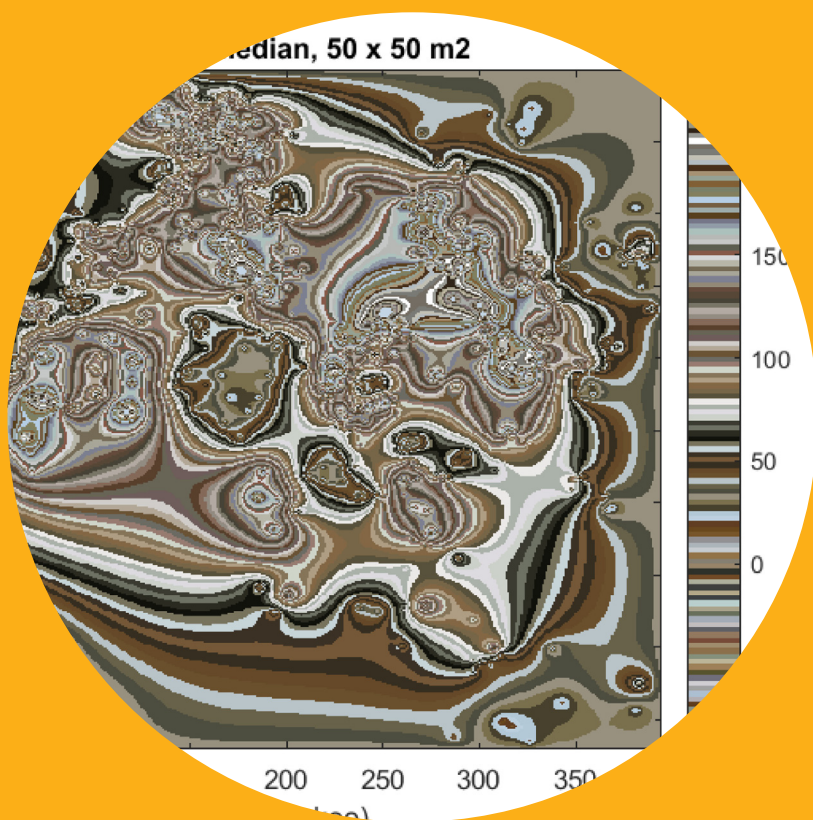


Nitrification in drinking water distribution and wastewater treatment

Reasons, consequences and the effects of the organic matter

Pirjo Liisa Rantanen



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Reasons, consequences and the effects of the organic
matter

Pirjo-Liisa Rantanen

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Abstract

This thesis concerns nitrification in different environments. Nitrification is a biochemical reaction of ammonium into nitrite and further nitrate. In drinking water distribution systems (DWDSs), nitrite formed in nitrification can be problematic because it is potentially harmful to humans. On the other hand, in wastewater treatment plants (WWTPs), nitrification is utilized in biological ammonium removal from wastewater. This thesis concerns the spatial and seasonal inspection of nitrite formation in full-scale DWDSs. In DWDSs, nitrite is formed by an added disinfection chemical, monochloramine, or ammonium in the raw water. Furthermore, this thesis inspects nitrification in relation to organic matter, in both WWTPs and in laboratory-scale simulated distribution systems (SDSs). The spatial analysis of water quality revealed that nitrite was forming rapidly after leaving the water treatment plant (WTP) in the DWDSs. The nitrite concentrations tended to be low in stagnating water. The normal low dose of monochloramine ($0.35\text{--}0.4\text{ mgCl}_2\text{ L}^{-1}$) was not high enough to prevent nitrite formation; however, it limited the maximum nitrite concentrations. Nitrite concentrations exhibited seasonal peaks either in the warm season or cold season, or there was no observable seasonal peak. The key drivers causing seasonality were water temperature and water age. The nitrite peaks in the cold season were caused by the decelerated ammonium oxidation. The dominant reaction at low water ages was ammonium oxidation into nitrite; and at high water ages, it was nitrite oxidation into nitrate. These results emphasize comprehensive and year-round nitrite monitoring in the DWDSs. In wastewater treatment, ammonium removal via nitrification was unexpectedly enhanced when the soluble organic matter concentrations were increased with pre-fermentation, retrofitted in a previously used pre-sedimentation basin. However, upon closer inspection, it was revealed that the organic load into the nitrification basin was reduced in the pre-fermentation line by the preceding denitrification and biological phosphorus removal, compared to the pre-sedimentation line. In non-disinfected conditions of tap water, decreasing the natural organic matter (NOM) in the water ($\text{TOC } 1.0\text{ mg L}^{-1}$) prevented nitrite formation in SDSs, compared to unreduced NOM ($\text{TOC } 1.6\text{ mg L}^{-1}$). When the results were interpreted with a pseudo first order reaction rate model, it was observed that the decreased nitrite concentrations were a result of enhanced nitrite oxidation. The maximum nitrite concentrations were strongly dependent on the ratio of the ammonium and nitrite oxidation activities. This study supports enhanced removal of NOM at the WTPs to also decrease the potentially harmful nitrite concentrations.

Keywords nitrification, nitrite, drinking water distribution, wastewater treatment

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Väitöskirjan nimi

Nitrifikaatio talousveden jakelussa ja jäteveden puhdistuksessa – Syyt, seuraukset ja orgaanisen aineen vaikutus

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Tämä väitöskirja käsittelee nitrifikaatiota erilaisissa ympäristöissä. Nitrifikaatiossa ammoniumtyppi hapettuu biokemiallisesti nitriitiksi ja edelleen nitraatiksi. Talousveden jakeluverkostoissa nitrifikaatio voi aiheuttaa terveydelle haitallisen nitriitin pitoisuuksien nousua. Toisaalta jätevedenpuhdistuksessa ammoniumtyyppiä poistetaan biologisesti nitrifikaation avulla. Väitöskirjassa tutkittiin nitriitin muodostumista talousveden jakeluverkostoissa spatiaalisesti ja kausitarkastelun avulla. Nitriitti muodostuu verkostoissa joko lisätystä desinfiointikemikaali monoklooriamiinista tai raakaveden sisältämästä ammoniumista. Lisäksi väitöskirjassa selvitettiin orgaanisen aineen vaikutusta nitrifikaatioon täyden mittakaavan jätevedenpuhdistamolla sekä laboratoriossa simuloituissa talousveden jakeluverkostoissa. Talousveden laadun paikkatietoon perustuva tarkastelu paljasti, että jakeluverkoston veden nitriittipitoisuudet nousivat jo lähellä vesilaitosta. Pitkään verkostossa viipyneessä vedessä nitriittipitoisuudet olivat enimmäkseen matalia. Talousvedeen normaalisti lisättävä pieni monoklooriamiiniannos ($0,35\text{--}0,4\text{ mgCl}_2\text{ L}^{-1}$) ei estänyt nitriitin muodostumista, mutta rajoitti sen maksimipitoisuuksia. Nitriittipitoisuudet vaihtelivat kausittain niin, että pitoisuuksien huippu osui joko lämpimään aikaan, kylmään aikaan, tai sitä ei esiintynyt lainkaan. Tärkeimmät nitriitin kausivaihteluun vaikuttavat tekijät olivat veden lämpötila ja veden ikä. Kylmässä lämpötilassa hidastunut ammoniumin hapettuminen aiheutti kylmään aikaan osuvat nitriittihuiput. Veden iän ollessa lyhyt nitriittipitoisuuksia hallitseva reaktio oli ammoniumin hapettuminen nitriitiksi ja veden iän ollessa pitkä hallitseva reaktio oli nitriitin hapettuminen nitraatiksi. Käytännössä tämän väitöskirjan tulokset puoltavat ympärivuotista ja koko jakeluverkoston kattavaan nitriitin tarkkailua. Jäteveden puhdistuksessa ammoniumitypen poisto nitrifikaation avulla yllättäen tehostui, kun liukoisen ja helposti hajoavan orgaanisen aineen pitoisuutta lisättiin esiselkeytyksen tilalle jälkiasennetun esifermentaation avulla. Lähemmässä tarkastelussa paljastui, että nitrifikaatiota edeltävät denitrifikaatio ja biologinen fosforinpoisto itse asiassa vähensivät nitrifikaatio-osastoon tulevaa orgaanisen aineen kuormaa esifermentaatiolinjalla verrattuna esiselkeytyslinjaan. Talousveden orgaanisen aineen (NOM) vähentäminen ($\text{TOC } 1,0\text{ mg L}^{-1}$) laboratoriomittakaavan simuloituissa jakeluverkostoissa ilman desinfiointia esti nitriittipitoisuuksien nousun verrattuna siihen, että NOM-pitoisuutta ei vähennetty ($\text{TOC } 1,6\text{ mg L}^{-1}$). Kun tuloksia tulkittiin ensimmäisen kertaluvun reaktionopeusmallilla, havaittiin, että nitriittipitoisuuksien väheneminen johtui tehostuneesta nitriitin hapettumisesta nitraatiksi. Teoreettiset maksiminitriittipitoisuudet riippuivat voimakkaasti ammoniumin hapettumisen ja nitriitin hapettumisen keskinäisestä suhteesta. Tulokset puoltavat NOM-pitoisuuden vähentämistä vedenkäsittelyssä myös terveydelle haitallisten nitriittipitoisuuksien vähentämiseksi.

Avainsanat nitrifikaatio, nitriitti, talousveden jakelu, jäteveden puhdistus**ISBN (painettu)** 978-952-64-0121-8**ISBN (pdf)** 978-952-64-0122-5**ISSN (painettu)** 1799-4934**ISSN (pdf)** 1799-4942**Julkaisupaikka** Helsinki**Painopaikka** Turku**Vuosi** 2020**Sivumäärä** 156**urn** <http://urn.fi/URN:ISBN:978-952-64-0122-5>

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Pirjo Rantanen

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List of publications

This doctoral dissertation consists of a summary and the following publications, which are referred to in the text by their numerals:

- I: Rantanen, P.-L., Keinänen-Toivola, M.M., Ahonen, M., Mellin, I., Zhang, D.Y., Laakso, T., and Vahala, R. (2017). The Spatial Distribution of Nitrite Concentrations in a Large Drinking Water Distribution System in Finland. *Journal of Water Resource and Protection*, 9, 1026–1042.
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- II: Rantanen P.-L., Mellin I., Keinänen-Toivola M.M., Ahonen M., and Vahala R. (2018). The Seasonality of Nitrite Concentrations in a Chloraminated Drinking Water Distribution System. *International Journal of Environmental Research and Public Health*, 15, 1756, 17 p.
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- III: Mikola, A., Rantanen, P. and Vahala, R. (2012). Full-Scale Investigation of the Influence of Flow Equalization and Prefermentation on Nitrification. *Water Environment Research*, 84, 5, 452-459.
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- IV: Rantanen, P.-L., Keinänen-Toivola, M.M., Ahonen, M., Gonzalez-Martinez, A., Mellin, I. and Vahala, R. (2020). Decreased natural organic matter in water distribution decreases nitrite formation in non-disinfected conditions, via enhanced nitrite oxidation, 21 p. Accepted for review in *Water Research* (acceptance date July 21st 2020)

Author's contribution

- I. P. Rantanen designed the study, made the analyses and maps, interpreted the results, and wrote the manuscript. All authors contributed to editing the paper.
- II. P. Rantanen designed the study, carried out the research, analyzed and interpreted the data, and wrote the manuscript. All authors contributed to editing the paper.
- III. P. Rantanen participated actively in the data analysis, data interpretation, and discussion. Furthermore, she participated in the study as a member of the steering group of the project as a specialist in nitrification. A. Mikola planned the study, carried out a part of the experimental work, analyzed the data and had the main responsibility for writing the paper. All authors contributed to editing the paper.
- IV. P. Rantanen planned the study, designed the experimental equipment and the laboratory analyses, and carried out the experiments. She also analyzed and interpreted the data and wrote the manuscript. A. Gonzalez-Martinez performed the molecular biology analyses. All authors contributed to editing the paper.

List of terms and abbreviations

Activated sludge = A biological wastewater treatment process, with the active microbial mass in suspension with the wastewater.

Alkalinity = The ability of a water solution to buffer against a decrease in pH.

AOA = Ammonia oxidizing archaea.

AOB = Ammonia oxidizing bacteria.

AOC = Assimilable organic carbon. A laboratory method of estimating the share of organic matter that is readily available for biofilm formation in distributed water.

Biofilm = Microbial growth on a surface. Biofilms grow on nearly all wet surfaces and, depending on the conditions, contain various kinds of micro-organisms and EPS.

BOD₇ = Biochemical oxygen demand with a seven-day incubation time. A laboratory method to estimate the organic matter concentration in wastewater.

BOD₇(ATU) = BOD₇ with added allyl thiourea to prevent oxygen consumption in nitrification. This method is commonly used in Finland.

C₅H₇NO₂ = The average elemental composition of bacterial mass, used in reactions.

COD_{Cr} = Chemical oxygen demand of wastewater analyzed with the dichromate method.

Drinking water = In this thesis, “drinking water” means treated and distributed water that has a good microbiological, chemical, and aesthetic quality according to legislation (European council, 1998, Finnish Ministry of Social Affairs and Health, 2015).

DWDS = Drinking water distribution system. Consists of the distribution pipes, water reservoirs, and other equipment permanently connected.

Equalization = A process unit in wastewater treatment. Its function is to equalize fluctuations in influent wastewater.

EPS = Extra-cellular polymeric substances.

Flotation filter = A combination of dissolved air flotation and bed filtration used as a unit process in wastewater treatment to polish the treatment result.

GAC = Granular activated carbon. In this thesis, this term is used in connection with water treatment. The unit process called GAC filtration removes organic substances from water and also has microbiological activity.

Normal NOM = The NOM concentration in tap water in the laboratory of Water Engineering, Aalto University, Espoo.

Hardness = The sum of the magnesium and calcium ion concentrations in water.

HPC = Heterotrophic Plate Count. A microbiological method of estimating the number of heterotrophic bacteria in water samples.

ICC = Intact Cell Count.

LoQ = Limit of quantification. The term is used for the determination limit of laboratory analyses. This should not be confused with the detection limit, which is lower and not quantifiable.

Reduced NOM = The NOM concentration in the mixture of tap water and RO water.

MLSS = Mixed liquor suspended solids. The concentration of biomass in activated sludge processes treating wastewater.

Municipal wastewater = Combined household and industrial wastewater and storm water.

Nitrification = Microbiological oxidation of ammonium and nitrite.

NOB = Nitrite oxidizing bacteria.

NOM = Natural organic matter. The term is used in connection with natural and distributed waters.

PE = The person equivalent of a WWTP, estimated from the influent BOD₇ load.

Pre-fermentation = A unit process in wastewater treatment to increase the easily biodegradable matter in the influent wastewater.

Pre-sedimentation basin = Primary settling basin.

Primary settling basin, primary settler, primary sedimentation basin = A basin where a share of suspended solids is removed from influent wastewater by settling.

RBCOD = Readily biodegradable COD, related to the organic matter of influent wastewater.

RO water = Water purified with reverse osmosis filtration for laboratory use.

SDS = Simulated distribution system.

Secondary disinfection = Disinfection of water in the DWDSs.

SI = Seasonality index.

Soluble COD_{Cr} = COD_{Cr} from a sample without suspended solids.

SRT = Sludge retention time.

SS = Suspended solids. A laboratory method of estimating the solids content of water samples.

Tap water = Distributed water that does not necessarily meet the requirements of good quality.

TOC = Non-purgeable total organic carbon, sometimes referred to as NPOC.

VFA = Volatile fatty acids. This term is used in connection with influent wastewater.

Wastewater = Water that has been used and in the consumption process has been contaminated with substances that restrict its further use.

WTP = Water treatment plant.

WWE = Water and wastewater engineering.

WWTP = Wastewater treatment plant.

List of symbols

i = Number of seasons when calculating SI values.

$\mu_{h,max}$ = Maximum growth rate of heterotrophic bacteria.

$\mu_{n,max}$ = Maximum growth rate of nitrification bacteria.

SI_i = Seasonal Index.

\bar{x} = Annual mean nitrite concentration when calculating the SI.

x_i = Mean nitrite concentration in a season i when calculating the seasonal index.

1 Introduction

1.1 Ubiquitous nitrification

Nitrification is a ubiquitous biochemical reaction in natural and artificial environments (Figure 1). It transforms aqueous ammonia (NH_3) into nitrite ions (NO_2^-) and further into nitrate ions (NO_3^-).

Natural environments form the vast majority of places where nitrification occurs. Much of the nitrogen mineralized in soils is released from dead microbes (Marumoto et al., 1982), and the end product is ammonium (Figure 2), which is the primary substrate of nitrification. Net mineralization of ammonium varies from 10 to 120 kgN ha⁻¹ a⁻¹, depending on soil type. However, ammonium is also a very desirable nutrient for plants and microbes, thus the actual amount of nitrified ammonium is difficult to estimate (Schlesinger and Bernhardt, 2013). Nevertheless, it is known that nitrification occurs to some extent in these environments.

This thesis concerns three of the environments mentioned in Figure 1—Water Distribution in Large Cities, Municipal Wastewater Treatment Processes, and Laboratories. In water distribution, nitrification may cause the formation of nitrite, which can be harmful to humans, especially infants (Jaffé, 1981). On the other hand, in wastewater treatment, nitrification enables the removal of ammonium from the influent wastewater. Furthermore, in laboratories, nitrification is studied in research. All the mentioned environments are artificial, or human-made, in contrast to soil and water environments, which are not altered or only slightly altered by humans. This implies the possibility to understand nitrification in artificial environments more profoundly because the boundaries and the inputs and outputs of the processes are less ambiguous.

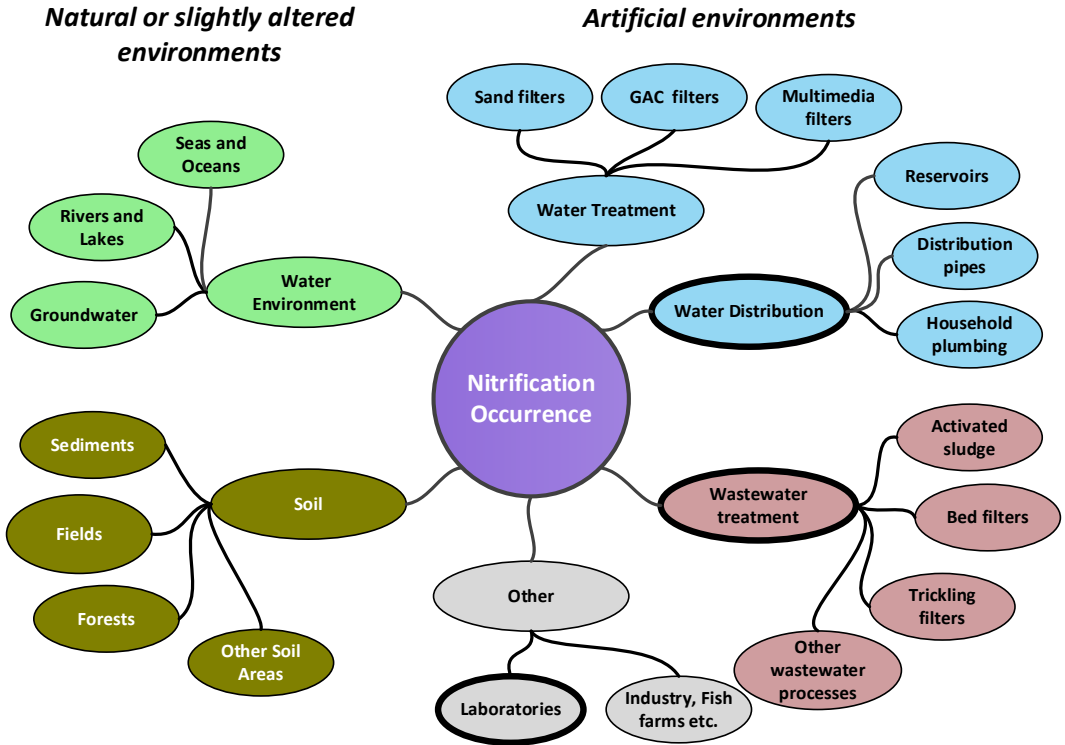


Figure 1. A mind map of nitrification occurrence. Highlighted occurrences are included in this thesis. Information combined from Crittenden et al., 2005; Paasonen-Kivekäs et al., 2016; Stumm and Morgan, 2009; Tchobanoglous et al., 2003; and Ward et al., 2011.

Figure 2 illustrates the part of the nitrogen cycle that concerns this thesis. It consists of the steps of ammonium formation—either from organic nitrogen compounds or monochloramine (National research council, 2006)—and successive nitrification and nitration. (Schlesinger and Bernhardt, 2013). The whole nitrogen cycle also includes other reactions, for example nitrogen fixation, denitrification, and anammox, which are discussed only briefly in this thesis.

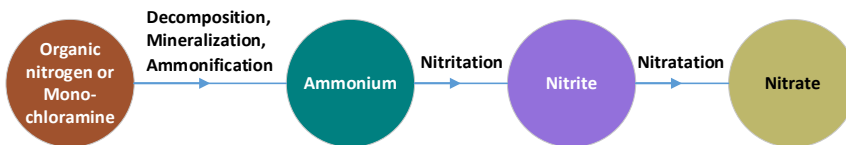


Figure 2. The part of the nitrogen cycle included in wastewater treatment and drinking water distribution, with preceding decomposition of organic nitrogen compounds or monochloramine and consequent nitrification (nitritation and nitrataion). Modified from Schlesinger and Bernhardt (2013).

1.2 The structure and the objectives of the thesis

This thesis consists of two connected parts (Figure 3). Part A describes the spatial and seasonal distribution of nitrite in drinking water distribution systems

(DWDSs). Part B describes nitrification in relation to varying concentrations of organic matter in both wastewater and tap water.

Title	Part	Publication
<p style="text-align: center;">Nitrification in drinking water distribution and wastewater treatment</p> <p style="text-align: center;">Reasons, consequences and the effects of the organic matter</p>	<p>A</p> <p>Nitrite formation in full-scale drinking water distribution systems</p>	<p>I The Spatial Distribution of Nitrite Concentrations in a Large Drinking Water Distribution System in Finland</p>
	<p>B</p> <p>The effect of organic matter on nitrification in wastewater treatment and tap water distribution</p>	<p>II The Seasonality of Nitrite Concentrations in a Chloraminated Drinking Water Distribution System</p>
	<p>III Full-Scale Investigation of the Influence of Flow Equalization and Prefermentation on Nitrification</p>	
	<p>IV The effect of organic matter on the nitrification rates in non-disinfected drinking water distribution</p>	

Figure 3. The structure of this thesis.

The overall objective of this thesis is to discover more information about nitrification in the above-mentioned artificial environments. The detailed objectives of the thesis consist of the following study questions:

Part A:

1. How can the existing obligatory monitoring data of drinking water quality be utilized to find out more about nitrite formation in a DWDS?
2. What is the spatial distribution of nitrite in a DWDS, and what are the reasons behind the spatial distribution?
3. What is the seasonal distribution of nitrite in a DWDS, and what are the main reasons for the observed seasonality?

Part B:

4. What are the effects of organic matter on nitrification in practical applications?
5. How does increasing the easily biodegradable organic matter in a nitrogen removal wastewater treatment plant (WWTP) affect ammonium removal by nitrification?
6. Can the nitrite levels in drinking water distribution be decreased by decreasing organic matter?

On the whole, the thesis provides more possibilities to control nitrification in artificial, human-made environments.

2 Background

2.1 Scientific connections

This thesis is based on various scientific disciplines related to Water and Wastewater Engineering (WWE). These disciplines are depicted in Figure 4, which includes the output fields of the thesis. The scope of this thesis lies between theoretical and practical science.

WWE links together the practical and theoretical scientific disciplines shown in Figure 4. Knowledge gaps arise from the practical disciplines linked to WWE, that is, environmental protection, environmental health, and public health. These are also the scientific fields that will utilize the results. In practice, the results will be utilized in everyday water quality monitoring, DWDS operation, and process design and operation.

WWE utilizes several theoretical scientific disciplines, including water chemistry, biochemistry, biogeochemistry, and microbiology. To complement these in this work, other theoretical disciplines were chosen by preference. These disciplines—experimental design, analytical chemistry, reaction engineering, and statistical analysis—were the tools used to produce data and derive information from the data.

All things considered, the focal point of this thesis arose from WWE. The other disciplines supported WWE. An effort was made to contain this thesis within WWE without going too deep into the other disciplines.

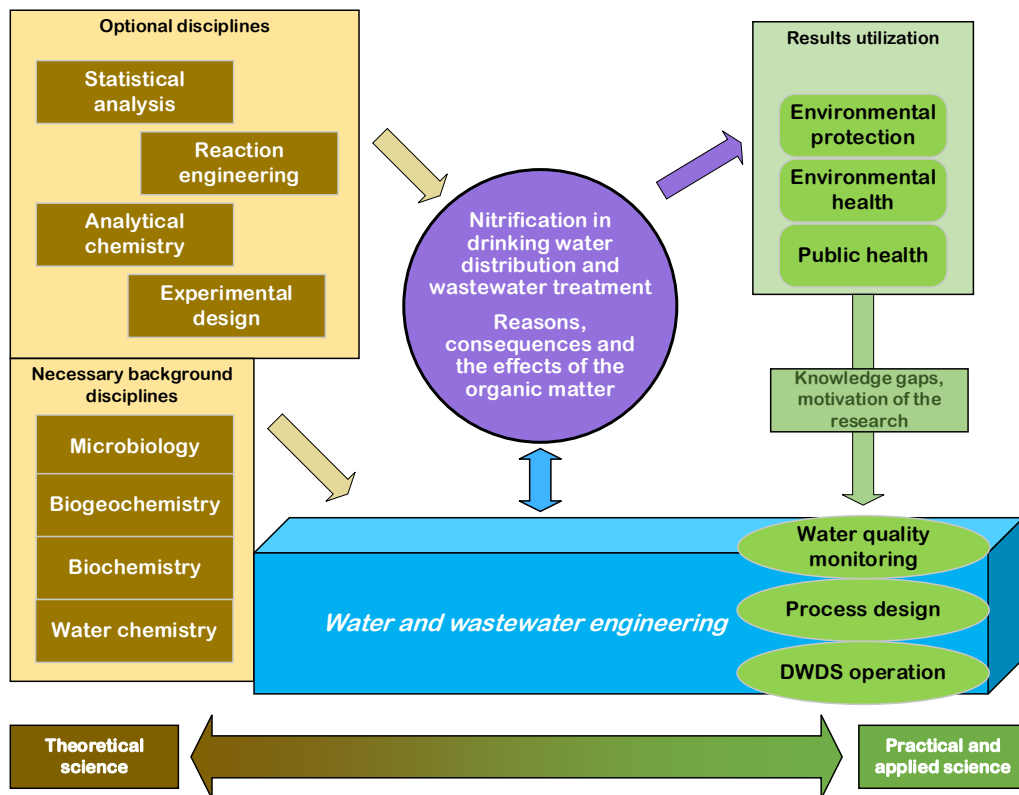


Figure 4. The scientific basis of this thesis and the output scientific fields.

Chapter 2 includes introductory texts for professionals who are acquainted only with drinking water distribution or wastewater treatment. Minimal references are used in these passages.

2.2 Nitrification

2.2.1 Historical highlights

The first nitrifying organisms on Earth were able to develop only after the oxygen atmosphere was created by plant life (Schlesinger and Bernhardt, 2013). The first nitrifiers were probably archaea (Schlesinger and Bernhardt, 2013), which have been found to dominate in soils (Leininger et al., 2006).

Nitrification was first reported in soil by Schoenbein (1846) when the added fertilizer contained ammonia. After a while, nitrate was noted in the fertilized soil. At that time, it was thought that nitrification might be an inorganic reaction. This supposition was refuted in 1888 by two separate researchers, Plath and Landolt, who observed that nitrification was a biological process (Chick, 1906). The nitrifying organisms were finally identified by Sergei Winogradsky (1890), the founder of modern microbiology. Nitrification was observed to be accomplished by two types of bacteria, *Nitrosomonas*, which oxidizes ammonia into nitrite (nitritation), and *Nitrobacter*, which oxidizes nitrite into nitrate (nitratation). Starting from these early years, it was clear that organic matter disturbed nitrification

because the growing media of that time contained organic matter that prevented the growth of the nitrifying organisms. Specific growth media were required without organic matter. Nitrifying organisms were found growing on inorganic carbon sources and are therefore called chemoautotrophic (or autotrophic) organisms (Winogradsky, 1890).

One of the pioneers of nitrification research in wastewater processes is Harriette Chick (Chick, 1906), who also formulated a law bearing her name, Chick's Law, concerning the inactivation of bacteria by disinfection (Chick, 1908). In fact, a modified Chick-Watson disinfection model has recently been used for modeling the disinfection of *Nitrosomonas europaea* with monochloramine (Wahman et al., 2009). In her research on wastewater, Chick (1906) noticed that nitrification functions better in higher temperatures. She also confirmed that nitrification is a two-step process and speculated that nitrifying bacteria may exist in symbiosis with other organisms.

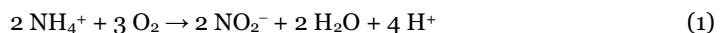
Furthermore, nitrification in drinking water distribution systems (DWDSs) was first noted by Feben (1935) when ammoniation of distributed water was used to prevent the development of chlorinous and chloro-phenolic tastes and odors. Unfortunately, nitrite was formed from the added ammonia in nitrification, causing increased chlorine demand. Feben concluded that the raw water contained unknown nitrifying bacteria and that the sand filters promoted the growth of these organisms after ammoniation of the water. He also postulated that it was impractical to control nitrification in the DWDS by chlorination.

Nitrification and other biochemical processes are commonly modeled with a Monod-type (Monod, 1949) kinetic model, which takes into account the bacterial growth in addition to the substrate concentration. The first computer-integrated differential equations of a Monod-type nitrification model were solved in (1965) by Knowles et al. The kinetic constants, estimated for both nitrification and nitrification, were shown to be temperature-dependent in this work.

Nitrospira-like bacteria have been observed as being capable of nitrifying ammonia all the way into nitrate (Daims et al., 2015; Daims et al., 2016; Kits et al., 2017). The reaction is called the comammox reaction. Nitrospira has been found abundantly in biofilms but not in purified water at water treatment plants (WTPs) (Xu et al., 2017).

2.2.2 Basics of nitrification

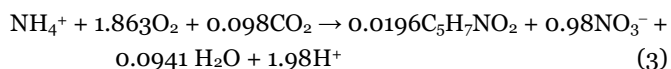
Nitrification consists of two main reactions: ammonium (NH_4^+) oxidation into nitrite (NO_2^-) and consequently nitrite oxidation into nitrate (NO_3^-):



As can be seen from the reaction equations, the products of nitrification reactions are nitrite, nitrate, and acidity. Equation 1 is called nitrification and Equation 2 is called nitrification. Furthermore, one end product of the reactions is more bacterial cells (Equation 3).

Unlike the heterotrophic bacteria, which consume organic matter as the carbon source, ammonia oxidizing bacteria (AOB) and nitrite oxidizing bacteria (NOB) consume carbon dioxide and carbonates as their carbon source. As a consequence, AOB and NOB gain less energy for the growth of new cells and thus grow slower than the heterotrophic bacteria. Therefore, the maximum growth rates of AOB and NOB ($\mu_{n,max}$) are low (0.2–0.9 g new cells (g cells d)⁻¹) compared to heterotrophic bacteria ($\mu_{n,max}$: 3.0–13.2 g new cells (g cells d)⁻¹) (Tchobanoglous et al., 2003).

On the whole, the reactions of ammonia oxidation, nitrite oxidation, carbon dioxide consumption, and cell growth are shown in Equation 3, as follows (Tchobanoglous et al., 2003):



In Equation 3, the compound C₅H₇NO₂ refers to bacterial mass.

2.2.3 The preconditions and consequences of nitrification

The main prerequisites of nitrification are ammonium, nitrifying organisms, and water. If these are fulfilled, nitrification occurs in many environments. However, nitrification is also sensitive. Because the organisms grow slowly, they easily lose the battle against other organisms, most often heterotrophic (Tchobanoglous et al., 2003). They also require high oxygen levels, do not tolerate well chemical or physical changes in the environment; furthermore, they can even destroy the environment for themselves by the extensive formation of hydrogen ions (Henze et al., 2002).

All these preconditions make nitrification not self-evident in WWTPs, although it can happen accidentally, especially in higher wastewater temperatures (Tchobanoglous et al., 2003). On the other hand, in DWDSs, getting rid of nitrification has proven to be a hard task, especially because nitrification organisms lodge in the sanctuary of biofilms (Zhang, Y. et al., 2009). Furthermore, in research, the initial starting of nitrification can be a challenge and can take months to establish, which was observed in **Publication IV**.

In DWDSs, the main consequences of nitrification are nitrite formation and the loss of monochloramine disinfectant (Anon., 2006). These are hard to prevent if the prerequisites of nitrification are fulfilled. Nitrification in the biofilm is persistent, because the structure of the biofilm protects all micro-organisms from environmental conditions (Yin et al., 2019). High doses of disinfecting chemicals can be used to prevent nitrification, but since the organisms are growing inside the biofilms, they can never be destroyed completely. Sooner or later, nitrification and its harmful effects will start again.

In wastewater treatment, nitrification not only has consequences in the operation of wastewater processes, but it also affects the actual design of the WWTPs (Henze et al., 2002; Tchobanoglous et al., 2003). For example, nitrifying processes are often designed to remove most of the organic matter first to decrease the organic load on the nitrifying unit. As another example from the everyday

operation of nitrification, alkaline chemicals are frequently added to the influent to compensate for the lowered pH.

2.3 Drinking water

2.3.1 Water treatment

The purpose of the drinking water treatment is to ensure a good chemical, microbiological, and aesthetic quality of the water for human consumption (Crittenden et al., 2005). The methods depend on the quality of the raw water, which can be groundwater, artificial groundwater, surface water, or in some cases, reclaimed wastewater. Groundwater can sometimes be good enough to be distributed to customers without any treatment (Lipponen et al., 2002; Schullehner et al., 2017). Artificial groundwater recharge aims to utilize the natural processes that result in groundwater (Neudorfer and Weyermayer, 2007). Furthermore, the quality of the surface waters and reclaimed wastewater can vary a lot, but in general, the purification requires several treatments in succession. Substances that are typically removed are turbidity, suspended solids, natural organic matter (NOM), and microbes (Crittenden et al., 2005). Additionally, the taste and odor are also improved in the treatment processes. Removal of undesirable chemicals and microorganisms from raw water is vital for public health protection (Xu et al., 2017).

Various treatment methods are used, for example, physical filtration, sedimentation, and physicochemical precipitation. When the raw water contains a significant concentration of NOM, the organic molecules may often be broken down by a high-energy treatment, for example, ozonation (Brunner et al., 2019). Ozonation is also an effective disinfection method. The disinfection operations at the WTP are called primary disinfection when the target is to inactivate microbes. The final phases of the treatment may include an additional physical-microbiological filtration, for example, with granular activated carbon (GAC) filters (Vahala, 2002). When a WTP provides water for a larger area where metal is used as a pipe material, the water quality may be enhanced by chemical additions for changing the pH of the water. Finally, the hygienic quality of the water is ensured with disinfection, e.g. with ultraviolet (UV) light, chlorination, or both.

2.3.2 Drinking water distribution

After treatment, the freshly produced drinking water is distributed to customers via DWDSs. Thus, the preceding treatment also has to take into account the distribution to avoid water quality changes and harmful effects on the distribution pipes. An important goal in distribution is to maintain the hygienic quality of the distributed water to the customers' taps. Maintaining a residual disinfectant in the distributed water is called secondary disinfection (Anon., 2006). This requires the addition of chlorine when the water enters the DWDS, and on the other hand, removal of substances that might cause extra consumption of the disinfection chemical.

In Finland, the quality of the distributed drinking water is regulated by the European Directive on the quality of water intended for human consumption (European Council, 1998) and the implementation of the Directive as a decree (Finnish Ministry of Social Affairs and Health, 2015). The decree states that the obligatory upper limit for nitrite is 0.5 mg L^{-1} (0.15 mgN L^{-1}) and for nitrate 50 mg L^{-1} (11.3 mgN L^{-1}). Furthermore, the value of the nitrate concentration divided by 50 plus the nitrite concentration divided by 3 must not exceed 1. The nitrite concentration in the water leaving the WTP must not exceed 0.1 mg L^{-1} (0.03 mgN L^{-1}). Ammonium, on the other hand, is not considered to be as harmful, and its targeted maximum value is 0.5 mg L^{-1} (0.5 mgN L^{-1}) (Valvira, 2018).

Drinking water distribution systems constitute separated environments because there are usually only one or very few points of entry for water, and elsewhere, only water outtake is possible. Thus, DWDSs form a relatively undisturbed environment for micro-organisms to grow, compared, for example, to activated sludge processes in wastewater treatment. Therefore, regular cleaning and flushing of the pipes is a good practice (Stinson, 1982). The environment is characterized by low concentrations of organic matter and other nutrients, but typically a high concentration of oxygen in the water. On the other hand, the deposits formed over the past decades can contain a substantial pool of nutrients. Therefore, the microbiological quality of the water introduced into DWDSs has to be good because the possibly harmful microbes have a chance to proliferate in the water and the biofilm (LeChevallier and Au, 2004).

2.3.3 Secondary disinfection

To sustain a good hygienic quality of distributed water to the customer's tap, secondary disinfection is used. This comprises adding chlorine containing chemicals at the WTP as the final step in water treatment. It is common practice to maintain a chlorine residual to suppress waterborne pathogens in drinking water distribution systems (Wilczak et al., 1996; Waak et al., 2018). However, in Europe, there are several countries where secondary disinfection is not used in distributing groundwater, for example, Finland, Denmark, and The Netherlands (Ahonen et al., 2008; Schullehner et al., 2017; Waak et al., 2018).

The chemical used in secondary disinfection is decomposed or consumed in the disinfection reactions with micro-organisms. On the other hand, it can also be consumed by reactions with NOM or other constituents of the distributed water. Thus, the concentration of the disinfection chemical is reduced when the distributed water progresses in the DWDS. The remaining disinfecting activity is measured as residual total chlorine, which is usually expressed as $\text{mgCl}_2 \text{ L}^{-1}$.

In the USA, the most common method for secondary disinfection was chlorine gas, as reported in a 2008 survey organized by the American Water Works Organization (Anon., 2008a). When dissolved in water, chlorine gas reacts into hypochlorite, which is the active agent in disinfection. Chlorine is capable of decreasing the total bacterial count in the distributed water (Rosenfeldt et al., 2009). In the USA, the most common alternative method was monochloramine disinfection (Anon., 2008b).

Li, W. et al. (2018) observed that total chlorine concentrations over 0.15 mg L^{-1} decreased the intact cell count (ICC) of the distributed water in full-scale DWDSs. They also concluded that monochloramine was more efficient in decreasing active bacterial cells than chlorine. In some cases, the bacterial concentrations may also increase in a disinfected DWDS. For example, Prest et al. (2014) observed that the total bacterial cell count increased in the DWDS from the initial $345 \times 10^3 \text{ cells mL}^{-1}$ to $425 \times 10^3 \text{ cells mL}^{-1}$ with chlorine dioxide disinfection (initial total chlorine concentration $0.1 \text{ mg Cl}_2 \text{ L}^{-1}$) in The Netherlands. In the latter case, the total chlorine in the DWDS was below the limit of quantification (LoQ).

2.3.4 Secondary disinfection with monochloramine

Monochloramine, NH_2Cl , is the product of the reaction of hypochlorite and ammonium (Equation 4) (Hale et al., 1919; Zhang, Y. et al., 2009). Dichloramine and nitrogen trichloride (NHCl_2 , NCl_3) may also form in the reaction, but the desired product is monochloramine, and its formation can be favored in practice by the lower ratio of chlorine to ammonia (Anon., 2005).



Monochloramine is inherently unstable, undergoing autodecomposition even in the absence of reactive substances (Ricca et al., 2019). However, it has been observed to penetrate biofilms better than chlorine because it is less reactive (Lee et al., 2011). Furthermore, monochloramine has been observed to be more stable when cement pipes are used and cause less corrosion of iron pipes than chlorine (Masters et al., 2015).

Monochloramine undergoes an auto-decay reaction depending on pH (Jafvert and Valentine, 1986; 1992). A higher pH reduces the auto-decay on monochloramine. The auto-decay reaction is initially catalyzed by reinforced concrete or concrete-lined ductile iron pipe surfaces because of the increased pH (Woolschlager et al., 2001).

Gomez-Alvarez et al. (2014) concluded that monochloramine was able to mitigate NOB activity when its concentration was above $0.4 \text{ mg Cl}_2 \text{ L}^{-1}$. On the other hand, they observed active ammonia oxidation by AOB at the above-mentioned monochloramine concentration.

Duirk et al. (2005) observed that monochloramine oxidized NOM in two pathways: a fast and direct oxidation of NOM and a slower reaction directed by HOCl formed from monochloramine. The latter was attributable to the main loss of monochloramine. Monochloramine loss occurred also by the organic soluble microbial products of nitrification (Bal Krishna et al., 2012).

Interestingly, it has been lately found that monochloramine can be co-metabolized by nitrifying bacteria directly to nitrite (Maestre et al., 2013; Maestre et al., 2016; Wahman et al., 2016). In fact, 30–60% of the monochloramine loss could be attributed to direct metabolism.

2.3.5 Biofilms in drinking water distribution

Biofilms are aggregates of various microorganisms that attach themselves to solid surfaces using self-secreted extracellular polymeric substances (EPS) (Al Marzooq, 2015). They form easily on the inside surfaces of the distribution pipes (Inkinnen et al., 2014). Generally, biofilms are not welcome in the DWDSs because they can degrade the water quality in distribution (Muhammad et al., 2020). However, biofilms are found even inside chlorine-disinfected distribution pipes (Bachmann and Edyvean, 2005). Low chlorine concentrations (less than 1.0 mg Cl₂ L⁻¹) may even promote surface attachment of micro-organisms (Liu, L. et al., 2015). Furthermore, pathogenic organisms may proliferate in DWDS biofilms and pose a health risk to consumers (Liu, G. et al., 2013).

Biofilms found in DWDSs comprise patchy and heterogeneous structures (Liu, G. et al., 2013). It is widely accepted that most of the microbial biomass in DWDSs is located within biofilms (Makris et al., 2014; Zacheus et al., 2001; Laurent et al., 1993). The microbial flora in DWDS biofilms is diverse (see Table 1) (Liu, G. et al., 2013). As can be seen, the phyla *Nitrospirae* is among the most common in DWDSs.

Table 1. Commonly found bacteria in DWDSs. (The table is compiled by Liu, G. et al., 2013)

	Commonly found bacteria in DWDSs	References
Predominant phyla in DWDSs	<i>Proteobacteria, Actinobacteria, Firmicutes, Verrucomicrobia, Nitrospirae, Bacteroidetes</i>	(Kalmbach et al., 1997; Schwartz et al., 1998; Schmeisser et al., 2003; Williams et al., 2004; Williams et al., 2005; Peng et al., 2010)
Predominant genera in DWDSs	<i>Acinetobacter, Aeromonas, Alcaligenes, Arthrobacter, Corynebacterium, Bacillus, Burkholderia, Citrobacter, Enterobacter, Flavobacterium, Klebsiella, Methylobacterium, Moraxella, Pseudomonas, Seratia, Staphylococcus, Mycobacterium, Sphingomonas, Xanthomonas</i>	(Batte et al., 2003; Berry et al., 2006; Simões et al., 2010)
Opportunistic pathogens	<i>Mycobacterium, Legionella, Pseudomonas, Klebsiella, Aeromonas</i>	(Anon., 2011)

In the recent years, the research concerning the bacteriology of biofilms has been revolutionized by the new molecular techniques in microbiology (Liu, G. et al., 2013). As a result several studies have been published lately (Muhammad et al., 2020). For example, hydraulic conditions have been found to affect the structure and population of bacterial communities in biofilms. Biofilms were found to change during the seasons when the microbial species in the frequent distribution pipe flushing were studied. Furthermore, the changes in water quality induced varying biofilm dynamics (Douterelo et al., 2016). Also, the treatment strategy at the WTP changed the biofilm bacterial populations (El-Chakhtoura et al., 2015). Gomez-Alvarez et al. (2014) concluded that biofilms change both temporally and geographically.

The bacterial community composition has been noted to differ between biofilms and bulk water samples. The bacteria capable of producing high quantities of an extracellular polymeric substance, and thus initiate the biofilm formation, were predominant in the biofilms. Furthermore, *Gammaproteobacteria*, the bacterial group including most of the known pathogens, was highly abundant in biofilms. This observation indicates the important role of biofilms in pathogenic contamination in DWDSs (Douterelo et al., 2013).

Kelly et al. (2014) noticed that there was no significant relationship between the concentration of monochloramine and the abundance of bacteria within the biofilms in a survey organized in a full-scale DWDS. The dominating taxa were *Methylomonas*, *Acinetobacter*, *Mycobacterium*, and *Xanthomonadaceae*, depending on the sampling time.

Boers et al. (2018) found seasonal variation in a non-monochloraminated full-scale DWDS. The biofilms consisted of a highly diverse bacterial environment, and only six species existed with a higher share than 5% as median (*Comamonadaceae*, *Deferrisoma*, *Gallionellaceae*, *Nitrospira*, *Parcubacteria*, and *Peribacterales*). The dominant species changed spatially from the beginning of the DWDS to the end of the DWDS.

Aggarwal et al. (2018) found that the biomass volumes of the biofilm in laboratory reactors with dechlorinated water were 10^2 – 10^3 times higher than in monochloraminated water. The dominant species in the monochloraminated laboratory biofilms were *Mycobacterium* or *Sphingopyxis*; but in the full-scale biofilms, the dominant species was only *Mycobacterium*. Furthermore, they found *Bradyrhizobium* in the biofilms growing without total residual chlorine, although the most abundant species was *Nitrospira*.

In addition to bacteria, other species have been found in the biofilms of DWDSs (Costerton, 1999). The fungi *Acremonium* and *Neocosmopora* have been observed in DWDS biofilms. The fungal diversity was markedly less than bacterial diversity and had a lag in responding to temporal dynamics (Douterelo et al., 2018).

Gomez-Alvarez et al. (2016) found that the biofilms in simulated DWDSs have resiliency, i.e., they tend to return to their initial state after a temporary disturbance, like changing the disinfection chemical from monochloramine to chlorine.

2.3.6 Ammonium in drinking water distribution

Ammonium in drinking water distribution originates either from added monochloramine or from the raw water source. For example, in China free ammonium concentrations of 0.1 to 3 mg L⁻¹ have been reported, and the highest values may reach more than 10 mg L⁻¹ (Zhang, X. et al., 2019). Also, in Denmark, the groundwater used as drinking water contained ammonium and nitrite (Schullehner et al., 2017). Monochloramine decomposes into ammonium either in consumption (disinfection) or decomposition. Moradi et al. (2017) pointed out that ammonium is not a good nitrification indicator, because the concentrations will change during the various stages of nitrification (Wilczak et al., 1996; Liu et al., 2005; Yang, J. et al., 2008). Zhang, Y. et al. (2009) have compiled in an extensive review article the reactions that may occur in monochloramine use and form ammonium. These

reactions include monochloramine decay (Vikesland et al., 2001), oxidation of organic matter by monochloramine (Woolschlager et al., 2001), reaction of monochloramine with corrosion products at pipe surfaces (Vikesland and Valentine, 2000), oxidation of nitrite by monochloramine (Valentine, 1985). However, it is unclear what the practical reaction rates of each reaction are.

The ammonium in the raw water can be removed at the WTP with nitrifying biological filters before distribution (Wagner et al., 2018). For example, GAC filters are a suitable filter type. Monochloramine is usually added to the water after the GAC filters because otherwise it would be decomposed in the filter.

2.3.7 Nitrification and nitrite formation in DWDSs

As mentioned earlier, nitrification in the DWDSs is almost inevitable if an ammonium source is present in the distributed water. Monochloramine provides ammonium when it is decomposed or consumed. In drinking water, the interest lies in minimizing the intermediate product of nitrification, nitrite, which is a potentially harmful compound when ingested by humans. In humans, nitrite can cause methemoglobinemia, which is a specific type of anemia. Infants younger than one year are more susceptible to methemoglobinemia than older children and adults. In methemoglobinemia, nitrite reacts with the hemoglobin of blood and disrupts oxygen transfer (Jaffé, 1981). Furthermore, nitrite has been observed to cause several types of cancer in animals and may potentially do so in humans. Moreover, nitrite has been found to be potentially cancerous in animal tests when ingested together with amines and amides or in conditions where the formation of organic nitroso compounds is possible (Mitchell, 2010).

Nitrite occurrence in DWDSs is often called a nitrification episode (Skadsen, 1993; Moradi et al., 2017). Elevated nitrite concentrations are usually noticed in the stagnating parts of DWDSs with high water age and low residual chlorine (Wilczak et al., 1996; Harrington et al., 2002; Liu et al., 2005; Zhang, Y. and Edwards, 2009). Wilczak et al. (2003) studied the seasonality of nitrite concentrations in summer and winter conditions in two sampling campaigns; they observed that the majority of the water samples with increased nitrite in the DWDSs were collected in the summer. However, elevated nitrite concentrations also occurred during the winter conditions. The number of ammonia oxidizing bacteria (AOB) in DWDSs has been found to be higher in summer than in winter (Wolfe et al., 1988; Ike et al., 1988; Wolfe et al., 1990; Pinto et al., 2014). Nitrite can also be formed in the premise plumbing systems (Zhang, Y. 2008). Rosenfeldt et al. observed a nitrite problem in two DWDSs with WTPs, including ozonation but no subsequent GAC filtration (Rosenfeldt et al., 2009).

Nitrification is often accompanied by several symptoms in the drinking water quality and quality monitoring (Moradi et al., 2017). When the secondary disinfecting chemical is reduced enough in the distributed water, nitrification is no longer inhibited by the disinfectant (Pintar et al., 2005). Consequently, the nitrite and nitrate concentrations increase in the distributed water (Wilczak et al., 1996; Pintar et al., 2005; Zhang, Y. et al., 2009). Other quality changes accompanied with nitrification episodes are oxygen depletion (Odell et al., 1996; Wilczak et al., 1996) and an increase in the heterotrophic plate count (HPC) (Skadsen, 1993;

Odell et al., 1996; Wilczak et al., 1996; Bal Krishna et al., 2013). Additionally, nitrification episodes have been connected to increased corrosion of the distribution pipe materials (Zhang, Y. et al., 2010a). Furthermore, Moradi et al. (2017) stated that other factors (pH, alkalinity, and temperature) indicating nitrification have been listed, but their effect is not clear (Odell et al., 1996).

The phosphorus needs for nitrification have been observed to remain unchanged in the interval of 5–1000 $\mu\text{gP L}^{-1}$ (Zhang, Y. 2008). On the other hand, the phosphorus concentration below 5 $\mu\text{gP L}^{-1}$ had a strong inhibiting effect on nitrification (Zhang, Y. and Edwards, 2010). Zhang, Y. and Edwards also noticed that nitrifiers can get their phosphorus from the pipe materials. Additionally, the bacterial biofilm on the pipe system also forms a phosphorus pool from endogenous decay.

2.3.8 Nitrification inhibition

Nitrification sustained by monochloramine can be mitigated, for example, by chlorine addition (Skadsen, 1993; Rosenfeldt et al., 2009). Rosenfeldt et al. noticed that the nitrogen species (ammonia, nitrite, and nitrate) decreased significantly when monochloramine was exchanged for chlorine.

Schranz et al. (2013) observed that high doses of monochloramine could also be used to inhibit nitrification. Monochloramine levels of 1.5 $\text{mgCl}_2 \text{L}^{-1}$ were capable of decreasing nitrification, and levels of 3.0 $\text{mgCl}_2 \text{L}^{-1}$ inhibited nitrification completely in a laboratory experiment. The inhibition mechanisms were either endogenous decay, inactivation by monochloramine, or trihalomethanes (THMs) cometabolism product toxicity. The inhibitory effect of THMs was previously noted by Speitel et al. (2011).

Furthermore, Skadsen (2002) observed that keeping the pH of the distributed water higher—at 9.4 instead of 8.5—inhibited nitrification. In a lower pH, 8.7–8.9 nitrification was observed every summer. Additionally, the high pH of 9.4 was able to maintain the monochloramine levels in the DWDS.

2.3.9 Denitrification

Denitrification is an anoxic reaction, forming gaseous nitrogen from nitrite and nitrate (Henze et al., 2002). Denitrification can utilize both nitrite and nitrate as the initial reactants. These oxidized forms of nitrogen are reduced in the reaction into elemental nitrogen. In denitrification, the nitrogen concentrations of the water phase decrease, because nitrogen is freed into gaseous form. Thus, the extent of denitrification can be estimated by calculating the nitrogen balance for the water phase.

The bacteria capable of denitrification are usually heterotrophic and more tolerant to environmental changes than AOB and NOB. The anoxic conditions are rarely reached in DWDSs because the dissolved oxygen is usually quite high in distributed water. However, denitrifying bacteria have been observed in DWDSs (Nagymate et al., 2016) and laboratory systems simulating drinking water distribution (Masters et al., 2015). In the latter case, denitrification was significant; it caused nitrogen loss from the water phase.

2.3.10 NOM in drinking water distribution

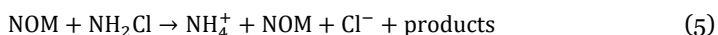
In raw water, organic compounds occur especially in surface waters. They originate from the long-term decay of living organisms (Stumm and Morgan, 2009); thus the term natural organic matter (NOM) is used. NOM has large molecular weights ranging from 200 g mol⁻¹ of the fulvic acids up to 200 000 g mol⁻¹ of the humic acids (An et al., 2017; Huang et al., 2016). It also has various functional groups in the chemical composition; for example organic acid, hydroxyl, and amino groups are common and occur in varying combinations (Pifer, 2012). Most compounds of NOM in surface water are anionic, with negative charge (Crittenden et al., 2005).

While the particulate NOM is removed during drinking water production, a fraction of the compounds still remains after the processes (Nissinen et al., 2001). NOM can be removed with chemical coagulation and separation of the resulting particulate matter, adsorption and membranes. It has been observed that NOM boosts biofilm formation in the pipes of the DWDSs (Huang et al., 2016).

NOM in drinking water is commonly analyzed as Total Organic Carbon (TOC) or Dissolved Organic Carbon (DOC). Specifically, the assimilable organic carbon (AOC) analysis was developed to estimate the capability of the distributed water to enhance the growth of biofilms in the distribution pipes (Van Der Kooij et al., 1982; Miettinen et al., 1999; van den Broeke et al., 2008; Ross et al., 2013). In addition, the biofilm formation potential can also be analyzed as biodegradable dissolved organic carbon (BDOC) (Escobar and Randall, 2001). A large study of AOC in the distributed water was performed in Belgium, and the resulting median of the AOC was 72 µg L⁻¹ (Polanska et al., 2005).

In DWDSs, NOM causes decay of the disinfection chemical (Powell et al., 2000; Vikesland et al., 2001; Wooschlager et al., 2001; Duirk et al., 2005; Huang et al., 2016). Furthermore, this generates higher consumption of disinfectants. In the presence of NOM, monochloramine loss was also accelerated (Ricca et al., 2019). As a result, part of the added monochloramine was lost.

The reaction of NOM with monochloramine can be approximated as follows (Wilczak et al., 2003):



Wilczak et al. (2003) noticed that a high degree of TOC removal with GAC or nanofiltration improved monochloramine stability. Apparently, monochloramine decay was prevented by the reduced concentration of organic compounds. On the other hand, an increase of 4 mg L⁻¹ of NOM, as dissolved organic carbon (DOC), doubled the demand of monochloramine (Thomas, 1987).

Moradi et al. (2017) developed a monochloramine decay index to predict nitrification in full-scale DWDSs. The index involved NOM concentrations of the molecular sizes 20 and 1000 g mol⁻¹. A high index indicated low monochloramine concentrations and vice versa. Li, W. et al. (2018) observed that when the total residual chlorine levels were below 0.15 mg/l, the AOC correlated positively with the ICC in full-scale DWDSs.

Zhang, Y. et al. (2010b) inspected the effect of organic matter on nitrite levels on a laboratory scale. The higher TOC concentration (3.0–4.0 mg L⁻¹) supported higher nitrite levels by increasing the rate at which monochloramine decomposed, compared to the lower TOC concentration (0.5–1.0 mg L⁻¹). Furthermore, it was observed that the higher levels of organic carbon promoted a higher amount of AOBs in the biofilm.

However, Scott et al. (2015) inspected two full-scale DWDSs in Canada and found no correlation between nitrite concentrations and NOM as TOC. In fact, they found no significant correlation between nitrite concentrations and the numbers of AOB and ammonia oxidizing archaea (AOA) in the collected water samples. It is possible that the range of the molecular size of the NOM affected this study. Moreover, Huang et al. (2016) noticed that the dissolved organic matter (DOM) in the molecular size range of 200–500 g mol⁻¹ correlated positively with oxidized nitrogen and also active bacterial cells in the DWDS disinfected with monochloramine. This was especially notable in those parts where the disinfectant concentrations had decreased in the DWDS.

Vahala and Laukkanen (1998) noticed that the concentration levels of nitrite rose in the DWDS when GAC filtration was commissioned to remove NOM from the drinking water in Helsinki, Finland. The levels of nitrite raised 5- to 10-fold compared to drinking water production without GAC. A similar observation had been made earlier in tests with simulated distribution systems (SDSs) (Vahala et al., 1999). In his doctoral thesis combining these two works, Vahala (2002) speculated that GAC filtration indirectly promoted nitrifying autotrophic bacteria by impairing the conditions for NOM-consuming heterotrophic bacteria by removing NOM from the drinking water.

Skadsen (1993) made an ostensibly similar notion as Vahala and Laukkanen (1998) concerning the commissioning of GAC filters. However, the WWTP at Ann Arbor, Michigan (USA), utilized two-point disinfection, and monochloramine was also dosed as pre-disinfection. Thus, the GAC filters further in the process train received an ammonium source, which functioned as a substrate in the filters to induce nitrification. The GAC material and the biofilm formed on the surfaces of the GAC granules both react with monochloramine freeing ammonia (Wilczak et al., 2003). Consequently, the water entering the DWDS was inoculated with nitrification bacteria from the GAC filters. This boosted the nitrification in the DWDS. Therefore, it can be concluded that the observations of Vahala and Laukkanen (1998) and Skadsen (1993) actually originate from different reasons, and moreover, the monochloramine concentrations were distinctly different. This leaves Vahala and Laukkanen (1998) and Vahala (2002) as the only ones who definitely observed increased nitrite concentrations after decreasing the concentration of NOM. As this text is written, the specific reasons for these contradictory observations are not known.

2.3.11 Formation of disinfection by-products

One of the main reasons for monochloramine use in secondary disinfection is the formation of chlorinated disinfection by-products (DBPs), mainly THMs with chlorine (Wilczak et al., 1996). However, monochloramine also forms DBPs, such

as N-nitrosodimethylamine (NDMA). Furthermore, dichloramine (if present) forms higher concentrations of NDMA-like DBPs (Selbes et al., 2018).

An et al. (2017) studied the effect of the molecular size of organic matter on the formation potential of THMs and NDMA in secondary disinfection with monochloramine. They found that DOC and the formation potential of the DBPs had linear relationships inside different molecular size categories. The smaller molecular sizes tended to have a higher potential to form DBPs. The potential was decreased by GAC filtration and sand filtration, both in total and within the molecular size categories.

Wahman et al. (2011) observed that four commonly observed THMs (trichloromethane, dibromochloromethane, bromodichloromethane, and tribromomethane) could be removed with biotransformation from treated drinking water by nitrifying biological filters or the re-suspended biomass from the filters.

2.4 Wastewater

2.4.1 Wastewater treatment

Nowadays, centralized wastewater treatment is considered one of the most important methods of sustaining good quality in the water environment in the vicinity of population centers. Wastewater originates from human feces and urine, chemicals, and other constituents flushed down the drain in households, offices, and other buildings, and, of course, the water used to flush all these. Other components may be industrial wastewater, landfill leachates (Fudala-Ksiazek et al., 2018), and water infiltrated into the sewer networks.

In Finland, the quality of the treated water at wastewater treatment plants WWTPs is regulated by the European Directive concerning urban wastewater treatment (European Council, 1991) and its implementation in Finnish legislation (Finnish Council of State, 2006). At WWTPs, influent and effluent wastewater is analyzed for its composition, mainly for organic matter, phosphorus, nitrogen, and other chemical, microbiological, and physical qualities. The requirements for the treated effluent quality are set for the first three constituents. The target of the requirements in wastewater treatment is to prevent eutrophication, waterborne diseases, oxygen depletion, toxic effects, and general environmental deterioration in the receiving water body and its vicinity.

The purpose of nitrification in wastewater treatment is to prevent the toxic effects and oxygen consumption of ammonium in the receiving water body and to prepare the nitrogen compounds for total nitrogen removal, most often via denitrification. Nitrification in municipal wastewater processes is commonly situated in the main treatment line as a part of the activated sludge or other biological treatment. Nitrification bacteria require a long time to grow, and therefore the basins designed for nitrification are usually larger than those for plain organics removal. A common practice is to remove a high percentage of organic matter first, either chemically or biologically, and ammonium only after that.

In the northern climate, the snow melting period in the spring is a challenge for nitrification. The snow melting causes a rapid drop in the wastewater temperature

at the same time as the flow of water increases due to infiltration or combined sewers. The flow increase may be several times the dry weather flow, depending strongly on the sewer network. These conditions set a limit to full ammonium removal with nitrification because nitrifiers are very sensitive to temperature drops, and the simultaneous large flows may mix up the hydraulics of the settling basins, thus causing the nitrifiers to be flushed out of the process. Various methods have been developed to ensure a good treatment result in these conditions, including equalization before the main process (Goel et al., 2005). The designer can also choose that a part of the highest flows may be bypassed to protect the nitrifying organisms inside the biological process. This may deteriorate the treatment result for other constituents unless the bypassed waters are treated separately.

Nitrite can be the intermediate product of nitrification in wastewater processes. Small concentrations of nitrite have been observed in activated sludge processes (Kaelin et al., 2009; Knapp and Graham, 2007). In these cases, it is considered to be a poor operation of the treatment process, possibly due to a lack of oxygen or insufficient alkalinity in the influent. These can be remedied by increasing aeration or adding an alkaline chemical.

2.4.2 Ammonium removal with nitrification

Ammonium in wastewater originates mostly from organic nitrogen compounds from feces and urine, or chemicals. Organic nitrogen decomposes into ammonium in microbial decomposition (Figure 2), with some exceptions.

Typical ammonium removal processes are biological treatment units with nitrification: activated sludge processes, trickling filters, biological filters and ponds (Tchobanoglous et al., 2003). Nowadays, ammonium removal can be organized, not only by nitrification, but also by several types of anammox and other processes (Schmidt et al., 2003). These all, however, must include at least partial nitrification—either a part of ammonium is nitrified or ammonium is nitrified only to the nitrite step (de Almeida et al., 2018; Zheng et al., 2019).

Ammonium removal typically occurs in the aerobic part of the WWTP (Henze et al., 2002). Furthermore, part of the ammonium removal occurs through assimilation, which is the consumption of ammonium as a nutrient for the growth of microbial mass (Loosdrecht and Jetten, 1998). The percentage of assimilation depends on the ratio of nitrogen and organic matter (typically 20–40%).

There is no practical limit for the possible ammonium removal percentage in WWTPs. Nevertheless, the snow melting period can decrease the percentage if the WWTP cannot handle the increased cold flows, as mentioned previously.

The optimum pH of nitrification is 7.5–8.5 (Le et al., 2019). This is particularly important because nitrification is easily inhibited by low pH in wastewater processes. Thus, if alkalinity is low in the influent water, the addition of an alkali chemical is needed to keep the pH high enough.

High organic loads from the sewer network can deteriorate nitrification in wastewater treatment (Henze et al., 2002). The optimum temperature for nitrification is 30–35 °C, but this is seldom reached in municipal wastewater treatment. Furthermore, nitrification in wastewater processes is vulnerable to temperature changes, especially sharp downward changes temporarily inhibit ammonium

removal (Henze et al., 2002). However, nitrification can also be operated at very low temperatures, even close to 0 °C (Rantanen, 2010). In light of recent findings by González-Cabaleiro et al. (2019), this observation may be the result of AOB changing their metabolism and benefiting from the bacterial population. The study concerning the thermodynamical modeling of AOB in wastewater processes concluded that the calculated maximum true yield ($0.16 \text{ g biomass (gN-NH}_3\text{)}^{-1}$) was actually lower than some observations (range $0.04\text{--}0.45 \text{ g biomass (gN-NH}_3\text{)}^{-1}$) (González-Cabaleiro et al., 2019). According to the authors, possible explanations are other energy sources utilized by AOB, e.g. pyruvate, which is a degradation product of heterotrophic micro-organisms. Thus, it is possible that in unfavorable conditions, AOB may benefit from commensalism with heterotrophs (González-Cabaleiro et al., 2019).

Johnston et al. (2019) observed that ammonia oxidizing bacteria maintained a stable population in the winter months, even though the ammonium removal performance of the full-scale WWTPs deteriorated. This suggests that nitrification failure at colder temperatures might result from different reaction kinetics of AOB and NOB, or that other organisms vulnerable to seasonal changes affect ammonium removal in the lowest temperatures (below 13 °C) (Johnston et al., 2019).

Nitrifying treatment processes usually require a slightly higher level of dissolved oxygen than processes that remove organic matter. Generally for good nitrification, dissolved oxygen levels below 2.0 mg L^{-1} should be avoided (Prosser, 1989; Coskuner and Jassim, 2008).

Nitrification is easily inhibited by certain metals and organic compounds in the influent wastewater. For example, copper concentrations of $0.05\text{--}0.56 \text{ mg L}^{-1}$ (Henze et al., 2002) and thiourea concentrations of 0.076 mg L^{-1} (Tomlinson et al., 1966) have been observed to be inhibitory. In practice, industrial wastewaters are the main source of inhibitory substances in municipal wastewater (Jönsson and Jansen, 1999). Furthermore, the reject waters from sludge dewatering or sludge incineration at the WWTP may also cause inhibition (Jönsson, 2001).

Nitrification by heterotrophic organisms has been observed in wastewater treatment (Chen et al., 2019; Jin et al., 2019; Zhang, N. et al., 2019). However, it is unclear if the reaction rates of heterotrophic nitrification are significant compared to autotrophic nitrification.

2.4.3 Nitrogen removal

Nitrogen removal involves the transformation of nitrogen compounds into gaseous nitrogen. The most common process in Finland is the recirculation activated sludge process, in which nitrification occurs as the last step and the activated sludge (including the nitrate) is recirculated back to the beginning of the process to be denitrified (Laitinen et al., 2014). This way, the organic matter of the influent can be utilized in denitrification, and the share of the aerated basin becomes smaller because part of the organic matter is already removed when ammonium is nitrified (Rantanen et al., 1999). The smaller aeration basin reduces the need for aeration, which is the biggest energy consumer at most WWTPs. Another benefit of denitrification is the increase in alkalinity by half of the amount that is

decreased by full nitrification. This reduces the consumption of alkali chemicals in the process.

The nitrite recirculation increases the percentage that can be attained in nitrogen removal: the higher the recirculation, the higher the attainable percentage. On the other hand, this is limited by the ratio of organic matter and nitrogen in the influent water: the higher the ratio, the higher the removal percentage (Henze et al., 2002). Furthermore, nitrate recirculation increases oxygen in the anoxic denitrification basin and may therefore reduce the effective volume available for denitrification.

The total nitrogen concentration in Finnish municipal wastewaters in 2009 was 58 mgN L⁻¹ as the median of the influents. The mean nitrogen reduction was 52% (Ruotsalainen, 2011).

2.4.4 Organic matter in wastewater

Organic matter in wastewater originates from feces and urine, unconsumed food remains, and organic chemicals. This organic matter varies in biodegradability and molecular size and has a wide range of functional groups and compounds.

The most common method of analyzing organic matter in wastewater is Biochemical Oxygen Demand (BOD) (Tchobanoglous et al., 2003). However, the digestion of BOD takes several days (typically five or seven), and this is not fast enough for practical operational decisions at the WWTPs. Instead, Chemical Oxygen Demand with the dichromate method (COD_{Cr}) is incubated only two hours, making it ideal for everyday operational decisions. Furthermore, soluble COD_{Cr} offers an easy method for estimating the biodegradability of the organic matter in wastewater (Mikola et al., 2007). Other more accurate methods (for example, readily biodegradable COD (RBCOD)) have been developed to evaluate the biodegradability of organic matter (Ziglio et al., 2001).

In Finland, BOD is analyzed with seven-day incubation and the addition of allyl thiourea to prevent ammonium oxidation during incubation (BOD₇(ATU)). The influent concentration of BOD₇(ATU) in the one hundred largest Finnish municipal WWTPs was 280 mgO₂ L⁻¹ in 2009 and COD_{Cr} 720 mgO₂ L⁻¹, as medians. The median removal rates were 96.6% and 91.9%, respectively (Ruotsalainen, 2011).

Part of the organic matter is removed by denitrification in nitrogen removal processes and by biological phosphorus removal when used. Most of the organic matter is removed by the growth of micro-organisms. However, chemical removal of organic matter is also possible and is occasionally used when the organic load needs to be diminished before nitrification.

As an unexpected but positive side effect, nitrifying WWTPs have been found to be able to effectively remove trace organic chemicals (Nsenga Kumwimba and Meng, 2019).

Pre-fermentation

Pre-fermentation of raw wastewater increases the easily biodegradable organic matter in the influent of the biological process. Pre-fermentation is organized as an anaerobic unit process, either in the main treatment line or in a side stream. The central aim is to enhance denitrification (Æsøy and Ødegaard, 1994; Canziani

et al., 1995; Goncalves et al., 1994; Pitman et al., 1988) or biological phosphorus removal (Brinch et al., 1994; Goncalves et al., 1994; Lötter and Pitman, 1992), or both. The easily biodegradable portion can be measured as RBCOD or volatile fatty acids (VFA) or simply as soluble COD_{Cr}.

The reported effects of pre-fermentation to nitrification are relatively rare in the literature. Pre-fermentation has been observed to either enhance nitrification (McCue, 2006; McCue et al., 2003) or inhibit nitrification (Delgado et al., 2004). The positive effects in the studies of McCue et al. were in the end unexplained. However, in all of the reported results, nitrification was systematically 2 to 8 percentage points higher with pre-fermentation than with pre-sedimentation. Moreover, the inhibiting effects observed by Delgado et al. were attributed to the high concentrations of VFA and the high C/N ratio in the wastewater. The influent wastewater was introduced directly into the nitrification basin in the study without the preceding consumption of organic matter by biological phosphorus removal or denitrification. This probably explains the antithetical results.

Generally, nitrification is suppressed by increased organic matter due to competition for space, oxygen, and ammonium between heterotrophic and autotrophic bacteria. More specifically, colloidal organic matter has been observed to be important in nitrification inhibition (Li, J. et al., 2002).

3 Materials and Methods

This thesis includes methods applied in data analysis, full-scale tests at a WWTP, and laboratory-scale tests with SDSs. Figure 5 illustrates the materials and methods. The processes and subjects are the same as in Figure 3 (“Part” column). The materials and methods are described here briefly and in more detail in **publications I–IV**.

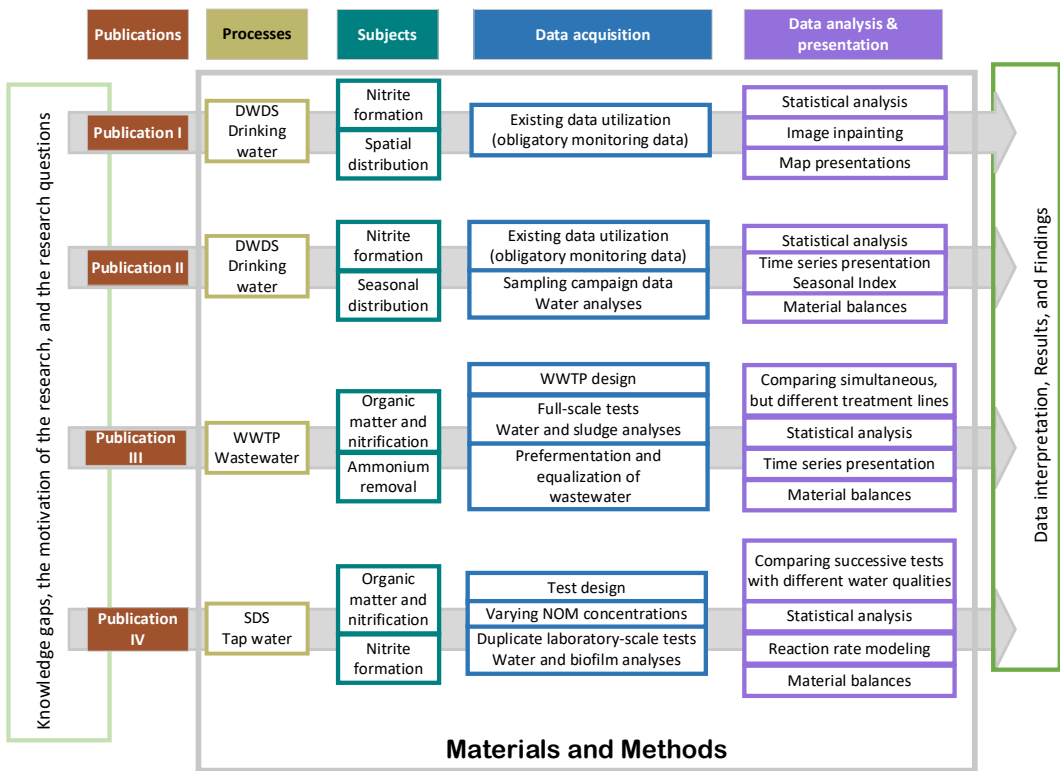


Figure 5. Materials and methods of the thesis. DWDS = Drinking Water Distribution System, WWTP = Wastewater Treatment Plant, SDS = Simulated Distribution System.

In **Publication I**, nitrite formation, its spatial distribution, and relations to other parameters were studied with contour maps and statistical methods. The data included the quality analyses of distributed drinking water from the obligatory monitoring program in the Helsinki metropolitan area (Kalso, 2013). In the study area, drinking water was supplied from two WTPs. The DWDS consisted of

364.2 km of water mains with larger than 200 mm diameter in Helsinki, and 255.7 km of similar mains in Vantaa. In Helsinki the pipe materials were cast iron and steel (99.7%), and in Vantaa plastic (61.5%), cast iron and steel (33.3%), and concrete (6.4%). The study site consisted of the geographical area defined by the locations of the sampled taps, which were situated in both residential and industrial areas.

The drinking water sampling locations, methods, and frequencies were decided by the municipal health authorities in each city. The sampling and analyses were organized by an accredited commercial laboratory, Metropolilab Ltd. In total, 2,176 samples from the years 2010–2013 were covered. The data was collected from pdf files into spreadsheets and the sampling locations were geocoded. All concentrations below the LoQs were also included in the analysis. The Student's t-test was used to compare differences in nitrite, ammonium and total residual chlorine concentrations between the cities. Furthermore, a skeleton hydraulic model of the DWDSs in Helsinki and Vantaa was devised by a consulting company (Laitala, 2015), and the maximum water age with the average flow was estimated for the 898 sampling locations with the model.

Nitrite, ammonium, total residual chlorine, and water age were depicted as contour maps, utilizing image inpainting (D'Errico, 2012) to visualize and interpolate the missing data in Matlab (version 2014a). Image inpainting has been developed for completing damaged images, e.g. photographs, but it has also been utilized in interpolating spatial environmental data (Jaimes Hernandez, 2014; Sproson and Sahlee, 2014). The contour maps were based on 50 m x 50 m squares with statistics—median, minimum, and maximum of nitrite; median of ammonium; total residual chlorine; and water age—calculated for each square.

In **Publication II**, the scrutiny of obligatory monitoring data was continued by estimating the seasonality of nitrite concentrations in the DWDS of Vantaa. The methods included finding the most complete time series in the data and categorizing them by seasonality type. In categorizing, the simplest possible method was used, a visual comparison to the temperature time series, and a method based on the seasonal index (SI, Equation 6) (Brendstrup et al., 2004; Hyndman and Athanasopoulos, 2013), which was calculated as follows:

$$SI_i = \frac{x_i}{\bar{x}} \quad (6)$$

where SI_i is the seasonal index based on one-year data in a two-month season i , x_i is the mean nitrite concentration in a two-month season i , \bar{x} is the annual mean nitrite concentration, and $i = 1-6$ are the numbers of the six two-month seasons starting from January. The calculation method of the SI was fine-tuned by a sensitivity analysis with four annual seasons and starting the seasons from December.

The nitrite data in the obligatory monitoring and the sampling campaign were not normally distributed (as assessed by the Anderson-Darling test), and thus non-parametric tests were used. The non-normality was caused by the abundance of values below the LoQ. Spearman's rank-order correlation coefficients were

used to define the correlation between two variables, with the limit of significance being $p < 0.05$.

Furthermore, the observations of the *SI* study were complemented by a sampling campaign of monthly samples for one year in a section of the Vantaa DWDS. The *SI* calculation method with six seasons (Equation 6), starting in January, was utilized in analyzing the data of the sampling campaign.

The sampling procedure in the sampling campaign was aiming at the quality of water in the service pipes instead of the household plumbing by increasing the flushing time from the taps before sampling. Thus, unlike in the standard SFS-ISO 5667-5 (Anon., 2009), the sampling procedure was to discharge for at least 15 min or 200 L of water, depending on the flow of the tap. A similar procedure was used by Roeselers et al. (2015). The samples were analyzed for ammonium, including monochloramine, as nitrogen (method: SFS 3032) (Anon., 1976), nitrite and nitrate as nitrogen (method: SFS-EN ISO 13395) (Anon., 1997) and total nitrogen (method: SFS-EN ISO 11905-1) (Anon., 1998), because the obligatory monitoring data did not include all these.

Furthermore, scatter images were utilized in evaluating the links between the different nitrogen fractions in the sampling campaign data. Finally, the significance of denitrification or anammox reactions was estimated with material balance calculations of the sums of the inorganic nitrogen compounds and total nitrogen. The statistical analyses were done in Matlab (version 2014a), and IBM SPSS Statistics.

In **Publication III**, tests at a full-scale WWTP (Figure 6) were performed. Two parallel treatment lines were compared, and one of them was equipped with pre-fermentation and equalization in the primary settling basin, and one line operated with an ordinary primary settler. The WWTP, with a person equivalent (PE) of 30,000, treats the wastewaters in the city of Savonlinna in the southeastern part of Finland. The plant is equipped with flotation filters as the final water purification unit. Thus, it is well-suited for testing novel treatment methods in the main process lines without endangering the water quality in the recipient.

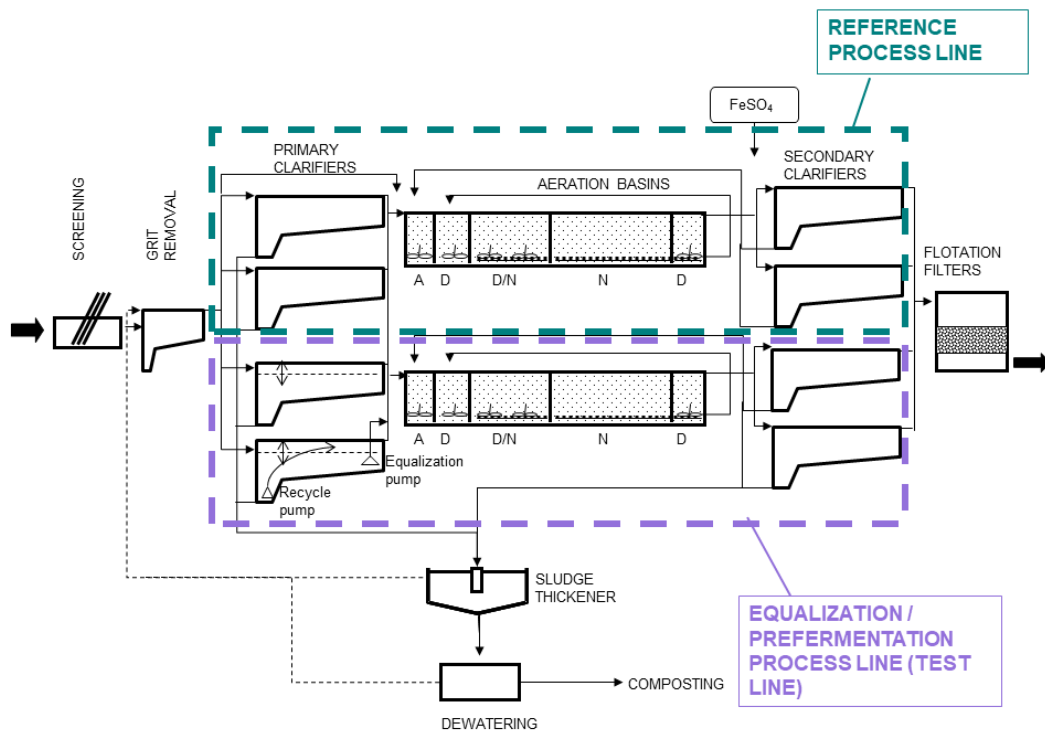


Figure 6. Pihlajaniemi WWTP, with the two parallel treatment lines (pre-fermentation and equalization and pre-sedimentation) in the full-scale tests of **Publication III**. A = Anaerobic basin, D = Anoxic denitrification basin, N = Aerobic nitrification basin.

The plant utilizes an adaptable operation strategy in nitrogen removal: The volumes of the aerobic and anoxic compartments in the activated sludge process are tailored to change during the year, thus optimizing nitrification first and then nitrogen removal. A high concentration of mixed liquor suspended solids (MLSS) is kept in the activated sludge. The process operation is described in more detail in **Publication III**, by Mikola et al. (2007; 2008) and Kiuru and Rautiainen (1998).

The pre-fermentation was organized with an internal raw sludge recycle, with a pump transferring raw sludge from the sludge pocket to the middle of the basin. The purpose of pre-fermentation is to increase the easily biodegradable organic matter in the wastewater. The retention time in the basin during the dry weather flow was 4 to 5 hours. In addition, 16% of the diurnal variation of the influent flow was equalized in the same basin. Other process conditions—such as total sludge retention time (SRT), MLSS, and dissolved oxygen—were kept similar for both process trains.

The treatment performance of the treatment lines was surveyed for COD_{Cr} , soluble COD_{Cr} , $\text{BOD}_7(\text{ATU})$, soluble $\text{BOD}_7(\text{ATU})$, RBCOD, and VFA to characterize the organic matter. In addition, alkalinity, suspended solids (SS), total nitrogen, NH_4^+ , NO_3^- , total phosphorus, orthophosphate (PO_4^{3+}), and pH were analyzed. The samples were 24-h composite samples. The nitrogen concentrations were analyzed with standard laboratory methods. The process was monitored with online measurements of the influent flow rate, dissolved oxygen, air flow, pH, and MLSS.

The results were interpreted for the ammonium removal efficiencies as time series and scatter plots. The snow-melt and rain episodes were inspected more closely than the rest of the data to reveal the ammonium removal capacity in critical conditions. The data was analyzed in a spreadsheet software (MS Excel).

In **Publication IV**, the effect of NOM on nitrification of tap water was studied on the laboratory scale at 18 °C. The two SDSs each consisted of a tank with 30 L of water and a pipe loop with a length of 22 m and a volume of 7.2 L (Figure 7). The water in the tank was pumped into the pipe loop with a volumetric flow of 100 L h⁻¹ and returned to the tank after flowing through the pipe loop. Two similar systems (SDS₁ and SDS₂) were operated in parallel. Before the actual tests, the systems were rinsed thoroughly and operated for seven months to grow a biofilm and a nitrifying population on the inner surface of the pipe loops.

Two levels of NOM were tested (Figure 7) to evaluate the effect of NOM concentrations on the degree of nitrite formation. To create the different levels of NOM, normal tap water and tap water diluted with reverse osmosis water (RO water) were employed. These are later referred to as normal NOM and reduced NOM, respectively. To ensure the repeatability of the nitrification test procedure, the tests with normal NOM were arranged in the beginning and repeated in the end.

The tests were organized as semi-continuous batch tests, with one test lasting for one week. Ammonium and nitrite were used separately as the initial substrates for nitrification (Figure 7). In commencing each test, either ammonium or nitrite was added to the influent water. Furthermore, in the tests with reduced NOM, the alkalinity and hardness of the water were compensated to the level of tap water. All tests were added with a concentration of 5 µgP L⁻¹ to ensure the growth of the microbes in the biofilm (Lehtola et al., 2002). Moreover, in nitrite tests, the small initial concentrations of ammonium were nitrified into nitrate by operating the batch system for one day.

The concentrations of ammonium, nitrite, nitrate, and total nitrogen were monitored by water samples and analyses during the tests. The samples were grab samples from the tank. The nitrogen concentrations were analyzed with the standard methods mentioned above, in the passage concerning **Publication II**. General water quality parameters were analyzed once a month (TOC, HPC, hardness, total chlorine (Cl₂), pH, alkalinity, and turbidity). See also Table 1 in **Publication IV**. NOM was analyzed as AOC and TOC during the tests with reduced NOM in a sampling campaign. The biofilm collectors were sent to a commercial laboratory for detachment of the biofilm samples. The microbial community of biofilms was analyzed once to get the share of AOB and NOB and the most abundant bacterial species. Other analyses performed from the biofilm samples were total bacterial count with the DAPI staining and suspended solids (SS).

The nitrification test results were interpreted in two ways: as apparent nitrite formation and as pseudo first order reaction rate models. The first provided information on whether nitrite concentrations increased or decreased in the chosen conditions. The latter enabled an evaluation of which of the reactions—nitrification or nitrification—was affected by the manipulated conditions of reduced NOM. The statistical analyses were done with Matlab (version 2019a). The data sets of

reaction rates and reaction rate constants were tested for normality with the Anderson–Darling test. The normally distributed data (the pseudo-first order reaction rate constants of nitrite, with normal and reduced NOM and with ammonium and nitrite as the initial substrate, and the separated data of SDS1 and SDS2 with normal and reduced NOM) were compared with Student’s t-test and non-normally distributed (the apparent reaction rates of nitrite and the pseudo-first order reaction rate constants of ammonium with normal and reduced NOM) with Wilcoxon’s rank-sum test.

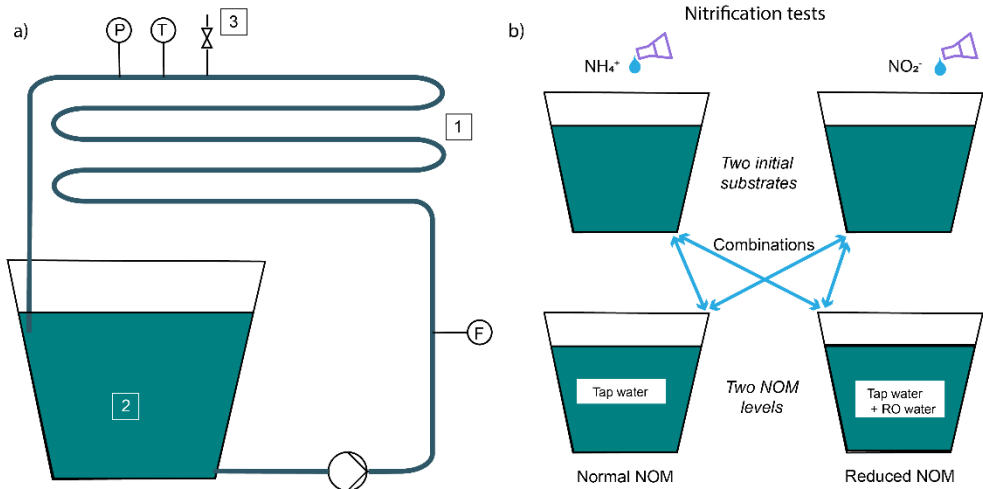


Figure 7. (a) A schematic diagram of the laboratory test equipment in **Publication IV**. 1 = a pipe loop of 22 m, 2 = a covered vessel with a water volume of 30 l, 3 = vent valve, F = water flow meter, P = pressure gauge, T = thermometer, dashed line = water level. Two similar pieces of equipment (P1 and P2) were used in the study. (b) Diagram of the performed tests. Both ammonium and nitrite tests were executed with Higher and Lower NOM.

4 Findings

4.1 Spatial and seasonal distribution of nitrite in a DWDS

The findings of Part A of the thesis, depicted in Figure 8, are the following. Nitrite was formed close to the WTPs in the DWDSs of Helsinki and Vantaa from monochloramine used for disinfection (Finding 1). Furthermore, low nitrite concentrations were more related to stagnant water than to fresh water. The added monochloramine concentrations were not able to mitigate nitrification in the biofilm. On the contrary, monochloramine provided an ammonium source for the AOB. Thus, added monochloramine supported nitrification. However, its concentration also limited the maximum nitrite concentrations. Nevertheless, the microbiological quality of the distributed water was good, according to the analyses of *E. coli*, coliforms, and *Clostridium perfringens*.

Contour maps illustrate several areas where the median nitrite concentrations were above $50 \mu\text{gN L}^{-1}$ (Figure 8). Nitrite levels were elevated (above $30 \mu\text{gN L}^{-1}$) almost throughout the entire study area. Unexpectedly, a low temperature did not significantly inhibit nitrite formation spatially.

The nitrite concentrations differed slightly, but significantly, between the cities of Vantaa and Helsinki. The lower concentrations in Vantaa were explained by a large share of concentrations below the LoQ. The nitrite concentrations below the LoQ were a result of full nitrification into nitrate.

Publication II studied the seasonality of the nitrite concentrations in the distributed water, partly with the same data as **Publication I**. Seasonality of nitrite in the obligatory monitoring data was observed in four different forms (Finding 2): (1) maximum nitrite concentrations occurred during the warm water period (summer maximum) or (2) during the cold water period (winter maximum); (3) the maximum or minimum values did not occur at any particular time during the year (mixed seasonality); (4) flat seasonality, with no values above the LoQ of the nitrite analysis. The summer maximum seasonality was related to low water ages, winter maximum to medium-high water ages, and flat seasonality to very high water ages. Additionally, in the sampling campaign data (which included all the inorganic fractions of nitrogen), it was observed that ammonium oxidation into nitrite was the dominant reaction in the summer maximum seasonality with lower water ages, and nitrite oxidation into nitrate was the dominant reaction in the winter maximum seasonality with a medium-high water age (Finding 3).

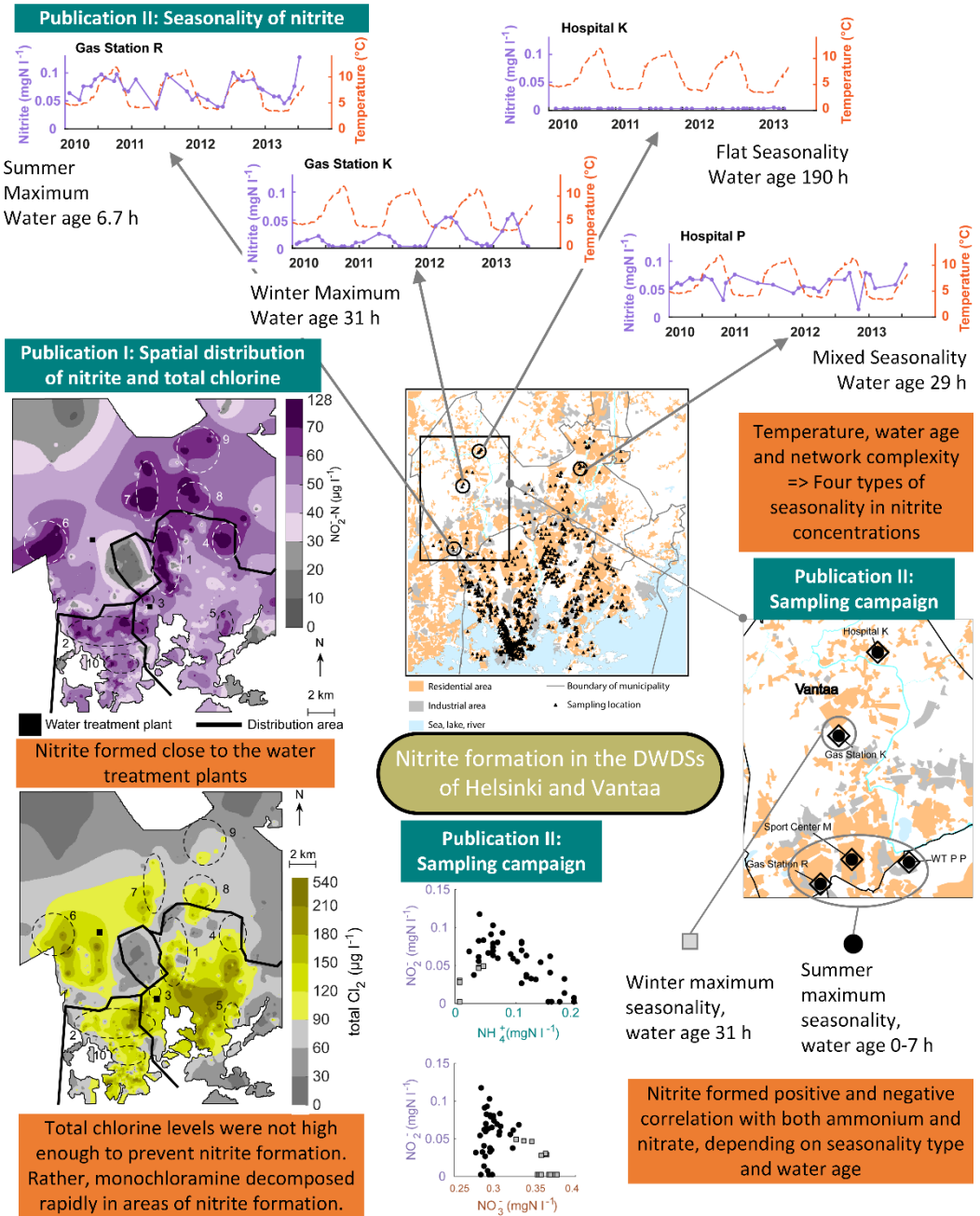


Figure 8. The findings of Part A. Middle: Map of the study area of both **publications I** and **II**. Middle left: The median of nitrite concentrations in distributed water in years 2010–2013 in the DWDSs of Helsinki and Vantaa, N = 2151. Bottom left: The respective map of total chlorine, N = 1850. Top: Examples of the seasonalities with Summer maximum, Winter maximum, Flat seasonality, and Mixed seasonality observed in the nitrite concentrations, with their respective temperature curves. Middle right: Area of the sampling campaign with the locations. Bottom middle: The correlation of ammonium to nitrite and the correlation of nitrate to nitrite, N = 13 for each four sampling points.

4.2 Nitrification and organic matter

The findings of Part B of the thesis are depicted in Figure 9. In its entirety, the effects of organic matter on nitrification were found to be ambiguous (Finding 4). The increase in soluble organic matter in the influent of a wastewater treatment plant did not deteriorate the nitrification capacity of the activated sludge process. On the contrary, the experimental process line that was equipped with pre-fermentation and equalization was capable of removing more ammonium than the conventional line with primary sedimentation (Figure 9). Thus, increasing the easily biodegradable organic matter in the influent flow of the nutrient removal process did not have adverse effects on nitrification. This was contrary to the hypothesis because nitrification is known to be inhibited by increased organic matter concentrations. The explanation for the antithetical observations was the consumption of organic matter in biological phosphorus removal and denitrification before the nitrification unit.

Furthermore, when organic matter was reduced in non-disinfected tap water in a simulated water distribution pipe, less nitrite was formed (Finding 5). This result was in line with the notion that organic matter inhibits nitrification. However, according to first order reaction rate modeling, the reason for this was the enhanced nitrite oxidation reaction (Finding 6). The ammonium oxidation reaction was not inhibited or enhanced significantly.

4.2.1 Ammonium removal and pre-fermentation of wastewater

The median ammonium concentration after the biological wastewater treatment was 2.2 mgN L^{-1} (mean removal 87%) in the pre-fermentation line and 8.0 mgN L^{-1} (mean removal 75%) in the pre-sedimentation line. As an average during the tests, 1.5 times more ammonium was removed in the pre-fermentation line than in the pre-sedimentation line. The difference in nitrification performance between the two process lines was more significant than expected. The better ammonium removal in the pre-fermentation line than at the pre-sedimentation line was a combination of better removal during the dry weather and faster recovery after storm water and snow melt episodes. Furthermore, the low temperature of the influent wastewater deteriorated nitrification in the pre-sedimentation process line more than in the pre-fermentation line.

The enhanced ammonium removal (Figure 9) was mostly attributed to pre-fermentation and the diurnal flow equalization during the dry weather. The process conditions were similar in the aeration for both process trains. Moreover, peak flows were not leveled out efficiently by the equalization basin. In addition, the pre-fermentation process line did not benefit from a lower hydraulic load because they were approximately 20% higher than the load on the reference process train.

Organic matter and pre-fermentation

Pre-fermentation increased soluble organic matter in the flow entering the biological treatment. The difference to the pre-sedimented water was more significant during summertime (more than 30%) than during the cold period (4–14%). Soluble organic matter (analyzed as BOD₇(ATU), VFA, RBCOD, and COD_{Cr}) in the water entering the biological treatment were impacted by the flow rate and thus the hydraulic retention time in the basins. The soluble COD_{Cr} in (Figure 9) decreased as the flow rate increased. However, the concentration in the pre-fermentation line was consistently higher than in the pre-sedimentation line, even during the high flow rates. In conclusion, pre-fermentation occurred during both dry weather flows and higher rain weather flows.

4.2.2 Nitrite formation in tap water

In nitrification tests with the SDSs, it was observed that nitrite increased with the normal NOM concentration of tap water (TOC 1.6 mg L⁻¹) and decreased when the NOM concentration was reduced by 43% (TOC 1.0 mg L⁻¹) (Figure 9). The nitrite formation or decrease evidently followed the changes in the NOM concentration. First, the NOM concentration was changed from the normal level to the reduced level, and then the NOM concentration was changed back to the normal level.

Furthermore, when the test results were interpreted with the pseudo first order reaction rate models, it was found out that the decreasing of NOM enhanced nitrite oxidation rates, and the resulting lower nitrite concentrations were a result of nitrite vanishing more rapidly. Ammonium oxidation was unaltered in the tests with reduced NOM. As a result of these two oxidation reactions, the median nitrite formation rates were with normal tap water NOM 2.7 µgN L⁻¹ h⁻¹, and with reduced NOM 2.4 µgN L⁻¹ h⁻¹. The difference in the rates was statistically significant. In addition, nitrite formation was noted to be dependent on the ratio of the pseudo first order reaction rate constants of ammonium oxidation and nitrite oxidation. The higher the ratio was, the more nitrite was formed.

Both AOB and NOB were detected in the biofilms of the SDSs. In a combined biofilm sample, the share of AOB (*Nitrosomonas* sp.) was 9.3%, and the share of NOB (*Nitrospira* sp.) was 8.7%. The high shares of AOB and NOB demonstrated the existence of nitrification activity in the biofilm. Furthermore, the possibility of reactions that change the total amount of nitrogen in the water phase (denitrification, anammox, and nitrogen accumulation) was evaluated by nitrogen balance calculations. A minor increase in nitrogen was observed (total nitrogen in SDS1 +1.1% of the feed, and SDS2 +2.0%; inorganic nitrogen in SDS1 +0.3%, and SDS2 +1.0%). The total amounts of the increase were, however, small compared to the weekly variation in the balances. Thus, the effect of the reactions accumulating or releasing nitrogen was not significant as a whole.

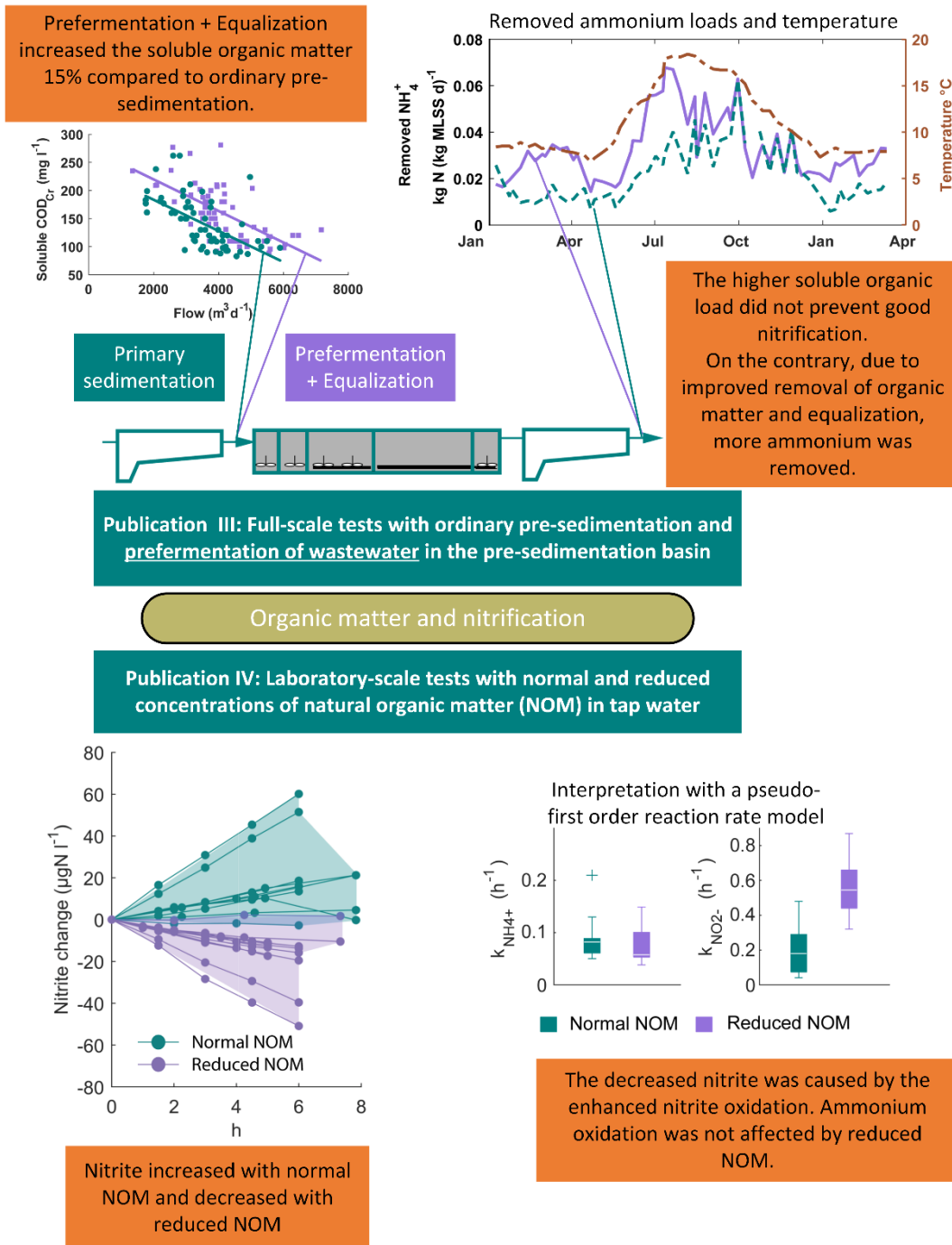


Figure 9. The findings of Part B. The top half of the figure concerns nitrification in wastewater treatment: Experiments were done on a full-scale WWTP with two process lines, pre-sedimentation and pre-fermentation. Top left: The relation of the influent flow and the soluble COD_{Cr} before the biological process. Top right: Time series of the removed ammonium load and temperature. The lower half concerns nitrite formation in tap water with two levels of NOM. Bottom left: Nitrite formation with two levels of NOM. Bottom right: Comparison of the reaction rate constants with the two NOM levels.

5 Discussion

5.1 Nitrogen reactions

In this work it was assumed that the nitrification and denitrification reactions occurred in biofilms or activated sludge. However, the microbiology of these systems was analyzed in only one occasion, in the end of the tests in **Publication IV**. In this chapter other possible nitrogen reactions are discussed to evaluate their significance. The discussion starts with wastewater treatment, because some of the reactions are utilized in WWTPs.

It is common knowledge that most nitrogen compounds are easily soluble, which prevents the chemical precipitation of nitrogen from wastewater, contrary to phosphorus removal. Thus biochemical nitrification and denitrification are utilized in wastewater treatment (Henze et al., 2002; Tchobanoglous et al., 2003). Another possibility for ammonium removal biochemically is called assimilation (Henze et al., 2002; Tchobanoglous et al., 2003), in which ammonium and other nitrogen compounds are utilized by micro-organisms as cell building materials. Depending on the ratio of organic matter and nitrogen, high percentages of ammonium may be removed by assimilation. However, most often the concentration of organic matter in municipal wastewater is not high enough to remove all ammonium (Tchobanoglous et al., 2003). In the case of Savonlinna WWTP, **Publication III**, assimilation explained approximately 15% of nitrogen removal. Furthermore, ammonium could be removed by stripping it into gaseous ammonia in pH 10-11 (Gustin and Marinsek-Logar, 2011), or precipitated as a sparingly-soluble magnesium ammonium phosphate (struvite, $\text{NH}_4\text{MgPO}_4 \times 6 \text{H}_2\text{O}$) (Crutchik et al., 2017). These methods need to be designed separately. Moreover, in Finnish wastewaters the concentrations of magnesium are not high enough to form struvite (Lehtinen, 2010). In addition, the pH at Savonlinna WWTP was not high enough for ammonium stripping. These notions considered, these reactions were unlikely in the wastewater treatment experiments of this thesis.

Magnesium ammonium phosphate precipitation was a possibility in the tests in **Publication IV**, especially because both magnesium and orthophosphate were amended into the tests. However, the orthophosphate concentration was so low that it would have explained less than one percent of the reacted ammonium. Furthermore ammonium stripping was unlikely because the pH was too low to form gaseous ammonia. Reactions of metallic lead or iron with nitrogen compounds (Huang and Zhang, 2005; Zhang, Y. et al., 2009) were unlikely in a pipe loop made of polyethylene, and a tank made of polypropylene. Furthermore the plastic materials were shock-chlorinated and rinsed with reverse osmosis water, as

explained in **Publication IV**, before the tests were started. The ammonium removal and nitrite formation activities in the SDSs were negligible during the starting period, which implies that the materials did not adsorb ammonium, nor ammonium or nitrite were extracted from the materials. Furthermore, it implies that the amount of suspended microbes in the water was not high enough to induce significant ammonium removal or nitrite formation via nitrification. Assimilation could have happened during the tests, when the microbes in the biofilm were using organic matter and nutrients in building microbial cells. However, significant decrease of NOM was not observed. If it is assumed that the decrease of NOM was $0.1 \text{ mg TOC L}^{-1}$, which could have been hidden in the error margins in the analyses of the influents and the effluents, it would have explained less than 5% of the decreased ammonium. Finally, the total nitrogen balance of the tests was calculated from the nitrogen in the influents, samples and effluents, and this was found to be slightly positive, from +0.3% to +2.0% of the feed. This implies that denitrification, anammox nor nitrogen fixation were not significant, as a whole, in the tests.

In the DWDSs of Helsinki and Vantaa (**publications I and II**), assimilation of nitrogen could have been possible. In **Publication II** the nitrogen loss by assimilation was estimated to be 2.7% of total nitrogen at the sampling location of Hospital K (Figure 8 in **Publication II**). Metallic lead can react with nitrate, forming nitrite and finally gaseous nitrogen (Zhang, Y. et al., 2009). However, the pipe materials in the cities of Helsinki and Vantaa did not include lead pipes. Thus, this reaction was unlikely to occur. Furthermore, metallic iron can reduce nitrate into ammonium (Huang and Zhang, 2005). Whether this reaction occurred, cannot be proven with the data of this thesis. Nevertheless, nitrate increased from the Pitkääkoski WTP to Hospital K, which implies that another reaction oxidized the possibly formed ammonium back into nitrate. This reaction was most probably biochemical nitrification.

To conclude, presupposing that the reactions of ammonium, nitrite, and nitrate were biochemical nitrification and denitrification is a realistic assumption. Thus, the role of biofilms and activated sludge was central to the observed nitrogen conversions.

5.2 Nitrite in drinking water distribution

Part A of the thesis, “Nitrite formation in full-scale DWDSs,” concerned the utilization of the vast pool of obligatory monitoring data of distributed water quality collected by the water works. Methods to visualize the nitrite concentrations in distributed water and to find the seasonal behavior of formed nitrite were studied. These methods were used to examine patterns in the nitrite concentrations. Additionally, total residual chlorine concentrations, ammonium concentrations, water age, and water temperature—complemented by sampling campaign data—were used to recognize the reasons for nitrite formation. The sampling campaign data included all inorganic nitrogen forms and total nitrogen in a relatively separated branch of a DWDS. The methods and findings are both discussed here.

5.2.1 Visualization of the spatial distribution

Statistical analyses of drinking water quality are often difficult because of missing data and the high share of values below the LoQ (Li, H. et al., 2019). For spatial analysis of the data, the most suitable methods depend on the purpose of the study. When interpolating non-existing spatial data, various methods are available, for example, kriging (van Beers and Kleijnen, 2003) or Bayesian spatial prediction (Le, N.D. and Zidek, 1992). The first is generally available in geographical software. The latter is an enhanced method developed on the basis of kriging, and more suitable for environmental analysis than kriging. However, these two methods are used mainly for prediction, while the purpose in **Publication I** was to illustrate nitrite concentrations as unequivocally as possible. In fact, the research method was in itself the visualization of the large data pool in an exploratory manner. For example, the effects of the underlying DWDS were not known. DWDSs are regularly organized spatially, but in a manner depending on the population, roads, industry, etc. Furthermore, the retention time in the household plumbing systems was not known because the water age had been modeled with a skeleton model without the service pipes (Laitala, 2015). Household plumbing has been noted to have a large effect on the observed nitrite levels (Zhang, Y., 2008).

The spatial data was interpolated by digital image inpainting (D'Errico, 2012; Garcia, 2010) in **Publication I**. In digital image inpainting, the goal is to interpolate smoothly from the boundaries of the existing data. Digital image inpainting has been used in interpolating data gaps concerning upwelling in the Baltic Sea (Sproson and Sahlee, 2014) and the land-atmosphere exchange of carbon, water, and energy in the Northern Chihuahua Desert (Jaimes Hernandez, 2014). In this thesis, the requirements for the application were formulated as follows:

- a) The resulting image should not react to the edges of the map.
- b) All existing values should be visible on the map as they are and not changed by the interpolation.
- c) No negative values were accepted.

In addition, the resulting image should be visually intuitive. Digital image inpainting protects the existing data because it is designed to fill only the missing parts of digital images. Thus, it already fulfills Requirement B.

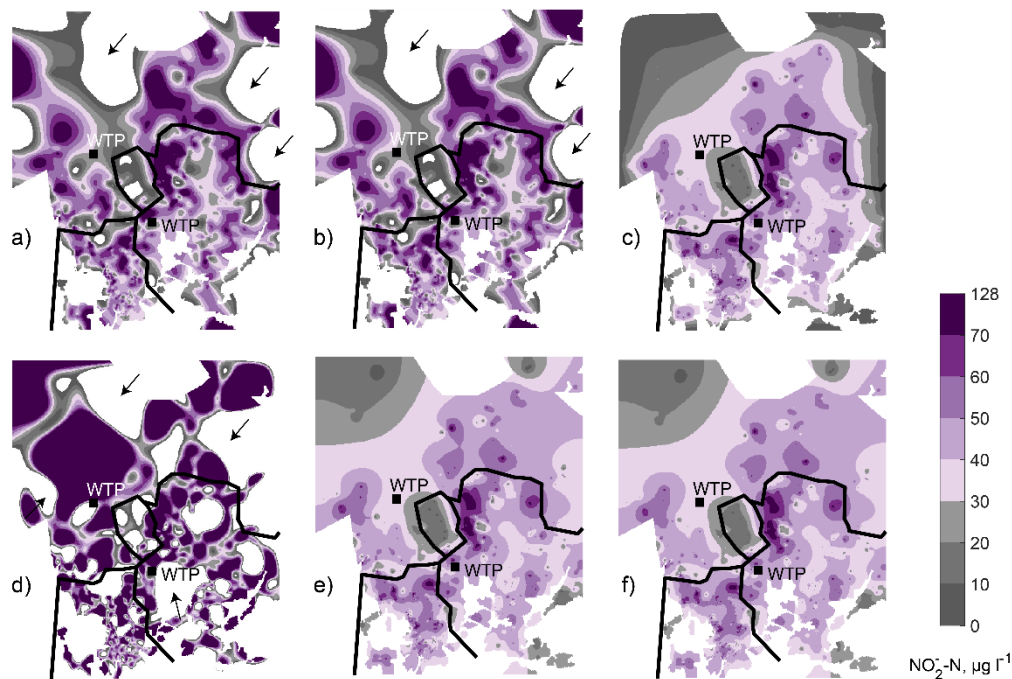


Figure 10. Illustrations depicting the boundary conditions of the interpolation of missing spatial data. (a) Method 0, (b) Method 1, (c) Method 2, (d) Method 3, (e) Method 4, and (f) Method 5 of the `inpaint_nans` function in Matlab (D’Errico, 2012). The chosen version was the map in Figure 10e, Method 4, and other maps should be compared to it. Arrows indicate examples of areas with less than zero values, interpolated by the inpainting methods.

It can be seen that Methods 0, 1, and 3 by D’Errico (2012) (figures 10a, 10c, and 10d) display negative values in areas where a non-negative value should have existed. These appear as white regions inside the mapping area, examples of which are indicated by arrows. Furthermore, the images in figures 10a, 10c, and 10d are not very illustrative or intuitive. Therefore, these interpolation methods were discarded. Method 2 (Figure 10c) reacted to the edges of the image area. This can be seen as grey areas of concentrations below 30 µg L⁻¹, close to the edges of the image. Thus, Method 2 was discarded, even though it fulfilled the rest of the requirements. Methods 4 and 5 (figures 10e and 10f) both fulfilled all the requirements and were practically equal. Without any other preconditions, Method 4 in Figure 10e was chosen. This method was used in all of the maps in **Publication I**: nitrite, total residual chlorine, ammonium, and water age.

5.2.2 Seasonality

Seasonality studies of environmental data often encounter a common problem: The sophisticated ARIMA models used for time series analysis (Faruk, 2010) require data with equidistant time intervals, which is not necessarily the case in environmental data. For example, Schullehner et al. (2017) had extensive data from Danish drinking water, including 54,000 analyses of drinking water from the years 2007–2016, but they did not utilize time series analysis. Instead, they studied seasonality with monthly boxplots. As another example, Salo et al. (2019) studied groundwater levels resulting from subsurface drainage applied with two

different methods from the years 2015–2017. Time series analysis could not be utilized because of unequal sampling intervals. Instead, they performed statistical analyses with several parametric and non-parametric methods.

One possibility to modify the time series is to fill the data gaps with interpolation. However, this may lead to artifacts in the data. Environmental sampling is time-consuming, and the analyses can frequently be expensive, which often leads to short time series (Pacheco et al., 2001; Woods et al., 2015) that are not suitable for time series modeling. Seasonally organized sampling campaigns are one option to inspect seasonally occurring phenomena (Serrano et al., 2015). This type of sampling strategy was also utilized in earlier studies concerning seasonality of nitrite concentrations in DWDSs (Wolfe et al., 1990; Wilczak et al., 1996).

With a large data pool, the requirement for time series analysis is whether the same location has been sampled and analyzed for the same variable often enough to form a long time series. This was the case in the obligatory monitoring data in Vantaa: there existed 16 locations with constant surveillance for 12–47 months. In Helsinki, the water quality monitoring did not have any long time series from the same sampling location.

Some of the original time series in Vantaa were suitable for evaluating the seasonality by comparing to the temperature curve (Figure 2 in **Publication II**). However, a more robust analysis tool could also categorize the equivocal time series. Furthermore, possible future changes in water quality could be analyzed with this method. A method that has been mostly used in evaluating sales in a small-scale, seasonal index, was chosen (Brendstrup et al., 2004; Hyndman and Athanasopoulos, 2013). The method was fine-tuned from the initial four-season method to a six-season method (Equation 6). Some of the data gaps were filled by forming six-season averages. Furthermore, the sensitivity to the starting month, whether it was January or December, was studied. The method was found to be robust for the initial month. The robustness against filling the missing data was also tested, and a conservative filling strategy was chosen: those gaps that had one missing value were filled.

The 16 time series were categorized with the seasonal index method. The index compares the value of each season to the annual average (Equation 6). Initially, it was evident that the nitrite time series of Vantaa did not demonstrate similar seasonal behavior. Some of the time series had a nitrite maximum during summer, as expected, but some had a visibly opposite winter maximum. Examples of seasonality with summer and winter maximums are shown in Figure 8. It turned out that different nitrification reactions were responsible for these phenomena: Nitrification was the key factor behind the summer maximum and nitratation behind the winter maximum.

One of the time series (Gas station K, Figure 8) had a possible growing trend in the obligatory monitoring data. Removing the trend before analyzing the seasonality would have been a logical choice if this had been an economical time series. Nevertheless, the added monochloramine concentration was limiting the maximum nitrite concentration, and thus the trend was not able to continue after the initial ostensible rise. This notion was corroborated by the data of the sampling

campaign with a lower peak at this location one year after the original time series ended (Figure 5e in **Publication II**).

In the sampling campaign, it was observed that nitrite was formed in minutes in the sampling line leading from a WTP to the laboratory at the site of the WTP. This was possibly an indication of direct monochloramine metabolism into nitrite, as observed by Wahman et al. (2016). However, this speculation cannot be proven by the data.

These results help in understanding where and when nitrite is formed in the DWDS and direct monitoring appropriately to gain exact knowledge of nitrite exposure. Also, possible future changes in the treatment process and additional disinfection measures can be designed appropriately to minimize extra nitrite exposure.

The problem in studying seasonality in environmental data was partially solved. A seasonal index can be used in analyzing trends once the annual seasonality is known. The applications are not limited to nitrite, but any variable in DWDSs or any other environmental data can be analyzed if the time series are long enough.

5.2.3 Combining seasonality and the spatial data

Combining the points of view in **publications I** and **II** resulted in an interesting chart (Figure 11). In the data used in spatial inspection, both summer and winter maxima can be seen in the monthly medians of nitrite, but only summer maximum in the highest values of the nitrite concentrations. In the monthly medians of nitrite, the summer maximum is visible in July, when the temperature was still rising, and the winter maximum in February, in the middle of the coldest period of the year. Furthermore, the monthly median of total chlorine was increased in July, which most probably increased the maximum nitrite by providing more ammonium substrate. However, the total chlorine concentration was not sufficient to inhibit nitrification. It must also be noted that the nitrite medians started to rise already in May, together with the first indications of a temperature rise. Moreover, when the temperature was at the highest, nitrite levels decreased. This may be a sign of disinfection inhibition. However, it was more probably a consequence of increased NOB activity in the higher temperature. As can be seen in Figure 11, the median and the highest value of nitrite both decrease in August. However, the total residual chlorine was still at the same level, as in July. The increase in total residual chlorine was obviously not the main reason for the elevated nitrite levels in July. A more likely reason was that when the temperature of the water remained at a high level, NOB activity increased. Consequently, the nitrite levels decreased.

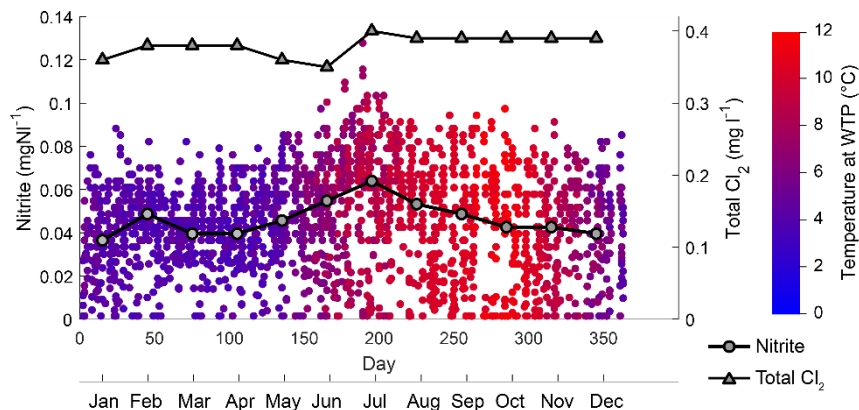


Figure 11. The combination of the data used in the spatial inspection and the seasonal point-of-view. The colored circles are all the nitrite concentrations ($N = 2151$) with the temperature indicated by color, the grey circles are the monthly medians of the nitrite concentrations, and the grey triangles are the monthly medians of the added monochloramine concentrations as total chlorine ($N = 1850$).

Interestingly, temperature did not significantly influence the spatial distribution of nitrite. On the other hand, the seasonality of nitrite concentrations evidently depended on temperature. The explanation for this paradox is that even though nitrite formation was decelerated by the low temperatures, it did not completely stop.

5.2.4 Water sampling strategies

The sampling strategies adopted in each city affected the resulting maps of the nitrite concentrations (**Publication I**). The pattern and level of the concentrations were rather similar in the lower half of the nitrite maps in figures 2a–c in **Publication I**, reflecting the sampling strategy in the area of Helsinki. The sampling included a few drinking water samples taken from each tap during the study interval. Consequently, the data in the area of Helsinki was geographically dense (830 sampling locations, Figure 8). In contrast, in Vantaa several drinking water samples were taken from each tap, but the tap locations were relatively few in number, leading to a geographically sparse collection of data (68 sampling locations, Figure 8). The Vantaa spatial data included wider spatial gaps between sampling locations, requiring larger areas to be interpolated compared to Helsinki. In conclusion, it can be said that the chosen method of spatial inspection suited the Helsinki data more than the Vantaa data. However, the Vantaa data was more suitable for time series analysis than the Helsinki data (**Publication II**).

Contrary to the earlier observations that concluded that nitrite is likely to occur in stagnating water (Cunliffe, 1991; Harrington et al., 2002), the opposite was revealed in **Publication I**: Nitrite was forming close to the water works in freshly produced water. The most probable reason was the low concentration of monochloramine, which was not able to prevent nitrification in the biofilm. However, the low monochloramine concentration also limited the maximum nitrite concentrations, and no nitrite value exceeded the statutory limit of 0.15 mg L^{-1} as

nitrogen. Furthermore, in stagnant water, the nitrite concentrations tended to be low. Unexpectedly, a low temperature did not significantly inhibit nitrification or nitrite formation. The findings of this study emphasize that nitrite concentrations should be monitored close to the WTPs. Focusing on stagnant water is not sufficient.

5.3 Organic matter and nitrification

Part B of this thesis, “The effect of organic matter on nitrification in wastewater treatment and tap water distribution,” studied ammonium removal in a full-scale WWTP and nitrite formation in an SDS. Organic matter consuming heterotrophic micro-organisms compete with the AOB and NOB; thus high organic matter concentrations decrease the activity of AOB and NOB. However, in practical occurrences of nitrification, the causes and effects are not always self-evident. Thus, two existing knowledge gaps were scrutinized: (1) ammonium removal with nitrification in a WWTP utilizing pre-fermentation to increase the concentration of soluble organic matter and (2) nitrite formation in non-disinfected conditions simulating tap water distribution.

5.3.1 Wastewater treatment

Controversially, the increased soluble organic matter enhanced the removal of ammonium in the tests at the Savonlinna WWTP (**Publication III**). The ammonium removal in the pre-fermentation line was not only higher than on the conventional pre-sedimentation line, but the treatment line equipped with pre-fermentation was capable of a faster recovery of the lost nitrification capacity.

Wastewater processes operate under a changing environment where balanced conditions are never reached. Thus, there are multiple causes leading to the enhanced nitrification on the pre-fermentation line compared to the pre-sedimentation line, and no single reason can be clearly pointed out. It is possible that the metabolism of AOB and NOB changed during the coldest period (Johnston et al., 2019) or that other organisms in commensalism with AOB were affected by the low temperature (González-Cabaleiro et al., 2019; Johnston et al., 2019). Furthermore, the numerous parameters influencing nitrification increase the number of reasons. The reasons are discussed in **Publication III**.

Here the focus is on the effects of organic matter and how the effects on nitrification were accomplished. Figure 12 depicts the effect of pre-fermentation as a process of increasing the soluble and easily biodegradable organic matter available for biological phosphorus removal and denitrification preceding nitrification. Here, the processes are divided into sub-processes to clarify the logic of the nitrification enhancement. The first phase includes non-soluble COD removal in pre-sedimentation compared to hydrolysis of non-soluble COD in pre-fermentation. The second phase includes the phosphorus release reaction of biological phosphorus removal and denitrification in anaerobic and anoxic conditions. Both of these reactions consume soluble COD. However, in the pre-fermentation line, the uptake was enhanced. As a result, the organic load on the following step, nitrification, was lower in the pre-fermentation line compared to the pre-sedimentation

line. Consequently, the heterotrophic growth was reduced in the aerated nitrification basin. Thus, the mass transfer of ammonia and nitrite inside the flocs to AOB and NOB was enhanced (Furumai and Rittmann, 1994; Rittmann and Manem, 1992). Furthermore, there was less competition for environmental resources. This all resulted in a higher capacity for ammonia removal compared to the conventional pre-sedimentation process.

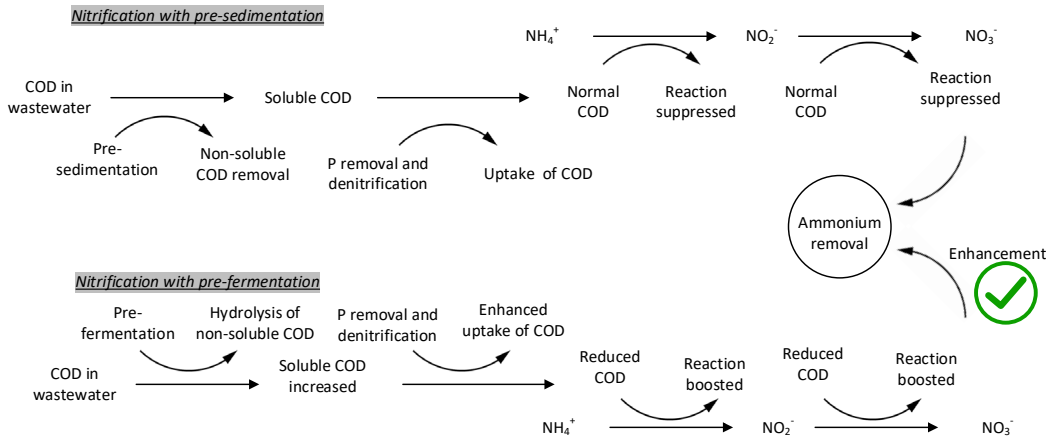


Figure 12. The comparison of nitrification with pre-sedimentation and pre-fermentation at a WWTP.

In conclusion, because ammonium removal was enhanced, it is probable that both reactions of nitrification were boosted, as shown in Figure 12. However, nitrite was not analyzed during the tests. If nitrite concentrations would have increased in the process, this would have been caused by operational problems such as low alkalinity in the influent or poor aeration (Kaelin et al., 2009; Knapp and Graham, 2007). These were not observed, which indicates that nitrite concentrations were not increased substantially. Moreover, the process was not specifically designed for removing nitrogen by nitrification-denitrification, in which nitrification is prevented at temperatures above 26 °C or oxygen levels below 0.4 mg L⁻¹ (van Dongen et al., 2001). Thus, the possibility of excessive nitrite formation by inhibited nitrification was negligible.

On the other hand, if the increased soluble organic load had been introduced directly into the aerobic compartment with nitrification, both nitrification reactions would have been suppressed, as observed by Delgado et al. (2004).

Furthermore, the nitrification in the tests at the Savonlinna WTP was not enhanced only in relation to organic matter, but the equalization improved the conditions of nitrification. However, the peak flows were not leveled out efficiently by the equalization basin. Thus, the effect of the diurnal equalization may have been less than the effect of the altered organic load.

5.3.2 Water distribution

In SDSs, nitrite was observed to increase with normal NOM of tap water but decrease with reduced NOM. Figure 13 compares the nitrification reactions with

normal and reduced NOM in the SDSs (**Publication IV**). As observed with the pseudo first order reaction rate model, this was the result of enhanced nitrite oxidation. Ammonium oxidation was not significantly enhanced or suppressed. Presumably, the critical factor was the availability of nitrite inside the biofilm, as the reduced NOM decreased the total amount of heterotrophic bacteria inside the biofilm. Similar observations have been made in wastewater treatment plants when nitrification has been disturbed by process conditions and the supply of nitrite to NOB was deteriorated (Kaelin et al., 2009; Knapp and Graham, 2007). Furthermore, the decreased amount of heterotrophic bacteria induces less competition for general environmental resources (Furumai and Rittmann, 1994; Rittmann and Manem, 1992).

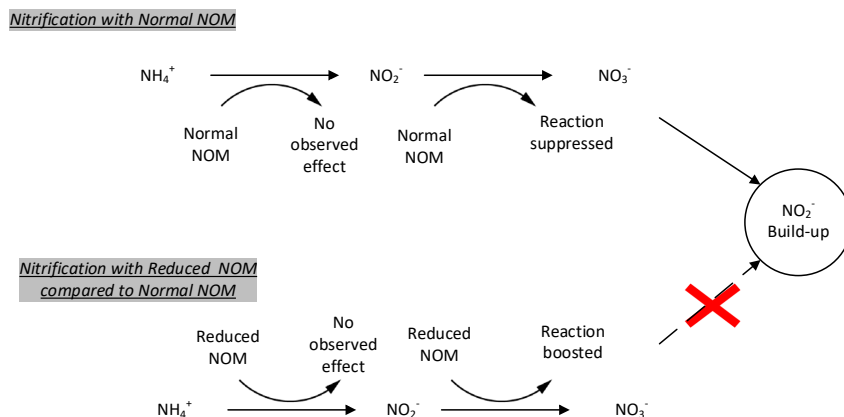


Figure 13. The comparison of nitrification with normal and reduced NOM in SDSs.

In DWDSs, there is a need to prevent nitrification because nitrite is potentially harmful to humans. This gives two options for the two nitrification reactions: either try to prevent ammonium oxidation or try to enhance nitrite oxidation. This notion gives new directions to explore nitrite formation in DWDSs. Purportedly, there may exist other conditions that enhance nitrite oxidation while being suitable for drinking water. From the thermodynamic perspective, affecting nitrite oxidation would be easier than ammonium oxidation because nitrite oxidation is four times less of a favorable reaction than ammonium oxidation (Stumm and Morgan, 2009). Thus, the NOB gain less energy from the reaction and are presumably more vulnerable to changes in the environment. For example, NOB have been observed to be affected by a lower monochloramine concentration than AOB (Gomez-Alvarez et al., 2014; Schrantz et al., 2013).

5.4 Organic matter and nitrification in a larger context

5.4.1 Benefits of the pre-fermentation process modification in wastewater treatment

It was apparent that the pre-fermentation process could remove more ammonium than the conventional pre-sedimentation process. Thus, in the case where

biological phosphorus removal and denitrification are combined with nitrification, a more efficient way to run the process is pre-fermentation enhanced with equalization. This design protects nitrification (McCue et al., 2006; McCue et al., 2004), which is of paramount importance in the cold northern climate. Furthermore, if an external carbon source were used, nitrification would not benefit similarly. On the contrary, remnants of an external carbon source could burden the nitrification basin. As a whole, pre-fermentation boosts both biological phosphorus removal (Brinch et al., 1994; Goncalves et al., 1994; Lötter and Pitman, 1992; Mikola et al., 2007) and denitrification (Goncalves et al., 1994; Brinch et al., 1994; Mikola et al., 2007; Pitman et al., 1988; Canziani et al., 1995) and ammonium removal (**Publication III**, McCue et al., 2006; McCue et al., 2004). The removal of organic matter was also improved (Mikola et al., 2007). The process change from pre-sedimentation to pre-fermentation was minor, and the costs were minimal (Mikola et al., 2007). Another beneficial observation was reduced production of waste activated sludge (Mikola et al., 2008). Thus, this relatively simple and low-cost modification is remarkably applicable at WWTPs. Furthermore, it is a good example of the circular economy, as it utilizes the organic matter in the influent wastewater instead of applying external carbon sources, which are industrial products. These benefits are summarized in Figure 14. The drawbacks related to pre-fermentation installed in existing pre-sedimentation tanks are largely related to the practical operation of the process (Dold et al., 1985; Wedi, 1992; Armiger et al., 1993; Christensson et al., 1998). However, pre-fermentation is a unit process that effectively supports a clean and healthy environment, and its use should be considered whenever a unit process that consumes organic matter precedes nitrification.

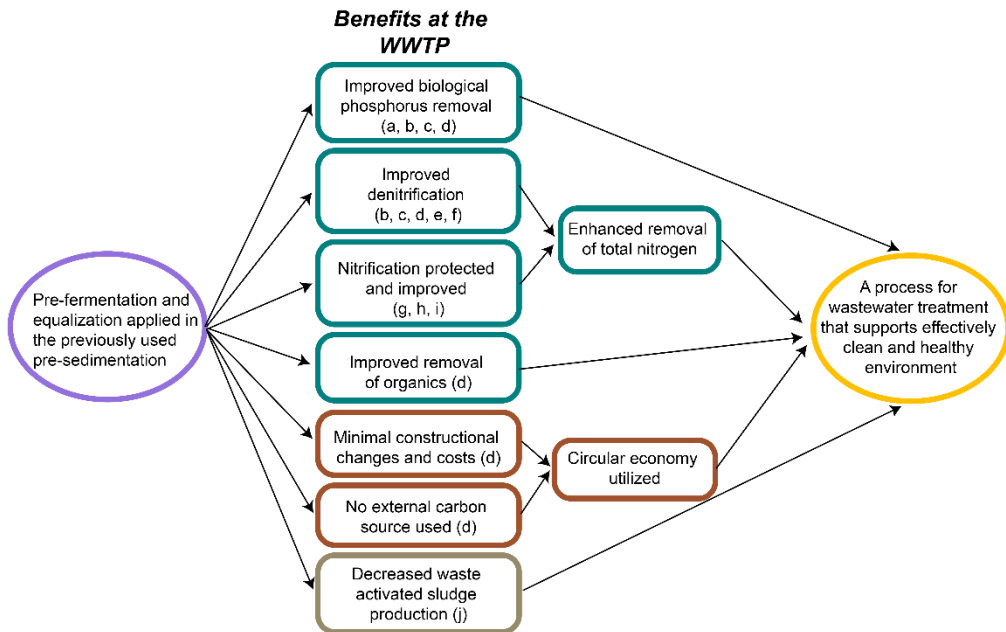


Figure 14. The benefits of the process with pre-fermentation and equalization built in a previous pre-sedimentation basin. (a) Lötter and Pitman, 1992, (b) Goncalves et al., 1994, (c) Brinch et al., 1994, (d) Mikola et al., 2007, (e) Pitman et al., 1988, (f) Canziani et al., 1995, (g) **Publication III**, (h) McCue et al., 2003, (i) McCue et al., 2006, (j) Mikola et al., 2008.

5.4.2 Enhanced removal of natural organic matter from distributed water

When the results concerning decreased nitrite formation with reduced NOM are positioned into a larger connection, they support enhanced removal of NOM at the WTPs. This, combined with other known consequences of reducing organic matter in DWDSs, forms a convincing case for reducing NOM at WTPs (Figure 15). Reducing NOM would reduce nitrite in conditions that are both disinfected with monochloramine (Harrington et al., 2002; Huang et al., 2016; Wilczak et al., 2003; Yang, X. et al., 2008; Zhang, Y. et al., 2010b) and non-disinfected (**Publication IV**). Furthermore, reduced NOM decreases heterotrophic growth in biofilms and slime build-up (Van Der Kooij et al., 1982; Miettinen et al., 1999; Escobar and Randall, 2001; van den Broeke et al., 2008; Ross et al., 2013). In disinfected DWDSs, decreasing NOM reduces the consumption of the disinfectant (Bal Krishna et al., 2012; Duirk et al., 2005) and DBPs (An et al., 2017) by reducing both reactants, leading to better water quality in distribution.

Water works spend a significant share of their budgets on renovating the distribution pipes. The value of this effort is enhanced if the distributed water is used for drinking, which is one of the primary functions of human beings. Thus, if the water quality could be improved enough to motivate customers to use tap water for drinking, this would be a more efficient use of the whole distribution network. For example, in Europe, consumption of packaged water was 115 L cap⁻¹ in 2017 (UNESDA, 2019), with Italy leading the consumption statistics by 200 L cap⁻¹. In the USA, consumption was 159 L cap⁻¹ in 2017 (Statista, 2018). On the other hand,

Finnish consumption was only 14 L cap⁻¹. These numbers reveal that in many countries, the water distributed by the water works is not favored for drinking purposes. By reducing the concentration of organic matter in the distributed water, the quality of water might increase enough for customers to approve distributed water for drinking.

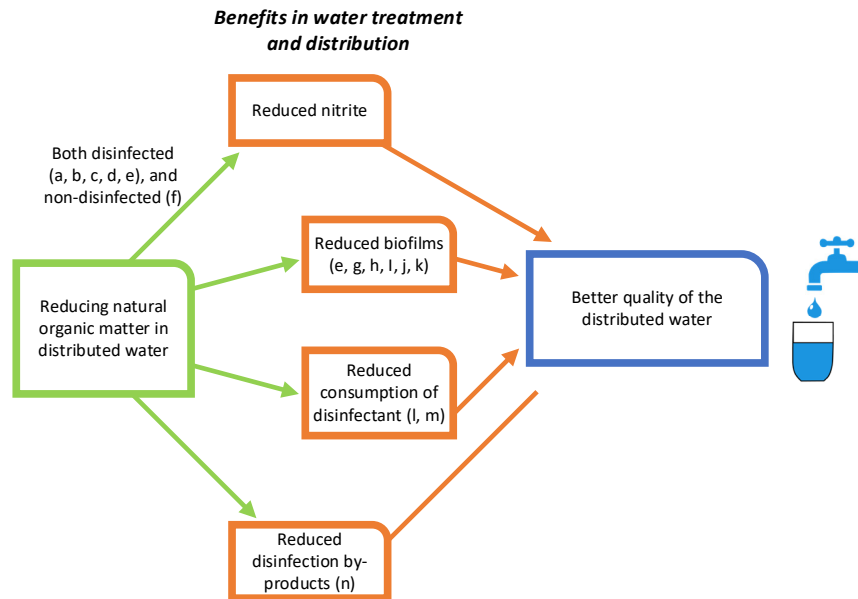


Figure 15. The key finding of **Publication IV** in a larger scope: Benefits of reducing NOM in water treatment and distribution. References: (a) Harrington et al., 2002, (b) Wilczak et al., 2003, (c) Yang, X. et al., 2008, (d) Zhang, Y. et al., 2010b, (e) Huang et al., 2016, (f) **Publication IV**, (g) Van Der Kooij et al., 1982, (h) Miettinen et al., 1999, (i) Escobar and Randall, 2001, (j) van den Broeke et al., 2008, (k) Ross et al., 2013, (l) Duirk et al., 2005, (m) Bal Krishna et al., 2012, and (n) An et al., 2017.

5.5 Practicality of the findings

The findings of this thesis relate to a very practical scientific discipline—water and wastewater engineering. The mapping and the time series analysis methods developed in **publications I** and **II** can be refined and improved for practical use in the everyday operation of WTPs and DWDSs. In this thesis, the methods have already revealed new knowledge on the formation of nitrite in DWDSs. Furthermore, the methods utilized the obligatory monitoring data collected by the water works.

Pre-fermentation was found to enhance nitrification in a full-scale study at a WWTP (**Publication III**). Thus, the process modification was put to the hardest test. The results of the study demonstrated various other benefits in wastewater treatment, and thus it can be recommended at WTPs with pre-denitrification or biological phosphorus removal, or both.

The results of **Publication IV** provide the possibility to decrease nitrite concentrations in non-disinfected DWDSs with ammonium or nitrite in the

distributed water. These kinds of DWDSs exist in Finland (Ahonen et al., 2008; Lipponen et al., 2002), Denmark (Schullehner et al., 2017), and The Netherlands (Waak et al., 2018). Furthermore, the mapping and time series analysis methods developed in **publications I** and **II** would be valuable in observing the consequences of a process modification in distributed water quality.

5.6 Further studies

This thesis raises some study questions for future research. A modification of an existing pre-sedimentation basin into a pre-fermentation and equalization basin was studied and found to be beneficial for numerous unit processes at the WWTP, including nitrification. The drawbacks were largely related to operational problems (Dold et al., 1985; Wedi, 1992; Armiger et al., 1993; Christensson et al., 1998). However, there are very few recent reports of this process modification in the scientific literature. Thus, a study concerning full-scale applications of retrofitted pre-sedimentation basins would reveal how successful operations of pre-fermentation and equalization have been realized in practice.

The observations concerning decreased nitrite formation in distributed water with reduced NOM need to be studied on a larger scale. The extent to which nitrite concentrations would actually be decreased remains to be seen in these tests. For example, the old biofilms in the DWDSs contain a pool of organic matter as microorganisms and extra-cellular polymeric substances (EPS). Moreover, changing the water quality will affect the microbial population of the biofilms and distributed water. These questions need to be studied further.

Other possible reasons for the suppression or enhancement of the nitrite oxidation reaction need to be surveyed. For example, the observations by Vahala (1999) and Vahala and Laukkanen (1998) of increased nitrite formation ostensibly when NOM was reduced may be explained by changes in other water quality parameters.

6 Conclusions

As conclusions, the answers to the study questions according to this thesis are compiled here.

1. *How can the existing obligatory monitoring data of drinking water quality be utilized to find out more about nitrite formation in a drinking water distribution system?*

In this thesis, it was observed that the obligatory monitoring data is useful for map presentations as a whole. The map presentation was developed utilizing interpolation with digital image inpainting. Furthermore, the time series included in the obligatory monitoring data were suitable for analyzing the seasonal properties of nitrite formation. A method based on a seasonal index was developed for this purpose to inspect the patterns of seasonal behavior (**Publications I and II**).

2. *What is the spatial distribution of nitrite in a drinking water distribution system, and what are the reasons behind the spatial distribution?*

The spatial distribution of nitrite revealed that nitrite was forming rapidly in the drinking water distribution systems. Moreover, the nitrite concentrations tended to be low with high water age. The monochloramine concentrations were not high enough to prevent nitrite formation. However, the maximum nitrite concentrations were limited by the added monochloramine. Unexpectedly, temperature did not significantly affect the spatial distribution. (**Publication I**)

3. *What is the seasonal distribution of nitrite in a drinking water distribution system, and what are the main reasons for the observed seasonality?*

Unexpectedly, nitrite exhibited four types of seasonality: (1) Nitrite maximum during summer or (2) winter, (3) mixed seasonality with concentrations above the Limit of Quantification (LoQ), and (4) flat seasonality with concentrations below the LoQ. The key drivers were temperature and water age. The winter maximum was caused by the decelerated ammonium oxidation. The dominant reaction at low water ages was ammonium oxidation into nitrite, and at high water ages, it was nitrite oxidation into nitrate (**Publication II**).

4. *What are the effects of organic matter on nitrification in practical applications?*

It is well known that organic matter suppresses nitrification reactions. However, in this thesis, nitrification in tap water conditions was suppressed by natural

organic matter. On the other hand, in wastewater conditions, nitrification was boosted by increased soluble organic matter (**publications III and IV**).

5. *How does increasing the easily biodegradable organic matter in a nitrogen removal WWTP affect ammonium removal by nitrification?*

Unexpectedly, ammonium removal via nitrification was enhanced when the soluble organic matter concentrations were increased with pre-fermentation in a previously used pre-sedimentation basin. However, when this observation was analyzed more deeply, it was revealed that the organic load was actually reduced by denitrification and biological phosphorus removal preceding the nitrification basin in the treatment line. Thus, the enhanced ammonium removal was in agreement with known theory (**Publication III**).

6. *Can the nitrite levels in drinking water distribution be decreased by decreasing organic matter?*

In non-disinfected conditions, decreasing natural organic matter prevented nitrite formation by enhancing the nitrite oxidation in a simulated distribution system. Furthermore, this observation supports reducing organic matter from current levels to decrease the nitrite concentrations in distributed water (**Publication IV**).

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