TALLINN UNIVERSITY OF TECHNOLOGY
SCHOOL OF ENGINEERING
Department of Environmental Engineering

ANALYSIS OF POLLUTION LOAD CALCULATION METHODS AND THE PROBABILITY OF EXCEEDING THE WATER QUALITY LIMIT VALUES IN THE NARVA AND EMAJÕGI RIVERS

NARVA- JA EMAJÕGI SAASTE KOORMUSE ARVUTAMISMEETODITE ANALÜÜS JA VEEKVALITEEDI PIIRVÄÄRTUSE ÜLETAMISE TÕENÄOSUS

MASTER THESIS

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(*On the reverse side of title page*)

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THESIS TASK

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Thesis topic:

(in English) Analysis of pollution load calculation methods and the probability of exceeding the water quality limit values in the Narva and Emajõgi rivers

(in Estonian) Narva- ja Emajõgi saaste koormuse arvutamismeetodite analüüs ja veekvaliteedi piirväärtuse ületamise tõenäosus

Thesis main objectives:

1. To calculate the pollution load of Narva River and Emajõgi and to choose the most reliable method for pollution load calculation.
2. To analyse and interpret the pollution load calculation results.
3. To build and analyse the load probability curves.
4. To compare the calculated pollution load with permissible limits of current water quality standards.

Thesis tasks and time schedule:

No	Task description	Deadline
1.	To define the study area and to review the methods for pollution load calculations.	15.10.19
2.	To calculate the pollution load of Narva and Emajõgi rivers and to interpret the results.	01.04.20
3.	To plot the probability curves and apply them to compare the actual pollution load with water quality limits.	01.05.20

Language: English **Deadline for submission of thesis:** "......."........2020.a

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PREFACE

The author is extremely grateful to her supervisor Alvina Reihan from Tallinn University of Technology. The completion of this thesis would not have been possible without her support. The author very much appreciates her valuable and constructive suggestions during the planning and development of this work.

The main aim of this study is to determine and analyze the magnitude, dynamics, and nature of the polluting load of the rivers Narva and Emajõgi. The study focuses on comparing the methods for pollution load calculation and application of probability curves for analysis of results obtained.

The study goes along with the NARVAWATMAN project (NarvaWatMan), which is conducted with the financial support of the Estonia–Russia Cross Border Cooperation Programme 2014-2020 (Cross Border Cooperation Programme). Estonia-Russia Cross Border Cooperation Programme 2014-2020 aims to foster cross-border cooperation across the borders between the Republic of Estonia and the Russian Federation to promote socio-economic development in the regions on both sides of the common borders.

The author would like to extend her sincere thanks to the reviewer of the thesis Enn Loigu from Tallinn University of Technology for expanding the topic of the work and adding new ideas to be thought.

The author would also like to extend her deepest gratitude to the Tallinn University of Technology as a whole for the great conditions for studying and doing research work, to all the lecturers and staff for the interesting and useful experience the author has received.

pollution load; probability curve; water quality; nutrients; master thesis

INTRODUCTION

Directive 2000/60/EC of the European Parliament and of the Council establishing a framework for Community action in the field of water policy (EU, 2000) set up a goal of achieving "good status" for all waters including surface waters and groundwater not only for human water uses but for the whole ecosystems. The "good water quality status" includes "good ecological" and "good chemical status".

Eutrophication is one of the major concerns nowadays as it has long-term negative consequences on biodiversity of water bodies. Water pollution occurs when the balance of nature is lost due to the increase of pollutant flow. The Baltic Sea is located in Northern Europe and remains one of the most polluted seas on our planet. The sea has limited water exchange with other seas, resulting in the accumulation of nutrients and pollutants and their very slow dilution.

The Baltic Marine Environment Protection Commission, also known as the Helsinki Commission (HELCOM), is an organization including 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). In 1974 it set up a goal of reducing the inputs of nutrients into the Baltic Sea.

Most of the pollution originates from inland activities and therefore it is important to identify the sources of pollution and reduce the input to achieve compliance with water quality standards. Most of the nutrient input to the Baltic Sea is riverine (HELCOM, 2018). Therefore, the good quality status of rivers is an important step toward achieving the goals set by the Helsinki Commission.

For this purpose, the Commission for the Protection of the Marine Environment of the Baltic Sea Area gathers data from contracting parties about the magnitude and sources of nutrient inputs into the sea, which should help to reduce the input (HELCOM, 2019).

Narva is a river belonging to the Baltic Sea catchment area flowing from the Peipsi Lake into the Narva Bay. Emajõgi flows through the Tartu County in Estonia. The concentrations of pollutants in this river are of great interest itself as well as the contribution to the loading into the Peipsi Lake.

The main aim of this study is to determine and analyse the magnitude, dynamics, and nature of the polluting load of the rivers Narva and Emajõgi.

The objectives of this study are:

- to analyse and interpret three methods for calculation pollution load described in HELCOM guideline (HELCOM, 2019);
- to calculate the pollution load of Narva River and Emajõgi by suitable methods;
- to choose the most reliable and convenient method for pollution load calculation of the studied rivers;
- to analyse and interpret the pollution load calculation results of the Narva River and Emajõgi;
- to build and analyse the probability curves of occurring the calculated amount of pollution in studied rivers; and
- to compare the calculated pollution load with permissible limits of water quality standards.

The full picture of the pollution loading and trends in Narva and Emajõgi rivers can help to define measures toward improving the water quality and status of the rivers and the Baltic Sea.

1 STUDY AREA

The study area of this thesis includes the parts of the catchment area of rivers Narva and Emajõgi.

1.1 Narva River

The Narva River is a river on the eastern border of Estonia, which starts from the Peipsi Lake near the Vasknarva village and flows into the Narva Bay. On the west bank of the river is the city of Narva, on the eastern bank of the river – Russian city Ivangorod.

Narva is a river belonging to the Gulf of Finland sub-basin of the Baltic Sea catchment area. Notwithstanding the fact that it is only 76.2 km long (Environmental Board, 2010), it is the biggest river in Estonia in terms of annual flow (with an annual volume of 400 m^3/s) (Piirsoo, Pall, Tuvikene, Viik, & Vilbaste, 2010) and the second-largest river entering the Gulf of Finland after the Neva River. Narva is also the largest river in Estonia by its catchment area of 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 (HELCOM, 2019). The basin area includes all rivers flowing into the Peipsi Lake and the Võrtsjärv Lake.

In terms of HELCOM classification (HELCOM, 2019), Narva is a border and a transboundary river. As the border river, it has an outlet to the Baltic Sea at the border between two countries – Estonia and Russia. That is the reason, why the inputs to the Baltic Sea from the Narva River are divided between these countries in relation to each country's share of total input. It is assumed 1/3 of total pollution load from the Narva River to the Baltic Sea is Estonian (Baltic Marine Environment Protection Commission, 2019). As a transboundary river, Narva is a river that crosses at the political border and has its outlet to the Baltic Sea in one of the HELCOM Contracting Parties. It is a natural border between Estonia and Russia upper the Peipsi Lake. These facts make studying pollution input to the Baltic Sea more difficult as an interaction between two countries must take place.

Into the Narva River flow many other rivers and streams. Most of the water is carried into the Narva River by tributaries entering from the right bank, and these also affect the chemical and ecological status of the river (Environmental Board, 2010).

The measurements of water flow and concentration of pollutant sampling are taken at hydrochemical stations. The description of these stations is available on the Estonian Weather Service website (Ajaloolised vaatlusandmed, 2020).

Hydrological measurements on the River Narva have been started in 1902. Nowadays there are two hydrochemical stations, 2 hydrological stations in Estonia on Narva River and one chemical monitoring station – 12 km from the mouth and one hydrological – 16 km from the mouth in Russia (HELCOM, 2019).

Vasknarva hydrometric Station was opened in 1902 and automated in 2010. It is located at the Narva River in Vasknarva village, Ida-Viru County, Estonia. Distance from the mouth of the river to the station is 76.4 km and the catchment area is 47800 km^2. Parameters measured, observed and calculated at this station are: water level; water temperature at the bottom of the river; manually measured water temperature in surface water (0.10-0.5 m) during flow measurement; flow rate [m^3/s] (2-3 times per month; 5-6 times per month during high water periods); drainage (calculated); ice events (if present) during flow measurement; description of aquatic vegetation (if any) during flow measurement; and air temperature (Vasknarva hüdromeetriajaam, 2020).

The hydrometric station of Narva city was opened in 2000 and automated in 2002. It is located at the Narva River in Narva city port, Ida-Viru County, Estonia. Distance from the mouth of the river to this station is 14.6 km and the catchment area is 56000 km^2. Parameters measured, observed and calculated at this station are the same as at the Vasknarva station except for air temperature (Narva linna hüdromeetriajaam).

The description of sampling methods on the Narva River from the Estonian side, description of methods for total nitrogen and total phosphorous analysis on the Narva River (based on Kati Roosalu table from Tallinn University of Technology) see in Appendices 1, 2 and 3.

1.2 Emajõgi

Emajõgi is the ninth largest river in Estonia with a length of 100 km. It connects the Võrtsjärv Lake through Tartu County with the Peipsi Lake, crossing the city of Tartu for 10 km. The Emajõgi basin covers almost a quarter of the area of mainland Estonia with the catchment area of 9745 km^2 (Kätlin Blank, 2017).

Emajõgi is the second largest river in Estonia by flow (after the Narva River) with the average flow at the mouth is 72 m^3/s and the only fully navigable river (Peipsi Alamvesikonna Kalurite Liit, 2008).

Emajõgi is unique in that way that it can flow in both directions. Usually flowing flows from west to east from the Võrtsjärv Lake to the Peipsi Lake, it can flow backward, i.e. towards the Võrtsjärv Lake if the water level of the Võrtsjärv Lake is lower (Peipsi Alamvesikonna Kalurite Liit, 2008).

The series of hydrological observations of Emajõgi started in 1867 and are the longest among Estonia's inland waters. National observation of the water quality of Emajõgi is conducted annually in its headwaters in Rannu-Jõesuu, the middle course in Tartu at Kvissentali, and lower course in Kavastu (Peipsi Alamvesikonna Kalurite Liit, 2008).

Tartu (Kvissentali) hydrometric station was opened in 1867 and automated in 2010. It is located at Emajõgi in Tartu city, Tartu County, Estonia. Distance from the station to the mouth of the river is 42.6 km and the catchment area is 7840 km^2. Measurable, observable and calculated parameters are: water level; 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; ice residues 2-3 times a month during flow measurement; thickness of ice and snow on the river 2-3 times a month during flow measurement; flow rate [m^3/s] 2-3 times a month, 5-6 times a month during high water; drainage (calculated); description of aquatic vegetation 2-3 times a month during flow measurement; and air temperature (Tartu (Kvissentali) hüdromeetriajaam).

2 DATA AND METHODS

2.1 Data

In this work datasets of water flow measurements from the Estonian Weather Service website (Ajaloolised vaatlusandmed, 2020) are used for calculation as well as databases of water quality characteristics of two monitoring stations at Narva River (Vasknarva and Narva city) and two stations at Emajõgi (Kavastu and Kvissentali) from Tallinn University of Technology and the State water quality monitoring program.

Initially available data are given Table 2.1.1.

Table 2.1.1 Data used for calculations

River	Narva		Emajõgi	
Station	Vasknarva	Narva city	Tartu (Kvissentali)	Kavastu
Hydrological characteristics	**Years**			
Water flow Q	1992-2018	2003-2018	1922-2018	
Pollutant concentrations (BOD_7)	1992-2009	1992-2009		1992-2009
Pollutant concentrations (BOD_5)	2009-2018	2009-2018		2009-2018
Pollutant concentrations (COD, NH_4, NO_3, N_{tot}, PO_4, P_{tot})	1992-2018	1992-2018		1992-2018

In this work the pollution load with Narva River and Emajõgi is calculated for the following water quality characteristics:

- BOD – biochemical oxygen demand (BOD_5);
- COD – chemical oxygen demand;
- NH_4 – ammonium nitrogen;
- NO_3 – nitrate;
- N_{tot} – total nitrogen;
- PO_4 – orthophosphate; and
- P_{tot} – total phosphorous.

BOD shows the amount of oxygen consumed by micro-organisms needed to degrade organic material (Water Education Foundation). High BOD means that there is less oxygen to support life and it indicates organic pollution. Until the year 2009 included, the amount of oxygen consumed over a seven-day period was reported (BOD_7) in the databases used in this thesis. Starting from 2010, the amount of oxygen consumed during a five-day period of incubation is presented as BOD_5.

The chemical oxygen demand is the amount of oxygen equivalent to the amount of oxidizing agent used in the water in the acidic medium to oxidize the organic substances in the water (Water Education Foundation).

Nitrogen is a vital nutrient that has a significant impact on the productivity of water bodies. The natural body of water contains nitrogen in various inorganic and organic compounds, as well as in molecular form. The inorganic (mineral) nitrogen compounds are NH_4^+ (ammonium), NO_2^- (nitrite) and NO_3^- (nitrate) ions. Total nitrogen N_{tot} is the sum of Kjeldhal nitrogen and oxidized nitrogen (NO_3, NO_2), where Kjeldhal nitrogen is the sum of organic nitrogen and ammonium (Weiner & Matthews, 2003).

Ammonium nitrogen NH_4 is the first intermediate stage for the conversion of organic nitrogen compounds into inorganic forms. High levels of ammonium compounds in surface water indicate recent pollution (Weiner & Matthews, 2003).

Nitrate NO_3 is the last stage of the biochemical conversion of nitrogen. The presence in water is mainly related to the processes in the water body, but it also occurs in water due to an inappropriate fertilization of fields or inappropriate result of farming.

Phosphorus is one of the main determinants of nutrient content, as it defines the productivity of the water body. Phosphorus compounds usually enter the river's water as mineral compounds in fertilizers and domestic wastewaters. The total phosphorus P_{tot} in the water sample is the sum of all forms of phosphorus: mineral (ortho- and polyphosphate) and organic phosphorus.

2.2 Methods for calculation of the pollution load from monitored rivers recommended by HELCOM

Pollution load is the mass of a substance that passes through a particular point of a river (for instance, hydrometric station) in a specified amount of time. Load is the product of water flow and the pollutant concentration in the water.

Water flow is the volume of water that passes a cross-section of a river in a specified amount of time (Donald W. Meals, R. Peter Richards, and Steven A. Dressing, 2013).

In HELCOM Guidelines (HELCOM, 2019) methods for calculation of the load from monitored rivers are divided based on the frequency of concentration and river flow measurement. Calculation methods differ from whether hydrological and chemical measurements are made at the same hydrochemical monitoring station or not.

Three methods described in the guide (HELCOM, 2019) can be applied if both hydrological and chemical measurements are performed at the same hydro-chemical monitoring station. The methods are listed from most recommended to least recommended.

The first method is based on daily water flow and daily concentration. If on the day t measurements were not taken, daily water flow (Q_t) and concentration values (C_t) can be interpolated linearly between days with data (HELCOM, 2019).

Annual pollution load is calculated using Formula 1.

$$L = 0.0864 \sum_{t=1}^{n} (Q_t \cdot C_t)_t \qquad (1)$$

where

∑ denotes summation;

n is number of days;

L is annual load [kg];

C_t is concentration on day t ([mg/l] for nutrients, and [µg/l] for hazardous substances); and

Q_t is water flow [l/s].

The estimate in the equation is multiplied by 0.0864 for nutrient to obtain the daily loads that are summarized in the equation over the whole year and by 0.0000864 for hazardous substances.

The advantage of this method is that it utilizes all of the water flow values available. The disadvantage is that it is very time consuming as many values are interpolated.

The second method uses mean monthly concentration and monthly river flow. Monthly river flow is calculated as water flow multiplied by the number of seconds in a month (HELCOM, 2019).

Annual pollution load is calculated using Formula 2.

$$L = 1/1000 \cdot \sum_{i=1}^{12} W_i \cdot C_i \tag{2}$$

where

L is annual load [kg];

∑ denotes summation;

W_i is volume of monthly river flow [m^3] in month *i*;

C_i is mean monthly concentration [mg/l] in month *i*; and

When concentration is in [µg/l] (hazardous substances) the equation must be divided with 1,000,000.

The advantage is that the method is less time consuming than the first method, as only 12 values per year (for each month) is needed to calculate. The disadvantage – is it needed to calculate an additional parameter – water flow. In case if there are months when water samples are not taken, the missing data are interpolated which adds errors to the estimation.

In the third method daily water flow and daily concentration regression is used. The calculation using daily regression should only be applied if there is a good relationship between the specific compound and the daily river flow (HELCOM, 2019).

Using Formula 3 pollution load is calculated, where concentration is calculated from regression (Formula 4).

$$L = m \sum_{i=1}^{n} Q_i \cdot C_{ri} \tag{3}$$

$$C_{ri} = \frac{a}{Q_i} + b + c \cdot Q_i \tag{4}$$

where

L is annual load [kg];

Q_i is daily water flow in day i (measured) [l/s];

C_{ri} is the regression value of the concentration for day in [mg/l];

m is conversion factor of units (0.0864 with concentration in [mg/l] (nutrients) and 0.0000864 with concentration [µg/l] (hazardous substances);

a, b, c are coefficients typical of each quality parameter, observation station and time series; and

n is number of days per year.

The disadvantage of this method is that the regression model is needed to be built. The method is the least recommended by HELCOM as it can increase errors to estimations.

2.3 Flow-normalised method

So-called "flow-normalised" method uses mean monthly concentrations and flow in a day of concentration measurement. This method has an advantage that the influence of water flow is eliminated. Intermediate data of flow-weighed concentrations can be used for additional analysis. In HELCOM guideline (HELCOM, 2019) methods proposed are not include the flow-normalised method, but before the trend analysis it is suggested to apply normalization first (HELCOM, 2015). This means that elimination of the effect of the hydrological conditions is mandatory anyway.

2.4 Comparison of methods and selection of the most suitable

The comparison of methods is done by such statistics as standard deviation and z-score.

Standard deviation is one of the most common measures of data dispersion. The more spread out a data distribution is, the greater its standard deviation. We will use it for comparing the difference in results of pollution load calculation obtained by three methods. Standard deviation is measured in the same units as the original data. For this it is more easily compared to the mean and other statistics that are measured in the same units as the original data (James, 2017).

Standard deviation is calculated by Formula 5.

$$s = \sqrt{\frac{\sum_{i=1}^{n}(x_i - \bar{x})^2}{n-1}} \tag{5}$$

where

s is standard deviation;

x_i is value, for which standard deviation is calculated;

$\bar{x}$ is mean value; and

n is number of methods.

While this statistics compare each year and each pollutant separately, in order to make a conclusion about the method results as a whole, we use such a statistics as z-score. It measures the number of standard deviations away from the mean a value is located. The mean value of the three methods by which pollution load is calculated is assumed to be the most probable value (James, 2017).

z-score is calculated by Formula 6.

$$z = \frac{x - \bar{x}}{s} \tag{6}$$

where

z is z-score;

x is value, for which z-score is calculated;

$\bar{x}$ is mean value; and

s is standard deviation.

2.5 Probability curve

Probability curves show in graphical form the time percentage during which the value of a hydrological characteristic is equalled or exceeded. The curves are used to analyse the water flow as well as water quality indicators.

The application of probability curves in developing the standards of water quality is described in several articled published by U.S. Environmental Protection Agency (Donald W. Meals, R. Peter Richards, and Steven A. Dressing, 2013), (U.S. Environmental Protection Agency; Office of Wetlands, Oceans and Watersheds, 2007), (U.S. Environmental Protection Agency, 2007). Probability curves help to define total maximum loads which are equal the maximum amount of a pollutant that a waterbody can receive without exceeding water quality standards.

To draw the probability curves graphical or analytical approaches can be applied. In this thesis, the graphical method is used for building the probability curves of average annual water flow and annual pollution load.

The sequence of plotting the curves begins with sorting the data from larger to smaller. Then each number is assigned with a rank: r=1 for largest and r=n for smallest. Probability is calculated using Formula 7:

$$P = \frac{r}{n+1} \cdot 100\%, \quad (7)$$

where

P is probability of certain average annual water flow or annual pollution load occurring in the range of years observed [%];

r is rank assigned to each average annual water flow or annual pollution load; and

n is number of years for which average annual water flow or annual pollution load is calculated (Vesilind & DiStefano, 2006).

Probability means a "1-in-*n*-year" chance of occurring of hydrological characteristics with a given value.

Another useful characteristic of the probability curve is the average recurrence interval which is an average length of time between two characteristics of a given size or larger. Average recurrence interval is inversely proportional to probability (see Formula 8):

$$T = \frac{1}{P} = \frac{n+1}{r}, \qquad (8)$$

where

T is average recurrence interval;

r is rank of the event; and

n is number of years of record.

After the probability is calculated, the scatter plot is built. On the horizontal axe is probability [%] and on the vertical axe is average annual water flow [m^3/s] or annual pollution load [t/a]. The plotted points are connected by a smooth curve. In this work, the exponential trendline curve is used.

The advantages of probability curves are that it is relatively easy to build using simple mathematical functions. No assumption should be made because only known values of water flow or pollution load are used. The probability curves demonstrate information in a clear and simple way and they are easy to interpret.

The more data used for building the curve, the more precise information the curve represents. But in case if hydrologic conditions of the water body have changed during the period of observation, the curve can give false representation.

The probability curve obtained on the basis of a limited number of actual observations does not accurately and fully reflect the patterns of changes in the hydrological characteristics. The end sections of the curve are especially poorly illuminated by observational data.

The probability curves can be divided into several zones according to different hydrologic conditions. For example, (U.S. Environmental Protection Agency; Office of Wetlands, Oceans and Watersheds, 2007) describes five hydrologic zones (high flows, moist conditions, mid-range flows, dry conditions, and low flows). Figure 2.5.1 illustrates this concept.

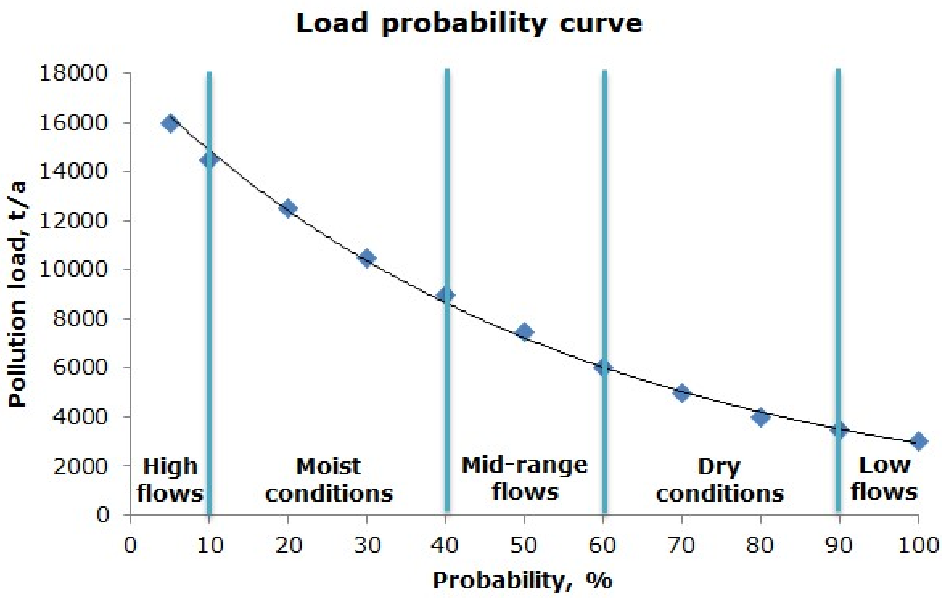

Figure 2.5.1 Hydrologic condition zones on probability curve (according to (U.S. Environmental Protection Agency; Office of Wetlands, Oceans and Watersheds, 2007))

Depending on the number of loads that are above or below the allowable limits we can determine the cause of pollution. The interpretation of the probability curve based on at which interval the ultimate values are exceeded is described in (Donald W. Meals, R. Peter Richards, and Steven A. Dressing, 2013). Figure 2.5.2 illustrates this concept.

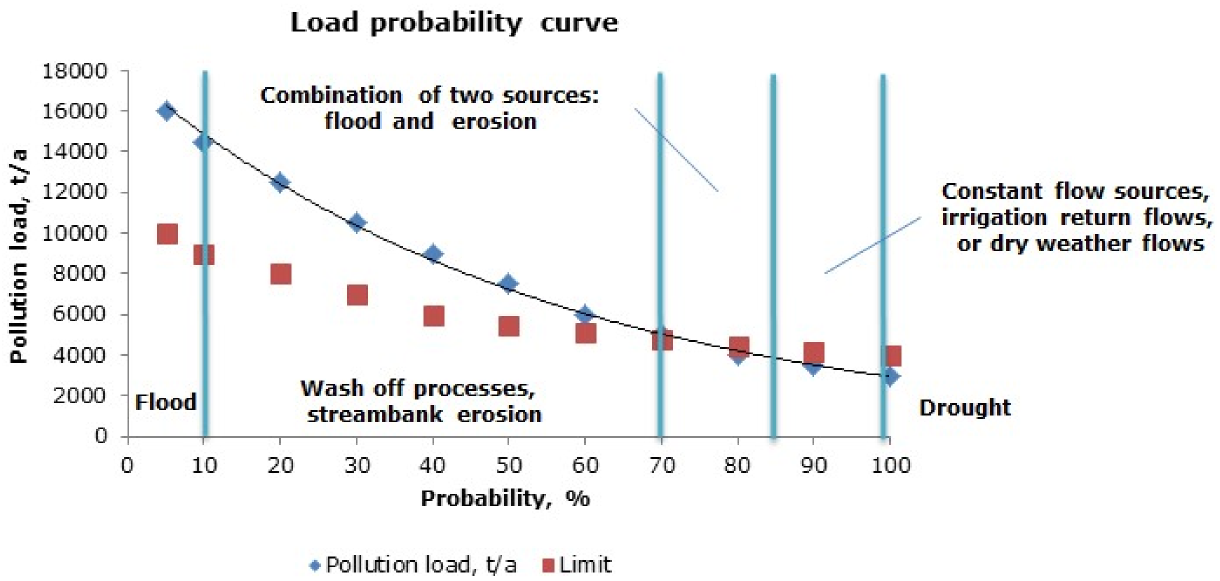

Figure 2.5.2 Determination of theoretical source of pollution based on probability curve (based on (Donald W. Meals, R. Peter Richards, and Steven A. Dressing, 2013))

According to this article loads above the limits occurring:

- at intervals less than 10% are due to extreme hydrologic conditions of a flood;
- at intervals of 85 to 99% (low flow conditions) showing the presence of constant flow sources (for instance, wastewater treatment plant), irrigation return flows, or dry weather flows;
- at intervals of 10 to 70% reflect wet weather contributions associated with sheet and rill erosion, wash off processes, and, potentially, streambank erosion;
- at intervals of 70 to 85%, have the cause of the combination of two mentioned above sources; and
- at intervals bigger than 99% have extreme hydrologic conditions of drought as the cause.

3 ANALYSIS

The calculations of annual pollution loads were done by three different methods. The first two methods, named “I method” and “II method” respectively, are the same as recommended by HELCOM guidelines (HELCOM, 2019). Another method named as “III method” is so-called flow-normalised method (see Chapters 2.3 and 3.4).

Annual pollution load is calculated only for those years, where more than 75% of data are available (at least 9 concentration measurements per year).

Pollution load of Narva River at Narva city station is calculated for years from 2003 to 2018.

In spite of the fact, that for at Vasknarva station concentration measurements were taken from 1992, pollution load calculations start from the year 1996 because in 1992 only two times per year concentration samples were taken, in 1993 – three, in 1994 – three and in 1995 – six times. Using such a small amount of data it is not feasible to receive realistic results of pollution load calculations. Therefore, for Vasknarva station it is calculated for years from 1996 to 2018.

The pollution load of Emajõgi at Kavastu station is calculated for years from 1992 to 2018.

The water flow at Kavastu station is not measured. To obtain water flow values for this station, the flows of Tartu (Kvissentali) are recalculated for Kavastu cross-section using Formula 9.

$$Q_{Kavastu} = \frac{Q_{Kvissentali} \cdot F_{Kavastu}}{F_{Kvissentali}}, \qquad (9)$$

where

$Q_{Kavastu}$ is water flow calculated for Kavastu station [m^3/s];

$Q_{Kvissentali}$ is water flow measured at Kvissentali station [m^3/s];

$F_{Kavastu}$ is catchment area of Kavastu, which is equal 8538 km^2; and

$F_{Kvissentali}$ is catchment area of Kvissentali, which is equal 7828 km^2.

For all the stations the biochemical oxygen demand is presented as BOD_5 since 2009. For years before 2009, BOD_7 was recalculated into BOD_5 using the conversion Formula 10 (European Environment Agency, 2015):

$$BOD_5 = \frac{BOD_7}{1.16}, \tag{10}$$

where

BOD_5 is the amount of oxygen consumed over a 5-day period [mg/l];

BOD_7 is the amount of oxygen consumed over a 7-day period [mg/l]; and

1.16 is conversion factor.

3.1 I method

I method used for pollution load calculation utilizes daily water flows and daily concentrations. While data on water flows is available for every day of a year, concentration samples are taken approximately once a month or for some years and stations even rarely. To obtain missing daily concentration values they are linearly interpolated between days of taking samples (as recommended by HELCOM guideline (HELCOM, 2019)).

This method can be interpreted in two ways depending on if interpolation takes into account water flow or not.

Linear interpolation is used to find coordinates of a point between two given points. In case of considering water flow into interpolation, we use linear interpolation to find unknown concentration value with the application of Formula 11 having three known water flow and two concentration values:

$$C_0 = \frac{(Q_0 - Q_1)(C_2 - C_1)}{Q_2 - Q_1} + C_1, \tag{11}$$

where

C_0 is interpolated concentration value [mg/l];

C_1 is lower concentration value [mg/l];

C_2 is higher concentration value [mg/l];

Q_0 is water flow of the day when concentration value is interpolated [m^3/s];

Q_1 is water flow of the day with higher concentration value [m^3/s]; and

Q_2 is water flow of the day with lower concentration value [m^3/s].

The problem with the usage of this method is that for non-linear collection of data, linear interpolation is often not accurate. Having concentration values only once a month we need to interpolate approximately thirty values between only two and taking into account the changing of water flows. In fact because of lack of data the relation between concentration and water flow seems not to be always linear, which means that sometimes the application of linear interpolation gives unreal concentration values.

For instance, we need to interpolate the NO_3 concentration value for 31.03.2003 between two days when samples were taken (20.03.2003 and 08.04.2003) at Narva city station using this method. The initial data is shown in Table 3.1.1.

Table 3.1.1 Data for illustration of linear interpolation of NO_3 concentration value

Date	**Q, m^3/s**	**NO_3, mg/l**
20.03.2003	295	0.14
31.03.2003	419	C_0 - ?
08.04.2003	367	0.86

As we can see, the water flow trendline is not linear. Moreover, logically, that with higher water flow the pollutant concentration should be lower, as a pollutant is diluted with water. But using linear interpolation, we cannot get a plausible result.

To show this, the data is substituted in the interpolating formula (Formula 12):

$$C_0 = \frac{(419 - 367)(0.86 - 0.14)}{295 - 367} + 0.14 = -0.38 \text{ [mg/l]}. \qquad (12)$$

Obviously, concentration value cannot be negative, which means that this method of interpolation cannot be used.

The same method is modified in order to obtain more realistic results and be simpler to use. The concentration values are interpolated not taking into account the water flows. In this case, Formula 13 applied in Microsoft Excel:

$$C_0 = C_1 + \frac{(C_2 - C_1)}{\left(ROW(C_2) - ROW(C_1)\right)}, \quad (13)$$

where

C_0 is interpolated concentration value [mg/l];

C_1 is lower known concentration value [mg/l];

C_2 is higher known concentration value [mg/l]; and

ROW([reference]) is Excel function that returns the row number of a cell reference.

When concentration values needed to be extrapolated behind the begging or end of observations, for example, from the first day of the month of the first year of the observations to the day of the same month when the first sample was taken; and from the last known concentration value to the end of that month, it is assumed the values do not change. We take one concentration values for all days from the begging of the month to the first day of the observations. In the same way, we take the same values for all days from the last day of the observations until the end of that month.

3.2 II method

II method is based on mean monthly concentration and monthly river flow and is recommended to use by HELCOM guide (HELCOM, 2019).

The concentrations are measured on a certain day in a month (usually once a month) and therefore approximately 12 concentration values per each year. It is assumed that these values are mean monthly concentrations. If there are less than 12 but more than 9 (included) concentration values per year, the concentration values are linearly interpolated for months with the lack of data between known values to have 12 in total (for each month of the year).

Sometimes two samples were taken in one month and no samples in the previous or following month. In this case, actual values are used in calculations and for a missing month no values are interpolated.

Using the database from the Estonian Weather Service website (Ajaloolised vaatlusandmed, 2020) the daily water flows are written down for the same days when concentration samples were taken.

The next step is to calculate a volume of river flow *W* for each month. For this, daily water flow is multiplied by the number of seconds in a month when samples were taken.

To calculate the monthly pollution load the average monthly concentration is multiplied by the monthly volume of river flow. In order to gain pollution load in tons, the result is divided by 1000000.

Formula 14 is used to calculate monthly pollution load.

$$L_i = \frac{Q_k \cdot t_i \cdot C_i}{1000000} = \frac{W_i \cdot C_i}{1000000}, \qquad (14)$$

where

L_i is monthly pollution load [t] in month i;

Q_k is water flow in a day of taking concentration sample [m^3/s] in day k;

t_i is amount of seconds in month I [s];

C_i is mean monthly concentration [mg/l] in month i;

W_i is volume of monthly river flow [m^3] in month I; and

1/1000000 is coefficient to convert the result in tons.

To calculate the annual pollution load all twelve monthly loads are summed up (see Formula 15):

$$L = \sum_{i=1}^{12} L_i = \sum_{i=1}^{12} W_i \cdot C_i, \qquad (15)$$

where

L is annual load [t];

$\sum$ denotes summation;

L_i is monthly pollution load [t] in month $_i$;

W_i is volume of monthly river flow [m^3] in month i; and

C_i is mean monthly concentration [mg/l] in month i.

3.3 Daily concentration regression method

The third method recommended by HELCOM guide (HELCOM, 2019) (based on daily concentration regression) is not applicable for giver data as there is no statistically significant relationship between the pollutants' concentrations and the daily water flows. This was shown by the regression model built in Excel.

To illustrate that, in Figure 3.3.1 is shown the regression analysis result for the BOD_5-Q relation at Vasknarva station.

As independent Variable 1 in regression analysis is used water flow Q and the dependent variable is BOD_5 concentration. The confidence level is 95%.

Correlation is 7.8%, which is quite low. The coefficient of determination shows that with this model we can describe only 0.6% of the variability of BOD_5 concentration values.

As the confidence interval for the water flow variable [-0.000939…0.000196] contains zero, this parameter is not statistically significant.

As we can see from the regression analysis result, the regression model cannot be used for prediction of concentration values of all days (population) as the whole model is not statistically significant: Significance F = 0.19910535 < α = 0.05.

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0,0782458
R Square	0,0061224
Adjusted R Square	0,0024277
Standard Error	0,5195535
Observations	271

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	0,44730366	0,4473037	1,657073	0,19910535
Residual	269	72,6127472	0,2699358		
Total	270	73,060050			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	1,9366591	0,0996194	19,440571	3,492E-53	1,74052617	2,132792
X Variable 1	-0,000371	0,0002886	-1,287273	0,199105	-0,000939	0,000196

Figure 3.3.1 Summary output of regression analysis for BOD_5-Q relation at Vasknarva station on Narva River

To create a dataset suited for regression analysis the model was improved by log-transforming both concentration and flow. But again, the regression model is not statistically significant and cannot be used for the prediction of unknown concentration values.

3.4 III method

The III method in result tables is "flow-normalised" described in the previous chapter. Like in the second method we assume that concentrations in a day of the month are mean monthly concentrations.

To calculate an annual pollution load Formula 16 is used:

$$L = \frac{\frac{\sum_{i=1}^{n} \frac{(Q_i \cdot C_i)}{1000}}{\sum_{i=1}^{n} Q_i} \cdot Q_{av} \cdot t}{1000} \qquad (16)$$

where

L is annual pollution load [t];

∑ denotes summation;

Q_i is water flow in a day of taking concentration sample [m^3/s];

C_i is mean monthly concentration [mg/l] in month i;

Q_{av} is average annual water flow [m^3/s];

t is amount of seconds in a year [s]; and

1/1000 are units converting coefficients.

4 RESULTS OF CALCULATION

Using the Microsoft Excel and the methods described earlier, the annual pollution load was calculated for two stations at the Narva River (Vasknarva and Narva city) and for Kavastu station at Emajõgi.

Results of calculations are presented in form of tables showing the total annual pollution load.

4.1 Narva River

Tables 4.1.1 – 4.1.3 show annual BOD_5, COD, NH_4, NO_3, N_{tot}, PO_4 and P_{tot} pollution load with Narva River at Vasknarva station from 1996 to 2018.

Table 4.1.1 Results of pollution load calculations for Vasknarva station on Narva River using I method

Year	Average annual water flow	Total annual pollution load						
		BOD_5	COD	NH_4	NO_3	N_{tot}	PO_4	P_{tot}
	m^3/s	t/a	t/a	t/a	t/a	t/a	t/a	t/a
1996	197	13152,29	69365,34	127,19	1219,00	3296,80	100,12	178,97
1997	300	22268,28	102987,57	215,66	724,37	4368,87	162,58	262,18
1998	450	28875,73	160727,69	507,12	2477,20	12770,09	230,29	376,96
1999	415	24815,93	150539,58	954,56	1913,20	9687,34	233,36	575,10
2000	268	15126,26	91577,99	249,38	1009,60	4389,63	217,66	473,91
2001	303	16876,30	102052,34	288,95	1227,97	5539,65	280,62	523,79
2002	290	15022,55	109506,92	444,71	797,13	4938,21	161,89	292,34
2003	245	12858,86	93373,94	229,79	520,42	2984,56	182,50	339,78
2004	378	16523,25	154764,37	396,75	627,11	5884,37	225,09	379,90
2005	360	18388,45	152580,15	225,51	614,78	6779,64	290,66	473,65
2006	200	11384,24	74903,68	181,43	608,26	5251,23	115,80	210,34
2007	258	15165,74	100494,83	261,36	1605,58	5682,61	250,28	311,93
2008	317	16510,56	141567,15	235,62	1418,90	7155,51	426,65	556,51
2009	396	20247,86	181256,43	265,74	1656,19	10708,66	399,69	688,30
2010	461	25733,90	201045,75	286,84	2318,29	12815,42	291,96	601,84
2011	381	20225,59	147489,90	194,99	1218,89	9157,55	297,06	616,80
2012	328	19373,85	147733,70	303,87	2145,84	8318,76	179,28	456,84
2013	372	21988,93	159272,21	214,52	899,68	6652,17	148,21	388,04
2014	281	16491,69	129243,24	171,36	911,98	4636,45	75,72	181,40
2015	276	15096,53	90717,11	172,31	1089,25	4425,46	88,00	171,93
2016	276	17883,29	124006,64	265,43	599,91	4450,75	105,62	256,03
2017	381	22754,39	203528,26	217,43	1294,01	6935,96	124,52	398,59
2018	329	21746,12	165700,94	271,05	1335,27	5982,40	77,82	256,09

Table 4.1.2 Results of pollution load calculations for Vasknarva station on Narva River using II method

Year	Average annual water flow	Total annual pollution load						
		BOD_5	COD	NH_4	NO_3	N_{tot}	PO_4	P_{tot}
	m^3/s	t/a	t/a	t/a	t/a	t/a	t/a	t/a
1996	206	13914,91	74144,61	140,50	1338,18	3116,86	100,99	161,91
1997	306	21469,58	100146,72	218,22	648,30	4499,86	147,77	266,21
1998	446	27541,53	161931,53	513,07	2676,62	13203,15	236,96	376,08
1999	418	25320,86	151065,02	943,78	1908,10	9902,69	224,23	563,72
2000	270	14329,56	87097,08	253,98	1090,02	4219,24	186,38	406,21
2001	305	16800,35	102668,87	281,40	1272,88	5631,71	279,56	513,72
2002	293	15260,71	110036,40	446,75	797,17	4891,04	160,70	292,53
2003	241	12641,48	92944,96	216,31	495,96	2920,48	180,64	330,80
2004	384	17024,19	159781,77	402,61	636,09	5998,31	225,56	390,06
2005	374	18936,50	153881,16	236,82	627,00	6931,51	301,74	489,25
2006	204	11510,50	76934,76	186,84	650,41	5449,86	116,82	214,28
2007	256	15113,77	99668,28	254,34	1567,81	5597,37	253,43	315,91
2008	327	17131,03	145368,95	243,83	1435,89	7389,08	455,11	594,76
2009	400	20392,29	182912,86	268,50	1696,10	10738,16	395,15	685,40
2010	465	25970,08	203707,48	287,87	2318,15	12837,89	292,07	610,40
2011	393	20905,39	152175,54	196,17	1266,38	9619,69	311,08	637,81
2012	325	19162,05	146532,50	302,45	2106,06	8172,87	175,60	464,74
2013	364	21516,25	153932,83	208,68	846,75	6460,66	143,36	379,58
2014	282	16584,76	130606,04	170,51	898,37	4639,85	74,88	181,10
2015	275	14892,91	90859,81	166,87	1094,65	4426,01	88,34	173,85
2016	277	18180,40	122876,93	267,67	590,57	4377,10	106,95	240,32
2017	379	22204,07	202879,62	215,28	1203,63	6929,10	120,33	397,56
2018	329	21714,14	167076,52	279,77	1322,28	5989,68	77,44	253,43

Table 4.1.3 Results of pollution load calculations for Vasknarva station on Narva River using III method

Year	**Average annual water flow**	**Total annual pollution load**						
		BOD_5	**COD**	**NH_4**	**NO_3**	**N_{tot}**	**PO_4**	**P_{tot}**
	m^3/s	**t/a**	**t/a**	**t/a**	**t/a**	**t/a**	**t/a**	**t/a**
1996	206	14140,86	74643,81	148,07	1301,49	3204,44	98,26	160,61
1997	307	21875,50	101698,15	230,25	681,18	4438,66	152,31	257,20
1998	445	26091,84	159469,52	506,31	2676,44	12889,39	247,57	375,08
1999	418	25370,35	151161,51	940,63	1909,54	9912,08	224,47	564,50
2000	270	14314,32	91291,02	262,53	1017,15	4274,75	189,99	429,31
2001	305	16782,73	102600,01	282,52	1277,23	5634,12	278,16	511,12
2002	293	15303,12	110986,22	454,35	802,30	4934,91	161,15	294,17
2003	241	12628,67	92741,59	215,50	499,77	2917,92	180,38	330,94
2004	384	17018,62	159461,22	401,57	637,69	5999,74	225,65	390,55
2005	374	18988,89	154442,30	239,50	629,62	6935,13	299,73	487,54
2006	204	11530,80	76910,00	186,19	646,09	5448,68	117,05	214,13
2007	256	15113,04	99456,66	253,43	1575,25	5601,03	252,99	315,55
2008	327	17121,53	145593,22	243,51	1444,41	7393,05	454,13	593,32
2009	400	20410,04	182769,52	269,03	1688,35	10708,73	394,13	680,61
2010	465	25908,40	203984,05	285,99	2336,53	12859,46	293,08	609,57
2011	393	20925,71	151990,38	195,67	1268,18	9581,43	310,07	635,95
2012	325	19165,81	146780,64	301,60	2103,68	8163,40	175,13	463,63
2013	364	21531,20	153985,03	210,50	849,01	6480,17	143,70	378,48
2014	282	16610,80	130559,04	170,70	904,61	4643,23	75,27	180,91
2015	275	14892,09	90947,20	168,94	1099,68	4422,42	88,63	173,99
2016	277	18192,37	123150,01	269,26	589,60	4379,18	106,80	240,39
2017	379	22164,29	203408,78	214,86	1195,85	6922,70	121,06	399,62
2018	329	21707,81	167435,14	281,38	1332,42	5998,33	77,69	252,88

Tables 4.1.4 – 4.1.6 show annual BOD_5, COD, NH_4, NO_3, N_{tot}, PO_4 and P_{tot} pollution load with Narva River at Narva city station from 2003 to 2018.

Table 4.1.4 Results of pollution load calculations for Narva city station on Narva River using I method

Year	Average annual water flow	Total annual pollution load						
		BOD_5	COD	NH_4	NO_3	N_{tot}	PO_4	P_{tot}
	m^3/s	t/a	t/a	t/a	t/a	t/a	t/a	t/a
2003	392	23149,40	154225,87	402,78	1762,31	6897,47	306,26	691,72
2004	488	28178,77	190290,26	479,36	1640,10	8771,79	403,27	740,80
2005	459	22529,12	177725,87	279,94	1151,18	10269,57	408,82	1194,94
2006	287	17433,49	137427,61	291,20	1418,28	7057,07	214,15	433,11
2007	351	17988,64	146511,33	217,08	2759,18	7123,47	360,43	435,50
2008	441	21209,93	249904,95	264,20	2232,39	11047,57	475,85	618,61
2009	495	23842,10	242157,39	306,90	3167,78	13753,53	397,33	537,97
2010	573	25603,15	259766,17	441,06	2893,71	17559,62	347,74	719,54
2011	514	28243,03	232551,94	297,20	2377,15	13490,84	337,20	906,43
2012	435	24614,20	192177,96	504,67	2956,33	9796,61	217,60	471,92
2013	486	27144,53	193362,61	342,70	2119,23	8992,19	216,39	443,37
2014	411	22979,06	194468,93	390,28	1867,88	7287,93	123,50	261,14
2015	390	20466,59	138084,61	280,12	1778,57	6877,60	141,07	240,91
2016	409	26446,42	198607,87	411,18	1310,36	7452,26	114,32	325,93
2017	579	34653,18	328943,26	343,55	1853,35	11476,11	246,40	601,62
2018	433	25168,73	212307,87	242,93	1702,01	8062,71	125,90	366,34

Table 4.1.5 Results of pollution load calculations for Narva city station on Narva River using II method

Year	Average annual water flow	Total annual pollution load						
		BOD_5	COD	NH_4	NO_3	N_{tot}	PO_4	P_{tot}
	m^3/s	t/a	t/a	t/a	t/a	t/a	t/a	t/a
2003	418	24663,33	162506,63	435,52	1984,62	7468,51	335,13	747,94
2004	494	28354,61	194836,03	442,63	1366,45	8709,85	425,34	793,99
2005	498	24272,31	189080,11	312,66	1275,49	11071,19	447,36	1239,55
2006	311	18214,23	146908,94	325,21	1614,35	7541,81	235,96	451,02
2007	365	18504,15	154237,56	211,69	2882,73	7249,95	381,39	459,20
2008	466	22488,02	266451,64	273,74	2414,69	11608,65	501,39	652,33
2009	533	24999,90	261505,67	331,64	3380,69	15054,13	423,50	574,16
2010	563	25153,21	255673,51	432,85	2975,37	17552,85	336,83	694,72
2011	560	30478,08	254575,35	311,21	2585,12	14785,70	373,01	1032,24
2012	471	26881,59	211292,50	528,67	3179,54	10569,87	234,71	519,76
2013	462	25674,68	183642,51	319,08	2045,41	8547,92	209,13	422,11
2014	441	25038,42	217918,05	407,69	2029,68	7864,95	133,73	284,14
2015	361	18942,38	128583,04	249,54	1596,13	6371,97	135,22	233,27
2016	426	28039,77	211554,55	418,52	1263,47	7784,97	119,06	358,03
2017	544	32666,60	313785,95	328,08	1784,35	10824,02	227,58	563,44
2018	402	23437,49	194419,35	235,93	1653,71	7512,76	112,84	332,89

Table 4.1.6 Results of pollution load calculations for Narva city station on Narva River using III method

Year	Average annual water flow	Total annual pollution load						
		BOD_5	COD	NH_4	NO_3	N_{tot}	PO_4	P_{tot}
	m^3/s	t/a	t/a	t/a	t/a	t/a	t/a	t/a
2003	418	24624,81	161990,18	436,14	1987,18	7463,55	335,54	748,60
2004	494	28280,24	194195,79	445,95	1378,78	8699,43	424,94	791,47
2005	498	24328,48	190120,56	313,70	1277,31	11110,55	446,92	1240,31
2006	303	17574,67	140913,96	333,84	1552,49	7367,17	231,29	447,53
2007	365	18478,24	153730,12	210,57	2876,92	7238,33	378,19	455,56
2008	466	22498,93	267272,52	274,03	2418,53	11620,55	500,61	650,98
2009	533	24988,66	260813,23	331,04	3354,43	14933,93	421,55	571,24
2010	563	25222,49	256012,40	433,06	3003,38	17557,09	338,24	694,43
2011	560	30411,48	254227,46	310,46	2600,41	14762,24	372,17	1029,22
2012	471	26879,83	211785,75	529,13	3187,25	10581,99	234,69	519,45
2013	462	25726,28	183163,72	319,83	2055,65	8570,04	209,25	421,98
2014	441	25081,11	218001,01	413,94	2041,18	7877,80	134,12	284,46
2015	361	18907,41	128560,45	251,54	1596,01	6361,76	135,51	233,37
2016	426	27998,21	211271,89	419,99	1272,38	7777,16	118,86	356,79
2017	544	32608,49	312260,01	327,33	1783,71	10783,42	226,23	560,31
2018	402	23421,79	194842,55	236,83	1666,41	7525,65	113,11	332,62

The comparison of results obtained by the three methods is provided in Chapter 5.

4.2 Emajõgi

Tables 4.2.1 – 4.2.3 present annual BOD_5, COD, NH_4, NO_3, N_{tot}, PO_4 and P_{tot} pollution load with Emajõgi at Kavastu station from 1992 to 2018.

Table 4.2.1 Results of pollution load calculations for Kavastu station on Emajõgi using I method

Year	Average annual water flow	Total annual pollution load						
		BOD_5	COD	NH_4	NO_3	N_{tot}	PO_4	P_{tot}
	m^3/s	t/a	t/a	t/a	t/a	t/a	t/a	t/a
1992	69,61	6347,31	29170,41	538,46	2445,28	4997,33	42,92	134,63
1993	51,09	4481,75	21215,66	507,33	1968,26	3717,58	52,17	132,33
1994	65,57	6012,24	29233,32	671,36	1737,53	3950,42	82,22	173,45
1995	72,99	5662,69	28800,05	355,61	1590,11	3761,15	58,22	156,66
1996	31,71	3329,28	10350,84	267,30	1381,55	2492,38	32,05	103,29
1997	54,15	5134,33	21832,56	301,85	2657,99	4681,40	33,62	129,54
1998	79,02	5863,21	40558,02	363,97	2600,66	4896,50	43,36	182,39
1999	73,77	5327,28	32914,01	466,89	1775,70	3445,21	45,99	165,05
2000	57,19	5159,15	22140,56	365,00	2154,31	3722,36	30,95	136,04
2001	62,26	5234,52	29745,01	380,73	2737,89	4192,75	45,83	157,28
2002	65,68	4907,82	28087,65	422,66	3036,66	4954,97	29,36	127,68
2003	51,32	3438,62	28015,81	473,68	2554,59	4343,44	52,47	148,27
2004	76,63	4460,24	41118,86	315,68	3885,33	5671,32	31,69	143,32
2005	73,36	4293,41	30689,64	343,33	3153,21	4786,99	26,77	135,46
2006	39,52	3128,67	14946,26	311,57	1918,94	2883,39	23,38	101,90
2007	55,57	3806,99	23754,07	219,06	3539,38	5045,67	18,30	97,08
2008	86,38	5025,88	49998,95	279,50	6480,17	8603,24	41,42	145,62
2009	91,90	5861,08	49868,59	376,88	4028,07	5886,52	54,69	148,40
2010	93,51	5957,86	50696,30	345,95	3834,66	5967,18	41,18	159,66
2011	78,23	4852,36	37807,27	365,26	3326,25	5221,48	43,68	122,55
2012	81,89	4156,05	46486,67	269,55	5631,83	7001,43	38,49	129,67
2013	68,18	4119,62	34077,92	345,72	2942,29	4278,91	25,50	88,96
2014	47,55	3182,34	22469,50	153,34	2423,92	3568,04	19,91	75,78
2015	59,88	4454,43	27800,11	121,81	3862,07	5328,44	25,87	89,19
2016	76,84	5121,26	44554,74	202,59	5368,13	7762,58	36,93	130,57
2017	71,42	4606,53	36987,07	138,62	3755,57	5226,57	24,24	92,21
2018	59,66	4138,49	27226,59	144,21	2381,78	4129,54	27,99	88,88

Table 4.2.2 Results of pollution load calculations for Kavastu station on Emajõgi using II method

Year	Average annual water flow	Total annual pollution load						
		BOD_5	COD	NH_4	NO_3	N_{tot}	PO_4	P_{tot}
	m^3/s	t/a	t/a	t/a	t/a	t/a	t/a	t/a
1992	70,08	6532,69	29888,93	536,68	2481,87	4947,21	41,21	136,22
1993	49,83	4401,72	21005,58	488,77	1950,29	3668,20	50,78	129,21
1994	66,01	6119,22	29491,28	707,28	1710,31	3994,30	87,48	179,89
1995	71,57	5478,95	28615,73	331,02	1580,01	3695,20	56,27	150,88
1996	33,16	3731,59	12127,50	284,53	1636,77	2824,99	36,63	114,05
1997	53,46	4993,22	21752,30	293,23	2818,09	4933,92	36,77	130,29
1998	74,29	5427,09	38318,86	332,68	2561,12	4729,95	40,36	171,62
1999	75,27	5508,37	33745,61	457,22	1781,02	3448,02	45,89	168,06
2000	54,61	4817,31	21099,61	334,81	2016,89	3508,99	26,84	125,42
2001	56,72	4939,50	27600,23	342,70	2527,91	3841,34	46,96	152,18
2002	65,37	4912,60	27935,22	416,60	3000,97	4862,12	27,85	124,78
2003	50,49	3379,46	27862,26	467,96	2450,96	4253,53	53,03	151,17
2004	75,25	4393,63	41628,94	304,09	3984,51	5768,91	35,67	143,68
2005	72,18	4287,20	30327,39	324,20	3060,15	4653,32	26,17	133,59
2006	39,87	3181,18	14947,68	323,78	1922,61	2892,74	26,02	106,04
2007	52,51	3566,40	22393,86	203,44	3240,94	4683,05	18,18	93,67
2008	82,93	4825,07	48321,06	250,99	6397,69	8499,30	40,21	140,33
2009	88,87	5765,83	49017,77	363,56	3987,18	5726,93	54,77	146,56
2010	96,68	6155,67	52476,19	363,40	4173,73	6357,07	43,68	165,46
2011	78,94	4921,69	37768,34	358,60	3123,50	4985,11	41,90	120,32
2012	86,74	4318,35	50333,07	279,19	6384,88	7876,87	40,82	135,15
2013	68,35	4028,22	34608,67	325,89	3016,07	4338,47	27,05	90,23
2014	46,41	3062,03	22305,25	148,03	2250,28	3380,58	18,35	74,13
2015	59,41	4361,32	27779,32	117,46	4137,06	5625,53	23,08	86,61
2016	78,45	5205,62	46062,78	210,61	5487,02	8027,01	41,12	136,91
2017	72,44	4459,49	37292,15	143,87	3980,48	5442,61	24,84	94,08
2018	60,46	4153,56	28664,80	129,67	2610,41	4136,76	27,96	88,34

Table 4.2.3 Results of pollution load calculations for Kavastu station on Emajõgi using III method

Year	Average annual water flow	Total annual pollution load						
		BOD_5	COD	NH_4	NO_3	N_{tot}	PO_4	P_{tot}
	m^3/s	t/a	t/a	t/a	t/a	t/a	t/a	t/a
1992	73,22	6789,46	31532,76	541,69	2674,19	5153,49	42,73	138,64
1993	49,83	4402,65	21069,35	489,59	1978,77	3693,02	50,92	129,30
1994	66,01	6098,38	29427,00	704,71	1714,33	3983,88	87,37	179,03
1995	71,57	5480,08	28524,11	332,79	1588,91	3703,94	56,63	151,22
1996	33,16	3456,69	11219,74	264,26	1516,67	2614,77	33,88	105,74
1997	53,46	5002,63	21721,24	294,02	2802,26	4910,88	36,65	130,09
1998	74,29	5424,26	38144,54	333,81	2555,29	4723,11	40,07	171,01
1999	75,27	5512,95	33829,01	457,47	1810,13	3481,49	46,39	168,25
2000	54,61	4818,31	21098,73	335,17	2023,32	3518,21	26,92	125,49
2001	56,72	4928,29	27506,52	341,36	2525,96	3835,67	46,65	151,27
2002	65,37	4924,36	28090,46	416,42	3045,55	4921,86	28,46	125,53
2003	50,49	3369,21	27818,13	469,16	2440,27	4240,63	52,98	151,01
2004	75,25	4399,30	41615,71	304,48	3992,05	5776,67	35,60	143,59
2005	72,18	4280,40	30511,73	324,41	3103,99	4701,70	26,45	133,75
2006	39,87	3182,60	14928,55	326,43	1924,04	2896,51	26,24	106,51
2007	52,51	3560,86	22530,22	203,05	3282,55	4725,12	18,11	93,95
2008	82,93	4821,51	48389,01	251,16	6415,62	8511,66	40,12	140,60
2009	88,87	5771,92	48815,01	364,67	4009,74	5748,18	55,18	146,67
2010	96,68	6142,47	52335,54	365,08	4182,84	6356,49	43,65	164,72
2011	78,94	4907,09	37774,16	360,78	3150,80	5007,85	42,16	120,62
2012	86,74	4305,01	50376,48	279,10	6416,61	7906,02	41,07	135,22
2013	68,35	4016,50	34490,07	327,31	3007,25	4327,56	27,04	90,05
2014	46,41	3069,23	22293,72	147,94	2262,16	3391,19	18,34	74,05
2015	59,41	4364,23	27844,50	118,35	4145,03	5635,36	23,02	86,64
2016	78,45	5215,47	45962,61	211,14	5489,00	8013,81	41,36	137,31
2017	72,44	4454,70	37178,46	145,04	3969,21	5438,17	24,74	93,75
2018	60,46	4136,64	28652,91	129,70	2620,20	4149,17	27,96	88,46

The average annual water flow was calculated for further analysis of the pollution load. In the method I it is presented as an average of 365 (or 366) days in a year. In methods II and III only the water flows on days when samples of chemical analysis were taken are included in calculations. This also affects the pollution load values as it is a product of concentration and water flow.

5 INTERPRETETION OF RESULTS

5.1 Comparison of the pollution load calculation results obtained by different methods

To compare the results of the three methods used for annual pollution load calculations, column charts are built for each pollutant. In this chapter results for BOD_5, NH_4, N_{tot} and P_{tot} quality indicators are shown as they define water quality class (Keskkonnaministeerium, 2009). Column charts of COD, NO_3 and PO_4 are shown in Appendices 4, 5 and 6.

In Figures 5.1.1-5.1.4 the total pollution loading with Narva River at Vasknarva station is shown from year 1996 to 2018.

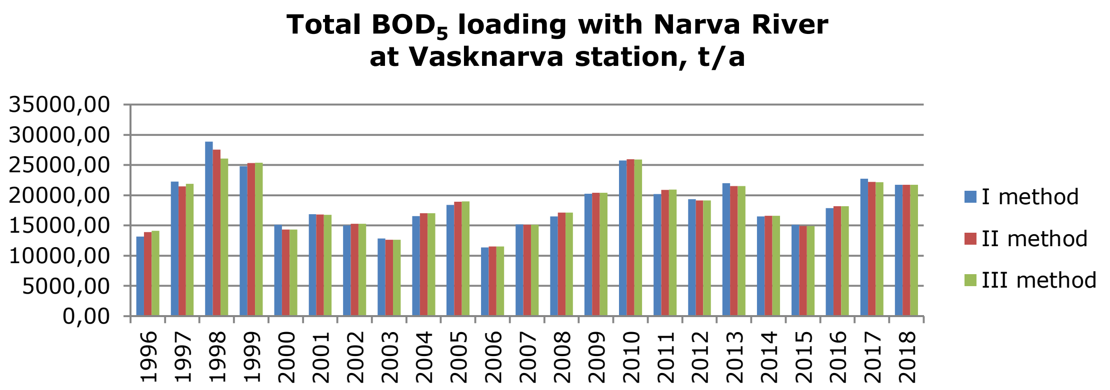

Figure 5.1.1 Total biochemical oxygen demand input with Narva River at Vasknarva station calculated by three different methods

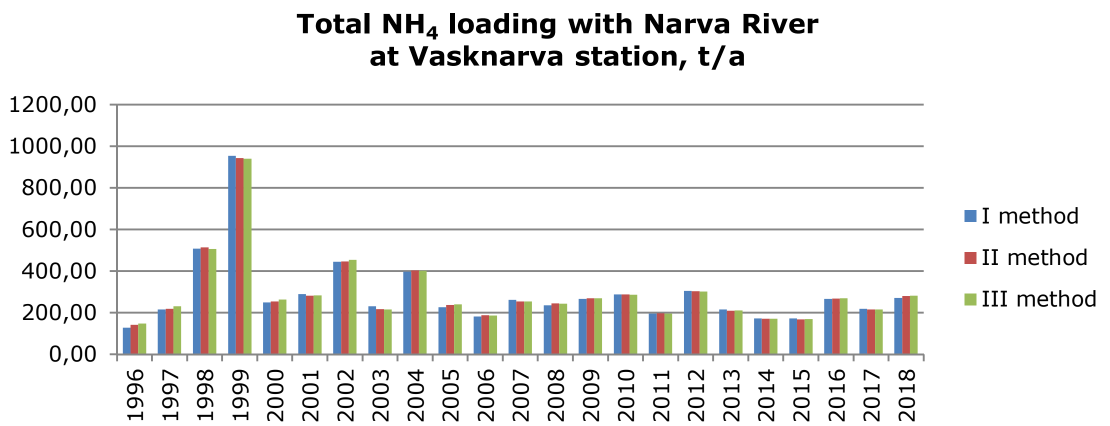

Figure 5.1.2 Total ammonia input with Narva River at Vasknarva station calculated by three different methods

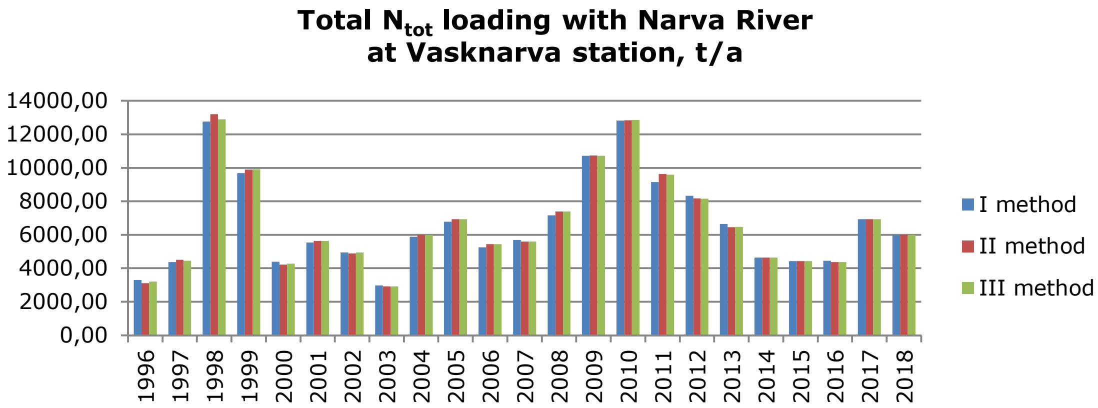

Figure 5.1.3 Total nitrogen input with Narva River at Vasknarva station calculated by three different methods

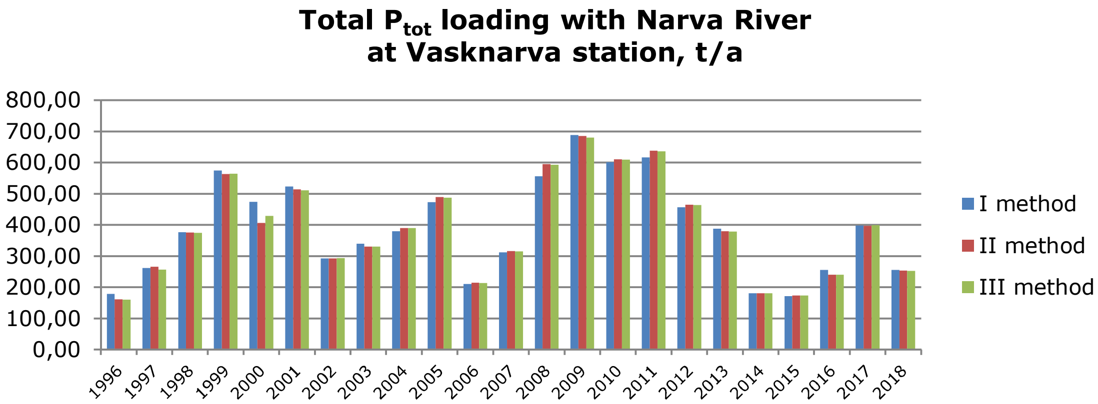

Figure 5.1.4 Total phosphorous input with Narva River at Vasknarva station calculated by three different methods

In Figures 5.1.5-5.1.8 total pollution loading with Narva River at Narva city station is shown from year 2003 to 2018.

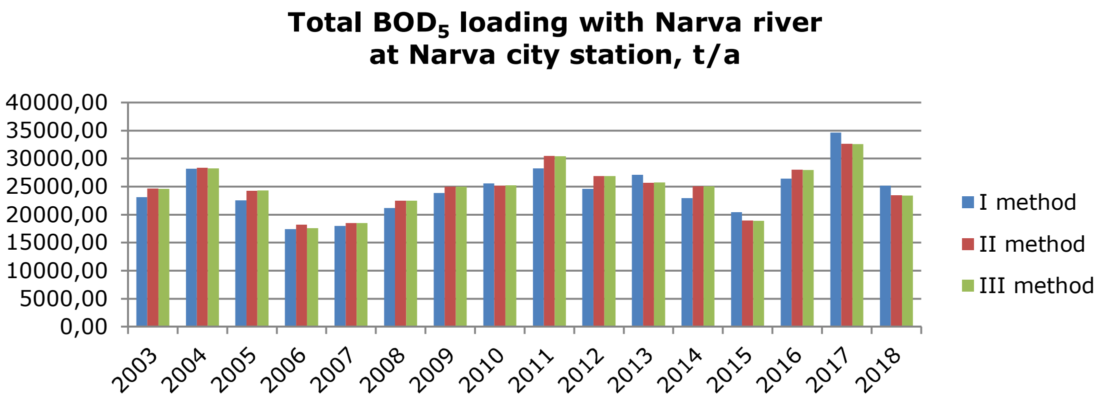

Figure 5.1.5 Total biochemical oxygen demand input with Narva River at Narva city station calculated by three different methods

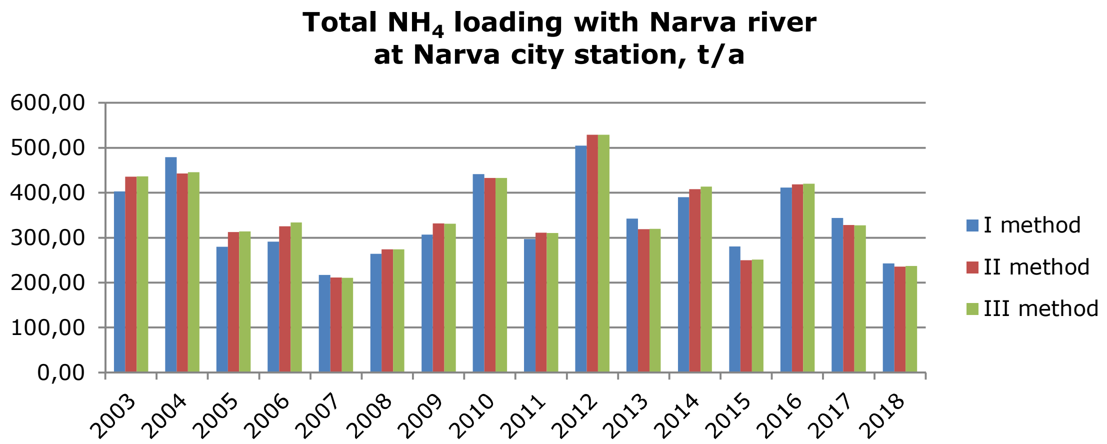

Figure 5.1.6 Total ammonia input with Narva River at Narva city station calculated by three different methods

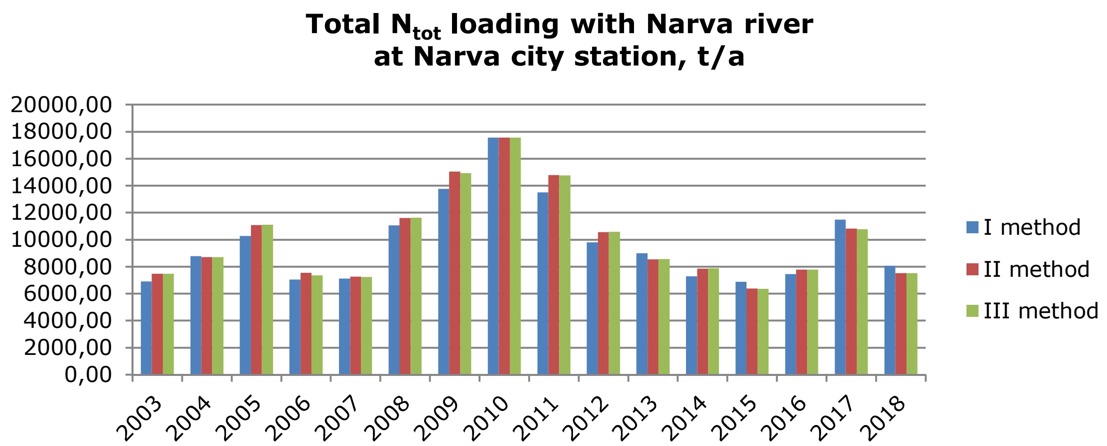

Figure 5.1.7 Total nitrogen loading with Narva River at Narva city station calculated by three different methods

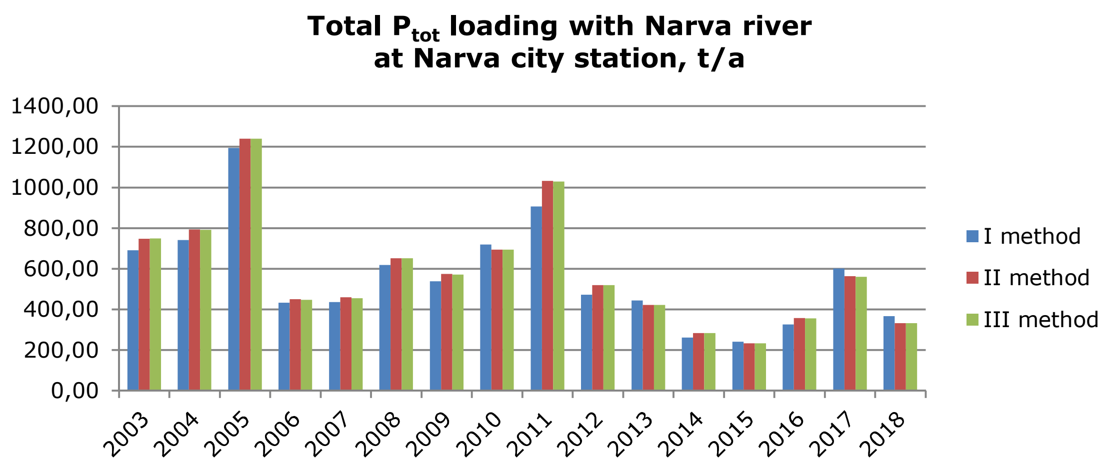

Figure 5.1.8 Total phosphorous input with Narva River at Narva city station calculated by three different methods

In Figures 5.1.9-5.1.12 total pollution loading with Emajõgi at Kavastu station is shown from year 1992 to 2018.

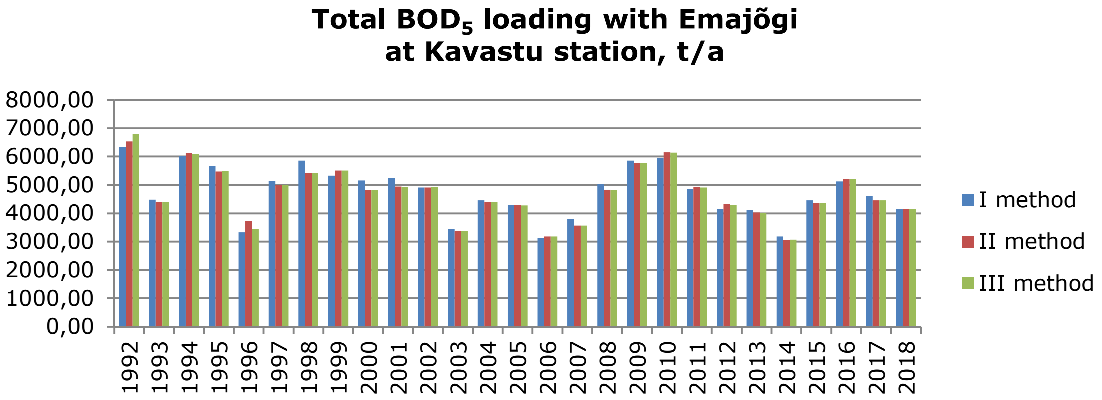

Figure 5.1.9 Total biochemical oxygen demand input with Emajõgi at Kavastu station calculated by three different methods

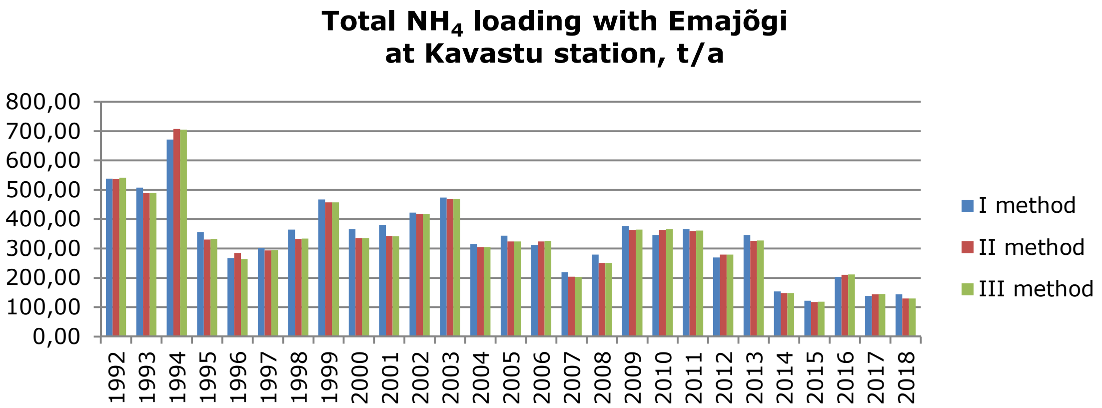

Figure 5.1.10 Total ammonia input with Emajõgi at Kavastu station calculated by three different methods

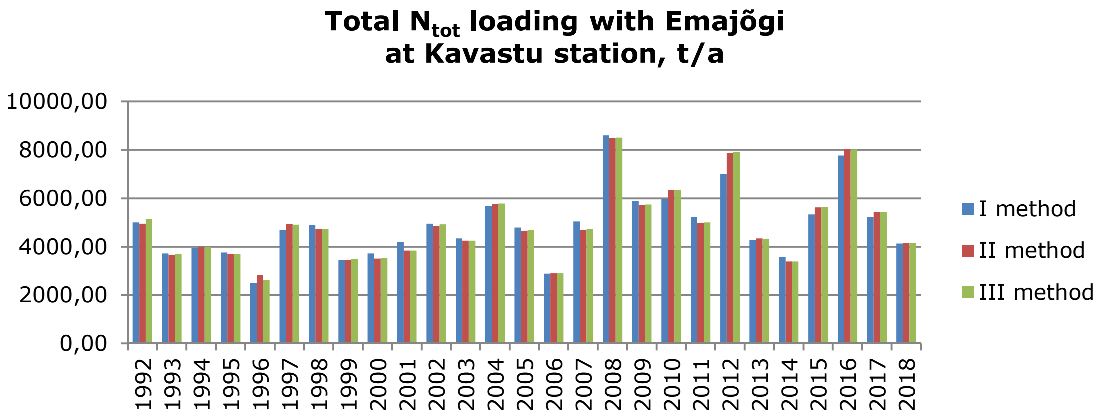

Figure 5.1.11 Total nitrogen input with Emajõgi at Kavastu station calculated by three different methods

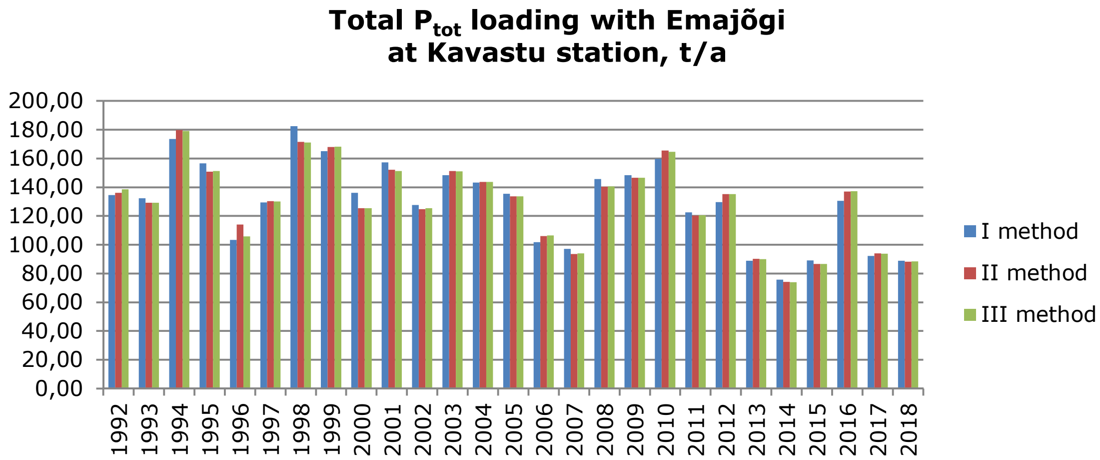

Figure 5.1.12 Total phosphorous input with Emajõgi at Kavastu station calculated by three different methods

On the charts it is seen that the methods give different values of annual pollution load. The differences are not constant and are analysed separately for each of the quality criteria by the standard deviation (see Chapter 2.4). In Tables 5.1.1-5.1.3 the average, maximum and minimum standard deviations and the years when they occurred during the period of observations are shown for each water quality indicator. This data is used in the following comparison of results obtained by different methods to make a conclusion about the most reliable one.

Table 5.1.1 Standard deviation of pollution load calculated for Vasknarva station on Narva River

Quality indicator	**Standard deviation**				
	Average	**Maximum**		**Minimum**	
	t	**t**	**Year**	**t**	**Year**
BOD_5	269,67	1392,34	1998	20,54	2018
COD	1269,44	3067,73	2013	116,14	2015
NH_4	4,14	10,57	1992	0,45	2014
NO_3	24,65	115,08	1998	2,63	1999
N_{tot}	74,55	256,49	2011	1,93	2015
PO_4	3,83	17,12	2000	0,19	2018
P_{tot}	6,65	34,42	2000	0,25	2014

Table 5.1.2 Standard deviation of pollution load calculated for Narva city station on Narva River

Quality indicator	Standard deviation				
	Average	Maximum		Minimum	
	t	t	Year	t	Year
BOD_5	806,99	1308,57	2012	88,27	2004
COD	7598,20	13562,36	2014	2271,39	2010
NH_4	11,96	22,54	2006	3,48	2007
NO_3	87,09	154,56	2004	24,90	2016
N_{tot}	323,28	740,91	2011	3,42	2010
PO_4	10,91	22,12	2005	2,68	2016
P_{tot}	22,15	71,78	2011	4,38	2015

Table 5.1.3 Standard deviation of pollution load calculated for Kavastu station on Emajõgi

Quality indicator	Standard deviation				
	Average	Maximum		Minimum	
	t	t	Year	t	Year
BOD_5	90,25	252,62	1998	6,51	2005
COD	543,34	2233,35	2012	10,66	2006
NH_4	9,00	22,35	2001	2,30	2015
NO_3	89,59	444,22	2012	2,63	2006
N_{tot}	110,50	514,05	2012	6,76	2006
PO_4	1,16	3,00	1994	0,01	2018
P_{tot}	2,32	6,40	1998	0,19	2004

From tables 5.1.1-5.1.3 we can estimate what is the difference in the results of different methods. For example, for Kavastu station the results of the methods differ from the most probable annual load of BOD_5 on average on 90.25 t.

The visual analysis of result graphs shows that the general tendency for each of the stations is that II and III methods give very close results while the method I almost for every year gives the result which differs from another two methods. This is supported by z-scores (see Chapter 2.4).

The average z-score for Vasknarva station of I the method is 1.04, the II – 0.58, and the III – 0.62. The average z-score for Narva city station of I the method is 1.14, the II – 0.61, and the III – 0.55. The average z-score for Kavastu station of I the method is 1.07, the II – 0.64, and the III – 0.56.

Based on z-scored we can make a conclusion that the III method gives the most closest to the most probable result. Taking into account that this method is quite simple to apply, we can assume that it is the best method to calculate the pollution load. Annual loads are largely dependent on streamflow but the large load does not always mean poor water quality. The III method uses a flow-weighted concentration that computed by dividing the sum of products of mean monthly concentrations and mean monthly water flow by the sum of mean monthly water flow. In this case, we eliminate the influence of possible dilution of pollutants during high flow periods and can use this intermediate data for additional analysis as well, for example, to compare the relative water quality of different basins as described in (Sether, Berkas, & Vecchia, 2004).

5.2 Dynamics of pollution load

Although different methods give an error in the estimated pollution load, this is not significant in trend analysis. What is important, in fact, is the effect of water flow.

The analysis of trends usually is recommended to be done after flow-normalization which removes the influence of hydrology variation (HELCOM, 2015). Indeed, the flow-normalized time series can give a more precise view of the causes of pollution and detect the contribution of anthropogenic activities.

The methods of normalization are statistical and their application resulting in a new time series of pollution input. Different authors define and describe several normalization methods (U.S. Geological Survey, 1982). In this work, we are not going deep into this topic. The simplest way nevertheless is to calculate the normalized pollutant concentrations by dividing the annual load by the annual water flow.

In chapter 5.1, the method III (flow-normalized) was recognized as the best. For the subsequent analysis of the calculation results, only it will be used since it uses the concentrations normalized by water flow to estimate the amount of pollution.

Figures 5.2.1-5.2.3 show the dynamics of pollution load and the average annual water flow at Vasknarva station on Narva River calculated using the III method from 1996 to 2018.

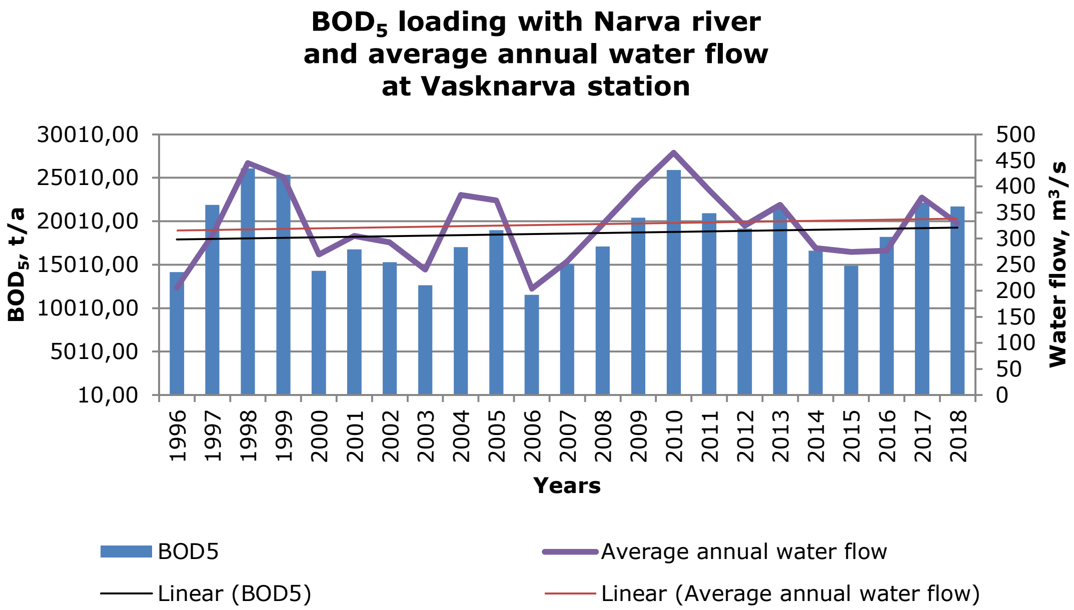

Figure 5.2.1 Dynamics of BOD_5 annual load and average annual water flow of Narva River at Vasknarva station

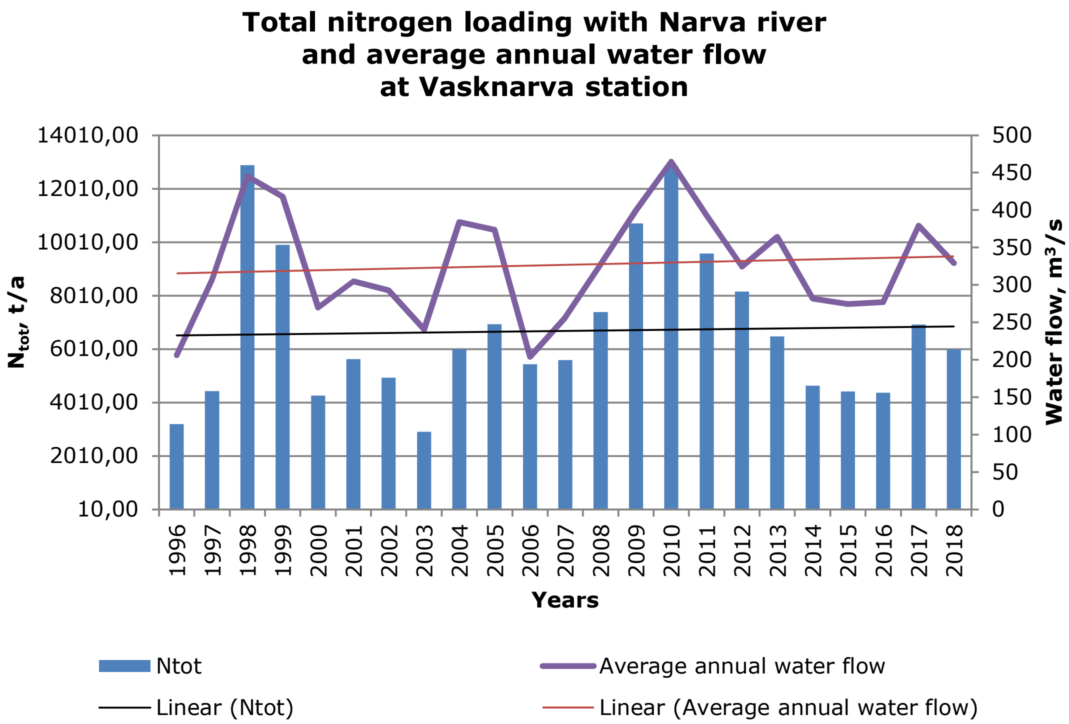

Figure 5.2.2 Dynamics of N_{tot} annual load and average annual water flow of Narva River at Vasknarva station

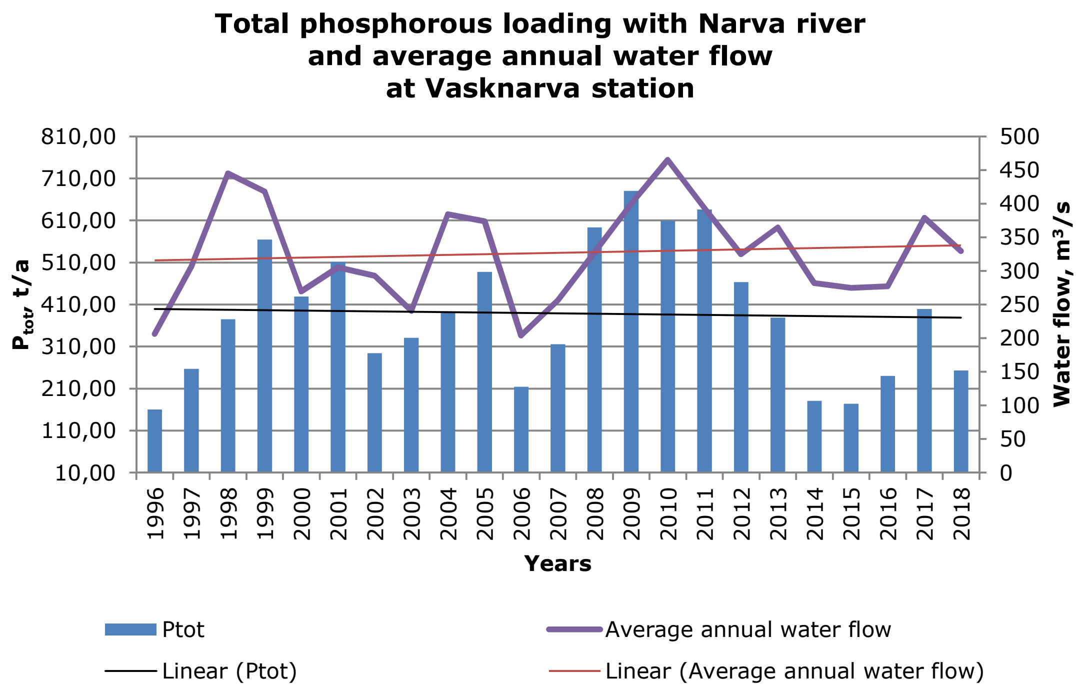

Figure 5.2.3 Dynamics of P_{tot} annual load and average annual water flow of Narva River at Vasknarva station

The trendline of BOD_5 and N_{tot} at Vasknarva station is positive for the last 22 years and proportional to the water flow trendline. This means that notwithstanding the fact that the pollution load is increasing, the concentrations are stable. At the same time an interesting situation is observed with P_{tot}. While the water flow trend is growing, the pollution load is decreasing. That shows that the measures applied in order to decrease the nutrient content in rivers are effective because of the concentrations of pollutants decrease. As the pollution at Vasknarva station depends largely on the state of the Peipsi Lake, all improvements towards the further purification of it reflect on the state of Narva River water quality as well. International projects, for instance, between Estonia and Russia, make focus on increasing the number of wastewater treatment plants and on the reduction of pollution input from Emajõgi and Velikaja river (Stalnacke, Loigu, Melnik, Nõrges, & Vetemaa, 2005).

In Figures 5.2.4-5.2.6 dynamics of pollution load and average annual water flow with Narva River at Narva city station are shown from the years 2003 to 2018.

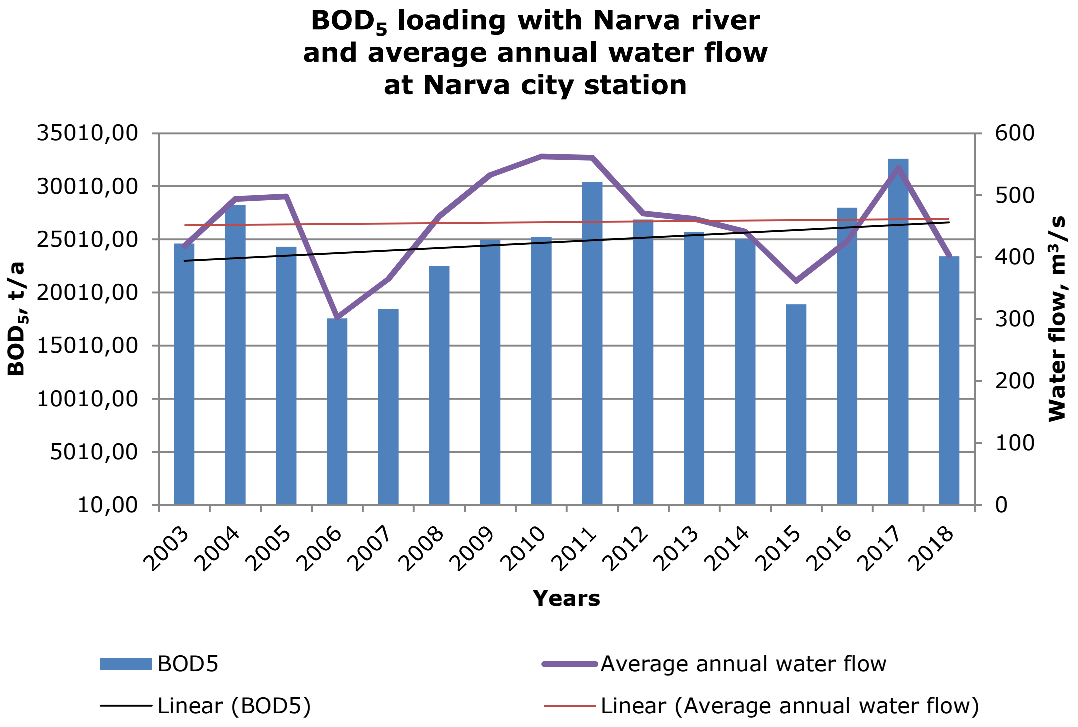

Figure 5.2.4 Dynamics of BOD_5 annual load and average annual water flow of Narva River at Narva city station

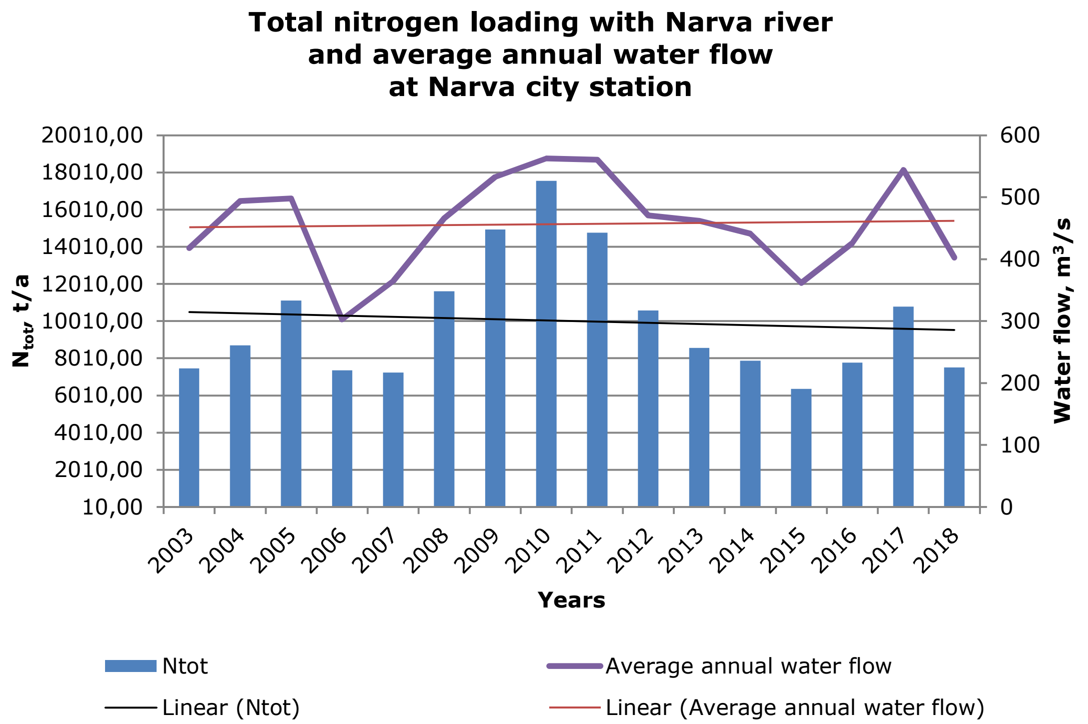

Figure 5.2.5 Dynamics of N_{tot} annual load and average annual water flow of Narva River at Narva city station

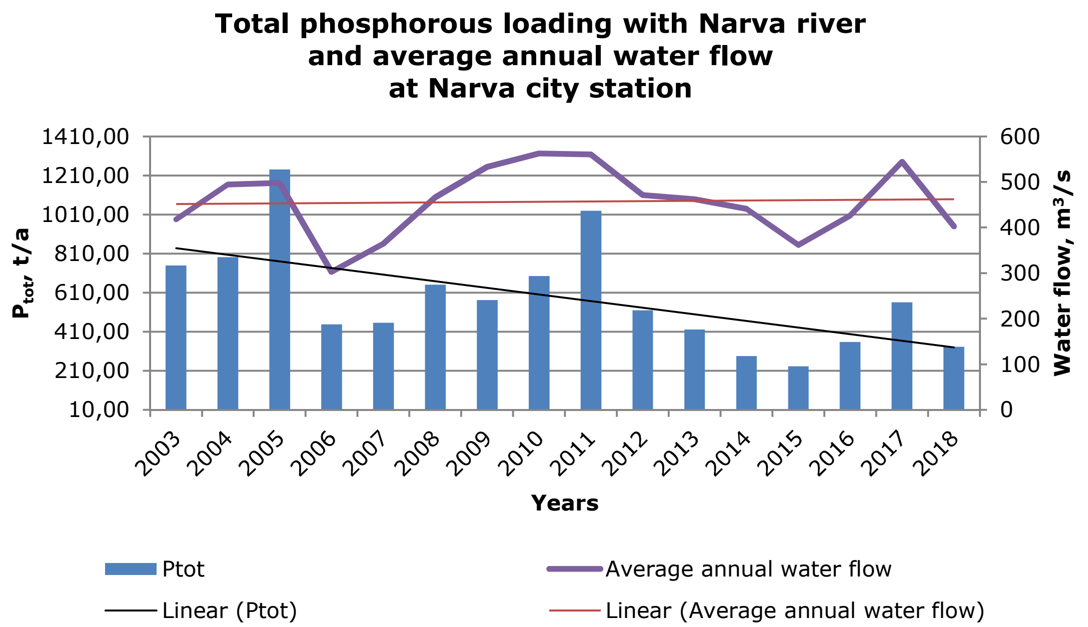

Figure 5.2.6 Dynamics of P_{tot} annual load and average annual water flow of Narva River at Narva city station

BOD_5 load is increasing for the last 15 years at Narva city station which can be explained by the fact that water flow is increased as well. As the load is growing faster than the flow the additional causes of pollution level increasing take place. As based on dynamics it is difficult to detect possible sources of pollutants, it will be done in the following chapters.

For nutrient pollution the situation is the opposite. As we can see from the figures, N_{tot} and P_{tot} load decline and, moreover, phosphorus is declining rapidly. The possible reason for it is the commissioning in 2001 of the sewage treatment plant in Ivangorod (Environmental Board, 2010). The water and wastewater pipes and wastewater treatment facility in Narva city were renovated on money received by Estonia primarily from the EU (Estonian Environment, 2010). The reducing P_{tot} content supports the tendency to decrease the level of eutrophication of water bodies as the result of the strategies of European water policy and HELCOM.

In Figures 5.2.7-5.2.9 dynamics of pollution load and average annual water flow with Emajõgi at Kavastu station are shown from the years 1992 to 2018.

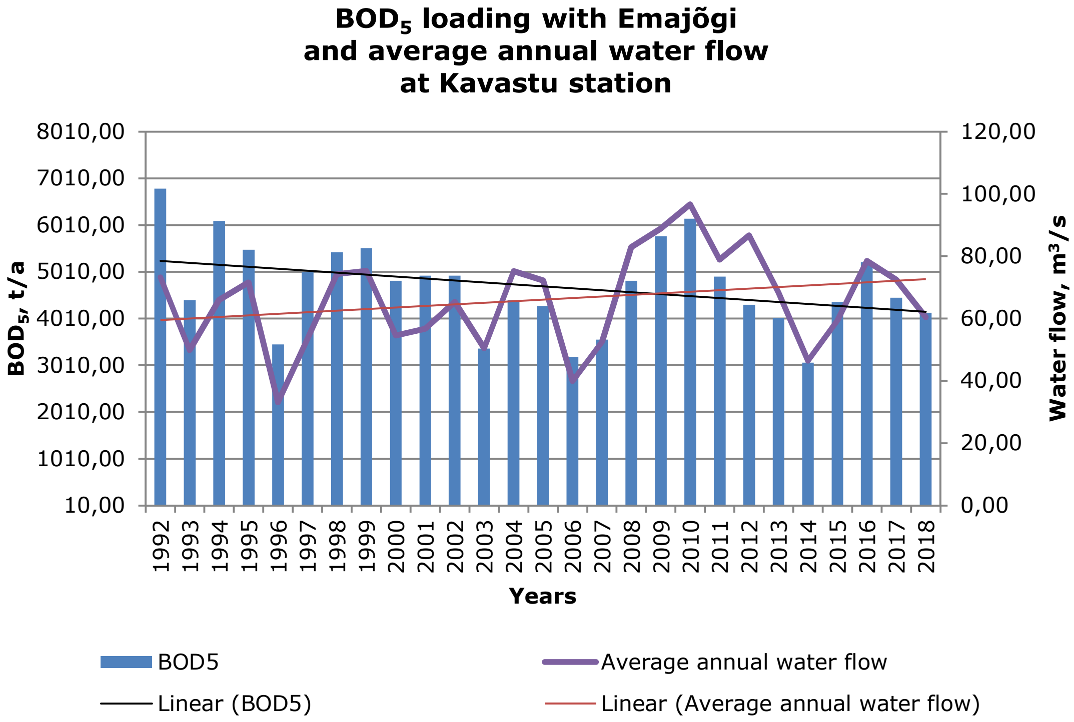

Figure 5.2.7 Dynamics of BOD_5 annual load and average annual water flow of Emajõgi at Kavastu station

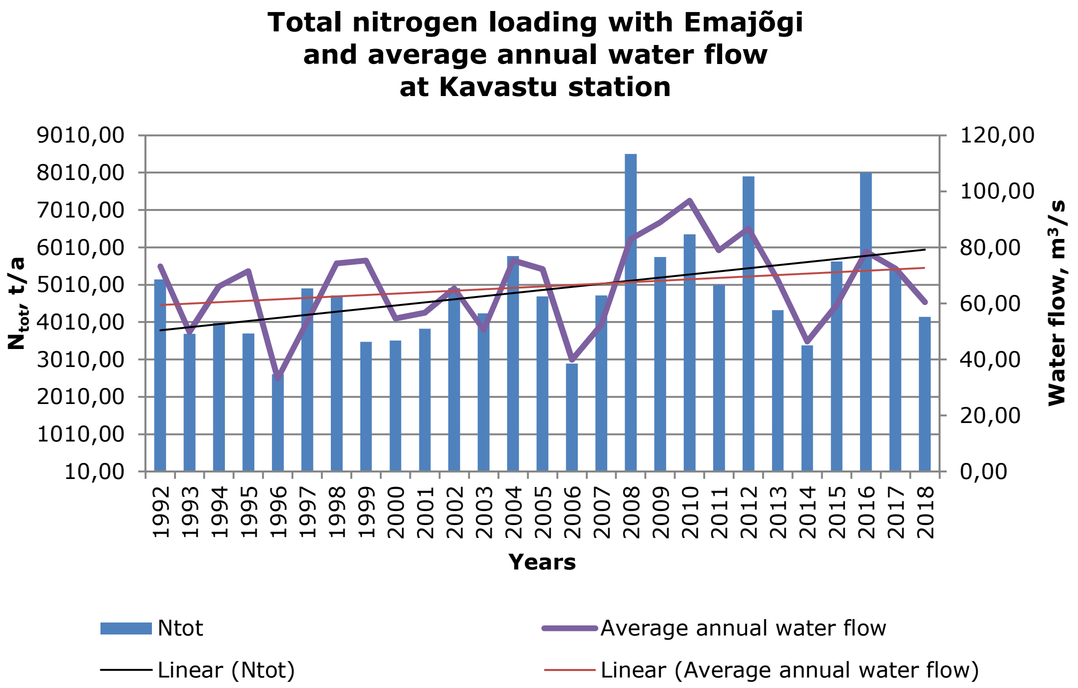

Figure 5.2.8 Dynamics of N_{tot} annual load and average annual water flow of Emajõgi at Kavastu station

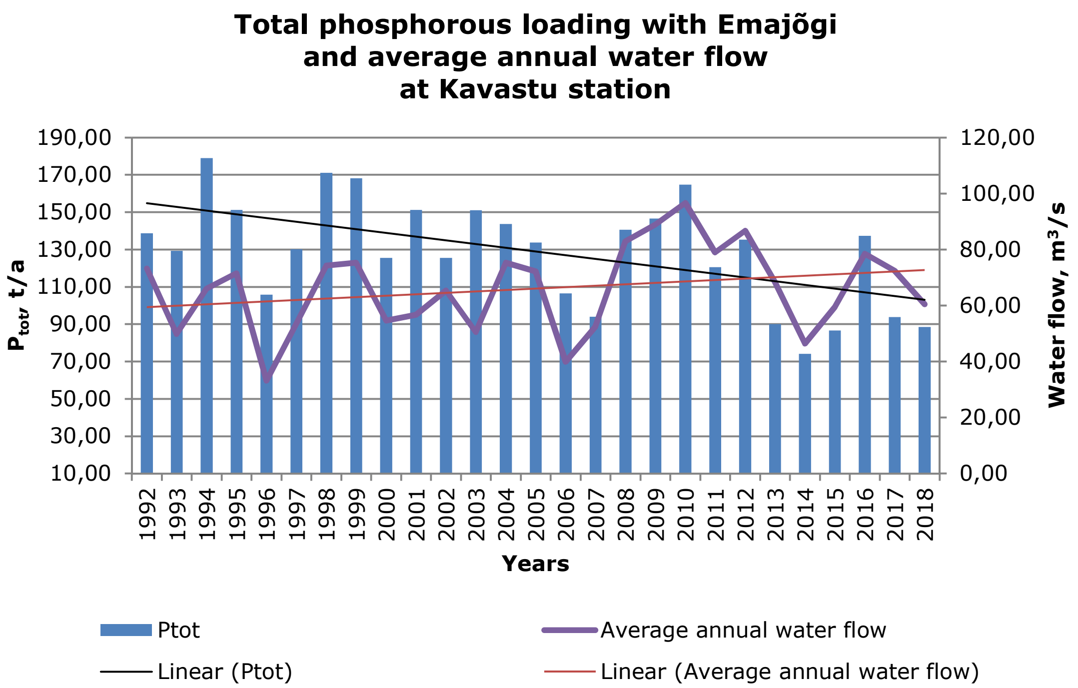

Figure 5.2.9 Dynamics of P_{tot} annual load and average annual water flow of Emajõgi at Kavastu station

At Kavastu station BOD_5 and P_{tot} load have a tendency to decrease during the period considered in this work. The reason for the phosphorous decline is probably the improved sewage systems as phosphorus enters rivers and other water bodies from untreated or badly treated sewage. In fact as it is stated in (Estonian Environment, 2010), from 2001 until 2008 Estonia received money for improvement of collection and treatment of wastewater in the Emajõgi river drainage area.

Soil erosion is another major source of phosphorus in water bodies, therefore measures towards soil protection can be effective.

Nitrogen load, as we can see, grows. That can be explained by the usage of fertilizers, from which nutrients enter the river. The catchment area of Emajõgi belongs to zone with 13-15.4% share of lands with intensive agriculture (Ministry of the Environment, 2018). The agriculture often contributes to pollution in water bodies as due to runoff, excess chemicals applied in fields can enter the water and deteriorate its quality. Moreover, this process is difficult to control and until special measures are taken on the farms, this problem will remain.

In order to summarise the results obtained, the average and pick values of water flow and pollution load are shown further. This gives a simple view of the variation of pollution during the observation period.

In Tables 5.2.1 and 5.2.6 are shown the average, minimum and maximum annual water flow and annual pollution load.

Table 5.2.1 The average, maximum and minimum annual water flow at Vasknarva station on Narva River

Hydrologic indicator	**Average**	**Maximum**		**Minimum**	
	m^3/s	**m^3/s**	**Year**	**m^3/s**	**Year**
Annual water flow	327	465	2010	204	2006

Table 5.2.2 The average, maximum and minimum annual pollution load at Vasknarva station on Narva River

Water quality indicator	Annual pollution load				
	Average	Maximum		Minimum	
	t	t	Year	t	Year
BOD_5	18599,51	26091,84	1998	11530,80	2006
COD	133715,87	203984,05	2010	74643,81	1996
NH_4	292,71	940,63	1999	148,07	1996
NO_3	1237,66	2676,44	1998	499,77	2003
N_{tot}	6684,48	12889,39	1998	2917,92	2003
PO_4	202,93	454,13	2008	75,27	2014
P_{tot}	388,70	680,61	2009	160,61	1996

In Tables 5.2.3 and 5.2.4 are shown the average, minimum and maximum annual water flow and annual pollution load for Narva River at Narva city station from the year 2003 to 2018.

Table 5.2.3 The average, maximum and minimum annual water flow at Narva city station on Narva River

Hydrologic indicator	Average	Maximum		Minimum	
	m^3/s	m^3/s	Year	m^3/s	Year
Water flow	457	563	2010	303	2006

Table 5.2.4 The average, maximum and minimum annual pollution load at Narva city station on Narva River

Water quality indicator	Annual pollution load				
	Average	Maximum		Minimum	
	t	t	Year	t	Year
BOD_5	24814,44	32608,49	2017	17574,67	2006
COD	208697,60	312260,01	2017	128560,45	2015
NH_4	349,21	529,13	2012	210,57	2007
NO_3	2128,25	3354,43	2009	1272,38	2016
N_{tot}	10014,41	17557,09	2010	6361,76	2015
PO_4	288,83	500,61	2008	113,11	2018
P_{tot}	583,65	1240,31	2005	233,37	2015

In Tables 5.2.5 and 5.2.6 are shown the average, minimum and maximum annual water flow and annual pollution load for Emajõgi at Kavastu station from the year 1992 to 2018.

Table 5.2.5 The average, maximum and minimum annual water flow at Kavastu station on Emajõgi

Hydrologic indicator	**Average**	**Maximum**		**Minimum**	
	m^3/s	**m^3/s**	**Year**	**m^3/s**	**Year**
Water flow	66,06	96,68	2010	33,16	1996

Table 5.2.6 The average, maximum and minimum annual pollution load at Kavastu station on Emajõgi

Water quality indicator	**Annual pollution load**				
	Average	**Maximum**		**Minimum**	
	t	**t**	**Year**	**t**	**Year**
BOD_5	4697,60	6789,46	1992	3069,23	2014
COD	31988,16	52335,54	2010	11219,74	1996
NH_4	327,37	704,71	1994	118,35	2015
NO_3	3135,06	6416,61	2012	1516,67	1996
N_{tot}	4865,42	8511,66	2008	2614,77	1996
PO_4	38,54	87,37	1994	18,11	2007
P_{tot}	128,98	179,03	1994	74,05	2014

From these tables we can see that in the years when the maximum and minimum water flow occurred, the pollution load does not always show the pick values. In this case, the reason for the high absolute values of pollution load is another than the high water flow. That follows to the conclusion that anthropogenic influence also makes a contribution to the pollution fluctuation and this contribution is not stable.

Because the definition of reasons why the pollution load changes is a key to identify the measures required to reduce the contaminants level, the catchment area of each monitoring station should be studied separately.

5.3 Probability curve

Figures 5.3.1-5.3.4 show the flow and load probability curves of BOD_5, NH_4, N_{tot} and P_{tot} for Narva River based on data gathered at Vasknarva station, covering the period from January 1996 to December 2018. Probability curves of water flow, COD, NO_3 and PO_4 see in Appendix 7.

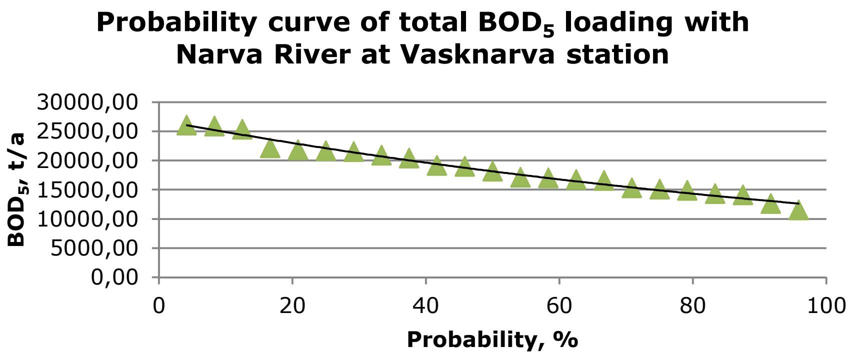

Figure 5.3.1 BOD_5 load probability curve for the Narva River at Vasknarva station

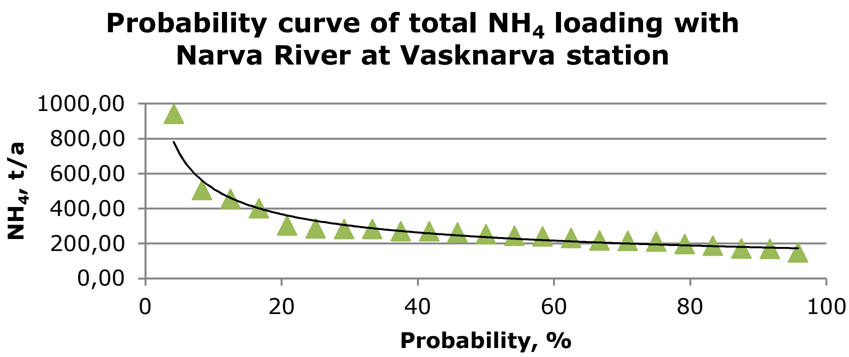

Figure 5.3.2 NH_4 load probability curve for the Narva River at Vasknarva station

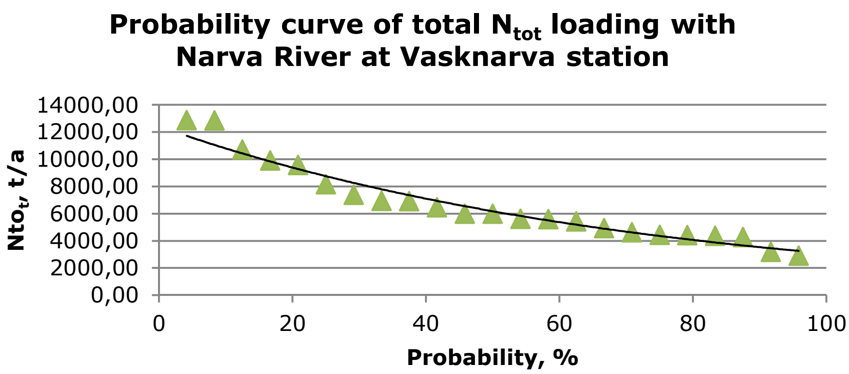

Figure 5.3.3 N_{tot} load probability curve for the Narva River at Vasknarva station

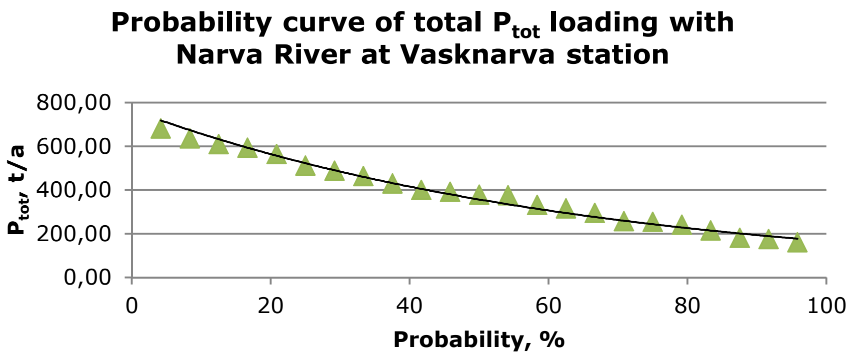

Figure 5.3.4 P_{tot} load probability curve for the Narva River at Vasknarva station

Figures 5.3.6-5.3.9 show the flow and load probability curves of BOD_5, NH_4, N_{tot} and P_{tot} for Narva River based on data gathered at Narva city station, covering the period from January 2003 to December 2018. Probability curves of water flow, COD, NO_3 and PO_4 see in Appendix 8.

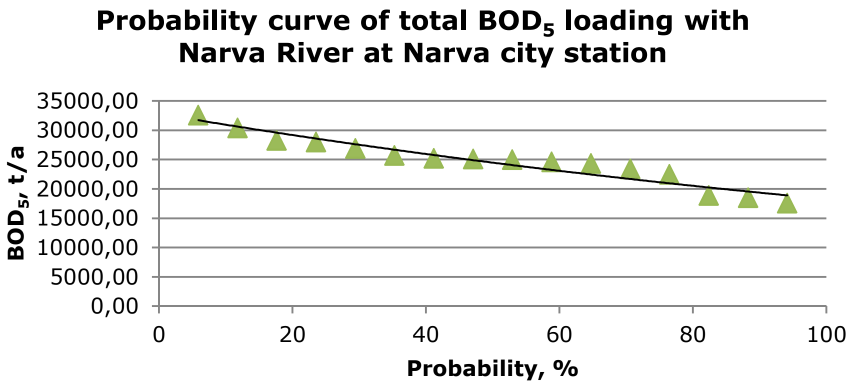

Figure 5.3.5 BOD_5 load probability curve for the Narva River at Narva city station

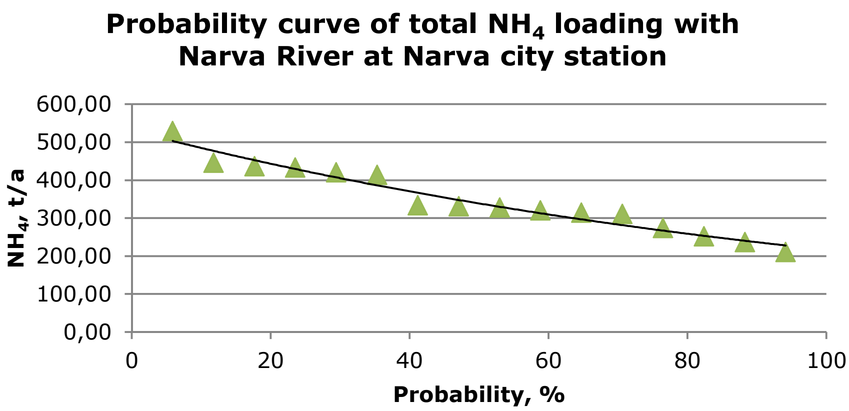

Figure 5.3.6 NH_4 load probability curve for the Narva River at Narva city station

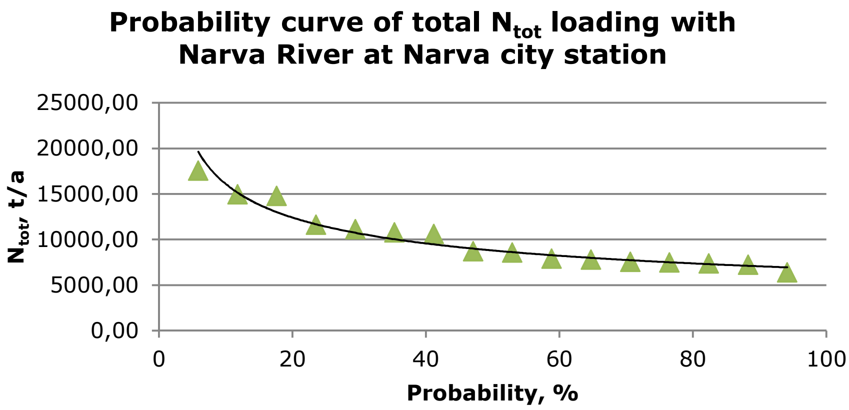

Figure 5.3.7 N_{tot} load probability curve for the Narva River at Narva city station

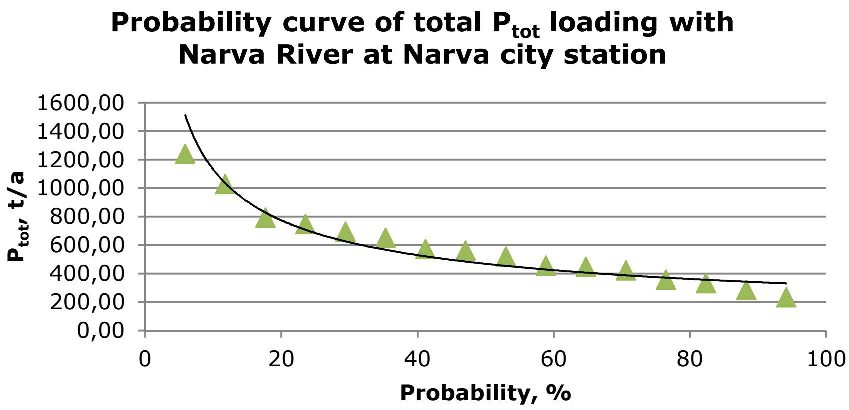

Figure 5.3.8 P_{tot} load probability curve for the Narva River at Narva city station

Figures 5.3.10-5.3.13 show the flow and load probability curves of BOD_5, NH_4, N_{tot} and P_{tot} for Emajõgi at Kavastu station covering the period from January 1992 to December 2018. Probability curves of water flow, COD, NO_3 and PO_4 see in Appendix 9.

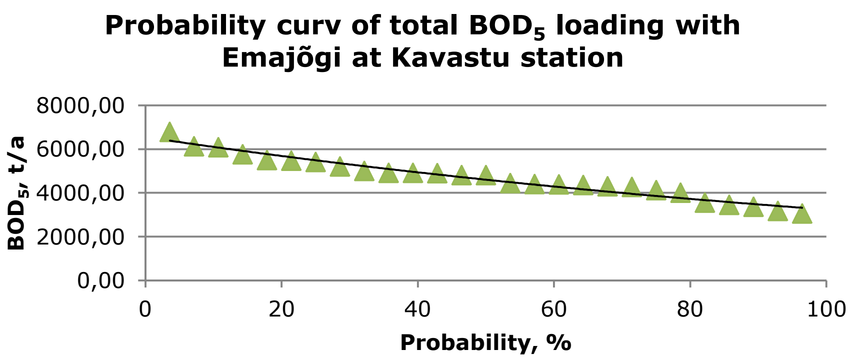

Figure 5.3.9 BOD_5 load probability curve for the Emajõgi at Kavastu station

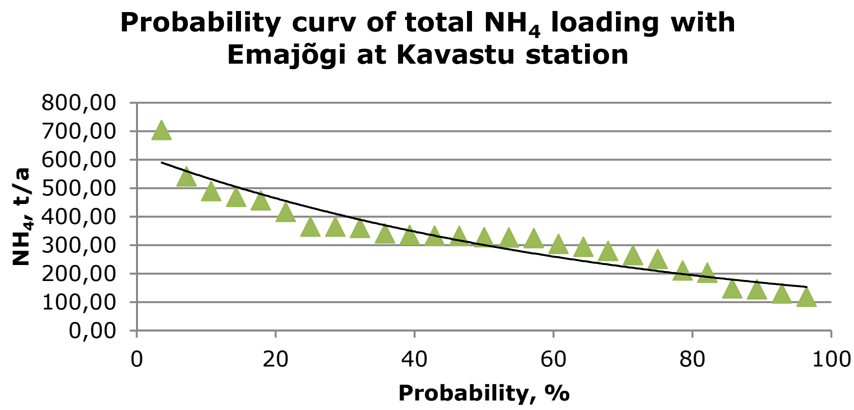

Figure 5.3.10 NH_4 load probability curve for the Emajõgi at Kavastu station

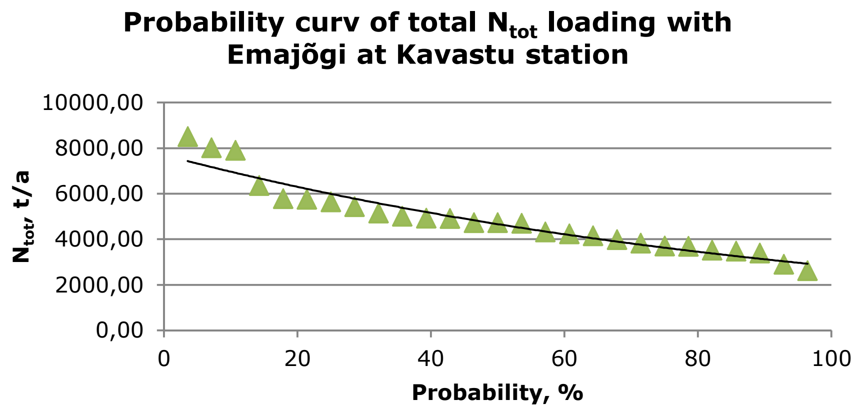

Figure 5.3.11 N_{tot} load probability curve for the Emajõgi at Kavastu station

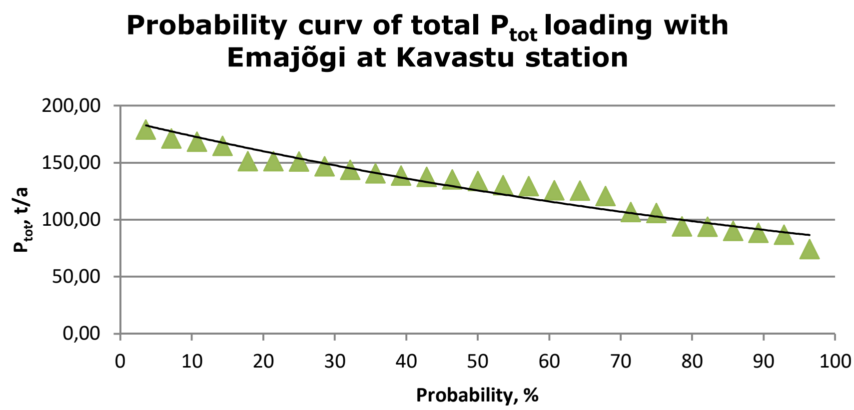

Figure 5.3.12 P_{tot} load probability curve for the Emajõgi at Kavastu station

In Table 5.3.1-5.3.3 are shown the average water flow and pollution load depending on hydrologic conditions according to (Donald W. Meals, R. Peter Richards, and Steven A. Dressing, 2013) (see Chapter 2.5). Values are calculated as medians of each hydrologic zone.

Table 5.3.1 Hydrologic and chemical water quality patterns for the Vasknarva station at Narva River based on hydrologic zones on probability curves

Hydrologic condition groups	Hydrologic zone on probability curve	Q	BOD_5	COD	NH_4	NO_3	N_{tot}	PO_4	P_{tot}
		m^3/s	t/a	t/a	t/a	t/a	t/a	t/a	t/a
High flows	up to 10%	443	25855	201345	501	2313	12644	386	633
Moist conditions	10-40%	382	21620	156952	284	1510	7778	266	499
Mid-range flows	40-60%	325	18192	145593	253	1196	5998	180	378
Dry conditions	60-90%	276	15208	100577	213	742	4541	119	255
Low flows	90-100%	209	12780	78314	169	594	3311	79	175

Table 5.3.2 Hydrologic and chemical water quality patterns for the Narva city station at Narva River based on hydrologic zones on probability curves

Hydrologic condition groups	Hydrologic zone on probability curve	Q	BOD_5	COD	NH_4	NO_3	N_{tot}	PO_4	P_{tot}
		m^3/s	t/a	t/a	t/a	t/a	t/a	t/a	t/a
High flows	up to 10%	561	30961	278519	467	3229	15590	460	1082
Moist conditions	10-40%	507	27159	254674	423	2670	11238	389	708
Mid-range flows	40-60%	464	25035	203057	329	2014	8635	285	540
Dry conditions	60-90%	414	23191	177870	301	1585	7510	191	406
Low flows	90-100%	347	18252	137826	230	1276	7019	117	272

Table 5.3.3 Hydrologic and chemical water quality patterns for the Kavastu station at Emajõgi based on hydrologic zones on probability curves

Hydrologic condition groups	Hydrologic zone on probability curve	Q	BOD_5	COD	NH_4	NO_3	N_{tot}	PO_4	P_{tot}
		m^3/s	t/a	t/a	t/a	t/a	t/a	t/a	t/a
High flows	up to 10%	88	6129	49908	526	6138	7981	56	170
Moist conditions	10-40%	75	5320	37959	365	3981	5537	45	149
Mid-range flows	40-60%	68	4818	29427	327	2802	4723	40	134
Dry conditions	60-90%	54	4209	25018	258	2143	3770	27	106
Low flows	90-100%	42	3239	16771	134	1627	3045	20	87

The probability curve gives an idea of the load distribution according to the probability of the appearance of a certain value, as well as depending on hydrological conditions.

Based on result obtained we can predict the possible level of pollution load in future if we now the hydrological pattern of a waterbody. That is why such tool is helpful in creating and adjusting the monitoring programs. In case of Narva River this is of high importance as due to its location on the border between two countries, the sampling method and frequency are influenced by political factors.

5.4 Interpretation of probability curves to assess water quality

According to Chapter 6 of the Procedure for designating status classes of surface water bodies (Keskkonnaministeerium, 2009), there are seven types of water bodies. Types depend on the surface waterbody catchment area and COD concentration (see Table 5.4.1).

Table 5.4.1 Description of the types of water bodies (Keskkonnaministeerium, 2009)

Type	Description	COD concentration	Catchment area
I A	Dark water and rich in humic substances rivers	90% COD_{Mn} > 25 mg O/l	10…100 km^2
I B	Light-water and low-organic-content rivers	90% COD_{Mn} < 25 mg O/l	10…100 km^2
II A	Rivers rich in dark water and humic substances	90% COD_{Mn} > 25 mg O/l	> 100…1000 km^2
II B	Light water and low organic matter rivers	90% COD_{Mn} < 25 mg O/l	> 100…1000 km^2
III A	Rivers rich in dark water and humic substances	90% COD_{Mn} > 25 mg O/l	> 1000…10,000 km^2
III B	Light water and low organic matter rivers	90% COD_{Mn} < 25 mg O/l	> 1000…10,000 km^2
IV	Narva River		> 10,000 km^2

Based on Table 5.4.1, types are assigned to studied rivers.

The Narva River has a catchment area of 58,126 km^2 and belongs to the IV type.

The Emajõgi has a catchment area of 9745 km^2 (Kätlin Blank, 2017) which is between 1000 and 10,000 km^2. The procedure of finding if 90% of COD concentration is more or less than 25 mg O/l is the same as for plotting the probability curve. We take all the data available and sort it from biggest to smallest. That the concentration values are ranked with rank 1 of the biggest value and so on. After that, we calculate the probability of each value occurring. From Table 5.4.2 we can see that only 1.78 % of COD exceeds 25.00 mg O/l, which makes Emajõgi belonging to type III B as light water and low organic matter rivers (90% COD_{Mn} value less than 25 mg O/l).

Table 5.4.2 The probability of occurrence of a COD concentration of more than 25 mg/l at the Kavastu station on the Emajõgi

COD sorted	**Rank**	**Probability**
mg/l		**%**
30,00	1	0,30
29,00	2	0,59
26,00	3	0,89
25,00	4	1,19
25,00	5	1,48
25,00	6	**1,78**
24,00	7	2,08
24,00	8	2,37
24,00	9	2,67
24,00	10	2,97
…	…	…

From the table in Annex 4 of the Procedure for designating status classes of surface water bodies (Keskkonnaministeerium, 2009) the ultimate values of "Very good class" are taken (see tables in Appendices 10 and 11 of this thesis).

For the Narva River ultimate values are:

- BOD_5 – 2.00 mg/l;
- NH_4 – 0.10 mg/l;
- N_{tot}- 0.50 mg/l;
- P_{tot} – 0.04 mg/l.

For the Emajõgi ultimate values are:

- BOD_5 – 1.80 mg/l;
- NH_4 – 0.10 mg/l;
- N_{tot}- 1.50 mg/l;
- P_{tot} – 0.05 mg/l.

Using these values, the ultimate annual pollution of BOD_5, NH_4, N_{tot}, and P_{tot} are calculated. For doing this, the limit concentration values are multiplied by annual average water flow (by the method I as it gives the most precise result), by the number of seconds per year and by the conversion factor of 1/1000000 to receive the result in tons per year.

The results of the calculation are shown in Tables 5.4.3-5.4.5.

Table 5.4.3 Maximum permissible annual pollution load with Narva River at Vasknarva station for "Very good" ecological status class

Year	Average annual water flow	Maximum BOD_5 loading	Maximum NH_4 loading	Maximum N_{tot} loading	Maximum P_{tot} loading
	m^3/s	t/a	t/a	t/a	t/a
1996	197	12489,74	624,49	3122,44	249,79
1997	300	18947,87	947,39	4736,97	378,96
1998	450	28362,36	1418,12	7090,59	567,25
1999	415	26199,76	1309,99	6549,94	524,00
2000	268	16958,94	847,95	4239,73	339,18
2001	303	19108,74	955,44	4777,19	382,17
2002	290	18293,13	914,66	4573,28	365,86
2003	245	15473,55	773,68	3868,39	309,47
2004	378	23901,35	1195,07	5975,34	478,03
2005	360	22733,74	1136,69	5683,44	454,67
2006	200	12625,29	631,26	3156,32	252,51
2007	258	16260,83	813,04	4065,21	325,22
2008	317	20071,58	1003,58	5017,90	401,43
2009	396	24957,33	1247,87	6239,33	499,15
2010	461	29106,78	1455,34	7276,69	582,14
2011	381	24033,54	1201,68	6008,39	480,67
2012	328	20732,54	1036,63	5183,14	414,65
2013	372	23486,28	1174,31	5871,57	469,73
2014	281	17726,86	886,34	4431,72	354,54
2015	276	17377,80	868,89	4344,45	347,56
2016	276	17467,83	873,39	4366,96	349,36
2017	381	24050,13	1202,51	6012,53	481,00
2018	329	20721,83	1036,09	5180,46	414,44

Table 5.4.4 Maximum permissible annual pollution load with Narva River at Narva city station for "Very good" ecological status class

Year	Average annual water flow	Maximum BOD_5 loading	Maximum NH_4 loading	Maximum N_{tot} loading	Maximum P_{tot} loading
	m^3/s	kg/s	kg/s	kg/s	kg/s
2003	392	24706,08	1235,30	6176,52	494,12
2004	488	30839,96	1542,00	7709,99	616,80
2005	459	28956,10	1447,80	7239,02	579,12
2006	287	18127,43	906,37	4531,86	362,55
2007	351	22132,40	1106,62	5533,10	442,65
2008	441	27874,20	1393,71	6968,55	557,48
2009	495	31247,25	1562,36	7811,81	624,95
2010	573	36155,46	1807,77	9038,87	723,11
2011	514	32394,30	1619,71	8098,57	647,89
2012	435	27502,50	1375,13	6875,63	550,05
2013	486	30634,50	1531,73	7658,63	612,69
2014	411	25895,46	1294,77	6473,87	517,91
2015	390	24594,97	1229,75	6148,74	491,90
2016	409	25863,84	1293,19	6465,96	517,28
2017	579	36517,13	1825,86	9129,28	730,34
2018	433	27279,94	1364,00	6819,98	545,60

Table 5.4.5 Maximum permissible annual pollution load with Emajõgi at Kavastu station for "Very good" ecological status class

Year	**Average annual water flow**	**Maximum BOD_5 loading**	**Maximum NH_4 loading**	**Maximum N_{tot} loading**	**Maximum P_{tot} loading**
	m^3/s	**t/a**	**t/a**	**t/a**	**t/a**
1992	70	3962,13	220,12	3301,78	110,06
1993	51	2900,06	161,11	2416,72	80,56
1994	66	3722,01	206,78	3101,68	103,39
1995	73	4143,43	230,19	3452,86	115,10
1996	32	1805,13	100,28	1504,27	50,14
1997	54	3073,82	170,77	2561,52	85,38
1998	79	4485,67	249,20	3738,06	124,60
1999	74	4187,38	232,63	3489,48	116,32
2000	57	3255,11	180,84	2712,60	90,42
2001	62	3534,22	196,35	2945,19	98,17
2002	66	3728,22	207,12	3106,85	103,56
2003	51	2913,04	161,84	2427,53	80,92
2004	77	4362,02	242,33	3635,01	121,17
2005	73	4164,24	231,35	3470,20	115,67
2006	40	2243,49	124,64	1869,57	62,32
2007	56	3154,57	175,25	2628,81	87,63
2008	86	4916,52	273,14	4097,10	136,57
2009	92	5216,69	289,82	4347,25	144,91
2010	94	5308,24	294,90	4423,53	147,45
2011	78	4440,81	246,71	3700,67	123,36
2012	82	4661,11	258,95	3884,26	129,48
2013	68	3870,11	215,01	3225,09	107,50
2014	48	2699,23	149,96	2249,36	74,98
2015	60	3399,32	188,85	2832,77	94,43
2016	77	4373,65	242,98	3644,71	121,49
2017	71	4053,90	225,22	3378,25	112,61
2018	60	3386,60	188,14	2822,17	94,07

Using the maximum annual pollution loads, the probability curves are plotted on the same graphs as the actual load calculated before.

Probability curves of actual and ultimate pollution loading with Narva River at Vasknarva station from January 1996 through December 2018 and calculated by III method are shown in figures 5.4.2-5.4.5. The probability curves are the black exponential trendlines and the blue crosses show the limit of "Very good" ecological status class (Keskkonnaministeerium, 2009).

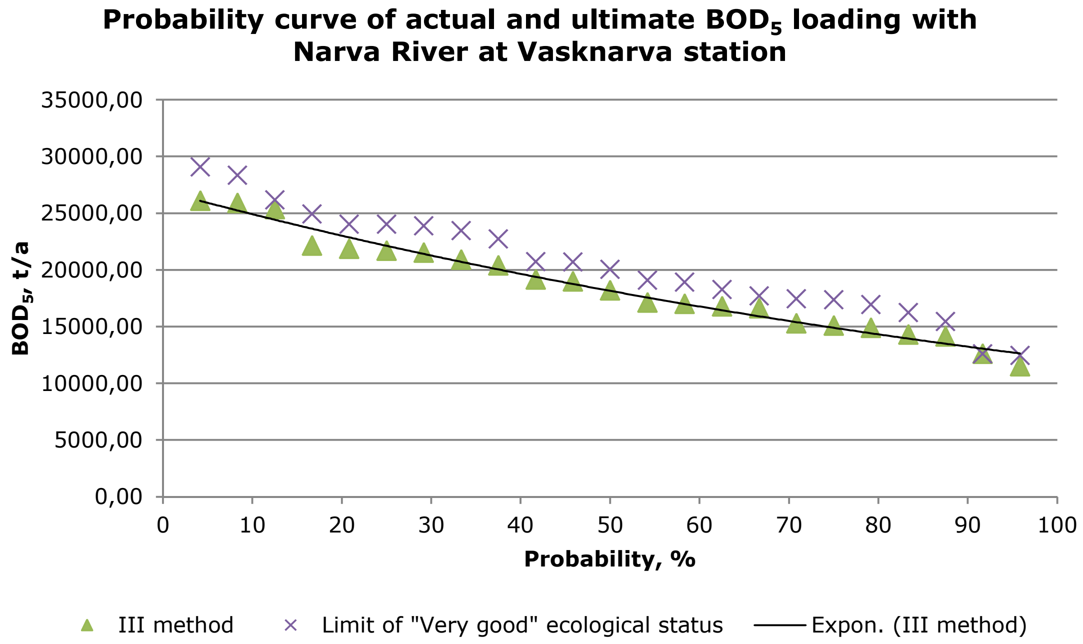

Figure 5.4.1 Comparison of actual and allowable biochemical oxygen demand for Narva River at Vasknarva station

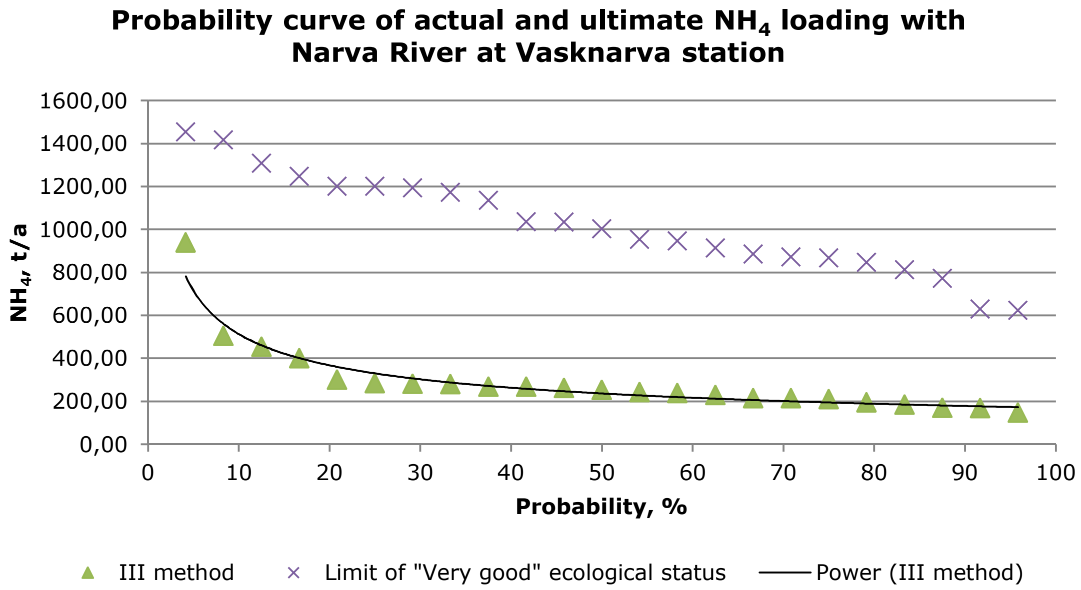

Figure 5.4.2 Comparison of actual and allowable ammonia loading with Narva River at Vasknarva station

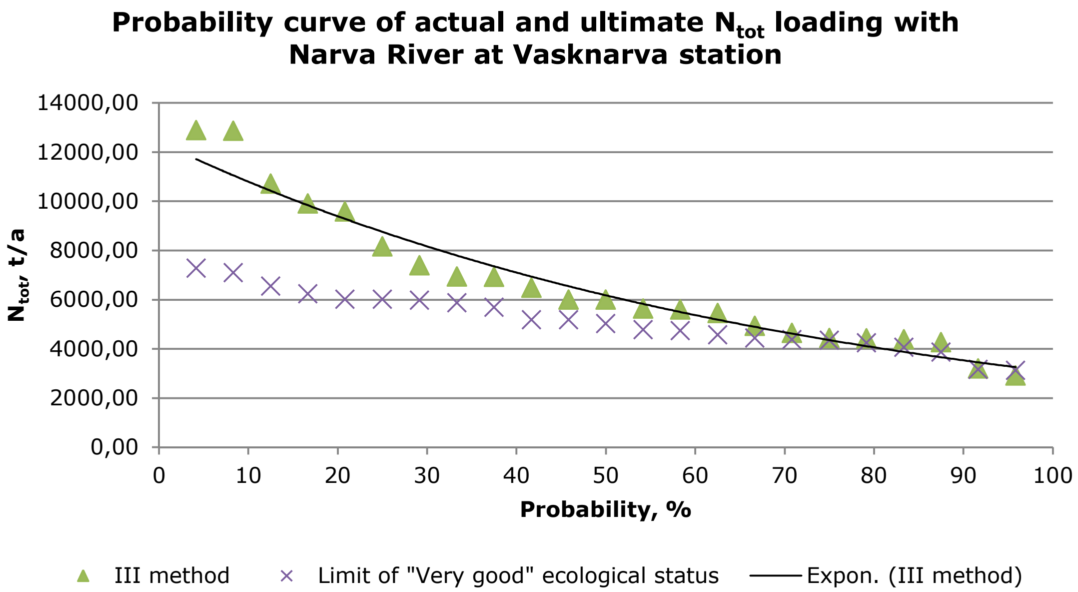

Figure 5.4.3 Comparison of actual and allowable total nitrogen loading with Narva River at Vasknarva station

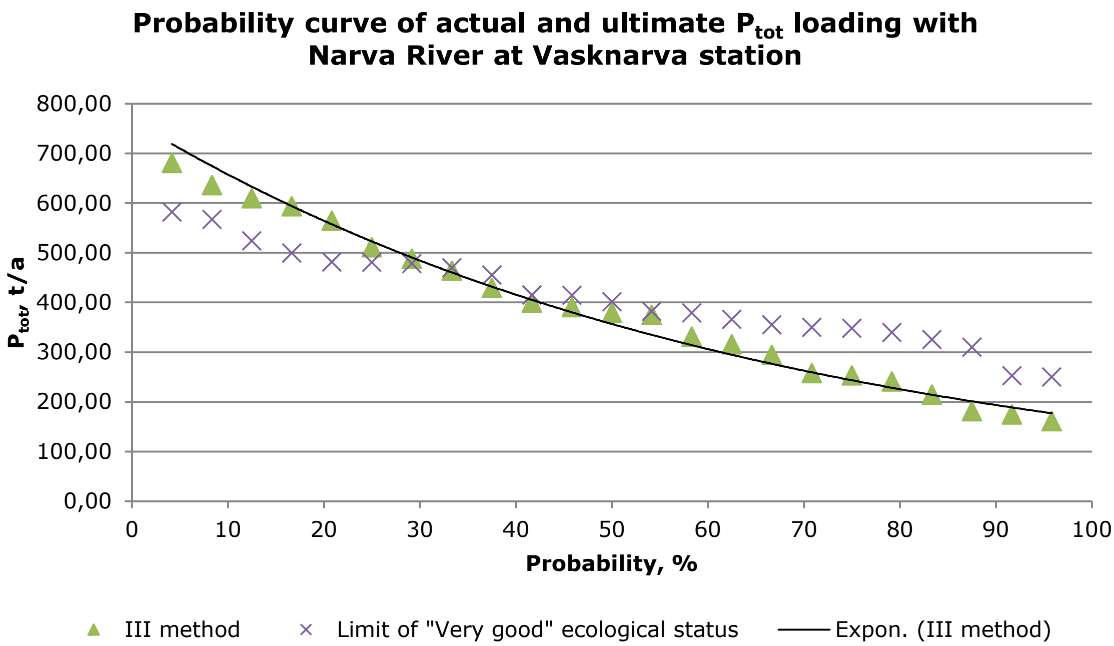

Figure 5.4.4 Comparison of actual and allowable total phosphorous loading with Narva River at Vasknarva station

Probability curves express compliance with standards in the graphical form. For the most precise analysis the summarised data is presented in the following tables, as the graphs do not show the exact reduction needs.

The of compliance of pollution load level with standards and possible measures to improve the water quality of Narva River at Vasknarva station are presented in table 5.4.6.

Table 5.4.6 Compliance of actual pollution load with water quality standards at Vasknarva station on Narva River

Quality indicator		**Hydrological conditions**				
		High flows	Moist conditions	Mid-range flows	Dry conditions	Low flows
		Hydrologic zone on probability curve				
		up to 10%	10-40%	40-60%	60-90%	90-100%
BOD_5	Actual, t/a	25854,60	21619,50	18192,37	15208,08	12779,89
	Limits, t/a	28146,10	23967,45	20071,58	17422,82	12910,11
	Additional capacity, t/a	2291,50	2347,94	1879,22	2214,74	130,22
	Additional capacity, %	**8,86**	**10,86**	**10,33**	**14,56**	**1,02**
NH_4	Actual, t/a	501,12	284,25	253,43	212,68	169,11
	Limits, t/a	1407,30	1198,37	1003,58	871,14	645,51
	Additional capacity, t/a	906,19	914,12	750,15	658,46	476,39
	Additional capacity, %	**180,83**	**321,59**	**296,00**	**309,60**	**281,70**
N_{tot}	Actual, t/a	12644,39	7778,23	5998,33	4540,95	3311,47
	Limits, t/a	7036,52	5991,86	5017,90	4355,70	3227,53
	Additional capacity, t/a	-5607,86	-1786,37	-980,44	-185,24	-83,94
	Additional capacity, %	**-44,35**	**-22,97**	**-16,35**	**-4,08**	**-2,53**
P_{tot}	Actual, t/a	633,31	499,33	378,48	255,04	174,68
	Limits, t/a	562,92	479,35	401,43	348,46	258,20
	Additional capacity, t/a	-70,39	-19,98	22,95	93,42	83,52
	Additional capacity, %	**-11,11**	**-4,00**	**6,06**	**36,63**	**47,81**
Reduction opportunities		Streambank stabilisation				
		Erosion control program	Erosion control program	Erosion control program		
			Riparian buffer protection	Riparian buffer protection	Riparian buffer protection	
					Municipal WWTP	Municipal WWTP

In this table with red colour are marked the percent on which pollution load should be reduced in order to fulfil requirements of water quality standards. With green colour is marked an additional capacity to receive pollutants.

We can see that actual BOD_5 and NH_4 levels are below the permissible limits. Especially good situation is with NH_4 load. N_{tot} exceeds limits during all hydrological conditions. Because the Vasknarva station is located near the Peipsi Lake, the high content of nitrogen can be explained by the bad water quality of it. The dominant cause of total nitrogen pollution in the Peipsi Lake from Estonian side is diffuse sources such as agriculture (Kätlin Blank, 2017). As this it rather difficult to eliminate in order to restore the water quality complex measures should be taken towards reducing the pollutant load.

Actual P_{tot} loading with Narva River at Vasknarva station exceeds the ultimate limits in high flow and moist conditions. As the level of exceeding is not high, the measures towards eliminating the erosion effect can improve the situation. The sampling frequency can be higher during hydrological conditions with exceeding pollution and lower when limits are not expected to be exceeded.

Probability curves of actual and ultimate pollution loading with Narva River at Narva city station from January 2003 through December 2018 and calculated by III method are shown in Figures 5.4.5-5.4.8.

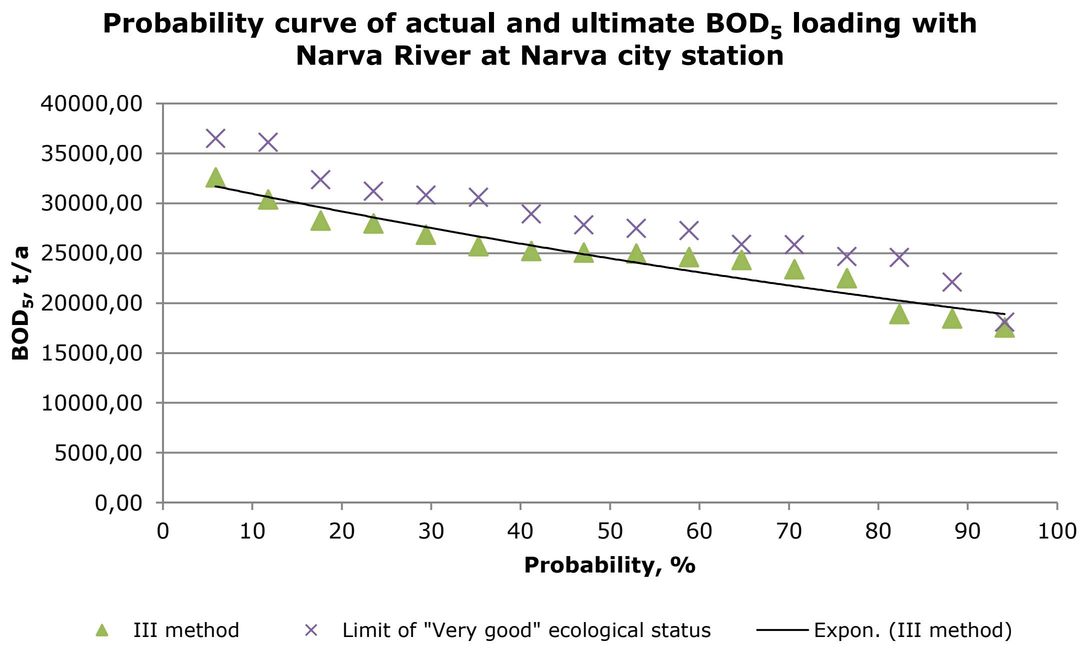

Figure 5.4.5 Comparison of actual and allowable biochemical oxygen demand for Narva River at Narva city station

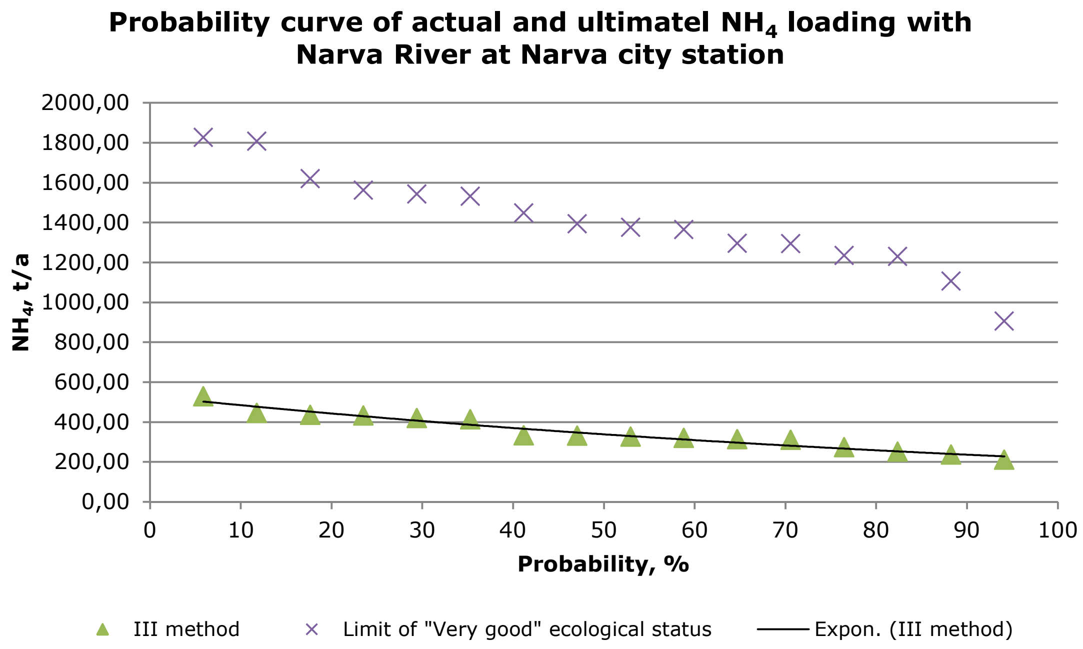

Figure 5.4.6 Comparison of actual and allowable ammonia loading with Narva River at Narva city station

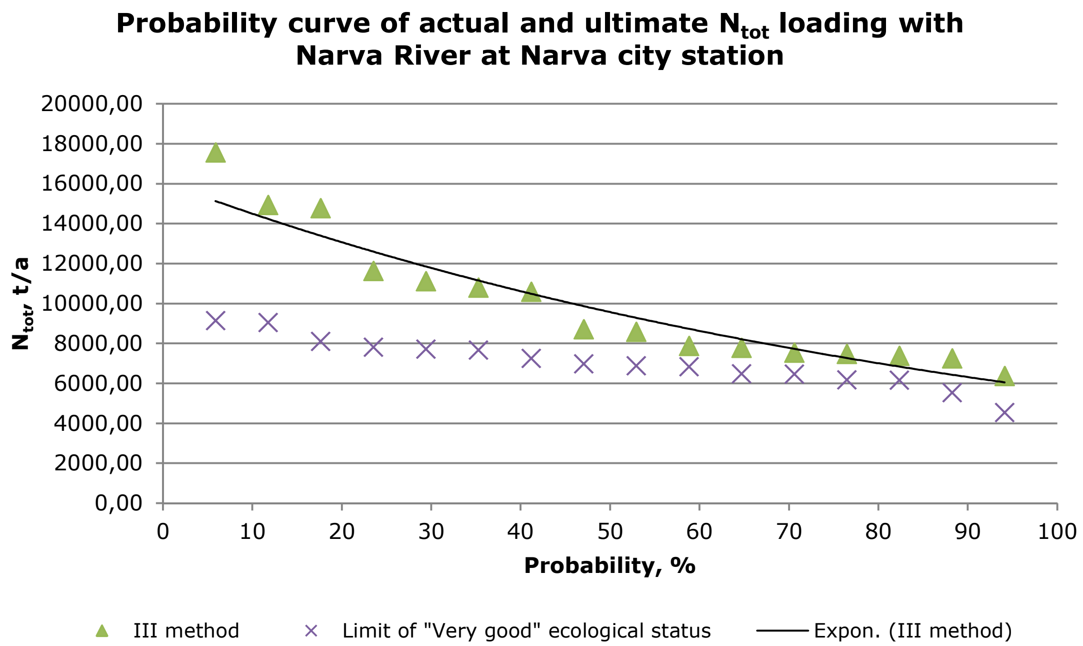

Figure 5.4.7 Comparison of actual and allowable total nitrogen loading with Narva River at Narva city station

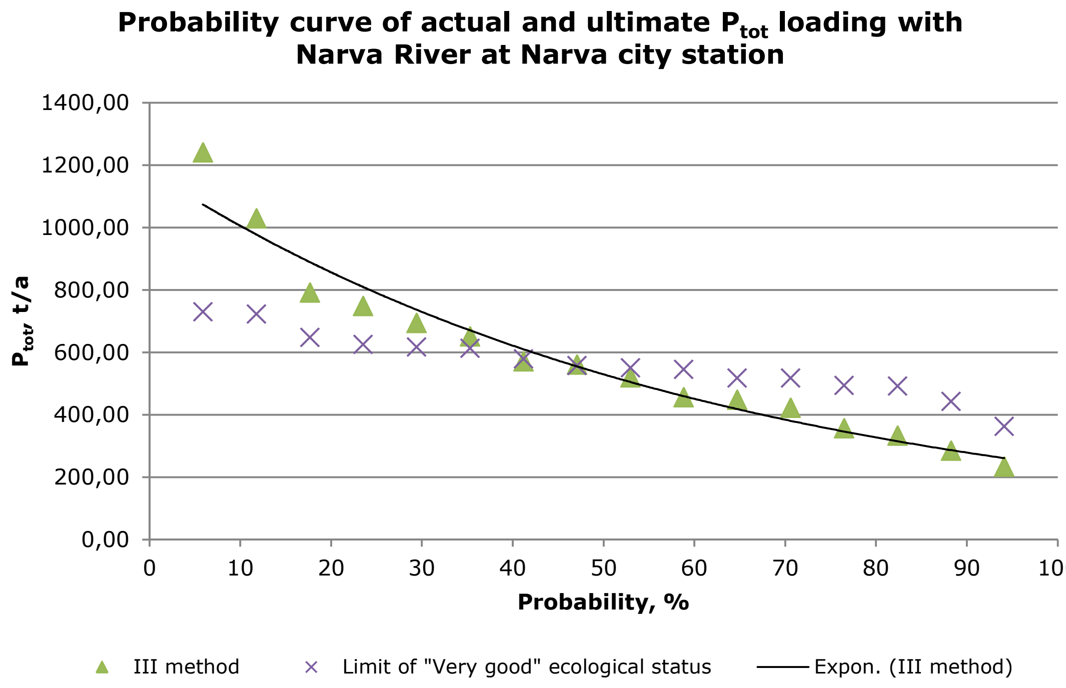

Figure 5.4.8 Comparison of actual and allowable total phosphorous loading with Narva River at Narva city station

The compliance of pollution load level with standards and possible measures to improve the water quality of Narva River at Narva city station are presented in table 5.4.7. With red colour marked the percent on which pollution load should be reduced in order to fulfil requirements of water quality standards. With green colour are marked indicators with an additional capacity to receive pollutants.

BOD_5 exceeds limits during the mid-range flows. Anthropogenic factors such as an introduction of excess fertilizers to a water body, wastewater treatment plants, and urban stormwater runoff can result in high BOD level.

In general, the pattern of pollution at both studied stations at Narva River is similar. As well as at Vasknarva station, the N_{tot} is high and exceeds the water quality limits at Narva city station, while, P_{tot} shows overload additionally during mid-range flows. As the amount of pollutant is bigger than can be received by the river without water quality decreasing, measures should be taken toward the elimination of the effect of wash off processes and streambank erosion.

Table 5.4.7 Compliance of actual pollution load with water quality standards at Narva city station on Narva River

Quality indicator		Hydrological conditions				
		High flows	Moist conditions	Mid-range flows	Dry conditions	Low flows
		Hydrologic zone on probability curve				
		up to 10%	10-40%	40-60%	60-90%	90-100%
BOD_5	Actual, t/a	30960,73	27159,43	25034,88	23191,07	18252,35
	Limits, t/a	36245,88	30941,78	21131,15	25574,40	21131,15
	Additional capacity, t/a	5285,15	3782,36	-3903,73	2383,33	2878,81
	Additional capacity, %	**17,07**	**13,93**	**-15,59**	**10,28**	**15,77**
NH_4	Actual, t/a	466,75	423,26	329,18	301,35	230,26
	Limits, t/a	1812,29	1547,09	1056,56	1278,72	1056,56
	Additional capacity, t/a	1345,54	1123,83	727,37	977,37	826,30
	Additional capacity, %	**288,28**	**265,52**	**220,96**	**324,33**	**358,85**
N_{tot}	Actual, t/a	15589,72	11238,05	8634,73	7510,12	7019,18
	Limits, t/a	9061,47	7735,45	5282,79	6393,60	5282,79
	Additional capacity, t/a	-6528,25	-3502,61	-3351,94	-1116,52	-1736,40
	Additional capacity, %	**-41,88**	**-31,17**	**-38,82**	**-14,87**	**-24,74**
P_{tot}	Actual, t/a	1082,00	707,97	539,88	405,68	271,69
	Limits, t/a	724,92	618,84	422,62	511,49	422,62
	Additional capacity, t/a	-357,08	-89,14	-117,26	105,81	150,93
	Additional capacity, %	**-33,00**	**-12,59**	**-21,72**	**26,08**	**55,55**
Reduction opportunities		Streambank stabilisation				
		Erosion control program				
			Riparian buffer protection			
					Municipal WWTP	

Probability curves of actual and ultimate pollution loading with Emajõgi at Kavastu station from January 1992 through December 2018 and calculated by III method see in Figures 5.4.10-5.4.13.

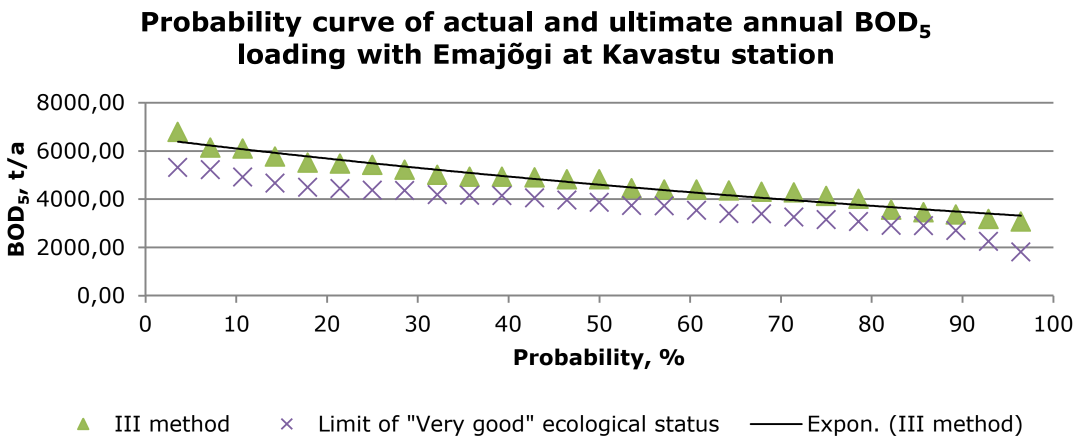

Figure 5.4.9 Comparison of actual and allowable biochemical oxygen demand for Emajõgi at Kavastu station

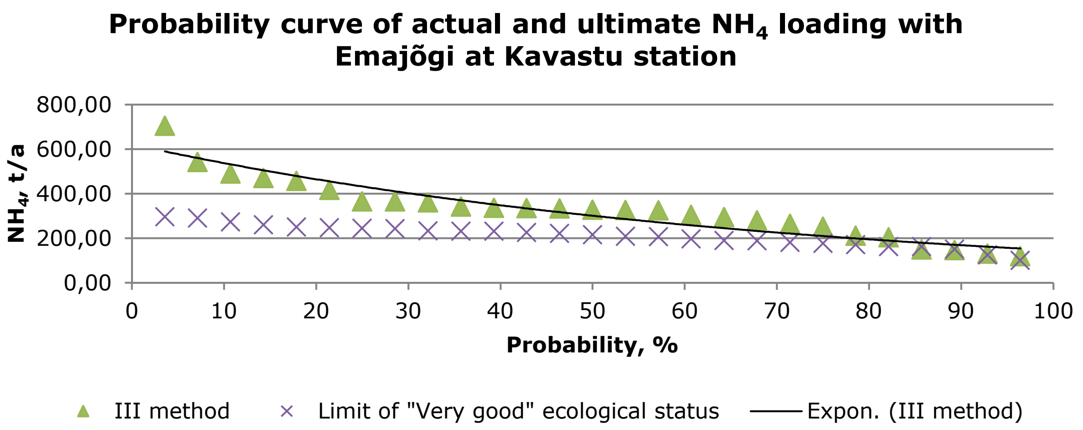

Figure 5.4.10 Comparison of actual and allowable ammonia loading with Emajõgi at Kavastu station

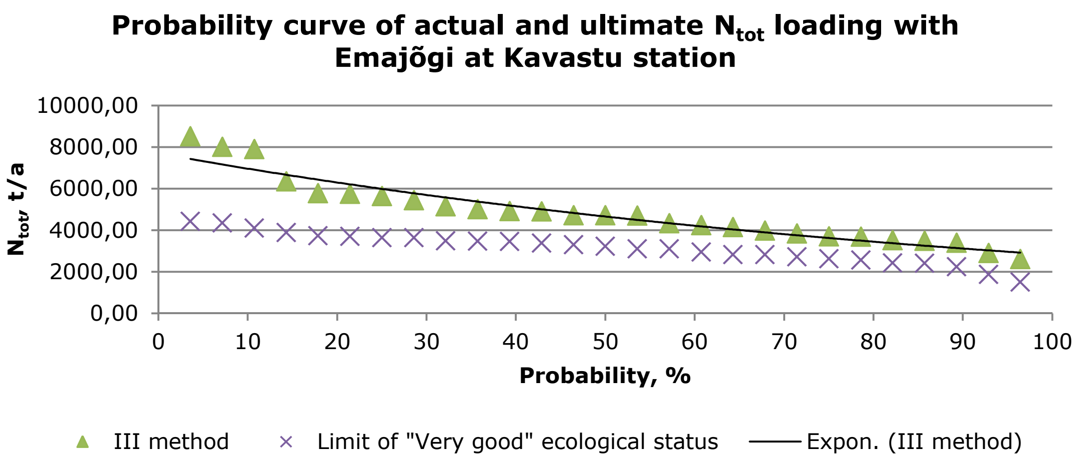

Figure 5.4.11 Comparison of actual and allowable total nitrogen loading with Emajõgi at Kavastu station

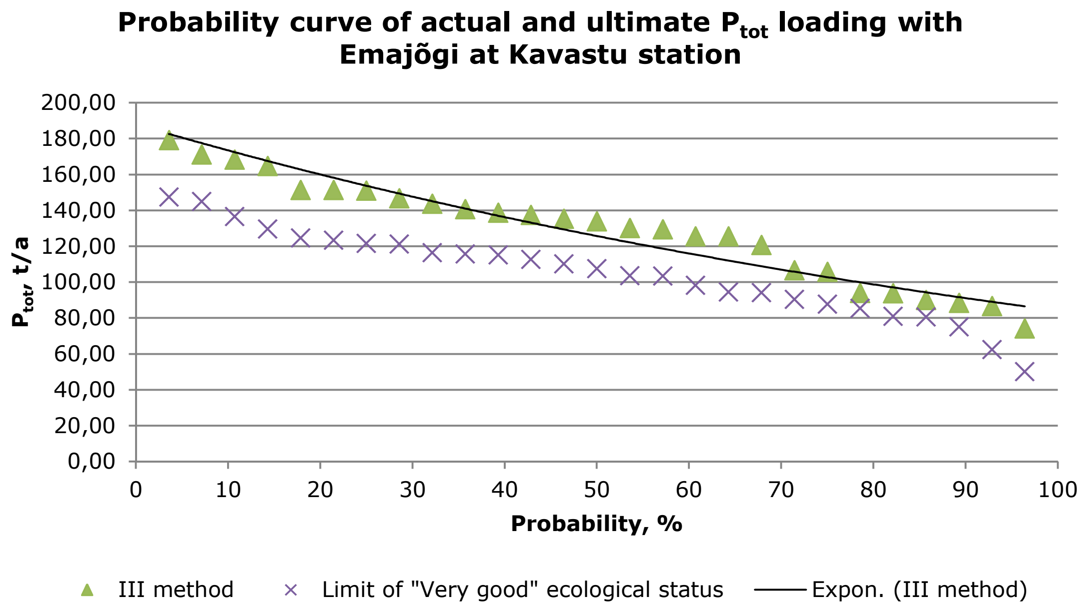

Figure 5.4.12 Comparison of actual and allowable total phosphorous loading with Emajõgi at Kavastu station

The compliance of pollution load level with standards and possible measures to improve the water quality of Emajõgi at Kavastu station are presented in table 5.4.8. With red colour marked the percent on which pollution load should be reduced in order to fulfil requirements of water quality standards. With green colour are marked indicators with an additional capacity to receive pollutants.

As it is seen from Figures 5.4.10-5.4.12 and Table 5.4.8, the situation with the pollution load in the Emajõgi needed to be improved. All studied water quality indicators showed the excess of quality standard limits during all hydrological conditions.

In fact, Emajõgi has bad water quality status. According to the assessment made by the Republic of Estonia Environmental Agency, it has the biological parameters that are significantly different from the reference conditions of the type (Keskkonnaagentuur). Until 2001 Emajõgi was responsible for 35% of all total nitrogen pollution into the Peipsi Lake and for 21% of total phosphorus input (Kätlin Blank, 2017).

The major reason of pollution is the usage of fertilizers (Kätlin Blank, 2017). While the problems with water quality are usually caused by mineral fertilizers, organic fertilizers can be associated with pollution as well. The region including the catchment area of Emajõgi is used intensively for agriculture. Runoff of fertilizers to a river can increase the nutrients content and decrease the amount of dissolved oxygen. Poorly operated wastewater treatment plants can lead to high level of nutrient load in waters as well. Nitrogen and phosphorous make a contribution to the high BOD as the increased amount of plants results in organic waste and in a high BOD level. High NH_4 concentration in river water can be a result of the discharge of domestic sewage and the application of nitrogen fertilizer along the riverbank.

Table 5.4.8 Compliance of actual pollution load with water quality standards at Kavastu station on Emajõgi

Quality indicator		**Hydrological conditions**				
		High flows	Moist conditions	Mid-range flows	Dry conditions	Low flows
		Hydrologic zone on probability curve				
		up to 10%	10-40%	40-60%	60-90%	90-100%
BOD_5	Actual, t/a	6129,24	5319,86	4818,31	4208,52	3238,58
	Limits, t/a	5126,64	4367,83	3870,11	3204,84	2380,21
	Additional capacity, t/a	-1002,60	-952,03	-948,21	-1003,68	-858,37
	Additional capacity, %	**-16,36**	**-17,90**	**-19,68**	**-23,85**	**-26,50**
NH_4	Actual, t/a	526,06	364,87	327,31	257,71	134,31
	Limits, t/a	284,81	242,66	215,01	178,05	132,23
	Additional capacity, t/a	-241,25	-122,22	-112,30	-79,66	-2,07
	Additional capacity, %	**-45,86**	**-33,50**	**-34,31**	**-30,91**	**-1,54**
N_{tot}	Actual, t/a	7981,47	5536,76	4723,11	3769,80	3044,91
	Limits, t/a	4272,20	3639,86	3225,09	2670,70	1983,51
	Additional capacity, t/a	-3709,27	-1896,90	-1498,02	-1099,10	-1061,40
	Additional capacity, %	**-46,47**	**-34,26**	**-31,72**	**-29,16**	**-34,86**
P_{tot}	Actual, t/a	170,18	148,84	133,75	106,13	87,18
	Limits, t/a	142,41	121,33	107,50	89,02	66,12
	Additional capacity, t/a	-27,78	-27,51	-26,25	-17,10	-21,07
	Additional capacity, %	**-16,32**	**-18,48**	**-19,62**	**-16,12**	**-24,16**
Reduction opportunities		Streambank stabilisation				
		Erosion control program				
			Riparian buffer protection			
					Municipal WWTP	

As we can see, the pollution is not independent and the excess of one quality indicator can cause to increase in another. Therefore, the complex measures should applied for improving water quality of Emajõgi.

CONCLUSION

The analysis of the methods recommended by the HELCOM guideline showed that the third method (the daily concentration regression method) is not applicable to the available data since there is no regression dependence of pollution on water flow.

The first (daily water flows and daily concentrations) and second (mean monthly concentration and monthly river flow) methods recommended by the manual can be used for calculation. With their help, the load of pollution of the Narva and Emaiõgi rivers was calculated. All methods give an error in the calculations. In the case when some data are not available (such as pollution concentrations), linear interpolation only increases the error. This is especially noticeable when using the second method since the annual load consists of exactly 12 components (1 for each method).

The magnitude of the annual pollution depends on the flow regime of the river. To eliminate this effect, before starting the analysis of the calculated load, data is recommended to be normalized. The easiest way is to divide the annual load by the total annual water flow.

The flow-normalized method, also used in this work, has the advantage that the intermediate step in the calculation is, in fact, the normalization by the flow. In addition, this method showed the closest results to the most probable ones and was recognized by the author as the most reliable and convenient to use.

Analysis of pollution trends showed that there is a significant reduction in phosphorus in the Narva River, especially at Narva city station. At the same time, total nitrogen is reduced only in recent years.

As for Emajõgi, phosphorus pollution is reduced, and nitrogen content, on the contrary, is growing.

Based on the probability curves, the probability of occurring of a certain amount of pollution was determined, depending on the hydrological conditions. But, more interesting is the use of curves to determine the status of water quality. In the course of this work, the actual loads were compared with the permissible limits and it turned out that for the Narva River at the Vasknarva station, the total nitrogen exceeds the limit under flood and erosion conditions, and at the Narva city station under any hydrological conditions. Phosphorus exceeds the limit in Narva River at Narva city station during high flows, moist conditions and mid-range flows.

As for Emajõgi, all the considered indicators of water quality showed an excess of permissible values.

Thus, in this work, such an analysis tool as probability curves was applied in practice. Since, with their help, it is possible to determine hydrological conditions, theoretical sources of pollution and compare compliance with current water quality standards, the author believes that this work will be useful in the subsequent study of water quality problems.

SUMMARY

Directive 2000/60/EC of the European Parliament and of the Council requires "good water quality status" for all waters.

Suffering from eutrophication the Baltic Sea requires measures to improve the water quality status. The Baltic Marine Environment Protection Commission, also known as the Helsinki Commission (HELCOM) set up a goal of reducing the inputs of nutrients into the Baltic Sea. As a major part of the pollution load is riverine, the analysis of pollution load and its trend in rivers belonging to the Baltic Sea catchment is of great importance.

In this study, the magnitude, dynamics, and nature of the polluting load of the rivers Narva and Emajõgi were studied based on hydrometric and hydrochemical data. The Narva River is a river on the eastern border of Estonia, which starts from the Peipsi Lake near the Vasknarva village and flows into the Narva Bay. Emajõgi is the ninth largest river in Estonia and connects the Võrtsjärv Lake through Tartu County with the Peipsi Lake, crossing the city of Tartu.

The analysis of pollution load calculation methods described by HELCOM showed that the daily river flow and daily concentration regression method is not suitable for available data additionally to the fact that it is the least recommended method in the guide. The other two methods have their own disadvantaged of applying connected with the lack of data for calculations. Therefore, the same assessment was also done by the flow-normalized method which showed the most reliable results and is the most convenient to apply.

The analysis of pollution loading trends helps to define the measures needed for achieving the goal of "good status" for all waters set by the Water Framework Directive. The flow-normalized data present a more precise picture of pollution situation eliminating the impact of water flow. The Narva River shows growth in BOD_5 loading at both studied station. The long term trend of the total nitrogen at Vasknarva station is positive but starting from 2010 the annual load is decreasing. At the Narva city station, N_{tot} is decreasing. The total phosphorous load at both stations on the Narva River shows a decreasing trend. Emajõgi shows a decreasing trend of BOD_5 and P_{tot}, while total nitrogen still is increasing.

The probability curves were built in order to predict and analyse the intensiveness of pollution and its connection to the water flow regime. The variation of flows is a key

part of adjusting the monitoring program. Knowing the hydrological condition we can predict the possible pollution load on a certain period of a year using the probability curve. It is important to focus on the possible source of pollution and monitor carefully the impact if the limit is about to be exceeded.

Knowing the limits set by water quality standards the actual pollution load was compared with allowable values. The analysis showed that in the Narva River the excess pollution of total nitrogen is observed at both Vasknarva and Narva city stations; total phosphorous load does not meet the requirements at Narva city station and partly at Vasknarva station. In the case of Emajõgi, serious measures towards the reduction of pollution should be applied as for all water quality indicators studied the limits are exceeded.

The author believes that all objectives of this study are met. The results obtained can help in further improvement of the water quality status of Narva and Emajõgi rivers. The probability curves presented in this work can be used in adjusting the monitoring program and focusing on possible sources of pollution causing the exceeding the water quality limits. This may form a subject of further studies.

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APPENDICES

Appendix 1 Description of sampling methods on the Narva River in Estonia (based on Kati Roosalu table from Tallinn University of Technology)

The samples at the Narva River were taken in the period from 1992 to 2018 from 20 m of shore and in the middle of the river, close to the border, about 100-110 m from the shore. All samples from the river were taken from a small boat with an outboard motor with the engine turned off to avoid vortex and the boat anchored to the place by bathometer.

There were three different locations where concentration samples were collected:

1) at the surface (~20 cm)

Sample was taken with long handled dipper with wide-mouth plastic mixing jug and then poured into 1 liter sampling bottle. Bottle number was recorded to the sampling protocol with the date and time of the sampling.

2) at 0,5 h of the river depth

Sample was taken with the bathometer which was lowered to the correct depth with rope, bathometer was closed and pulled up with the sample. Portion of the sample was poured into sampling bottle with volume of 1 liter.

3) at 0,8 h of the river depth

Sample was taken with the bathometer which was lowered to the correct depth with rope, bathometer was closed and pulled up with the sample. Portion of the sample was poured into 1 liter sampling bottle.

The depth of the river was measured either with measuring stick or with a graduated rope with weight at the end (deeper sections of the river).

After taking, samples were stored in the cooling box with ice packages during the transportation back to the laboratory. After arrival to the laboratory they are placed into the refrigerator at 1…5°C.

Analyses are supposed to start next morning after samples taking. Otherwise, they are freezed at -18°C.

Appendix 2 Description of methods for total nitrogen analyses in the Narva River (based on Kati Roosalu table from Tallinn University of Technology)

Measurement is carried in compliance with FOSS Application notes 5202 and 5201, based on ISO 11905 and ISO 13395 by using photometric method after nitrogen compound mineralization with potassium peroxodisulfate ($K_2S_2O_8$).

The analysis id done to undiluted sample 0.1-5 mg/l (if necessary, samples can be diluted with distilled water).

Equipment used is FIAstar 5000 Analyzer unit with wavelenght λ=540 nm.

Samples are collected in polyethene bottles. Samples are analyzed as soon as possible, but not more than 48 hours. Before analyses the samples are stored in a fridge at temperatures 1-5^{o}C. If it is not possible to analyze the samples in 48h they are freezed at -18^{o}C. Like this they can be stored up to 1 month.

Preliminary procedure: 15 ml unfiltered sample is placed in the mineralization bottle and 3 ml of mineralization solution* is added, mixed well. The sample is boiled under pressure for 30 min and cooled to room temperature.

Mineralization solution preparation: 10 g $K_2S_2O_8$ is added to 100 ml of NaOH (0.375 M) + 6 g H_3BO_3, diluted with water to volume of 200 ml.

By the previous procedure all inorganic and organic nitrogen compounds are oxidized to nitrates with $K_2S_2O_8$ solution.

Method description: the nitrate ions formed after mineralization procedure are futher analyzed with the FOSS autoanalyzer (FIAstar 5000), where nitrate is reduced to nitrite in a cadmium redactor. Nitrite formed from reduction of nitrate will form a diazo compound on the addition of an acidic sulphanilamide solution*. This compound is coupled with NED** (N-(1-naphtyl)-ethylene diamine dihydrochloride) solution to form a purple azo dye, which is measured in FIAstar 5000 at λ=540 nm.

**Sulphanilamide solution preparation*: Place 150 ml of distilled water and 25 ml of conc. H_3PO_4 In a volumetric flask with volume of 250 ml, dissolve 2.5 g of sulphanilamide ($C_6H_8N_2O_2S$) in this solution, dilute to volume with distilled water.

***NED solution preparation*: 0.25 g $C_{12}H_{14}N_2$2HCL is dissolved in 150 ml of distilled water. This solution is diluted to volume of 250 ml with distilled water.

Expanded uncertainty (k=2) is 9.3% in range 0.13-5 mg/l.

Appendix 3 Description of methods for total phosphorous analyses in the Narva River (based on Kati Roosalu table from Tallinn University of Technology)

Measurement is carried in compliance with ISO 6878:2004 by using spectrophotometric method after phosphorous compounds are converted to orthophosphate by mineralization with potassium peroxodisulfate ($K_2S_2O_8$).

The analysis id done to undiluted sample 0.003-0.8 mg/l (if necessary, samples can be diluted with distilled water).

Equipment used is spectrophotometer Hach DR/2800 with ƛ=880 nm.

Samples are collected in polyethene bottles. Samples are analyzed as soon as possible, usually in 24 h from sample collection. Before analyses the samples are stored in a refridgerator at temperatures 1-5^{o}C. If it is not possible to analyze the samples in 24h they are freezed at -18^{o}C. Like this they can be stored up to 1 month.

Preliminary procedure: 25 ml of unfiltered sample is placed in the mineralization bottle and 5 ml of $K_2S_2O_8$ solution* is added. Then the samples are boiled under pressure for 30 min and cooled to room temperature.

**$K_2S_2O_8$* *solution preparation*: 5 ml of 4 M H_2SO_4 and 5 g of $K_2S_2O_8$ in 100 ml of distilled water.

Phosphorous compounds are converted to orthophosphate by mineralization with peroxodisulfate. Orthophosphate ions react in acid solution containing molybdate and antimony ions to form an antimony phosphomolybdate complex.

Method description: to the mineralized sample 1 ml of ascorbic acid* and after 30 sec, 1 ml of molybdate solution** is added and mixed well. The absorbance of this blue solution is measured by spectrometer at 880 nm after a period between 10 min and 30 min. Blank sample (distilled water + chemicals) is used in the reference cell. Blank samples absorption is measured against distilled water. In the range from 0,003-0,15 mg/l 5 cm cuvette is used, in the range >0,15 mg/l 1 cm cuvette is used.

**Ascorbic acid solution preparation*: 5 g of $C_6H_8O_6$ diluted up to 100 ml with distilled water.

**Molybdate solution preparation*: 13 g $[(NH_4)_6Mo_7O_{24}*4H_2O]$ + 0,35 g $[K(SbO)C_4H_4O_6]$ + H_2SO_4 solution (120 ml conc. H_2SO_4+170 ml H_2O) add up to 500 ml with distilled water.*

An antimony phosphomolybdate complex is reduced with ascorbic acid to form a strongly coloured molybdenum blue complex.

Expanded uncertainty (k=2) in the range of 0.003-0.01 mg/l is 18.4%; 0.01-0.03 mg/l is 11.9%; 0.03-0.5 mg/l is 9.8%.

Appendix 4 Total COD, NO_3 and PO_4 loading with the Narva River at Vasknarva station calculated by three different methods

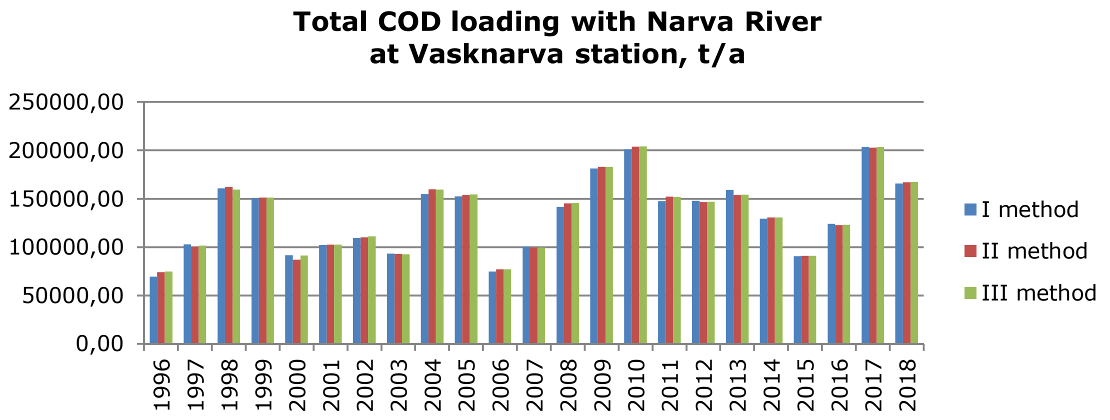

Figure Total chemical oxygen demand in Narva River at Vasknarva station

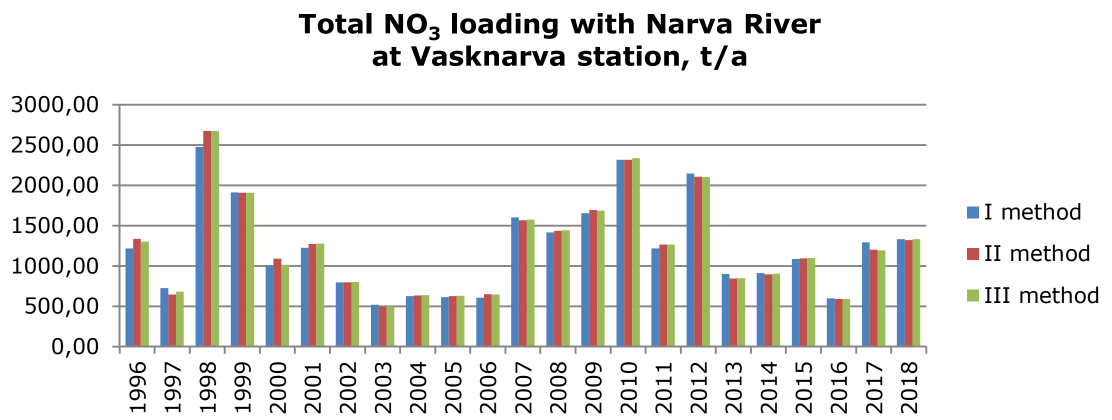

Figure Total nitrate input with Narva River at Vasknarva station

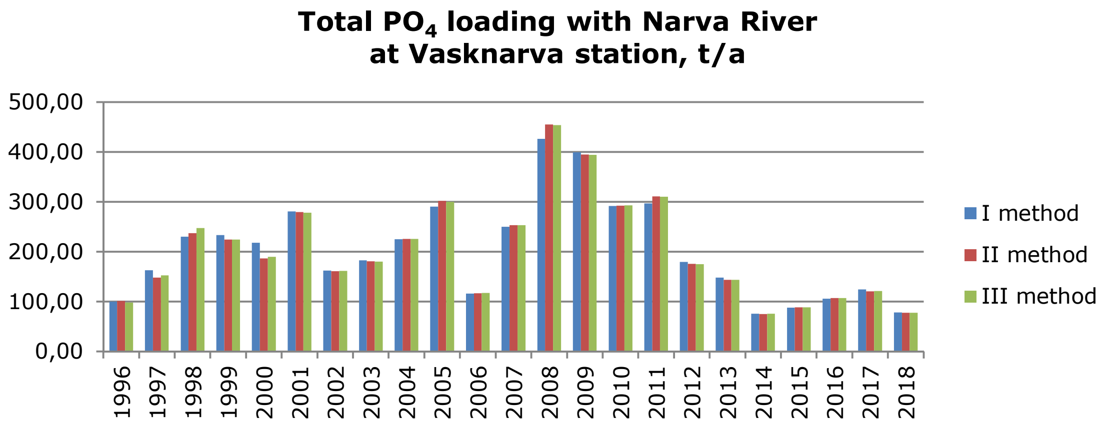

Figure Total orthophosphate input with Narva River at Vasknarva station

Appendix 5 Total COD, NO_3 and PO_4 loading with the Narva River at Narva city station calculated by three different methods

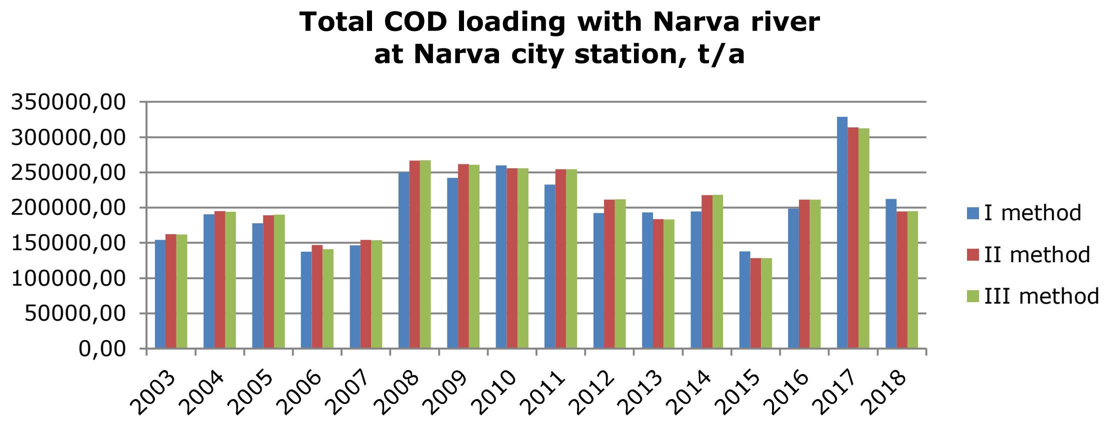

Figure Total chemical oxygen demand in Narva River at Narva city station

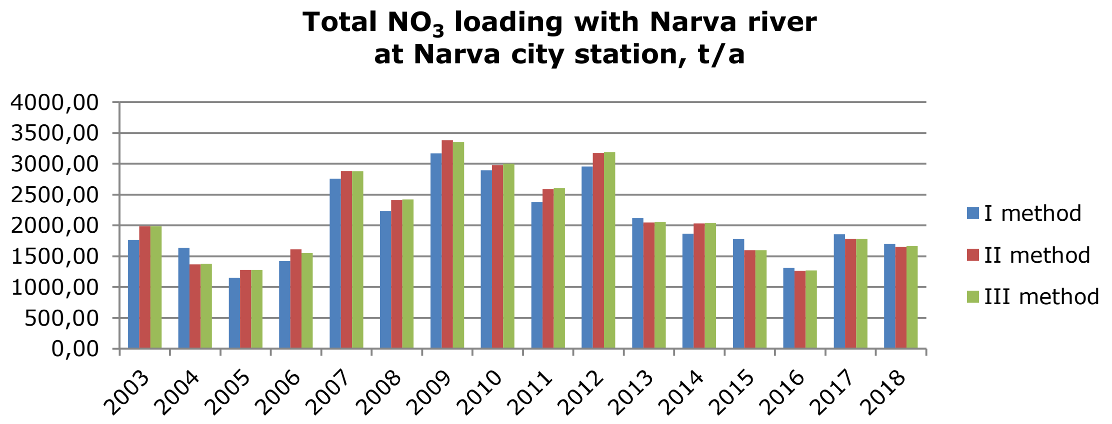

Figure Total nitrate input with Narva River at Narva city

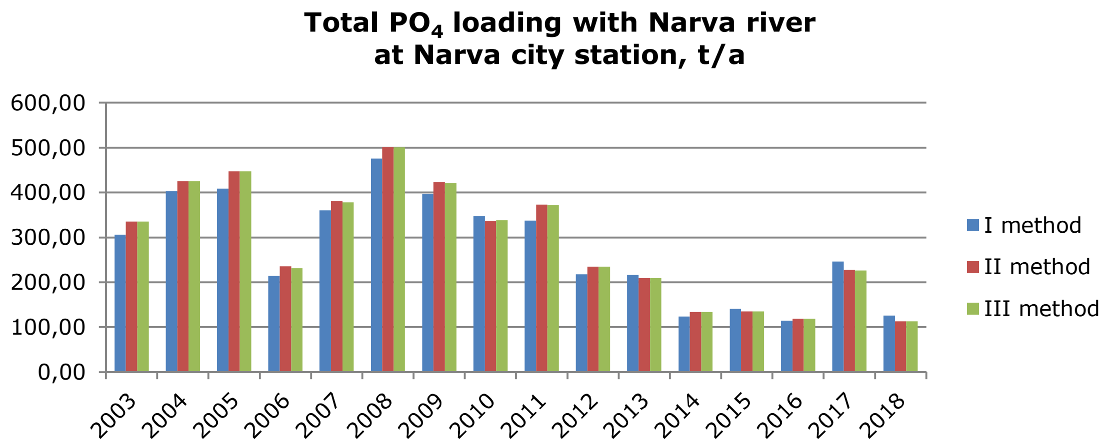

Figure Total orthophosphate loading with Narva River at Narva city station

Appendix 6 Total COD, NO_3 and PO_4 loading with Emajõgi at Kavastu station calculated by three different methods

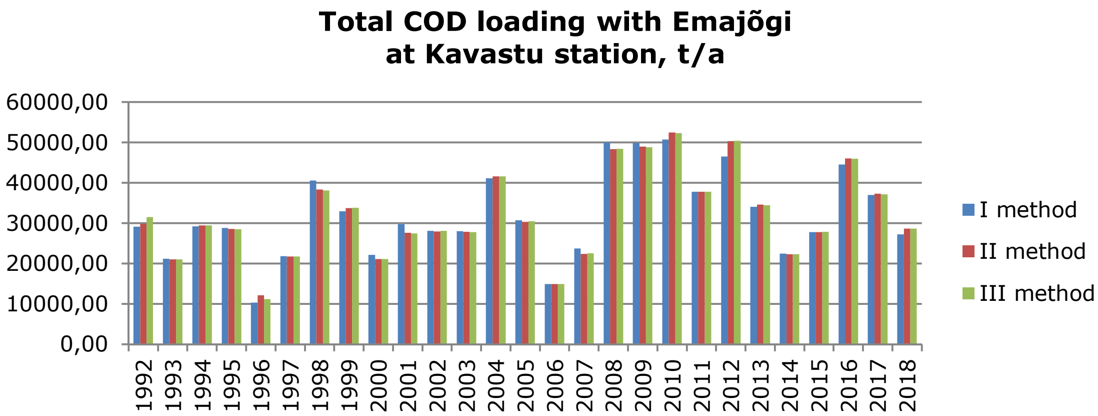

Figure Total chemical oxygen demand in Emajõgi at Kavastu station

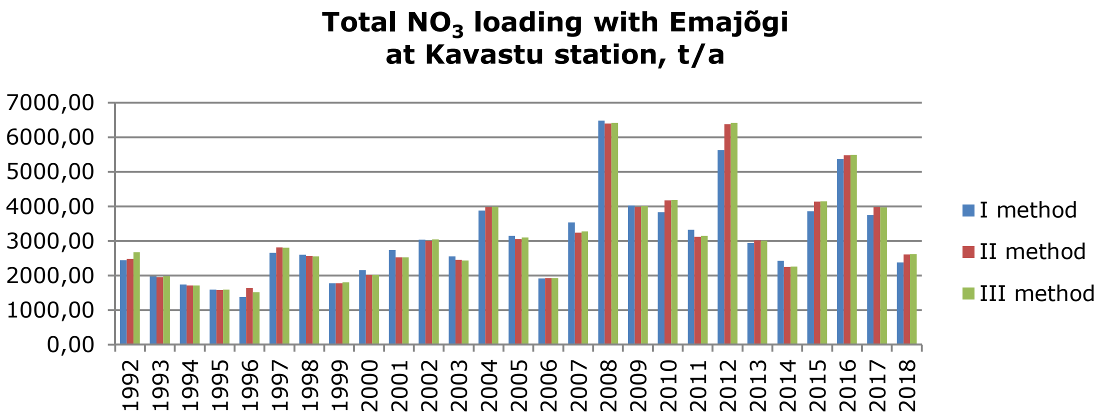

Figure Total nitrate input with Emajõgi at Kavastu station

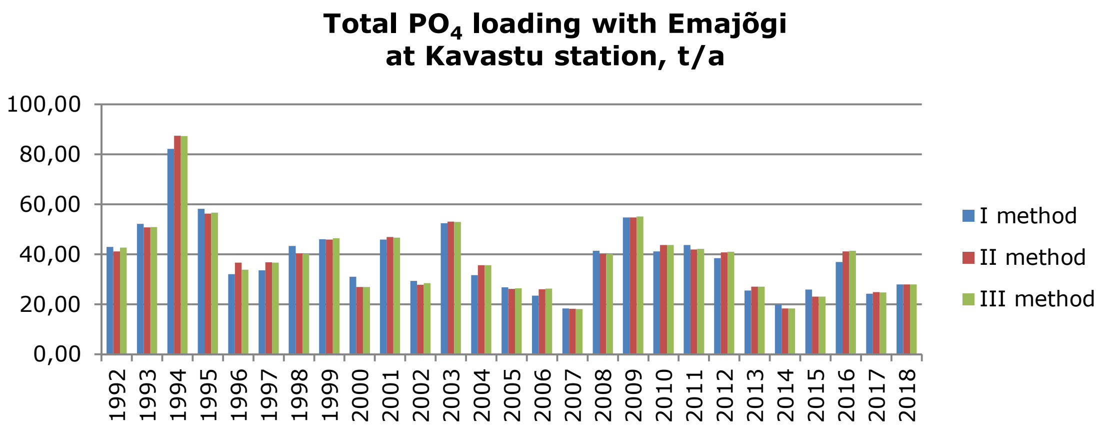

Figure Total orthophosphate input with Emajõgi at Kavastu station

Appendix 7 Probability curves of average annual water flow, COD, NO_3 and PO_4 of Narva River based on data gathered at Vasknarva station covering the period from January 1996 to December 2018

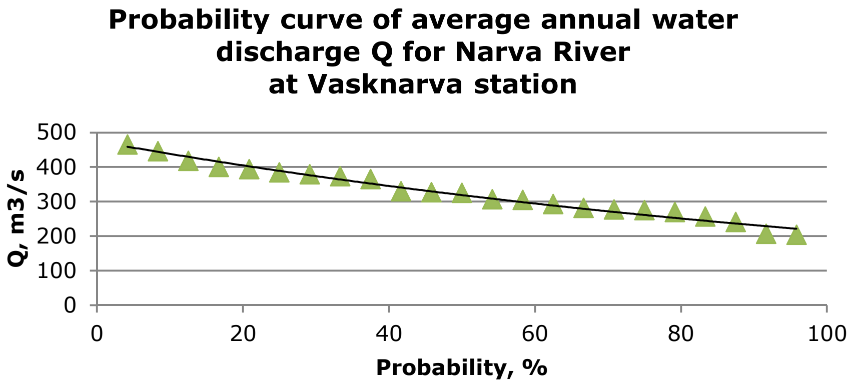

Figure Flow probability curve for the Narva River at Vasknarva station

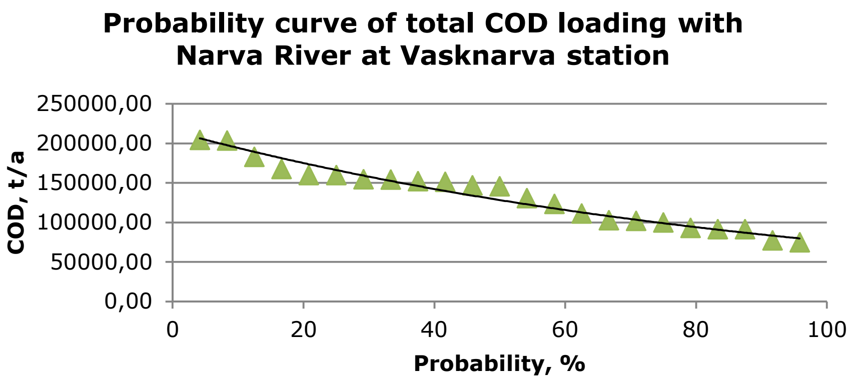

Figure COD load probability curve for the Narva River at Vasknarva station

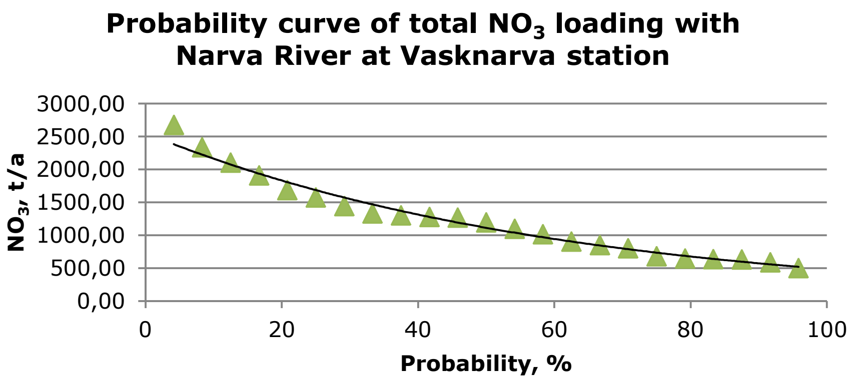

Figure NO_3 load probability curve for the Narva River at Vasknarva station

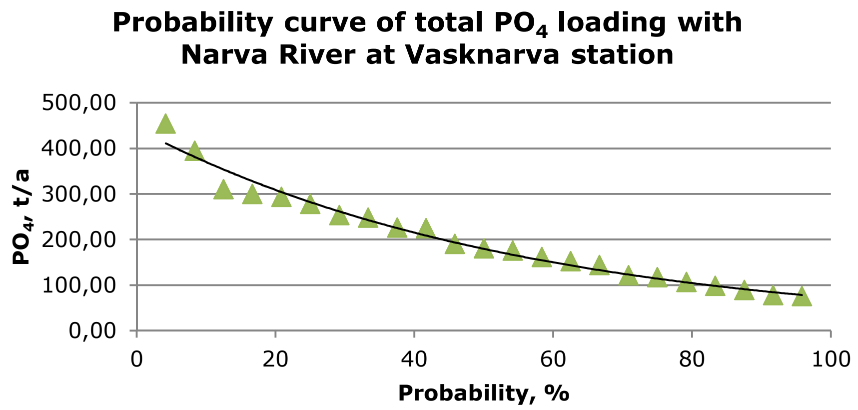

Figure PO_4 load probability curve for the Narva River at Vasknarva station

Appendix 8 Probability curves of average annual water flow, COD, NO_3 and PO_4 of Narva River based on data gathered at Narva city station covering the period from January 2003 to December 2018

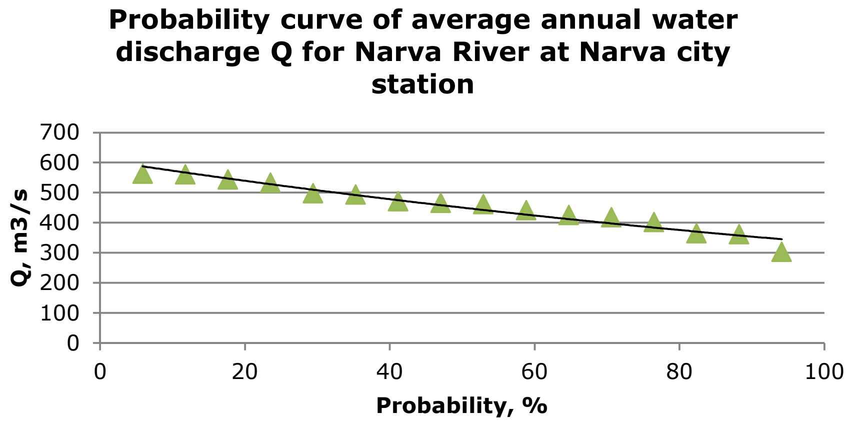

Figure Flow probability curve for the Narva River at Narva city station

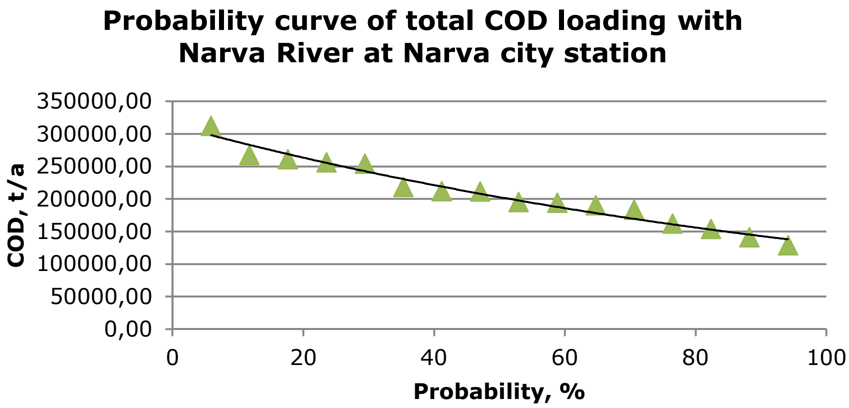

Figure COD load probability curve for the Narva River at Narva city station

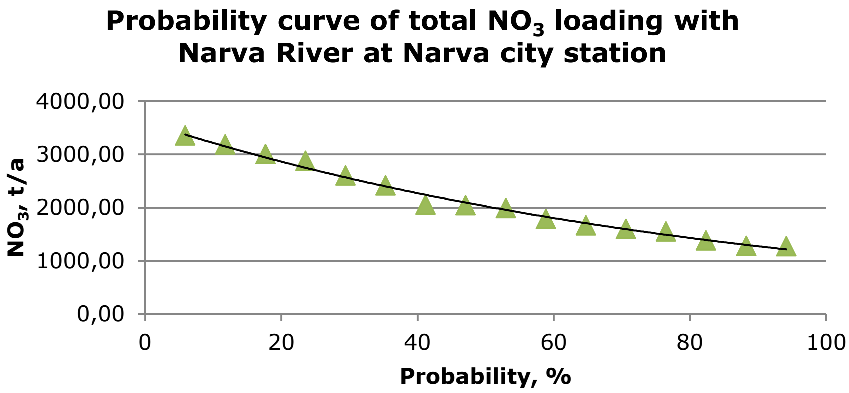

Figure NO_3 load probability curve for the Narva River at Narva city station

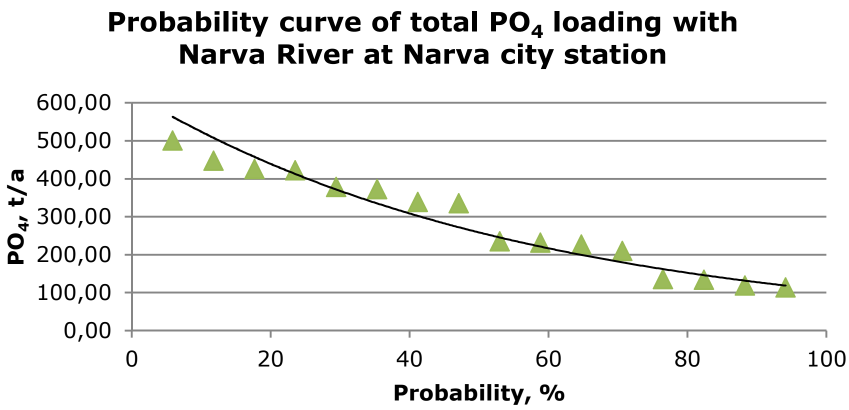

Figure PO_4 load probability curve for the Narva River at Narva city station

Appendix 9 Probability curves of average annual water flow, COD, NO_3 and PO_4 of Emajõgi based on data gathered at Kavastu station covering the period from January 1992 to December 2018

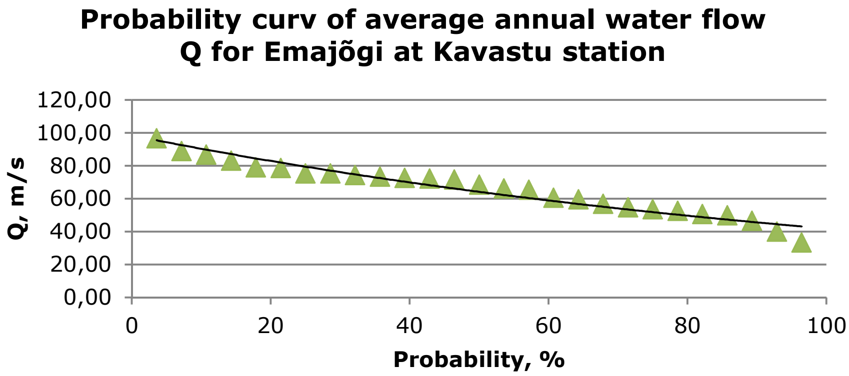

Figure Flow probability curve for the Emajõgi at Kavastu station

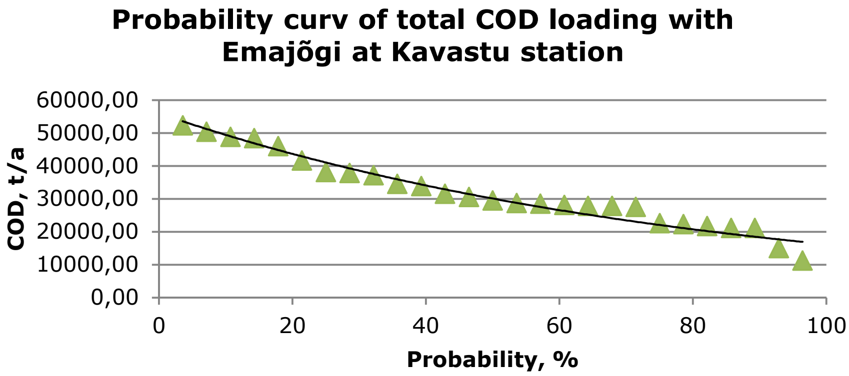

Figure COD load probability curve for the Emajõgi at Kavastu station

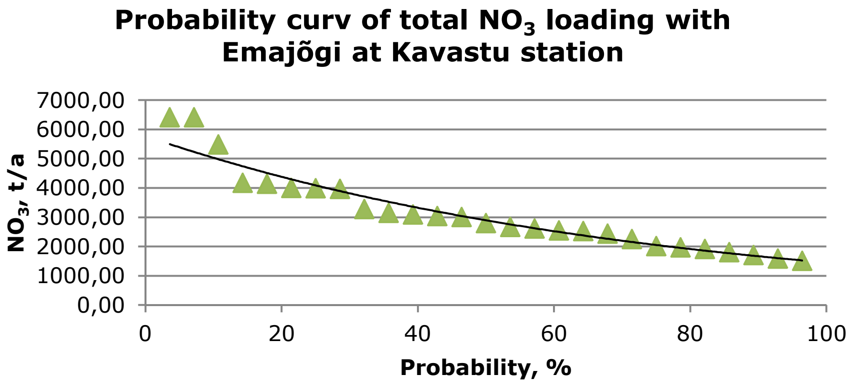

Figure NO_3 load probability curve for the Emajõgi at Kavastu station

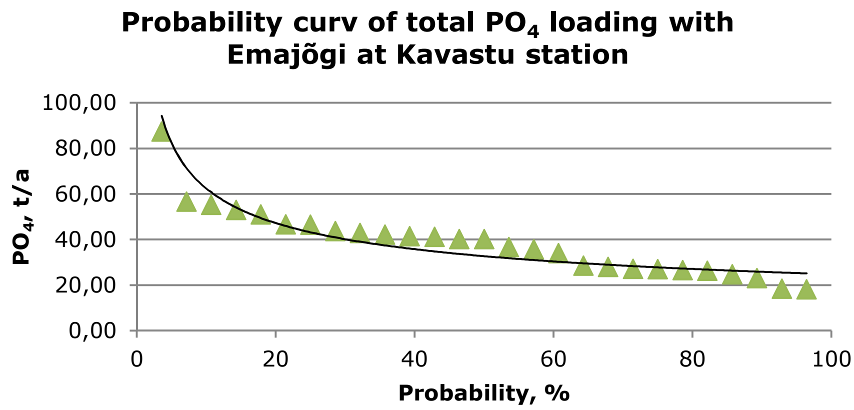

Figure PO_4 load probability curve for the Emajõgi at Kavastu station

Appendix 10 Limits of ecological status classes of surface water bodies of watercourses of type IV according to the values of general physico-chemical conditions *(Keskkonnaministeerium, 2009)*

Quality indicator		**Unit**	**Very good class**	**Good class**	**Medium class**	Bad class	Very bad class
Type IV: catchment area of more than 10,000 km^2 (Narva River)							
Biochemical oxygen demand (BOD_5)	Arithmetic mean	mg O_2/l	<2,0	2,0–2,5	>2,5–4,0	>4,0–5,0	>5,0
Nitrogen content (N_{tot})	Arithmetic mean	mg N/l	<0,5	0,5–0,7	>0,7–1,0	>1,0–1,5	>1,5
Phosphorus content (P_{tot})	Arithmetic mean	mg P/l	<0,04	0,04–0,06	>0,06–0,08	>0,08–0,1	>0,1
NH_4^+	90% guaranteed value	mg N/l	<0,10	0,10-0,30	0,30-0,45	0,45-0,60	>0,60

Appendix 11 Limits of ecological status classes of surface water bodies of watercourses of type III B according to the values of general physico-chemical conditions *(Keskkonnaministeerium, 2009)*

Quality indicator		**Unit**	**Very good class**	**Good class**	**Medium class**	**Bad class**	**Very bad class**
Type III B: light water and low organic matter rivers (90% COD_{Mn} value less than 25 mg O/l) with a catchment area > 1000–10,000 km^2							
Biochemical oxygen demand (BOD_5)	Arithmetic mean	mg O_2/l	<1,8	1,8–3,0	>3,0–4,0	>4,0–5,0	>5,0
Nitrogen content (N_{tot})	Arithmetic mean	mg N/l	<1,5	1,5-3,0	>3,0-6,0	>6,0-8,0	>8,0
Phosphorus content (P_{tot})	Arithmetic mean	mg P/l	<0,05	0,05–0,08	>0,08–0,1	>0,1–0,12	>0,12
NH_4^+	90% guaranteed value	mg N/l	<0,10	0,10-0,30	0,30-0,45	0,45-0,60	>0,60