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Eutrophication Study of Lake Liesjärvi

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<p>Vesistön rehevöitymisellä tarkoitetaan orgaanisten eliöiden määrän kasvamista sen luonnollisen sietokyvyn ylitse. Rehevöitymistä aiheuttaa ravinteiden epätasapaino, jolloin vedessä on enemmän ravinteita, kuten fosforia ja nitraatteja, kuin mitä vesistön eliöt kuluttavat. Epätasapainon seurauksena vaatimattomammat kasvit ja eläimet lisääntyvät, ja elinympäristöltään vaativammat lajit katoavat.</p> <p>Tässä tutkimuksessa käydään läpi rehevöitymisen taustaa ja kemiaa. Saatua tietoa sovelletaan Etelä-Suomessa sijaitsevaan Liesjärveen. Kyseinen järvi on valittu tutkimuksen kohteeksi, sillä osittain sen ranta-alue on rauhoitettu kansallispuistoksi, mutta järven valuma-alueella on 2010-luvulla avattu turvekaivanto.</p> <p>Vedenlaatuanalyysia varten Liesjärvestä nostettiin näytteitä vuoden 2014 helmikuussa viidestä eri kohdasta. Näytteiden ottopaikat valittiin järven sisään- ja ulosvirtaamien, ja keskikohdan mukaisesti.</p> <p>Paikan päällä oli mahdollista mitata järven lämpötila, sähkönjohtokyky, happipitoisuus ja pH -arvo. Laboratoriotutkimuksissa mitattiin kemikaalien hapenkulutus, fosfori-, nitraatti-, nitriitti-, kloridi-, ja sulfaattioksidipitoisuudet. Kemiallinen hapenkulutus mitattiin hapettamalla näytteet käsittelyn jälkeen permanganaatilla ja ravinteiden määrä mitattiin ioninvaihtokromatografilla.</p> <p>Tutkimuksen tuloksia verrattiin toisiinsa ja aikaisempina vuosina tehtyihin mittaustuloksiin. Analyysin tuloksena todettiin, että veden laadussa ei ole tapahtunut merkittäviä muutoksia 50-vuoteen. Liesjärvi on siis edelleen hyvässä kunnossa, joskin se on vieläkin alueelle tyypillisesti lievästi rehevöitynyt.</p>	
Avainsanat	Rehevöityminen, järvi, vesitekniikka, veden laatu, veden laadun testaus, vesianalyysi, veden ravinteet

Abstract

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<p>Eutrophication is defined as a greater inflow of nutrients to an aquifer than is consumed. Excess nutrients cause over population of lower-quality organisms, thus decreasing the quality of water. When the living conditions worsen, the more demanding quality vegetation and fauna disappear.</p> <p>This research project studied about the chemistry and effects of eutrophication. Gained information was applied to Liesjärvi lake that is located in Southern Finland. This lake was chosen due to a natural park and a recently opened peat swamp dig site located within the drainage basin.</p> <p>The sampling for this project was done in January 2014. There were 5 sampling points selected at the inflow and outflow points of water and also in the middle of the lake.</p> <p>In situ measurements included temperature, conductivity, dissolved oxygen quantity and pH. Chemical oxygen demand (COD) and nutrient content was measured in a laboratory. Measured nutrients include phosphorus, nitrate, nitrite, sulphite oxide, and chlorides. COD was measured by oxidizing pretreated samples with permanganate, and nutrients were measured with ion exchange chromatographer.</p> <p>The results were compared with each other and with those of previous measurements. Analyses showed that Liesjärvi's water is of good quality, and the quality has remainder the same for the last 50 years. The lake is mildly eutrophicated, which is typical or humus, rich waters.</p>	
Keywords	Eutrophication, water quality study, water engineering, lake, surface water, water quality, water nutrients, water sampling

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1 Nomenclature

<i>biodiversity</i>	the variety of organisms in a selected area.
<i>bio manipulation</i>	gained by calculating changes to the ecosystem by adding or removing species
<i>decomposition</i>	happens when organic matter breaks down into simpler forms. Plantation decomposition starts with water leaching, where soluble carbon compounds are liberated. Afterwards decomposition occurs by fungi and bacteria. Different compounds decompose in different rates for it is dependent on their chemical structure.
<i>delay time</i>	the time between two occurrences
<i>dredging</i>	excavation activity that happens at least partly under water. It is used to remove debris and sediments from the bottom of a surface water area.
<i>ecosystem</i>	defined as the interaction of the organisms as a group and with their surroundings. It is a complex system that considers all the relationships between and amongst living and non organic material within a system.
<i>endangered species</i>	those species that are likely to become extinct.
<i>eutrophication</i>	the growth of vegetation above sustainable limit of an ecosystem.
<i>hypolimnetic/ hypolimnion</i>	the bottom layer of a thermally stratified lake. Water is non-circulating and permanently cold.
<i>inflow</i>	the source of water to a water body
<i>macrophyte</i>	a plant that grows in or nearby water and is emergent, sub emergent or floating.
<i>nutrients</i>	substances that give energy and are vital for growth and repair.
<i>outflow</i>	the exit point of water of a water body
<i>peat</i>	formed from partially decomposed plants and organic matter. Peat lands are known for their very high CO ₂ content and are harvested as an energy source. Peat is not considered as a renewable source of energy due to slow regeneration time.
<i>photosynthesis</i>	the process of plants, where CO ₂ and water is converted into

<i>redox reaction</i>	sugar and oxygen by using sun light as an energy source defined as a change in an atoms oxidation state. Oxidation means the loss of electrons and reduction is the gain of electrons
<i>retention time</i>	in hydrology is the time that water takes to flow from inflow to outflow point.
<i>runoff area/ catchment area</i>	the total area where water flows into a water body.
<i>sediment</i>	forms the bottom layer of a water body; it is formed from any naturally settled material like dirt and plant debris.
<i>settlement time</i>	the time that it takes particles to fall onto the bottom of a water body
<i>sustainable development</i>	defined by United Nation World Commission on Environment and Development as 'development that meets the needs of the present without compromising the ability of future generations to meet their own needs'. [1]
<i>trash species</i>	organisms that have low requirement for their living environment.
<i>trophic state</i>	the weight of biomass in a water body.

2 Introduction

When an aquifer has a higher nutrient content than consumption the vegetation starts to grow. The overgrowth of vegetation is known as eutrophication and it is one of the signs of decrease in water quality.

When nutrients, like nitrogen and phosphorus, is consumed by overgrown vegetation oxygen demand increases. As the oxygen is consumed by plants the biodiversity suffers and simplifies. Symptoms of an eutrophicated aquifer include vegetation overgrowth, high oxygen demand and lack of quality species.

In this case study thesis the effects and symptoms of eutrophication are discussed and the gained information is applied to a small Finnish lake called Liesjärvi. This lake was chosen to this case study because Liesjärvi is part of European Union's Natura 2000 programme due to its environmental purity, but the water quality might be compromised by a newly opened peat swamp located within the catchment basin

Natura 2000 –programme is designed by the European Union to protect Europe's most endangered and valued species, such as the flying squirrel for example. Part of the programme is to ensure sustainable development within and around a Natura 2000 site to ensure longevity of rare species.

The biggest influence to Liesjärvi water quality originates from VAPO energy manufacturer, who have opened a peat swamp digging site 6 kilometres to the north-east of the lake in 2010. This peat swamp called Rinnansuo has a direct water flow to Lake Liesjärvi. Due to this direct passage, it is important that any leakages from the swamp site are purified.

Previous Liesjärvi water quality study was done in 2005, as a part of a municipal lake water quality research project called Järki -Programme. The project investigated the quality of all the lakes around Häme municipality and found Liesjärvi to be in good condition albeit mildly eutrophicated. [1]

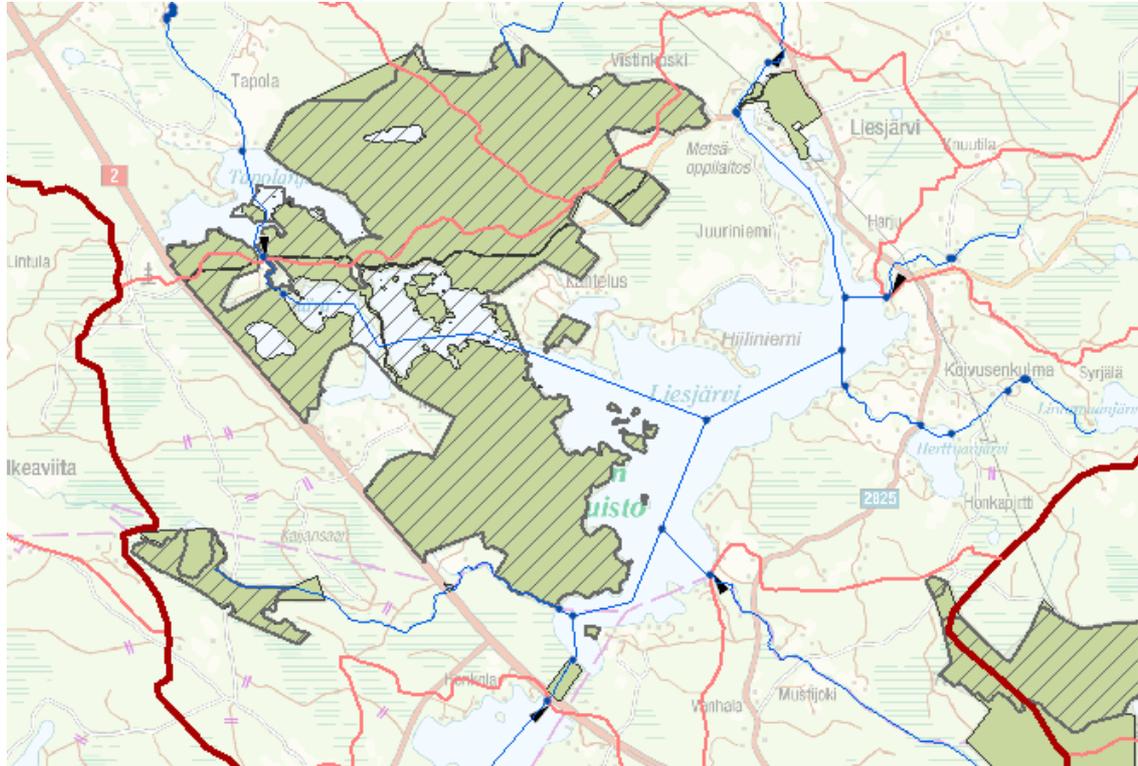
To prevent excess vegetation growth, it is important to continuously monitor Liesjärvi's water quality. Increased phosphorus and nitrogen levels have to be noticed before they

set any permanent changes to the lake. Peat swamps are very high in nutrient content therefore it is even more important to mitigate any possible leakages.

Visible changes take years to occur, and it is very time consuming and costly to return the lake to the previous state after it has been compromised. As the quality of the lake decreases, so does the estate values because the landscape has altered. Therefore, it is not only the interest of environmental preservation but also capital value that motivates protection of Liesjärvi.

3 Lake Liesjärvi

Liesjärvi is located in Tammela municipality, South Finland (Picture 1). It is the greatest lake in River Loimijoki water system and is the central lake of Turpoo area. The coordinates for Lake Liesjärvi are: longitude 60.670217° and latitude 23.909500°.



Picture 1 Water inflow and outflow points, and Natura 2000 area.

The last comprehensive study was done for JÄRKI –project in 2005, which surveys the current status of lakes in the Häme municipality area. The research concluded that Liesjärvi is in a good condition.

The surface area of Liesjärvi is 883 ha and volume is $26.5 \times 10^6 \text{ m}^3$. The length of the lake is 7.4 km and the greatest width is 4.5 km. Liesjärvi has a relatively smooth lake bottom surface and is shallow; the deepest point is 12 m in Bay Hiiliniemi's basin. The average depth of the lake is 3 metres. It has 54.7 km of shoreline from which 7 km belongs to islands. [1, 3]

Liesjärvi's runoff area is 5.972 ha, with 73 % forests, 18 % aquifers, 3 % agriculture, 3 %, housing, and 1 % other in 2005. A notable usage for shore line is summer cottages. Part of the inflow area is included in the Natura 2000 network.

Historically, Liesjärvi was used to transport trees, but all industrial usage ended in 1979. There has been water level regulation due to this, and there are still some signs of changing water level on the shorelines. The earliest water quality tests date to 1969, but the annual measurements have started only in the late 2000 century. The results of these measurements have been quite consistent: water quality is good albeit slightly acidic and mildly eutrophic. [1,3]

3.1 Lake ecology

Geology, climate and soil usage determines the water composition of a lake. The shape, size and depth influence water flow direction, velocity and settling times. If the lake has many multiple bays and capes, and is also shallow, there are many settling points and the current does not flow with high velocity. All that happens around a lake's catchment area influences the water composition, especially industrial and residential areas.

Suspended particles originate from inflowing rivers, resuspension of sediments, shore erosion, and production of organic material. Bed sediments are resuspended and settled depending on the water currents and wave action.

Organic debris contains degraded parts of dead organisms and faecal material. There is also suspended dust and sand in the flowing waters. The relationship between particulate matter and the sediment characteristics with respect to particle size and organic matter content play a significant role in a lake's carbon cycle functionality. If a lake is shallow and eutrophic, there is usually net P transport during summer when orthophosphates are released from sediments. [4]

Seasonal variation in the life cycle creates differences in the composition of water. Nutrient concentration is highest during winter due to vast amounts of plantation debris that is left to decompose in the water in the autumn. During summer nutrient content is low after a vast growth phase in the spring.

Phosphorus content also depends on the inflow rate of rivers and waste water. If the total phosphorus level is less than 0.5 mg/l, there is no significant variation between winter and summer concentrations. [1]

3.2 Hydrology, flora and fauna of Lake Liesjärvi

Crucial element to the surface water ecology is sunlight that is crucial for photosynthesis. With sunlight, green plants are able to grow and produce oxygen. [1]

Water flow in lakes varies from 0.001 to 0.01 m s^{-1} . Water velocity is positively related to water discharge and the slope gradient of the water level and is inversely related to the roughness of water bed. Liesjärvi has a runoff area that is about 130 m^2 . Outflow from the lake happens through River Turpoonjoki to Lake Kuivajärvi. The theoretical delay time for water is 360 days. [1]

Due to the protective nature of the Natura 2000 –programme, Liesjärvi area is rich in flora and fauna. Many different animals live there due to diverse and clean living conditions.

There are several different kinds of birds in the area: black woodpecker, great spotted woodpecker, three-toed woodpecker, gray spotted woodpecker, and lesser spotted woodpecker. Chaffinches, willow warblers, redwings, spotted flycatchers, and robins are the most common birds in the national park. Black-throated diver can be heard throughout summer (Picture 2) and red necked grebes and whooper swans like to nest in the bays. Moose and white-tailed deer can be seen in the forests. An endangered flying squirrel resides at the site.



Picture 2: Black-throated diver. [4]

Most common fish in Liesjärvi are perch, ruffe and roach. These are known as trash fish as they can be found in lesser quality waters. There are also sweet water clams living in the bottom of the lake. Clams live in good condition aquifers, thus their disappearance would be a sign of decrease in water quality. [3]

Liesjärvi has 52 different kinds of water plant species. From these, 11 live in meso-eutrophic waters and 5 in eutrophic waters. Some of these plants do not originate in rough or humus waters. Recently-entered species are water fever (*Elodea canadensis*) (Picture 3), duckweed (*Lemna minor*), blunt-leaved pondweed (*Potamogeton obtusifolius*), arrowhead (*Sagittaria sagittifolia*), Elantine hydropiper (*Elatine orthosperma*), long-leaved hook moss (*Drepanocladus longifolius*), ja crystalwort (*Riccia fluitans*).



Picture 3: *Elodea canadensis* [5]

Elantine hydropiper has been observed in five different places that have increased vegetation growth. Yellow iris (*Iris pseudacorus*) and acute sedge (*Carex acuta*) are typical plants for eutrophicated shallow waters, and there are small amounts of them growing in Liesjärvi (Picture 4). Moss (*Drepanocladus sordidus*) and long-leaved hook moss (*Drepanocladus longifolius*) are also signs of eutrophication.



Picture 4: *Carex acuta*

There is no sign of significant growth of plants that are typical for strongly eutrophicated areas. There is only one eutrophication indicator plant growing: duckweed, and only in small number.

There are two endangered plant species in the lake; fontinalis moss (*Fontinalis Diche-lymoides*) and elantine hydropiper. Both of these plants can be found on the northern side of Hiiliniemenlahti and the later in Taipaleenlahti. Water lobelia (*Lobelia dort-manna*) (Picture 5), elantine hydropiper, spring quillwort (*Isoëtes Echinospora*), lake quillwort (*Isoëtes lacustris*), and water awlwort (*Subularia aquatica*) are part of Finland's international responsibility for threatened species. All of these can be found in Liesjärvi. [1, 8]



Picture 5: Lobelia dortmanna [6]

4 Legislations

To ensure protection and fair usage of our resources legislations have been set in place by the Finnish government and European Union. All EU member states must develop the EU directives into local laws and regulations within a certain period of time. Typically nations have set stricter legislations than what is advised in EU directives.

4.1 Water resource legislations

Finland has set several protective legislations to ensure that the quality of our waters is consistently at least good in the water bodies of the country. Many of these legislations are based and abrade on the Act of Water Resources Management.

Act on Water Resources Management (1299/2004, Finlex)

The aim of Water Resources Management act is to protect, improve and restore waters thus ensuring that surface and ground water quality does not fall below good. It supplies conditions for water resources management and for the related analysis work, resources management and related international cooperation in water resources management. The act does not only focus on the quality of water but also on sufficient and sustainable use.

Government Decree on Water Resources Management (1040/2006, Finlex)

This act sets provisions on the accounts to be included in a water resources management plan, on the assessment and monitoring of the status of water, and on the preparation of a water resources management plan

Government Decree on Water Resources Management Regions (1303/2004, Finlex)

This act determines water resources management regions, coordinating regional environment centres, cooperation groups and their duties, steering group and coordination, and measures in international water resources management regions.

4.2 Controlling water pollution and hydrological engineering

Legislation designed to prevent the pollution of water bodies is included in broader environmental protection statutes that came into force in the year 2000.

Environmental Protection Act (86/2000, Finlex)

Environmental Protection Act is the most central environmental legislation. Its objective is to prevent environmental pollution, to repair and reduce damage caused by pollution, to ensure an environment that is healthy, pleasant and rich in biodiversity, and to prevent and mitigate generation and effects of harmful waste.

Environmental Protection Decree (169/2000, Finlex)

This decree is an addition to the Environmental Protection Act that adds details to the activities where a permit is a requirement.

Decree on Substances Dangerous and Harmful to the Aquatic Environment (1022/2006, Finlex)

The base of act 1022/2006 is the Environmental Protection Act 86/2000, and it is designed to protect surface waters and improve their quality by preventing and minimizing effects of harmful and dangerous substances.

Government Decree on Urban Waste Water Treatment (888/2006, Finlex)

The base of act 1022/2006 is the Environmental Protection Act 86/2000 and Water Services Act 119/2001. It sets the requirements for urban waste water treatment.

Government Decree on the restriction of discharge of nitrates from agriculture into waters (931/2000, Finlex)

Finland's Nitrates Decree is based on the EU Nitrates Directive, and controls the use of nitrate fertilisers in all farms across the country. It also sets the base to act 1022/2006 and the Environmental Protection Act 86/2000 and implements them into the restrictions of discharge of nitrates from agriculture.

Act on Water Services (119/2001, Finlex)

The aim of this act is to provide pure water and sewage to all households.

5 Eutrophication

Eutrophication is caused by increased nutrient levels in aquifers. It is one of the significant features in water quality studies, especially when natural surface waters are being studied. The condition of an ecosystem can be described by its trophic state, i.e. the degree of eutrophication or the lack of it.

There are three different trophic states:

1. Oligotrophic: low productivity ecosystems
2. Mesotrophic: intermediate productivity ecosystem
3. Eutrophic: high productivity ecosystem.

Eutrophication increases biomass production and diminishes biodiversity. Excess nutrients are consumed by water weeds and algae. Algal blooms and water plant growth change the water quality and living conditions. As the quality of water decreases, more sensitive organisms start to disappear.

Extra plant growth consumes more oxygen than what is produced by photosynthesis, thus decreasing the amount of dissolved oxygen (DO). Plants floating on the surface prevent aqueous photosynthesis, which also lessens DO.

The excess growth, such as phytoplanktons and weeds, eventually die and settle in to the sediments. As the oxygen is consumed by decomposition, DO-levels drop on the bottom layer of lake. Sediment oxygen demand (SOD) is therefore high in deep places of reservoirs where the amount of dissolved oxygen is low.

Dissolved oxygen is produced by phytoplankton during the day but is consumed during night time. If there is excess amount of algae more oxygen is consumed than produced, and this will cause oxygen depletion. Due to the lack of oxygen, more surrounding sensitive species will suffer and disappear from the ecosystem. Therefore, it is important to measure the dissolved oxygen to analyse the quality of water.

Due to increased macrophyte growth, water flow changes in velocity and route. This will change its channel carrying capacity, aeration and navigation. Plantation growth will also have an effect on the aesthetics of the aquifer with algal mats and decaying vegetation, which causes change in odour and colour. This decreases the market value of the site.

Certain algae blooms are hazardous to human health: blue algae (cyano bacteria) cause liver damage, for example. Decomposition increases growth rate of harmful bacteria and the amount of particles in the water.

Plants and particles on the water body's surface prevent necessary sun rays entering the water, thus obstructing photosynthesis. Therefore there is less of oxygen production and only species that require low oxygen containing surroundings can survive.

It is quite clear that eutrophication is a self-feeding system that only needs a small change in the ecosystem in order it to start. In nutrient rich environments, it is natural to

have eutrophicated surroundings, but those that are still mesotrophic should stay as such.

The amount of nutrients depends on the yearly life cycle. During the growing season nutrients are absorbed from waters therefore the concentrations are lower than normal in the spring. In the autumn' vegetation causes a lot of organic debris which increases the water nutrient content when it decomposes. Hence the nutrient concentration is typically higher during the winter than summer; all nutrients released from decomposed nutrients are stored under a layer of ice and not consumed by growing organisms. [3]

There is a peak in the water flow rate during the spring. This is due to melting snow and rainwater both entering waterways. As the upper ground is still frozen from winter, it does not absorb water as well as during summer, which also increases the amount of flowing water. All loose organic material flow to the lakes and rivers during this peak. Therefore, there is also a peak in the nutrient content.

5.1 Phosphate

Phosphorus is most commonly found in natural waters, waste waters, sediments, and sludge. Anthropological sources include fertilizers, several detergents, and cleaning solutions. It is released to waters from waste water discharge, fertilizer leakages and soil erosion.

Phosphorus is used in the production of vital proteins like DNA. It has a part in transformation of cells, early root growth stimulation, and in fruit and seed production. In animals it is a part of teeth and bone growth in the form of calcium phosphate.

Natural source of dissolved inorganic phosphorus is mineral apatite. In pH 7 or higher phosphates precipitate as calcium phosphate. Typically P concentrations are twentieth smaller than nitrogen or potassium. [1, 10]

Table 1 Typical phosphorus concentrations of surface water [1]

	Surface water P mg l ⁻¹
Total P	–
TP (< 0.45)	0.01 – 2.1
RP (< 0.45)	0.003 – 1.9

Table 1 shows typical phosphorus concentrations of surface water. Where TP is total phosphorus, describing both inorganic and organic species, and RP is reactive phosphorus. The number in brackets is filter density in μm .

Dissolved phosphorus is consumed by primary producers and some bacteria. As much as 60 % of organic phosphorus is in molecular compounds, but some of it is in humus polymers. 'In general, the soil organic phosphorus correlates well with organic matter content and organic nitrogen, but the C: organic P ratio displays more variation than the C:N ratio, because organic phosphorus is less associated with large humus polymers than organic nitrogen'. [4]

The availability of phosphorus depends on pH, redox conditions and organic matter content. Most efficient pH for plant uptake is between 6 and 7 or under anaerobic conditions.

Phosphorus content also depends on the inflow rate of rivers and waste water. If the total phosphorus level is less than 0.5 mg/l, there is no significant variation between winter and summer concentrations. If the total phosphorus level is higher, P levels are three times higher during summer than in winter. [4]

5.2 pH

Hydrogen ion $[\text{H}^+]$ concentration in aqueous solutions is called pH. Acids increase hydrogen concentration when dissolved in water, and base solutions counteract: they accent hydrogen ions.

In a neutral solution pH value is always 7. In an acidic solution the value is less than 7 and in a basic solution it is greater than seven.

Primary producers produce carbonic acid in photosynthesis which increases pH -value. Also high level of carbonates and non-limited growth of algae cause rise in pH. Most lakes have neutral or mildly basic pH value between 6-7. [10]

5.3 COD

Chemical oxygen demand is commonly used in water quality measurements as an indicator of organic compounds in surface or waste water. It is defined as 'a measure of the oxygen equivalent of the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant'. These organics include humus, wastewater, manure or leakages. [11]

COD has been proven to have a relationship with biological oxygen demand (BOD), which is the measure of the amount of oxygen consumed by bacteria. The correlation has to be first established in every sample; therefore BOD is not measured in this research.

COD is greater than BOD but less than 20 mg in unpolluted waters. [12]

Lake Liesjärvi's average COD value is 14 mg l^{-1} and increases when measured closer to the bottom due to organic deposit. Decomposition of organic material increases COD during winter.

5.4 Nitrogen

The main forms of dissolved nitrogen are nitrate (NO_3^-) and ammonium (NH_4). Nitrite (NO_2^-) is also a very common nitrogen compound in waters. Sources of nitrates and nitrites are typically fertilizers and from tree cuttings. Ammonium is a typical sight of manure, 83 % is produced from decomposition of manure, and is usually sourced from runoffs from farms or human waste stations.

Nitrogen is one of the main components in nucleic acids, proteins and plant chlorophyll. In high concentrations inorganic aqueous nitrogen is toxic to plants, animals and hu-

mans. Typical nitrogen concentrations can be seen in table 2. Excess amounts of nitrate or nitrite can cause a fatal blood disorder called methemoglobinemia in infants, and ammonia is toxic to plants in soil and fish in waters. Nitrogen is also one of the causes of eutrophication. [4]

Table 2: Typical nitrogen concentrations in surface water [1]

	Surface water N mg l ⁻¹
Total N	0.56 – 17
NO ₃ ⁻	0.04 – 10.5
NH ₄	0.004 – 7.5

Nitrogen in the form of ammonium and aqueous nitrate is consumed by primary producers and bacteria. The absorption of nitrogen by plants and bacteria is called nitrogen fixation. It can occur only in waters that have temperature above 10 °C and a pH between 6.6 and 8. Therefore, during early spring, late autumn and winter, there is no nitrogen fixation. Thus, nitrogen concentrations are higher during winter than during summer.

Ammonium's toxicity causes it to be quickly transformed into organic nitrogen in waters. Organic nitrogen is released during decomposition. 'Nitrate is toxic to human health, and chronic exposure to high concentrations of nitrate may cause methemoglobinemia'. Maximum limit in US is 10 mg nitrate as nitrogen [10]

5.5 Lake restoration methods

In the 1950's, eutrophicated lakes were restored by using fire service pumps to mix oxygen to the water. Since then restoration methods have become more sophisticated and wider in scale.

Restoration projects focus on the input of a lake: the first step is to mitigate the inflow of harmful nutrients and material. If the input of nutrients continues to exceed the loading capacity, the lake will become eutrophicated again. The main idea is to gain sustainability on the lake.

Restoration is a time and capital consuming process; therefore it has to be planned carefully. In smaller scale, dredging can be used to clear waterways and pick up excess deposits, but it is necessary to clear the whole lake side area in badly contaminated cases. Small-scale dredging is not registered as official restoration projects.

There are many ways to control eutrophication:

- **Hypolimnetic aeration:** oxygen-rich surface water is mixed with oxygen-poor bottom water layer also known as hypolimnion. This method is the most efficient one.
- **Food chain restoration:** the amount of cyprinidae fish is controlled. This method is efficient if more than 200 to 400 kg ha⁻¹ is removed.
- **P-inactivation:** phosphorus is inactivated with FeSO₄, AlSO₄, FeCl₃, AlCl₃, and polyalumchlorides. One treatment is effective for 3 years.
- **Stabilizing lake sediment layers:** There are three different methods:
 1. Mixing and ploughing the sediment layers. There are encouraging results
 2. Covering the sediment layer with clay. This method is still in an experimental stage.
 3. By-product of an industrial process ferric gypsum has been tested in hyper-eutrophic lakes with the result of significant P-inactivation.
- **Hypolimnetic water withdrawal:** a siphon pipe is installed from the deepest point of the lake to the outlet. This method is used with other techniques.

In the 70's, aeration and plant removal were the most popular methods of restoration. The latter is still commonly used, but dredging and biomanipulation are getting more common. As new ways of control are discovered, lake restoration is becoming more about chemistry than manual labour. Even so biological and chemical methods are not used together. [9]

5.6 Eutrophication in Lake Liesjärvi

Liesjärvi is a mildly eutrophicated lake. There is only one outflow point that has to stay as it is or the water level starts rising. If the water way is obstructed the water flow velocity decreases and eutrophication process accelerates. Finally, the whole part of the lake will be fully grown and the water will sit still.

Some mitigation methods are already used; the surroundings of the bridge at the exit point are annually dredged. This ensures open pathway for water. Also the state of the lake is monitored annually by the Lake Liesjärvi preservation society.

In Liesjärvi area only 2 % of the area is used for farming; thus possible ammonium sights originate from humans.

In Järki –programme locals voiced their concern about vegetation growth and increased murkiness of the water. There are some newly entered species that known to live in eutrophic waters. The fish are known as trash fish, i.e. species that have low requirements for their living environment. [1]

6 Equipment and Chemicals

In this chapter all the equipment used during the sampling and the analysis methods are explained in detail.

All the equipment was first washed in a dishwasher and then rinsed with ion-exchanged water. Between handling they were again rinsed with ion-exchanged water to minimize contamination.

Sensors

SevenGo Duo Pro™ pH/ORP/Ion/Conductivity meter SG78 was used to measure pH, conductivity and temperature.

Luminescent Dissolved Oxygen Probe: Model LDO10101 was used to measure dissolved oxygen.

Ion-chromatography

761 Compact IC was used for ion-chromatography analysis. A 2 ml syringe was used for injecting a sample through a 25 mm syringe filter with 0.45 µm Nylon membrane into the IC. Samples were stored in 100 ml burettes for easier handling.

Lab equipment and chemicals for COD_{Mn} analysis [13]

In COD analysis 10 ml, 5 ml, 2ml, 1ml, and 0.5 ml pipettes, clamp, burette, beakers, dropper, test tubes, test tube holders, heater, and pots were used.

The following chemicals were used for COD_{Mn} –analysis:

- Sodium permanganate 0.02 M
- Sodium permanganate 0.002 M
- Phosphoric acid 4 M
- Starch solution
- Natrium sulphate 0.01 M

7 Methodology

Sampling points were chosen due to historical data and location (Picture 5). Taipaleenlahti, Hietaniemenselän syväne, Vanaja-suonlahti and Karjusilta have previously recorded data. Cape Kyynärä's measurement point does not have historical records, but its location is important for water quality measurements for it is in the bay of the Natura 2000 site and it also is at the entering point of an inflow river. Bay Taipaleenlahti's measurement point is similarly close to the Natura 2000 site and at an inflow point.



Picture 6: Measuring points Source: [2]

Samples were taken from 5 different points of the lake: Kynnärä, Taipaleenlahti, Hietaniemenlahti, Vanajasuonlahti and Karjusilta. These points were selected due to their geographical locations:

- Taipaleenlahti and Kynnärä are close to the inflow rivers
- Hietaniemenlahti is at the centre of the lake
- Karjusilta is at the outflow point
- Vanajasuonlahti is located close to the inflow point of Swamp Rinnansuo river

Cape Hietalahdenniemi –measurement point is located in the centre of the lake and also has the deepest point. Cape Kynnärä's measurement point is close to the outflow river. Bay Vanajasuonlahti measurement point was chosen due to historical data, and it is located close to a swamp area

Measurements were taken twice; the second measurement was taken two weeks after the first one. The sampling points were selected as close to each other as it was possible. There is no significant difference between the different sampling locations because they are only a couple of metres apart from each other.

Samples that were used in ion-chromatography were stored in 250 ml plastic bottles. Chemical oxygen demand samples were stored in 250 ml glass bottles with 2.5 ml sulphuric acid for conservation.

During laboratory experiments protective gear was used. They included a laboratory jacket, safety gloves and safety glasses.

During the sampling process sensors were rinsed with ion-exchanged water between every sample. IC samples were taken straight into the bottles, but COD samples were first taken in a 500 ml glass bottle and then poured carefully into the storing container. Sampling bottles were lowered into the water with a sampling bottle holder.

7.1 In-situ measurements

In situ temperature, pH, dissolved oxygen, and conductivity were measured. Measurements were taken thrice from each sample except for Taipapaleenlahti, where measurements were taken only once.

Dissolved oxygen was measured from the bottle as soon as the sample was taken. This creates an error in the results, since air is mixed in the sample as the bottle is lowered in the water. Dissolved water sample should be taken straight from the source to ensure accurate readings. As such these values cannot be used in this thesis. The measurement was performed incorrectly due to a misunderstanding that the sensor cannot be lowered in water.

Temperature measurements were taken from two sensors; pH and conductivity. These sensors were placed in the sample bottle after dissolved oxygen was measured. Measurements were taken three times, and an average of those is used in this thesis. All samples were stored in dark and at a temperature of +4 °C to ensure maximum storage time. IC samples were analysed two days after the samples were taken, while COD samples were analysed the next day.

7.2 Ion-chromatography

Ion exchange chromatography separates ions and polar molecules by attracting them to an ion exchanger. It is a quick way to detect charged molecules such as proteins and nucleotides.

A 2 ml sample was taken with a syringe and injected into an ion chromatographer through a filter. Results were recorded and printed.

7.3 COD_{Mn}

Chemical Oxygen Demand (COD) was attained by using the Finnish standard method SFS 3036. In this method, the sample is oxidized with permanganate and thus chemical oxygen demand is gained.

Samples were prepared for storage by adding 2.5 ml of 4 M sulphuric acid (1 ml of H₂SO₄ per 100 ml of sample) and placed in a dark place at a temperature of 4 °C.

The laboratory procedure is done in following four steps:

1. 0.5 ml of 4 M sulphuric acid and 2 ml of 0.002 M potassium permanganate were added to 10 ml of sample. Solution was boiled for 20 minutes.
2. After boiling sample was immediately cooled down to room temperature, and 1 ml 0.1 M potassium iodide solution and 5 drops of starch solution were added.
3. Sample was titrated with 0.01 M natrium sulphate solution until blue colour disappears. It is very important to mix the sample while being titrated.
4. Blank sample was prepared in the same manner. 10 ml of ion exchange water was used as a blank sample.

Results were calculated by using the following formula:

$$COD_{Mn} = (V_2 - V_1) \times c_1 \times 800 \times f$$

Where

COD_{Mn} is Chemical oxygen demand, mg/l

V_2 is the amount of natriumtiosulphate that is consumed in titration of a sample, ml

V_1 is the amount of natriumtiosulphate that is consumed in titration of a blank sample, ml

C_1 is the concentration of natriumtiosulphate, mol/l

800 is half of oxygen's molemass in milligrams and decided by sample volume

f is the dilution factor; volume of diluted sample by volume of undiluted sample

Samples were preserved by adding 4 M sulphuric acid and were stored in glass bottles.

[13

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8 Results

This chapter presents the results of the measurements taken in the winter of 2014 and a table of long term measurements taken at Hietalahdenniemi

8.1 Results of Measurements Taken During Winter 2014

First measurements taken were temperature, pH, dissolved oxygen in milligrams per litre, conductivity in micro Siemens per centimetre, and saturation of water. Table 3 gives the results.

Table3: Temperature, dissolved oxygen, pH, conductivity, and saturation with average values and standard deviation

Station	DO				
	T	[mg/l]	pH	Conductivity [μS/cm]	%
Taipaleenlahti	1.3	12.90	5.68	50.3	
	1.1	13.18	6.06	48.7	
Karjusilta	1.4	12.64	6.02	50.2	93.3
	1.3	12.57	6.04	50.2	92.8
Hietaniemenlahti	1.3	12.57	6.09	50.3	89.9
	1.3	12.57	6.14	50.2	90.0
Kynnärä	1.2	12.39	6.21	49.6	88.5
	1.1	12.19	6.23	48.8	86.9
Vanajasuonlahti	1.0	11.99	6.26	48.2	85.3
	1.2	12.07	6.17	49.7	86.1
average	1.22	12.51	6.09	49.6	89.1
standard deviation	0.12	0.37	0.17	0.78	2.96

The standard deviations indicate we can see that the water quality is consistent throughout the lake.

Dissolved oxygen is very high due to a measurement error. The results cannot be considered as true values, but as the measurement error is the same in all of the results, it can be stated that the dissolved oxygen quantity is about the same in all measurement point although it cannot be said what that exact quantity is.

Temperature is low as can be expected from a winter measurement. The sample water was taken from 1-metre depth so it was quite close to the frozen surface. On the bottom of the lake, the water temperature would be higher.

Like in any mildly eutrophicated water, the pH is a bit acidic. The pH value is at its highest in Kynnärä and Vanajasuonlahti.

Conductivity is almost the same in every measurement point. The highest values were gotten at the deepest point, Hietaniemenlahti and the lowest ones at Vanajasuonlahti.

Table 4 presents the measurement results for ion-chromatography:

Table4: Chlorine, fluorine, nitrogen dioxide, nitrogen trioxide, sulphate, and phosphate concentrations in mg l⁻¹, and traces of acetate.

Station	CL-	F-	NO ₂	NO ₃	SO ₄	PO ₄	Acetate
Taipaleenlahti	2.906	0.153	0	0.335	0.306	0	
	2.326	0.149	0	0.341	0.306	0	
Karjusilta	2.819	0.172	0	0.356	0.343	0	x
	2.294	0.148	0	0.373	0.358	0	
Hietaniemenlahti	2.25	0.149	0	0.354	0.338	0	x
	2.356	0.148	0	0.341	0.4	0	
Kynnärä	2.944	0	0	0.367	0.351	0	
	2.934	0.147	0	0.37	0.356	0	
Vanajasuonlahti	2.38	0.148	0	0.345	0.354	0	x
	2.344	0.147	0	0.341	0.358	0	x
average	2.555	0.14	0	0.4	0.342	0	
standard deviation	0.30	0.05	0.00	0.01	0.02	0	

Nutrient concentrations are very consistent around Liesjärvi. Also, all nutrient values were really low. This is due to the time of the year, since nutrients do not rise from the bottom depositions or there is no surface vegetation to decompose in the water.

The only notable difference between the measuring points is a trace of acetate concentration. The samples did not contain enough acetate to get a proper reading, but there were signs of small concentrations. The amount does not have any significant effect on the quality of the water; nevertheless, it suggests that there is some leakage from swamp areas around Hietaniemenlahti, Vanajasuonlahti and Karjusilta.

There are two inflow points of two different swamps at Vanajasuonlahti. The other swamp is used as a peat dig site; therefore, the leakages from there should be monitored. From these measurements it can be concluded that there are no significant leakages from the dig site as the nutrient values are similar in all measuring points.

Table 5 presents the measurement results for chemical oxygen demand analysis.

Table5: Chemical oxygen demand in milligrams per litre

Station	COD [mg/l]
Taipaleenlahti	23.33
	26.13
Karjusilta	32.53
	27.33
Hietaniemenlahti	34.53
	35.73
Kynnärä	34.53
	34.13
Vanajasuonlahti	35.73
	34.93
average	31.89
standard deviation	4.54

Chemical oxygen demand was measured with a permanganate titration method (ST 3036) where the samples were pretreated and then oxidized with permanganate. This method is very prone to error and a systematic error can clearly be seen from the results: the values are exceptionally high when compared to previous measurements.

Due to the high values these results cannot be compared with earlier measurements but can be compared within the same results.

8.2 Comparison between results from winter 2014 and previous measurements

This section compares the readings gotten from phosphorus, total nitrogen, pH, conductivity, and COD measurements between years 1968 and 2014. Historical values were gotten from the Järki –study Närhi H. & Jutila H. 2005: *Tammelan Liesjärven tila ja kuormitus*. Table 4 presents the measurement results.

Table 6: Phosphorus, total nitrogen, pH, conductivity, and chemical oxygen demand values from 1968 to 2014 at Hietaniemenlahti

Year	Phosphorus	Total Nitrogen	pH	Conductivity	COD (Mn)
1968	20.0		6.4	4.3	20.0
1972	12.5	390	6.2	5.3	8.0
1973	5.0	495	6.5	5.0	13.0
1974	7.5	310	6.2	5.5	9.0
1975	25.0	330	6.0	5.6	18.0
1978	15.0	495	6.3	6.5	14.0
1983	17.5	650	6.0	5.1	16.0
1984	12.7				
1986	16.0	610	6.1	4.5	12.0
1991	10.0	790	5.9	5.9	8.0
1992	12.7				
1995	13.5	510	6.3	6.0	11.5
1998	14.0	505	6.2	6.7	13.0
2001	16.0	700	6.0	6.0	18.0
2002	15.0	700	6.0	6.0	19.0
2003	17.0	490	6.2	6.5	13.0
2004	11.0				
2005	17.5				
2014	0.0	338	5.8	5.0	35.1
Average	13.6	522.4	6.1	8.6	15.2
SD	5.1	158.11	0.2	0.6	8.9

There has not been any consistent time schedule for measuring for Liesjärvi. The earliest measurements were taken in 1968 and the latest in 2014. Between years 1968 and 2003, there has not been notable variations in the measured values. Therefore it can be said that the Liesjärvi's water has been in a stable condition since the beginning of measurements.

When the 2014 results are compared to earlier ones, it is clear that pH and nitrogen concentrations have not changed. There was a small peak in conductivity in late 90's, but it has since returned close to early values. Phosphorus was not found in the 2014 sample, but it is highly unlikely that this result is accurate. The COD value has doubled from 2003 which is highly unlikely since nitrogen and phosphorus levels have decreased. Therefore, it can be stated that the result for COD measurement is false.

9 Analysis

When the results from the measurements are compared, it is quite easy to conclude that Lake Liesjärvi is in good condition and the water quality is consistent. In this section the results are compared and analysed.

9.1 2014 Winter Measurements

The limit value for phosphorus concentration is less than 1 mg l⁻¹ and for nitrogen concentration is between 0.56 and 17 mg l⁻¹. As the phosphorus concentration is typically extremely low, it explains why there were no phosphorus readings gotten from the samples.

Figures 1 and 2 show the results for the ion-chromatography and the average of the results. The averages and standard deviations of the results are listed in Table 7.

Table 7: Averages and standard deviations for nutrient measurements

Station	Cl-	F-	NO ₂	NO ₃	SO ₄	PO ₄
Average	2.555	0.136	0.000	0.352	0.342	0
SD	0.302	0.048	0.000	0.014	0.020	0

Figure 1: Measured nutrient concentrations in mg l⁻¹.

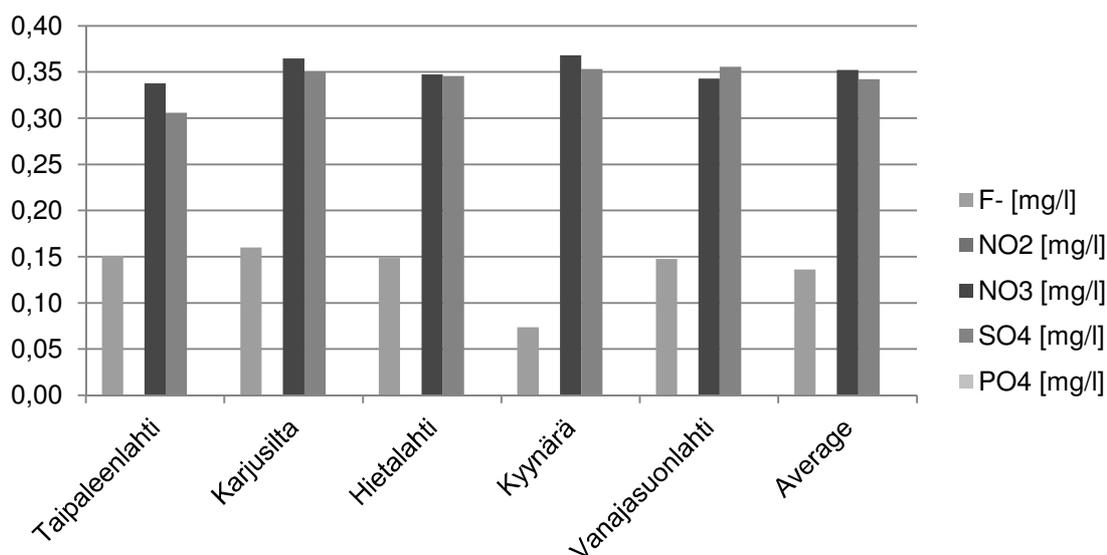
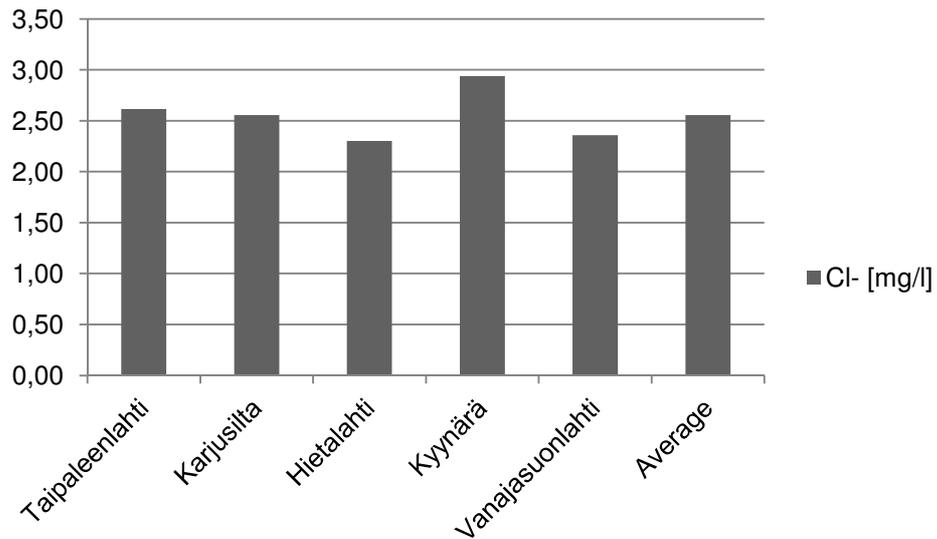
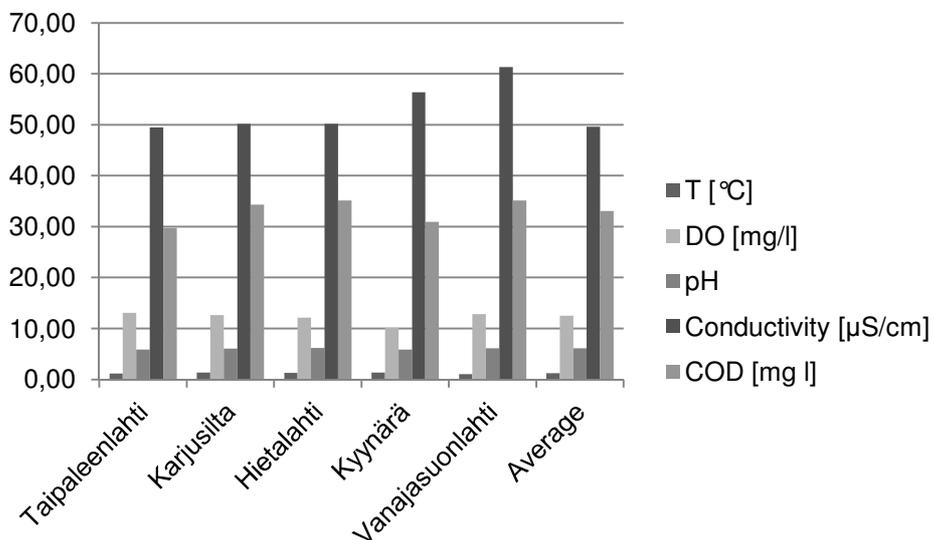


Figure 2: Chloride measurement results in mg l^{-1} 

The samples that were taken show only little variation. Chlorides have the most variation with the standard deviation slightly above 1 (Figure 2). Most of the nutrient values are below 0.5. There are no signs of eutrophication. It is clear that the quality of Liesjärvi is good, and there is no variation of quality in it.

Figure 3: Temperature, DO, pH, Conductivity, and COD**Table 8** Average values and standard deviation of in situ measurements and COD

Station	T	DO [mg l^{-1}]	pH	Conductivity [$\mu\text{S cm}^{-1}$]	%	COD [mg l^{-1}]
Average	1.208	12.507	6.090	49.620	89.108	33.05
SD	0.117	0.366	0.165	0.784	2.959	2.54

Temperature, dissolved oxygen, pH, and conductivity also show little variance (Figure 3, Table 8). There is the same systematic error in all of the DO measurements and therefore the results can be compared between each other. Water is mildly acidic which is typical for humus rich waters. Temperature is quite low due to the measuring point; only 1 meter below surface.

Chemical oxygen demand exhibits the most of variation. The average value of COD is 33.05 mg l^{-1} , and the standard deviation is 2.54. COD is at its lowest at the inflow points of the lake, Taipaleenlahti and Kynärä and at its highest at the centre point Hietalahdenniemi. There is no great variation at the three high value points: the centre, out-flow point Kynärä and near the inflow point of the peat swamp.

Lower COD means more oxygen is diluted in the water. Lower COD levels can be expected near a national park due to the protective systems to the ecosystem.

Because Liesjärvi water is in good condition, and there is no significant variation between different measuring points, it can be said that there is no reason to take annual measurements from all 5 points of the lake.

The best point to take these measurements is the middle of the lake, where the two inflow currents unite and start to flow out of the river. Even though taking measurements from Hietalahdenniemi does not include the effect of any of leakages to the north end of the lake, the middle point shows a good average of the whole area.

9.2 Measurements between 1960-2014

To understand the progression of the water quality it is necessary to compare historical data with the current results. In Figure 4 there is a graphical representation of the historical data and Table 9 shows the average and standard deviation of them.

Figure 4: Phosphorus, total nitrogen, pH, conductivity, and COD values at the centre point of Lake Liesjärvi between years 1968 and 2014

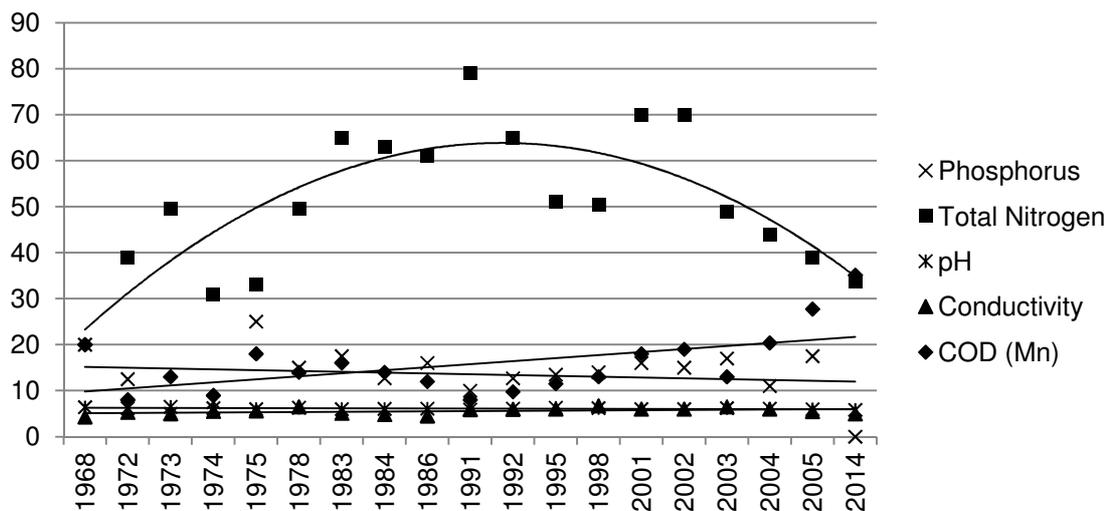


Table 9 Average and standard deviation of annual measurements

	Phosphorus	Total Nitrogen	pH	Conductivity	COD (Mn)
Average	13.57	52.24	6.14	5.59	15.17
SD	5.51	15.07	0.19	0.73	6.72

Most fluctuation has occurred in nitrogen values. The highest concentration of nitrogen that has been recorded was in 1991 with 79 mg l^{-1} and lowest in 1974 with 31 mg l^{-1} . Nitrogen has the highest mean concentration of all the measured components and also has the highest standard deviation.

Nitrogen intake depends on the surrounding influences like waste input and chemical waste. There are many summer houses and cottages which increased in number in the 20th century. With more housing, there are also more detergents led in to the lake and leakages from the summer cottages.

Housing legislations have had great influence on human behaviour around lake areas. There are regulations about distances of waste and toiletry stations and also mitigation of the chemical inputs: carpets are not allowed to be washed in lakes anymore, for example. All these measures have had an impact on the nitrogen concentration.

There is no significant variation between other measured values. For example, pH and conductivity have been quite regular throughout the years. Phosphorus has greater standard deviation due to fluctuations in the 60's and early 70's and also due to the

2014 result of 0. If the most recent measurement is not considered, it can be said that phosphorus concentration has not changed significantly since the end of 70's.

Chemical oxygen demand is also fairly regular. There is a high peak at the 2014 measurement but that can be stated as false due to the high systematic error.

It can also be seen how phosphorus regulates the COD value. The two main nutrients, phosphorus and nitrogen, are both major factors in eutrophication. But as stated before the one that is lower in quantity regulates the growth rate of vegetation in a lake. Phosphorus is the regulatory chemical.

10 Conclusion

There are no significant changes in the water quality of Liesjärvi. The quality is consistent throughout the whole lake; therefore, there is no reason to take samples from multiple points around the lake.

There should be annual measurements to ensure consistency of stable conditions around the natural park. Even minor changes can have big effects after 10 or 20 years. The housing areas, recreational usage and roads around the lake all create leakages that can offset a change.

Strict legislations and active community have played an important role in keeping Liesjärvi as clean as it is now. When the Rinnansuo peat swamp dig site became active, the whole Liesjärvi community demanded more proof that there was not going to be any effects on the lake.

It is impossible to forecast what the future of Liesjärvi will be but at the moment it looks quite bright.

10.1 In Effects of Swamp Rinnansuo peat dig on Liesjärvi water quality

The motive of this thesis was to estimate the effect of Rinnansuo peat swamp operations on Liesjärvi's water quality and the possible increase of eutrophication level. The peat site has been active from 2012, thus, the effects should be non-existent or minimal if present. If there were major changes to be found in water quality, it would mean that drastic mitigation methods would be required.

Geologically, the inflow from River Rinnansuojoki enters Lake Liesjärvi at an optimal point since it is at the outflow branch of the Lake. The inflow point is located behind Cape Hiiliniemi, where the lake narrows; therefore, the current is stronger towards the outflow point at Bridge Karjusilta.

The major concern of changes in water quality is focused on the western side of the lake, where the Natura 2000 site is based at. There are two endangered water plant species and some that are in Finland's international responsibility for threatened species. It can be said that this area is not threatened by peat swamp leakage due to the water flow direction: the water runs away from these areas.

This does not mean that the leakages would not have any significant effects on the water quality and the vegetation at the northern side of the Liesjärvi area known as Lake Soukkajärvi. There are summer cottages, a forestry education centre and a few permanent residents living in that area. Decrease in water quality and increased amount of vegetation would mean that the property values would descent.

Also there is a small natural site at Karjusilta. Increased water vegetation would have significant effects on this area.

The biggest concern of major eutrophication at the northern bay is that it is the only outflow point of the whole lake. Even though it is highly unlikely to completely fully grow on vegetation, increased vegetation could slow water flow, and then vegetation growth rate would increase. If the narrow point of Karjusilta would completely be covered in vegetation, the water level would increase and that would change all the shorelines around Liesjärvi.

Even though this scenario is taken to the extreme, it shows how important the protection of water quality is. There should be continuous annual measurements of water so that any major changes can be noticed immediately and then mitigated.

The effects of peat swamps are not immediate but can be seen after 10 or 20 years. From earlier cases it can be seen how lakes have had significant vegetation growth and how biodiversity has decreased as a result of this.

10.2 Peat leakage effects

There are no mentions of acetate in previous studies, which means that either there have not been any findings or the findings have not been recorded. As there has been inflow from swamp areas close by, the latter seems more probable. As acetate is found only as small traces it, is not a significant factor in water quality.

When talking about traces of acetate, the amount of acetate is so small that the quantity does not show in measurements. Acetate can typically be found in swamp areas; thus, it is natural to detect it in when nutrients are measured.

Acetate was also shown in Hietalahdenniemi's measurements, which also could be expected. The samples were taken at the intersection where the two currents from the inflow points unite. Water in Liesjärvi travels next to forestry areas and swampy areas; therefore, nutritious water qualities can be expected to show in measurements.

Karjusilta had the highest nutrition quantities, which could be expected from the only outflow point of the whole river. This northern area also has a farm and a small ship yard on the shoreline, which also has an impact on the water quality. It cannot be determined from these experiments how much they affect the water quality, but neither of them is highly industrialized nor work in large scale; hence the effects can be estimated as minimal.

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Appendix 1: Insitu Measurement Results and Sampling Point Coordinates

		T	DO [mg/l]	pH	Conductivity [μS/cm]	%	Latitude/Longitude
Taipaleenlahti	A	1.3	12.9	5.68	50.3		60.64509066
	B	1.1	13.18	6.06	48.7		23.89394796
Karjusilta	A	1.5	12.8	6.05	50.1	91.9	
	A	1.4	12.57	6.01	50.1	98.7	
	A	1.4	12.54	6.01	50.3	89.4	60.69794145
	B	1.2	12.6	6.11	50.3	90.2	
	B	1.3	12.56	6.15	50.2	90	
	B	1.3	12.55	6.15	50.2	89.9	32.92333349
Hietaniemi	A	1	12.05	6.34	48.3	85.7	
	A	1	11.98	6.2	48	85.2	
	A	1.1	11.95	6.23	48.2	85	60.67288404
	B	1.7	12.28	6.07	53	88.1	
	B	1.6	12.21	6.05	52	87.7	
	B	1.6	12.18	6.05	51.5	87.5	23.91465361
Kynnärä	A	1.4	10.17	5.89	56.2	72,9	
	A	1.4	10.15	5.83	56.1	72.8	
	A	1.4	10.10	5.83	56.9	72.4	60.68122928
	B	1.3	10.10	5.99	56.6	72.4	
	B	1.4	10.06	5.92	56.3	72.1	
	B	1.4	10.02	5.87	56.3	71.8	23.85064345
Vanajasuonlahti	A	1.35	12.86	6.02	60.2	91.3	
	A	0.85	12.81	6.07	60.7	90.1	
	A	0.8	12.79	6.1	61	90	60.67919817
	B	1.05	12.89	6.25	62.5	91.5	
	B	1	12.85	6.2	62	91.2	
	B	1	12.82	6.15	61.5	91.1	23.95369937
Average		1.150	11.730	6.040	59.400	83.390	60.67526872
SD		0.235	1.429	0.140	2.560	9.666	25.70725558

Appendix 2: COD Measurement results and Sampling Point Coordinates

		wash	Mn con [ml]	Latitude/longitude
Taipaleenlahti	A	P	13.9	60.64530062
		P	14.8	
	B		12.1	23.89379885
			13.4	
Karjusilta	A		13.9	60.69794145
			12.5	
	B	P	13.8	23.92333349
		P	13.9	
Hietalahti	A		12.5	60.67271800
			13.4	
	B		12.6	23.91522710
			13.0	
Kynnärä	A		12.8	60.68113469
			12.8	
	B	P	12.8	23.85010915
		P	13.2	
Vanajasuonalahti	A	P	13.1	60.68113469
		P	13.0	
	B	P	12.6	23.95331321
		P	12.1	
Blank	A		17.2	
	B		17.1	
			17.5	