



DEFRA

**NDMA - CONCENTRATIONS IN DRINKING WATER
AND FACTORS AFFECTING ITS FORMATION
(CSA7240 / WT02049 / DWI 70/2/210)**

FINAL REPORT

**DEFRA 7348
March 2008**

NDMA - CONCENTRATIONS IN DRINKING WATER AND FACTORS AFFECTING ITS FORMATION (CSA7240 / WT02049 / DWI 70/2/210)

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SUMMARY

I OBJECTIVES

The general objective of this project was to review the occurrence of NDMA (N-nitrosodimethylamine) in drinking water supplies in England and Wales and to identify possible implications for future regulation and for water companies. The project was carried out in two phases:

- Phase 1 - A literature review and an assessment of the findings of the review with regard to water treatment.
- Phase 2 - A seasonal survey of NDMA in drinking water in England and Wales at treatment works selected as being most likely to give rise to the formation of NDMA.

II REASONS

NDMA has been detected in drinking water at low concentrations at some treatment works, mostly in North America. Where found, NDMA has also most often been associated with the practice of chloramination and in this respect NDMA is considered to be a disinfection by-product.

NDMA has been classified as “probably carcinogenic to humans” by the International Agency for Research on Cancer (IARC) and similarly by the US Environmental Protection Agency (USEPA). A guideline value for NDMA in drinking water of 100 ng/l is to be included in the second addendum to the 3rd edition of the World Health Organization (WHO) Guidelines for Drinking-water Quality and it is likely that the USEPA will assign a maximum contaminant concentration for NDMA in the near future but its value is unknown at present. The California Department of Public Health (CDPH) has established a notification level for NDMA of 10 ng/l whilst the Ontario Ministry of the Environment (MOE) has set a Maximum Acceptable Concentration (MAC) for NDMA at 9 ng/l.

There is no EU or UK national standard for NDMA in drinking water. It is possible that NDMA will be a candidate for any revision of the Drinking Water directive. Accordingly, Defra, through the Drinking Water Inspectorate (DWI), wants to understand the implications of any possible new standard.

Defra/DWI commissioned WRc to review existing data on NDMA and, based on the review, to carry out a representative survey of NDMA concentrations in drinking water in England and Wales.

III CONCLUSIONS

1. Forty-one treatment works in England and Wales were selected for sampling because of the presence of key factors known to be associated with the formation of NDMA. NDMA was detected in final waters at three of these works (Works C11, C12 and D18) in four quarterly surveys at concentrations up to 5.8 ng/l. Final water NDMA concentrations were within the current concentrations of concern in North America (9-10 ng/l) and substantially lower than the future WHO guideline value. Should future UK drinking water regulations

restrict NDMA to similar concentrations, this would have only minor impact on the UK water industry.

2. NDMA was detected at one other works (Works C16) in a sample of clarified water but not in samples of final water from this works. This raises the possibility that NDMA may have been present following coagulation at other works in the survey but was not detected in final water samples.
3. Key factors associated with the formation of NDMA identified from the literature review included organic precursors, the use of polyDADMAC or Epi-DMA polyelectrolytes in water treatment, and chloramination. The use of polyDADMACs and Epi-DMA in treatment in England and Wales is not believed to be widespread.
4. While the key factors identified from the literature review were present at the treatment works where NDMA was detected, they were also present at works where NDMA was not formed. It is believed that the source of the NDMA was in fact the coagulant used at these works (see Conclusion 5) and it is concluded that - for the water qualities and operating regimes at the treatment works sampled in the survey - the key factors identified had negligible effect on the formation and presence of NDMA.
5. A common factor at the treatment works where NDMA was detected was the use of a ferric coagulant. Laboratory tests on samples of this coagulant from Works C11 and C16 indicated that NDMA was a possible contaminant. However, the same coagulant was also dosed at works where NDMA was not detected in final waters.
6. At Works C12, NDMA was detected in the supernatant recycled to water treatment at 31.5 and 39.1 ng/l. Although the ferric coagulant from this works was not analysed directly for NDMA, it is probable that this elevated concentration of NDMA in the recycled supernatant was due to the coagulant dosed in the magnetite/backwash recovery process. The concentration of NDMA in the supernatant could be responsible for downstream concentrations of NDMA found in the treated water at this works.
7. Final water NDMA concentrations found in the four quarterly surveys showed no consistent trends. Although the number of samples taken was limited, there was no clear evidence to indicate a temperature-related - or other seasonal-related - effect on NDMA formation.
8. Concentrations of NDMA in samples from distribution were generally comparable to concentrations found in final waters. Although the number of samples taken in distribution was very limited, there was no clear evidence to indicate continued formation of NDMA in distribution.

IV RECOMMENDATIONS

1. The possibility of other coagulants being a source of NDMA in drinking water warrants further investigation.
2. The removal of NDMA in water treatment should be investigated more rigorously, including the possibility that NDMA is present at the coagulation stage but is not subsequently detected in the final water. This investigation should address coagulant type and dose, the range of treatment processes and chemicals used commonly in England and Wales, and possible seasonal affects. The investigation should enable the

development of appropriate control procedures to minimise concentrations of NDMA in drinking water.

3. The fate of NDMA in distribution should be investigated more rigorously including possible seasonal affects and the effect of residence time.

1. INTRODUCTION

1.1 Objectives

The general objective of this project was to review the occurrence of NDMA (N-nitrosodimethylamine) in drinking water supplies in England and Wales and to identify possible implications for future regulation and for water companies. The project was carried out in two phases:

- Phase 1 - A literature review and an assessment of the findings of the review with regard to water treatment.
- Phase 2 - A seasonal survey of NDMA in drinking water in England and Wales at treatment works selected as being most likely to give rise to the formation of NDMA.

1.2 Background

NDMA has been detected in drinking water at low concentrations at numerous treatment works, mostly in North America. Concentrations up to about 100 ng/l have been reported, although lower concentrations are more common. In one study of 21 treatment works in the US and Canada, NDMA was detected in 28 of 81 final water samples at concentrations between 0.7 and 30 ng/l. Where previously identified, the presence of NDMA has most often been associated with the practice of chloramination and in this respect NDMA is considered to be a disinfection by-product.

NDMA has been classified as “probably carcinogenic to humans” by the International Agency for Research on Cancer¹ (IARC) and similarly by the US Environmental Protection Agency (USEPA). A guideline value for NDMA in drinking water of 100 ng/l based on an upper-bound excess lifetime cancer risk of 10^{-5} (WHO, 2006)² is to be included in the second addendum to the 3rd edition of the World Health Organization (WHO) Guidelines for Drinking-water Quality. Using a different risk assessment approach, the USEPA identify a theoretical 10^{-6} lifetime risk level of cancer from NDMA exposure at 0.7 ng/l. It is likely that the USEPA will assign a maximum contaminant level for NDMA in the near future but its value is unknown at present. The California Department of Public Health (CDPH) has established a notification level for NDMA of 10 ng/l³. The Ontario Ministry of the Environment (MOE), Ontario, Canada, has set a Maximum Acceptable Concentration (MAC) for NDMA at 9 ng/l⁴.

¹ IARC (1987). Lyon, International Agency for Research on Cancer. Overall Evaluations of Carcinogenicity: An Updating of IARC Monographs, Volumes 1-42, Supplement No. 7.

² WHO (2006). N-Nitrosodimethylamine in Drinking Water. Background Document for the Development of WHO Guidelines for Drinking-Water Quality. World Health Organization, Geneva.

³ Fulmer, A and Khiari, D (2007). *Nitrosamines in Drinking Water*, Drinking Water Research, Nov/Dec 2007.

⁴ Najm, I and Trussell, R R (2000). *NDMA Formation in Water and Wastewater*, Paper presented at the AWWA Water Quality Technology Conference, Salt Lake City, November 2000.

There is no EU or UK national standard for NDMA in drinking water. It is possible that NDMA will be a candidate for any revision of the Drinking Water Directive. Accordingly, Defra, through the Drinking Water Inspectorate (DWI), wants to understand the implications of any possible new standard.

There are few data on concentrations of NDMA in drinking water in England and Wales. The DWI commissioned WRc to review existing data on NDMA and, based on the review, to carry out a representative survey of NDMA concentrations in drinking water in England and Wales.

1.3 Report format

The report includes the following sections:

- Section 1 – Describes the objectives and background to the project.
- Section 2 – Presents a brief summary of the literature review relating to NDMA in drinking water.
- Section 3 – Describes the development and validation of the analytical method for NDMA in drinking water used in this study.
- Section 4 – Summarises and discusses the results of the four seasonal sampling surveys for NDMA, carried out in December 2006, February 2007, June 2007 and September 2007. The results of an additional survey carried out in November 2007 and a programme of laboratory tests are also discussed.
- Section 5 - Presents the conclusions from this work.
- Section 6 - Makes recommendations for future work.

A series of appendices is also included:

- Appendix A - Presents the detailed literature review.
- Appendix B - Describes DWI guidance on sampling design, specifically on the design and implementation of stability trials.
- Appendix C - Presents full details of the sampling surveys and the laboratory tests.
- Appendix D - Presents process descriptions of the three works where NDMA was detected throughout the sampling survey: Works C11, C12 and D18.
- Appendix E - Presents full details of an extension to the main contract to investigate the possible contamination of a small number of coagulants with NDMA.

2. LITERATURE REVIEW

The first phase of this project required a review and assessment of the literature relating to the formation and occurrence of NDMA in drinking water. The specific objectives were:

- to carry out a literature review to identify studies relating to the occurrence of NDMA in drinking water; and
- to assess and summarise the findings of the studies identified from the literature review and their relevance to drinking water treatment practice in England and Wales.

A summary of the literature review is presented below; the full detailed review is presented in Appendix A.

The literature review identified numerous laboratory investigations of NDMA formation in drinking water. Generally, these investigations have been carried out to elucidate reaction mechanisms and have used unrealistically high concentrations of reactants compared with those occurring in water treatment.

The principal mechanism of NDMA formation in water treatment is probably through the reaction of monochloramine with organic precursors, particularly secondary and tertiary amines. The precursor mentioned most commonly - and the one used in most laboratory studies to investigate mechanisms - is dimethylamine (DMA), although a wide range of other precursors could occur in raw water sources.

There is considerable evidence in the literature of water samples taken from treatment works and in distribution containing NDMA at concentrations up to about 100 ng/l, although usually at much lower concentrations. Factors implicated in the formation of NDMA include raw water source, influence of sewage effluent and agricultural/industrial inputs (i.e. as sources of precursors), chemicals used in water treatment and treatment processes, particularly ion exchange and chloramination.

Findings from the literature review of particular relevance to water treatment in England and Wales included:

- Formation of NDMA can result from preformed chloramine or from separate addition of ammonia and chlorine. This has significance in relation to both treatment and distribution where chloramination is used. It will also be significant where ammonia occurs naturally in the raw water and is removed by chlorination.
- NDMA may also be formed through the reaction of nitrite with precursors, known as nitrosation, enhanced by the presence of chlorine. There are water treatment processes based on these mechanisms for ammonia or nitrate removal, but they have little or no implementation in the UK. However, the mechanism may occur in other processes such as granular activated carbon (GAC) adsorbers or filters to produce measurable concentrations of nitrite.
- Some polyelectrolytes used in water treatment, particularly the Epi-DMA (epichlorohydrin-dimethylamine) and polyDADMAC (polydiallyldimethylammonium chloride) products,

contain the precursor DMA. However, these chemicals are not believed to be widely used for drinking water treatment in England and Wales.

- Strong base anion exchange resins used for nitrate removal may provide a source of precursors for NDMA formation, particularly when new (and possibly also on decay with ageing).
- NDMA is a very hydrophilic compound with a high water solubility, hence is poorly adsorbed onto activated carbon. NDMA removal observed in some GAC adsorbers may be due to biological activity and biodegradation.

As there are few data on concentrations of NDMA in drinking water in England and Wales, it was recommended that a sampling survey be carried out, with samples taken quarterly to determine the extent of NDMA in water supplies and to capture any effects of seasonal changes in water quality and temperature.

3. NDMA ANALYSIS - METHOD DEVELOPMENT AND VALIDATION

3.1 Determination of NDMA in waters by solid phase extraction and GC-MS (Method LP/R/541)

3.1.1 Introduction

Laboratory accreditation

The analytical method described in this section (Section 3), including method development, validation and stability tests, relates to work done by Spencer House Laboratory, Thames Water. Spencer House Laboratory analysed all the samples from Surveys 1 to 5 (Section 4.2) and the additional laboratory studies (Section 4.3). Spencer House Laboratory is UKAS accredited (Registration No. 0677) and all work is performed to strict quality control standards (ISO 17025). Although NDMA is not included in its UKAS schedule of accreditation, the laboratory has wide-ranging experience in the analysis of trace levels of organic pollutants in water using methods including GC-MS and GC-MS-MS.

The analysis of samples for the contract extension work (Section 4.4) was conducted by a university laboratory. The method employed and validation conducted by this laboratory are described in Appendix E.

Principle

This method is for the determination of NDMA in waters.

Samples were spiked with a known concentration of deuterated internal standard (d6-NDMA) and extracted by passing the sample through a solid phase extraction (SPE) cartridge containing coconut charcoal. The cartridge was dried under vacuum and the NDMA was eluted from the cartridge with dichloromethane (DCM). The DCM extract was dried and concentrated down to approximately 200 µl. The extract was analysed by GC-MS using a 1 µl splitless injection on the PTV inlet.

Existing methodologies referred to in the method development:

Munch, J W and Bassett, M V (2004). Method 521: Determination of nitrosamines in drinking water by solid phase extraction and capillary column gas chromatography with large volume injection and chemical ionization tandem mass spectrometry (MS/MS). Version 1.0. EPA Document No. EPA/600/R-05/054. National Exposure Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, Ohio 45268 (www.epa.gov/nerlcwww/m_521.pdf).

Cheng, R C, Andrews-Tate, C, Hwang, C J, Guo, Y, Grebel, J E and Suffet, I H (2005). Comparison of alternative nitrosamine analyses for water reuse samples. Water Reuse

Association, California Section, 2005 Annual Conference, San Diego, CA. (www.watereuse.org/ca/2005conf/papers/A1_rcheng.pdf).

Range of application and reporting limits

The range of application was up to 40 ng/l NDMA. Concentrations above the range of application could be determined by dilution.

The minimum reporting limit was 0.9 ng/l NDMA.

3.1.2 Sampling and preservation

Samples were collected in 1-litre plastic PET bottles containing 40 mg of ascorbic acid. In the stability trials, to simulate initial sampling and conditions during transport, spiked NDMA samples were maintained at room temperature for approximately 17 hours prior to refrigeration.

On receipt into the laboratory, samples were stored in the dark at $4^{\circ}\text{C} \pm 2^{\circ}\text{C}$ prior to extraction. Samples were stable for up to 3 weeks when stored in the dark at $4^{\circ}\text{C} \pm 2^{\circ}\text{C}$ and extracts for 3 weeks when stored in the dark at $-15^{\circ}\text{C} \pm 5^{\circ}\text{C}$.

Every batch of samples was analysed with a procedural blank sample⁵.

3.1.3 Extraction procedure

Conditioning SPE cartridges

SPE cartridges were washed with DCM and methanol before being conditioned with methanol and ultrapure water.

Preparation of standards and AQC

One litre of ultrapure water was dechlorinated with ascorbic acid and spiked up with internal standard / standard / AQC as appropriate. The calibration range was as follows: 0, 4, 10, 20 and 40 ng/l NDMA with an AQC at 10 ng/l. The internal standard used was d6-NDMA at 40 ng/l.

Preparation of samples

One litre of sample was spiked up with internal standard at 40 ng/l.

⁵ NDMA was not found in any procedural blank sample, confirming that NDMA was not present as a contaminant of the test method.

Extraction

The extraction was performed using a Vacmaster 20 system. The waters were drawn through the SPE cartridges under vacuum.

Drying, elution and concentration

The cartridges were dried under vacuum and eluted with DCM. The DCM extract was dried with sodium sulphate to remove any residual water and concentrated using a stream of nitrogen to approximately 200 µl. The extract was transferred to an amber vial with insert and analysed by GC-MS.

3.1.4 Instrumental procedure

GC-MS conditions

- Method – NDMA.
- Agilent GC-MS: MS13 (6890GC, 5973 inert MS, 7683 injector) / MS15 (6890GC, 5975 MS, 7683B injector).
- Rtx5-amine column with deactivated pre-column.
- Helium carrier gas, constant pressure mode.
- PTV splitless injection mode - 1 µl injection.
- Oven ramp - 35°C up to 280°C.
- Transfer line heated to 280°C.
- Electron impact (EI) ionisation mode.
- SIM Mode - NDMA ions: 74, 42, 43 and d6-NDMA Ion: 80. (Note: M/z 74 and m/z 80 are quantifying ions, with m/z 74 being the molecular ion for NDMA and m/z 80 being the molecular ion for d6-NDMA. M/z 42 and m/z 43 are qualifying ions.)

3.2 Validation

The validation results for the two mass spectrometers MS13 and MS15 are shown in Sections 3.2.1 and 3.2.2, respectively. The results of the 21-day stability trials are shown in Section 3.2.3.

3.2.1 Precision results for the determinand NDMA - MS13

See Table 3.1.

3.2.2 Precision results for the determinand NDMA - MS15

See Table 3.2.

3.2.3 Stability trials

The stability trial design was as described in DWI Information Letter 12/05, *Guidance on Sample and Sample Extract Stability Trials and the Preservation and Preparation of Samples for Metals Analysis*. The DWI Guidance on Sample and Sample Extract Stability Trials is reproduced in Appendix B.

The stability trials used a chlorinated water and this was dechlorinated with ascorbic acid as per procedure used throughout the survey.

The results for in-bottle and in-vial stability trials for NDMA, demonstrating stability at 7, 14 and 21 days, are shown in Tables 3.3 to 3.7, respectively.

Table 3.1 Precision results for the determinand NDMA - MS13 (ng/l)

Solution		Blank	LOD	Low spike	High Spike	Tap Water	Tap Water Spike	AQC
True Concentration		0	4	10	30	0	10	10
Sample	Replicate							
1	1	0.41	3.77	8.87	29.95	0.47	9.33	9.57
1	2	0.56	3.67	9.26	28.13	0.42	9.05	9.63
2	1	0.54	3.64	9.19	28.68	0.60	9.61	9.39
2	2	0.61	3.62	9.50	28.76	0.55	8.97	9.33
3	1	0.38	4.16	9.88	29.61	0.36	9.94	9.65
3	2	0.34	4.22	10.08	30.21	0.66	9.80	9.65
4	1	0.46	4.30	10.34	31.85	1.04	10.84	9.67
4	2	0.44	4.23	9.92	30.66	0.82	10.05	9.75
5	1	0.21	4.23	9.76	28.03	0.31	9.57	9.52
5	2	0.22	4.09	9.50	31.31	0.22	9.98	9.36
6	1	0.34	4.03	9.61	30.42	0.35	9.97	9.17
6	2	0.29	4.43	10.70	31.98	0.33	10.17	9.41
7	1	0.30	4.35	9.48	30.10	0.35	9.93	9.47
7	2	0.36	4.08	9.92	31.15	0.30	9.84	9.77
8	1	0.12	3.98	9.42	30.21	0.16	10.27	9.30
8	2	0.12	3.75	10.02	29.82	0.14	10.28	9.73
9	1	0.65	4.30	9.38	28.14	0.66	10.19	9.61
9	2	0.66	4.42	9.81	30.20	0.66	9.58	9.32
10	1	0.04	3.89	10.25	27.67	0.03	9.14	9.83
10	2	0.03	4.22	9.40	28.93	0.05	11.02	10.14
11	1	0.17	3.92	9.08	27.86	0.18	9.44	9.88
11	2	0.21	4.14	9.11	29.57	0.26	9.60	9.92
Mean		0.3391	4.0655	9.6582	29.6927	0.4055	9.8441	9.5941
Between-batches mean square		0.0736	0.1102	0.2757	2.0549	0.1290	0.3004	0.0915
Within-batches mean square		0.0017	0.0225	0.1446	1.2862	0.0073	0.2400	0.0252
F-value		43.3225	4.8877	1.9058	1.5976	17.5584	1.2518	3.6376
Significance		***	**	NS	NS	***	NS	*
Within-batches SD		0.041	0.150	0.380	1.134	0.086	0.490	0.159
Between-batches SD		0.190	0.209	0.256	0.620	0.247	0.174	0.182
Total SD		0.194	0.258	0.458	1.292	0.261	0.520	0.242
Relative SD		57%	6%	5%	4%	64%	5%	3%
F 0.05		1.83	1.69	1.58	1.58	1.79	1.57	1.67
F-value		8.191	0.100	0.056	0.047	10.365	0.070	0.016
Estimated DF		10	14	19	19	11	20	15

Notes:

- | | |
|--|--|
| 1. NS | Not significant |
| 2. * | Significant at the 0.05 level |
| 3. ** | Significant at the 0.01 level |
| 4. *** | Significant at the 0.001 level |
| 5. Pass | St not significantly larger than target |
| 6. Date of analysis | 17/11/2006 |
| 7. Limit of detection | 0.45 ng/l (Calculated as 3x Sw (LOD solution)) |
| 8. Absolute target: | 0.05 |
| 9. Percentage target | 20% |
| 10. Conc of standard used for spiking | 200000 ng/l |
| 11. Vol of standard solution | 0.05 ml |
| 12. Vol of sample used | 1000 ml |
| 13. Conc added in spiking | 9.9995 ng/l |
| 14. Conc 'recovered' | 9.4387 ng/l |
| 15. Grand mean recovery | 94.39% |
| 16. Standard error of mean recovery | 1.35% |
| 17. 95% confidence limits on mean recovery | $\pm 2.46\%$ |
| 18. Best possible recovery | 96.85% |
| 19. Recovery acceptable if not significantly outside the range 95-105% | Pass |
| 20. Assessment of recovery | Pass |

Table 3.2 Precision results for the determinand NDMA - MS15 (ng/l)

Solution		Blank	LOD	Low spike	High Spike	Tap Water	Tap Water Spike	AQC
True Concentration		0	4	10	30	0	10	10
Sample	Replicate							
1	1	0.12	4.22	9.31	29.96	0.59	10.55	10.09
1	2	0.34	4.00	10.01	29.45	1.33	9.89	10.51
2	1	0.34	3.88	9.58	28.27	0.62	9.97	9.72
2	2	0.30	4.19	9.45	30.65	0.68	9.91	9.39
3	1	0.00	3.84	9.53	30.81	0.00	10.13	9.68
3	2	0.00	3.72	10.29	30.00	0.00	9.74	9.60
4	1	0.27	3.91	10.53	30.69	0.71	10.38	9.63
4	2	0.40	4.38	9.72	30.63	0.51	9.73	9.70
5	1	0.39	3.97	9.37	28.10	0.60	9.29	9.54
5	2	0.46	4.27	9.58	30.20	0.59	10.27	9.45
6	1	0.54	3.62	9.94	30.87	0.37	10.78	9.47
6	2	0.18	4.13	10.86	30.03	1.39	10.18	9.72
7	1	0.00	4.24	9.79	30.84	0.34	10.44	9.61
7	2	0.31	4.36	10.41	30.75	0.40	10.30	9.45
8	1	0.01	3.74	9.87	29.76	0.08	10.27	9.58
8	2	0.40	3.98	10.19	30.02	0.09	10.33	9.54
9	1	0.27	4.05	10.14	29.45	0.28	10.18	9.67
9	2	0.28	3.91	9.98	31.07	0.22	10.24	9.50
10	1	0.05	3.70	10.31	31.59	0.04	10.39	9.58
10	2	0.06	4.59	10.13	31.69	0.04	10.75	9.66
11	1	0.49	4.13	9.91	29.46	0.51	10.66	10.30
11	2	0.57	3.94	9.27	30.66	0.49	9.93	9.54
Mean		0.2627	4.035	9.9168	30.225	0.4491	10.1959	9.6786
Between-batches mean square		0.0488	0.0463	0.193	0.9503	0.2169	0.1198	0.1101
Within-batches mean square		0.0207	0.075	0.163	0.7204	0.0745	0.1374	0.0458
F-value		2.354	1.6192	1.1843	1.319	2.9103	1.1476	2.4042
Significance		NS	NS	NS	NS	*	NS	NS
Within-batches SD		0.144	0.274	0.404	0.849	0.273	0.371	0.214
Between-batches SD		0.118	0.000	0.123	0.339	0.267	0.000	0.179
Total SD		0.186	0.274	0.422	0.914	0.382	0.371	0.279
Relative SD		71%	7%	4%	3%	85%	4%	3%
F 0.05		1.62	1.57	1.57	1.57	1.64	1.57	1.62
F-value		12.595	0.115	0.045	0.023	18.060	0.033	0.021
Estimated DF		17	20	21	20	16	21	17

Notes:

- | | |
|--|---|
| 1. NS | Not significant |
| 2. * | Significant at the 0.05 level |
| 3. ** | Significant at the 0.01 level |
| 4. *** | Significant at the 0.001 level |
| 5. Pass | St not significantly larger than target |
| 6. Date of analysis | 17/11/2006 |
| 7. Limit of detection | 0.822 ng/l (Calculated as 3x Sw (LOD solution)) |
| 8. Absolute target: | 0.05 |
| 9. Percentage target | 20% |
| 10. Conc of standard used for spiking | 200000 ng/l |
| 11. Vol of standard solution | 0.05 ml |
| 12. Vol of sample used | 1000 ml |
| 13. Conc added in spiking | 9.9995 ng/l |
| 14. Conc 'recovered' | 9.7468 ng/l |
| 15. Grand mean recovery | 97.47% |
| 16. Standard error of mean recovery | 1.30% |
| 17. 95% confidence limits on mean recovery | $\pm 2.35\%$ |
| 18. Recovery acceptable if not significantly outside the range 95-105% | |
| 19. Assessment of recovery | Pass |

Table 3.3 NDMA stability study: In-bottle trial (Day 14)

Replicate	Day 0	Day 14	
1	11.28	9.84	
2	10.00	9.89	
3	9.76	11.45	
4	9.57	11.35	
5	9.80	11.43	
6	11.81	11.53	
7	11.40	10.36	
8	11.36	10.41	
9	10.47	10.61	
10	10.48	10.77	
N	10	10	
Mean	10.59	10.76	
Standard Deviation	0.81	0.65	
			Comparison
Pooled St. Dev., s			0.73
Mean diff, d Numerical value of change			0.17
SE (diff)			0.329
t statistic Observed value of t			0.520
Degrees of freedom			18
Critical value (0.05) Tabulated value of t			2.101

Notes:

1. Conclusion: The difference between the means is not significant.

Target diff, 5%		0.53	t statistic	1.612 ¹
Target diff, 10%		1.06	t statistic	3.224 ²
Target diff, 12.5%	Target change numerical data	1.32	t statistic	4.030 ³

Notes:

1. A 5% difference would not be significant.
2. A 10% difference would be significant.
3. A 12.5% difference would be significant.

Acceptance Criteria

Mean difference > target change value	No
Observed t > tabulated t	No
Target change t statistic > tabulated t	Yes

Conclusion **Stable**

Table 3.4 NDMA stability study: In-bottle trial (Day 21)

Replicate	Day 0	Day 21
1	9.67	10.19
2	9.20	10.03
3	9.40	10.06
4	9.21	9.96
5	9.85	9.48
6	9.62	10.31
7	9.23	10.69
8	9.08	9.97
9	9.36	10.35
10	9.13	9.37
N	10	10
Mean	9.38	10.04
Standard Deviation	0.26	0.39
		Comparison
Pooled St. Dev., s		0.33
Mean diff, d	Numerical value of change	0.67
SE (diff)		0.149
t statistic	Observed value of t	4.481
Degrees of freedom		18
Critical value (0.05)	Tabulated value of t	2.101

Notes:

1. Conclusion: There is a real difference between the means.

Target diff, 5%		0.47	t statistic	3.154 ¹
Target diff, 10%		0.94	t statistic	6.308 ²
Target diff, 12.5%	Target change numerical data	1.17	t statistic	7.885 ³

Notes:

1. A 5% difference would be significant.
2. A 10% difference would be significant.
3. A 12.5% difference would be significant.

Acceptance Criteria

Mean difference > target change value	No
Observed t > tabulated t	Yes
Target change t statistic > tabulated t	n/a

Conclusion	Stable
-------------------	---------------

Table 3.6 NDMA stability study: In-vial trial (Day 14)

Replicate	Day 0	Day 14	
1	9.84	10.97	
2	9.89	10.49	
3	11.45	10.90	
4	11.35	10.68	
5	11.43	10.51	
6	11.53	11.20	
7	10.36	9.88	
8	10.41	11.73	
9	10.61	10.87	
10	10.77	9.97	
N	10	10	
Mean	10.76	10.72	
Standard Deviation	0.65	0.55	
			Comparison
Pooled St. Dev., s			0.60
Mean diff, d	Numerical value of change		0.04
SE (diff)			0.269
t statistic	Observed value of t		0.164
Degrees of freedom			18
Critical value (0.05)	Tabulated value of t		2.101

Notes:

1. Conclusion: The difference between the means is not significant.

Target diff, 5%		0.54	t statistic	2.001 ¹
Target diff, 10%		1.08	t statistic	4.003 ²
Target diff, 12.5%	Target change numerical data	1.35	t statistic	5.003 ³

Notes:

1. A 5% difference would not be significant.
2. A 10% difference would be significant.
3. A 12.5% difference would be significant.

Acceptance Criteria

Mean difference > target change value	No
Observed t > tabulated t	No
Target change t statistic > tabulated t	Yes

Conclusion Stable

Table 3.7 NDMA stability study: In-vial trial (Day 21)

Replicate	Day 0	Day 21
1	9.84	11.89
2	9.89	11.73
3	11.45	11.78
4	11.35	11.37
5	11.43	10.52
6	11.53	11.53
7	10.36	10.42
8	10.41	12.45
9	10.61	11.64
10	10.77	10.32
N	10	10
Mean	10.76	11.37
Standard Deviation	0.65	0.71
		Comparison
Pooled St. Dev., s		0.68
Mean diff, d	Numerical value of change	0.60
SE (diff)		0.304
t statistic	Observed value of t	1.975
Degrees of freedom		18
Critical value (0.05)	Tabulated value of t	2.101

Notes:

1. Conclusion: The difference between the means is not significant.

Target diff, 5%		0.54	t statistic	1.769 ¹
Target diff, 10%		1.08	t statistic	3.537 ²
Target diff, 12.5%	Target change numerical data	1.35	t statistic	4.421 ³

Notes:

1. A 5% difference would not be significant.
2. A 10% difference would be significant.
3. A 12.5% difference would be significant.

Acceptance Criteria

Mean difference > target change value	No
Observed t > tabulated t	No
Target change t statistic > tabulated t	Yes

Conclusion **Stable**

4. NDMA SAMPLING SURVEY

4.1 Selection of treatment works

A literature review was carried out as part of the first phase of this project to identify factors affecting the formation of NDMA in water treatment and its occurrence in drinking water (see Appendix A). Key factors identified from the review included:

- raw water source (e.g. groundwater, lowland surface water, upland surface water) and quality (e.g. presence of organics, ammonia, nitrite);
- proximity of sewage effluent or agricultural/industrial inputs;
- use of treatment chemicals (e.g. polyDADMAC or Epi-DMA polyelectrolytes);
- use of treatment processes (e.g. ion exchange, GAC adsorption, chloramination); and
- distribution characteristics.

It was recommended as a result of the literature review to carry out a survey of NDMA in drinking water in England and Wales, sampling from treatment works that exhibited one or more of the above factors.

Subsequently, a survey of 41 treatment works from 11 water utilities was carried out. In addition, two works where none of the key factors for NDMA formation were exhibited were included as 'controls', i.e. works where the formation of NDMA would not be expected. Relatively few 'control' works were included in order to focus the available resources on those works perceived to be at high risk.

At the beginning of the survey, it was intended to take quarterly samples from 20 works (including the two 'control' works) to determine the extent of NDMA in drinking water and any seasonal effects. However, as the project progressed, it was considered greater overall value would be obtained by including a larger number of works though not sampling every works every quarter. The benefits of this approach were considered to outweigh any potential disadvantages, such as reducing the strength of the seasonal effects and other possible statistical analyses. Consequently, works where NDMA was not detected in successive surveys were excluded from subsequent surveys; works where NDMA was detected in final water were sampled more intensively in subsequent surveys, including sampling of raw water, within treatment and from distribution. An anonymised list of the participating water utilities and treatment works, together with a summary of the surveys participated in, is given in Table 4.1.

In addition to the quarterly sampling surveys, a fifth additional survey and a series of laboratory tests were carried out to elucidate the results from the preceding surveys.

NDMA analysis for Surveys 1-5 and the laboratory tests was carried out by Spencer House Laboratory. NDMA analysis for the work described under Contract Extension (Section 4.4) was carried out by a university laboratory.

Table 4.1 List of participating water utilities and treatment works

Works Ref.	Works Description	Survey No.			
		1	2	3	4
Utility A					
A1	<i>Source:</i> Reservoir, Agricultural input, Sewage effluent input, High colour/TOC, Algae, Pesticides <i>Treatment:</i> RGF, Ozonation, GAC, Chloramination <i>Chemicals:</i>	X	X		
A2	<i>Source:</i> Groundwater, High colour/TOC <i>Treatment:</i> Coagulation, RGF, GAC, Chloramination <i>Chemicals:</i> Ferric coagulant	X	X		
A3	<i>Source:</i> Lowland river/reservoir, Agricultural input, Sewage effluent input, High colour/TOC, Algae, Ammonia, Nitrate, Pesticides <i>Treatment:</i> Coagulation, RGF, Recycle, Ozonation, GAC, Chlorination <i>Chemicals:</i> Aluminium coagulant	X	X		
A4	<i>Source:</i> Lowland river/reservoir, Agricultural input, Sewage effluent input, High colour/TOC, Algae, Ammonia, Nitrate, Pesticides <i>Treatment:</i> Coagulation, RGF, Recycle, Ozonation, GAC, Ion exchange, Chlorination <i>Chemicals:</i> Aluminium coagulant	X	X		
A5	<i>Source:</i> Groundwater, Ammonia <i>Treatment:</i> Chlorination <i>Chemicals:</i>	X	X		
A6	<i>Source:</i> Groundwater, Agricultural input, Nitrate, Pesticides <i>Treatment:</i> Ion exchange, GAC, Chlorination <i>Chemicals:</i>	X	X		
A7	<i>Source:</i> Groundwater, Nitrate, Pesticides <i>Treatment:</i> Ion exchange, GAC, Chlorination <i>Chemicals:</i>	X	X		
A8	<i>Source:</i> Lowland river/reservoir, Agricultural input, Sewage effluent input, High colour/TOC, Algae, Ammonia, Nitrate, Pesticides <i>Treatment:</i> Coagulation, RGF, Ozonation, GAC, Chloramination <i>Chemicals:</i> Ferric coagulant	X	X		
AC1 ('Control')	<i>Source:</i> Groundwater <i>Treatment:</i> Chlorination <i>Chemicals:</i>	X	X		
Utility B					
B9	<i>Source:</i> Upland reservoir, High colour/TOC <i>Treatment:</i> Coagulation, Pressure filtration, Pre-chlorination, RGF (manganese removal), Chlorination <i>Chemicals:</i> Aluminium coagulant	X	X		
B10	<i>Source:</i> Lowland Reservoir (fed by canal), Agricultural input, Sewage effluent input, High colour/TOC, Algae, Pesticides <i>Treatment:</i> Coagulation, Pressure filtration, GAC, Chlorination <i>Chemicals:</i> Aluminium coagulant	X	X		
BC2 ('Control')	<i>Source:</i> Groundwater, Pesticides (trace) <i>Treatment:</i> Chlorination <i>Chemicals:</i>	X	X		
Utility C					
C11 ¹	<i>Source:</i> Upland, High colour/TOC <i>Treatment:</i> Coagulation, Pre-chlorination (~1 mg/l), RGF, Chloramination <i>Chemicals:</i> Ferric coagulant, Polyacrylamide	X	X	X	X
C12 ¹	<i>Source:</i> Upland, High colour/TOC <i>Treatment:</i> Sirofloc, Pre-chlorination (~1 mg/l), RGF, Chlorination <i>Chemicals:</i> PolyDADMAC (2-3 mg/l)	X	X	X	X
C13	<i>Source:</i> Lowland river, Agricultural input, Algae, Ammonia, Nitrate, Pesticides <i>Treatment:</i> Coagulation, Ozonation, RGF/GAC, Chlorination <i>Chemicals:</i> Aluminium coagulant, PolyDADMAC (0.7-1.4 mg/l), Polyelectrolyte	X	X		
C14	<i>Source:</i> Lowland river, Agricultural input, Sewage effluent input, Pesticides <i>Treatment:</i> Actiflo, RGF, Ozonation, GAC, Chlorination <i>Chemicals:</i> Polyelectrolyte (FloPam AN905 SEP)	X	X		

Works Ref.	Works Description	Survey No.			
		1	2	3	4
C15	<i>Source:</i> Lowland river, Agricultural input, Algae, Pesticides <i>Treatment:</i> Pre-ozonation (2-3 mg/l), Coagulation, Direct RGF, Chlorination <i>Chemicals:</i> Ferric coagulant (~1 mg/l), PolyDADMAC (1-2 mg/l)	X	X	X	
C16 ¹	<i>Source:</i> Upland reservoir, High colour/TOC <i>Treatment:</i> Coagulation, RGF1, RGF2 (Mn removal), Chlorination <i>Chemicals:</i> Ferric coagulant, Polyacrylamide		X	X	
C17	<i>Source:</i> River, High colour/TOC, Pesticides <i>Treatment:</i> Coagulation, RGF, GAC, Chloramination <i>Chemicals:</i> Aluminium coagulant, Polyacrylamide		X	X	
Utility D					
D16	<i>Source:</i> Reservoir, Ammonia, Pesticides <i>Treatment:</i> Coagulation, RGF, GAC, Chlorination, Dechlorination (NaHSO ₄) <i>Chemicals:</i> Ferric coagulant, Starch-based polyelectrolyte (Wisprofluc)	X	X		
D17	<i>Source:</i> River, Reservoir, Ammonia, Nitrate, Pesticides <i>Treatment:</i> Coagulation, RGF, Ozonation, GAC, Chlorination, Dechlorination (SO ₂) <i>Chemicals:</i> Ferric coagulant, Polyacrylamide (LT22S)	X	X		
D18	<i>Source:</i> Reservoir, Ammonia, Nitrate, Pesticides <i>Treatment:</i> Coagulation, RGF, GAC, Chlorination, Dechlorination (SO ₂) <i>Chemicals:</i> Ferric coagulant, Polyacrylamide (LT22), Epi-DMA	X	X	X	X
D19 ²	<i>Source:</i> Lowland river <i>Treatment:</i> Sedimentation, Pre-ozonation, Coagulation, RGF, Ozonation, GAC, Chlorination, Dechlorination (SO ₂) <i>Chemicals:</i> Aluminium or Ferric coagulant			X	X
Utility E					
E19	<i>Source:</i> Upland reservoir, High colour/TOC <i>Treatment:</i> Coagulation, Direct RGF, SSF, Ozonation (infrequent), Chlorination <i>Chemicals:</i> Aluminium coagulant, Polyacrylamide, PolyDADMAC		X	X	
E20	<i>Source:</i> Upland reservoir, High colour/TOC <i>Treatment:</i> Coagulation, RGF1, RGF2 (Mn removal), Chlorination <i>Chemicals:</i> Ferric coagulant, Polyacrylamide		X	X	
E21	<i>Source:</i> Upland reservoir, Agricultural input <i>Treatment:</i> Coagulation, RGF, Chlorination <i>Chemicals:</i> Aluminium coagulant, Polyacrylamide, polyDADMAC		X	X	
E22	<i>Source:</i> Upland river, Agricultural input, Sewage effluent input (limited), Ammonia, Pesticides <i>Treatment:</i> Coagulation, RGF1, RGF2 (Mn removal), GAC, Chlorination <i>Chemicals:</i> Aluminium coagulant, Polyacrylamide (LT22S)		X	X	
E23	<i>Source:</i> E19, E22 <i>Treatment:</i> Coagulation, RGF, Chlorination <i>Chemicals:</i> PolyDADMAC (LT35), Polyacrylamide (A120)		X	X	
Utility F					
F1 ²	<i>Source:</i> Lowland reservoir, Agricultural input, Sewage effluent input, Pesticides <i>Treatment:</i> Coagulation, RGF, Backwash recycle, Ozonation (2-3 mg/l), GAC, Chlorination <i>Chemicals:</i> Ferric coagulant			X	X
Utility G					
G1 ²	<i>Source:</i> Lowland river (with bankside storage), Agricultural input, Sewage effluent input, Algae, Ammonia, Nitrate, Pesticides <i>Treatment:</i> Pre-ozonation (1.5 mg/l), Coagulation, RGF, Backwash recycle, Ozonation (0.2 mg/l residual), GAC, Chlorination <i>Chemicals:</i> Aluminium coagulant, Polyacrylamide			X	X
G2 ²	<i>Source:</i> Lowland river / Groundwater, Agricultural input, Sewage effluent input, High colour/TOC, Pesticides <i>Treatment:</i> Coagulation, RGF1, RGF2 (Mn removal), Backwash recycle, Ozonation (0.6-1.0 mg/l), GAC, Chlorination <i>Chemicals:</i> Aluminium coagulant, Polyacrylamide			X	X

Works Ref.	Works Description	Survey No.			
		1	2	3	4
Utility H					
H1 ²	<i>Source:</i> Lowland river, Agricultural input, Sewage effluent input, Algae, Ammonia, Nitrate, Pesticides <i>Treatment:</i> Pre-ozonation (0.7-1.0 mg/l), Coagulation, RGF, Ozonation (1.8-1.2 mg/l), GAC, Chlorination <i>Chemicals:</i> Ferric coagulant, Polyacrylamide			X	X
H2 ²	<i>Source:</i> Lowland river, Agricultural input, Sewage effluent input, Algae, Ammonia, Nitrate, Pesticides <i>Treatment:</i> Pre-ozonation (0.7-1.0 mg/l), Coagulation, RGF, Ozonation (1.8-1.2 mg/l), GAC, Chlorination <i>Chemicals:</i> Ferric coagulant, Polyacrylamide			X	X
H3 ²	<i>Source:</i> Lowland river, Agricultural input, Sewage effluent input, Algae, Ammonia, Nitrate, Pesticides <i>Treatment:</i> Pre-ozonation (0.8-1.5 mg/l), Coagulation, RGF, Ozonation (0.8-1.2 mg/l), GAC, Chlorination (contact tank), Chloramination (distribution) <i>Chemicals:</i> Ferric coagulant			X	X
H4	<i>Source:</i> Lowland river, Agricultural input, Sewage effluent input, Algae, Ammonia, Nitrate, Pesticides <i>Treatment:</i> Pre-ozonation (0.8-1.2 mg/l), Coagulation, RGF, Ozonation (0.3-0.8 mg/l), GAC, Chlorination (contact tank), Chloramination (distribution) <i>Chemicals:</i> Ferric coagulant, Polyacrylamide, PolyDADMAC			X	X
H5	<i>Source:</i> Lowland reservoir, Agricultural input, Sewage effluent input, Algae, Ammonia, Pesticides <i>Treatment:</i> Pre-ozonation (0.7-1.5 mg/l), Coagulation, RGF, Ozonation (1.0-1.5 mg/l), GAC, Chlorination (contact tank), Chloramination (distribution) <i>Chemicals:</i> Ferric coagulant, Polyacrylamide			X	X
H6	<i>Source:</i> Lowland river, Lowland reservoir, Agricultural input, Sewage effluent input, Algae, Ammonia, Pesticides <i>Treatment:</i> Coagulation, RGF, Backwash recycle, Ozonation (1.3-1.7 mg/l), GAC, Chlorination (contact tank), Chloramination (distribution) <i>Chemicals:</i> Ferric coagulant, Polyacrylamide			X	X
H7	<i>Source:</i> Lowland reservoir, Agricultural input, Algae, Ammonia, Pesticides <i>Treatment:</i> Slow sand filtration, RGF, GAC, Chlorination (contact tank), Chloramination (distribution) <i>Chemicals:</i> None			X	X
Utility J					
J1	<i>Source:</i> Lowland river/groundwater, Agricultural input, Sewage effluent input, High colour/TOC, Algae, Ammonia, Nitrate, Pesticides <i>Treatment:</i> Coagulation, RGF, Chlorination <i>Chemicals:</i> Aluminium coagulant (130 mg/l), Polyacrylamide (0.11 mg/l)			X	X
J2	<i>Source:</i> Upland reservoir <i>Treatment:</i> Coagulation, RGF, Ozonation (5 mg/l), GAC, Chlorination <i>Chemicals:</i>			X	X
J3	<i>Source:</i> Lowland reservoir, High colour/TOC, Algae <i>Treatment:</i> Coagulation, RGF, GAC, Chlorination, Chloramination <i>Chemicals:</i> Aluminium coagulant (6 mg/l)			X	X
Utility K					
K1	<i>Source:</i> Lowland reservoir, Algae, Pesticides <i>Treatment:</i> Pre-chlorination, Coagulation, RGF, Backwash & waste liquor recycle, GAC, Aeration, Chlorination (contact tank), Chloramination (distribution) <i>Chemicals:</i> Aluminium coagulant (18 mg/l Al ₂ O ₃), Starch-based polyelectrolyte (Wisprofloc - 2 mg/l; also used in sludge treatment)				X
Utility L					
L1 ¹	<i>Source:</i> Reservoir, Agricultural input, High colour / TOC, Algae, Pesticides <i>Treatment:</i> Coagulation, RGF, Backwash recycle (occasional via membrane), GAC, Chlorination <i>Chemicals:</i> Polyaluminium chloride (8-15 mg/l Al ₂ O ₃), PolyDADMAC (1-2 mg/l)				

Notes:

1. Works C11, C12, C16 and L1 were also sampled in Survey 5.
2. Works D19, F1, G1, G2, H1, H2 and H3 were also included in a survey conducted by Bayer CropScience AG.

4.2 Summary of survey results

Quarterly sampling surveys were carried out in December 2006, February 2007, June 2007 and September 2007. A fifth additional survey was carried out in November 2007. Full details of these surveys are presented in Appendix C; a summary of the results is given below.

4.2.1 Survey 1 (December 2006)

The first sampling survey was carried out during week beginning 4 December 2006. Samples of final water were taken from 18 treatment works from four utilities (Utilities A, B, C and D), including samples from two 'control' works.

NDMA was found at concentrations between 1.6 - 5.8 ng/l in final water from three of the 18 treatment works sampled: Works C11, C12 and D18. NDMA was not detected in the samples from the two 'control' works nor in samples from Utilities A or B, or the other works from Utilities C or D.

The highest concentration of NDMA (5.6-5.8 ng/l) was found in the final water from Works C11 that treats a highly-coloured upland water by coagulation (with ferric coagulant), filtration and chloramination.

NDMA was also found in the final water sampled from Works C12 (1.6-1.8 ng/l) that treats a highly-coloured upland water and includes dosing of polyDADMAC, and Works D18 (1.6-1.8 ng/l) that treats a reservoir water by coagulation (with ferric coagulant) and includes dosing of Epi-DMA.

4.2.2 Survey 2 (February 2007)

The second survey was carried out during week beginning 26 February 2007. Samples were taken from 17 of the works participating in Survey 1 together with an additional seven works - including five works from a fifth utility, Utility E.

NDMA was found at concentrations between 1.3 - 3.2 ng/l in samples from three of the 24 treatment works sampled: Works C11, C12 and D18, where NDMA was also detected in Survey 1. NDMA was not detected in the samples from the two 'control' works nor in samples from Utilities A, B or E, or the other works from Utilities C or D.

The highest concentration of NDMA was again found in samples from Works C11. A concentration of 3.2 ng/l was found in a chlorinated sample taken before ammoniation. Chloraminated final water was sampled from Main No.1 (1.3 ng/l) and Main No.2 (2.5 ng/l). The two mains were dosed independently with ammonium sulphate, proportional to the chlorine concentration measured following the 'Final Tank'.

NDMA (1.5 ng/l) was found in the final water sampled from Works C12. A concentration of 1.7 ng/l was found in water sampled prior to polyDADMAC dosing but NDMA was not detected in a sample of polyDADMAC-dosed water prior to chlorination.

NDMA (1.9-2.0 ng/l) was found in the final water sampled from Works D18. An NDMA concentration of 2.1 ng/l was found in water sampled prior to dosing Epi-DMA.

4.2.3 Survey 3 (June 2007)

The third survey was carried out during week beginning 11 June 2007. Samples were taken from 25 works, including 13 works from four 'new' utilities (Utilities F, G, H and J) and an additional works from Utility D (Works D19). Works that had been sampled in both Surveys 1 and 2 where NDMA had not been detected were excluded from further sampling: all works at Utilities A and B, Works C13, C14, D16 and D17.

Seven works (Works D19, F1, G1, G2, H1, H2 and H3) were included for the first time as these had been included in a survey conducted by Bayer CropScience AG because of concern about the formation of NDMA as a result of ozonation of dimethylsulfamide, a metabolite of the fungicide tolyfluanid (see Appendix A).

Samples of final water only were taken from 22 treatment works. More intensive sampling - including sampling of raw water, within treatment and from distribution - was carried out at Works C11, C12 and D18.

NDMA was found at concentrations between 1.1 - 10.0 ng/l in samples from three of the 25 treatment works sampled: Works C11, C12 and D18, where NDMA was also detected in Surveys 1 and 2. NDMA was not detected in samples from Utilities E, F, G, H or J, nor in samples from other works in Utilities C and D.

At each of the works sampled intensively (C11, C12 and D18), NDMA was detected throughout water treatment and in distribution but not in the raw water.

The highest concentrations of NDMA (9.9 - 10.0 ng/l) were found in the post-clarified and RGF filtered samples from Works C11. The measured concentration in distribution (6.8 ng/l) was not substantially different to that found in the final water leaving the works (5.1 ng/l).

At Works C12, NDMA (2.7 - 2.9 ng/l) was found in samples of water taken following polyDADMAC dosing and from distribution.

At Works D18, the highest concentration of NDMA (3.7 ng/l) was found in the post-clarified sample. Samples taken downstream of GAC adsorption, including from distribution, measured 1.1 ng/l or less.

4.2.4 Survey 4 (September 2007)

The fourth sampling survey was carried out during week beginning 24 September 2007. Samples were taken from 18 works, including one works from a 'new' utility (Utility K). Works that had been sampled in previous successive surveys where NDMA had not been detected were excluded from further sampling: all works at Utility E and Works C15, C16 and C17.

Samples of final water only were taken from 15 treatment works. More intensive sampling was again carried out at Works C11, C12 and D18.

NDMA was found at concentrations between 1.0 - 39.1 ng/l in samples from three of the 18 treatment works sampled: Works C11, C12 and D18, where NDMA was detected in Surveys 1, 2 and 3. NDMA was not detected in samples from Works D19 or from Utilities E, F, G, H, J or K.

As observed for Survey 3, at each of the works sampled intensively, NDMA was detected throughout water treatment and in distribution but not in the raw water. The highest concentration (39.1 ng/l), found in recycled supernatant sampled at Works C12, was an order of magnitude greater than other NDMA concentrations found at this works. The recycled supernatant originates from the magnetite/backwash recovery process. Here 'spent' magnetite from water treatment is processed and the recovered magnetite is recycled to water treatment. Wastewater from the recovery process is dosed with ferric coagulant (in the order of 100 mg/l as Fe³⁺). Following flocculation and thickening, the resultant supernatant is recycled to the head of the treatment works. The ferric coagulant used in the recovery process was the same coagulant as used at works C11 and D18.

At Works C11, NDMA was found at concentrations between 1.5 - 4.3 ng/l. The measurements within treatment were generally consistent (3.6 - 4.3 ng/l), with a lower concentration found in distribution (1.5 ng/l). The NDMA concentration found in the recycled supernatant from sludge thickening (3.6 ng/l) was consistent with measurements in water treatment.

At Works C12, NDMA was found at concentrations between 2.2 - 3.1 ng/l in samples of water taken following recycle of supernatant and polyDADMAC dosing, and from distribution. The NDMA concentrations found in water treatment and distribution could be accounted for by the dilution of the NDMA in the recycled supernatant. The recycled supernatant constitutes about 5 - 7% of the flow at the works intake, thus the resultant dilution would give calculated NDMA concentrations in the order of 2.0 - 2.7 ng/l.

At Works D18, the highest concentration of NDMA (3.4 ng/l) was found in the post-clarified sample. Samples taken downstream of GAC adsorption again measured 1.1 ng/l or less.

4.2.5 Survey 5 (November 2007)

A fifth sampling survey was carried out during week beginning 12 November 2007 to include further works dosing polyDADMAC or Epi-DMA, and also to elucidate some of the results from Survey 4. Thus samples were taken from a works that dosed polyDADMAC from a 'new' utility (Utility L), Works C11 and C12 (both recycled supernatant samples), and Works C16 (raw and clarified water samples).

NDMA was not detected in the final water sampled from Works L1.

NDMA (1.9-2.3 ng/l) was found in the recycled supernatant samples from Works C11, comparable with the concentration found in Survey 4 (3.6 ng/l).

NDMA (31.5 ng/l) found in the recycled supernatant sample from Works C12 confirmed the magnitude of the recycled supernatant sample found in Survey 4 (39.1 ng/l). The supernatant sample was taken following dosing of a ferric coagulant in the order of 100 mg/l Fe; NDMA was not detected in a sample taken immediately before coagulant dosing. Although the coagulant dosed at Works C12 was not analysed directly for NDMA, this result together with the evidence given above (Section 4.2.4) provides very strong circumstantial evidence that the ferric coagulant used at the site was the source of the NDMA.

NDMA (2.7 ng/l) was detected in the clarified water sampled from Works C16, but not in the raw water. Works C16 treats a highly coloured raw water by ferric coagulation. NDMA was not detected in samples of final water taken from this works in Surveys 2 and 3.

4.2.6 Discussion

NDMA was detected in final waters at three works in each of the four quarterly surveys: Works C11, C12 and D18. The seasonal variation in NDMA detected at these works is shown in Table 4.2.

The NDMA concentrations found in the final water samples were below current concentrations of concern in North America and substantially lower than the likely WHO guideline value for NDMA. The highest concentration in water treatment (i.e. excluding the recycled supernatant samples from Works C12) was 10.0 ng/l found immediately after coagulation and pH adjustment at Works C11; the concentration entering supply was lower at 5.1 ng/l.

Table 4.2 Seasonal variation in NDMA concentration (ng/l) found at Works C11, C12 and D18

Sample	Survey 1 (December 06)	Survey 2 (February 07)	Survey 3 (June 07)	Survey 4 (September 07)
Works C11				
Raw	-	-	< 0.9	< 0.9
Recycle	-	-	-	3.6
Post-clarifier (pre-chlorine)	-	-	10.0	3.9
Post-RGF (chlorinated)	-	-	9.9	3.7
Post-contact tank (chlorinated)	-	3.2	5.2	4.2
Final (chloraminated)	5.6 / 5.8	1.3 / 2.5	5.1	4.3
Distribution	-	-	6.8	1.5
Works C12				
Raw	-	-	< 0.9	< 0.9
Recycle	-	-	-	39.1
Pre-polyDADMAC ¹	-	1.7	-	-
Post-clarifier (post- polyDADMAC / pre-chlorine)	-	< 0.9	2.9	2.3
Post RGF (chlorinated)	-	-	2.9	3.1
Final (chlorinated)	1.6 / 1.8	1.5	2.8	2.5
Distribution	-	-	2.7	2.2
Works D18				
Raw	-	-	< 0.9	< 0.9
Pre Epi-DMA	-	2.1	-	-
Post-clarifier (post Epi-DMA)	-	-	3.7	3.4
Post GAC (pre-chlorine)	-	-	< 0.9	< 0.9
Final (chlorinated)	1.6 / 1.8	1.9 / 2.0	1.1	1.0
Distribution	-	-	1.1	1.1

Note:

1. Nominally sampled pre-polyDADMAC dosing, but possibly affected by backmixing caused by the hydraulic dosing arrangement.

Several factors associated with the formation of NDMA were present at Works C11, C12 and D18. Possible contributory factors included treatment of highly-coloured upland waters, dosing of polyDADMAC or Epi-DMA polyelectrolytes, and chloramination. However, these factors were also present at works where NDMA was not detected.

The NDMA concentration (39.1 ng/l) found in the recycled supernatant from magnetite regeneration at Works C12 could account for the downstream concentrations of NDMA found

in water treatment at this works. The supernatant sample was taken following dosing of a ferric coagulant in the order of 100 mg/l Fe. This, and other results from Survey 4, indicated the possibility that the ferric coagulant was a factor in the occurrence of NDMA.

In Survey 5, NDMA (2.7 ng/l) was detected in the clarified water sampled from Works C16 where treatment included ferric coagulation. NDMA had not been detected in samples of final water taken from this works in Surveys 2 and 3. This raises the possibility that NDMA may have been formed as a result of coagulation at other works in the survey, but was not detected in final water samples.

NDMA was detected at four works that dosed the same ferric coagulant: Works C11, C16 and D18 where the coagulant was dosed directly into treatment, and Works C12 where the coagulant was dosed in the magnetite recovery process and the resultant supernatant was recycled to water treatment. Subsequent laboratory tests (see Section 4.3) also implicated the ferric coagulant as a source of NDMA. However, the same ferric coagulant was dosed at treatment works where NDMA was not detected in final waters: Works C15, D16, D17, D19 (during summer), H1, H2, H4, H5, H6 and H7. Other ferric coagulants were also dosed at works where NDMA was not detected in final waters: Works A2 and A8 - ferric sulphate (supplied by a second manufacturer), Works E20 - ferric sulphate (supplied by a third manufacturer), Works F1 and H3 - ferric chloride.

To try to relate the formation of NDMA with seasonal raw water quality, raw waters from Works C11, C12 and D18 were analysed for pH, turbidity and selected organic and nitrogen parameters (see Table 4.3).

The results of the raw water analysis showed the organic content of the raw waters to Works C11 and C12 to be comparable and greater than that of the raw water to Works D18. The nitrate concentration to Works D18 was substantially greater than the nitrate concentration to Works C11 and C12, and the nitrite concentration - a key factor in NDMA formation - was substantially greater for Works D18 in Survey 3.

The final water NDMA concentrations found for Works C12 and D18 show no consistent seasonal trends: highest NDMA concentrations for Works C12 (2.5-2.8 ng/l) were found in Surveys 3 (June 2007) and 4 (September 2007), whilst the highest concentrations for Works D18 (1.6-2.0 ng/l) were found in Surveys 1 (December 2006) and 2 (February 2007). The highest final water concentrations for Works C11 (5.6-5.8 ng/l) were found in Survey 1 (December 2006) but the lowest concentrations (1.3-2.5 ng/l) were found in Survey 2 (February 2007). Unfortunately, water temperature was not recorded at the time of sampling but there is no evidence from the above results to indicate a temperature-related - or other seasonal-related - effect on NDMA formation. A similar observation regarding the correlation of NDMA with water temperature and other parameters was made by the University of Waterloo⁶, while Graham *et al*⁷ suggested that the phenomenon of slightly elevated NDMA concentrations observed during winter periods was more likely attributable to greater preservation of precursors than to NDMA formation mechanics.

⁶ AWWA Research Foundation/WERF (2005). Factors affecting the formation of NDMA in water and occurrence.

⁷ Graham, J E *et al* (1995). Factors affecting NDMA formation during drinking water treatment. In Proc. Water Quality Technology Conf., New Orleans, La., American Water Works Association.

Table 4.3 Summary of raw water quality: Works C11, C12 and D18

Parameter	Survey 2	Survey 3	Survey 4
Works C11			
pH	6.46	6.73	6.71
Turbidity (NTU)	8.7	4.2	1.9
TOC (mg/l C)	6.34	3.00	12.7
True UV ₂₅₄ (AU/m)	32.7	13.3	62.8
True colour (°H)	44.1	13.7	90.2
Ammonia (mg/l NH ₃ as N)	< 0.021	0.018	< 0.3
Nitrite (mg/l NO ₂ as N)	0.008	0.093	< 0.1
Nitrate (mg/l NO ₃ as N)	1.87	5.67	< 0.3
Works C12			
pH	6.40	5.95	6.56
Turbidity (NTU)	2.8	2.0	1.5
TOC (mg/l C)	5.82	4.89	10.4
True UV ₂₅₄ (AU/m)	30.9	28.8	55.1
True colour (°H)	44.1	40.2	89.2
Ammonia (mg/l NH ₃ as N)	0.025	0.010	< 0.3
Nitrite (mg/l NO ₂ as N)	0.011	0.012	< 0.1
Nitrate (mg/l NO ₃ as N)	2.85	3.13	0.4
Works D18			
pH	7.55	7.54	7.79
Turbidity (NTU)	1.0	1.9	1.5
TOC (mg/l C)	4.79	5.22	6.8
True UV ₂₅₄ (AU/m)	12.2	14.8	15.3
True colour (°H)	7.8	11.8	12.7
Ammonia (mg/l NH ₃ as N)	< 0.021	0.100	< 0.3
Nitrite (mg/l NO ₂ as N)	0.014	0.329	< 0.1
Nitrate (mg/l NO ₃ as N)	30.1	32.8	7.0

Concentrations of NDMA in samples from distribution were generally comparable to final water samples for Works C12 and D18, suggesting no further formation following treatment. Results for Works C11 showed one increased concentration in distribution compared with final water (6.8 ng/l cf. 5.1 ng/l) and one decreased concentration (1.5 ng/l cf. 4.3 ng/l). In the literature, the University of Waterloo⁴ reported initial increases in NDMA concentration (from 0-1.25 ng/l to 1.75-2.5 ng/l) in distribution with increasing time of travel. However, decreases in NDMA concentration were observed at distant sampling locations with time of travel greater than 24-48 hours.

4.3 Summary of laboratory tests

Laboratory tests were carried out in September and November 2007 to try to elucidate the formation of NDMA observed in the sampling survey. Full details of these tests including methodology and results are presented in Appendix C; a summary of the results is given below.

The laboratory tests carried out in September simulated treatment at Works C11 and D18. Tests were carried out in a standard laboratory jar tester using raw waters (from both works) and recycled thickener supernatant (from Works C11 only) sampled at the time of the fourth survey. Chemicals were dosed to one-litre samples of raw water (or raw water/recycled supernatant) to simulate the various stages of the treatment process and to allow comparison of NDMA measurements with samples taken during the site visits. The ferric coagulant used in the tests was sampled from Works C11. Results are summarised in Table 4.4.

The results of the tests generally showed higher concentrations of NDMA in the laboratory-derived samples than in samples from Works C11 or D18, although of a similar order of magnitude. NDMA was found in the ferric coagulant-dosed water (7.2 / 5.0 ng/l) suggesting that NDMA was formed as a result of coagulation and pH adjustment. NDMA concentrations found in subsequent samples were greater than the coagulant-dosed water concentrations by up to 20%, indicating a possible small affect due to subsequent dosing of Epi-DMA, chlorination or chloramination.

Table 4.4 Comparison of NDMA (ng/l) in laboratory-treated water with samples from Works C11 and D18

Sample	Laboratory Sample (ng/l)	Works Sample (ng/l)
Works C11		
Raw water	-	< 0.9
Recycle (Ref LC12)	3.0	3.6
Coagulant-dosed water (Ref LC1)	7.2 ¹	-
Coagulant / polyelectrolyte-dosed water (Ref LC2)	8.5 ¹	3.9
Coagulant / polyelectrolyte-dosed water - chlorinated (Ref LC3)	9.1	3.7 / 4.2
Coagulant / polyelectrolyte-dosed water - chloraminated (Ref LC11)	5.4	4.3
Coagulant dosed raw water / 5% recycle (Ref LC5)	8.8	-
Coagulant dosed raw water / 10% recycle (Ref LC6)	7.7	-
Coagulant dosed raw water / 20% recycle (Ref LC7)	8.7	-
Coagulant / polyelectrolyte dosed raw water / 5% recycle (Ref LC8)	6.8 ¹	-
Coagulant / polyelectrolyte dosed raw water / 5% recycle - chlorinated (Ref LC9)	8.9	-
Coagulant / polyelectrolyte dosed raw water / 5% recycle - chloraminated (Ref LC10)	8.8	-
Works D18		
Raw water	-	< 0.9
Coagulant-dosed water (Ref LD1)	5.0	-
Coagulant / polyelectrolyte (LT22)-dosed water (Ref LD2)	5.4	-
Coagulant / polyelectrolyte (LT22) / Epi-DMA-dosed water (Ref LD3)	5.9	3.4
Coagulant-dosed water - chlorinated (Ref LD4)	5.2	-
Coagulant / polyelectrolyte (LT22)-dosed water - chlorinated (Ref LD5)	4.8	-
Coagulant / polyelectrolyte (LT22) / Epi-DMA-dosed water - chlorinated (Ref LD6)	4.9	-

Note:

1. Interference on qualifier ion; ion ratio did not match.

A second series of laboratory tests was carried out in November 2007 to supplement and clarify the results from September. Tests were carried out to simulate coagulation at Works C11 and C16 using raw waters and coagulants sampled from both works. Results are summarised in Table 4.5.

Table 4.5 Comparison of NDMA (ng/l) in laboratory-treated water with samples from Works C11 and C16

Sample	Laboratory Sample (ng/l)	Works Sample (ng/l)
Works C11 raw water (- sample retained from Survey 4) (Ref: LC11)	< 0.9	< 0.9
Works C11 laboratory-clarified water (C11 coagulant 12.85 mgFe/l, pH 4.6 adjusted with NaOH) (Ref: LC11/C11/C)	3.9	3.9
Works C16 laboratory-clarified water (C16 coagulant 12.0 mgFe/l, pH 3.8 adjusted with Ca(OH) ₂) (Ref: LC16/C16/L)	2.7	2.7
Works C16 laboratory-clarified water (C11 coagulant 12.0 mgFe/l, pH 3.8 adjusted with Ca(OH) ₂) (Ref: LC16/C11/L)	3.6	-

Table 4.5 shows that NDMA found in laboratory-coagulated samples of raw waters from Works C11 and C16 was at concentrations similar to those found in comparable samples from the respective works. NDMA was formed as a result of coagulation using the ferric coagulant sampled from both treatment works.

A further series of tests was carried out to investigate the possibility of contamination of the coagulant with NDMA. Samples of deionised or distilled water were dosed with the coagulant and/or sodium hydroxide (caustic) or calcium hydroxide (lime) as used at Works C11 and C16. Results are summarised in Table 4.6.

Table 4.6 Comparison of NDMA (ng/l) in laboratory-treated water with samples from Works C11 and C16

Sample	Laboratory Sample (ng/l)	Works Sample (ng/l)
Deionised coagulated water (C11 coagulant 12.85 mgFe/l, pH 4.6 adjusted with NaOH) (Ref: Deion/C11/C)	3.9	(3.9)
Distilled coagulated water (C11 coagulant 12.85 mgFe/l, pH 4.6 adjusted with NaOH) (Ref: Dist/C11/C)	4.7	(3.9)
Distilled coagulated water (C16 coagulant 12.0 mgFe/l, pH 3.8 adjusted with Ca(OH) ₂) (Ref: Dist/C16/L)	3.7	(2.7)
Distilled water (pH 4.6 adjusted with NaOH) (Ref: Dist/C)	< 0.9	-
Distilled water (pH 3.8 adjusted with Ca(OH) ₂) (Ref: Dist/L)	< 0.9	-
Distilled water (blank)	< 0.9	-
Deionised water (blank)	< 0.9	-

The results from Table 4.6 confirmed the possibility that the coagulant was the source of the NDMA. Subsequently, a final set of tests was carried out to analyse samples of the coagulant (ex. Works C11) diluted successively with distilled water. The results are shown in Table 4.7 and Figure 4.1.

Table 4.7 Measurements of NDMA in diluted coagulant

Sample	NDMA (ng/l)
Sample 1 (Dilution factor 1/1000 (0.0010))	70
Sample 2 (Dilution factor 1/2000 (0.0005))	38.4
Sample 3 (Dilution factor 1/5000 (0.0002))	14.0
Sample 4 (Dilution factor 1/10,000 (0.0001))	7.6
Sample 5 Distilled water (blank)	< 0.9

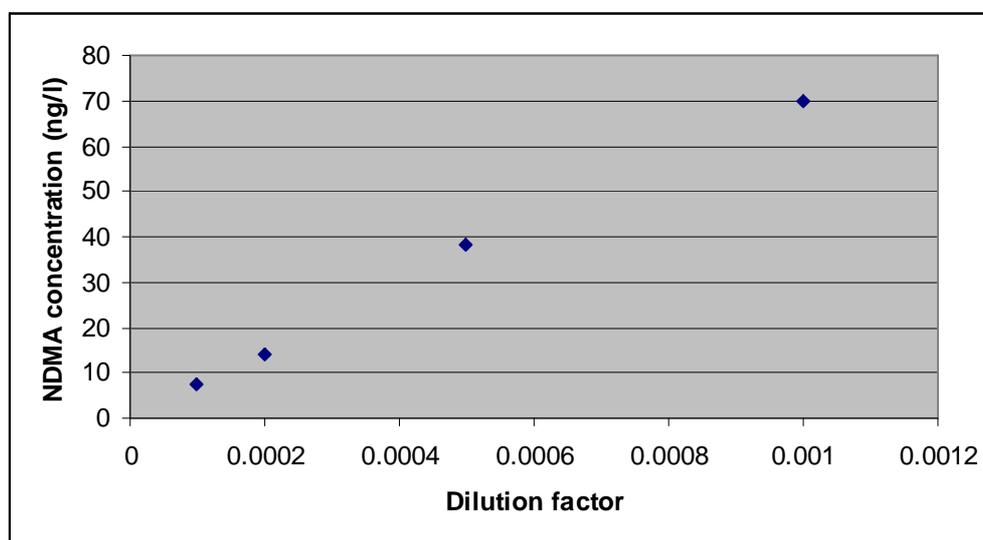


Figure 4.1 Measurements of NDMA in diluted coagulant

The results showed NDMA found in each of the diluted samples at concentrations consistent with the dilution of the coagulant. NDMA was not detected in the distilled water 'blank'. Based on these results, it is calculated that the sample of coagulant contained in the order of 70,000 ng/l (70 µg/l) NDMA.

These results became available late in the project by which time it was not possible to investigate details such as product batch number or production details. However, given the number of sites affected it seems most unlikely that contamination was restricted to a single batch of coagulant.

D17 Fe ₂ (SO ₄) ₃ I	96.3 - 339.9 µg/l (mean: 214.7 µg/l)
Fe ₂ (SO ₄) ₃ I supplied directly	46.9 - 166.6 µg/l (mean: 109.0 µg/l)
Fe ₂ (SO ₄) ₃ II supplied directly	13.3 - 72.5 µg/l (mean: 51.9 µg/l)
FeCl ₃	< MDL - 5.33 µg/l

The calculated NDMA concentration in the ferric sulphate coagulant sampled from Works C11 can be compared with 70 µg/l calculated previously (see Appendix C7).

In addition to the coagulant dilution tests, samples of clarified and final waters were taken for NDMA analysis from Works D17 and D18 to investigate possible removal within treatment. Results of the tests are summarised in Table 4.9.

Table 4.9 Results for analysis for NDMA in Works D17 and D18 clarified and final water samples

Sample code	Description	Conc (ng/l)	Sample code	Description	Conc (ng/l)
S1	Distilled water blank	< MDL	S16	D17 clarified water	2.20
S14	D18 clarified water	< MDL	S17	D17 final water	< MDL
S15	D18 final water	< MDL	S30	Distilled water blank	2.77

Note:

1. MDL = Method Detection Limit (1.47 ng/l).

At Works C11 and C16, where contamination of the ferric sulphate coagulant was determined, NDMA was detected in corresponding clarified and/or final water samples in previous surveys. Contamination of the coagulant from Works D17 was also determined and NDMA was detected in the corresponding clarified water (2.20 ng/l). However, as this concentration was close to the MDL and lower than 'detected' in one of the distilled water blanks, the clarified water result must be considered inconclusive. NDMA was not detected in the final water when sampled from Works D17 at the same time, nor in samples of final water taken in Surveys 1 and 2.

NDMA was not detected in the clarified or final water from Works D18, although NDMA had been detected in each of the four seasonal surveys at concentrations between 3.4-3.7 ng/l in clarified water and 1.0-2.0 ng/l in final water. These concentrations are close to the MDL.

5. CONCLUSIONS

1. Forty-one treatment works in England and Wales were selected for sampling because of the presence of key factors known to be associated with the formation of NDMA. NDMA was detected in final waters at three of these works (Works C11, C12 and D18) in four quarterly surveys at concentrations up to 5.8 ng/l. Final water NDMA concentrations were within the current concentrations of concern in North America (9-10 ng/l) and substantially lower than the future WHO guideline value. Should future UK drinking water regulations restrict NDMA to similar concentrations, this would have only minor impact on the UK water industry.
2. NDMA was detected at one other works (Works C16) in a sample of clarified water but not in samples of final water from this works. This raises the possibility that NDMA may have been present following coagulation at other works in the survey but was not detected in final water samples.
3. Key factors associated with the formation of NDMA identified from the literature review included organic precursors, the use of polyDADMAC or Epi-DMA polyelectrolytes in water treatment, and chloramination. The use of polyDADMACs and Epi-DMA in treatment in England and Wales is not believed to be widespread.
4. While the key factors identified from the literature review were present at the treatment works where NDMA was detected, these were also present at works where NDMA was not formed. It is believed that the source of the NDMA was in fact the coagulant used at these works (see Conclusion 5) and it is concluded that - for the water qualities and operating regimes at the treatment works sampled in the survey - the key factors identified had negligible effect on the formation and presence of NDMA.
5. A common factor at the treatment works where NDMA was detected was the use of a ferric coagulant. Laboratory tests on samples of this coagulant from Works C11 and C16 indicated that NDMA was a possible contaminant. However, the same coagulant was also dosed at works where NDMA was not detected in final waters.
6. At Works C12, NDMA was detected in the supernatant recycled to water treatment at 31.5 and 39.1 ng/l. Although the ferric coagulant from this works was not analysed directly for NDMA, it is probable that this elevated concentration of NDMA in the recycled supernatant was due to the coagulant dosed in the magnetite/backwash recovery process. The concentration of NDMA in the supernatant could be responsible for downstream concentrations of NDMA found in the treated water at this works.
7. Final water NDMA concentrations found in the four quarterly surveys showed no consistent trends. Although the number of samples taken was limited, there was no clear evidence to indicate a temperature-related - or other seasonal-related - effect on NDMA formation.
8. Concentrations of NDMA in samples from distribution were generally comparable to concentrations found in final waters. Although the number of samples taken was very limited, there was no clear evidence to indicate continued formation of NDMA in distribution.

6. RECOMMENDATIONS

1. The possibility of other coagulants being a source of NDMA in drinking water warrants further investigation.
2. The removal of NDMA in water treatment should be investigated more rigorously, including the possibility that NDMA is present as a result of coagulation but is not subsequently detected in the final water. This investigation should address coagulant type and dose, the range of treatment processes and chemicals used commonly in England and Wales, and possible seasonal affects. The investigation should enable the development of appropriate control procedures to minimise concentrations of NDMA in drinking water.
3. The fate of NDMA in distribution should be investigated more rigorously including possible seasonal affects and the effect of residence time,

APPENDIX A LITERATURE REVIEW

A1 NDMA

A1.1 Mechanisms of NDMA formation in drinking water

Many studies have investigated the formation of NDMA in drinking water. The principal mechanism of NDMA formation is probably the reaction of chloramines with organic precursors, particularly secondary and tertiary amines. The most commonly quoted precursor is dimethylamine (DMA), which is considered to be ubiquitous in water and because it forms NDMA via classical nitrosation by nitrite (Challis and Challis, 1982; Keefer and Roller 1973), although other precursors have been investigated. The chemical structure of DMA is described in Figure A1.

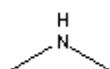


Figure A1 Chemical structure of dimethylamine (DMA (C₂H₆NH))

The presence of nitrite in water can be as a result of nitrification of ammonia by micro-organisms, or by denitrification of nitrate by either micro-organisms or UV radiation (Mole and Fielding, 1996). Nitrosation of amines occurs most rapidly in acidic conditions; an optimal pH of 3.4 has been reported. However, NDMA formation has been reported to occur in neutral and alkali conditions (Mole and Fielding, 1996). The chemical structure of NDMA is described in Figure A2.

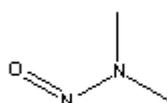


Figure A2 Chemical structure of N-nitrosodimethylamine (NDMA (C₂H₆N₂O))

In an experiment to assess the formation of NDMA utilising various substrates, DMA was reacted with nitrite, monochloroamine, free chlorine, and free chlorine and ammonia (Awwa Research Foundation/WERF, 2005). Each compound was present at a concentration of 0.1 mM (5.5 mg/l DMA, 7.2 mg/l Cl₂ for both chlorine and monochloramine, and 1.4 mg/l N for ammonia). No NDMA contaminants were present in any of the individual reactant solutions. Reaction of the solutions took place for 24 hours at pH 7 and 25°C in dark conditions. The reaction of DMA with nitrite produced an NDMA concentration of 2.1 µg/l; the reaction of DMA with monochloramine resulted in an NDMA concentration of 12.3 µg/l; the control reaction of DMA with free chlorine resulted in an NDMA concentration of 0.5 µg/l, which increased to 10.5 µg/l in the presence of ammonia. The reaction between DMA and monochloramine continued over a forty-hour period, reaching a concentration of 18 µg/l. The formation potential did not appear exhausted after forty hours (Choi *et al.*, 2002).

It has been reported that addition of chlorine to DMA and nitrite can significantly enhance the formation of NDMA (Awwa Research Foundation/WERF, 2005). In the absence of chlorine, NDMA formation was reported to increase from 0.34 to 0.65 µg/l as nitrite concentration was increased from 0.05 to 1.0 mM (2.3 – 46 mg/l). Following addition of 0.1 mM HOCl (5.25 mg/l), NDMA formation was reported to increase from 0.14 to 15.47 µg/l as nitrite concentration increased from 0.01 to 0.1 mM (0.46 – 4.6 mg/l).

Choi and Valentine (2002) have investigated the effect of varying ammonia concentrations on NDMA formation. Monochloramine and DMA concentrations were fixed at 0.1 mM (~5 mg/l) and ammonia concentration was varied from 0.14 to 1 mM (2.4 – 17 mg/l). NDMA formation was found to slightly increase with decreasing ammonia concentration, due to an increasing Cl:N ratio. However, it should be noted that some monochloramine decomposition occurred during this study and decomposition of monochloramine increased with decreasing ammonia concentration.

However, in a study by Choi *et al.* (2002), 0.1 mM (7 mg/l) chlorine was added to 0.2 mM (10.6 mg/l) DMA and the concentration of ammonia was varied up to 1.0 mM (17 mg/l). Increasing the concentration of ammonia was reported to increase the formation of NDMA. Over 25 µg/l NDMA was produced at an ammonia concentration of 1.0 mM (17 mg/l). It was also reported that NDMA formation increased with increasing monochloramine concentration up to 2 mM (102 mg/l), at which point NDMA formation appeared to plateau.

It should be noted that most of the studies summarised above used excessive concentrations of disinfectant and other chemicals compared with normal use concentrations during water treatment.

A mechanism proposed to account for NDMA formation in chlorinated water containing DMA and ammonia is summarised in Figure A3.

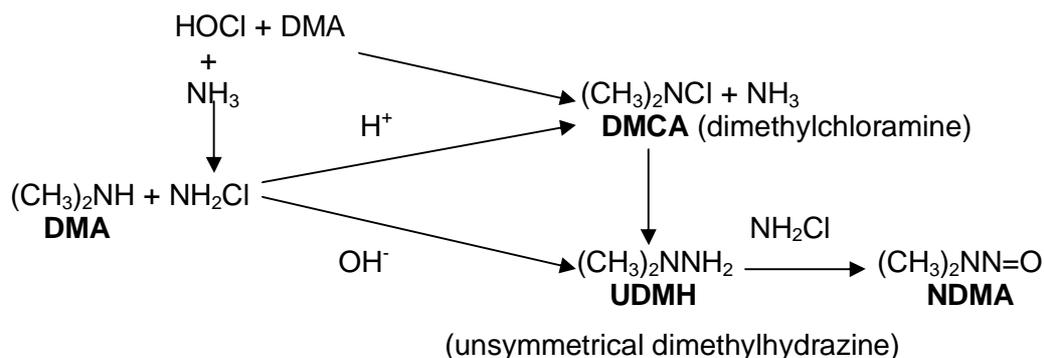


Figure A3 Proposed mechanism of NDMA formation in chlorinated water in the presence of DMA and ammonia (Awwa Research Foundation/WERF, 2005)

It has been suggested that NDMA can also be formed via reactions with bromamines (Figure A4). Bromamines are generally more reactive than chloramines and therefore would be expected to react more readily with DMA. Oxidation of bromide by monochloramine to bromamine is reported to be relatively slow and NDMA formation is expected to increase more or less continuously at a rate governed by the rate of formation of bromamine. A second, short-lived pathway for the rapid formation of NDMA in the presence of bromide has also been

proposed. HOCl oxidises bromide to produce HOBr, which then rapidly reacts with ammonia to form bromamines (Awwa Research Foundation/WERF, 2005).

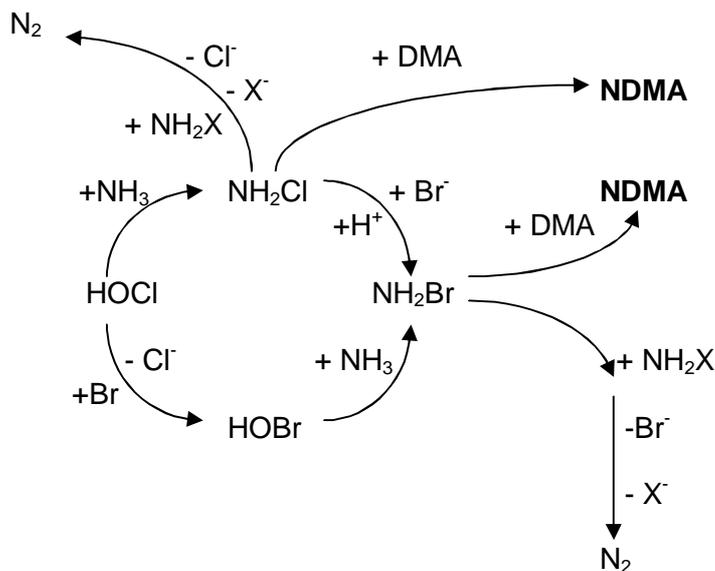


Figure A4 Enhanced NDMA formation in the presence of bromide (X- = Br- or Cl-) (Awwa Research Foundation/WERF, 2005)

In an experiment to compare the formation of NDMA by DMA and monochloramine in the presence and absence of bromide, only 5 $\mu\text{g/l}$ NDMA was produced in the absence of bromide, compared to 90 $\mu\text{g/l}$ in its presence at 2 mM (160 mg/l) (Awwa Research Foundation/WERF, 2005). Chlorination of solutions of DMA, bromide and ammonia also enhanced NDMA formation compared with monochloramine, but only at comparatively high bromide concentrations (up to 0.2 mM (16 mg/l) and 0.8 mM (64 mg/l) at pH 7.0 and 8.5, respectively (Awwa Research Foundation/WERF, 2005).

It has also been reported that NDMA can be formed by reaction of nitrite with several nitrogenous precursors including 1,1,3,3-tetramethyl-2-thiourea (TMTU), 1,1-dimethyl-3-(4-methoxyphenyl)-2-thiourea (DMPTU), sodium dimethyldithiocarbamate (DMDTC) and tetramethylthiuram (TMT). These compounds produced 5 to 30 times more NDMA compared with equivalent molar concentrations of DMA. It was observed that these compounds have a thiocarbonyl functional group rather than a carbonyl functional group as in DMA (Awwa Research Foundation/WERF, 2005).

Humic substances can act as precursors for the formation of NDMA by reaction with monochloramine. Iowa river water and 'synthetic' water containing the same TOC concentration (3.4 mg/l) prepared from reverse osmosis concentrate from the same water were treated with 50 mg/l pre-formed monochloramine at pH 7. After 7 days the 'NDMA formation potentials' were 112 and 100 ng/l respectively (Chen and Valentine 2007).

UV-A irradiation of 53 mg/l DMA in the presence of 46 mg/l nitrite yielded approximately 15 $\mu\text{g/l}$ NDMA after 30 minutes (Lee and Yoon 2007). The significance of this mechanism for NDMA formation during water treatment is unclear, especially as NDMA is photolysed by UV irradiation (e.g. Lee *et al.* 2005).

Strong ionic resins have been reported as a potential source of NDMA (Mole and Fielding, 1996). Nitrosamines are reported to be present in the resin as a manufacturing contaminant (Kimoto *et al.*, 1980). These authors reported that nitrosamines are not expected to be retained on the resins and would therefore be expected to wash out after several deionisation-regeneration cycles. In an experiment in which tap water was passed through a mixed bed of new cation and anion resins, NDMA concentrations of 1.26 to 2.03 ng/l were detected in the treated water. No NDMA was detected in the tap water prior to the study, indicating that the presence of NDMA was a consequence of contact with the resins. In another study (Najm and Trussell, 2001), NDMA was found at concentrations up to 130 ng/l when various resins were contacted with deionised water or groundwater (neither containing chlorine). Only resins containing trimethyl or dimethyl-ethanol quaternary amine functional groups produced NDMA.

Whilst DMA acts as a precursor for NDMA formation, several studies have shown that the concentrations of DMA present in water sources cannot account for the quantities of NDMA formed during disinfection. In one study, it was reported that the fungicide thiram (Figure A5) was a more efficient precursor than DMA (Graham *et al.*, 1996). Possible NDMA precursors were listed by Siddiqui and Atasi (2001) and Mitch *et al.* (2003).

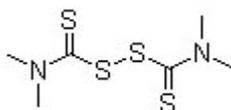


Figure A5 Chemical structure of thiram (dimethyldithiocarbamate)

Other pesticides, like thiram, have been reported to be precursors for NDMA formation, however, they are not expected to form significant NDMA concentrations in drinking water (Mole and Fielding, 1996).

Although it is claimed that NDMA appears not to be formed during ozonation (Najm and Trussell, 2001), there is current concern with regard to ozonation of the fungicide tolyfluanid (Figure A6) (DWI, 2007). Dimethylsulfamide, a metabolite of tolyfluanid, may potentially react with ozone during water treatment to form NDMA.

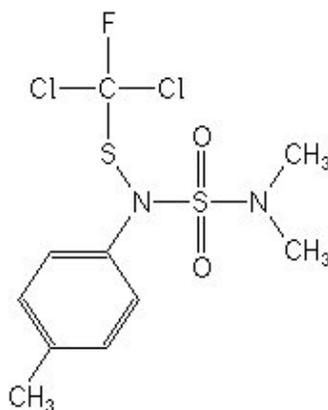


Figure A6 Chemical structure of tolyfluanid (N-trihalomethylthio)

Other pesticides, such as bromacil, benazolin, 2,4-D, dicamba, MCPA and mecoprop are also reported to contain NDMA as a microcontaminant (WHO, 2002). Tertiary dimethylamines, such as ranitidine (Figure A7) - a pharmaceutical drug used to treat certain stomach conditions - can be converted to NDMA. Ranitidine is reported to show a conversion rate 83-fold greater than DMA (Schmidt *et al.*, 2006).

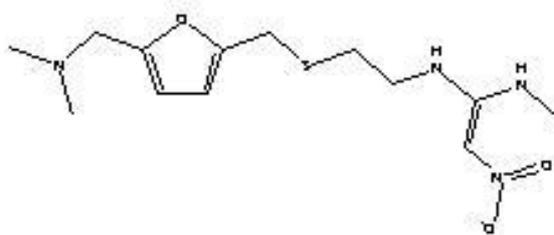


Figure A7 Chemical structure of ranitidine

Cationic polyelectrolytes (Epi-DMA and polyDADMAC products) can also act as precursors for the formation of NDMA by reaction with chloramines. NDMA concentrations of 180 to 400 ng/l were produced when five commercial polyDADMACs were chlorinated then ammoniated (Wilczak *et al.*, 2003). NDMA concentrations could be reduced by chlorinating after filtration. Delaying the addition of ammonia following chlorination also decreased NDMA formation but possibly at the expense of greater formation of chlorinated by-products such as THMs. Laboratory coagulation tests were used to examine any effect of the age of polyelectrolyte solutions (0 to 50 hours) on the yield of NDMA (Kohut and Andrews, 2003). Tap water was spiked with 500 µg/l nitrite then treated with aluminium sulphate (4.7 mg/l Al), either polyDADMAC (10 mg/l) or Epi-DMA (20 mg/l), and sodium hypochlorite (4 mg/l). NDMA concentrations were found to increase with the age of Epi-DMA solutions but this effect was not significant with polyDADMAC. The maximum yields of NDMA were approximately 20 ng/mg Epi-DMA (reached after 3 hours) and 8 ng/mg polyDADMAC (reached after 50 hours).

A1.2 NDMA detected in drinking water

In one major study in Canada and the United States (Awwa Research Foundation/WERF, 2005) concentrations of NDMA were monitored at 21 drinking water treatment facilities. The facilities selected represented various presumed vulnerability factors, including raw water source, being downstream of a wastewater plant, being affected by agricultural/urban runoff, raw water pH, treatment by ion exchange, disinfection process (chlorine vs. chloramination) and distribution characteristics. Samples of works influent and final water and water from distribution were collected quarterly. Analytical detection limits ranged from 0.2 to 0.3 ng/l, although results were reported based on a minimum reporting level (MRL) of three times greater than the limit of detection (0.6 to 1 ng/l).

Influent samples (raw water): NDMA was detected above the MRL in six of the 81 influent water samples (Table A1). The concentration of NDMA in these samples ranged from 0.6 to 1.8 ng/l. Three of the samples with NDMA concentrations detected above the MRL at the influent were

sampled in the autumn, two were sampled in the winter and one was sampled in the spring. The spring sample contained the highest detected concentration (1.8 ng/l).

Table A1 Raw water samples with NDMA concentrations above the MRL from a study of 21 drinking water treatment facilities in Canada and the United States (Awwa Research Foundation/WERF, 2005)

Drinking water treatment facility code	Season	NDMA concentration (ng/l)	Description
2678-05	Autumn	0.6	River in central Canada affected by spring runoff, agriculture, algal blooms, ice cover, industrial and multiple wastewater discharge upstream.
2678-05	Winter	0.6	River in central Canada affected by spring runoff, agriculture, algal blooms, ice cover, industrial and multiple wastewater discharge upstream.
2678-07	Spring	1.8	Ground water source in western United States.
2678-18	Autumn	0.8	River impaired by significant wastewater discharges in north-eastern United States.
2678-18	Winter	0.6	River impaired by significant wastewater discharges in north-eastern United States.
2678-22	Autumn	0.9	River in central Canada, wastewater plant 10 km upstream.

Final water samples: NDMA was detected above the MRL in 28 of the 81 final water samples at concentrations ranging from 0.7 to 30.0 ng/l (Table A2). The four highest concentrations (24.0-30.0 ng/l) were found in water from one works that used anion exchange for nitrate removal from groundwater, with the highest concentration detected in the spring. This is the same works at which an influent concentration of 1.8 ng/l was detected. NDMA was detected at concentrations ranging from 4.2 to 6.6 ng/l at a works utilising chloramination, again with the highest concentration found in the spring. The NDMA concentrations in the final waters from the other sites ranged from 0.6 to 4.7 ng/l.

Drinking water samples (distribution): NDMA was detected in the majority of drinking water distribution samples at concentrations ranging from 0.6 to 24.0 ng/l (Table A3). The highest concentration occurred in the spring at the same works as the highest detected influent and final water concentrations. Summer and winter concentrations at this site were reported to be 10.0 and 12.0 ng/l, respectively. No sample was available for the autumn. High concentrations of NDMA (9.0-21.6 ng/l) were also detected throughout the year at a site utilising chloramination, again with the highest concentration detected in the spring. NDMA was detected at above 5 ng/l in a further four samples, three sampled in the spring and one in the winter. The remaining samples with NDMA detected above the MRL were below 5 ng/l.

Distribution samples generally had higher concentrations of NDMA than works final waters, except where final water was blended with other water prior to distribution.

The University of Waterloo collected influent, final water and distribution samples from Utility 2678-22, a surface water treatment works utilising alum coagulation, ozonation, chlorination and chloramination (prior to distribution) (Awwa Research Foundation/WERF, 2005). In distribution, in general, NDMA concentrations increased with increasing time of travel, from 0 - 1.25 ng/l to 1.75 - 2.5 ng/l. However, decreases in concentration were observed at distant sampling locations, with time of travel greater than 24 - 48 hours.

Table A2 Final water samples with NDMA concentrations above the MRL from a study of 21 drinking water treatment facilities in Canada and the United States (Awwa Research Foundation/WERF, 2005)

Drinking water treatment facility code	Season	NDMA concentration (ng/l)	Description
2678-03	Spring	6.6	Chloramine disinfection
2678-03	Summer	6.5	Chloramine disinfection
2678-03	Autumn	4.2	Chloramine disinfection
2678-03	Winter	4.4	Chloramine disinfection
2678-05	Spring	2.2	Not reported
2678-05	Summer	0.9	Not reported
2678-05	Autumn	0.6	Not reported
2678-07	Spring	30.0	Anion exchange; sodium hypochlorite.
2678-07	Summer	24.0	Anion exchange; sodium hypochlorite.
2678-07	Autumn	20.0	Anion exchange; sodium hypochlorite.
2678-07	Winter	25.7	Anion exchange; sodium hypochlorite.
2678-08	Spring	4.7	Chlorine used from October to May and chloramines from May to October.
2678-08	Summer	1.7	Chlorine used from October to May and chloramines from May to October.
2678-08	Winter	0.9	Chlorine used from October to May and chloramines from May to October.
2678-09	Summer	0.8	River water blended with groundwater. River water is treated with PAC and ferric chloride and blended with groundwater before lime softening, ferric chloride addition and sand filtration; partial treatment by ion exchange.
2678-09	Autumn	2.4	River water blended with groundwater. River water is treated with PAC and ferric chloride and blended with groundwater before lime softening, ferric chloride addition and sand filtration; partial treatment by ion exchange.
2678-09	Winter	1.2	River water blended with groundwater. River water is treated with PAC and ferric chloride and blended with groundwater before lime softening, ferric chloride addition and sand filtration; partial treatment by ion exchange.
2678-15A	Spring	1.5	Chloramines
2678-15A	Summer	2.2	Chloramines
2678-15A	Autumn	2.7	Chloramines
2678-15A	Winter	1.4	Chloramines
2678-15B	Summer	0.7	Chloramines
2678-18	Autumn	1.0	Not reported
2678-18	Winter	1.1	Not reported
2678-23	Summer	0.6	Not reported
2678-23	Autumn	0.6	Not reported
2678-23	Winter	1.1	Not reported
2678-24	Autumn	1.7	Chloramine residual, retention time about 9 hours.

Table A3 Distribution water samples with NDMA concentrations above the MRL from a study of 21 drinking water treatment facilities in Canada and the United States (Awwa Research Foundation/WERF, 2005)

Drinking water treatment facility code	Season	NDMA concentration (ng/l)	Description
2678-03	Spring	21.6	Fluoride and phosphate added.
2678-03	Summer	16.3	Fluoride and phosphate added.
2678-03	Autumn	15.3	Fluoride and phosphate added.
2678-03	Winter	9.0	Fluoride and phosphate added.
2678-05	Spring	5.0	3-5 days detention time.
2678-05	Summer	1.7	3-5 days detention time.
2678-05	Winter	0.6	3-5 days detention time.
2678-06	Summer	1.3	Approximately 6 days detention time, ductile iron pipe.
2678-07	Spring	24.0	Plant final water blended with groundwater that has not passed through anion exchange, 200 minute detention time, asbestos/concrete pipe.
2678-07	Summer	10.0	Plant final water blended with groundwater that has not passed through anion exchange, 200 minute detention time, asbestos/concrete pipe.
2678-07	Winter	12.0	Plant final water blended with groundwater that has not passed through anion exchange, 200 minute detention time, asbestos/concrete pipe.
2678-08	Spring	4.7	1-3 day detention time, cast-iron pipe.
2678-08	Summer	1.7	1-3 day detention time, cast-iron pipe.
2678-08	Winter	0.9	1-3 day detention time, cast-iron pipe.
2678-09	Summer	1.9	Detention time less than 1 day.
2678-09	Autumn	0.6	Detention time less than 1 day.
2678-09	Winter	0.7	Detention time less than 1 day.
2678-11A	Summer	1.9	1-2 days detention time, PVC and asbestos/cement pipes.
2678-11A	Autumn	0.6	1-2 days detention time, PVC and asbestos/cement pipes.
2678-11A	Winter	0.7	1-2 days detention time, PVC and asbestos/cement pipes.
2678-11B	Summer	1.1	1-7 days detention time, PVC and asbestos/cement pipes.
2678-11B	Autumn	0.7	1-7 days detention time, PVC and asbestos/cement pipes.
2678-14	Spring	6.0	2-3 days detention time, ductile iron pipe.
2678-14	Summer	1.7	2-3 days detention time, ductile iron pipe.
2678-14	Autumn	2.2	2-3 days detention time, ductile iron pipe.
2678-14	Winter	2.5	2-3 days detention time, ductile iron pipe.
2678-15A	Spring	2.0	Detention time approximately 24 hours from plant.
2678-15A	Summer	3.2	Detention time approximately 24 hours from plant.
2678-15A	Autumn	3.3	Detention time approximately 24 hours from plant.
2678-15A	Winter	2.4	Detention time approximately 24 hours from plant.
2678-15A	Spring	1.6	Covered finished water reservoir influent. Detention time about 24 hours from plant final water on a different line than location above.
2678-15A	Summer	2.2	Covered finished water reservoir influent. Detention time about 24 hours from plant final water on a different line than location above.
2678-15A	Autumn	2.7	Covered finished water reservoir influent. Detention time about 24 hours from plant final water on a different line than location above.

Drinking water treatment facility code	Season	NDMA concentration (ng/l)	Description
2678-15A	Winter	2.3	Covered finished water reservoir influent. Detention time about 24 hours from plant effluent on a different line than location above.
2678-15A	Spring	3.1	Covered finished water. Detention time from the reservoir influent is 3.4 days.
2678-15A	Summer	2.8	Covered finished water. Detention time from the reservoir influent is 3.4 days.
2678-15A	Autumn	3.6	Covered finished water. Detention time from the reservoir influent is 3.4 days.
2678-15A	Winter	3.6	Covered finished water. Detention time from the reservoir influent is 3.4 days.
2678-15B	Spring	1.4	Covered finished water influent. Detention time about 24 hours from plant effluent.
2678-15B	Summer	1.2	Covered finished water influent. Detention time about 24 hours from plant effluent.
2678-15B	Autumn	1.1	Covered finished water influent. Detention time about 24 hours from plant effluent.
2678-15B	Winter	1.6	Covered finished water influent. Detention time about 24 hours from plant effluent.
2678-15B	Spring	2.9	Covered finished water. Detention time 3.1 days from reservoir influent.
2678-15B	Summer	2.1	Covered finished water. Detention time 3.1 days from reservoir influent.
2678-15B	Autumn	2.1	Covered finished water. Detention time 3.1 days from reservoir influent.
2678-15B	Winter	2.5	Covered finished water. Detention time 3.1 days from reservoir influent.
2678-18	Autumn	0.7	Not reported
2678-18	Winter	1.2	Not reported
2678-20	Autumn	3.2	8 day detention time, concrete lined water main.
2678-20	Winter	2.6	8 day detention time, concrete lined water main.
2678-22	Spring	0.6	Detention time approximately 38 hours.
2678-22	Winter	0.6	Detention time approximately 38 hours.
2678-23	Spring	2.4	Ductile iron pipe
2678-23	Summer	2.8	Ductile iron pipe
2678-23	Autumn	2.9	Ductile iron pipe
2678-23	Winter	1.1	Ductile iron pipe
2678-24	Autumn	1.7	Detention time about 42 hours.
2678-27	Winter	0.7	Detention time >24 hours, cast iron pipe.
2678-30	Summer	5.8	Detention time from plant final water to distribution system about 44 hours, ductile iron pipes, pre-stressed concrete mains pipe.
2678-30	Winter	0.9	Detention time from plant final water to distribution system about 44 hours, ductile iron pipes, pre-stressed concrete mains pipe.

The University of Waterloo collected samples from Utility 2678-22 in March, May and August 2002, and attempted to correlate NDMA concentrations with, *inter alia*, water temperature but found no clear relationship (Awwa Research Foundation/WERF, 2005). Graham *et al* (1995) suggested that the phenomenon of slightly elevated NDMA concentrations observed during winter periods was more likely attributable to greater preservation of precursors than to NDMA formation mechanics.

In a separate study, Kimoto *et al.* (1981) analysed tap water in Philadelphia. Water was sampled for 8.5-11.75 hours, twice a week from 23rd May to 14th June 1978 and for 64-95

hours, twice a week from 28th July to 31st August 1978. NDMA was detected in the tap water at concentrations ranging from 3 to 6 ng/l. Recovery of added NDMA to separate samples was reported to range from 69-83%.

NDMA has been reported in drinking water wells near a rocket engine test facility in Sacramento County, California (Mitch *et al.*, 2003). Although concentrations of NDMA in drinking water were not reported, groundwater concentrations were as high as 400 µg/l at the test facility and 20 µg/l in groundwater outside the test facility. As a result, drinking water wells were closed. Mitch *et al.* (2003) also reported NDMA in two drinking water production wells recharged by water from an advanced wastewater treatment system in Orange County, California. NDMA was also detected in treated water in Orange County that had not been impacted with wastewater effluent. In 2001, a survey of chloraminated drinking water supplies reported NDMA concentrations greater than 10 ng/l in 3 of 20 drinking water systems (Mitch *et al.*, 2003). No supplies that utilised only free chlorine during disinfection reported NDMA concentrations greater than 5 ng/l, while one of four drinking water systems that used anion exchange treatment reported an NDMA concentration in excess of 10 ng/l.

In a 2003 survey of NDMA in water in California, 32 water treatment works were sampled and NDMA concentrations were found in samples of the influent, final water and from distribution (OEHHA, 2006). Of the 45 influent samples, 14 were reported to contain NDMA concentrations above the limit of detection (1 ng/l) with the highest reported to be 9.4 ng/l.

Thirty of 58 final water samples were reported to be above the limit of detection, with the highest concentration reported to be 63.7 ng/l (OEHHA, 2006). Other final water samples from this works were reported to contain 26.2 ng/l, 2 ng/l and <1 ng/l. A different treatment works reported a concentration of 18.3 ng/l in a final water sample, with a second sample from this site containing of 2 ng/l. A final water sample from another treatment facility also had a notably high concentration of NDMA (10.4 ng/l). However, other samples from this facility were below the limit of detection. The remaining samples contained NDMA concentrations of less than 5.5 ng/l.

Thirty-four of 58 samples taken from distribution had NDMA concentrations above the limit of detection, with the highest concentration reported to be 28.3 ng/l (OEHHA, 2006). A second sample from this site reported a concentration of 1.1 ng/l. A different site reported NDMA concentrations of 15.8 and 13.4 ng/l. This was the same site that had reported NDMA concentrations of 18.3 and 2 ng/l in the works final water. Another treatment works reported an NDMA concentration of 7.4 ng/l in the distribution sample, with a concentration of 3.8 ng/l reported in a second sample. A fourth treatment works reported NDMA concentrations of 6.8 and 2.6 ng/l. None of the remaining treatment facilities reported NDMA concentrations above 5 ng/l.

In a survey of eleven different drinking water utilities in Missouri, US, NDMA concentrations measured from 3 to 48 ng/l (Schmidt *et al.*, 2006). One of the drinking water facilities utilised free chlorine disinfection and reported an NDMA concentration of 6.1 ng/l. The remaining ten facilities utilised chloramination; four of these utilities reported NDMA concentrations above 10 ng/l.

In 1986, treated drinking water from Oshweken, Canada, was contaminated with NDMA at concentrations between 5 and 115 ng/l (Schmidt *et al.*, 2006). In 1990, NDMA was detected in the municipal aquifer in Elmira, Canada, at a concentration range of 1.3 to 2.9 µg/l. The NDMA in the aquifer was attributed to contamination from a nearby chemical facility (Environment Canada, 2001). In the Drinking Water Surveillance Programme undertaken in

Ontario, Canada, between 1994 and 1996, NDMA was detected in 140 of 313 samples taken from 100 different sites (Environment Canada, 2001). The limit of detection in this study was reported to be 1 ng/l and the mean NDMA concentration was reported to be 2.7 ng/l. The highest concentration (4 ng/l) was found in drinking water plants using a pre-blended polyamine/alum coagulant. All 20 samples from four water treatment works using this coagulant reported detectable concentrations of NDMA.

In 2003, drinking water samples were collected from two cities in Alberta, Canada. Samples were collected in July and September. Both cities utilised surface water sources for their drinking water and were located 40 km apart. One city utilised chloramination and UV in drinking water treatment, the other city only used chloramination. Samples were collected within the distribution systems in both cities, but samples of the final water were only taken from the treatment works using chloramination and UV. The concentration of NDMA in distribution of the facility that used only chloramination was reported to be 2 ng/l; in the facility that used both chloramination and UV, the concentration was reported to be 14 ng/l. The concentration of NDMA in the final water from this works was reported to range from 57 to 81 ng/l (Charrois *et al.*, 2004).

It has been suggested that water treatment utilities that use wastewater effluent dominated surface water sources may be susceptible to NDMA formation. The Oshweken and Brantford drinking water plants in Ontario, Canada, which rely on water from the Grand River, received approximately 10% of their water supply from wastewater, and have reported an average NDMA concentration of 13 ng/l (Schmidt *et al.*, 2006).

In an analysis of drinking water performed in 2006 in the UK by one major utility, no NDMA was detected at a concentration above the reported limit of detection of 10 ng/l (Personal Communication, 2006; see Table A4). Treatment works sampled in the survey included those thought most likely to form NDMA plus one 'control' works not expected to produce NDMA. The LoD used in the survey was significantly higher than the LoDs reported by Awwa Research Foundation/WERF (2005). It should also be noted that the survey was only carried out on ten samples during the winter. The highest detected concentrations of NDMA in the survey undertaken in the United States and Canada were found in spring (Awwa Research Foundation/WERF, 2005).

Table A4 UK Water Utility NDMA survey (Personal Communication, 2006)

Works Ref.	No. Samples	Result (ng/l)	Comments
A1	1	< 10	Chloramination used for residual disinfection.
A2	1	< 10	Chloramination used for residual disinfection; ammonia in raw water.
A3	1	< 10	Chemical processes used.
A4	1	< 10	Chemical processes used.
A5	1	< 10	Ammonia high in raw water.
A6	1	< 10	Nitrate removal plant.
A7	1	< 10	Nitrate removal plant.
A8	2	< 10	Chloramination used for residual disinfection.
AC1	1	< 10	Clean source used as control.

Note:

1. Works reference codes as used in the WRc survey of NDMA in England and Wales (WRc Report DEFRA 7348).

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A2 TOLYFLUANID AND DICHLOFLUANID

The DWI was alerted to an issue at the beginning of March 2007 concerning a fungicide called tolyfluanid, and the potential for one of its metabolites, dimethylsulfamide, to react with ozone during water treatment to form NDMA.

As a result of this concern, tolyfluanid was suspended from use and its manufacturer (Bayer CropScience AG) conducted a brief sampling survey at selected treatment works (Table A5).

Table A5 Results of monitoring (Bayer CropScience AG, 2007)

Works Ref.	Dimethylsulfamide (ng/l)		NDMA (ng/l)	
G1	Raw water intake 1	232	Tap water	< loq
G1	Raw water intake 2	235	Tap water	< loq
G2	Borehole water	< loq	Tap water	< loq
G2	River water	< loq	Tap water	< loq
F1	Borehole water	61	Tap water	< loq
F1	Reservoir water	212	Tap water	< loq
D19	River water intake	< loq	Tap water	< loq
H1	River water	< loq	Domestic water	< loq
H2	River water	63	Domestic water	3
H3	River water	89	Domestic water	< loq

Notes:

1. loq = limit of quantification.
2. Works reference codes as used in WRc NDMA survey.

The results of the survey showed traces of dimethylsulfamide in raw waters at four works at concentrations between 61-235 ng/l. NDMA was found in only one of the corresponding treated waters, at a concentration of 3 ng/l.

The above works were subsequently included in the third and fourth NDMA sampling surveys.

A brief review of the literature pertaining to tolyfluanid and a related product, dichlofluanid, is presented below.

A2.1 Tolyfluanid

Chemical Structure

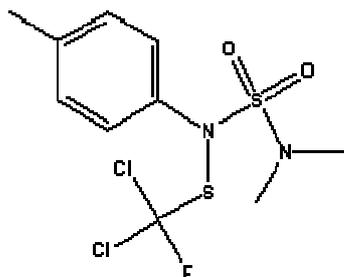


Figure A8 Chemical structure of tolyfluanid

Use and occurrence

Tolyfluanid (CAS RN: 731-27-1) (also spelt Tolyfluanid) is currently approved as the active ingredient in two pesticide products in the UK; 'Elvaron Multi' and 'Talat' (PSD, 2006). 'Talat' also contains the pesticide fenhexamid. Both products are approved for use in the UK until 31st December 2013. However, following information from the European Commission that the German Regulatory Authorities suspended use of the tolyfluanid containing product 'Euparen M WG', Bayer CropScience Ltd. agreed to voluntarily suspend sale and supply of 'Elvaron Multi' and 'Talat' in the UK (PSD, 2007).

No data were located on the occurrence of tolyfluanid in water.

Information has been located on the usage of tolyfluanid in general, dating back from 1998 to 2004 and usage levels on specific crops have been located for 2004.

General usage

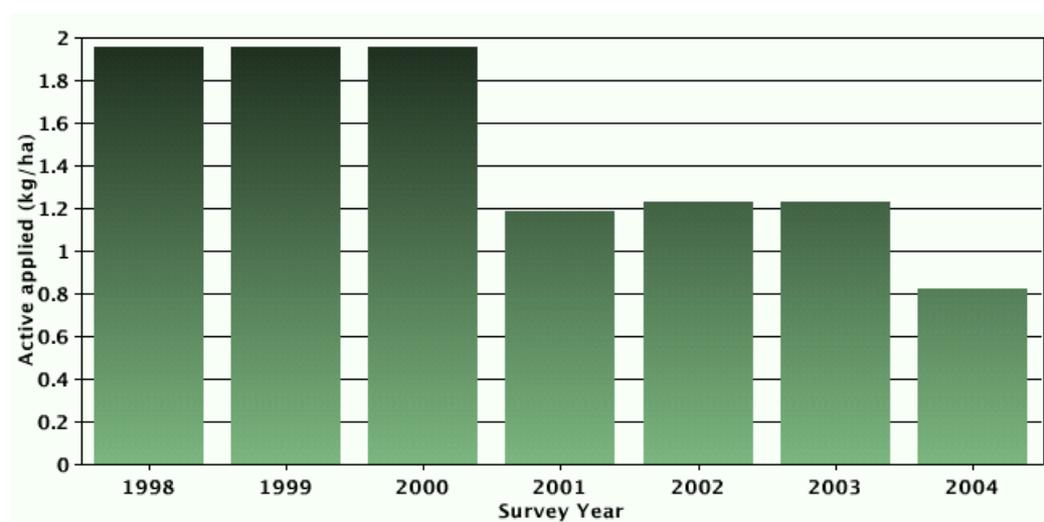
Table A6 contains information on the levels of tolyfluanid applied to crops in Great Britain between 1998 and 2004 (CSL, 2006a). Note that the 'Total Area Treated' refers to the active substance treated area, i.e. the area treated by tolyfluanid, multiplied by the number of times the area was treated. For example, if a field of 3 hectares is treated four times, the treated area is 12 hectares (3x4).

Table A6 Levels of tolyfluanid applied to crops in Great Britain between 1998 and 2004 (CSL, 2006a)

Year	Total Area Treated (ha)	Total Weight Applied (kg)
1998	127	250
1999	127	250
2000	127	250
2001	5123	6103
2002	5706	7041
2003	5783	7153
2004	15811	13100

Although these data do not differentiate between levels of tolyfluanid applied to different crops, these statistics are based on application rates to arable crops, bulbs and flower crops, fodder, forage and grassland crops, protected crops, hardy nursery stock, hops, mushrooms, orchard crops, soft fruit crops and vegetable crops. Surveys were conducted on different crops in different years, therefore extrapolation was performed for those years where a particular crop was not surveyed (CSL, 2006a).

It should be noted that the amount of tolyfluanid applied per hectare of treated area (kg/ha) has decreased in recent years. In 2004, the amount of tolyfluanid applied per hectare of treated area was less than 50% the level of 1998 (Figure A9).

**Figure A9 Levels of tolyfluanid applied to crops in Great Britain between 1998 and 2004 (CSL, 2006a)**

Specific crop usage levels

In a survey of pesticide usage on orchards and fruit stores conducted in England and Wales in 2004, tolyfluanid accounted for approximately 5% of total applied fungicides (CSL, 2006c). Levels of tolyfluanid applied to specific crops are given in Table A7.

Table A7 Usage of tolyfluanid on orchards and fruit stores in 2004 (CSL, 2006c)

Crop	Spray (ha)	Active substance applied (kg)
Dessert apples – Cox	2275	1476
Dessert apples – Others	3285	1949
Culinary apples – Bramley	2510	1641
Culinary apples – Others	22	19
Pears	2259	1611
Cider apples and cherry pears	261	189
Total	10612	6886

In 2003, a survey was conducted of pesticide usage on edible and ornamental protected crops conducted in England, Wales and Scotland (CSL, 2005). Levels of tolyfluanid applied to specific crops are given in Tables A8 and A9.

Table A8 Usage of tolyfluanid on edible crops in 2003 (CSL, 2005)

Crop	Spray (m²)	Active substance applied (kg)
Tomatoes	501	-
Cucumbers	34451	-
Lettuce	204326	-
Celery	9743	-
Peppers	-	-
Other vegetables	68033	-
Edible plants in propagation	554661	-
Strawberries	152315	100
Other fruit	-	-
Total	1024032	100

Table A9 Usage of tolyfluanid on ornamental crops in 2003 (CSL, 2005)

Crop	Spray (m²)	Active substance applied (kg)
Chysanthemums for cutting	-	-
Carnations and plants	-	-
Alstroemeria	-	-
Other flowers and foliage	-	-
Potted chysathemums	-	-
Other pot plants	6063	1
Plants in propagation	28262	2
Hardy nursery stock	82241	8
Total	116566	11

Environmental fate and behaviour

Water

Tolyfluanid is of low water solubility (0.9 mg/l at 25°C) (SRC, 2007). It is expected to bind to sediment and suspended solids, based on an experimental log K_{ow} of 3.9 (SRC, 2007). Tolyfluanid is not expected to volatilise from water surfaces, based on an estimated Henry's Law constant of 7.61×10^{-7} atm.m³/mole and a vapour pressure of 1.5×10^{-6} mmHg (SRC, 2007). Tolyfluanid is reported to be susceptible to hydrolysis, with reported hydrolytic half-lives of 12 days, 5.6 days and 42.5 hours at pH 4, 7 and 9, respectively (EFSA, 2005). Tolyfluanid is not expected to undergo photolysis and is reported not to be readily biodegradable (EFSA, 2005).

Soil

In soil, tolyfluanid is expected to be rapidly hydrolysed to dimethylamino sulfotoluidide (DMST); half-lives of 2-11 days have been reported (Tomlin, 2006). DMST is further degraded to methylaminosulfotoluidide, 4-(dimethylaminosulfonylamino)benzoic acid and 4-(methylaminosulfonylamino)benzoic acid which eventually degrades to carbon dioxide (Tomlin, 2006).

Summary of ecotoxicity, fate and behaviour data

Tolyfluanid appears to be of moderate acute toxicity to freshwater algae, of moderate chronic toxicity to insects, of high acute and moderate chronic toxicity to freshwater crustaceans and of high acute and of moderate-to-high chronic toxicity to freshwater fish. It also appears to be of low chronic toxicity to annelids and birds.

Tolyfluanid is of low water solubility and, in water, is expected to bind to suspended solids and sediment. It is not expected to undergo volatilisation, photolysis or biodegradation, but will rapidly undergo hydrolysis.

A2.2 Dichlofluanid

Chemical structure

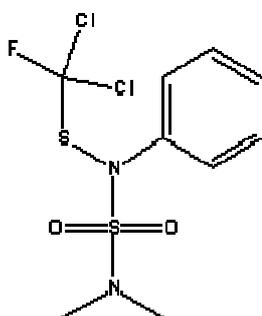


Figure A10 Chemical structure of dichlofluanid

Usage and occurrence

In 2006, dichlofluanid (CAS RN: 1085-98-9), for use in wood preservatives (PT8), was accepted for inclusion on to Annex I of the Biocidal Products Directive (98/8/EC) (HSE, 2006).

The next official steps are:

The Assessment Report that was voted on at the SCBP (the Inclusion Directive for Dichlofluanid) has to be translated into the EC official languages.

The above translated documents are then published in the EU Official Journal (OJ) and the date of publication establishes the date of inclusion.

This Inclusion Directive then has to be processed within the EU Commission to arrive at the formal date of inclusion of Dichlofluanid into Annex I of the BPD – this is 1 March 2009.

All products in PT 8 containing Dichlofluanid have to be authorised, or withdrawn from the market by 28th February 2011.

In a survey of UK coastal waters conducted in 1998, dichlofluanid was not detected (Thomas *et al.*, 2004).

Table A10 contains information on the levels of dichlofluanid applied to crops in Great Britain between 1990 and 2004 (CSL, 2006d). Note that the 'Total Area Treated' refers to the active substance treated area, i.e. the area treated by dichlofluanid, multiplied by the number of times the area was treated. For example, if a field of 3 hectares is treated four times, the treated area is 12 hectares (3x4).

Table A10 Levels of dichlofluanid applied to crops in Great Britain between 1990 and 2004 (CSL, 2006d)

Year	Total area treated (ha)	Total weight applied (kg)
1990	28 800	45 101
1991	29 426	45 745
1992	29 426	45 745
1993	29 660	46 121
1994	30 747	40 924
1995	30 468	40 731
1996	30 468	40 731
1997	30 848	40 778
1998	22 597	30 232
1999	22 505	29 960
2000	22 505	29 960
2001	10 260	12 901
2002	10 260	12 901
2003	10 218	12 902
2004	10 218	12 902

Surveys were conducted on different crops in different years; therefore extrapolation was performed for those years where a particular crop was not surveyed (CSL, 2006d).

Environmental fate and behaviour

Air

No data were located. However, dichlofluanid is structurally very similar to tolyfluanid, therefore it may be expected to undergo a similar fate in the atmosphere.

Water

Dichlofluanid is only sparingly soluble (1.3 mg/l at 25°C) (SRC, 2007). It is expected to bind to sediment and suspended solids, based on an experimental log K_{ow} of 3.7 (SRC, 2007) and is not expected to volatilise from water surfaces, based on an estimated Henry's Law constant of 3.78×10^{-8} atm.m³/mole and an experimental vapour pressure of 1.12×10^{-7} mmHg (SRC, 2007). Dichlofluanid is reported to undergo rapid hydrolysis at pH 7, with 65-70% degradation occurring after 40 hours (JMPR, 1983).

Soil

In studies conducted in aerobic soils, half-lives of 2-3 days were reported for dichlofluanid. The major metabolite detected in soils was dimethylamnosulfanilide (PSD, 2003). Dichlofluanid is also degraded to carbon dioxide; in highly humus and moderately humus soils, 77.5 and 98.8%, respectively, of an applied dose of dichlofluanid was recovered as carbon dioxide after 63 days (PSD, 2003).

Summary of ecotoxicity, fate and behaviour data

Data on the toxicity of dichlofluanid to the aquatic environment are extremely limited. It appears to be of moderate chronic toxicity to the one species of freshwater algae tested, of moderate acute toxicity to the one species of freshwater crustacean tested, of high-to-moderate acute toxicity to molluscs and of high acute toxicity to freshwater fish. It appears to be of moderate acute toxicity to the one species of marine crustacean tested and of high acute toxicity to the one species of marine fish tested. Dichlofluanid appears to be of low toxicity to annelids and birds.

Dichlofluanid is of low solubility and, in water, is expected to bind to sediment and suspended solids. It is not expected to undergo volatilisation from water surfaces, but is expected to hydrolyse rapidly.

A2.3 References

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A3 WATER TREATMENT PROCESS IMPLICATIONS

A3.1 Mechanisms of NDMA formation in drinking water

Numerous laboratory investigations of NDMA formation in drinking water have been reported, utilising a range of reactants including secondary and tertiary amines, nitrite, free chlorine ammonia and chloramines. Generally, these investigations have been carried out to elucidate reaction mechanisms and have used unrealistically high concentrations of reactants compared with those occurring in water treatment in order to provide easily measurable effects. Whilst the results should be considered with this in mind, they probably provide reasonable indications of the mechanisms involved and the implications for water supply.

The principal mechanism of NDMA formation in water treatment and distribution is probably through the reaction of monochloramine with organic precursors, particularly secondary and tertiary amines. In this respect NDMA is considered to be a disinfection by-product.

The precursor mentioned most commonly - and the one used in laboratory studies to investigate mechanisms - is DMA, although in real situations at water treatment works a wide range of other precursors could occur.

Bromide can increase the production of NDMA from monochloramine and DMA, through the production of bromamines, but this requires bromide concentrations substantially higher than those found in raw waters so is unlikely to be significant in terms of water treatment.

Another mechanism for NDMA formation is through the reaction of nitrite with precursors, known as nitrosation, enhanced by the presence of chlorine. This enhancement is surprising considering the very rapid reaction between nitrite and chlorine, but is believed to occur through the production of a highly reactive intermediate, N_2O_4 , in the oxidation of nitrite to nitrate. This mechanism is enhanced at higher pH (Awwa Research Foundation/WERF, 2005).

NDMA may be potentially formed as a result of the ozonation of dimethylsulfamide, a metabolite of the fungicide, tolyfluanid (DWI, 2007).

A3.2 Significance to water supply

Although many laboratory investigations have used largely unrealistic concentrations of reactants, there is considerable evidence in the literature of samples taken from treatment works and in distribution containing NDMA at concentrations up to about 100 ng/l, although usually at much lower concentrations. Factors implicated in the formation of NDMA include raw water source and influence of sewage effluent and agricultural/industrial inputs (i.e. as a source of precursors), chemicals used in treatment and treatment processes, particularly ion exchange and chloramination.

The formation of NDMA can result from preformed chloramine or from separate addition of ammonia and chlorine, and therefore has significance in relation to both treatment and distribution where chloramination is used. It will also be significant where ammonia occurs naturally in the raw water and is removed by chlorination.

Nitrite rarely occurs naturally to any significant extent in raw waters, but can be produced as a stable intermediate in biological nitrification (oxidation of ammonia to nitrate under aerobic conditions) or biological denitrification (reduction of nitrate to nitrogen under anoxic conditions). There are water treatment processes based on these mechanisms for ammonia or nitrate removal, but they have little or no implementation in the UK. However, the mechanism may occur in other processes such as granular activated carbon (GAC) adsorbers or filters to produce measurable levels of nitrite.

Studies have shown that nitrosation can occur on the surface of GAC when nitrite, produced from the nitrification of ammonia on the biofilm surrounding the GAC reacts with a build-up of amines that the GAC has adsorbed (DiGiano *et al*, 1986).

NDMA exhibits a log K_{ow} value of -0.57, indicating that it is a very hydrophilic compound with a high water solubility (Schmidt, 2006). Consequently, NDMA is poorly adsorbed onto activated carbon and other polymeric materials. However, in some activated carbon filters, an increase in removal efficiency for NDMA has been observed with increasing running time. Schmidt suggests that this effect can most likely be explained by an increased biological activity and that biodegradation is the dominant mechanism of removal.

The results of the survey of drinking water for NDMA as a result of the ozonation of dimethylsulfamide showed one positive result (Bayer CropScience AG, 2007). A concentration of 3 ng/l NDMA was found in a drinking water from a works treating a raw water containing 63 ng/l dimethylsulfamide. However, as a result of the continuing suspension of tolyfluanid in the UK and Europe, it is unlikely that this formation pathway will be of future concern.

A3.3 Sources of precursors

Precursors are ubiquitous in raw waters, including naturally occurring organics in raw water and organics arising from sewage effluent inputs or from industrial/agricultural sources. Precursors also arise from chemicals and materials used in water treatment processes.

Strong base anion exchange resins used for nitrate removal may provide a source of precursors, particularly when new (and possibly also on decay with ageing).

Some polyelectrolytes used in water treatment, particularly the Epi-DMA (epichlorohydrin-dimethylamine) and polyDADMAC (polydiallyldimethylammonium chloride) products, contain DMA. The precursor concentrations may increase on storage of polyelectrolyte solutions. These chemicals are not believed to be widely used for drinking water treatment in England and Wales.

A3.4 Minimising NDMA formation

A wide range of organic nitrogen precursors can occur in raw waters. Conventional treatment such as coagulation or GAC adsorption may be effective at removing some of these precursors and reducing NDMA formation potential.

Nitrite formation by biological denitrification can be prevented by avoiding low dissolved oxygen (DO) conditions in filters and, probably more significantly because of higher levels of adsorbed organics and biomass, in GAC adsorbers. Denitrification should not be significant during normal operation. However, after long periods out of service, when low DO conditions

can develop, filters and GAC beds should be backwashed before return to operation, and ideally the backwash water should not be recycled.

Nitrite formation by nitrification of ammonia is also more likely to be significant when filters or GAC beds are out of service, because of the long contact time between the water and biomass that would produce higher nitrite concentrations. Again, backwashing before return to service will reduce the potential for NDMA formation. On balance, biological nitrification in filters and GAC during routine operation is likely to be beneficial in terms of reducing NDMA formation, because the removal of ammonia prior to chlorination will more than offset the NDMA formation potential from low concentrations of nitrite.

The most likely source of NDMA in water supplies will be from chloramination, because of the long contact times in distribution. Monochloramine concentrations should be kept to a minimum for the distribution requirements, and care should be taken to minimise nitrite formation from nitrification in distribution.

Laboratory experiments showed that contact with free chlorine for 2 hours prior to chloramination reduced NDMA formation by over 90%. A comparison of NDMA formation at two full-scale treatment plants found much lower NDMA concentrations at the plant that had 2-4 hours contact with free chlorine prior to ammonia addition compared to the second plant where ammonia was added a few seconds after chlorine (Charrois and Hruday 2007). However, this study did not examine the possible effects on the formation of other disinfection by-products such as THMs.

At sites that may be susceptible to NDMA production, the formation potential can be reduced by avoidance of polyDADMAC or Epi-DMA products, using polyacrylamide products in preference. The potential for other undesirable contaminants from these products, e.g. acrylamide monomer from polyacrylamide, needs also to be considered. PolyDADMAC and Epi-DMA products should, where possible, be used as quickly as possible after preparation of dosing solutions, to minimise release of precursors during storage.

Ion exchange resin should be rinsed well before use, which would normally be in accordance with supplier's recommendations. After chemical regeneration or acid washing of the resin, there may be an increased potential for low level precursor release, so effective rinsing is needed. Old resins may also release more precursors, and earlier replacement of resin should be considered compared with replacement on the basis of loss of capacity.

A3.5 References

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A4 CONCLUSIONS AND RECOMMENDATIONS

The literature review has identified numerous laboratory investigations of NDMA formation in drinking water. Generally, these investigations have been carried out to elucidate reaction mechanisms and have used unrealistically high concentrations of reactants compared with those occurring in water treatment.

The principal mechanism of NDMA formation in water treatment is probably through the reaction of monochloramine with organic precursors, particularly secondary and tertiary amines. The most commonly mentioned precursor - and the one used in laboratory studies to investigate mechanisms - is DMA, although a wide range of other precursors could occur at water treatment works.

There is considerable evidence in the literature of samples taken from treatment works and in distribution containing NDMA at concentrations up to about 100 ng/l, although usually at much lower concentrations. Factors implicated in the formation of NDMA include raw water source and influence of sewage effluent and agricultural/industrial inputs (i.e. as sources of precursors), chemicals used in treatment and treatment processes, particularly ion exchange and chloramination.

Based on these findings, it is recommended that a sampling survey should be carried out to determine the range of concentrations of NDMA in water supplies in England and Wales. Sampling should be carried out quarterly to capture any effects of seasonal changes in water quality and temperature.

The survey should be designed to address the principal factors identified from the literature review, including:

- raw water source (e.g. groundwater, lowland surface water, upland surface water) and quality (organics, ammonia, nitrite);
- proximity of sewage effluent or agricultural/industrial inputs;
- treatment chemicals (e.g. polyDADMAC or Epi-DMA polyelectrolytes);
- treatment processes (e.g. ion exchange, GAC adsorption, chloramination); and
- distribution characteristics (e.g. residence time).

The first sampling survey should be carried out to identify treatment works where NDMA is formed and is present in the final water exiting the works. Further sampling surveys will be informed by the results of the first survey and could include more intensive sampling within treatment and in distribution.

APPENDIX B DWI GUIDANCE ON SAMPLE AND SAMPLE EXTRACT STABILITY TRIALS⁸

B1 PURPOSE

The purpose of these trials was to demonstrate that the maximum permitted delay between sampling and analysis does not result in “a material alteration in the concentration or value for the measurement or observation of which the sample is intended” (regulation 16(2)(c)).

In terms of a statistical trial, the hypothesis to be tested is that the change in the mean of repeated measurements before and after storage is not greater than a target figure.

A successful stability trial must be conducted prior to adopting sample preservation conditions or sample extract preservation conditions which differ from, or storage times which are longer than, those documented in ISO 5667 Part 3:2003, or other authoritative source, i.e. a standard method. Each sample matrix of interest must be fully tested. In practice, only the worst case or worst cases need be tested. For example testing nitrite stability in waters with low colony counts will not yield useful information.

Results of trials carried out in other laboratories may be used, provided the laboratory can show that the preservation and storage conditions are identical (not just similar) and that the sample matrices of interest to the laboratory were included in the trial and the results of the trial were fully satisfactory and robust (i.e. reproduced in three or more independent laboratories).

B2 SPECIFICATION OF REQUIREMENT

For regulatory analysis the appropriate target value is one half of the maximum permitted trueness error. For most parameters this is 5% of the value at the PCV. For many organic parameters it is 12.5%. Significance is at the two-sided 95% confidence level, and the power is set at 90%. Each sample matrix type of interest must be tested separately.

The specification, design, calculation and interpretation given in this document are all derived from NS30 pages 113 to 120, 137 to 139 and 148.

B3 DESIGN OF TRIAL

The trial should consist of spiking of a pre-determined number of samples to the PCV. All samples must be collected by filling a series of bottles from the same source (e.g. a single tap). The true concentrations of the parameter must show negligible variation from one sample to another. If filling a series of bottles directly from the tap may not yield such samples, a bulk sample should be taken which is then mixed and sub-divided into a series of bottles. Precision of spiking is of paramount importance and more important than the absolute value spiked. If precision of spiking is likely to cause problems, consideration should be given to spiking a bulk sample, which can then be sub-divided into a series of bottles.

⁸ DWI Information Letter 12/05 (<http://www.dwi.gov.uk/reggs/infolett/2005/info1205.shtm>).

One set of samples is analysed on Day 0, with a further set analysed at each selected time interval with all sample preservation and storage conditions applied exactly as it is intended to apply them to regulatory samples. It would be prudent to also include times less than the full period desired for routine storage of samples in the trial.

The estimated minimum number of samples (n) required to be analysed on each day of testing to show whether the change is significant is given below

Standard deviation (%PCV)	Number of samples to detect 12.5% change	Number of samples to detect 10% change	Number of samples to detect 5% change
1	2	2	2
2	2	2	5
3	2	3	10
4	3	7	17
5	5	7 (mercury)	26
6	6	10	38
7	9	13	51
8	11	17	67
9	14	22	85
10	17	26 (tetrachloromethane)	104
11	21	32	126
12	24	38	150
12.5	26	41	163
38	38	59	234
20	67	104	416

These figures are minimum values of n for which the equation $(t\alpha + t\beta) s\sqrt{(2/n)} \leq \delta$ is true, where δ is the target change, subject to a minimum of 2 for a statistical comparison to be made. This indicates that the test will probably be sufficiently powerful to identify the target change as being a statistically significant difference. Figures in bold relate to the maximum permitted precision relevant to the maximum permitted change. These numbers are only estimates of the actual numbers required because the actual distribution of data will not be known until after the test is completed, and either more or fewer replicates may be needed in practice. Reasons for large deviations from the expected standard deviation should be investigated to determine if there is any reason for the unexpected change in performance, which may invalidate the trial. Large within batch variations can also lead to wrong conclusions being drawn. Prior to undertaking trials steps should be taken to ensure that between batch errors are not significant. The most common cause of significant between batch errors is variation in the true value of calibration standards. If it is not possible to reduce such errors to a magnitude which will not adversely affect the trial, means should be adopted to measure and compensate for such errors, such as those described in NS30 or DD ISO ENV 13530:1998

The same design can also be used to test alternative preservation and pre-treatment methods. In these cases, storage times should be the same and between batch errors can be eliminated by analysing both sets of samples in the same analytical batch.

B4 CALCULATION

The significance of any observed difference is determined using a t-test. The following is an example calculation, with expected standard deviation of 2% and target change 5%

	Day zero	Day x
	101.0	94.0
	100.3	93.2
	98.8	92.9
	101.2	96.5
	99.9	92.8
Mean	100.225	94.05
Standard deviation	1.11	1.72
Pooled standard deviation	1.45	
Mean difference	6.175	
Standard Error (of differences)	1.024	
t statistic (calc)	6.032	
Degrees of freedom	6	
Critical value (.05) (from tables)	2.447	

Conclusion: there is a real difference between the means.

B5 INTERPRETATION

$t_{0.05}$ for 6 degrees of freedom = 2.447 (from tables). The observed value is greater than the tabulated value and therefore there is a real difference between the two means. The numerical value of the change is also greater than the target value and therefore there is a significant change.

If the observed value of t is greater than the tabulated value and the change was less than or equal to the target change, the change is less than (or equal to) the target and samples may be stored for up to the tested period under the conditions tested.

If the observed value of t is less than the tabulated value and the change was equal to or greater than the target change, the trial was not sufficiently powerful to show a significant change and must be repeated with more replicates.

If the change is less than the target change and the observed value of t was less than the tabulated value then, provided the trial was sufficiently powerful and would have identified any difference in excess of the target change as being significant, there has been no significant change and samples may be stored for up to the tested period under the conditions tested. The test is sufficiently powerful if the target change is substituted for mean difference in the formula for the t test and the value of t then calculated is greater than the tabulated value. If it is not greater then the trial was not sufficiently powerful to show a significant change and must be repeated with more replicates.

In summary:

Mean difference greater than target?	Observed t greater than tabulated value?	Would difference equal to target change have observed t greater than tabulated value?	Proposed new storage arrangements satisfactory?
Yes	Yes	N/A	No
Yes	No	N/A	No*
No	Yes	N/A	Yes
No	No	No	No*
No	No	Yes	Yes

* Trial not sufficiently powerful to test the original hypothesis. Repeat trial using more replicates.

APPENDIX C RESULTS OF SURVEYS AND LABORATORY TESTS

C1 INTRODUCTION

Quarterly sampling surveys were carried out in December 2006, February 2007, June 2007 and September 2007. Details of these surveys are presented in below.

C2 SURVEY 1 - DECEMBER 2006

C2.1 Sampling

The first sampling survey was carried out during week beginning 4 December 2006. Samples of final water were taken from 18 treatment works, including two 'control' works. Two works identified for sampling were excluded because of ongoing operating difficulties.

Samples from Utility A were taken by Utility A Samplers and returned directly to the analysing laboratory (Spencer House Laboratory).

Samples from Utilities B and D were taken by WRc personnel. Samples from Utility C were taken by WRc personnel (Samples C11 and C12) and Utility C Samplers (Samples C13, C14 and C15). Samples were returned to WRc in ice-packed cool boxes on the day of sampling and stored in the dark at 4°C until submission to the analysing laboratory within approximately 48 hours of sampling.

Samples C11, C12 and D18 were taken in duplicate as a check on the analytical procedure.

C2.2 Results

Results from the first sampling survey are shown in Table C1. Sample chromatograms are shown in Figures C1 to C4.

Table C1 Results of Sampling Survey 1 (December 2006)

Works Ref.	Works Description	Sample Code	NDMA (ng/l)
Utility A			
A1 Final	<i>Source:</i> Reservoir, Agricultural input, Sewage effluent input, High colour/TOC, Algae, Pesticides <i>Treatment:</i> RGF, Ozonation, GAC, Chloramination <i>Chemicals:</i>	M1837158	< 0.9
A2 Final	<i>Source:</i> Groundwater, High colour/TOC <i>Treatment:</i> Coagulation, RGF, GAC, Chloramination <i>Chemicals:</i> Ferric coagulant	M1837159	< 0.9
A3 Final	<i>Source:</i> Lowland river/reservoir, Agricultural input, Sewage effluent input, High colour/TOC, Algae, Ammonia, Nitrate, Pesticides <i>Treatment:</i> Coagulation, RGF, Recycle, Ozonation, GAC, Chlorination <i>Chemicals:</i> Aluminium coagulant	M1837160	< 0.9

Works Ref.	Works Description	Sample Code	NDMA (ng/l)
A4 Final	<i>Source:</i> Lowland river/reservoir, Agricultural input, Sewage effluent input, High colour/TOC, Algae, Ammonia, Nitrate, Pesticides <i>Treatment:</i> Coagulation, RGF, Recycle, Ozonation, GAC, Ion exchange, Chlorination <i>Chemicals:</i> Aluminium coagulant	M1837161	< 0.9
A5 Final	<i>Source:</i> Groundwater, Ammonia <i>Treatment:</i> Chlorination <i>Chemicals:</i>	M1837162	NS
A6 Final	<i>Source:</i> Groundwater, Agricultural input, Nitrate, Pesticides <i>Treatment:</i> Ion exchange, GAC, Chlorination <i>Chemicals:</i>	M1837163	< 0.9
A7 Final	<i>Source:</i> Groundwater, Nitrate, Pesticides <i>Treatment:</i> Ion exchange, GAC, Chlorination <i>Chemicals:</i>	M1837164	< 0.9
A8 Final	<i>Source:</i> Lowland river/reservoir, Agricultural input, Sewage effluent input, High colour/TOC, Algae, Ammonia, Nitrate, Pesticides <i>Treatment:</i> Coagulation, RGF, Ozonation, GAC, Chloramination <i>Chemicals:</i> Ferric coagulant	M1837165	< 0.9
AC1 Final ('Control')	<i>Source:</i> Groundwater <i>Treatment:</i> Chlorination <i>Chemicals:</i>	M1837166	< 0.9
Utility B			
B9 Final	<i>Source:</i> Upland reservoir, High colour/TOC <i>Treatment:</i> Coagulation, Pressure filtration, Pre-chlorination, RGF (manganese removal), Chlorination <i>Chemicals:</i> Aluminium coagulant	M1837167	NS
B10 Final	<i>Source:</i> Lowland Reservoir (fed by canal), Agricultural input, Sewage effluent input, High colour/TOC, Algae, Pesticides <i>Treatment:</i> Coagulation, Pressure filtration, GAC, Chlorination <i>Chemicals:</i> Aluminium coagulant	M1837168	< 0.9
BC2 Final ('Control')	<i>Source:</i> Groundwater, Pesticides (trace) <i>Treatment:</i> Chlorination <i>Chemicals:</i>	M1837169	< 0.9
Utility C			
C11/1 Final	<i>Source:</i> Upland, High colour/TOC <i>Treatment:</i> Coagulation, Pre-chlorination (~1 mg/l), RGF, Chloramination <i>Chemicals:</i> Ferric coagulant, Polyacrylamide	M1837170	5.8
C11/2 Final (Duplicate)	<i>Source:</i> Upland, High colour/TOC <i>Treatment:</i> Coagulation, Pre-chlorination (~1 mg/l), RGF, Chloramination <i>Chemicals:</i> Ferric coagulant, Polyacrylamide	M1837171	5.6
C12/1 Final	<i>Source:</i> Upland, High colour/TOC <i>Treatment:</i> Sirofloc, Pre-chlorination (~1 mg/l), RGF, Chlorination <i>Chemicals:</i> PolyDADMAC (2-3 mg/l)	M1837172	1.8
C12/2 Final (Duplicate)	<i>Source:</i> Upland, High colour/TOC <i>Treatment:</i> Sirofloc, Pre-chlorination (~1 mg/l), RGF, Chlorination <i>Chemicals:</i> PolyDADMAC (2-3 mg/l)	M1837173	1.6
C13 Final	<i>Source:</i> Lowland river, Agricultural input, Algae, Ammonia, Nitrate, Pesticides <i>Treatment:</i> Coagulation, Ozonation, RGF/GAC, Chlorination <i>Chemicals:</i> Aluminium coagulant, PolyDADMAC (0.7-1.4 mg/l), Polyelectrolyte	M1837174	< 0.9
C14 Final	<i>Source:</i> Lowland river, Agricultural input, Sewage effluent input, Pesticides <i>Treatment:</i> Actiflo, RGF, Ozonation, GAC, Chlorination <i>Chemicals:</i> Polyelectrolyte (FloPam AN905 SEP)	M1837175	< 0.9
C15 Final	<i>Source:</i> Lowland river, Agricultural input, Algae, Pesticides <i>Treatment:</i> Pre-ozonation (2-3 mg/l), Coagulation, Direct RGF, Chlorination <i>Chemicals:</i> Ferric coagulant (~1 mg/l), PolyDADMAC (1-2 mg/l)	M1837176	< 0.9
Utility D			
D16 Final	<i>Source:</i> Reservoir, Ammonia, Pesticides <i>Treatment:</i> Coagulation, RGF, GAC, Chlorination, Dechlorination (NaHSO ₄) <i>Chemicals:</i> Ferric coagulant, Starch-based polyelectrolyte (Wisprofloc)	M1837177	< 0.9

Works Ref.	Works Description	Sample Code	NDMA (ng/l)
D17 Final	<i>Source:</i> River, Reservoir, Ammonia, Nitrate, Pesticides <i>Treatment:</i> Coagulation, RGF, Ozonation, GAC, Chlorination, Dechlorination (SO ₂) <i>Chemicals:</i> Ferric coagulant, Polyacrylamide (LT22S)	M1837178	< 0.9
D18/1 Final	<i>Source:</i> Reservoir, Ammonia, Nitrate, Pesticides <i>Treatment:</i> Coagulation, RGF, GAC, Chlorination, Dechlorination (SO ₂) <i>Chemicals:</i> Ferric coagulant, Polyacrylamide (LT22), Epi-DMA	M1837179	1.6
D18/2 Final (Duplicate)	<i>Source:</i> Reservoir, Ammonia, Nitrate, Pesticides <i>Treatment:</i> Coagulation, RGF, GAC, Chlorination, Dechlorination (SO ₂) <i>Chemicals:</i> Ferric coagulant, Polyacrylamide (LT22), Epi-DMA	M1837180	1.8

Note:

1. NS Not sampled.

C2.3 Discussion

NDMA was found at concentrations between 1.6 - 5.8 ng/l in drinking water from three of the 18 treatment works sampled: Works C11, C12 and D18. The measured concentrations are below current concentrations of concern in North America and substantially lower than the likely WHO guideline value. NDMA was not detected above the limit of detection (0.9 ng/l) in the samples from the two 'control' works nor in samples from Utilities A or B.

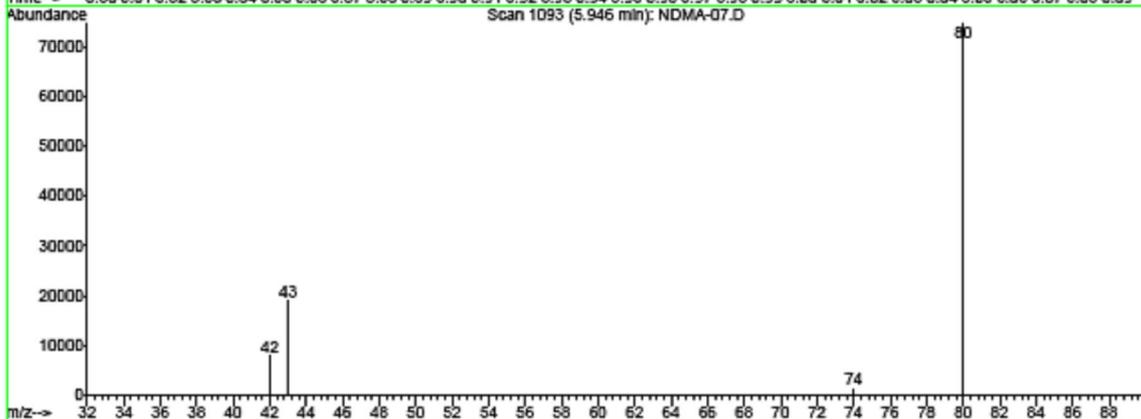
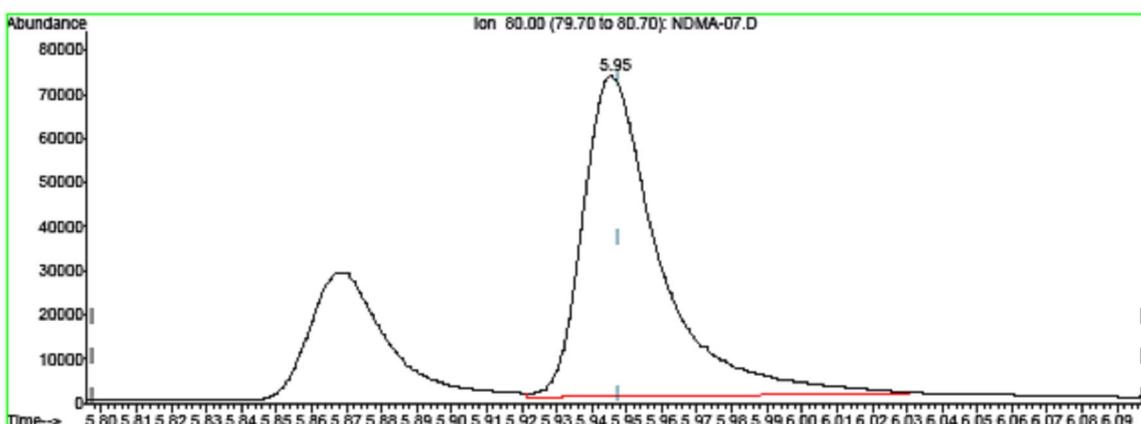
The highest concentration of NDMA (5.6-5.8 ng/l) was found in the duplicate samples from Works C11. This works treats a highly-coloured upland water by coagulation (ferric coagulant), filtration and chloramination.

NDMA (1.6-1.8 ng/l) was found in the duplicate samples taken from a second works from Utility C, Works C12. This works treats a highly-coloured upland water using the Sirofloc process, filtration and chlorination. Treatment includes dosing of polyDADMAC.

Quantitation Report (Qedit)

Data Path : D:\DATA\NDMA\Batch 1\
 Data File : NDMA-07.D
 Acq On : 13 Dec 2006 16:10
 Operator : DT
 Sample : 1837158
 Misc :
 ALS Vial : 6 Sample Multiplier: 1

Quant Time: Dec 14 08:51:21 2006
 Quant Method : C:\MSDCHEM\1\METHODS\NDMA 14DEC06.M
 Quant Title : NDMA
 QLast Update : Thu Dec 14 08:48:13 2006
 Response via : Initial Calibration



TIC: NDMA-07.D

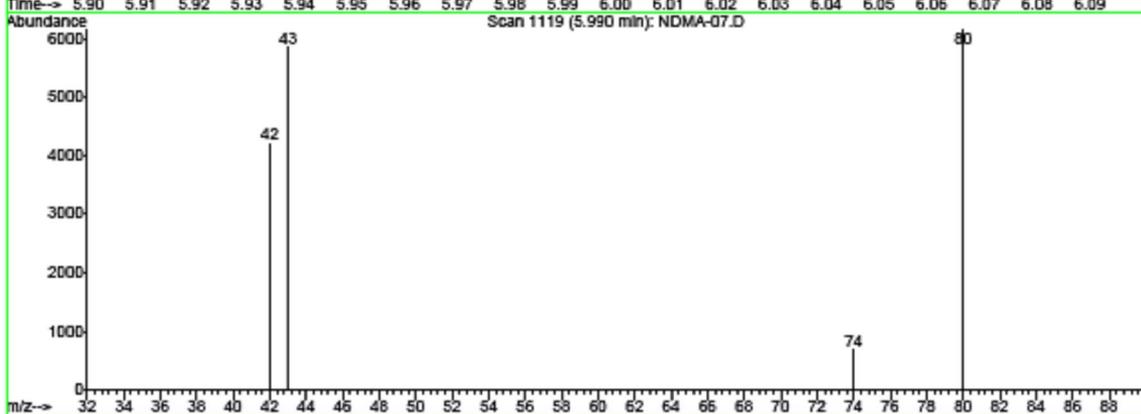
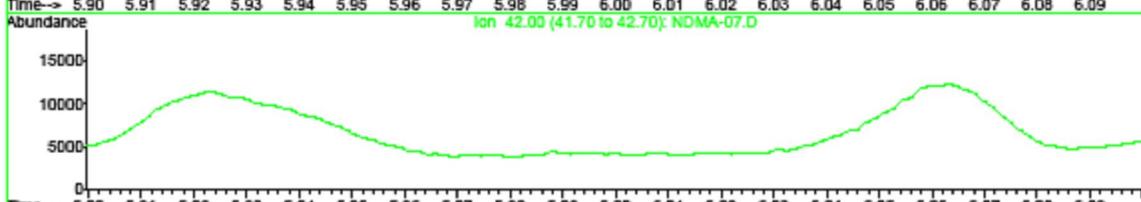
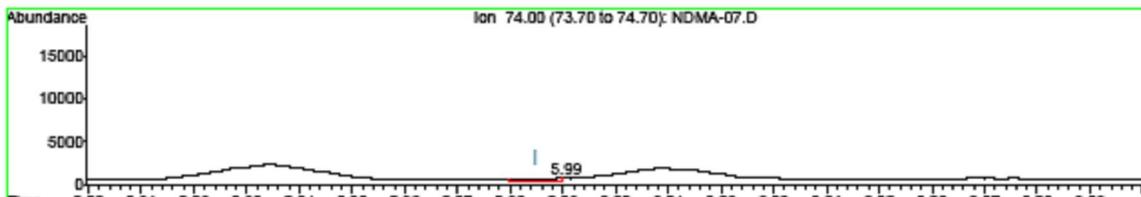
(1) D6-NDMA		
5.946min (-0.002) 40.00ng/l		
response 111149		
Ion	Exp%	Act%
80.00	100	100
0.00	0.00	0.00
0.00	0.00	0.00
0.00	0.00	0.00

Figure C1 Survey 1: Sample A1 (M1837158) - d6-NDMA

Quantitation Report (Qedit)

Data Path : D:\DATA\NDMA\Batch 1\
 Data File : NDMA-07.D
 Acq On : 13 Dec 2006 16:10
 Operator : DT
 Sample : 1837158
 Misc :
 ALS Vial : 6 Sample Multiplier: 1

Quant Time: Dec 14 08:51:21 2006
 Quant Method : C:\MSDCHEM\1\METHODS\NDMA 14DEC06.M
 Quant Title : NDMA
 QLast Update : Thu Dec 14 08:48:13 2006
 Response via : Initial Calibration



TIC: NDMA-07.D

(2) NDMA
 5.990min (+0.005) 0.26ng/l m
 response 142

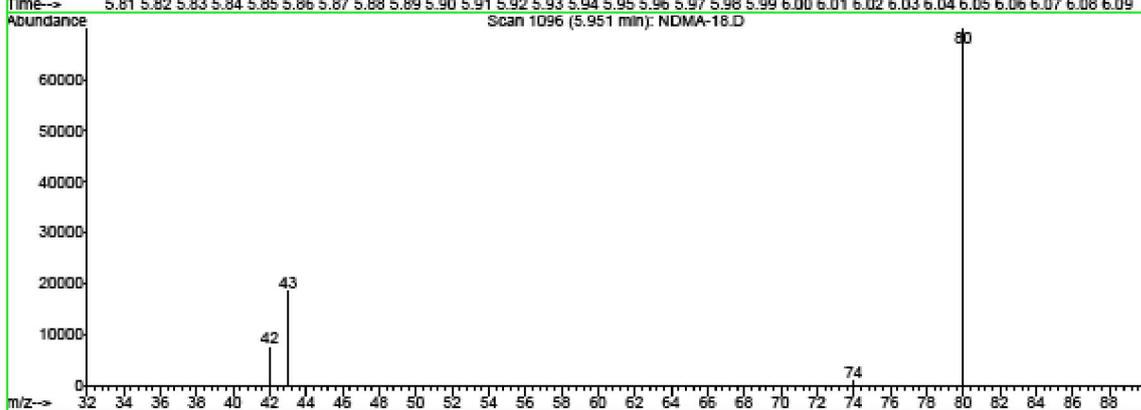
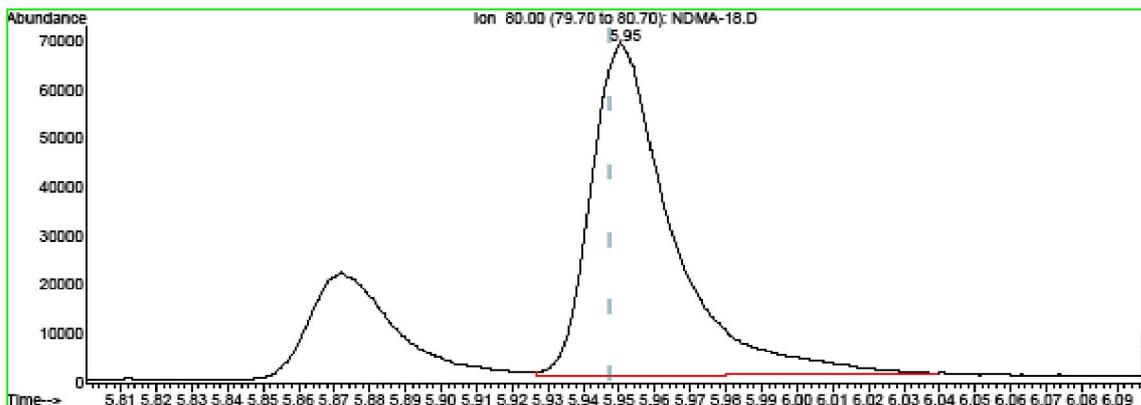
Ion	Exp%	Act%
74.00	100	100
42.00	41.60	0.00#
0.00	0.00	0.00
0.00	0.00	0.00

Figure C2 Survey 1: Sample A1 (M1837158) - NDMA

Quantitation Report (Qedit)

Data Path : D:\DATA\NDMA\Batch 1\
 Data File : NDMA-18.D
 Acq On : 13 Dec 2006 20:57
 Operator : DT
 Sample : 1837170
 Misc :
 ALS Vial : 17 Sample Multiplier: 1

Quant Time: Dec 14 08:55:38 2006
 Quant Method : C:\MSDCHEM\1\METHODS\NDMA 14DEC06.M
 Quant Title : NDMA
 QLast Update : Thu Dec 14 08:48:13 2006
 Response via : Initial Calibration



TIC: NDMA-18.D

(1) D6-NDMA		
5.951min (+0.003)	40.00ng/l	
response	107660	
Ion	Exp%	Act%
80.00	100	100
0.00	0.00	0.00
0.00	0.00	0.00
0.00	0.00	0.00

Figure C3 Survey 1: Sample C11/1 (M1837170) - d6-NDMA

Quantitation Report (Qedit)

Data Path : D:\DATA\NDMA\Batch 1\
 Data File : NDMA-18.D
 Acq On : 13 Dec 2006 20:57
 Operator : DT
 Sample : 1837170
 Misc :
 ALS Vial : 17 Sample Multiplier: 1

Quant Time: Dec 14 08:55:38 2006
 Quant Method : C:\MSDCHEM\1\METHODS\NDMA 14DEC06.M
 Quant Title : NDMA
 QLast Update : Thu Dec 14 08:48:13 2006
 Response via : Initial Calibration

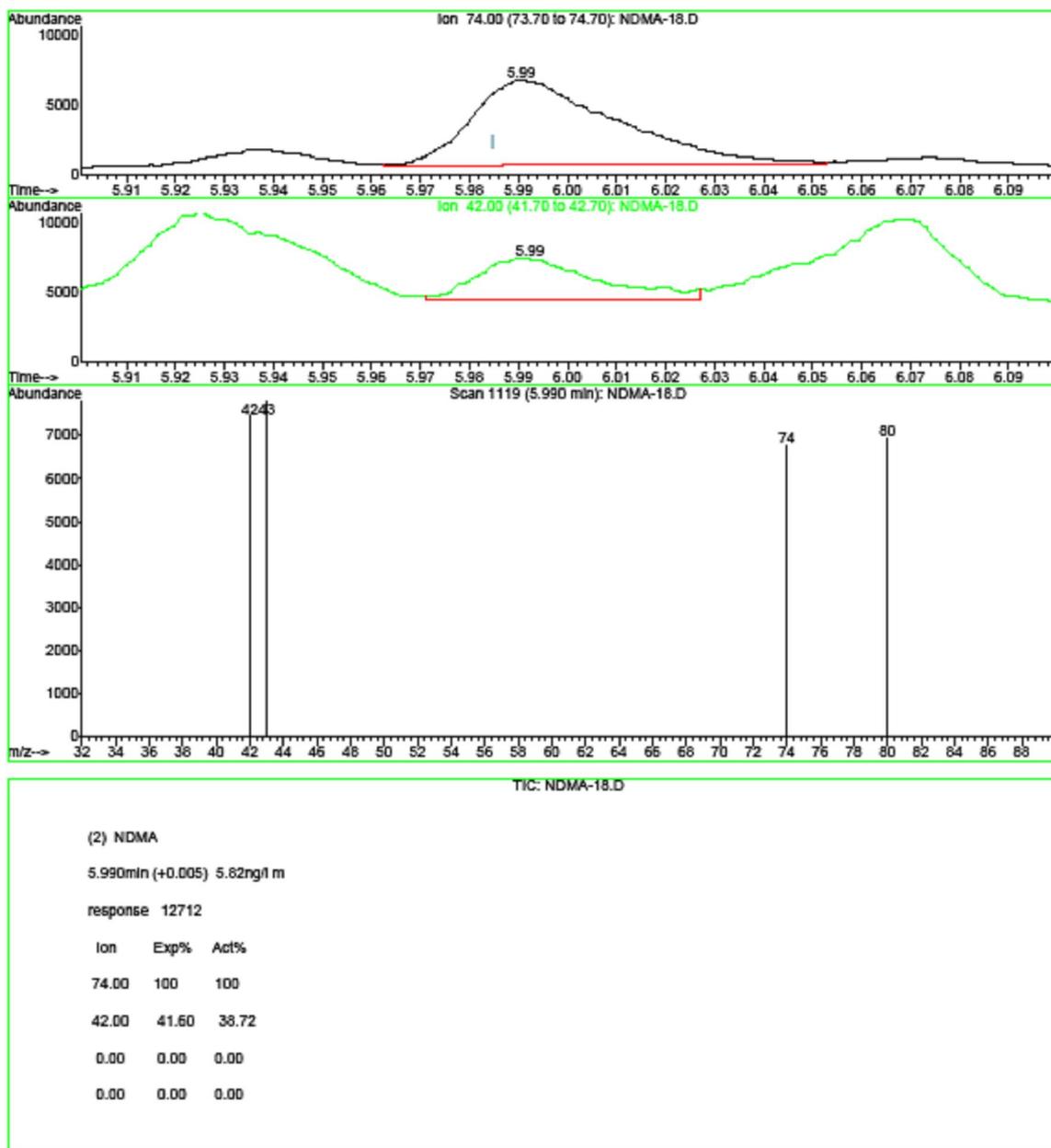


Figure C4 Survey 1: Sample C11/1 (M1837170) - NDMA

NDMA (1.6-1.8 ng/l) was found in the duplicate samples taken a works from Utility D, Works D18. This works treats a reservoir water by coagulation (ferric coagulant), filtration, GAC adsorption and chlorination. Treatment includes dosing of Epi-DMA.

Two of the three works where NDMA was detected treat highly-coloured upland waters with both works including additional factors: chloramination at Works C11 and dosing of PolyDADMAC at Works C12. Works D18 does not treat highly-coloured water but notably includes dosing of Epi-DMA in water treatment.

High colour/TOC is indicated at several works where NDMA was not detected. However, this indication is subjective and further quantitative data will be sought to allow comparison between these works and Works C11 and C12.

Chloramination is utilised at several works from Utility A where NDMA was not detected.

Use of polyDADMAC and Epi-DMA appears not to be widespread. NDMA was detected at two of the three works utilising these polyelectrolytes: Works C12 (polyDADMAC) and Works D18 (Epi-DMA).

The measured concentrations of NDMA are below the 9 ng/l standard included in legislation introduced by the Ministry of Environment (MoE) in Ontario, Canada, below the notification level of 10 ng/l established by the California Department of Health Services (CDHS) and substantially below the WHO guideline value of 100 ng/l.

C2.4 Conclusions

- Sixteen works were sampled because their raw water source and/or treatment included factors associated with the formation of NDMA. NDMA was detected at three of these works.
- NDMA was not detected at the two 'control' works.
- Where NDMA was detected, possible contributory factors included highly-coloured upland waters, chloramination and use of polyDADMAC or Epi-DMA. However, these factors were also present at works where NDMA was not detected.
- The measured concentrations of NDMA (1.6-5.8 ng/l) were lower than current concentrations of concern in North America and substantially lower than the WHO guideline value.

C3 SURVEY 2 - FEBRUARY 2007

For the second survey, samples were again taken from the treatment works participating in the first survey; additional 'intra-works' sampling was carried out at the three works that showed measurable concentrations of NDMA from the first survey. Sampling was also carried out at an additional seven works - including five works from a fifth utility, Utility E - exhibiting one or more of the factors indicated in the formation of NDMA: highly-coloured raw water, dosing of polyDADMAC or Epi-DMA, and chloramination.

C3.1 Sampling

The second sampling survey was carried out during week beginning 26 February 2007.

Samples of final water were taken from 24 treatment works, including two 'control' works. Additional 'intra-works' sampling was carried out at Works C11, C12 and D18. Two works identified for sampling were excluded because of ongoing operating difficulties and a sample from a third works was spoiled and the analysis cancelled.

Samples from Utility A were taken by Utility A Samplers and returned directly to the analysing laboratory (Spencer House Laboratory).

Samples from Utilities B, D and E were taken by WRc personnel. Samples from Utility C were taken by WRc personnel (Samples C11, C12 and C17) and Utility C Samplers (Samples C13, C14, C15 and C16). Samples from Utilities B, D and E were returned to WRc in ice-packed cool boxes on the day of sampling and stored in the dark at 4°C until submission to the analysing laboratory within approximately 48 hours of sampling. Samples from Utility C were collected and stored in ice-packed cool boxes and submitted directly to the analysing laboratory within approximately 12 - 48 hours of sampling.

C3.2 Results

Results from the second sampling survey are shown in Table C2.

Table C2 Results of Sampling Survey 2 (February 2007)

Works Ref.	Works Description	Sample Code	NDMA (ng/l)
Utility A			
A1 Final	<i>Source:</i> Reservoir, Agricultural input, Sewage effluent input, High colour/TOC, Algae, Pesticides <i>Treatment:</i> RGF, Ozonation, GAC, Chloramination <i>Chemicals:</i>	M1949727	< 0.9
A2 Final	<i>Source:</i> Groundwater, High colour/TOC <i>Treatment:</i> Coagulation, RGF, GAC, Chloramination <i>Chemicals:</i> Ferric coagulant	M1949728	NS
A3 Final	<i>Source:</i> Lowland river/reservoir, Agricultural input, Sewage effluent input, High colour/TOC, Algae, Ammonia, Nitrate, Pesticides <i>Treatment:</i> Coagulation, RGF, Recycle, Ozonation, GAC, Chlorination <i>Chemicals:</i> Aluminium coagulant	M1949729	< 0.9
A4 Final	<i>Source:</i> Lowland river/reservoir, Agricultural input, Sewage effluent input, High colour/TOC, Algae, Ammonia, Nitrate, Pesticides <i>Treatment:</i> Coagulation, RGF, Recycle, Ozonation, GAC, Ion exchange, Chlorination <i>Chemicals:</i> Aluminium coagulant	M1949730	< 0.9
A5 Final	<i>Source:</i> Groundwater, Ammonia <i>Treatment:</i> Chlorination <i>Chemicals:</i>	M1949731	NS
A6 Final	<i>Source:</i> Groundwater, Agricultural input, Nitrate, Pesticides <i>Treatment:</i> Ion exchange, GAC, Chlorination <i>Chemicals:</i>	M1949732	< 0.9
A7 Final	<i>Source:</i> Groundwater, Nitrate, Pesticides <i>Treatment:</i> Ion exchange, GAC, Chlorination <i>Chemicals:</i>	M1949733	< 0.9

Works Ref.	Works Description	Sample Code	NDMA (ng/l)
A8 Final	<i>Source:</i> Lowland river/reservoir, Agricultural input, Sewage effluent input, High colour/TOC, Algae, Ammonia, Nitrate, Pesticides <i>Treatment:</i> Coagulation, RGF, Ozonation, GAC, Chloramination <i>Chemicals:</i> Ferric coagulant	M1949734	< 0.9
AC1 Final ('Control')	<i>Source:</i> Groundwater <i>Treatment:</i> Chlorination <i>Chemicals:</i>	M1949735	< 0.9
Utility B			
B9 Final	<i>Source:</i> Upland reservoir, High colour/TOC <i>Treatment:</i> Coagulation, Pressure filtration, Pre-chlorination, RGF (manganese removal), Chlorination <i>Chemicals:</i> Aluminium coagulant	M1949736	< 0.9
B10 Final	<i>Source:</i> Lowland Reservoir (fed by canal), Agricultural input, Sewage effluent input, High colour/TOC, Algae, Pesticides <i>Treatment:</i> Coagulation, Pressure filtration, GAC, Chlorination <i>Chemicals:</i> Aluminium coagulant	M1949737	< 0.9
BC2 Final ('Control')	<i>Source:</i> Groundwater, Pesticides (trace) <i>Treatment:</i> Chlorination <i>Chemicals:</i>	M1949738	< 0.9
Utility C			
C11/1 Final No.1	<i>Source:</i> Upland, High colour/TOC <i>Treatment:</i> Coagulation, Pre-chlorination (~1 mg/l), RGF, Chloramination <i>Chemicals:</i> Ferric coagulant, Polyacrylamide	M1949739	1.3
C11/2 Final No.2	<i>Source:</i> Upland, High colour/TOC <i>Treatment:</i> Coagulation, Pre-chlorination (~1 mg/l), RGF, Chloramination <i>Chemicals:</i> Ferric coagulant, Polyacrylamide	M1949763	2.5
C11/3 Chlorinated, pre-ammonia	<i>Source:</i> Upland, High colour/TOC <i>Treatment:</i> Coagulation, Pre-chlorination (~1 mg/l), RGF, Chloramination <i>Chemicals:</i> Ferric coagulant, Polyacrylamide	M1949764	3.2
C12/1 Final	<i>Source:</i> Upland, High colour/TOC <i>Treatment:</i> Sirofloc, Pre-chlorination (~1 mg/l), RGF, Chlorination <i>Chemicals:</i> PolyDADMAC	M1949741	1.5
C12/2 PolyDADMAC dosed, pre-chlorine	<i>Source:</i> Upland, High colour/TOC <i>Treatment:</i> Sirofloc, Pre-chlorination (~1 mg/l), RGF, Chlorination <i>Chemicals:</i> PolyDADMAC	M1949765	< 0.9
C12/3 Pre-polyDADMAC	<i>Source:</i> Upland, High colour/TOC <i>Treatment:</i> Sirofloc, Pre-chlorination (~1 mg/l), RGF, Chlorination <i>Chemicals:</i> PolyDADMAC	M1949766	1.7
C13 Final	<i>Source:</i> Lowland river, Agricultural input, Algae, Ammonia, Nitrate, Pesticides <i>Treatment:</i> Coagulation, Ozonation, RGF/GAC, Chlorination <i>Chemicals:</i> Aluminium coagulant, PolyDADMAC (0.7-1.4 mg/l), Polyelectrolyte	M1949743	< 0.9
C14 Final	<i>Source:</i> Lowland river, Agricultural input, Sewage effluent input, Pesticides <i>Treatment:</i> Actiflo, RGF, Ozonation, GAC, Chlorination <i>Chemicals:</i> Polyelectrolyte (FloPam AN905 SEP)	M1949744	< 0.9
C15 Final	<i>Source:</i> Lowland river, Agricultural input, Algae, Pesticides <i>Treatment:</i> Pre-ozonation (2-3 mg/l), Coagulation, DAF, RGF, Ozonation (?), GAC, Chlorination <i>Chemicals:</i> Aluminium coagulant, PolyDADMAC (1-2 mg/l)	M1949745	Cancelled
C16 Final	<i>Source:</i> Upland reservoir, High colour/TOC <i>Treatment:</i> Coagulation, RGF1, RGF2 (Mn removal), Chlorination <i>Chemicals:</i> Ferric coagulant, Polyacrylamide	M1949767	< 0.9
C17 Final	<i>Source:</i> River, High colour/TOC, Pesticides <i>Treatment:</i> Coagulation, RGF, GAC, Chloramination <i>Chemicals:</i> Aluminium coagulant, Polyacrylamide	M1949768	< 0.9
Utility D			
D16 Final	<i>Source:</i> Reservoir, Ammonia, Pesticides <i>Treatment:</i> Coagulation, RGF, GAC, Chlorination, Dechlorination (NaHSO ₄) <i>Chemicals:</i> Ferric coagulant, Starch-based polyelectrolyte (Wisprofloc)	M1949746	< 0.9

Works Ref.	Works Description	Sample Code	NDMA (ng/l)
D17 Final	<i>Source:</i> River, Reservoir, Ammonia, Nitrate, Pesticides <i>Treatment:</i> Coagulation, RGF, Ozonation, GAC, Chlorination, Dechlorination (SO ₂) <i>Chemicals:</i> Ferric coagulant, Polyacrylamide (LT22S)	M1949747	< 0.9
D18/1 Final	<i>Source:</i> Reservoir, Ammonia, Nitrate, Pesticides <i>Treatment:</i> Coagulation, RGF, GAC, Chlorination, Dechlorination (SO ₂) <i>Chemicals:</i> Ferric coagulant, Polyacrylamide (LT22), Epi-DMA	M1949748	2.0
D18/2 Final (Duplicate)	<i>Source:</i> Reservoir, Ammonia, Nitrate, Pesticides <i>Treatment:</i> Coagulation, RGF, GAC, Chlorination, Dechlorination (SO ₂) <i>Chemicals:</i> Ferric coagulant, Polyacrylamide (LT22), Epi-DMA	M1949749	1.9
D18/3 Pre Epi-DMA	<i>Source:</i> Reservoir, Ammonia, Nitrate, Pesticides <i>Treatment:</i> Coagulation, RGF, GAC, Chlorination, Dechlorination (SO ₂) <i>Chemicals:</i> Ferric coagulant, Polyacrylamide (LT22), Epi-DMA	M1949752	2.1
Utility E			
E19 Final	<i>Source:</i> Upland reservoir, High colour/TOC <i>Treatment:</i> Coagulation, Direct RGF, SSF, Ozonation (infrequent), Chlorination <i>Chemicals:</i> Aluminium coagulant, Polyacrylamide, PolyDADMAC	M1949750	< 0.9
E20 Final	<i>Source:</i> Upland reservoir, High colour/TOC <i>Treatment:</i> Coagulation, RGF1, RGF2 (Mn removal), Chlorination <i>Chemicals:</i> Ferric coagulant, Polyacrylamide	M1949751	< 0.9
E21 Final	<i>Source:</i> Upland reservoir, Agricultural input <i>Treatment:</i> Coagulation, RGF, Chlorination <i>Chemicals:</i> Aluminium coagulant, Polyacrylamide, polyDADMAC	M1949753	< 0.9
E22 Final	<i>Source:</i> Upland river, Agricultural input, Sewage effluent input (limited), Ammonia, Pesticides <i>Treatment:</i> Coagulation, RGF1, RGF2 (Mn removal), GAC, Chlorination <i>Chemicals:</i> Aluminium coagulant, Polyacrylamide (LT22S)	M1949755	< 0.9
E23 Final	<i>Source:</i> E19, E22 <i>Treatment:</i> Coagulation, RGF, Chlorination <i>Chemicals:</i> PolyDADMAC (LT35), Polyacrylamide (A120)	M1949757	< 0.9

Notes:

1. NS = Not sampled.
2. C11/1 = Final water main No.1; C11/2 = Final water main No.2; C11/3 = Chlorinated water, pre-ammonia.
3. C12/1 = Final water; C12/2 = PolyDADMAC dosed, pre-chlorine; C12/3 = Pre-polyDADMAC.
4. C15 extensively refurbished between Surveys 1 and 2.
5. C15 analysis cancelled.
6. D18/1 = Final water; D18/2 = Final water (duplicate); D18/3 = Pre-Epi-DMA.
7. Works E23 retreats water from Works E19 and E22 after storage in open reservoirs.

C3.3 Discussion

NDMA was found at concentrations between 1.3 - 3.2 ng/l in drinking water from three of the 24 treatment works sampled, Works C11, C12 and D18; the same three works as in Survey 1. The measured concentrations are below current concentrations of concern in North America and substantially lower than the likely WHO guideline value. NDMA was not found above the limit of detection (0.9 ng/l) in the samples from the two 'control' works nor in samples from Utilities A, B or E.

The highest concentration of NDMA was again found in samples from Works C11. This works treats a highly-coloured upland water by coagulation (ferric coagulant), filtration and chloramination. A concentration of 3.2 ng/l was found in a chlorinated sample taken before ammoniation. Chloraminated final water was sampled from Main No.1 (1.3 ng/l) and Main No.2 (2.5 ng/l). The two mains were dosed independently with ammonium sulphate, proportional to the chlorine concentration measured following the 'Final Tank'.

NDMA (1.5 ng/l) was found in the sample of final water taken from a second works in Utility C, Works C12. This works treats a highly-coloured upland water using the Sirofloc process, filtration and chlorination. Treatment includes dosing of polyDADMAC. An NDMA

concentration of 1.7 ng/l was found in water sampled prior to polyDADMAC dosing but NDMA was not detected in a sample of polyDADMAC-dosed water prior to chlorination.

NDMA (1.9-2.0 ng/l) was found in the duplicate samples of final water taken from Utility D, Works D18. This works treats a reservoir water by coagulation (ferric coagulant), filtration, GAC adsorption and chlorination. Treatment includes dosing of Epi-DMA. An NDMA concentration of 2.1 ng/l was found in water sampled prior to dosing Epi-DMA.

Two of the three works where NDMA was detected treat highly-coloured upland waters with both works including additional factors: chloramination at Works C11 and dosing of PolyDADMAC at Works C12. Works D18 does not treat highly-coloured water but notably includes dosing of Epi-DMA in water treatment.

Samples of raw water were analysed for selected parameters at the three treatment works where NDMA had been detected previously (Works C11, C12 and D18) and at Works C17, a works treating a highly-coloured river water by chloramination (see Table C3).

Table C3 Raw water analysis from selected works (Survey 2)

Works ref.	pH	Turbidity (NTU)	TOC (mg/l C)	True UV ₂₅₄ (AU/m)	True colour (°H)	Ammonia (mg/l NH ₃)	Nitrite (mg/l NO ₂)	Nitrate (mg/l NO ₃)
C11	6.46	8.7	6.34	32.7	44.1	< 0.021	0.008	1.87
C12	6.40	2.8	5.82	30.9	44.1	0.025	0.011	2.85
C17	6.90	12.0	6.97	31.0	40.2	< 0.021	0.029	5.57
D18	7.55	1.0	4.79	12.2	7.8	< 0.021	0.014	30.1

Note:

1. NH₃, NO₂ and NO₃ measured as N.

Although the organic content of the raw waters from the three works from Utility C was similar, NDMA was detected only at Works C11 and C12. NDMA was not detected at Works C17 even though the final water was chloraminated. NDMA was again detected at Works D18 even though the organic content of the raw water was significantly lower than at the Utility C works. Works D18 nitrate concentration was substantially higher than at the Utility C works, although its nitrite concentration - a key factor in NDMA formation - was generally comparable.

High colour/TOC is indicated at several other works where NDMA was not detected. However, this indication is subjective and further quantitative data will be sought to allow comparison between these works and Works C11 and C12.

Chloramination is utilised at several works from Utility A where NDMA was not detected.

Use of polyDADMAC and Epi-DMA appears not to be widespread. NDMA was detected at two of the three works utilising these polyelectrolytes: Works C12 (polyDADMAC) and Works D18 (Epi-DMA).

The measured concentrations of NDMA are below the 9 ng/l standard included in legislation introduced by the Ministry of Environment (MoE) in Ontario, Canada, below the notification

level of 10 ng/l established by the California Department of Health Services (CDHS) and substantially below the WHO guideline value of 100 ng/l.

C3.4 Conclusions

- Twenty-two works were sampled because their raw water source and/or treatment included factors associated with the formation of NDMA. NDMA was detected at three of these works - Works C11, C12 and D18; the same three works as in Survey 1.
- NDMA was not detected at the two 'control' works.
- Where NDMA was detected, possible contributory factors included highly-coloured upland waters, chloramination and use of polyDADMAC or Epi-DMA. However, these factors were also present at works where NDMA was not detected.
- Limited 'intra-works' sampling at Works C11, C12 and D18 showed NDMA formation prior to chloramination (at Works C11) and dosing of polyDADMAC (Works C12) and Epi-DMA (Work D18).
- The measured concentrations of NDMA (1.3-3.2 ng/l) were lower than current concentrations of concern in North America and substantially lower than the WHO guideline value.

C4 SURVEY 3 - JUNE 2007

The third survey sampled 25 works, including at 13 works from four 'new' utilities (F, G, H and J) and an additional works from Utility D (Works D19). Works that had been sampled in both Surveys 1 and 2 where NDMA had not been detected were excluded from sampling. Thus all works at Utilities A and B were excluded, as were Works C13, C14, D16 and D17.

Seven works (Works D19, F1, G1, G2, H1, H2 and H3) had been included in a separate survey carried out by Bayer CropScience AG because of concern about the formation of NDMA as a result of ozonation of dimethylsulfamide, a metabolite of the fungicide tolyfluamid.

C4.1 Sampling

The third sampling survey was carried out during week beginning 11 June 2007.

Samples of final water only were taken from 22 treatment works. More comprehensive sampling - including raw water, 'intra-works' samples and samples from distribution - was carried out at the three works where NDMA had been detected previously: Works C11, C12 and D18.

Samples from Utilities D, E, F, G and J were taken by WRc personnel. Samples from Utility C were taken by WRc personnel (Samples C11 (excluding distribution), C12 (excluding distribution) and C17) and Utility C Samplers (Samples C11 (Distribution), C12 (Distribution), C15 and C16). Samples from Utility H were taken by Utility H Samplers.

Samples from Utilities D, E, F and G were collected and returned to WRc in ice-packed cool boxes on the day of sampling. Samples from Utility C were collected and stored in ice-packed

cool boxes and returned to WRc within approximately 12 - 36 hours of sampling. Samples from Utility J were returned to WRc in ice-packed cool boxes within approximately 36 hours of sampling. At WRc, samples were stored in the dark at 4°C until transported to the analysing laboratory in ice-packed cool boxes within approximately 48 hours of sampling. Samples from Utility H were collected and stored in ice-packed cool boxes and returned to a central laboratory for refrigerated storage until collected by WRc within 24-72 hours of sampling. WRc then collected and transported the samples in ice-packed cool boxes directly to the analysing laboratory.

Sample C12 (Distribution) was collected and stored in an ice-packed cool box and returned to a central laboratory for refrigerated storage until dispatched in an ice-packed cool box to WRc by courier approximately 96 hours after sampling. Upon arrival at WRc, the temperature of this sample had increased to 10°C. This sample was then transported to the analysing laboratory in an ice-packed cool box some 120 hours after sampling.

C4.2 Results

Results from the third sampling survey are shown in Table C4.

Table C4 Results of Sampling Survey 3 (June 2007)

Works Ref.	Works Description	Sample Code	NDMA (ng/l)
Utility C			
C11 Raw	<i>Source:</i> Upland, High colour/TOC	M2061889	< 0.9
C11 Postclar	<i>Treatment:</i> Coagulation, Pre-chlorination (~1 mg/l), RGF,	M2061891	10.0
C11 RGFfilt	Chloramination	M2061892	9.9
C11 Preamm	<i>Chemicals:</i> Ferric coagulant, Polyacrylamide	M2061893	5.2
C11 Final		M2061894	5.1
C11 Distribution		M2061890	6.8
C12 Raw	<i>Source:</i> Upland, High colour/TOC	M2061896	< 0.9
C12 Postpoly	<i>Treatment:</i> Sirofloc, Pre-chlorination (~1 mg/l), RGF, Chlorination	M2061899	2.9
C12 RGFfilt	<i>Chemicals:</i> PolyDADMAC	M2061900	2.9
C12 Final		M2061901	2.8
C12 Distribution		M2061931	2.7
C15 Final	<i>Source:</i> Lowland river, Agricultural input, Algae, Pesticides <i>Treatment:</i> Pre-ozonation (2-3 mg/l), Coagulation, DAF, RGF, Ozonation (?), GAC, Chlorination <i>Chemicals:</i> Aluminium coagulant, PolyDADMAC (1-2 mg/l)	M2061903	< 0.9
C16 Final	<i>Source:</i> Upland reservoir, High colour/TOC <i>Treatment:</i> Coagulation, RGF1, RGF2 (Mn removal), Chlorination <i>Chemicals:</i> Ferric coagulant, Polyacrylamide	M2061904	< 0.9
C17 Final	<i>Source:</i> River, High colour/TOC, Pesticides <i>Treatment:</i> Coagulation, RGF, GAC, Chloramination <i>Chemicals:</i> Aluminium coagulant, Polyacrylamide	M2061905	< 0.9
Utility D			
D18 Raw	<i>Source:</i> Reservoir, Ammonia, Nitrate, Pesticides	M2061906	< 0.9
D18 Postclar	<i>Treatment:</i> Coagulation, RGF, GAC, Chlorination, Dechlorination (SO ₂)	M2061907	3.7
D18 PostGAC	<i>Chemicals:</i> Ferric coagulant, Polyacrylamide (LT22), Epi-DMA	M2061908	< 0.9
D18 Final		M2061909	1.1
D18 Distribution		M2061910	1.1
D19 Final	<i>Source:</i> Lowland river <i>Treatment:</i> Sedimentation, Pre-ozonation, Coagulation, RGF, Ozonation, GAC, Chlorination, Dechlorination (SO ₂) <i>Chemicals:</i> Aluminium or Ferric coagulant	M2061911	< 0.9

Works Ref.	Works Description	Sample Code	NDMA (ng/l)
Utility E			
E19 Final	<i>Source:</i> Upland reservoir, High colour/TOC <i>Treatment:</i> Coagulation, Direct RGF, SSF, Ozonation (not dosed), Chlorination <i>Chemicals:</i> Aluminium coagulant, Polyacrylamide, PolyDADMAC (0.5 mg/l)	M2061912	< 0.9
E20 Final	<i>Source:</i> Upland reservoir, High colour/TOC <i>Treatment:</i> Coagulation, RGF1, RGF2 (Mn removal), Chlorination <i>Chemicals:</i> Ferric coagulant, Polyacrylamide	M2061913	< 0.9
E21 Final	<i>Source:</i> Upland reservoir, Agricultural input <i>Treatment:</i> Coagulation, RGF, Chlorination <i>Chemicals:</i> Aluminium coagulant, Polyacrylamide, polyDADMAC (not dosed)	M2061914	< 0.9
E22 Final	<i>Source:</i> Upland river, Agricultural input, Sewage effluent input (limited), Ammonia, Pesticides <i>Treatment:</i> Coagulation, RGF1, RGF2 (Mn removal), GAC, Chlorination <i>Chemicals:</i> Aluminium coagulant, Polyacrylamide (LT22S)	M2061915	< 0.9
E23 Final	<i>Source:</i> E19, E22 <i>Treatment:</i> Coagulation, RGF, Chlorination <i>Chemicals:</i> PolyDADMAC (LT35 0.5 mg/l), Polyacrylamide (A120)	M2061916	< 0.9
Utility F			
F1 Final	<i>Source:</i> Lowland reservoir, Agricultural input, Sewage effluent input, Pesticides <i>Treatment:</i> Coagulation, RGF, Backwash recycle, Ozonation (2-3 mg/l), GAC, Chlorination <i>Chemicals:</i> Ferric coagulant	M2061917	< 0.9
Utility G			
G1 Final	<i>Source:</i> Lowland river (with bankside storage), Agricultural input, Sewage effluent input, Algae, Ammonia, Nitrate, Pesticides <i>Treatment:</i> Pre-ozonation (1.5 mg/l), Coagulation, RGF, Backwash recycle, Ozonation (0.2 mg/l residual), GAC, Chlorination <i>Chemicals:</i> Aluminium coagulant, Polyacrylamide	M2061918	< 0.9
G2 Final	<i>Source:</i> Lowland river / Groundwater, Agricultural input, Sewage effluent input, High colour/TOC, Pesticides <i>Treatment:</i> Coagulation, RGF1, RGF2 (Mn removal), Backwash recycle, Ozonation (0.6-1.0 mg/l), GAC, Chlorination <i>Chemicals:</i> Aluminium coagulant, Polyacrylamide	M2061919	< 0.9
Utility H			
H1 Final	<i>Source:</i> Lowland river, Agricultural input, Sewage effluent input, Algae, Ammonia, Nitrate, Pesticides <i>Treatment:</i> Pre-ozonation (0.7-1.0 mg/l), Coagulation, RGF, Ozonation (1.8-1.2 mg/l), GAC, Chlorination <i>Chemicals:</i> Ferric coagulant, Polyacrylamide	M2061920	< 0.9
H2 Final	<i>Source:</i> Lowland river, Agricultural input, Sewage effluent input, Algae, Ammonia, Nitrate, Pesticides <i>Treatment:</i> Pre-ozonation (0.7-1.0 mg/l), Coagulation, RGF, Ozonation (1.8-1.2 mg/l), GAC, Chlorination <i>Chemicals:</i> Ferric coagulant, Polyacrylamide	M2061921	< 0.9
H3 Final	<i>Source:</i> Lowland river, Agricultural input, Sewage effluent input, Algae, Ammonia, Nitrate, Pesticides <i>Treatment:</i> Pre-ozonation (0.8-1.5 mg/l), Coagulation, RGF, Ozonation (0.8-1.2 mg/l), GAC, Chlorination (contact tank), Chloramination (distribution) <i>Chemicals:</i> Ferric coagulant	M2061922	< 0.9
H4 Final	<i>Source:</i> Lowland river, Agricultural input, Sewage effluent input, Algae, Ammonia, Nitrate, Pesticides <i>Treatment:</i> Pre-ozonation (0.8-1.2 mg/l), Coagulation, RGF, Ozonation (0.3-0.8 mg/l), GAC, Chlorination (contact tank), Chloramination (distribution) <i>Chemicals:</i> Ferric coagulant, Polyacrylamide, PolyDADMAC	M2061923	< 0.9
H5 Final	<i>Source:</i> Lowland reservoir, Agricultural input, Sewage effluent input, Algae, Ammonia, Pesticides <i>Treatment:</i> Pre-ozonation (0.7-1.5 mg/l), Coagulation, RGF, Ozonation (1.0-1.5 mg/l), GAC, Chlorination (contact tank), Chloramination (distribution) <i>Chemicals:</i> Ferric coagulant, Polyacrylamide	M2061924	< 0.9

Works Ref.	Works Description	Sample Code	NDMA (ng/l)
H6 Final	<i>Source:</i> Lowland river, Lowland reservoir, Agricultural input, Sewage effluent input, Algae, Ammonia, Pesticides <i>Treatment:</i> Coagulation, RGF, Backwash recycle, Ozonation (1.3-1.7 mg/l), GAC, Chlorination (contact tank), Chloramination (distribution) <i>Chemicals:</i> Ferric coagulant, Polyacrylamide	M2061925	< 0.9
H7 Final	<i>Source:</i> Lowland reservoir, Agricultural input, Algae, Ammonia, Pesticides <i>Treatment:</i> Slow sand filtration, RGF, GAC, Chlorination (contact tank), Chloramination (distribution) <i>Chemicals:</i> None	M2061926	< 0.9
Utility J			
J1 Final	<i>Source:</i> Lowland river/groundwater, Agricultural input, Sewage effluent input, High colour/TOC, Algae, Ammonia, Nitrate, Pesticides <i>Treatment:</i> Coagulation, RGF, Chlorination <i>Chemicals:</i> Aluminium coagulant (130 mg/l), Polyacrylamide (0.11 mg/l)	M2061927	< 0.9
J2 Final	<i>Source:</i> Upland reservoir <i>Treatment:</i> Coagulation, RGF, Ozonation (5 mg/l), GAC, Chlorination <i>Chemicals:</i>	M2061928	< 0.9
J3 Final	<i>Source:</i> Lowland reservoir, High colour/TOC, Algae <i>Treatment:</i> Coagulation, RGF, GAC, Chlorination, Chloramination <i>Chemicals:</i> Aluminium coagulant (6 mg/l)	M2061929	< 0.9

Notes:

1. C11 and C12 recycle samples not taken; C11 Pre-poly sample not taken.
2. C12 RGFilt is (chlorinated) filtrate from Filter No.1 - blended sample not taken.
3. C11 raw water was from the Nidd aqueduct.
4. C15 extensively refurbished between Surveys 1 and 2.
5. Works E23 retreats water from Works E19 and E22 after storage in open reservoirs.
6. H1 River treated water blended with groundwater source (ion exchange nitrate removal).
7. H2 Alternative groundwater available (disinfection only).

C4.3 Discussion

NDMA was found at concentrations between 1.1 - 10.0 ng/l in samples from three of the 25 treatment works sampled (Works C11, C12 and D18); the same three works as in Surveys 1 and 2. The measured concentrations are generally below current concentrations of concern in North America and substantially lower than the WHO guideline value. NDMA was not found above the limit of detection (0.9 ng/l) in samples from Utilities E, F, G, H or J or at other works in Utilities C and D.

The highest concentrations of NDMA (9.9 - 10.0 ng/l) were found in the post-clarified and RGF filtered samples from Works C11. This works treats a highly-coloured upland water by coagulation (ferric coagulant), filtration and chloramination. The measured concentration in distribution (6.8 ng/l) was not significantly different to that found in the final water leaving the works (5.1 ng/l).

At Works C12, NDMA was found at consistent concentrations (2.7 - 2.9 ng/l) in samples of water taken following polyDADMAC dosing and from distribution. This works treats a highly-coloured upland water using the Sirofloc process, filtration and chlorination.

At Works D18, the highest concentration of NDMA (3.7 ng/l) was found in the post-clarified sample. Downstream concentrations, including from distribution, were lower (up to 1.1 ng/l). This works treats a reservoir water by coagulation (ferric coagulant), filtration, GAC adsorption and chlorination. Treatment includes dosing of Epi-DMA.

At each of the works sampled intensively, NDMA was detected throughout water treatment and in distribution but not in the raw water. At Works C11, NDMA was first detected following clarification (i.e. after dosing with ferric coagulant and polyacrylamide polyelectrolyte); at

Works C12, NDMA was first detected following clarification (i.e. after dosing with magnetite and polyDADMAC polyelectrolyte); and at Works D18, NDMA was first detected following clarification (i.e. after dosing with ferric coagulant, polyacrylamide polyelectrolyte and Epi-DMA). It was noted that backwash wastewaters were recycled to water treatment at both Works C11 and C12, although the concentration of any NDMA in the wastewater would be greatly diluted by the influent raw water; backwash wastewater was not recycled at Works D18.

Samples of raw water were analysed for selected parameters at the three treatment works where NDMA had been detected previously (Works C11, C12 and D18) and at Works C17, a works treating a highly-coloured river water by chloramination (see Table C5).

Table C5 Raw water analysis from selected works (Survey 3)

Works ref.	pH	Turbidity (NTU)	TOC (mg/l C)	True UV ₂₅₄ (AU/m)	True colour (°H)	Ammonia (mg/l NH ₃)	Nitrite (mg/l NO ₂)	Nitrate (mg/l NO ₃)
C11	6.73	4.2	3.00	13.3	13.7	0.018	0.093	5.67
C12	5.95	2.0	4.89	28.8	40.2	0.010	0.012	3.13
C17	6.18	2.9	5.12	29.0	37.3	0.009	0.013	1.68
D18	7.54	1.9	5.22	14.8	11.8	0.100	0.329	32.8

Note:

1. NH₃, NO₂ and NO₃ measured as N.

Although the raw water quality to the three works from Utility C was similar in terms of overall organic content, as indicated by TOC, UV₂₅₄ and colour, NDMA was detected only at Works C11 and C12. NDMA was not detected at Works C17 even though the final water was chloraminated. NDMA was again detected at Works D18. The raw water to D18 was comparable to the Utility C works in terms of TOC, but lower in organics as indicated by UV₂₅₄ and colour. Nitrite - a key factor in NDMA formation - and nitrate were notably higher at Works D18 at 0.33 mg/l and 32.8 mg/l, respectively.

C4.4 Conclusions

- Twenty-five works were sampled because their raw water source and/or treatment included factors associated with the formation of NDMA. NDMA was detected at three of these works, Works C11, C12 and D18; the same three works as in Surveys 1 and 2.
- Where NDMA was detected, possible contributory factors included highly-coloured upland waters, chloramination and use of polyDADMAC or Epi-DMA. However, these factors were also present at works where NDMA was not detected.
- At each of the works sampled intensively - Works C11, C12, D18 - NDMA was detected throughout water treatment and in distribution but not in the raw water. Backwash wastewaters were recycled to water treatment at both C11 and C12, although the concentration of any NDMA in the wastewater would be greatly diluted by the influent raw water; backwash wastewater was not recycled at D18.

- The measured concentrations of NDMA (1.1-10.0 ng/l) were substantially lower than the WHO guideline value. The highest NDMA concentration (10.0 ng/l) observed was comparable to the concentrations of concern in North America. However, NDMA concentrations in all treated drinking waters (1.1 - 5.1 ng/l) were lower than the concentrations of concern in North America.

C5 SURVEY 4 - SEPTEMBER 2007

The fourth survey sampled 18 works, including one works from a 'new' utility (Works K1). Works that had been sampled in successive surveys where NDMA had not been detected were excluded from sampling. Thus all works in Utility E were excluded, as were Works C15, C16 and C17.

Seven works (Works D19, F1, G1, G2, H1, H2 and H3) included in a separate survey carried out by Bayer CropScience AG because of concern about the formation of NDMA as a result of ozonation of dimethylsulfamide, a metabolite of the fungicide tolyfluanid, were sampled for a second time.

C5.1 Sampling

The fourth sampling survey was carried out during week beginning 24 September 2007.

Samples of final water only were taken from 15 treatment works. Intensive sampling - including raw water and samples from treatment and distribution - was carried out at the three works where NDMA had been detected previously, i.e. Works C11, C12 and D18.

Samples from Utilities D, F, G, J and K were taken by WRc personnel. Samples from Utility C were taken by WRc personnel with the exception of distribution samples that were taken by Utility C Samplers. Samples from Utility H were taken by Utility H Samplers.

Samples from Utilities C (with the exception of Sample C12 (Distribution)) D, F, G, J and K were collected and returned to WRc in ice-packed cool boxes on the day of sampling. Sample C12 (Distribution) was collected and stored in an ice-packed cool box and returned to a central laboratory for refrigerated storage until collected and returned to WRc some 120 hours after sampling. At WRc, samples were stored in the dark at 4°C until transported to the analysing laboratory in ice-packed cool boxes, mostly within 24 - 72 hours of sampling. Samples from Utility H were collected and stored in ice-packed cool boxes and returned to a central laboratory for refrigerated storage until collected by WRc within 24-96 hours of sampling. WRc then collected and transported the samples in ice-packed cool boxes directly to the analysing laboratory.

C5.2 Results

Results from the fourth sampling survey are shown in Table C6.

Table C6 Results of Sampling Survey 4 (September 2007)

Works Ref.	Works Description	Sample Code	NDMA (ng/l)
Utility C			
C11 Raw	<i>Source:</i> Upland, High colour/TOC	M2230627	< 0.9
C11 Rec	<i>Treatment:</i> Coagulation, Pre-chlorination (~1 mg/l), RGF,	M2230628	3.6
C11 Postclar	Chloramination	M2230629	3.9
C11 RGFfilt	<i>Chemicals:</i> Ferric coagulant, Polyacrylamide	M2230630	3.7
C11 Preamm		M2230631	4.2
C11 Final		M2230632	4.3
C11 Distribution		M2230633	1.5
C12 Raw	<i>Source:</i> Upland, High colour/TOC	M2230634	< 0.9
C12 Rec	<i>Treatment:</i> Sirofloc, Pre-chlorination (~1 mg/l), RGF, Chlorination	M2230635	39.1
C12 Postpoly	<i>Chemicals:</i> PolyDADMAC	M2230637	2.3
C12 RGFfilt		M2230638	3.1
C12 Final		M2230639	2.5
C12 Distribution		M2230640	2.2
Utility D			
D18 Raw	<i>Source:</i> Reservoir, Ammonia, Nitrate, Pesticides	M2230644	< 0.9
D18 Postclar	<i>Treatment:</i> Coagulation, RGF, GAC, Chlorination, Dechlorination (SO ₂)	M2230645	3.4
D18 PostGAC	<i>Chemicals:</i> Ferric coagulant, Polyacrylamide (LT22), Epi-DMA	M2230646	< 0.9
D18 Final		M2230647	1.0
D18 Distribution		M2230649	1.1
D19 Final	<i>Source:</i> Lowland river <i>Treatment:</i> Sedimentation, Pre-ozonation, Coagulation, RGF, Ozonation, GAC, Chlorination, Dechlorination (SO ₂) <i>Chemicals:</i> Aluminium or Ferric coagulant	M2230650	< 0.9
Utility F			
F1 Final	<i>Source:</i> Lowland reservoir, Agricultural input, Sewage effluent input, Pesticides <i>Treatment:</i> Coagulation, RGF, Backwash recycle, Ozonation (2-3 mg/l), GAC, Chlorination <i>Chemicals:</i> Ferric coagulant	M2230656	< 0.9
Utility G			
G1 Final	<i>Source:</i> Lowland river (with bankside storage), Agricultural input, Sewage effluent input, Algae, Ammonia, Nitrate, Pesticides <i>Treatment:</i> Pre-ozonation (1.5 mg/l), Coagulation, RGF, Backwash recycle, Ozonation (0.2 mg/l residual), GAC, Chlorination <i>Chemicals:</i> Aluminium coagulant, Polyacrylamide	M2230657	< 0.9
G2 Final	<i>Source:</i> Lowland river / Groundwater, Agricultural input, Sewage effluent input, High colour/TOC, Pesticides <i>Treatment:</i> Coagulation, RGF1, RGF2 (Mn removal), Backwash recycle, Ozonation (0.6-1.0 mg/l), GAC, Chlorination <i>Chemicals:</i> Aluminium coagulant, Polyacrylamide	M2230658	< 0.9
Utility H			
H1 Final	<i>Source:</i> Lowland river, Agricultural input, Sewage effluent input, Algae, Ammonia, Nitrate, Pesticides <i>Treatment:</i> Pre-ozonation (0.7-1.0 mg/l), Coagulation, RGF, Ozonation (1.8-1.2 mg/l), GAC, Chlorination <i>Chemicals:</i> Ferric coagulant, Polyacrylamide	M2230659	< 0.9
H2 Final	<i>Source:</i> Lowland river, Agricultural input, Sewage effluent input, Algae, Ammonia, Nitrate, Pesticides <i>Treatment:</i> Pre-ozonation (0.7-1.0 mg/l), Coagulation, RGF, Ozonation (1.8-1.2 mg/l), GAC, Chlorination <i>Chemicals:</i> Ferric coagulant, Polyacrylamide	M2230660	< 0.9
H3 Final	<i>Source:</i> Lowland river, Agricultural input, Sewage effluent input, Algae, Ammonia, Nitrate, Pesticides <i>Treatment:</i> Pre-ozonation (0.8-1.5 mg/l), Coagulation, RGF, Ozonation (0.8-1.2 mg/l), GAC, Chlorination (contact tank), Chloramination (distribution) <i>Chemicals:</i> Ferric coagulant	M2230661	< 0.9

Works Ref.	Works Description	Sample Code	NDMA (ng/l)
H4 Final	<i>Source:</i> Lowland river, Agricultural input, Sewage effluent input, Algae, Ammonia, Nitrate, Pesticides <i>Treatment:</i> Pre-ozonation (0.8-1.2 mg/l), Coagulation, RGF, Ozonation (0.3-0.8 mg/l), GAC, Chlorination (contact tank), Chloramination (distribution) <i>Chemicals:</i> Ferric coagulant, Polyacrylamide, PolyDADMAC	M2230662	< 0.9
H5 Final	<i>Source:</i> Lowland reservoir, Agricultural input, Sewage effluent input, Algae, Ammonia, Pesticides <i>Treatment:</i> Pre-ozonation (0.7-1.5 mg/l), Coagulation, RGF, Ozonation (1.0-1.5 mg/l), GAC, Chlorination (contact tank), Chloramination (distribution) <i>Chemicals:</i> Ferric coagulant, Polyacrylamide	M2230663	< 0.9
H6 Final	<i>Source:</i> Lowland river, Lowland reservoir, Agricultural input, Sewage effluent input, Algae, Ammonia, Pesticides <i>Treatment:</i> Coagulation, RGF, Backwash recycle, Ozonation (1.3-1.7 mg/l), GAC, Chlorination (contact tank), Chloramination (distribution) <i>Chemicals:</i> Ferric coagulant, Polyacrylamide	M2230664	< 0.9
H7 Final	<i>Source:</i> Lowland reservoir, Agricultural input, Algae, Ammonia, Pesticides <i>Treatment:</i> Slow sand filtration, RGF, GAC, Chlorination (contact tank), Chloramination (distribution) <i>Chemicals:</i> None	M2230665	< 0.9
Utility J			
J1 Final	<i>Source:</i> Lowland river/groundwater, Agricultural input, Sewage effluent input, High colour/TOC, Algae, Ammonia, Nitrate, Pesticides <i>Treatment:</i> Coagulation, RGF, Chlorination <i>Chemicals:</i> Aluminium coagulant (130 mg/l), Polyacrylamide (0.11 mg/l)	M2230666	< 0.9
J2 Final	<i>Source:</i> Upland reservoir <i>Treatment:</i> Coagulation, RGF, Ozonation (5 mg/l), GAC, Chlorination <i>Chemicals:</i>	M2230667	< 0.9
J3 Final	<i>Source:</i> Lowland reservoir, High colour/TOC, Algae <i>Treatment:</i> Coagulation, RGF, GAC, Chlorination, Chloramination <i>Chemicals:</i> Aluminium coagulant (6 mg/l)	M2230668	< 0.9
Utility K			
K1 Final	<i>Source:</i> Lowland reservoir, Algae, Pesticides <i>Treatment:</i> Pre-chlorination, Coagulation, RGF, Backwash & waste liquor recycle, GAC, Aeration, Chlorination (contact tank), Chloramination (distribution) <i>Chemicals:</i> Aluminium coagulant (18 mg/l Al ₂ O ₃), Starch-based polyelectrolyte (Wisprofloc - 2 mg/l; also used in sludge treatment)	M2230669	< 0.9

C5.3 Discussion

NDMA was found at concentrations between 1.0 - 39.1 ng/l in samples from three of the 18 treatment works sampled, Works C11, C12 and D18; the same three works as in Surveys 1, 2 and 3. The concentration found in recycled supernatant from Works C12 (39.1 ng/l) was an order of magnitude greater than other measurements from this (and the other) works. NDMA was not detected in samples from Works D19 or from Utilities E, F, G, H, J or K.

With the exception of the concentration found in the recycled supernatant, concentrations were below current concentrations of concern in North America and substantially lower than the WHO guideline value.

At Works C11, NDMA was found at concentrations between 1.5 - 4.3 ng/l. This works treats a highly-coloured upland water by coagulation (ferric coagulant), filtration and chloramination. Generally the measurements within treatment were consistent (3.6 - 4.3 ng/l), with a lower concentration found in distribution (1.5 ng/l). Recycled supernatant contained 3.6 ng/l - too

small to account for downstream concentrations of NDMA. As in Survey 3, NDMA was not detected in the raw water.

At Works C12, NDMA was found at consistent concentrations (2.2 - 3.1 ng/l) in samples of water taken following polyDADMAC dosing and from distribution. Supernatant recycled to water treatment contained 39.1 ng/l - sufficient to account for downstream concentrations of NDMA. This works treats a highly-coloured upland water using the Sirofloc process, filtration and chlorination. As in Survey 3, NDMA was not detected in the raw water.

At Works D18, the highest concentration of NDMA (3.4 ng/l) was found in the post-clarified sample. Downstream samples, following GAC adsorption, measured <0.9 - 1.1 ng/l. This works treats a reservoir water by coagulation (ferric coagulant), filtration, GAC adsorption and chlorination. Treatment includes dosing of Epi-DMA. As in the previous survey, NDMA was not detected in the raw water.

At each of the works sampled intensively, NDMA was detected throughout water treatment and in distribution but not in the raw water; a similar observation was made for Survey 3.

- At Works C11, NDMA was detected following clarification (i.e. after dosing with ferric coagulant and polyacrylamide polyelectrolyte); NDMA was found in the thickener supernatant (3.6 ng/l) but even if recycled at 5 - 10% of the raw water flow, this would not account for the NDMA detected in water treatment.
- At Works C12, NDMA was detected following clarification (i.e. after supernatant recycle and dosing of magnetite, and polyDADMAC polyelectrolyte); NDMA was found in the recycled supernatant (39.1 ng/l) which if recycled at 5 - 10% of the raw water flow could account for the NDMA detected in water treatment.
- At Works D18, NDMA was detected following clarification (i.e. after dosing with ferric coagulant, polyacrylamide polyelectrolyte and Epi-DMA); sludge/backwash supernatant is not recycled at this works.

Samples of raw water were analysed for selected parameters at these three treatment works (see Table C7).

Table C7 Raw water analysis from selected works (Survey 4)

Works ref.	pH	Turbidity (NTU)	TOC (mg/l C)	True UV254 (AU/m)	True colour (°H)	Ammonia (mg/l NH ₃)	Nitrite (mg/l NO ₂)	Nitrate (mg/l NO ₃)
C11	6.71	1.9	12.7	62.8	90.2	< 0.3	< 0.1	<0.3
C12	6.56	1.5	10.4	55.1	89.2	< 0.3	< 0.1	0.4
D18	7.79	1.5	6.8	15.3	12.7	< 0.3	< 0.1	7.0

Note:

1. NH₃, NO₂ and NO₃ measured as N.

The raw water quality to the two works from Utility C was similar in terms of overall organic content as indicated by TOC, UV₂₅₄ and colour, and the nitrogen parameters, NH₃, NO₂ and NO₃. The raw water to Works D18 was lower in organics than Works C11 and C12, but

notably higher in nitrate at 7.0 mg/l. Nitrite - a key factor in NDMA formation - was not detected (< 0.1 mg/l) at any of the works.

C5.4 Conclusions

- Eighteen works were sampled because their raw water source and/or treatment included factors associated with the formation of NDMA. NDMA was detected at three of these works - Works C11, C12 and D18; the same three works as in Surveys 1, 2 and 3.
- Where NDMA was detected, possible contributory factors included highly-coloured upland waters, chloramination and use of polyDADMAC or Epi-DMA. However, these factors were also present at works where NDMA was not detected.
- At each of the works sampled intensively - Works C11, C12, D18 - NDMA was detected throughout water treatment and in distribution but not in the raw water. NDMA found in the supernatant recycled to water treatment at Works C12 (39.1 ng/l) would be sufficient to account for the downstream concentrations of NDMA.
- With the exception of the concentration found in the recycled supernatant, the measured concentrations of NDMA (1.1-4.3 ng/l) were below current concentrations of concern in North America and substantially lower than the WHO guideline value.
- The results of the NDMA measurements (Surveys 1 - 4) showed no significant seasonal trends nor evidence of continued formation of NDMA following treatment.

C6 SURVEY 5 - ADDITIONAL SAMPLING

C6.1 Sampling

Additional sampling was carried out during week beginning 12 November 2007, with the objective of identifying and sampling final waters from further works dosing polyDADMAC or Epi-DMA in water treatment.

The sampling carried out in Surveys 1 - 4 had largely concentrated on the major water utilities, with 8 of the 11 utilities in England and Wales sampled. In addition, two water-only companies were sampled.

A telephone survey of 10 of the remaining water-only companies received 8 responses, with one works identified that used an Epi-DMA polyelectrolyte periodically to treat algae in bankside storage (- not being dosed at the time of the enquiry) and one works that dosed polyDADMAC in water treatment. A sample of final water was taken subsequently from the latter works (Works L1).

In addition, to confirm and clarify some of the results from Survey 4 (including results from the laboratory trials - see Section 3.8), further samples of recycled liquors were taken from Works C11 and C12, and Works C16 was sampled for raw and clarified water.

All samples were taken by WRc personnel and returned to WRc in ice-packed cool boxes on the day of sampling. At WRc, samples were stored in the dark at 4°C until transported to the analysing laboratory in ice-packed cool boxes, within 8 - 120 hours of sampling.

C6.2 Results

Results are shown in Table C8.

Table C8 Results of additional sampling (November 2007)

Works Ref.	Works Description	Sample Code	NDMA (ng/l)
Utility C			
C11 Recycle (Backwash supernatant)	<i>Source:</i> Upland, High colour/TOC <i>Treatment:</i> Coagulation, Pre-chlorination (~1 mg/l), RGF, Chloramination	M2305414	2.3
C11 Recycle (Thickener supernatant)	<i>Chemicals:</i> Ferric coagulant, Polyacrylamide	M2305415	1.9
C12 Recycle (Pre-coagulant)	<i>Source:</i> Upland, High colour/TOC <i>Treatment:</i> Sirofloc, Pre-chlorination (~1 mg/l), RGF, Chlorination	M2305416	< 4.5 ¹
C12 Recycle (Post-coagulant)	<i>Chemicals:</i> PolyDADMAC	M2305417	31.5
C16 Raw	<i>Source:</i> Upland reservoir, High colour/TOC	M2305418	< 0.9
C16 Clarified	<i>Treatment:</i> Coagulation, RGF1, RGF2 (Mn removal), Chlorination <i>Chemicals:</i> Ferric coagulant, Polyacrylamide	M2305419	2.7
Utility L			
L1 Final	<i>Source:</i> Reservoir, Agricultural input, High colour / TOC, Algae, Pesticides <i>Treatment:</i> Coagulation, RGF, Backwash recycle (occasional via membrane), GAC, Chlorination <i>Chemicals:</i> Polyaluminium chloride (8-15 mg/l Al ₂ O ₃), PolyDADMAC (1-2 mg/l)	M2305427	< 0.9

Note:

1. Highly-coloured sample diluted fivefold for analysis, hence limit of detection = 4.5 ng/l.

The results of the Works C11 Recycle analyses were comparable with the previous result for Works C11 Recycle (i.e. thickener supernatant). Similarly, the Works C12 Recycle (Post-coagulant) confirmed the magnitude of the previous Works C12 Recycle (39.1 ng/l). Significantly, NDMA was not detected in the Works C12 Recycle (Pre-coagulant) sample. This 'undosed' sample was highly alkaline and highly coloured due to the treatment process, and was subsequently dosed with coagulant in the order of 100 mg/l Fe⁹.

The samples taken from Works C16 showed NDMA detected in the clarified water (2.7 ng/l) but not in the raw water. Works C16 treats a highly coloured water by ferric coagulation. NDMA was not detected in samples of final water taken from this works in Surveys 2 and 3.

NDMA was not detected in the final water sampled from Works L1.

⁹ Estimate based on daily usage of coagulant and flow of waste liquor for 1 October - 14 November 2007: range 38 - 168 mg/l Fe; mean 103 mg/l Fe.

C6.3 Conclusions

- NDMA was detected in the clarified water sampled from Works C16 where treatment included ferric coagulation. NDMA had not been detected in samples of final water taken from this works in Surveys 2 and 3.
- The Works C12 Recycle (post-coagulant) sample (31.5 ng/l) confirmed the magnitude of the previous Works C12 Recycle sample (39.1 ng/l). NDMA was not detected in a sample taken immediately before dosing coagulant, which was dosed in the order of 100 mg/l Fe. The NDMA in the recycled supernatant could account for the concentrations of NDMA detected throughout treatment and in the final water at this works.

C7 LABORATORY TESTS

C7.1 September 2007

Laboratory tests were carried out to simulate treatment at Works C11 and D18 to try to elucidate the formation of NDMA at these works.

Tests were carried out in a standard laboratory jar tester using raw water (from both works) and recycled thickener supernatant (from Works C11 only) sampled at the time of the fourth survey. Chemicals were dosed to one-litre samples of raw water (or raw water/recycled supernatant) to simulate the various stages of the treatment process and to allow comparison of NDMA measurements with samples taken during the site visits. The ferric coagulant used in these tests was sampled from Works C11.

C7.1.1 Works C11

NDMA had been detected in the final water from Works C11 in each of the four quarterly surveys. Intensive sampling (Survey 3) showed that NDMA was not present in the raw water but was present in samples downstream of coagulation, following dosing of ferric coagulant and cationic polyacrylamide polyelectrolyte (SNF Flopam FO4190¹⁰) but prior to dosing of chlorine. Supernatants from washwater recovery and sludge thickening may be recycled to water treatment, upstream of polyelectrolyte dosing. It is believed that supernatant was not being recycled during the period of sampling.

Following dosing of chlorine prior to the RGFs and the contact tank, sodium bisulphite is dosed to reduce the chlorine residual to 0.6 mg/l Cl₂ prior to dosing ammonium sulphate (ammonium sulphate (37.5%)) at a 5:1 Cl:N mass ratio.

Works conditions during the site visit:

Flow	16.5 Ml/d
Coagulant dose	12.85 mg/l (as Fe)
Coagulation pH	4.5 (pH adjusted with sodium hydroxide)
Polyelectrolyte dose	0.2 mg/l (dosed as 0.24% w/w solution)

¹⁰ SNF Flopam FO4190 is also dosed to aid sludge thickening.

Sodium hypochlorite	1.2 mg/l Cl ₂ residual (post clarifiers)
Sodium hypochlorite	1.1 mg/l Cl ₂ residual (post RGFs)
Sodium bisulphite	Dosed to reduce chlorine residual to 0.6 mg/l
Ammonium sulphate	Dosed to 0.6 mg/l Cl at 5:1 Cl:N ratio (dosed as a 2.3% solution)

Laboratory tests were carried out to simulate treatment at the works. Tests were carried out using raw water and recycled supernatant sampled from Works C11 at the time of the fourth survey. Specifically, tests were carried out as indicated in Table C9 to try to elucidate the formation of NDMA.

Table C9 Works C11 laboratory test programme

Sample reference	Raw water (ml)	Recycle (ml)	Coagulant dose (mgFe/l)	NaOH dosed to pH ...	Polymer dose (mg/l)	NaOH dosed to pH ...	NaOCl dosed to residual ... (mgCl/l)	(NH ₄) ₂ SO ₄ dosed to residual ... (mgCl/l)
LC1	1000	-	12.85	4.5	-	-	-	-
LC2	1000	-	12.85	4.5	0.2	-	-	-
LC3	1000	-	12.85	4.5	0.2	8.2	1.00	-
LC4	Abandoned due to inaccurate coagulant dose							
LC5	950	50	12.85	4.5	-	-	-	-
LC6	900	100	12.85	4.5	-	-	-	-
LC7	800	200	12.85	4.5	-	-	-	-
LC8	950	50	12.85	4.5	0.2	-	-	-
LC9	950	50	12.85	4.5	0.2	8.2	1.00	-
LC10	950	50	12.85	4.5	0.2	8.2	1.00	0.11
LC11	1000	-	12.85	4.7	0.2	8.2	1.35	0.15
LC12	-	1000	-	-	-	-	-	-

Notes:

1. Coagulant: Ferric sulphate dosed as 2 gFe/l solution.
2. Sodium hydroxide (NaOH) dosed as 0.1M solution.
3. Polymer: Flopam dosed as 0.24 g/l solution.
4. Sodium hypochlorite dosed as 2 gCl/l solution.
5. Ammonium sulphate ((NH₄)₂SO₄) dosed as 2.3 g/l solution.
6. Test LC4 abandoned due to inaccurate coagulant dose - test repeated (LC11).
7. LC12 sludge supernatant only.

C7.1.2 Works D18

NDMA has been detected in the final water from Works D18 in each of the four quarterly surveys. Intensive sampling (Survey 3) showed that NDMA was not present in the raw water but was present in samples downstream of coagulation, following dosing of ferric coagulant, polyelectrolyte (Magnafloc LT22) and Epi-DMA (Nalco 8210) but prior to dosing of chlorine. Raw water nitrate is typically high and the likely precursors to NDMA formation are nitrate and/or Epi-DMA.

Following possible dosing of chlorine prior to the contact tank, sulphur dioxide is dosed to reduce the chlorine residual from 2.0 mg/l to 0.5 mg/l.

Sludge and backwash wastewater are discharged to lagoon hence there is no recycling to water treatment.

Works conditions during the site visit:

Flow	42.0 Ml/d
Coagulant dose	11.0 mg/l (as Fe)
Coagulation pH	7.8 (pH adjusted with sodium hydroxide)

Polyelectrolyte dose	0.1 mg/l
Epi-DMA dose	1.0 mg/l
Sodium hypochlorite	2 mg/l Cl ₂ residual (post contact tank)
Sulphur dioxide	Dosed to reduce chlorine residual to 0.5 mg/l Cl ₂ for distribution

Laboratory tests were carried out to simulate treatment at Works D18 using raw water sampled from the works at the time of the fourth survey. Specifically, tests were carried out as indicated in Table C10 to try to elucidate the formation of NDMA.

Table C10 Works D18 laboratory test programme

Sample reference	Raw water (ml)	Coagulant dose (mgFe/l)	NaOH dosed to pH ...	Polymer (LT22) dose (mg/l)	Polymer (epiDMA) dose (mg/l)	NaOCl dosed to residual ... (mgCl/l)
LD1	1000	11.0	7.8	-	-	-
LD2	1000	11.0	7.8	0.1	-	-
LD3	1000	11.0	7.8	0.1	1.0	-
LD4	1000	11.0	7.8	-	-	2.6
LD5	1000	11.0	7.8	0.1	-	2.6
LD6	1000	11.0	7.8	0.1	1.0	2.6

Notes:

1. Coagulant: Ferric sulphate dosed as 2 gFe/l solution.
2. Sodium hydroxide (NaOH) dosed as 0.1M solution.
3. Polyacrylamide polyelectrolyte: Magnafloc LT22 dosed as 0.5 g/l solution.
4. Epi-DMA polyelectrolyte: Nalco 8210 dosed as 0.5 g/l
5. Sodium hypochlorite dosed as 2 gCl/l solution.

C7.1.3 Results

Results are summarised in Tables C11 and C12.

The results of the laboratory samples (Table C11) generally showed higher concentrations of NDMA than detected in samples from Works C11, although of a similar order of magnitude. NDMA was found in the coagulant-dosed water (7.2 ng/l) and in the coagulant-dosed water/recycle (7.7-8.8 ng/l), and in all subsequent samples at similar concentrations. The results suggest that NDMA was present as a result of ferric coagulation and pH adjustment but was not significantly affected by subsequent chlorination or chloramination.

Table C11 Comparison of NDMA (ng/l) in laboratory-treated water with samples taken from Works C11

Sample	Laboratory sample	Works C11 sample
Raw water	-	< 0.9
Recycle (Ref LC12)	3.0	3.6
Coagulant-dosed water (Ref LC1)	7.2 ¹	-
Coagulant / polyelectrolyte-dosed water (Ref LC2)	8.5 ¹	3.9
Coagulant / polyelectrolyte-dosed water - chlorinated (Ref LC3)	9.1	3.7 / 4.2
Coagulant / polyelectrolyte-dosed water - chloraminated (Ref LC11)	5.4	4.3
Coagulant dosed raw water / 5% recycle (Ref LC5)	8.8	-
Coagulant dosed raw water / 10% recycle (Ref LC6)	7.7	-
Coagulant dosed raw water / 20% recycle (Ref LC7)	8.7	-
Coagulant / polyelectrolyte dosed raw water / 5% recycle (Ref LC8)	6.8 ¹	-
Coagulant / polyelectrolyte dosed raw water / 5% recycle - chlorinated (Ref LC9)	8.9	-
Coagulant / polyelectrolyte dosed raw water / 5% recycle - chloraminated (Ref LC10)	8.8	-

Note:

1. Interference on qualifier ion; ion ratio did not match.

Table C12 Comparison of NDMA (ng/l) in laboratory-treated water with samples taken from Works D18

Sample	Laboratory sample (ng/l)	Works sample (ng/l)
Raw water	-	< 0.9
Coagulant-dosed water (Ref LD1)	5.0	-
Coagulant / polyelectrolyte (LT22)-dosed water (Ref LD2)	5.4	-
Coagulant / polyelectrolyte (LT22) / Epi-DMA-dosed water (Ref LD3)	5.9	3.4
Coagulant-dosed water - chlorinated (Ref LD4)	5.2	-
Coagulant / polyelectrolyte (LT22)-dosed water - chlorinated (Ref LD5)	4.8	-
Coagulant / polyelectrolyte (LT22) / Epi-DMA-dosed water - chlorinated (Ref LD6)	4.9	-

The results of the laboratory samples (Table C12) showed a higher concentration of NDMA than in the one comparable sample from Works D18, although of a similar order of magnitude.

Again, NDMA was found in the coagulant-dosed water (5.0 ng/l) and in all subsequent samples at similar concentrations. The results suggest that NDMA was present as a result of ferric coagulation and pH adjustment but was not significantly affected by dosing of polyelectrolyte (LT22) or Epi-DMA, or subsequent chlorination.

C7.2 November 2007

Laboratory tests were carried out during week beginning 12 November 2007 with the objective of supplementing and clarifying the results of the laboratory tests carried out in September, and to clarify the occurrence of NDMA observed in the sampling surveys.

Tests were carried out in a standard laboratory jar tester using the raw water previously sampled from Works C11 (- this had been retained at WRc, stored in the dark at 10°C) and raw water sampled from Works C16.

Chemicals were dosed to one-litre samples of the raw waters to simulate pH adjustment and coagulation at Works C11 and C16, to allow comparison with the previous laboratory tests and with samples taken during the site visits.

A series of tests was carried out to simulate coagulation at Works C11 and C16. Tests were carried out using raw waters and coagulants sampled from each of the works, with pH adjusted by sodium hydroxide (caustic) or calcium hydroxide (lime), as appropriate, using standard laboratory reagents. Specifically, tests were carried out as indicated in Table C13.

Table C13 Laboratory test programme (November 2007)

Sample reference	Water source	Water volume (ml)	¹ Coagulant source	¹ Coagulant dose (mgFe/l)	² NaOH dosed to pH ...	³ Ca(OH) ₂ dosed to pH ...
LC11	Works C11	1000	-	-	-	-
LC11/C11/C	Works C11	1000	Works C11	12.85	4.6	-
LC16/C16/L	Works C16	1000	Works C16	12.00	-	3.8
LC16/C11/L	Works C16	1000	Works C11	12.00	-	3.8
Deion/C11/C	Deionised	1000	Works C11	12.85	4.6	-
Dist/C11/C	Distilled	1000	Works C11	12.85	4.6	-
Dist/C16/L	Distilled	1000	Works C16	12.00	-	3.8
Dist/C	Distilled	1000	-	-	4.6	-
Dist/L	Distilled	1000	-	-	-	3.8
Distilled blank	Distilled	1000	-	-	-	-
Deionised blank	Deionised	1000	-	-	-	-

Notes:

1. Coagulant: Ferric sulphate dosed as 2 gFe/l solution.
2. Sodium hydroxide (NaOH) dosed as 0.1M solution.
3. Calcium hydroxide (Ca(OH)₂) dosed as saturated solution.

C7.2.1 Results

Results are summarised in Table C14.

Table C14 Comparison of NDMA (ng/l) in laboratory-treated water with samples taken during Survey 5

Sample	Laboratory Sample (ng/l)	Works Sample (ng/l)
Works C11 raw water (- sample retained from Survey 4) (Ref: LC11)	< 0.9	< 0.9
Works C11 laboratory-clarified water (C11 coagulant 12.85 mgFe/l, pH 4.6 adjusted with NaOH) (Ref: LC11/C11/C)	3.9	3.9
Works C16 laboratory-clarified water (C16 coagulant 12.0 mgFe/l, pH 3.8 adjusted with Ca(OH) ₂) (Ref: LC16/C16/L)	2.7	2.7
Works C16 laboratory-clarified water (C11 coagulant 12.0 mgFe/l, pH 3.8 adjusted with Ca(OH) ₂) (Ref: LC16/C11/L)	3.6	-
Deionised coagulated water (C11 coagulant 12.85 mgFe/l, pH 4.6 adjusted with NaOH) (Ref: Deion/C11/C)	3.9	-
Distilled coagulated water (C11 coagulant 12.85 mgFe/l, pH 4.6 adjusted with NaOH) (Ref: Dist/C11/C)	4.7	-
Distilled coagulated water (C16 coagulant 12.0 mgFe/l, pH 3.8 adjusted with Ca(OH) ₂) (Ref: Dist/C16/L)	3.7	-
Distilled water (pH 4.6 adjusted with NaOH) (Ref: Dist/C)	< 0.9	-
Distilled water (pH 3.8 adjusted with Ca(OH) ₂) (Ref: Dist/L)	< 0.9	-
Distilled water (blank)	< 0.9	-
Deionised water (blank)	< 0.9	-

Table C14 shows that NDMA was found in laboratory coagulated samples of raw waters from Works C11 and C16 at concentrations similar to those found in comparable samples from the respective works. NDMA was formed as a result of dosing coagulants sampled from Works C11 and C16 to raw waters, deionised and distilled waters, with pH adjusted by NaOH or Ca(OH)₂.

It was considered a strong possibility that NDMA was a contaminant of the coagulant. Accordingly, a further series of tests was carried out to analyse samples of the coagulant (ex. Works C11) diluted with distilled water. The four dilutions were prepared using aliquots from the same sample of coagulant. The results are shown in Table C15.

Table C15 Measurements of NDMA in diluted coagulant

Sample	NDMA (ng/l)
Sample 1 (1/1000 dilution)	70
Sample 2 (1/2000 dilution)	38.4
Sample 3 (1/5000 dilution)	14.0
Sample 4 (1/10,000 dilution)	7.6
Sample 5 Distilled water (blank)	< 0.9

The results in Table C15 show NDMA found in each of the diluted samples at concentrations consistent with the dilution of the coagulant. NDMA was not detected in the distilled water 'blank'. Based on these results, it is calculated that the sample of coagulant contained in the order of 70,000 ng/l (70 µg/l) NDMA.

C7.3 Conclusions

- September 2007: The results of the laboratory tests generally showed higher concentrations of NDMA than found at Works C11 and D18. NDMA appeared to be present as a result of coagulation with ferric sulphate and pH adjustment. NDMA concentrations found in subsequent samples increased by up to 20% as a result of dosing polyelectrolytes or subsequent chlorination or chloramination.
- November 2007: The results of the laboratory tests showed concentrations of NDMA comparable to those found at Works C11 and C16 following coagulation with ferric sulphate and pH adjustment. NDMA was detected in successive dilutions of ferric sulphate but not in the distilled water blank, suggesting possible contamination of the coagulant with up to 70 µg/l NDMA.

APPENDIX D PROCESS DESCRIPTIONS OF WORKS C11, C12 AND D18

D1 INTRODUCTION

NDMA was detected in samples from Works C11, C12 and D18 in each of the quarterly surveys.

Descriptions of Works C11, C12 and D18 are given below.

D2 WORKS C11

A process schematic of Works C11 is shown in Figure D1.

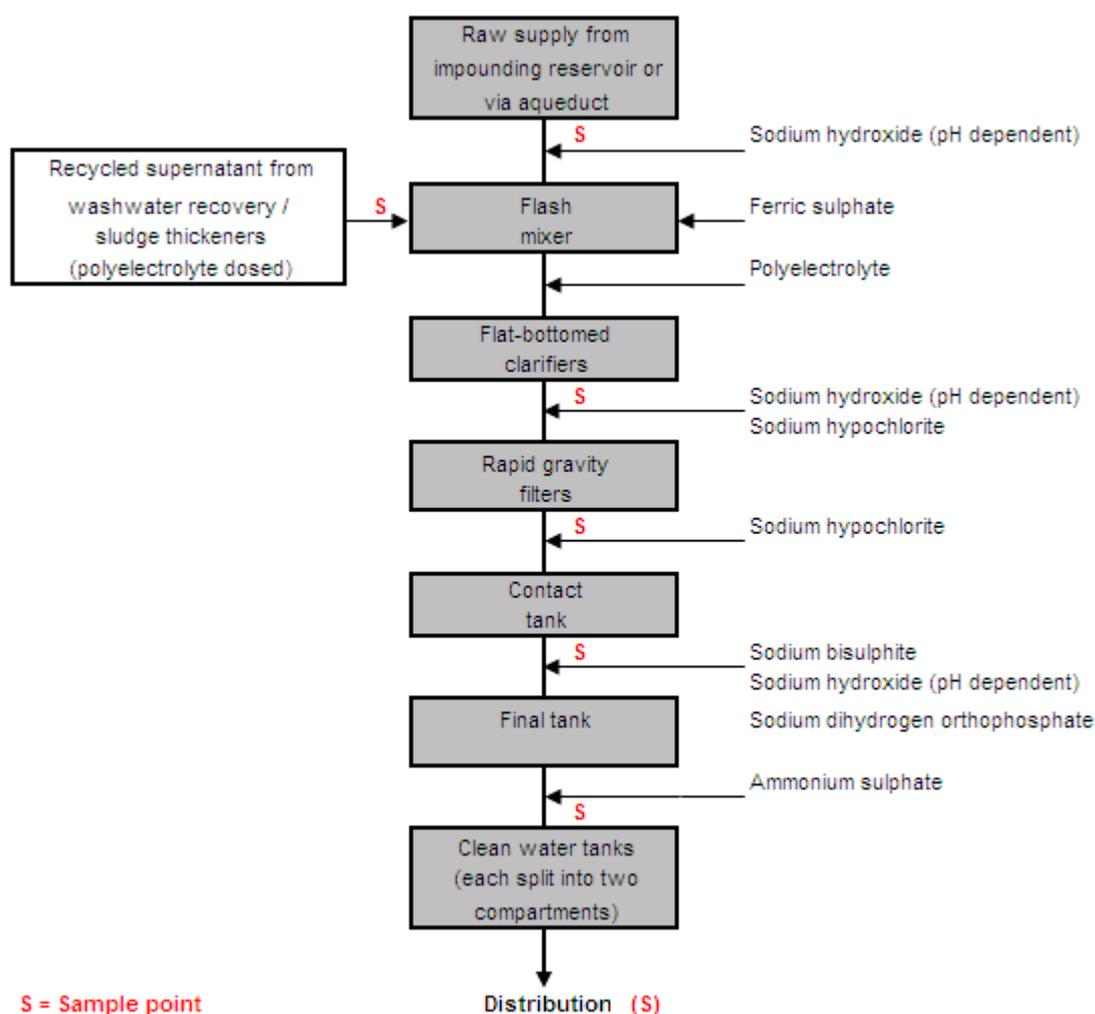


Figure D1 Process schematic of Works C11

D2.1 Water treatment

The catchment area for Works C11 is upland moorland with some minor agricultural activity. The raw water typically has high concentrations of colour/TOC.

Raw water is stored in an impounding reservoir which also receives water from a similar catchment via aqueduct. Raw water flows to the works inlet flash mixer via the raw water inlet main.

The raw water is dosed with coagulant (ferric sulphate) approximately half way into the flash mixer; if required for pH correction, sodium hydroxide (caustic soda) is dosed prior to the flash mixer. Supernatant water from washwater recovery and sludge thickening is recycled to the flash mixer downstream of the coagulant dosing point but upstream of polyelectrolyte dosing. Polyelectrolyte is dosed as the raw water weirs over from the flash mixer into the clarifier inlet channel.

The dosed raw water is fed into flat-bottomed clarifiers via the clarifier inlet channel. From the clarifiers, water flows into a common filter inlet channel where it is dosed with caustic soda and chlorine (to aid removal of manganese) prior to the rapid gravity filters.

Dosed, clarified water passes through the rapid gravity filters to a chlorine contact tank via a common filtered outlet channel. Chlorine is dosed to the filtered water prior to the contact tank.

After passing through the contact tank, sodium bisulphite is dosed to reduce the chlorine residual and caustic soda is dosed to raise the treated water pH to its final target value. Sodium dihydrogen orthophosphate is dosed to provide plumbosolvency protection in distribution.

The chlorinated water is then passed through a final tank after which ammonium sulphate is dosed to provide a residual disinfectant (chloramine) in distribution.

D2.2 Sludge treatment

Sludge from the clarifiers is collected in a holding tank from where it is pumped to sludge thickeners, dosed en-route with polyelectrolyte. Supernatant water from the sludge thickeners is recycled to the inlet flash mixer. The thickened sludge is gravity fed to holding tanks and is tankered from site.

Backwash wastewater from the rapid gravity filters is passed to holding tanks where the wastewater is settled. After settlement, supernatant water is pumped back to the inlet flash mixer whilst the settled sludge is fed to a holding tank from where it is pumped to the sludge thickeners.

D3 WORKS C12

A process schematic of Works C12 is shown in Figure D2.

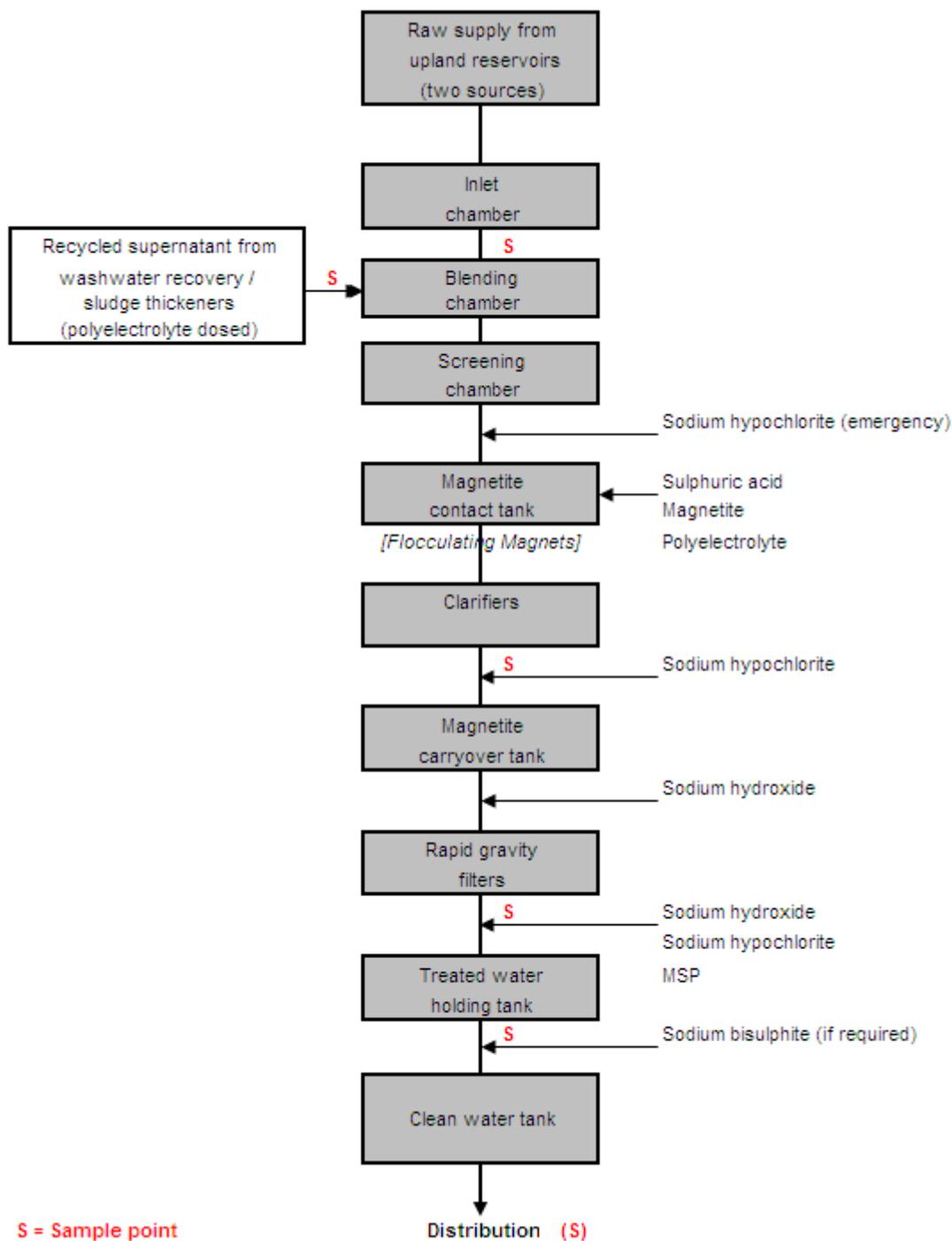


Figure D2 Process schematic of Works C12

D3.1 Water treatment

The catchment area for Works C12 is upland moorland (with some minor agricultural activity). The raw water typically has high concentrations of colour/TOC.

Works C12 uses the 'Sirofloc' process, a novel form of treatment that manipulates the charge on particles of magnetite to remove impurities from the raw water.

Raw waters from two upland reservoirs flow under gravity to the works inlet chamber where they are blended with supernatant water recycled from the magnetite/backwash wastewater recovery plant.

From the inlet chamber, the blended water passes through a series of three contact tanks. Regenerated magnetite and sulphuric acid are dosed in the first contact tank (- the acid produces a positive charge on the surface of the magnetite which attracts the negatively-charged colloidal impurities in the raw water). Polyelectrolyte (Posifloc CL45CLV) is dosed in the second contact tank to enhance coagulation.

The magnetite suspension flows from the third contact tank to the clarifiers. En-route to the clarifiers, the suspension flows past flocculating magnets that enhance the flocculation of the magnetite particles. The larger flocculated particles settle rapidly and can be easily separated from the clarified water.

The spent magnetite is thickened in the outlet cone of the clarifier and is then pumped to a dedicated regeneration train where it is regenerated for re-use.

The clarified water is dosed with sodium hypochlorite solution before any remaining magnetite is deposited in the magnetite recovery tank prior to the rapid gravity sand filters. The clarified water is then dosed with sodium hydroxide (for manganese removal) before passing through the filters.

The filtered water is trim dosed with sodium hypochlorite and sodium hydroxide prior to entering the treated water holding tank. Monosodium phosphate (MSP) is also dosed for control of plumbosolvency in distribution.

From the treated water holding tank, water is pumped to the clean water tank - dosed en-route with sodium bisulphite to trim the residual chlorine - and then passes into supply.

D3.2 Sludge treatment

The spent magnetite is dosed with sodium hydroxide to pH 10.5-12.5 in the magnetite reactivation tank (- the increased pH reverses the polarity on the surface of the magnetite, repelling the negatively charged colloidal impurities removed from the raw water). The magnetite slurry is then sequentially diluted and passed through two magnetic drum separators where the regenerated magnetite is separated from the dirty water.

The regenerated magnetite is collected in the regenerated magnetite tank where dilution water is added and the resultant slurry is pumped by a variable speed pump to the magnetite contact tanks, the flow rate being determined by the raw water flow rate to the inlet works.

The dirty water from the magnetic drum separators flows by gravity into magnetite recovery tanks and overflows to flocculation tanks in the washwater recovery plant. The water is dosed with ferric sulphate and either sulphuric acid or sodium hydroxide for pH adjustment. The coagulant-dosed water is pumped to sludge thickeners, dosed en-route with an anionic polyelectrolyte. Thickened sludge is pumped to holding tanks in the centrifuge building while the supernatant is discharged to the supernatant holding tank.

Backwash wastewater from the rapid gravity filters flows by gravity to the washwater recovery plant. The supernatant from the recovery tanks gravitates to the supernatant holding tank, while the settled sludge is pumped to a filter sludge holding tank in the centrifuge building.

Supernatant from the Supernatant Holding Tank is pumped to the works inlet chamber to mix with the incoming raw water.

Supernatant from the filter sludge holding tank is decanted and pumped to the centrate holding tank. The settled sludge is transferred to the thickened sludge holding tanks.

Thickened sludge is dosed with polyelectrolyte (Posifloc PW80) and dewatered by centrifuge. The centrate from the centrifuges flows to the centrate holding tank and is typically returned to the flocculation tanks over a 24-hour period.

D4 WORKS D18

D4.1 Water treatment

A process schematic of Works D18 is shown in Figure D3.

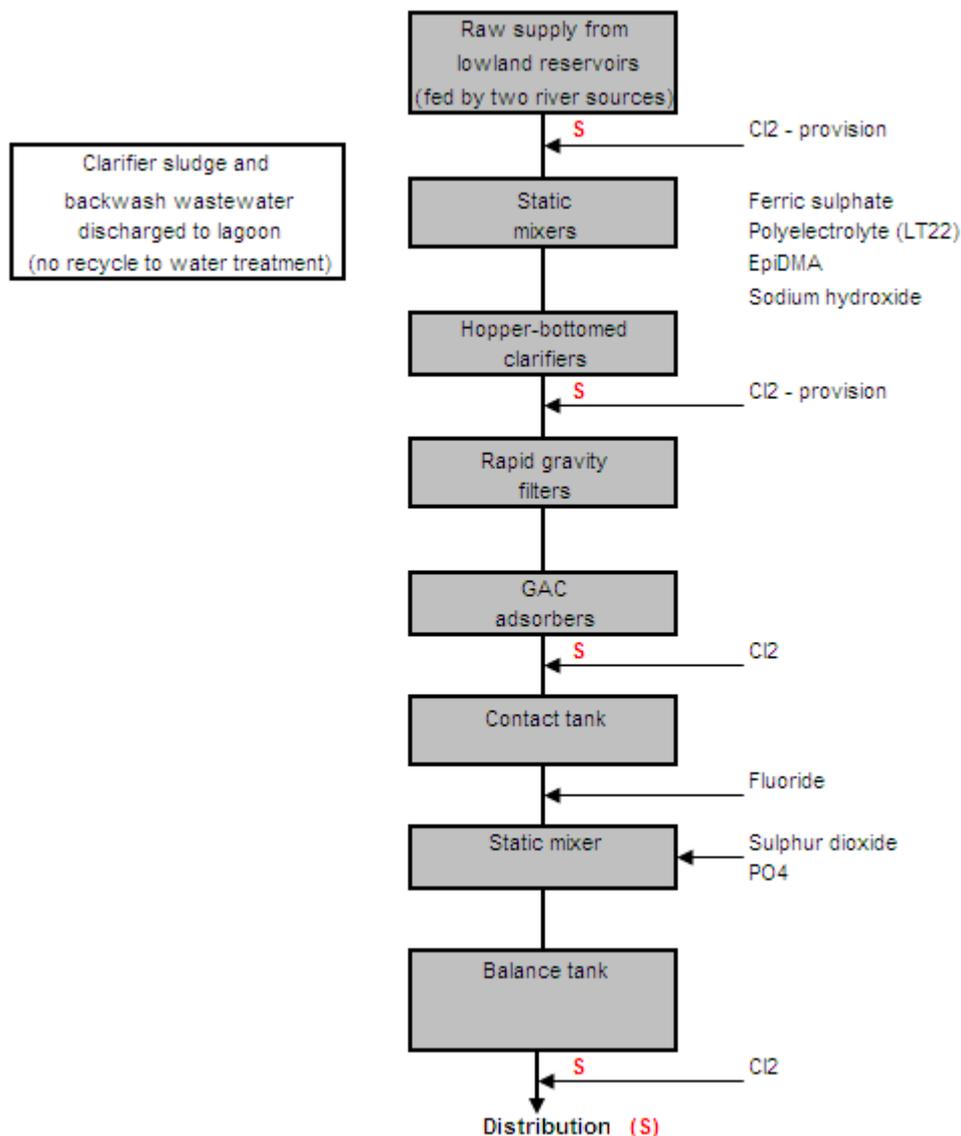


Figure D3 Process schematic of Works D18

Raw water is pumped from a lowland reservoir, fed from two lowland rivers, to flash mixers where ferric sulphate, polyelectrolyte (LT22), Epi-DMA (Nalco 8210) and sodium hydroxide are dosed. If required, chlorine can be dosed to the raw water prior to the flash mixers.

The dosed raw water is fed to hopper-bottomed clarifiers. Sludge from the clarifiers is discharged to lagoons while clarified water flows to sand/anthracite rapid gravity filters. If required, chlorine can be dosed prior to the filters.

Filtered water is pumped to GAC adsorbers to remove pesticides. After the adsorbers, chlorine is dosed to 2 mg/l prior to the contact tank. After the contact tank, the chlorine residual is reduced to about 0.5 mg/l with sulphur dioxide, and fluoride and phosphate are dosed. The dosed water enters a balance tank from where high lift pumps pump into supply. Additional chlorine is dosed in distribution as required.

D4.2 Sludge treatment

Sludge from the clarifiers is discharged to the lagoons.

Backwash waters from the RGFs and GAC adsorbers flows are discharged to washwater 'recovery' tanks, which in turn discharge to the lagoons.

There is no recycling to water treatment. Supernatant from the lagoons is discharged to watercourse while settled sludge is periodically removed and disposed of to sewage treatment.

APPENDIX E CONTRACT EXTENSION

E1 INTRODUCTION

In the principal survey reported in Appendix C, NDMA was detected in final waters at three works (Works C11, C12 and D18) and in clarified water at a fourth works (Works C16). A common factor at these works was the use of a specific ferric coagulant. Subsequent laboratory tests on samples of the coagulant taken from two of the affected works (Works C11 and C16) indicated that NDMA was a possible contaminant. However, this and other ferric coagulants were dosed at treatment works where NDMA was not detected in final waters.

The possibility of NDMA being a contaminant of a ferric coagulant widely used in the water industry warranted further investigation.

E2 SCOPE OF WORK

1. The coagulant dilution tests carried out on the ferric sulphate coagulant sampled from Works C11 (see Table C15) were repeated. Four samples were prepared for analysis: 1/1000 dilution, 1/2000 dilution, 1/5000 dilution, 1/10,000 dilution. A distilled water 'blank' was also submitted.
2. Similar dilution tests were carried out on samples of ferric sulphate sampled from Works C16¹¹, i.e. a works where NDMA had been detected in treatment, and from Works D17, i.e. a works where NDMA had not been detected in treatment.
3. Samples of clarified and final waters were taken for NDMA analysis from Works D17 and D18 to investigate possible removal within treatment.
4. Dilution tests were carried out on other ferric coagulants used in the water industry in England and Wales to determine whether they contained NDMA and if so at what concentration. Tests were carried out on:
 - Ferric sulphate (I and II)
 - Ferric chloride

Duplicate samples for each coagulant were prepared, with the dilutions calculated to give NDMA concentrations of 10 ng/l and 50 ng/l assuming that NDMA was present in the coagulant such that when dosed at 12.85 mg/l as Fe³⁺ (i.e. the dose used in treatment at Works C11), the coagulant would give rise to an NDMA concentration in water treatment of 1 ng/l.

¹¹ It had been planned to sample coagulant from Works D18, but this had not proved possible because of health and safety restrictions at the works.

E3 METHODOLOGY

E3.1 Analysis

Towards the end of December 2007, the analysing laboratory employed throughout this study ceased performing commercial chemical analysis. As a result, a university laboratory was contracted to perform the NDMA analysis for this contract extension.

The university laboratory was not UKAS accredited.

E3.1.1 Method description

NDMA analysis was accomplished using a solid phase extraction (SPE), isotope dilution gas chromatography/mass spectrometry (GC/MS) methodology similar to that originally proposed by Taguchi *et al* (1994) and used by others (Luo *et al*, 2003; Valentine *et al*, 2005). Briefly, 500 ml of water sample was extracted with 125 mg of carbonaceous polymeric beads (Ambersorb 348, Aldrich) by shaking for 1 hour at 200 RPM. The Ambersorb beads were then filtered onto a glass fibre filter. After air drying for roughly 30 minutes, they were transferred to a 2 ml amber vial containing 300 µl fused-glass insert (Chromacol) and 0.250 ml methylene chloride was added to re-extract the adsorbate. The methylene chloride phase was then used for gas chromatography injection. A 5 µl aliquot of methylene chloride extract was injected into Pelkin Elmer gas chromatography system coupled with a Clarus 500 mass spectrometer (Shelton, CT, USA). A DB1701 capillary column was used.

Peak identifications were based on the comparison of the experimental full scan mass spectrum with standard NDMA mass spectrum. d6-NDMA was used as the internal standard and added at the beginning of the analytical procedure. Because the internal standard is a labelled analogue of the analyte, the procedure presumes that internal standard recovery during method procedures is equal to unlabelled NDMA recovery. Therefore, each calculated sample NDMA concentration has been compensated for losses during sample preparation using the internal standard compound. Quantifications were accomplished using selective ion monitoring (SIM) based on the characteristic mass peaks of NDMA in EI mode, specifically, m/z 74 for NDMA and m/z 80 for d6-NDMA.

E3.1.2 Method verification

Calibration curve

The calibration curve (Figure E1) established a linear relationship between the NDMA concentration in water and the responding ratio, which is the ratio of NDMA peak area to d6-NDMA peak area. This calibration curve was then used for determining the NDMA concentration in the WRc samples of unknown NDMA concentration. A deviation from linearity was observed, particularly at concentrations below about 10 ng/L.

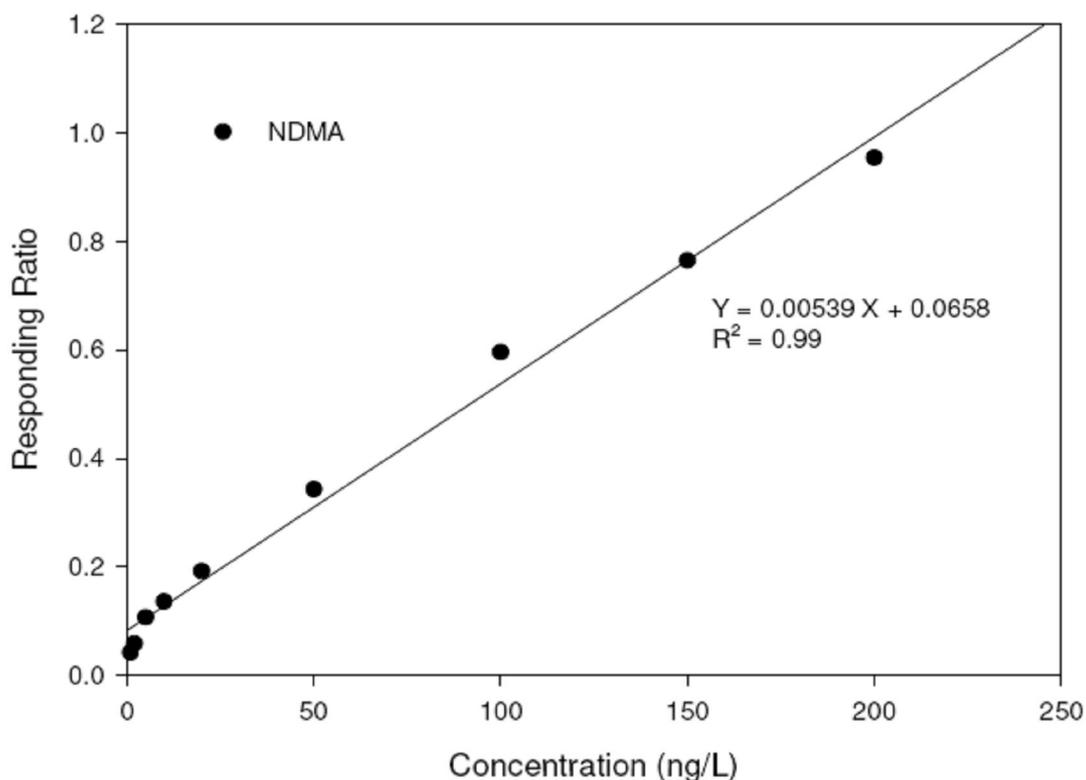


Figure E1 Calibration curve for NDMA determination from 1 to 200 ng/l

MDL determination

The method detection limit (MDL) for NDMA analysis in water samples was determined using a USEPA approach (USEPA, 2004), which indicates the minimum concentration of a substance that can be measured and reported with 99% confidence. Seven replicate samples were analyzed. The MDL was the product of the standard deviation multiplied by the upper critical value of Student's t distribution with six degrees of freedom and $\alpha = 0.01$, which is 3.143. Seven 500 ml standard samples containing 10 ng/l of NDMA were analyzed according to the method described above. The MDL was determined to be at 1.47 ng/l (Table E1).

NDMA recovery tests

NDMA recovery test results are shown in Table E2.

Table E1 MDL determination for NDMA analysis

Sample No.	Conc. of NDMA spiked (ng/l)	Conc. of NDMA determined (ng/l)
1	10	10.46
2	10	10.28
3	10	9.68
4	10	9.48
5	10	9.07
6	10	9.84
7	10	9.70
STDEV		0.47
MDL		1.47

Table E2 NDMA recovery tests

Sample No.	Conc. of NDMA spiked (ng/l)	Conc. of NDMA determined (ng/l)
1	5	5.08
2	5	4.09
3	5	4.91
4	20	19.87
5	20	18.90
6	20	20.90
7	100	102.24
8	100	100.89
9	100	98.20

E3.2 Sampling

Samples of coagulant were taken from Works D17 (ferric sulphate) on 26 February 2008 and from a treatment works in Utility A (ferric chloride) on 29 February. Dilution tests were also carried out on samples of the ferric sulphate coagulant taken previously from Works C11 and C16 (and stored under refrigeration) and on samples of the same and a second ferric sulphate coagulant supplied directly.

Samples of clarified and final waters were taken from Works D18 and D17 on 26 February. NDMA had been detected in the final water from Works D18 in each of the four seasonal surveys and also from within treatment. NDMA had not been detected in the final water from Works D17 in either Survey 1 or 2.

Water samples were collected in 1-litre PET bottles containing 40 mg ascorbic acid preservative and stored in the dark at 4°C ± 2°C at WRc until delivered in ice-packed cool boxes to the University laboratory for analysis.

D17 Fe ₂ (SO ₄) ₃ I	96.3 - 339.9 µg/l (mean: 214.7 µg/l)
Fe ₂ (SO ₄) ₃ I supplied directly	46.9 - 166.6 µg/l (mean: 109.0 µg/l)
Fe ₂ (SO ₄) ₃ II supplied directly	13.3 - 72.5 µg/l (mean: 51.9 µg/l)
FeCl ₃	< MDL - 5.33 µg/l

The calculated NDMA concentration in the ferric sulphate coagulant sampled from Works C11 can be compared with 70 µg/l calculated previously (see Appendix C7).

At Works C11 and C16, where contamination of the ferric sulphate coagulant was determined, NDMA was detected in corresponding clarified and/or final water samples in previous surveys. Contamination of the coagulant from Works D17 was also determined and NDMA was detected in the corresponding clarified water (2.20 ng/l). However, as this concentration was close to the MDL and lower than 'detected' in one of the distilled water blanks, the clarified water result must be considered inconclusive. NDMA was not detected in the final water sampled from Works D17 at the same time, nor in samples of final water taken in Surveys 1 and 2.

NDMA was not detected in the clarified or final water from Works D18, although NDMA had been detected in each of the four seasonal surveys at concentrations between 3.4-3.7 ng/l in clarified water and 1.0-2.0 ng/l in final water. These concentrations are close to the MDL.

E5 CONCLUSIONS

1. Despite a large degree of scatter within the analysis, the results of the coagulant dilution tests confirmed the presence of NDMA in two ferric sulphate coagulants supplied by the same manufacturer.
2. It is probable that the one other coagulant tested, ferric chloride, was not contaminated by NDMA.
3. Given the scope of the validation of this method, the deviation from linearity of the calibration curve at low concentrations and the detection of NDMA in a sample of distilled water, the results from this laboratory below 10 ng/l need to be interpreted with caution.

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