N-nitrosodimethylamine (NDMA) in Purified Recycled Water

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The UWSRA is a $50 million partnership over five years between the Queensland Government, CSIRO's Water for a Healthy Country Flagship, Griffith University and The University of Queensland. The Alliance has been formed to address South East Queensland's emerging urban water issues with a focus on water security and recycling. The program will bring new research capacity to South East Queensland tailored to tackling existing and anticipated future issues to inform the implementation of the Water Strategy.

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FOREWORD BY THE URBAN WATER SECURITY RESEARCH ALLIANCE

Water is fundamental to our quality of life, to economic growth and to the environment. With its booming economy and growing population, Australia's South East Queensland (SEQ) region faces increasing pressure on its water resources. These pressures are compounded by the impact of climate variability and accelerating climate change.

The Urban Water Security Research Alliance, through targeted, multidisciplinary research initiatives, has been formed to address the region's emerging urban water issues.

As the largest regionally focused urban water research program in Australia, the Alliance is focused on water security and recycling, but will align research where appropriate with other water research programs such as those of other SEQ water agencies, CSIRO's Water for a Healthy Country National Research Flagship, Water Quality Research Australia, eWater CRC and the Water Services Association of Australia (WSAA).

The Alliance is a partnership between the Queensland Government, CSIRO's Water for a Healthy Country National Research Flagship, The University of Queensland and Griffith University. It brings new research capacity to SEQ, tailored to tackling existing and anticipated future risks, assumptions and uncertainties facing water supply strategy. It is a $50 million partnership over five years.

Alliance research is examining fundamental issues necessary to deliver the region's water needs, including:

- ensuring the reliability and safety of recycled water systems.
- advising on infrastructure and technology for the recycling of wastewater and stormwater.
- building scientific knowledge into the management of health and safety risks in the water supply system.
- increasing community confidence in the future of water supply.

This report is part of a series summarising the output from the Urban Water Security Research Alliance. All reports and additional information about the Alliance can be found at http://www.urbanwateralliance.org.au/about.html.

C. Davis

Chris Davis
Chair, Urban Water Security Research Alliance

FOREWORD BY WATERSECURE AND VEOLIA WATER AUSTRALIA

The Western Corridor Recycled Water Scheme and the Gold Coast Desalination Plant are two major assets forming part of the South East Queensland (SEQ) Water Grid. These assets are owned by the Queensland Manufactured Water Authority, trading as WaterSecure, with their operation and maintenance outsourced to Veolia Water Australia. They are designed to provide drought resilient high quality water for this fast growing area in years and decades to come.

This infrastructure relies on world class innovations and technologies and both WaterSecure and Veolia Water Australia are committed to ensuring the Western Corridor Recycled Water Scheme and the Gold Coast Desalination Plant remain at the leading edge of the water purification industry. WaterSecure, Veolia Water Australia and The University of Queensland have entered into a $2.45 million research collaboration in January 2008 in order to embrace the pace of change in technology and maintain the efficiency, reliability and sustainability of these assets.

Water quality management and monitoring are key elements of the strategy underpinning this collaboration, aiming at driving scientific research to inform decision making processes with regards to new potential contaminants in indirect potable reuse and desalination applications. This report presents some significant outputs from this collaboration generated in partnership with the Urban Water Security Research Alliance.

Keith Davies
CEO, WaterSecure

Ben Bowen
Regional Manager, Veolia Water Australia

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EXECUTIVE SUMMARY

With traditional methods of harvesting water being no longer enough to meet growing demands, new options to supply water to communities and industry are currently being explored. In South East Queensland (SEQ), a plan for meeting water supply requirements for the next 50 years was implemented through the South East Queensland Water Strategy (2008). The production of Purified Recycled Water (PRW) in the framework of the Western Corridor Recycled Water Project (WCRWP) plays an important role in this water strategy. To that end, three Advanced Water Treatment Plants (AWTP) were built in the SEQ region - the Luggage Point AWTP and Gibson Island AWTP (located on both sides of the Brisbane river estuary) and Bundamba AWTP (located inland, near Ipswich).

The production of PRW in this Project is based on the treatment of wastewater to the highest standards through a seven-barrier process. These are, in summary: (1) Source Control; (2) Wastewater Treatment Plants (WWTPs); (3) Micro-Filtration or Ultra-Filtration (MF/UF); (4) Reverse Osmosis (RO); (5) Advanced Oxidation Processes (AOP); (6) natural environment blending; and, finally (7) Water Treatment Plant (WTP) (www.qwc.qld.gov.au). Barriers (3), (4) and (5) are provided by the AWTP.

As described in the South East Queensland Regional Plan 2009-2031, the purpose of the South East Queensland Water Strategy is to ensure water in the region is managed on a sustainable and integrated basis to provide secure and reliable supplies of acceptable quality for all uses for the long term. Public health and safety will not be compromised and the highest water quality standards appropriate to use will always be maintained. During the AWTP treatment train, the water is disinfected with chloramines to minimise biofouling on the RO membranes. However, the addition of a disinfectant to secondary treated effluents with relatively high concentrations of organic matter has the potential to produce hazardous disinfection by-products (DBPs).

One of the most concerning DBPs that is found in water treatment plants when disinfecting wastewater by means of chloramination is *N*-nitrosodimethylamine (NDMA). The US Environmental Protection Agency (US EPA) classifies NDMA as a "B2 carcinogen - reasonably anticipated to be a human carcinogen" (EPA, 2008) and a 10^{-6} cancer risk level in drinking water at 0.7 ng/L has been determined (EPA, 2001). Moreover, Public Health Regulations in Queensland require that NDMA concentrations in recycled water for augmentation of drinking water supplies are less than 10 ng/L (QPC, 2005). In the SEQ context, NDMA was found at medium to high ng/L levels before the AOP during the commissioning phase of Bundamba 1A AWTP (Poussade et al., 2009). This was not the case for Luggage Point AWTP where values of NDMA across the plant were always lower than the 10 ng/L guideline value. Although the AOP used at Bundamba 1A AWTP proved to be very effective in destroying NDMA to below the guideline concentration, the need for understanding and managing NDMA formation to minimise the risk of the presence of nitrosamines in the environment and drinking water supplies emerged. As a result of this knowledge gap, two projects were independently funded in a collaborative approach to carry out applied research on NDMA formation and management in PRW at the Advanced Water Management Centre (AWMC), at The University of Queensland (UQ).

The first two-year project, funded by the Urban Water Security Research Alliance (UWSRA), was focused on the NDMA formation potential (FP) in source water used for the production of PRW. The NDMA FP is a measure of the maximum NDMA concentration that can be obtained as a result of an extreme exposure of the water to chloramines. The first aim of that project was to identify source streams and operating conditions with increased NDMA FP in relevant recycled water sources in SEQ. After establishing the required methodologies for NDMA analysis, systematic analysis of the NDMA formation potential from a number of source waters was performed; particularly the effluents of the treatment plants providing feed flows to the AWTPs, but also other treatment plants with much lower treatment performance, e.g. Fairfield Sewage Treatment Plant (STP). A second aim of this project was to establish if there was a possible correlation between wastewater plant treatment level/performance and the NDMA FP for the specific situation in SEQ. To answer that question, the relation of NDMA FP with other chemical parameters commonly measured at the WWTPs, such as dissolved organic nitrogen and carbon, was evaluated.

Results obtained from this project showed that the NDMA FP of the evaluated effluents ranged between 350 and 1,020 ng/L, showing remarkable differences among individual WWTPs. The actual concentration of NDMA in those effluents was normally lower than 5 ng/L and never higher than 25 ng/L. When trying to relate chemical parameters to NDMA FP, it was found that the ammonium concentration in the secondary effluent could not be used to predict the formation of NDMA in the disinfection process, since high values of NDMA precursors were observed in the presence of high and low concentration of ammonia. However, a weak correlation between dissolved organic nitrogen (DON) and non-purgable organic carbon (NPOC) and NDMA FP was observed ($R^2 = 0.4$ for both parameters).

In an attempt to identify specific NDMA precursors in the SEQ context, a search on chemistry databases was performed and a list of potential anthropogenic NDMA precursors that can be found in secondary treated effluent was developed and included in this report. However, the measurement of all these potential precursors was beyond the scope of this project. Quaternary ammonium chloride compounds are commonly used as disinfectants in industrial, cosmetic and household products and have been identified as NDMA precursors. In a collaboration with CSIRO, benzalkonium chlorides were measured in all source waters used to generate PRW because reported levels in wastewater vary widely around the world, depending on local usage patterns. However, results showed that concentrations of benzalkonium chloride in SEQ plants were lower than 100 ng/L. Therefore, this compound is unlikely to significantly contribute to the NDMA FP of the PRW source waters in SEQ.

A second project funded by The University of Queensland, Veolia Water Australia and WaterSecure, focused on the understanding of the fate of NDMA and NDMA precursors across the different AWTPs in order to better characterise and reduce the concentrations of NDMA and its precursors along the PRW production train. It was observed that more than 98.5% of NDMA precursors were effectively removed by the RO membranes and no major changes in the NDMA precursor concentrations were identified in the remaining parts of the treatment train (except coagulation stage for Bundamba 1A AWTP). The high removal of NDMA precursors by the RO membranes drastically reduces any potential for reformation of NDMA after the RO stage, even if chloramines were present (or added) there or later during drinking water treatment and distribution. To complement these findings, the NDMA FP of different size fractionations of secondary effluents was measured. It was observed that more than 75% of NDMA precursors were found in the fraction smaller than 1,000 Da.

However, only 10% of the NDMA that was formed prior to the RO filtration stage was rejected by the RO membrane at Bundamba 1A AWTP. Thus, based on the poor NDMA rejection in comparison to the high rejection for NDMA precursors, the minimisation of NDMA formation before the RO membranes was identified as a key point to overcome the problem of high NDMA concentrations observed during the commissioning phase of Bundamba 1A AWTP (Poussade et al., 2009). Therefore, the operational parameters that influence the kinetics of formation of NDMA were investigated at the bench scale. It was observed that the disinfection of secondary effluents with pre-formed monochloramine generated significantly less NDMA than monochloramine formed in-line in the treatment train. Following this strategy, it is possible to minimise the formation of dichloramine, the main chloramine species responsible for the NDMA formation. The NDMA formation increased with the disinfectant dose applied. However, the contact time of the disinfectant with the wastewater was the most important parameter when aiming to minimise the NDMA formation. From these results, it was concluded that a contact time lower than six hours was an acceptable value to keep NDMA formation below the regulation limit when chloramine dose was lower than 10 mg/L Cl_2, independently of the disinfection strategy. The findings of this research were successfully implemented at Bundamba 1A AWTP, reducing the NDMA formation during the production of PRW by a factor of 20 by modifying the reagent dosing point.

Finally, working with scientists involved in the UWSRA Enhanced Treatment project, the research team assessed the fate of NDMA and NDMA precursors in processes such as denitrification, ozonation and biological activated carbon (BAC) filtration at the South Caboolture Water Reclamation Plant. Results showed that NDMA was not generated across that reclamation plant. On the other hand, BAC seemed to be a key step for the NDMA precursors removal in the treatment train, since 50% of the initial NDMA FP was eliminated by the BAC stage, even when the influent to this process was not pre-treated with ozone (actually, 80% of NDMA FP removal in the BAC stage when comparing inlet and outlet concentrations for this process). The pre-ozonation step and dissolved air flotation removed 20% and 18% of NDMA FP respectively and 40% of the initial concentration of NDMA precursors was removed when ozone was used before BAC filtration. Actually, 66% of NDMA FP was removed by ozonation when comparing inlet and outlet concentration of this process. NDMA and NDMA FP in the final effluent were around 2 ng/L and 50 ng/L, respectively.

Although both projects were independently funded, they were managed and executed in close collaboration; Dr Farré being the leader of both projects. As a consequence, it was agreed among project partners and funding institutions to publish a joint, comprehensive report covering the entire set of results. Therefore, the report presents results from the research generated in a joint effort between the Advanced Water Management Centre, National Research Centre for Environmental Toxicology (both part of The University of Queensland), Veolia Water Australia, WaterSecure and the Urban Water Security Research Alliance.

1. INTRODUCTION: N-NITROSODIMETHYLAMINE, A CHALLENGE IN THE SOUTH EAST QUEENSLAND CONTEXT

One of the key projects addressing the water shortage in South East Queensland (SEQ) is the Western Corridor Recycled Water Project (WCRWP) in which secondary effluent from different wastewater treatment plants is to be recycled for indirect potable reuse. The primary aim of the WCRWP is the production of purified recycled water (PRW). To achieve this, three Advanced Water Treatment Plants (AWTP) have been built in the SEQ region using coagulation, Ultra/Micro Filtration (UF/MF), Reverse Osmosis (RO) and the Advanced Oxidation Process (AOP) technology for water treatment. During this treatment train, water is disinfected at several points. Disinfection serves a number of purposes, including destroying or deactivating disease-producing microorganisms, ensuring water safety, and limiting biological fouling of the RO thin-film composite membranes. Although chlorine disinfection is widely applied as the most traditional water disinfection technique (Hasse, 1936), the active layer (polyamide) of the RO membranes can be corrupted by chlorine in solution, thus chloramines are normally used at the AWTPs. However, whilst effective at fouling control and disinfection, chloramination may also produce adverse effects, such as the formation of so-called disinfection by-products (DBPs). These compounds can be toxic and/or carcinogenic and are not always well rejected by the different physical barriers used.

One of the most concerning chemical compounds that has been found in AWTPs when disinfecting wastewater by means of chloramination is N-nitrosodimethylamine (NDMA). The US Environmental Protection Agency (EPA) classifies NDMA as a “B2 carcinogen - reasonably anticipated to be a human carcinogen” (EPA, 2008) and a 10^{-6} cancer risk level in drinking water at 0.7 ng/L has been determined (EPA, 2001). Moreover, Public Health Regulations in Queensland require that NDMA concentrations in recycled water to augment a supply of drinking water are less than 10 ng/L (QPC, 2005). The first evidence of NDMA in drinking water was reported in Canada in 1986 where this compound was measured at concentrations between 5 and 115 ng/L in the Oshweken water supply (Jobb, 1994). Since then, significant efforts have been made to investigate the chemistry of NDMA as well as to understand the key parameters that enhance NDMA formation. Several critical parameters driving NDMA formation in water treatment have already been identified. These parameters include the operational conditions for chloramination and the nature of precursor compounds (i.e. the specific composition of source water). However, to our knowledge, the NDMA formation assessment data has been predominantly undertaken in the United States and Canada. Moreover, a report has extended this assessment to other water facilities in Germany and one plant in Australia (Sacher et al., 2008).

High concentrations of formed NDMA were measured before the AOP during the first 16 months of operation at Bundamba AWTP, one of the three AWTPs of the WCRWP in SEQ. NDMA was safely removed in the AWTP by means of UV/H_2O_2, proving the effectiveness of the system and ensuring 100% compliance with the regulation. Nevertheless, the need for a better understanding of the formation of this hazardous compound was identified. Two independent projects were funded, by the UWSRA on one hand and Veolia Water Australia, WaterSecure and The University of Queensland on the other, in a collaborative approach to investigate different issues concerning NDMA in PRW in SEQ. The main targets of the research can be summarised as follows: (i) identify the NDMA formation potential (FP) of source water for PRW in SEQ; (ii) evaluate the fate of NDMA and NDMA precursors across AWTP during the production of PRW; and (iii) propose strategies to minimise the formation of NDMA during the production of PRW.

2. LITERATURE REVIEW

2.1. Chemistry of N-Nitrosodimethylamine at Advanced Water Treatment Plants

N-Nitrosodimethylamine, or NDMA, is the simplest dialkylnitrosamine, with a molecular formula of $(CH_3)_2N\text{-}NO$ and a molecular mass of 74.08 g/mol.

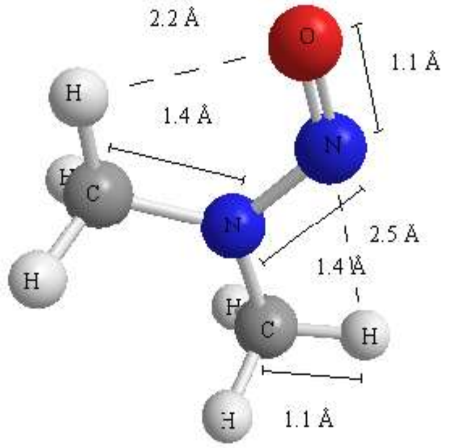


Figure 1. 3D chemical structure of NDMA with bond length (—) and close contacts (---) (drawn with ChemBio 3D Ultra 11.0).

As previously stated, NDMA has been classified as a "B2 carcinogen - reasonably anticipated to be a human carcinogen" (EPA, 2008). Protonation of the oxygen in the nitroso group makes NDMA a reactive alkylating agent, capable of transferring methyl groups to nucleophilic sites in biological molecules, such as DNA. DNA methylation is an important regulator of gene transcription, but alterations in DNA methylation may alter gene expression and may initiate the development of cancer. At ambient temperature, NDMA is a volatile, combustible, yellow, oily liquid with no distinct odour. Table 1 describes the physico-chemical properties of this polar molecule (Callahan et al., 1979; EPA, 2008).

Table 1. Physico-Chemical Properties of NDMA.

Property	Value
CAS Number	62-75-9
Boiling point (°C)	151–154
Molecular weight (g/mol)	78.08
Hydrophobicity soil - Log K_{oc}	1.079
Hydrophobicity water - Log K_{ow}	-0.57
Vapour pressure (Pa)	1,080 (25 °C)
Henry's law constant (Pa m^3/mol)	3.34 (25 °C)
Density (kg/L)	1.006 (20 °C)
Solubility in water (g/L)	Miscible 100 (19 °C)

Due to the low Henry's law constant, volatilisation from natural waters and air stripping are unlikely to result in significant removal of NDMA from solution. As a small, uncharged molecule, NDMA is poorly removed via RO. Moreover, due to the presence of a polar functional group, NDMA is hydrophilic with a log K_{ow} of -0.57. Thus, NDMA sorbs poorly to soil, activated carbon, and other sorbents (Mitch et al., 2003b).

Biodegradation of NDMA in aqueous and soil system has been well studied and it is established that anaerobic and aerobic biodegradation may be possible (EPA, 2008). Fundamental research by Sharp et al. (2005) has identified the enzymes responsible for NDMA biotransformation. Research conducted at wastewater treatment plants (Sedlak et al., 2005), in landscape irrigation systems (Arienzo et al., 2006), and during filtration at a drinking water treatment plant (Schmidt and Brauch, 2008) have demonstrated that NDMA biotransformation occurs.

Photochemically, NDMA exhibits two absorption bands, with one maximum at 228 nm (molar extinction coefficient ε_{228nm}= 7,378 $M^{-1}cm^{-1}$) and one at 332 nm (ε_{332nm}=109 $M^{-1}cm^{-1}$) for the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions respectively (Stefan and Bolton, 2002). Figure 2 shows the absorption spectra of this photo-sensitive compound. As a consequence, the most common method to treat NDMA in drinking water is photolysis by ultraviolet (UV) radiation in the wavelength range of 225 to 250 nm (EPA, 2008).

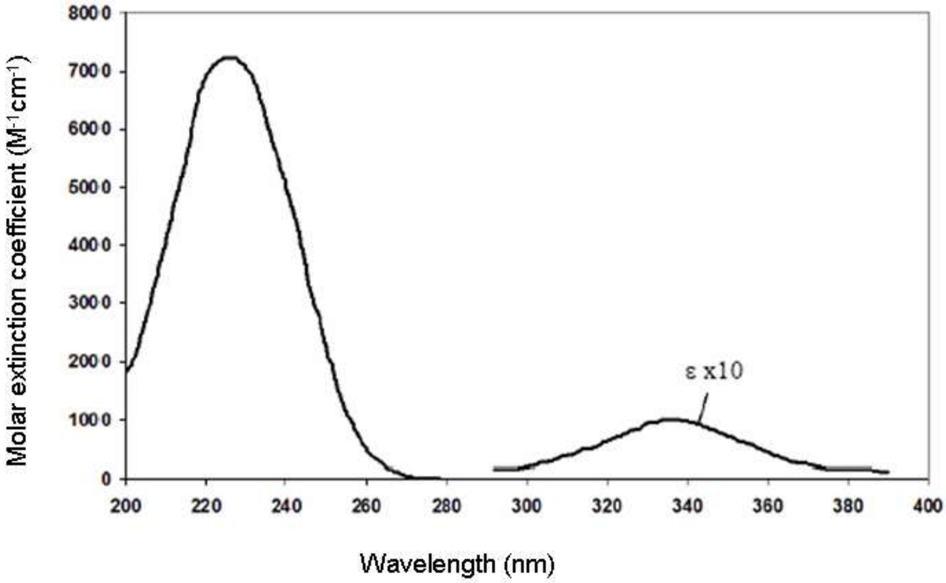


Figure 2. Absorption Spectrum of NDMA (Sacher et al., 2008).

The major nitrosamine absorption band near 230 nm is below the wavelength range present in natural sunlight, but the less intense band at 330-340 nm overlaps with the irradiance spectrum of natural sunlight, and thus, is responsible for the photodecay of nitrosamines in the environment. Plumlee and Reinhard (2007) modelled NDMA photolysis in a non-specific surface water with a depth of one metre and intermediate light screening by the water at midday solar intensity for January to December at three locations representing a range of latitudes. The predicted rates corresponded to half-lives over the year of 8-38 hours (h) in London (51° N latitude), 7-14 h in Irvine (33° N latitude), and 6-7 h in Ecuador (2° S latitude). Experimental results showed that removal of NDMA by sunlight photolysis could be achieved (Mitch et al., 2003b). Nevertheless, it should be mentioned that the characteristics of natural water bodies may vary considerably regarding water depth and UV transparency, which has a substantial influence on the removal by sunlight. For this reason, photolysis in Wivenhoe Dam (barrier 6, water depth 67 m at full capacity), may not be particularly efficient, and is not considered to form part of the NDMA treatment strategy.

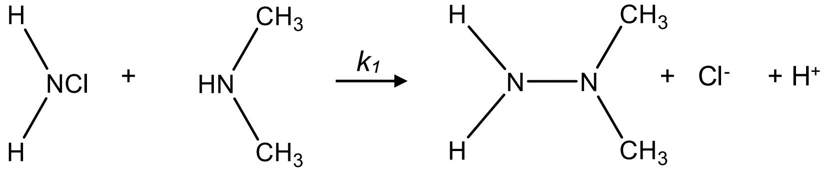
2.2. Review of the Formation of N-Nitrosodimethylamine at Advanced Water Treatment Plants

The chemistry of nitrosamine formation has frequently been described as extremely complex. Although a great deal of research has been done, the formation mechanisms are not completely described. Hence, additional research to fill these knowledge gaps has been identified recently (Sacher et al., 2008). The complexity is mainly related to: (a) the possibility that many reactions occur simultaneously; (b) an intimate dependence on the exact reaction conditions, including concentrations of reactants, catalysts and inhibitors; and (c) the relevance of other reactions that can compete for the nitrosation agents.

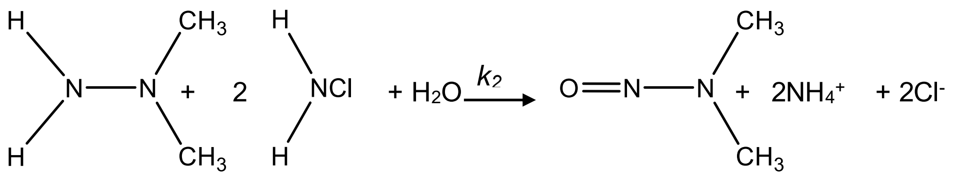
Some principles for NDMA formation have been already established. Two pathways are generally used to describe NDMA formation during disinfection of wastewater with chloramines: (a) the reaction of monochloramine with aliphatic amines to form unsymmetrical dimethylhydrazine (UDMH); and (b) the reaction of dichloramines to form chlorinated UDMH. Subsequently, both molecules are oxidised to NDMA. It is important to note, that when disinfecting wastewater by means of chloramination, monochloramine (NH_2Cl), dichloramine ($NHCl_2$) or trichloramine (NCl_3) can be formed at different proportions with a maximum of two inorganic chloramines coexisting at specific conditions. The proportion of the species present in solution is dependent on the ratio of chlorine to ammonia and on the pH used. At pH levels usually present in drinking waters (i.e. pH = 6-8), the predominant chloramine species are monochloramine and dichloramine. Since the Cl:N ratio employed in water disinfection is below 1, monochloramine can be considered as the main species present in solution (Mitch et al., 2005; Schreiber and Mitch, 2005).

A third mechanism of NDMA formation is based on the nitrosation of nitrogen-containing compounds by nitrosation agents, mainly nitrite (HNO_2) (pathway c) (Mirvish, 1975). Recently, Choi and Valentine (2003) proposed another possible pathway for NDMA formation by nitrosation of DMA involving a reaction of DMA with nitrite that is catalysed by free chlorine. They predicted that the effective nitrosation agent dinitrogen tetroxide (N_2O_4) was formed through oxidation of nitrite by free chlorine at neutral pH (Choi and Valentine, 2003). However, nitrosation agents are normally removed in the biological treatment at WWTP. Moreover, it has been shown already that nitrite formation during chloramination could be ruled out (Diyamandoglu and Selleck, 1992; Diyamandoglu, 1994). Thus, this mechanism should not be particularly relevant for NDMA formation during disinfection of waters with chloramine at the AWTPs. Nevertheless, it has not been excluded from this review in order to better understand the chemistry of NDMA formation, since this is the most traditional and well known mechanism.

The first mechanism concerning the formation of NDMA during chloramination of aliphatic amines to UDMH was studied deeply by Valentine, Sedlak and co-workers (Choi et al., 2002; Choi and Valentine, 2002a, b; Mitch and Sedlak, 2002). This proposed mechanism accounted for the fact that NDMA formation was observed during disinfection with chlorine and chloramines even in the absence of nitrosation agents. A two-step mechanism was proposed, as depicted in Equations 1 and 2.



Equation 1

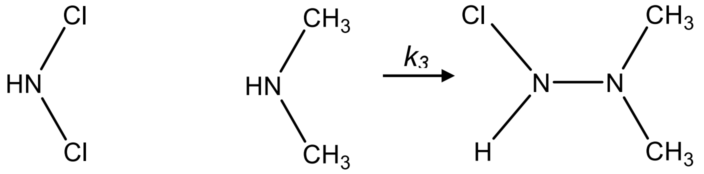


Equation 2

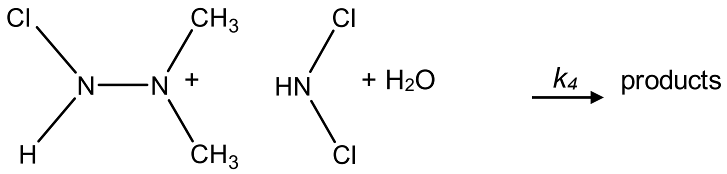
The first step of the mechanism involves a nucleophilic substitution of the chlorine in monochloramine (NH_2Cl) by DMA to form the UDMH intermediate. In the second step, NH_2Cl oxidises the UDMH intermediate to form NDMA. In addition, a side reaction between DMA and monochloramine that produces dimethylchloramine (DMCA) can also occur during the chloramination process. DMCA cannot react to UDMH. This side-reaction may limit the DMA availability for NDMA formation. If chloramine is formed in-situ by addition of hypochlorous acid, or any hypochlorite salt and ammonia, DMA can also combine with hypochlorous acid to form DMCA and, as explained before, reduce the DMA availability for NDMA formation.

Choi and Valentine (2002a) assessed rate constants for these two steps as $k_1 = 6.4\ M^{-1}s^{-1}$ and $k_2 = 0.3\ M^{-1}s^{-1}$ and determined an optimum DMA:monochloramine molar ratio for maximum NDMA formation of approximately one. Nevertheless, these results were criticised by Schreiber and Mitch (2006), who suggested that the model lacked robustness at different Ph values. Yagil and Anbar (1962) and Delalu et al. (1981) had previously reported a rate constant for UDMH formation from NH_2Cl and DMA of $0.081\ M^{-1}s^{-1}$, two orders of magnitude lower than proposed by Choi and Valentine. At AWTPs, the hydraulic retention time of the water in the entire process is several hours. The NDMA reaction formation by the above described mechanism takes place over several days (Mitch et al., 2003a). Thus, a different, faster mechanism for the NDMA formation during disinfection process may be more relevant in this specific context.

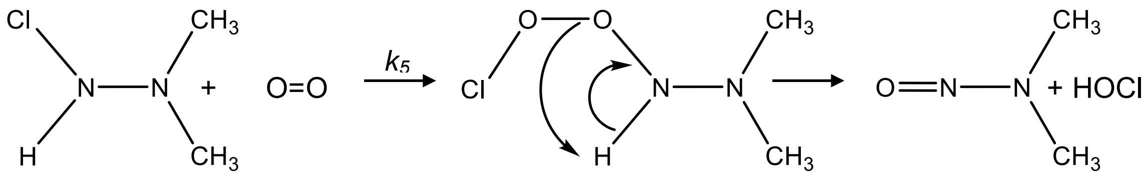
After revision of the first mechanism, Schreiber and Mitch (2006) suggested that the initial step in the pathway involves a nucleophilic substitution reaction of a chlorine atom at dichloramine ($NHCl_2$) by secondary amines to form chlorinated unsymmetrical dialkylhydrazine intermediates (e.g. UDMH-Cl for DMA) rather than UDMGH (see Equations 3-5). In this new mechanism, the non-polar nature of the N-Cl linkage in the structure of chlorinated UDMH enables the incorporation of dissolved oxygen to its subsequent oxidation to NDMA. This oxidation can also be conducted directly by chloramines. Schreiber and Mitch proposed 52, 0.8 and 1.4 $M^{-1}s^{-1}$ values for the rate constants k_3, k_4 and k_5 respectively.



Equation 3



Equation 4

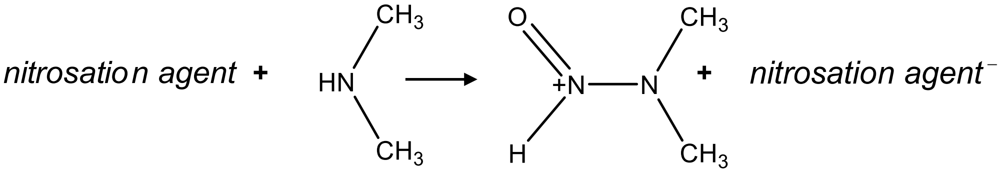


Equation 5

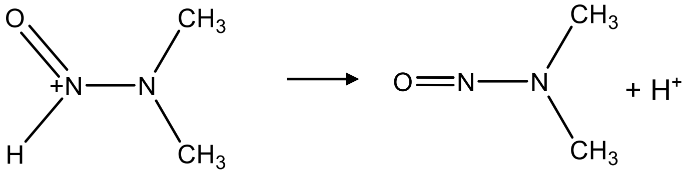
As stated before, monochloramine is the predominant chloramine species under typical chloramination conditions (Cl:N <1). Hence, this model predicts NDMA formation based solely on the low levels of dichloramine formed via disproportionation of monochloramine.

Finally, we describe NDMA formation via the nitrosation mechanism. Although this mechanism is perhaps the best known, it is not relevant for NDMA formation at AWTP because nitrosation agents are normally removed from water prior to the AWTPs during biological treatment in WWTPs. Moreover, it has been proven already that nitrite formation during chloramination can be excluded (Diyamandoglu and Selleck, 1992; Diyamandoglu, 1994).

Equations 6 and 7 show the formation of NDMA by a general nitrosation of DMA.



Equation 6



Equation 7

This reaction is strongly pH dependent. Nitrous acid (HNO_2), for instance, in aqueous acidic solution ($pH < 5$) is known to form nitrosating agents of the type $NO\delta^{+}–Y\delta^{-}$ (indicating complexes of the nitrosonium ion (NO^{+}) with stable anions). However, in neutral or alkaline aqueous solutions, the reaction of DMA with HNO_2 produces insignificant amounts of NDMA, as no nitrosating agents can be formed from the nitrite ion (NO_2^{-}) (pK_a of $HNO_2 = 3.37$) (Patai, 1982). On the other hand, nitrosation can be also enhanced via catalysis by metal salts as Cu, Fe, Zn, (Challis et al., 1978) by nucleophilic anions, such as thiocyanate, halides, formaldehyde, chloral, phenols and fluvic acids (Sacher et al., 2008a).

2.3. Review of the N-Nitrosodimethylamine Precursors at Advanced Water Treatment Plants

In general, the two key precursors involved in the formation of nitrosamines are organic nitrogen compounds and inorganic nitrogen containing species like monochloramine or dichloramines.

Traditionally, dimethylamine (DMA) was the first NDMA precursor considered during water chloramination since direct reaction between this molecule and chloramine produces the carcinogenic compound. Dimethylamine is not only the typical metabolic product of proteins in animals and plants (implying a typical concentration in urine of 40 μg/L) or faeces (0.41 μg/L) (van Rheenan, 1962; Brooks et al., 1972; Tricker et al., 1994) but also is the most frequently used amine among all aliphatic amines produced in the chemical industry. Dimethylamine is involved in the industrial production of N,N-dimethylformamide (70%), N,N-dimethylacetamide, fungicides or herbicides (10%), and as a vulcanisation accelerator in the rubber industry (11%). It is also used as a solvent, flotation chemical, absorber for acidic gases, antioxidant, tanning agent and insect attractant. Finally, this compound also is an important intermediate in the production of other chemical products such as dyes, propellants and pharmaceuticals. Dimethylamine can accumulate as a residual during the production of all these products, but may also be generated in their decomposition. Since DMA can also be formed by demethylation of trimethylamine (TMA), this tertiary amine is also a possible direct NDMA precursor. Trimethylamine is present in plants, fish, and algae (Cromwell and Richardson, 1966; Ayanaba and Alexander, 1974). It is produced during biodegradation of nitrogen-containing organic molecules in plants and mammals and, like DMA, it is also involved in many processes in the chemical industry, either directly applied or as an important intermediate in the production of other chemicals (Sacher et al., 2008).

DMA concentrations in primary wastewater effluents are typically in the range of 20-80 µg/L (Mitch et al., 2003a; Mitch et al., 2003b; Mitch and Sedlak, 2004). Since DMA is degraded by bacteria, levels in secondary wastewater effluents are lower (<10 µg/L), corresponding in general to a 30-95% removal efficiency (Mitch et al., 2003a; Mitch et al., 2003b; Mitch and Sedlak, 2004; Sedlak et al., 2005; Pehlivanoglu-Mantas and Sedlak, 2006b).

The usual test used to quantify the concentration of organic precursors of NDMA that could be formed during disinfection of water with chloramination is the NDMA formation potential (FP) test. This test was first developed by Mitch et al. (2003a) and is based on the measurement of the NDMA formed after the application of a high dose of monochloramine to a pH-buffered sample during a contact time of several days. This test was used to evaluate the NDMA formation potential at the AWTPs in SEQ, and is described further in the text (see experimental section).

Studies based on the NDMA FP have shown that DMA was the precursor of only 0.4-12% of the NDMA formed in WWTP effluents (Gerecke and Sedlak, 2003; Mitch et al., 2003a; Mitch and Sedlak, 2004; Sedlak et al., 2005). The molar conversion rate of DMA to NDMA has been determined as 0.76% (Sacher et al., 2008a). Consequently, DMA is not the only precursor for NDMA formation, and may only be a minor component.

It has been reported that application of the NDMA FP test to synthetic waters containing dimethylethanolamine and dimethylaminobenzene also resulted in appreciable NDMA concentrations, while amines without having two methyl substituents, such as methylamine, methylethylamine, diethylamine and triethylamine did not form significant amounts of NDMA (Mitch and Sedlak, 2004). In this study, the authors suggested an NDMA formation mechanism from tertiary amines having two methyl substituents. The initial step of this mechanism is the dealkylation of the tertiary amine during chloramination, resulting in the formation of dimethylamine, which then is transformed to NDMA as previously explained. According to the authors, an iminium ion ($R_2C=(NR_2)^+$) is formed as an intermediate of the dealkylation step.

Recently, a study concerning different NDMA precursors has been published (Sacher et al., 2008). This work shows that NDMA formation is substantially enhanced or decreased for some tertiary amines depending upon certain structural characteristics. These are: (a) NDMA formation is typically slow for a structure with the dimethylamine group next to a carbonyl or a sulfonyl group; while (b) very high NDMA conversion rates have been observed for structures with the dimethyl group being coupled over a methylene group in α-position to an electron-rich, heterocyclic, 5-membered ring system (e.g. furan or thiophen (see Figure 3)).

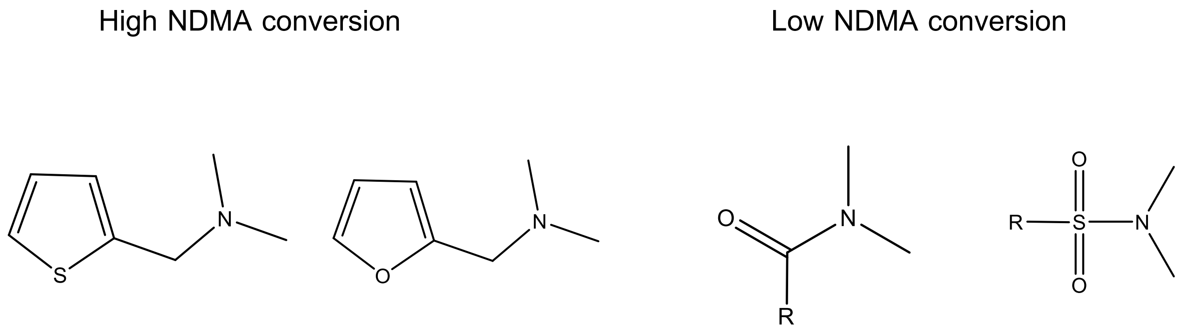


Figure 3. Structural Characteristics of Tertiary Dimethylamines Facilitating or Blocking NDMA Formation during Chloramination (Sacher et al., 2008).

Among the evaluated substances, ranitidine (see Figure 4), a pharmaceutical often used to treat gastritis, showed the highest conversion efficiency in that report. This finding confirmed the previous observations of Mitch et al. (2003a).

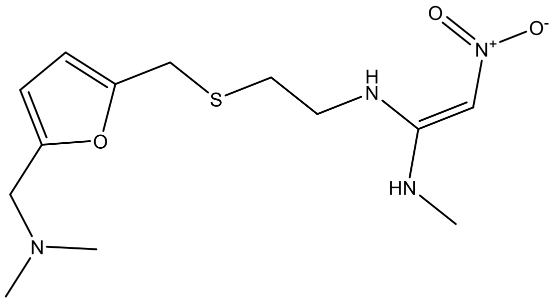


Figure 4. Ranitidine Structure.

Although the ranitidine concentration in the raw water entering Bundamba AWTP was always below the method detection limit (0.02 µg/L), this is a clear example of how NDMA formation during chloramination can be attributed and predicted on the basis of structural similarities. Nevertheless, the complete identity of the major precursors is still unknown (Sacher et al., 2008). It seems clear that mesomeric and inductive effects of potential precursors, as well as stability of final products, are playing an important role in the explanation of the NDMA conversion efficiency. Also the formation of an iminium ion as an intermediate of the dealkylation step seems to be related to the NDMA formation.

In addition to anthropogenic compounds, natural organic matter has been demonstrated to be another typical source of NDMA (Westerhoff and Mash, 2002; Chen and Valentine, 2006, 2007, 2008). WWTPs remove 90% of dissolved organic nitrogen (DON) prior to entering the AWTP. The typical concentration of DON remaining after treatment at WWTPs is in the range from 1 to 5 mg N/L (Pehlivanoglu-Mantas and Sedlak, 2006b). The remaining 10% DON that enters the AWTP consists of either difficult-to-remove DON species, or DON produced during biological treatment. At this point, an important analytical limitation must be considered since approximately 70% of the compounds related to DON are difficult to identify. Thus, the NDMA FP is difficult to predict. In order to resolve such a difficulty related to the unidentified fraction of DON entering the AWTP, a method for the characterisation of molecular weight distribution and fractionation of DON using solid phase extraction (SPE) has been recently published (Pehlivanoglu-Mantas and Sedlak, 2008). This analytical strategy may provide useful information to identify wastewater derived DON that could act as NDMA precursors during the reuse of wastewater as potable water after chloramination.

Apart from precursor compounds such as DMA, tertiary amines or other DON, polyelectrolytes and ion-exchange resins used as coagulants have also been related to the NDMA formation in several water treatments plants (Kohut and Andrews, 2003; Wilczak et al., 2003).

Also, studies conducted by the Orange County Sanitation District demonstrated the presence of NDMA in raw sewage in residential and industrial areas. Spikes in influent wastewater NDMA concentrations were attributed to batch discharges form industrial plating operations, circuit board manufacturing, carpet dyeing and use of herbicides such as metam sodium (dimethyldithiocarbamates) in sewers for root control (OCSD, 2002). Studies at Los Angeles County Sanitation District also demonstrated high concentration of NDMA in used antifreeze and drum recycler discharge (Carr et al., 2003).

2.4. N-Nitrosodimethylamine Removal in South East Queensland Advanced Water Treatment Plants

Reverse Osmosis (RO) acting as a physical barrier used in the AWTPs in SEQ does not effectively retain NDMA (Plumlee et al., 2008). Data from Bundamba 1A AWTP showed that the NDMA concentration before RO could be above 200 ng/L with less than 10% removal in the RO filtration step.

Many factors influence the rejection of contaminants in RO filtration, including charge, size, hydrophobicity, hydrogen bonding capacity and dipole moment of the molecule (Bellona et al., 2004). Steinle-Darling et al. (2007) studied the impacts of membrane type, coating, fouling and chemical properties of seven nitrosoalklyamines, including NDMA, by three different RO composite polyamide membranes under varying conditions. They found that nitrosamine infiltration was rapid and rejection attained a constant value almost instantaneously, indicating that this class of contaminant was not adsorbed by the membrane matrix. Moreover, when assessing the relative rejection of the seven nitrosamines they found that this was a function of size and not hydrophobicity, a tendency which had been also previously reported for non-absorbing trace organics (Ng and Elimelech, 2004). They also found that ionic strength and pH had some influence on the rejection of nitrosamines. Furthermore, additional material on the membrane surface, such as coatings and/or foulant accumulation could increase or decrease the rejection of nitrosamines. Therefore, since the nitrosamines, in particular NDMA, are rejected to different degrees by different membrane types, the optimum solution is not universal and these effects should be investigated more thoroughly on a case-by-case basis.

Each of the AWTPs in SEQ operates using different RO membranes. These differences also affect plant operation, particularly chloramination, since different manufacturers limit the chloramine doses to different ranges for the membrane warranty. At Bundamba and Gibson Island AWTPs, the levels of monochloramine are between 2-4 mg/L as specified by the membrane providers (KMS and Hydranautics respectively), while at Luggage Point AWTP, the maximum limit of operation to maintain the membrane manufacturer warranty (Toray) is 1-2 mg/L of chloramine. Effective management of NDMA therefore requires a case-by-case study.

2.4.1. Direct Removal of N-nitrosodimethylamine

Since NDMA is not well retained by the RO composite polyamide membranes, UV/H_2O_2 Advanced Oxidation Process (AOP) is the current standard procedure used to remove residual NDMA from recycled water at SEQ AWTPs to avoid further reformation.

AOPs are chemical oxidation techniques able to produce in situ reactive free radicals, as such the hydroxyl radical (HO), by means of different reacting systems. The concept was originally established by Glaze et al. (1987) as “oxidation processes which generate hydroxyl radical in sufficient quantity to affect water treatment”. The hydroxyl radical is a non-selective oxidant that is able to oxidise a wide range of organic molecules with rate constants usually in the order of 10^6-10^9 $M^{-1}\cdot s^{-1}$ (Haag and Yao, 1992; Buxton et al., 1998).

Specifically, the rate constant for the reaction of NDMA with HO·was reported to be $(4.30 \pm 0.12) \times 10^8$ M^{-1} s^{-1} (Mezyk et al., 2004). The mechanism of NDMA destruction upon irradiation with UV_{254nm} is dependent on the ratio of NDMA and H_2O_2 concentrations (Ho et al., 1996). They found that most UV radiation was absorbed by NDMA and the main reaction pathway was via direct photolysis of NDMA when the H_2O_2/NDMA ratio is below 10. However, if the ratio increased above 100, the UV was mainly absorbed by H_2O_2, forming HO and·leading to NDMA degradation.

The main disadvantage of AOPs is that their energy consumption is high. The electrical energy per order (EEO) of a particular design is defined as the number of kilowatt hours of electrical energy required to reduce the concentration of a pollutant by 1 order of magnitude in a unit volume of contaminated water. EEO reported in different UV systems at AWTPs in USA ranges from 0.3 to 1.28 kWh/order/1,000gal (Loveland, 2002). This figure-of-merit is independent of the initial contaminant concentration under the assumption that the degradation kinetics follows first or pseudo-first order with respect to the contaminant concentration. The AOP step at the Bundamba 1A AWTP was initially designed to accomplish 1.0-log removal of NDMA, based on an expected influent concentration to the UV/H_2O_2 reactor of 50 ng/L NDMA (i.e. the concentration of the RO permeate). Nevertheless, the measured concentrations before the AOP are almost four times higher than previously assumed. Before the start of this project, the Bundamba 1A AWTP achieved final effluent concentrations lower than 10 ng/L of NDMA after the UV treatment (most data is lower than 5 ng/L, but some analyses are around 6-7 ng/L). This reduction in concentration is possible because of the safety factor built into the design of the reactor (Poussade et al., 2009 personal communication).

Other technologies that may be available to remove NDMA are ozone oxidation, and adsorption onto activated carbon, among others. Nevertheless, the study of alternative NDMA removal techniques has not been included in this review since the main objective of SEQ Water Strategy is to avoid NDMA formation and the NDMA control method is via UV/H_2O_2.

2.4.2. Indirect Removal of N-nitrosodimethylamine

Direct removal of NDMA by UV/H_2O_2 treatment is a technology with high energy consumption. The irradiance by the light source (also called UV fluence or UV dose) is proportional to the NDMA concentration to be removed. Thus, the minimisation of this contaminant could be recommended also from an environmental impact and operational cost savings point of view. Nevertheless, the quality of PRW is the main aim in this discussion. In that sense, it is not considered satisfactory to rely on a single barrier in the AWTP for the direct removal of NDMA within the general approach of the seven-barriers process proclaimed by the SEQ water strategy.

As previously stated, the formation of NDMA can be reduced indirectly by means of NDMA minimisation strategies developed based on a better understanding of the mechanisms of NDMA formation, or by simply removing NDMA precursors. From previous literature, some strategies for the reduction of NDMA formation can be summarised as follows.

When disinfecting wastewater by means of chloramination, the relative proportion of monochloramine (NH_2Cl), dichloramine ($NHCl_2$) or trichloramine (NCl_3) depends upon both the ratio of chlorine to ammonia, and pH (with a maximum of two inorganic chloramines coexisting at any specific set of conditions). Moreover, the concentration of dichloramine relative to a monochloramine solution decreases with increasing pH, becoming negligible at pH 8.0 (Schreiber and Mitch, 2005). Dichloramine reacts much faster than monochloramine with organic matter to form NDMA (Mitch et al., 2005; Schreiber and Mitch, 2005). Once formed, dichloramine is relatively stable. Thus, one way to reduce NDMA formation is to avoid dichloramine formation in the disinfection step. Dichloramine formation is favoured when the Cl:N ratio is above 1. Although free chlorine is never added at higher ratios, this proportion can be achieved locally during the addition of hypochlorite to an ammonia solution before complete mixing is achieved. Hence, the first strategy to minimise NDMA formation is the addition of preformed chloramine (prepared separately at high pH), or addition of free chlorine prior to ammonia to avoid Cl:N ratios higher than 1.

It has been observed that the reaction of chlorinated NDMA precursors with chloramines does not result in any significant production of NDMA. Thus, another strategy to minimise NDMA formation is the chlorination of organic matter prior to chloramine addition (Mitch and Sedlak, 2002; Mitch et al., 2005; Schreiber and Mitch, 2005). Nevertheless, in those cases, the formation of free chlorine disinfection by-products of toxicological relevance cannot be omitted, as well as the possibility of RO membrane damage. Further, a chlorinated UDMH pathway is possible at the AWTPs. This mechanism was based on the formation of NDMA by the direct dissolved oxygen incorporation in the chlorinated UDMH intermediate. Hence, limiting the NDMA formation via the chlorinated pathway requires a concomitant reduction in the concentration of dissolved oxygen (Schreiber and Mitch, 2006).

One interesting finding of the work presented in this report is that the NDMA can be reduced if the contact time between the chloramines and the wastewater is minimised. This contact time minimisation decreases the conversion of monochloramine to dichloramine, which is the main species related to the NDMA formation.

Apart from that, another strategy to minimise NDMA formation at AWTPs is the removal of precursor compounds prior to chlorination. Techniques reported in the literature are related to coagulation, flocculation and sedimentation, oxidation or adsorption.

From previous research, it has been concluded that coagulation, flocculation and sedimentation could not be regarded as efficient treatment options since precursor compounds for nitrosamine formation could not be significantly removed by these processes (Randtke and McCarty, 1979; Pietsch et al., 2001; Sacher et al., 2008). Ferric chloride is the coagulant used at the AWTP. Iron can act as catalyst for the NDMA formation when considering nitrosation of nitrogen containing compounds. Even though the mechanism during chloramination is different from the nitrosation pathway, it has been previously reported that metal ions might enhance the oxidation of UDMH to NDMA (Choudhary and Hansen, 1998; Sacher et al., 2008). Thus, the residual iron after the coagulation step at the AWTP could be a potential catalyst for NDMA formation and must be assessed. This hypothesis was studied in this project and the catalytic effect was not observed.

Studies based on the adsorption of NDMA precursors onto activated carbon (AC) have produced mixed results, with low removal efficiency of small aliphatic amine precursors (Hwang et al., 1994), but higher removal efficiencies for other precursor compounds (Sacher et al., 2008). Sacher et al. (2008) concluded that adsorption onto activated carbon might be an option just for a partial removal of precursor compounds for NDMA formation during disinfection. This is mainly due to the hydrophilic/hydrophobic nature of different NDMA precursor compounds that can be present in water sources (Pehlivanoglu-Mantas and Sedlak, 2008).

Whilst oxidation is a possibility, general conclusions cannot be drawn due to the contradictory data presently available in the literature. This is due to the wide variation in nature of NDMA precursors. Recently, results reported by Sacher et al. (2008) showed that oxidation of NDMA precursors at laboratory as well as full-scale tests with ozone (O_3) and chlorine dioxide (ClO_2) significantly reduced NDMA FP. Nevertheless, Zhao et al. (2008) studied the formation of nine nitrosamines following different disinfection treatments in water from various locations in North America. They found that ClO_2 could increase NDMA from some precursors as trimethylamine (TMA), 3-(dimethylaminomethyl)indole (DMAI), and 4-dimethylaminoantipyrine (DMAP). These results were consistent with previously reported research (Andrzejewski et al., 2005; Lee et al., 2007). The same conclusions were extracted from ozone oxidation, given results which show that NDMA is produced from the reaction of ozone with DMA, especially at higher pH (Andrzejewski et al., 2008). They also found that O_3 pre-treatment released DMA by partial oxidation from other NDMA precursors including dimethylaminobenzene (DMAB), 3-(dimethylaminomethyl)indole (DMAI), and 4-dimethylaminoantipyrine (DMAP) and thus increasing NDMA formation potential (Andrzejewski et al., 2005; Lee et al., 2007). In general, they conclude that the effectiveness of different oxidants to remove nitrosamines may require optimisation according to source water quality, since the nature of precursors in source waters is usually not known. This conclusion can be extrapolated to all the above described processes.

3. MATERIALS AND METHODS

3.1. Chemicals

All chemicals used for chemical analysis were of analytical grade and commercially purchased. NDMA and other nitrosamines had a purity of >99.9% and were obtained from Supelco. Deuterated d_6-NDMA and d_{14}-NDPA (N-nitrosodipropylamine) were used as surrogate and internal standard, respectively (>98.9%, Accustandard and Ultra Scientific, respectively). For the NDMA FP test, ammonium chloride (TraceSELECT®, $\geq$ 99.9% purity), sodium hydroxide (SigmaUltra, $\geq$ 98%, pellets) and sodium hypochlorite solution (reagent grade, available chlorine $\geq$ 4%) were used. Potassium dihydrogenphosphate (KH_2PO_4, Fluka, puriss. p.a., $\geq$ 99.5%) and disodium hydrogenphosophate ($Na_2HPO_4 \cdot 2H_2O$, Fluka, puriss. p.a., $\geq$ 99.5%) were used to prepare pH buffer solutions. To quench the chloramine solution, sodium sulphite (Fluka, puriss. p.a., $\geq$ 98.0%) was employed. Commercial DPD test kits (Hach) were used for the analysis of free and total chlorine (DPD Total and Free Chlorine Reagent, Test 'N Tube Vials 2105545 and 2105645). To standardise the chlorine solution, sodium thiosulphate (SigmaUltra, $\geq$ 99.5%), potassium dichromate (SigmaUltra, $\geq$ 99.5%), acetic acid (ReagentPlus®, $\geq$ 99%), soluble starch (ACS reagent) and potassium iodide (ReagentPlus®, 99%) were used. For solid phase extraction (SPE), we used EPA commercial charcoal optimised for NDMA analysis (Restek). HPLC-grade dichloromethane, methanol and water were used for conditioning and cleaning the solid phase extraction (SPE) cartridges. Anhydrous sodium sulphate, granular 10-60 mesh from Mallinckrodt, was used to remove water from the extracts. Finally, 99% decane (Sigma-Aldrich) was used as keeper in the last concentration steep.

3.2. Site Description and Sample Collection

Water samples were obtained from different WWTP effluents located in SEQ. The WWTPs were operated by two local governments, Brisbane City Council and Ipswich City Council. The details of the WWTPs where the samples were collected are summarised below. All samples were collected from the secondary effluent (without disinfection), since this is the source water for the AWTPs. All of them, except Fairfield STP, include biological nutrient removal and achieve typical total nitrogen levels of 5 mg/L or lower. Phosphorus removal varies between the plants, with total phosphorus averaging around 3 mg/L. Salinity (TDS) is generally of the order of 500 mg/L, but is significantly higher at Luggage Point (typically more than 1,000 mg/L and up to 2,000 mg/L) because of tidal ingress that is apparent within the catchment. The WWTPs generally deliver water of high secondary standards (Traves et al., 2008). Fairfield STP was included in the study to assess the effect of the tertiary treatment concerning the NDMA FP. 24-hour composite samples were taken to assess NDMA and total NDMA precursors (measured by means of the NDMA FP test) seasonally between December 2008 and December 2009. All samples were taken in amber glass bottles, packed on ice and shipped to The University of Queensland. 2.5 mg/L of sodium thiosulfate was added to samples for NDMA analysis immediately after sampling (Sacher et al., 2008a). Those samples were extracted the same day at the AWMC laboratory and extracts, kept at 4 °C, were analysed at Queensland Health Forensic and Scientific Services (QHFSS) within 3-4 days. The NDMA FP test was initiated on the day of sampling.

To evaluate the fate of NDMA and NDMA precursors during the production of purified recycled water at the AWTPs, different grab samples were taken across the treatment train in both Bundamba 1A AWTP and Luggage Point AWTP. Bundamba 1A AWTP reclaims effluent from Bundamba WWTP, Goodna WWTP, Wacol WWTP and Oxley WWTP. Luggage Point AWTP treats water from Luggage Point WWTP. The treatment capacity at both plants is 66 ML/day. Advanced treatment at both AWTPs includes the following common steps: coagulation with ferric chloride; disinfection by chloramination; Micro-Filtration/Ultra-Filtration (MF/UF); Reverse Osmosis (RO); and an ultraviolet-hydrogen peroxide Advanced Oxidation (UV-AOP, Trojan Technologies UVPhox). Differences between both plants are mainly related to the monochloramine addition but also to the different RO membranes used. Bundamba 1A AWTP generates the monochloramine in-line by adding sodium hypochlorite to the wastewater containing ammonia; while at Luggage Point the monochloramine is preformed prior to injection in the treated water. Table 2 shows the different membranes used in both plants. Also, Bundamba 1A AWTP uses UF after pre-treatment, while Luggage Point AWTP applies MF. Finally, Luggage Point AWTP occasionally employs a polyacrylamide polymer to assist in the pre-treatment. Another important difference between both plants is the holding tanks' capacities across both plants, directly affecting the contact time between the water and the chemicals added during the treatment. This important difference is discussed further in the text.

Gibson Island, the third AWTP forming the Western Corridor Recycled Water Project, was not monitored since it was still undergoing commissioning work at the time of the experimental campaign of this study.

Table 2. Specifications of the Membranes Used at the AWTPs.

	MF/UF Membrane	RO Membrane
Bundamba 1A AWTP	Siemens CP PVDF Nominal pore size: 0.04 μm	KMS 18"TFC MegaMagnum HR 3 stages: 85% recovery.
Luggage Point AWTP	Pall Microza PVDF Nominal pore size: 0.1 μm	Toray TML 20-400 3 stages: 85% recovery.

3.2.1. Bundamba Wastewater Centre

The Bundamba Wastewater Centre is a 23 ML/d- BNR plant, currently servicing approximately 75,000 people and industries around Ipswich. The outline if the process is given in Table 3 (Gardner et al., 2008).

Table 3. Characteristics of the Bundamba Wastewater Centre.

Process Stage	Description
Primary treatment	Screening and aerated grit channel
Secondary Treatment (inc. nutrient removal)	Secondary treatment is by carousel-type extended aeration oxidation ditch, with mechanical surface aerators. The bioreactor is followed by secondary sedimentation tanks
Tertiary treatment	Currently, disinfection is by gas chlorination
Effluent quality (nutrients)	Total Nitrogen < 3.6 mg/L Total Phosphorus < 1.1 mg/L

3.2.2. Oxley Creek Wastewater Treatment Plant

The Oxley Creek WWTP is a full nitrogen and phosphorus removal plant that was newly upgraded in 2006 to a 65 ML/d BNR plant servicing 260,000 people and industries in Brisbane's southern suburbs. The source breakdown is 80% domestic and 20% industrial. The outline of the process is given in Table 4 (Gardner et al., 2008).

Table 4. Characteristics of the Oxley Creek WWTP.

Process Stage	Description
Primary treatment	Screening and grit removal
Secondary Treatment (inc. nutrient removal)	Secondary treatment is by an oxidation ditch configuration for N removal and some biological P removal. Additional phosphorus removal is achieved with alum precipitation. The bioreactor is followed by secondary sedimentation tanks.
Tertiary treatment	Disinfection by ultraviolet light
Effluent quality (nutrients)	Total Nitrogen < 5 mg/L Total Phosphorus < 3 mg/L

3.2.3. Gibson Island Wastewater Treatment Plant

The Gibson Island WWTP is a full nitrogen and phosphorus removal plant of 46 ML/d, servicing 200,000 people and industries in east Brisbane. The outline if the process is given in Table 5 (Gardner et al., 2008).

Table 5. Characteristics of Gibson Island WWTP.

Process Stage	Description
Primary treatment	Screening and aerated grit channel
Secondary Treatment (inc. nutrient removal)	A small anaerobic mixing zone is followed by a carousel-type oxidation ditch, with anoxic and aerobic zones. Some EBPR occurs in the anaerobic zone, but there is no additional chemical precipitation of phosphorus. The oxidation ditch is followed by secondary sedimentation tanks.
Tertiary treatment	N/A
Effluent quality (nutrients)	Total Nitrogen < 2.5 mg/L Total Phosphorus < 3.8 mg/L

3.2.4. Luggage Point Wastewater Treatment Plant

The Luggage Point WWTP is a 132 ML/d BNR plant, servicing 572,000 people and industries from northern and western Brisbane. The outline if the process is given in Table 6 (Gardner et al., 2008).

Table 6. Characteristics of Luggage Point WWTP.

Process Stage	Description
Primary treatment	Screening, aerated grit channel and primary sedimentation
Secondary Treatment (inc. nutrient removal)	Currently, the 5-stages Bardenpho configuration has a total anaerobic fraction of 3.5-7.5%, total anoxic fraction of 30-41.5% and total aerobic fraction of 55-62.5%. There is limited EBPR in the anaerobic zone and no chemically-assisted P precipitation. The bioreactors are followed by secondary sedimentation tanks.
Tertiary treatment	N/A
Effluent quality (nutrients)	Total Nitrogen < 6.2 mg/L Total Phosphorus < 6.5 mg/L

3.2.5. Goodna Wastewater Treatment Plant

The Goodna WWTP is a full nitrogen removal plant with no major phosphorus removal and mainly a domestic catchment. It is a 22 ML/d plant that serves 40,000 people and industries in the western suburbs of Brisbane and Ipswich. The outline if the process is given in Table 7 (Gardner et al., 2008).

Table 7. Characteristics of Goodna WWTP.

Process Stage	Description
Primary treatment	Screening and grit removal
Secondary Treatment (inc. nutrient removal)	Biological nutrient removal by the Modified Ludzack-Ettinger process, followed by secondary sedimentation tanks
Tertiary treatment	Disinfection by chlorine gas
Effluent quality (nutrients)	Total Nitrogen < 5 mg/L Total Phosphorus < 6.7 mg/L

3.2.6. Wacol Wastewater Treatment Plant

The Wacol WWTP is a 5.6 ML/d BNR plant, servicing 33,600 people. The outline if the process is given in Table 8 (Gardner et al., 2008).

Table 8. Characteristics of Wacol WWTP.

Process Stage	Description
Primary treatment	Screenings and Grit Removal
Secondary Treatment (inc. nutrient removal)	Activated Sludge
Tertiary treatment	UV disinfection
Effluent quality (nutrients)	Total nitrogen <2.2 mg/L
	Total phosphorus <3.3 mg/L

3.2.7. Fairfield Sewage Treatment Plant

The Fairfield STP is a 2.7 ML/day plant, servicing 12,000 people. The outline if the process is given in Table 9 (Gardner et al., 2008). Fairfield STP is the only non-BNR plant left in the Brisbane area. This plant was included in the study to evaluate the effect of biological nutrient removal on NDMA precursors.

Table 9. Characteristics of Fairfield STP.

Process Stage	Description
Primary treatment	Screenings and Grit Removal and sedimentation
Secondary Treatment (inc. nutrient removal)	Activated Sludge
Tertiary treatment	Disinfection by liquid sodium hypochlorite solution
Effluent quality (nutrients)	Total nitrogen < 50 mg/L
	Total phosphorus < 4.6 mg/L

3.3. Trace-Level Analysis of N-Nitrosodimethylamine in Water Samples

Samples were mainly analysed at Queensland Health Forensic and Scientific Services (QHFSS). The method used for N-nitrosamines analysis is based on EPA Method 251 (Munch and Bassett, 2004). In that analysis, water is passed through a carbon solid phase extraction (SPE) cartridge and the N-nitrosamines are eluted off with dichloromethane. The extracts are concentrated by evaporation under nitrogen to 1 mL and analysed by capillary gas chromatograph-mass spectrometer (GC-MS) in Positive Chemical Ionisation (PCI) mode with anhydrous ammonia as the chemical ionisation gas (Finnigan Trace G.C. Ultra and Finnigan Trace DSQ Mass Spectrometer with Ammonia Chemical Ionization).

Fifty microlitres of a 0.5 mg/L deuterated NDMA stock solution in methanol solvent was added as a surrogate to each 1 L sample to evaluate the percentage of recovery of the extraction (25 ng/L). For SPE, commercial EPA coconut carbon cartridges for NDMA analysis (Restek) were used. Methanol, dichloromethane (HPLC grade) and MilliQ water were used as solvents. Glass fibre filters were obtained from Whatman. Teflon 1/8” tubing, weights, tubes, tube adaptors, and a 12-port vacuum manifold for performing SPE were purchased from Supelco. The charcoal cartridge was conditioned with 8 mL of dichloromethane, followed by 15 mL of methanol and 25 mL of HPLC water. The cartridge was allowed to dry during dichloromethane and methanol cleaning but not during the last cleaning with HPLC water. The flow rate for sample loading was adjusted to < 10 mL/min. After finishing the loading, cartridges were cleaned with 10 mL of HPLC water and dried under vacuum for 10 minutes.

For elution, 30 mL of dichloromethane was passed first trough the charcoal cartridge and then through a 6 mL tube packed with previously dried sodium sulphate. A final 1 mL was collected for analysis. 50 ng/L of internal standard was added to the final 1 mL. Every batch was accompanied by a standard spiked solution and a blank to determine the performance of the extraction and the possible NDMA contamination in the water.

2 µL samples were splitless injected into the gas chromatograph at 250 °C. The column used was ZB-5MS (30x0.25x1.0). The initial temperature of the oven was 40 °C for 1 min. Then a ramp was programmed at 40 °C/min to 265 °C. Final temperature was held for 5.4 minutes. Helium gas at 1 mL/min was used as carrier. Anhydrous ammonia gas, 99.99% pure, was used in the mass spectrometer to facilitate positive chemical ionization. The reagent gas flow for CI was 3.5 mL/min. The NDMA detection limit for the technique was 5 ng/L.

To reduce the detection limit of NDMA, a high resolution mass spectrometer (HRMS) was used. A GC/HRMS, HP 5890 II GC, coupled with VG AutoSpec, was used in splitless injection mode with an injector temperature of 200 °C. Separation was achieved using a J&W Scientific DB-1701 column (30m × 0.25mm i.d., 0.25mm film thickness) with ultra-high purity helium carrier gas; temperature program of 38 °C for 1 min, 25°C/min to 250 °C and held for five minutes; total run-time 10 minutes. The mass spectrometer operating conditions were: ion source and transfer line temperatures 250 °C; ionisation energy 38 eV; trap current 500 µA; electron multiplier voltage set to produce a gain of 106. Resolution was maintained at 5,000 (10% valley definition) throughout the sample sequence. Selective Ion Recording (SIR) experiments were performed in the electron impact mode monitoring the exact masses of appropriate ions for native compounds. Figure 5 shows the correlation obtained for both analytical methods. The limits of reporting for NDMA with this analytical technique was 1 ng/L.

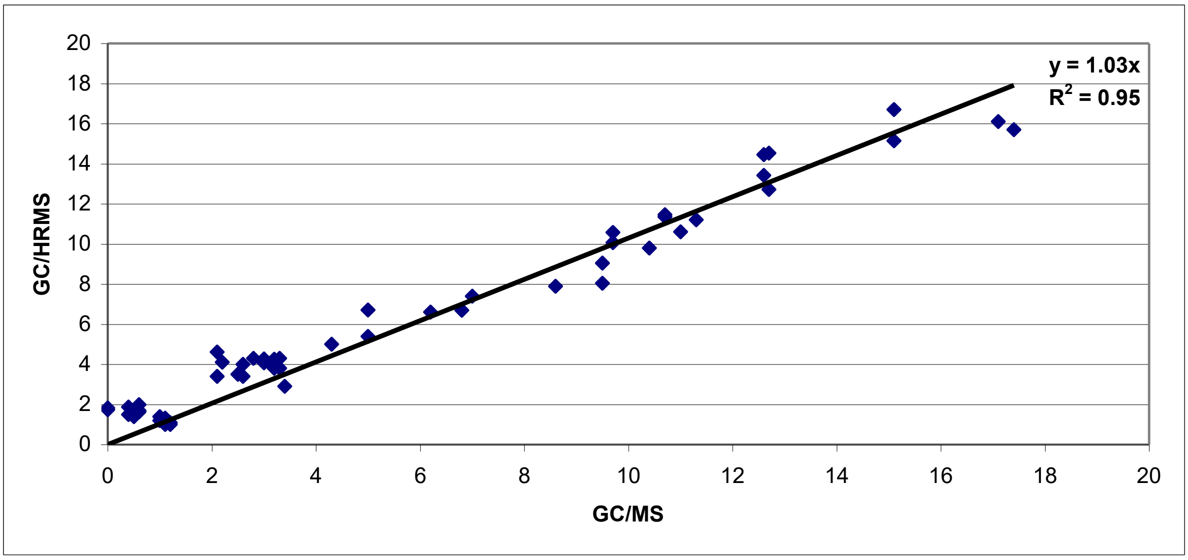


Figure 5. Correlation between the GC/HRMS and GC/MS for NDMA concentration (all data is expressed in ng/L).

3.4. Determination of NDMA Formation Potential

N-nitrosodimethylamine Formation Potential (NDMA FP) test is performed to characterise water samples with regard to their potential to form nitrosamines. To quantify the total concentration of NDMA precursors, water samples are exposed to relatively high concentrations of monochloramine for an extended period. The levels of NDMA formed in this test serve as an indicator of all compounds that can be converted into NDMA during chloramination (i.e. the measured NDMA concentration in the formation tests is an indicator for the NDMA precursor concentration). As a consequence, this test can be used to compare the potential of different waters to form nitrosamines during chloramination (Sacher et al., 2008).

The experimental design of the NDMA FP test followed closely the procedure described as nitrosamine precursor test by Mitch et al (2003a). For the preparation of stock solutions, MilliQ water was used. A 24 mM aqueous ammonium chloride solution was prepared by dissolving 1.3 g in 1 L of MilliQ water and adjusting the pH to 8.0 by addition of small amounts of sodium hydroxide (0.5 M). For the NDMA FP experiments, a chloramine stock solution was prepared by slowly adding a hypochlorite solution to this aqueous stirred ammonium chloride solution to form monochloramine as per Equation 8. The adjustment of the pH to 8 and the slow addition are necessary in order to avoid dichloramine formation.

$$NH_3 + HClO \rightarrow NH_2Cl + H_2O \qquad \text{Equation 8}$$

Prior to the preparation of the chloramine solution, the free chlorine concentration in the hypochlorite stock solution was determined by a N-N-diethyl-p-phenylenediamine (DPD) test kit (Eaton et al., 1989) (DPD Free Chlorine Reagent, Test 'N Tube Vials) from Hach. Based on the free chlorine concentration in the hypochlorite solution, the volume of hypochlorite stock solution was calculated that was necessary to achieve a molar ratio of ammonia to free chlorine of 1.2:1 in the final chloramine stock solution. That is, 20 mM hypochlorite to achieve a 20 mM monochloramine (around 1,400 mg/L free Cl_2) as shown in Equation 9. The respective volume of hypochlorite stock solution was then added to 500 mL of ammonium chloride solution. Before and after each NDMA FP test, the concentration of bound chlorine was determined by the DPD test kit (DPD Total Chlorine Reagent, Test 'N Tube Vials).

$$V_{Cl_2}(mL) = \frac{1400\,ppmCl_2 \times 500\,mL}{measured_{ppmCl_2}} \qquad \text{Equation 9}$$

In this test, 1,400 ppm Cl_2 is 20 mM NaOCl, which is 0.8% of the 24 mM ammonium chloride solution.

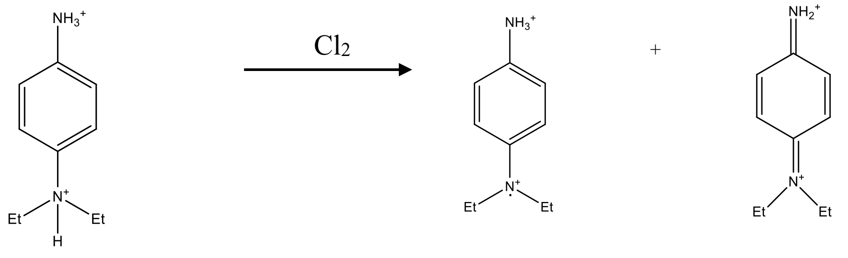
A concentration of 2 mM (140 mg/L Cl_2) was used to determine the NDMA FP of the selected waters. The test was performed at pH 6.8 which was achieved by adding 700 mg/L KH_2PO_4 and 880 mg/L $Na_2HPO_4 \cdot 2H_2O$ to the water sample (10 mM phosphate buffer). To evaluate the NDMA FP test, dimethylamine (DMA) was added to the solution as a known NDMA precursor as described previously in the literature (Gerecke and Sedlak, 2003; Mitch et al., 2003a). All experiments were performed in 2 L amber glass bottles, which were stored at room temperature (23±2 °C) in the dark for seven days. The total chlorine was measured daily. On the seventh day, the residual chloramine concentration was quenched with 2.5 g/L sodium sulphite (added in solid phase to the sample) to prevent further NDMA formation as depicted in Equation 10. Then the samples were analysed for NDMA. Data obtained from this experiments was compared with the results reported in the literature (Gerecke and Sedlak, 2003; Mitch et al., 2003a).

$$NH_2Cl + SO_3^{2-} + H_2O \rightarrow SO_4^{2-} + NH_4^{+} + Cl^{-} \qquad \text{Equation 10}$$

3.5. DPD Method

N-N-diethyl-p-phenylenediamine (DPD) is used as an indicator of the colorimetric procedure to determine free and total chlorine in water (Eaton et al., 1989).

The chemical basis for the DPD chlorine reaction is depicted in Equation 11. The DPD amine is oxidised by chlorine to two oxidations products. At a near neutral pH and in absence of iodide ion, the primary oxidation product is a semi-quinoid, cationic compound known as a Wurster dye. This relatively stable free radical species accounts for the pink colour in the DPD colorimetric test. DPD can be further oxidised to a relatively unstable, colourless imine compound. When DPD reacts with small amounts of chlorine at a near neutral pH, the Wurster dye is the principal oxidation product.



Equation 11

colourless coloured colourless

Subsequent addition of a small amount of iodide acts catalytically to cause monochloramine to produce a pink colour.

The DPD Wurster dye colour has been measured photometrically at wavelengths ranging from 490 to 555 nm. For maximum sensitivity, absorption measurements are recommended at 510 and 515 nm. Monochloramine and dichloramine are slow to react directly with DPD at a near neutral pH. To quantify this species, the test is performed under slightly acidic conditions in the presence of iodide ion. The iodide reacts with the chloramine to form iodine as the triiodide ion as shown in Equations 12 and 13.

$$NH_2Cl + 3I^- + H_2O + H^+ \longrightarrow NH_4OH + Cl^- + I_3^- \qquad \text{Equation 12}$$

$$NHCl_2 + 3I^- + H_2O + 2H^+ \longrightarrow NH_4OH + 2Cl^- + I_3^- \qquad \text{Equation 13}$$

The triiodide, in turn, reacts with DPD, forming the Wurster oxidation product (Harp, 2002).

For the detection of free and bound chlorine a Varian 50 Conc UV-Vis spectrophotometer was used at a wavelength of 530 nm using a 1 cm cuvette. Commercial DPD test kits from Hach were used for the analysis (DPD Total and Free Chlorine Reagent, Test 'N Tube Vials 2105545 and 2105645).

3.6. Other Analytical Methods

Non-purgeable organic carbon (NPOC) was measured at the AWMC using a JENA multi N/C 3100 instrument. For the NPOC analysis, the samples were acidified adding 17 µL of 2 M hydrochloride acid in a 20 mL sample bottle and 99.99% pure oxygen with a flow rate of 200 mL/min was fed into the analyser for the combustion. CeO_2 was used as an oxidation catalyst and 200 µL was added into the samples. Afterwards, the samples were injected into a combustion tube and heated at 850 °C. This was done for 20 sec under constant stirring and the purge flow rate was about 100 mL/min. The standard solutions for calibration purposes were 0.5-100 mg/L potassium hydrogen phthalate. Dissolved organic nitrogen (DON) was calculated to be the difference between Total Kjeldahl Nitrogen (TKN) and NH_4–N nitrogen. TKN was measured using a Lachat QuickChem method 10-107-06-2-D. Ammonium nitrogen was measured on a Lachat flow injection analyser as per the Lachat QuickChem method 31-107-06-1-A. Nitrate and nitrite were also measured on a Lachat flow injection analyser as per the Lachat QuickChem method. Monochloramine (MCA) and dichloramine (DCA) measurement were performed spectrophotometrically solving the two equations below.

$$A_{245} = \varepsilon_{MCA,245}\, C_{MCA}\, d + \varepsilon_{DCA,245}\, C_{DCA}\, d \qquad \text{Equation 14}$$

$$A_{295} = \varepsilon_{MCA,295}\, C_{MCA}\, d + \varepsilon_{DCA,295}\, C_{DCA}\, d \qquad \text{Equation 15}$$

Where $\varepsilon_{MCA,245}$=445 M^{-1} cm^{-1}, $\varepsilon_{DCA,245}$=14 M^{-1} cm^{-1}, $\varepsilon_{MCA,295}$=208 M^{-1} cm^{-1}, $\varepsilon_{DCA,295}$=267 M^{-1} cm^{-1} (Valentine, 1986).

3.7. Size Fractionation

A stirred cell Amicon Model 8200 (Millipore cat. no 5123) apparatus was used. Maximum operating pressure allowed is 5.3 bar (530 kPa) and the relief valve setting pressure is 6.3 bar (630 kPa). Compressed nitrogen was used to supply pressure. Stirred cell fractionations were done using cellulose Ultracel membranes at 63.5 mm diameter. The molecular weight sizes used were 0.5 kDa, 1 kDa, 3 kDa, 5 kDa and 10 kDa (Millipore). Washing was also applied to minimise contamination. Since samples were already fractionated into size ranges, the only correction made was based on mass balancing to correct for up-concentration.

3.8. Preformed and In-line Preparation of Disinfecting Agent and Experimental Set-up

Monochloramine was prepared freshly before every experiment because of its ability to auto-decompose. Prior to the preparation of the chloramine solution, the free chlorine concentration in the hypochlorite stock solution was determined. Based on the free chlorine concentration in the hypochlorite solution, the volume of hypochlorite stock solution to be added was calculated to achieve molar ratio ammonia to free chlorine of 1.2:1 in the final 20 mM monochloramine stock solution (around 1,400 mg/L Cl_2). The respective volume of hypochlorite stock solution was added drop-wise to the ammonium chloride solution. Dichloramine was obtained by lowering the pH of the monochloramine solution with sulphuric acid to pH 3.7 and aging for one hour (Valentine et al., 1986). In–line monochloramine was obtained by adding the specific amount of ammonium chloride and sodium hypochlorite to the mixing reactor. The kinetic experiments were conducted in 10 litre glass reactors protected from light at 25 °C using 10 mM phosphate buffer (pH 6.9) during 24 hours of contact time. Samples were collected after 15 min, 30 min, 1 h, 2 h, 4 h, 6 h, 8 h and 24 h of reaction time and quenched with sodium sulphite to stop NDMA formation. The samples were stored overnight in the fridge and extracted by SPE the following day. For storage, acid pre-washed and acetone rinsed amber bottles baked overnight at 105 °C were used.

4. NDMA FORMATION POTENTIAL TEST IN SOURCE WATERS FOR PURIFIED RECYCLED WATER IN SOUTH EAST QUEENSLAND

The aim of this chapter is to scan the actual situation in SEQ concerning the presence of NDMA precursors in source waters used to produce PRW. For that purpose, three different goals were set:

- Quantify the NDMA precursors present in different wastewater treatment plant effluents that are being used for the production of PRW in SEQ;
- Evaluate the fate of NDMA precursors across the AWTPs in SEQ; and
- Relate NDMA precursors to other parameters commonly measured at the WWTP in order to be able to predict the NDMA FP during the disinfection of secondary effluents to generate PRW.

NDMA FP test was adapted from the literature and those results are also presented in that chapter.

4.1. Adaptation of NDMA Formation Potential Test

As a first attempt to investigate the NDMA FP test, different results of experiments already published in the literature were reproduced. On the one hand, Mitch et al. (2003a) carried out the test to determine the yield of NDMA from the reaction between dimethylamine (DMA) and monochloramine when establishing the NDMA FP test for the first time. They measured the NDMA formed after 11 days of contact time between DMA (73,000 ng/L) and monochloramine (2 mM) in a 2.5 mM phosphate buffered solution. Results showed that the conversion yield of DMA to NDMA was 0.5%, thus obtaining a concentration of 569 ng/L NDMA after the 11 days contact period.

On the other hand, Gerecke et al. (2003) carried out the test to determine the yield of NDMA from the reaction between DMA and monochloramine when reducing the contact time to seven days. To do this, they spiked water with 4,500 ng/L of DMA. The monochloramine dose was 1 mM in a 10 mM phosphate buffered solution for seven days. Results showed that the conversion of DMA to NDMA was 0.6%, thus obtaining a concentration of 44.5 ng/L NDMA after the seven days. Both experiments were reproduced at the AWMC during seven days in a 10 mM phosphate buffered solution at 23 ± 2 °C in duplicates. Samples A and B correspond to the experiment reproducing Gerecke et al. results (Gerecke and Sedlak, 2003), while samples C and D correspond to the experiments reproducing Mitch et al. results (Mitch et al., 2003a). Figure 6 shows the results of daily total chlorine measurements.

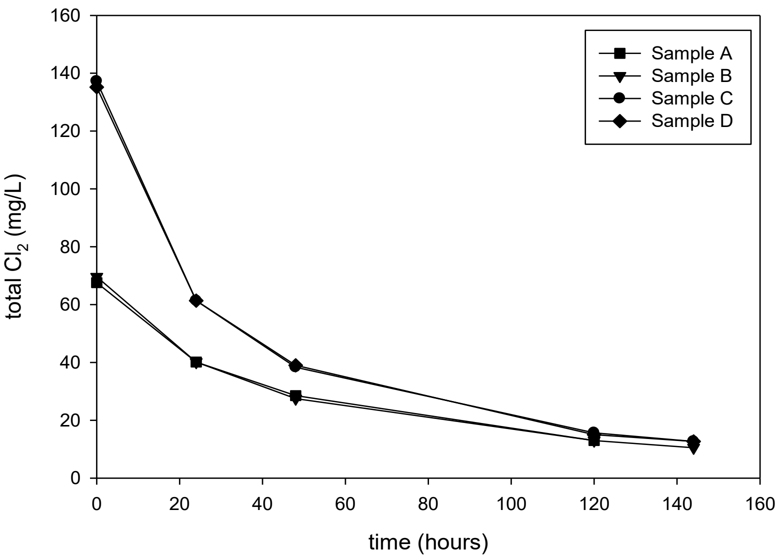


Figure 6. Total Chlorine (mg Cl2/L) Decay during NDMA FP Test.

As seen in Figure 6, the monochloramine concentration decreases rapidly at first from approximately 70 mg/L Cl_2 to 28 mg/L Cl_2 for samples A and B, and from approximately 140 mg/L Cl_2 to 39 mg/L Cl_2 for samples B and C within 48 hours. After 48 hours, the monochloramine decay slowed down. It has been generally reported that monochloramine disappearance is controlled by auto-decomposition rather that by chlorine demand (Jafvert and Valentine, 1992; Vikesland et al., 1998, 2001; Mitch et al., 2003a).

After seven days, residual chlorine was quenched with sodium sulphite and analyses were performed at QHFSS, as described before. Table 10 shows the results obtained.

Table 10. NDMA Results for the NDMA FP Test. *(Mitch et al., 2003a), **(Gerecke and Sedlak, 2003).

Sample	Dimethylamine (ng/L)	Reported % molar yield	NDMA precursor analysis (reported value) ng/L	NDMA precursor analysis (experimental value) ng/L
A, B (n=4, α=0.05)	4,500	0.6*	44.5 ± 1.9	44.0 ± 8.0
C, D (n=4, α=0.05)	73,000	0.5**	569 ± 84	570 ± 110

4.2. NDMA and NDMA Formation Potential Test in Source Water for Recycling

NDMA precursors in source waters for the production of PRW in SEQ were examined by means of the NDMA FP test. This test quantifies the concentration of the organic precursors of NDMA that could be formed during chloramination of water and wastewater. This method was firstly developed by Mitch and co-workers (Mitch et al., 2003a) and has been continuously referenced and used (Pehlivanoglu-Mantas et al., 2006; Schreiber and Mitch, 2006; Mitch and Schreiber, 2008; Sacher et al., 2008). The method involves applying a high dose of monochloramine to a pH-buffered water sample during seven days of contact period to produce NDMA.

Although the test is not thought to predict concentration levels of nitrosamine formed in disinfection systems (Mitch et al., 2003a), the levels of nitrosamine formed in this test can be used to compare the potential of different waters to form nitrosamines during chloramination and to estimate an approximate value of NDMA according to Gerecke and Sedlak's observations (Gerecke and Sedlak, 2003). Results of different sampling days are presented in Figure 7.

Fairfield STP is not a source water for PRW. As explained in the experimental section, Fairfield STP is a WWTP that does not include biological nutrient removal in the treatment train. This plant was included in the study to evaluate the effects of the nutrient removal stage at the WWTP on the NDMA FP. These results will be discussed further.

Concentrations of NDMA in the source waters prior to the formation potential tests were generally lower than the reporting limit (5 ng/L) and never higher than 25 ng/L. No other nitrosamines were measured above the QHFSS limit of reporting (LOR) in this sampling campaign (i.e., *N*-nitrosodiethylamine LOR = 10 ng/L, *N*-nitrosopiperidine LOR = 20 ng/L, *N*-nitrosodibuthylamine LOR = 20 ng/L, *N*-nitrosomorpholine LOR = 10 ng/L). NDMA FP concentrations presented in Figure 7 correspond to the NDMA generated during the formation potential test corrected for initial NDMA concentration when this value was higher than the reporting limit (i.e. 5 ng/L).

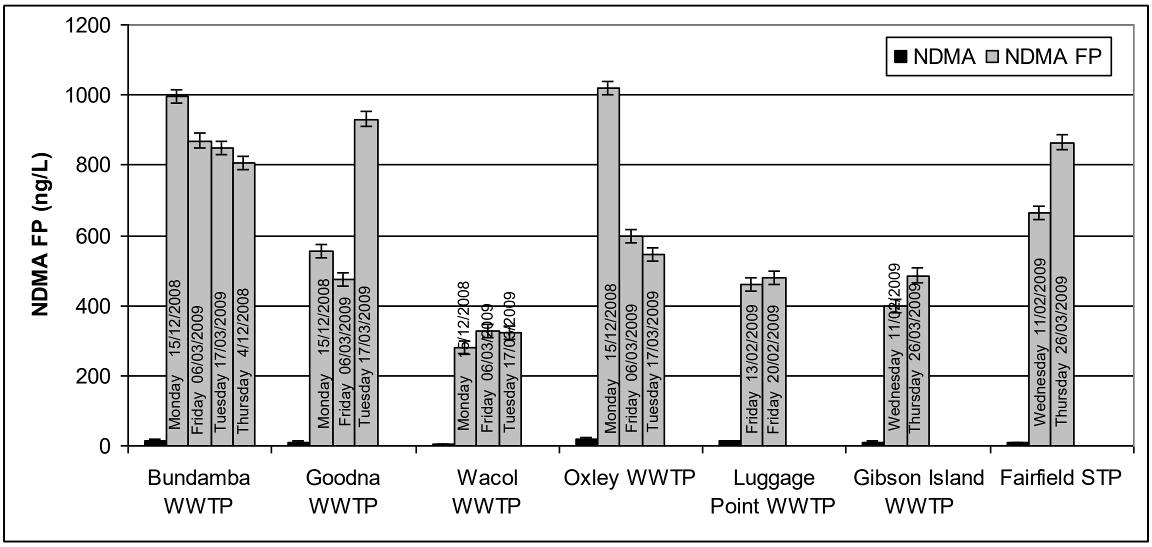


Figure 7. NDMA FP of the different WWTPs providing water to the AWTPs in SEQ, except Fairfield STP, which is not a water source for Purified Recycled Water.

As observed in Figure 7, NDMA FP concentrations in WWTP secondary effluents were between 350 and 1,020 ± 20 ng/L, showing remarkable differences among single WWTPs, probably due the different degrees of industrial contribution in the different plants. Bundamba WWTP was the plant that consistently showed comparably high potential to generate NDMA upon disinfection. This sewer catchment is 85% residential and 15% commercial/industrial and has four major trade waste costumers that are a chicken abattoir, a dairy producer, an aluminium extruder and a beverage manufacturer. No further relation could be established between single industrial waste streams and high levels of NDMA precursors. However, in general, results shown in Figure 7 are in accordance with previous research performed in other countries. Pehlivanoglu and Sedlak reported that NDMA precursor concentrations between 200 and 1,200 ng/L were observed in secondary wastewater effluents (Pehlivanoglu-Mantas and Sedlak, 2006a). In addition, Sedlak and collaborators studied the NDMA FP of different municipal WWTPs in the USA, where the concentration of NDMA precursors in wastewater effluent ranged from 660 to <2,000 ng/L (Wilczak et al., 2003; Sedlak and Kavanaugh, 2005).

Although NDMA FP results of secondary effluents evaluated in this work were not high when comparing them with other published data, Gerecke and Sedlak (2003) showed that an NDMA precursor concentration of approximately 50 ng/L typically results in the formation of more than 10 ng/L of NDMA after chloramination under typical drinking water treatment conditions. Therefore, based on the prediction suggested by Gerecke and Sedlak, the formation of NDMA in the secondary effluents of the above mentioned WWTP could reach values as high as 70 to 200 ng/L after disinfection with chloramines, 10 ng/L being the regulation limit for PRW (QPC, 2005). Indeed, concentrations ranging between 10 and 270 ng/L (150 ng/L on average) could be easily observed at Bundamba 1A AWTP prior to the Advanced Oxidation Process during the optimisation phase of the disinfection strategy (Poussade et al., 2009) while values lower than 10 ng/L were always found at Luggage Point AWTP. In order to better understand the absolute concentration of NDMA precursors, the NDMA FP load of the different WWTP was calculated as well. To achieve this, the concentration was multiplied for the average flow of the WWTP the day of the sampling. NDMA precursor loads are represented in Figure 8.

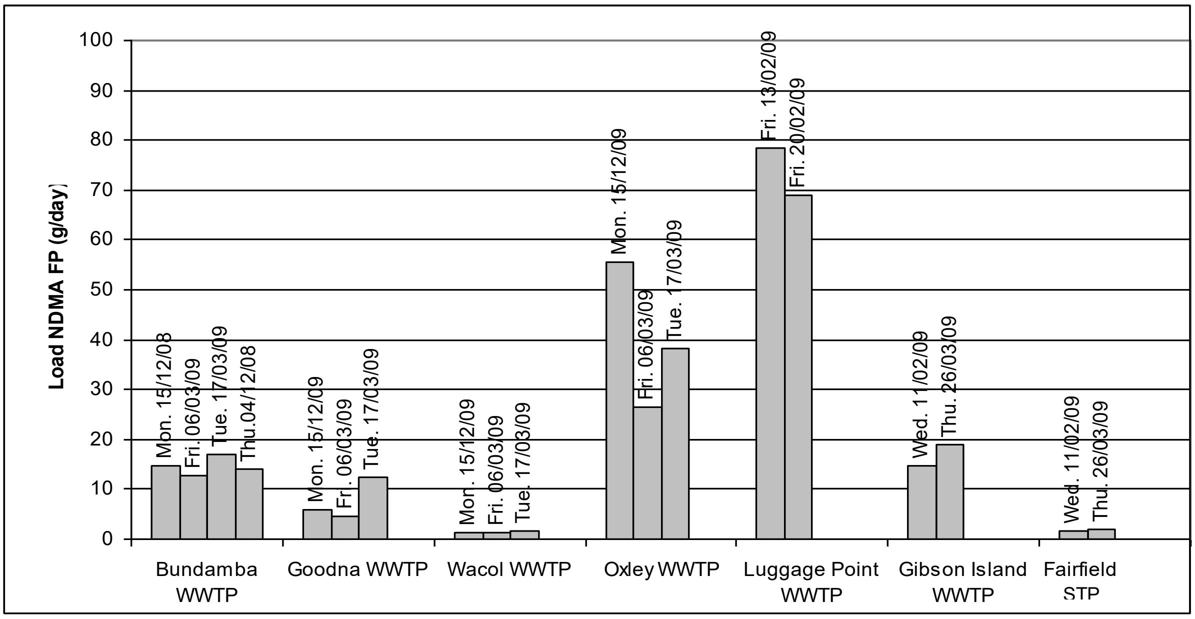


Figure 8. Absolute loads of NDMA precursors during 24 hours for the different WWTP in SEQ. Fairfield STP is not a water source for Purified Recycled Water.

As seen in Figure 8, the maximum loads of NDMA precursor were observed at Luggage Point WWTP. Average flows during the two sampling days were 171 and 144 ML/day. These high flows explain why the NDMA FP concentration measured in those samples was not as high as revealed when assessing the absolute load. Nevertheless, it must be mentioned that Luggage Point is the biggest WWTP with a higher industrial contribution. Thus it is normal to observe this highest value in the absolute load of NDMA precursors. More surprising was the high concentration measured on Monday 15th December 2008 at Oxley WWTP. Average flows at Oxley WWTP were 54.6, 44.3 and 70.3 ML/day on Monday 15th December, Friday 6th March and Tuesday 17th March, respectively. Nevertheless, absolute loads of NDMA precursors were 55.6, 26.4, and 38.3 g, respectively. One hypothesis that explained the high load on the 15th December could be that normally industries clean their processes during the weekend, thus, a high NDMA load after the weekend could indicate that NDMA precursors may have been used as such. In an attempt to understand the relation between the WWTP flow and the absolute load of NDMA FP, Figure 9 represents the average 24 hours sampling flow and the NDMA load measured at each WWTP.

From Figure 9, it is observed that, in general, the NDMA precursor loads in the secondary effluent of the WWTPs studied increase proportionally in relation to the flow. In general, increases in WWTP flows are not related to a higher human activity, thus a constant load of pollutants at the influent of the WWTP should be expected. Nevertheless, this proportional increase of NDMA precursors load observed when increasing the flow at the WWTP indicates that the degradation of the NDMA precursors is related to the activity of the plant. That means that when the flow at the WWTP increases, the hydraulic retention time decreases, thus decreasing the efficient contact time between the microorganisms at the WWTP and the NDMA precursors. This causes a lower efficiency of NDMA precursor removal at the WWTP.

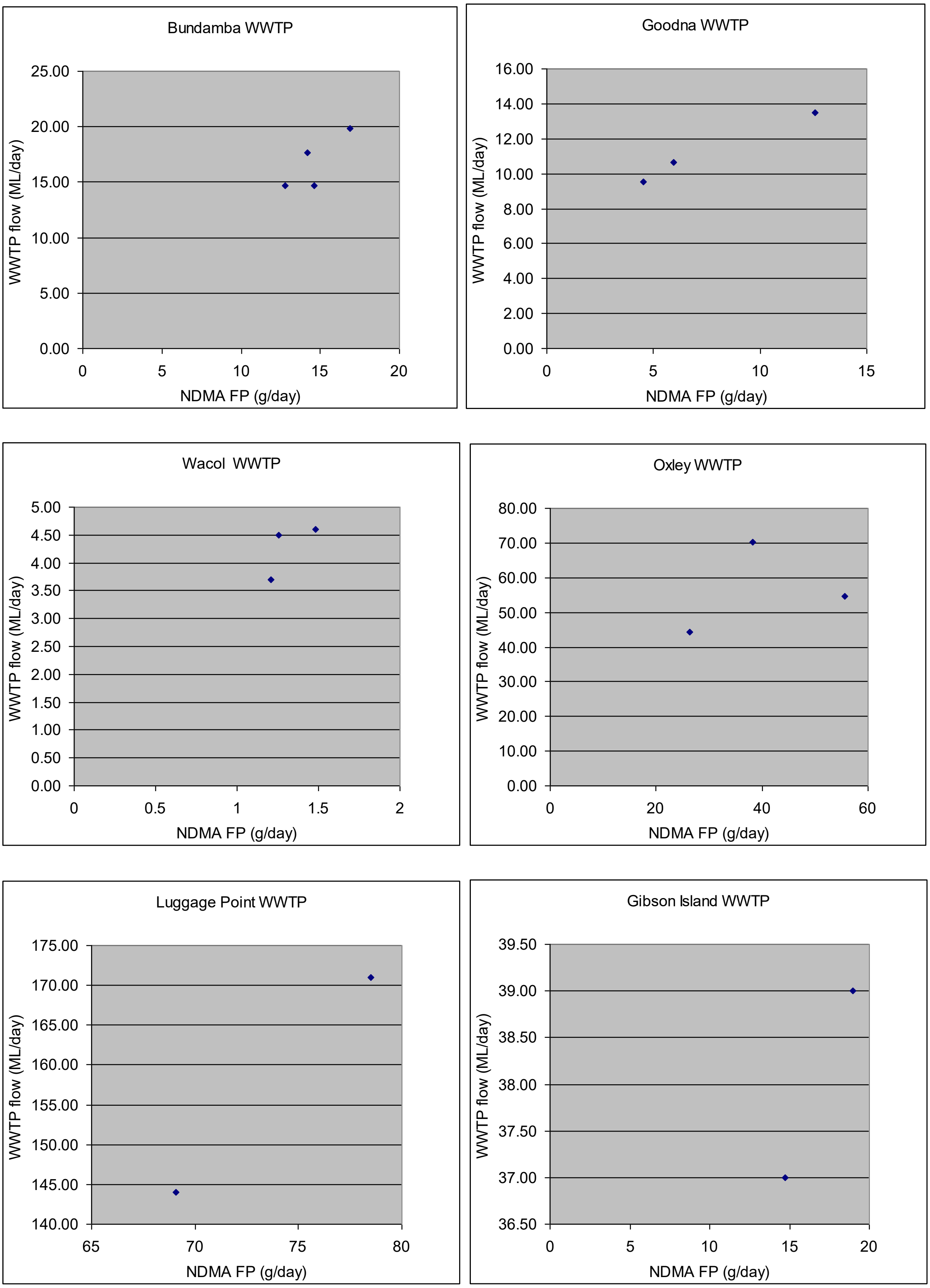


Figure 9. Relation between WWTP flow (ML/day) and NDMA FP load (g/day).

The assessment of different nitrogen species and organic carbon was performed in all water sampled in order to allow a possible prediction of NDMA formation based on simple measurements.

Table 11 shows all the pertinent chemical parameters measured at the different WWTPs. The correlation between these parameters and the NDMA FP is represented in Figure 10.

Table 11. Chemical Parameters Measured at the Secondary Effluent of the Wastewater Treatment Plants during the Different Sampling Days.

	% of Design Flow	NPOC mg/L	NH_4-N mg/L	NO_2-N mg/L	NO_3-N mg/L	DON mg/L
Bundamba (05/12/2008)	77	-	-	-	-	-
Bundamba (15/12/08)	64	15.9	0.08	0.02	3.19	2.01
Bundamba (06/03/09)	64	12.11	0.13	0.16	1.68	1.83
Bundamba (17/03/09)	86	12.38	0.14	0.17	2.44	1.74
Goodna (15/12/08)	49	24.0	0.34	0.10	0.96	1.98
Goodna (06/03/09)	43	10.10	0.12	0.04	1.15	1.40
Goodna (17/03/09)	61	11.07	1.09	0.13	0.59	1.27
Wacol (15/12/08)	80	11.2	0.02	0.01	0.97	1.50
Wacol (06/03/09)	66	9.84	0.03	0.01	0.78	1.09
Wacol (17/03/09)	82	10.70	0.04	0.02	1.16	1.09
Oxley (15/12/08)	84	15.6	0.01	0.01	1.35	2.09
Oxley (06/03/09)	68	15.39	0.04	0.00	1.03	2.13
Oxley (17/03/09)	108	11.31	0.10	0.00	0.92	1.27
Luggage Point (13/02/09)	130	13.37	0.49	0.13	4.07	1.31
Luggage Point (20/02/09)	109	12.06	0.23	0.04	2.18	1.54
Gibson Island (11/02/09)	80	12.96	0.37	0.21	0.77	1.57
Gibson Island (26/03/09)	85	11.91	0.10	0.05	0.05	1.31
Fairfield (26/03/09)	88	18.47	47.32	0.23	0.07	-
Fairfield (11/02/09)	89	16.12	46.88	0.05	0.00	4.48

High ammonia concentrations in secondary effluents normally indicate a certain nitrification inhibition in the WWTP and can be an indicator for a non-optimal process performance in the WWTP. This non-optimal performance could be related to a high NDMA formation. Nevertheless, contrary to this assumption, ammonia concentration of the secondary effluent could not be used to predict the formation of NDMA in the disinfection process since high values of NDMA precursors were observed in the presence of both high and low concentrations of ammonia (see Figure 10). On the other hand, there appears to be a weak trend of increasing NDMA FP with increasing dissolved organic nitrogen (DON) and non-purgeable organic carbon (NPOC) concentrations, which may assist with predicting the NDMA formation potential. Other analysed parameters, like nitrite or nitrate, did not provide further information. Fairfield STP was not included in this part of the study due to the high levels of nitrogen present in the secondary effluent (no nutrient removal applied in that STP). Average values of NH_4^+, DON, and NPOC were 47 mg/L, 4.5 mg/L, and 17.3 mg/L, respectively for Fairfield STP.

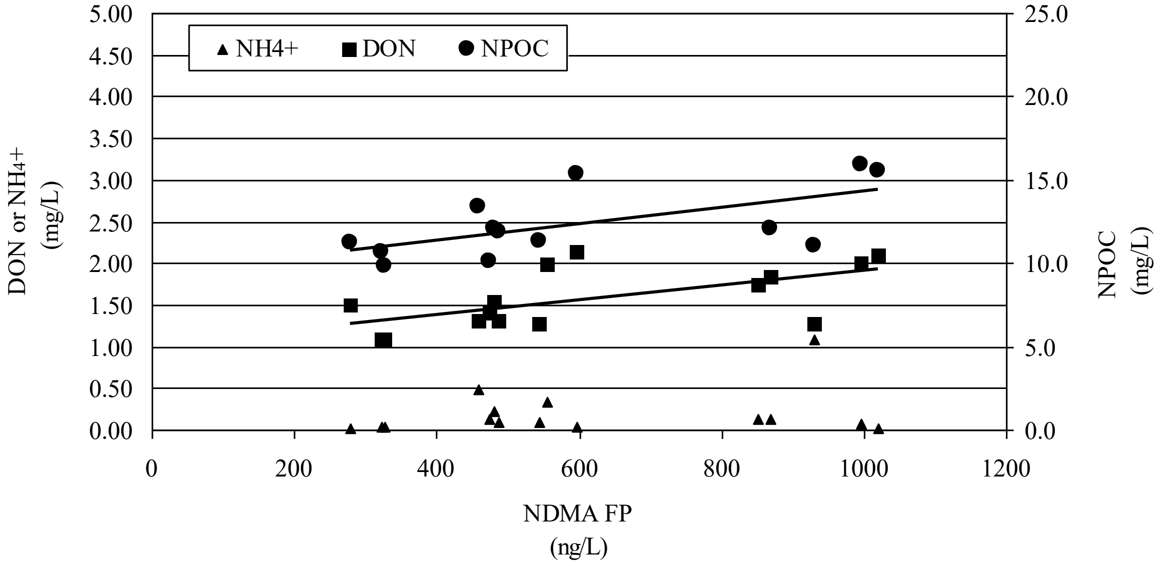


Figure 10. Relation of NDMA FP and DON, NH4+, and NPOC concentration of different water sources for the AWTPs in the SEQ context.

Finally, the effect of the biological nutrient removal treatment at WWTPs on the NDMA FP was evaluated. All WWTPs supplying water to the different AWTPs in SEQ are currently implementing biological nutrient removal as advanced treatment. In order to better understand the effect of this advanced treatment on the removal of NDMA precursors, a secondary WWTP without biological nutrient removal treatment was included in the study (i.e. Fairfield STP). Results from Wacol WWTP and Fairfield STP were compared. These both treat 100% domestic wastewaters and the main difference is the nutrient removal treatment in Wacol WWTP. NDMA FP values of Fairfield STP were twice as high as the values obtained from Wacol WWTP. These results support biological nutrient removal as an efficient barrier to control the formation of NDMA during disinfection of secondary effluent through chloramination (Sedlak et al., 2005).

4.3. NDMA Formation Potential across Advanced Water Treatment Plants

To evaluate the fate of NDMA precursors across the AWTPs, two different plants with different membranes were monitored. Figure 11 shows the NDMA FP of different samples taken across Bundamba 1A and Luggage Point AWTPs.

These results show that coagulation has an effect on the removal of NDMA precursors for the specific secondary effluents used as influent into Bundamba 1A AWTP (i.e. a mixture of Bundamba WWTP, Goodna WWTP, Wacol WWTP and Oxley WWTP). Both plants use ferric chloride to remove phosphate within the pre-treatment step of secondary effluents. Nevertheless, the pre-treatment at Luggage Point seems to have a lesser effect on the removal of NDMA precursors. This difference could be the result of a different pre-treatment efficiency rate or the different nature of NDMA precursors present in the influent. Microfiltration and ultrafiltration do not seem to have any effect on the removal of NDMA precursors since no statistical difference was found when measuring the concentration of those precursors from the pre-treatment with $FeCl_3$ to the reverse osmosis in either of the plants. Also no differences concerning the NDMA precursor rejection was found when using either MF or UF.

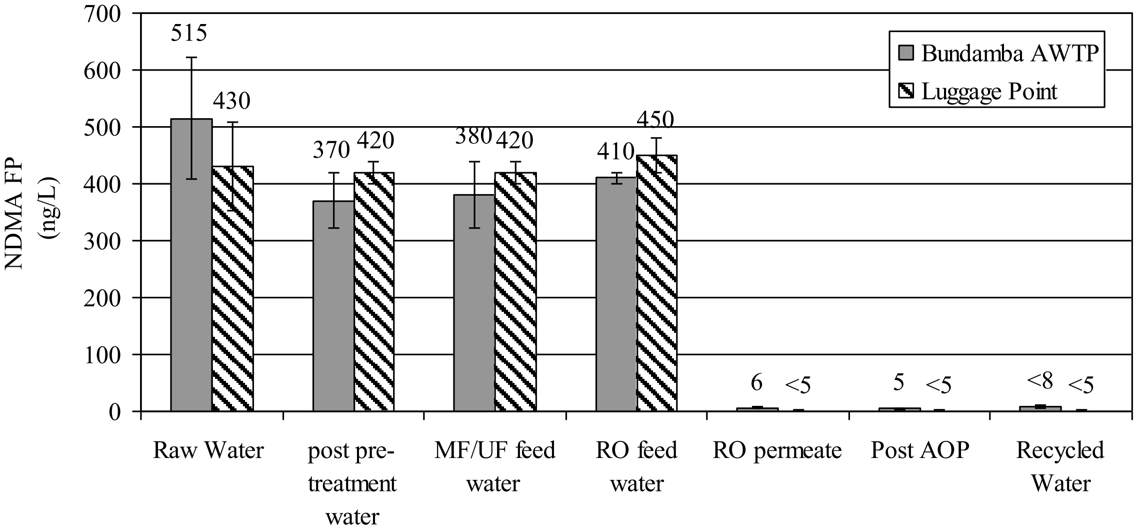


Figure 11. Concentration of NDMA Precursors across the different steps of Bundamba 1A and Luggage Point AWTP.

On the contrary, the reverse osmosis membrane filtration achieved an NDMA precursors removal of 98.5 ± 0.5% and >98.9± 0.5% at Bundamba 1A and Luggage Point AWTP, respectively. In fact, the use of reverse osmosis membrane treatment prior to chlorine disinfection has been suggested as a safety strategy for preventing NDMA formation (Mitch and Sedlak, 2004). However, since the AWTPs evaluated in the present study employ secondary wastewater effluent as source water for recycled water, disinfection prior to the reverse osmosis filtration is a required step in order to limit biofouling and maintain performance and productivity of the RO membranes. Since the presence of NDMA precursors cannot be avoided in this case, the dosing and operating conditions for the chloramination process within the AWTPs need to be carefully optimised to avoid the excessive formation of NDMA in the treatment process. Finally, NDMA FP of RO permeate remained constant and lower than the guideline at 10 ng/L until the end of the treatment (i.e. 5-8 ± 2 ng/L NDMA precursors at Bundamba 1A, and lower than the reporting limit for Luggage Point AWTP).

The 3-stage RO membrane configuration used at both AWTPs is designed to achieve 85% water recovery, therefore a reverse osmosis concentrate (ROC) stream (15% of incoming water) is produced as a main drawback of this process. The concentration of NDMA precursor in the ROC was measured at 1,600 ± 200 ng/L for Bundamba 1A and 2,200 ± 200 ng/L for Luggage Point AWTP. Due to the location of Bundamba 1A AWTP, this concentrate effluent cannot be directly discharged to the river due to the elevated nutrient concentrations present. Thus, a nitrification-denitrification system is employed in conjunction with an additional phosphorus precipitation step at this AWTP achieving a final NDMA FP concentration of 1,100 ± 200 ng/L.

Wastewater-derived NDMA precursors are relatively stable in river waters (Gerecke and Sedlak, 2003). Thus, the high concentration of NDMA precursors in the effluent may have important implications in effluent-derived surface waters that are used as a source for drinking water. However, it is noteworthy to remark that the load of NDMA precursors discharged by the AWTP is lower than the amount discharged by the WWTP. As seen in Figure 11, a relatively high percentage of NDMA precursors are removed at the pre-treatment step by means of coagulation with ferric chloride at Bundamba 1A AWTP. In this specific AWTP, NDMA precursors concentration in the WWTP effluents ranged from 350 to 1,020 ± 20 ng/L. The concentration factor of the RO membranes at both AWTP is 6.7 (corresponding to 85% rejection). Hence, without any removal of NDMA precursors across the AWTP, values at the ROC would reach 2,350-6,830 ng/L. Nevertheless, values measured at the final treated ROC were always lower. Therefore, it is clear that the AWTP is improving the NDMA precursors discharge to the environment in comparison to direct WWTP discharge. Nevertheless, additional options are being considered at the AWTPs to further minimise ROC discharge impacts to the environment.

Complementary chemical analyses were performed at the different representative treatment steps of both Bundamba 1A AWTP and Luggage Point AWTP. Those results are shown in Figure 12. The parameters monitored were NPOC, ammonia (as nitrogen), nitrate (as nitrogen) and DON. Nitrite (as nitrogen) was also measured across the plant, but concentrations were always lower than 0.1 mg/L for both plants, and hence those values were not included in the chart. Results from each sampling location are represented individually for each AWTP. Values shown in every column correspond to the concentration of the mentioned measured parameters. The red and green lines correspond to average NDMA FP concentration across the treatment train for Bundamba 1A and Luggage Point AWTP, respectively.

Results presented in Figure 12 support most of the previous statements of the present study. Bundamba 1A AWTP raw water contained a higher concentration of NPOC and DON than Luggage Point AWTP, hence NDMA FP of Bundamba 1A AWTP was higher than Luggage Point AWTP. After the pre-treatment with ferric chloride coagulation, the NPOC and DON concentrations of the water treated at Bundamba 1A AWTP decreased significantly and proportionally to the NDMA FP. Contrary to that observation, DON and NPOC did not decrease during the pre-treatment with ferric chloride at Luggage Point AWTP and NDMA FP remained constant during this first step of the treatment train. Following this process, the concentration of the chemical parameters measured in the treated water remained constant until reaching the reverse osmosis membrane. Also, NDMA FP concentration was constant from the pre-treatment to reverse osmosis membrane at both plants. These observations agree with previous findings that NPOC and DON may be useful parameter to predict the potential of NDMA formation of specific water. NPOC and DON concentrations measured after the reverse osmosis membrane were always lower than the analytical quantification limit of the method at both plants (i.e. 0.1 mg/L), thus making the comparison of these two plants hard in regards to the prediction of the potential of NDMA formation based on the NPOC or DON concentrations.

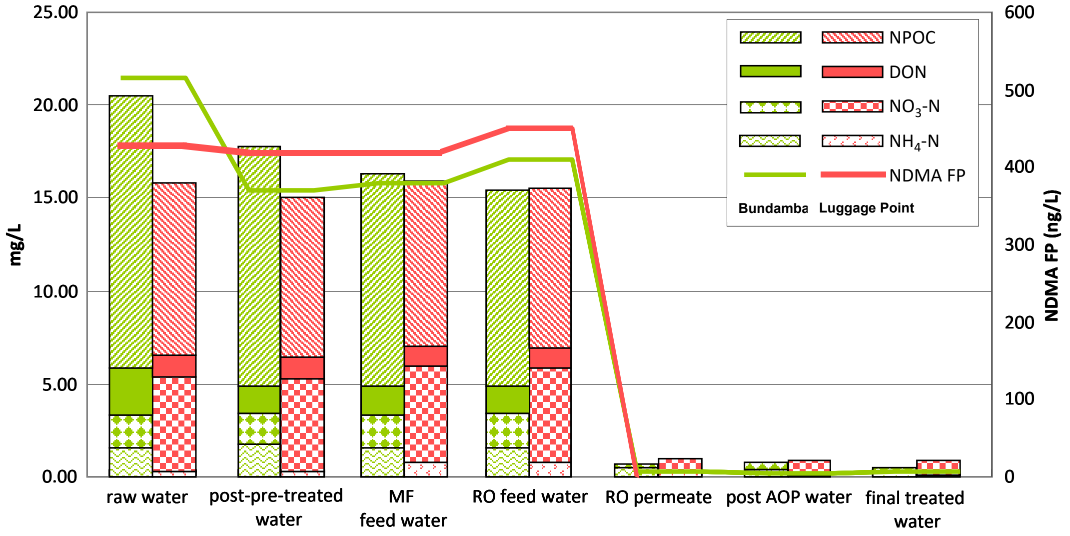


Figure 12. Fate of different chemical parameters across the Bundamba 1A AWTP and Luggage Point AWTP and average values of NDMA FP. Not to be contemplated as accumulative numbers.

Size fractionation of the wastewater effluent used as source water for PRW at Luggage Point AWTP was performed in order to understand some physical properties of NDMA precursors.

Figure 13 shows the results of the NDMA formation potential after this fractionation.

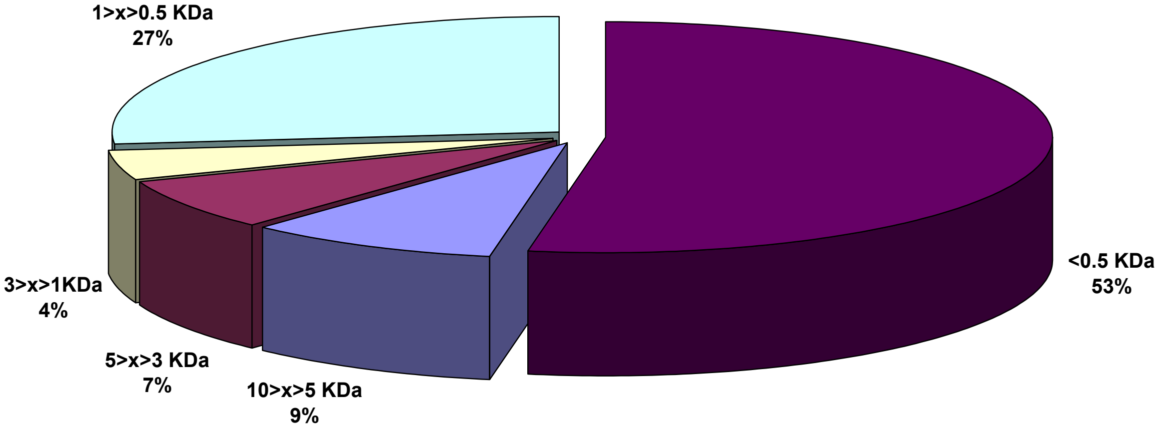


Figure 13. **Size Fractionation of Secondary Effluent used as Source Water for PRW.**

As seen in Figure 13, more than 75% of the NDMA precursors have a molecular weight lower than 1,000 Da. However, based on the previous data presented concerning the fate of NDMA precursors across the AWTP, more than 98% of the NDMA FP was rejected by the RO membranes. Hence, those precursors may be found between the range of 1,000 Da and 100 Da, that is, the molecular weight cut-off (MWCO) normally estimated for RO membranes. However, size is not the only property affecting solute rejection by the active layers of RO membranes. Charge and hydrophilicity/hydrophobicity are other important parameters that may affect the rejection of NDMA precursors by the membranes. In general, contaminant rejection in RO membranes has been reported to be higher for larger, more hydrophobic, and more negatively charged contaminants (Bellona et al., 2004; Kim et al., 2005). Rejection is more effective for negatively charged contaminants because active layers are usually negatively charged above pH = 5, and thus anions are excluded by the electric Donnan mechanism (Ohki and Ohshima, 1985). Also the presence of organics in the water can either increase or decrease contaminant rejection depending on how the interactions between organics and membrane, and organics and solute, affect the charge of both membrane and contaminants, and the steric effects experienced by the contaminant in the active layers (Bellona et al., 2004). The presence of organics in the water also causes membrane fouling which furthers hampers the ability to predict changes in performance. Therefore, the observed 98% rejection of the NDMA FP by the RO membrane should be contemplated as a conjunction of all the above described parameters and not by the size only.

The NDMA FP of the size fractions was also related to the NPOC and DON. Again, the trend between NPOC, DON and NDMA FP which may assist with predicting the NDMA FP could be observed. In that case, that trend was observed to be stronger for DON than for NPOC. These results are represented in Figure 14 and Figure 15.

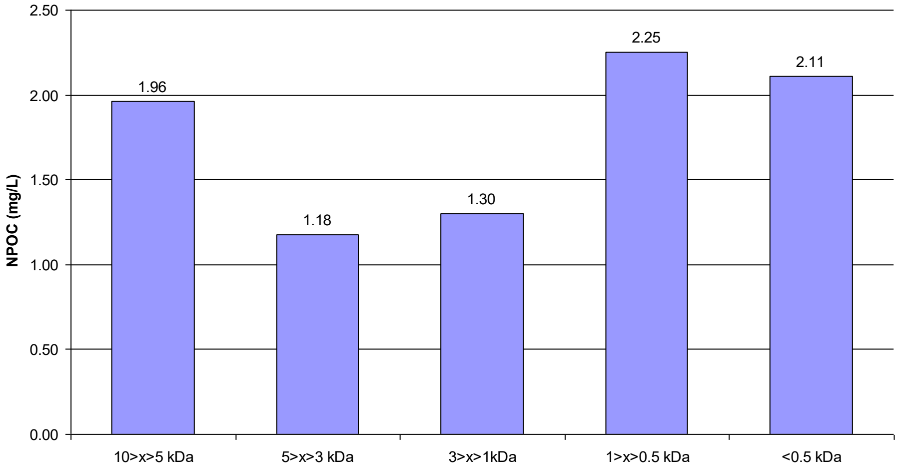


Figure 14. **Relation of NPOC in the Different Size Fractions of Luggage Point WWTP Effluent.**

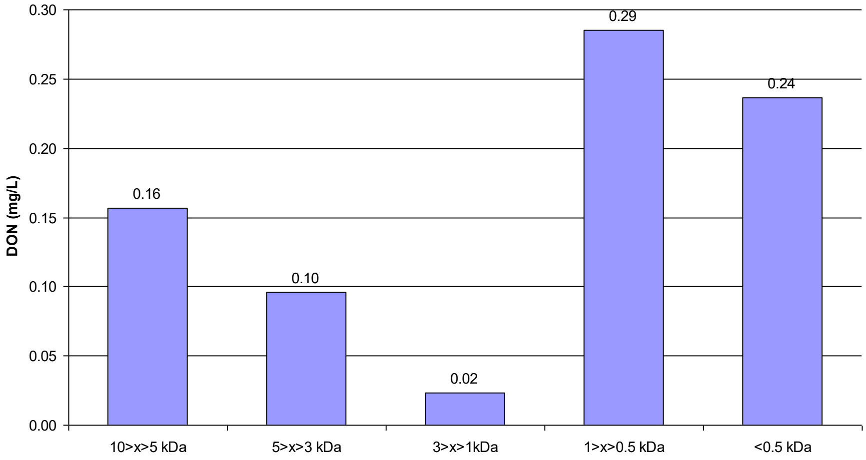


Figure 15. **Relation of DON in the Different Size Fractions of Luggage Point WWTP Effluent.**

From these results, it is clear that most of the DON is capable of passing through a 1kDa filter and also that the higher NDMA FP is encountered in that fraction. These results agree with previous data published by Pehlivanoglu-Mantas and Sedlak (2008), where they measured the NDMA FP in dissolved organic nitrogen forms in wastewater effluents. In that publication, they warned about the potential of NDMA formation by low-molecular weight wastewater-derived DON that can happen during the reclamation or reuse of wastewater after disinfection.

For further characterisation of the organic matrix, secondary effluent from Bundamba WWTP, Goodna WWTP, Wacol WWTP and Oxley WWTP were analysed by LC-OCD-OND technique (LC stands for liquid chromatography, OCD for organic carbon detector, and OND for organic nitrogen detector). All experiments were performed in collaboration with the University of New South Wales (UNSW), Australia. The respective results are given in Figure 16, Figure 17, and Figure 18 and Table 12. Using the LC-OCD-OND technique, samples are analysed without any further pre-treatment. First, natural organic matter (NOM) is fractionated by size exclusion chromatography (SEC) and then the organic carbon and organic nitrogen content of the separated fractions is detected as carbon dioxide and as nitrate, respectively, after photo-oxidation in a thin-film reactor. Fractionation of NOM during SEC is based on three effects, size exclusion, ionic and hydrophobic interactions, making the interpretation of the chromatograms rather complex. However, in agreement with Sacher et al (2008), NDMA FP correlates better with hydrophobic organic carbon (HOC, $R^2 = 0.95$), the DON in the biopolymer fraction ($R^2 = 0.93$), and the organic carbon in the low molecular weight (LMW) neutrals fraction ($R^2 = 0.72$). From Figure 18, it can be seen that the peak at 53 minutes, which corresponds to LMW neutrals, correlates also with the NDMA FP. Bundamba WWTP has by far the highest peak nitrogen diagram and also has the highest NDMA FP.

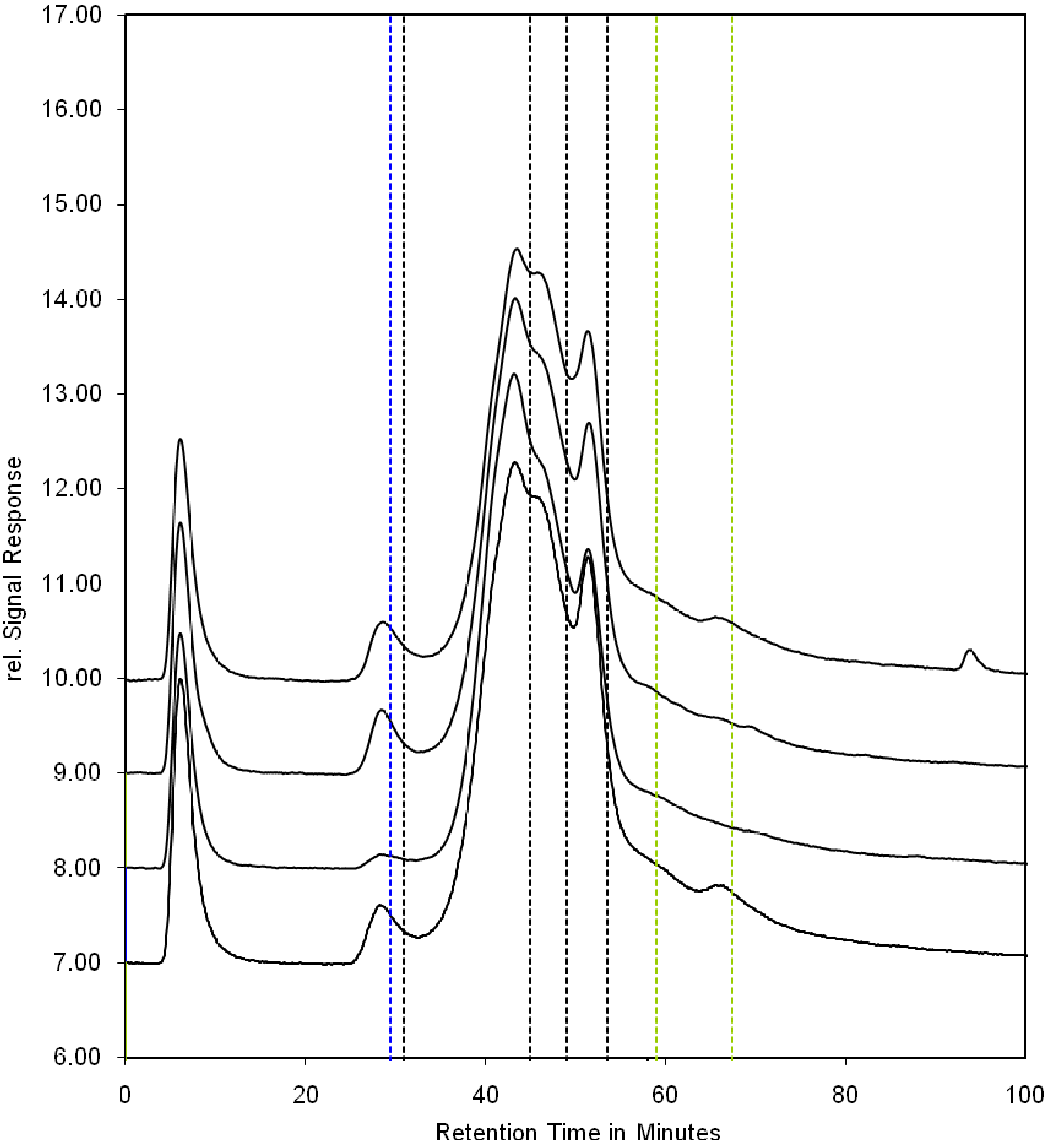


Figure 16. Comparing OCD in Bundamba WWTP, Goodna WWTP, Wacol WWTP and Oxley WWTP. Chromatograms from the top to the bottom are Bundamba WWTP, Goodna WWTP, Wacol WWTP and Oxley WWTP respectively.

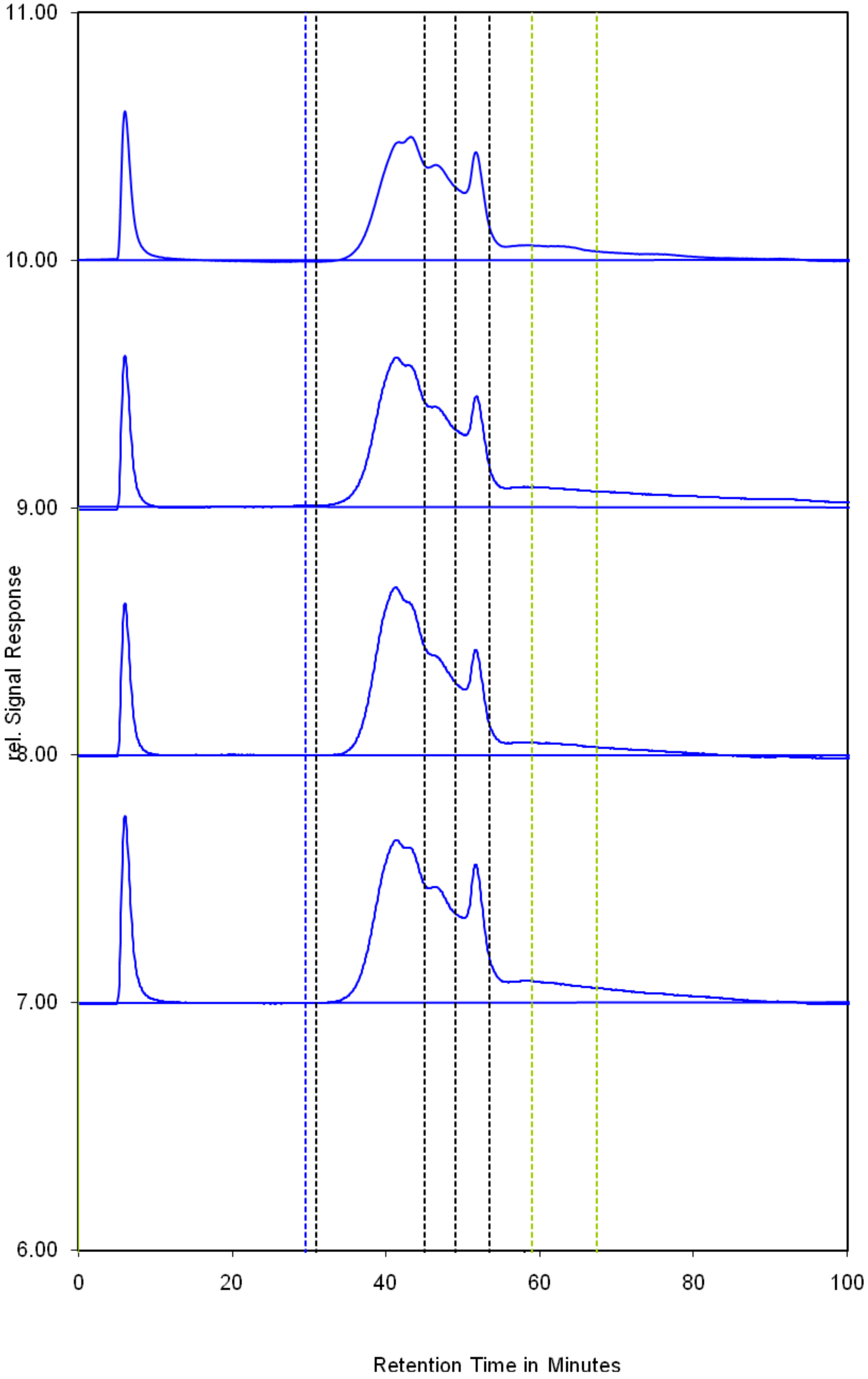


Figure 17. Comparing UVD in Bundamba WWTP, Goodna WWTP, Wacol WWTP and Oxley WWTP. Chromatograms from the top to the bottom are Bundamba WWTP, Goodna WWTP, Wacol WWTP and Oxley WWTP respectively.

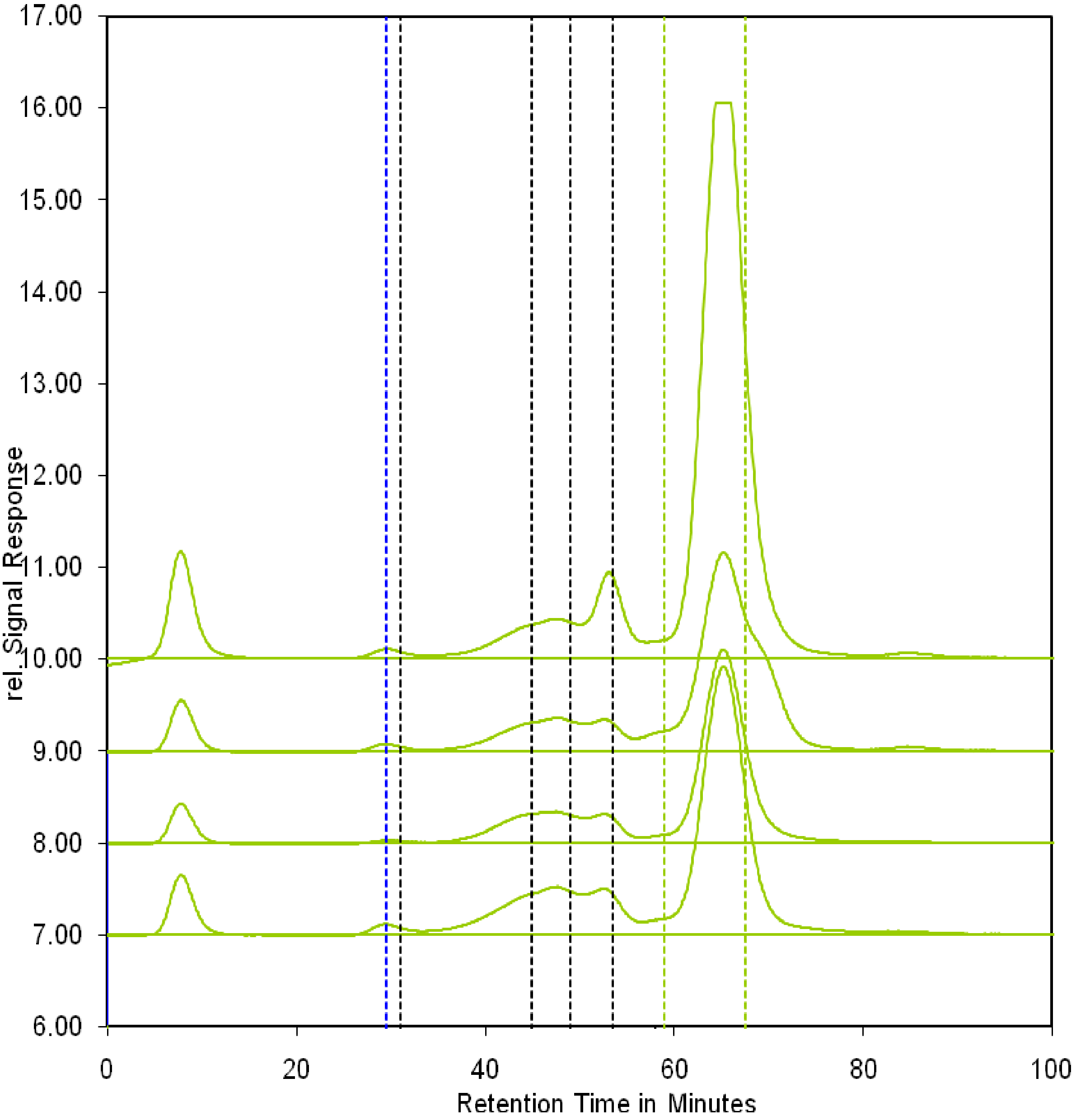


Figure 18. **Comparing OND in Bundamba WWTP, Goodna WWTP, Wacol WWTP and Oxley WWTP. Chromatograms from the top to the bottom are Bundamba WWTP, Goodna WWTP, Wacol WWTP and Oxley WWTP respectively.**

Table 12. Results of LC-OCD-OND Measurements of Selected Surface Water Samples.

	DOC Dissolved	HOC Hydrophobic	CDOC Hydrophilic	BIO-polymers	DON (Norg)	N/C	% Proteins in BIOpol.*	Humic Subst. (HS)	DON (Norg)	N/C	Aromaticity (SUVA-HS)	Mol-Weight (Mn)	Position in HS diagram	Building Blocks	LMW Neutrals	LMW Acids	Inorganic Colloids SAC	SUVA (SAC/DOC)
								approximate molecular weights (g/mol):										
				>>20.000				~1000 (see separate HS-diagram)						300-500	<350	<350		
	ppb-C	ppb-C	ppb-C	ppb-C	ppb-N	µg/µg	% BIOpol.	ppb-C	ppb-N	µg/µg	L/(mg*m)	g/mol	--	ppb-C	ppb-C	ppb-C	(m^{-1})	L/(mg*m)
	% DOC	% DOC	% DOC	% DOC	--	--	--	% DOC	--	--	--	--	--	% DOC	% DOC	% DOC	--	--
Bundamba WWTP NDMA FP=995ng/L	**11609**	**3047**	**8562**	**413**	**57**	**0.14**	**41**	**4761**	**293**	**0.06**	**3.22**	**573**	**A**	**1483**	**1905**	**n.q.**	**n.q.**	**3.02**
	100%	26.2%	73.8%	3.6%	--	--	--	41.0%	--	--	--	--	--	12.8%	16.4%	--	--	--
Goodna WWTP NDMA FP=556ng/L	**11417**	**2387**	**9030**	**400**	**41**	**0.10**	**31**	**4363**	**247**	**0.06**	**4.22**	**738**	**B**	**2304**	**1857**	**106**	**0.33**	**3.00**
	100%	20.9%	79.1%	3.5%	--	--	--	38.2%	--	--	--	--	--	20.2%	16.3%	0.9%	--	--
Wacol WWTP NDMA FP=280ng/L	**10350**	**1945**	**8405**	**92**	**15**	**0.16**	**49**	**4907**	**266**	**0.05**	**3.70**	**680**	**C**	**1815**	**1568**	**23**	**0.08**	**3.16**
	100%	18.8%		0.9%	--	--	--	47.4%	--	--	--	--	--	17.5%	15.2%	0.2%	--	--
Oxley WWTP NDMA FP=1020ng/L	**13175**	**2815**	**10360**	**377**	**55**	**0.15**	**44**	**5123**	**383**	**0.07**	**4.14**	**724**	**D**	**2499**	**2305**	**55**	**0.05**	**3.26**
	100%	21.4%	78.6%	2.9%	--	--	--	38.9%	--	--	--	--	--	19.0%	17.5%	0.4%	--	--

LMW = low-molecular weight
DON = Dissolved organic nitrogen
n.q. = not quantifiable (< 1ppb calculated)
n.m. = not measured
*:under the presumption that all org. N in the BIOpolymer fraction originates from proteins
"Biopolymers" = Polysaccharides, Proteins, Aminosugars
"Building Blocks" = breakdown products of humics
"Neutrals" include mono-oligosaccharides, alcohols, aldehydes, ketones
"Acids" = Summary value for monoprotic organic acids < 350 Da

4.4. Conclusions

The NDMA FP of secondary effluents in SEQ was studied in order to evaluate the presence of NDMA precursors in water sources for PRW. Results obtained showed values between 350 and 1,020 ng/L for NDMA FP in the secondary effluents, with remarkable differences between individual WWTPs. Concentrations of NDMA in the source waters prior to the formation potential tests were generally lower than the reporting limit (5 ng/L) and never higher than 25 ng/L. No other nitrosamines were measured above the QHFSS limit of reporting (LOR) in this sampling campaign.

More than 98.5% of NDMA precursors were effectively removed by Reverse Osmosis (RO) membranes at both AWTPs. No major changes in relation to the NDMA precursor concentration were experienced during the rest of the treatment train except at the coagulation step from Bundamba 1A AWTP.

Ammonia concentration of the secondary effluent could not be used to predict the formation of NDMA in the disinfection process since high values of NDMA precursors were observed in the presence of both high and low concentration of ammonia. On the other hand, there appears to be a trend of increasing NDMA FP with increasing dissolved organic nitrogen (DON) and non-purgeable organic carbon (NPOC) concentrations, which may assist with predicting the NDMA formation potential. When evaluating the NDMA formation of different size fractions of secondary effluent, it was found that 75% of the NDMA precursors were found at the size fraction <1,000 Da.

Because there is a possibility of NDMA generation at the AWTP, the disinfection strategy must be well understood and optimised in order to minimise that formation. The next chapters of this technical report deal with that objective.

5. UNDERSTANDING THE PARAMETERS AFFECTING NDMA FORMATION AT AWTPS

The aim of this chapter is to understand the operational parameters employed at the AWTPs that most affect the formation of NDMA during the production of PRW. The following aspects were evaluated using dimethylamine, as a well known NDMA precursor, and real secondary effluents:

- Disinfection strategy;
- Source water;
- Chloramine dose; and
- Effect of ferric chloride as a possible catalyst for NDMA formation.

Controlled experiments at bench scale were performed to understand the most significant operational parameters affecting the formation of NDMA during the production of PRW at the AWTPs. Solutions of dimethylamine, which is a well known NDMA precursor (Mitch et al., 2003b), and secondary effluent from Bundamba WWTP, Luggage Point WWTP and Goodna WWTP (see Table 13) were disinfected by different disinfection strategies during 24 hours contact time.

Table 13. Chemical Parameters, Initial NDMA, NDMA Formation Potential and NDMA Generated after 24 hours of Chloramine-10mg/L Cl2-/Wastewater Contact Time of Secondary Effluents Used as Source Water for PRW.

	NPOC (mg/L)	NH_4-N (mg/L)	NO_2-N (mg/L)	NO_3-N (mg/L)	TKN (mg/L)	DON (mg/L)	Total N (mg/L)	$NDMA_o$ (ng/L)	$NDMA_{24h}$ (ng/L)	NDMA FP (ng/L)
Bundamba WWTP	10.4	0.10	0.06	1.2	1.82	1.72	3.10	5	16	294
Luggage Point WWTP	10.6	0.20	0.01	0.33	1.26	1.06	1.60	6	18	246
Goodna WWTP	8.89	0.04	0.03	2.75	1.22	1.18	4.00	3	38	324

5.1. NDMA Formation Kinetics with Dimethylamine as a well Known NDMA Precursor

Experiments with dimethylamine at 0.1 mg/L were performed at 4 mg/L Cl_2, which is a usual concentration to be considered in a full-scale plant application. Three disinfection scenarios were evaluated in this study: (1) disinfection with pre-formed monochloramine; (2) disinfection with monochloramine formed in-line; and (3) disinfection with dichloramine. Figure 19 shows the evolution of the NDMA formation during 8 hours and after 24 hours of chloramine/dimethylamine solution contact time when using the three different disinfection scenarios. No NDMA was found in the original dimethylamine solution. The darker line in the figure at 10 ng/L represents the NDMA guideline value for PRW in Queensland (QPC, 2005). As observed in Figure 19, pre-formed monochloramine formed only 0.20±0.02 µg/L of NDMA after 24 hours of contact time in comparison to 0.78±0.02 µg/L NDMA when using in-line monochloramine and 3.30±0.20 µg/L NDMA created with dichloramine.

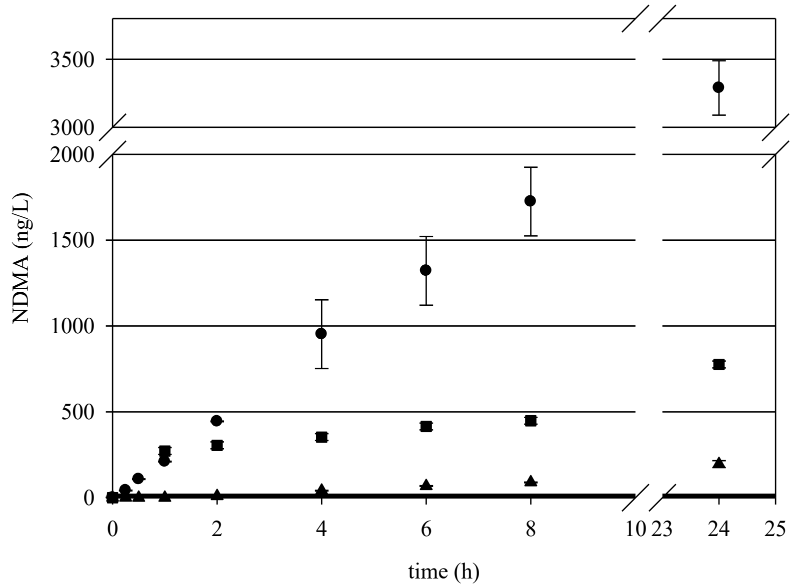


Figure 19. **NDMA formation during 24 hours using a 0.1 mg/L solution of dimethylamine as standard NDMA precursor. pH = 6.9, disinfectant dose 4 mg/L Cl2. (•) dichloramine, (▪) in-line monochloramine, and (▲) pre-formed monochloramine.**

Figure 20 shows the chlorine decay of dimethylamine disinfection following strategies 1-3 at an initial chlorine dose of 4 mg/L Cl_2. As seen, the fastest chlorine decay was observed when adding dichloramine followed by in-line monochloramine. On the other hand pre-formed monochloramine did not decay significantly even after eight hours of contact time. These results correlate with the formation of NDMA in each specific scenario, being higher for dichloramine, followed by in-line and pre-formed monochloramine, showing the reaction of the chlorinated species with NDMA precursors.

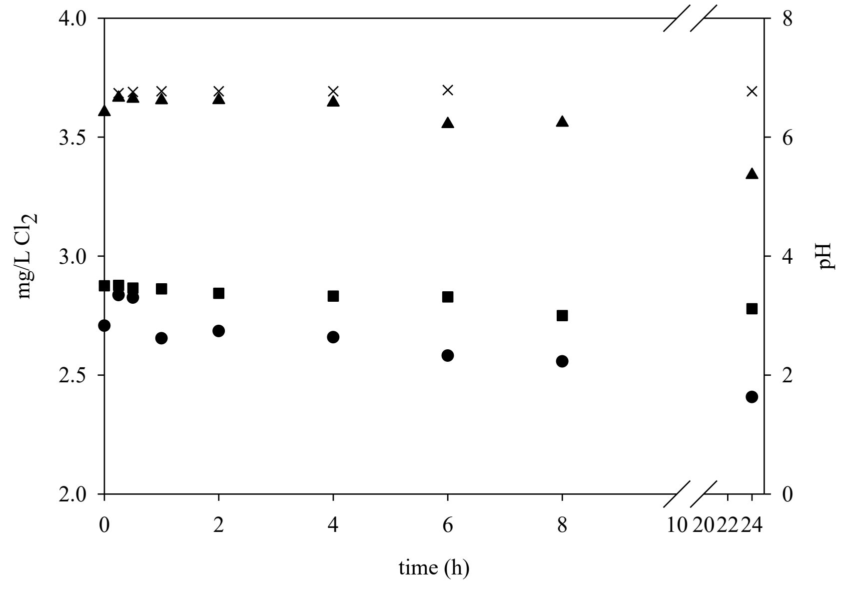


Figure 20. **Chlorine decay during 24 hours disinfection of 0.1 mg/L solution of dimethylamine as standard NDMA precursor. Initial disinfectant dose 4 mg/L Cl2. Time zero correspond to the first sample taken after mixing. (•) dichloramine, (▪) in-line monochloramine, (▲) pre-formed monochloramine, (x) Average pH.**

Schreiber et al. (2005) suggested that dichloramine is the main species related to NDMA formation. Even though this species is not the desired compound for disinfection purposes, dichloramine can be generated during disinfection. Therefore, disinfection must be well controlled at the AWTP to avoid the presence of this species. In fact, when water is disinfected by means of chloramination, monochloramine (NH_2Cl), dichloramine ($NHCl_2$) and trichloramine (NCl_3) can be formed in different proportions. Since these species are in a chemical equilibrium, all three may be present, although the concentration of one or two of them may be very low. The proportion of the species present in solution is dependent on the ratio of chlorine to ammonia and on pH. At pH levels usually present in secondary effluents (pH = 6-8), the predominant chloramine species are monochloramine and dichloramine. The Cl:N molar ratio employed in the disinfection strategy is usually below 1, therefore monochloramine can be considered as the main species present in solution (Mitch et al., 2005; Schreiber and Mitch, 2005). However, although normally a Cl:N molar ratio < 1 is used, locally, due to incomplete mixing, dichloramine can be present in excess, leading to the generation of NDMA (Sedlak and Kavanaugh, 2005). This could be the case when monochloramine is generated in-line by adding chlorine to an ammonia solution, as initially implemented in Bundamba 1A AWTP.

To investigate this effect we compared the formation of NDMA during a 24-hour contact time when adding in-line or pre-formed monochloramine to a dimethylamine solution. Figure 18 shows that a higher NDMA concentration was generated when using in-line formed monochloramine in comparison to pre-formed monochloramine. As already stated, the significantly higher NDMA formation when monochloramine is generated in-line can be explained by the possible formation of dichloramine at the reagents' mixing point since the order of reagent addition used (i.e. ammonia before sodium hypochlorite) fosters a high localised chlorine concentration (Schreiber and Mitch, 2005). When monochloramine is pre-formed by adding ammonia over a chlorine solution, the possibility of high free chlorine concentrations in contact with ammonia is minimised, which results in less dichloramine and ultimately less NDMA formation.

Apart from high local chlorine concentration, dichloramine can also be generated in solution due to the decomposition of monochloramine to dichloramine following reactions 16 and 17. Equation 16 shows the disproportionation reaction of monochloramine to free chlorine, while equation 17 is outlining the reaction of monochloramine with free chlorine to finally form dichloramine.

$$NH_2Cl + H_2O \leftrightarrow OCl^- + NH_4^+ \qquad \text{Equation 16}$$

$$HOCl + NH_2Cl \rightarrow NHCl_2 + H_2O \qquad \text{Equation 17}$$

To evaluate this effect, we measured the conversion of pre-formed monochloramine to dichloramine at the bench scale, also following the generation of NDMA. The results of these experiments are plotted in Figure 21. This figure shows that NDMA was generated at <1 ng/L up to one hour of monochloramine/dimethylamine solution contact time. Monochloramine decreased mainly due to self decomposition. However, dichloramine could be measured after 1.5 hours of contact time. The appearance of this species could be related to the formation of NDMA based on the mechanism proposed by Schreiber and co-authors (Schreiber and Mitch, 2006). In our experiment, we could measure a rate constant of $3.1 \times 10^{-5}\ s^{-1}$ for the monochloramine decomposition equation 16, which compares favourably to the value reported in the literature $2.1 \times 10^{-5}\ s^{-1}$ (Jafvert and Valentine, 1992). For equation 17, Jafvert et al. suggest that a good estimate may lie within the range of 150-425 $M^{-1}s^{-1}$.

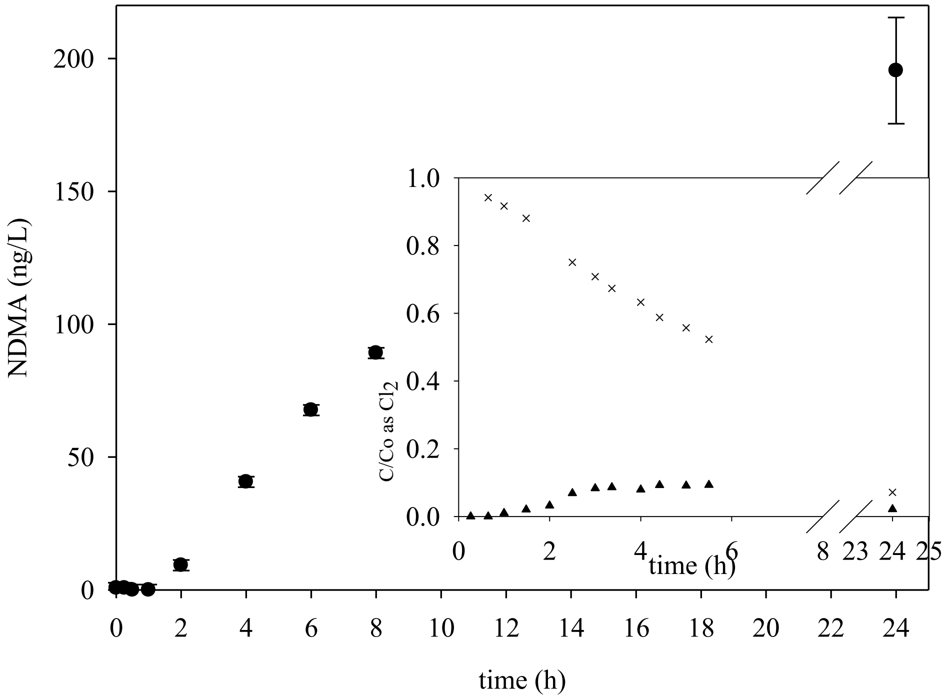


Figure 21. **NDMA formation during 24 hours using a 0.1 mg/L solution of dimethylamine as standard NDMA precursor and pre-formed monochloramine as disinfectant agent at pH = 6.9, disinfectant dose 4 mg/L Cl2. Secondary figure correspond to the dichloramine measured during the time as a result of the disproportionation of monochloramine. (•) dimethylamine, (x) monochloramine, (▲) dichloramine.**

5.2. Effect of Disinfection Strategy and Contact Time on NDMA Formation

In order to evaluate the influence of the disinfection strategy on NDMA formation, three different experiments were conducted with secondary effluent from Bundamba 1A and Luggage Point WWTP. To this aim, either: (1) 10 mg/L monochloramine (MCA) pre-formed; (2) 10 mg/L MCA formed in-line; or (3) 10 mg/L dichloramine (DCA) were added to the secondary effluent buffered at pH 6.9. The high chlorine dose was required in order to obtain high enough concentrations of formed NDMA that allow the comparison between the different source waters as discussed later. Samples were taken after 15 min, 30 min, 1 h, 2 h, 4 h, 6 h, 8 h and 24 h of reaction time. Figure 22 and Figure 23 show the evolution of the NDMA formation during 8 hours of disinfection of the Bundamba 1A and Luggage Point secondary effluent with scenarios (1)-(3) (left axis). The columns show the NDMA concentration after 24 hours (right axis). These values were calculated by subtracting the initial NDMA concentration from the total NDMA generated in the sample. The yellow line represents the Public Health Regulations limit in Queensland at 10 ng/L.

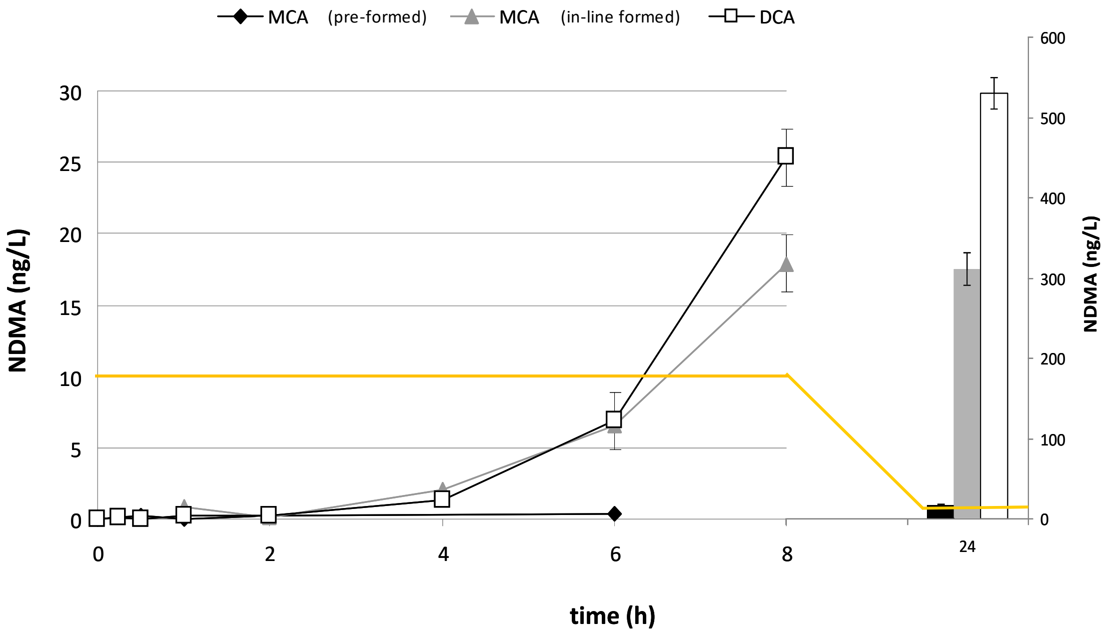


Figure 22. NDMA formation during 24 hours with Bundamba secondary effluent at pH 6.9. Disinfectant dose of 10 mg/L Cl_2.

In general, dichloramine formed significantly more NDMA compared to monochloramine. This result is consistent with previous results published in the literature in which Schreiber et al (2005) suggested that dichloramine is the main species related to NDMA formation. In-line formed monochloramine was synthesised by adding ammonium chloride (NH_4Cl) followed by chlorine HOCl to the reactor. This disinfection strategy simulates the current scheme used at Bundamba 1A AWTP. As already expected both plants show a higher NDMA concentration after 24 hours when forming the monochloramine in line in comparison to the NDMA formed by adding the pre-formed monochloramine. The significantly higher NDMA formation with the in-line formed MCA in comparison to the NDMA formed when pre-formed monochloramine was used can be explained by the formation of dichloramine at the mixing point. The order of reagent addition used, NH_4Cl before HOCl, fosters dichloramine formation at the mixing point due to high localised Cl:N molar ratios prior to complete mixing (Schreiber and Mitch, 2005). When monochloramine is pre-formed the possibility of high free chlorine concentrations in contact with ammonia is minimised, which results in less dichloramine formation and less NDMA. Thus, adding pre-formed monochloramine instead of in-line formed monochloramine seems to be an important parameter to be considered when designing the treatment train for the production of PRW.

However, monochloramine decomposed to dichloramine over the time (see previous section), the latter being the main species related to the NDMA formation. Thus, the contact time between disinfectant and wastewater seems to be the most important parameter to consider when the minimisation of NDMA formation is required during the production of PRW. From the results obtained, it can be concluded that a contact time between 6 and 8 hours is an acceptable value to keep NDMA formation below the regulation limit.

5.3. Effect of Source Water on NDMA Formation

Different secondary effluents used as source water for the production of PRW may have a very different yield of NDMA formation, depending on the presence of specific NDMA precursors. To evaluate the effect of the source water on the NDMA formation, secondary effluent samples taken from Bundamba WWTP, Luggage Point WWTP and Goodna WWTP were used for these experiments.

Pre-formed MCA at 10 mg/L Cl_2 was added to the wastewater buffered at pH 6.9. NDMA concentrations were monitored after 15 min, 30 min, 1 h, 2 h, 4 h, 6 h, 8 h and 24 h reaction time. In Figure 23, the lines show the NDMA formation kinetics of the three different source waters over 8 hours (left axis) and the columns show the NDMA formation after 24 hours (right axis). These values were calculated by subtracting the initial NDMA concentration from the total NDMA generated in the sample. The yellow line indicates the regulation limit at 10 ng/L.

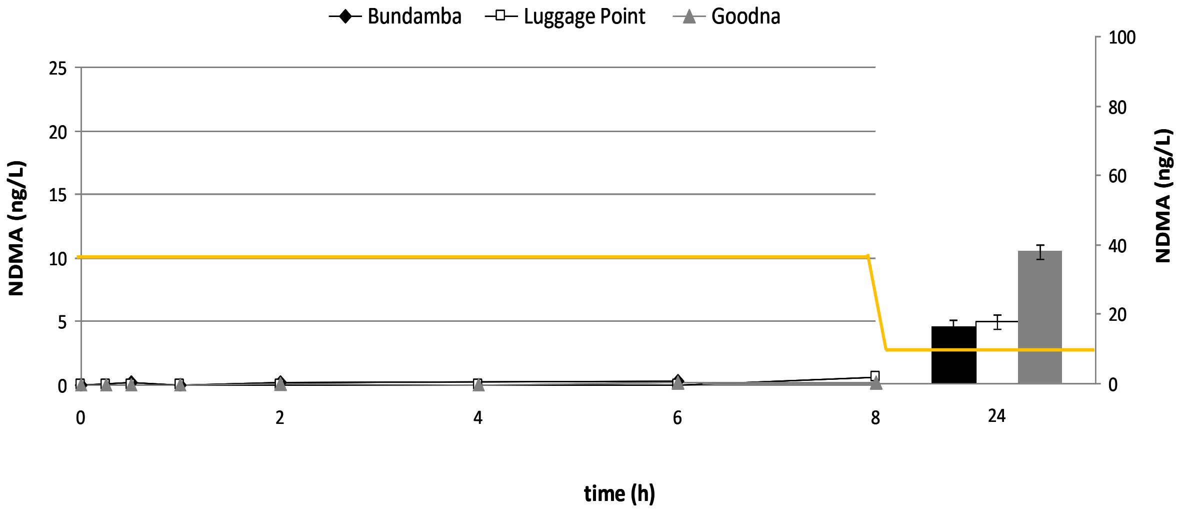


Figure 23. NDMA formation kinetics over 24 hours of three different secondary WWTP effluents with MCA added pre-formed at 10 mg/L Cl_2.

During the first 8 hours, no difference in the NDMA formation of the three source waters could be seen since all values ranged below the LOR. After 24 hours, differences can be observed between Goodna and the other two plants (e.g. 38.1 ng/L for Goodna, 16.4 ng/L for Bundamba, 17.8 ng/L for Luggage Point). Although NDMA generated is two times higher when disinfecting the Goodna WWTP effluent than the NDMA formed during disinfection of Bundamba and Luggage Point WWTP effluents, it must be noted that the final value after 24 hours varies in a low range of order of magnitude. The fact that there is no difference in the NDMA formation during the production of PRW over a contact time of 8 hours and a minimal variation at 24 hours, implies that the impact of these specific source waters can be considered negligible on NDMA formation.

5.4. Effect of Monochloramine Dose on NDMA Formation

Figure 24 shows the kinetics of NDMA formation over 24 hours with three different pre-formed monochloramine doses (i.e. 4 mg/L Cl_2, 10 mg/L Cl_2, 15 mg/L Cl_2) applied to the secondary effluent of Bundamba WWTP. The lines show the NDMA formation of the three different disinfectant doses over 8 hours (left axis) and the columns show the NDMA formation after 24 hours (right axis). These values were calculated by subtracting the initial NDMA concentration from the total NDMA generated in the sample. The yellow line indicates the regulation limit at 10 ng/L.

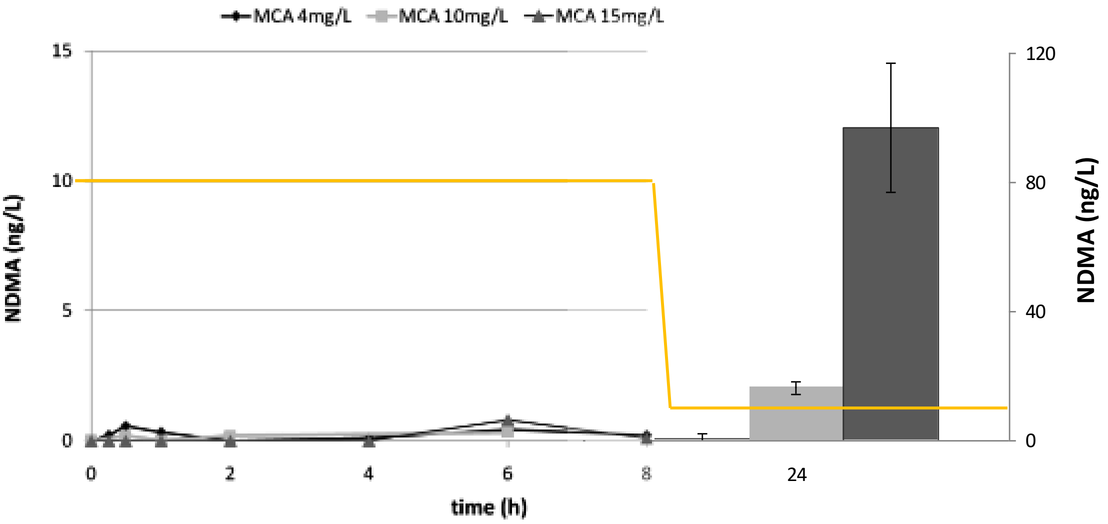


Figure 24. NDMA formation kinetics over 24 hours at different pre-formed MCA doses (4mg/L Cl_2, 10mg/L Cl_2, 15mg/L Cl_2) using real water effluent from Bundamba WWTP.

After 24 hours, a higher monochloramine concentration resulted in higher NDMA formation (i.e. 0.3 ng/L NDMA for 4 mg/L Cl_2; 16.4 ng/L NDMA for 10 mg/L Cl_2; and 97.0 ng/L NDMA for 15 mg/L Cl_2). With a monochloramine dose of 10 mg/L Cl_2, and even with applying 15 mg/L Cl_2, the NDMA formation was less than 5 ng/L after 8 hours.

During the production of PRW, the monochloramine dose used at the AWTPs ranges from 2 to 5 mg/L which draws attention particularly to the results obtained at the lowest pre-formed MCA dose (4 mg/L Cl_2). The results imply that no NDMA formation would be expected when adding monochloramine at normal disinfectant dosages and using pre-formation as the disinfection strategy.

5.5. Effect of Ferric Chloride on NDMA Formation

A previous study suggested that metal ions like copper, iron and nickel might enhance the NDMA formation (Sacher et al., 2008). Therefore, the residual iron left from the coagulation pre-treatment might act as a catalyst for NDMA formation during PRW production. To evaluate the possible catalytic effect of the iron on the formation of NDMA, secondary effluent samples were taken from Bundamba WWTP and Luggage Point WWTP. To avoid ferric chloride ($FeCl_3$) precipitation, the phosphate buffer could not be used in those experiments. Thus, no buffer was applied in those experiments since the water samples′ buffer capacity was sufficient to keep the pH around 7 after adding the disinfectant. Monochloramine was formed in-line by adding NH_4Cl first, followed by $FeCl_3$ (48 mg/L) and HOCl last, simulating the treatment process at the initial configuration of Bundamba 1A AWTP. The $FeCl_3$ dose of 48 mg/L is used to simulate the maximum dose of iron that can be present in solution in the real AWTP. In these experiments, a disinfectant dose of 10 mg/L Cl_2 was applied.

Figure 25 shows the kinetics of the in-line formed monochloramine at 10 mg/L Cl_2 in the presence and absence of the coagulant $FeCl_3$ for secondary effluents of Bundamba and Luggage Point WWTP. The lines show the NDMA formation over 8 hours (left axis) and the columns show the NDMA formation after 24 hours (right axis). These values were calculated by subtracting the initial NDMA concentration from the total NDMA generated in the sample. The yellow line indicates the regulation limit at 10 ng/L.

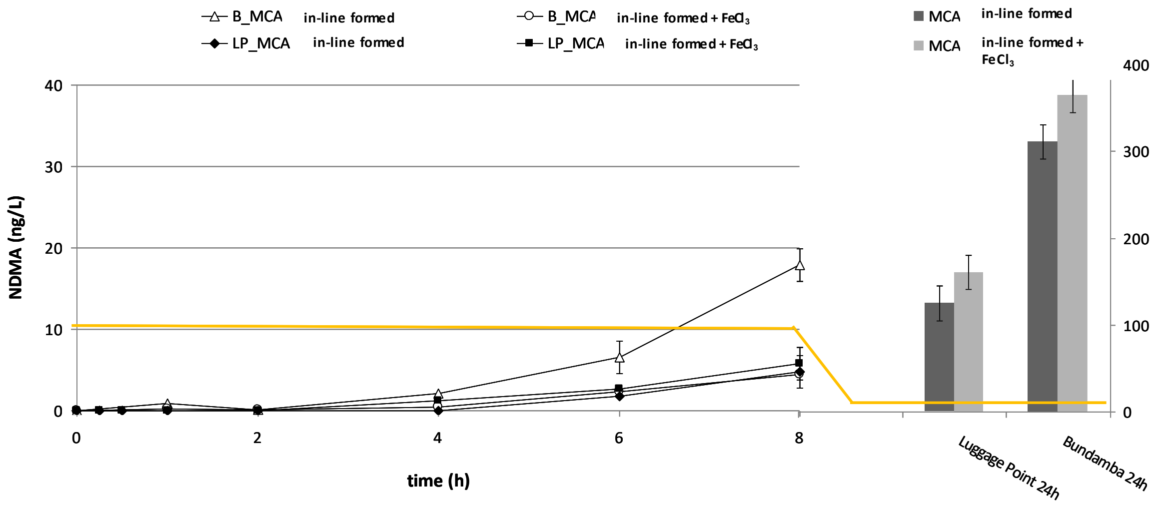


Figure 25. NDMA formation kinetics over 24 hours with 10 mg/L Cl_2 in-line formed MCA in the presence and absence of $FeCl_3$ (48 mg/L). B = Bundamba, LP= Luggage Point.

No statistical differences were found when comparing the NDMA generated after 24 hours in the presence and absence of $FeCl_3$ for Luggage Point secondary effluent. For the secondary effluent of Bundamba WWTP, the NDMA concentration was around 10 ng/L higher after 24 hours in the presence of $FeCl_3$. This variation however, is of low importance considering the long contact time of 24 hours between the wastewater and the disinfectant.

For a contact time of 8 hours, no statistical difference was observed for the NDMA formed in the presence and the absence of $FeCl_3$. NDMA concentrations monitored ranged around the LOR except for Bundamba secondary effluent, for which, in the absence of $FeCl_3$, NDMA was formed above the LOR. No explanation could be found for this observation. Nevertheless, it can be concluded that the addition of the coagulant ferric chloride seems not to have a catalytic effect on NDMA formation for the time frame of 8 hours. Even after 24 hours, the variation of the NDMA formation is within, or is close to, the statistical errors.

5.6. Conclusions

The aim of this part of the project was to study the parameters that control NDMA formation during the disinfection of secondary effluent used as source water for PRW at the AWTPs. From the results of this work, it can be concluded that the disinfection of secondary effluents with pre-formed monochloramine generates significantly less NDMA than monochloramine formed in-line in the treatment train. Following this strategy, the formation of dichloramine, the main chloramine species related to NDMA formation, is minimised.

Also, the NDMA formation increases with the disinfectant dose applied. Less than 5 ng/L of NDMA was formed after 24 hours of contact time when pre-formed monochloramine was added at 4 mg/L Cl_2 to a real secondary effluent. Considering that monochloramine dose applied during the production of PRW at the real AWTPs ranges from 2 to 5 mg/L Cl_2, minimal NDMA formation would be expected when using pre-formed monochloramine as the disinfectant agent.

However, the contact time between disinfectant and wastewater is an important parameter to consider when the minimisation of NDMA formation is required during the production of PRW. From the results presented in that work, it can be concluded that a contact time lower than 6 hours is acceptable to keep NDMA formation below the regulation limit when chloramine dose is lower than 10 mg/L Cl_2 independent of the disinfection strategy. Finally, no catalytic effect could be observed from ferric chloride used as a coagulant at the AWTPs on NDMA formation.

The reduction of the contact time between wastewater and chloramines was tested at Bundamba AWTP and the results are presented in next chapter.

6. NDMA FORMATION POTENTIAL ACROSS THE ADVANCED WATER TREATMENT PLANTS

The results obtained at bench scale were used to explain the high concentrations of NDMA generated at the AWTP during the first 16 months of operation (Poussade et al., 2009). Controlling the contact time as well as using pre-formed monochloramine can successfully minimise the formation of NDMA in a full-scale plant application. Contact time at Bundamba 1A AWTP was reduced, with excellent results concerning the reduction of NDMA formation. To reduce the contact time, sodium hypochlorite was added downstream from the coagulation tank, in the UF/MF water, instead of before the coagulation as was initially configured. This operational modification reduced the contact time between the chloramine and the water before reaching the RO membranes from approximately 8-27 hours to 1-3.5 hours depending on the flow used at the plant.

To evaluate the fate of NDMA and NDMA precursors across the AWTPs, grab samples were taken at different points of the treatment train seasonally between February and June 2009. Table 14 shows the sampling dates and average flows at each plant during the selected sampling dates.

Table 14. Average Flow and Sampling Dates for Bundamba 1A and Luggage Point AWTP.

	Bundamba AWTP	Luggage Point AWTP
	Average flow m^3/h	Average flow m^3/h
1st sampling	3/2/2009	18/5/2009
	0.831	1.369
2nd sampling	7/5/2009	15/6/2009
	1.850	1.644

6.1. NDMA and NDMA FP Analysis across Bundamba 1A

The initial disinfection strategy of the initial configuration (configuration 1) at Bundamba 1A AWTP consisted of the addition of both disinfecting reagents (i.e. ammonium sulphate and sodium hypochlorite) before the pre-treatment of the raw water. In April 2009, the disinfection configuration at Bundamba 1A AWTP was modified. The modified configuration (configuration 2) changed the addition point of sodium hypochlorite further in the treatment train to the micro-filtration (MF) feed water. Due to the large size of the tanks used to pre-treat and store the MF feed water at that plant (i.e. 24 ML in total), the contact time between chloramines and wastewater was greatly reduced (from 8-27 hours to 1-3.5 hours) when the disinfection configuration changed. This reduction of the contact time greatly reduced the formation of NDMA across the plant as described in the previous chapter.

Apart from that change to the plant configuration, a second modification of the disinfection strategy was the reduction of chloramine concentration in the water to achieve a safe value of 1-2.5 mg/L at the RO feed (previous concentrations were maintained at 3-5 mg/L at the RO feed water). Figure 26 and Figure 27 show the fate of NDMA and NDMA precursors during the treatment train at Bundamba 1A - configuration 1 and 2, respectively. Each column of the chart corresponds to one specific sampling point. The purple section corresponds to the initial NDMA concentration while the magenta section is the concentration of NDMA precursors present in the water that have not been converted to NDMA during the treatment train, but that could be potentially transformed to NDMA. NDMA in the Reverse Osmosis Concentrate (ROC) was not measured during configuration 1. A standard spike (50 ng/L NDMA) was included in the analysis as a control. This standard was treated as the rest of the samples in terms of extraction, concentration and quantification. No other nitrosamines were measured above the QHFSS detection limit in this sampling campaign (i.e. *N*-nitrosodiethylamine 10 ng/L, *N*-nitrosopiperidine 20 ng/L, *N*-nitrosodibuthylamine 20 ng/L, *N*-nitrosomorpholine 10 ng/L).

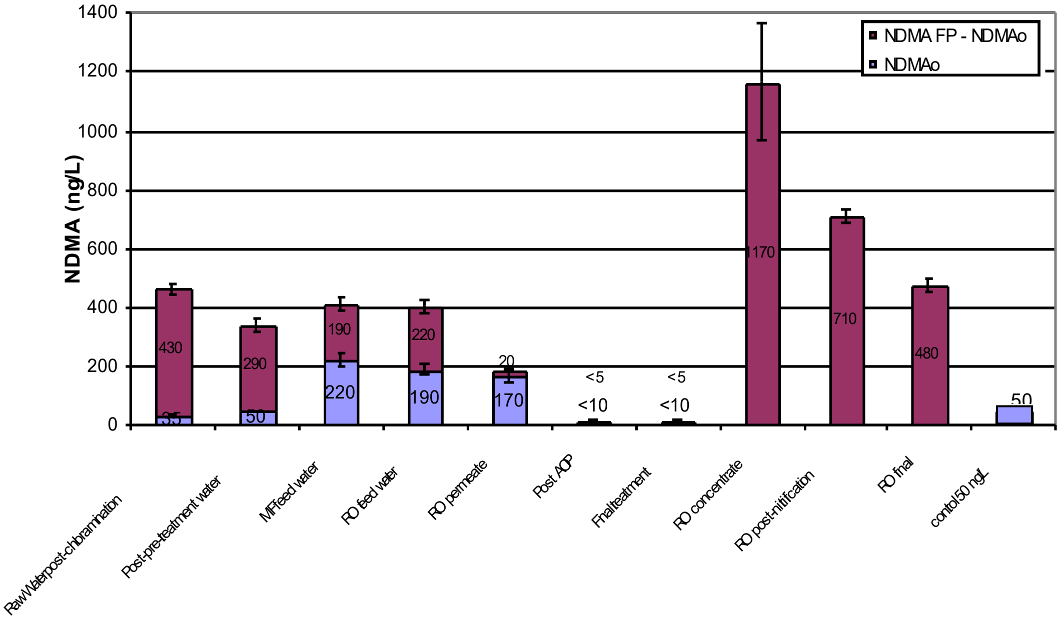


Figure 26. **NDMA and NDMA precursors along the treatment train at Bundamba 1A for configuration 1 (i.e. disinfectant addition point; Raw water). At RO Concentrate, ROC post-nitrification and ROC final, initial NDMA levels were not measured.**

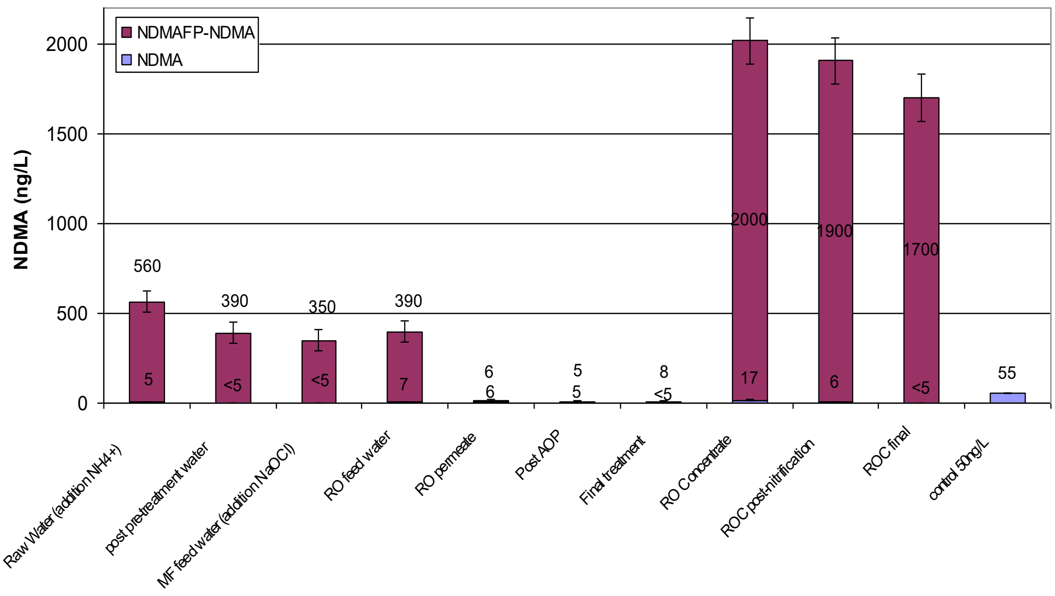


Figure 27. **NDMA and NDMA precursors along the treatment train at Bundamba 1A for configuration 2 (i.e. disinfectant addition point; MF feed water).**

As observed in Figure 26 and Figure 27, initial NDMA levels at the raw water were low during the two sampling dates. However, with configuration 1, NDMA concentration increased, achieving a maximum value of 220 ng/L observed in the MF feed water. This increase was related to the long monochloramine/wastewater contact time (i.e. approximately 8-27 hours, depending on the flow). NDMA rejection by microfiltration or RO membranes was around 10%. As a result, NDMA concentration in the RO permeate was around 170 ng/L.

Contrary to that observation, NDMA concentrations were noticeably decreased when changing the disinfection configuration at Bundamba 1A AWTP. NDMA concentration at Bundamba 1A configuration 2, were never higher than 7 ng/L. The reduction of the NDMA formation across the plant can be explained by the reduction of monochloramine/wastewater contact time when relocating the chlorination dosing point (i.e. approximately 1-3.5 hours depending on the flow). NDMA concentrations lower than the QHFSS reporting limit of 5 ng/L were observed in the final treated water for any configuration.

Figure 26 and Figure 27 also show the NDMA precursors concentration across the treatment plant. As seen in both figures, coagulation has an effect on the removal of NDMA precursors for the specific wastewater used as source water for the recycled water at Bundamba 1A. On the other hand, MF does not seem to have any effect on the removal of NDMA precursors since no statistical difference was found when measuring the concentration of those precursors from the pre-treatment with $FeCl_3$ to the RO membrane. Finally, 98.5 ± 0.5% NDMA precursors removal was observed at the RO membrane. NDMA formation potential at the RO permeate remained constant and lower that the recommended 10 ng/L value until the end of the treatment. These observations are described in Chapter 4.

It is also interesting to mention the good correlation between the total values (i.e. NDMA + NDMA FP) for both sampling dates across the plant. The difference between the values observed at the ROC treatment is explained by the difference between the NDMA formed at the plant depending on the configuration. In configuration 1 the NDMA FP at the ROC was measured as 1,170 ± 200 ng/L. This value matches the 85% concentration factor of the RO feed water (220 ng/L x 6.7 = 1,474 ng/L). However, in configuration 2, the NDMA FP value at the RO feed water corresponding to precursors was higher due to the lower NDMA formation. Thus, the NDMA FP of the ROC should be also higher (390 ng/L x 6.7 = 2,613 ng/L). In fact, the value observed at the ROC at configuration 2 was 2,000 ± 200 ng/L.

The removal of NDMA precursors at the ROC treatment in configuration 1 was much higher than in configuration 2. It should be mentioned again that NDMA formation at configuration 1 was much higher than at configuration 2. The difference observed during the removal of the NDMA precursors at the nitrification-denitrification system at Bundamba 1A AWTP during the two different configurations, suggests that the less biodegradable precursors are more easily converted to NDMA during the chloramination step. This assumption could be explained by the different nature of NDMA precursors observed at the plants. On the one hand, specific pharmaceuticals or industrial compounds can be easily converted to NDMA but they are generally biorecalcitrant. On the other hand, proteins or compounds of biological origin can be further removed by a stronger biological treatment and they are not so easily converted to NDMA. Nevertheless, this is a hypothesis which would need further research to prove, but is out of the scope of the present project.

6.2. NDMA and NDMA FP Analysis across Luggage Point

Figure 29 and Figure 29 show the fate of NDMA and NDMA precursors during the treatment train at Luggage Point AWTP. NDMA concentrations were not obtained for the first sampling due to operational problems related with contamination, thus only some NDMA FP concentration are represented in Figure 29. This contamination problem was quickly identified through the analysis of blanks and control samples performed in each of the analysed batches as suggested in the analytical method (EPA, 2004). No other nitrosamines were measured above the QHFSS detection limit in this sampling campaign (i.e. *N*-nitrosodiethylamine 10 ng/L, *N*-nitrosopiperidine 20 ng/L, *N*-nitrosodibuthylamine 20 ng/L, *N*-nitrosomorpholine 10 ng/L).

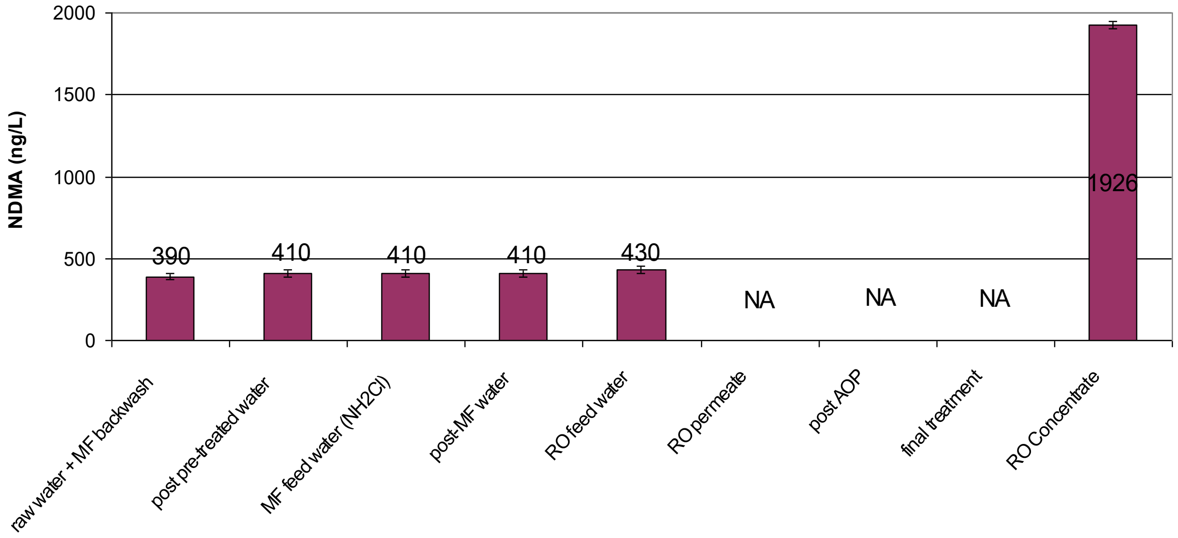


Figure 28. NDMA precursors concentration across the treatment train at Luggage Point AWTP. NA: not analysed.

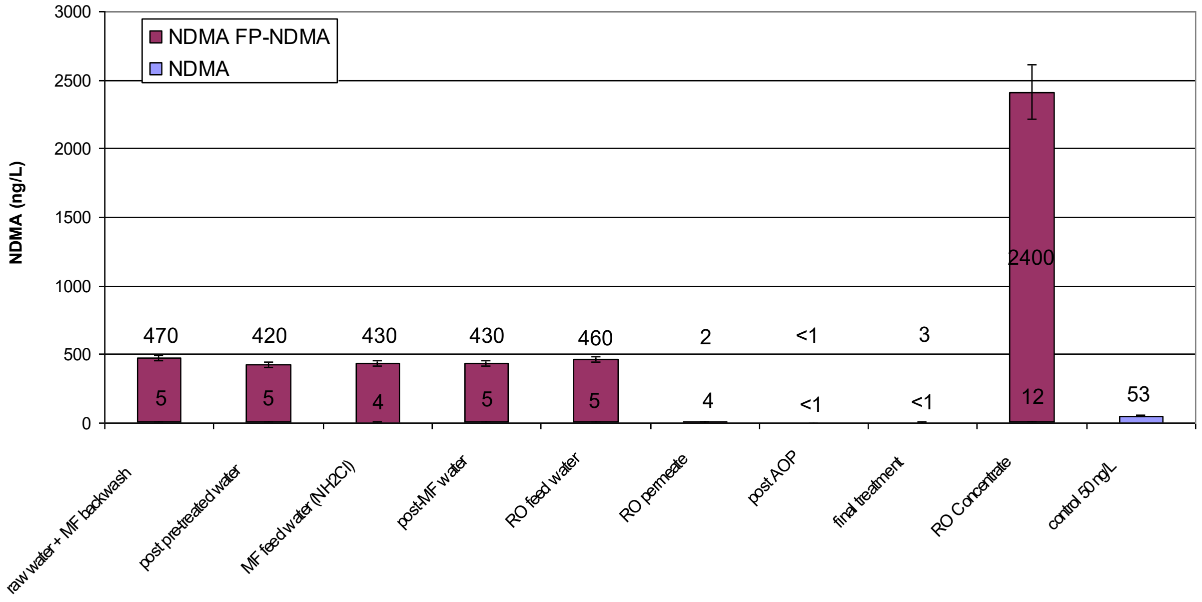


Figure 29. NDMA and NDMA precursors concentration across the treatment train at Luggage Point AWTP. Values lower than 5 ng/L were analysed and confirmed at EnTox by means of GC/HRMS.

It is noteworthy that monochloramine addition strategy can be done in two different ways at Luggage Point AWTP. The chloramine addition point could be placed before or after the pre-treatment. Due to the short contact time of the pre-treatment step at that specific plant, little difference in NDMA formation is expected when the disinfection strategy is changed. Nevertheless, it must be pointed out that, during the two sampling days, monochloramine was added to the pre-treated water which is also the main disinfection configuration at Luggage Point.

Values of NDMA and NDMA FP expressed in Figure 29 were analysed at EnTox by GC/HRMS. The limit of quantification for NDMA with this analytical method is 1 ng/L. As observed in this figure, NDMA concentrations were lower than 5 ng/L during all the treatment train.

Figure 29 and Figure 29 show the NDMA precursors' fate across the plant. Contrary to what was observed at Bundamba 1A AWTP, coagulation did not have any effect on the removal of NDMA precursors. Also, MF did not seem to have any effect on the removal of NDMA precursors. A 99.5 ± 0.5% of NDMA precursors removal was observed by the RO membrane. NDMA formation potential of RO permeate remained constant and lower than the recommended 10 ng/L value until the end of the treatment. A good correlation between the total values (i.e. NDMA + NDMA FP) for both sampling dates across the plant can be also observed in that plant. Finally, it is also important to remark that the NDMA FP measured at the ROC matched the 6.7 concentration factor (460 ng/L x 6.7 = 3,082 ng/L, measured value = 2,400 ± 200 ng/L). Those results were also presented in Chapter 4.

6.3. Conclusions

The decrease of the contact time between wastewater and disinfectant was tested at Bundamba 1A AWTP by changing the plant configuration. This new configuration (i.e. chlorine addition after pre-treatment) reduced the contact time from 20-22 hours to 1-2 hours and dramatically decreased the NDMA formation across that specific plant. With this configuration, NDMA has not been detected at concentrations higher than 10 ng/L in any step of both Bundamba 1A and Luggage Point AWTP. NDMA concentration of final treated water was lower than QHFSS reporting limit (i.e. < 5 ng/L) at both plants.

NDMA precursors were present in the raw water at concentrations up to 560 ± 20 ng/L. At Bundamba 1A AWTP, 30% of NDMA precursors were removed at the pre-treatment of raw wastewater. Contrary to that observation no NDMA precursor removal was observed at any step of Luggage Point AWTP before RO membrane filtration. RO membranes showed a high percentage of NDMA precursor removal at both plants. In general, more than 98.5 ± 0.5% NDMA precursors were effectively removed by RO membranes. Remaining NDMA precursor concentration was lower than 10 ng/L after RO treatment at both plants.

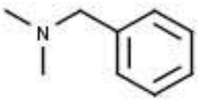
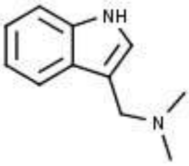
7. NDMA PRECURSORS IN SOUTH EAST QUEENSLAND

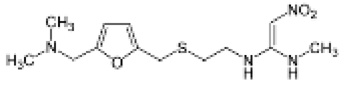
7.1. Database Search on Possible NDMA Precursors in the Environment

In order to investigate possible NDMA precursors present in the secondary effluents of WWTPs that are used as source water to produce PRW, a search of the REAXYS® database was done. The search criteria were based on the substructure $CH_2–N(CH_3)_2$ and the results were limited to those where their occurrence in the environment had been reported in the literature. Table 15 shows the compounds that were found in this search.

Table 15. NDMA Potential Precursors

Source: data from REAXYS® database. Notes: table continues over several pages; NF=not found.

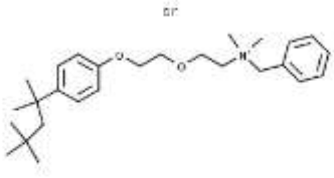
	**Use:** catalyst for the formation of polyurethane foams and epoxy resins **Chemical Name**: benzyl-N,N-dimethylamine **Molecular Formula**: $C_9H_{13}N$ **CAS Registry Number**: 103-83-3 **Molecular Weight**: 135.209 **Linear Structure Formula**: $N(CH_3)2CH_2C_6H_5$ **Type of Substance**: isocyclic **Reported molar yield of conversion:** 61% (Kemper et al., 2010)		**Use**: starting material for tryptophan syntheses **Chemical Name**: 3-(dimethylamino)methyl indole; donaxine; grammine; gramine **Molecular Formula**: $C_{11}H_{14}N_2$ **CAS Registry Number**: 87-52-5 **Molecular Weight**: 174.246 **Linear Structure Formula**: $C_8H_5NHCH_2N(CH_3)2$ **Type of Substance**: heterocyclic **Reported molar yield of conversion:** 2.9% (Sacher, Schmidt et al. 2008)



Use: is a histamine H2-receptor antagonist that inhibits stomach acid production

Chemical Name: Ranital; ranitidine; N-(2-(((5-((dimethylamino)methyl)-2-furanyl)methyl)thio)ethyl)-N'-methyl-2-nitro-1,1-ethenediamine
Molecular Formula: $C_{13}H_{22}N_4O_3S$
CAS Registry Number: 66357-35-5; 82530-72-1
Molecular Weight: 314.409

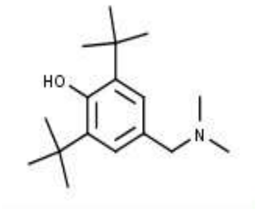
Reported molar yield of conversion: 62.9% (Sacher, Schmidt et al. 2008)



Use: surfactant, antiseptic, and anti-infective properties,

Chemical Name: diisobutylphenoxyethoxyethyl dimethyl benzyl ammonium chloride;
Molecular Formula: $C_{27}H_{42}NO_2$*Cl
CAS Registry Number: 121-54-0
Molecular Weight: 448.089

Reported molar yield of conversion: NF

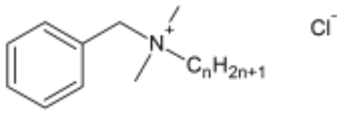


Use: NF

Chemical Name: N,N-dimethyl-3,5-di-tert-butyl-4-hydroxybenzylamine
Molecular Formula: $C_{17}H_{29}NO$
CAS Registry Number: 88-27-7
Molecular Weight: 263.423

Chemical Name: hexadecyldimethylbenzylammonium chloride
Molecular Formula: $C_{25}H_{46}N$*Cl
CAS Registry Number: 122-18-9
Molecular Weight: 396.1

Reported molar yield of conversion: NF



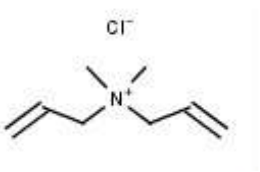
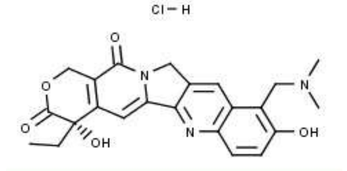
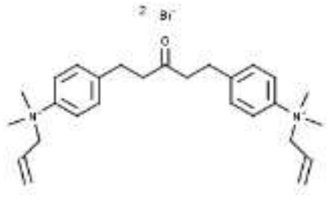
n = 8, 10, 12, 14, 16, 18

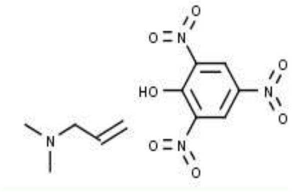
Use: cationic surfactant, belonging to non-oxidizing biocide. antimicrobial

Chemical Name: benzalkonium chloride
Molecular Formula: variable
CAS Registry Number: 139-07-1
Molecular Weight: variable

Chemical Name: N-tetradecyl-N-benzyl-N,N-dimethylammonium chloride
Molecular Formula: $C_{23}H_{42}N$*Cl
CAS Registry Number: 139-08-2
Molecular Weight: 368.046

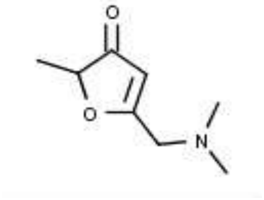
Reported molar yield of conversion: 0.3% (Sacher, Schmidt et al. 2008)

 **Use:** flocculant in water treatment **Chemical Name**: N,N-dimethyl-N,N-diallylammonium chloride. DADMAC **Molecular Formula**: $C_8H_{16}N*Cl$ **CAS Registry Number**: 7398-69-8 **Molecular Weight**: 161.675 **Reported molar yield of conversion:** NF	 **Use:** chemotherapy agent to treat ovarian cancer and lung cancer, as well as other cancer types **Chemical Name**: 4-(S)-10-(dimethylamino)-methyl-4-ethyl-4,9-dihydroxy-H-pyrano[3',4':6,7]indolizino-[1,2-b]quinoline-3,14(4H,12H)dione hydrochloride; topotecan hydrochloride; **Molecular Formula**: $C_{23}H_{23}N_3O_5*ClH$ **CAS Registry Number**: 119413-54-6; 123949-07-5 **Molecular Weight**: 457.914 **Reported molar yield of conversion:** NF
 **Use:** Parasympathetic drugs that inhibit or inactivate the enzyme acetylcholinesterase, allowing prolonged activity of acetylcholine. **Chemical Name**: 1,5-bis(4-allyldimethylammoniumphenyl)pentane-3-one dibromide **Molecular Formula**: $2Br*C_{27}H_{38}N_2O$ **CAS Registry Number**: 402-40-4 **Molecular Weight**: 566.42 **Reported molar yield of conversion:** NF	 **Use:** NF **Chemical Name**: 2-N,N-dimethylaminomethyl-5-methylfuran; **Molecular Formula**: $C_8H_{13}NO$ **CAS Registry Number**: 14496-35-6 **Molecular Weight**: 139.197 **Reported molar yield of conversion:** NF



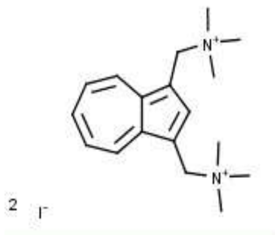
Use: NF

Chemical Name: allyldimethylamine picrate; picric acid
Molecular Formula: $C_5H_{11}N*C_6H_3N_3O_7$
CAS Registry Number: 26128-89-2; 91969-13-0
Molecular Weight: 314.255
Reported molar yield of conversion: NF



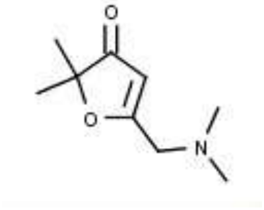
Use: NF

Chemical Name: 5-Dimethylaminomethyl-2-methyl-3-oxo-2,3-dihydrofuran;
Molecular Formula: $C_8H_{13}NO_2$
CAS Registry Number: 1007-46-1; 92096-10-1
Molecular Weight: 155.197
Reported molar yield of conversion: NF



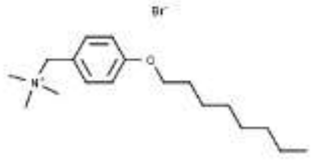
Use: NF

Chemical Name: N,N'-<1,3-Azulenylenbis(methylen)>bis(trimethylammonium)-diiodid; azulene-1,3-bis<(trimethylammonium)methyl> diiodide;
Molecular Formula: $C_{18}H_{28}N_2*2I$
CAS Registry Number: 38303-40-1
Molecular Weight: 526.243
Reported molar yield of conversion: NF



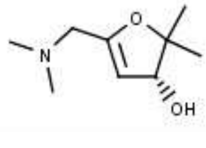
Use: NF

Chemical Name: 5-dimethylaminomethyl-2,2-dimethyl-furan-3-one; 5-Dimethylaminomethyl-2,2-dimethyl-2,3-dihydrofuran-3-on
Molecular Formula: $C_9H_{15}NO_2$
CAS Registry Number: 1009-66-1
Molecular Weight: 169.224
Reported molar yield of conversion: NF



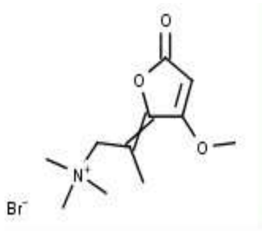
Use: NF

Chemical Name: p-Octyloxybenzyltrimethylammonium bromide; p-Octyloxybenzyltrimethylammonium
Molecular Formula: $Br*C_{18}H_{32}NO$
Molecular Weight: 358.362
Reported molar yield of conversion: NF



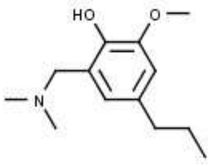
Use: NF

Chemical Name: cis-5-Dimethylaminomethyl-2,2-dimethyl-3-hydroxy-furan
Molecular Formula: $C_9H_{17}NO_2$
Molecular Weight: 171.239
Linear Structure
Reported molar yield of conversion: NF



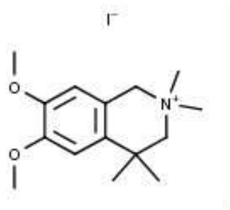
Use: NF

Chemical Name: [2-((Ξ)-3-methoxy-5-oxo-5*H*-[2]furylidene)-propyl]-trimethyl-ammonium; bromide; [2-((Ξ)-3-Methoxy-5-oxo-5*H*-[2]furyliden)-propyl]-trimethyl-ammonium; Bromid
Molecular Formula: $Br*C_{11}H_{18}NO_3$
Molecular Weight: 292.173
Reported molar yield of conversion: NF



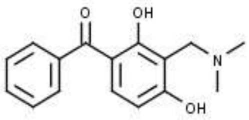
Use: NF

Chemical Name: 2-Dimethylaminomethyl-6-methoxy-4-propyl-phenol; 6-Dimethylaminomethyl-4-propyl-guaiacol
Molecular Formula: $C_{13}H_{21}NO_2$
CAS Registry Number: 54675-70-6
Molecular Weight: 223.315
Reported molar yield of conversion: NF



Use: NF

Chemical Name: 6,7-Dimethoxy-2,2,4,4-tetramethyl-1,2,3,4-tetrahydro-isochinolinium-jodid
Molecular Formula: $C_{15}H_{24}NO_2*I$
CAS Registry Number: 97767-60-7
Molecular Weight: 377.266
Reported molar yield of conversion: NF



Use: NF

Chemical Name: 3-(dimethylaminomethyl)-2,4-dihydroxybenzophenone
Molecular Formula: $C_{16}H_{17}NO_3$
Molecular Weight: 271.316
Reported molar yield of conversion: NF

7.2. Benzalkonium Chloride

Quaternary amines such as benzalkonium chloride (BC) were identified as a possible NDMA precursor (Kemper et al., 2010). It was also identified in our search previously presented. Benzalkonium chloride is a quaternary amine biocide commonly found in consumer products including shampoos, detergents, and fabric softeners. Previous research showed that the concentrations of benzalkonium chloride ranged between 120 and 149 ng/L in three wastewater effluents in the USA (Kemper et al., 2010) and around 30-600 ng/L in Austrian wastewater effluents (Clara et al., 2007). Higher levels up to 36.6 µg/L have been found in surface water samples collected downstream from different wastewater treatment discharges, thus indicating its input and persistence through the wastewater treatment process (Ferrer, 2001). Although the percentage of NDMA conversion has been reported as lower than 1% molar, their presence was measured in SEQ source water for PRW. Table 16 shows the BC concentration measured in the different source waters for PRW and its contribution to NDMA formation potential. Because of the low concentrations of BC encountered in SEQ waters, less than 5 ng/L of NDMA in the NDMA formation potential could be explained by the presence of this compound. Therefore it is not expected that BC is a major contributor to NDMA FP in source waters for PRW.

Table 16. Contribution of Benzalkonium Chloride (BC) to the NDMA Formation Potential in SEQ Source Water for PRW.

	NDMA observed (mg/L)	NDMA FP (ng/L	BC (ng/L)	NDMA expected by BAC conversion (ng/L)	NH_4-N (mg/L)	Nox-N (mg/L)	NO_2-N (mg/L)	NO_3 (mg/L)	TKN (mg/L)	DON (mg/L)	TN (mg/L)	TOC (mg/L)
Bundamba	<5	926	63	**4**	0.3	1.9	0.1	1.8	2.7	2.4	4.6	10.1
Goodna	<5	565	51	**3**	0.3	2.4	0.1	2.3	2.0	1.7	4.3	10.4
Wacol	<5	463	74	**5**	0.0	0.5	0.0	0.5	1.1	1.0	1.6	12.4
Oxley	<5	544	13	**1**	0.1	0.2	0.0	0.2	1.7	1.5	1.9	11.9
Luggage Point	<5	470	59	**4**	0.4	1.6	0.1	1.4	2.1	1.8	3.7	12.3
Gibson Island	<5	442	59	**4**	0.1	0.2	0.0	0.2	1.5	1.5	1.7	12.4
Fairfield	<5	749	27	**2**	47.4	0.4	0.0	0.4	46.1	0.0	46.5	14.4

7.3. Conclusions

A search of the REAXYS® database was undertaken to investigate possible NDMA precursors present in the secondary effluents of WWTP that are used as source water to produce PRW. The search criteria were based on the substructure $CH_2–N(CH_3)_2$ and the results were limited to those where their occurrence in the environment had been reported in the literature. Benzalkonium chloride was identified within this search as a possible source of NDMA during the disinfection of secondary effluents. However, less than 5 ng/L of NDMA FP could be predicted by the concentrations obtained in the wastewater treatment plants used as source water for PRW in SEQ. Therefore, benzalkonium chloride does not contribute significantly to the NDMA FP in that context.

8. NDMA FORMATION POTENTIAL AT SOUTH CABOOLTURE WATER RECLAMATION PLANT

In an attempt to understand the NDMA and NDMA precursors in other reclamation plants apart from the ones within the Western Corridor Recycled Water Scheme, the South Caboolture Water Reclamation Plant was monitored in October/November 2009. This study was performed in collaboration with Dr Julien Reungoat and the UWSRA Enhanced Treatment Project.

The South Caboolture Water Reclamation Plant was designed to reduce riverine pollution from the 40,000 population equivalent wastewater treatment plant and to provide recycled water to industry and community consumers. Whilst the plant provides water for non-potable applications, it has been designed to meet drinking water standards. The treatment process, detailed in Figure 30, incorporates biological denitrification, pre-ozonation, coagulation/flocculation/dissolved air flotation-sand filtration (DAFF), main ozonation, biological activated carbon filtration and final ozonation for disinfection. The activated carbon was renewed in March 2008 after nine years of service; its adsorption capacity was assumed not to be exhausted at the time sampling took place, four months later. Van Leeuwen et al. (2003) published more details on the process and its performances. For this specific study, two sets of 24-hour composite samples were collected across the plant (sampling points S1 to S7) and from the effluents of pilot-scale slow biofilters connected to the full-scale process (Figure 30 and Table 17). A fraction of the sample was analysed immediately to quantify NDMA levels across the plant. Another fraction was used to determine the NDMA formation potential by adding chloramine to the samples and then leaving it to react for seven days.

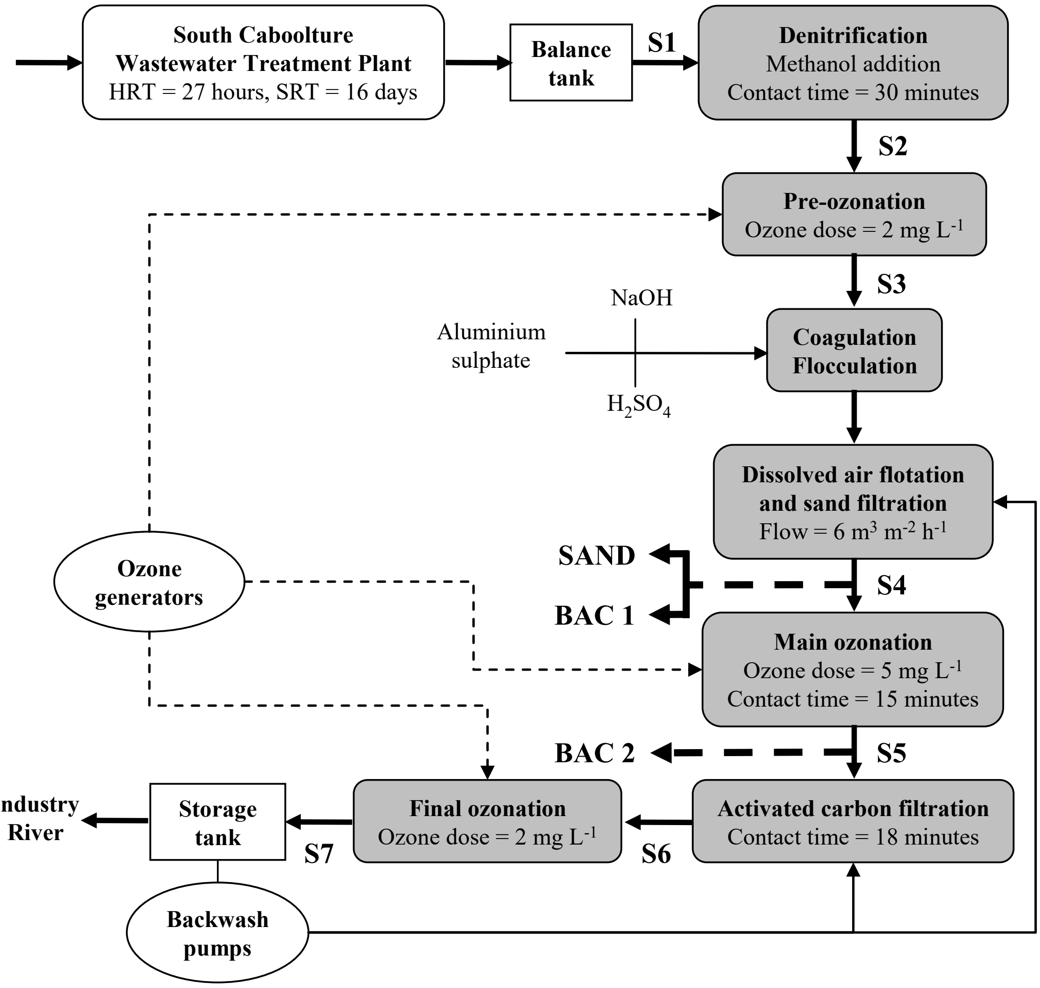


Figure 30. South Caboolture Water Reclamation Plant.

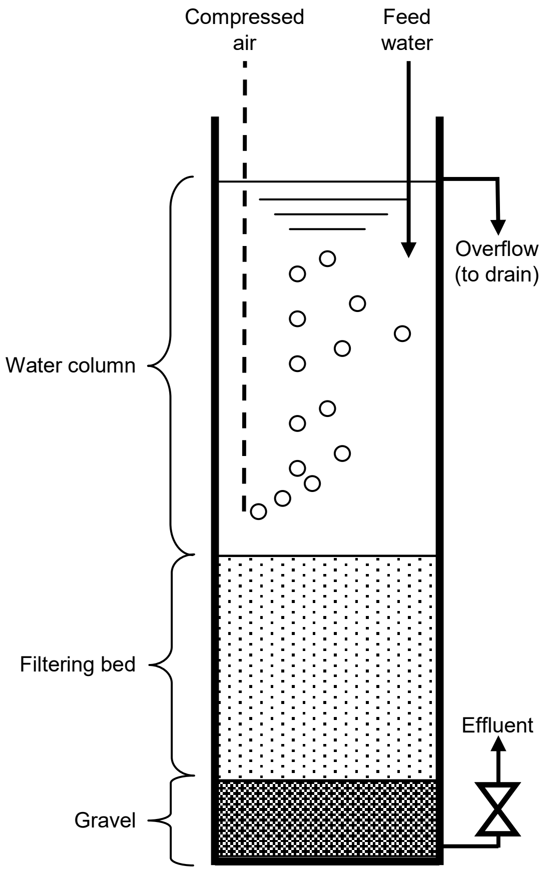


Figure 31. Pilot-Scale Biofilters.

Table 17. Pilot-Scale Biofilters Characteristics.

Filter	Media	Bed (cm)	Feed Water	EBCT (min)
SAND	Sand	80 ± 1	Ozonated (S5)	60 ± 5
BAC 1	Granular Activated Carbon	80 ± 1	Filtered, non-ozonated (S4)	60 ± 5
BAC 2	Granular Activated Carbon	80 ± 1	Ozonated (S5)	60 ± 5

The results (Figure 33) show that NDMA levels remain very low across the treatment train, below 5 ng/L. The NDMA formation potential is 423±55 ng/L in the raw water (secondary effluent from the wastewater treatment plant) and remains the same after denitrification. Pre-ozonation and DAFF reduced the NDMA FP by around 20% each, bringing the level down to 260±31 ng/L. The main ozonation was the most effective step, reducing the NDMA FP by another 66% to levels below 100 ng/L (40% removal of initial NDMA FP). The activated carbon filter and the final ozonation further reduced the NDMA FP by 35% and 11% respectively. The NDMA FP in the final effluent was 51±8 ng/L.

The BAC 1 filter was able to reduce the NDMA FP by more than 80% (50% of initial NDMA FP), which is better than the ozonation alone, and the effluent level was 48±6 ng/L, similar to the effluent of the main plant. The sand filter was not able to reduce the NDMA FP after ozonation but the BAC 2 filter decreased NDMA FP by 56%, down to 39±12 ng/L, which is slightly better than BAC 1 filter but still a very similar level.

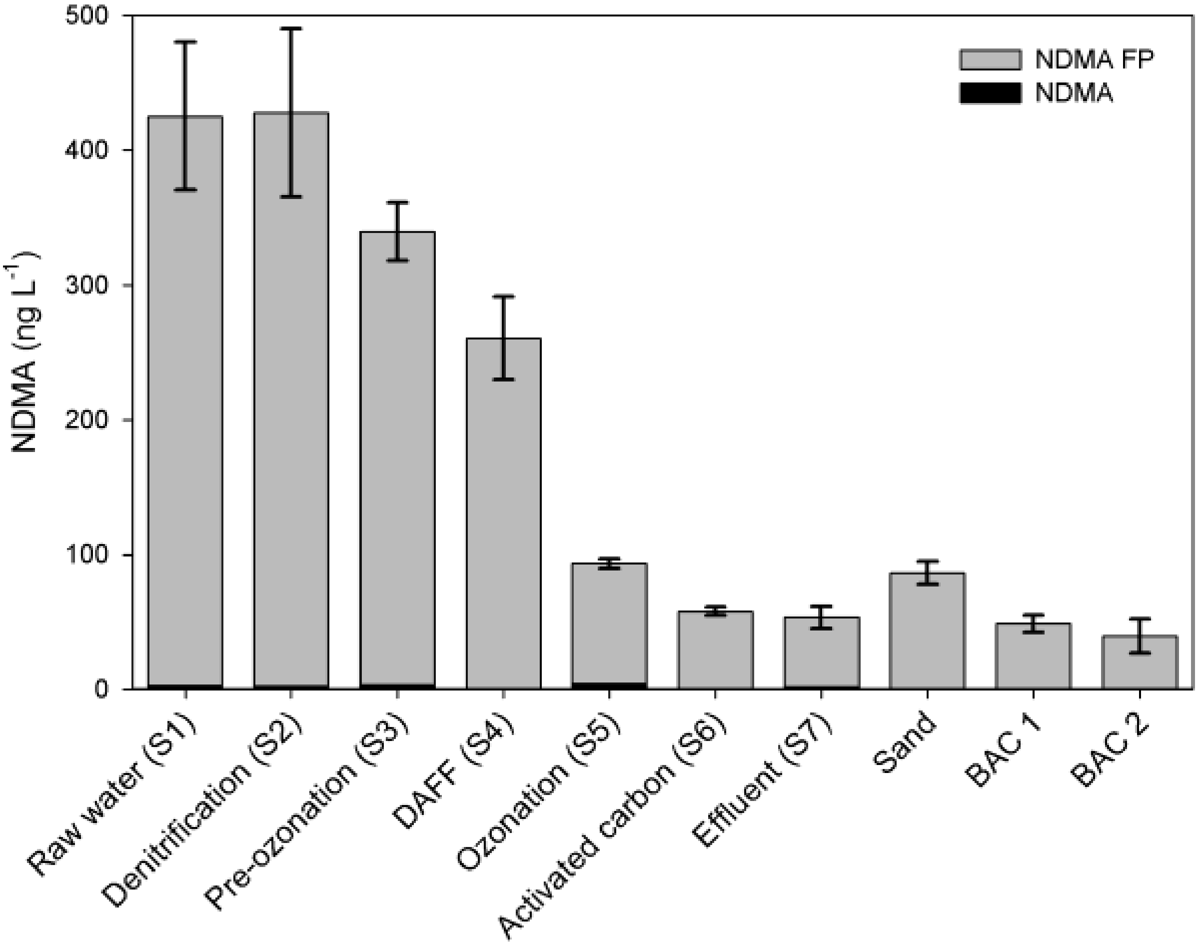


Figure 32. NDMA Levels and NDMA Formation Potential Across South Caboolture Water Reclamation Plant and Pilot-Scale Biofilters.

8.1. Conclusions

NDMA concentration and NDMA formation potential were measured across the South Caboolture Water Reclamation Plant. Results show that NDMA is always below 5 ng/L across that reclamation plant. On the other hand, BAC filtration seems to be a key step for NDMA precursor removal in the treatment train since 80% NDMA FP can be eliminated at the BAC stage even when the influent of this process is not ozonised-water. 20% and 18% of NDMA FP is removed at the pre-ozonation and dissolved air flotation steps, respectively. NDMA precursors were removed by 66% by ozone when this process was included in the treatment train. NDMA and NDMA FP in the final effluent are around 2 ng/L and 50 ng/L, respectively.

LIST OF PUBLICATIONS

The following publications have been delivered from this research:

Maria José Farré, Katrin Doederer, Laurence Hearn, Yvan Poussade, Jurg Keller and Wolfgang Gernjak. Understanding the parameters affecting NDMA formation at Advanced Water Treatment Plants. **Journal of Hazardous Materials,** 185 (2011), 1575-1581.

Maria Jose Farré, Jurg Keller, Neil Holling, Yvan Poussade and Wolfgang Gernjak. Occurrence of NDMA precursors in wastewater treatment plant effluent and their fate during UF-RO membrane treatment. Accepted in **Water Science and Technology** 63 (4) (2011) 605-612.

Maria José Farré, Howard S. Weinberg, Bonny Lyon, Yvan Poussade, Jurg Keller and Wolfgang Gernjak. Fate of disinfection by-products and their precursors across reverse osmosis membranes when producing high quality recycled water. Platform presentation.**2010 Water Quality Conference and Exposition** in November 2010, Georgia, USA.

Katrin Döderer, Laurence Hearn, Wolfgang Gernjak, Jurg Keller, Yvan Poussade, and Maria José Farré. Fate of NDMA and its precursors across UF/RO membranes during the production of high quality recycled water. Platform presentation. **Membranes in the Production of Drinking and Industrial Water** in June 2010, Trondheim, Norway.

Maria Jose Farré, Jurg Keller, Neil Holling and Wolfgang Gernjak. Evaluation of the NDMA Potential of Water Sources for Purified Recycled Water in South East Queensland. Platform presentation. **7th IWA World Congress on Water Reclamation and Reuse**, September 2009, Brisbane, Australia.

Maria José Farré, Katrin Doederer, Laurence Hearn, Neil Holling, Jochen Mueller, Jurg Keller, Yvan Poussade, Cedric Robillot and Wolfgnag Gernjak. Minimising the NDMA Formation during the Production of Purified Recycled Water. **UWSRA Science Forum 2010**.

Maria Jose Farre Olalla, Neil Holling, Jurg Keller and Wolfgnag Gernjak. Occurrence of NDMA precursors in wastewater source for purified recycled water. **UWSRA Science Forum 2010.**

GLOSSARY

AC	Activated Carbon
AOP	Advanced Oxidation Process
AWMC	Advanced Water Management Centre
AWTP	Advanced Water Treatment Plants
BAC	Biological activated carbon
BC	Benzalkonium chloride
CAS	Chemical Abstract Service
DBP	Disinfection By-Products
DCA	Dichloramine
DCMA	Dimethylchloramine
DMA	Dimethylamine
DON	Dissolved Organic Nitrogen
DPD	N-N-diethyl-p-phenylenediamine
EEO	Electrical Energy per Order
EPA	Environmental Protection Agency
FP	Formation Potential
LOR	Limit of Reporting
MCA	Monochloramine
MF	Micro Filtration
MWCO	Molecular weight cut off
NDMA	N-nitrosodimethylamine
NOM	Natural Organic Matter
NPOC	Non-purgable Organic Carbon
PRW	Purified Recycled Water
QHFSS	Queensland Health Forensic and Scientific Services
RO	Reverse Osmosis
ROC	Reverse Osmosis Concentrate
SEQ	South East Queensland
SPE	Solid Phase Extraction
STP	Sewage Treatment Plant
TMA	Trimethylamine
UDMH	Unsymmetrical dimethylhydrazine
UF	Ultrafiltration
UV	Ultraviolet
UWSRA	Urban Water Security Research Alliance
WWTP	Wastewater Treatment Plant
WTP	Water Treatment Plant
WCRWP	Western Corridor Recycled Water Project

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