TALLINN UNIVERSITY OF TECHNOLOGY
School of Engineering
Environmental Engineering and Management

ORGANIC SUBSTANCES AND NUTRIENT CONTENT IN THE SELECTED ESTONIAN RIVERS OF GULF OF FINLAND

ORGAANILISE- JA TOITAINE SISALDUS VALITUD EESTI JÕGEDES SOOME LAHE VALGALAS

Master's Thesis

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Tallinn 2020

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THESIS TASK

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Study programme: Environmental Engineering and Management EABM 03

main speciality:

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In Estonian : Orgaanilise- ja toitaine sisaldus valitud Eesti jõgedes Soome Lahe valgalas

Thesis main objectives:

1. Assessment of nutrient load trends in the selected 12 Estonian rivers flowing into the Gulf of Finland with Mann Kendall Test.
2. Evaluation of Chemical status and Eutrophication level with Nitrogen to Phosphorus ratio and study changes in before and after implementation of BSAP.

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PREFACE

The basis for this research originally stemmed from my passion for water-related courses. The courses I undertook for my Master's program mainly the Water bodies, Water Quality, and Water Conservation study deeply rooted my interest. It really inspired me to recognize the general importance of water in our day to day activities and the necessity of managing the water resources in the community. The Environmental Policy course helped me recognize the various fundamental regulations that are being adopted and implemented by respective countries to protect their water resources in local communities and nations.

In this research, the most important indicators of eutrophication and organic pollution have been taken into consideration in 12 selected rivers flowing from Estonian territory to the Gulf of Finland. The current thesis covers the situation during the years 1992-2019 for 11 rivers and 1997-2019 for one.

I could not have done this without the constant support and advice from my supervisor Professor Karin Pachel for her timely guidance and ideas.
I want to dedicate this thesis to my parents and my family for their love, understanding, and support. Besides, I also want to acknowledge Tallinn University of Technology for this opportunity.

Keywords: Eutrophication, Gulf of Finland, Baltic Sea, Mann Kendall test, Trend Analysis, Estonia

The thesis is in English and contains [60] pages of text, [7] chapters, [42] figures, [17] tables.

List of Abbreviations

BOD_5	Biological Oxygen Demand for 5 days
BOD_7	Biological Oxygen Demand for 7days
BSAP	Baltic Sea Action Plan
CART	Country Allocated Reduction Targets
DO	Dissolved Oxygen
DON	Dissolved Organic Nitrogen
EQR	Ecological Quality Ratio
EU	European Union
GOF	Gulf of Finland
HELCOM	Helsinki Commission
MAI	Maximum Allowable Input
MK test	Mann Kendall Trend Test
NAP	Nitrates Action Program
NH_4	Ammonium
NO_2	Nitrite
NO_3	Nitrate
O_2 Sat	Oxygen Saturation
PLC	Pollution Load Compilation
PO_4	Orthophosphate
RBMP	River Basin Management Plans
T-N	Total Nitrogen
T-P	Total Phosphorus
WFD	Water Framework Directive
WWTP	Wastewater Treatment Plant

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1 INTRODUCTION

Surface water quality deterioration is a serious global concern due to increased pollution and climate change. As a result, countries have already implemented water quality protection measures and monitoring regimens. To better understand water resource conditions, it is critical to assess water quality, especially the major contributors to its spatial and temporal variations. The water quality is the physical, chemical, and biological characteristics of water in relation to a set of standards. The primary importance of surface water quality can be related for its purpose as drinking water, for safety of human contact, and for the overall health of the ecosystem.

The Baltic Sea is distinctly known as one of the most vulnerable marine ecosystems in the world, mainly due to the wide number of human activities that happen in and around the sea. Being the most isolated bodies of brackish water due to its semi-enclosed character and hydrography, it leads to the accumulation of nutrients as well as persistent pollutants [1]. The sea receives an excessive amount of P and N, making it susceptible to marine problems like algal blooms, turbidity, and oxygen depletion problems. Eutrophication and overfishing have been pointed out as the main threats to the ecosystem in the Baltic Sea. One of nine sub catchments of the Baltic Sea is the Gulf of Finland (GOF), which is also experiencing environmental problems marked distinctly to the sea. The GOF is one of the most heavily loaded sub-basins in the Baltic Sea, with the area-specific N and P loads being two to three times higher than those of the entire Baltic Sea [2] [3]. GOF extends largely between Finland, Estonia, and Russia.

In the year 2014, experts from these regions worked together to establish a healthier and safe gulf. The eutrophication state of the GOF is amongst the highest of all basins of the Baltic Sea, but it has shown a decreasing trend, especially after the early 2000s [4]. The key activities that were addressed to reduce the impact in the Gulf of Finland 2014 were;

- Marine Littering – In both marine and freshwater, plastic littering is one of the most ubiquitous environmental problems.
- Unsustainable farming practices,
- Unsustainable shipping- GOF has been one subject to most dense traffic. The volume of maritime traffic in the GOF is increasing [4].
- Accidental oil spills.

The GOF is heavily polluted by nutrients and thus eutrophication is one of the major environmental concerns [5] since it receives most of its land-based nutrient load from the riverine export of the three countries, and some atmospheric deposition originating from other countries. Thus, being a trans-boundary matter, the solution needs to be trans-national. Consequently, in 2007, the Baltic Sea Action Plan (BSAP) was adopted by HELCOM's (Baltic Marine Environment Protection Commission-Helsinki Commission) Contracting Parties and the EU to work together and achieve an unaffected Baltic sea from eutrophication.

Currently, the countries are bound to implement the Directive 2000EC/60. Accordingly, Maximum Allowable Inputs (MAI) into the Baltic Sea were identified, and country allocated reduction targets (CARTs) were also constituted for respective parties, followed by the Water Framework Directive (WFD) regional River Basin Management Plans (RBMP) in 2007 [6]. The good status of all surface water, including coastal water, by a set deadline, is the directive's key objective. This is implemented to all the water bodies (rivers, lakes, stretches of coastal water, and groundwater). However, further reduction of inputs to meet the ambitious nutrient reduction goals of HELCOM and WFD seems to be a challenge, particularly for Finland and Estonia [5].

The two main components of the nutrient reduction scheme MAI and CART specify the maximum level of N and P inputs allowed into the Baltic Sea sub-basins to achieve the target of a non-eutrophic sea. The BSAP is built on four strategic ecological objectives [7].

1. The Baltic Sea unaffected by Eutrophication.
2. Favorable conservation status of Baltic Sea Diversity.
3. The Baltic Sea Life undisturbed by hazardous substances.
4. Maritime Activities in the Baltic Sea carried out in an environmentally friendly way.

In this regard, reporting the nutrient loads of the following constituents and defining the chemical status of the river is obligatory for the contracting parties, according to PLC [7]. Ultimately, the chemical status and eutrophication level of the rivers were also indicated in the study as to the national limit values and nitrogen to phosphorus ratio criteria. Mann Kendall Test is used as the statistical method to validate the results of the trend analysis. The mean monthly concentration method is used to find the nutrient and BOD concentration while, the 90th percentile is used to find the NH_4-N. The 10th percentile is used to find the DO concentration. The chemical status of rivers is defined based on the following constituents in mg/l.

- Biochemical oxygen demand for 5 days (BOD_5)
- Total nitrogen T-N is the sum of total Kjeldahl nitrogen (NH_4-N, organic and reduced nitrogen) and NO_2-N, NO_3-N.
    - Ammonium ion (NH_4-N)
    - Nitrite ion (NO_2-N)
    - Nitrate ion (NO_3-N)
- Total phosphorus T-P is the sum of organic P and PO_4-P
    - Orthophosphate ion (PO_4-P)
- Dissolved Oxygen

1.1 Physico-chemical indicators

Physical and chemical indicators are used in water quality assessment and analysis. They include pH, temperature, dissolved oxygen, salinity, and nutrients. Although physico-chemical indicators can identify the cause of the problem, they only give limited information on the extent to which pollutants impact the fauna and flora. For that matter, biological indicators are needed [8] which is not included in the study. Some of the water quality indicators used in this study is explained below.

pH: The pH value is an indicator to monitor acidity and alkalinity of a water from a scale of 0-14. The pH lower than 7 is considered as acidic and pH greater is considered basic. The water quality criteria in Europe are between the ranges 6-9. Lower and extreme pH is not suitable for the marine biodiversity as it is harmful to the fish and insects [9].

Suspended Solids: It is the amount of suspended particles within the water body. If there is a high concentration of such particles, it restricts light penetration and ultimately hinders photosynthesis. The suspended particles can also damage the fish gills causing problems in the ecosystem. Analytically, it is determined by filtering a known volume of water through 0.45 µm filter paper and weighing the sample. It is measured in mg/l.

Turbidity: It is the degree to which light is scattered by the suspended solids in water in the presence of the salts, clay, silts, etc. suspended in water bodies. It is caused by soil erosions, excess nutrients, and waste pollutants. Such particles increase the temperature of the water by absorbing the heat from the sunlight, decreasing the DO content. This, in turn, further reduces the photosynthesis process in plants harming the overall marine biodiversity. It can be measured with an electronic turbidimeter and reported in units of Nephelometric Turbidity Unit (NTU).

Temperature: It impacts the rates of metabolism and growth of aquatic organisms, the rate of plants photosynthesis, the solubility of oxygen in river water, and organism's sensitivity to disease, parasites, and toxic materials [9]. When the temperature in water bodies increases, plants grow and die faster, leaving behind matter that requires oxygen for decomposition. It is an important parameter as it can alter the physical and chemical properties of the water. Heat transfer from the air, sunlight, or thermal pollution can cause changes in the temperature.

Biochemical Oxygen Demand (BOD): It is the amount of dissolved oxygen needed by aerobic biological organisms to break down organic material present in a given water sample at a certain temperature over a specific time period. The BOD value is most commonly expressed in mg of oxygen consumed per liter of the sample during 5 or 7 days of incubation at 20 °C. BOD_5 is used in the study. It is also used as an indicator of organic pollution in water bodies.

Organic Nitrogen: In the river and lakes are dissolved organic nitrogen (DON), which is produced either from the photosynthesis of algae and plants or excreted as nitrogenous waste by animals. The leachate from the soil, sewage discharges, and deposition from the atmosphere can also produce organic nitrogen in the water bodies. Most of the DON compounds in freshwater are usually amino acids, proteins, nucleic acids (RNA and DNA), and Urea.

Inorganic Nitrogen: It is the sum of Ammonia and Total oxidized Nitrogen, namely Nitrate and Nitrite.

Nitrate (NO_3): It is the most stable and oxidized form of nitrogen in the water bodies. It is formed by the complete oxidation of the nitrogen compounds. It is the primary form of nitrogen used by the plants as a nutrient for their growth. However, excessive amounts of nitrogen result in phytoplankton or macrophyte proliferations, which is toxic to the infants at a high level. It is determined using spectrophotometric or chromatographic methods as mg/l N or mg/l NO_3 [10].

The following conversion factor applies:

Table 1 Showing conversion Factor from mg/l NO_3 to mg/l N [10]

From	To	Divide by
mg/l NO_3	mg/l N	4.43

Nitrite (NO_2): It is an intermediate nutrient formed during the oxidation of ammonia to nitrate in a process called nitrification. Effluents like sewage are rich in ammonia, which can gradually lead to the formation of nitrite and increase its concentrations in receiving waters. Thus, higher levels of nitrite in the river may indicate pollution. Although this form of nitrogen can be used as a source of nutrients for plants and its presence promotes plant proliferation, however, NO_2 is toxic to aquatic life even at lower concentrations. It is determined using spectrometric methods.

Table 2 Showing conversion factor from mg/l NO_2 to mg/l N [10]

From	To	Divide By
mg/l NO_2	mg/l N	3.28

Ammonia Nitrogen: It occurs in the water bodies naturally due to the microbiological decomposition of nitrogenous compounds in organic matter. Aquatic organisms like fish also excrete ammonia. It exists in aqueous solutions in two forms, ionized (NH_4^+) and un-ionized (NH_3). The un-ionized fraction is toxic to freshwater fish at very low concentrations. Its concentration depends on temperature, pH, and salinity. The concentration of NH_3 increases with increase in temperature and pH with reducing salinity. Analytically, NH_3 is usually determined by titration or colorimetric tests. The units are mg/l N, mg/l $NH_{3,}$ or mg/l NH_4 with the proper conversions.

Table 3 Showing conversion from mg/l NH_3 and mg/l NH_4 [10]

From	To	Divide by
mg/l NH_3	mg/l N	1.22
mg/l NH_4	mg/l N	1.29

Total Nitrogen (TN): It is the measure of all forms of organic Nitrogen and inorganic Nitrogen. Total Nitrogen is determined by digesting the sample following the colorimetric measurement. Its unit is mg/l N. It is an essential nutrient for plants and animals. However, an excess amount of nitrogen in a waterway may lead to low levels of DO and negatively impact various plant life and organisms. Sources of nitrogen may include WWTP, runoff from fertilized lawns and croplands, failing septic systems, runoff from animal manure and storage areas, and industrial discharges [11].

$$Total\ Nitrogen(mg/l\ N) = \text{Total Kjeldahl Nitrogen} + \text{Total Oxidised Nitrogen} \quad (1.1)$$

Total Phosphorus (TP): It is the sum of both inorganic and organic phosphorus. An increase in P content can lead to an algal bloom, accelerated plant growth, and low DO content. The sources may include soil and rocks, wastewater treatment plants (WWTP), runoff from fertilized lawns and cropland, failing septic systems, runoff from animal manure storage areas, commercial cleaning preparations, etc. The phosphorus in natural water and wastewaters can be found in the form of phosphates (PO_4).

- Inorganic form (including orthophosphates and condensed phosphates)
- Organic form (organically-bound phosphates)

Orthophosphate: It is the most readily available form for uptake during photosynthesis. But higher concentrations generally occur when it co-exists with the algal blooms. The orthophosphate is determined colorimetrically and is typically reported as mg/l P.

Table 4 Showing conversion from mg/l PO_4 to mg/l P [10]

From	To	Divide By
mg/l PO_4	mg/l P	3.07

Dissolved Oxygen (DO): It is the free (not-bonded) oxygen compound present in water bodies. It has an immense influence on the organisms living within the water body. A DO level that is both too high and too low can harm aquatic life and affect water quality. Since the photosynthesis is light-dependent, DO tend to peak during the day and decline during the night. This parameter is vital for marine life and is a critical indicator of pollution and eutrophication in rivers. The solubility of the oxygen depends on temperature and salinity. It can be reported in % saturation as well as mg/l O_2 in terms of concentration. Several Factors can cause variation in DO. Such deviations can be caused by

- River Morphology
- Seasonal changes in Temperature
- Oxygen consumption
- **Eutrophication** – It is triggered by excessive amounts of nutrients washed into the sea. In eutrophic rivers, the oxygen exchange between the flora and water leads to high oxygen content during the day and sharp decreases at night.

1.2 Aim of the Thesis

The main goal of the current thesis is to assess trends and estimate nutrient loads with the Mann Kendall Trend Test for 12 monitoring rivers (Pühajõgi, Purtse, Kunda, Selja, Loobu, Valgejõgi, Pudisoo, Jägala, Vääna, Keila, Pirita and Vihterpalu) in Estonia that flow into the Gulf of Finland catchment area. Subsequently, another goal is to evaluate the chemical status and eutrophication level of these rivers regarding national criteria and nitrogen to phosphorus ratio during the years 1992 to 2019 for 11 rivers and 1997-2019 for one river (River Pirita).

2 STUDY AREA, MATERIALS AND METHODS

2.1 Study Area

The North Estonian coastal sea stretches for about 300 km from west to east along the GOF, which has an area of 29 500 km^2 and an average depth of 37 m [12]. The Gulf receives large pollution from three municipalities (Tallinn, St. Petersburg and Helsinki) and industries as well as wastewater sludge (from St. Petersburg) and rivers [13]. The riverine export varies from year to year due to the fluctuation in river flow and weather conditions, especially rainfall, which affects annual nutrient export.

In this study, the main selected rivers located at the West Estonian river basin (Lääne-Viru), East Estonian (Ida-Viru), and Harju County are considered for organic substances and nutrient content assessment (Figure 1 and Figure 2).

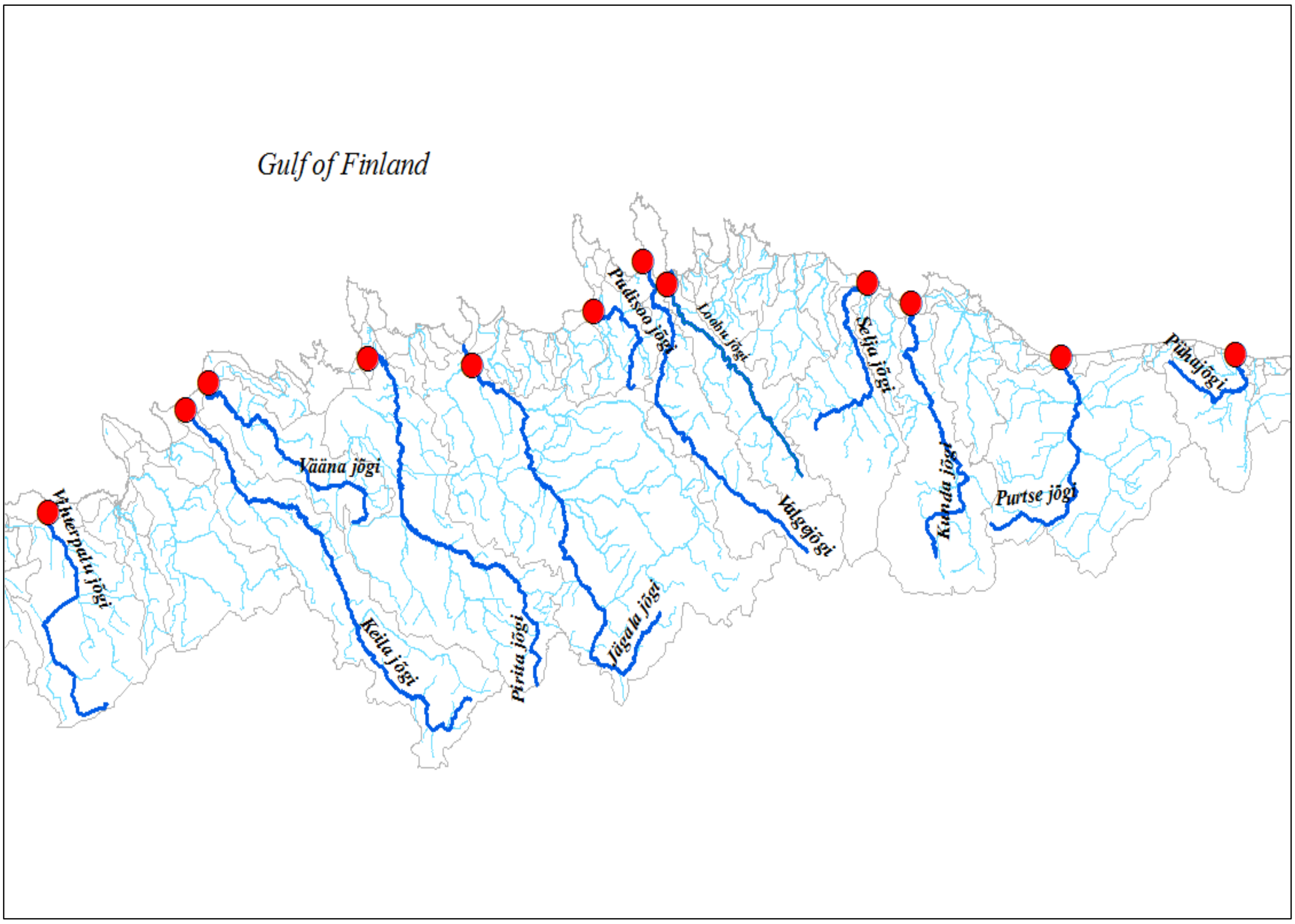

Figure 1. Sampling locations

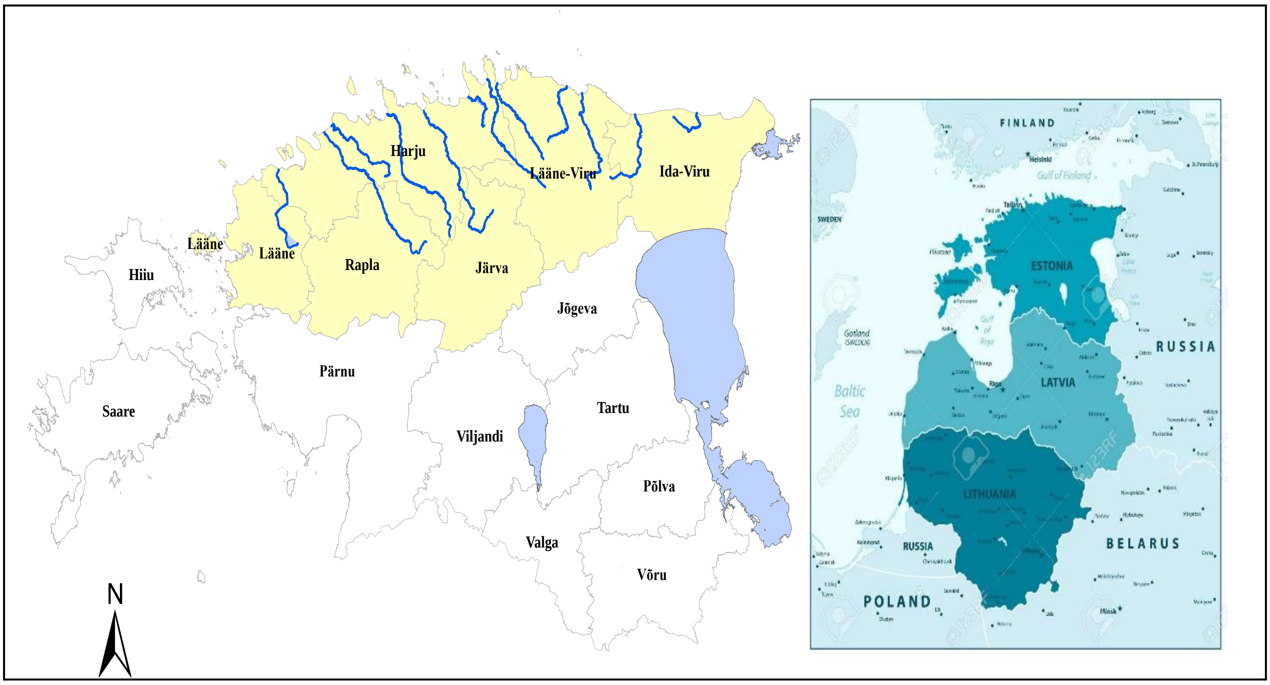

Figure 2. The study area: North Estonia (source of rivers) and Gulf of Finland

2.1.1 Catchment Properties

The catchment area of the GOF covers 422 580 km^2, of which 25.32% belongs to Finland, 67.58% to Russia, 6.25% to Estonia, and less than 1% to Latvia (Table 5). The city of St. Petersburg and adjacent regions, Karelia and Estonia, are the main contributors to the Gulf pollution [13]. 23% of the runoff of Estonian rivers flows into the GOF. There are hydro-chemical monitoring stations on 13 rivers flowing from Estonia, which accounts for 85% of the catchment area. Out of the 26 400 km^2 of the GOF drainage area in Estonia, the runoff is checked on 21 545 km^2 or 81.6% of the catchment area [14].

Table 5 Division of the GOF catchment area between the contracting parties (km^2) [15]

Sub-basins/Country	Estonia	Finland	Russia	Latvia
GOF Catchment Area proportion (km^2)	26400	107000	285580	3600

Tallinn is home to 401 500 inhabitants, i.e., about 30% of the population of Estonia. It was originally included in the HELCOM List of Hot Spots as the largest source of pollution in Estonia [5] in the early 1990s. Due to the construction of WWTPs over the last two decades, the pollution load has been decreasing. Tallinn's WWTP was removed from the Hot Spots list in 2006, and by the end of 2014, the wastewater treatment results complied with the HELCOM recommendations for both P and N [5].

2.1.2 The Main Factors that influence Water Quality

The northern part of Estonia is heavily industrialized with oil shale based chemical industry and power plants, cement and pulp mills, and a soviet-era depository of radioactive wastes that have impacted virtually every component of the Baltic Sea environment. It is also the major pollution source and is a hot spot for the Baltic environment [12]. This region embodies the largest industrial (Kunda Nordic Cement, Viru Keemia Grupp AS, Kiviõli Keemiakombinaat, etc.) and energy (Baltic and Estonian thermal power plants) enterprises. Nutrients may enter the Baltic Sea not only as riverine export but also as direct point source loads and atmospheric deposition.

1. Pulp and Paper Industry

In the early years, there were two large pulp and paper mills (Tallinn mill and Kehra) in Tallinn, which discharged either directly or via rivers to the GOF, impacting its water quality. Some adverse aspects of the pulps were not monitored then. Conversely, today, most pulp mills are required to utilize chlorine-free bleaching processes around the Baltic Sea. Yet about 50% of the total organochlorine inputs from pulp mills since the early 1940s still reside in the Baltic Sea, mainly in the bottom sediments [12]. Large-sized pulp and paper industries primarily located in land-lakes discharge substantial amounts of organic substances and nutrients. Pulp and paper industry plays a significant role in the discharge of oxygen-consuming, nutrient-rich, and slowly degradable substances to the receiving waters.

2. Oil Shale Power Plants

The two large oil shale burning power plants located near the city of Narva are the critical source of atmospheric emissions in Estonia. The majority of mined oil shale is used for the generation of electricity in two thermal power plants. As oil shale is a low-grade fossil fuel, each year 4-5 million tons of oil shale ash and semi-coke is dumped near the power plants where residual organic matter is prone to self-ignition and gives gaseous emissions (e.g., SO_2, NO_x) influencing rivers of Narva, Purtse, Valgejõgi and Jägala [12].

3. Wastewater Treatment Plants (WWTP)

Municipal sewage and industrial water flowing from Russia and Estonia were principal causes of water quality in the GOF that contributed to the problem significantly in earlier days. Since the early 1990s, after the development in the WWTPs, the P load from the city of Tallinn (Estonia's largest municipal source), has decreased by 90%, while the N load has decreased by 75% in the GOF (2016) [5].

4. Agricultural effluents

Run-off from agricultural sources is known to be one of the main sources of diffuse pollution in Estonia, and it is the most difficult to control. Large scale livestock production is still dominant in Estonia. Arable land currently occupies about 690000 ha [16]. The agricultural pressure from crop production is mainly achieved through the intensive use of pesticides and chemical fertilizers. Although the mineral fertilizers and pesticide uses decreased as prices increased in earlier days, now the main legal act, regulating water protection in Estonia, is the Water Act, which governs and implements EU Nitrates Directive (91/676/EEC) and WFD (2000/60/EC). With growing livestock, a new class of agricultural pollutants in the form of veterinary medicines (antibiotics, vaccines, and growth promoters) also emerged [17]. Action programs, like RBMP and Nitrates Action Program (NAP), were also launched according to the Water Act. The EC (Good Agricultural Practice for Protection of Waters) Regulations 2006 allow farm inspection by local authorities.

5. Solid Waste

Careless and illegitimate dumpings may cause adverse environmental problems contributing to contamination of local rivers, aquifers, and ultimately the gulf and the sea. Destruction of such waste through uncontrolled incineration without the treatment of flue gas can also lead to pollution. The hazardous waste from households and industries should be handled separately from regular wastes and treated properly.

6. Radioactive Discharges

The Baltic Sea has been affected due to the Chernobyl accident and nuclear weapon tests in the atmosphere. This kind of discharge is typically manmade. At Sillamäe in North-Eastern Estonia, there was a waste deposit with radioactive waste close to the Baltic Seashore. Its closure and sanitation of the depository in 1998-2008 became one of the highest priority environmental projects over the whole Baltic Sea basin [12].

2.2 Dataset

Data series for water quality with new national monitoring program and changed methodology in laboratories began in 1992 and have continued up to today [18]. State monitoring of river water quality involves 61 stations on 47 rivers and streams [19]. The state keeps account over water resources and their status. In Estonia, an account of water resources is kept in the National Environmental Register as a water cadastre. The purpose of keeping the state water cadastre is to keep a record of the amount, quality, use, and users of water in Estonia, as well as the long-term holding and issuing of data [20].

A minimum of 12 datasets should be collected over a year for all monitored rivers to estimate the annual input load. The samples do not need to be collected at regular monthly intervals, but it should be at a frequency that appropriately shows the expected river flow pattern. This is mainly important if only 12 samples are taken annually, and there is a marked annual variation in the flow pattern [21].

The monitoring database from the Estonian Environmental Register is used to analyze water quality in the North Estonian Rivers. The study includes historical data over the period 1992-2019 for 11 rivers and 1997-2019 for one. Although there was some data missing on organic pollution nutrients, it is sufficient for identifying trends in rivers. For most of the rivers studied in this research, sampling frequency was once a month. The unit of values in hydro-chemistry data was on mg/l. Analyses on the water samples have been carried out using standardized methods - ISO 6878 for TP, ISO11905 for TN, and ISO 10304-1 for nitrate [19]. Regular pollution control in coastal waters began in 1967 for water samples from North-Estonian rivers by the Tallinn Technological University. They were responsible for the analysis until 2014. Now, the two Estonian laboratories involved in sampling are the Estonian Environmental Research Centre (EKUK) and the Estonian Marine Institute (University of Tartu). They include laboratory analysis and studies for both the historical data and the more recent data from the national monitoring program [12].

2.3 Methods

The condition of the indicators measures the evaluation of the ecological status of the surface water bodies. The member states should make an ecological status classification based on relevant biological elements, physico-chemical elements, and hydromorphological in the assessment of ecological status, as shown in Table 6. The trend assessment method is discussed in section 2.3.2.

Table 6 Quality elements to be used for the assessment of ecological status based on the list in Annex V, Table 1.1, of the Directive [22].

Surface Rivers
Biological Elements • Composition and abundance of aquatic flora • Composition and abundance of benthic invertebrate fauna • Composition, abundance and age structure of fish fauna
Chemical and physico-chemical elements • Thermal conditions • Oxygenation conditions • Salinity • Acidification status • Nutrient conditions • Specific pollutants   ○ Priority pollutants and non-pollutants identified by the member states
Hydromorphological elements • Quantity and dynamics of water flow • Connection to ground water bodies • River continuity • River depth and width variation • Structure and substrate of the river bed • Structure of the riparian zone

2.3.1 Ecological Status Classification

Excerpts from the Water Framework Directive [23] pertaining to ecological status:

Article 2 (21): "Ecological status" is an expression of the quality of the structure and functioning of aquatic ecosystems associated with surface waters, classified in accordance with Annex V.

In the Directive, Annex V provides a general definition of ecological quality in each of the five status classes (See Table 7). The basic principle for the classification of ecological status is based on Ecological Quality Ratio (EQR);

$$EQR = \frac{Observed\ Biological\ Value}{Reference\ Biological\ Value} \tag{2.1}$$

The assessment principles used for eutrophication status and biodiversity status are summarized in the table below. Member States are obliged to provide a map for each river basin district displaying the classification of the ecological status for each body of water. It is color-coded in accordance with the second column of the table set out below to indicate the ecological status classification of the body of water [24]. The overall quality is represented by the worst biological quality element, expressed in five-level classification statuses from high to bad.

Table 7 The assessment of Ecological status EC WFD 2000 [23] for more details

classification	**colour code**	**status**
High	Blue	Acceptable
Good	Green	
Moderate	Yellow	Impaired
Poor	Orange	
Bad	Red	

The point of reference is given by undisturbed conditions showing no or minor human impacts [22]. The good status for surface water means it has a good ecological status and a good chemical status. For each indicator, good status is defined by setting a threshold value against which the current status can be achieved. The observed value in response to threshold conditions can be interpreted as if the status is high; the disturbance is none or minor deviation from the reference period. While if the status is Good > Slight Deviation, Moderate > Moderate Deviation, Poor > Major Deviation and Bad > Severe Deviation.

2.3.2 Statistical Analysis

The PLC-6 assessment and the development of HELCOM core input pressure indicators need parties to perform trend analysis on normalized time series of nutrient inputs to different parts of the Baltic Sea. This is done to evaluate if nutrient inputs are reduced and determine whether the CARTs have been achieved.

There are a number of different trend analysis methods, which can be both non-parametric and parametric. The method performed in this research for the trend analysis is known as the Mann-Kendall's trend test (hereby MK test), a non-parametric trend method. Most of the non-parametric methods for trend detection in water quality time series are based on this classical test [25] [26]. MK test is used to determine whether a time series has a monotonic upward or downward trend [27] for the water quality time series. The results are graphically presented in section 5.2. Concerning trend analysis, this method is chosen for testing the significant monotone trend in the water quality data time series due to its following advantages.

- The method is reasonably robust as irregularly spaced observations and missing data does not impact the yearly time series of nutrient inputs.
- Outliers which can be due to the detection limit of the measurement method can also be handled appropriately by the nonparametric tests [28] [29]. Water quality data time series often show such limiting characteristics.
- This non-parametric method can be used on raw nutrient time series, normalized time series, and runoff (climate) time series. If it is decided to use monthly input time series in the future, the Kendall trend test has been extended to a seasonal version [30] [31].
- Parametric methods are most powerful if data is normally distributed. However, since the marginal distribution of water quality data is often skewed [30] [28], nonparametric tests have a higher power in non-normality.

Disadvantages

- The power of the Kendall trend method is slightly lower than ordinary linear regression if the time series data are Gaussian distributed, and the trend is actually linear, as this will encompass slightly less restrictive assumptions.

Test interpretation

In this test, the null hypothesis H_0 states that there is no trend, and the alternative hypothesis states that there is a monotonic trend in the two-sided test or that there is an upward (or downward trend) in the one-sided test by comparing the p-value to significance level alpha. Hence, on rejecting the H_0, the result is said to be statistically significant. For the time series X_1 ..,X_n, the MK statistics (*S)* is given by [27]:

$$S = \sum_{i=1}^{n-1} \sum_{j=k+1}^{n} \text{sign}(x_j - x_i) \quad (2.2)$$

$$sign(x_j - x_i) = 1 \; if x_j - x_i > 0$$

$$= 0 \; if \; x_j - x_i = 0$$

$$= -1 \; if \; x_j - x_i < 0$$

Note that the data values are evaluated as an ordered time series. If MK stat, $S > 0$, then observations later in the time series are larger in number than those in front in the time series, while if $S < 0$, the reverse is true. A very high positive net value of S suggests an increasing trend, and a low negative net value indicates a decreasing trend. To compute the probability associated with S and the sample size, n, and to statistically quantify the significance of the trend; the variance of the S is given by:

$$var = \frac{1}{18}[n(n-1)(2n+5) - \sum_{t=1}^{g} f_t(f_t - 1)(2f_t + 5)] \quad (2.3)$$

Where n is the number of data points, g is the number of tied groups, t varies over the set of tied ranks, and f_t is the number of times that rank t appears. Another statistic obtained by running the MK test is Kendall's tau, which measures the strength of the relationship between two variables. It ranges between +/- 1 and +1.

The MK test uses the following Z test statistics to measure the statistical significance for sample size N>10:

$$Z = 3 * \frac{\tau_b \sqrt{n(n-1)}}{\sqrt{2(2n+5)}} \quad (2.4)$$

where Z score = the measure of standard deviations, $\tau_b = \text{Kendall's Tau}$ and n = number of observations. This is also used to test the null hypothesis. If $|Z|$ is greater than $Z_{\alpha/2}$, where α corresponds to the chosen significance level (e.g., at 5% with $Z_{0.025}$ =1.96) then the $H_{0,}$ null hypothesis is considered to be invalid.

In this research, the trend is based on the assessment of the nutrient load T-N and T-P calculated by the software Addinsoft's XLSTAT 2020, and linear trend lines are plotted for each using Microsoft Excel 2007.

2.3.3 Data and Assumptions

Monitoring data were collected between the years 1992-2019 in all except one of the rivers, particularly River Pirita, as its monitoring only started in 1997. Based on the MK test, the River Vääna had the maximum number of data (334) and River Pudisoo the least (219). River Pirita had samples of 23 years only (since 1997-2019) compared to the rest of the rivers that had readings for the last 28 years (1992-2019). Two key assumptions were used for processing the data.

- It is assumed that when multiple samples were collected in a single month, the mean value of those samples was considered as the representative sample. This was necessary as the MK analysis required only one data point at a given instant of time (see section 3.1, page 39).
- The probability level of significance used in the test is 5%. At $\alpha = 0.05$, the null hypothesis of no trend is rejected implying that the trend is significant, if the z score, $|z|$ => 1.96 or < -1.96 (according to formula 2.4).

Applied Coefficients

Conversion factor for BOD

From the historical data series, it can be said that BOD_7 was measured from 1992 through 2009. During the fifth Baltic Sea Pollution Load compilation [32], it was decided to report BOD_5 in place of BOD_7. To convert BOD_7 to BOD_5, in the PLC assessment, a conversion factor as follows is used.

$$BOD_5 = \frac{BOD_7}{1.15} \qquad (2.5)$$

where BOD_5- Biological Oxygen Demand in 5 days, BOD_7- Biological Oxygen Demand in 7 days

2.4 Classification of Surface Waters

Excerpt from the Directive 2000/60/EC about surface water bodies:

Article 2, point 10: “Body of surface water” means a discrete and significant element of surface water such as a lake, a reservoir, a stream, river or canal, part of a stream, river or canal, a transitional water or a stretch of coastal water.

According to Regulation No. 44 of the Minister of the Environment-Estonia, the typology of rivers here is based on size and geological characteristics (soil conditions) and content of organic matter.

Table 8 Typology of Estonian Rivers [33]

Class		**COD (mg/l)**
Class A-Light Water	Low Content	<25
Class B-Dark Water	High Content	>25

According to the table above, the low COD is classified under light water (class A), and the dark water (class B) indicates high organic content. The classification based on the catchment area is shown below in Table 9 Classification by the catchment area.

Table 9 Classification by the catchment area

Type	**Size of Basin (km^2)**	**Classification**
I	10-100	Small
II	100-1000	Medium
III	1000-10000	Large
IV	>10000	Very Large

2.5 Hydrology of monitoring catchment areas

- **River Pühajõgi**

Pühajõe is a village in Toila parish, Ida-Viru County. It has a catchment area of size 219.7 km^2. It flows into the Narva Bay. The catchment consists largely of forest (48%) and farmlands (32%) [19].

Basic Hydrological Facts [34]

Type: II B

Size of catchment Area: 219.7 km^2

River Length:32.6 km

Station: Suue (1 km from the mouth) [14]

❖ River Purtse

Purtse is a village in Lüganuse Parish, Ida-Viru County in north-eastern Estonia. The monitoring station is the Tallinn-Narva mnt, which is 1 km away from it. It flows to the Narva Bay. The catchment consists mostly of forest (48%) [19]. In 2009 there were nine closed and two operational oil mines in its watershed. From operating mines, the water is pumped out while from the closed mines, it flows freely [35].

Basic Hydrological Facts [34]

Type: II A

Size of catchment Area: 811 km^2

River Length: 51.2 km

Station: Tallinn-Narva mnt (1 km from the mouth) [14]

❖ River Kunda

The source of this river is Vinni Parish in Lääne-Viru County. It flows into the basin of GOF. The River Kunda has two tributaries, rivers Ädara and Vaeküla. The catchment consists more of Farmland (37%) and Forests (49%) [19]. One of the major pollution sources for this river was the large Kunda cement factory, but its emissions decreased over the decade. However, in 2006, AS Estonian Cell, a new aspen pulp mill, was opened near Kunda. The factory features sulphur-free, chlorine-free bleaching production [36].

Basic Hydrological Facts [34]

Type: II B

Size of catchment Area: 535.9 km^2

River Length: 65.8 km

Station: Suue (2 km from the mouth) [14]

❖ River Valgejõgi (White River)

The source of River Valgejõgi starts at the lake Pandivere, which is in Lääne-Viru County. The river is a salmon and sea trout river flowing into the GOF. The catchment area largely embodies farmland (29%) and forests (47%) [19]. This river does not have any significant tributaries. It belongs to Natura 2000 Network.

River Valgejõgi - Basic Hydrological Facts [34]

Type: II B

Size of catchment Area: 451.5 km^2

River Length: 89.5 km

Station: Loksa jalak.sild (1 km from the mouth) [14]

- **River Selja**

This salmon and sea trout river flow from the Pandivere Upland to the GOF (Lääne-Viru County). The catchment area is mainly farmland (66%) [19]. Most of the area where spawning is located belongs to the Natura 2000 network. The river Selja has one major tributary called River Sõmeru [35] [19].

Basic Hydrological Facts [34]

Type: II B

Size of catchment Area: 422.6 km^2

River Length: 46.4 km

Station: Suue (1 km from the mouth) [14]

- **River Loobu**

The Loobu River originates from the Lääne-Viru County and drains to the Eru Bay in Lahemaa National Park. The River Loobu has three major tributaries, rivers Udriku, Vohnja, and Läsna. There is more farmland (43%) and forest (45%) in the catchment area [19].

Basic Hydrological Facts [34]

Type: II B

Size of catchment Area: 314 km^2

River Length: 60.6 km

Station: Vihasoo (1 km from the mouth) [14]

❖ River Jägala

The River Jägala is a salmon river and a historical sea trout river flowing to the Gulf of Finland. The catchment area mostly consists of farmland (31%) and forests (48%) [19]. The river begins from the Pandivere and flows into the lhasalu Bay (Harju County). There are two hydroelectric power dams on it. The River Jägala has six major tributaries, namely River Ambla, Jänijõgi, Mustjõgi, Aavoja, Soodla, and Jõelähtme. All of them occupy resident brown trout populations. The river belongs to the Natura 2000 network from the river mouth to the waterfall [35].

Basic Hydrological Facts [34]

Type: III B
Size of catchment Area: 1481.3 km^2
River Length: 98.8 km
Station: Linnamäe (1 km from the mouth) [14]

❖ River Pudisoo (The Pearl River)

Pärlijõgi or Pudisoo River is a river in Harju County. This river also occupies river trout. It flows into the Kolga Bay. There are 5 numbers of dams on the river. This river has been registered as one of the objects of pristine nature in Estonia, and a Pearl River special Protection Area has been established to protect this river and its biota [37]. The catchment area consists of 60% forest cover [19].

Basic Hydrological Facts [34]

Type: II A
Size of catchment Area: 143.7 km^2
River Length: 31.8 km
Station: Pudisoo hp (3 km from the mouth) [14]

- **River Vihterpalu**

57% of the catchment consists of forests and 26% of wetlands [19]. Vihterpalu River is a river in western Harju, Änglema Village. It is also called as Änglema River. It has nine tributaries, including Piirsalu River.

Basic Hydrological Facts [34]

Type: II A

Size of catchment Area: 481.1 km^2

River Length: 48 km

Station: Vihterpalu hp (2.4 km from the mouth) [14]

- **River Keila**

The Keila River is in Harju County, Keila-Joa, rural municipality. The water body is protected as a habitat for salmons. The catchment area mainly consists of farmlands (46%), and the share of swamps (12%) and forest (38%) is small [19]. It has two major tributaries, namely Atla and Maidla.

Basic Hydrological Facts [34]

Type: II B

Size of catchment Area: 669.3 km^2

River Length: 116 km

Station: Suue (1 km from the mouth) [14]

- **River Vääna**

Vääna River is a sea trout and Salmon River in Harju County flowing into the GOF. 44% of the catchment area consists of farmlands and 35% of forests [19]. It has two major tributaries namely, river Pääsküla and Vanamõisa stream.

River Vääna Basic Hydrological Facts [34]

Type: II B

Size of catchment Area: 315 km^2

River Length: 64.3 km

Station: Suue (1 km from the mouth) [14]

- **River Pirita jõgi**

Pirita River is a river in Northern Estonia that discharges into the Tallinn Bay, which is a part of the GOF. The River has four major tributaries, namely rivers Kuivajõgi, Leiva, Angerja, and Tuhala. The catchment area consists mostly of farmland (37%) and forest (44%) [19].

Basic Hydrological Facts [34]

Type: II B

Size of catchment Area: 807.8 km^2

River Length: 106.9 km

Station: Lükati [14]

2.6 Surface Water Quality Criteria

An excerpt from the Directive pertaining to setting quality class boundaries is given in the following Sections of the WFD:

Annex V: 1.4.1 (iii) Each Member State shall divide the ecological quality ratio scale for their monitoring system for each surface water category into five classes ranging from high to bad ecological status, by assigning a numerical value to each of the boundaries between the classes.

In the history of water policies in Europe, the establishment of the Water Framework Directive was a milestone for Europe. On December 22, 2000, the Water Framework Directive (or the Directive 2000/60/EC of the European Parliament) was published in European Communities.

In this research, the content of Biochemical Oxygen Demand (BOD_5) and ammonia (NH_4^+) has been selected as parameters showing organic pollution and T-N and T-P, indicating eutrophication. The following table 10 and table 11 show the numeric surface water quality criteria. The water quality criteria for nutrients (see Table 10 below) applies to all class I, class II, and class III rivers. The quality class boundaries of surface water quality provided in table 11 shall be applied to class IV rivers and in Estonia, mainly River Narva.

Table 10 The quality class boundaries of hydro-chemical variables of rivers with catchment types I, II and III [33]

indicator	river type	unit	high	good	moderate	poor	bad
BOD_5	Class A Class B	mg O_2/l	<2.2 <1.8	2.2-3.5 1.8-3.0	>3.5-5.0 >3.0-4.0	>5.0-7.0 >4.0-5.0	>7.0 >5.0
T-N	all	mg N/l	<1.5	1.5-3.0	>3.0-6.0	>6.0-8.0	>8.0
T-P	all	mg P/l	<0.05	0.05-0.08	>0.08-0.1	>0.1-0.12	>0.12
NH_4	all	mg N/l	<0.1	0.1-0.3	0.3-0.45	0.45-0.6	>0.6
O_2%	Type A Type B	Saturation %	>60 >70	60-50 70-60	<50-40 <60-50	<40-35 <50-40	<35 <40
pH	all		6-9	6-9	6-9	6-9	<6-9>

Table 11 The quality class boundaries of hydro-chemical variables of rivers with catchment types IV [33]

indicator	river type	unit	high	good	moderate	poor	bad
BOD_5	IV-Narva River	mg O_2/l	<2.0	2.0-2.5	>2.5-4.0	>4.0-5.0	>5.0
T-N		mg N/l	<0.5	0.5-0.7	>0.7-1.0	>1.0-1.5	>1.5
T-P		mg P/l	<0.04	0.04-0.06	>0.06-0.08	>0.08-0.1	>0.1
NH_4		mg N/l	<0.1	0.1-0.3	0.3-0.45	0.45-0.6	>0.6
O_2		Saturation %	>70	70-60	60-50	50-40	<40
pH			6-9	6-9	6-9	6-9	<6-9>

2.6.1 Hydro chemical Status Calculation

In order to compare these national criteria with actual values, we considered the 90th percentile of monthly values in a year in the case of NH_4^+. For BOD_5, T-P, and T-N; we used the annual mean values. In the case of O_2 Saturation, we used the lowest 10th percentile as the worst-case scenario for all sites (appx. A2.1.6).

The overall result of the present (2019) hydro chemical condition in this study is calculated following the water quality classification according to Regulation No. 44 of the Minister of the Environment [33];

If the pH value is within the limits, the other five variables are calculated:

- high – 5 points;
- good – 4 points,
- moderate – 3 points,
- poor – 2 points,
- bad – 1 point.

The overall result is determined by the sum of the five variables:

- 23-25 – high;
- 18-22 – good;
- 13-17 – moderate;
- 8-12 – poor;
- <8 – bad.

3 DATA GAP

Generally, data quality should be ensured by checking the data for gaps, i.e., missing values, and for suspect values or outliers. A first task in establishing a data quality routine is the precise identification of gaps in the dataset, which spot variables that are missing and the length of the missing period, followed by determination of the type of gap which is not measured, measured, but not reported, etc. Data gaps in time series on nutrient input may occur for several different reasons [31] :

- Measurements are missing from a sub-catchment for certain periods of time.
- Measurements of nutrient concentrations are missing.
- Nutrient and runoff data are both missing for a certain period of time.
- Measurements could not be made due to external conditions (e.g., ice cover).
- Data has not been reported for unknown reasons.

In this research, missing nutrients concentration and runoff data in studied rivers are as follows:

1. River Pühajõgi

- 1^{st} and 3^{rd} month data are missing for all the parameters in the year 1992.
- 6^{th} and 10^{th} month data are missing for the DO parameter and 6^{th}, 7^{th}, and 8^{th} data for O_2 Sat in the year 1992.
- 7^{th} month data is missing for all parameters in the year 1996, 2002, and 2003.
- 4^{th} month data is missing for all parameters in the year 2003.
- 5^{th} month data is missing for SS in the year 2005.
- First four months' data is missing for all parameters in the year 2010.

2. River Purtse jõgi

- 1^{st}, 3^{rd}, 7^{th}, and 10^{th} month data is missing for all parameters in the year 1992.
- 7^{th} and 12^{th} month data are missing for all parameters in the year 1993.
- 6^{th} and 12^{th} month data are missing for all parameters in the year 1995.

- 7^{th} data is missing for all parameters 1996, 1998-2004.
- First four months' data is missing for all parameters in the year 2010.

3. River Kunda jõgi

- 11^{th} month data is missing for O_2 Parameter and TN in 1992.
- 1^{st}, 2^{nd}, 3^{rd}, and 7^{th} month data is missing for all parameters in the year 1992.
- Data for 2^{nd} month is missing for all parameters in the year 1993.
- 3^{rd} month nutrient concentration data is missing in the year 2006.
- First four months' data is missing for all parameters in the year 2010.
- 1^{st} month data is missing for all parameters in the year 2019.

4. River Selja jõgi

- 1^{st}, 3^{rd}, and 7^{th} data are missing for all parameters in the year 1992.
- 2^{nd} month data is missing for all parameters in the year 1993.
- 12^{th} month data is missing in the year 1994, 1995, 1997-2002.
- First four-month data is missing in the year 2010.

5. River Loobu jõgi

- 1^{st}, 2^{nd}, 3^{rd}, and 7^{th} month data is missing for all parameters in the year 1992.
- 7^{th} month data is missing for all the parameters in the year 1997 and 1998.

6. River Valgejõgi

- 1^{st}, 2^{nd}, 3^{rd}, and 7^{th} month data is missing in 1992 for all parameters.
- 7^{th} month data is missing in the years 1995, 1997, and 1998 for all the parameters.
- 6^{th} month DO data is missing in the year 2003.

7. River Jägala jõgi

- 1^{st}, 3^{rd}, and 7^{th} month data are missing for all parameters in the year 1992.
- 5^{th} month data and 11^{th} month data is missing for TP in the year 1992 and 1994, respectively.
- 7^{th} month data is missing in the years 1997 and 1998 for all the parameters.

8. River Pudisoo jõgi

- All month data is missing except 5^{th}, 6^{th}, and 11^{th} data for most parameters in the year 1992.
- Every month data except November for the T-P parameter is missing in the year 1992.
- 5^{th} data is missing for DO, and O_2 sat parameters in the year 1993.
- Every alternative, even-month data is missing for all parameters in the years 1993 and 1994 (e.g., Feb, April, June, etc.).
- Every alternate odd-month data is missing for all parameters in the years 1995-2010 (e.g., Jan, Mar, May, etc.).
- 1^{st} month data is missing for all parameters in the year 2011.

9. River Vihterpalu jõgi

- 1^{st}, 3^{rd}, 7^{th}, 8^{th}, 10^{th}, and 12^{th} month data is missing for all parameters in the year 1992.
- Every alternate even-month data is missing for all parameters in the years 1993 and 1994.
- Every alternate odd-month data is missing for all parameters in the years 1995-2010.
- First-month data is missing for all parameters in the year 2011.

10. River Keila jõgi

- 1^{st}, 3^{rd}, 7^{th}, and 9^{th} month data is missing for all parameters in the year 1992.
- 7^{th} month data is missing for all parameters in the years 1993 and 1998.
- 8^{th} month data and 6^{th} data are missing for O_2 sat and DO parameters in 1993 and 1994, respectively.
- 3^{rd} month data is missing for BOD_5 in the year 1995.
- 8^{th} month data is missing for TN in the year 1999.
- 7^{th} month data are missing for O_2 sat and DO parameters in the year 2006.

11. River Vääna jõgi

- 1^{st}, 3^{rd}, and 7^{th} month data is missing for all parameters in the year 1992.
- 8^{th} month data is missing for O_2 sat and DO parameters in the year 1993.

- 7th month data is missing for parameters in the year 1998.
- 3rd month data is missing for all parameters in the year 2015.
- 7th and 8th month data are missing for DO, and O_2 sat in the year 2006.
- 5th month data is missing for DO, and O_2 sat in the year 2014.

12. River Pirita jõgi

- 1st and 2nd month data are missing for all the parameters in the year 1997.
- 7th month data is missing for all the parameters in the year 1998.
- 7th month data is missing for DO in the year 2006.

3.1 PLC Missing data Guidelines

One of the tasks agreed under PLC-6 is the development of a standardized methodology to calculate uncertainties in national datasets, including a methodology for filling in data gaps and missing data [31].

Several different methods are available for filling in data gaps. The following method is applied in this study to fill in the gap in the MK test. In case there were 2 readings or more in the same month(x_1, x_2), then the mean of adjacent values is taken as the representative reading (x_a):

$$x_a = \frac{x_1 + x_2}{2} \quad (3.1)$$

4 RESULTS

4.1 Changes in concentration with national criteria

Eutrophication and acidification have been identified as the two major causes of downgrading of water quality in standing waters across Europe [22]. Of the different nutrients found in the aquatic environment, T-N, T-P (including organic and inorganic compounds) with BOD_5 play a key role as limiting factor in primary production, and these nutrients have been used as indicators of pollution loads. In Estonia, for most rivers, the dataset is measured every month, and this is taken as a mean monthly concentration. As mentioned above, on the available initial series data, BOD_5 and NH_4 were used as an indicator of organic pollution and T-N and T-P loads as a measure of eutrophication hazard. The pH was used to determine the acidification status. The amounts of average, maximum, minimum, median, 90th percentile and 10th percentile are calculated for every year (appx. A2.2).

The 90th percentile is a figure in an interval showing that 90% of observations on that interval are less than it, and only 10% of observations are greater than 90th percentile. Overall, significant changes have taken place in Estonia since the 1992 level. The 2019 hydrochemical condition was calculated from study section 2.6.1 (calculations in appx. A1.3).

1. **Pühajõgi**

The status of the river in terms of both the nutrients T-P and T-N concentration is found to be impaired in the earlier years since 1992, as shown in Figure 3, which is due to the intensive use of the catchment area as farmland. So, the runoff from agricultural sources is one source of diffuse pollution here. However, in recent years the condition has improved significantly. The T-P concentration in this river improved a little in 2004. It then fluctuated between moderate, excellent, and good conditions in the next consecutive years. Currently, the status of T-P content is in excellent status.

In 1992, the 10th percentile of oxygen saturation was ranked as the worst condition compared to all the years showing poor ecological quality (appx. A2.1.6). The annual mean of BOD_5 is in moderate and poor conditions since 1992-1998. However, since the

2000s, the status improved drastically, securing a high status. In recent years it is in slight deterioration to just satisfactory good condition (see Figure 4). For NH_4-N, the 90th percentile of the five consecutive years from 1992 shows that the river was earlier in extremely bad condition showing eutrophication. Although there was a slight improvement in the coming years, in 2003 again, a sudden increase in the concentration of NH_4 was observed, putting it back to a high level of eutrophication status. Nevertheless, since 2010, it has witnessed fluctuations of good, moderate, and high status.

2019 Physical-chemical status : Good

2. Purtse jõgi

The nutrient condition was very bad at the beginning of the assessment years, but TP started improving after the third year (1994) and stayed mostly in high status until 2019 (See Figure 5). As per TN, it fluctuated to moderate status in the next year 1993-1999. Since the 2000s, all the wastewater from oil shale processing has been treated in a WWTP and drained through a pipe directly into the Baltic Sea [35], improving the water quality. As a result, the water quality in River Purtse has significantly improved as the status shifted to good and excellent classes.

The annual mean concentration of BOD_5 has been in good and moderate status in the early six years since 1992. After that, it significantly improved securing excellent status in the later years with a small fluctuation to slightly moderate in a few years, in 2012 and 2016. In terms of NH_4-N, the 90th percentile of assessment shows it to be in the worst condition in the years 1992, 1993, and 1995. Even though the status improved in 1994 to moderate but in 1995, it peaked deteriorating downstream. After that year, NH_4 status started improving to good status, and following 2004 it gradually improved to excellent status in the recent year (Figure 6).

2019 Physical-chemical status: High

3. Kunda jõgi

The status of the river in terms of the annual mean of BOD_5 is excellent and satisfactorily good in all the studied years. 90th percentiles of NH_4 concentrations are also in Good or High status except in the early years of 1992 and 1993 (see Figure 8). From Figure 7, we can say that the T-N is fluctuating between moderate and good status, while T-P is steadily changing between good and excellent class status. In terms of physical and chemical status, the overall water quality in the recent year 2019 is classified as excellent condition (see table 18 for more details).

2019 Physical-chemical status (River Kunda): High

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4. Loobu jõgi

Since 1992 the TN has been found to be in good status. There was a sharp increase in the concentration of T-N, deteriorating it to moderate status, particularly in 2007-2009, as observed in Figure 9. There was a deep economic crisis in that period, and the state had to arrange its economic policy due to the crisis [38]. The T-N has still been classified under a slightly satisfactorily moderate condition in 2019. Meanwhile, T-P was in a really poor status at the beginning of the 1990s, but it saw a decreasing trend over the years, improving to excellent status in 2019. The possible reason may be due to the construction of the new WWTP in Kadrina in the year 2000 [20]. While all the last decades from 1992, NH_4 remained in a steady excellent condition. The BOD_5 is also under satisfactorily good and excellent status (Figure 10).

2019 Physical-chemical status: Good

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5. Selja jõgi

The overall hydrochemistry of this river currently falls mainly within excellent conditions in terms of BOD_5, NH_4, and TP (Figure 11 and Figure 12). However, TN has been in a fluctuating trend indicating moderate and poor conditions. Due to intensive agricultural land use in the catchment area, the nutrient concentration is high. Especially in 2019, TN concentration has been marked as a poor status since the nitrate level is elevated (appx. A2.1.2). Still, the overall physical and chemical status in the same year is good.

Strong cases in the years 2008 and 2009 witnessed high nutrient concentrations. TP has been in bad status since 1992-2006 and remained poor, preceding the recession. The reason could be due to the wastewater from the settlements and food industry, coming as pollution from livestock farms and fields. Accordingly, population density is high in this area, with 74.5 inhabitants per square kilometer, making it one of the populous catchments (see Figure 29 appx. A2.1.1). It started seeing an improving trend towards the end of 2019, securing excellent condition.

2019 Physical-chemical status (River Selja continued): Good

6. Valgejõgi

The water quality is presently classified as an excellent oligotrophic river and poses no threat to salmon [35]. The NH_4 is in excellent status since 1992-2019, with further showing a decreasing concentration trend over the years. The organic matter parameter BOD_5 (Figure 14), is also currently showing high or natural status quality. TP is mostly in class I status all the years except for few fluctuations to good status in the years 1992, 1993, and 2016. The TN is mostly in good status over the study period (Figure 13).

2019 Physical-Chemical status: High

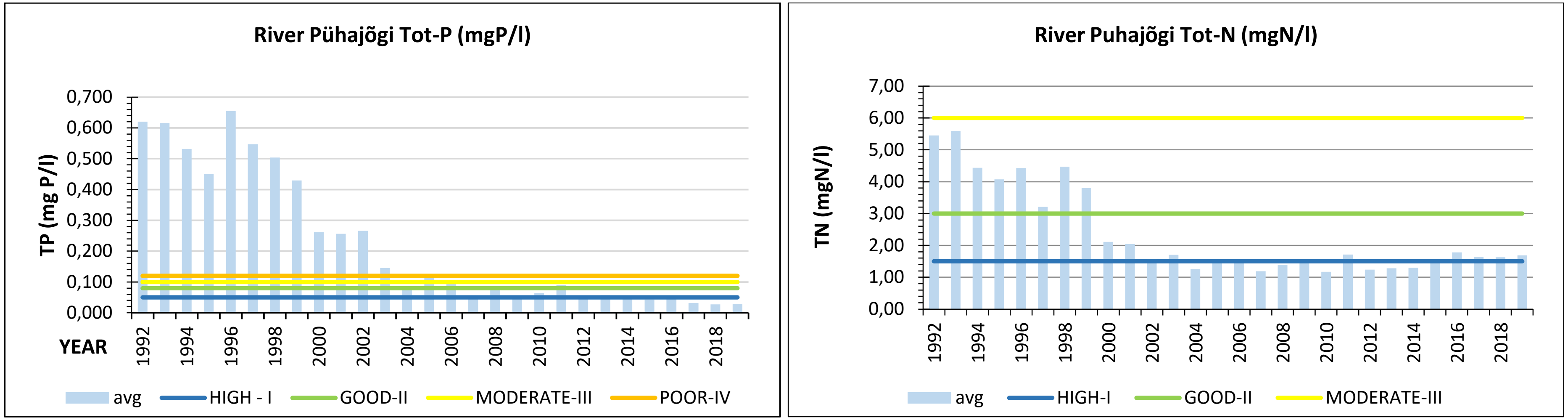


Figure 3. River Pühajõgi T-P and T-N and national criteria

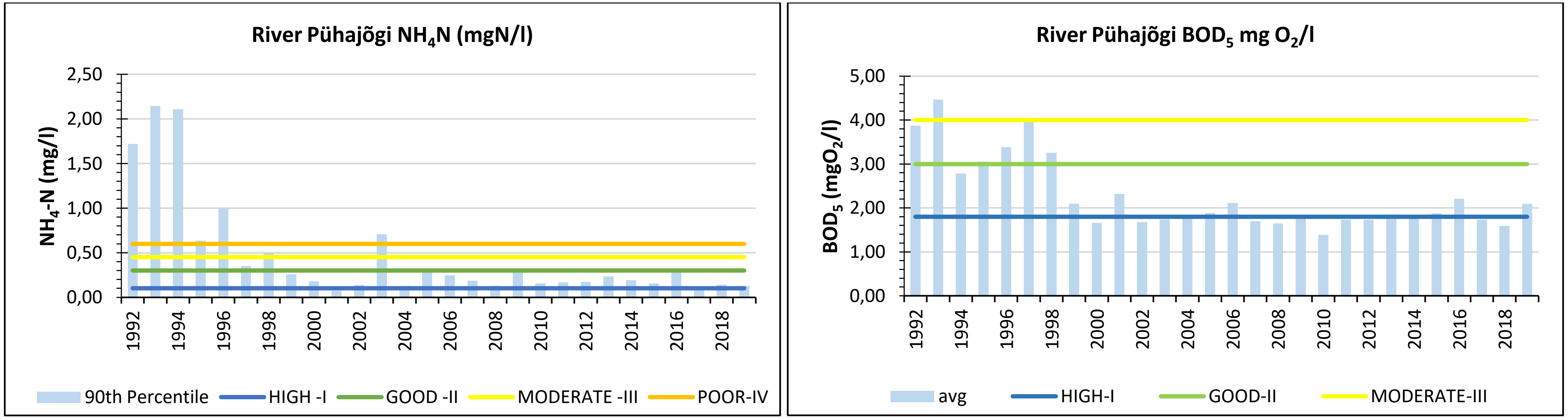


Figure 4. River Pühajõgi NH_4N and BOD_5 and national criteria

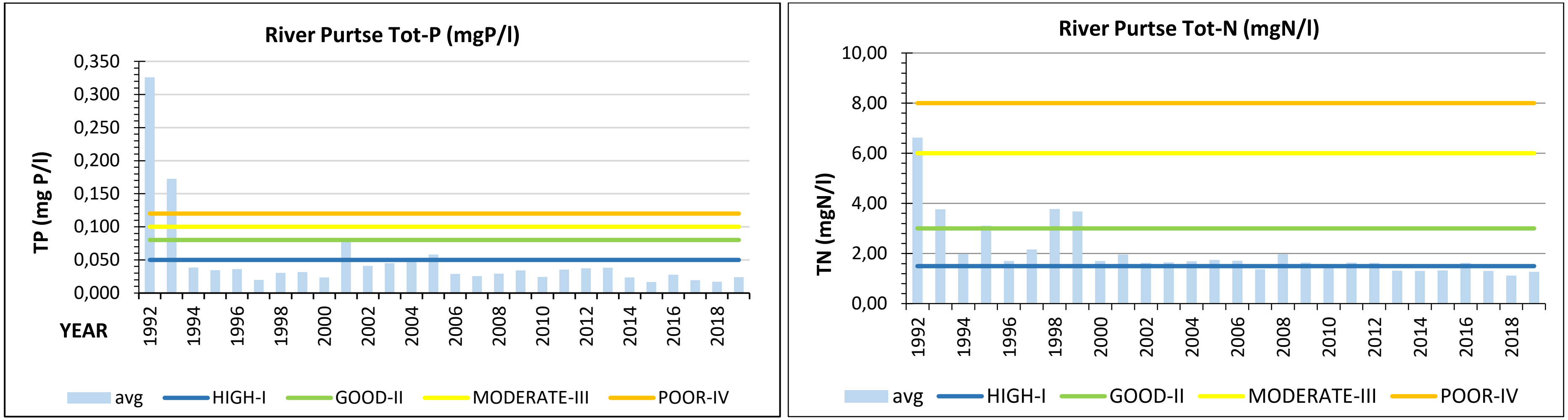


Figure 5. Purtse River Tot-P and Tot-N and national criteria

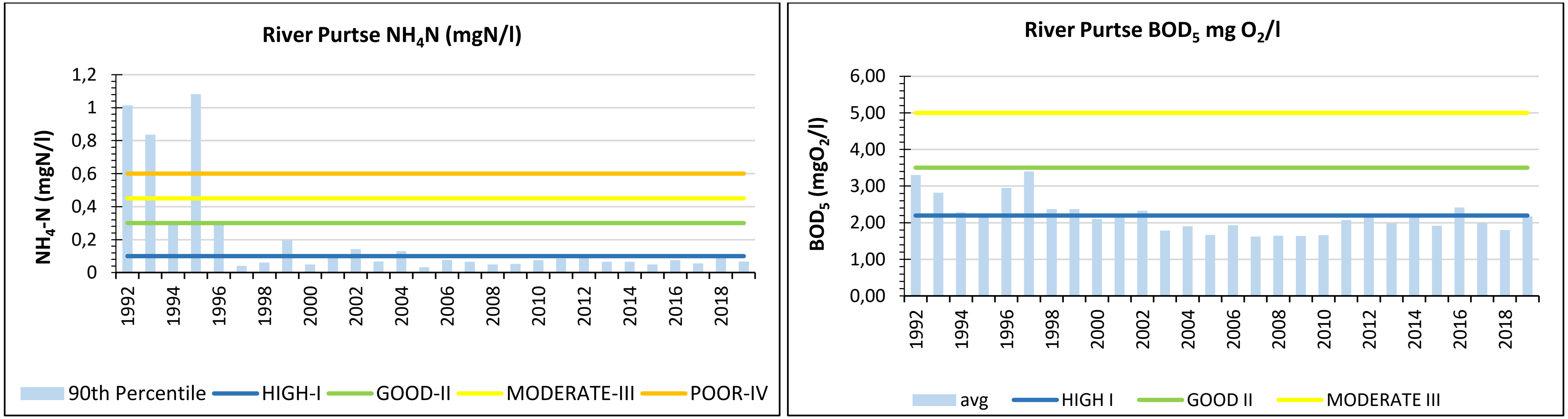


Figure 6. Purtse River NH_4N and BOD_5 and national criteria

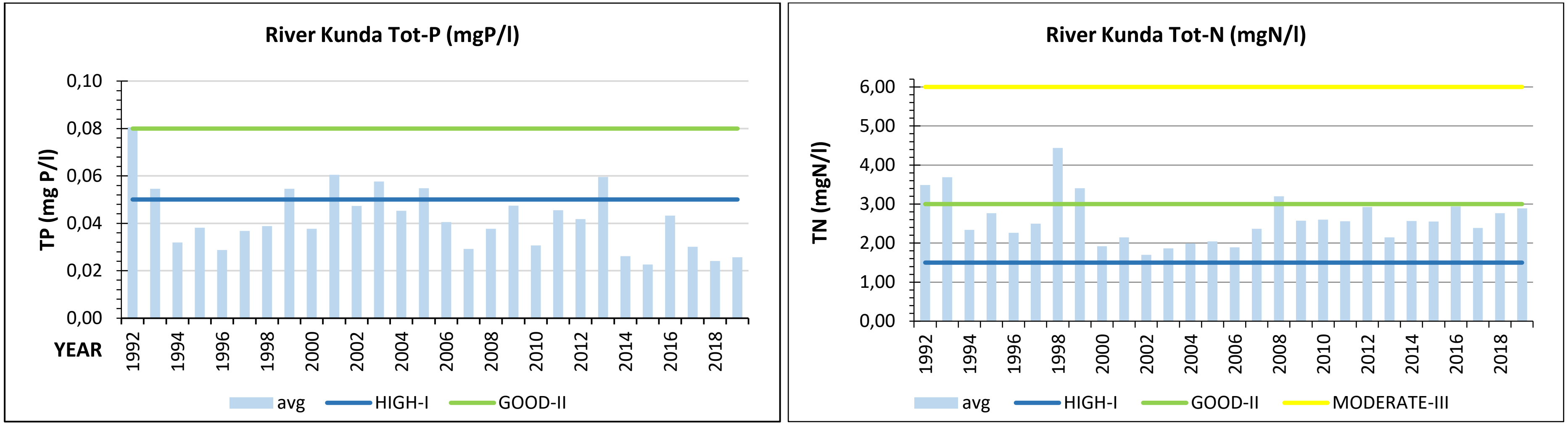


Figure 7. River Kunda Tot-P and Tot-N and national criteria

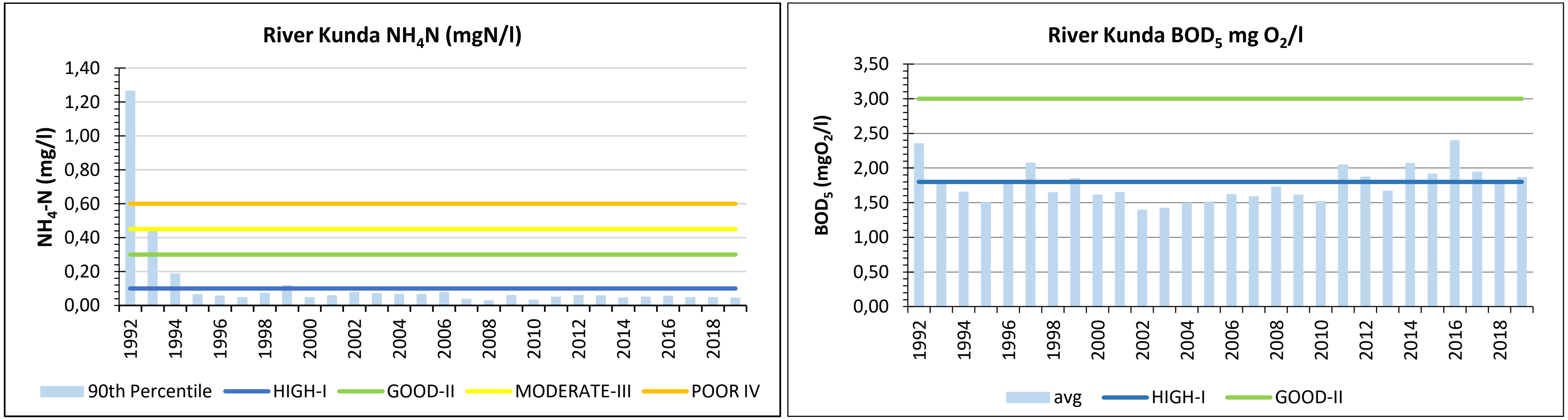


Figure 8. River Kunda NH_4N and BOD_5 and national criteria

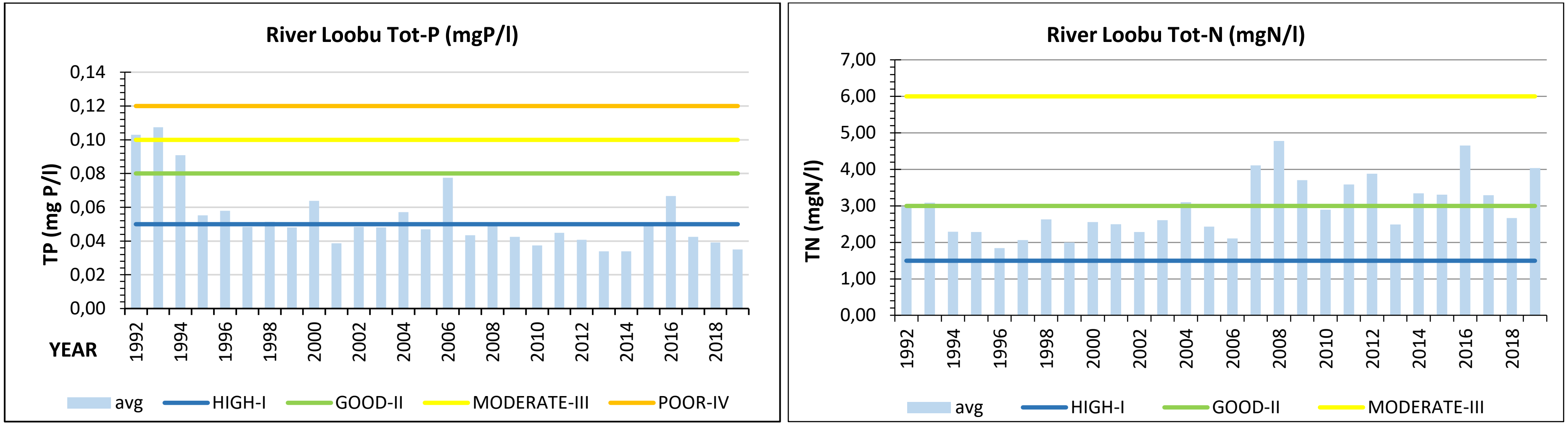


Figure 9. River Loobu Tot-P and Tot-N and national criteria

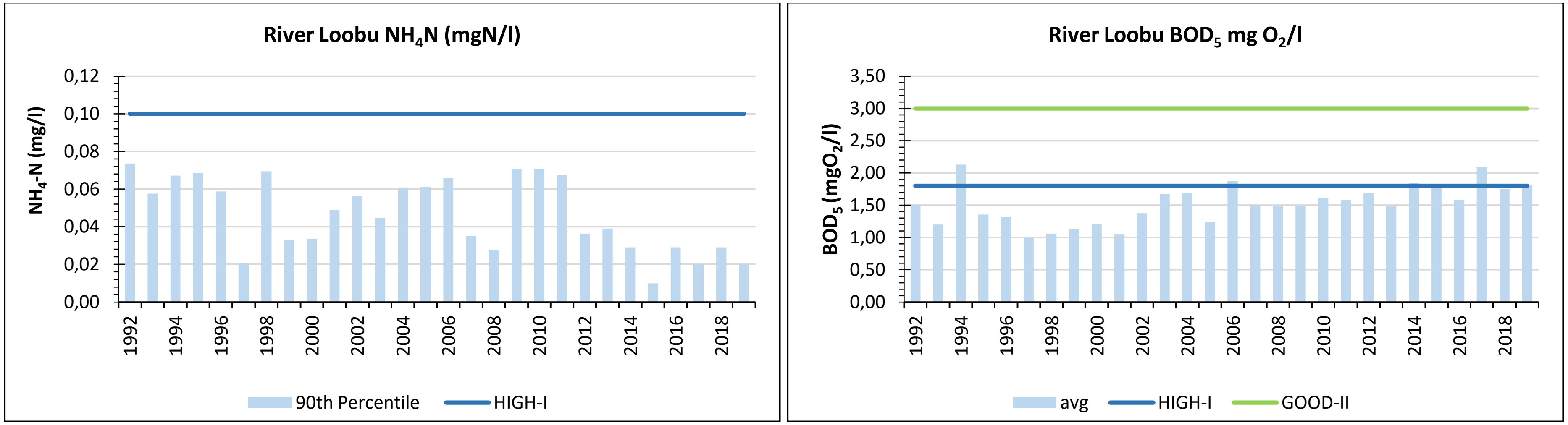
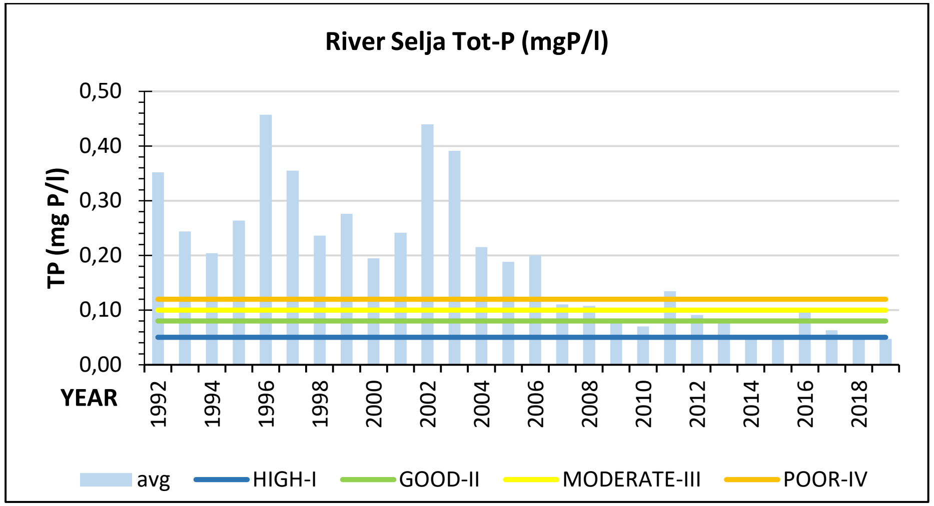


Figure 10. River Loobu NH_4N and BOD_5 and national criteria



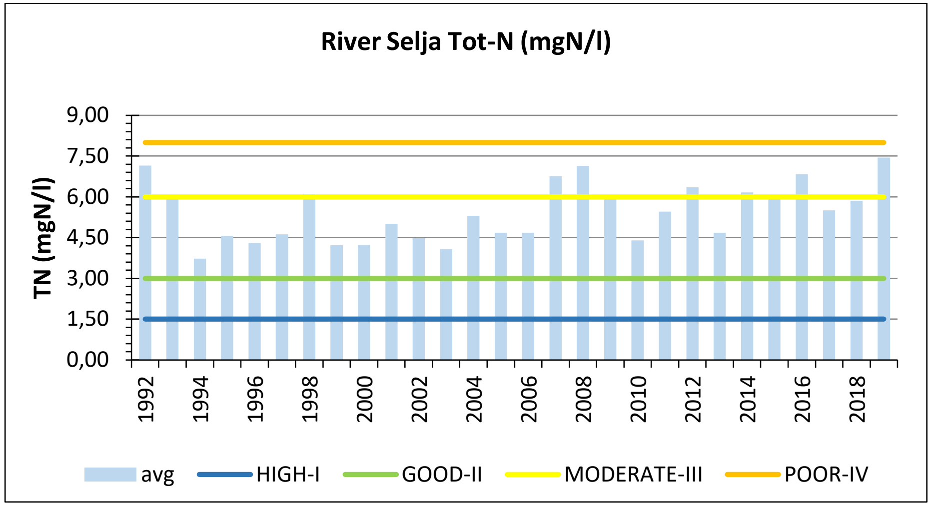
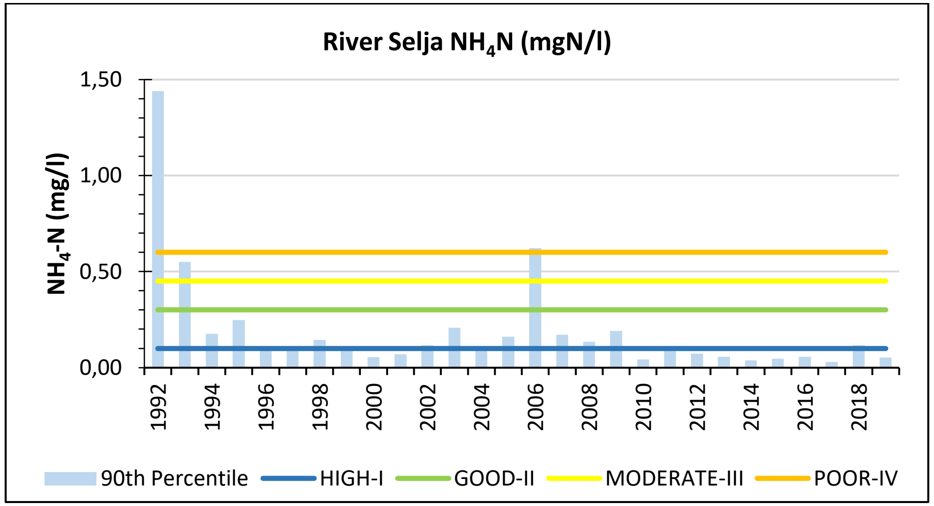


Figure 11. River Selja Tot-P and Tot-N and national criteria



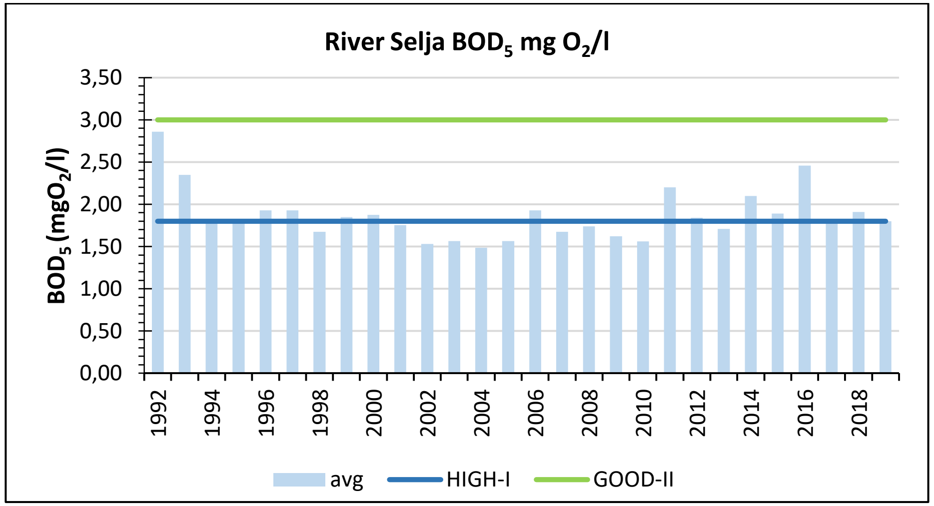


Figure 12. River Selja NH_4N and BOD_5 and national criteria

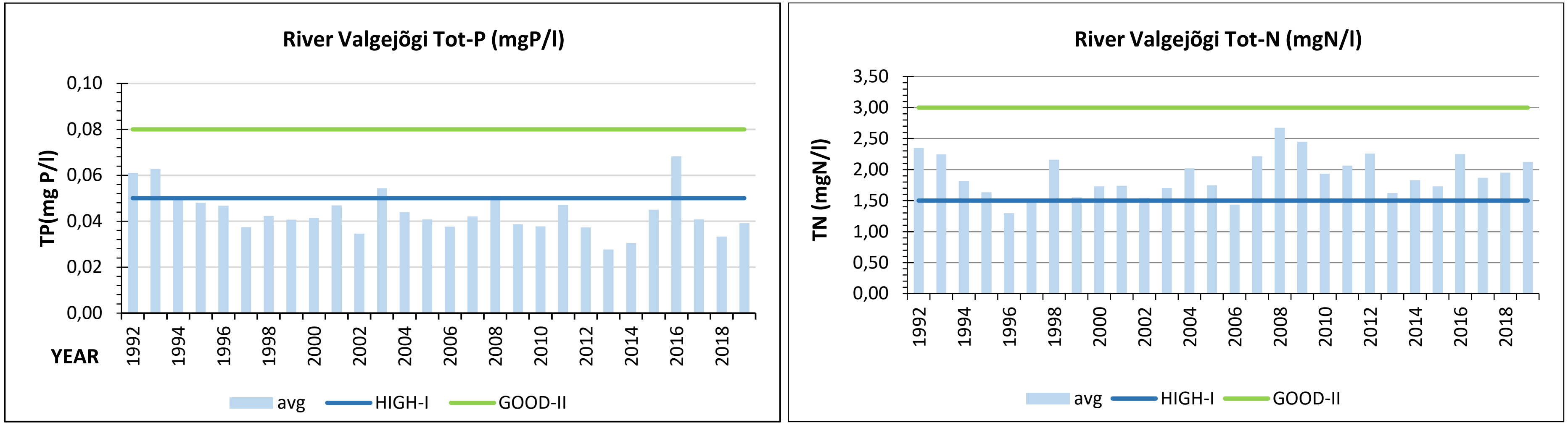


Figure 13. River Valge Tot-P and Tot-N and national criteria

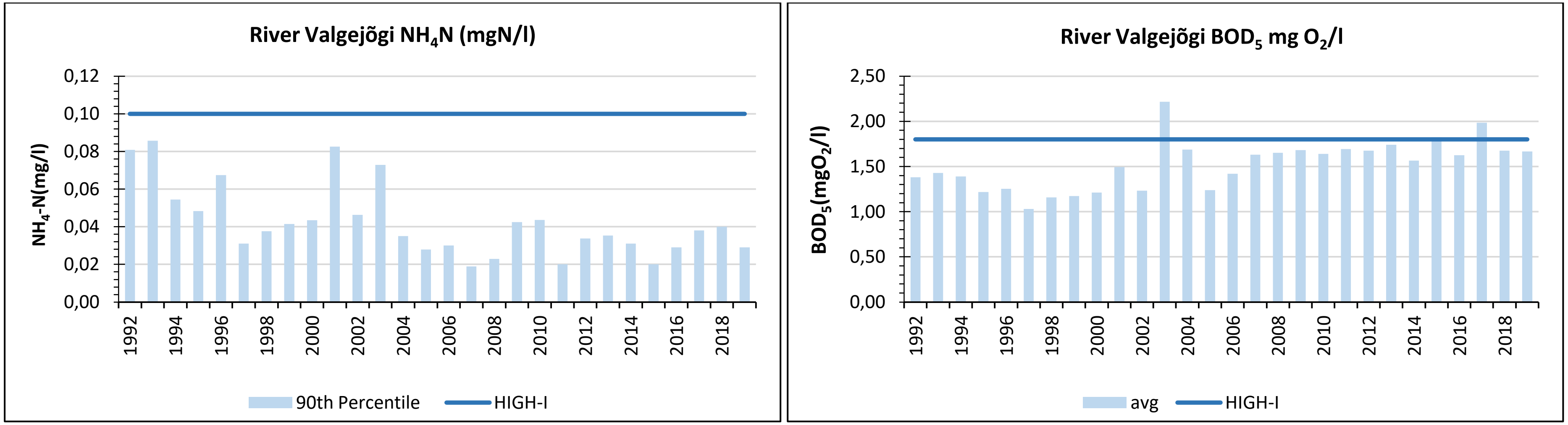


Figure 14. River Valge NH_4N and BOD_5 national criteria

7. Pudisoo jõgi/ Pärli jõgi

The overall physico-chemical status for the recent year is in excellent quality. All the parameters are currently in class I excellent status except for T-P, which is in moderate status (see Figure 15 and Figure 16). The general trend of T-N and T-P was characterized by large fluctuations throughout the assessment period. Although TN is in good and high status, the TP is mostly in moderate status with few sudden peaks to bad status observed in the year 2006, resulting in very high eutrophication due to a lower supply of Nitrogen. This can be as a result of salmon stocking. Although there are measures taken by the local government to reduce anthropogenic-input of Phosphorus, today, it is still at high risk of eutrophication. The average BOD_5 and NH_4 have both mostly remained in an excellent state over the years.

2019 Physical-chemical status: High

8. Vihterpalu jõgi

The biological (BOD_5) monitoring is mostly in excellent and good conditions, as shown in figure 18. The Vihterpalu river basin is characterized by low population density and low impact of human activities (Figure 29, appx. A2.1.1). Both the nutrient conditions are also steadily in good quality (Figure 17). The 10^{th} percentile scenario of O_2 Sat in the year 1993 also explains that the situation deteriorated (section A2.1.6), since the NH_4 condition is comparatively higher in the same year.

2019 Physical-chemical status: High

9. Keila jõgi

The nutrient conditions are mostly under less satisfactory moderate conditions, as seen in figure 19. It is not in good condition due to the intensive agricultural land use, scattered dwellings and settlements wastewater in the catchment area (appx. A2.1.1). The T-P status was bad, specifically in the years 2002 and 2003. However, the water quality in terms of phosphorus concentration improved in later years, achieving a good class by 2019.

In contrast, NH_4 concentration is mostly under good status except for the extremely poor status in the years 2002, 2003, 2006, and 2009. The 10^{th} percentile of oxygen saturation also shows a poor condition in the year 2003 (appx. A2.1.6). The BOD_5 is mostly in excellent conditions as well (Figure 20).

2019 Physical-chemical status (River Keila continued): High

10. Vääna jõgi

As shown in figure 22, the BOD_5 condition is mostly in good, class II condition for most of the years except in a few years where they are in slightly less satisfactory class III conditions, mainly in 1996, 2002-2004. Meanwhile, the nutrient conditions, particularly TP, are in poor conditions even to the year 2019. This may be due to the intensive agricultural use of the catchment area and impact from scattered dwellings wastewater. The condition of the Vääna River is probably also affected by its tributary, the Pääsküla River, next to which, is a landfill. The landfill is closed for now. On the other hand, the TN concentration improved while fluctuating between moderate and poor condition (see Figure 21). The 90^{th} percentile of NH_4 concentration drastically only improved from the year 2006, achieving excellent status by the end of the study period years.

2019 Physical-chemical status: Good

11. Jägala jõgi

The river is an oligotrophic river with excellent physical-chemical status in the year 2019. The NH_4 conditions and BOD_5 are under a steady excellent status (Figure 24). As per the nutrient conditions, TN is mostly found to be under good status. However, in the case of TP, there were sudden spikes in the concentration of TP, which placed it under a bad situation in the year 1995 and poor status in the year 2006. The state has improved since then, and hence it has been under an excellent condition in recent years (Figure 23).

2019 Physical-chemical status: High

12. Pirita jõgi

All the parameters like NH_4 and BOD_5 are all mostly under good and excellent conditions. Some impact of agricultural and urban effluents can be observed on the catchment. In case of TN, there is a presence of high nutrient load compared to TP. It is mostly under moderate and good conditions (see Figure 25 and Figure 26), while the TP has been under good conditions since 2009.

2019 Physical-chemical status: Good

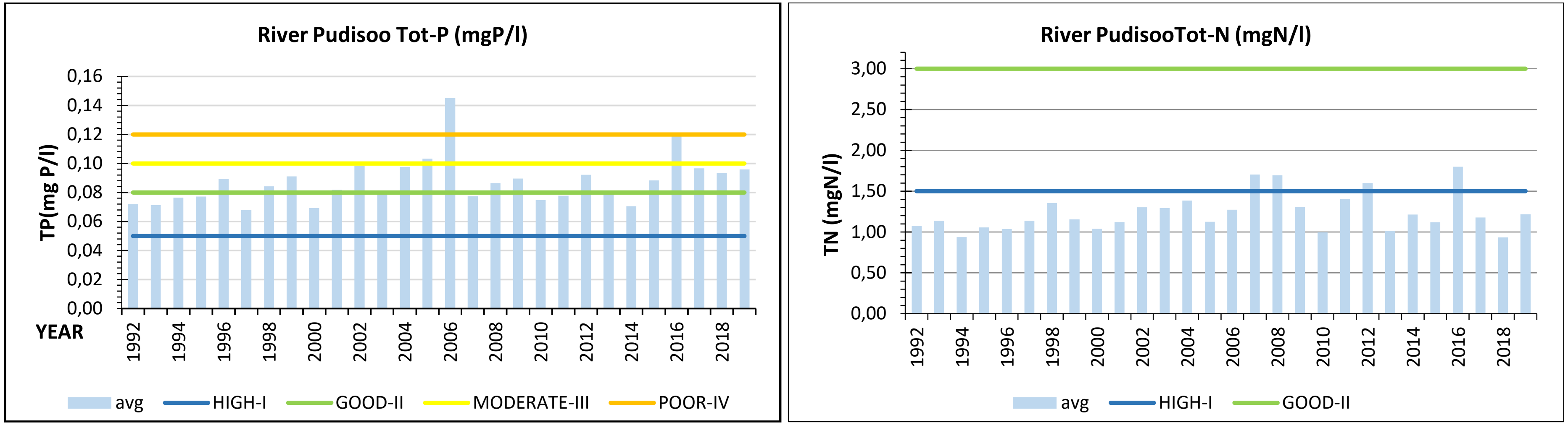


Figure 15. River Pudisoo Tot-P and Tot-N and national criteria

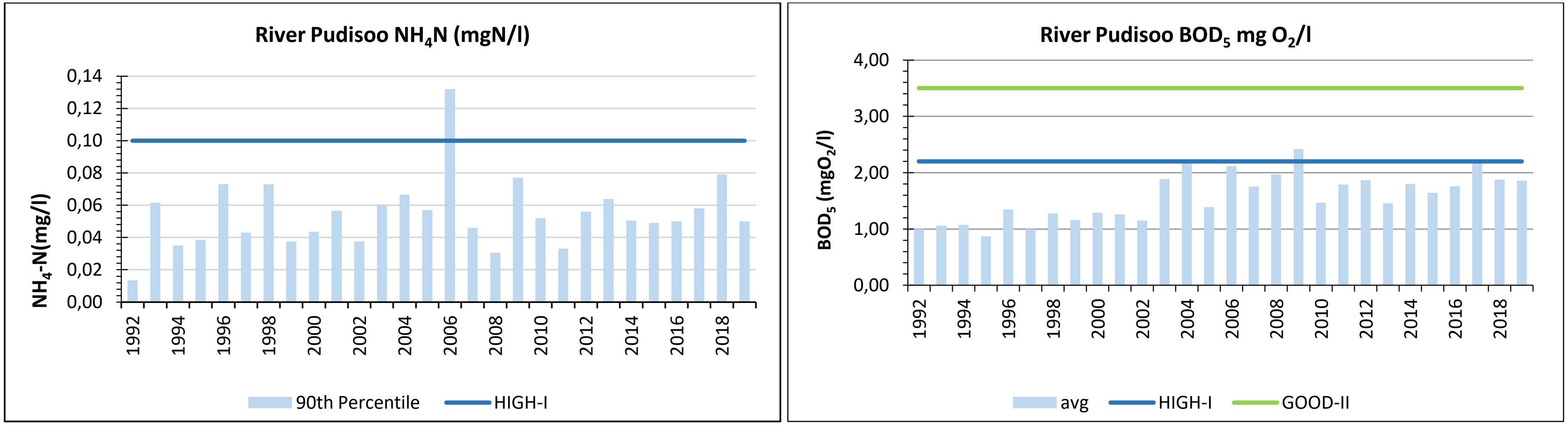


Figure 16. River Pudisoo NH_4N and BOD_5 and national criteria

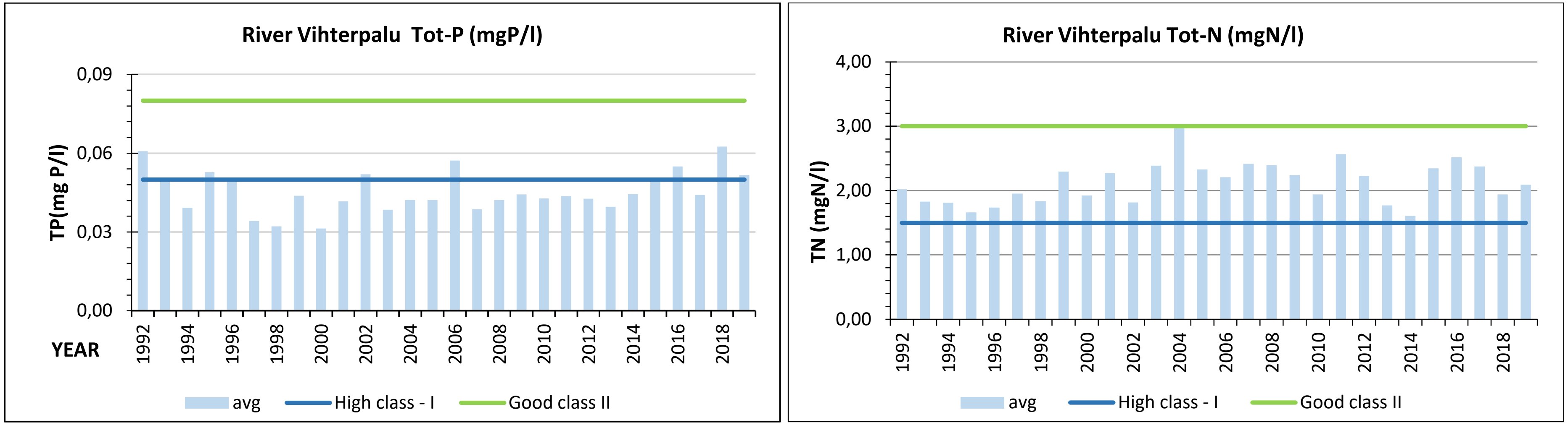


Figure 17. River Vihterpalu Tot-P and Tot-N and national criteria

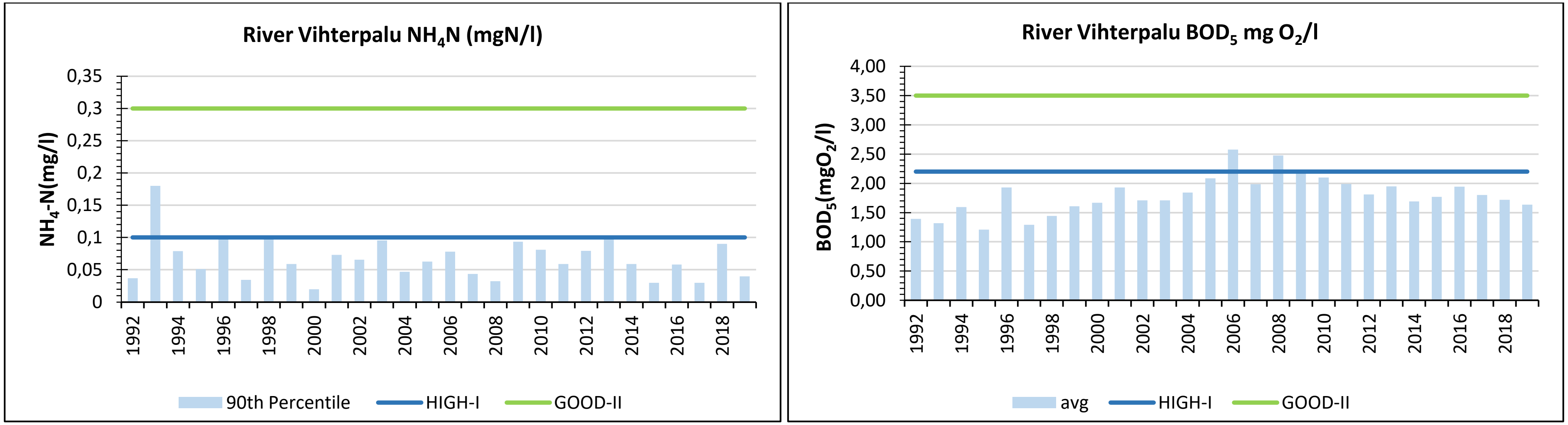


Figure 18. River Vihterpalu NH_4N and BOD_5 and national criteria

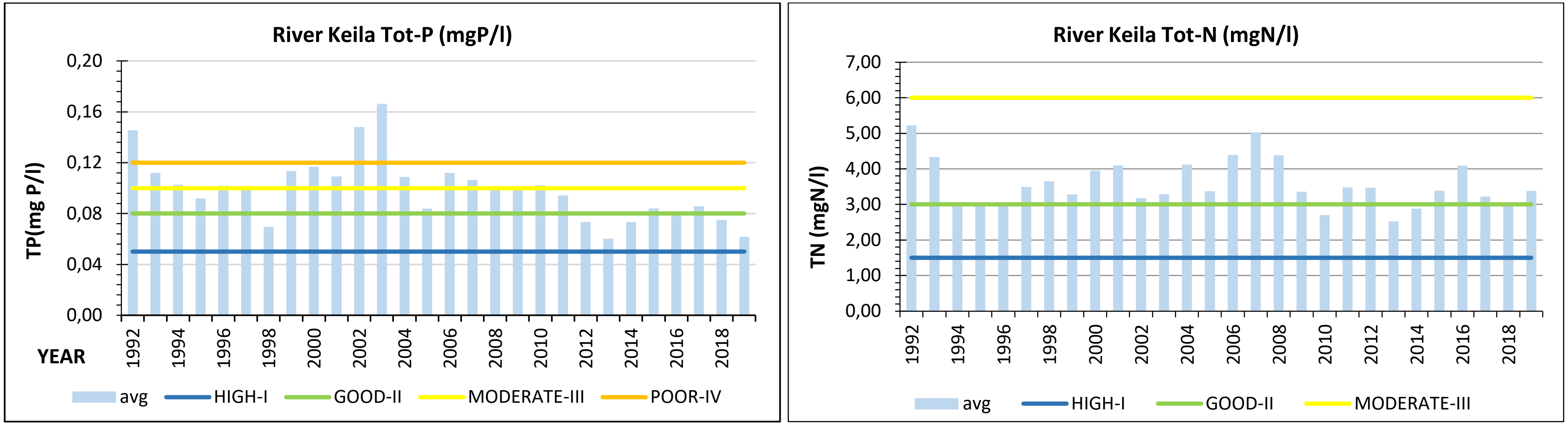


Figure 19. River Keila Tot-P and Tot-N and national criteria

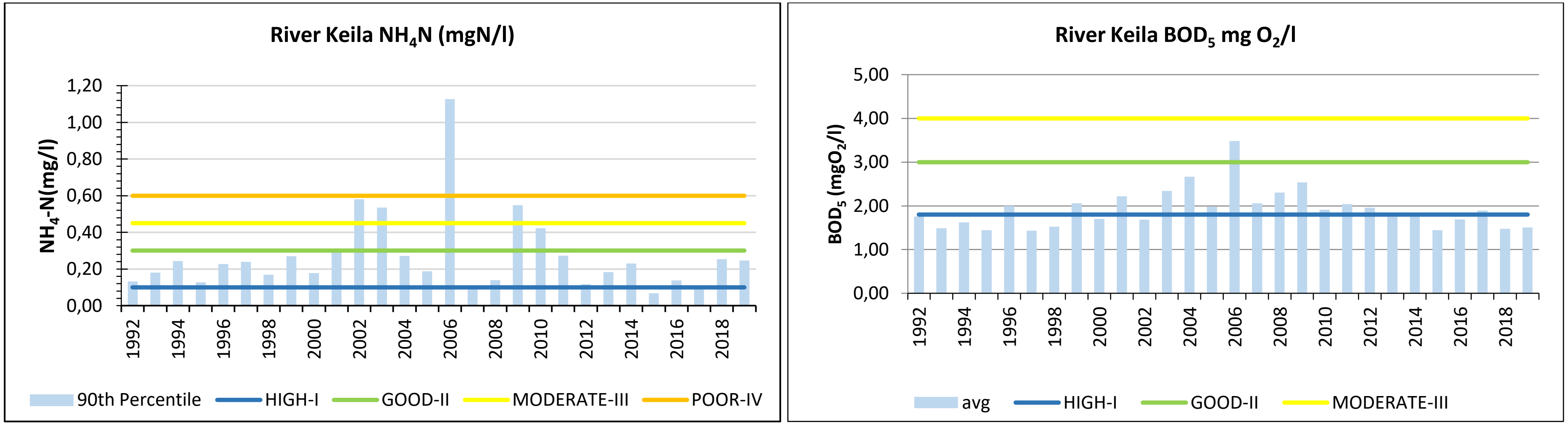


Figure 20. River Keila NH_4N and BOD_5 and national criteria

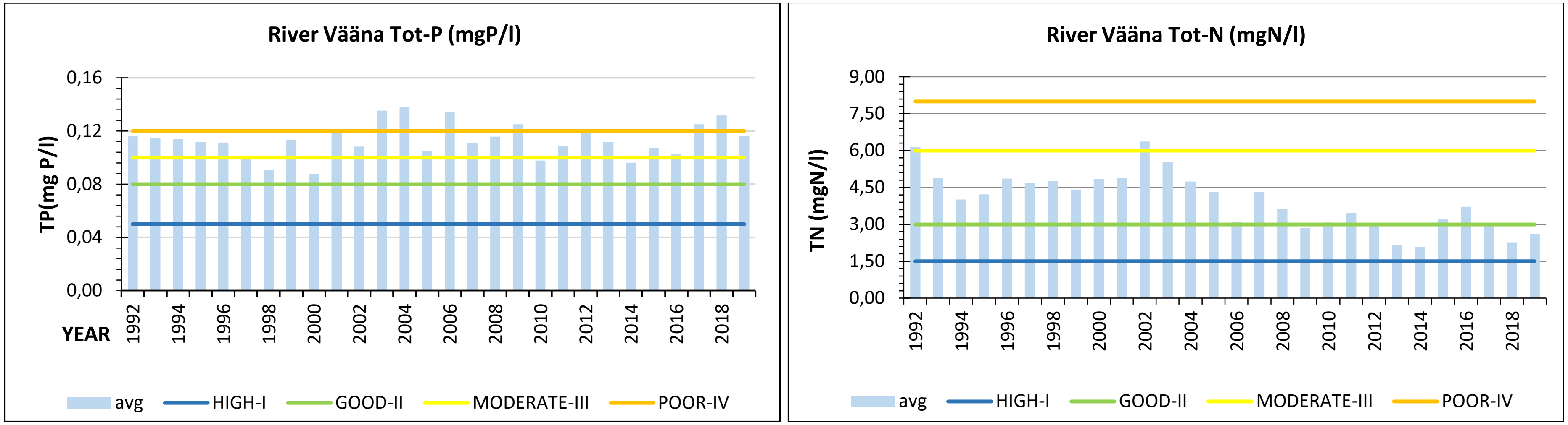


Figure 21. River Vääna Tot-P and Tot-N and national criteria

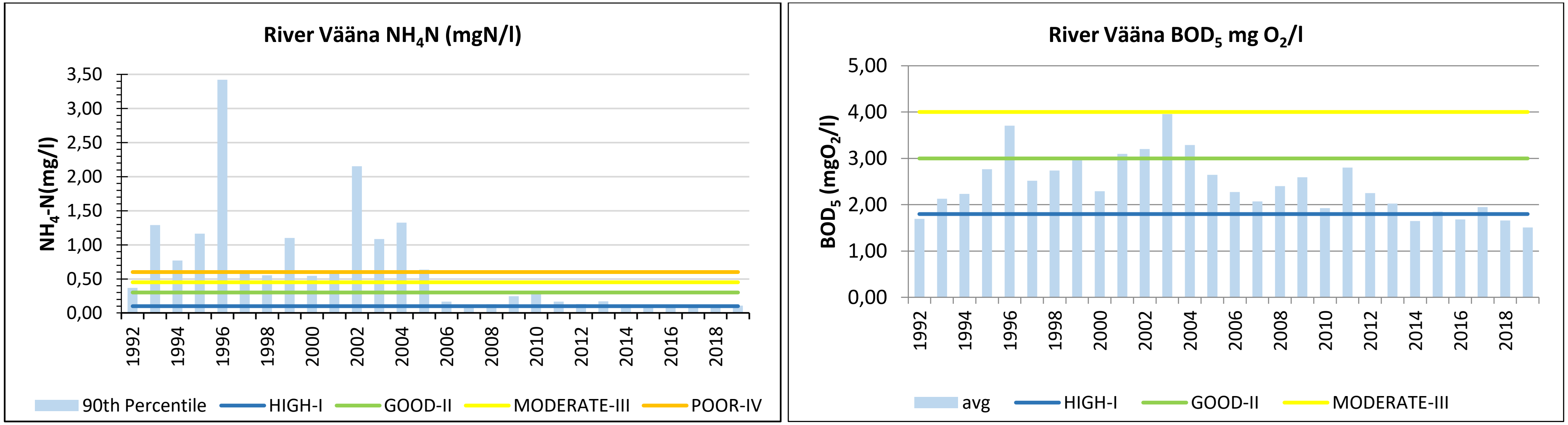
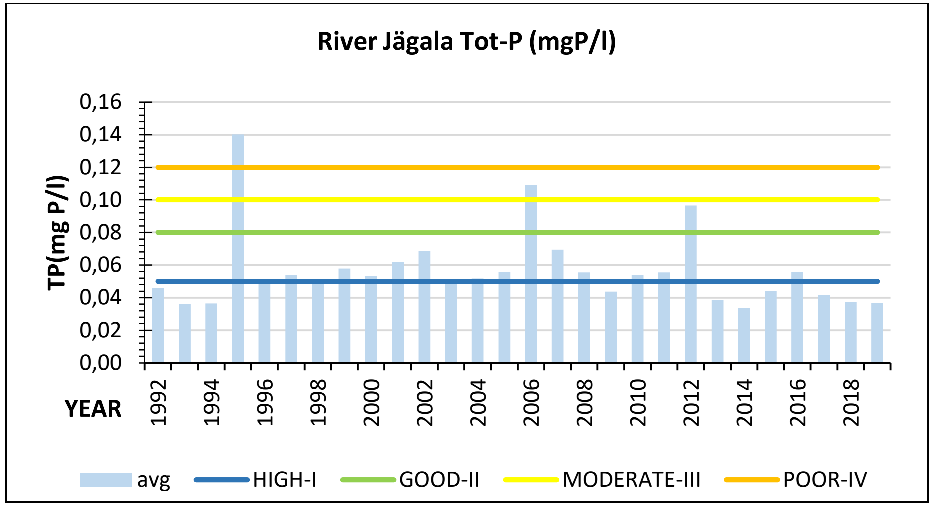


Figure 22. River Vääna NH_4N and BOD_5 and national criteria



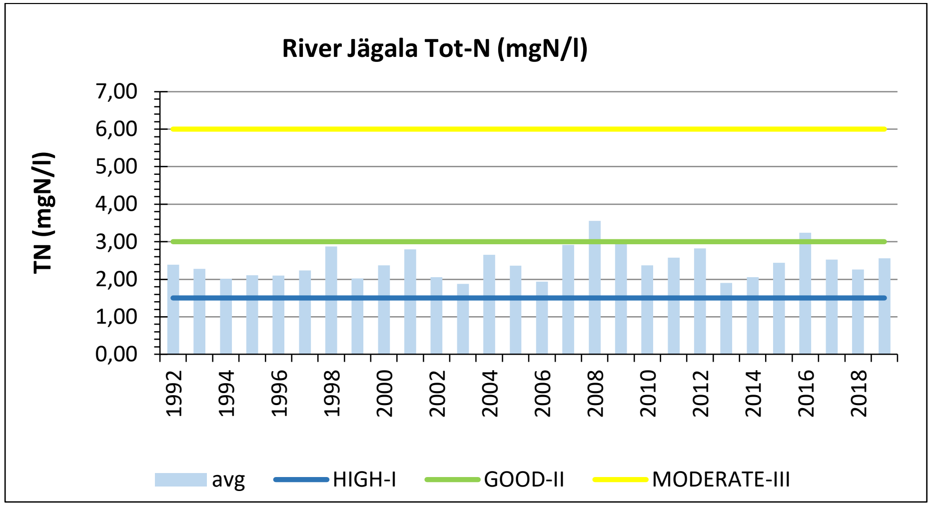
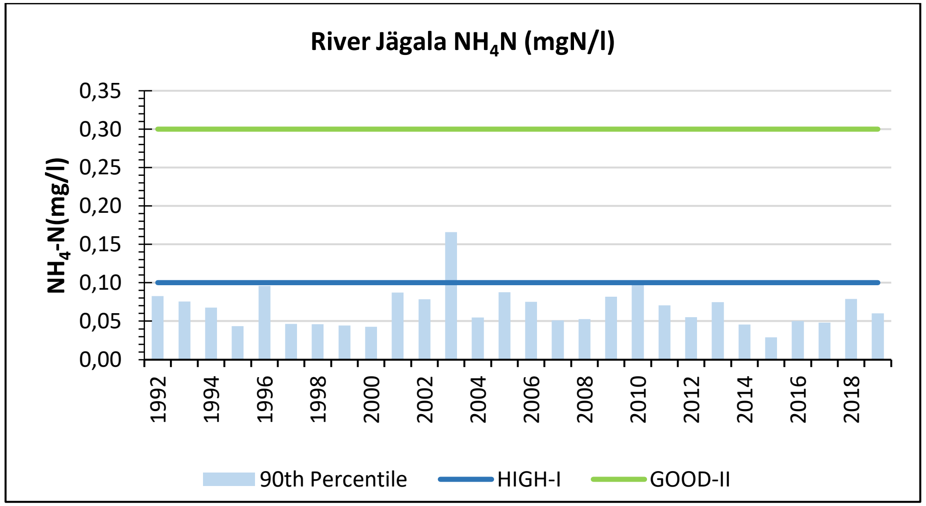


Figure 23.River Jägala Tot-P and Tot-N and national criteria



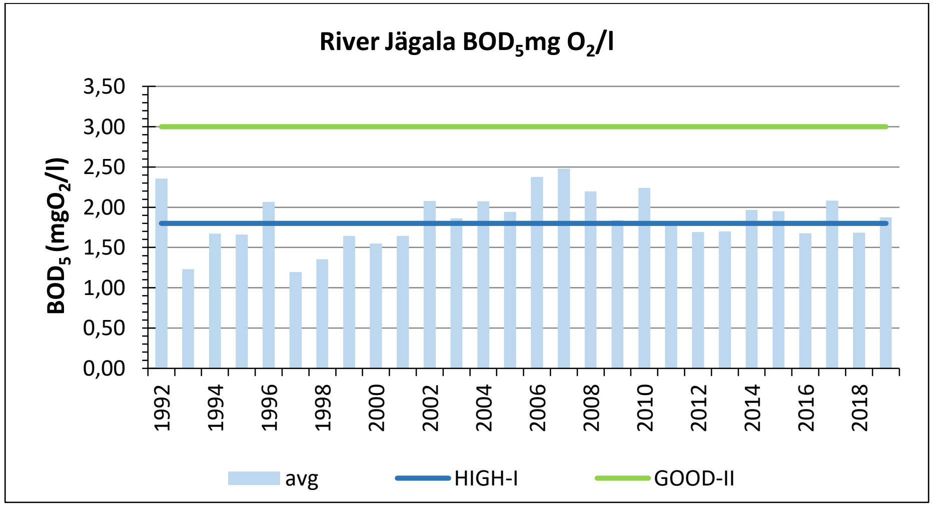
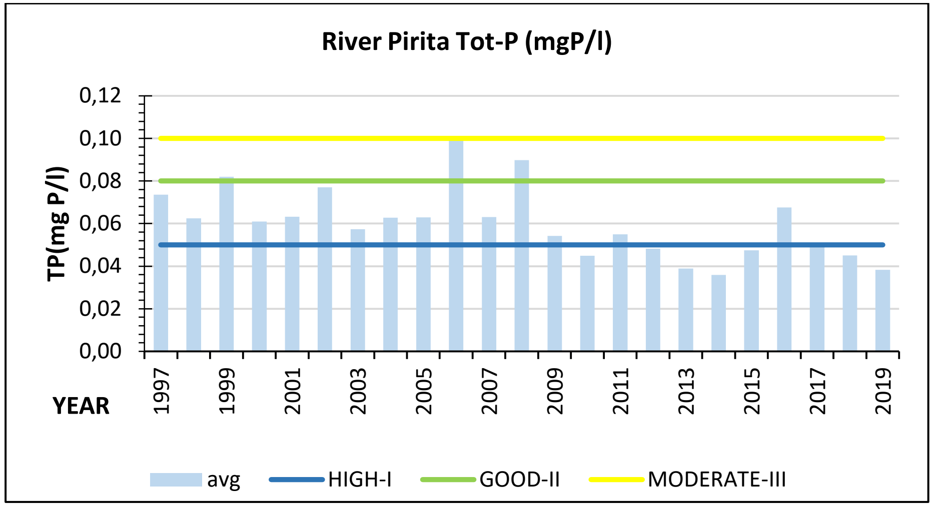


Figure 24. River Jägala NH_4N and BOD_5 and national criteria



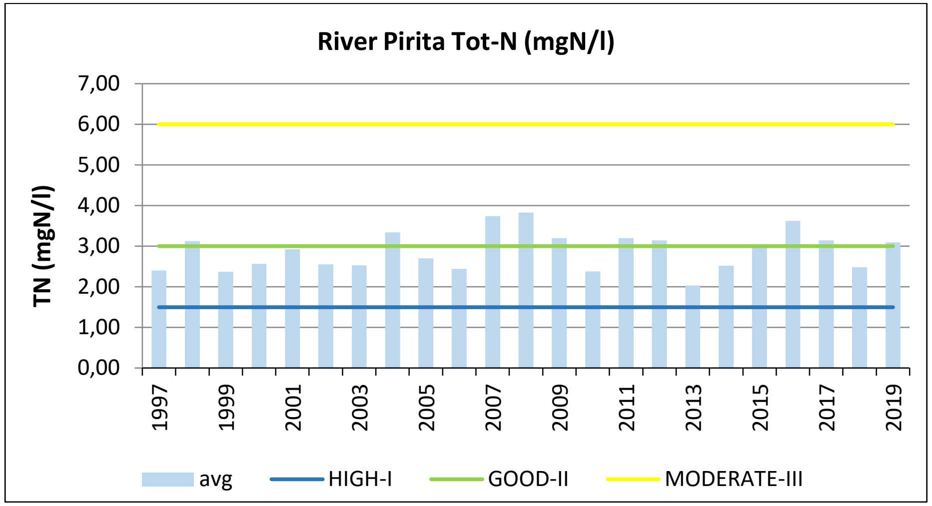
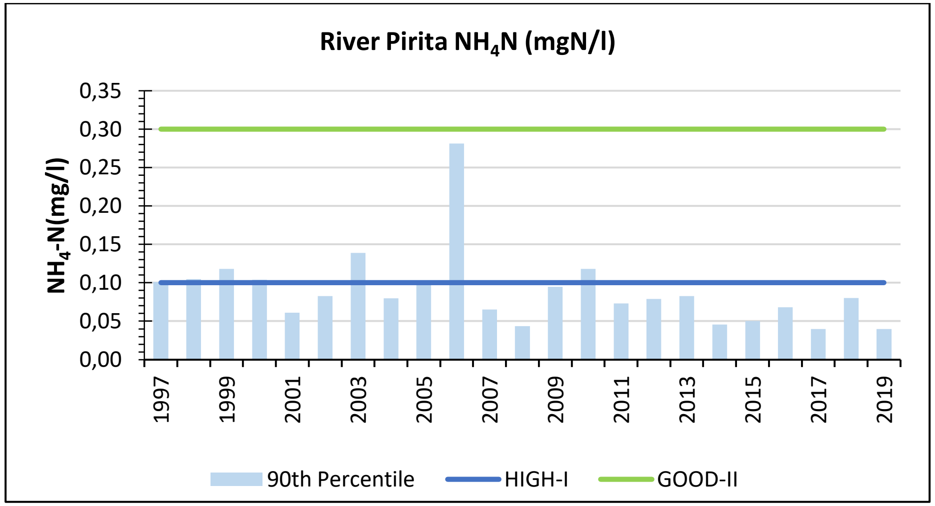


Figure 25. River Pirita Tot-P and Tot-N and national criteria



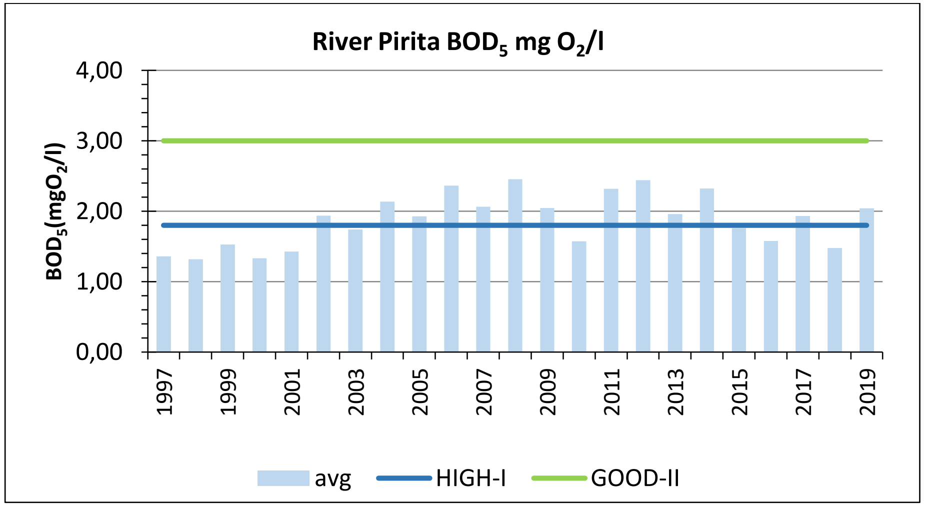


Figure 26. River Pirita NH_4N and BOD_5 and national criteria

5 DISCUSSIONS

5.1 Comparison of N/P Ratio in two intervals

A higher trophic level index correlates with a lower N/P ratio, which can be understood as a loss of Nitrogen. Denitrification is mainly responsible for the loss of Nitrogen in eutrophic lakes. Denitrification is a process facilitated microbially that reduces NO_3 to molecular Nitrogen (N_2), which escapes to the atmosphere. This results in a primary cause of nitrogen loss from water bodies associated with lower N/P ratios. To sum up, the N/P ratio is an indicator of eutrophication, and in shallow water bodies, the more eutrophic level accounts to the lower of the N/P ratio [39]. Nitrogen supply and eutrophication level in a water body can be categorized as the table below, which is related to the threshold ratios of Total Nutrients (TN: TP).

Table 12 N/P Ratio criteria to indicate eutrophication level **[40] [41]**

N/P Ratio	**Supply of Nitrogen**	**Eutrophication Level**
N/P>30	Extremely high	Oligotrophic
25<N/P<30	Very High	Very Low Level of Eutrophication
20<N/P<25	High	Low Level of Eutrophication
15<N/P<20	Moderate	Standard Level
10<N/P<15	Low	High Level of Eutrophication
5<N/P<10	Very Low	Very High level of Eutrophication
N/P<5	Extremely Low	Extremely High Level of Eutrophication

In this chapter, the nitrogen to phosphorus ratio from the studied rivers is presented to mainly understand the relationship between the N/P ratio and the eutrophication. It is also to highlight observations in the condition of the water quality from the year the HELCOM Nutrient Reduction Scheme was implemented in 2007. Thus, the N/P Ratio, in mainly two intervals, is compared. The first interval is from 1992-2007 and the second interval from 2008-2019 (after implementation of BSAP). In order to calculate the N/P ratio, the average annual amount of T-N and T-P in specific ranges is calculated.

Table 13 N/P ratio of studied catchment area

River	N/P Ratio (1992-2007)	N/P Ratio (2008-2019)	*Δ (%)
1. Pühajõgi	8.60	29.39	241.95
2.Kunda jõgi	55.60	74.22	33.50
3. Loobu jõgi	41.96	82.57	96.76
4. Purtse jõgi	42.84	53.54	24.98
5. Selja jõgi	18.07	77.88	330.97
6. Valgejõgi	39.32	49.86	26.81
7. Pudisoo jõgi	13.76	14.31	4.01
8. Jägala jõgi	37.18	52.84	42.10
9.Vihterpalu jõgi	47.91	45.51	-5.01
10.Keila jõgi	33.76	40.43	19.77
11. Vääna jõgi	41.92	25.80	-38.45
	N/P Ratio (1997-2007)	**N/P Ratio (2008-2019)**	***Δ (%)**
12.Pirita jõgi	40.25	57.92	43.89

*Δ (%) gives the changes in percentage from, before-BSAP (1992-2007) level. (+) % for increase or (-) % for decrease (formula in appx. A1.1)

From the table above, we can say that N/P ratio from BSAP implementation, increased three-fold the ratio in 1992-2007 for Pühajõgi presenting a significant change in the eutrophication level from the status of a very high level of eutrophication to a very low level of eutrophication which means the supply of Phosphorus reduced. This shows a lot of improvement in surface water quality. Even in the case of Selja jõgi, there is a change in the supply of Nitrogen level from moderate to extremely high supply of Nitrogen, showing a good ecological condition in recent years. The nitrate condition, particularly in Selja River, was significantly higher because of the use of the catchment as mostly farmlands (66%) explaining the strong relationship between intensive agricultural land use, and the increase in nutrient conditions (appx. A2.1.1).

In the rest of the rivers like Kunda, Loobu, Purtse, Valge, Vihterpalu, Jägala, Pirita, and Keila, the N/P ratio is in excellent status for both the study intervals with a high supply of Nitrogen keeping eutrophication status to the oligotrophic state. While in River Pudisoo, the situation before the implementation of BSAP and after does not show much difference with an increase of just 4% in the ratio between the two intervals. However, both the cases conclude that the N/P ratio is in a high level of eutrophication as there is a low supply of Nitrogen over Phosphorus, which means the condition is disappointing. The water quality of the Vääna jõgi changed from being oligotrophic to being a very low eutrophic river over the years due to a lower supply of Nitrogen over Phosphorus. This may be an impact of the scattered dwellings wastewater since the catchment has a population density of about 58 inhabitants per square kilometer (Figure 29).

5.2 MK Test Result

A spreadsheet-based XLSTAT [42] was used within excel's spreadsheet. This tool is used to process the input water quality input time-series data, perform the trend analysis, and finally report the results of the MK test. The nutrient concentration data on the 12 monitored rivers was analyzed using the aforementioned XLSTAT tool (refer to section 2.3.2). The trend is statistically significant if P-value is < 0.05 (alpha). A positive MK statistic suggests that the nutrient concentration is increasing with time, while a negative MK statistic states the opposite. There is no trend if the computed probability is larger than the level of significance.

N Concentration

Based on the test run, for TN loading, a statistically increasing trend (p-value < 0.05; two-sided test) is observed in 2 rivers, namely Rivers Selja and Loobu. Since the probability for both is < 0.0001, it shows a minimal chance the data is random and 99.99% confident that the data is significant, rejecting the null hypothesis. Kendall's tau for Selja is 0.182, and for Loobu is 0.193, indicating the weakest acceptable correspondence as it is far from being a perfect positive monotonous relation (+1). At the same time, 3 rivers (Pühajõgi, Purtse, and Vääna) have a significantly decreasing trend with a weaker correlation. The remaining 7 rivers (Valgejõgi, Pudisoo, Jägala, Vihterpalu, Keila, Kunda, and Pirita) did not have a trend accepting the null hypothesis denoting that the data is independent and randomly ordered. Since the testing trend is performed at 5% significance level, when p-value > 0.05, the alternate hypothesis is rejected, stating that there are high chances that data is random, which is not acceptable as we want 95% confidence. In the case of all the 7 rivers, their Z value is in the range of the critical Z score values (i.e., -1.96 and +1.96) and the p values associated with it are greater than alpha (0.05). This kind of pattern is likely one version of a random pattern. On the other hand, an interesting case is observed when the Z values fall outside the critical range with smaller probabilities. It could mean there is spatial clustering of either high values or low values [43]. For instance, with Pühajõgi, the low negative *Z* score, i.e., -11.55 indicates an intense spatial clustering of low values. In terms of River Loobu, with a high *Z* score (5.25), it means there is spatial clustering of high values. No trends were even observed in catchments dominated by farmlands and forest covers. We can say that this test validated the previous method of concentration analysis since the MK trends gave the same results in terms of significant trends. The results are shown in Table 14, and the same results are presented visually in Figure 27.

Table 14 MK statistics and trends for TN concentration in study catchments

Total Nitrogen							
River Name	No of observations	Years monitored	MK-stat (S)	Kendall's Tau	Normalized Test Statistics(*Z*)	p-Value	Trend (5% level of significance)
1. Pühajõgi	329	1992-2019	-22720	-0.427	-11.55	< 0.0001	Decreasing
2. Purtse jõgi	317	1992-2019	-17693	-0.359	-9.53	< 0.0001	Decreasing
3. Vääna jõgi	334	1992-2019	-18622	-0.335	-9.14	< 0.0001	Decreasing
4. Selja jõgi	316	1992-2019	9001	0.182	4.83	< 0.0001	Increasing
5. Loobu jõgi	333	1992-2019	10654	0.193	5.25	< 0.0001	Increasing
6. Valgejõgi	332	1992-2019	3704	0.068	1.84	0.067	No trend
7. Pudisoo jõgi	219	1992-2019	734	0.031	0.68	0.4983	No trend
8. Jägala jõgi	334	1992-2019	3657	0.066	1.80	0.073	No trend
9.Vihterpalu jõgi	222	1992-2019	890	0.036	0.81	0.421	No trend
10.Keila jõgi	331	1992-2019	-2602	-0.048	-1.30	0.196	No trend
11.Kunda jõgi	312	1992-2019	-809	-0.017	-0.45	0.660	No trend
12.Pirita jõgi	274	1997-2019	1400	0.037	0.92	0.3557	No trend

P Concentration

For TP, the results of MK tests were statistically significant from 12 Rivers (Table 15) with 8 downward trends (Pühajõgi, Kunda, Loobu, Purtse, Selja, Valgejõgi, Keila, and Pirita), 2 upward trends (Vihterpalu and Pudisoo) and 2 rivers not showing any significant trend (River Jägala and River Vääna). In the previous section, the N/P ratio stated that the Vihterpalu jõgi is in an oligotrophic state while the Pudisoo is in the high eutrophic condition, because of the low supply of nitrogen as compared to phosphorus.

From the MK test results, we can confirm that the concentration of TP is in increasing trend for both the rivers. In terms of Kendall's tau, both the Rivers Vihterpalu (0.160) and Pudisoo (0.148) are showing a weak correlation. Their *Z* values indicate a spatial clustering of high values since it is a high positive score for both (3.54 and 3.24 respectively). However, for the rivers with decreasing trends, Pühajõgi and Selja exhibited a moderate correlation as opposed to a perfect positive monotonous relation (with $\tau = -0.66$ and -0.55 respectively). In contrast, the rest of the other 6 rivers showed the weakest acceptable relationship. At the same time, their low negative *Z* scores indicate a strong clustering of low values. As for the Vääna and Jägala, no trend was detected indicating no monotonous relation at all at 5% significance level with p-value indicating randomness and less confidence. The *Z* value for both was within the range of +1.96 and -1.96 standard deviations representing a random pattern. Statistically significant trends were indicated in varying catchment size (appx. A2.1.1). Overall our study suggests that there is a clear trend in most of the rivers for TP concentrations as compared to the TN concentration (Figure 28).

Table 15 MK statistics and trends for TP concentration in study catchments

Total Phosphorus							
Site Name	No of observations	Years monitored	MK-Stat(S)	Kendall's Tau	Normalized Test Statistics (Z)	p-Value	Trend (5% level of significance)
1. Pühajõgi	329	1992-2019	-35707	-0.664	-17.98	< 0.0001	Decreasing
2.Kunda jõgi	313	1992-2019	-8188	-0.170	-4.49	< 0.0001	Decreasing
3. Loobu jõgi	332	1992-2019	-14316	-0.263	-7.16	< 0.0001	Decreasing
4. Purtse jõgi	321	1992-2019	-17693	-0.115	-3.08	0.0025	Decreasing
5. Selja jõgi	317	1992-2019	-27555	-0.553	-14.69	< 0.0001	Decreasing
6. Valgejõgi	331	1992-2019	-9518	-0.177	-4.80	< 0.0001	Decreasing
7.Keila jõgi	332	1992-2019	-10296	-0.188	-5.12	< 0.0001	Decreasing
8.Pirita jõgi	274	1997-2019	-7919	-0.214	-5.28	< 0.0001	Decreasing
9. Pudisoo jõgi	216	1992-2019	3407	0.148	3.24	0.001	Increasing
10.Vihterpalu jõgi	222	1992-2019	3862	0.160	3.54	0.0005	Increasing
11. Vääna jõgi	334	1992-2019	1192	0.022	0.59	0.559	No trend
12. Jägala jõgi	332	1992-2019	-2555	-0.047	-1.28	0.206	No trend

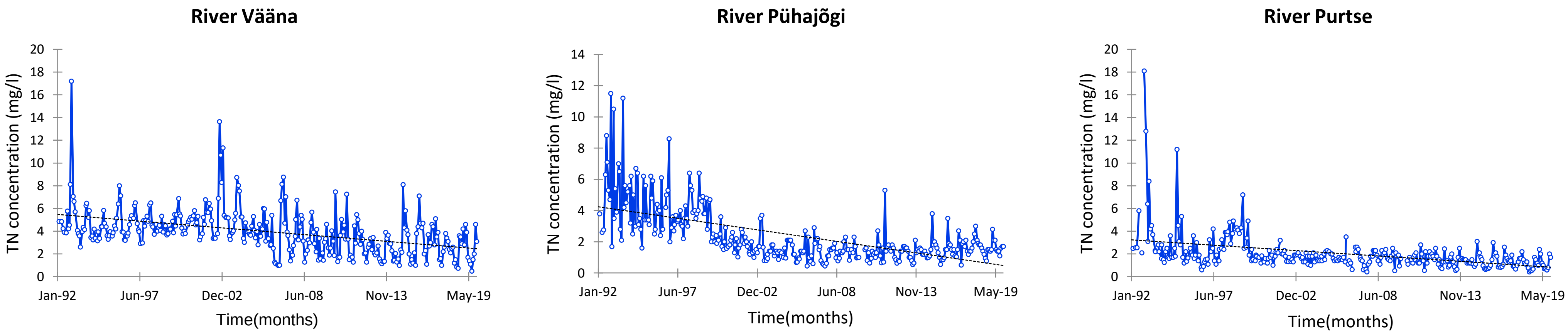


Figure 27a. Time Series of TN Concentration showing decreasing trend

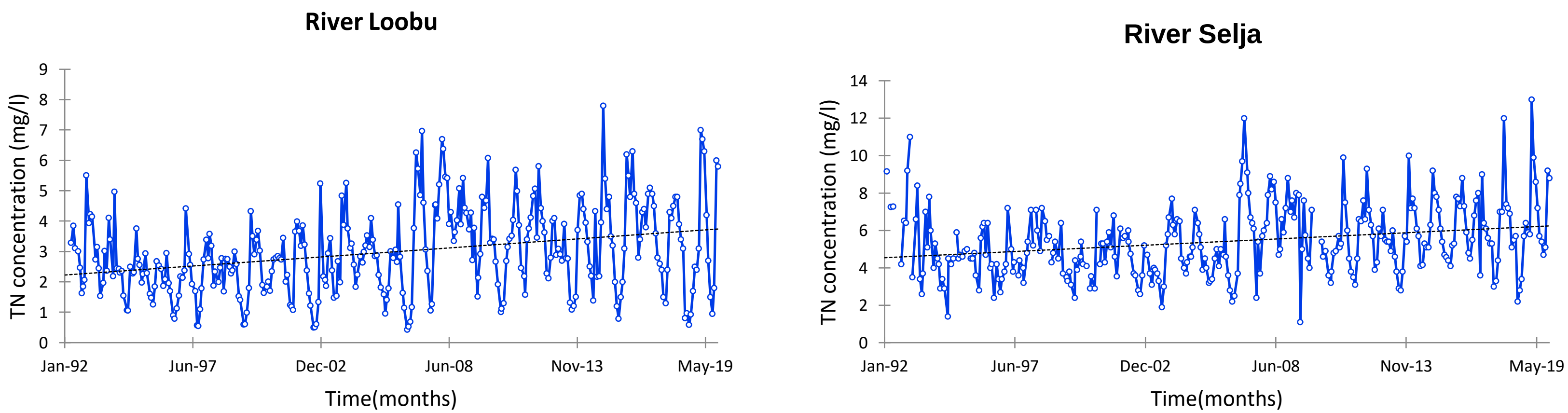


Figure 27b. Time Series of TN Concentration showing increasing trend

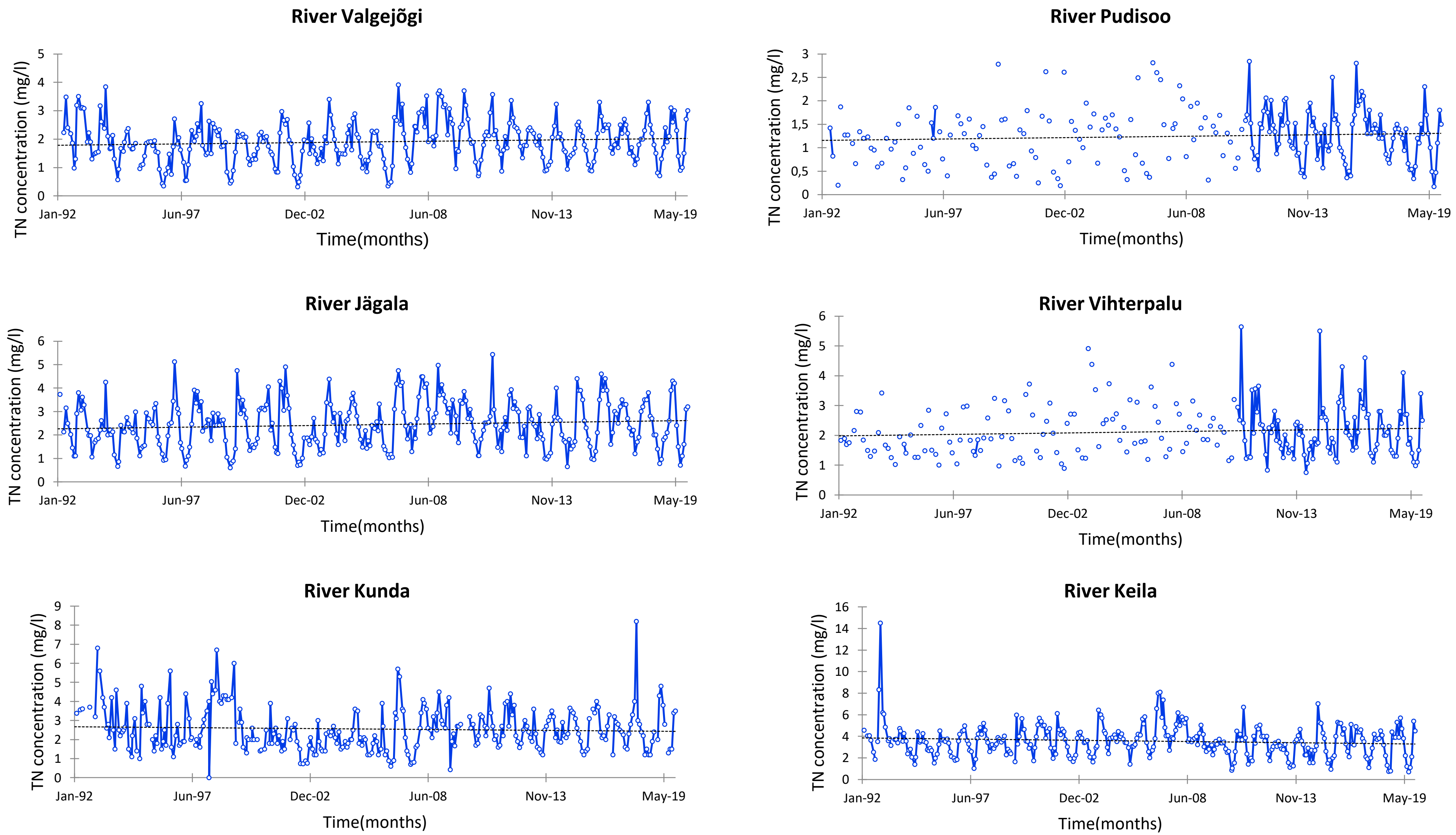


Figure 27c. Time Series of TN Concentration showing no trend

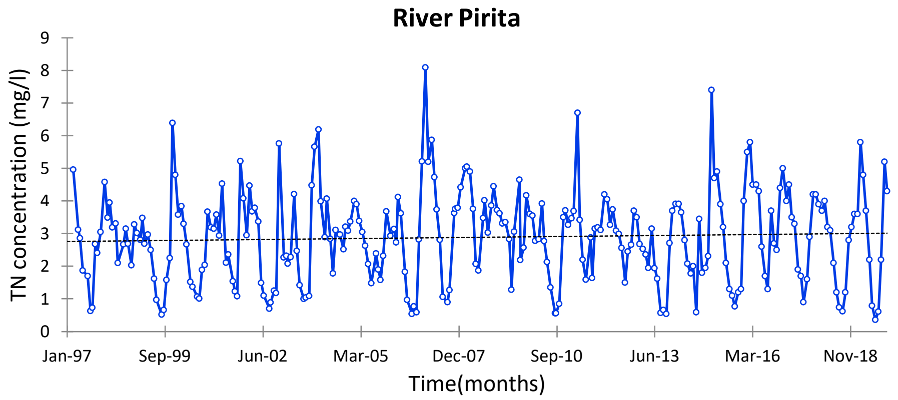
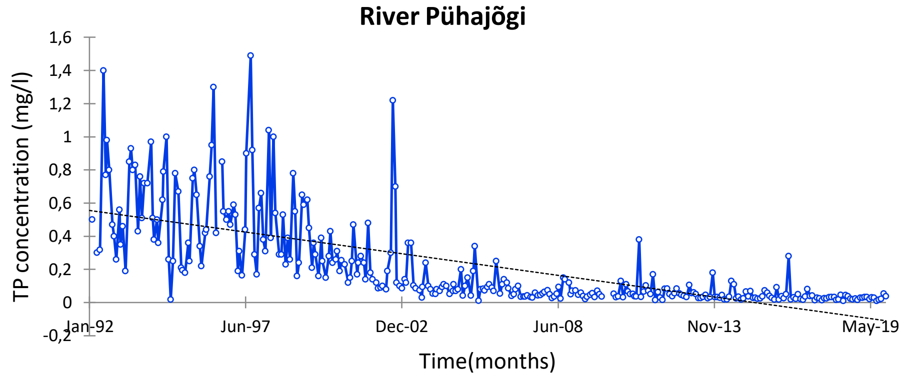
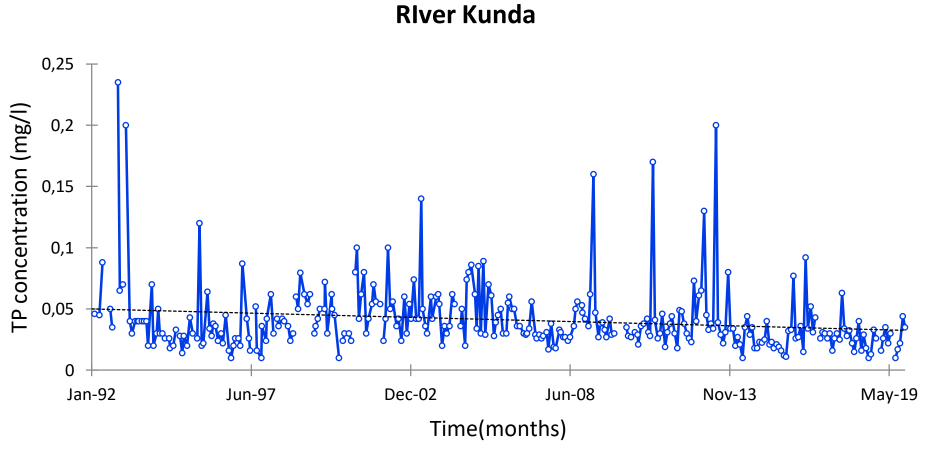


Figure 27c Time Series of TN Concentration showing no trend





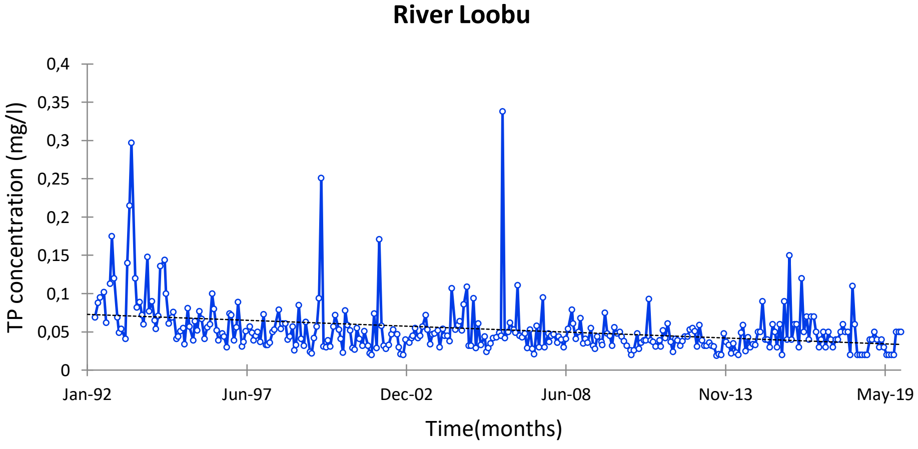


Figure 28a. Time Series of TP Concentration showing decreasing trend

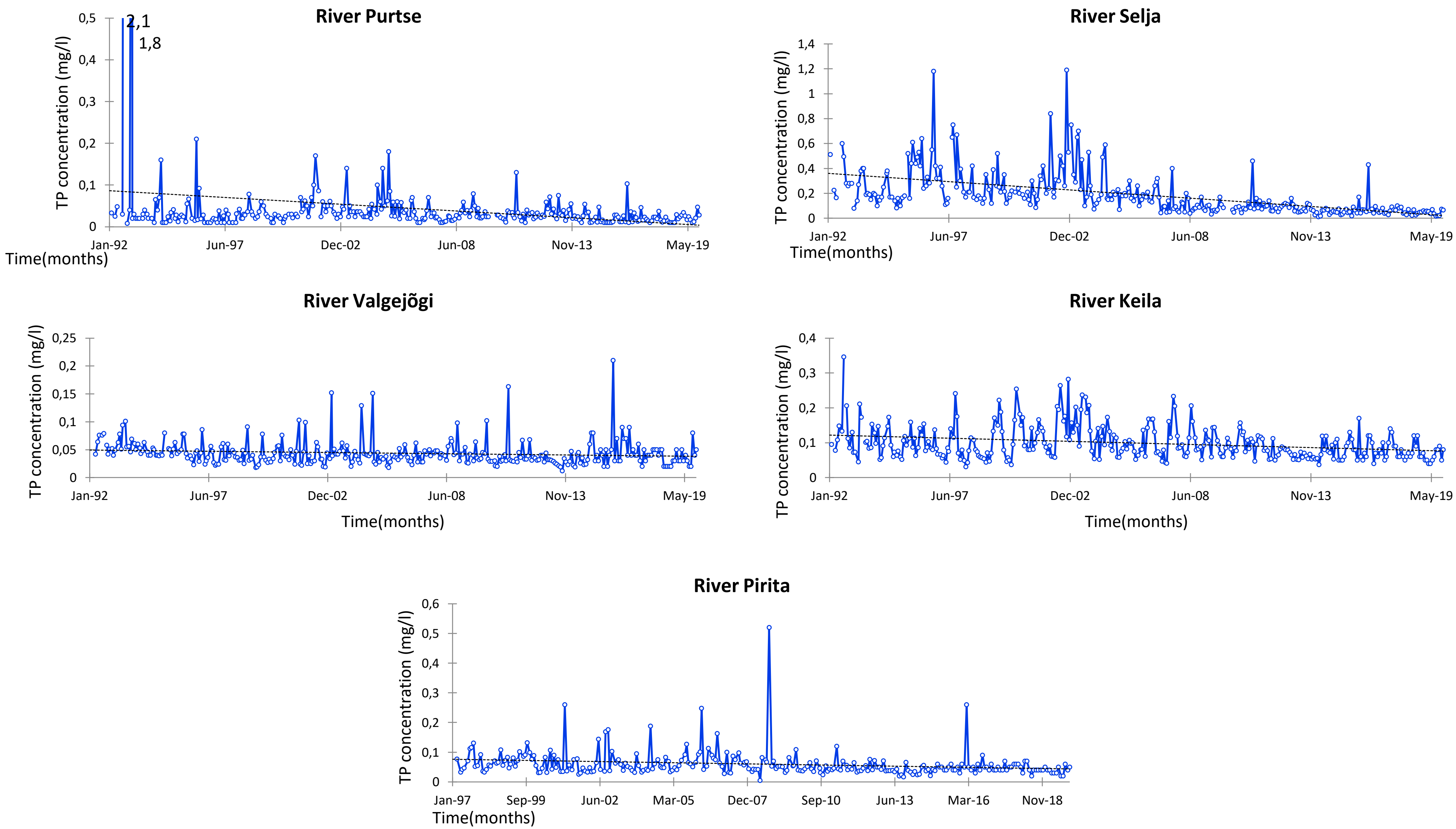


Figure 28a. Time Series of TP Concentration showing decreasing trend

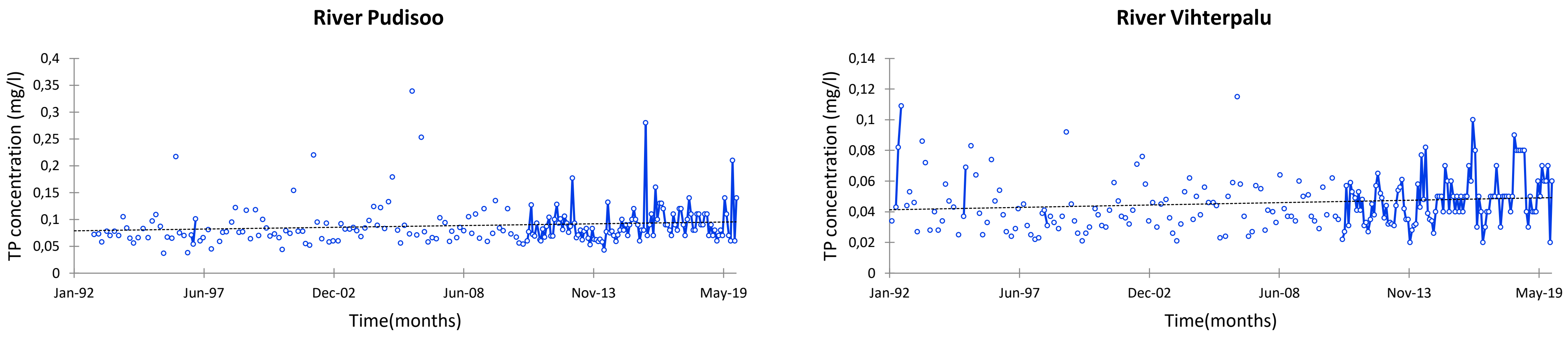


Figure 28b. Time Series of TP Concentration showing increasing trend

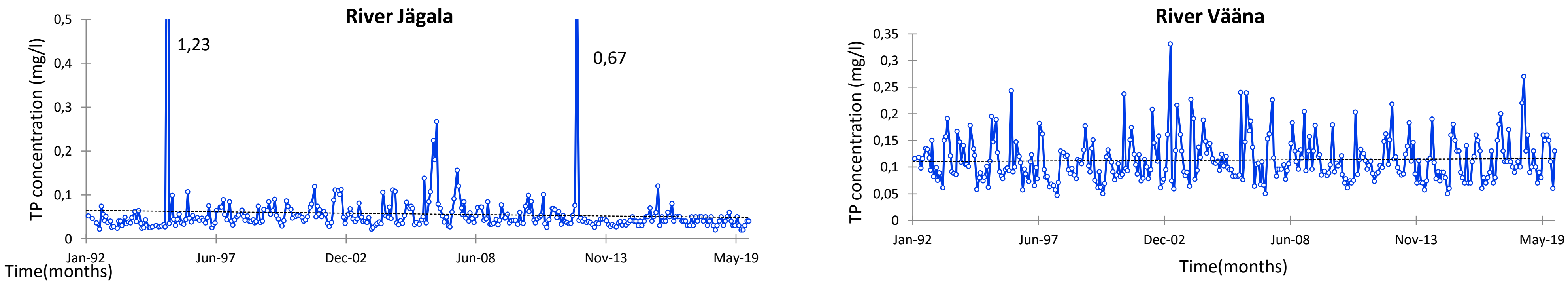


Figure 28c. Time Series of TP Concentration showing no trend

6 CONCLUSION

The protection of the Baltic Sea and the GOF requires reliable information on the nutrient inputs and their sources. All the surrounding countries need to monitor the surface rivers for nutrient concentration to improve the current situation and check if it meets the HELCOM recommendations. However, during the last two decades, the condition improved concerning the nutrient conditions in the surface water mainly after the development of WWTPs. Since the early 1990s, the P load from Tallinn decreased by 90%, while the N load reduced by 75% into the GOF basin based on a study done in 2016. The major pollution sources at the regional level can be related to North-Eastern Estonia mainly due to the reason that most of the Energy and Chemical industry here is based on oil shale mines and agricultural activities as well. The nutrient loads and trend of selected Estonian rivers flowing into the GOF catchment was studied using two methods. The first method was the concentration method with national criteria, and the second was the nonparametric MK test using XLSTAT to examine the trends statistically. Overall the outlook looks positive as it indicates good progress in several rivers towards cleaner surface water in terms of its physico-chemical status. However, this indicator can identify only the cause of the problem, and give limited information on the extent to which pollutants are impacting the fauna and flora. For that matter, biological indicators are also needed to understand the ecological status.

As the objective of this research was to assess organic substances and nutrient content levels in the selected Estonian rivers flowing into the GOF in the period 1992-2019, we can conclude that the water quality of the studied rivers has improved over the years, with significant changes taken place. When accounting for the reduction in the nutrient content, it can be estimated that the TP reduced by 46% since the 1992 level taken as an average from all the studied rivers and TN by 15% (annex A1.2). The main cause of eutrophication, as studied in the research, was the excessive nutrient loads from human settlements, industries, and agriculture.

The study also points out the impacts of emissions of nutrients on the water quality and lack of or weak responses in rivers can be reported from rivers showing higher nutrient loads. For that reason, the research also offers remarkable insights and new perspectives for policymakers and planners to help build monitoring strategies. Due to possible sampling errors, wide ranges of minimum and maximum values were observed. For instance, the 10^{th} percentile of O_2 Sat condition in River Vääna with 4.9%, in the year 1995 is a suspect (see appx. A2.1.6). There were also many reported data gaps marked in the study, especially in River Pudisoo and Vihterpalu. Hence, before analysis is performed for such a dataset, it would be good to increase the sampling frequency from once a month to once every two weeks in the monitoring program. This can ensure accuracy, and one can monitor compliance with national criteria standards and indicate a need for enforcement actions where noncompliance is identified.

After the implementation of BSAP in the year 2007, it was observed that there were vast improvements in the quality of most surface water, which was especially evident for the N/P ratio of River Pühajõgi and River Selja showing the effectiveness of such action programs. However, in the case of River Pudisoo due to the increasing trend in phosphorus concentration, it is in the state of a high level of eutrophication with N/P 14.31 in the second interval (2008-2019), and as to River Vääna, the N/P decreased by nearly 40% in the same interval falling to the risk of being a low eutrophic river. Hence, a low N/P ratio may increase the probability of nitrogen limitations in the surface water. It shows that there is a need for further monitoring and control by the relevant authorities to ensure if compliance with good physico-chemical status criteria is met in smaller catchments.

In the MK test, statistically significant (two-sided tests at 5% level) downward/upward trends and no trend for both nutrient loads were performed for all the rivers. A decline in the TN was noted in 3 rivers (Pühajõgi, Purtse, and Vääna) and an increase in 2 rivers (Selja and Loobu) out of the 12 catchment rivers. The rivers did not show any trend in the remaining 7 (Jägala, Valgejõgi, Pudisoo, Vihterpalu, Keila, Kunda, and Pirita). While in the case of TP, 8 rivers showed a significant decreasing trend (Pühajõgi, Kunda, Loobu, Purtse, Selja, Valgejõgi, Keila, and Pirita), and 2 rivers (Vihterpalu and Pudisoo) displayed an increasing trend. 2 (Jägala and Vääna) rivers supported the null hypothesis of no trend. Understandably, several rivers have responded to the decrease in inorganic and organic

fertilizers and better farm practices. The statistical test validated the results of the nutrient mean monthly concentration method with similar conclusions for significant trends.
The source of Phosphorus, however, in the surface water usually originates from the municipalities depending on the treatment efficiency. Better treatment efficiency in the WWTP depending on the use of chemicals for phosphorus precipitation can be a mitigation effort to cut the pollution at its source and also by controlling the phosphorus discharge from households and industries. The nutrient loads, particularly from the agricultural pressure with the application of excess manure, need to be reduced. In order to achieve that reduction, there needs to be proper management in the farming and livestock sectors to decrease NO_3 leaching to the water bodies. Phosphorus trapping or moving substantial amounts of N and P by transporting the manure to nutrient-deficit croplands could be done, although it may be costly and less energy effective due to the requirement of transportation. Introducing new technologies for nutrient recovery from manure in intensive livestock environments can also be effective. However, additional responses like regulations, use of economic incentives such as government subsidies, education and creating awareness, and more research and innovations are needed to promote wide adoption and reduce nutrient pollution.

There is a further need for efficient industrial and municipal wastewater treatment. In subject to industries, intensive R&D is needed to achieve closed circulations of process waters in chemical bleaching and even alternately substitute it with chlorine and sulfur-containing chemicals. It was found that some mills have already ceased to use chlorine bleaches, and gradually chlorine-free productions will dominate, which is a hopeful situation. The reduced nutrient load will benefit not only the marine ecosystems, but also the health, environment, and even economy, provided that the Best Available Technology and Best Environmental Practice principles are fully recognized and applied.

SUMMARY

The research gives an overview of pollution and eutrophication in the rivers of the heavily industrialized North Estonia flowing into the Gulf Of Finland (GOF) catchment. It presents trends computed for the 28-year period of monthly surface water flows obtained from 11 basins - Pühajõgi, Purtse, Kunda, Selja, Loobu, Valgejõgi, Pudisoo, Jägala, Vääna, Keila, and Vihterpalu river during the years 1992-2019 and 23-year period in river Pirita (1997-2019), to evaluate the surface water quality of the rivers flowing into the GOF by analyzing water samples for physico-chemical properties with an emphasis on BOD_5, NH_4N, TN and TP indicators.

The largest proportions of nutrient inputs in Finland and Estonia originate from diffuse sources, especially from agriculture [5] as a result of surface runoffs. On the available initial time-series data, concentrations of BOD_5 and NH_4 were used as the indicators of organic pollution, and T-N and T-P were used as the indicators of eutrophication. The mean, maximum, minimum, 90^{th} percentile, 10^{th} percentile, and the median has been calculated for every year to follow the course of changes in concentrations of mentioned constituents during the studied years. Ultimately, the chemical status and eutrophication level of the rivers were also indicated as to the national limit values and nitrogen to phosphorus ratio criteria. Mann Kendall Test (5% significance level) is used as the statistical method to validate the results of the trend analysis for all the 12 rivers.

Integrated assessment results in brief

- According to the N/P ratio, River Pudisoo is in the state of high-level eutrophication.
- River Pühajõgi and Purtse have shown a significant decrease in nutrient concentration since the beginning of the study period (appx. A2.1).
- The MK test revealed 3 rivers (Pühajõgi, Purtse, and Vääna) with statistically significant downward trends and 2 rivers (Selja and Loobu) with statistically significant upward trend in terms of TN out of the total 12 catchments. The 7 remaining rivers showed no trend.
- There were 8 rivers with a statistically decreasing trend and 2 rivers (Pudisoo and Vihterpalu) with increasing trend in terms of TP out of all the studied rivers. 2 rivers showed no trend (Jägala and Vääna).

7 LIST OF REFERENCES

[1] C. Agrell, K. Okla, G. Bremle, N. Johansson, M. Klavins and A. Zelechowska, A system Analysis of Baltic Sea, vol. 148, Ecological Studies , 2001, pp. 149-150.

[2] H. Pitkänen, J. Lehtoranta and A. Räike, “Internal nutrient fluxes counteract decreases in external load: the case of the estuarial eastern Gulf of Finland Ambio 30,” pp. 195-201, 2001.

[3] GOF year 2014 team “Gulf Of Finland 2014 Assessment,” 2014, p. 31. Available: https://www.kik.ee/sites/default/files/5457.pdf

[4] S. Outi and M. Raateoja, “The gulf of Finland assessment,” Finnish Environment Institute, p.7, 2016.

[5] S. Knuutila and et al., “Nutrient inputs into the Gulf of Finland: Trends and water protection targets,” pp. 54-64, 2016.

[6] “HELCOM (2013a): HELCOM Copenhagen Ministerial Declaration - Taking Further Action to Implement the Baltic Sea Action Plan - Reaching Good Environmental Status for a healthy Baltic Sea,” 2013.

[7] HELCOM 2010 Ecosystem Health of the Baltic Sea 2003–2007: HELCOM Initial Holistic Assessment., Balt. Sea Environ. Proc. No. 122, 2010, pp. 6-13.

[8] “The State of Queensland (Department of Environment and Science) ,last updated on 03/09/2018,” Queensland Government, [Online]. Available: https://environment.des.qld.gov.au/management/water/health-indicators.

[9] “NASA Summer Camp 95,” The crooked river project, n.d. [Online]. Available: https://www.grc.nasa.gov/WWW/k-12/fenlewis/Cuyahoga_River.html.

[10] “EPA Ireland,” [Online]. Available: https://www.epa.ie/pubs/reports/water/waterqua/iwqmolou/App%207.pdf.

[11] “EPA, United States,” 2013 . [Online]. Available: https://www.epa.gov/sites/production/files/2015-09/documents/totalnitrogen.pdf.

[12] O. Roots and Ü. Suursaar, “Hazardous Substances in the water,biota and sediments of the North Estonian coastal sea,” Popov,V;Brebbia,C.A. (Toim.). Environmental Toxicology III. Southampton,Boston: WIT Press, pp. 79-90, 2010.

[13] “HELCOM 1993 The Baltic sea Environmental Proceedings,” the Baltic Sea Joint Comprehensive Environmental Action Programme Balt.Sea Environ.Proc. Copyright 1993 No. 48, p. 3-4, 1993.

[14] “Environmental Report 7,1993,Water Pollution And Quality In Estonia, Environmental Data Center,” National board of Waters and Environment, Helsinki, pp. 23,49, 1993.

[15] R. Antti, O. Natalia and et al., “Background information on the Baltic Sea catchment area for the Sixth Baltic Sea Pollution load compilation (PLC 6),” Baltic Marine Environment Protection Commission, p.4, 2019.

[16] “Agricultural land and cultivated area of crops - Statistics Estonia,” Statistics Estonia, [Online]. Available: https://www.stat.ee/34243. [Accessed 20 3 2020].

[17] J. M. Sagasta, S. M. Zadeh and H. Turral, “Water pollution from agriculture: a global review,” The Food and Agriculture Organization of the United Nations Rome. The International Water Management Institute on behalf of the Water Land and

Ecosystems Research, p.3, 2017.
[18] A. Roose and O. Roots, “Monitoring of priority hazardous substances in Estonian water bodies and in the coastal Baltic Sea.,” Boreal Env.Res.10:89-102, p.99, 2005.
[19] A. Iital, K. Pachel and E. Loigu, “Recent trends in nutrient concentrations in Estonian rivers as a response to large-scale changes in land-use intensity and life-styles,” Journal of Environmental Monitoring 12, p.178-188, 2010.
[20] K. Pachel, “Water Resources, Sustainable Use and Integrated Management in Estonia,PhD thesis,” Tallinn University Of Technology, Tallinn, pp. 24,28, 2010.
[21] “HELCOM Guidelines for the annual and periodical compilation and reporting of waterborne pollution inputs to the Baltic sea (PLC-water),” pp. 20-21, 2015.
[22] “Common Implementation strategy for the Water Framework Directive (2000/60/EC) Guidance Document No 10, Rivers and Lakes – Typology, reference conditions and classification systems,” Working Group 2.3 – REFCOND, 2003.
[23] “European Commission,Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for community action in the field of water policy,” Off. J. Eur. Communities , pp. 7,21,59, 2000.
[24] European Communities Environmental Objectives (Surface Waters) Regulations . Article 26, 2009, p. 15.
[25] H. B. Mann, “Non parametric test against trend,” *Econometrica,* no. 13, pp. 245-259, 1945.
[26] M. G. Kendall, “Rank Correlation Methods,” vol. 4th Ed, 1975.
[27] C. Zaiontz, “Real Statistics in Excel Mann-Kendall Test 2012-2019,” 2019. [Online]. Available: https://www.real-statistics.com/time-series-analysis/time-series miscellaneous/mann-kendall-test/. [Accessed 20 3 2020].
[28] O.Thas, L.Van Vooren, J.P.Ottoy, “Selection of Nonparametric Methods for Monotonic trend Detection in Water Quality,” BIOMATH Department,University of Gent, Belgium, p.2-5, 1996.
[29] D. Berryman, B. Bobee, D. Cluis and J. Haemmerli, “Non parametric test for trend detection in water quality time series,” *Water Resources Bulletin,* no. 24(3), pp. 545-556, 1988.
[30] R. M. Hirsch and J. R. Slack, “A non parametric trend test for seasonal data with serial dependence,” *WATER Resources Research,* pp. 727-732, 1984.
[31] S. Larsen, “2013,” Danish Centre For Environment and Energy, Statistical Aspects in relation to Baltic Sea Pollution Load Compilation” Task1 under HELCOM, p. 7.
[32] “HELCOM, 2011. The Fifth Baltic Sea Pollution Load Compilation (PLC-5) Balt. Sea Environ. Proc. No. 128,” Helsinki Commission, Finland, p. 97, 2011.
[33] “Regulation No. 44 of the Ministry of the Environment - Annex 4,” 28 07 2009. [Online].
[34] “Estonian Environmental Register,” [Online]. Available: http://register.keskkonnainfo.ee/envreg/main#HTTPn4dsji7NdBnRXRGS4n2jAIljbXy614.
[35] “HELCOM,2011,Salmon and Sea Trout Populations and Rivers in Estonia – HELCOM assessment of salmon (Salmo salar) and sea trout (Salmo trutta) populations and habitats in rivers flowing to the Baltic Sea,” Balt.Sea Environ.Proc. No. 126B, pp.11,13, 2011.
[36] Suursaar, Aps, Martin, P. and Kaljurand, “Monitoring of pulp mill effluents in the

coastal waters of North Estonia," Estonian Marine Institute, University of Tartu, Estonia, p. 3, 2008.

[37] "'Pearl River'.," Wikipedia, (2019). [Online]. Available: https://libguides.ioe.ac.uk/c.php?g=482485&p=3299863. [Accessed 25 Feb 2020].

[38] O. Raju, "Economic crisis and economic policy in Estonia 2007-2010," University of Tartu, Tartu, p. 141, 2011.

[39] Y. Zhang, C. Song, L. Ji, Y. Lui, J. Xiao, X. Cia and Y. Zhou, "Cause and effect of N/P ratio decline with eutrophication aggravation in shallow lakes," Science of Total Environment 627, p. 7, 2018.

[40] S. Farshadi, "Organic Substances and Nutrients Content and Load in the Rivers of Lake PEIPSI Catchment Area in 1992-2017," Masters Thesis,Tallinn University Of Technology, Tallinn, pp. 56-81, 2019.

[41] Prof. LOIGU, Interviewee, *Nitrogen Supply and Eutrophication level categorization.* [Interview]. 2019.

[42] Addinsoft, "XLSTAT statistical and data analysis solution," Newyork, USA, 2020.

[43] "What is a Z score What is a p-value," [Online]. Available: http://resources.esri.com/help/9.3/arcgisdesktop/com/gp_toolref/spatial_statistics_toolbox/what_is_a_z_score_what_is_a_p_value.htm. [Accessed 22 04 2020].

[44] "HELCOM (2007a): The HELCOM Baltic Sea Action Plan.".

[45] O. Roots, "Report of a survey of the state of the Environment in the Estonia,Latvia and Lithuania," Ministry of the Environment of the Estonia, (1999).

[46] R. M. Hirsch, J. R. Slack and R. A. Smith, "Techniques of trend analysis for monthly water quality data," Water Resources Research, pp. 727-732, 1982.

[47] "Kendall's Tau (Kendall Rank Correlation Coefficient)," Statistics How To, [Online]. Available: https://www.statisticshowto.com/kendalls-tau/. [Accessed 22 04 2020].

APPENDICES

Appendix 1 Calculations

A1.1 Nitrogen to Phosphorus Ratio

Table 16 Showing average N/P ratio in two intervals

River Name	Parameter	1992-2007	2008-2019
Vihterpalu	T-N	2.092	2.161
	T-P	0.044	0.047
Kunda	T-N	2.504	2.668
	T-P	0.045	0.036
Pühajõgi	T-N	2.968	1.489
	T-P	0.345	0.051
Purtse	T-N	2.409	1.471
	T-P	0.056	0.027
Keila	T-N	3.753	3.327
	T-P	0.111	0.082
Jägala	T-N	2.311	2.610
	T-P	0.062	0.049
Valgejõgi	T-N	1.784	2.063
	T-P	0.045	0.041
Vääna	T-N	4.742	2.918
	T-P	0.113	0.113
Selja	T-N	4.924	6.032
	T-P	0.272	0.077
Loobu	T-N	2.549	3.554
	T-P	0.061	0.043
Pudisoo	T-N	1.199	1.283
	T-P	0.087	0.089
		1997-2007	**2008-2019**
Pirita	T-N	2.794	2.968
	T-P	0.069	0.051

***Δ changes in percentage:** Note that for Pirita, the monitoring started only from 1997.

$$* \Delta\,(\%) = 100 * ((N/P)_{(1992-2007)} - (N/P)_{(2008-2019)})/(N/P)_{(1992-2007)}) \quad (A1.1)$$

A1.2 Changes in nutrient concentration since 1992

Table 17 Showing changes from beginning of study period and 2019

River Name	% increase or decrease since 1992 (since 1997 for Pirita*)					
	BOD_5	**TN**	**TP**	**NH_4**	**NO_3**	**PO_4**
Vihterpalu	-17.4	-3.58	15,07	-8.11	-54.98	-7.14
Kunda	20.77	17.19	68.10	96.45	-71.64	71.46
Pühajõgi	45.95	69.01	95.32	92.67	29.30	96.97
Purtse	34.18	80.79	92.64	93.38	35.83	95.19
Keila	14.22	35.23	57.67	-86.36	8.61	67.46
Jägala	20.43	-7.12	20.48	27.36	-61.19	17.65
Valgejõgi	-20.63	9.49	35.79	64.11	-32.49	54.08
Vääna	11.05	57.51	0.06	70.57	40.26	9.07
Selja	37.03	-4.12	86.65	96.37	-44.15	88.34
Loobu	-20.53	-35.64	66.02	72.83	-130.16	69.26
Pudisoo	-85.83	-13.15	-33.10	-270.37	-61.04	28.29
Pirita*	-50.51	-28.974	47.92	60.40	-92.11	53.51
Avg	-0.94	14.72	46.05	25.77	-36.15	53.68

(-) value   % increase from 1992

(+) value   % decrease from 1992

Formula:

$$\% = 100 * \frac{(X_{1992} - X_{2019})}{X_{1992}} \quad \text{(A1.2)}$$

Where X_{1992} = Average parameter in the year 1992 (for BOD_5, TN, TP, NO_3, PO_4)
90th percentile in the year 1992(for NH_4)

X_{2019} = Average parameter in the year 2019 (for BOD_5, TN, TP, NO_3, PO_4)
90th percentile in the year 2019 (for NH_4)

*Note that the monitoring for River Pirita started only from 1997.

A1.3 Physical-chemical Status in 2019 (Check section 2.6.1 page 34)

class B Rivers																		
	Pühajõgi		**Kunda**		**Loobu**		**Selja**		**Valgejõgi**		**Keila**		**Pirita**		**Vääna**		**Jägala**	
PH	8.26	In Range	8.34	In Range	8.85	In Range	8.367	In Range	8.308	In Range	8.214	In Range	8.242	In Range	8.228	In Range	8.23	In Range
BOD_5	2.09	4	1.87	4	1.817	4	1.8	5	1.667	5	1.508	5	2.042	4	1.508	5	1.88	4
NH_4	0.13	4	0.045	5	0.02	5	0.052	5	0.029	5	0.246	4	0.04	5	0.108	4	0.06	5
TN	1.69	4	2.89	4	4.038	3	7.442	2	2.125	4	3.383	4	3.097	3	2.616	4	2.56	4
TP	0.029	5	0.026	5	0.035	5	0.047	5	0.039	5	0.062	5	0.038	5	0.116	2	0.04	5
O_2 Sat	88.3	5	84	5	94.4	5	90	5	90.3	5	83.2	5	70.3	5	90	5	87.60	5
Total		**22**		**23**		**22**		**22**		**24**		**23**		**22**		**20**		**23**

Table 18 showing physical-chemical status in 2019 for all rivers

class A Rivers						
	Purtse		**Pudisoo**		**Vihterpalu**	
PH	7.98	In Range	8.075	In Range	8.017	In Range
BOD_5	2.18	5	1.858	5	1.633	5
NH_4	0.067	4	0.05	5	0.04	5
TN	1.273	5	1.22	5	2.09	4
TP	0.024	5	0.096	3	0.052	4
O_2 Sat	83	5	87.2	5	88.25	5
Total		**24**		**23**		**23**

Results

- 23-25 – high
- 18-22 – good
- 13-17 – moderate
- 8-12 – poor
- <8 – bad.

Appendix 2 Additional Charts

A2.1 Comparison of all the rivers

A2.1.1 Main characteristics of the monitored rivers

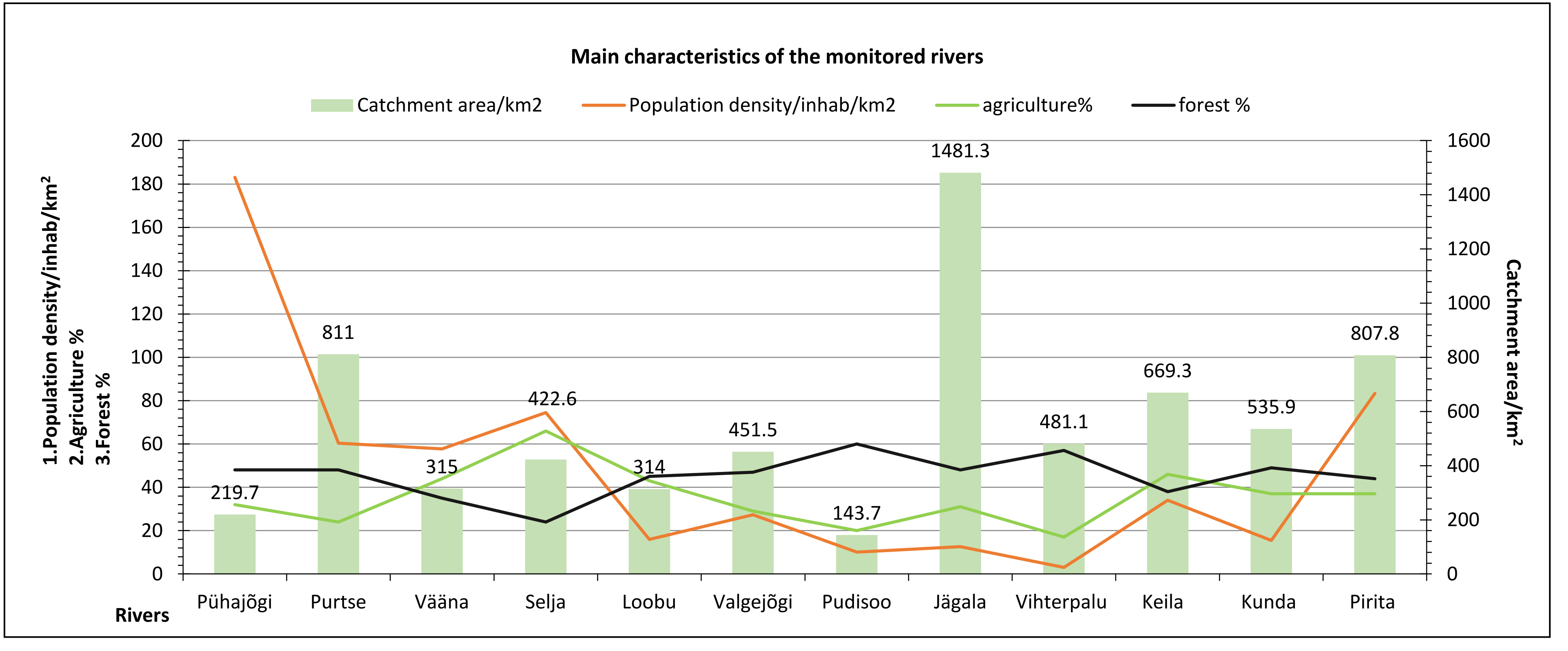


Figure 29. Showing characteristics of the monitored rivers

- **A2.1.2 Average Nitrate concentration**

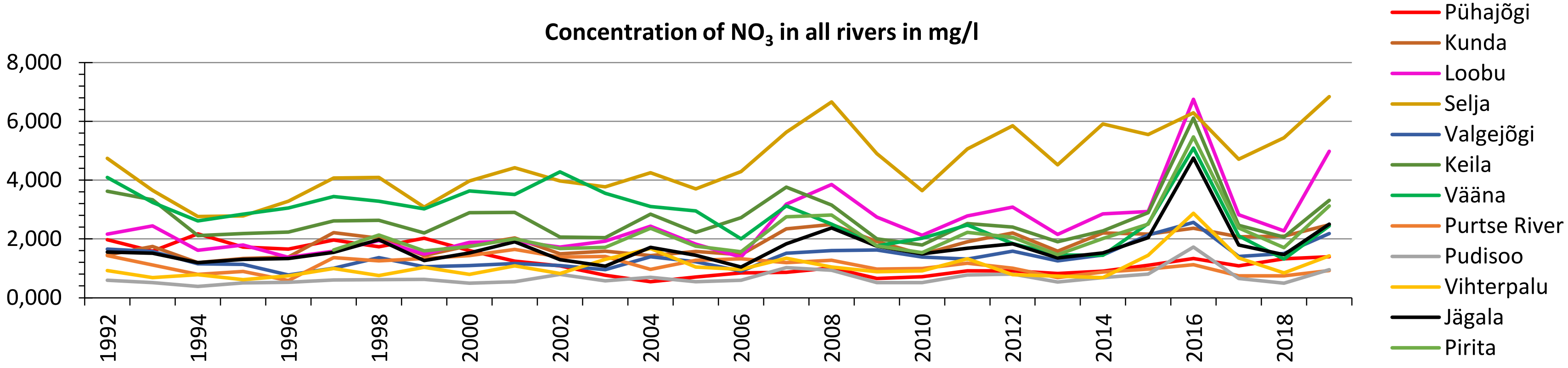


Figure 30a. Chart showing average NO_3 concentration in all the studied rivers

- **A2.1.3 Average Phosphate concentration**

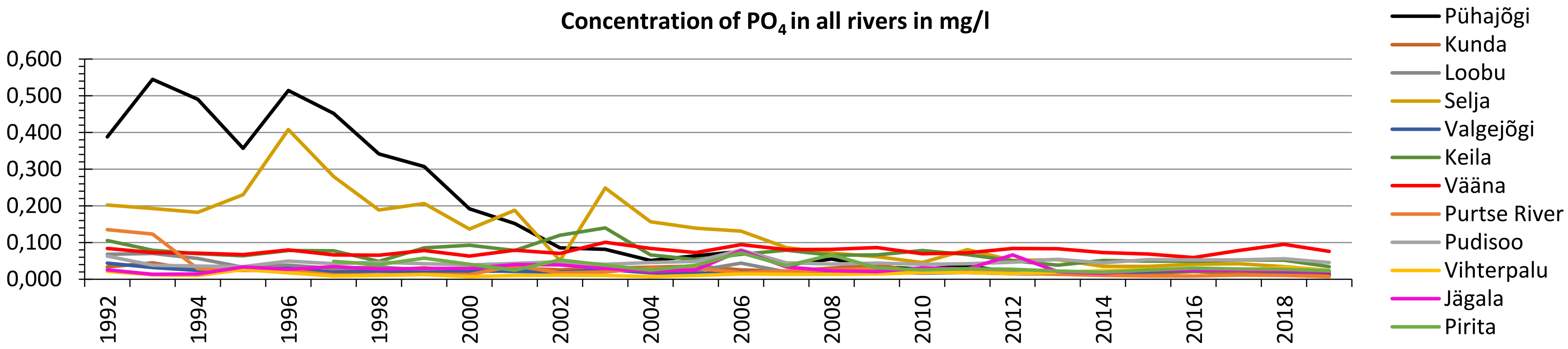


Figure 30b. Chart showing average PO_4 concentration in all the studied rivers

- **A2.1.4 Average TN concentration in mg N/l**

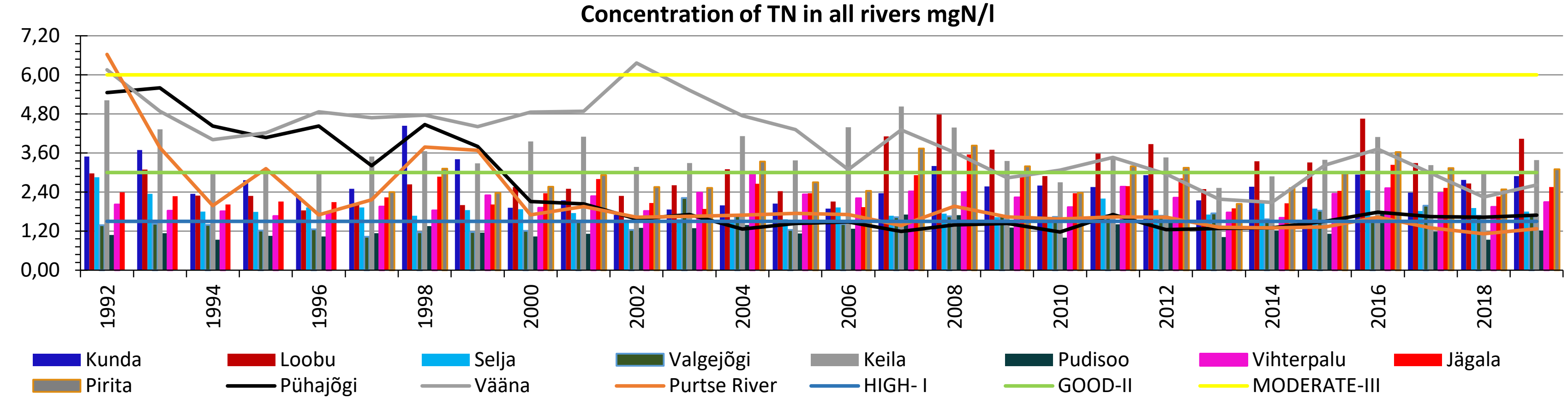


Figure 30c. Chart showing average TN concentration in all the studied rivers highlighting Pühajõgi, Purtse and Vääna

- **A2.1.5 Average TP concentrations in mg P/l**

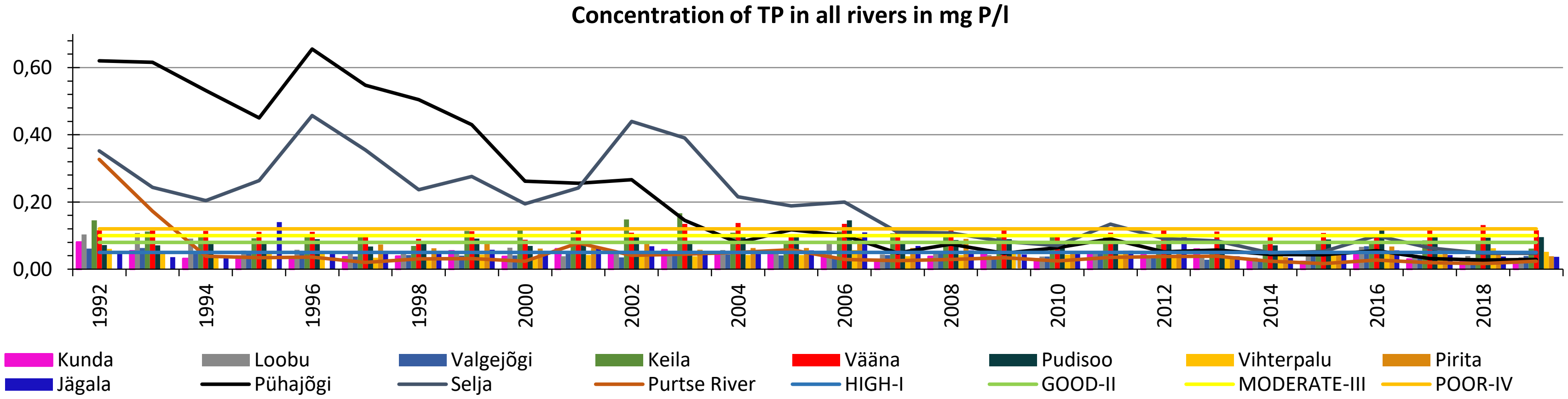
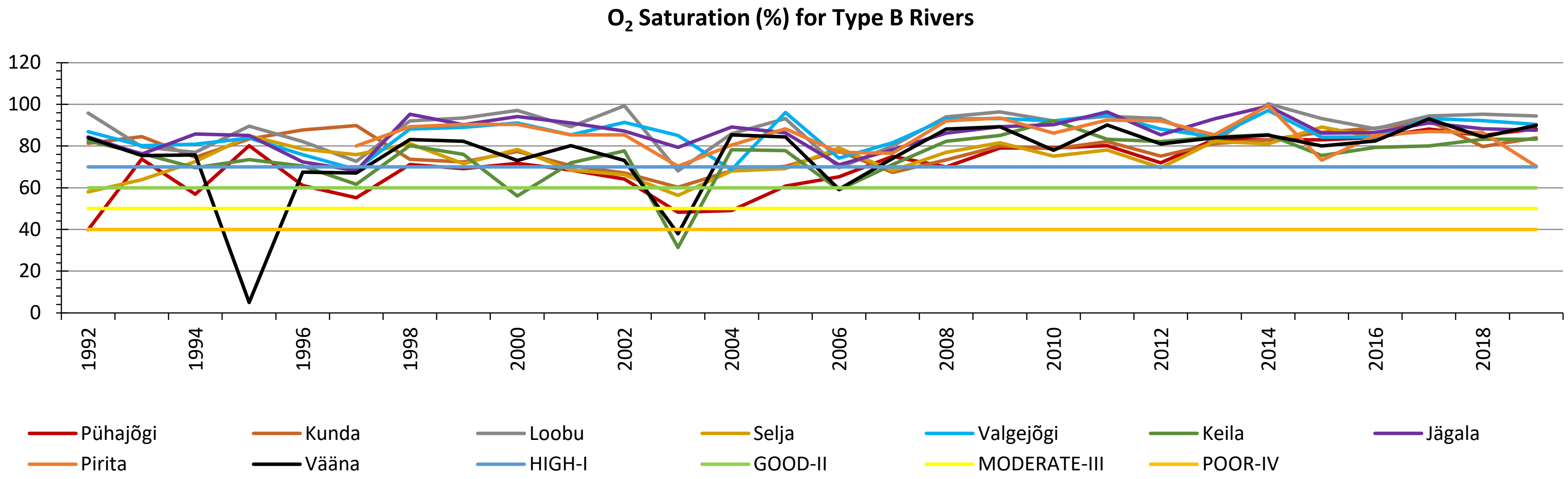


Figure 30d. Chart showing average TP concentration in all the studied rivers highlighting Pühajõgi, Purtse and Selja

- **A2.1.6 10th percentile of O_2 Sat concentration in %**



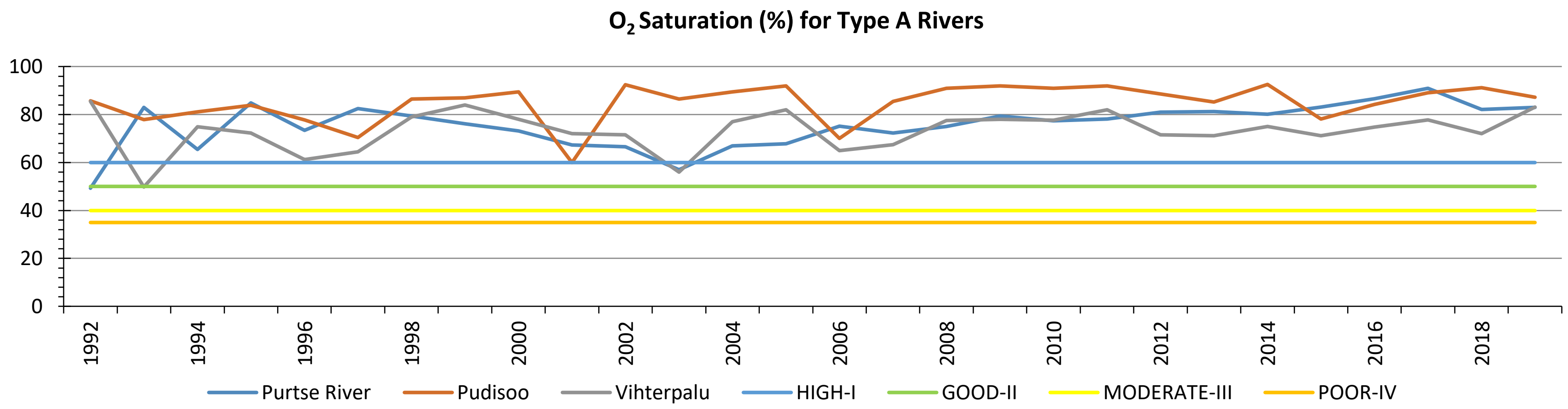
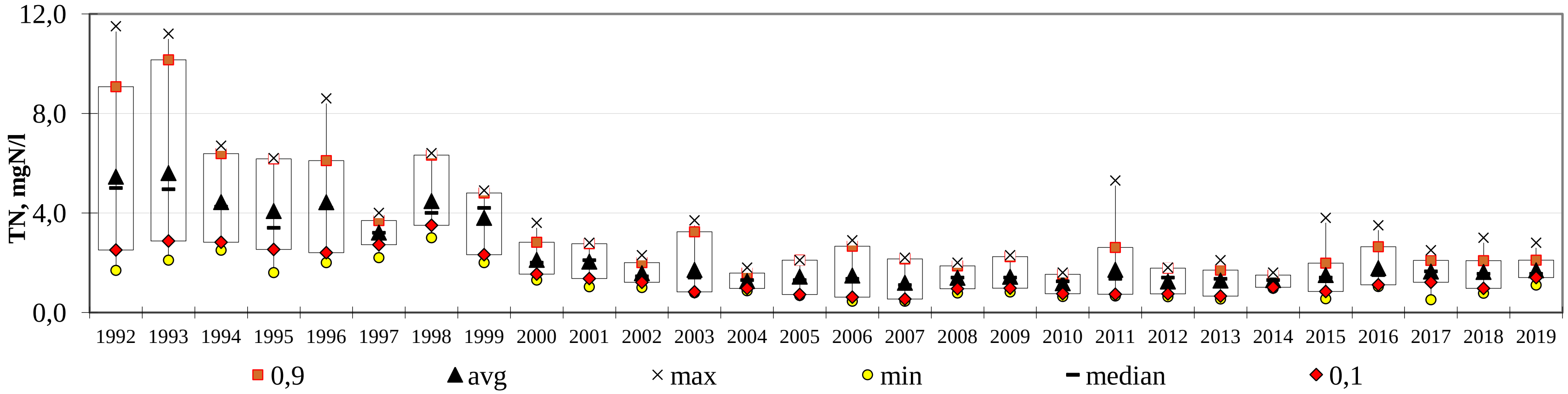


Figure 30e. Chart showing 10th percentile concentration of O_2 Sat in all the studied rivers

A2.2 Box plot showing concentration of Hydro-chemical monitoring stations.

1. River Pühajõgi



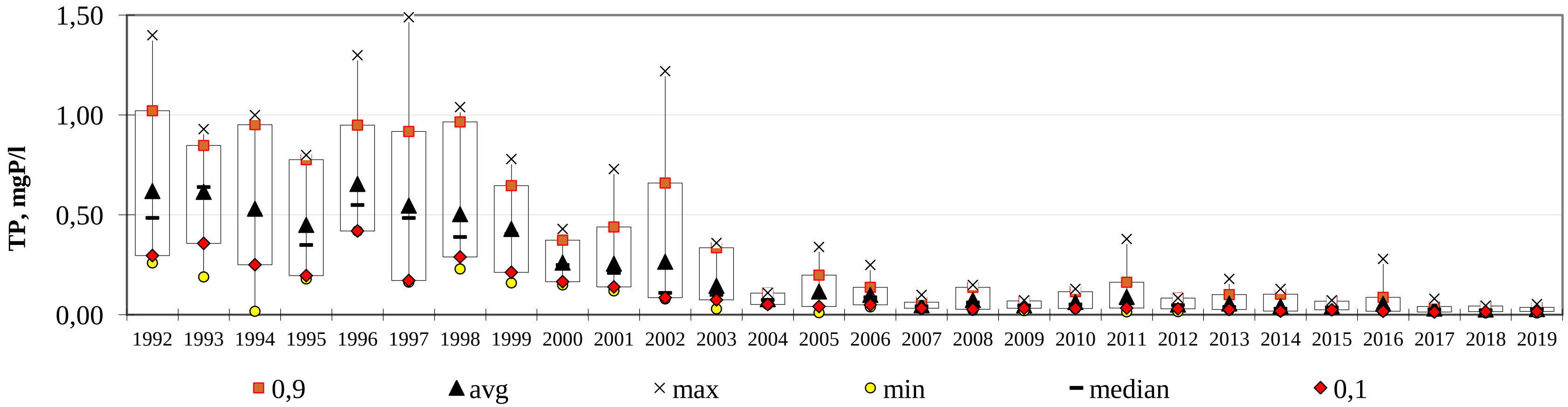
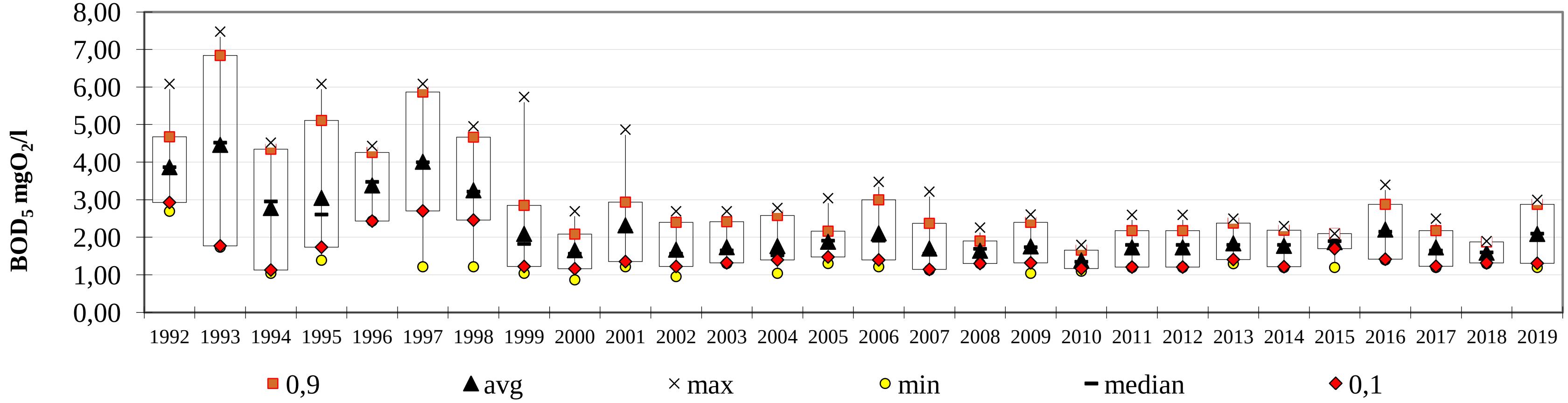


Figure 31a. Changes in concentration of TN and TP

1. River Pühajõgi



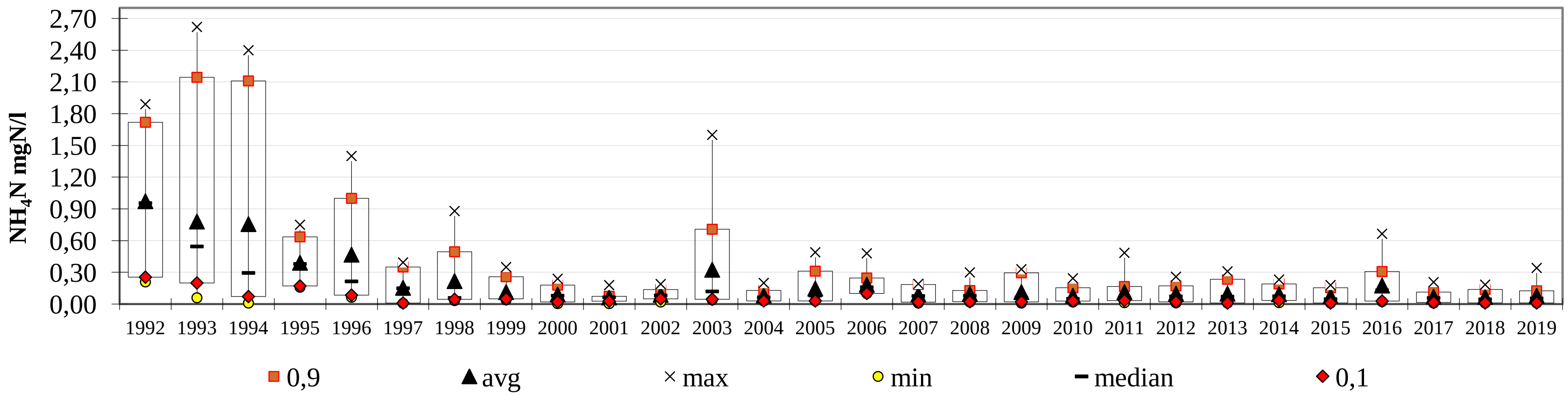


Fig 31b. Changes in concentration of BOD_5 and NH_4

2. River Purtse

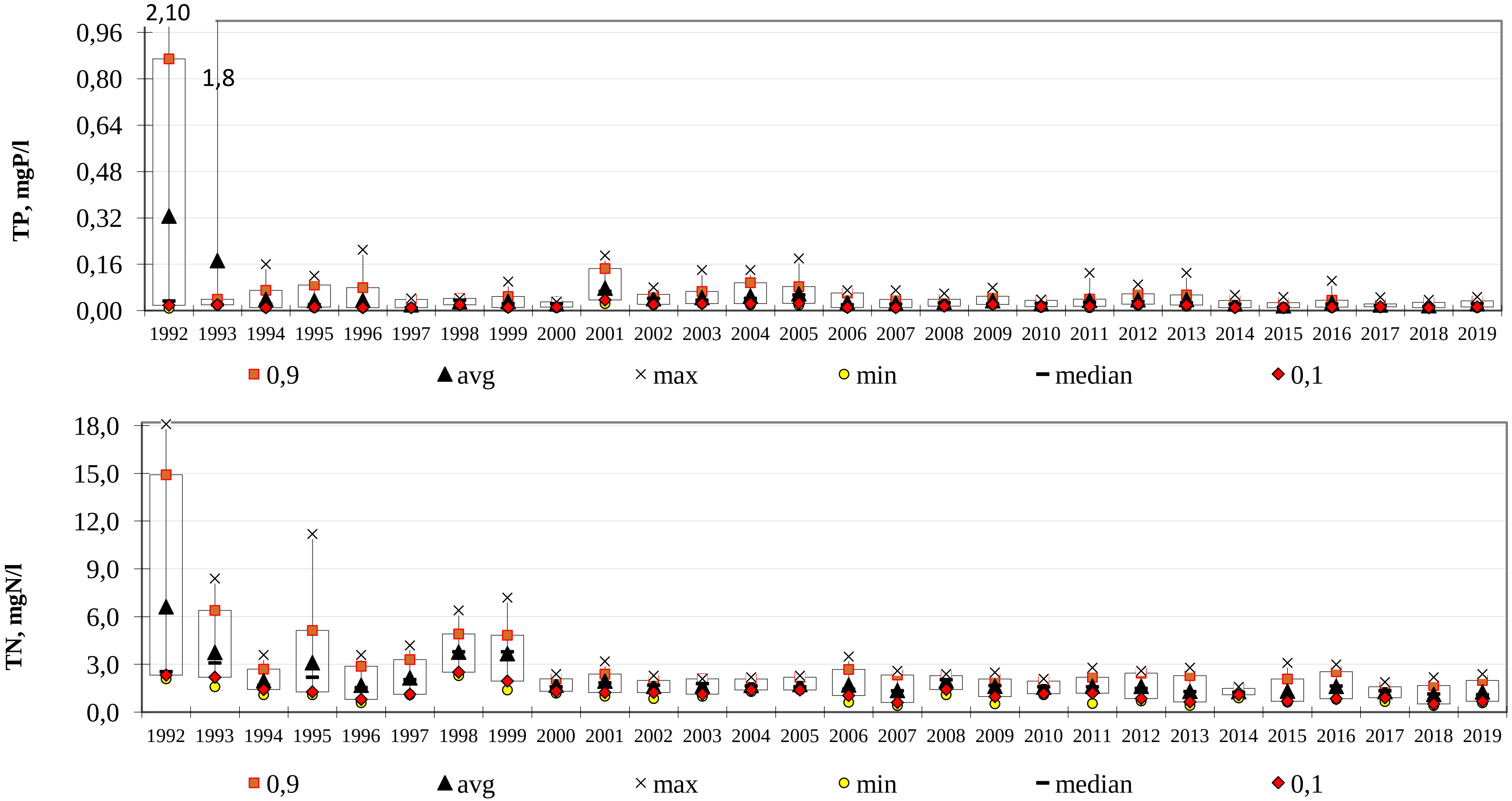


Figure 32a. Changes in concentration of TN and TP

2. River Purtse

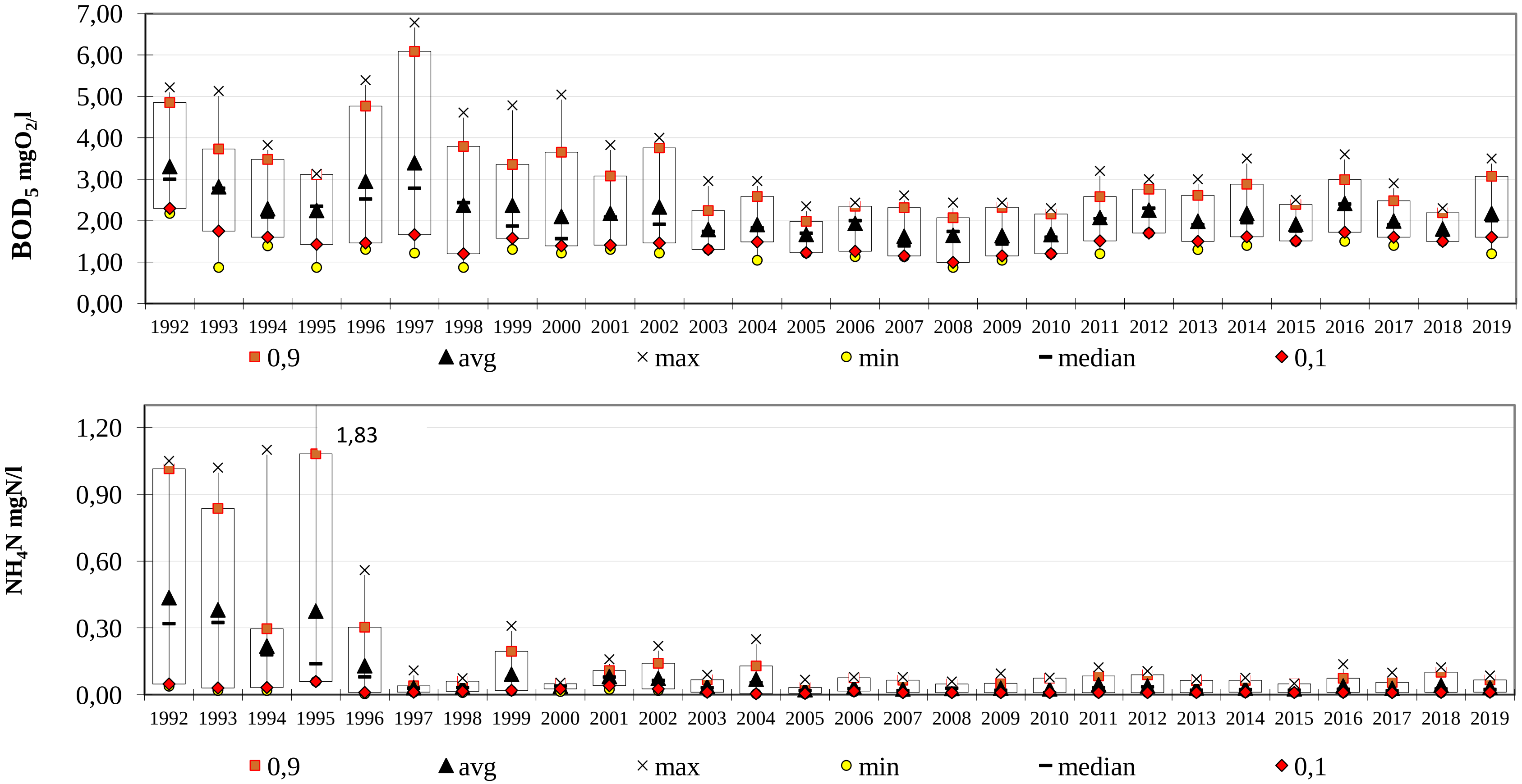
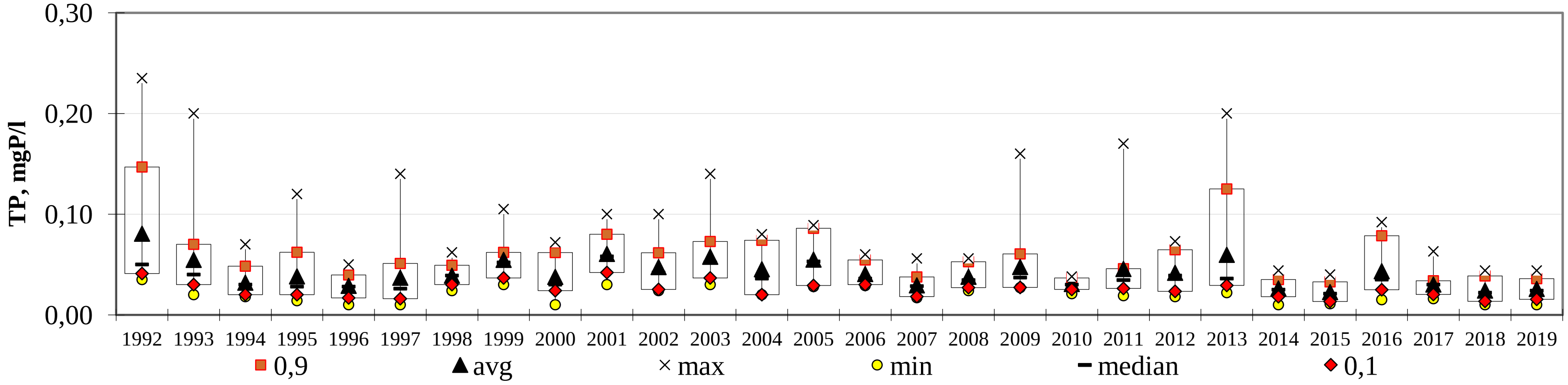


Fig 32b. Changes in concentration of BOD$_5$ and NH$_4$

3. River Kunda



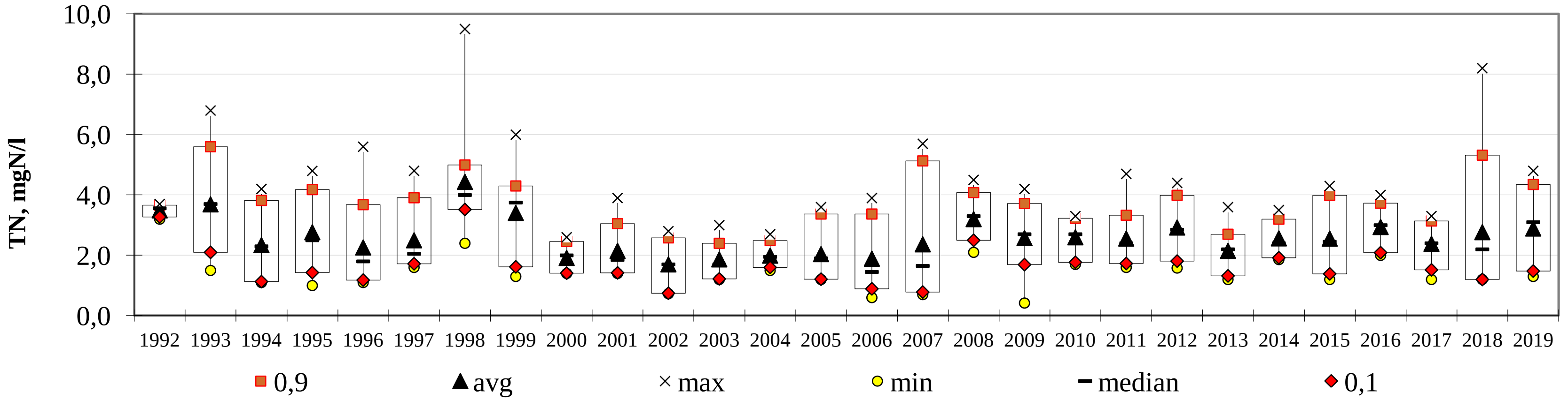


Figure 33a. Changes in concentration of TN and TP

3. River Kunda

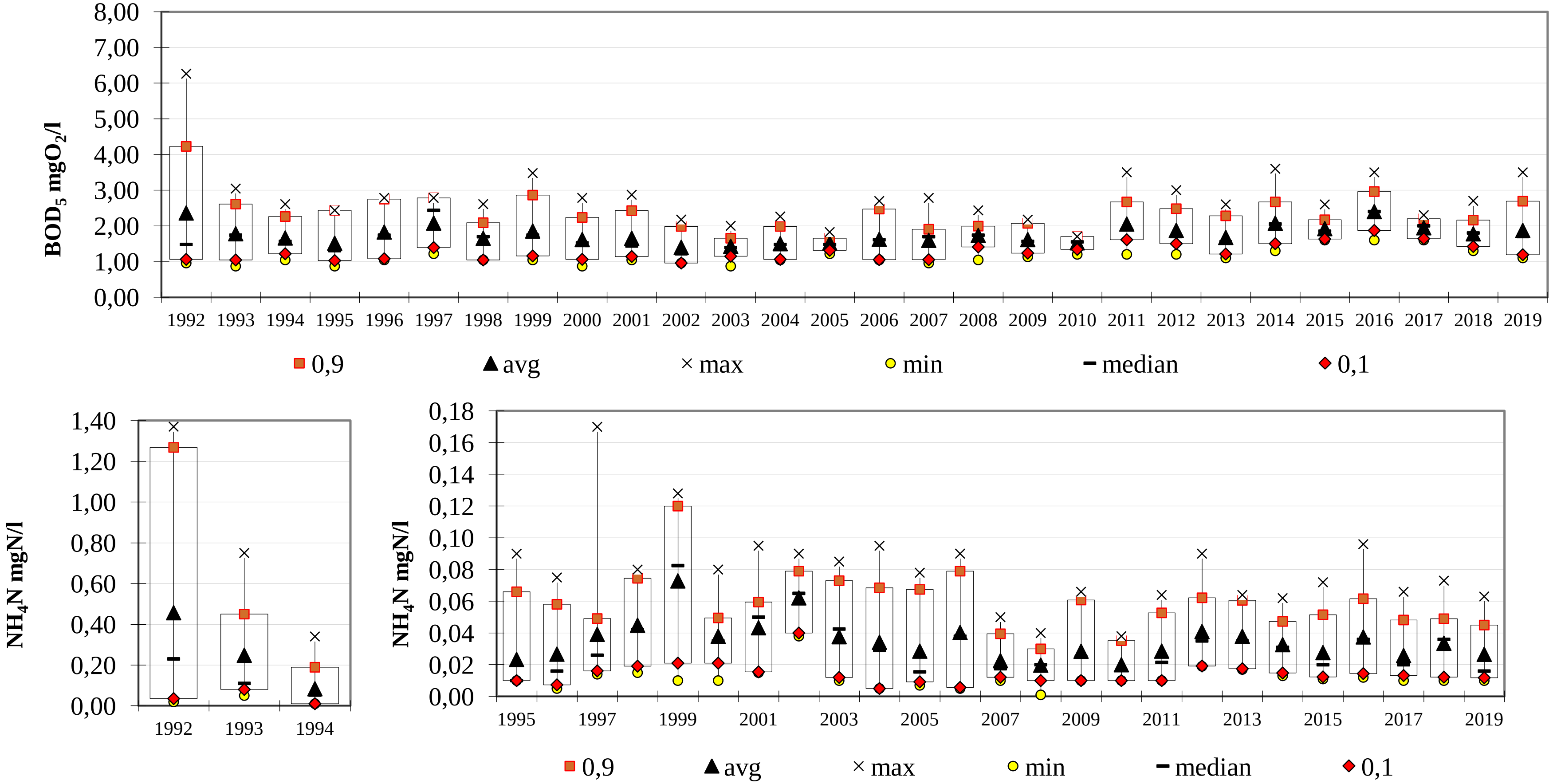


Fig 33b. Changes in concentration of BOD_5 and NH_4

4. River Loobu

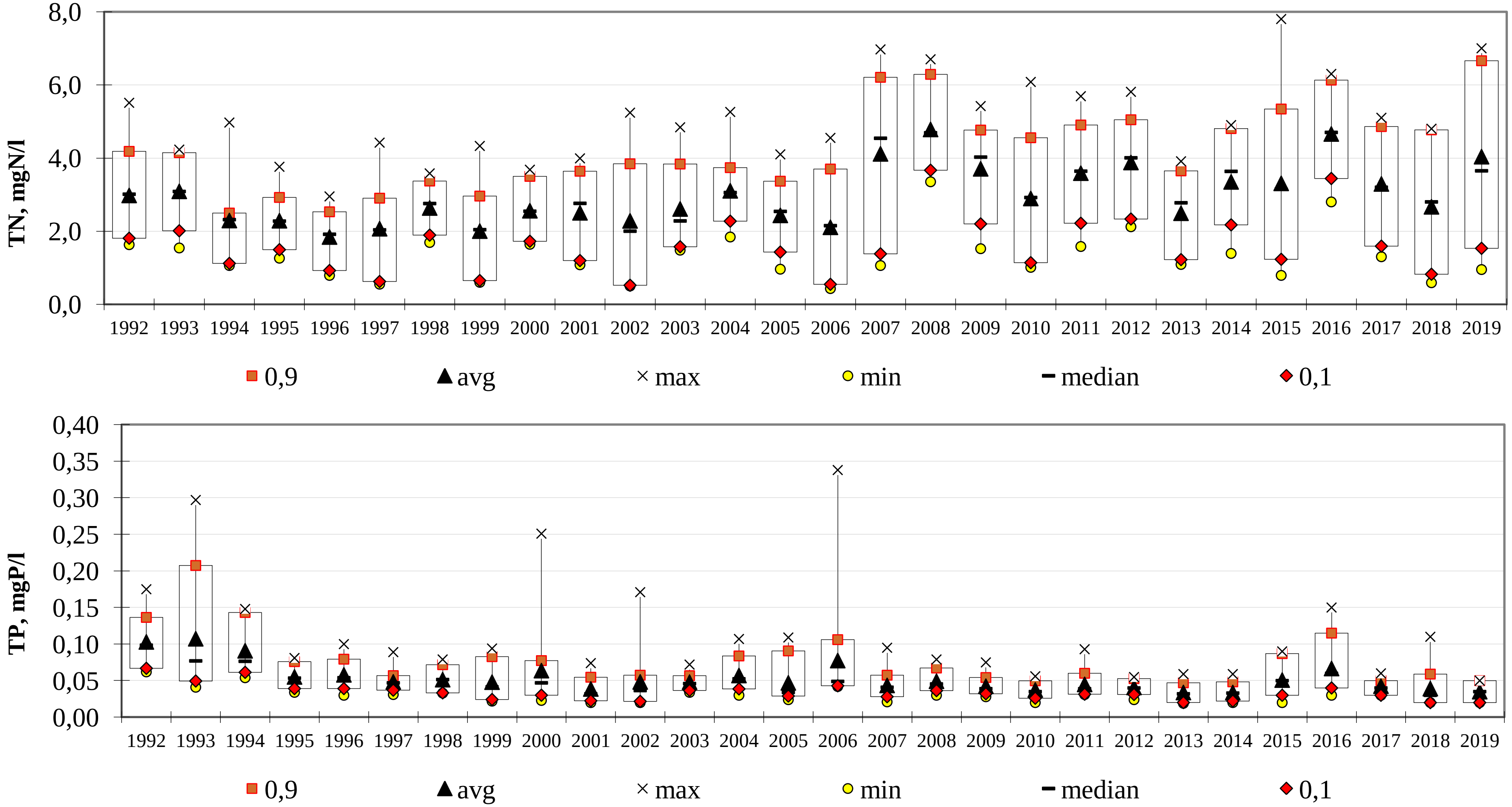
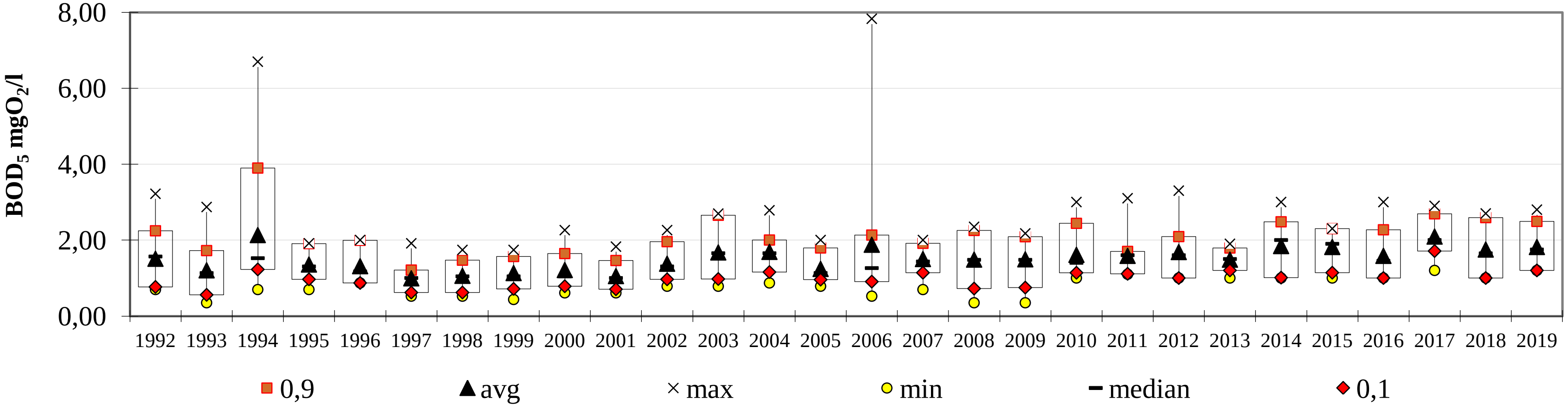


Figure 34a. Changes in concentration of TN and TP

4. River Loobu



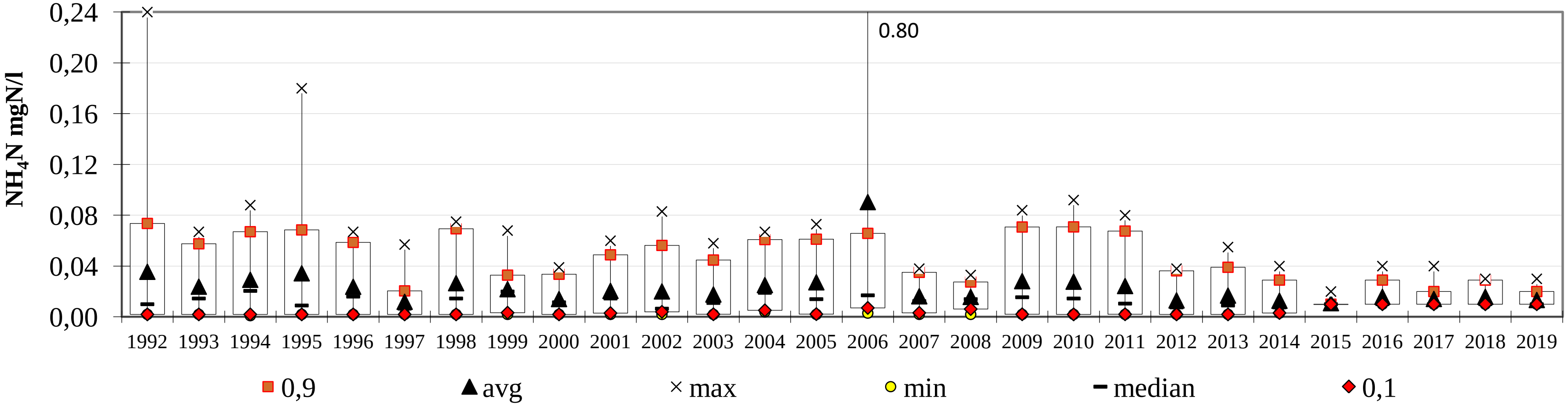
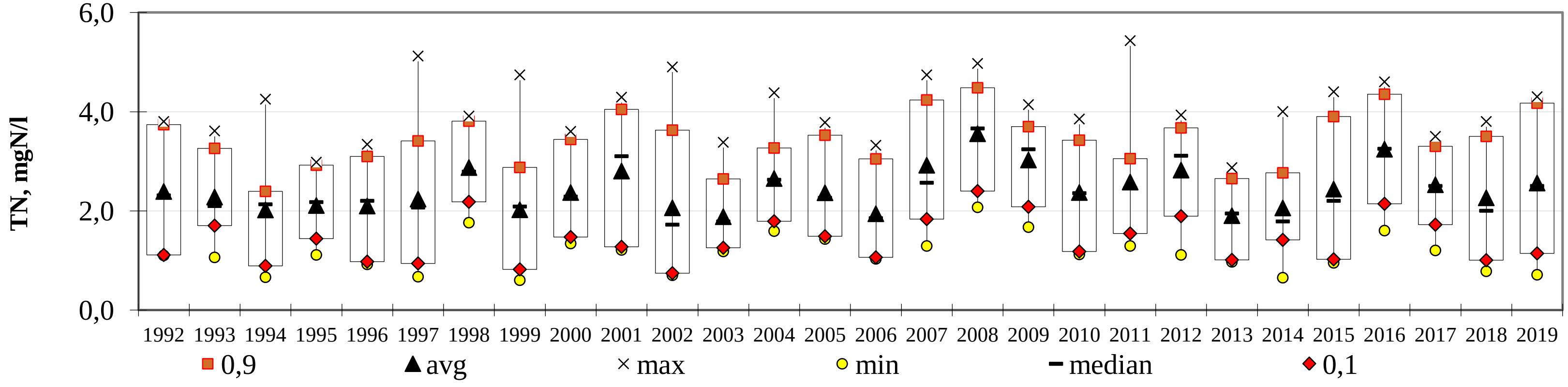


Fig 34b. Changes in concentration of BOD_5 and NH_4

5. River Jägala



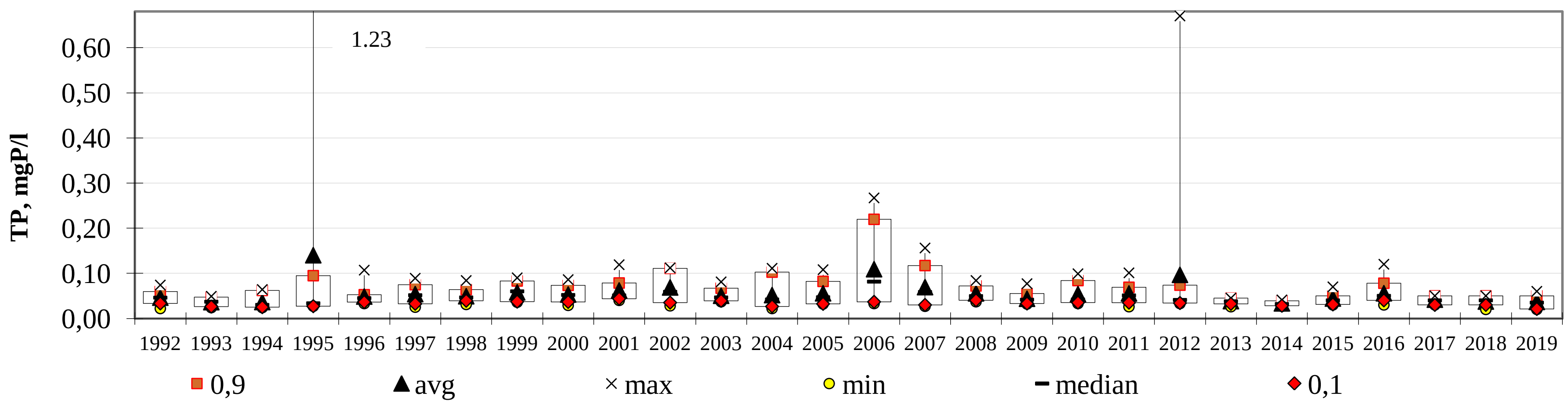
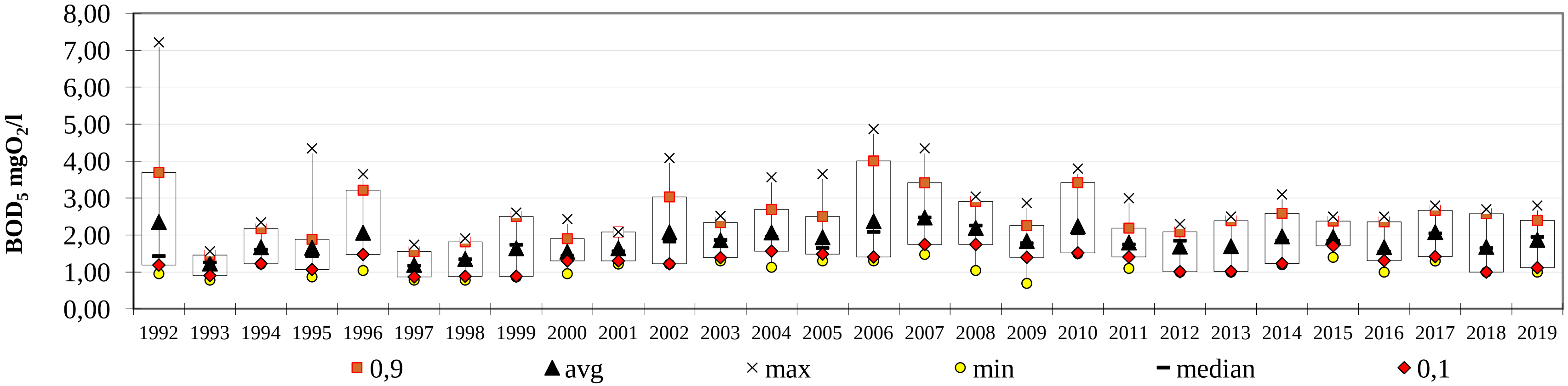


Figure 35a. Changes in concentration of TN and TP

5. River Jägala



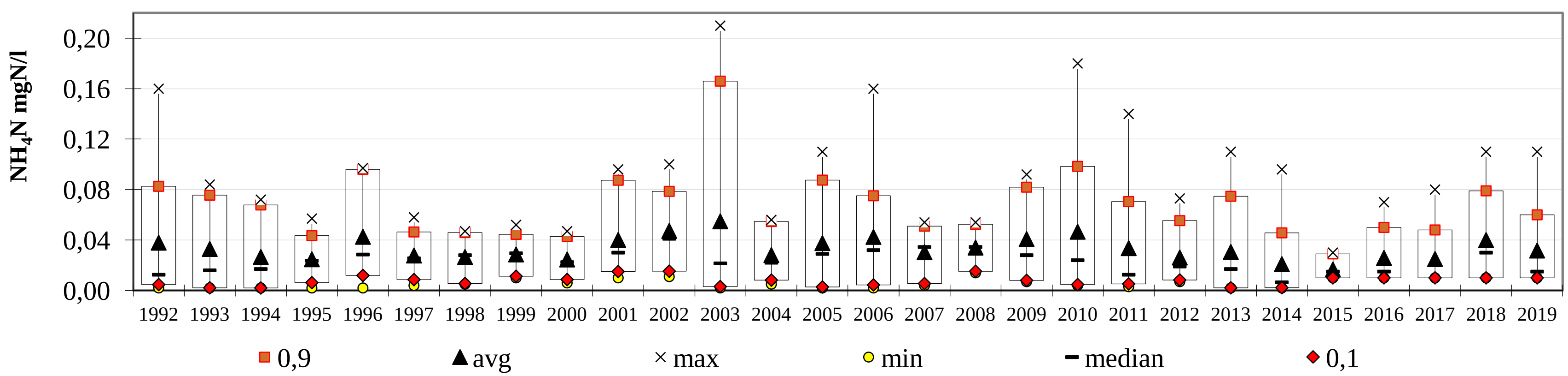
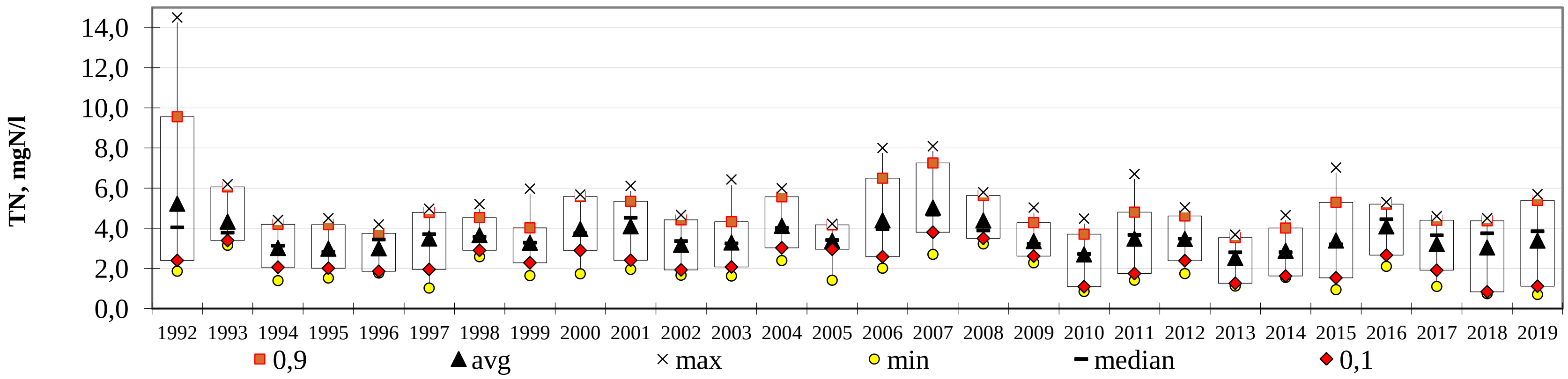


Fig 35b. Changes in concentration of BOD_5 and NH_4

6. River Keila



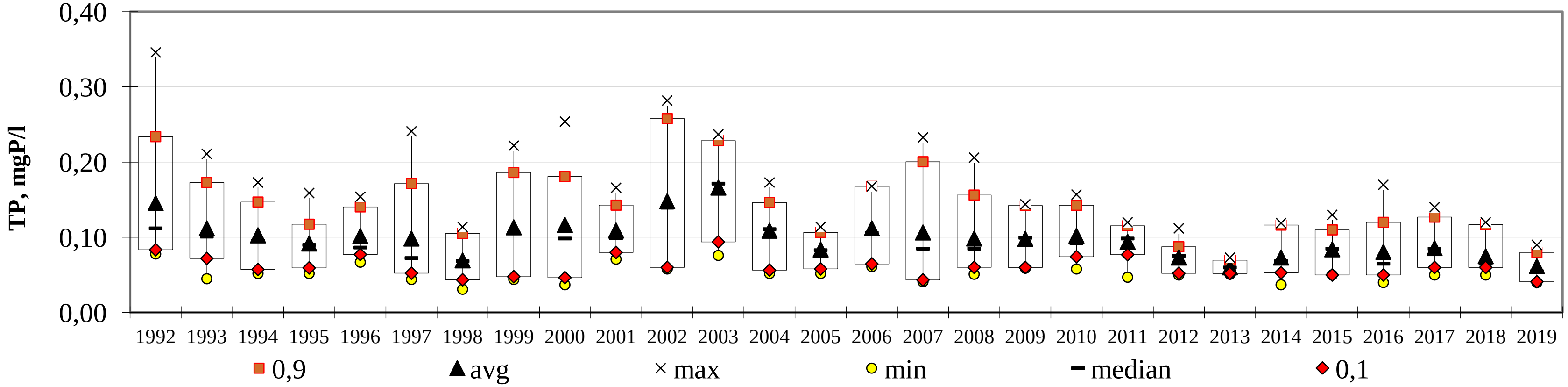
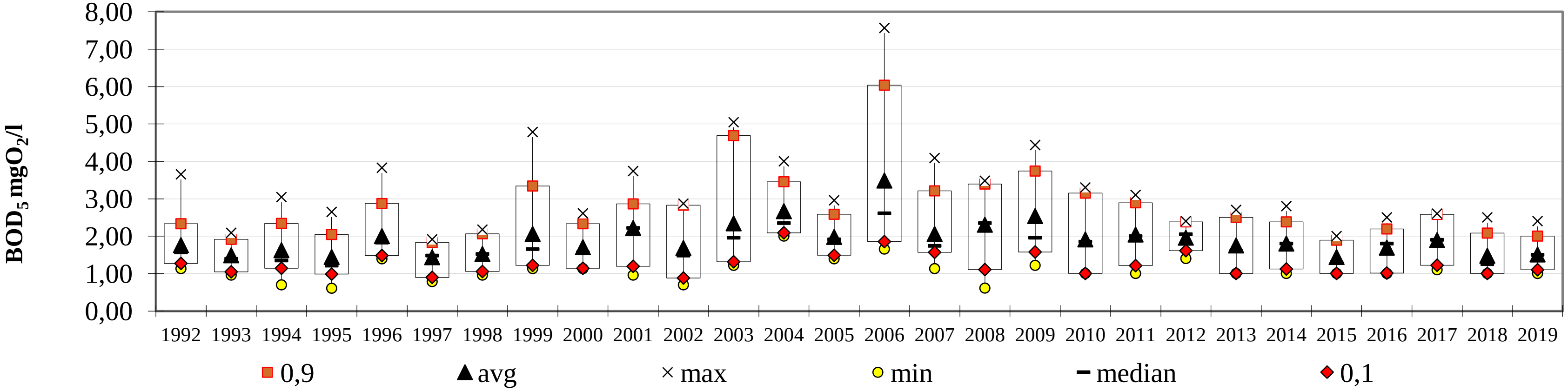


Figure 36a. Changes in concentration of TN and TP

6. River Keila



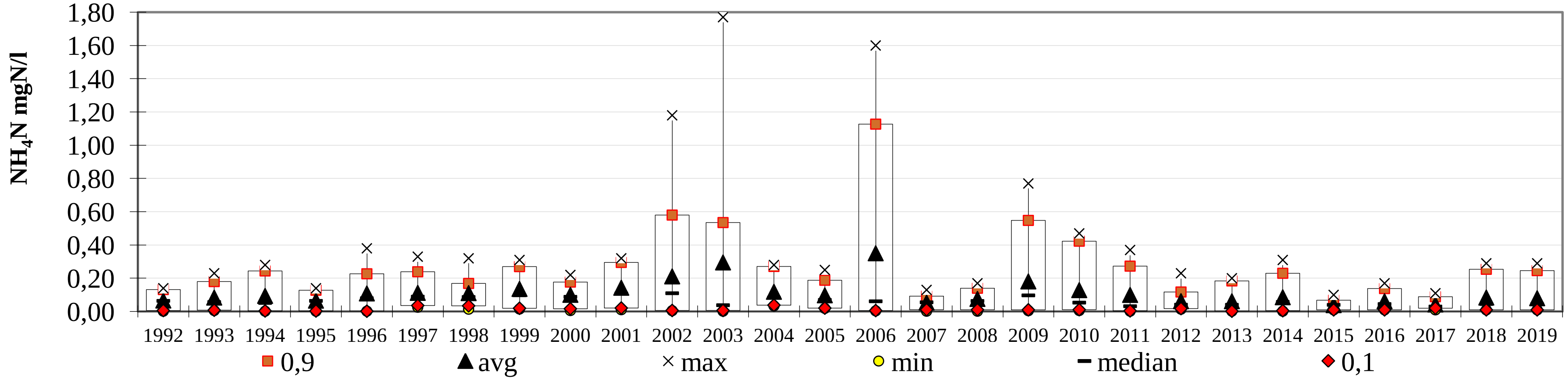
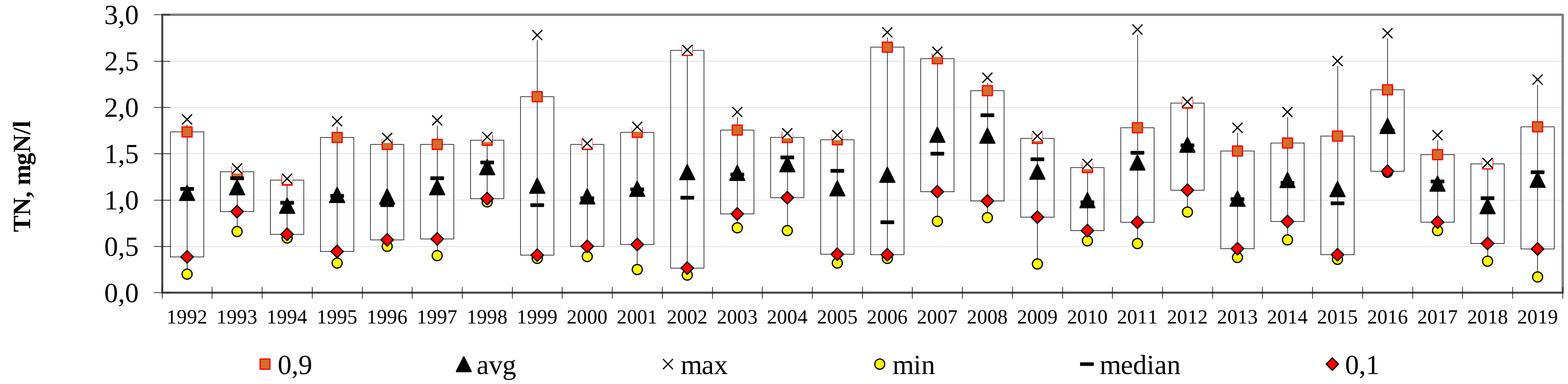


Fig 36b. Changes concentration of BOD_5 and NH_4

7. River Pudisoo



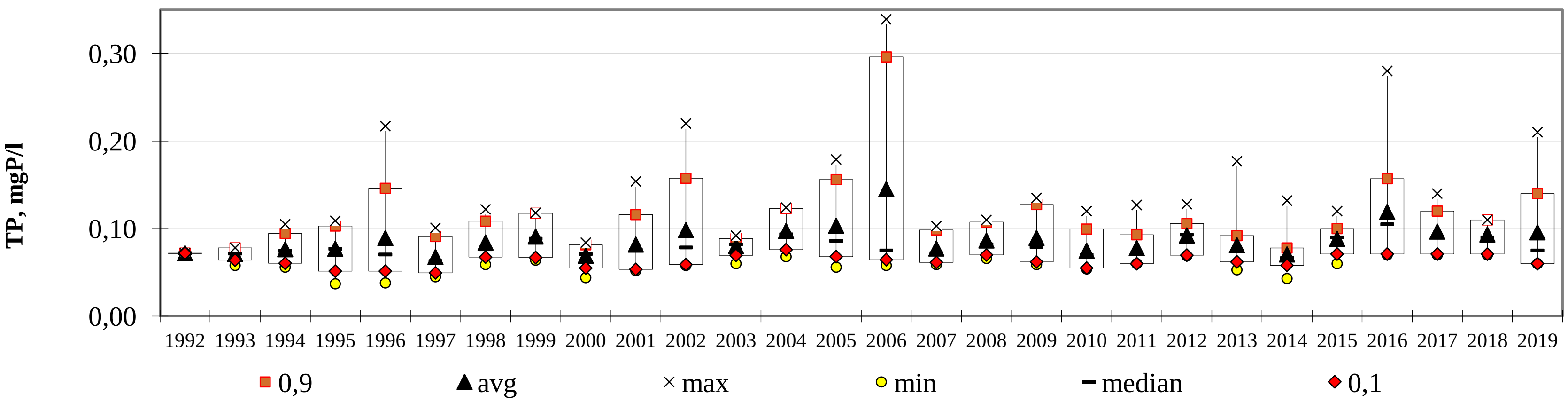
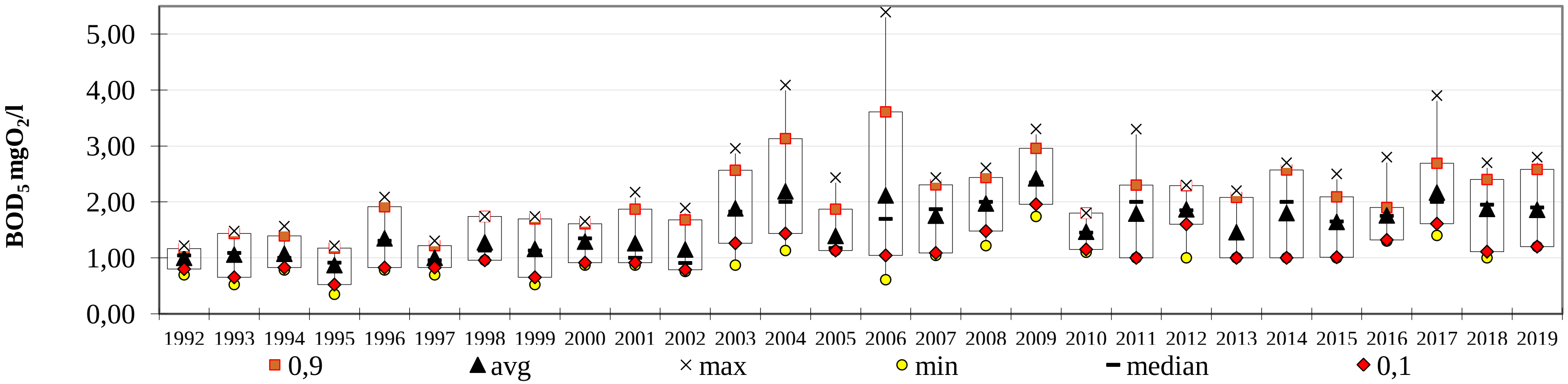


Figure 37a. Changes in concentration of TN and TP

7. River Pudisoo



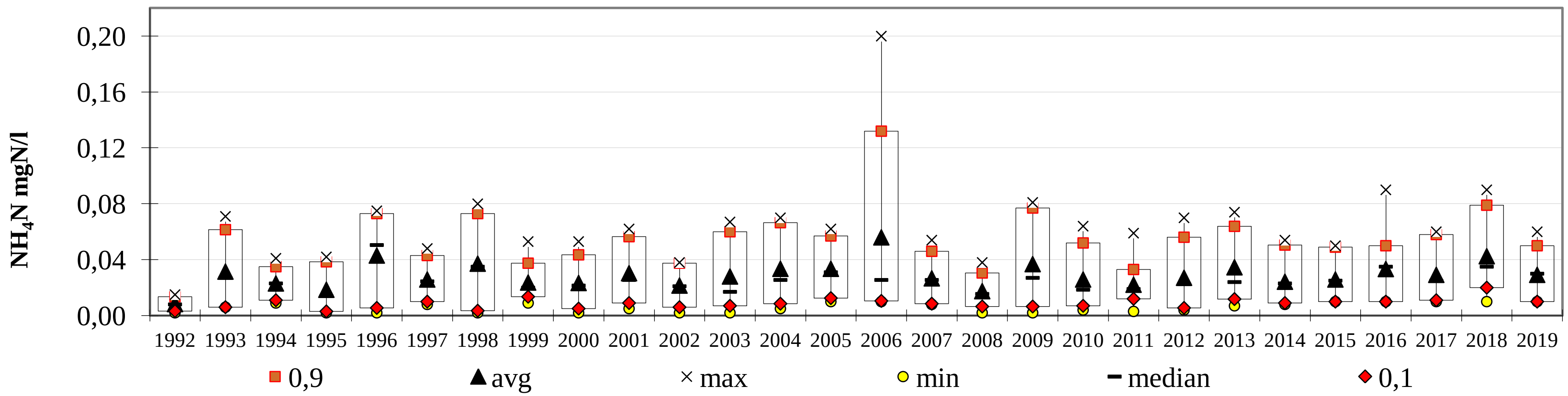


Fig 37b. Changes in concentration of BOD_5 and NH_4

8. River Vääna

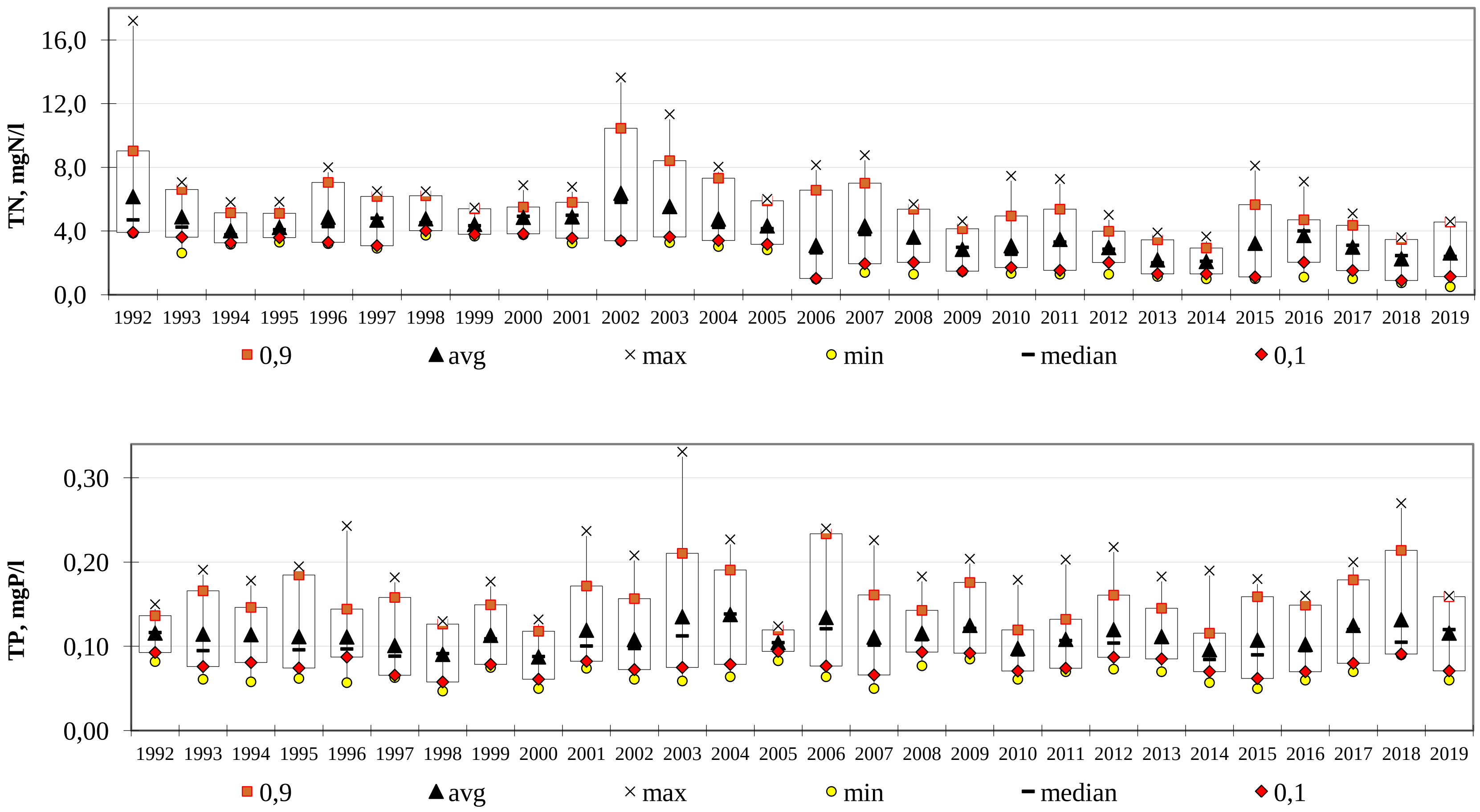
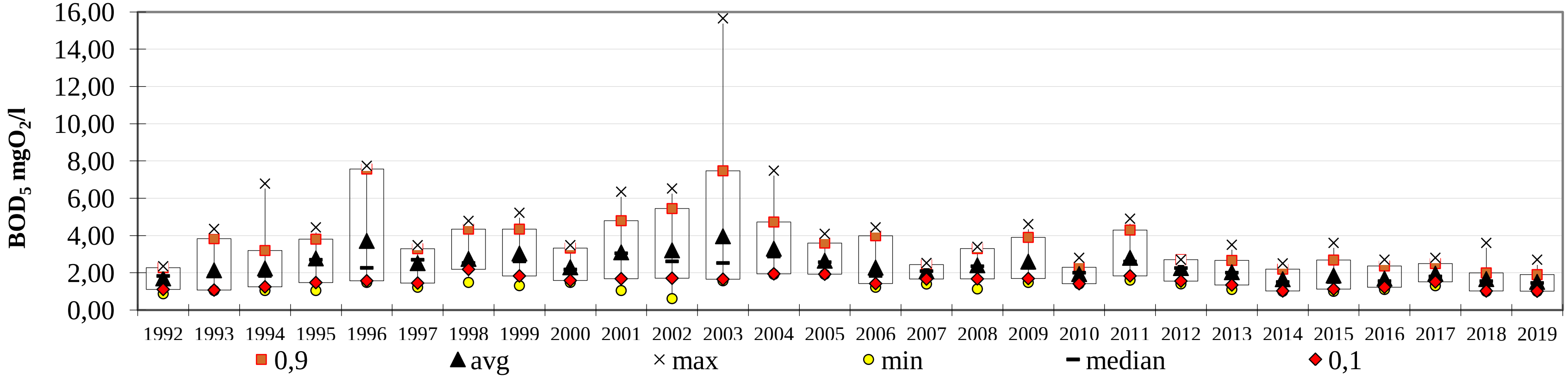


Figure 38a. Changes in concentration of TN and TP

8. River Vääna



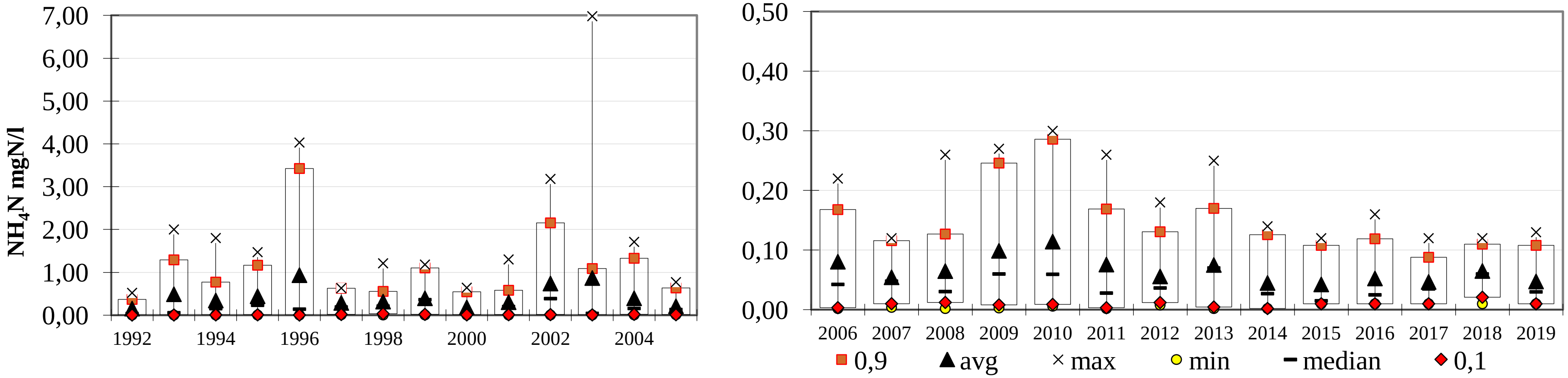
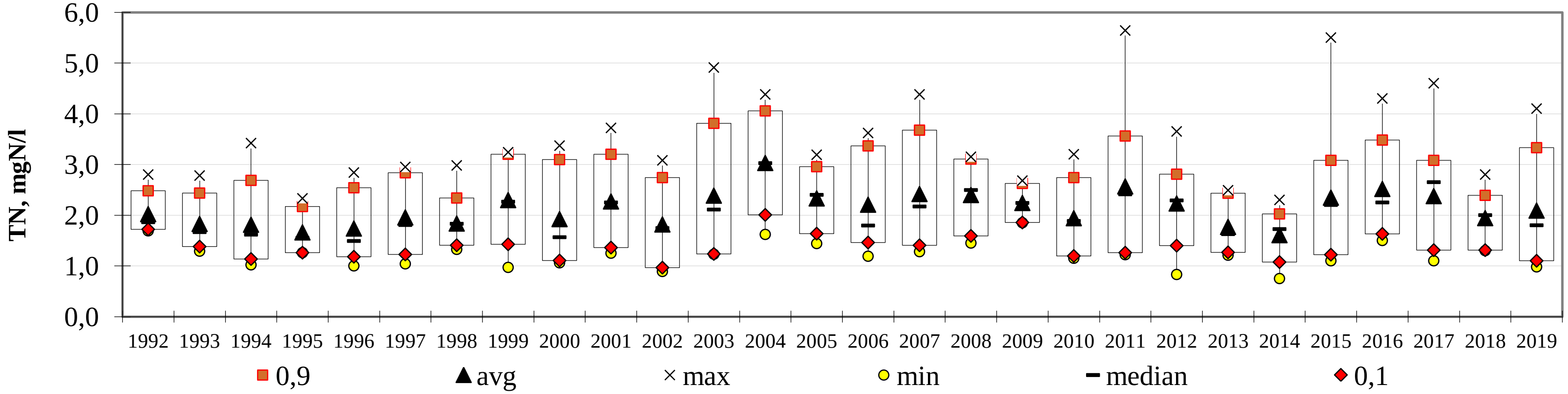


Fig 38b. Changes in concentration of BOD_5 and NH_4

9. River Vihterpalu



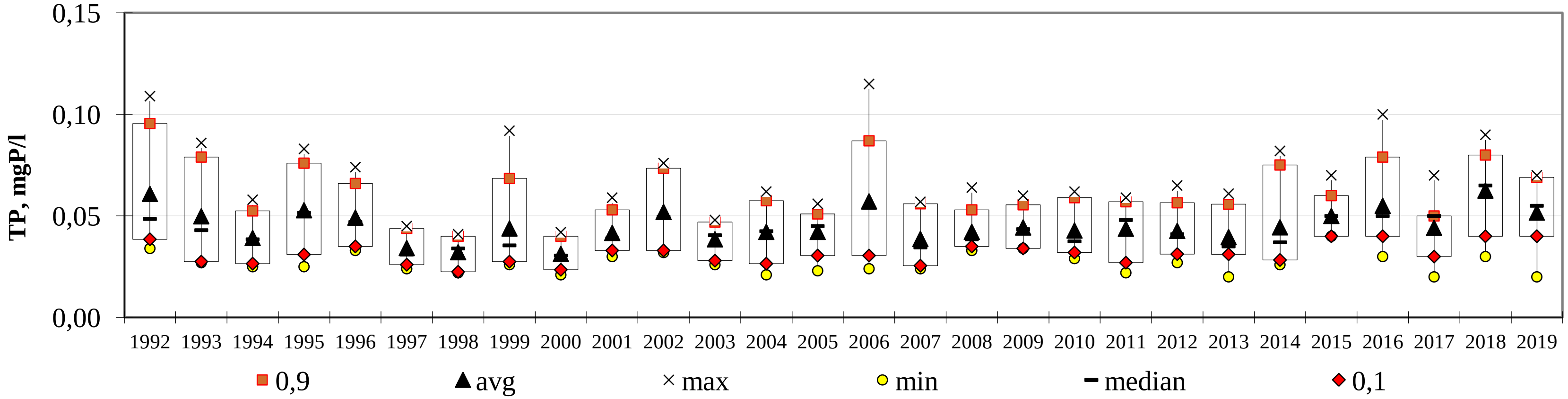
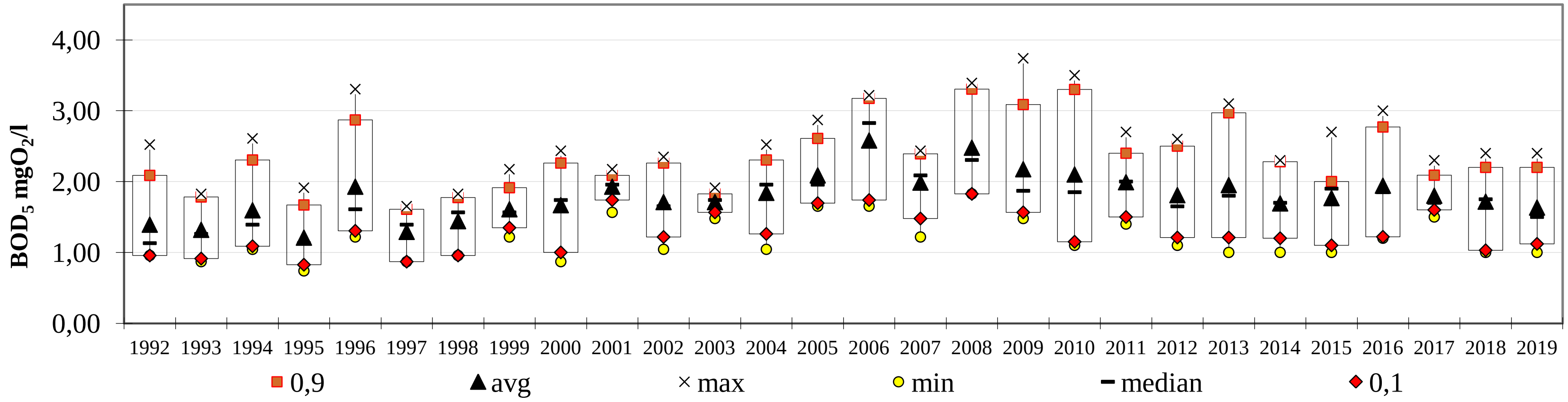


Figure 39a. Changes in concentration of TN and TP

9. River Vihterpalu



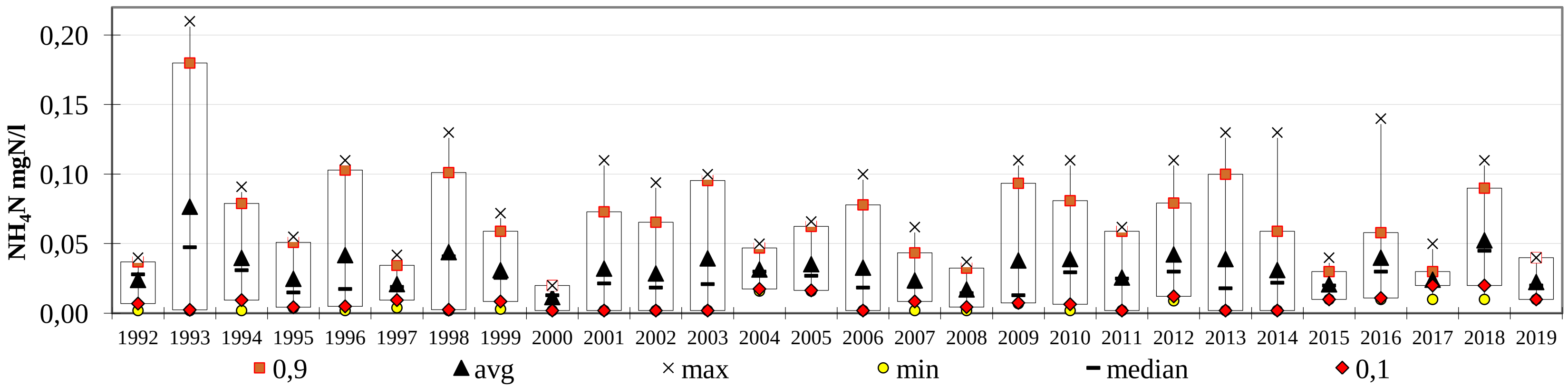


Fig 39b. Changes in concentration of BOD_5 and NH_4

10. River Selja

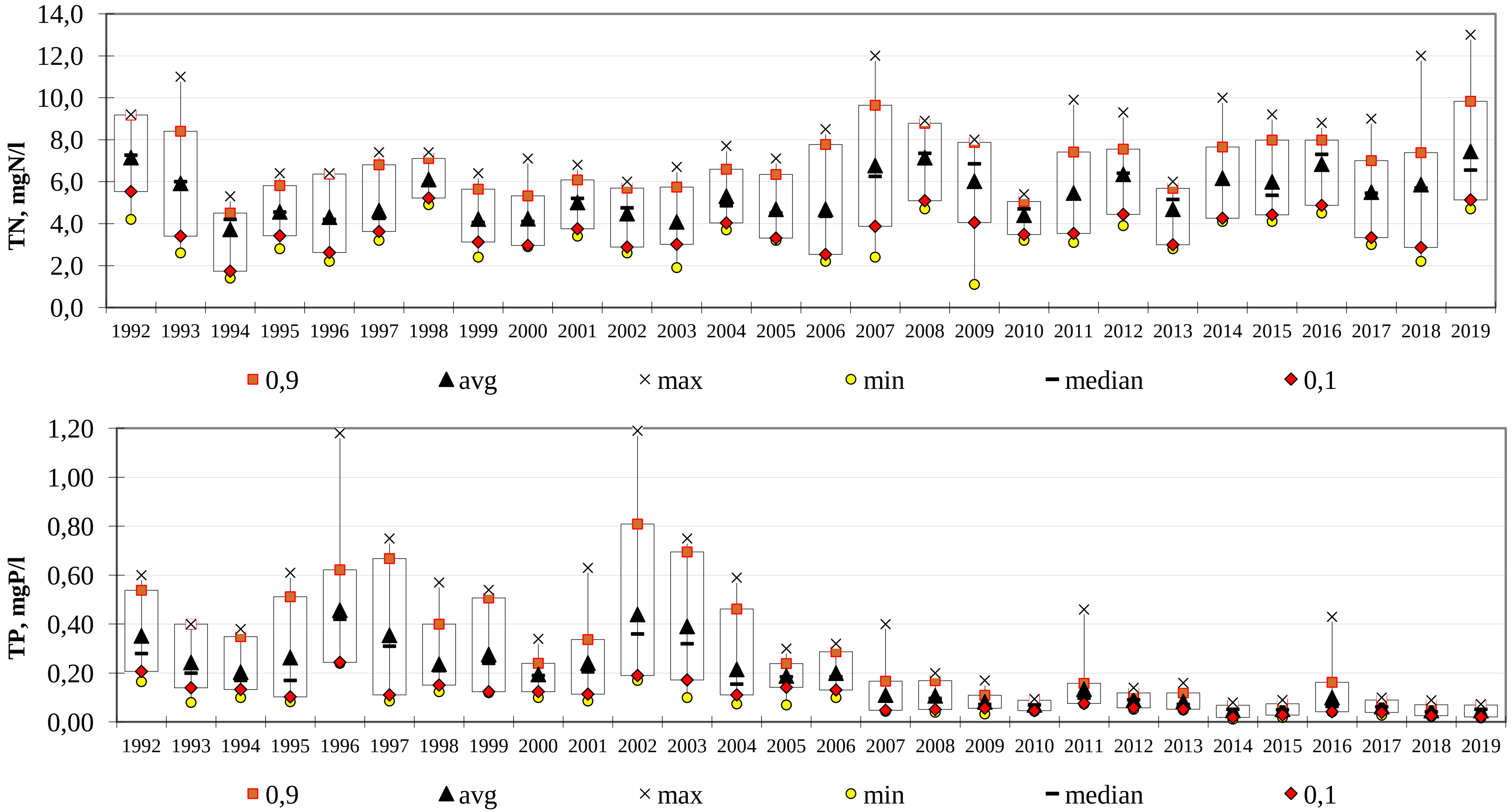
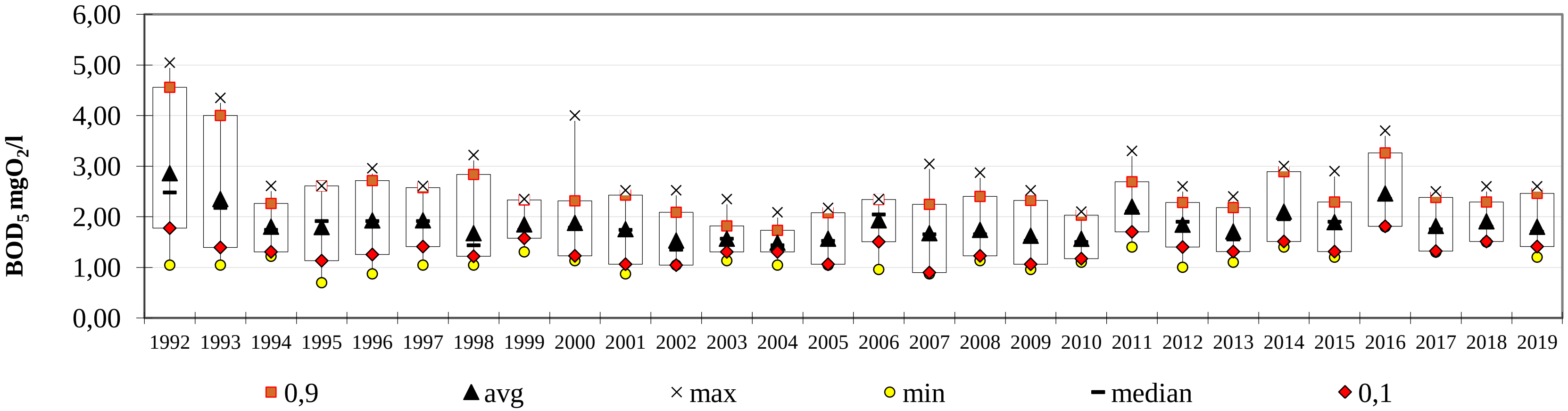


Figure 40a. Changes in concentration of TN and TP

10. River Selja



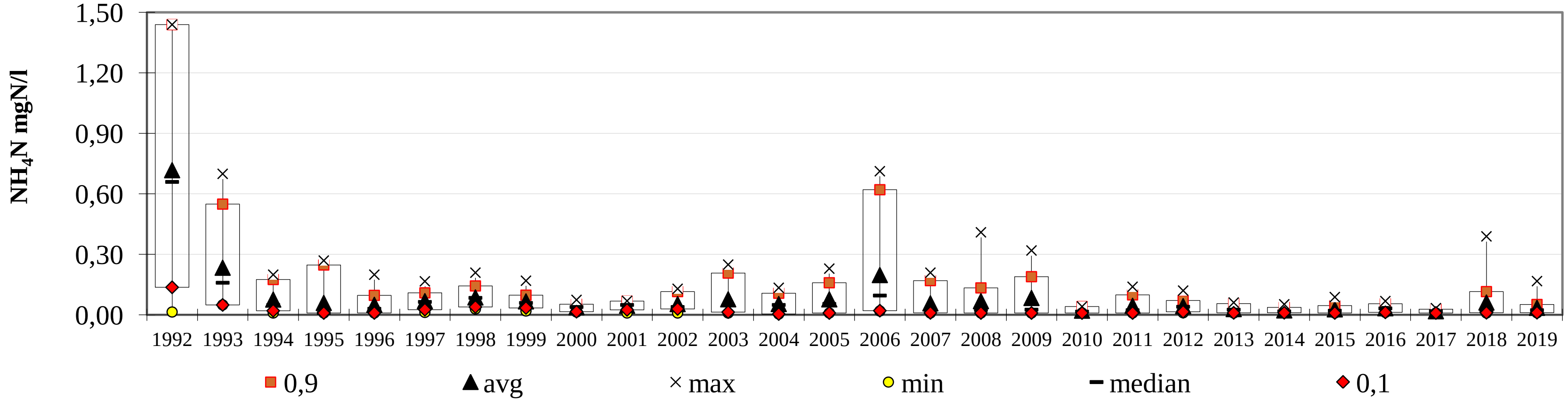
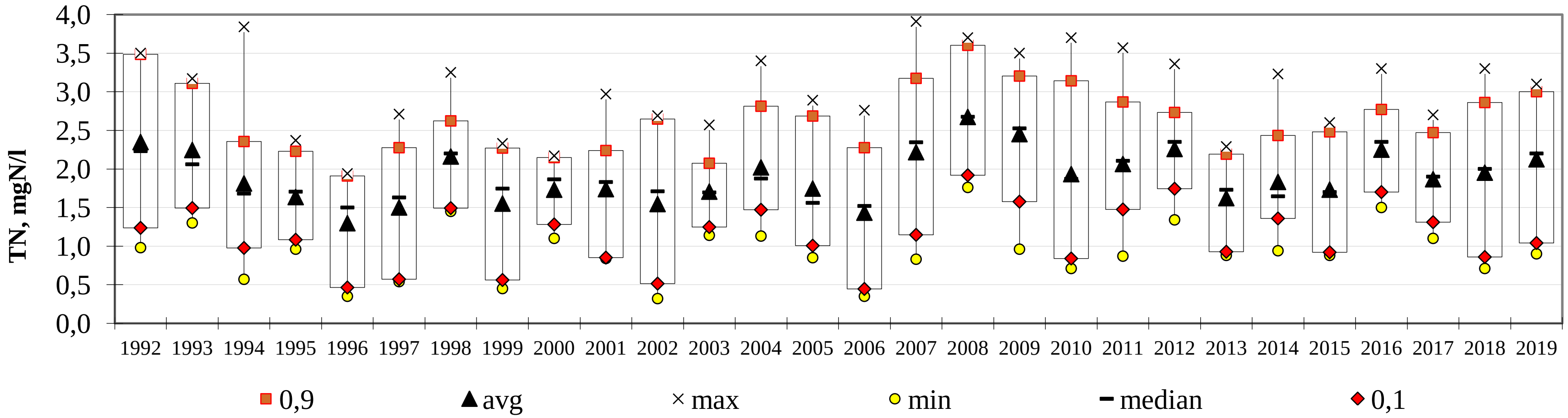


Fig 40b. Changes in concentration of BOD_5 and NH_4

11. River Valgejõgi



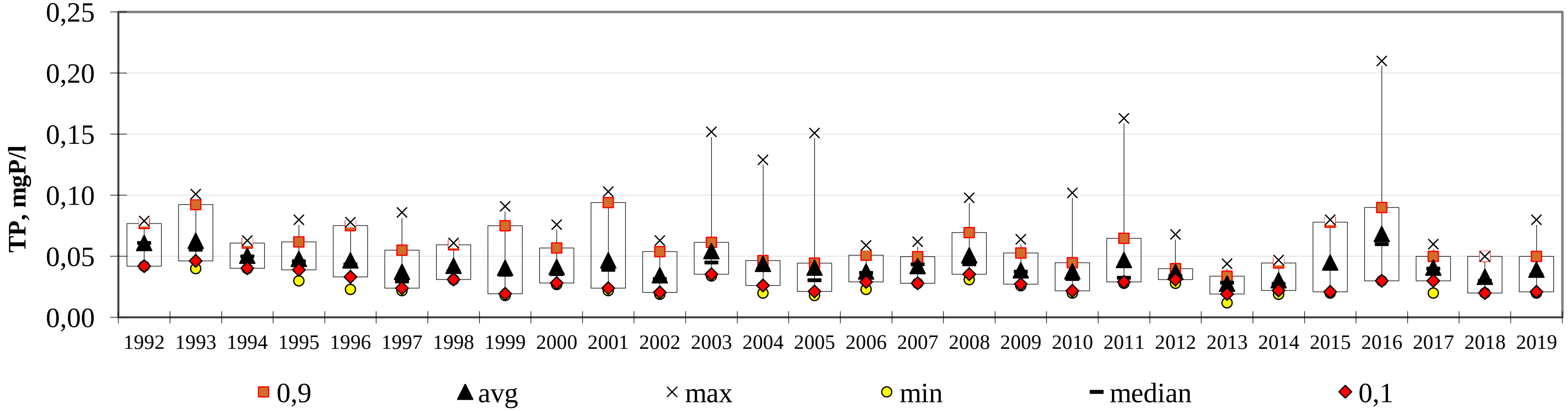
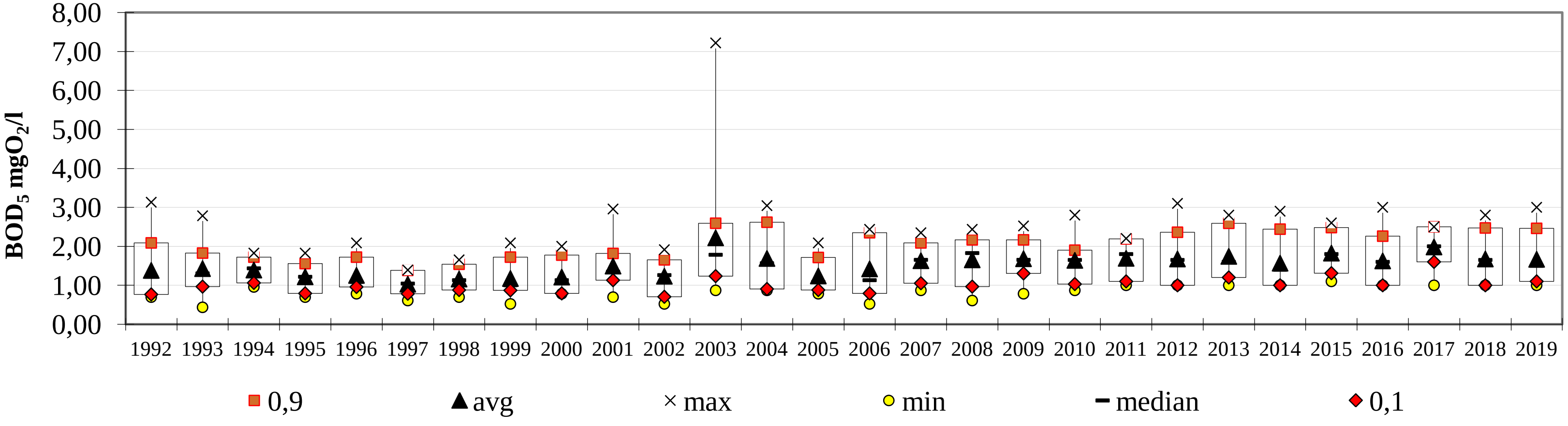


Figure 41a. Changes in concentration of TN and TP

11. River Valgejõgi



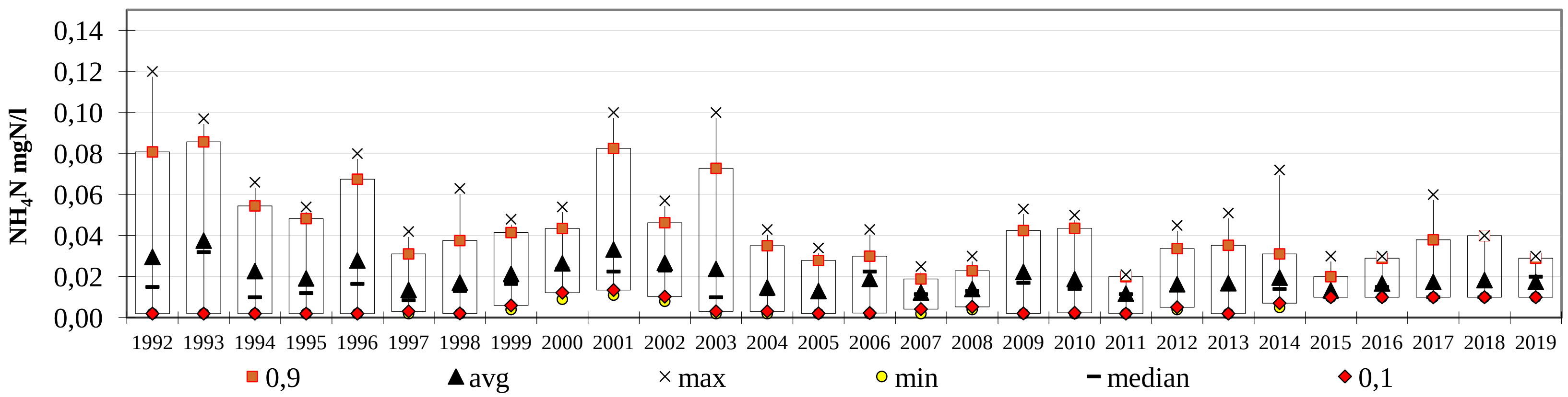
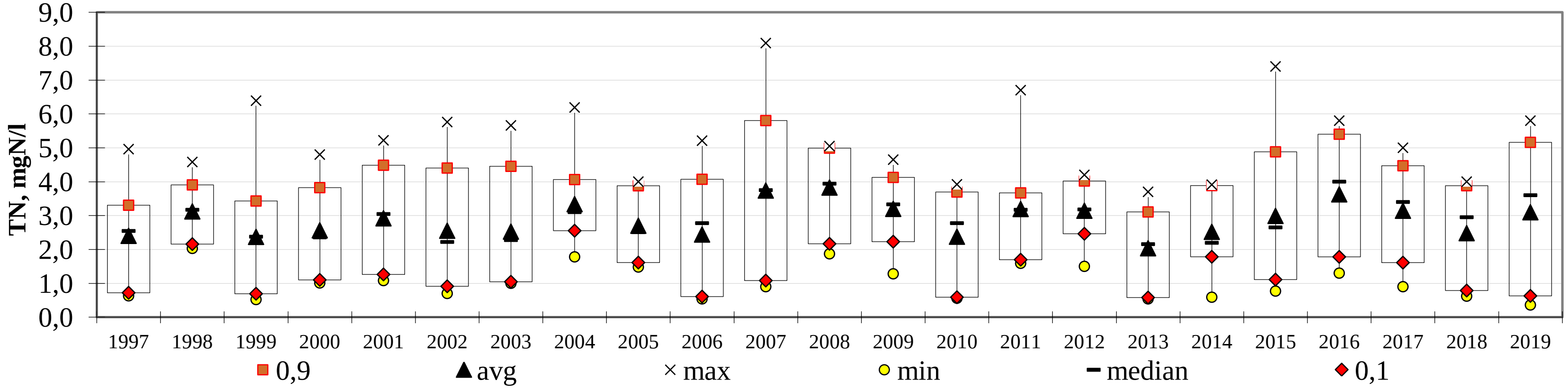


Fig 41b. Changes in concentration of BOD_5 and NH_4

12. River Pirita



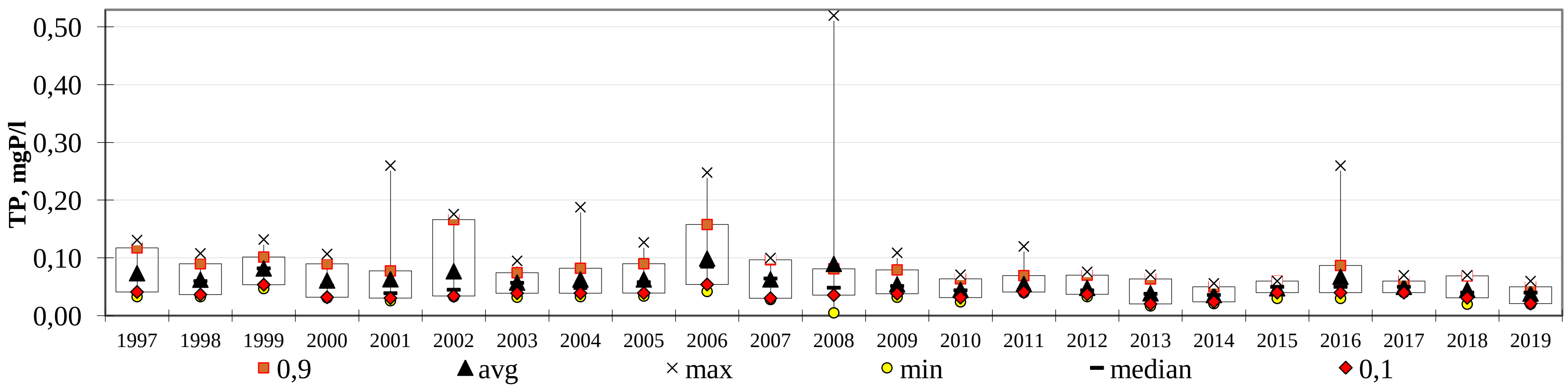
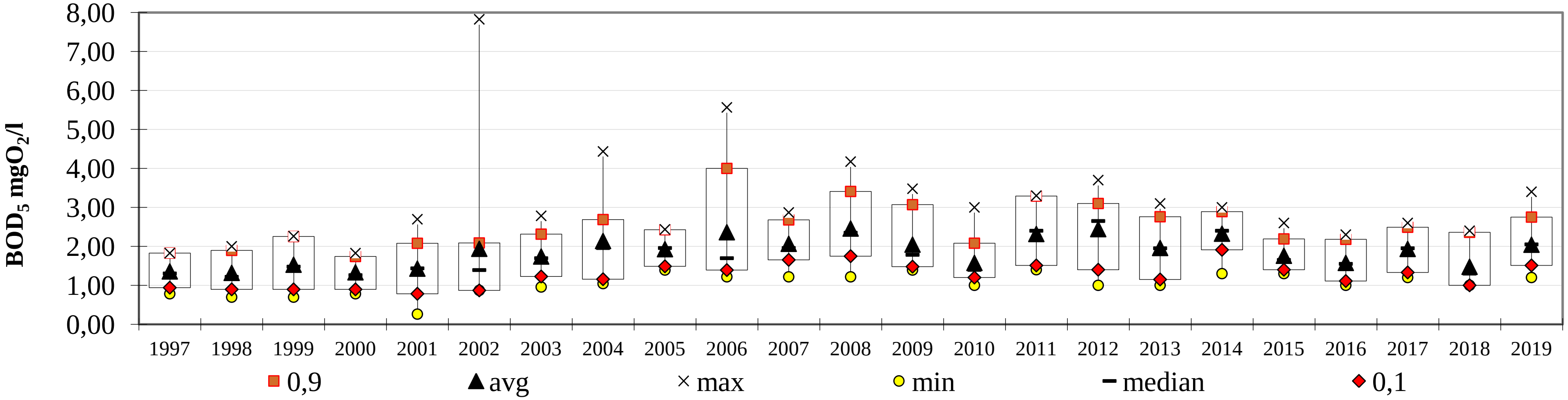


Figure 42a. Changes in concentration of TN and TP

12. River Pirita



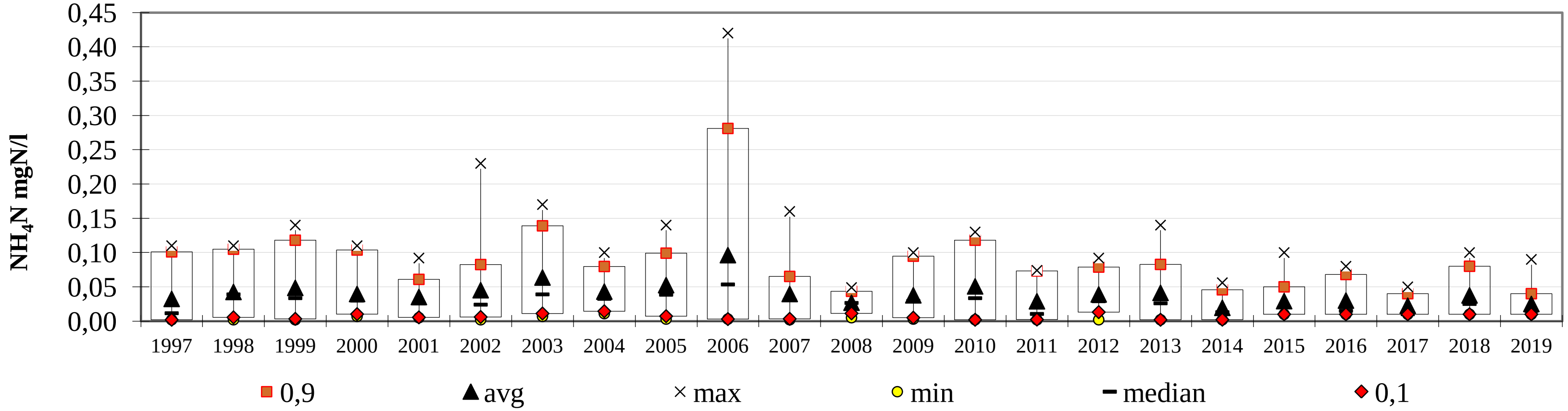


Fig 42b. Changes in concentration of BOD_5 and NH_4