TALLINN UNIVERSITY OF TECHNOLOGY
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Department of Civil Engineering and Architecture

NITROGEN CONTENT IN THE RIVERS DURING PERMANENT COLD WINTER SEASON

LÄMMASTIKU SISALDUS JÕGEDES TALVISEL KESTVAL KÜLMAPERIOODIL

MASTER THESIS

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AUTHOR’S DECLARATION

Hereby I declare, that I have written this thesis independently.
No academic degree has been applied for based on this material.
All works, major viewpoints and data of the other authors used in this thesis have been referenced.

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TASK FOR THE FINAL PAPER

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The purpose of this master thesis is to assess a hypothesis about the relation of river water quality to the status of groundwater body during permanent cold winter season of 2008-2011. The study area includes three observational regions according to the hydrological station. Majority of the work centralizes around the nitrate sensitive zone. Research is based on monitored data about the concentration of total nitrogen, NH_4^+ and NO_3^- in given time frame. This approach is relatively new in determining the hydrochemical state of water bodies making it as an interesting topic for master thesis.

Summary in Estonian:

Talvise kestva külmaperioodi seireandmete analüüsist selgus, et ökoloogilised tingimused 13 uuritud jões kogu lämmastiku sisalduse alusel on enamasti kesises, halvas või väga halvas klassis. $NH4^+$ sisaldus, mis üldiselt viitab värskele reostusele jäi heasse või väga heasse klassi. NO_3^- sisaldus jõgedes on regiooniti varieeruv, kuid tugevalt on mõjutatud karstialad, ning piirkonnad, kus esineb intensiivseid põllumajanduslikke tegevusi. Kontsentratsioonid jõgedes jäävad tihti sihtväärtuse piirnormi (25 mg/L) vahetus lähedusse või alla selle, kuid esineb mõningaid erandeid, kus väärtused küündivad 40 mg/L ligilähedale. Uurimustöö käigus vaadeldi 4 seirejaama, kus oli mõõdetud nitraaditundliku ala põhjavee NO_3 sisaldust. Uurimustöö esimeses pooles püstitati hüpotees, mis leidis analüüsi lõppedes kinnitust. Mida kestvam külmaperiood, seda madalamad kontsentratsioonid, mis tähendab, et pikal perioodil jõed toituvad põhjaveest mõjutades samaaegselt viimase kvaliteeti.

Summary in English:

According to the analysis of monitored data in 13 rivers the ecological state based on total nitrogen is in poor, bad or very bad class. The content of $NH4^+$ lies within good or very good state. The NO_3^- content shows strong variation and the most affected by pollution are karst or intensive agricultural areas. Big portion of the concentrations in rivers stay close or below the target value of 25 mg/L, with some exceptions, where the values nearly reach 40 mg/L. During the research 4 monitoring stations were closely assessed to evaluate the amount of NO_3 in groundwater. In the first half of this thesis a hypothesis was set that found proof. The longer the permanent cold period, the lower the concentrations, which means that during the drought period rivers are dependent on groundwater and are affecting the quality of it.

Date of accepting the task: **February 20, 2018**

Supervisor:	**Karin Pachel**	....
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ABBREVIATIONS

As - arsenic

BOD_5 – biological oxygen demand

Cd - cadmium

COD – chemical oxygen demand

EEA – Estonian Environmental Agency

EPA – The Environmental Protection Agency

EU – European Union

Hg - mercury

N_2 – dinitrogen

NH3 - ammonia

NH_4^+ - ammonium

NO_2^- - nitrite

NO_3^- – nitrate

O_2 – oxygen

Pb - lead

PCE - tetrachloroethylene

pH – hydrogen ion exponent

TCE - trichloroethylene

TP – total phosphorus

TN – total nitrogen

WFD – Water Framework Directive

1. INTRODUCTION

1.1 Background and description of the problem

From ancient times for ecosystems as well as human kind the water has always been essential part of life that serves important role in global arena. Due to this reason it is not only mandatory but even strictly compulsory to maintain and observe the water quality in local, regional and national levels.

The majority of the World's countries are aiming towards best available techniques and practices to achieve sustainable use of water that maintains the quality and good status of naturally occurred phenomena called ''The Water''. In order to accomplish all of the goals mentioned previously there is a need for higher support, what assures the framework for all the necessary activities. The EU as one of the sustainable development influencers has established multiple strategies and policies with a perspective to make sustainability into action and monitor required parameters.

Estonian Water Act provides the base for the use of water. It claims that the cleanliness and ecological state of different types of water bodies, which include inland, transboundary and groundwater should be kept under protection. The aim is to guarantee and arrange good water management that will meet with the objectives set up in the present Act [1]. Monitoring programs are used to provide comprehensive information about the conditions in the nature, which creates the base for environmental management.

Nowadays water quality monitoring hands over adequate data, that serves several purposes along with trend analysis, control of transboundary pollutants, locating critical areas, conformity to regulations, measurement as well as evaluation of efficiency of all kinds of programs and conservation practices, model validation and calibration, defining water quality problems and conducting research based on provided data [2]. All member states in the EU are obligated to employ all the requirements into action that are ruled by EU WFD. Article 8 in EU WFD is a separate section for monitoring of surface and groundwater status and ensures that an extensive overview of the water bodies shall be provided by EU states [3].

In Estonia the surface water and groundwater conditions are constantly monitored during national environmental monitoring providing different qualitative and quantitative information. Besides scientists and specialists the monitoring is officially arranged and controlled by EEA in the fields of air, meteorology, water and etc.

It is known to be true that water quality significantly changes during the time when temperatures drop below zero degrees of Celsius. In this thesis the aim is to investigate available monitored data primarily during the cold period months in North of Estonia and compare the concentrations of total nitrogen, ammonia and nitrates in surface water. Based on the information received from surface water it is possible to evaluate nitrate concentration in groundwater. Gathered data should provide answers about the ecological and chemical state of rivers in studied area during hydrological season of winter. After data analysis it is possible to make assumptions and conclusions about the situation in researched regions.

The master thesis is divided into 4 different sections. The first chapter provides introduction into the topic and presents the objectives of thesis. Second chapter concentrates on literature overview regarding the topic. In the third chapter the topic development is proceeded further by describing the source of data and applied methodologies. The fourth and final chapter involves the practical part, where monitored data is analysed.

1.2 Objectives

The main objectives of current master thesis are following:

- To give literature overview about the topic;
- To provide information about sources of data and to introduce applicable methodology for data analysis;
- To assess the duration of permanent cold winter season and its compliance with nitrogen content in rivers and groundwater as well as constructing illustrative graphs and tables of the monitored data;
- To evaluate the state of groundwater based on the quality of rivers;
- To analyse gathered information and make conclusions based on findings.

2. LITERATURE OVERVIEW

2.1 Distribution of water

Water is the only naturally occurring substance that can have three different forms: liquid, solid and gaseous. The chemical formula of water consists of two hydrogen atoms covalently bonded to a single oxygen atom. The molecule itself is polar meaning that it possesses net positive charge on the hydrogen atoms and a net negative charge on the oxygen atom [4].

On the Earth water is known to be essential from the early beginnings as it is the largest source and main reason for the existent of life. Hydrology is referred to as the science of water that investigates and researches all the characteristics of water [5]. This field looks deeper into the occurrence, circulation, distribution of water as well as the biological, chemical and physical properties and their relation towards the environment [6].

Principally the water can be found in any accessible environment on or near the Earth's surface (air, streams, lakes, oceans, soil etc). It is said that the total amount of water on this planet is approximately 1.4x10^9 km^3 and it is distributed into different types of water bodies. The main classification of water reservoirs is introduced in Figure 1 [7]:

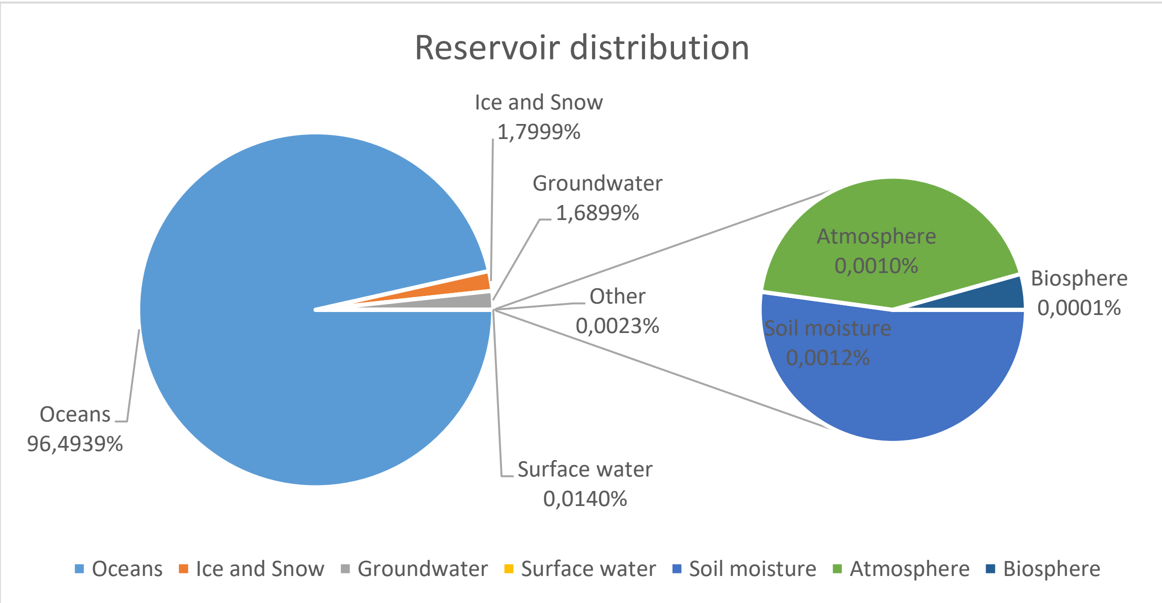


Figure 1. Reservoir distribution on Earth [7]

According to the figure oceans, ice and snow, groundwater and surface water (lakes and rivers) hold up the majority of water resources. Freshwater that is abundant for survival can be mainly found in the last three. Groundwater and surface water are by far the most frequently used freshwater reservoirs firstly, because it is easily accessible and secondly, a big portion of freshwater is locked in the glaciers [7]. Therefore it is important to control and monitor biological, physical and chemical indicators in surface as well as groundwater.

2.1.1 Survey of Estonian rivers

Based on the watersheds Estonia has four different drainage areas that include following catchment areas: Narva River and Lake Peipsi, Gulf of Riga, Gulf of Finland, the islands (Saaremaa, Hiiumaa) [8].

From the result of the geographical location and natural conditions morphometry of rivers and distribution of water resources are only some of the special characteristics of Estonia. The amount of watercourses according the official register (1982) there are 1,755 rivers, streams, main ditches and channels, from which 133 catchment areas are only over 100 km^2 and and 1000 km^2 in 14 rivers [23]. Rivers are relatively short with a small catchment area that are mostly poor in water (Northern Estonia). Due to the reason that rivers are naturally divided into small and uneven sections of water bodies sets up limitations for its use as a resource from the economic point of view [8].

Võhandu (162km), Pärnu (144km), Põltsamaa, Pedja, Kasari, Keila and Jägala hold the title of longest rivers. The mean width depends largely on the river starting from 40 meters up to 600-900 meters and width at their lower reaches varies between 15 to 20 meters. The depth at lowest reaches is from 2 to 5 meters ending up with a mean value from 5 to 15 meters [8].

One of the particular phenomenas in North Estonia and in islands is called karst, which refers to the dissolution of the limestone and river discharge into the underground water network. This allows for some rivers (Jõelähtme, Tuhala, Kuivajõgi) to run underground [8].

The runoff takes place mainly in the borders of Estonia and the annual distribution of it varies. The mean runoff is 8.2 l/s per 1 km^2 and it takes place mostly during the spring floods, which start in March and accomplish high peak in April. Dry and low water periods occur from June to the end of September that transmits to autumn runoff until the second half of November. December to March the air temperatures are reaching below 0 degrees of Celsius which refers to winter low water conditions [8].

2.1.2 Survey of groundwater in Estonia

Hydrogeology is a science of groundwater and aquifers, their sustainable use and protection [9]. The EPA classifies all available and existent groundwater as drinking water unless it is specifically released to have another purpose and, as such, must be according to applicable discharge and meet up with clean up standards. The flow of groundwater can be relatively fast through crevices and caves in karst terrain or slow through an impermeable materials (clay) and permeable soil (sand) [16].

The cross-section of geological base in Estonia is formed by monolithic layer that consists of crystalline metamorphic and igneous rocks. The layers from bottom to top are Vendian, Cambrian, Ordovician, Silurian and Devonian sedimentary stones and surface layer which consists of quaternary deposits [9].

Groundwater that is a part of natural water cycle refers to water in the pores of rocks and sediments that moves in the upper crust due to gravity and pressure. It has a vital importance as a resource of fresh water especially during dry periods and as supporter of maintaining good aquatic conditions. This describes how groundwater is in constant cyclic movement. In Estonia plenty of groundwater can be found all over the national territory near the ground and it is considered as easily accessible. There are 3000 to 10000 springs in Estonia, most of which are small and around 500 that are slightly larger [9].

A situation where water typically percolates (drains) downwards from the upper soil layer to groundwater is called recharge. This process takes place mainly in vadose zone, which can be explained as the region on top of the water table up to the roots of the plants. Usually recharge happens naturally (water cycle) or artificially where rainwater is channeled into subsurface [4].

The amount of precipitation in Estonia is around 600-800 mm and approximately 70 mm (10%) remains for groundwater supply as a result of infiltration [12]. The amount of infiltrated water depends on the level of moisture, permanency, the network and characteristics of the pores of the soil [4]. Intensive infiltration takes place during the spring, fall rain and snowmelt through the surface into the lower parts of the Earth. Despite the fact that water absorbs well some shortages are still existant. In late spring-summer rain evaporates and in winter precipitation water stays as a snow on the ground. In Estonia groundwater nutrition is high in the Pandivere Upland, up to 200-300 mm in a year and lowest in the west, in Võrtsjärv and Peipsi lowland and in bogs, up to 0-50 mm in a year. Precipitation doesn't affect not only groundwater resources but also the natural composition of it by enriching it with minerals [9]. Pandivere Upland is with vital importance in nitrate sensitive area, where the majority of rivers ecological and chemical state are dependent on.

2.2 The water cycle

The water cycle or hydrologic cycle [4] that is powered by the Sun by giving energy for the circulation [15] refers to pathways that involves the processes where nature's water moves in its different phases from the Earth's surface down over and through the land to the atmosphere and returns to the surface as precipitation or condensation [4,5].

The circulation is divided into two sections - large and small water cycle. Small cycle involves only atmosphere and hydrosphere where vaporized water from the sea and ocean emerges back as the precipitation. Inversely large cycle comprises all four spheres-atmosphere, hydrosphere, lithosphere and biosphere [9]. The main idea behind the water cycle is that the water is not lost and regained over time, but the quantity of water in different spheres, water bodies and other components are in constant change due to the dynamics of natural hydrologic cycle [4].

The precipitation water from the atmosphere that includes rainfall, hail, sleet and snow is not directly channeled back up via evapotranspiration. Part of it flows to the stream channels over the soil surface in the form of overflow or surface runoff [4, 5]. The surface runoff that is referred as water flowing over Earth's surface will transform itself into streamflow what conclusively will find its end in a water body (lakes, rivers) [4]. The portion of stream flow that migrates in the saturated zone to discharge back is called baseflow [7]. Another part moves into the soil by infiltration [4, 5], where water can rapidly flow through the soil straight into springs and adjacent streams [5] or it percolates at slow rate through compacted, wet, clayey soil into the groundwater [15] where it eventually streams into the natural river system, lakes and other open water bodies.

The hydrologic cycle is closed by evaporation or transpiration (collectively evapotranspiration) which is a process where the water is transported back into the atmosphere through various paths and stages [5].

2.3 Importance of monitoring

The monitoring of various substances and the purpose of several researches is to observe constantly and systematically the changes in quality of water bodies using specific hydrophysical and hydrochemical indicators to reduce or avoid the vulnerability [10].

Local national environmental monitoring in Estonia is aiming towards an overview of the state of the environment and the changes happening within. The legislative base for state-operative monitoring was carried out in 1992. Over twenty years that it has been conducted there are different smaller and bigger changes implemented, but still the monitoring is required to be dynamic enough, so that it is possible in timely manner to react according to the circumstances [10].

Relevant legislation governing the organization of environmental monitoring in Estonia are the law of Environmental Monitoring (RT I, 18.05.2016, 1) and Environmental Register Act (RT I, 08.07.2014, 18). The Environmental Register Act stipulates in the keeping, manintaining, issuing and publishing of the monitored data. According to the law the constant control is mainly keeping a track over environmental status and the factors affecting it, which includes environmental observations and data analysis.

Environmental Monitoring act establishes the objectives of monitoring [11]:

- assess and analyse environmental factors;
- to monitor, evaluate and predict changes in meteorological and hydrological aspects;
- to determine the status and amount of renewable resources;
- to identify environmental changes that require additional measures for implementation or further research;

- to monitor transboundary pollution and make comparisson researches based on international agreements;
- to develop and supplement the system of indicators describing the state of the environment;
- to receive primary data for pursuing development projects for plans and programs [11].

Importance of the observations in necessary to comply with national and international goals that are first and foremost adopted by EU. Environmental monitoring can be divided into two different sections: a part that concentrates on supervision over nature's resources and a part that specifies inspection over the environmental state. With the efficient monitoring it is possible to ascertain environmental risks and afterwords act on them accordingly. The outcome of the process allows to verify and restrict the sources of the problems and avoid any situation, where there is need to deal and fight against worst case scenarios [11].

As an example the results of groundwater monitoring are used for evaluation of groundwater resources, hydrogeological prognosis, modelling, assessing the flow of water in the extraction of mineral resources, determining the regional hydrogeological conditions, calculating the groundwater balance, the linkages and trends of natural and technogenic factors, migration of waste materials and study between surface and groundwater interactions [12].

2.4 Main water quality parameters under monitoring

2.4.1 Surface water

Surface water includes all terrestrial waters with the exception of groundwater. According to Estonia's Ministry of the Environment regulation RT I, 25.11.2010, 15 that specifies in surface waters has a register of objects needed to be monitored and clearly classifies quality elements that will describe the conditions in an observable object. Main parameters for watercourse are illustrated in Figure 2 [13].

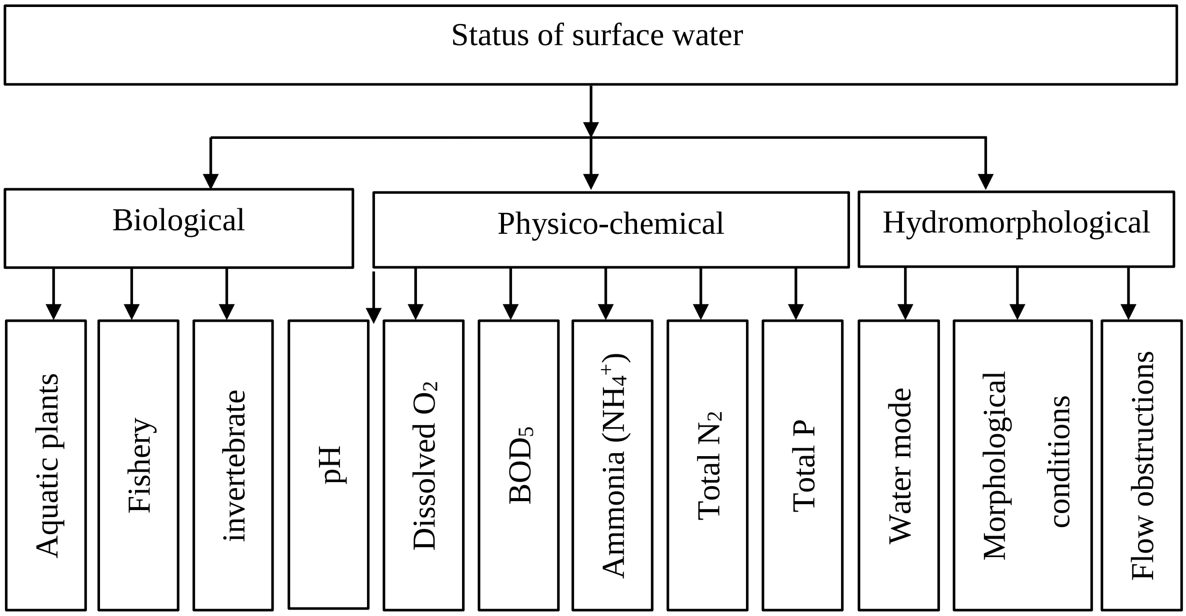


Figure 2. Water quality paramteres for surface waters [3,13].

Biological parameters include aquatic plants (phytobenthos), fishery and invertebrates. Main physico-chemical components are pH, dissolved O_2, BOD_5, NH_4^+, TN and TP. Hydromorphological indicators are water mode - mainly flow rate, flow obstructions - along and across the river, morphological conditions contain the nature and reach of river bank and bottom area and the width of the river[13].

2.4.2 Groundwater

In a broad sense groundwater refers to water that flows in the ground. The Directive 2000/60/EC establishes framework for water policy and sets up core parameters that shall be monitored in all the selected groundwater bodies: oxygen content, pH value, conductivity, NO_3^-, NH_4^+ [3].

Estonian Ministry of the Environment has established a regulation RT I, 12.07.2016, 2 in the field of groundwater. The document sets up register of objects of which conditions should be determined along with classification, list of pollutants together with limit values. Main parameters that are named in the act and 2000/60/EC are illustrated in Figure 3 [14].

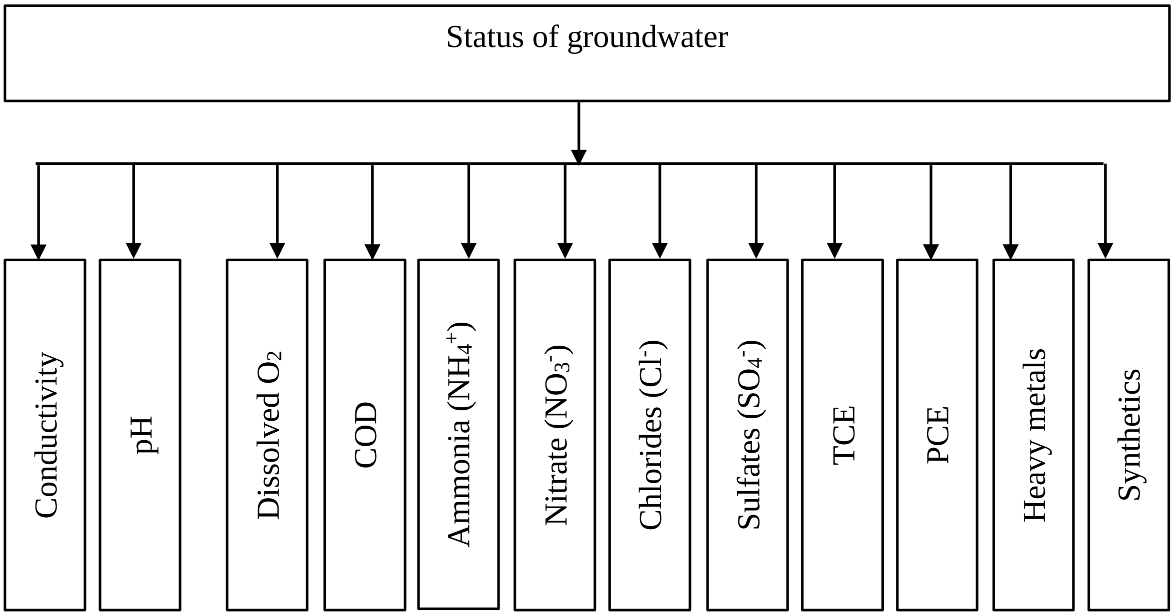


Figure 3. Required parameters for groundwater monitoring [14].

Elements that are required to be monitored include conductivity, pH, dissolved O_2, COD, ammonia, nitrate, chlorides, sulfates TCE and PCE. Heavy metals in groundwater can occur naturally or from anthropogenic sources. In the document it is stated that As, Cd, Pb, Hg should be monitored. Synthetic materials are not specified in present regulation [14].

2.4.3 Nitrogen in the aqautic environment

The N_2 is the most abundant natural element in the environment holding up 99% of all atmospheric gases [24] and maintains equilibrium concentrations in surface waters [25]. Besides organic matter addition and contribution from weathering rocks the main source of organic N_2 include fixation by special types of bacteria and plants [4]. The element is transformed by biochemical reactions into dissolved inorganic substances that mainly include gaseous NO, NO_3^-, NO_2^- and $NH4^+$. The biochemical reactions are illustrated in Figure 4 [24].

The organic N breaks into NH_3 or NH_4^+ by fixation, followed by oxidation into NO_3^-, which is more suitable form for plants due to assimilation, where NO_3^- and ammonia are united by plants and animals. After the process there are still remains of organic N, which need to be converted into NH_4^+ by ammonification. For the reasoning of oxygen absence denitrification can convert NO_3^- back to NH_4^+ by anaerobic bacteria [4] and N into gaseous state [24]. The organic nitrogen content in streams is usually in low quantities and the concentrations may be as low as 0.2 mg/L in surface waters and in groundwater in levels where there is no need for concern [25].

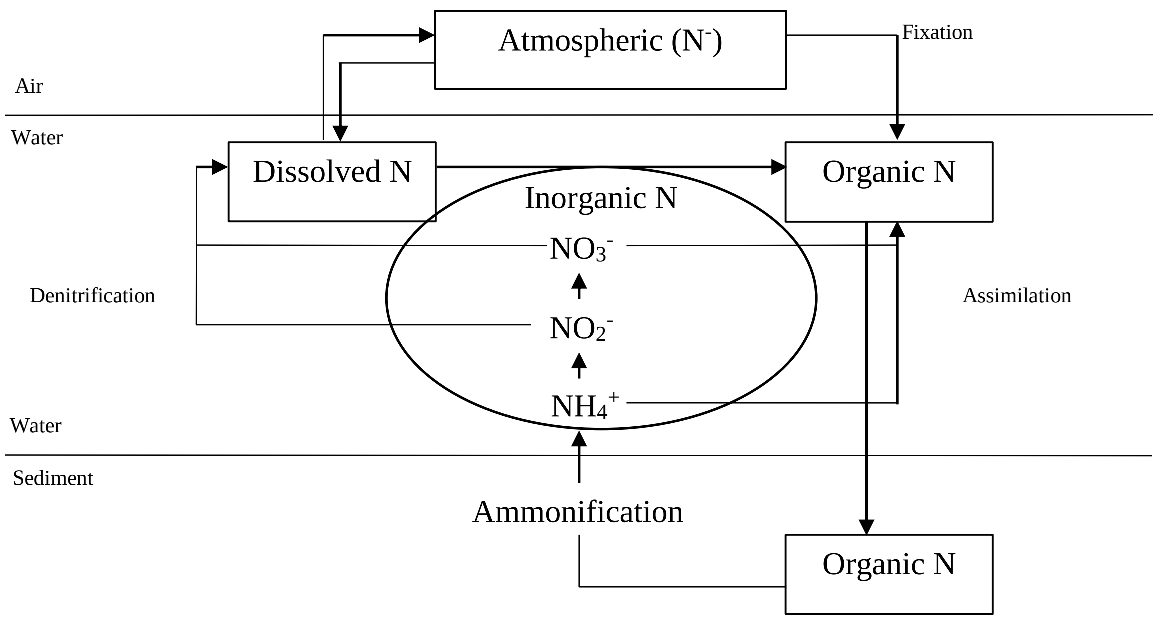


Figure 4. The nitrogen cycle in aquatic conditions [24].

Large concentrations of ammonia (NH_3 and NH_4^+) are toxic to biota and the presence of it characterizes organic substance hydrolysis. Ammonia is soluble depending on the temperature and the interaction between NH_3 and NH_4^+ is described by equation 1 [16]:

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^- \quad (1)$$

With pH below 7.0 ammonia is mostly present as ionized $NH4^+$. With pH increasing $NH4^+$ is changed into NH_3 and the toxicity of water body increases [16]. According to EU Fresh water Fish Directive non-ionized ammonia permissible value is 0.025 mg/l [49] and the level of value expresses recent or fresh pollution. The concentrations that exceed the value of 0.5 mgN/L is found to be very toxic to fish and other organisms. In groundwater the content is considerably low due to sorption of ammonia into soil. In monitoring results ammonia is presented as NH_3-N or NH_4-N ions, where the N shows the degree of pollution and the distance it may have traveled, which is later converted into NH_3 or NH_4 by massbalance [25].

Nitrite is the intermediate product in nitrogen cycle and the content of it characterizes the amount of oxidezed N_2. The usual concentraton in unpolluted streams ranges below 0.01 mgN/L and does not exceed the level of 0.5 mgN/L. The presence of nitrate referres to fresh contamination from sources.

Nitrate is a well-known pollutant that is derived from decaying vegetation, fertilizer and animal waste [15]. At the monitoring point of view in surface and groundwater bodies it is used as indicator for the presence of organics [16] and it characterizes totally oxidized nitrogen. NO_3^- as nitrogen or NO_3-N as an ion is strongly related to land-use and watershed management policies [4]. The natural concentration generally varies between 1-2 mgN/L. Streams that have interaction with shallow groundwater draining agricultural areas have an occurance of higher concentrations of nitrates (for example 10 mgN/L) [16]. The high concentration can accelerate the growth of algae and aquatic plats. In drinking water the content of 45 mg/L and above affects people health strongly and is toxic to infants [4]. According to RT I, 27.09.2017,2 that sets up the requirements for drinking water quality and control as well as analyze methods, the limit value for nitrates is 50 mg/L [51].

Total nitrogen presented in monitored data refers to all nitrogen bound elements found in water, which include NH_3, NH_4^+, NO_3^-, NO_2^- and organic N_2.

The nitrogen cycle processes are of with great importance in intensively managed croplands, where N fertilizers are largely in use [4]. From anthropogenic sources the nitrogen balance in surface water is affected mainly by fertilizers used in agriculture. Streams and rivers that are depending on deep groundwater draining agricultural areas are threatened by contamination with nitrates. Other ways include industrial activities such as discharged wastewater into streams, fossil fuel burning or runoff. Naturally nitrogen compounds provide nutrients for the growth of aquatic plants such as phytoplankton that in turn maintain living conditions for ecosystem [25].

Nitrogen compounds are parameters for evaluation of ecological status class in surface and groundwater. It is possible to compare the concentrations in each of them to find any proof wether there is interference existant between the two components during the permanent cold periods where precipitation is not an option for rivers and streams to receive nutrients. For example, natural groundwater in some cases owns detectable concentrations of NH_4^+ produced by microbial degradation of N-bearing compunds in organic matter. Especially in sedimentary groundwaters the ammonium concentrations can be higher due to sedimentary rocks that contain N compunds that are modified into NH_4^+ [26].

2.5 Surface and groundwater interactions

Surface water and groundwater are considered as renewable natural resources and the task is to ensure the good status by long-term planning and taking action respectively. Qualitative and quantitative aspects of both need to be integrated [3] as in several exchanges between surface and groundwater that are strongly interdependent can escalate into variety of hydrological problems or advantages such as the flow and chemistry [18].

Anthropogenic sources have had serious impacts on groundwater level and flows during the recent centuries. In spite of the nonvisibility factor, groundwater owns an important function as source of drinking water, groundwater recharge and ecological effects. Moreover, groundwater is vital for rivers and water bodies during dry periods. Based on named factors, my hypothesis is that the water quality of the rivers of long-term low-flow water periods must characterize groundwater quality. This indicates that the water quality in rivers during drought season is characterized by the status of groundwater in a territorially large area.

Europe's anthropogenic sources have many impacts to the quality of surface and groundwater. Approximately 20% of the groundwater is labelled as poor chemical status and 50% of surface waters are failing in conserving and maintaining the ecological state [19]. To efficiently manage water resources, in this context river basin, it is substantial to determine if the connection between surface and groundwater is present or not and to what extent. The interaction can be described as effluent or influent [17]. An influent water body leaks into the ground and it could be hydraulically connected or disconnected from the groundwater. This indicates that surface water moves into the groundwater domain and vice versa. Inversely effluent water body occur in regions where the water table is near the land surface [15] and the discharge happens from the saturated zone up into surface waters [7]. Both, influent and effluent, are driven by the pressure difference between the surface and groundwater. The pressure and the hydraulic gradient can be changed and modified by several factors therefore any change can affect either of the component [20].

As mentioned previously surface and groundwater are generally not considered as two separate components rather than closely linked and interacted over wide range of important physiographic and catchment settings that are part of hydrological cycle [19]. Parameters affected by the joint operation includes quantity, quality and the ecological wellbeing of water where the subsurface region proximal to surface water bodies regulates nutrient and contaminant transfer [21]. The interaction exists almost in all naturally occurring water bodies, such as lakes, wetlands, rivers, ocean, coast and estuaries [20].

Due to the cooperation of both the use and development and contamination of one another has a great potential to have positive or negative effect on the other component of the system [19]. Groundwater discharge can contaminate water bodies by degrading or conversely it can supply with vital nutrients as well as converse the ecological function [21]. For example in lowland streams many aquatic ecosystems are reliant on the resources of groundwater referred also as groundwater dependent ecosystems [19]. In case of contamination it is crucial to understand the mass flow rates between the components to apply measures of restoration [22].

The transition zone is called region between surface water environments and groundwater systems [21] where the exchange, transport, degradation, transformation, precipitation and sorption of water and nutrients takes place. It has a considerable role in the mediation of interactions due to the characteristics of permeable sediments, saturated conditions and low flow velocities. It is referred to as the hyporheic zone being responsible for the biota and metabolism of streams [22].

In order for discharge into streams and rivers from groundwater the height of the river stage must be lower than groundwater surface stream[27], therefore the flow usually changes from upstream to downstream. The movement is characterized as spatially and temporally heterogeneous [19] in response to natural factors such as climate variability [27]. Groundwater flow paths are typically run by hydrostatic forces arising from topography and geology. The surface water flow paths temporarily enter into the subsurface where the blend of two components occur [21].

3. SOURCES OF DATA AND METHODOLOGY

3.1 Monitoring stations in Estonia

The water monitoring program in Estonian provides complete overview on surface and groundwater. To accomplish and maintain a good aquatic environment the base of representative monitoring is guaranteed by various activities. Monitoring data provides information about ecological status in surface water, chemical conditions in surface and groundwater, quantitative status in groundwater. In order to ensure the technical and data collection capability, the status assessments are divided into three groups [28]:

- Surveillance monitoring – conducted to assess long-term changes;
- Operational monitoring – provides further information for overview monitoring. Necessary for making sure if additional measures are required and to get a clear picture about general conditions and important changes in the aquatic environment;
- Investigative monitoring – seeks out for reasons why environmental targets have not been achieved [28].

Monitoring stations in Estonia are located across the country. According to environmental register there are approximately 472 different stations for surveillance of river hydrochemical conditions, 395 for support network groundwater or groups of bodies and 39 in nitrate sensitive areas [29].

3.1.1 Surface water monitoring

The revision for surface water monitoring programme in Estonia took place in 1992 [30] and in 1994 hydrochemical monitoring was added [31]. The distribution of surface monitoring stations in Estonia can be seen in figure 5 [37].

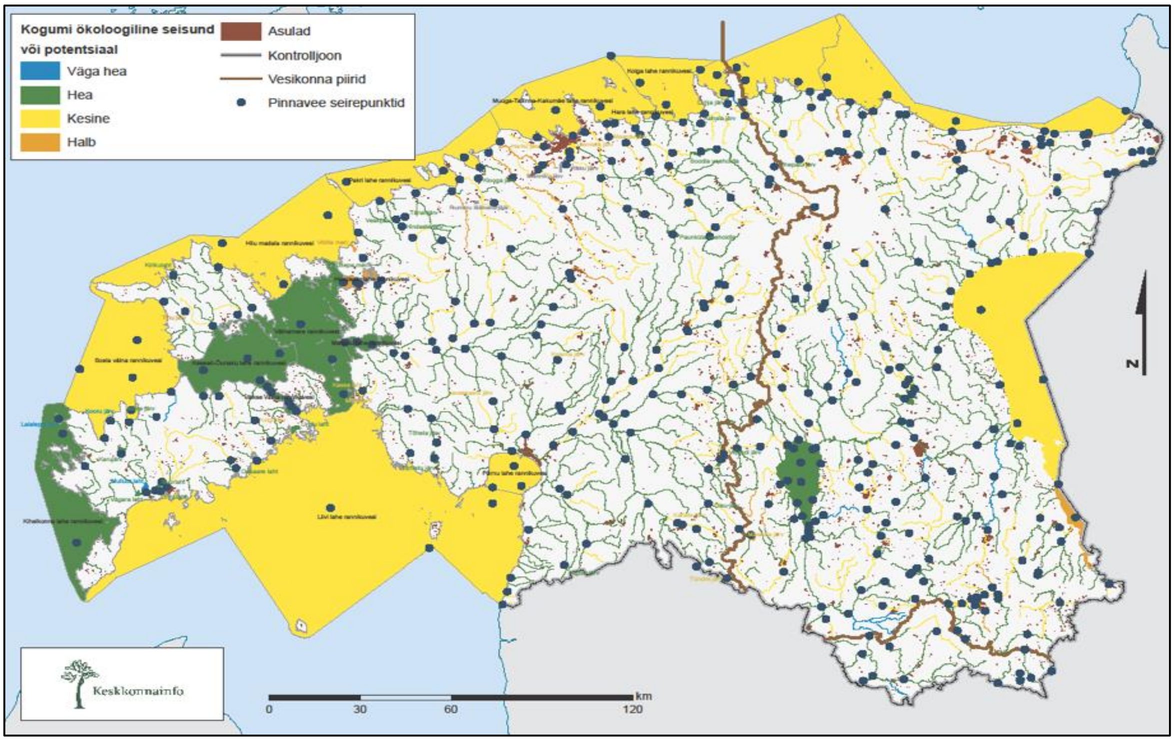


Figure 5. Distribution of surface water monitoring stations [37].

Over 30 years ago the physical-chemical monitoring was conducted at 54 stations on 27 rivers and today the number has increased according to trends, requirements and changes in legislations, directives and acts [30]. Based on physical-chemical parameters the ecological state and quality class is determined [32]. The types of watercourses under monitoring are:

1) Type I A – dark colored, rich in humic rivers with a catchment area 10-100 km^2;
2) Type I B – rivers that are light colored, contain low organic matter content and with a catchment area 10-100 km^2;
3) Type II A - dark colored, rich in humic rivers with a catchment area 100-1000 km^2;
4) Type II B - rivers that are light colored, contain low organic matter content and with a catchment area 100-1000 km^2;
5) Type III A - dark colored, rich in humic rivers with a catchment area 1000-10000 km^2;
6) Type III B - rivers that are light colored, contain low organic matter content and with a catchment area 1000-10000 km^2;
7) Type IV – rivers with the catchment area over 10000 km^2 [13].

The monitoring program is mainly divided into 4 sections: South, North, Northeast and Southwest of Estonia [31]. The number of stations must be at least 1 per 1000 km^2 in agricultural and industrial areas and 1 per 1700 km^2 in areas that are not affected by anthropogenic sources. Sampling procedure is conducted 6-12 times a year according to the need that are set by the government [13].

Agricultural areas own special and frequent monitoring program in Estonia. This program was implemented by Tallinn University of Technology by which it is possible to describe the state of the environment, impact of human activities and apply environmental measures in nitrate vulnerable area. Pandivere and Adavere-Põltsamaa are regions considered as nitrate sensitive and following water courses are monitoring the surface water: Võisiku-Võisiku, Põltsamaa-Rutikvere, Alastvere main ditch-Põltsamaa-Jõgeva, Jänijõgi-Jäneda. Sampling in these water bodies are conducted once a month [30]. Generally the requirement for surface water monitoring in agricultural areas is 6 times per year at equal intervals by making sure that at least one is collected during high water period and at least one at low water period [34].

3.1.2 Groundwater monitoring in Estonia

Groundwater possesses essential value and it is a part of national monitoring program. The main task is to investigate the natural condition of groundwater (water level, chemical composition), to observe quality, water level and resource changes due to human impact (direct and indirect consumption, pollution) [33], for modelling, to assess water recharge, to conduct hydrogeological prognosis, to investigate pollutant migration and to receive proof about surface and groundwater interactions [12]. Based on named parameters it is possible to receive necessary information on national level for decision making and for international communication or cooperation. On EU level the limit values for nitrate ions and pesticides are set up for groundwater. European council directive 2006/118/EC states that the maximum permitted limit for nitrate is 50 mg/l [33].

Generally springs are preferred as the monitoring location. Supporting networks give an overview of the conditions in groundwater. The territory of Estonia identifies 15 groundwater bodies on what observational network has been established to monitor quantitative and chemical status. During the process water level is examined and samples are collected to determine chemical composition and hazardous substances presence and concentration [33].

Purpose of the review of chemical composition in groundwater bodies besides detecting various substances is to describe natural changes within, to evaluate human impact and the effectiveness of monitoring program, to assess the achievement of environmental targets in areas that are strongly dependent on groundwater and to assign the status class [34], which are good (mainly natural waters) or bad (polluted or strongly polluted waters) [14]. The distribution of chemical monitoring stations of groundwater are presented in Figure 6 [37].

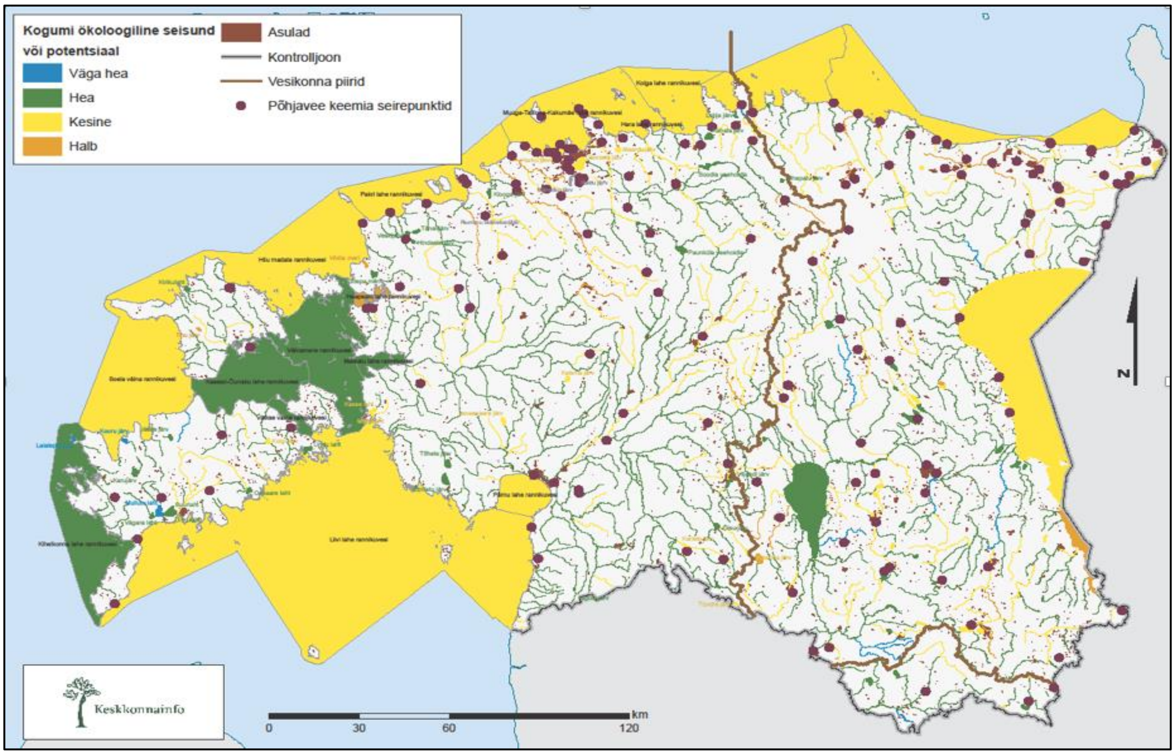


Figure 6. Distribution of groundwater chemical stations [37].

The requirements for groundwater monitoring time and frequency in observational monitoring is once per year during summer low water period, for operational monitoring once per year at equal intervals and in nitrate sensitive areas 4 times in basic monitoring points and once a year in supporting monitoring stations [34]. The reason behind multiple sampling in nitrate vulnerable areas is that in Pandivere upland the contamination of groundwater with nitrogen compounds is with decisive importance in water quality formulation for the rivers starting from the slopes that are predominantly feeding on surface aquifers [35]. These aquifers are referred to as groundwater bodies and their groups which mainly appear on the ground are related to the surface water and are to a greater or lesser extent affected my human activities [33]. The layer of surface coating is below 2 metres and precipitation water has a quick access into groundwater due to infiltration [35].

3.2 Study area

Nitrogen content in the rivers can be assessed across the country. This work is based on available data that focuses on the areas that fall under the region of North of Estonia. The trend in nitrogen content increase could be the object of interest primarily because of the expansion of agricultural area as well as the majority of industries are assembled and continue to be assembled in North side of Estonia.

Several meteorological observation networks are spread between counties and cities. In total there are 35 stations that monitor the temperature (air and ground), air humidity and pressure, wind speed, sunshine duration, amount of precipitation, height and amount of clouds, visibility distance, weather phenomena, types of radiation and ultraviolet radiation. In this thesis air temperature is the main parameter under interest. On Figure 7 the distribution of meteorological stations is illustrated [36].

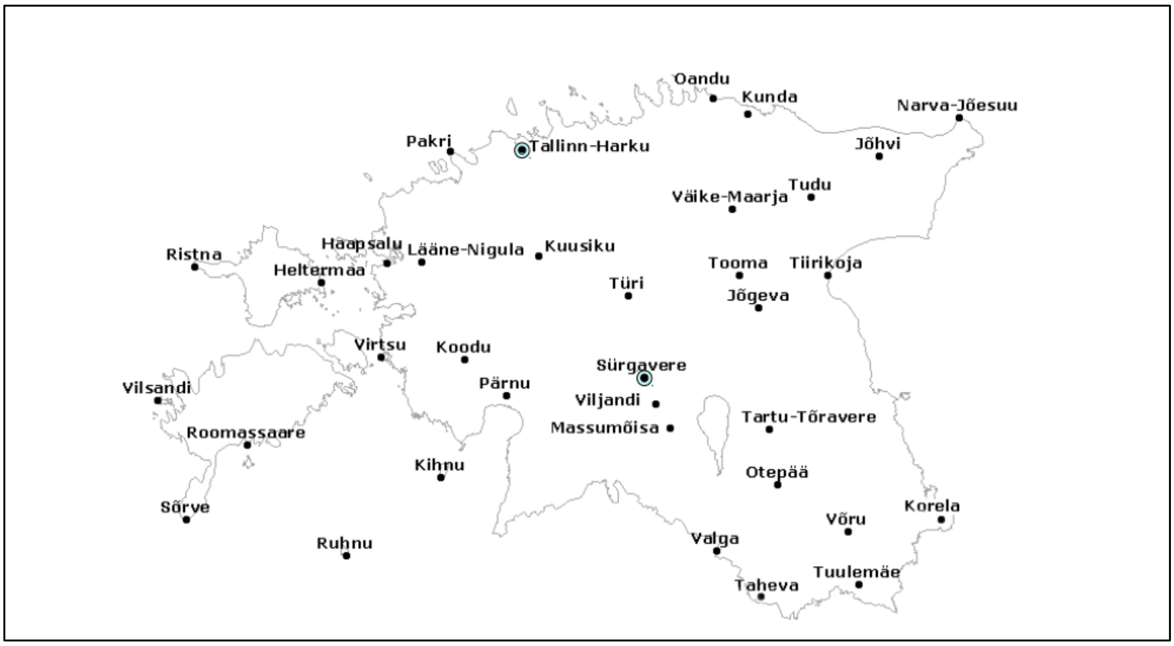


Figure 7. Distribution of meteorological stations in Estonia [36]

From the variety of selection 3 stations were picked out to characterize climatic situation during the period from December to February to assess permanent cold period in North of Estonia. Each of the three would represent different areas: West side (Tallinn-Harku), East side (Jõhvi) and nitrate sensitive area (Väike-Maarja). The monitoring stations of rivers surface water were selected accordingly that would fit near the area of dominant meteorological station and groundwater station were picked based on the close radius of appropriate river monitoring station.

As previously mentioned several surface and groundwater monitoring points were selected according to the meteorological station due to the opportunity to provide evidence wether the available nitrogen content data in both (surface and groundwater) were monitored during permanent cold period, where air temperatures are below zero. Based on that it is possible to evaluate groundwater condition based on river water quality. Monitored stations are listed in Table 1.

Table 1. List of monitoring stations under study

Nr.	Monitoring station code	Name of the hydrochemical station	Region	Matrix	Type
1	SJA4852000	Leivajõgi: Pajupea	Tallinn-Harku	Surface water	I A
2	SJA1764000	Alastvere peakraav	Väike-Maarja	Surface water	I B
3	SJA8358000	Jänijõgi: Jäneda	Väike-Maarja	Surface water	II B
4	SJA1354000	Kääpa jõgi: Kääpa	Väike-Maarja	Surface water	I B
5	SJA2802000	Oostriku jõgi: Oostriku	Väike-Maarja	Surface water	I B
6	SJA4253000	Preedi jõgi: Varangu	Väike-Maarja	Surface water	II B
7	SJA7946000	Põltsamaa jõgi: Rutikvere	Väike-Maarja	Surface water	II B
8	SJA3989000	Räpu jõgi	Väike-Maarja	Surface water	I B
9	SJA9895000	Valgejõgi: Porkuni, Oruveski talust põhjasuunas	Väike-Maarja	Surface water	I B
10	SJA0106000	Võisiku peakraav (Riivli oja)	Väike-Maarja	Surface water	I B
11	SJA9303000	Kunda: Lavi allikad	Väike-Maarja	Surface water	I B
12	SJA8796000	Porijõgi - Reola	Väike-Maarja	Surface water	II B
13	SJA8127000	Alajõgi - Alajõe	Jõhvi	Surface water	II A
14	SJA2641000	AD47: Kalme küla, Kääri talu	Väike-Maarja	Groundwater	-

Table 1 continued

Nr.	Monitoring station code	Name of the hydrochemical station	Region	Matrix	Type
15	SJA9706000	ADA30: Sopa allikas	Väike-Maarja	Groundwater	-
16	SJA8442000	ADKK21: Kõrkküla küla, Kuusiku talu	Väike-Maarja	Groundwater	-
17	SJA8435000	PAA15: Aravete allikas	Väike-Maarja	Groundwater	-

The rivers are selected purposely by couple different factors, besides the location of hydrological stations. Karst area that divides into to – Põltsamaa and Pandivere- is one of the indicators that would demonstrate the nutrient concentrations changes in time. Põltsamaa karst are is represented by rivers of Räpu, Põltsamaa and main ditches in Võisiku, Alastvere. Pandivere highland karst area is characterised by rivers of Oostriku, Preedi, Valgejõgi, Jänijõgi and Kunda. Rivers Kunda, Alajõgi, Porijõgi, Leivajõgi and Kääpa are exceptions from Põltsamaa and Pandivere karst, which will be explained more in chapter 4.

3.2.1 Nitrate sensitive area

The land area in Estonia is 43 200km^2 that makes up approximately 96% of the total area (45 227km^2) [48]. In general nitrate sensitive area is considered as region, where groundwater bodies nitrate ion content can exceed the value of 50 mg/L due to the agricultural activities or surface water bodies that are eutrophic or on the verge of eutrophication for the same reasoning [35]. Nitrate sensitive zone (Figure 8) is characterised as karst area with relatively thin (<2 m) surface cover on limestone layer. The area (approximately 7.7% of Estonia) is continously through the years affected by intensive agricultural production. Besides influencing river water quality the groundwater quality is also under danger, due to large accumulation of it in the Northern Part of the region. Agricultural activities are popular in this zone, because the soil is considered as one of the best in Estonia [46]. With the Estonian Act RT I, 29.04.2014, 6 the clear boundaries are established, where agricultural influence on water bodies is significantly stronger compared to other locations [35]. The main portion of this thesis is focused on nitrate sensitive area of Pandivere and Adavere-Põltsamaa in Estonia.

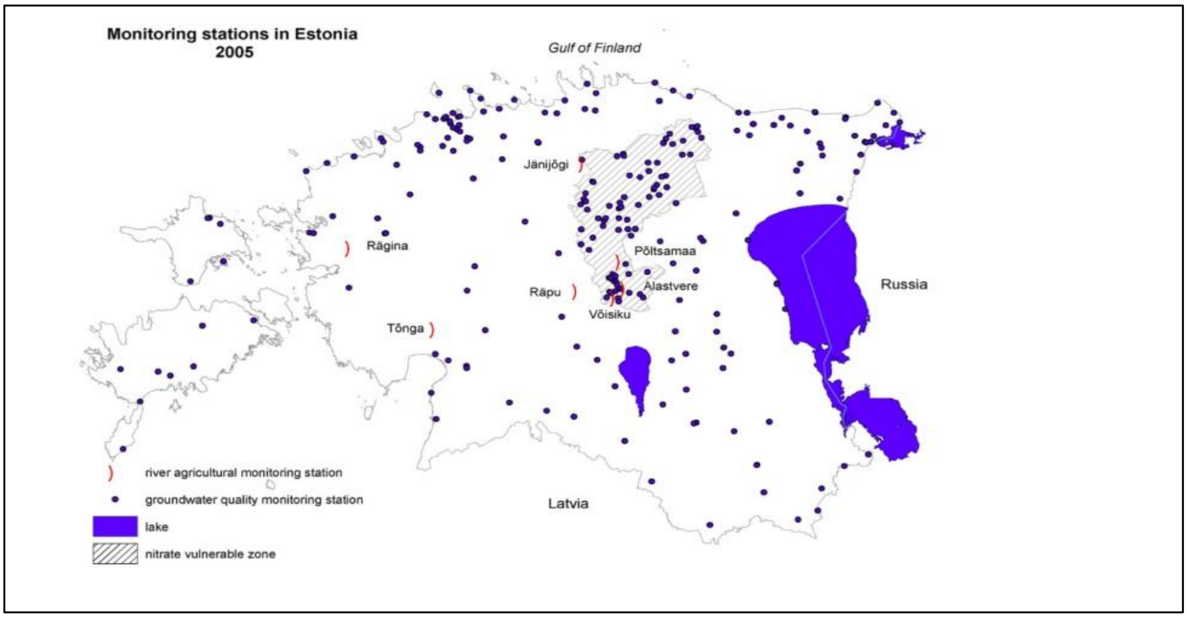


Figure 8. Distribution of water quality monitoring stations in agricultural catchments in Estonia for ground and surface water [46]

According to the Water Act more stringent environmental protection requirements have been put in place. In 2015 Estonian Parliament approved the draft to make changes in the Water Act due to the need of more relevant requirements to restrict the water pollution from agricultural areas. Estonia's water condition is considered as bad in surface and groundwater and the increasing trend continous due to the occurrence of nitrate ions, which in turn leads to higher risk of pollution [35].

Up to these days the land use and management, especially leaching of nitrates, is also considered as one of the top influencers of pollution [48]. To assess the importance of agricultural land impact, mostly in nitrate sensitive area, there is a need for knowledge of the percentage of agricultural and arable land that constitutes from the catchment area. In table 2 the main characteristics and corresponding values are presented.

Table 2. Main characteristics if catchments of the monitored rivers [48]

No.	Name of the hydrochemical station	Catchment area/km^2	Agricultural (%)	Arable (%)
1	Alajõgi/Alajõe	140	15	2
2	Põltsamaa/Rutikvere	861	41	24
3	Kääpa/Kose	282	28	15

Table 2 continued

No.	Name of the hydrochemical station	Catchment area/km^2	Agricultural (%)	Arable (%)
4	Porijõgi/Reola	241	54	13
5	Preedi/Varangu	34.8	56	34
6	Oostriku/Oostriku	29.7	70	53
7	Valgejõgi/Porkuni	57	67	37
8	Kunda/Lavi	362	28	13
9	Kunda/mouth	528	37	17
10	Vodja/Vodja	52	59	35
11	Leivajõgi/Pajupea	96	36	11
12	Räpu/Arkma	25.5	61	39

According to the table 2 it can be seen that the percent of agricultural and arable land is quite high in most of rivers except Alajõgi, where the area is mostly covered by forest (65%). Overall the nitrate sensitive area is characterized as fertile and relatively productive.

3.4 Sampling

Sampling is referred to a procedure that mainly involves physical collection from a water body under surveillance for later analysis and the taken portion represents the whole condition in terms of selected parameters. Representativeness is a major concern due to the fact that errors can occur in sampling part as well as analysis part. The main purpose is to gather useful data followed by informative results that will eventually meet with the monitoring porgram objectives at least cost [24].

It is essential that sampling is conducted with same methods so that it is possible to compare the results. Therefore in the Baltic region and in countries nearby usually water sampling and analysis is governed by standards that are adopted by EU [38]. The sampling techniques taken from monitored stations processed in this thesis are in accordance with following standards:

- EVS-EN ISO 10304-1 Water quality – Determination of dissolved anions by liquidchromatography of ions – Part 1: Determination of bromide, chloride, fluoride, nitrate, nitrite, phosphate and sulphate;
- ISO 5667-6 Water quality – Sampling – Part 6: Guidance on sampling of rivers and streams;
- ISO 5667-11 Water quality – Sampling – Part 11: Guidance on sampling of groundwaters [39].

Grab technique has been found to be most common and cost effective technique in surface water monitoring. In this scenario water samples are collected manually from a watercourse over fixed period of time and as frequently as required. After collection samples are transported into the laboratory and analysed by in-house methodology [30]. Most of the groundwater can be sampled by pumping systems and analysed in laboratory similarly as surface water. Assessing different nutrient concentrations regularly provides an insight into the condition of aqueous environments [24].

In Nordic countries including Estonia automatic stations are used to continuously register water discharge and to sample pollution loads in agricultural areas. Advantages of automatic systems include constant data flow on water level and discharge, storage of data in memory of data-logger or virtual files, keep constant check on station functionality and receive data via wireless connection, saves time by sampling several parameters at the same time [30].

3.3 Methodology

To efficiently keep control over the quantity and quality of aquatic resources it is essential to understand the interconnections between groundwater and river systems in general, although it sets up a challenge because it is mostly poorly understood in many catchments all over the world. It is known that the interaction is present in geological, topographical and climatic settings where rivers have varying degrees of connection with groundwater systems [27].

Hydrogeologists and hydrologists often apply techniques such as groundwater flow systems, topography, geology/aquifer systems, climate and rainfall-runoff process that characterise physical state within a river basin [27]. To carry out complete monitoring ending up with trustworthy results integral design need to be applied for data analysis. Beforehand the seasonal variations need to be separated because the changes in water quality can be rapid due to natural fluctuations [30]. In Estonia there are four different seasons throughout the year where water quality transforms from ‘’wall to wall’’. According to the theme of this thesis the cold period from December 2008 up to February 2011 is under interest primarily in the following months: December, January, February. The temperature is the main parameter assessed to support the results that the sampling timing occurred during the period where climatic conditions where below zero degrees of Celsius specifying real time conditions within the rivers in selected three regions. To conduct necessary hydrographs a mathematical expression (equation 2) was applied to demonstrate cumulative distribution of air temperatures from highest (minus degrees) to lowest (plus degrees).

$$P = \left(\frac{m}{n+1}\right) * 100 \quad (2)$$

where

P	Percent of the date sorted from highest to lowest
m	Order of series of numbers
n	A number of the date of the month

For evaluation of chemical indicators one of the applicable approaches is to collect already existing hydrometric data from different catchments handing over an opportunity to analyse data patterns [27]. Statistical descriptive statistics provide different opportunities to examine water quality data (nutrient concentrations) that is generally not normally distributed. This can be logically explained due to characteristics of the nature as well as seasonal patterns influenced by water discharge [30]. The idea is to apply statistical methods in interpreting available results of the concentrations of TN, NH_4^+ and NO_3^- in rivers and in groundwater (if available) during winter period. In result it is possible to make assumptions how rivers maintain ecological state during difficult conditions and evaluate groundwater condition based on that.

In surface waters it is possible to assess the ecological state of physio-chemical parameters. According to act RT I, 25.11.2010, 15 appendix 4 the ecological state is divided into 5 categories based on the type of the watercourse (Table 3) [13]. Majority of the monitored rivers fall under the type of I A, II A, I B or II B. To facilitate determination of each status class the limitation values have been set. State of the watercourses is assessed based on parameters of TN and NH_4^+ that are in compliance with the previously named act.

Table 3. Determination of ecological state based on physio-chemical values in watercourses [13]

Quality parameter		Unit	Very good class	Good class	Poor class	Bad class	Very bad class
Type I A, II A, III A							
TN	Arithmetic mean	mg/L	<1.5	1.5-3.0	> 3.0-6.0	>6.0-8.0	>8
NH_4^+	90% probability value	mgN/L	<0.10	0.10-0.30	> 0.30-0.45	>0.45-0.60	>0.60
Type I B, II B, III B							
TN	Arithmetic mean	mg/L	<1.5	1.5-3.0	> 3.0-6.0	>6.0-8.0	>8
NH_4^+	90% probability value	mgN/L	<0.10	0.10-0.30	> 0.30-0.45	>0.45-0.60	>0.60

The 90% probability value calculation of NH_4^+ is based on logarithmic normal distribution. The logarithmic values of arithmetic mean and standard deviation are calculated based on the method of moments (equations 3,4) [45].

$$M = \ln \frac{m}{\sqrt{\ln\ (1+\frac{s^2}{m^2}}} \qquad (3)$$

where

M	monitored data logarithmic mean
m	arithmetic mean of monitored data
s	standard deviation of monitored data

$$S = \sqrt{\ln 1 + \frac{s^2}{m^2}} \quad (4)$$

where

S monitored data logarithmic standard deviation

m arithmetic mean of monitored data

s standard deviation of monitored data

The value corresponding to 90%, which means that 90% of the monitored nutrient concentration is less or equal than percentile content can be found with equation 5 [45].

$$Q = e^{(M+1.2816 \times S)} \quad (5)$$

Where

e is a constant, because $\ln(e) = 1$

S monitored data logarithmic standard deviation

M monitored data logarithmic mean

s standard deviation of monitored data

Monitored data of NO_3^- is generally reported as equivalent nitrogen concentration and referred to as nitrate nitrogen (NO_3-N). The preferred concentration unit of mgN/L is common amongst environmental engineers and other specialists investigating polluted streams. Equivalent concentration can cause minor confusion, but on the other hand provides useful information in water quality studies by expressing nitrogen elements in terms of nitrogen. When receiving the concentrations from the rivers the modification with mass balance needs to be applied in order for the possibility to compare the results with limit values. Mass balance can be easily performed by dividing the molar mass of NO_3 (62 g/mol) by the molar mass of nitrogen atom (14 g/mol), which results in 1 mgN/L=4.43 mgNO3/L [25]. All the monitored concentrations are required to be multiplied by the conversion factor of 4.43 in order to use it for further data comparison.

4. PRACTICAL PART - DATA ANALYSIS

4.1 Evaluation of weather conditions

From year to year it becomes more clear that there is a strong need for climatic data. In Estonia the monitoring and measurement of climatic status was started in the end of 18th century when Tartu Observatory was constructed [40]. Seasonal runoff conditions are determined by hydrological seasons and govern following time periods:

- Fall – from October to November;
- Winter – from December to February;
- Spring – from March to May;
- Summer – from June to August [41].

4.1.1 Hydrological season of 2008-2009

All the three months – December, January, February - were warmer from the average 3-4°C, 3.7°C and 2.2°C respectively. For the most part the minuscule temperatures occurred in the beginning of January and often changed to periods that were close to 0°C. East, Northeast and South-East of Estonia was rich in rainfall and the period in general is described as insufficient in snow [41].

In Tallinn-Harku the average temperature in December was 0.4°C, in January -1.9°C and in February -4.3°C. The distribution of air temperatures in Tallinn-Harku aerological station during the winter season in 2008-2009 is presented in Figure 9.

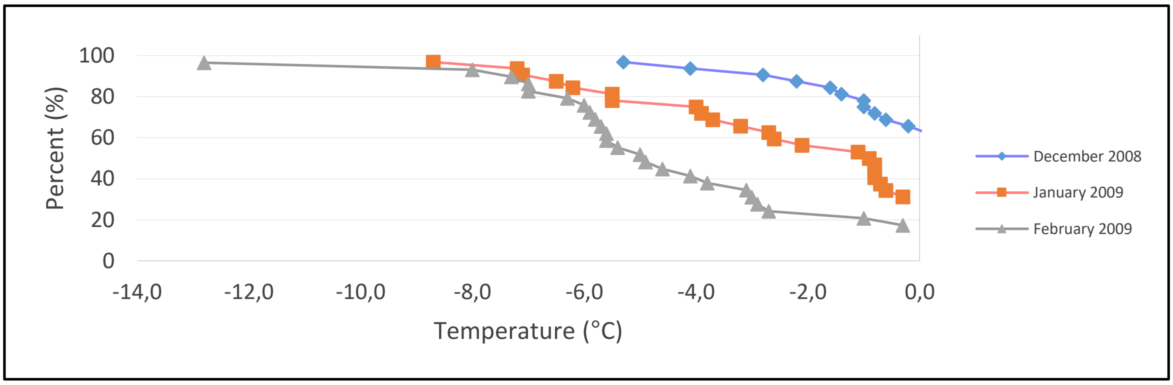


Figure 9. Air temperatures in Tallinn-Harku during permanent cold period in 2008-2009

From all the three months December was described as warmest where the majority of the month was above 0°C. January and February were slightly better in describing permanent cold period where only 4-9 days were warmer. Maximum temperatures reached in December -5.3°C, in January -7.4°C and in February -6.6°C.

December in Jõhvi meteorological station was measured with the average temperature of 0.9°C and 15 days out of 31 occurred to be below 0°C. The average temperature in January was measured as -3°C and in February -5.5°C. The maximum temperatures in Jõhvi during December, January and February were -7.4°C, -10.7°C, -15.2°C respectively (Figure 10).

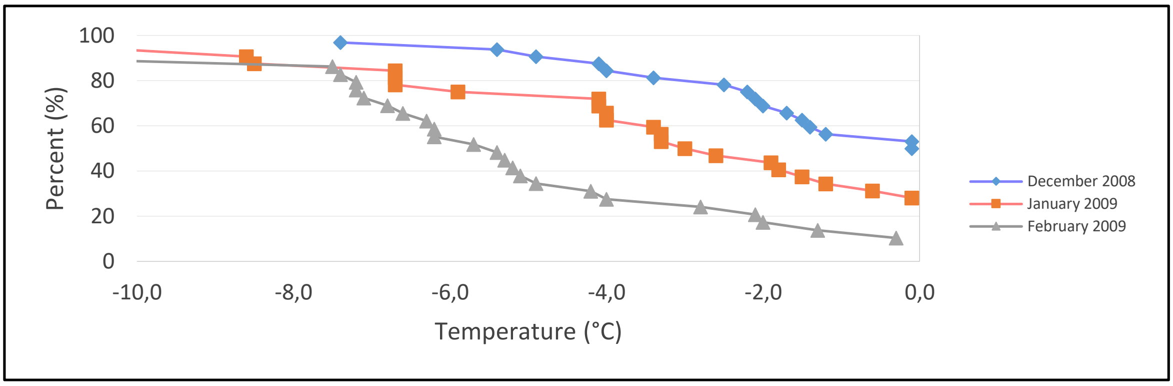


Figure 10. Air temperatures in Jõhvi during permanent cold period in 2008-2009

Väike-Maarja region was the coldest during hydrological season out of three observational locations. Average temperatures varied from -1.2°C up to -6.1°C. The coldest month was February, where the majority of temperatures stayed below 0°C. Maximum lowest temperature in Väike-Maarja region was reached in February 2009 -16.8°C, followed by -13.1°C in January and -6.6 in December (Figure 11).

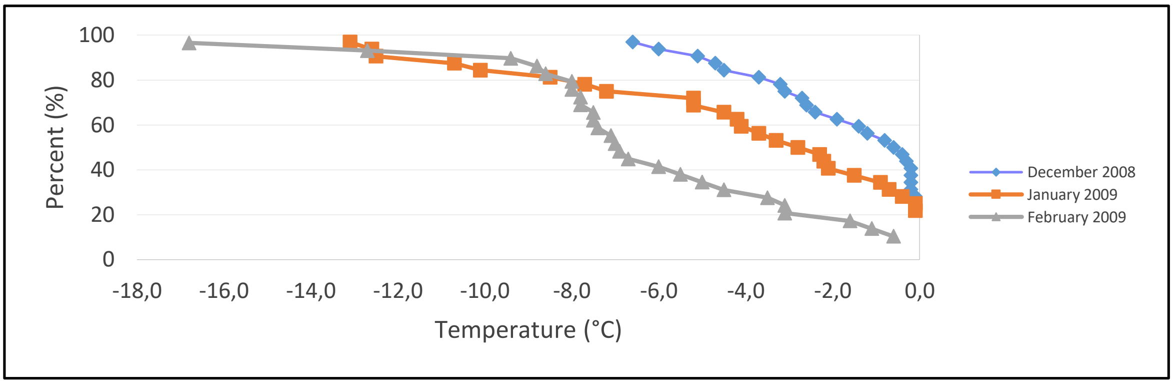


Figure 11. Air temperatures in Väike-Maarja during permanent cold period in 2008-2009

4.1.2 Hydrological season of 2009-2010

In 2009 the climatic winter started in December in the end of first decade where the Estonian mainland was covered with snow [40]. Since the middle of December sudden air temperature decrease occurred where permanent minus degrees (-21°C up to -6°C) remained approximately for a week followed by another week of slightly warmer weather (-7°C up to +6°C) [42]. The end of the month was colder from the ordinary up to -20°C. January in 2010 is described as rich in snow and sunny making it as permanent cold month. Daily average ranged from -5°C to -3°C during warmer days of the month and from -26°C to -15°C in the cold days. In February the weather was predominantly colder from the average and rich in snow all over Estonia [40]. All in all the three winter months are characterized by cold air temperatures, blizzard and thick ice layer. The temperature was 3.8°C lower from the average from previous years and there was 11% more snowfall. The air temperature with Estonian average of -7.5°C positioned 8^{th}-9^{th} place during the last half of a century [42].

The water temperature in rivers decreased from 0.2°C in the middle of December. In the rivers Valgejõe, Tagajõe and Avijõe had the thickest ice coverage. In the end of 2009 the water level and drainage were quite high and for this reason it continued to be in the normal range or higher in most of the rivers in January. The low water period started in February and the flow rates decreased and made up 20-80% from the norm [42].

The average temperatures in Tallinn-Harku region in the hydrological season of 2009-2010 were -3.9°C in December, -11°C in January and -7.7 °C in February. Maximum air temperatures were varied from -15.5°C to -21.8°C (Figure 12).

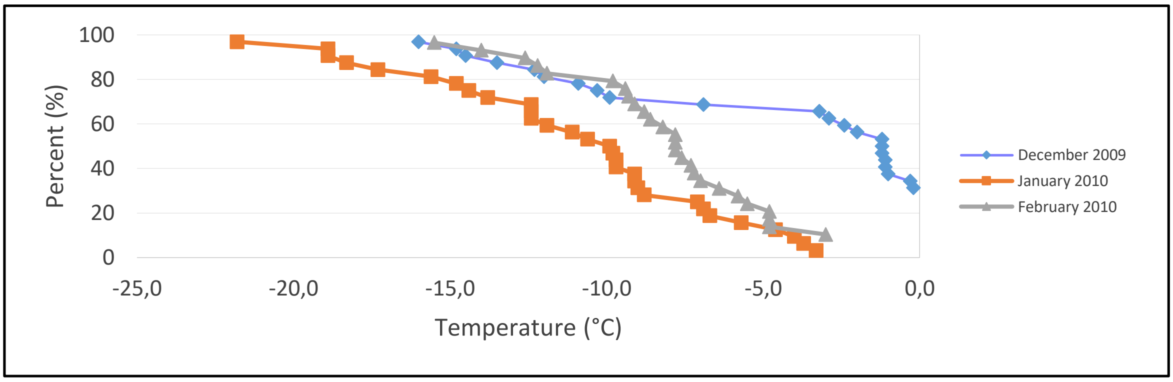


Figure 12. Air temperatures in Tallinn-Harku during permanent cold period in 2009-2010

Hydrological season in Jõhvi during 2009-2010 was described as cold and with the average temperatures -5.6°C in December, -12.8°C in January and -8.9°C in February. From the Figure 13 schematic distribution of air temperatures can be seen that January is the best month for describing permanent cold period, because all the days of the month were below 9°C.

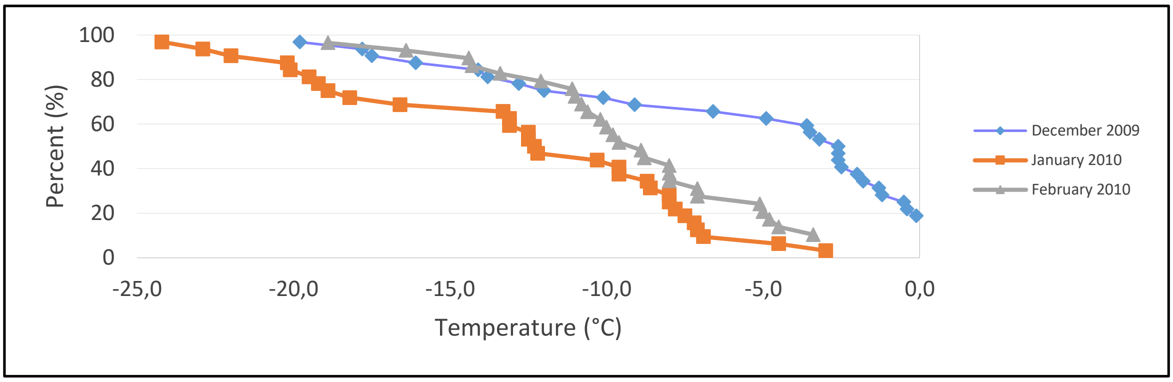


Figure 13. Air temperatures in Jõhvi during permanent cold period in 2009-2010.

In Väike-Maarja region the average temperatures were -5.3°C in December, -13.3°C in January and -9°C in February. In the first and third month of hydrological season 6 out of 31 days and 2 out of 28 days respectively were slightly above zero. The maximum temperature during at the given time frame was -23.5°C measured in January (Figure 14). In Väike-Maarja, likewise Jõhvi, all the temperatures were in minuses representing idealistic permanent cold period in which the nutrient concentration could be determined for assessing the possibility of surface water groundwater interaction.

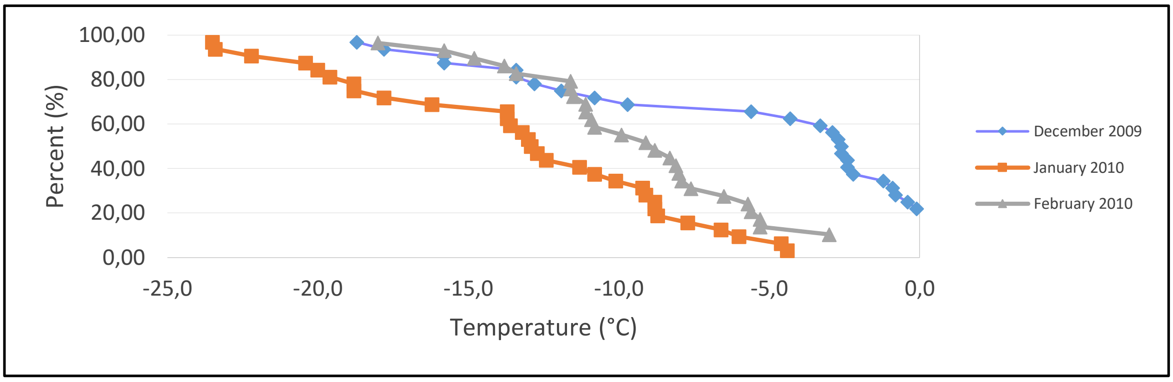


Figure 14. Air temperatures in Väike-Maarja during permanent cold period in 2009-2010.

4.1.3 Hydrological season of 2010-2011

During the hydrological season in 2010-2011 the air temperatures are characterized as low in December and February – from the usual 4.4°C and 5.3°C colder respectively [43]. In December 2010 the weather was considerably colder and snowy followed by slightly warmer January. The first third of February 2011 appeared to be warmer out of the ordinary. The second and third decade was mostly without precipitation, sunny and frosty permanent winter weather which was last seen in 1996 [36].

The amount of snow was higher from the normal in December and January. Thickness of the ice was above average varying from half a meter, for example 59 cm in Valgejõe, up to approximately 1 meter. In general the air temperatures compared to previous years was 3.1°C colder and the amount of precipitation was 24% higher. The water level at different areas was affected by fluctuations due to frost and melting and in several places it exceeded the long-term average [43].

In Tallinn-Harku aerological station the average temperatures were measured -6.3°C in December, -3.5°C in January and -9.6°C in February. The permanent cold period started already in December due to the fact that all 31 days were below 0°C, but still the maximum lowest temperature was reached in February -20.8°C (Figure 15). In December and January the lowest peaks were -10.8°C and -12.6°C. The minimum temperatures varied from 0°C up to 1.9°C and during the three months the warmer days occurred only during couple of times.

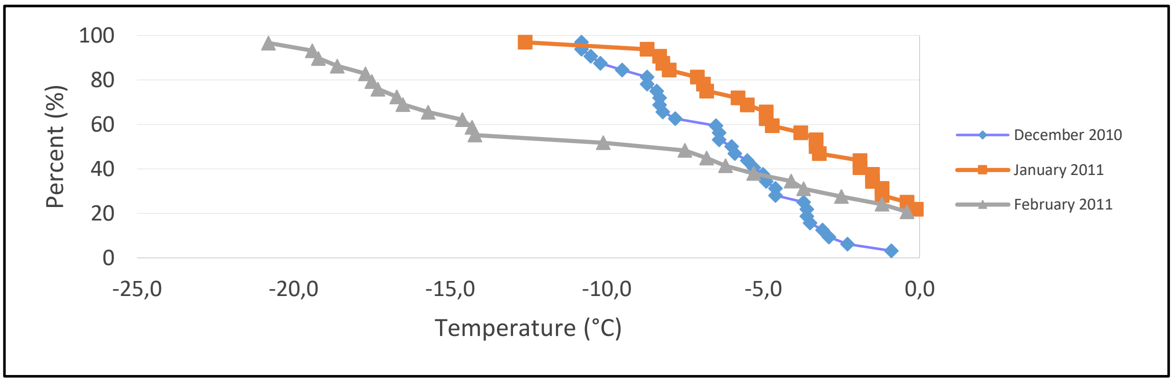


Figure 15. Air temperatures in Tallinn-Harku during permanent cold period in 2010-2011

Average temperatures in Jõhvi during three months varied from -5.2°C up to -11.9°C. December started with relatively cold temperatures with a mode of -9.3°C. The highest peaks of the month were reached at the end of the second decade and the beginning of third decade with temperatures around -12°C. In January 2011 the weather is characterised as periods that were warmer and colder. The temperatures during the month mostly ranged from +1.6°C to -15.8°C. Despite the fact approximately 10% of the month stayed below 0°C. The beginning of February in Jõhvi meteorological station was measured slightly warmer out from the ordinary where temperature fluctuated from 0.5°C to -4°C. With the start of the second decade the ambient condition changed rapidly and the maximum temperature reached up to -25.5°C. The distribution curves of cold temperatures on Jõhvi meteorological station is illustrated in Figure 16.

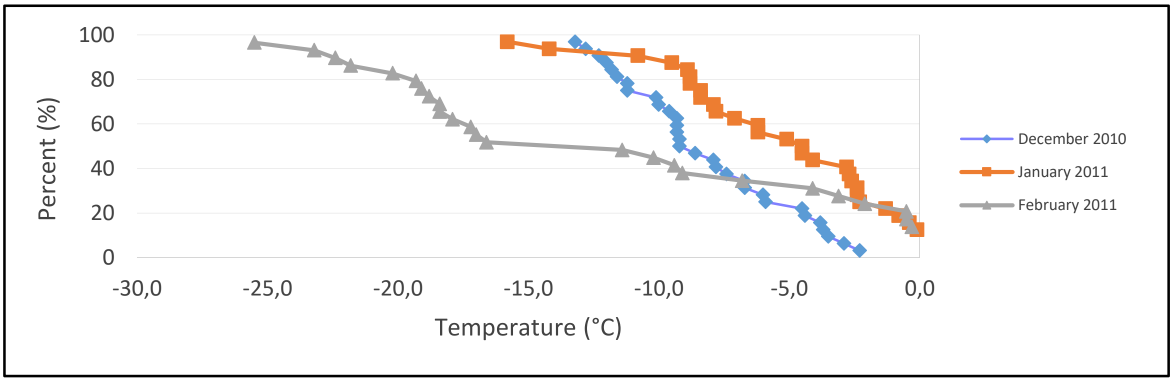


Figure 16. Air temperatures in Jõhvi during permanent cold period in 2010-2011

In Väike-Maarja just as in Tallinn-Harku and Jõhvi all observed temperatures at the last month of 2010 stayed below 0°C. The measured parameter ranged from -1.7°C to -13.5°C with the average of -8.6°C. The permanent cold period continued throughout January where approximately 94% of the time the weather conditions where low. The minimum temperature +1.1°C took place in the last day in the first decade and the maximum temperature -17.2°C occurred in the middle of second decade. The average temperature in Väike-Maarja in January was -5.3°C. February in 2011 compared to previous two months had the lowest mean of -11.7°C. Observed parameters varied from 0.1°C up to -24°C. The coldest period started from the second decade and lasted until the end of the month. The schematic distribution of permanent cold temperatures in Väike-Maarja can be seen in Figure 17.

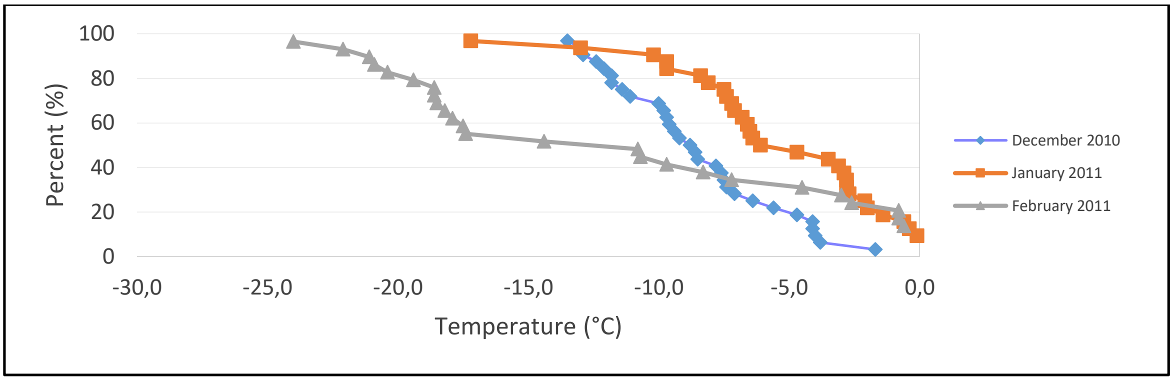


Figure 17. Air temperatures in Väike-Maarja during permanent cold period in 2010-2011.

4.2 The ecological state of rivers

The ecological state of the rivers is assessed based on the concentrations of TN (Table 4) and NH_4 (Table 5) during the hydrological winter seasons in 2008-2009, 2009-2010, 2010-2011. TN refers to all nitrogen compounds in any form. NH_4 is generally a degradation product in water and the presence of the element is aiming towards possible contamination from anthropogenic sources. The quality classes are divided into 5 different sections that provide information about conditions in rivers during permanent cold winter season.

Table 4. The ecological state of rivers based on TN

No.	Name of the hydrochemical station	Type	Parameter	Unit	Concentration		
					2008-2009	2009-2010	2010-2011
1	Leivajõgi: Pajupea	I A	TN	mg/L	6.73	5.18	5.15
2	Alastvere peakraav	I B	TN	mg/L	9.2	10.7	8.1
3	Jänijõgi: Jäneda	II B	TN	mg/L	8.4	7.6	5.9
4	Kääpa jõgi: Kääpa	I B	TN	mg/L	2.1	1.5	-
5	Oostriku jõgi: Oostriku	I B	TN	mg/L	6.6	5.8	2.8
6	Preedi jõgi: Varangu	II B	TN	mg/L	5.3	4.4	3.9
7	Põltsamaa jõgi: Rutikvere	II B	TN	mg/L	4.5	3.8	3.7
8	Räpu jõgi	I B	TN	mg/L	7.7	5.5	6.4

Table 4 continued

No.	Name of the hydrochemical station	Type	Parameter	Unit	Concentration		
					2008-2009	2009-2010	2010-2011
9	Valgejõgi: Porkuni, Oruveski talust põhjasuunas	I B	TN	mg/L	6.1	6.5	2.0
10	Võisiku peakraav (Riivli oja)	I B	TN	mg/L	5.5	3.9	3.8
11	Kunda jõgi: Lavi allikad	I B	TN	mg/L	1.2	-	0.28
12	Porijõgi	II B	TN	mg/L	2.55	1.7	2.0
13	Alajõgi	II A	TN	mg/L	1.2	0.7	1.0

Blue- very good; green - good; yellow - poor; orange - bad; red - very bad

In the winter period of 2008-2009 the concentrations of TN in rivers in all three regions had the ecological state of very good in Kunda and Alajõgi. Good conditions occurred in Porijõgi and Kääpa. The low mean average concentrations are understandable, because these rivers generally have low nutrient content compared to others. Võisiku main ditch, Põltsamaa and Preedi classify under the quality status of poor, which are a part of karst area. 4 rivers out of 13 are considered as bad (Leivajõgi, Oostriku, Räpu, Valgejõgi). In Leivajõgi the possible reason behind bad quality state could be the excessive run-off due to the fact that highest concentrations occurred in December when climatic winter hadn't started. Decreasing concentration trend continued up to February. Alastvere peakraav and Jänijõgi had the highest mean concentrations and are strictly classified as very bad condition.

Permanent cold period of 2009-2010 can be described slightly better than the previous period and the status of some rivers redeemed the status class. Very bad condition occurred only in Alastvere peakraav. In Jänijõgi and Valgejõgi the ecological state was bad. The occurrence of bottom two conditions in previously named rivers can be explained by the pollution load from agricultural areas as well as high nitrogen contamination in groundwater that are affecting surface water quality by the interactions between the two components. The average concentration maintained ecological quality class of poor in following rivers: Leivajõgi, Oostriku, Preedi, Põltsamaa, Räpu and Võisiku. Alajõgi preserved very good, Kääpa and Porijõgi remained in the good status.

Nutrient concentrations in December of 2010, January of 2011 and February 2011 stayed in the same class (poor) in 4 rivers (Leivajõgi, Preedi, Põltsamaa and Võisiku main ditch) that had available monitored data compared to permanent cold period in 2009-2010. Alastvere main ditch from year to year stays in the same concentration frames with a label of very bad conditions although the concentration is somewhat lower, which could lead to the fact that it was colder period and ice coverage occurred sooner than usually. Räpu river average concentration had a slight change of 0.9mg/L automatically positioning into level down (bad ecological status) compared to last period. Oostriku and Valgejõgi had the change into good condition. The low concentration occurrence could result in the weather condition, because climatic winter started relatively early (in December) and rivers were covered with ice.

Table 5. The ecological state of rivers based on NH_4^+

No.	Name of the hydrochemical station	Type	Parameter	unit	Concentration		
					2008-2009	2009-2010	2010-2011
1	Leivajõgi: Pajupea	I A	NH_4	mgN/L	0.387	0.514	0.258
2	Alastvere peakraav	I B	NH_4	mgN/L	0.088	0.093	-
3	Jänijõgi: Jäneda	II B	NH_4	mgN/L	0.059	0.089	0.151
4	Kääpa jõgi: Kääpa	I B	NH_4	mgN/L	0.060	0.124	-
5	Oostriku jõgi: Oostriku	I B	NH_4	mgN/L	-	-	-
6	Preedi jõgi: Varangu	II B	NH_4	mgN/L	-	-	-
7	Põltsamaa jõgi: Rutikvere	II B	NH_4	mgN/L	0.171	0.121	0.080
8	Räpu jõgi	I B	NH_4	mgN/L	0.114	0.127	0.093
9	Valgejõgi: Porkuni, Oruveski talust põhjasuunas	I B	NH_4	mgN/L	-	-	-
10	Võisiku peakraav (Riivli oja)	I B	NH_4	mgN/L	0.063	0.109	0.055
11	Kunda jõgi: Lavi allikad	I B	NH_4	mgN/L	-	-	0.022
12	Porijõgi	II B	NH_4	mgN/L	0.131	0.150	0.112
13	Alajõgi	II A	NH_4	mgN/L	0.196	0.159	0.060

Blue- very good; green - good; yellow - poor; orange - bad; red - very bad

Due to the shortcoming of monitored data the concentration of NH4 is totally or partially absent in 6 rivers (Alastvere, Kääpa, Oostriku, Preedi, Valgejõgi, Kunda) during all the observational periods. Majority of the ecological state varies between very good or good state which could infer that agricultural fresh pollution at colder permanent periods is at minimum. In Leivajõgi the concentrations compared to others is relatively higher. In 2008-2009 the average concentration is labelled as poor, in 2009-2010 as bad and in 2010-2011 the status improved into good. Because Leivajõgi is located near intensive agricultural area the lower quality classes occurred probably due to the lack of organic substance degradation.

Generally the total nitrogen content during cold period don't exceed the EU level of 50mg/L or even the target value of 25 mg/L. The winters of 2008-2011 especially 2010 are considered as good representatives of permanent cold winter seasons, which could describe the ecological state in rivers when precipitation or run-off is not an option and other alternative causes are taken into account for assessing the fluctuation of nitrogen content. The biggest pollution according to the TN numbers can be found in Alastvere main ditch. The concentrations are constantly high regardless of the ambient condition or change in water level. It is a strong karst area with thin surface layer, which refers to the fact that most of the precipitation has infiltrated into groundwater. The amount of ammonia is comparatively low during winter periods, which is understandable due to the fact that agricultural areas are inactive since fall and there is no fresh pollution from agricultural areas.

4.3 Permanent cold winter season duration based on NO_3 concentrations

The meaning behind permanent cold time is non-occurrence of molten period. In Estonia the weather during the winter is generally quite fluctuating, where temperatures can vary even with 30°C amplitude. To assess groundwater quality based on river nutrient concentrations the periods of 2008 December up to February 2011 were investigated as in being a good representatives of drought periods.

The main concept of the idea is to evaluate the distribution of nitrates during the cold winter, where concentrations are higher because rivers are under the coverage of ice and most likely are groundwater fed. Precipitation can't access into water bodies and it remains on the ground as snow. The longer the cold season the lower is the amount of substances. The increase in nitrate content is due to the slowed down process of denitrification, where plants as the utmost users of nitrogen are deactivated. To schematically present the amount of nitrate content in 13 observational rivers and the downward trend during the cold times an illustration (Figure 18) was conducted, where researched objects are gathered. The method relies on hydrological data where the days of cold period were counted since the date that the river was sampled in December 2008 – February 2011. According to the applicable numbers the data was distributed according to the years and days of the cold period. In some rivers the monitoring frequency is slightly higher (Räpu, Jänijõgi, Võisiku, Kääpa, Leivajõgi) providing 1 extra day per yearly period. Trendline was added on all statistical graphs, which proves the decreasing trend in concentration and shows that the data set is linear. All obtainable data is converted with conversion factor from mass balance (4.43) from mgN/L to mg/L in order to compare the results with existing target and limit values and with nearby groundwater monitoring station concentrations if data is available.

From the Figure 18 it can be seen that there is a strong connection between the river and the geographical location. In 5 rivers (Kunda, Kääpa, Alajõgi, Porijõgi) the concentration of NO_3 is considerably lower out of 13, because they are objects that each have their own exception. Kunda Lavi springs are reckoned with regional features. In Pandivere karst area the NO_3 concentrations are lower in the East in slope springs and inversely higher in Southern region. With permanent cold period duration of 25 days the concentration value is measured as 5.3 mg/L and in 65 days it has significantly decreased with a value of 1.0 mg/L. In Kääpa the NO_3 content (mg/L) in 2009 winter is 6.6 (34 days), 5.8 (61 days) and in 2010 4.9 (32 days), 4.4 (57 days). The lower values can be explained by the fact that the catchment area of Kääpa river begins from the bog area that has natural characteristics and the numbers remain in the frames of natural NO_3 concentration (4.4-8.8 mg/L).

Nearby Alajõgi there are cultural grasslands and animal production, which contribute to the low occurrence of NO_3. The decreasing trend can be seen in 2010-2011, where the concentrations are 9.7 mg/L (39 days), 5.8 mg/L (57 days) and 9.3 mg/L (50 days), 5.8 (62 days) respectively.

Figure 18. NO_3 concentrations (mg/L) in 13 observational rivers

Porijõgi is another river with an exception of lower concentrations (8.4 mg/L, 7.5 mg/L, 6.6 mg/L) with decreasing trend during the years of 2008-2011 due to moderate agricultural activities that are out from the borders of nitrate sensitive area. The 5 days permanent period in 2011 occurred in the beginning of December, where climatic winter season started with low temperatures (up to -12°C). Leivajõgi is a river that doesn't qualify under the nitrate sensitive area, but the amount of NO_3 is relatively higher compared to some rivers that are located in the Pandivere or Adavere-Põltsamaa region. The reason behind the fact is the intensive agriculture taking place near Leivajõgi. The decreasing concentrations (mg/L) in 2009 are 18.2 (7days), 12.8 (17days), in 2010 12.6 (25days), 9.4 (53 days) and in 2011 20.5 (5 days), 12.3 (33 days).

The rest of 8 rivers out of 13 under research have significantly higher NO_3 concentrations compared to others. These rivers are mostly situated on the karst in Põltsamaa (Räpu, Põltsamaa, Võisiku, Alastvere) and Pandivere (Oostriku, Preedi, Valgejõgi, Jänijõgi). The most vulnerable areas towards NO_3 pollution are karst regions or unprotected groundwaters, therefore higher values are justified.

In Oostriku the trendline confirms the nutrient diminishing over period of time. After 19 days have passed with permanent cold in 2009 the concentration is 28.8 mg/L. This value exceeds the targets that are set by EU (25 mg/L). In 2010 the concentration is slightly lower (22.6 mg/L) after 57 days have passed and 12.0 mg/L in 2011 after 65 days have passed. Near the monitoring station of Oostriku river a sampling was conducted in Sopa spring groundwater with a 6 days difference. The measured result is 23 mg/L (26.01.2010) which is very close to the value of 22.6 mg/L (01.02.2010) analysed in Oostriku surface water. This example is the idealistic proof material that supports the aim of this thesis. The probability of surface and groundwater interference is high and the groundwater quality is most likely dependent on the ecological state of the river.

Preedi/Varangu river and Valgejõgi monitored results are approximately in the same range as Oostriku. In Preedi the concentration decrease is following 21.7 mg/L (20 days), 17.3 (57 days), 16.4 mg/L and in Valgejõgi 22.6 mg/L (17 days), 21.7 mg/L (57 days), 6.0 mg/L (65 days). None of the maximum values in either of them exceed the permissible limit, but yet very close by missing with couple of mg/L.

Jänijõgi that is located in the intensive agricultural area the concentrations are much higher compared to other Pandivere highland karst area rivers. In years section the amount of NO_3 seems to have decreasing trendline. In 2009 with 33 days of permanent cold the content of NO_3 is 35.4 mg/L, which exceeds the target value with 10 mg/L. In 2010 the concentrations are 26.4 mg/L (29 days) and 24.3 mg/L (57 day). In 2011 the concentration stayed as constant after 5 and 69 days of permanent period. In that year the winter started very early and probably rivers were covered with ice sooner than usual. The longer the winter the more stable is the amount of NO_3 in rivers. The nearest groundwater monitoring station that would describe the local area near Jänijõgi and had available data was Aravete spring. Sample is taken on the 27th of January in 2010 (27 mg/L) and is with 5 days difference from surface water analysis taken on the 1st of February 2010 (24.3 mg/L). Concentrations are very similar due to the fact that Jänijõgi feeds on Pandivere groundwater and due to the interaction the water under the ground is affected by the river quality.

Räpu is one of the rivers that is located on Põltsamaa karst area, where agricultural activities play a big role in contributing the rivers with NO_3 pollution. The highest value during the 3 yearly periods was measured in 2009 with concentration of 32.2 mg/L (14 days) followed by almost 50% decrease (19.1 mg/L) after the amount of cold period days reached to 19. In 2010 the concentration with average value of 19.4 mg/L was constant after 31 days of permanent cold as well as 59 days. Concentrations in 2011 were in the same range with the results of 21.1 mg/L (7 days), 18.3 mg/L (36 days).

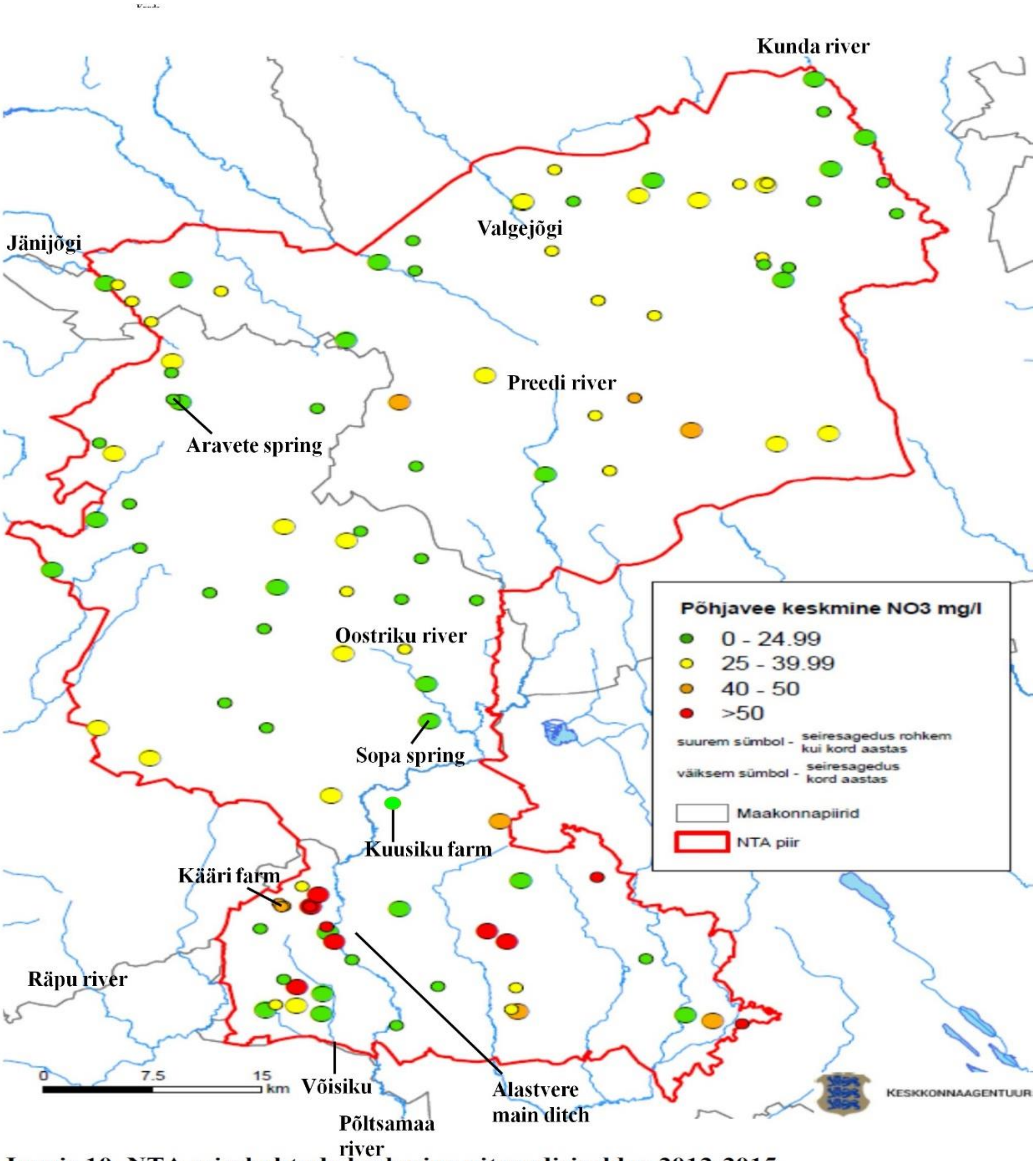
Põltsamaa river is situated in the same district as Räpu. During the years of 2008-2011 the concentration with increasing days of continuous winter is diminishing. The amount of NO_3 in surface water was measured under the target limit of 25 mg/L with values of 20.4 mg/L, 17.3 mg/L and 13.7 mg/L according to longevity of cold days 19, 57, 65 respectively. From monitoring station in Kõrkküla village an analysis was conducted on 26th of January 2010 with the amount of 24 mgNO_3/L. At the same time frame (1st of February 2010) the concentration in surface water was 17.3 mg/L, which is 28% less than in groundwater. The change in the values is based on the size of the water body or sampling site.

Similarly to Põltsamaa river the Võisiku stream is showing decreasing trend in NO_3. In the permanent cold period. The values in 2009 were found to be 22.1 mg/L (34 days) and 20.4 (61 days), which are slightly under 25 mg/L. In 2010 the concentrations are moving little bit downward from previous year and are staying in the close range during long cold period – 17.3 mg/L (32 days), 15.1 mg/L (57 days). The same trend continuous up to 2011 where the results of analyses are 15.9 mg/L (7 days) and 14.6 (65 days). The stable concentration is due to the very long duration of time, where temperatures were below 0°C. From Kalme küla (Kääri farm) groundwater sampling was taken on 26.01.2010 (51 mg/L), when the duration of cold period had been approximately 51 days. The change in surface (sample taken in 1st of February 2010) and groundwater value is approximately 67%. The distance and size between the sampling sites make the comparison complicated. In Kääri farm sample has been collected from the bore hole, that are relatively low and the water originates from upper soil layers, where pollution load is the highest. The river inversely characterizes integrated nitrate concentration on larger land area by feeding on deeper groundwater layers. All in all this is the reason why river concentration is significantly lower than in shallow groundwaters.

Alastvere main ditch is one of the four observational surface water objects that is geographically under the Põltsamaa karst area. The amount of NO_3 during cold winter ranged between 39.6 mg/L (20 days in 2009) to 35.7 mg/L (61 days in 2009) ranking it to the top of the list with high values. All of the data exceeded the target value of 25 mg/L but stayed under the maximum permissible value of 50 mg/L. Besides the fact that it is situated on karst area another indicator of concentration is the presence of pig farm in Alastvere that distributes its organic waste on the field in spring sowing time. The waste is oxidized into NO_3 in the soil, which in turn leads to old pollution occurrence [50].

Any of the concentrations measured in all 13 rivers did not exceed the limit value of 50 mg/L. If EU would officially lower limit value from 50 mg/L to 25 mg/L then the concentrations in Estonia, especially in nitrate sensitive area would almost or totally exceed the set value. In real life scenario lowering the maximum level is not applicable. The problem doesn't consider only rivers but also groundwater that are affected by the surface water quality. The concentrations in water in the bottom of the Earth's crust are found to be higher in some cases than the 50 mg/L (Kalme village – 51 mg/L) limit according to the monitored stations. In Figure 19 the average groundwater concentrations are illustrated in nitrate sensitive area of Estonia, which indicates that majority of the NO_3 values range between 0-

40 mg/L in the Northern part and 0-50 mg/L in the Southern part. From the data analysis it was found that in highland surface water and in well the content of NO_3 is relatively high.



Joonis 10. NTA seirekohtade keskmine nitraadisisaldus 2012-2015.

Figure 19. Groundwater average concentrations of NO_3 during 2012-2015 [51]

It is important to raise awareness about the problem and take action towards better solutions. It is known that most of Estonia is dependent on groundwater as a source of drinking water, therefore it is essential to work towards the aim of best available managing techniques of NO_3 in rivers and groundwater.

4.4 Regional specifics in NO_3 concentrations

In many cases the amount of NO_3 concentration is peculiar to certain regions. In order to manage river water quality the values of NO_3 are used as a tool to determine regional specifics or sources of contamination. The methodology or solution to interpret the results must be presented clearly. The data set consists of NO_3 values during the years of 2008-2011 including all hydrological seasons. All the 13 rivers that were assessed in previous sections are not included in this subpoint. The rivers were handpicked (Kunda, Jänijõgi, Põltsamaa, Alastvere, Kääpa, Alajõgi, Leivajõgi) by their characteristics and geographical locations that would show the variation in best available way. Alajõgi and Leivajõgi will present the Jõhvi and Tallinn-Harku region respectively and the rest of the rivers are presenting Väike-Maarja or more precisely nitrate sensitive area.

The regional specifics will be presented with box and whisker chart that will display the variation within a set of data. In order to graphically construct the data, statistical calculations need to be conducted. The minimum, maximum value from the whole population as well as 10th, 50th and 90th percentiles were calculated using excel functions. The lower and upper whisker is a minimum and maximum value respectively from monitored data. The 10th percentile will indicate that 10% of the data the concentrations are lower and 90% are higher from the found value. The 50th percentile is a median in a data set that eliminates lower and upper values from each other. The 90th percentile provides a value that defines the 10% values that are higher from calculated result and 90% that stay under the computed number.

According to Figure 20 the regional variation is clearly seen and numbers support the features, which have been discussed throughout the thesis. Kunda, Kääpa and Alajõgi are the 3 bottom rivers with lowest concentrations. In Kunda jõgi the maximum concentration during three years is 6.6 mg/L and the minimum value is 0.5 mg/L. With the 10th percentile it is possible to say that about 90% of the values are above 0.7 mg/L and 10% below. The median of 1.5 mg/L separates the highest and lowest values from the middle point. About 10% of the values are higher than 4.4 mg/L and 90% are under. For site specific reasons the concentrations are low.

River Kääpa that is characterised as natural area the maximum and minimum values are 0.2 mg/L and 12.0mg/L. The highest and lowest concentrations are divided by 3.6 mg/L. The

10th percentile is 0.7 mg/L and 90th percentile 9.7 mg/L. In Alajõgi the minimum (0.1 mg/L) and maximum (9.3 mg/L) values are slightly lower than in Kääpa river. Approximately 10% of the values are lower than 0.2 mg/L and higher than 2.7 mg/L with a median of 0.8 mg/L.

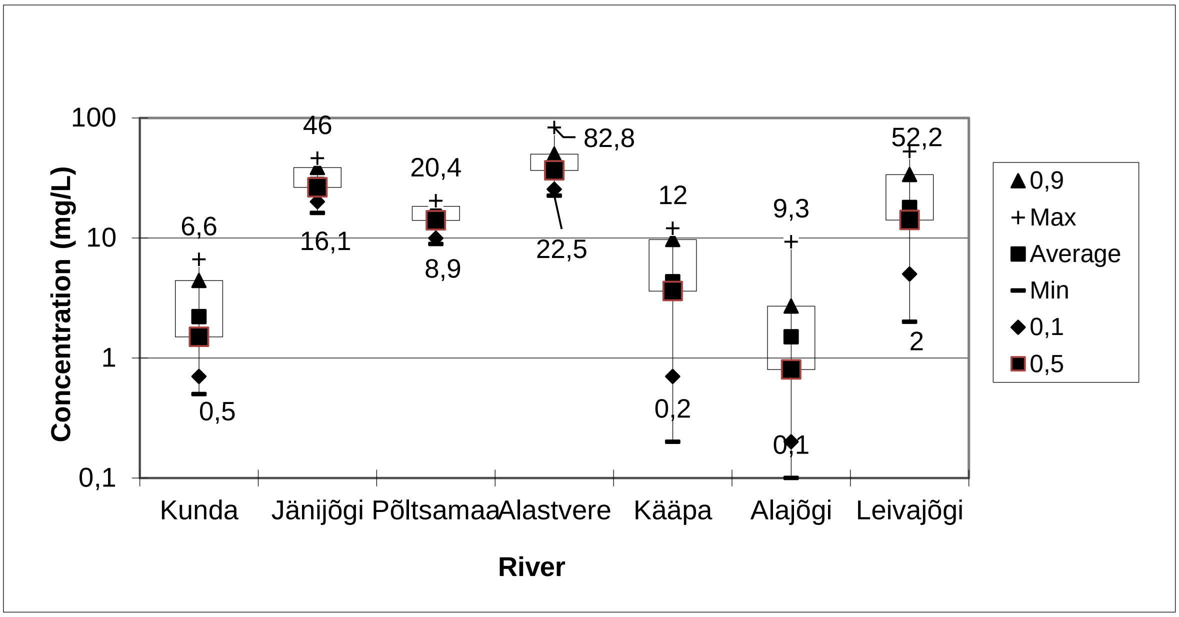


Figure 20. The regional specifics distribution of NO_3 concentration in 2008-2011

Põltsamaa and Alastvere surface water monitoring stations have measured the median of 14 mg/L and 36.5 mg/L both of which are located in the Põltsamaa karst area. The minimum and maximum values in Põltsamaa range between 8.9 mg/L to 20.4 mg/L and in Alastvere from 22.5 mg/L to 82.8 mg/L. In Alastvere the 90th percentile is a parallel with concentration of 50 mg/L that is the limit of NO_3 in water. The difference between the two variables is significant although they classify under the same region.

Jänijõgi that is ranked on the third place according to the graph owns a minimum and maximum value of 16.1 mg/L and 46 mg/L respectively. The median is located slightly below the mean, which refers that there are more upper values than lower values. The 90th percentile indicates that 10% of the values are above 38.5 mg/L and 90% are below the value.

Second largest variation belongs to Leivajõgi, due to the intensive agriculture presence in the area. The minimum and maximum value are as 2.0 mg/L and 52.2 mg/L, which exceeds the permissible value of 50 mg/L. The median (14.1 mg/L) is positioned in the lower part of the chart leading towards an assumption that 90% of the values are lower than 33.7 mg/L and higher than 5.0 mg/L.

As suspected the regional variations are strongly present and the specifics have reached to the surface. Areas that are out of the borders of nitrate sensitive zones (Alajõgi, Kääpa) have significantly lower concentrations, where intensive agriculture or farming are not playing major role. Kääpa river lies outside of the nitrate sensitive area, where usually concentrations are smaller. The measured maximum values are approximately 25% of the 50 mg/L limit value. Leivajõgi is another exception that isn't a part of karst area, but the concentrations and statistical analysis shows elevated values due to the presence of active agricultural activities. In Figure 20 the average is higher from the median, which means that there are more maximum values than minimum. Rivers Alastvere, Põltsamaa and Jänijõgi are all situated in the karst area, which usually leads to higher concentrations, with a highest value of 10.7 mg/L.

In order to harmonize the regional specifics a good management plan and renewed technologies need to be applied. Agricultural activities clearly can't be stopped, otherwise situation would turn its course, where there are large food shortages. In Estonian nitrate sensitive area concentrations in Southern part are somewhat higher than in the Northern part. Majority of the rivers are located near agricultural or farming areas, which also lead to increase in NO_3 content. Good agricultural practice manual provides many solutions for farmers and production sites with the aim of maintaining the healthy environment and natural resources. Environmental management system technique is not wide spread amongst farmers. Applying it in every agricultural production site would probably help to make some changes in decreasing NO_3 concentrations.

SUMMARY

The nutrient occurrence and concentration in water bodies have been a problematic field for years of time. During the Soviet Union period agriculture and farming was major part of normal everyday life. After the collapse in the 1990s there was decreasing trend in previously named activities. With EU overtake in 2004 a new wave of opportunities entered to the market in terms of finances, which led to the increase of intensive land cultivation. Nowadays renewed methods, *e.g.* mineral fertilizers, are available in order to reduce inexcessive pollutant leaching.

The seasonal variation and patterns have an effect on the quality of water. The conventional agricultural activities in Estonia take place in early spring ending up in the middle of the fall and are on hold for months in time. The inactive period is called permanent cold winter season. This particular time is under interest due to the fact that the vegetation and flow of water has been slowed down. The period under study involves 3 hydrological winter seasons from December 2008 – February 2011 in 3 regions (Tallinn-Harku, Väike-Maarja, Jõhvi). As a matter of fact Väike-Maarja hydrological station air temperature monitored statements were used to describe the nitrate sensitive area in Estonia over specified period of time. The objective of this thesis focused on investigating the duration of cold period in winter and the change in nutrient concentration while drought season in rivers and groundwater.

N_2 compounds are abundant for aquatic ecosystems and are necessary in rather low quantities. There are many chemical forms of N_2 that are presence in water bodies and each of them indicate towards different factors. In this thesis the amount of TN, NH_4^+ were assessed to seek out information about the ecological state of 13 rivers during permanent cold season. The TN content in rivers is relatively high in karst areas, where the soil layer is thin and due to intensive agricultural activities nearby the water quality is easily affected by pollutants. The highest values were detected in Alastvere main ditch (10.7 mg/L). The good and very good state is present mainly in rivers (Kääpa, Porijõgi, Alajõgi) that are geographically out of the borders from nitrate leaching fields. The natural concentration of NH_4^+ is very low in bodies of water and the increase in concentration directly pinpoints to the fresh pollution from anthropogenic sources. The majority of the rivers gained a good or

very good status class, which is explainable by permanent cold period, where rivers are covered with ice and surface run-off cannot occur.

The aim of current thesis is to find proof for hypothesis that states that during drought periods the water quality of rivers should mirror the groundwater quality on the example of nitrate concentrations. The limit value of 50 mg/L for NO_3 is set by EU as well as the target value that is exactly half less (25 mg/L) from the latter value. Regional specifics as well as location of agricultural areas largely characterize the concentration pattern trends in NO_3. In nitrate sensitive areas the concentration approximately varies between 12-40 mg/L, which quite often exceeds the target value, but doesn't reach the limit.

In 4 areas it was possible to compare the available data in rivers as well as groundwater, where the values were very similar 75% of the time. In Oostriku river the surface water was sampled with a value of 22.6 mg/L and in groundwater of Sopa spring 23 mg/L. Jänijõgi that is situated on intensive area had a measurement of 24.3 mg/L and in Aravete spring the groundwater received a value of 23.5 mg/L. The comparison of these numbers strongly support the hypothesis that was formulated previously. The permanent cold in both had lasted for approximately 57 days, that results in slightly lower concentrations and the river is most likely fed by groundwater. In Võisiku main ditch the concentration between groundwater (51 mg/L) and surface water (15.1 mg/L) differs quite a lot, which can be explained by the possibility of old pollution occurrence in groundwater. In Põltsamaa region the monitored data in groundwater and surface water was 24 mg/L and 17.3 mg/L respectively. Reasoning behind the variation of ~6 mg/L can be the fact that Põltsamaa river is under type II B watercourse, which means that the NO_3 concentration characterizes large catchment area and the concentration could be slightly lower.

According to the research conducted in the thesis there is strong relation between permanent cold period and decrease in nutrient concentration. The hypothesis that was set by the author found an evidence, during the comparison of the values, which leads to final conclusion that the quality of river is affecting the quality of groundwater during permanent cold winter period.

KOKKUVÕTE

Kasvava majanduse ja tootmisega põllumajandusvaldkonnas on väetiste kasutamine tekitanud probleeme pinna- ja põhjavee kogumites. Suure osa panusest annab omalt poolt kaasa aastaaegade vahetus, mis muudab vee füüsikalis-keemilisi tingimusi. Talvine kestev külmaperiood aastatel 2008-2011 oli peamiseks vaatluspunktis Põhja-Eestis, kus valiti 3 hüdroloogilist seirejaama (Tallinn-Harku, Väike-Maarja ja Jõhvi) klimaatilise olukorra hindamiseks. Nitraaditundlik ala Eestis asub Pandivere ja Adavere-Põltsamaa piirkonnas ning peamine fookus on adresseeritud just antud regioonile koos mõne erandiga eemalolevatest asukohtadest.

Peamine eesmärk antud magistritöö raames on uurida püstitatud hüpoteesi, mis põhineb teoorial, kus pikaaegsel külmal madala vooluga perioodil on võimalik jõevee kvaliteedi alusel hinnata põhjavee seisundit. Kestev külmaperiood on aeg, kus maapind ning jõed on külmunud ja sademed üldjuhul ladestuvad maapinnale lumena. Seetõttu ei saa toimuda infiltratsiooni maapinda ning jõgede veerežiim ei toitu sademetest. Antud lähenemine on mitmeti uudne suund hüdrokeemiliste seireandmete analüüsil.

Töö põhineb seireandmete analüüsil, kus hinnatakse lämmastikusisaldust jõgedes ning põhjavees. Talvise kestva külmaperioodi seireandmete analüüsist selgus, et ökoloogilised tingimused 13 uuritud jões kogu lämmastiku sisalduse alusel on enamasti kesises, halvas või väga halvas klassis. $NH4^{+}$ sisaldus, mis üldiselt viitab värskele reostusele jäi heasse või väga heasse klassi. NO_3^- sisaldus jõgedes on regiooniti varieeruv, kuid tugevalt on mõjutatud karstialad, ning piirkonnad, kus esineb intensiivseid põllumajanduslikke tegevusi. Kontsentratsioonid jõgedes jäävad tihti sihtväärtuse piirnormi (25 mg/L) vahetus lähedusse või alla selle, kuid esineb mõningaid erandeid, kus väärtused küündivad 40 mg/L ligilähedale (Alastvere peakraav).

Uurimustöö käigus vaadeldi 4 seirejaama, kus oli mõõdetud nitraaditundliku ala põhjavee NO_3^- sisaldust. Tulemused viitasid tõsiasjale, et pinnavee NO_3^- sisaldus jõgedes ühtib suures plaanis põhjavee seire andmetega. Uurimustöö esimeses pooles püstitati hüpotees, mis leidis analüüsi lõppedes kinnitust. Mida kestvam külmaperiood, seda madalamad kontsentratsioonid, mis tähendab, et pikal perioodil jõed toituvad põhjaveest mõjutades samaaegselt viimase kvaliteeti.

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