Tampere University of Applied Sciences

NITROGEN CONCENTRATION IN BARLEY AND SOIL WITH DIFFERENT FERTILIZER TREATMENTS

Trung Dang Viet

BACHELOR'S THESIS
April 2019
Degree Programme in Energy and Environmental Engineering

ABSTRACT

Tampereen ammattikorkeakoulu
Tampere University of Applied Sciences
Degree Programme in Energy and Environmental Engineering

Trung Dang
Nitrogen Concentration in Barley and Soil with Different Fertilizer Treatments

Bachelor's thesis 36 pages, appendices 9 pages
April 2019

The use of waste as a resource is a part of the circular economy concept. Human urine, a readily available human waste, could be a cost effective alternative to conventional mineral fertilizer. However, the feasibility of this application requires testing of the environmental impacts as well as the plants grown with human urine. This thesis aimed to study the nitrogen concentration in the barley crop grown with human urine as nitrogen is one of the most important macro nutrients directly impacting plant growth. Another aim of this thesis was to compare the total nitrogen content between the barley crop treated with human urine and mineral fertilizer. This was done by determining the total nitrogen content of barley grains, straws and barley-grown soil of both treatments.

The samples were analysed with two methods: the automatic analyser Elementar vario TOC select and the manual Kjeldahl digestion method. The soil samples were analysed with the vario TOC select while grains and straws were analysed with the Kjeldahl digestion.

The test resulted in an insignificant difference in the total nitrogen content across the samples of both treatments as well as when compared to the reference database from the Natural Resources Institute Finland. In addition, the dry weather of summer 2018 negatively affected the barley grain quality of both treatments. The results suggested the feasibility of human urine to replace mineral fertilizer in terms of nitrogen content and the need to further study the effects of weather conditions on barley crops' nitrogen uptake.

Total nitrogen, human urine, mineral fertilizer, nitrogen uptake, nitrogen concentration, Kjeldahl digestion

CONTENTS

GLOSSARY or ABBREVIATIONS AND TERMS (choose one or other)

This thesis work used abbreviations for each treatment studied.

TAMK	Tampere University of Applied Sciences
cr	credit
kg N/ha	Kilogram of nitrogen per hectare
TN_b	Total nitrogen bound
TKN	Total Kjeldahl nitrogen
UF18	Urine fertilized treatment (Fall 2018)
MF18	Mineral fertilized treatment (Fall 2018)
UF17	Urine fertilized treatment (Fall 2017)
MF17	Mineral fertilized treatment (Fall 2017)
US17	Urine fertilized treatment (Spring 2017)
MS17	Mineral fertilized treatment (Spring 2017)
UF16	Urine fertilized treatment (Fall 2016)
MF16	Mineral fertilized treatment (Fall 2016)
NF16	Treatment without fertilizer (Fall 2016)
H_2SO_4	Sulfuric acid
H_3BO_3	Boric acid
H_2BO_3	Dihydrogen borate
HNO_3	Nitric acid
N_2	Nitrogen (gaseous form)
NH_4^+	Ammonia
NO	Nitric oxide
NO_2^-	Nitrite
NO_3^-	Nitrate
$NaCO_3$	Sodium carbonate
$NaCO_3 \cdot 10H_2O$	Sodium carbonate decahydrate
$(NH_4)_2SO_4$	Ammonium sulphate
O_3	Ozone
O_2	Oxygen (gaseous form)
SO_4	sulphate
hv	Photon energy

1 INTRODUCTION

This thesis work used the materials from project Hierakka, carried out during the period 2016-2018. Project Hierakka – Hiedanranta as a development area for urban nutrient studied the application of human urine as a fertilizer replacing the use of mineral fertilizer (Viskari et al. 2018). This thesis work aims to determine the nitrogen concentration in the barley crop grown during the project. This was achieved by analysing the total nitrogen content in barley grains, straws and the soil used to grow the plants and comparing the result of the human urine treatment and mineral fertilizer treatment. This work has a supportive role in determining the possibilities and feasibility of using human urine as a fertilizer. This is a step toward sustainability as well as circular economy as it explores the use of readily available waste as materials. The main principles of circular economy include the use of waste as resource, reuse and recycle materials found as waste and eco-design (Acciona 2019).

There are three main types of samples analysed in this thesis work: grains, straws and soil. The samples were harvested from the barley crop field in Iittala. There were two types of treatment carried out: human urine and mineral fertilizer. The quantity of samples was not the same as they were harvested during different seasons. Thus, the analysis and outcome of the study was done with the available samples and comparisons were drawn where possible. Picture 1 showed the urine spreading process during the original project.

PICTURE 1. Urine spreading

The expected outcome of the study is the comparison of total nitrogen content of the samples between the treatment of human urine and mineral fertilizer and the concentration of nitrogen in the plant and soil. Similar total nitrogen content across the treatment indicates the feasibility of the project in practice.

2 THEORY

In this section, the background information of important subject in this thesis was provided, including the significance of nitrogen in plant, nitrogen translocation in plants, nitrogen uptake in plants, total nitrogen and the weather effect on plant growth and nitrogen.

2.1 Significance of nitrogen

2.1.1 Nitrogen as an element

On earth, nitrogen is one of the most available elements that is important for any living organisms. Nitrogen is a colourless and tasteless non-metal element with atomic weight of 14 Nitrogen is essential in the formation of macro molecules such as protein, amides, enzyme, nucleic acids, chlorophyll, etc. Nitrogen has 14 unstable isotopes with the only stable isotope being ^{15}N, also being used to study agricultural plant nutrition. Another use for this isotope is as an indicator of nitrogen compounds and organic pollutants (Baset 2015, 51).

2.1.2 Nitrogen in crop plants and soil

There are many ways to classify nutrients in plants e.g. quantity of nutrient, biochemical functions, mobility in soil or within the plant or functions in the plant, etc. In any of the known classifications, nitrogen is considered one of the most important nutrients, being one of the macro nutrients, meaning it is needed in larger quantities than other elements. Nitrogen, in ionic forms e.g. NO_3^-, NH_4^+ are essential for organ and organelle in plants as they are the main forms of nitrogen uptake by plants.

Nitrogen is considered the limiting nutrient in crop production as it directly affects plant growth, the critical concentration of nitrogen refers to the concentration of nitrogen that most plant growth takes place (Baset 2015, 52). Hence, suitable

amount of nitrogen is the key to crop productivity. In the malting process, it is suggested that the optimal concentration of nitrogen in barley grains is less than 2.16% (21.6 gram/kilogram) to achieve low nitrogen levels, high grain yields and high quality of malting (Baethgen, Christianson, Lamothe 1995). On the other hand, plants growth halts without enough nitrogen nutrient as they are not able to produce proteins and nitrogen compounds. The deficiency of nitrogen is shown in symptoms of plants such as pale green leaves as the shortage of chlorophyll up to the point of leaves turning yellow early and fall off. In general, lack of nitrogen can lead to slow growth rate and plant root grows more than shoot as well as lower quantity and quality of grains. These symptoms serve as indicators for nitrogen deficiency (Baset 2015, 65).

In soil, nitrogen is mostly present in organic matter, largely unavailable to plants without microorganisms' activities of nitrogen fixation, cycling, ammonification, nitrification and denitrification, turning complex compounds into simple inorganic forms, suitable for the uptake of plants (Miransari 2012, 159). The process of organisms converting complex organic nitrogen into ammonium is called ammonification. Ammonium will then be converted into nitrite by bacteria e.g. Nitrosomonas spp. And Nitrococcus spp., then oxidized into nitrate. This is known as nitrification. The rate of the nitrification process is affected by the pH of soil e.g. the rate is hastened at neutral pH of 7.0 while slower in acidic soils with pH less than 6.0 (Miransari 2012, 83). The nitrogen will be returned to the atmosphere by the denitrification process of reduction where nitrate is converted into nitrogen (gaseous form) by bacteria e.g. Thiobacillus denitrificans, Micrococcus denitrificans, Pseudomonas spp., etc. (figure 1) (Baset 2015, 55).

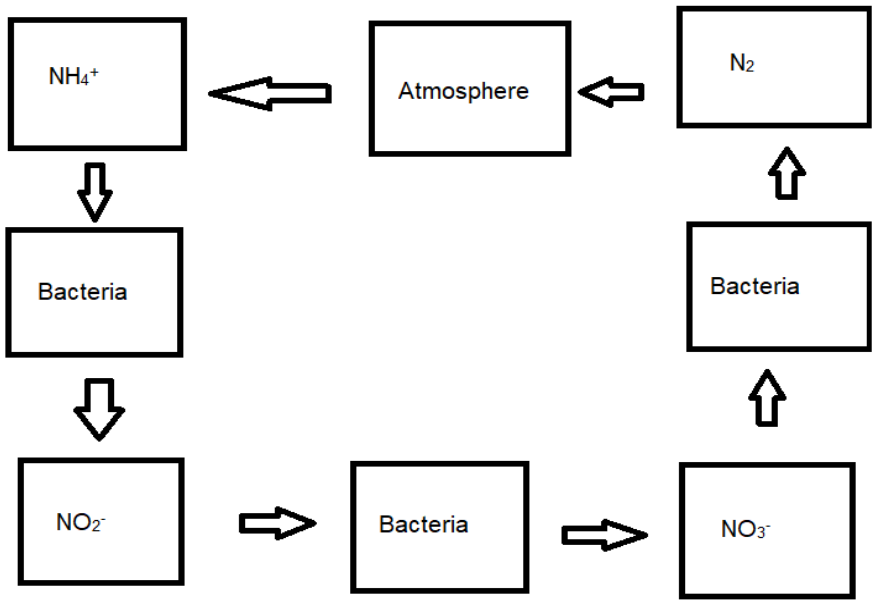


FIGURE 1. Nitrogen cycle

2.2 Nitrogen translocation in plants

Nitrate, ammonium and amino acids are transported from root to shoot through xylem vessel, which is a vascular tissue that transports water and different dissolved minerals from plant's root to its body as well as providing physical support. There are three processes that take place to transfer nutrients in plant's body: short distance & long distance transport and remobilization of nitrogen.

2.3 Nitrogen uptake in plants

Nitrogen is utilized by plants mostly in forms of nitrate (NO_3^-) and ammonium (NH_4^+). Essentially, the analysis of total nitrogen in plants refer to the measurement of these compounds. The amount of nitrate and ammonium needed for plants varies depending on the conditions of the plants e.g. upland or submerged. In the case of barley, which is grown in upland condition, nitrate is preferred over ammonium (Baset 2015, 54). In addition, nitrate is not adsorbed on soil but absorbed by roots at micromolar or above concentrations. while being mobile by mass flow or diffusion (Tinker, Nye, Peter 2000).

2.4 Total nitrogen

Total nitrogen or total bound nitrogen (TNb) is defined as the inorganic nitrogen (ammonia, nitrate and nitrite) and organic nitrogen. This is different from total Kjeldahl nitrogen (TKN), which consists of ammonia nitrogen and organic nitrogen. Essentially, total nitrogen is the sum of TKN, nitrate and nitrite (Manivasakam 2016).

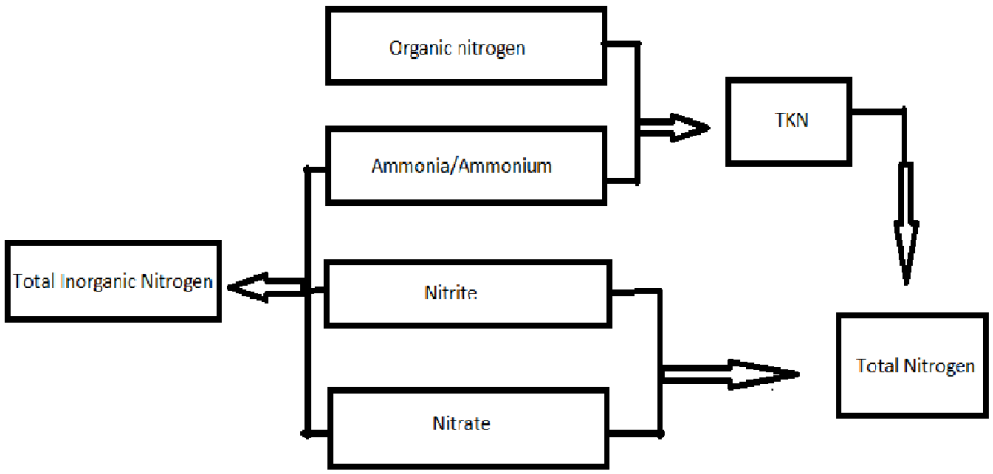


FIGURE 2. Nitrogenous compounds

The most common method to determine the total nitrogen is the Kjeldahl digestion, which is one of the main methods used in this thesis.

2.5 Fertilization effects

The optimal nitrogen supply from fertilization is difficult to control due to the ecosystem, environmental conditions, crop management, etc. Thus, the control of nitrogen supply from fertilization based on the crop's need is important to improve crop performance, specifically grain's quantity and quality upon harvest. Mineral fertilizer, being the costliest investment for barley farmers (Vicente et al. 2019), offers more precise control over nutrient supplementation compared to organic

materials (Nkurunziza et al. 2017). Urine, one the other hand, offers high concentration of nitrogen as in mineral fertilizer while being more readily available (Grunbaum 2010). However, the nitrogen released from using urine may not be taken up effectively without proper management, resulting in possible downgrades in grain quantity and quality, as well as the risk of leaching (Nkurunziza et al. 2017). Thus, optimal yield is achieved by the quantity and timing of fertilizer application (Vicente et al. 2019).

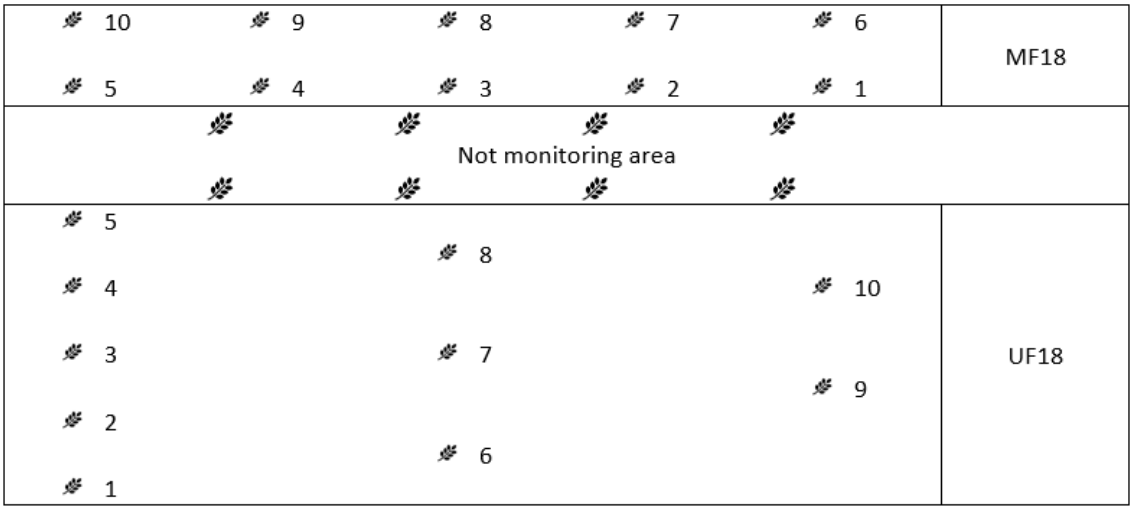
According to the study done by Vicente et al. (2019), grain yield of barley improved drastically with the use of nitrogen fertilization up to a limit. The study suggested that a 130 kg N/ha application of nitrogen fertilizer improved the grain yield by 65%. However, further application of 170 kg N/ha improved the grain yield by another 10%. Regarding the quantity of grains, the gain from 170 kg N/ha from 130 kg N/ha was marginal while reducing the quality of grains, as the thousand grain mass is reduced. The level of fertilizer application is also dictated by the availability of nitrogen in soil in different seasons (Baethgen et al. 1995).

2.6 Effects of weather

Weather is an important factor regarding crop growth. The temperature and precipitation amount can have an impact on the microorganisms in the soil, as well as the growth of plants. Plants tend to favour increasing temperature up to a point. Extreme high or low temperature have a negative effect on plants growth as well as seed germination. Precipitation, in the form of rain during summer, affects all plant growth functions. Too much water will reduce the oxygen available in soil and may cause erosion (Knox County Master Gardeners 2014). On the other hand, drought may negatively affect the quality of malting, notably by raising the nitrogen levels in grains (Baethgen et al. 1995). For these reasons, it is important to discuss the changes in temperature in accordance with the respective analysis results to assess the implication weather has on the treatments.

3 METHODS

In the Hierakka project, two treatments were applied onto the barley crop: human urine and mineral fertilizer (picture 2). The nitrogen level applied was 100 kg N/ha. The mineral fertilizer used in the 2018 treatment was Yara CAN27 and Yara Mila 3 for the 2016 and 2017 treatments (Viskari et al. 2018). The amount of human urine applied was determined so that the nitrogen level applied was similar to mineral fertilizer. The allocation of nitrogen was determined by comparing the amount of nitrogen in three parts of the barley crop: soil, grains and straw. Five samples per fertilizer treatment were analysed from the sampling plots in the field. There were different methods of determining the nitrogen concentration in said samples, each posing its own limitation, which were discussed below. Thus, two methods including the automatic analyser Elementar vario TOC select and the Kjeldahl digestion were applied.

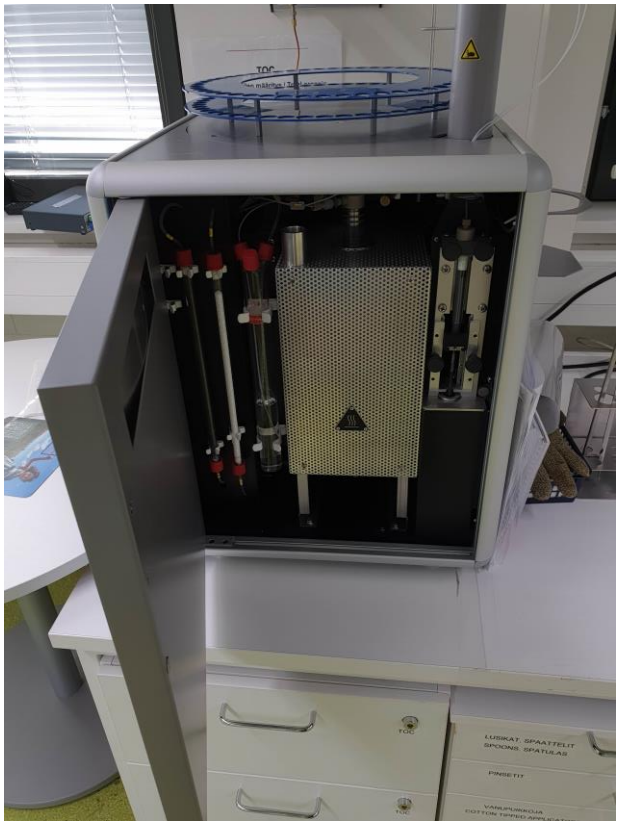


PICTURE 2. Example of sample plots for human urine fertilizer and mineral fertilizer treatments in 2018

3.1 Total nitrogen in soil using vario TOC select analyser

The Elementar vario TOC select is a multifunctional device mainly used to measure the total organic Carbon of solid and liquid samples (picture 3). The main principle of the device is the combustion of samples at high temperature in an

oxygen stream above 680° Celsius (Flyer vario TOC select 2019). This high temperature also enables the analysis of total bound nitrogen. In this study, the function used was TNb. After test runs using all the sample types, it was concluded that the method was viable to determine the total nitrogen in soil samples due to the unavailability of standard samples for grains and straws.



PICTURE 3. Elementar vario TOC select

3.1.1 Sample preparation

The raw soil samples were sieved into finer grains using a soil sampling sieve tool (picture 4). The amount of soil needed for the measurement was approximately 200 grams for each treatment, thus the sieved samples were divided into smaller containers.

PICTURE 4. Soil sieve

The vario TOC select analyser can measure up to 60 samples in solid mode with ten slots to be used for standard samples and one blank sample. For every sample used for this measurement, it was required to have at least three replicates to ensure the accuracy and prevent drastic differences in the result. Thus, five samples were chosen for each treatment.

3.1.2 Foiled-samples preparation

The vario TOC select measured the samples in solid mode, requiring all the samples to be put and compressed inside a tinfoil with known mass, including the blank, standards and samples. This was done with a compressor provided by the device manufacturer (picture 5).

First, the blank sample was prepared by weighting an empty sheet of tinfoil and the mass of the tinfoil was used. Next, the standard samples were prepared by using a soil sample with known concentration of nitrogen provided by the analyser manufacturer. For this measurement, ten standard samples were chosen with mass ranging from 10 mg to 90 mg. The purpose was to cover the expected range of the soil sample total nitrogen content and to create a standard curve that would fit best with the measurement. It was important that for every measurement, a set of ten standard samples was prepared due to the change in moisture. Next, the soil samples were prepared by weighting three replicates of each sample with different masses between 20mg and 60mg. The samples were contained in the

same tinfoil used for the blank sample and standard samples. The samples were chosen based on availability and variety so that the whole treatment result could be best conveyed.

PICTURE 5 Foiled sample and compressor

3.1.3 TN analysis

The measurement principle of the analyser was to convert the nitrogen found in the sample into nitrogen monoxide. The general rate of conversion is more than 80% depending on the combustion temperature, nitrogen compound and catalyst used. The detector inside the analyser produces ozone that reacts with the nitrogen monoxide to create nitrogen dioxide in an electronic excited state. This form of nitrogen dioxide is converted into normal nitrogen dioxide by emitting photons with wavelength between 600-3000nm, sometimes as high as 1200nm. The conversion equations are as follow (Operating instructions vario TOC cube/select 2019):

$$TN_b + O_2 \rightarrow NO$$
$$NO + O_3 \rightarrow NO_2^*$$
$$NO_2^* \rightarrow NO_2 + hv$$

The analysis was done as following. First, the ash finger solid meter was checked and replaced if necessary. The synthetic air valve was opened. The temperature of the device suitable for the analysis was 850 Celsius degrees. The suitable pressure used was between 1180 and 1200mbar. The synthetic air flow was 200ml/min. After the analysis had been completed by the device, the results were calibrated, and the standard curve was created using the standard sample results. The unfavourable standards were excluded (those further away from the curve). The standard curve used had polynomial degree 1 or 2. Afterward, the sample results were calculated using said calibration. The result for each sample was calculated as the average of the replicates. The final result for the treatment analysis was the average of all the samples. The analyser was put into maintenance for the next run.

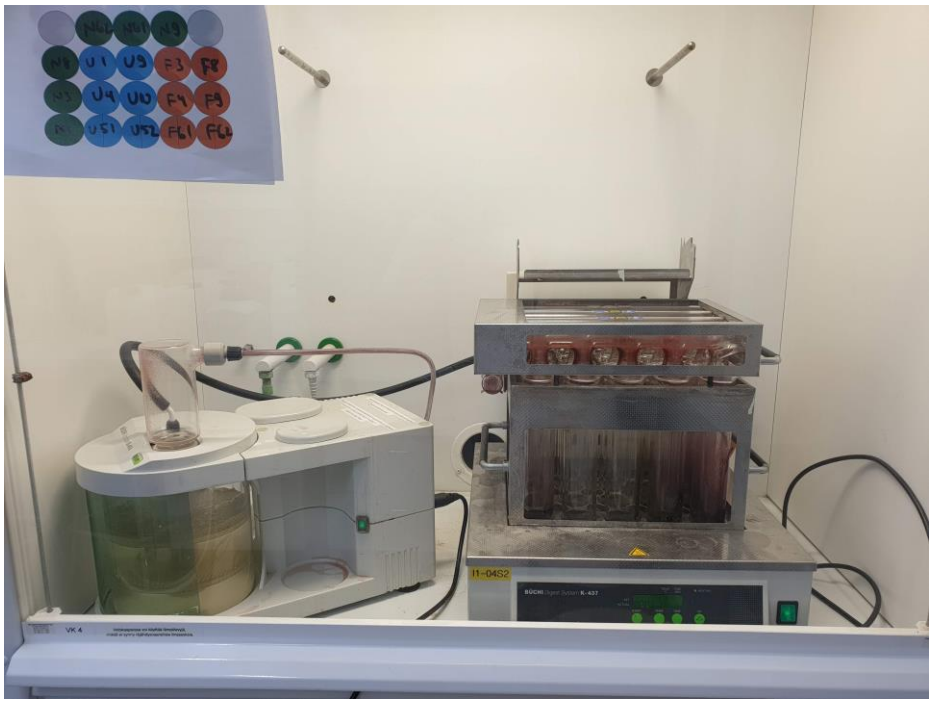
3.2 Total Kjeldahl nitrogen in grains and straws

The Kjeldahl digestion method was used to analyses the total nitrogen content in barley grains and straws. The principle of the Kjeldahl digestion is the conversion of organic matter into ammonium sulphate under the presence of sulfuric acid. Then, excess amount of alkali is added to release ammonia from ammonium sulphate. It is then distilled and absorbed in solution of boric acid and titrated with sulfuric acid as shown below (Manivasakam 2016).

$$2HNO_3 + 2H_3BO_3 \rightarrow 2NH_4^+ + 2H_2BO_3^-$$
$$H_2SO_4 \rightarrow 2H^+ + SO_4^{2-}$$
$$2NH_4 + 2H_2BO_3^- + 2H^+ + SO_4^{2-} \rightarrow (NH_4)_2SO_4 + 2H_3BO_3$$

The capacity of the digestion system was twenty samples per run. Five samples were analysed for each treatment, with one sample having two replicates. Two blanks samples were made for each run.

The Kjeldahl digestion process consisted of three steps: digestion, distillation and titration. There were preparations required for each step. The system used for the digestion was Büchi K-437 and Büchi K-415 Scrubber unit (picture 6), the distillation unit used was Büchi K-350 (picture 7) (Büchi 2019).



PICTURE 6. Büchi K-437 Kjeldahl digestion system and Büchi K-415 Scrubber unit

PICTURE 7. Büchi K-350 distillation unit

3.2.1 Preparation for Kjeldahl digestion process

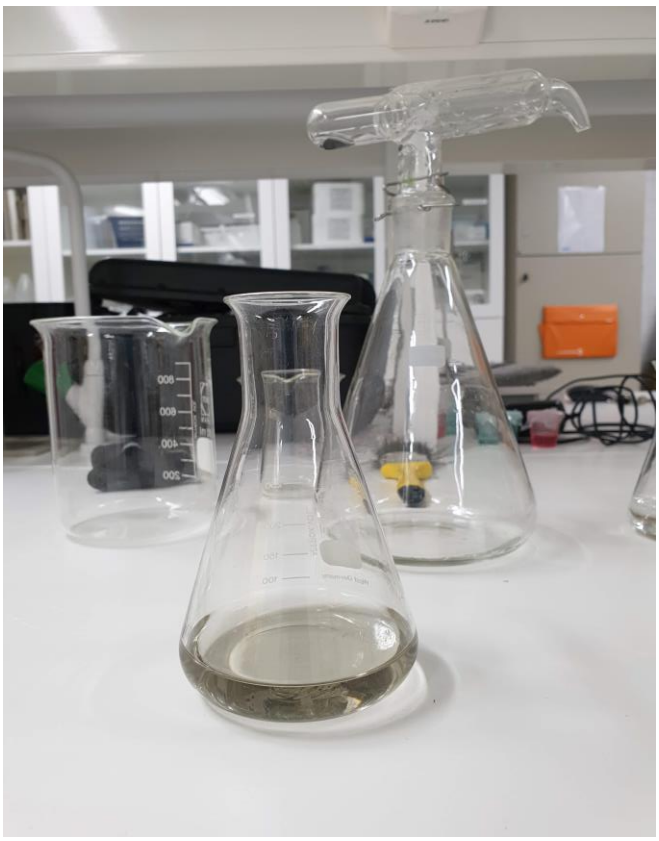
First, the solution for the scrubber unit was prepared by diluting $NaCO_3$ in warm distilled water to create $NaCO_3$ 30%. This was done either by diluting concentrated $NaCO_3$ or $NaCO_3 \cdot 10H_2O$, following the instruction from the device manufacturer.

The preparation of samples followed the same guideline: the sample size was 1 millimetre in diameter with mass of 1 gram approximately. For the grain samples, the samples were grinded and the mass used was 0.8 gram approximately. For the straw samples, the samples were blended and the mass used was 1 gram. The straw samples mass used were bigger than grain samples due to the expected nitrogen content in straw to be less than grain. Sample selection was done

so that for every fertilizer treatment e.g. human urine fertilized barley grain from Fall 2018, mineral fertilized barley straws from Fall 2017, etc., five samples were chosen, four without replicates and one with two replicates. With this method, six samples in total were analysed for each fertilizer treatment, hence the differences in each treatment were covered to maintain accuracy while reducing the time and resources used for the experiment.

After the samples were prepared, the samples were put into the 300 millilitre glass vials (18 of 20 slots) and the remaining two vials were used as blanks. Blank samples were prepared and treated with the same amount of reagent as normal samples. Next, two Kjeldahl tablets were put into each vial along with three drops of paraffin oil (mineral oil) to reduce foaming during the digestion process. Finally, 20 millilitre of concentrated sulfuric acid 98% was poured into each vial. Due to the expected lower nitrogen content of straw, more sample was weighted and thus the foaming potential was higher. Uncontrolled foaming would ruin the whole process and required most attention while doing the digestion. This could be minimized by having the reagents added and left overnight before the digestion.

In the steam distillation process, the receiving vessels were prepared by adding 60 millilitres of boric acid 2% into an Erlenmeyer flask. Next, three drops of Kjeldahl indicator solution was added (picture 8).



PICTURE 8. Receiving vessel for distillation

In the titration process, the titration acid was prepared by diluting 0.25M sulfuric acid in 2 litters of distilled water to create 0.5N sulfuric acid solution.

3.2.2 Kjeldahl digestion process

The digestion system was sealed tight before running and was connected to the scrubber. The samples were first pre-heated to 370 degrees Celsius. However, direct pre-heat could cause foaming and thus, a lower temperature e.g. 200 degree Celsius was chosen. After the samples were heated without foaming to the set temperature, it was raised by an increment from 30 to 50 degree Celsius until reaching 370 degrees Celsius. The samples were then left for one hour at 370 degrees Celsius. The desired outcome was a translucent liquid with no solid sample left. At any point that the samples would start foaming, the pre-heating was stopped until the samples stabilized.

After the digestion was done, the system was left to cooldown in four hours. Next, 50 millilitres of distilled water were added to each vial and shaken well. In case

of crystallization, the samples would be shaken until the samples dissolved or the vial would fit in the distillation unit. This was done because the crystallized samples would interfere with the hose of the distillation unit (picture 9).

PICTURE 9. Digested samples mixed with distilled water

The samples were then ready for the distillation process. A prepared receiving vessel was put into the device so that the hose was covered in the boric acid solution. Next, a sample vial was attached to the device tightly. Sodium hydroxide 32% was added as reagent until its reaction with the sample solution stopped. The process was set to run in four minutes. The receiving vessel was then ready for the titration process. The digestion vial was carefully taken out of the device with a rubber-tipped tong as it was heated during the distillation process (picture 10).

PICTURE 10. Distillation process

The receiving vessel was then put into the titration device using the prepared 0.5N sulfuric acid solution. The titration warning colour was blue and finished when the sample's colour turned into grey-brown (picture 11). The titration amount was read from the device and used to calculate the total nitrogen using formula 1 (shown below).

$$\%N = \frac{(V_1 - V_{BI}) \times c \times f \times M(N) \times 100}{m \times 1000}$$ (Viskari 2019) (1)

Where,

%N = the total nitrogen of the samples, %

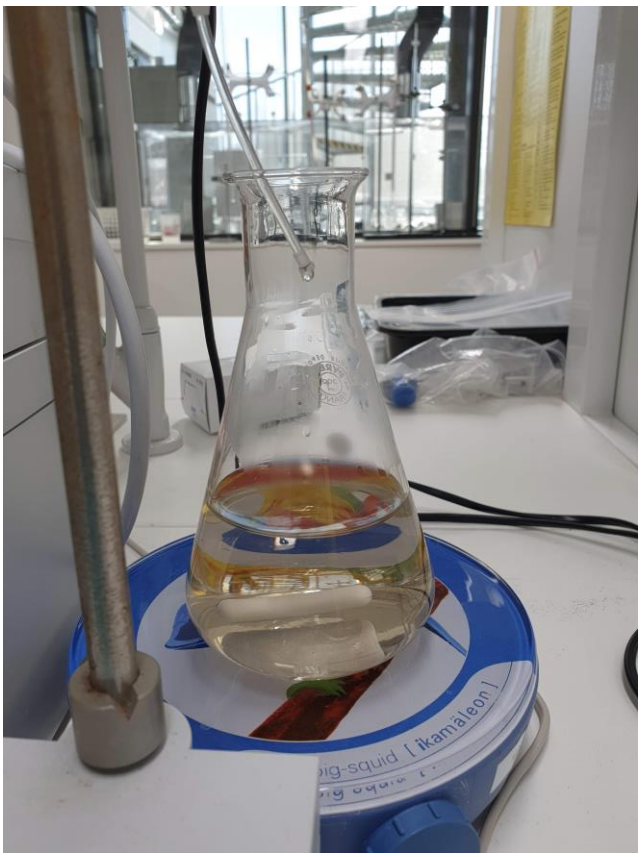
V_1 = consumption of 0.5N sulfuric acid in titration, ml

V_{BI} = consumption of 0.5N sulfuric acid in blank sample titration, ml

c = concentration of sulfuric acid (0.25M used in this measurement)

f = factor of acid (2 in this measurement)

M(N) = molar mass of nitrogen = 14g/mol



PICTURE 11. Titration process

3.3 Dry matter content

In this study, the sample mass was used for all the calculations. However, as there was water content in every sample, thus, the dry matter content was calculated.

The dry matter content was measured using the Precisa XM60 (picture 12). First, a small amount of sample was weighted into a metal weighting pan e.g. 2 grams. The device heated up the samples and gave result in percentage of dry matter in the given sample. For every sample, two to three duplicate runs were carried out and the results were the average of the duplicates. This result was used to calculate the real mass of samples in the total nitrogen calculation (formula 2).

$$\%N_{final} = \frac{\%N}{\%m_{dry}} \qquad (2)$$

Where,

$\%N_{final}$ = total nitrogen of the dry sample, %

$\%m_{dry}$ = percentage of dry matter content, %

PICTURE 12. Dry matter content determination using Precisa XM60

4 RESULTS

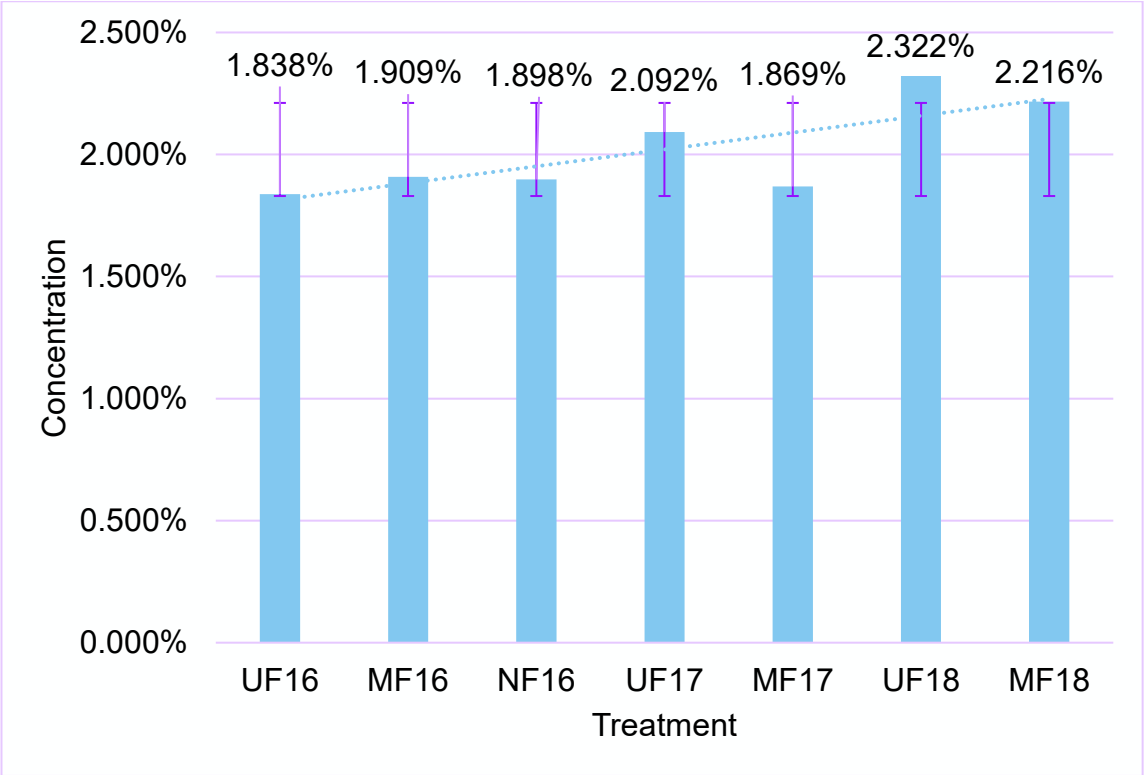
In this section, the results for each experiment were shown. During the experiments, samples were analysed with duplicates and the results were the average of the duplicates, where applicable. Two duplicates for each sample were used for dry mass analysis with the average being the result.

4.1 Total Kjeldahl nitrogen in barley grains

The TKN results for barley grains determined by using Kjeldahl digestion method were shown below (table 1). The amount of grains samples was fewer than soil as there were no samples collected from Spring 2017. Graphical representation was shown below (graph 1). For the full database see Appendix 1.

TABLE 1. Average total Kjeldahl nitrogen in barley grains in different fertilizer treatments and years

Treatment	TKN (%)
UF18	2.322
MF18	2.216
UF17	2.092
MF17	1.869
UF16	1.838
MF16	1.909
NF16	1.898



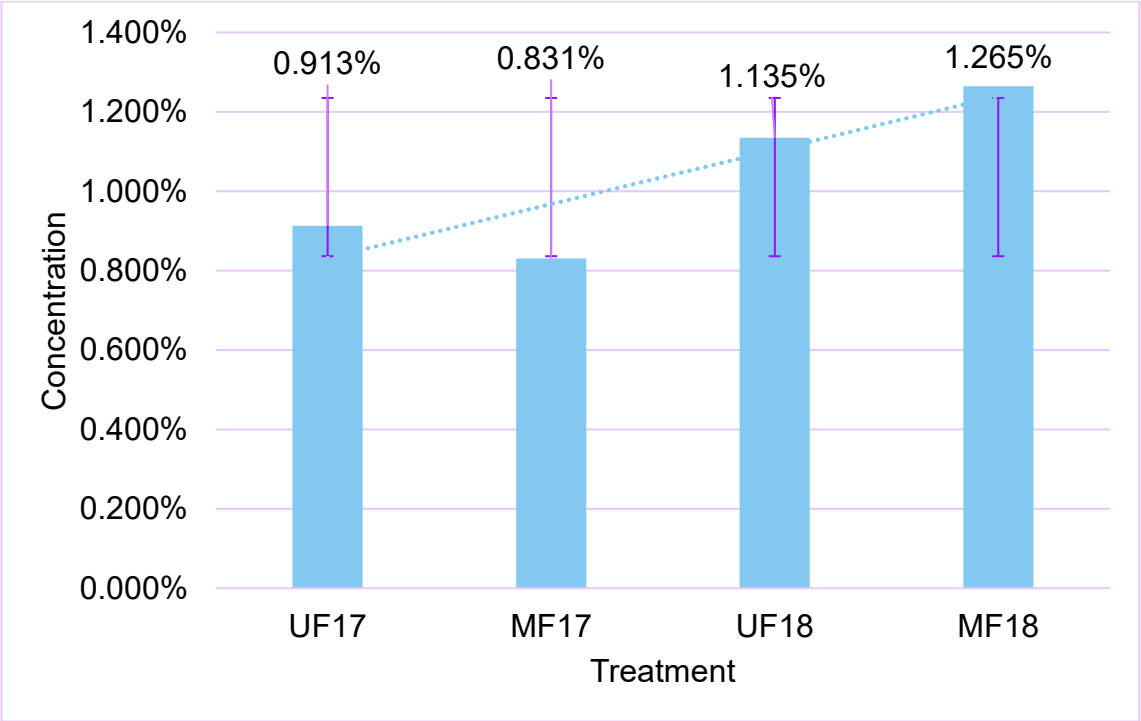
GRAPH 1. Average total Kjeldahl nitrogen in barley grains in different fertilizer treatments and years

4.2 Total Kjeldahl nitrogen in barley straw

The TKN results for barley straws determined by using the Kjeldahl digestion method were shown below (table 2). Graphical representation was shown below (graph 2). For the full database see Appendix 2.

TABLE 2. Average total Kjeldahl nitrogen in barley straws in different fertilizer treatments and years

Treatment	TKN (%)
UF18	1.135
MF18	1.265
UF17	0.913
MF17	0.831



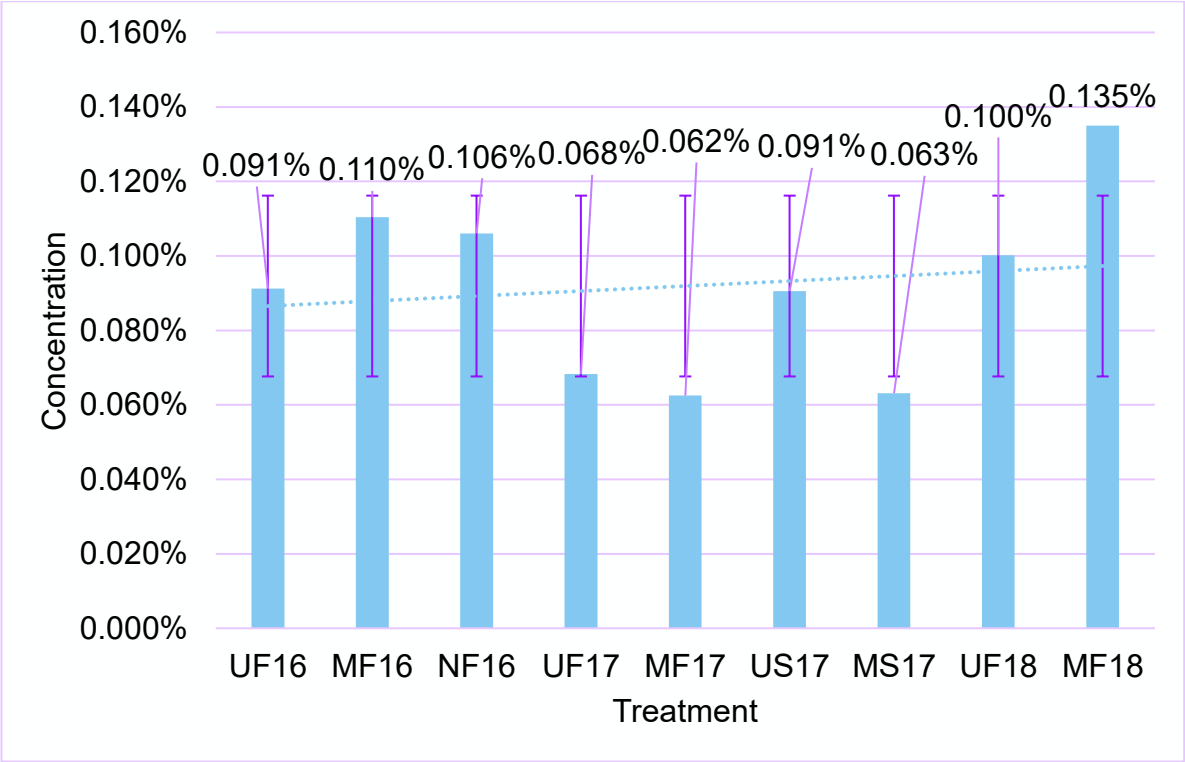
GRAPH 2. Average total Kjeldahl nitrogen in barley straws in different fertilizer treatments and years

4.3 Total nitrogen in soil

The TNb for soil was determined using the vario TOC select method (table 3). For the full database, see Appendix 3. The comparative graph was shown below (graph 3).

TABLE 3. Average total nitrogen in soil in different treatments and years

Treatment	TNb (%)
UF18	0.100
MF18	0.135
UF17	0.068
MF17	0.062
US17	0.091
MS17	0.063
UF16	0.091
MF16	0.110
NF16	0.106



GRAPH 3. Average total nitrogen in soil in different treatments and years

5 DISCUSSION

5.1 Barley grains

The average TNb in human urine fertilized barley grains was 2.084%, 1998% for mineral fertilized grains and 1.898% for barley grown without fertilizer (graph 1). The difference of less than 0.1% implying the insignificant effect of the type of fertilizer on barley grains. However, either types of fertilizer yielded more nitrogen content than barley grown without fertilizer. Comparing the data from the same time, the difference was consistence. The treatments from summer 2018 yielded most nitrogen and there was more nitrogen found in urine fertilized barley than mineral fertilizer. Compared to the reference database (Maaseutuvirasto 2008), the nitrogen content of human urine fertilized grains from 2017 was the closest to the reference 2.02%, implying that the urine fertilized barleys were less prone to nitrogen deficiency that would affect growth rate, maturity, quantity and quality of grains as well as tillering (Baset 2015, 65). On the other hand, the nitrogen contents from the 2018 treatments were consistently higher than the optimal nitrogen level of 2.16% for the malting process, indicating that the quality and size of grain yields were low (Baethgen et al. 1995). In addition, further study on the optimal level of human urine application to compensate for the weather conditions and increase grain quality and quantity must be conducted (Vicente et al. 2019).

5.2 Barley straws

The average TNb in human urine fertilized barley straws was 1.024% and 1.048% for mineral fertilized straws (graph 2). Compared to the reference database (Maaseutuvirasto 2008), the 2018 treatments yielded approximately double the reference total nitrogen content of 0.64% while the 2017 treatments were closer. This was due to the dry weather during summer 2018 that affected the nitrogen uptake of plants.

5.3 Soil

As shown in graph 3, the most recent treatments yielded the most nitrogen content, followed by the treatments from 2016. The mineral fertilizer treatment in 2017 summer and spring yielded much lower nitrogen content, with average of 0.093%. Compared to the average of 0.088% of the human urine fertilized treatment, the difference was insignificant. However, the analysis results from the mineral fertilizer treatments had greater variety, with the most recent treatment having as much as double the results than in 2017. During the 2016 treatments, the difference between three treatments were insignificant, implying similar amount of nitrogen taken up by plants, as well as similar conditions of soil including possible leaching and emission (Nkurunziza et al. 2017).

5.4 Weather effects

The weather data was collected from the Finnish Meteorological Institute including the monthly records of the temperature and precipitation at the Hattula Lepaa (2018) and Hämeenlinna Katinen (2017 and 2016) weather stations (table 4).

TABLE 4. Weather data 2018 (Finnish Meteorological Institute 2016, 2017 and 2018, modified)

Year	Month	Monthly precipitation amount (mm)	Monthly mean temperature (degC)
2016	6	71.4	15.3
2016	7	47.3	17.3
2016	8	69.8	15.4
2017	6	84.1	13.3
2017	7	62.7	15.3
2017	8	106.4	15
2018	6	40.8	15
2018	7	46.8	20.5
2018	8	41.8	17.3

It could be seen that in 2018, the average temperature during summer was higher than 2017 and 2016 while precipitation was drastically lower. The precipitation during summer 2017 was the highest. The temperature of summer 2018 was the highest, followed by summer 2016 and 2017 respectively. This caused a drought

stress in 2018. Regarding the TNb content of grains, straws and soil, the 2018 treatments yielded the highest TNb, followed by the treatments in 2017 and the lowest was 2016. The dry weather during summer 2018 treatments increased the nitrogen level pass the optimal concentration for plant growth, consequently lowered the malting quality (Baethgen et al. 1995). Thus, proper management of nitrogen fertilizer and analysis of nitrogen available in the soil must be conducted to maintain grain yields quality.

The TNb of treatments in 2017 was the closest to the database published by the Natural Resources Institute Finland (Maaseutuvirasto 2008). The database suggested the TNb content of barley grains of 2.02%, compared to the findings of this thesis of 2.092% and 1.869% for human urine and mineral fertilizer respectively. Thus, it can be concluded that the weather conditions of summer 2017 and 2016 were most suited for barley crop growth.

6 CONCLUSION

In conclusion, to serve the growing population in the future, it is important to develop a sustainable food production process. Human urine, under good treatment and usage, can be a potential sustainable fertilizer that not only replace conventional mineral fertilizer, but also contribute to the bigger picture that is circular economy. By using waste as resource, the use of mineral fertilizer that carries unwanted side effects on the environment can be mitigated. However, the use of human urine as a fertilizer must be tested before putting into practice. The test of total nitrogen bound in different parts of crop plant serve as part of the bigger study as nitrogen is one of the most important macro elements impacting crop growth. If human urine can replace mineral fertilizer, it must produce crops with similar properties compared to mineral fertilizer. The aim of this thesis work was to determine the total nitrogen content of barley grains, straws and the soil used to grow the plants that were treated with human urine and mineral fertilizer, compare and assess the results.

By applying different methods, both automatic and manual, it was possible to determine the total nitrogen content in the samples from all treatments. The analysis was a success and results were favourable. The total nitrogen content of the barley parts grown with human urine were similar to that of mineral fertilizer, as well as the database done by the Natural Resources Institute Finland.

The drastic difference in weather condition during the original study imply the effects of weather on the total nitrogen content. The barley crops grown during summer 2017 yielded the closest total nitrogen content compared to the reference database (Maaseutuvirasto 2008) and the crops during summer 2018 with little rain yielded the lowest quality of grains due to the highest nitrogen concentration.

It can be said that in terms of total nitrogen content, human urine is a feasible replacement for mineral fertilizer. The barley crops grown with human urine yielded similar properties, physically and chemically to mineral fertilizer. How-

ever, poor weather conditions can negatively affect the quality of crop yields, especially during the era of global warming. Thus, the optimal amount of human urine fertilized must be further studied to compensate for the changes of nitrogen available in soil for plant uptake under different weather conditions.

This thesis work was successful in determining the total nitrogen content of different parts of the barley crop from the treatment of human urine and mineral fertilizer and helped prove the possibilities and feasibility of human urine as a fertilizer.

REFERENCES

Acciona. What is circular economy?. Accessed: 25.04.2019. https://www.activesustainability.com/sustainable-development/what-is-circular-economy/

Baethgen W.E., Christianson C.B., Lamothe A.G. 1995. Nitrogen Fertilizer Effects On Growth, Grain Yield, And Yield Components Of Malting Barley. Field Crops Research 43.

Büchi – Products & Solutions. Distillation Unit K-350. Accessed: 25.04.2019. https://www.buchi.com/en/products/kjeldahl-dumas/distillation-unit-k-350-k-355

Baset M. 2015. Nutrition of Crop Plants. Nova Science Publishers, Inc. USA.

Elementar – Products. vario TOC select. Accessed 25.04.2019. https://www.elementar.de/en/products/toc-water-analysis/vario-toc-select.html

Elementar – Products. vario TOC select. Operating instructions vario TOC cube vario TOC select.

Finnish Meteorological Institute. 2016. Hämeenlinna Katinen. Accessed on 25.04.2019. https://cdn.fmi.fi/fmiodata-convert-api/preview/bcaf5fe4-eaac-434c-8b9c-4b752ade3a7a/?locale=en

Finnish Meteorological Institute. 2017. Hämeenlinna Katinen. Accessed on 25.04.2019. https://cdn.fmi.fi/fmiodata-convert-api/preview/9aa9bd85-b459-4f7a-941f-f1acf9903a5a/?locale=en

Finnish Meteorological Institute. 2018. Hattula Lepaa. Accessed on 25.04.2019. https://cdn.fmi.fi/fmiodata-convert-api/preview/6a64861b-1dbe-43d3-b75a-def9d6dec057/?locale=en

Grunbaum M. 2010. Human Urine Is Shown to Be an Effective Agricultural Fertilizer. Accessed on 03.05.2019. https://www.scientificamerican.com/article/human-urine-is-an-effective-fertilizer/

Knox County Master Gardeners. 2014. How Weather Affects Plants. Garden Tips. University of Illinois Extension. Accessed: 25.04.2019. https://web.extension.illinois.edu/hkmw/downloads/55040.pdf

Maaseutuvirasto. 2008. Ravinnetaseohje. Accessed on 25.04.2019. http://rae.savonia.fi/tietopankki/maatilan-tietopaketti/finish/14-ravinnetase/25-ravinnetaseohje-2008/0

Manivasakam N. 2016. Industrial effluents: origin, characteristics, effects, analysis & treatment. Chemical Publishing Company Inc.

Miransari M. 2012. Soil nutrients. Nova Science Publishers, Inc. USA.

Nkurunziza L., Chongtham I.R., Watson C.A., Marstorp H., Öborn I., Bergkvist G., Bengtsson J. 2017. Understanding effects of multiple farm management practices on barley performance. European Journal of Agronomy.

Tinker P. B., Nye, Peter H. 2000. Solute Movement in the Rhizosphere. Oxford University Press, New York. USA.

Vicente R., Vergara-Díaz O., Kerfal S., López A., Melichar J., Bort J., Serret M.D., Araus J.L., Kefauver S.C. 2019. Identification Of Traits Associated With Barley Yield Performance Using Contrasting Nitrogen Fertilizations And Genotypes. Plant Science.

Viskari E.L. 2019. Kjeldahl digestion instruction. TAMK.

Viskari E.L., Honkala I., Haapamäki S., Pakula S. 2018. Virtsa Lannoitteena Peltoviljelyssä – Hyödyt, Riskit Ja Mahdollisuudet. Käymäläseura Huussi ry. Finland.

APPENDICES

Appendix 1. Total Kjeldahl nitrogen in barley grains

Treatment	Titration acid (ml)	Sample Mass (g)	Dry Matter Content (%)	Total Nitrogen (%)	Replicate Average (%)	Total Average (%)
Blank L	0.153	0				
Blank R	0.126	0				
UF182	2.038	0.892	92.93	1.604088445		
UF183	2.762	0.874	92.29	2.277007973		
UF187	2.612	0.808	91.81	2.334264607		
UF189	2.73	0.834	92.10	2.361962775		
UF1851	3.358	0.814	91.85	3.015009765		
UF1852	3.944	0.951	91.85	3.050373672	3.032691718	2.322003103
MF183	2.61	0.794	91.70	2.376478195		
MF185	2.348	0.799	92.21	2.09936395		
MF189	2.542	0.813	92.22	2.244206758		
MF1810	2.692	0.854	91.91	2.277633667		
MF1861	2.364	0.814	92.05	2.079327686		
MF1862	2.392	0.82	92.05	2.090094287	2.084710986	2.216478711
UF171	2.29	0.87	92.19	1.877911265		
UF173	2.432	0.806	92.59	2.151536929		
UF175	2.252	0.808	91.86	1.993414846		
UF179	2.954	0.876	91.97	2.446750606		
UF17101	2.296	0.817	91.32	2.024308208		
UF17102	2.268	0.833	91.32	1.959647164	1.991977686	2.092318266

Treatment	Titration acid (ml)	Sample Mass (g)	Dry Matter Content (%)	Total Nitrogen (%)	Replicate Average (%)	Total Average (%)
Blank L	0.08	0				
Blank R	0.108	0				
NF161	2.038	0.813	92.28	1.814833528		
NF163	2.062	0.865	91.86	1.734593356		
NF168	1.938	0.8567	91.80	1.642118907		
NF169	2.696	0.8379	92.24	2.357949408		
NF1661	2.464	0.8496	92.37	2.115151797		
NF1662	2.064	0.847	92.37	1.763561114	1.939356456	1.897770331
UF161	2.046	0.7957	91.95	1.868604847		
UF164	1.988	0.8943	92.41	1.605152892		
UF169	2.254	0.8345	92.72	1.955206086		
UF1610	2.032	0.807	92.55	1.817267869		
UF1651	2.39	0.8715	92.18	2.001734521		
UF1652	2.126	0.8181	92.18	1.887205952	1.944470237	1.838140386
MF163	2.208	0.8354	92.27	1.920724714		
MF164	2.146	0.8752	91.79	1.789012884		
MF168	2.252	0.8578	92.15	1.91198813		
MF169	2.316	0.8462	92.40	1.990280076		
MF1661	2.314	0.8754	92.01	1.930412564		
MF1662	2.322	0.8775	92.01	1.932732567	1.931572566	1.908715674
MF171	2.534	0.962	92.56	1.87430713		
MF174	2.102	0.859	92.53	1.71908233		
MF177	2.286	0.866	92.81	1.86037437		1.869295241
MF179	2.39	0.815	92.92	2.07074102		
MFIF61	2.27	0.908	93.08	1.755916527	1.821971353	
MF1762	2.314	0.862	93.08	1.88802618		

Appendix 2. Total Kjeldahl nitrogen in straws

Treatment	Titration acid (ml)	Sample Mass (g)	Dry Matter Content (%)	Total Nitrogen (%)	Replicate Average (%)	Total Average (%)
Blank L	0.21	0				
Blank R	0.092	0				
MF182	1.664	1.075	94.79	1.039934491		
MF184	2.252	0.987	94.52	1.577249214		
MF188	1.846	1.001	94.76	1.251551203		
MF1810	2.164	1.024	94.32	1.459748986		
MF1861	1.702	1.002	93.20	1.16317028		
MF1862	1.26	1.01	93.20	0.825105331	0.994137805	1.26452434
UF182	1.222	0.972	94.74	0.814569002		
UF183	1.528	1.117	94.05	0.918037009		
UF187	1.824	1.029	94.69	1.202517991		
UF189	1.686	1.072	93.97	1.06718448		
UF1851	3.19	1.194	94.25	1.891298802		
UF1852	2.154	1.026	94.25	1.450665767	1.670982284	1.134658153
UF172	1.756	1.074	94.70	1.105245715		
UF174	1.426	1.04	94.61	0.907565312		
UF178	1.692	1.14	95.03	0.996265387		
UF179	1.446	1.068	94.13	0.902212125		
UF1761	1.288	1.077	94.30	0.78405802		
UF1762	0.922	1.093	94.30	0.523887042	0.653972531	0.913052214
MF172	1.47	1.045	94.42	0.88398244		
MF173	1.33	1.076	94.33	0.767390939		0.830777398
MF178	1.396	1.041	94.54	0.886015106		
MF1710	1.308	1.049	94.41	0.772454671		

MF1741	1.432	1.051	94.01	0.853614034	0.844043833	
MF1742	1.414	1.06	94.01	0.834473632		

Appendix 3. Total nitrogen in barley-grown soil

Treatment	TNb (%)	Replicate Average TNb (%)	Dry Matter Content (%)	Sample Mass (mg)	Total Average (%)
MF1811	0.145			39.88	
MF1811	0.15			29.68	
MF1813	0.146	0.1438542	97.86	68.71	
MF1831	0.054			67.79	
MF1832	0.131			44.54	
MF1833	0.167	0.114810667	97.85	28.1	
MF1851	0.128			37.03	
MF1852	0.151			27.45	
MF1853	0.106	0.1255485	97.83	64.74	
MF1871	0.177			32.8	
MF1872	0.137			61.42	
MF1873	0.155	0.152894	97.80	53	
MF1891	0.154			56.14	
MF1892	0.134			30.46	
MF1893	0.135	0.1376301	97.61	43.98	0.134947493
UF1611	0.098			28.17	
UF1612	0.08			57.69	
UF1613	0.098	0.0907856	98.68	36.25	
UF1621	0.099			48.01	
UF1622	0.101			26.42	
UF1623	0.071	0.0889964	98.52	41.96	
UF1631	0.103			20	
UF1632	0.089			38.55	0.091191307
UF1633	0.08	0.089170667	98.35	47.47	
UF1641	0.098	0.1007574	98.46	41.04	

UF1642	0.127			23.23	
UF1643	0.082			60.08	
UF1651	0.097			27.55	
UF1652	0.089			36.2	
UF1653	0.077	0.086246467	98.38	45.12	
UF1811	0.103			45.84	
UF1812	0.09			27.06	
UF1813	0.095	0.094368	98.30	64.52	
UF1831	0.119			34.8	
UF1832	0.1			51.35	
UF1833	0.1	0.104546933	98.32	66.42	
UF1851	0.102			60.47	
UF1852	0.095			44.82	
UF1853	0.079	0.0903164	98.17	75.52	
UF1871	0.185			33.73	
UF1872	0.08			54.78	
UF1873	0.094	0.1174648	98.16	73.72	
UF1891	0.094			58.85	
UF1892	0.083			73.65	
UF1893	0.11	0.094002067	98.26	38.88	0.10013964
MF1611	0.092			32.71	
MF1612	0.109			48.03	
MF1613	0.101	0.098894933	98.24	63.96	
MF1621	0.115			27.93	
MF1622	0.112			42.1	
MF1623	0.097	0.106218	98.35	53.31	
MF1631	0.111			29.31	
MF1632	0.112	0.1036164	98.37	35.56	0.11037838

MF1632	0.093			48.49	
MF1641	0.159			24.14	
MF1642	0.102			37.35	
MF1643	0.089	0.114823333	98.42	51.6	
MF1651	0.165			24.04	
MF1652	0.135			29.56	
MF1653	0.091	0.128339233	98.47	43.17	
NF1611	0.121			35.47	
NF1612	0.125			57.05	
NF1613	0.139	0.126061833	98.23	17.78	
NF1621	0.194			20.55	
NF1622	0.079			42.55	
NF1623	0.037	0.101339	98.07	56.63	
NF1631	0.087			27.02	
NF1632	0.122			42.34	
NF1633	0.03	0.074193567	93.13	60.85	
NF1641	0.118			25.78	
NF1642	0.107			33.13	
NF1643	0.046	0.088897033	98.41	56.43	
NF1651	0.152	0.1397792	91.96	31.76	0.106054127
UF1711	0.082			30.19	
UF1712	0.069			36.8	
UF1713	0.064	0.070426833	98.27	50.56	
UF1731	0.043			35.82	
UF1732	0.08			27.56	
UF1733	0.059	0.0601146	99.09	43.93	
UF1751	0.057			24.59	
UF1752	0.088	0.067745667	99.14	41.6	0.068288727

UF1753	0.06			35.71	
UF1771	0.062			27.29	
UF1772	0.064			41.87	
UF1773	0.068	0.063916533	98.84	35.42	
UF1791	0.086			31.01	
UF1792	0.097			26.29	
UF1793	0.057	0.07924	99.05	41.23	
US1711	0.102			38.51	
US1712	0.109			49.61	
US1713	0.148	0.118350333	98.90	57.72	
US1731	0.123			66.37	
US1732	0.133			44.24	
US1733	0.127	0.126364467	98.98	52.25	
US1751	0.11			45.75	
US1752	0.074			51.02	
US1753	0.088	0.089696533	98.93	65.62	
US1771	0.034			49.95	
US1772	0.058			60.24	
US1773	0.06	0.050089067	98.86	76.84	
US17101	0.073			51.39	
US17102	0.072			64.52	
US17103	0.063	0.068300267	98.51	57.18	0.090560133
MS1711	0.059			43.78	
MS1712	0.048			53.56	
MS1713	0.085	0.0632128	98.77	67.8	
MS1731	0.038			45.7	
MS1732	0.058			58.54	
MS1733	0.063	0.052364	98.80	67.27	0.063124733

MS1741	0.071			46.48	
MS1742	0.053			57.71	
MS1743	0.1	0.073800533	98.84	69.85	
MS1751	0.068			43.72	
MS1752	0.052			53.14	
MS1753	0.067	0.061572867	98.78	66.14	
MS1771	0.06			58.17	
MS1772	0.055			67.06	
MS1773	0.081	0.064673467	98.99	41.78	
MF1751	0.064			44.44	
MF1752	0.057			58.32	
MF1753	0.078	0.065577133	98.86	63.81	
MF1761	0.053			58.08	
MF1762	0.053			46.27	
MF1763	0.069	0.057773333	99.04	71.15	
MF1771	0.057			57.38	
MF1772	0.059			73.88	
MF1773	0.078	0.0640006	98.97	43.91	
MF1791	0.059			62.17	
MF1792	0.06			49.33	
MF1793	0.053	0.0566396	98.79	59.04	
MF17101	0.049			49.78	
MF17102	0.074			61.96	
MF17103	0.086	0.068412667	98.20	67.48	0.062480667