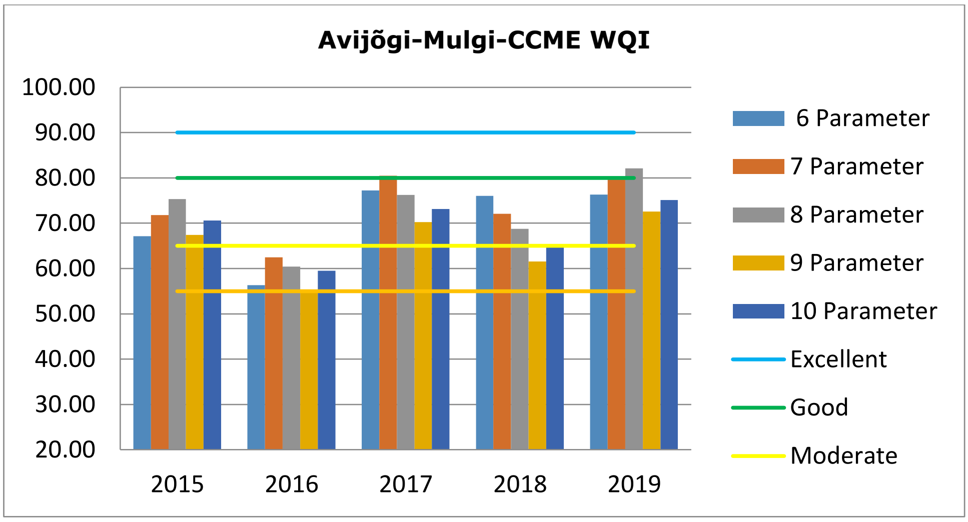

Figure 7.2.6: Comparison of the CCME WQI using different parameters in the Avijõgi-Mulgi.

Table 7.2.7 explains that the quality status was slightly oscillating with the addition of separate parameters, except in 2015, where the moderate water quality class remains constant. The addition of COD_{Mn} values impacts to depreciate one step the water quality class between 2016 and 2018. Moreover, in 2019 the quality status was improved when the 10th-parameter was added. The high concentration of BOD_5, COD_{Mn}, and oxygen deficit were the main reasons to impact the water quality in the Alajõgi river.

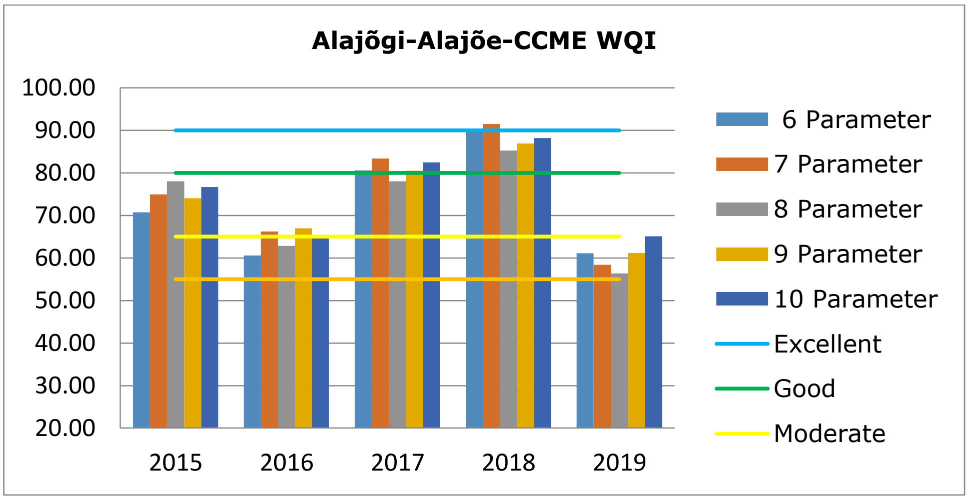

Figure 7.2.7: Comparison of the CCME WQI using different parameters in the Alajõgi-Alajõe.

Figure 7.2.8 depicts that the water quality index score continued to fall from 2015 to 2017, and fluctuated in 2018 and 2019 by using different parameters. Furthermore, the electrical conductivity lowered one step the quality grade in 2016, 2017, and 2019, and nitrates depreciate quality grade in 2015 and 2019, and then added phosphates dropped the quality into bad grade in 2017. The total nitrogen, electrical conductivity, nitrates, and phosphates were the main driving force to the significant decline in the index score and quality class of the Kullavere river.

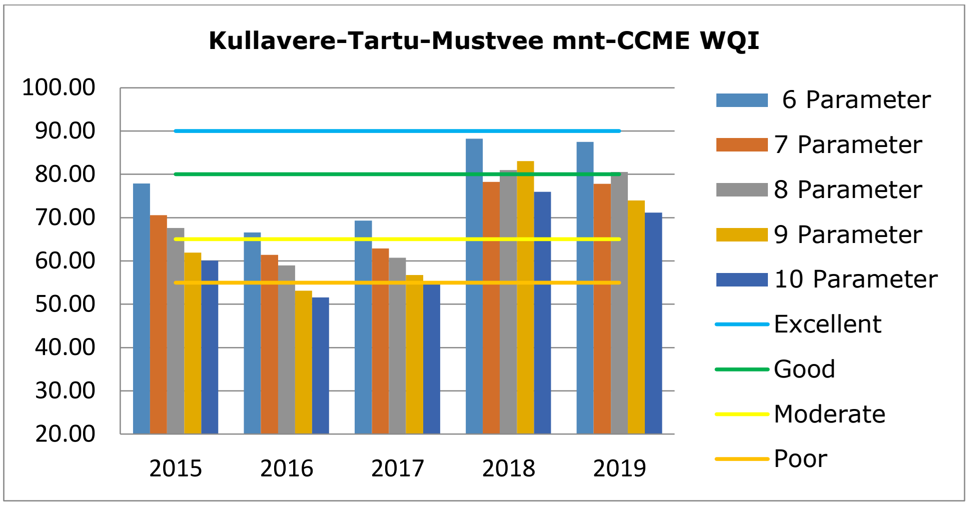

Figure 7.2.8: Comparison of the CCME WQI using different parameters in the Kullavere-Tartu-Mustve mnt.

Figure 7.2.9 illustrates that the index score fluctuated in all years studied by adding parameters. The quality grade remains constant (moderate) in 2015. The addition of EC impacted a quality class to depreciate one step in 2018 and 2019, and COD_{Mn} steps down the class in 2016 and 2017. The concentration of EC, BOD_5, and COD_{Mn} was impacting the water quality in the Rannapungerja river.

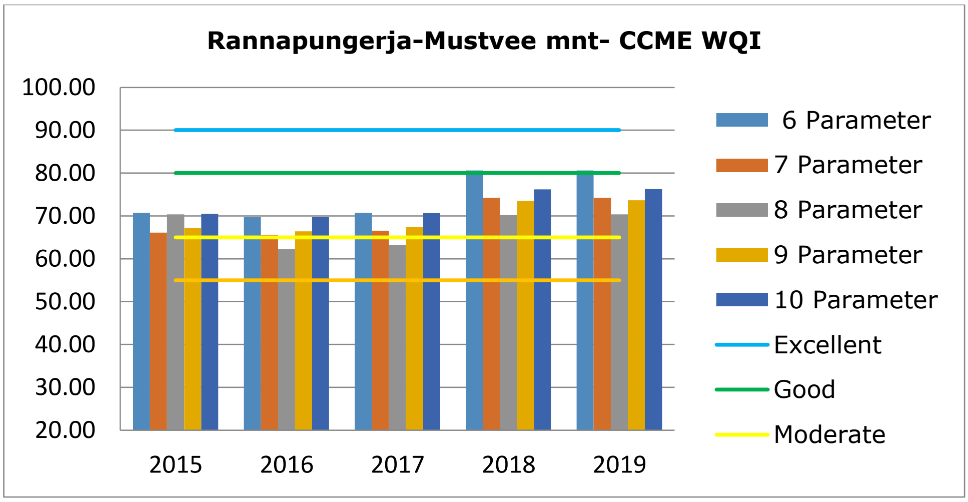

Figure 7.2.9: Comparison of the CCME WQI using different parameters in the Rannapungerjia-Mustvee mnt.

Figure 7.2.10 explains that the index score was changing in the Mustajõgi river as in all other rivers. Again, the significant influence to decrease the water quality for one step for all calculated years was marked adding the electrical conductivity. After that, the quality grade remains constant, except in 2018, it increases by using COD_{Mn}. The concentration of total nitrogen, nitrates, and EC caused to impact on the water quality in the Mustajõgi river.

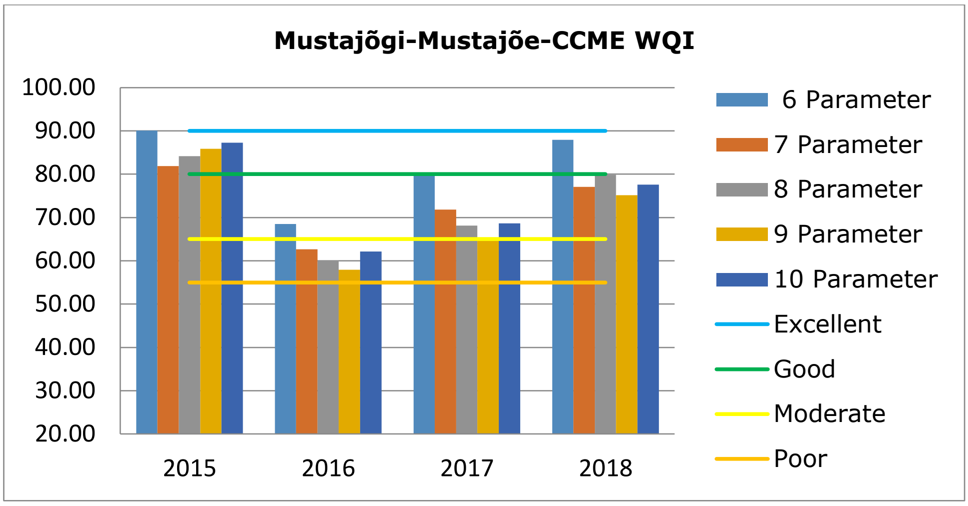

Figure 7.2.10: Comparison of the CCME WQI using different parameters in the Mustajõgi-Mustajõe.

7.3 Comparison of the CCME WQI (NarvaWatMan) score by using different sampling frequencies in a year in the Emajõgi and Narva River

To determine the water quality class by considering different sampling frequencies and different variables per year in the Emajõgi and Narva rivers (figures 7.3.1-7.3.4). This analysis was performed different times per year using six parameters (pH, BOD_5, O_2%, NH_4, N_{tot}, P_{tot}), then 8 (pH, BOD_5, O_2%, NH_4, N_{tot}, P_{tot}, EC, COD_{Mn}), and finally 10 (pH, BOD_5, O_2%, NH_4, N_{tot}, P_{tot}, EC, COD_{Mn}, PO_4, NO_3).

Figures 7.3.1-7.3.3 illustrate the variation of the index score between the different periods in a year, different parameters used, and observe the conversion of the water quality class for Emajõgi river. It is visible that the water quality index score for the year (12 months) and season 1 (Jan/Mar/May/Jul/Sep/Nov) was almost the same, and the quality grade was constant for a different set of parameters. However, the WQI index score for season 2 (Feb/Apr/Jun/Aug/Oct/Dec, 3rd column) provides a better score than for season 1 and upgrades the quality class for a combination of 6, 8, and 10 parameters. The quality grade was more or less the same for season 2, season 3 (Jan/Apr/Jul/Oct), and season 4 (Feb/May/Au/Nov). However, in most cases, season 5 (Mar/Jun/Sep/Dec) gives a better index score and the higher class of the quality of water compared to the other seasons and the whole year for different parameters used.

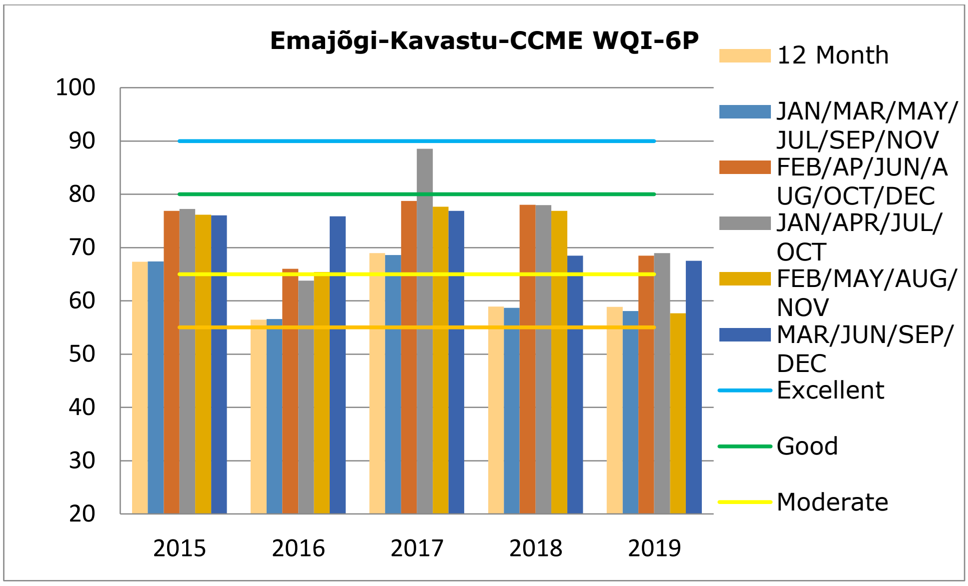

Figure 7.3.1: Comparison of the CCME WQI by different sampling frequencies using 6 parameters in the Emajõgi-Kavastu.

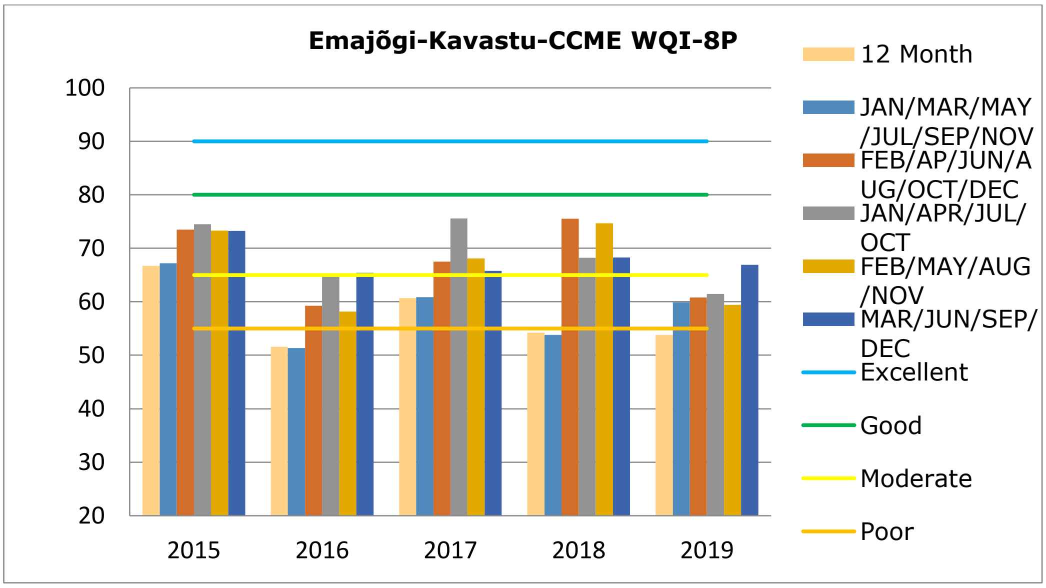

Figure 7.3.2: Comparison of CCME WQI by different sampling frequencies using 8 parameters in the Emajõgi-Kavastu.

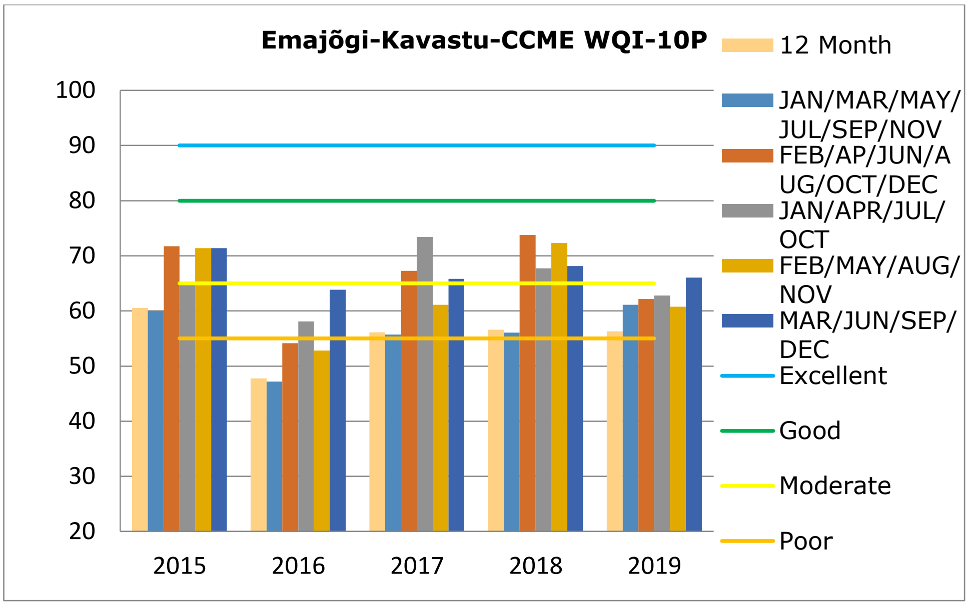

Figure 7.3.3: Comparison of the CCME WQI by different sampling frequencies using 10 parameters in the Emajõgi-Kavastu.

Figure 7.3.4 illustrates the overall index score fluctuated between 12 months, January to June and July to December December in Narva river only for 6 parameters (pH, BOD_5, O_2%, NH_4, N_{tot}, P_{tot},). The index score for 12 months was less than the calculated for two periods: January-June and July-December. If we compare the separate periods in a year (Jan to Jun and Jul to Dec) with 12-months quality class, then the quality is improving for the period January-June in 2015-2019, as well in July-December in 2019.

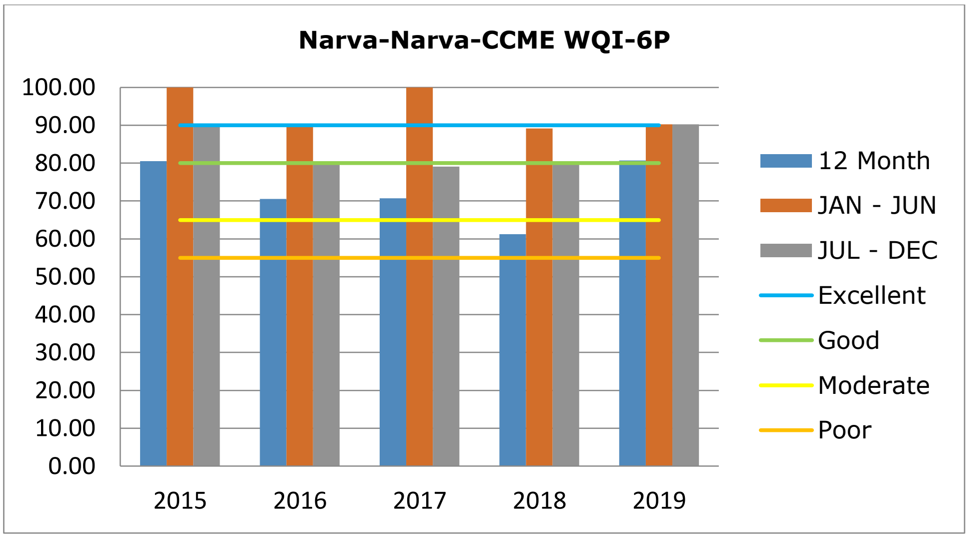

Figure 7.3.4: Comparison of the CCME WQI by different sampling frequencies in the Narva-Narva.

8 DISCUSSION

In the chapter mentioned above, it has been stated that three scenarios were considered for the comparison of the results of the water quality index calculation using the CCME WQI, WA WQI, and MCWQI methods. In the first scenario, six parameters (pH, BOD_5, O_2%, NH_4^+, N_{tot}, P_{tot}) were used to compare the CCME WQI (limit values from EST Act 19 and NarvaWatMan), MCWQI, and WA WQI methods. In the second scenario, to form a comparison between six parameters, seven parameters, eight parameters, nine parameters, and ten parameters the CCME WQI (NarvaWatMan limit values) method was used. The third scenario compares the water quality index by taking different sampling frequencies each year with six, eight, and ten parameters using the CCME WQI (NarvaWatMan) method for the Emajõgi and Narva rivers.

The detailed calculations and results for all monitoring stations considering various methods are documented in an excel sheet. In the first scenario, it was observed that the water quality index scores for the MCWQI and CCME WQI tended to be very high, whereas the WA WQI scores indicate the lower water quality class. Thus in general MCWQI scores are are higher than the CCME WQI scores. The MCWQI indicates that the waterbodies status is in the excellent and good category and rarely moderate for all the studied rivers. Furthermore, the CCME WQI (NarvaWatMan) method shows a score that depicts the water quality status as good and moderate, rarely excellent. Notably, the WA WQI illustrates the worse results compared to the other methods, indicate moderate to bad water quality class when applied for the same monitoring stations.

Moreover, In chapter 6 the comparison between the Estonian WQI and the CCME WQI (EST Act No 19) is shown, using the same limit values and six parameters (pH, BOD_5, O_2%, NH_4^+, N_{tot}, P_{tot}). In most cases, both indicate the same water quality class, except in the Narva river, Emajõgi river, and Kullavere river. The Estonian WQI shows excellent water quality in the Narva and Kullavere river, while the CCME WQI (EST Act No. 19) indicates that the water quality ranges are moderate to excellent. In the Emajõgi river, the Estonian WQI depicts the good quality of water, whereas the CCME WQI illustrates the changes in water quality ranges from poor to excellent. The reasons for the water quality status fluctuation between those methods could be: the CCME WQI consider every single bad sample along with the values, while the Estonian WQI evaluates the annual mean or certain percentile result of the values. Furthermore, the Estonian WQI and the MCWQI indicate the same water quality categories in most cases, except in the Võhandu, Avijõgi, and Kullavere rivers. The main cause could be that the Estonian WQI was considering the limit values of Act 19, while the MCWQI was following the more strict limit values received from the NarvaWatMan project.

In the second scenario, the CCME WQI (NarvaWatMan) was rerun using different parameters each year. The water quality index scores obtained for all the monitoring stations showed a fluctuation when adding more parameters (from 6 to 10). EC, COD_{Mn}, NO_3^- and PO_4^{3-} are significant changes in the index scores. It is notable that sometimes the CCME WQI scores dropped by using the 10-parameters compared to 6-parameters. As a result, the water quality class is step down by lowering the index score. In comparison, most of the water quality categories remained unchanged. The CCME WQI method application showed that when adding EC, COD_{Mn}, NO_3^-, PO_4^{3-}, the water quality status changes are insignificant. The major drivers for the changes of the water quality status are N_{tot}, NO_3^-, P_{tot} , pH, BOD_5, NH_4^+.

Furthermore, in Narva river, the higher concentration of the BOD_5 and electrical affected the water quality class at Narva station, and BOD_5, pH were responsible for the changes in the Vasknarva station. The high concentration of total nitrogen, nitrates, ammonium nitrogen, BOD_5, and electrical conductivity were accountable to deteriorate the water quality in the Emajõgi river. The phosphates, total phosphorous, and electrical conductivity were the causes that affect the water quality class in the Piusa river. The liable parameters to change the water quality rank in the Võhandu river were phosphates, total phosphorus, nitrates, and lack of oxygen saturation. The excess amount of total nitrogen and nitrates was culpable to the water quality category in the Avijõgi river. The BOD_5, COD_{Mn}, and deficit of oxygen were influenced the water quality rank in the Alajõgi river. The high concentration of total nitrogen, electrical conductivity, nitrates, and phosphates were the main driving force to decline the quality class of the Kullavere river. In the Rannapungerja River, the water quality grade changed due to the higher concentration of EC, BOD_5, and COD_{Mn}. The concentration of total nitrogen, nitrates, and EC influenced the water quality level of the Mustajõgi river.

In the third scenario, the water quality index score of the Emajõgi river was determined using the CCME WQI method with different parameters for five seasons (Season 1- Jan/Mar/May/Jul/Sep/Nov, Season 2 - Feb/Apr/Jun/Aug/Oct/Dec, Season 3- Jan/Apr/Jul/Oct, Season 4- Feb/May/Aug/Nov, Season 5- Mar/Jun/Sep/Dec) and a full year (12 months). It was noteworthy that the water quality index score for a year and season 1 (Jan/Mar/May/Jul/Sep/Nov) was almost the same, and the quality level remained constant. However, season 2(Feb/Apr/Jun/Aug/Oct/Dec) brings a high index score compare to season 1 and upgrades the quality rank. The quality grade more or less the same for season 2, season 3 (Jan/Apr/Jul/Oct), season 4 (Feb/May/Au/Nov). In 70% of cases, the quality level of season 5 (Mar/Jun/Sep/Dec) was better compared to the other seasons and full year in the Emajõgi River. In Narva river, the overall index score fluctuated between different periods of sampling. The index score for 12 months was less than for the others two sampling periods in a year. Selected the sampling period (Jan to Jun) improved water quality rank compared to the other (Jul-Dec) sampling period.

The CCME WQI method has a pathological memory effect due to the factor F_1. The CCME WQI will never forget any bad sample, this behavior of the CCME WQI methos is denoted as a pathological memory effect [40]. For instance, considering 6 times frequency in a year (F_1 = 100, F_2 = 20.5, F_3 = 2.25), and 12 times frequency in a year (F_1 = 100, F_2 = 9.05, F_3 = 1.10), results, CCME WQI provide index score as 41.05 and 42.03. Whereas MCWQI presents, the index score is 83.35 and 90.01. This comparison shows that the CCME WQI values slightly change, while the MCWQI index score rises more than 6 points for two sampling periods. MCWQI depicts the water quality status for one year as excellent, while CCME WQI reflects the water quality as bad for the considered whole period due to the pathological memory effect. [40]

Furthermore, the frequency factor F_2 has an effect on the CCME WQI. For example, if all sampling tests fail but only barely (F_1 = 100, F_2 = 100, and F_3 = 2.50), in this case, the water quality status cannot be bad. As a result, CCME WQI represents the score of 18.34, while MCWQI presents the value of 70.76. The MCWQI reflects moderate water quality, whereas CCME WQI shows bad water quality. MCWQI smoothens the effect of F_1 and F_2 using the geometric multiplication between them and it could be better formula to calculate the water quality index. [40]

The overall the treated water quality index score was determined using the abovementioned methods for all studied rivers and is represented graphically in figures.

9 CONCLUSION

To recapitulate regarding index score analyses from studied ten monitoring sites using six physical and chemical parameters data for the Narva river and the rivers of the Lake Peipsi basin from 2015 to 2019. The MCWQI model tended to be the most rigorous model for ranking the water quality status, nearest comparable model was CCME WQI (NarvaWatMan). In contrast, the WA WQI models provided a moderate to bad ranking water quality compared the other two models for all studied monitoring stations. The MCWQI represents the water quality ranking better than the CCME WQI (NarvaWatMan) because it is free of the pathological memory effect due to the factor F_1. Moreover, the Estonian WQI and the CCME WQI (EST Act No 19) indicate the same water quality class, except in the Narva river, Emajõgi river, and Kullavere river. The main cause is that the CCME WQI will never forget a bad sample, while the Estonian WQI considers the arithmetic mean value of the year. Additionally, the Estonian WQI and the MCWQI indicate the same water quality categories in most cases, except in the Võhandu, Avijõgi and Kullavere river, because both are using different limit values.

As reported by the random parameter addition experiment to check the water quality index score using six to ten parameters, a minimum of six parameters should be used in the CCME WQI method. The right choice of parameters could impact the index values compared to the number of many parameters selected. The overall index score will be lower in the monitoring stations by including many variables with exceedances of objectives. The author suggested that the main parameters to impact the water quality status were N_{tot}, NO_3^-, P_{tot}, EC, BOD_5 for all studied rivers in Estonia.

Furthermore, this study, considered a minimum of four sampling frequencies and a maximum of 12 sampling times in a year, and the index value was fluctuating compared to each other. At least, the minimum number of sampling frequency (4 times in a year) should be incorporated to get accurate index scores. However, the higher sampling frequency will provide a more stable index score in a year. Moreover, the selection of sampling periods (months) affects the water status class. The results obtained are exceeding the limit values in some months and not in others, so sampling should be done in all seasons.

SUMMARY

The main objectives of the study were gathering the physical-chemical parameters data of the Narva river and the rivers of the Lake Peipsi basin. The data was used to determine the water quality index score by applying different water quality index methods and compare the calculated index score based on the quality rank and scale.

The analysis of water quality status considered different index methods (WA WQI, MCWQI, and CCME WQI), using both physical and chemical parameters data. For comparison, the water quality status of rivers according to the current Estonian water quality evaluation method (Act 19) was presented. Virtually MCWQI method presents the range of the water quality as excellent and good, while the WA WQI method produces the range between moderate to bad. The widely used the CCME WQI method (NarvaWatMan) shows the water quality status in the class between excellent to poor category with more variables. To recapitulate, the CCME WQI (NarvaWatMan) is not bad all the time. Furthermore, the author compares the Estonian WQI and CCME WQI (EST Act No 19) indicating that the same water quality class in most cases, except in the Narva, Emajõgi, and Kullavere river, due to the pathological memory effect of the CCME WQI. Similarly, the Estonian WQI and the MCWQI also indicate the same water quality categories in most cases, except in the Võhandu, Avijõgi, and Kullavere rivers. The main cause could be that the Estonian WQI was considering the limit values of Act 19, while the MCWQI was following the more strict limit values received from the NarvaWatMan project.

The CCME WQI (NarvaWatMan) was rerun to evaluate the water quality class by adding more parameters. It was noteworthy that the water quality index scores were waving by adding new parameters (EC, COD_{Mn}, NO_3^-, PO_4^{3-}) to the existing six variables (pH, O_2%, BOD_5, NH_4^+, P_{tot}, N_{tot}). The remarkable point is that the most common parameters that affected the water quality rank are N_{tot}, NO_3^-, P_{tot}, EC, BOD_5 for all of the studied rivers in Estonia. Furthermore, the overall water quality class was affected by different sampling frequencies and selection of the sampling months per year. The minimum number of sampling frequency (4 times per year) should be incorporated for accurate index scores. However, the higher amount of experiment could provide a more stable index score per year, but it does depends on the selection of sampling months.

It is not easy to select compatible water quality index methods that indicate water quality status accurately. The CCME WQI has few weaknesses, pathological memory

effect, due to the factor F_1, F_2, F_3 in the CCME WQI formula. Furthermore, this formula shows strange behaviour due to the failed variables (F_1). In that case, the author applied the geometric mean instead of arithmetic mean, which (MCWQI) shows a better index score compared to the CCME WQI method.

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