



Special Publications

Disinfection By-products in Drinking Water

Edited by K Clive Thompson, Simon Gillespie
and Emma H Goslan



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Preface

The international conference, Disinfection By-products in Drinking Water (DBP2014) was held between October 27th and 29th, 2014 in the Municipal Hall, Mülheim an der Ruhr, alongside the banks of the River Ruhr. It brought together international experts on disinfection by-products (DBPs) to review and debate recent developments and current thinking in the field. It was attended by delegates from around 20 different countries from Europe, Asia, North America and Australasia.

The conference focussed on the challenges faced by water utilities and regulatory authorities around the world in balancing the risk of microbial contamination against the potential health risks associated with DBPs. It brought delegates up to date on the latest technology for monitoring DBPs, on treatment processes for minimising their formation, on research into the health and toxicological concerns of DBPs, and on the potential direction of future regulation.

Chlorination was first used to disinfect public drinking water supplies in the UK in Maidstone as early as 1897 and in the USA in 1908, with ozone and other disinfectants introduced in Europe around the same time. However it wasn't until the early 1970s that Johannes Rook in Rotterdam and Tom Bellar in Ohio independently discovered higher levels of chloroform in treated drinking water than in the source water, and the whole field of disinfection by-product research was born.

Whether it is in the production of safe, clean drinking water, or the management of swimming pools in communal recreational facilities, the disinfection of water to protect against microbial contamination carries the risk of producing harmful DBPs. Chlorination of the naturally occurring organic matter in water results in a wide range of toxic halogenated organic compounds. Carcinogenic nitrosamines are a potential by-product of chloramination, and ozonation oxidises bromide to bromate as well as producing a plethora of small organic molecules. There are at least 600 known disinfection by-products, and the count continues to rise.

Worldwide, regulation governing the control of DBPs has become more stringent. Most countries in the developed world have set regulatory standards for trihalomethanes and bromate. In the USA, the EPA additionally sets standards for haloacetic acids and chlorite. In Europe the disinfection by-product rule of the 1998 EU Drinking Water Directive requires water utilities to “design, operate and maintain the disinfection process so as to keep disinfection by-products as low as possible without compromising the effectiveness of the disinfection; and to verify the effectiveness of the disinfection process.” Water treatment works designed in Europe since January 2010 should have taken the disinfection by-product rule into account and companies should have included this requirement in their regulatory risk assessments. As our understanding of DBPs and their associated health effects increases, so to do the challenges of ensuring that they are effectively regulated, monitored and minimised.

The DBP2014 conference was a cooperative venture organised by IWW Water Centre (DE), RSC (UK) and SCI (UK). This book represents the proceedings of that conference, and we, the editors, hope that you enjoy reading it.

Simon Gillespie
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Disinfection By-products Formation

THE NEXT GENERATION OF DRINKING WATER DISINFECTION BY-PRODUCTS: OCCURRENCE, FORMATION, TOXICITY, AND NEW LINKS WITH HUMAN EPIDEMIOLOGY

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1 INTRODUCTION

Drinking water disinfection by-products (DBPs) are an unintended consequence of using disinfectants to kill harmful pathogens in drinking water. They are formed primarily by the reaction of disinfectants with natural organic matter (NOM) and bromide or iodide¹, but can also be formed from pollutants, such as pesticides, pharmaceuticals, antibacterial agents, estrogens, textile dyes, bisphenol A, parabens, surfactants, and algal toxins²⁻⁴. Popular disinfectants for drinking water include chlorine, chloramines, ozone, chlorine dioxide, and UV.

Eleven DBPs are regulated in the United States⁵, but more than 600 have been identified¹. And, despite this large number of DBPs identified, more than 50% of the halogenated material formed in chlorinated drinking water is still unknown, as well as the toxicological risk that it poses to human health^{2, 6}.

Adverse health concerns include bladder cancer, miscarriage, and birth defects^{1, 7-12}. While bladder cancer is the primary cancer observed in humans, none of the 11 regulated DBPs cause bladder cancer in animals; consequently, many researchers believe that the regulations are not adequately controlling for these effects in humans. As a result, there is intensive research in emerging, unregulated DBPs. These include iodo-trihalomethanes, iodo-acids, haloamides, halonitromethanes, halofuranones, haloacetonitriles, haloacetaldehydes, nitrosamines, and halobenzoquinones. Many of these unregulated DBPs are more genotoxic or cytotoxic than those currently regulated^{1, 13-15}. For example, iodoacetic acid is the most genotoxic DBP identified to-date, and is 2x more genotoxic than bromoacetic acid¹. Iodoacetic acid was also recently shown to be tumorigenic in mice¹⁶.

Nitrogen-containing DBPs (N-DBPs) have become a major focus because they are generally more toxic than DBPs that do not contain nitrogen. For example, many nitrosamines are known to be carcinogens¹. Nitrosamines were on the U.S.

Environmental Protection Agency's (EPA's) Unregulated Contaminant Monitoring Rule¹⁷, and are currently being considered for regulation in the United States.

DBPs can also form in disinfected swimming pool water¹⁸⁻²². Some swimming pool DBPs are the same as those found in drinking water, but some are different, due to the additional human precursors that can be present in pools (e.g., urine, sweat, hair, sunscreens, lotions, personal care products etc.)^{22, 23}. For example, trichloramine is a common DBP found in chlorinated swimming pools, and it is formed by the reaction of urea (from urine or sweat) with chlorine²⁴. While trichloramine is produced in the water, it is quickly transported to the air phase above, due to its high Henry's Law constant. Trichloramine is suspected as the causal agent in the increased asthma in epidemiologic studies of elite swimmers^{25, 26}. One study has also shown increased incidence of bladder cancer with heavy exposure from swimming pools²⁷.

Newer potential health concerns include severe skin rashes, and respiratory and digestive issues resulting from exposure to chloraminated drinking water. However, there has not yet been a controlled scientific study to examine these issues. Chloramination has become a popular disinfectant in the U.S., due to tightened DBP regulations⁵, and is also used in other countries, including the UK and Australia. The use of chloramines can result in ~90% reduction in the levels of regulated trihalomethanes (THMs) and haloacetic acids (HAAs) compared to chlorination, and it also allows longer residual disinfection in distribution systems.

DBP formation depends on the type of disinfectant, dose, and the type of organic matter or other precursors present in the water^{1, 28-31}. Formation mechanisms for several DBPs and DBP classes have been investigated, including iodo-DBPs, halonitromethanes, nitrosamines, haloamides, halopyroles, and halobenzoquinones. A review of their formation follows.

2 IODO-DBPs

Iodo-DBPs identified to-date include iodo-THMs (dichloroiodomethane, bromochloroiodomethane, dibromoiodomethane, chlorodiiodomethane, bromodiiodomethane, and iodoform); iodo-acids (iodoacetic acid, bromoiodoacetic acid, chloroiodoacetic acid, diiodoacetic acid, (*Z*)-3-bromo-3-iodopropenoic acid, (*E*)-3-bromo-3-iodopropenoic acid, and (*E*)-2-iodo-3-methylbutenedioic acid)^{6, 32-35}; iodo-amides (bromoiodoacetamide and chloroiodoacetamide)^{1, 14, 36}; and the recently reported iodoacetaldehyde^{37, 38}.

Iodo-THMs were the first iodo-DBPs to be discovered, back in the mid-1970s,³⁹ and have been measured in drinking waters treated with chlorination or chloramination^{6, 31, 40-44}. Highest levels are consistently observed in chloraminated water (up to 15 µg/L), and total iodo-THM levels can be as much as 81% of the regulated THMs⁶. Point-of-use treatment with iodine⁴⁵, and chlorination or chloramination of hydraulic fracturing (HF) wastewater can also produce iodo-THMs⁴⁶.

Iodo-acids, which are the most genotoxic of the iodo-DBPs^{35, 47}, were first identified in a U.S. Nationwide Occurrence Study^{6, 41, 47}, and levels up to 1.7 µg/L were reported in a 23 city survey of chloraminated and chlorinated drinking water from the U.S. and

Canada³⁵. Chlorine dioxide was also reported to form iodoacetic acid when reacted with source waters⁴⁸, and iodo-acids were also tentatively identified in simulated drinking waters treated with chlorine, monochloramine, and chlorine-chloramine³². Finally, iodoacetic acid and chloroacetic acid can form when chlorinated tap water is allowed to react with iodized table salt (containing potassium iodide) or with potassium iodide itself³². The rank order for genotoxicity is iodoacetic acid >> diiodoacetic acid > bromoiodoacetic acid > (*E*)-2-iodo-3-methylbutenedioic acid > (*E*)-3-bromo-3-iodopropenoic acid > (*E*)-3-bromo-2-iodopropenoic acid. Iodoacetic acid is also teratogenic, producing developmental effects (neural tube closures) in mouse embryos, at low nM levels similar to levels that induce DNA damage in mammalian cells^{49, 50}. Iodoacetic acid is also tumorigenic in mice¹⁶.

Iodoacetamides—bromoiodoacetamide and chloroiodoacetamide—have been identified in drinking water treated with chloramines or chlorine. Bromoiodoacetamide was originally found in chloraminated drinking water from several cities in the U.S.¹⁴; later, both bromoiodoacetamide and chloroiodoacetamide were found in chloraminated and chlorinated drinking water from three provinces in China³⁶. Haloacetamides can form by hydrolysis of the corresponding haloacetoneitriles^{51, 52}, or by an independent pathway⁵³; they are preferentially formed with chloramination vs. chlorination⁵³. Both of these iodoacetamides are highly cytotoxic and genotoxic in mammalian cells¹⁴. As a class, haloamides are the most cytotoxic of all DBP classes measured to-date, and they are the second-most genotoxic DBP class, close behind the halonitriles.

Chloramination increases the formation of all of these iodo-DBPs. In practice, drinking water plants can add preformed monochloramine (NH₂Cl, formed by the reaction of chlorine and ammonia), but generally chlorine is added first and allowed to react for a certain amount of time (free chlorine contact time) before the ammonia is added, to enable a higher level of microbial inactivation. Most research shows that a lower free chlorine contact time (increased NH₂Cl contact time) increases the formation of iodo-DBPs^{6, 29, 32, 35, 54, 55}, consistent with a mechanism proposed by Bichsel and von Gunten, which involves competing mechanisms to form iodate and organic iodo-DBPs^{36, 57}. Reaction of aqueous chlorine (HOCl) with iodide initially forms hypoiodous acid (HOI), which then reacts quickly with HOCl to form iodite and iodate. The corresponding reactions to form organic iodo-DBPs (e.g., iodo-THMs and iodo-acids) are much slower, favoring the formation of iodate instead of organic iodo-DBPs. On the other hand, reactions of NH₂Cl with HOI to form iodite and iodate are much slower, such that NH₂Cl favors the formation of organic iodo-DBPs over iodate. New research indicates that ozone pretreatment at lower pH might be used to minimize iodo-DBP (and bromate) formation by selectively oxidizing iodide to iodate⁵⁸.

Natural iodide is believed to be the major source of iodine in the formation of iodo-DBPs, but, new research has revealed that compounds used for medical imaging (i.e., iodinated X-ray contrast media (ICM)) can also be a source of iodine⁵⁹⁻⁶¹. ICM are excreted within ~24 h after medical imaging, are stable during wastewater treatment, and can be present up to 100 µg/L in rivers and creeks⁶² and up to 2.7 µg/L in drinking water reservoirs⁵⁹. These ICM structures have 3 iodines attached to a benzene ring that also contains 3 amide side chains, and can react with chlorine or chloramine to form iodo-THMs and iodo-acids. NOM and pH can significantly impact their formation, and OCl⁻ is hypothesized as the reacting disinfectant species. Moreover, new controlled laboratory studies indicate that iodo-THMs are favored at low chlorine doses⁶¹.

Iopamidol appears to be more reactive than other ICM investigated (e.g., iopromide, iohexol, iomeprol, diatrizoate, hiztodenz, and iodixanol)⁵⁹⁻⁶¹. New mechanistic research using liquid chromatography (LC)-high resolution MS/MS and nuclear magnetic resonance (NMR) spectroscopy has revealed the initial points of reaction on the iopamidol structure, along with the initial high molecular weight DBPs formed⁶⁰. Proposed reaction mechanisms involve cleavage of one of side chains, substitution of chlorine for iodine on the benzene ring, amide hydrolysis, cleavage of the other side chains, and oxidation of NH₂ to NO₂. Structures for 19 high molecular weight DBPs were proposed.

3 NITROSAMINES

N-Nitrosodimethylamine (NDMA) was discovered to be a DBP in 2002^{63, 64}, and created significant interest due to its potent carcinogenicity¹. NDMA was initially discovered in chlorinated drinking waters from Ontario, Canada⁶⁵, and was later found in many other locations^{63, 64, 66}. Other nitrosamines have also been found as DBPs, including *N*-nitrosopiperidine, *N*-nitrosodiphenylamine, *N*-nitrosopyrrolidine, and *N*-nitrosomorpholine^{67, 68}. A new total nitrosamine (TONO) assay indicates that the nitrosamines identified so far only represent 5-10% of the total nitrosamines formed in drinking water and recreational waters^{69, 70}. Tobacco-specific nitrosamines—4-(methylnitrosamino)-1-(3-pyridyl)-1-butanone and 4-(methylnitrosamino)-1-(3-pyridyl)-1-butanol—were also recently discovered as chloramination DBPs⁷¹.

California regulates NDMA at 10 ng/L⁷² and Ontario, Canada at 9 ng/L⁷³. A Canadian national drinking water guideline was also recently established, limiting NDMA to 40 ng/L in drinking water⁷⁴, and the U.S. EPA is considering its regulation. NDMA, *N*-nitrosodiethylamine, *N*-nitrosodibutylamine, *N*-nitrosodipropylamine, *N*-nitrosomethylethylamine, and *N*-nitrosopyrrolidine were measured in drinking waters across the U.S. due to inclusion on the U.S. EPA's second Unregulated Contaminants Monitoring Rule (UCMR-2). National occurrence data revealed a maximum level of 530 ng/L for NDMA in chloraminated drinking water¹⁷, which surpassed the previous maximum (180 ng/L) observed in Canadian chloraminated drinking water⁶⁷. NDMA and 4 other nitrosamines are also on the U.S. EPA's Contaminant Candidate List (CCL-3), a priority list of drinking water contaminants⁷⁵.

NDMA is generally maximized with chloramination. Early research indicated that the nitrogen in monochloramine (NH₂Cl) was incorporated into the structure of NDMA⁶³, and subsequent research revealed that it was actually dichloramine (NHCl₂), which always coexists with NH₂Cl, that was the primary reactant⁷⁶. Nitrite can also be a nitrosamine precursor in reactions with chlorine^{77, 78}. NDMA can also sometimes form in chlorination reactions when nitrogen precursors are present (e.g., natural ammonia in source waters or when nitrogen-containing coagulants or ion-exchange resins are used in water treatment)⁷⁹⁻⁸². Consumer products, including shampoos, laundry detergents, dish washing liquids, and fabric softeners, can also be precursors, with quaternary amine polymers surprisingly more reactive than the monomers⁸³. Similarly, diallyldimethylammonium chloride (DADMAC) polymers, which are used as coagulants in drinking water treatment are more reactive than the monomers^{82, 84, 85}. Amino acids, hydrophilic/low molecular weight dissolved organic nitrogen, amine-based

pharmaceuticals, and diphenylamine can also serve as NDMA precursors⁸⁶. The Lifestraw®, a point-of-use device that uses I₃⁻ complexed resins with an activated carbon filter, can also produce NDMA, but levels rapidly decline to low ng/L levels after the first few flushes of water⁴⁵. An excellent review was recently published on the formation, precursors, control, and occurrence of nitrosamines in drinking water⁸⁷.

NDMA was recently identified in ozonated drinking water from Germany, which was a surprise because it had not been found previously in drinking water treated with ozone⁸⁸. A fungicide, tolylfluanide, containing a dimethylamine group in its structure, was found to be the precursor⁹¹, and trace levels of bromide can catalyze its formation⁸⁹. In addition, dithiocarbamate pesticides can react with NH₂Cl, O₃, Cl₂, or ClO₂ to form NDMA⁹⁰. Finally for the tobacco-specific nitrosamines just identified in 2014, tobacco alkaloids, including nicotine, nornicotine, and anabasine were determined to be precursors to their formation in chloraminated drinking water⁷¹.

4 HALOAMIDES

Haloamides can form in reactions with either chlorine or chloramine,^{6, 14, 41, 91, 92} but preferentially form with monochloramine⁵³. The mechanism can involve hydrolysis of the corresponding haloacetonitriles^{51, 52}, or reaction of organic nitrogen precursors with NH₂Cl⁵³. ¹⁵N-labeled NH₂Cl studies showed an initial rapid formation of both dichloroacetamide and dichloroacetonitrile, with the nitrogen originating from organic nitrogen precursors. Reactions of asparagine as a model precursor also suggested that dichloroacetamide can be formed without a dichloroacetonitrile intermediate, and humic substances were more potent precursors for dichloroacetamide formation, while wastewater effluents and algal substances were more potent precursors for dichloroacetonitrile formation⁵³. Therefore, independent mechanisms are also involved in the formation of haloacetamides, in addition to the hydrolysis of the haloacetonitriles. Amino acids, including aspartic acid, histidine, tyrosine, tryptophan, glutamine, asparagine, and phenylalanine, can also react with chlorine to form dichloroacetamide⁹³.

5 HALONITROMETHANES

Chloropicrin (trichloronitromethane) is the most commonly measured halonitromethanes, but a total of 9 have been identified in drinking water. Brominated nitromethanes show significant toxicity³⁴, with a cytotoxicity and genotoxicity greater than most DBPs currently regulated, and they have been found at levels up to 3 µg/L^{6, 34, 41, 94, 95}. Halonitromethanes are also mutagenic in *Salmonella*⁹⁶, with potencies greater than that of the regulated THMs⁹⁷. The greater cytotoxic and mutagenic activities of the halonitromethanes is likely due to the greater intrinsic reactivity conferred by the nitro group⁹⁷. Pre-ozonation used prior to chlorination or chloramination vastly increases the formation of bromonitromethanes^{6, 41}. Nitrite can also play a role in the formation of the nitro group in these DBPs⁹⁸.

Trihalonitromethanes (including tribromo-, bromodichloro-, and chlorodibromonitromethane) require particular analytical conditions for their analysis because they can thermally decompose with commonly used injection port temperatures

during gas chromatography (GC)-electron capture detection (ECD) or GC/mass spectrometry (MS) analysis⁹¹.

6 HALOPYRROLES

2,3,5-Tribromopyrrole was first reported as a DBP in 2003, and was found in finished drinking water treated with pre-chlorination followed by treatment with combined ClO₂-Cl₂ or ClO₂-NH₂Cl⁹⁹. This identification resulted from the first study of chlorine dioxide DBPs formed under high bromide/iodide conditions. 2,3,5-Tribromopyrrole is 8x more cytotoxic than dibromoacetic acid (a regulated DBP) and has about the same genotoxic potency as MX⁹⁹, a carcinogen¹⁰⁰. Tribromopyrrole forms primarily from humic acid (vs. fulvic acid), and it is interesting that a soil humic model proposed by Schulten and Schnitzer¹⁰¹ includes a pyrrole group in its structure¹⁰¹. In none of the samplings from this research was tribromopyrrole found in waters treated with chlorine only, therefore, the combination of chlorine dioxide and chlorine (or chloramines) may be necessary for its formation, or chloramination may also be important in its formation. New research also shows that halopyrroles can form as DBPs in chlorinated saline wastewater effluents¹⁰². Tri- and tetra-halopyrroles were identified, including brominated, chlorinated, and iodinated analogues.

7 HALOBENZOQUINONES

Four halobenzoquinones (HBQs)—2,6-dichlorobenzoquinone, 2,6-dibromobenzoquinone, 2,6-dichloro-3-methylbenzoquinone, and 2,3,6-trichlorobenzoquinone—were recently identified as new DBPs in drinking water treated with chlorine, chloramines, chlorine-chloramines, ozone-chloramines, and chloramines-UV^{103, 104}. Levels ranged up to 275 ng/L. 2,6-Dichlorobenzoquinone, 2,3,6-Trichloro-1,4-benzoquinone, 2,3-dibromo-5,6-dimethyl-1,4-benzoquinone, and 2,6-dibromo-1,4-benzoquinone were also recently identified in chlorinated swimming pools¹⁰⁵, and subsequent research revealed the formation of hydroxylated HBQs with UV treatment¹⁰⁶. Haloquinones are predicted to be highly toxic, with the chronic lowest observed adverse effect levels (LOAELs) of haloquinones predicted at low µg/kg body weight per day, which is 1000x lower than most regulated DBPs, except bromate. Controlled laboratory studies using phenol as a precursor showed highest levels of 2,6-dichlorobenzoquinone with chlorination, with highest levels of 2,6-dibromobenzoquinone resulting from preozonation in the presence of bromide. In the formation of HBQs in swimming pools, UV filters and other aromatic compounds found in lotions and sunscreens were found to be important precursors¹⁰⁵.

8 NEW LINKS WITH HUMAN EPIDEMIOLOGY

In 2012, for the first time, chemistry and toxicology and epidemiology were combined for a multicountry epidemiology study of drinking water and adverse birth outcomes in Europe. In this study called “HiWATE” (Health Impacts of Long-Term Exposure to Disinfection Byproducts in Drinking Water), Jeong et al. published an integrated study of chemistry (target DBP quantification and comprehensive identification) with toxicology

(in vitro mammalian cell toxicity of complex drinking water samples) and epidemiology findings¹⁰⁷. In total, 11 drinking water samples were collected from five European countries, each corresponding to a separate epidemiology study for the HiWATE program. More than 90 DBPs were identified, and THMs and HAAs were quantified. The range and type of DBPs reflected the diverse collection sites, the different disinfection processes, and the different characteristics of the source waters. Results showed a correlation of the mammalian cell cytotoxicity with the number of DBPs identified and several DBP chemical classes. DBP occurrence, cytotoxicity, and genotoxicity also correlated with epidemiology results (low birth weight and small for gestational age) from two countries. Specifically, % small for gestational age (SGA) correlated with the number of DBPs and the genotoxicity potency index values for cities in Spain, and risk of low birth weight (LBW) correlated with the number of DBPs, levels of DBPs, cytotoxic potency, and genotoxicity potency in two locations in Lithuania.

References

1. S. D. Richardson, M. J. Plewa, E. D. Wagner, R. Schoeny and D. M. DeMarini, *Mutat. Res.* 2007, **636**, 178.
2. S. D. Richardson and C. Postigo in *Emerging Organic Contaminants and Human Health - The Handbook of Environmental Chemistry*, ed. D. Barcelo, Springer-Verlag Berlin Heidelberg, Germany, 2012, Vol. 20, p 93.
3. C. Postigo and S. D. Richardson, *J. Hazard. Mater.* 2014, **279**, 461.
4. S. D. Richardson and C. Postigo in *In Occurrence, Formation, Health Effects, and Control of Disinfection By-Products*, ed. T. Karanfil, W. Mitch, P. Westerhoff and X. Yuefeng, ACS Symposium Series, ACS Publications, Washington, DC, 2014, in press.
5. U.S. Environmental Protection Agency (U.S. EPA). Drinking Water Contaminants. <http://goo.gl/90OBMZ> (accessed November, 2014).
6. S. W. Krasner, H. S. Weinberg, S. D. Richardson, S. J. Pastor, R. Chinn, M. J. Scilimenti, G. D. Onstad and A. D. Thruston Jr., *Environ. Sci. Technol.* 2006, **40**, 7175.
7. K. P. Cantor, C. M. Villanueva, D. T. Silverman, J. D. Figueroa, F. X. Real, M. Garcia-Closas, N. Malats, S. Chanock, M. Yeager, A. Tardon, R. Garcia-Closas, C. Serra, A. Carrato, G. Castaño-Vinyals, C. Samanic, N. Rothman and M. Kogevinas, *Environ. Health Perspect.* 2010, **118**, 1545.
8. C. M. Villanueva, K. P. Cantor, S. Cordier, J. J. K. Jaakkola, W. D. King, C. F. Lynch, S. Porru and M. Kogevinas, *Epidemiology* 2004, **15**, 357.
9. K. Waller, S. H. Swan, G. DeLorenze and B. Hopkins, *Epidemiology* 1998, **9**, 134.
10. D. A. Savitz, P. C. Singer, K. E. Hartmann, A. H. Herring, H. S. Weinberg, C. Makarushka, C. Hoffman, R. Chan and R. Maclehose, *Drinking Water Disinfection By-Products and Pregnancy Outcome*; AWWA Research Foundation, Denver, CO., 2005; p 212.
11. M. J. Nieuwenhuijsen, M. B. Toledano, N. E. Eaton, J. Fawell and P. Elliott, *Occup. Environ. Med.* 2000, **57**, 73.
12. F. Bove, Y. Shim and P. Zeitz, *Environ. Health Perspect.* 2002, **110**, 61.
13. M. J. Plewa and E. D. Wagner, *Mammalian Cell Cytotoxicity and Genotoxicity of Disinfection By-Products*. Water Research Foundation: Denver, CO, 2009; p 134, 2009.

14. M. J. Plewa, M. G. Muellner, S. D. Richardson, F. Fasano, K. M. Buettner, Y. T. Woo, A. B. McKague and E. D. Wagner, *Environ. Sci. Technol.* 2008, **42**, 955.
15. M. J. Plewa, J. E. Simmons, S. D. Richardson and E. D. Wagner, *Environ. Mol. Mutagen.* 2010, **51**, 871.
16. X. Wei, S. Wang, W. Zheng, X. Wang, X. Liu, S. Jiang, J. Pi, Y. Zheng, G. He and W. Qu, *Environ. Sci. Technol.* 2013, **47**, 5913.
17. U.S. Environmental Protection Agency (U.S. EPA) Unregulated Contaminant Monitoring Rule 2 - UCMR 2. <http://goo.gl/EQD8bI> (accessed November, 2014).
18. J. Li and E. R. Blatchley III, *Environ. Sci. Technol.* 2007, **41**, 6732.
19. C. Zwiener, S. D. Richardson, D. M. DeMarini, T. Grummt, T. Glauner and F. H. Frimmel, *Environ. Sci. Technol.* 2007, **41**, 363.
20. S. D. Richardson, D. M. DeMarini, M. Kogevinas, P. Fernandez, E. Marco, C. Lourencetti, C. Ballesté, D. Heederik, K. Meliefste, A. B. McKague, R. Marcos, L. Font-Ribera, J. O. Grimalt and C. M. Villanueva, *Environ. Health Perspect.* 2010, **118**, 1523.
21. W. A. Weaver, J. Li, Y. Wen, J. Johnston, M. R. Blatchley and E. R. Blatchley III, *Water Res.* 2009, **43**, 3308.
22. S. Chowdhury, K. Al-hooshani and T. Karanfil, *Water Res.* 2014, **53**, 68.
23. H. Kim, J. Shim and S. Lee, *Chemosphere* 2002, **46**, 123.
24. C. Schmalz, F. H. Frimmel and C. Zwiener, *Water Res.* 2011, **45**, 2681.
25. V. Bougault and L. P. Boulet, *Brit. J. Sport. Med.* 2012, **46**, 402.
26. A. Florentin, A. Hautemaniere and P. Hartemann, *Int. J. Hyg. Environ. Health.* 2011, **214**, 461.
27. M. Kogevinas, C. M. Villanueva, L. Font-Ribera, D. Liviach, M. Bustamante, F. Espinoza, M. J. Nieuwenhuijsen, A. Espinosa, P. Fernandez, D. M. DeMarini, J. O. Grimalt, T. Grummt and R. Marcos, *Environ. Health Perspect.* 2010, **118**, 1531.
28. L. Liang and P. C. Singer, *Environ. Sci. Technol.* 2003, **37**, 2920.
29. G. Hua and D. A. Reckhow, *Water Res.* 2007, **41**, 1667.
30. A. D. Shah and W. A. Mitch, *Environ. Sci. Technol.* 2012, **46**, 119.
31. Z. Zhang, S. Echigo, R. A. Minear and M. J. Plewa in *Natural Organic Matter and Disinfection By-Products: Characterization and Control in Drinking Water*, ed. S. E. Barrett, S. W. Krasner and G. L. Amy, American Chemical Society, Washington, D.C., 2000, p 299.
32. G. Ding and X. Zhang, *Environ. Sci. Technol.* 2009, **43**, 9287.
33. A. Becalski, B. P. Y. Lau, T. J. Schrader, S. W. Seaman and W. F. Sun, *Food Addit. Contam.* 2006, **23**, 957.
34. M. J. Plewa, E. D. Wagner, P. Jazwierska, S. D. Richardson, P. H. Chen and A. B. McKague, *Environ. Sci. Technol.* 2004, **38**, 62.
35. S. D. Richardson, F. Fasano, J. J. Ellington, F. G. Crumley, K. M. Buettner, J. J. Evans, B. C. Blount, L. K. Silva, T. J. Waite, G. W. Luther, A. B. McKague, R. J. Miltner, E. D. Wagner and M. J. Plewa, *Environ. Sci. Technol.* 2008, **42**, 8330.
36. W. Chu, N. Gao, D. Yin, S. W. Krasner and M. R. Templeton, *J. Chromatogr. A* 2012, **1235**, 178.
37. C. H. Jeong, C. Postigo, S. D. Richardson, J. E. Simmons, S. Y. Kimura, B. J. Marinas, D. Barcelo, E. D. Wagner and M. Plewa, *Environ. Sci. Technol.* 2014, submitted.
38. C. Postigo, C. H. Jeong, S. D. Richardson, E. D. Wagner, M. Plewa, J. E. Simmons and D. Barcelo in *Occurrence, Formation, Health Effects, and Control of Disinfection By-Products*, ed. T. Karanfil, W. Mitch, P. Westerhoff and X.

- Yuefeng, ACS Symposium Series, ACS Publications, Washington, DC, 2014, submitted.
39. H. J. Brass, M. A. Feige, T. Halloran, J. W. Mello, D. Munch and T. R.F. in *Drinking Water Quality Enhancement Through Source Protection*, ed. R. B. Pojasek, Ann Arbor Science, Ann Arbor, MI, 1977, p 393.
 40. S. W. Krasner, M. J. McGuire, J. G. Jacangelo, N. L. Patania, K. M. Reagan and E. M. Aieta, *J. Am. Water Works Assoc* 1989, **81**, 41.
 41. H. S. Weinberg, S. W. Krasner, S. D. Richardson and J. A. D. Thruston, *The Occurrence of Disinfection By-Products (DBPs) of Health Concern in Drinking Water: Results of a Nationwide DBP Occurrence Study*; National Exposure Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Athens, GA. : 2002.
 42. B. Cancho, F. Ventura, M. Galceran, A. Diaz and S. Ricart, *Water Res.* 2000, **34**, 3380.
 43. X. Wei, X. Chen, X. Wang, W. Zheng, D. Zhang, D. Tian, S. Jiang, C. N. Ong, G. He and W. Qu, *PLoS ONE* 2013, **8**.
 44. J. Criquet, S. Allard, E. Salhi, C. A. Joll, A. Heitz and U. von Gunten, *Environ. Sci. Technol.* 2012, **46**, 7350.
 45. E. M. Smith, M. J. Plewa, C. L. Lindell, S. D. Richardson and W. A. Mitch, *Environ. Sci. Technol.* 2010, **44**, 8446.
 46. K. M. Parker, T. Zeng, J. Harkness, A. Vengosh and W. A. Mitch, *Environ. Sci. Technol.* 2014, **48**, 11161.
 47. M. J. Plewa, E. D. Wagner, S. D. Richardson, A. D. Thruston Jr., Y. T. Woo and A. B. McKague, *Environ. Sci. Technol.* 2004, **38**, 4713.
 48. T. Ye, B. Xu, Y. L. Lin, C. Y. Hu, L. Lin, T. Y. Zhang and N. Y. Gao, *Water Res.* 2013, **47**, 3006.
 49. I. E. S. Hunter, E. H. Rogers, J. E. Schmid and A. Richard, *Teratology* 1996, **54**, 57.
 50. E. S. I. Hunter and J. A. Tugman, *Teratology* 1995, **52**, 317.
 51. V. Glezer, B. Harris, N. Tal, B. Iosefzon and O. Lev, *Water Res.* 1999, **33**, 1938.
 52. D. A. Reckhow, A. L. MacNeill, T. L. Platt, A. L. MacNeill and J. N. McClellan, *J. Water Supp. - Res. Technol. - AQUA* 2001, **50**, 1.
 53. H. Huang, Q. Y. Wu, H. Y. Hu and W. A. Mitch, *Environ. Sci. Technol.* 2012, **46**, 10624.
 54. D. B. Jones, A. Saglam, A. Triger, H. Song and T. Karanfil, *Environ. Sci. Technol.* 2011, **45**, 10429.
 55. D. B. Jones, H. Song and T. Karanfil, *Water Res.* 2012, **46**, 5491.
 56. Y. Bichsel and U. von Gunten, *Environ. Sci. Technol.* 1999, **33**, 4040.
 57. Y. Bichsel and U. von Gunten, *Environ. Sci. Technol.* 2000, **34**, 2784.
 58. S. Allard, C. E. Nottle, A. Chan, C. Joll and U. von Gunten, *Water Res.* 2013, **47**, 1953.
 59. S. E. Duirk, C. Lindell, C. C. Cornelison, J. Kormos, T. A. Ternes, M. Attene-Ramos, J. Osiol, E. D. Wagner, M. J. Plewa and S. D. Richardson, *Environ. Sci. Technol.* 2011, **45**, 6845.
 60. F. M. Wendel, C. Lütke Eversloh, E. J. Machek, S. E. Duirk, M. J. Plewa, S. D. Richardson and T. A. Ternes, *Environ. Sci. Technol.* 2014, **48**, 12689.
 61. T. Ye, B. Xu, Z. Wang, T. Y. Zhang, C. Y. Hu, L. Lin, S. J. Xia and N. Y. Gao, *Water Res.* 2014, **66**, 390.
 62. T. A. Ternes and R. Hirsch, *Environ. Sci. Technol.* 2000, **34**, 2741.
 63. J. Choi and R. L. Valentine, *Water Res.* 2002, **36**, 817.

64. W. A. Mitch and D. L. Sedlak, *Environ. Sci. Technol.* 2002, **36**, 588.
65. D. B. Jobb, R. Hunsinger, O. Meresz and V. Y. Taguchi in *Proceedings of the Fifth National Conference on Drinking Water*, Winnipeg, Manitoba, Canada, 1992.
66. J. M. Boyd, S. E. Hrudey, X. F. Li and S. D. Richardson, *TrAC - Trends Anal. Chem.* 2011, **30**, 1410.
67. J. W. A. Charrois, M. W. Arend, K. L. Froese and S. E. Hrudey, *Environ. Sci. Technol.* 2004, **38**, 4835.
68. Y. Y. Zhao, J. Boyd, S. E. Hrudey and X. F. Li, *Environ. Sci. Technol.* 2006, **40**, 7636.
69. P. Kulshrestha, K. C. McKinstry, B. O. Fernandez, M. Feelisch and W. A. Mitch, *Environ. Sci. Technol.* 2010, **44**, 3369.
70. N. Dai and W. A. Mitch, *Environ. Sci. Technol.* 2013, **47**, 3648.
71. M. Wu, Y. Qian, J. M. Boyd, S. Leavey, S. E. Hrudey, S. W. Krasner and X. F. Li, *Environ. Sci. Technol.* 2014, **48**, 1828.
72. California Department of Health - Drinking Water Program. Drinking Water Notification Levels and Response Levels: An Overview. <http://goo.gl/XvsT74> (accessed November, 2014).
73. Ontario Regulation 169/03. Ontario Drinking Water Quality Standards. Safe Drinking Water Act, 2002. <http://goo.gl/6OTIkI> (accessed November 2014).
74. Health Canada. Guidelines for Canadian Drinking Water Quality: Guideline Technical Document - N-Nitrosodimethylamine (NDMA). Water, Air and climate Change Bureau, Healthy Environments and Consumer Safety Branch, Health Canada, Ottawa, Ontario (Catalogue No H128-1/11-662E) 2011 <http://goo.gl/yAUstU> (accessed November, 2014).
75. U.S. Environmental Protection Agency (U.S. EPA) Contaminant Candidate List 3 - CCL 3. <http://goo.gl/6M90rO> (accessed November, 2014).
76. I. M. Schreiber and W. A. Mitch, *Environ. Sci. Technol.* 2006, **40**, 6007.
77. J. Choi and R. L. Valentine, *Environ. Sci. Technol.* 2003, **37**, 4871.
78. I. M. Schreiber and W. A. Mitch, *Environ. Sci. Technol.* 2007, **41**, 7039.
79. W. A. Mitch, A. C. Gerecke and D. L. Sedlak, *Water Res.* 2003, **37**, 3733.
80. W. A. Mitch, J. O. Sharp, R. R. Trussell, R. L. Valentine, L. Alvarez-Cohen and D. L. Sedlak, *Environ. Eng. Sci.* 2003, **20**, 389.
81. J. M. Kemper, P. Westerhoff, A. Dotson and W. A. Mitch, *Environ. Sci. Technol.* 2009, **43**, 466.
82. A. Wilczak, A. Assadi-Rad, H. H. Lai, L. L. Hoover, J. F. Smith, R. Berger, F. Rodigari, J. W. Beland, L. J. Lazzelle, E. G. Kincannon, H. Baker and C. T. Heaney, *J. Am. Water Works Assoc* 2003, **95**, 94.
83. J. M. Kemper, S. S. Walse and W. A. Mitch, *Environ. Sci. Technol.* 2010, **44**, 1224.
84. S. H. Park, P. Piyachaturawat, A. E. Taylor and C. H. Huang, *Water Sci. Technol.* 2009, **9**, 279.
85. S. H. Park, S. Wei, B. Mizaikoff, A. E. Taylor, C. Favero and C. H. Huang, *Environ. Sci. Technol.* 2009, **43**, 1360.
86. E. Pehlivanoglu-Mantas and D. L. Sedlak, *Water Res.* 2008, **42**, 3890.
87. S. W. Krasner, W. A. Mitch, D. L. McCurry, D. Hanigan and P. Westerhoff, *Water Res.* 2013, **47**, 4433.
88. C. K. Schmidt and H. J. Brauch, *Environ. Sci. Technol.* 2008, **42**, 6340.
89. U. V. Gunten, E. Salhi, C. K. Schmidt and W. A. Arnold, *Environ. Sci. Technol.* 2010, **44**, 5762.

90. L. P. Padhye, J. H. Kim and C. H. Huang, *Water Res.* 2013, **47**, 725.
91. P. H. Chen, S. D. Richardson, S. W. Krasner, G. Majetich and G. L. Glish, *Environ. Sci. Technol.* 2002, **36**, 3362.
92. W. Chu, N. Gao, D. Yin and S. W. Krasner, *J. Hazard. Mater.* 2013, **260**, 806.
93. W. H. Chu, N. Y. Gao, Y. Deng and S. W. Krasner, *Environ. Sci. Technol.* 2010, **44**, 3908.
94. S. D. Richardson, A. D. Thruston Jr., T. V. Caughran, P. H. Chen, T. W. Collette, T. L. Floyd, K. M. Schenck, B. W. Lykins, G.-R. Sun and G. Majetich, *Environ. Sci. Technol.* 1999, **33**, 3368.
95. S. W. Krasner, R. Chinn, C. J. Hwang and S. Barrett in *Proceedings of the 1990 American Water Works Association Water Quality Technology Conference*, American Water Works Association, Denver, CO, 1991.
96. B. Kundu, S. D. Richardson, P. D. Swartz, P. P. Matthews, A. M. Richard and D. M. DeMarini, *Mutat. Res.* 2004, **562**, 39.
97. B. Kundu, S. D. Richardson, C. A. Granville, D. T. Shaughnessy, N. M. Hanley, P. D. Swartz, A. M. Richard and D. M. DeMarini, *Mutat. Res.* 2004, **554**, 335.
98. J. Choi and S. D. Richardson in *Proceedings of the International Workshop on Optimizing the Design and Interpretation of Epidemiologic Studies to Consider Alternative Disinfectants of Drinking Water*, Raleigh, NC, 2005.
99. S. D. Richardson, A. D. Thruston Jr., C. Rav-Acha, L. Groisman, I. Popilevsky, O. Juraev, V. Glezer, A. B. McKague, M. J. Plewa and E. D. Wagner, *Environ. Sci. Technol.* 2003, **37**, 3782.
100. T. A. McDonald and H. Komulainen, *J. Environ. Sci. Health - C* 2005, **23**, 163.
101. H. R. Schulten and M. Schnitzer, *Naturwissenschaften* 1993, **80**, 29.
102. M. Yang and X. Zhang, *Environ. Sci. Technol.* 2014, **48**, 11846.
103. F. Qin, Y. Y. Zhao, Y. Zhao, J. M. Boyd, W. Zhou and X. F. Li, *Angew. Chem. Int. Ed.* 2010, **49**, 790.
104. Y. Zhao, J. Anichina, X. Lu, R. J. Bull, S. W. Krasner, S. E. Hrudey and X. F. Li, *Water Res.* 2012, **46**, 4351.
105. W. Wang, Y. Qian, J. M. Boyd, M. Wu, S. E. Hrudey and X. F. Li, *Environ. Sci. Technol.* 2013, **47**, 3275.
106. Y. Qian, W. Wang, J. M. Boyd, M. Wu, S. E. Hrudey and X. F. Li, *Environ. Sci. Technol.* 2013, **47**, 4426.
107. C. H. Jeong, E. D. Wagner, V. R. Siebert, S. Anduri, S. D. Richardson, E. J. Daiber, A. B. McKague, M. Kogevinas, C. M. Villanueva, E. H. Goslan, W. T. Luo, L. M. Isabelle, J. F. Pankow, R. Grazuleviciene, S. Cordier, S. C. Edwards, E. Righi, M. J. Nieuwenhuijsen and M. J. Plewa, *Environ. Sci. Technol.* 2012, **46**, 12120.

N-NITROSODIMETHYLAMINE PRECURSORS IN WASTEWATER: REMOVAL VIA ACTIVATED SLUDGE TREATMENT

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1. INTRODUCTION

Disinfection by-products (DBPs) are recognized as a potential health concern in treated drinking water, but have not been as extensively studied in recycled water. However, our analysis of chemicals in secondary wastewater after treatment with microfiltration (MF) and reverse osmosis (RO) has demonstrated that DBPs are often the most frequently detected chemicals in recycled water, and that DBPs may be more frequently detected in RO-treated recycled water than in secondary wastewater.¹⁻³ As part of the MF/RO treatment process, it is standard practice to chloramine to minimize RO membrane fouling.⁴ Dosed chlorine reacts with ammonia present in, or added to, the wastewater to form monochloramine, and this process leads to formation of DBPs.^{1,3,5} Despite increased detection, the concentrations of most DBPs in recycled water are well below health values.^{1,3} However, this is not the case for *N*-nitrosodimethylamine (NDMA), which has been identified as a potential health concern for both drinking water^{6,7} and recycled water.^{2,5,8} NDMA has primarily been reported by water utilities using chloramination,^{9,10} though it is now recognised that NDMA can be formed during both chlorine and chloramine treatment, depending on the precursors present and the process conditions.^{9,11} More recently, ozonation has also been identified to result in a significant NDMA formation from some precursors.¹²⁻¹⁴

The importance of *N*-nitrosamines as disinfection by-products of health concern is illustrated by the publication of a number of recent literature reviews describing their occurrence and control,¹⁵⁻¹⁷ and increasing recognition of their cancer potencies and toxicities.^{18,19} While *N*-nitrosamine concentrations in recycled water can be minimised by additional treatment with UV irradiation and advanced oxidation processes,^{20,21} it is also possible that concentrations could be minimised by reduction of precursors present in the secondary wastewater.²² While NDMA precursors are often modeled using dimethylamine, the majority of NDMA precursors in wastewater are unidentified organic nitrogen species that have not been fully characterized.²³ In this study, we investigated the factors that influence the removal of NDMA precursors during activated sludge treatment, and the potential impact of different chloramination or ozonation strategies on NDMA formation in recycled water.

2. METHODOLOGY

2.1. Sampling Sites

Samples were collected from Beenyup Wastewater Treatment Plant (WWTP) and Beenyup Advanced Water Recycling Plant (AWRP) in Perth, Western Australia during 2010 and 2011. Beenyup WWTP is a conventional activated sludge treatment plant with continuous flow that treats predominantly domestic wastewater, with a small proportion of industrial wastewater (~2%).¹ The activated sludge system has a pre-anoxic zone for denitrification, combined with an aerated zone to promote nitrification (Figure 1). Recycling pumps located at the end of each tank pump aerated mixed liquors, which are rich in nitrate from the end of the tank back to the head without oxygen addition to increase denitrification. Additional denitrification occurs in the secondary sedimentation tanks, where liquid-solid separation occurs. The plant has a sludge handling system that uses polyacrylamide-based polymeric flocculants for the dewatering of the excess sludge using dissolved air flotation thickeners as well as for the dewatering of the anaerobic digested sludge by centrifugation. Effluent from the dissolved air flotation thickeners is returned to the treatment process just before primary sedimentation, while centrate from sludge handling is returned to the head of the WWTP (Figure 1). Beenyup WWTP has a capacity of 135 ML/day, and flow into the plant has two maxima in each 24 hour period, one around midday and another one between 9 and 11 pm. The retention time in the aeration tanks and the clarifiers varies between 6 to 8 hours depending on flow.²⁴ Samples from Beenyup WWTP were collected at the primary wastewater sampling point and at the combined secondary wastewater sampling point (Figure 1).

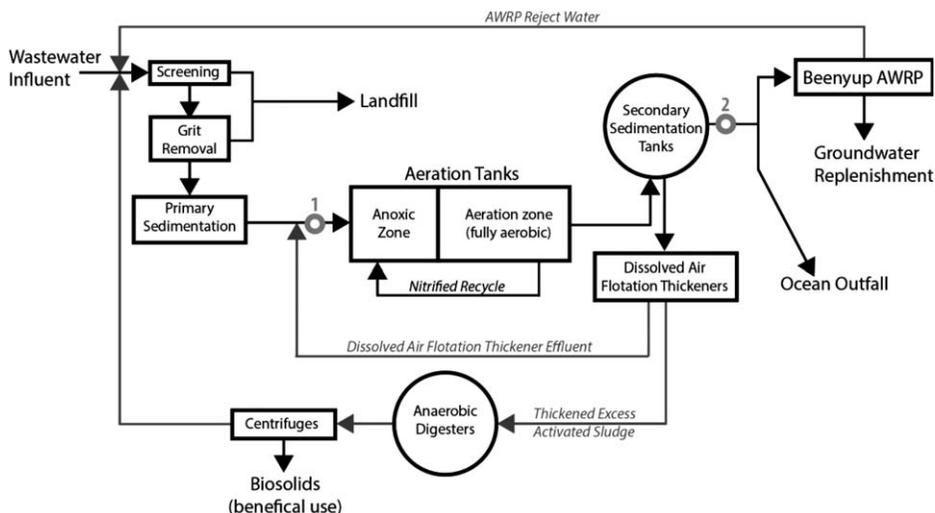


Figure 1 Schematic of Beenyup Wastewater Treatment Plant, showing 1) primary and 2) secondary wastewater sampling points. Pathways by which polyacrylamide-based polymeric flocculants are introduced into the treatment plant are in grey.

Primary wastewater has undergone solids removal by screening, grit removal and primary sedimentation. Therefore, the sample obtained had a lower solids content than the raw influent into the WWTP. However, previous research has shown close agreement between total NDMA precursor concentrations for wastewater influent and primary wastewater,²⁵ and therefore, precursor removal during primary treatment is expected to be minimal. Most secondary wastewater from Beenyup WWTP is discharged into the Indian Ocean. However, between March 2010 and September 2014, 7 ML/day of secondary wastewater from Beenyup WWTP fed into the Beenyup AWRP^{26,27} as part of the Water Corporation of Western Australia's Groundwater Replenishment Trial. Beenyup AWRP was commissioned between March and November 2010, after which time reinjection into a deep underground aquifer commenced. Treatment at the AWRP consisted of chloramination to minimise biofouling on membranes, ultrafiltration (UF), RO, and UV disinfection. After UF/RO/UV treatment, about 4.5 ML/d of treated water was injected into the aquifer for replenishment, while the RO reject (about 2.5 ML/d) was sent to the head of the WWTP.

All samples were collected as grab samples. Samples for *N*-nitrosamine precursor or concentration analysis were collected in glass containers, filled to zero headspace, kept cool (in an ice box) and away from light until reaching the laboratory, where they were then stored at 4 °C until analysis. Samples for *N*-nitrosamine concentration contained ascorbic acid (20 mg/L) as a quenching agent. Trip and field blanks containing ultrapure water and ascorbic acid (20 mg/L), if appropriate, were also included during each sampling occasion to determine if there was any contamination through the sampling process, storage and transport. Trip blanks remained unopened until analysis, and field blanks were opened at each sampling location. Samples for total organic carbon (TOC) analysis were subsampled (40 mL) from glass containers used to collect samples for *N*-nitrosamine precursor analysis. Samples for nutrients were collected in high density polyethylene (HDPE) bottles.

N-nitrosamine precursor concentrations throughout both Beenyup WWTP and Beenyup AWRP were measured in July 2010 (during Beenyup AWRP commissioning) and February 2011 (see Figure 2 for sampling points). In addition, to investigate the effect of nitrification and denitrification on NDMA precursor removal in Beenyup WWTP, matched primary and secondary wastewater were collected in two separate sampling campaigns, as described in Table 1.

Sampling was undertaken during high, medium and low flow conditions, related to the demand on the WWTP at the time of sampling. The retention time in the aeration tanks and sedimentation tanks was taken into account when estimating the time lag between the sampling of the primary wastewater and the secondary wastewater, calculated to be 6, 7 and 8 hours for high, medium and low flow events, respectively.

2.2. *N*-Nitrosamine Precursor Analysis and Formation Studies

The total concentration of *N*-nitrosamine precursors was determined using a previously published NDMA precursor analysis protocol,²⁸ also known as the NDMA formation potential test. This protocol has been employed in many studies to quantify *N*-nitrosamine precursors in natural waters and wastewaters,^{23,28,29} and applies a high dose of monochloramine (140 mg/L Cl₂) to a buffered sample with a contact time of 10 days. A modified version with 7 days contact time was used in this study, as preliminary tests indicated there was little *N*-nitrosamine formation after 7 days.

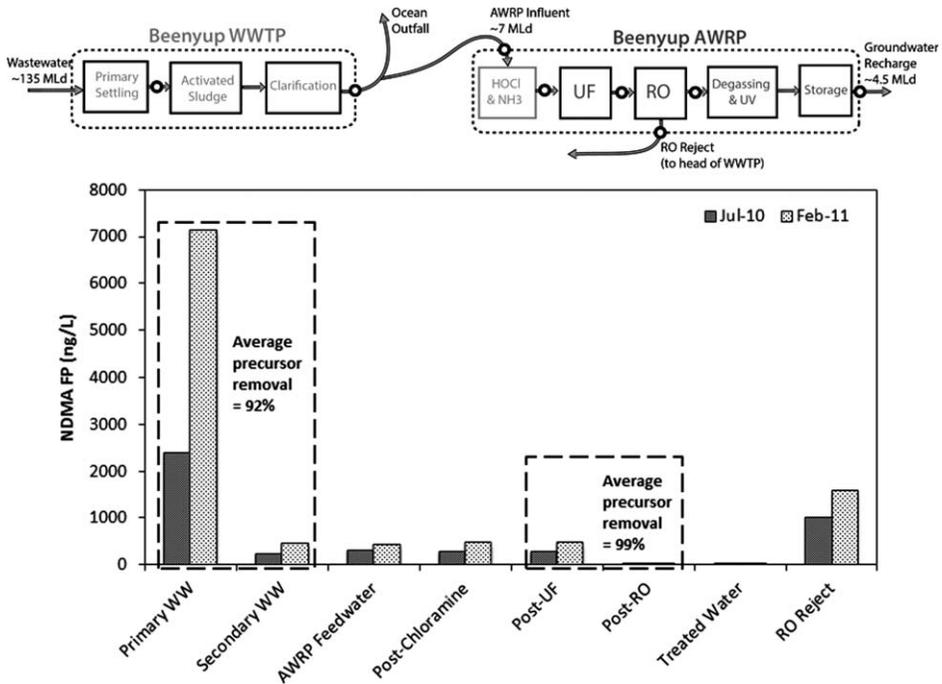


Figure 2 NDMA precursors, as measured by formation potential, in Beenyup WWTP and AWRP. Sampling points for each plant are identified (bold circles) in the schematic.

Table 1 Overview of sampling dates in Beenyup WWTP including detention times

	Target Flow rate	Detention time	Flow Rate (L s ⁻¹)				
			Initial	Final	Ave.	Min.	Max.
2010 Sampling Campaign							
Tue, 7 Sep 10	Low	8 hr	612	1597	1687	612	2126
Tue, 14 Sep 10	Low	8 hr	618	1688	1746	618	2197
Sat, 18 Sep 10	Medium	7 hr	2496	1924	2053	1813	2513
Sat, 11 Sep 10	Medium	7 hr	2654	1990	2165	1903	2667
Mon, 20 Sep 10	High	6 hr	1867	1968	1563	1387	1968
Mon, 11 Oct 10	High	6 hr	1901	1918	1543	1346	1957
2011 Sampling Campaign							
Mon, 13 Jun 11	Medium	7 hr	1843	1962	1605	1409	1962
Tue, 14 Jun 11	Low	8 hr	606	1815	1520	597	1901
Thu, 16 Jun 11	Low	8 hr	607	1528	1536	602	1913
Sat, 18 Jun 11	High	6 hr	2550	1981	2110	1889	2551
Mon, 20 Jun 11	Medium	7 hr	1805	1947	1617	1437	1953
Tue, 21 Jun 11	Low	8 hr	617	1655	1562	617	1928
Thu, 23 Jun 11	Low	8 hr	603	1521	1505	596	1907
Sat, 25 Jun 11	High	6 hr	2529	2004	2141	1903	2534

In addition to the *N*-nitrosamine precursor analysis, a series of experiments was conducted to measure *N*-nitrosamine formation in Beenyup secondary wastewater using lower chloramine concentrations (1, 3 and 10 mg/L Cl₂), closer to the typical concentrations used in water recycling plants (3 mg/L Cl₂ at Beenyup AWRP). These chloramination experiments used either preformed monochloramine, or simultaneously-dosed hypochlorite and ammonium chloride solutions, to form monochloramine inline. All reactions were carried out in amber glass bottles at pH 7 with phosphate buffer (10mM), where the disinfectant stock solution was added in one-tenth of the total sample volume, to make up the desired dose. Samples were collected after 24 hours, quenched with ascorbic acid to stop the reaction, and analysed for *N*-nitrosamines.

For ozonation experiments, ozone stock solutions were prepared using an oxygen-fed generator (American Ozone Systems, Inc., Chicago, Illinois) to diffuse ozone into ultrapure water. The concentration of the ozone stock solution was measured on an Agilent Technologies Cary 60 UV/Vis spectrophotometer at 600 nm using the indigo method.³⁰ An appropriate volume was added into samples to achieve the desired ozone to TOC ratios (0.1-0.5), taking dilution into account. Samples were sealed, mixed by inverting, and left at room temperature for one day to ensure ozone residual was zero before analysing for NDMA.

2.3. *N*-Nitrosamine Analysis

N-Nitrosamines were analysed after sample preconcentration on an Agilent Technologies 7890A gas chromatograph coupled with a 5975C mass spectrometer, operating in positive chemical ionization mode with ammonia as the reagent gas (flow = 0.5 mL/min). Sample preconcentration was undertaken either by liquid-liquid extraction (LLE) for NDMA precursor analysis samples, when higher concentrations of *N*-nitrosamines were expected, or by solid-phase extraction (SPE) for lower *N*-nitrosamine concentrations or experiments with lower disinfectant doses (1-10 mg/L Cl₂). For LLE, an aliquot of sample (50 mL) containing deuterated *N*-nitrosamines (80 ng/L) as the surrogate standards, was adjusted to pH 8 with sodium hydrogen carbonate or sodium carbonate. Sodium chloride (15 g) was added, and the sample vial shaken until all salt dissolved. The sample was then extracted with dichloromethane (5 mL) and the organic layer dried through anhydrous magnesium sulphate. The extract was concentrated to ~200 µL in a heating block (40 °C) under a gentle stream of nitrogen. The final extract was transferred to a GC microvial containing diphenylamine-*d*₁₀ (50 µg/L) as the internal standard.

The SPE procedure was based on the method of Charrois et al.¹⁹ with minor modifications. SPE cartridges were prepared in-house with LiChrolut® EN (0.35 g) and Carboxen™ 572 (0.5 g) and were conditioned with hexane (10 mL), dichloromethane (20 mL), methanol (20 mL) and ultrapure water. An aliquot of sample (1L) containing deuterated *N*-nitrosamines (14 ng/L) as the surrogate standards, was adjusted to pH 8 with sodium hydrogen carbonate. Each sample was passed through a SPE cartridge. After transfer, the cartridge was dried under vacuum for a few hours and eluted with dichloromethane (18 mL). The extract was concentrated to ~200 µL using the same procedure as for LLE. While the method used is able to measure 8 different *N*-nitrosamines, only NDMA was detected in significant concentrations. Limits of detection for NDMA were calculated based on the 95% confidence interval for triplicates of a low concentration standard according to the USEPA procedure³¹ and were typically 1-3 ng/L for LLE preconcentration and ≤1 ng/L for SPE preconcentration.

2.4. Other Chemical Analyses

Conductivity, pH, and temperature were all measured in the field using portable probes (HQ40d, Hach Co., USA). Other water quality parameters measured by standard methods³² included TOC (5310-TOC C), ammonia (4500-NH₃ G, LOR = 0.01 mg/L), nitrate and nitrite (4500-NO₃⁻ F, LOR = 0.01 mg/L), and total nitrogen (4500-N C, LOR = 0.01 mg/L). Dissolved organic nitrogen (DON) was determined as the difference between total nitrogen and the sum of nitrate, nitrite and ammonia.

2.5. Data Analysis

The normality of each chemical dataset was tested by calculation of the Kolmogorov-Smirnov Statistic and the Shapiro-Wilk Statistic, with most found to have a poor fit to the normal distribution curve. Therefore, non-parametric tests were used to determine whether the dataset showed significant differences with respect to either plant flow rate, or sampling event. The Kruskal–Wallis one-way analysis of variance by ranks was used to determine whether nitrogen removal was affected by low, medium or high flow rates, while the Mann–Whitney *U*, the non-parametric equivalent of the student's *t*-test, was used to determine whether nitrogen removal was different in the 2010 and 2011 sampling events. All statistical analysis was undertaken using SPSS Statistics v22 (IBM).

3. RESULTS AND DISCUSSION

3.1. Removal of NDMA Precursors

N-Nitrosamine precursor concentrations through both Beenyup WWTP and Beenyup AWRP were measured in July 2010 (during Beenyup AWRP commissioning) and February 2011 via the *N*-nitrosamine formation potential test (Figure 2). Formation of *N*-nitrosamines other than NDMA was always below 25 ng/L, except for *N*-piperidine (average 104 ng/L formation) and *N*-pyrrolidine (average 479 ng/L formation), both detected in primary wastewater but not secondary wastewater. Overall NDMA formed at least 90% of *N*-nitrosamine precursors on a molar basis. The concentration of NDMA precursors in primary wastewater was very variable (2400 ng/L in July 2010, and 7100 ng/L in February 2011). This variation might be due to seasonal changes, as other studies have found higher concentrations of NDMA precursors during summer sampling events than in winter sampling,^{33,34} but more summer sampling in particular would be required to confirm this. Despite the difference in NDMA precursor concentrations in primary wastewater, there was consistent removal of NDMA precursors for both sampling events during the activated sludge treatment (average of 92% removal) and also during RO treatment (average 99% removal). The removal of NDMA precursors by RO treatment was comparable to that found in other studies,^{23,35} and considerably better than the removal of NDMA itself, typically around 50%.^{1,8,36} The rejection measured for NDMA precursors in this study was similar to measured rejection of dimethylamine and other alkylamines by both nanofiltration and RO membranes.³⁷ Rejection of these small molecules is high because they are positively charged at neutral pH.

In absolute terms, the largest removal of NDMA precursors was during activated sludge treatment in the Beenyup WWTP, comparable or higher to that found in other

studies.^{33,34,38} During activated sludge treatment, indigenous waterborne microorganisms utilise dissolved and suspended organic material, producing a secondary wastewater with lower C and N content. The two key processes for transformation and, ultimately, removal of N from wastewater are nitrification and denitrification. During nitrification, ammonia is oxidised into nitrite by nitrifying bacteria in the presence of oxygen, and the nitrite is then further oxidised to nitrate.³⁹ During denitrification, nitrate is reduced to nitrogen gas under anoxic conditions, thus completely removing N from the system. Biodegradable organic N, particularly urea, amino acids and proteins, can also be removed in this process, through conversion to ammonia by either hydrolysis or ammonification through heterotrophic bacteria,⁴⁰ although typically removal of organic N is less efficient than inorganic N.⁴¹ Removal of NDMA precursors has also been previously linked to biological treatment, although variations in removal efficiency could not be linked to differences in treatment processes.^{33,34} Formation of other DBPs from effluent organic matter has also previously been linked to the level of wastewater treatment.²²

3.2. Nitrogen Removal During Activated Sludge Treatment

While activated sludge treatment involves both nitrification and denitrification steps, it is nitrification that has been found to strongly control concentrations of inorganic and organic nitrogen in secondary wastewater, and also correlate with biodegradable dissolved organic carbon (BDOC), dissolved organic carbon (DOC) and DBP formation potential.⁴² Assessment of the nitrifying and denitrifying efficacy of Beenyup WWTP, using the quantitative classification scheme of Krasner et al.^{22,42} (Figure 3), indicated that, in general, Beenyup WWTP has good nitrification (ammonia < 2 mg/L-N) and partial denitrification (nitrate > 5 mg/L-N). At higher flow rates, hydraulic overloading, which reduces the retention time, and higher organic matter loading has been found to reduce the efficacy of the nitrification and denitrification processes at Beenyup WWTP.⁴³

To investigate the effect of nitrification and denitrification on NDMA precursor removal at Beenyup WWTP, matched primary and secondary wastewater were collected over a variety of different flow rates in two separate sampling campaigns, and a variety of N species, as well as NDMA precursors, were measured (Table 2). The total N in primary wastewater was dominated by ammonia and DON, while total N in secondary wastewater was dominated by nitrate, with some DON and ammonia. While NDMA precursors make up a component of DON, the calculated percentage by mass in Beenyup secondary wastewater was always less than 0.02%. Previous analysis by Pehlivanoglu-Mantas and Sedlak⁴⁴ suggests that DON in secondary wastewater is relatively low molecular weight (<10 kDa) and hydrophilic, which is consistent with its persistence in wastewater through both primary and secondary wastewater treatment. The same study suggested NDMA precursors are typically <1 kDa and may be more hydrophobic than bulk DON.

The Kruskal–Wallis one-way analysis of variance by ranks was used to determine whether nitrogen concentrations (i.e., ammonia, nitrate, nitrite, DON, total N, and NDMA precursors) in either primary or secondary wastewater were significantly different during low, medium or high flow rates. However, the null hypothesis (that there was no difference in distribution over different flow categories) was retained for all variables tested, except for NDMA precursors in secondary wastewater ($p = 0.044$). There was also a weak positive correlation between NDMA precursors and average event flow rate (Spearman's rho = 0.563, $p = 0.03$), which would indicate that there is

less NDMA precursor removal at shorter retention times. However, overall there were much more significant differences between the two sampling campaigns than between different flow rates.

While N concentrations in primary wastewater were higher in the June 2011 sampling campaign, the concentration of ammonia and NDMA precursors in the secondary wastewater was lower, suggesting better removal in this second sampling campaign.

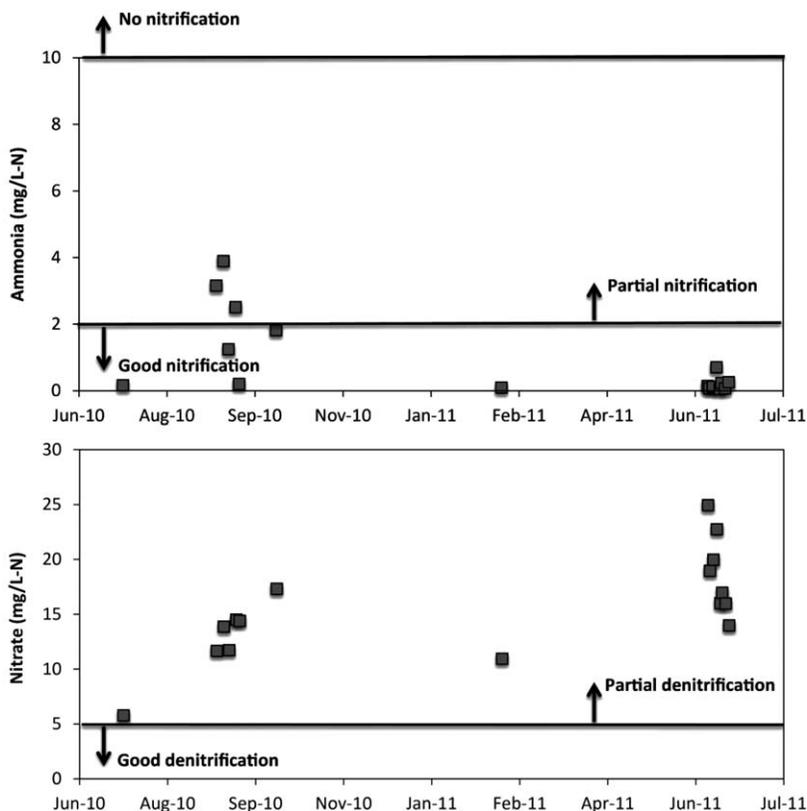


Figure 3 Concentration of ammonia and nitrate in Beenyup WWTP secondary wastewater

Table 2 Average concentration of target N species in matched primary and secondary wastewater samples during the 2010 and 2011 sampling campaigns.

	Avg Sept 2010 (n = 6)		Avg June 2011 (n = 8)	
	Primary WW	Secondary WW	Primary WW	Secondary WW
Ammonia (mg/L-N)	57 ± 7.8	2.0 ± 1.3	65 ± 16	0.2 ± 0.2
Nitrate (mg/L-N)	0.8 ± 0.47	14 ± 2.1	0.02 ± 0.007	19 ± 3.7
Nitrite (mg/L-N)	0.06 ± 0.08	0.18 ± 0.06	< 0.01	0.05 ± 0.08
DON (mg/L-N)	7 ± 1.7	1.6 ± 0.02	14 ± 13	4.8 ± 4.3
Total N (mg/L-N)	71 ± 7.9	19 ± 2.6	79 ± 14	24 ± 2.6
NDMA FP (ng/L)	4100 ± 397	420 ± 22	4900 ± 620	394 ± 38

In order to remove the influence of primary wastewater concentrations, percentage removals of ammonia, nitrate, DON, total N, and NDMA precursors were calculated for activated sludge treatment (Figure 4). The percentage removal of nitrate was estimated by assuming that all removed ammonia was transformed to nitrate. Comparison using the Mann Whitney U test confirmed that there was a significant difference ($p < 0.05$) in removal between the two sampling campaigns for all N species, except DON, which had much higher variability. This variability was probably related to both the relatively low DON concentrations, and also the method of estimation. The percentage removal of both ammonia and NDMA precursors was higher in the 2011 sampling campaign, when good nitrification was always achieved. In contrast, both total N and nitrate had poorer removal in the 2011 sampling campaign, reflecting poorer denitrification and a higher concentration of nitrate in the secondary wastewater.

In contrast to previous studies,³⁵ there was a correlation between NDMA precursors and ammonia concentrations in secondary wastewater (Spearman's rho = 0.648, $p = 0.012$), which provides additional support to the hypothesis that NDMA precursor reduction is related to the nitrification process. There was no correlation between NDMA precursors and DON in either primary (Spearman's rho = 0.196) or secondary (Spearman's rho = 0.033) wastewater, confirming that NDMA precursors are a minor and specific fraction of DON.

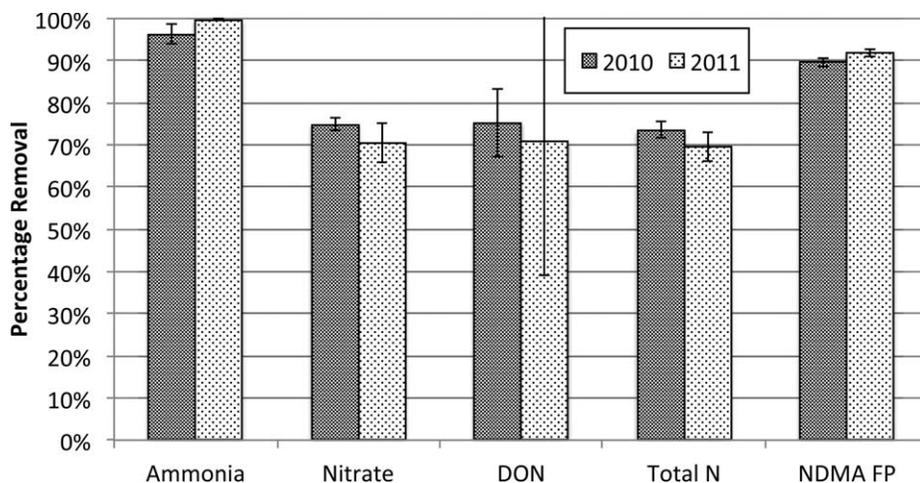


Figure 4 Percentage removals of ammonia, nitrate, DON, TN, and NDMA precursors between primary and secondary wastewater, for the 2010 and 2011 sampling campaigns.

3.3. NDMA Precursors in Primary Wastewater

As previously discussed, there was significant variability in the concentration of NDMA precursors measured in primary WW, ranging from 2400 to 7100 ng/L. Previous researchers have attributed variability in primary wastewater precursors to seasonal impacts,^{33,34} or the presence of specific industries in the wastewater catchment, such as circuit board manufacture.²⁵ Another potential source of NDMA precursors within the treatment plant is amine-based cationic polyacrylamide polymers, often used for

coagulation in WWTPs. Previous studies have shown formation of NDMA in the order of $\mu\text{g/L}$ after chloramination of polyacrylamide compounds.²³ Increases in NDMA precursor concentrations between primary and secondary treatment have been attributed to the use of cationic polymers during clarification in other studies.²⁵ At Beenyup WWTP and AWRP, there are three polymers that may contribute to NDMA precursors within the primary wastewater: Flopam FO 4350 SH is used in the dissolved air flotation thickeners to thicken excess sludge before digestion, EMA 8845 MBL is used in Beenyup sludge handling, and NALCO[®] PC-1521T is an anti-scalant used in the Beenyup AWRP. Effluent from the dissolved air flotation thickeners is returned to the treatment process just before primary sedimentation, while centrate from sludge handling and reject water from Beenyup AWRP are returned to the head of the WWTP (Figure 1). Assessment of NDMA precursors in polymer solutions (10 mg/L) made with ultrapure water, using the 7 day precursor analysis protocol produced NDMA concentrations between 56 and 372 ng/L (Figure 5), much

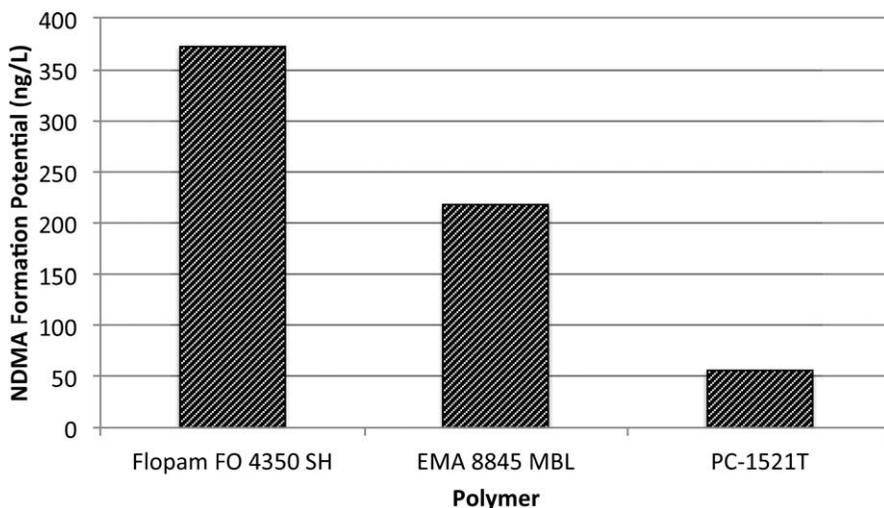


Figure 5 Seven day NDMA precursor experiments for polymers (10 mg/L solutions) used in Beenyup WWTP and AWRP. Flopam FO 4350 SH is used in the dissolved air flotation thickeners to thicken excess sludge before digestion, EMA 8845 MBL is used in Beenyup sludge handling, and NALCO[®] PC-1521T is an anti-scalant used in Beenyup AWRP.

lower than the concentrations of NDMA precursor measured in primary wastewater. Therefore, it appears that NDMA precursors in Beenyup primary wastewater are not significantly affected by the use of polymers. Previous research has attributed most NDMA precursors to domestic sources which are difficult to control²⁵ and therefore source control activities may have limited effect on reducing NDMA precursors in primary wastewater.

3.4. NDMA Formation from Ozonation and Chloramination of Secondary Wastewater

To investigate the potential formation of NDMA during water recycling treatment, laboratory experiments were undertaken using either ozonation or chloramination. Ozone is of benefit for potable water reuse applications as it reduces the concentrations of both pathogens and trace organic chemicals, and it can be implemented before and after traditional disinfection or membrane processes. While typical secondary amines, such as dimethylamine, and related compounds have been shown to be NDMA precursors upon ozonation, molar conversion yields are typically very low (i.e. 0.02%).^{12,45} In contrast, ozonation of precursors in which dimethylamine is bonded directly to a nitrogen atom or separated with a good leaving group (e.g. CO₂, SO₂) leads to much higher molar conversion yields of NDMA (>50%), particularly when the reaction is catalysed by bromide.^{12,13} Ozone is not currently part of the treatment strategy at Beenyup WWTP or AWRP, and therefore the effect of ozone on NDMA formation in treated wastewaters could not be tested in the full-scale plant. In laboratory experiments, relatively low concentrations of NDMA formed in Beenyup secondary wastewater after ozonation (Figure 6a), though the net NDMA formation did increase from 2 ng/L to 12 ng/L as the ozone to TOC ratio increased from 0.1 to 0.5. Previous research has found that ozonation can remove up to 95% of NDMA precursors, as measured using the NDMA formation potential test,^{45,46} and so there may be opportunities to reduce the concentration of NDMA precursors in the AWRP feedwater before UF/RO treatment, without significant NDMA formation upon ozonation. Ozone dose optimisation is required to minimise production of ozone-DBPs,^{47,48} and further investigations are required to measure the effects of the presence of ammonia, bromide and polyacrylamide sludge treatment polymers, which have recently been implicated in increased NDMA formation during ozonation of wastewater.⁴⁹

Chloramination in water recycling plants is achieved by addition of preformed monochloramine, or by separate addition of ammonia and chlorine to the wastewater stream (inline-formation), which can lead to formation of both monochloramine and dichloramine.⁵⁰ Understanding chloramine speciation is important for minimising DBP formation, particularly formation of NDMA. For example, dichloramine enhances (between 3 to 30 times) NDMA formation compared to monochloramine during chloramination of secondary wastewaters, depending on the wastewater and contact time.⁵¹ The effect of monochloramine dose was investigated by treating secondary wastewater with preformed or inline-formed monochloramine at 1, 3, and 10 mg/L Cl₂. Comparison of formation results after 24 hours (Figure 6b) showed similar concentrations (25-28 ng/L) of NDMA at 1 mg/L Cl₂ and 3 mg/L Cl₂ of both pre-formed and inline-formed monochloramine. While the concentrations of NDMA formed in these experiments are higher than the current Australian Guidelines for Water Recycling (10 ng/L),⁵² additional laboratory tests using the conditions employed at Beenyup AWRP (3 mg/L Cl₂, pH 6-7 and contact time of 3 hours) demonstrated that NDMA formation was well below 5 ng/L for both pre-formed and inline-formed monochloramine, and therefore no further optimisation of the chloramination process is required for NDMA minimisation. These laboratory results are consistent with extensive monitoring of final product water from the Beenyup AWRP which showed that NDMA concentrations were almost always <10 ng/L.⁵³

Increasing the dose of monochloramine from 3 to 10 mg/L Cl₂ resulted in 3 times (90 ng/L) and 7.6 times (190 ng/L) higher NDMA concentrations from preformed and inline-formed monochloramine, respectively. Choi et al.¹⁰ has previously evaluated the

effect of monochloramine dose on NDMA formation and observed a generally linear increase in NDMA concentration when preformed monochloramine was applied from 0.01-0.2 mM (0.7-14 mg/L Cl_2) to a fixed concentration of dimethylamine (0.1 mM). This is in contrast to the non-linear increase in NDMA formation reported in this study, and also by Farré et al.⁵ during the application of preformed monochloramine from 4-15 mg/L Cl_2 to secondary wastewater. This non-linear increase in formation emphasises the presence of other organic matter (i.e. besides dimethylamine) can also act as NDMA precursors. At 10 mg/L Cl_2 , inline-formed monochloramine produced twice as much NDMA as preformed monochloramine, which is also in agreement with previous research.⁵ Higher concentrations of dichloramine and organic chloramines have been observed in Beenyup wastewater dosed with 10 mg/L Cl_2 inline-formed monochloramine, compared to 3 mg/L Cl_2 inline-formed monochloramine.⁵⁴ Overall, the results suggest that the monochloramine dose should be controlled carefully in full-scale plants that use inline-formed monochloramine in order to minimize NDMA formation.

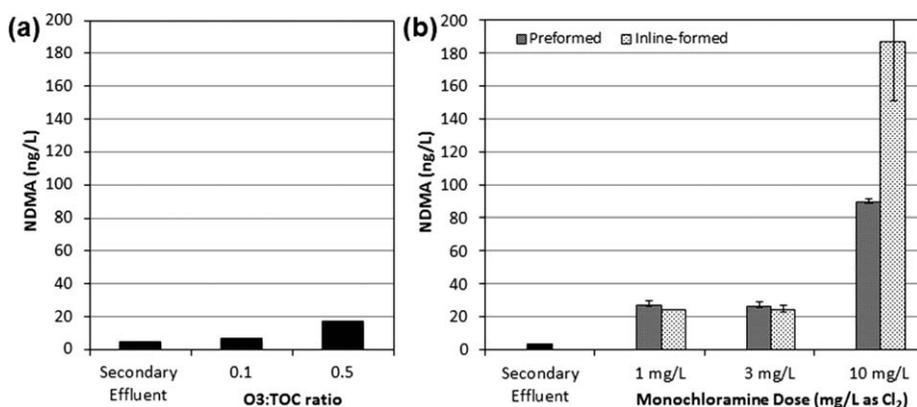


Figure 6 NDMA formation from a) ozonation and b) preformed and inline-formed chloramination

4. CONCLUSIONS

The two key barriers for *N*-nitrosamine precursor removal were found to be activated sludge treatment and RO. Reverse osmosis is much more effective in removing NDMA precursors than NDMA itself. Precursor removal during activated sludge treatment was related to the removal of ammonia, suggesting that nitrification is the most important removal mechanism for NDMA precursors. Hence, ensuring that the WWTP is operating well (in terms of nitrification) will promote maximum removal of NDMA precursors. Significant variability in the concentration of NDMA precursors in the primary wastewater led to variability in the concentration of NDMA precursors in secondary wastewater. Further investigations are required to understand the contribution of seasonal influences, influent flow rates or other sources of precursors to this variability. Analysis of treatment polymers used at the Beenyup WWTP and AWRP suggest that there would be little contribution from the polymers to NDMA formation.

Actual NDMA concentrations in secondary wastewater were much lower than NDMA precursor concentrations and did not correlate with precursor concentrations.

Although inline-formed monochloramine has been found to produce higher levels of dichloramine and organic chloramines than preformed monochloramine, the impact on *N*-nitrosamine formation was dose dependent. Increasing the chloramine dosage from 3 to 10 mg/L Cl₂, resulted in significantly more NDMA from inline-formed monochloramine than from preformed monochloramine. It is therefore important to control the dose at the treatment plant since a slight increase in dose could result in a significant increase in NDMA formation. Ozonation of Beenyup secondary wastewater did not lead to significant NDMA formation and therefore may have promise for NDMA precursor removal. However, ozone will produce its own suite of DBPs, and therefore it is important to test the formation of other DBP classes before any oxidation pre-treatment step is employed.

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References

1. P. Van Buynder, R. Lugg, C. Rodriguez, M. Bromley, J. Filmer, P. Blair, M. Handyside, S. Higginson, N. Turner, O. Lord, P. Taylor, K. Courtney, C. Newby, A. Heitz, K. Linge, J. Blythe, F. Buseti and S. Toze, *Premier's Collaborative Research Program (2005-2008): Characterising Treated Wastewater For Drinking Purposes Following Reverse Osmosis Treatment. Technical Report* ISBN: 978-0-9807477-0-6, Department of Health, Western Australia, 2009.
2. K. L. Linge, P. Blair, F. Buseti, C. Rodriguez and A. Heitz, *J. Water Supply Res. T.*, 2012, **61**, 494.
3. K. L. Linge, J. W. Blythe, F. Buseti, P. Blair, C. Rodriguez and A. Heitz, *Sep. Purif. Technol.*, 2013, **104**, 221.
4. C. R. Bartels, M. Wilf, K. Andes and J. Iong, *Water Sci. Technol.*, 2005, **51**, 473.
5. M. J. Farré, K. Döderer, L. Hearn, Y. Poussade, J. Keller and W. Gernjak, *J. Hazard. Mat.*, 2011, **185**, 1575.
6. J. M. Boyd, J. W. A. Charrois, R. Hofmann and S. E. Hrudey, in *Disinfection By-Products – Relevance to Human Health*, eds. S. Hrudey and J. W. A. Charrois, IWA Publishing, London, 2012.
7. J. W. A. Charrois, J. M. Boyd, K. L. Froese and S. E. Hrudey, *J. Environ. Eng. Sci.*, 2007, **6**, 103.
8. T. Fujioka, S. J. Khan, J. A. McDonald, A. Roux, Y. Poussade, J. E. Drewes and L. D. Nghiem, *Water Res.*, 2013, **47**, 6141.
9. S. D. Richardson, *Global NEST J.*, 2005, **7**, 43.
10. J. Choi and R. L. Valentine, *Water Res.*, 2002, **36**, 817.
11. Y. Y. Zhao, J. M. Boyd, M. Woodbeck, R. C. Andrews, F. Qin, S. E. Hrudey and X. F. Li, *Environ. Sci. Technol.*, 2008, **42**, 4857.
12. E. J. Marti, A. N. Pisarenko, J. R. Peller and E. R. V. Dickenson, *Water Res.*, in press, <http://dx.doi.org/10.1016/j.watres.2014.08.047>.