DEFRA

INVESTIGATION INTO THE POTENTIAL FORMATION AND REMOVAL OF NITROSAMINES IN DRINKING WATER TREATMENT (DWI 70/2/239)

FINAL REPORT

WRc Ref: Defra 8196.05
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Report No.: Defra 8196.05

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SUMMARY

Objectives

The principal objectives of this project were to:

- determine NDMA concentrations in all iron and aluminium coagulants used in drinking water treatment in England and Wales;
- conduct detailed process investigations at the sites and distribution systems where NDMA was detected in the final water in a previous Defra/DWI study[1] ("the 2008 Defra/DWI study") and at other selected sites;
- investigate the potential formation and removal of nitrosamines in water treatment in a series of laboratory-based studies; and
- determine NDMA concentrations in selected ferric coagulants.

Reasons

In 2006, Defra/DWI commissioned a research project entitled "NDMA - A Survey of Levels in Drinking Water and Factors Affecting its Formation" (Ref: DWI 70/2/210). This survey was completed in early 2008. The study examined water from 43 treatment works and at over 90% of these sites, no detectable levels of NDMA were found in the final water. NDMA was detected at a few works but concentrations in final water never exceeded 10 ng/l. There was some evidence that NDMA may have been formed but subsequently removed within the treatment process. These results appeared to implicate a particular coagulant ('Coagulant A1') as the source of NDMA at these works.

Early in 2008 DWI commissioned a toxicological risk assessment for NDMA in drinking water. The key conclusions of this assessment were that NDMA is a potent animal carcinogen by several routes of exposure and genotoxic both *in vitro* and *in vivo* and consequently that exposure should be as low as reasonably practicable. However the advice also recognised that drinking water is not a major route of exposure and was reassuring in that it did not recommend immediate public health action in respect of the very low concentrations of NDMA (<10 ng/l in final water) reported in the above study.

In 2008, the Inspectorate notified the manufacturer of the findings of the research and as a consequence the manufacturer took steps to address the problem.

DWI wished to confirm that the steps taken by the manufacturer had been effective and determine whether NDMA was found in other coagulants used in England and Wales. DWI let a project to investigate the possible presence of NDMA in coagulants, the formation and removal of NDMA within treatment and distribution and to include investigation of the formation and removal of other nitrosamines.

[1] Dillon, G.R. *et al.* (2008). *NDMA Concentrations in Drinking Water and Factors affecting its Formation: Final Report*. WRc Report DEFRA7348, March 2008.

Defra/DWI commissioned WRc to carry out this study. Severn Trent Services (STS) (formerly Severn Trent Laboratories (STL)) undertook the analytical work.

Conclusions

Literature review

The International Agency for Research on Cancer (IARC) has classified several nitrosamines as either Group 2A ("probably carcinogenic to humans") or Group 2B ("possibly carcinogenic to humans"); NDMA, the most widely reported nitrosamine, is classified as Group 2A. WHO has issued a Guideline Value for NDMA in drinking water of 100 ng/l based on an upper bound excess lifetime cancer risk of 10^{-5}.

NDMA has been found at treatment works and in distribution at concentrations up to 100 ng/l in North America, although usually at concentrations less than 10 ng/l. In the UK, NDMA has been detected in final waters from a small number of treatment works at concentrations up to 5.8 ng/l. Reports of other nitrosamines in drinking water suggest that their concentrations are considerably less: NDEA has been detected in the US at up to 0.7 ng/l, NPYR and NMOR have been detected in Canada following chloramination, and NDBA has been detected in one distribution system in the UK.

Prevention of contamination of drinking water by nitrosamines can be achieved by removal of formation precursors or removal of nitrosamines once formed. Some removal of precursors may be achieved by biodegradation, adsorption on activated carbon and pre-chlorination. Once formed, nitrosamines may be removed to varying degrees and efficacies by biofiltration, adsorption on carbonaceous resins (claimed to be more effective than activated carbon), advanced oxidation processes and UV irradiation.

Coagulant survey

Coagulant usage: A survey of water companies in England and Wales identified the use of twenty-eight ferric- and aluminium-based coagulants supplied by seven manufacturers/ suppliers.

In the initial survey carried out in 2009, NDMA was either not detected or detected only as a trace contaminant in 22 coagulants. Allowing for dilution in the tests, NDMA concentrations in these coagulants were typically <1 µg/l and close to the limit of detection of 0.48 µg/l; it is probable that many of these results were false positives. In six coagulants higher concentrations (up to 19 µg/l) were detected but these were well below the concentrations detected during the 2008 Defra/DWI study. The six contaminated coagulants were all ferric sulphates produced by three manufacturers.

Contract Extension 1 (2010): Towards the end of the 2008-2009 water treatment survey (see below), significantly increased NDMA concentrations were detected in treated waters and distribution. Investigation revealed the NDMA concentration in Coagulant A1 had increased considerably, believed as a result of an NDMA precursor contained in a raw material used in the manufacturing process.

A subsequent 5-month analytical survey (June-October 2010) monitored NDMA concentrations in Coagulant A1 and Coagulant B2 (manufactured by a similar process to Coagulant A1).

NDMA concentrations in Coagulant A1 were reduced following a partial replacement of the affected raw material in the manufacturing process. NDMA concentrations in coagulant samples taken during delivery ('ex. delivery') to Works D20 reduced from 195 µg/l to 67 µg/l while concentrations in samples supplied directly to WRc by the manufacturer ('ex. production') were generally lower and reduced to 18 µg/l by mid-October. However, the NDMA concentration in the final 'ex. production' coagulant sample submitted at the end of October increased to 325 µg/l. The reason for the substantial increase was unexplained.

NDMA concentrations in samples of Coagulant B2 taken from Works C12 ('ex. works') were initially high due to contamination from residual Coagulant A1 in the coagulant holding tanks. By the end of the 5-month survey, NDMA concentrations in 'ex. works' samples reduced to 27 µg/l, comparable to 'ex. production' samples supplied directly to WRc by the manufacturer.

At both Works C12 and D20, NDMA concentrations in water samples taken throughout treatment generally decreased in proportion to the reduction in NDMA in the coagulant.

Contract Extension 2 (2011): As a result of the unexplained increase in NDMA in Coagulant A1 at the end of October 2010, a second survey was carried out to confirm that NDMA concentrations had been subsequently reduced.

It was not possible to obtain samples of Coagulant A1 because production had ceased and no residual stock of coagulant could be sourced from water treatment works. The survey therefore investigated NDMA concentrations in Coagulant B2.

A five-month analytical survey (June-October 2011) showed that NDMA concentrations in Coagulant B2 sampled from Works C12 measured 26-36 µg/l. If dosed at typical values used in water treatment, Coagulant B2 would increase the NDMA concentration in coagulated water by 0.4-2.7 ng/l. NDMA was detected in only one sample of final water, at 0.9 ng/l.

NDMA concentrations in the 'ex. works' coagulant samples were consistently higher than in 'ex. production' samples (3.8-9.2 µg/l) supplied directly to WRc by the manufacturer.

NMOR concentrations measured in Coagulant B2 sampled from Works C12 measured 4.3-28 µg/l, potentially giving rise to NMOR concentrations in coagulated water between 0.03-2.12 ng/l. NMOR was not detected in any samples of final water.

NMOR concentrations in the 'ex. works' coagulant samples were consistently lower than in 'ex. production' samples (22-143 µg/l) supplied directly to WRc by the manufacturer.

Water treatment works survey

A 12-month survey measuring NDMA concentrations in water from six selected water treatment works was carried out between November 2008 and November 2009. Towards the end of the survey, results were affected by a large increase in NDMA concentration in Coagulant A1 used at the works. In Surveys 1-9 (November 2008-August 2009), NDMA concentrations detected in final waters and distribution were generally not detectable and occasionally low ng/l. Surveys 10-12 (September 2009-November 2009) showed significantly increased levels, typically low ng/l levels but up to 24 ng/l. No samples of treated water were found to exceed the WHO guideline value of 100 ng/l. Reduction in NDMA concentrations in coagulants (described above) lead to corresponding reductions in final water concentrations.

Generally, NDMA was not detected in raw water with some exceptions at Works D18 and H5, where concentrations were typically 1-2 ng/l (though a single sample contained 12 ng/l).

NDMA measured within treatment was usually attributed to the contaminated coagulant (and raw water at Works D18 and H5). Works D17, D18 and H5 used lower coagulant doses than Works C11, C12 and C16, and the effect of the contaminated coagulant was not as significant.

There was some evidence that NDMA concentrations in post-coagulated water increased as a result of ozonation, and that NDMA was removed by RGF and GAC, presumably by a biological mechanism and/or adsorption. At Works C11 and D18, there was evidence of NDMA concentrations in distribution increasing with retention time.

Laboratory studies

NDMA formation and removal: Laboratory trials were carried out to investigate NDMA formation and removal, simulating observations from the water treatment works survey. The results showed the removal of NDMA from post-coagulated clarified water and nitrosamine-spiked tap water by RGF media (sampled from Works C16) indicating a possible biological removal mechanism. Trials simulating the formation of NDMA in distribution proved inconclusive.

Nitrosamine formation and removal: Laboratory trials were carried out to investigate the formation and removal of a range of nitrosamines by water treatment processes.

In trials dosing Coagulant B2 to highly coloured upland water from Works C12, NDMA and NMOR were detected in the various post-coagulated water samples; NMOR was also detected in the raw water. Increases in NDMA and NMOR in post-coagulated water samples were almost certainly due to contamination of the coagulant used in the tests and, in the investigation of DAF, possible contamination of the equipment used.

Ozonation and/or GAC generally reduced concentrations of NDMA and NMOR. Storage of chlorinated or chloraminated water for 48 hours – simulating retention in distribution - generally showed a small increase in concentration of both nitrosamines.

In trials spiking pre-formed nitrosamines to tap water, all the spiked nitrosamines were removed effectively by GAC or ozonation/GAC. Ozonation alone had little effect on nitrosamine concentration.

Suggestions

The principal source – or potential source - of nitrosamines (NDMA and NMOR) in drinking water appears to be contaminated ferric coagulants. It is suggested that manufacturers be required to analyse coagulants for nitrosamines and provide results to water companies to ensure that this contamination route is controlled.

Should nitrosamines in drinking water continue to be a concern, removal by GAC adsorption may be particularly effective based on the results of laboratory tests with virgin GAC (Chemviron F400). If appropriate, further tests should be carried out on GAC to fully investigate the process, including optimum GAC type, EBCT, bed life, etc.

1. INTRODUCTION

1.1 Objectives

The general objectives of this project were to:

(i) determine NDMA concentrations in all iron and aluminium coagulants used in drinking water treatment in England and Wales;

(ii) conduct detailed process investigations at the sites and distribution systems where NDMA was detected in the final water in a previous Defra/DWI study[2] ("the 2008 Defra/DWI study") and at other selected sites;

(iii) investigate the potential formation and removal of nitrosamines in water treatment in a series of laboratory-based studies; and

(iv) determine NDMA concentrations in selected ferric coagulants.

Specific objectives are listed below:

1. Review the scientific literature to identify the formation, occurrence and toxicity of nitrosamines.

2. Develop and performance test a method of analysis that unambiguously determines NDMA concentration in drinking water with a limit of detection close to 1 ng/l.

3. Obtain samples of all iron and aluminium coagulants used in drinking water treatment in England and Wales.

4. Determine NDMA concentrations in all iron and aluminium coagulants obtained.

5. Measure NDMA concentrations throughout the process stream and within the distribution system of the three works where NDMA was detected in the final water in the 2008 Defra/DWI study.

6. Measure NDMA concentrations throughout the process stream of three works where Coagulant A1 identified in the 2008 Defra/DWI study is used but where NDMA was not detected in the final water.

7. Informed by the findings of the process stream study, devise and conduct laboratory-based studies to investigate the potential formation of and removal of nitrosamines by different drinking water treatment processes.

8. Determine NDMA concentrations in selected ferric coagulants.

[2] Dillon, G.R. *et al.* (2008). *NDMA Concentrations in Drinking Water and Factors affecting its Formation: Final Report*. WRc Report DEFRA7348, March 2008.

1.2 Background

In 2006, Defra/DWI commissioned a research project entitled “NDMA - A Survey of Levels in Drinking Water and Factors Affecting its Formation” (Ref: DWI 70/2/210). This survey - referred to in this report as “the 2008 Defra/DWI study” - was completed in early 2008. The study examined water from 43 treatment works and at over 90% of these sites, no detectable levels of NDMA were found in the final water. NDMA was detected at a few works but concentrations in final water never exceeded 10 ng/l. There was some evidence that NDMA may have been formed but subsequently removed within the treatment process. These results appeared to implicate a particular coagulant (‘Coagulant A1’) as the source of NDMA at these works.

Early in 2008 DWI commissioned a toxicological risk assessment for NDMA in drinking water. The key conclusions of this assessment were that NDMA is a potent animal carcinogen by several routes of exposure and genotoxic both *in vitro* and *in vivo* and consequently that exposure should be as low as reasonably practicable. However the advice also recognised that drinking water is not a major route of exposure and was reassuring in that it did not recommend immediate public health action in respect of the very low concentrations of NDMA (<10 ng/l in final water) reported in the above study.

In 2008, the Inspectorate notified the manufacturer of the findings of the research and as a consequence the manufacturer took steps to address the problem.

DWI wished to confirm that the steps taken by the manufacturer had been effective and determine whether NDMA was found in other coagulants used in England and Wales. DWI let a project to investigate the possible presence of NDMA in coagulants, the formation and removal of NDMA within treatment and distribution and to include investigation of the formation and removal of other nitrosamines.

Defra/DWI commissioned WRc to carry out this study. Severn Trent Services (STS) (formerly Severn Trent Laboratories (STL)) undertook the analytical work.

1.3 Resumé of Content

This final report includes the following:

- Section 1: A statement of the objectives of the project and background information.
- Section 2: A summary of the literature review covering the formation, occurrence and toxicity of nitrosamines. The full review is presented in Appendix A.
- Section 3: A summary of the methodology developed for the analysis of NDMA and other nitrosamines in drinking water. The full methodology is presented in Appendix B.
- Section 4: Results of the NDMA analysis of iron and aluminium coagulants used in England and Wales, together with temporal analysis for selected ferric coagulants. Supporting information is presented in Appendix C.
- Section 5: A summary of the results from the monthly surveys at six selected treatment works. Supporting information is presented in Appendix D.

- Section 6: A summary of results from laboratory tests investigating the formation and removal of NDMA and other nitrosamines. Supporting information is presented in Appendix E.

- Sections 7 and 8: Conclusions and Suggestions, respectively.

2. LITERATURE REVIEW

2.1 Introduction

In 2006, Defra commissioned a survey to investigate the formation and occurrence of N-nitrosodimethylamine (NDMA), a 'probable human carcinogen' and one of a group of chemicals known as nitrosamines. The survey, carried out during 2006-2008, examined water from 43 treatment works in England and Wales (Dillon *et al.*, 2008). NDMA was detected in final water at three works at concentrations less than 10 ng/l, with the probable source being a contaminated ferric coagulant. It is possible that other nitrosamines might be formed within water treatment and be present in final water. Accordingly, Defra commissioned WRc to investigate the potential formation and removal of nitrosamines in drinking water treatment.

A literature review was carried out to investigate the formation, occurrence, toxicity and removal of several nitrosamines potentially formed during drinking water treatment, listed in Table 2.1.

Table 2.1 Nitrosamines potentially formed during water treatment

Nitrosamine	Abbreviation	Structure
N-Nitrosodimethylamine	NDMA	$O=N\text{-}N(CH_3)_2$
N-Nitrosomethylethylamine	NMEA	$O=N\text{-}N(CH_2CH_3)CH_3$
N-Nitrosodiethylamine	NDEA	$O=N\text{-}N(CH_2CH_3)_2$
N-Nitrosopyrrolidine	NPYR	$(C_4H_8)N\text{-}N=O$
N-Nitrosodipropylamine	NDPA	$O=N\text{-}N(C_3H_7)_2$
N-Nitrosopiperidine	NPIP	$(C_5H_{10})N\text{-}N=O$
N-Nitrosodibutylamine	NDBA	$O=N\text{-}N(C_4H_9)_2$
N-Nitrosomorpholine	NMOR	$O=N\text{-}N(C_4H_8O)$

The major physical-chemical properties of these nitrosamines are shown in Table 2.2.

Table 2.2 Physical-chemical properties of selected nitrosamines

Nitrosamine	Mol. Wt. (g/mol)	Density (g/ml)	Water Solubility (g/100 ml)	Vapour Pressure (hPa)[1]	Boiling Point (°C)[2]
NDMA	74.08	1.006 (20°C)	>10 (19°C)	2.1	151-153
NMEA	88.11	0.9448 (18°C)	-	1.1	163
NDEA	102.14	0.9431 (20°C)	9.3	0.81	175-177
NPYR	100.12	-	-	0.072	214
NDPA	130.19	0.9163 (20°C)	0.9894	0.086	206
NPIP	114.15	1.06 (20°C)	1-5 (22°C)	0.092	217-219
NDBA	158.24	0.8997 (20°C)	Slightly soluble	0.03	235
NMOR	116.12	-	>10 (19°C)	0.036	224-225

Notes:
1. At 20°C.
2. At 760 mmHg.
3. Source: www.chemfinder.com.

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

2.2 Formation and Occurrence

The formation of nitrosamines is complex and depends on many factors including concentrations of reactants, catalysts and inhibitors, and other competing reactions. Most published work focuses on the formation of NDMA. However, most of the principles directing NDMA formation should be valid (at least on a qualitative basis) to the formation of other nitrosamines.

The three major pathways by which nitrosamines might be formed are:

- Nitrosation of nitrogen-containing compounds by nitrosating agents.
- Reaction of monochloramine with aliphatic amines (e.g. dimethylamine (DMA)) to unsymmetrical dimethylhydrazine (UDMH) and subsequent oxidation to nitrosamines.
- Reaction of dichloramine with aliphatic amines to chlorinated UDMH and subsequent oxidation to nitrosamines by either monochoramine or dissolved oxygen.

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 concentrations less than 10 ng/l. There are less data with regard to the formation and occurrence of other nitrosamines although several (NDEA, NPYR, NDPA, NPIP, NDBA) have been formed in laboratory trials at low ng/l concentrations as a result of chloramination and

several (NMEA, NPYR, NPIP, NDBA, NMOR) have been detected in river water in the US. NDEA has been detected in the US in drinking water at a concentration up to 0.7 ng/l; NPYR and NMOR have been detected in Canada at treatment works and in distribution following chloramination; and NDBA has been detected in the UK in one distribution system.

2.3 Toxicity

The International Agency for Research on Cancer (IARC) classified several nitrosamines as either Group 2A ("probably carcinogenic to humans") or Group 2B ("possibly carcinogenic to humans"). The EPA IRIS database includes nine aliphatic nitrosamines with significant health concerns. NDMA, the most widely reported nitrosamine, is classified by IARC as Group 2A and has a WHO Guideline Value of 100 ng/l based on an upper bound excess lifetime cancer risk of 10^{-5}. The California Department of Health Services (CDHS) established a notification level in 1998 for NDMA of 10 ng/l. In 2004 and 2005, notification levels of 10 ng/l for NDEA and NDPA were also established.

In 2002, CDHS requested a Public Health Goal (PHG) from the Office of Environmental Health Hazard Assessment (OEHHA). In December 2006, OEHHA developed a PHG for NDMA in drinking water of 3 ng/l, based on a cancer risk of 10^{-6} for lifetime exposure to NDMA in drinking water.

The toxicity of specific nitrosamines is reviewed in Appendix A.

2.4 Removal

Prevention of contamination of drinking water by nitrosamines can be achieved by removal of precursors, i.e. prevention of formation, or actual removal once formed.

According to literature and laboratory studies, some removal of nitrosamine precursors may be achieved by biodegradation, activated carbon and pre-chlorination. Biodegradation, e.g. during underground passage, achieved good removal of aliphatic amines and some nitrogen-containing precursors. Activated carbon achieved good removal of precursors for nitrosamine removal and dissolved organic nitrogen (DON) but was less effective for aliphatic amines. Pre-chlorination is reported to reduce NDMA formation potential substantially.

Nitrosamines may be removed to varying degrees and efficacies by biofiltration, adsorption on carbonaceous resins, advanced oxidation processes (AOPs) and UV irradiation. Aerobic biofiltration under laboratory conditions gave good microbial degradation of NDMA but was less effective for other nitrosamines (NDMA>>NDBA>NDEA>NPIP>NDPA>NMEA> NPYR>NMOR). Carbonaceous resins were more effective than GAC for adsorption of nitrosamines but still low compared to other organic substances. UV irradiation was effective for NDMA removal but at high dosage, e.g. one order of magnitude NDMA reduction required about 10 times the dose for virus removal.

The removal of specific nitrosamines is reviewed in Appendix A.

3. DETERMINATION OF NDMA AND OTHER NITROSAMINES IN DRINKING WATER

Severn Trent Services (STS) (formerly Severn Trent Laboratories (STL)) undertook the analytical work.

STS Analytical Services division are quality and environmentally assured through the international standards:

- ISO 17025:2005
- ISO 9001:2008
- ISO 14001:2004
- BS OHSAS 18001:2007 certification

which are assessed by the United Kingdom Accreditation Service (UKAS) and certification bodies that are accredited by UKAS. STS Analytical Services are also accredited for MCERTS for the chemical analysis of soils and the performance standard for organisations undertaking sampling and chemical testing of water (Version 1.1).

An analytical method was developed by STS to determine NDMA in water with a limit of detection of 0.48 ng/l. The method describes a procedure for the determination of NDMA in drinking water using a solid phase extraction (SPE) cartridge containing 2 g of 80-120 mesh coconut charcoal analysed using gas chromatography mass spectrometry (GCMS).

The method described has been shown to be suitable for the determination of NDMA in drinking water samples. All NDMA results within this report have been determined by this method (unless stated otherwise) and have been blank corrected.

The method described was also used to determine NDMA in diluted samples of coagulants.

The method may be applicable to untreated source waters (with suitable adaptation) and to other types of water samples, but it has not been evaluated for these uses.

An analytical method was developed by STS to determine other nitrosamines in drinking water based on liquid chromatography tandem mass spectrometry (LCMSMS).

The NDMA and other nitrosamine analytical methods are presented in Appendix B.

4. COAGULANT SURVEY

4.1 Coagulant Usage in England and Wales

A request for information on coagulant usage (types and quantities) was sent to each of the water companies in England and Wales. The responses from the companies are summarised by region in Table 4.1.

The survey identified 28 coagulants supplied by seven manufacturers/suppliers.

Five water companies reported not using coagulants in their treatment processes.

Table 4.1 Coagulant usage (tonnes/year) in England and Wales by region

Coagulant	Central & Eastern	London & South East	Northern	Western	Wales
Ferric sulphate	51053	827	52113	8236	9201
Aluminium sulphate	6328	3225	21739	8718	11060
Polyaluminium chloride	3100	10800	24	9020	400
Ferric chloride	1319	3924	0	395	350
Aluminium chloride hydroxide	0	0	0	0	2400
Ferrous chloride	0	565	0	207	0
Aluminium chloride	0	0	0	152	0
Ferric aluminium sulphate	0	0	[1]	0	0

Note:
1. One company reported using ferric aluminium sulphate but no quantity was indicated.

4.2 Coagulant NDMA Analysis

4.2.1 All Coagulants

Samples of the ferric and aluminium coagulants used in water treatment in England and Wales were obtained direct from manufacturers/suppliers and analysed for NDMA. The results are shown in Table 4.2 ('2009' data).

Table 4.2 Diluted coagulant NDMA analysis (ng/l): All coagulants

Manufacturer	Coagulant type	Product Ref.	Dilution	NDMA (2009) GCMS[1] (ng/l)	NDMA (2010) GCMS (ng/l)
Manufacturer A	Ferric sulphate	Coagulant A1	1:1000 1:5000 1:10000	9.2 (5.1) 2.2 1.5	231 - -
		Coagulant A2	1:1000 1:5000 1:10000	2.9 (20) 1.1 0.87	66 - -
Manufacturer B	Ferric sulphate	Coagulant B1	1:1000 1:5000 1:10000	9.7 (8.5) 2.8 1.9	17[2] - -
		Coagulant B2	1:1000 1:5000 1:10000	15.0 (9.0) 3.1 1.9	20 - -
		Coagulant B3	1:1000 1:5000 1:10000	8.8 (6.1) 2.0 1.2	16 - -
		Coagulant B4	1:1000 1:5000 1:10000	1.0 < 0.48 < 0.48	17[2] - -
	Aluminium sulphate	Coagulant B5	1:1000 1:5000 1:10000	< 0.48 < 0.48 < 0.48	- - -
	Polyaluminium chloride	Coagulant B6	1:1000 1:5000 1:10000	< 0.48 < 0.48 < 0.48	- - -
		Coagulant B7	1:1000 1:5000 1:10000	< 0.48 < 0.48 < 0.48	- - -
Manufacturer C	Ferric chloride	Coagulant C1	1:1000 1:5000 1:10000	< 0.48 < 0.48 < 0.48	 - -
	Ferric sulphate	Coagulant C2	1:1000 1:5000 1:10000	0.92 1.1 0.90	< 0.48 - -
		Coagulant C3	1:1000 1:5000 1:10000	0.91 1.0 0.80	- - -
		Coagulant C4	1:1000 1:5000 1:10000	5.0 (2.9) 1.6 1.2	2.1 - -
	Aluminium sulphate	Coagulant C5	1:1000 1:5000 1:10000	0.85 0.54 0.64	- - -
	Polyaluminium chloride	Coagulant C6	1:1000 1:5000 1:10000	0.51 0.59 0.51	- - -
		Coagulant C7	1:1000 1:5000 1:10000	0.60 0.52 < 0.48	- - -

Manufacturer	Coagulant type	Product Ref.	Dilution	NDMA (2009) GCMS[1] (ng/l)	NDMA (2010) GCMS (ng/l)
	Aluminium chloride hydroxide	Coagulant C8	1:1000 1:5000 1:10000	0.55 < 0.48 0.57	- - -
		Coagulant C9	1:1000 1:5000 1:10000	0.53 0.70 < 0.48	- - -
Manufacturer D	Ferrous chloride	Coagulant D1	1:1000 1:5000 1:10000	0.79 0.72 0.69	< 0.48 - -
	Ferric chloride	Coagulant D2	1:1000 1:5000 1:10000	0.81 0.91 0.52	- - -
	Aluminium chloride	Coagulant D3	1:1000 1:5000 1:10000	1.2 0.98 0.77	- - -
	Polyaluminium chloride	Coagulant D4	1:1000 1:5000 1:10000	0.74 0.70 0.74	- - -
		Coagulant D5	1:1000 1:5000 1:10000	0.68 0.82 0.74	- - -
Manufacturer E	Ferric aluminium sulphate (low manganese)	Coagulant E1	1:1000 1:5000 1:10000	0.66 (1.97) 0.64 (0.99) 0.51	2.4 - -
	Aluminium sulphate	Coagulant E2	1:1000 1:5000 1:10000	1.0 1.1 0.95	- - -
	Polyaluminium chloride	Coagulant E3	1:1000 1:5000 1:10000	< 0.48 < 0.48 0.49	- - -
Manufacturer F[3]	Ferric sulphate	See result for Coagulant B4			
Manufacturer G	Ferrous chloride	Coagulant G1	1:1000 1:5000 1:10000	< 0.48 < 0.48 < 0.48	< 0.48 - -
	Ferric chloride	Coagulant G2	1:1000 1:5000 1:10000	< 0.48 0.64 1.1	< 0.48 - -

Notes:
1. GCMS analysis confirmed by GCMSMS. GCMSMS values shown in brackets.
2. Single sample provided by manufacturer.
3. Ferric sulphate supplied by Manufacturer F is manufactured by Manufacturer B.

The results of the 2009 survey showed that NDMA was a contaminant in several of the coagulants, notably the ferric sulphates. Allowing for the dilution used in the analytical procedure, six coagulants contained appreciable concentrations of NDMA up to 19.0 µg/l:

- Manufacturer A (Coagulant A1, 9.2-15.0 µg/l; Coagulant A2, 2.9-8.7 µg/l).
- Manufacturer B (Coagulant B1, 9.7-19.0 µg/l; Coagulant B2, 15.0-19.0 µg/l; Coagulant B3, 8.8-12.0 µg/l).
- Manufacturer C (Coagulant C4, 5.0-12.0 µg/l).

The higher positive results were subsequently confirmed by repeat analysis using GCMSMS (data shown in brackets).

NDMA was not detected, or was detected at trace concentrations, in 22 ferric and aluminium coagulants. Since the trace concentrations were near to the limit of detection and no

significant differences or conflicting results were obtained for different dilutions, it is probable that these were false positives.

4.2.2 Ferric coagulants

Concurrent with the 2009 analytical survey of all coagulants used in water treatment in England and Wales, a monthly analysis was carried out on fresh samples of Coagulant A1 - the ferric coagulant that had been identified in the 2008 Defra/DWI study as being responsible for concentrations of NDMA detected at Works C11, C12, C16 and D18 – and Coagulant A2. Results of analysis carried out on samples of these coagulants submitted between November 2008 and March 2009 are shown in Table 4.3.

Table 4.3 Diluted coagulant NDMA analysis (ng/l): Coagulants A1 and A2

Sample Date	Sample Code	Dilution		
		1/1000[1]	1/5000[1]	1/10000[1]
November 2008	M531/700/2 A1	9.4	2.4	1.6
	M531/700/1 A2	2.8	1.2	< 1.0
December 2008	A1	5.9 (6.19)	2.0 (2.15)	1.3 (1.53)
	A2	4.1 (4.04)	1.4 (1.64)	1.1 (1.42)
January 2009	A1	3.3 (3.66)	1.8 (1.05)	0.85 (1.04)
	A2	3.1 (3.52)	-	-
February 2009	A1[2]	4.3 (4.91)	2.4 (1.20)	0.54 (0.75)
	A2	5.5 (6.07)	-	-
March 2009	A1[3]	7.9 (8.97)	-	-
	A2	4.8 (5.82)	-	-

Notes:
1. GCMS analysis confirmed by GCMSMS (values shown in brackets).
2. Coagulant A1 was re-analysed after 12-months storage to February 2010: NDMA concentration = 7.7 ng/l (1/1000 dilution).
3. Coagulant A1 was re-analysed after 11-months storage to February 2010: NDMA concentration = 12 ng/l (1/1000 dilution).

Analysis of Coagulant A1 in the 2008 Defra/DWI study had indicated a concentration of NDMA in the order of 70 µg/l. As a result of this finding, the manufacturer implemented changes to its manufacturing process. The results of the analysis in Table 4.3 indicate a reduction in NDMA concentration by a factor of about 10-20.

At typical coagulant doses used in water treatment, detection of NDMA in drinking water was not expected as a result of dosing ferric coagulant containing NDMA at the concentrations indicated in Table 4.4. This was generally observed during the water treatment works survey, with some exceptions at Works C12 and Works H5. However towards the end of the survey (September-November 2009), NDMA concentrations detected in treatment and distribution increased considerably. Coagulant A1 was suspected as the source of the NDMA and further analysis was carried out on fresh samples of Coagulant A1 obtained from various treatment works and direct from the manufacture (see Table 4.4).

Table 4.4 Diluted Coagulant A1 NDMA analysis

Source of Coagulant A1	Date Sampled	NDMA[1] (ng/l)	NDMA (ng/mgFe)
Works C11	27/10/2009	386	1.91
Works C12	6/11/2009	245	1.22
Works D17	25/11/2009	283	1.40
Works D17	29/11/2009	233	1.16
Works D18	20/11/2009	312	1.55
Works D18	26/11/2009	294	1.46
Works D18	29/11/2009	295	1.46
Works H5	19/11/2009	380	1.88
Works H5	22/12/2009	271	1.34
Manufacturer A	11/2009	282/341[2]	1.40/1.69[2]

Notes:
1. Coagulant samples diluted 1/1000.
2. Duplicate analysis.

The results in Table 4.4 show NDMA concentrations in the coagulants sampled from the treatment works in the range 233-386 μg/l. This level of contamination corresponds to a mean 1.49 ng NDMA/mg Fe in the coagulants, clearly indicating the potential for the elevated NDMA concentrations measured towards the end of the treatment works survey when dosed in the range 3 to 15 mg Fe/l.

There was a concern that NDMA concentrations in other ferric coagulants might also have increased. Accordingly, fresh samples of Coagulant A1 and the other ferric coagulants in which NDMA had been detected during the 2009 survey were analysed to confirm whether or not there had been any significant change. Results are shown in the right-hand column in Table 4.2 ('2010' data).

The results of the 2010 analysis of the ferric coagulants showed significant changes in the concentration of NDMA in Coagulants A1, A2 and B4. The concentration of NDMA in Coagulants A1 and A2 had increased substantially since the 2009 analysis but were lower than measured during October-December 2009 (Table 4.4) when the manufacturer was experiencing production problems. Coagulants B1 and B4 were effectively the same formulation and a single sample was provided by the manufacturer for the 2010 analysis. In 2009, separate samples were provided, with Coagulant B4 obtained several months after Coagulant B1.

4.3 Further Coagulant NDMA Analysis

4.3.1 Contract Extension 1 (2010)

The NDMA in Coagulant A1 was believed to have been formed during manufacture from a precursor in a raw material. The raw material used at this time ('Raw Material 1') had been outsourced by the coagulant manufacturer. Subsequent to this finding, the manufacturer

sourced an alternative supply of the raw material ('Raw Material 2'). The two supplies were blended in manufacturing in a 1:4 ratio (Raw Material 1:Raw Material 2) in order to reduce the formation of NDMA in the coagulant.

To monitor NDMA concentrations in Coagulant A1 and to compare with concentrations in Coagulant B2 – a ferric coagulant manufactured by a similar process - a 5-month survey was carried out between June and October 2010. NDMA concentrations were measured in samples of the two coagulants supplied directly to WRc by the manufacturers, from two treatment works using the coagulants (Works C12 and Works D20, selected because of ease of access for sampling) and in water samples from these works. The results of the survey are summarised in Tables 4.5 and 4.6; full details are presented in Appendix C.

Table 4.5 Contract Extension 1: NDMA (ng/l unless stated) measured at Works C12

Sample Point	Works C12 Sample Date				
	24/06/10	**26/07/10**	**25/08/10**	**20/09/10**	**25/10/10**
Raw water	<0.48	<0.48	<0.48	<0.48	<0.48
Recycled water 2	60	42	21	16	15.1
Post-clarification	2.2	1.0	0.78	1.0	0.53
Coagulant B2[1] (ex. works)	125	92	39	29	27.3
Coagulant B2[1] (ex. production)	26 (12/06/10)[2]	27 (14/07/10)[2]	31 (09/08/10)[2]	25 (04/09/10)[2]	5.8 (21/10/10)[2]

Notes:
1. Coagulant samples µg NDMA/l.
2. Coagulant production date.

Works C12 switched from using Coagulant A1 to Coagulant B2 in May 2010, with the first delivery of Coagulant B2 made on 17/05/10. Coagulant B2 sampled from the works was initially contaminated with NDMA from the residual Coagulant A1 contained in the coagulant holding tanks. The level of contamination was reduced with successive deliveries of Coagulant B2 until NDMA measured in the coagulant sampled from the works was comparable to that measured in samples obtained direct from the manufacturer; there was no known reason for the reduction in NDMA in the sample submitted by the manufacturer in October. NDMA concentrations measured in samples from water treatment were generally consistent with the concentrations measured in the works coagulant.

Table 4.6 Contract Extension 1: NDMA (ng/l unless stated) measured at Works D20

Sample Point	Works D20 Sample Date				
	24/06/10	**26/07/10**	**25/08/10**	**20/09/10**	**25/10/10**
Raw water	< 0.48	3.0	< 0.48	< 0.48	< 0.48
Post coagulation	8.5	3.5	1.9	2.5	0.83
Final water	< 0.48	< 0.48	< 0.48	1.7	< 0.48
Coagulant A1[1] (ex. delivery)	149 (16/06/10)[2]	195 (30/06/10)[2]	75 (24/08/10)[2]	67 (22/09/10)[2]	76 (11/10/10)[2]
Coagulant A1[1] (ex. production)	140 (25/06)[3] 31 (05/07)[3]	132 (21/07)[3] 22 (04/08)[3]	22 (18/08)[3,4] 19 (30/08)[3]	24 (16/09)[3] 23 (28/09)[3]	18 (13/10)[3,5] 325 (28/10)[3]

Notes:
1. Coagulant samples µg NDMA/l.
2. Coagulant delivery date.
3. Coagulant production date.
4. A 'non-blended' coagulant sample produced using only 'Raw Material 2' was also submitted to WRc by the manufacturer. The NDMA content of this sample measured 16 µg/l (production date 18/08/10).
5. A 'non-blended' coagulant sample produced using only 'Raw Material 2' was also submitted to WRc by the manufacturer. The NDMA content of this sample measured 12 µg/l (production date 10/10/10).

The NDMA concentrations in samples of Coagulant A1 taken directly from tankers delivering to Works D20 remained high over the period of the survey, although there was a large reduction in August when the concentration approximately halved to 75 µg/l. Concentrations of NDMA detected in the post-coagulation water samples were generally consistent with the concentration of NDMA detected in the works coagulant. With the exception of the September sample (1.7 ng/l), NDMA was not detected in the final water, possibly as a result of removal within treatment by RGF or GAC.

The NDMA concentrations in coagulants sampled from deliveries to the works were greater than measured in samples supplied direct to WRc by the manufacturer, particularly from August to early October (18-24 µg/l). The samples supplied directly were 'ex. production' samples and were expected to show no significant difference to the 'ex. delivery' samples. Two samples of Coagulant A1 manufactured using only Raw Material 2, i.e. 'non-blended' samples, contained 12-16 µg NDMA/l. The reason for the discrepancy between the 'ex. delivery' and 'ex. production' samples is unexplained.

The NDMA concentration in the final sample submitted direct to WRc by the manufacturer in late October increased substantially to 325 µg/l; a result confirmed by repeat analysis. The reason for the substantial increase was unexplained.

4.3.2 Contract Extension 2 (2011)

As a result of the high NDMA concentration (325 µg/l) detected in the final 'ex. production' sample of Coagulant A1 in Contract Extension 1 (Section 4.3.1), it was decided to continue to analyse samples of this coagulant. However, before sampling commenced, production of

Coagulant A1 ceased and no residual stock of coagulant could be sourced from water treatment works.

The same raw material used in the manufacture of Coagulant A1 was also used in the manufacture of Coagulant B2, so it was decided to carry out a 5-month survey between June and October 2011 measuring concentrations of NDMA and NMOR (which had been detected in the laboratory tests; see Section 6.3) in Coagulant B2. Samples of this coagulant were obtained from Works C12 ('ex. works') and from the manufacturer ('ex. production), submitted directly to WRc.

Manufacturer B received its raw material from three distinct sources: Source F, Source N/G and Source S. Raw material from a single source was used in the batch manufacturing process, thus it was possible to sample and analyse coagulants produced with material from each of these sources.

Samples were collected from Works C12 monthly between June and October 2011, and obtained directly from the manufacturer for comparison. The results of the survey are summarised in Tables 4.7 and 4.8; full details are presented in Appendix C.

Table 4.7 Contract Extension 2: NDMA (ng/l unless stated) measured at Works C12

Sample Point	**Works C12 Sample Date**				
	15/06/11	**13/07/11**	**24/08/11**	**21/09/11**	**12/10/11**
Final water	-	-	< 0.48	< 0.48	0.90
Coagulant B2[1] (ex. works)	34	36	27.4	26.1	27.5
Coagulant B2[1] (ex. production): Raw material = Source F					
	7.0 (03/05/11)[2]	7.7 (19/07/11)[2]	-	-	-
Coagulant B2[1] (ex. production): Raw material = Source N/G					
	5.1 (28/05/11)[2]	-	-	-	3.8 (30/10/11)[2]
Coagulant B2[1] (ex. production): Raw material = Source S					
	-	7.9 (07/07/11)[2]	9.2 (26/08/11)[2]	-	-

Notes:
1. Coagulant samples µg NDMA/l.
2. Coagulant production date.

Table 4.8 Contract Extension 2: NMOR (ng/l unless stated) measured at Works C12

Sample Point	Works C12 Sample Date				
	15/06/11	**13/07/11**	**24/08/11**	**21/09/11**	**12/10/11**
Final water	-	-	<1.54	<1.54	<1.54
Coagulant B2[1] (ex. works)	12	4.3	2.04	7.06	28.3
Coagulant B2[1] (ex. production): Raw material = Source F					
	143 (03/05/11)[2]	85.7 (19/07/11)[2]	-	-	-
Coagulant B2[1] (ex. production): Raw material = Source N/G					
	68 (28/05/11)[2]	-	-	-	22.4 (30/10/11)[2]
Coagulant B2[1] (ex. production): Raw material = Source S					
	-	35 (07/07/11)[2]	49.1 (26/08/11)[2]	-	-

Notes:
1. Coagulant samples µg NMOR/l.
2. Coagulant production date.

The coagulant samples taken from Works C12 from June to October 2011 contained 26-36 µg NDMA/l and 4.3-12 µg NMOR/l. The 'ex. works' NDMA concentrations were higher than the concentrations measured in the 'ex. production' samples (3.8-9.2 µg/l). The NDMA concentrations in the 'ex. production' samples were similar irrespective of the source of the raw material. The NMOR concentrations in the 'ex. works' samples were significantly lower than the concentrations measured in the 'ex. production' samples (35-143 µg/l). NMOR concentrations were highest in the coagulant produced with raw material from Source F.

At the NDMA and NMOR concentrations measured in the coagulant sampled from Works C12, concentrations in water treatment following dosing of the coagulant at typical doses (3-15 mg Fe/l) could measure about 0.4-2.7 ng NDMA/l and 0.03-2.12 ng NMOR/l. Actual concentrations measured in final waters would depend on the extent of any removal in water treatment.

NDMA was detected in only one sample of final water (0.9 ng/l) whilst NMOR was not detected (limit of detection 1.54 ng/l).

5. WATER TREATMENT WORKS SURVEY

5.1 Introduction

A survey of water treatment works was conducted over a period of one year (November 2008 - November 2009) with samples taken monthly from six works from sampling points throughout treatment and in distribution. The selection of works and sample points was discussed and agreed with DWI prior to the survey. The principal requirement was that all works used Coagulant A1: three works where NDMA had been detected in the 2008 Defra/DWI study in final water samples (Works C11, C12 and D18) and three works where NDMA had not been detected (Works C16, D17 and H5). In addition to this requirement, the works were selected to provide a wide and representative range of treatment processes and treatment chemicals.

Samples were collected in 1-litre plastic PET bottles containing 40 mg of ascorbic acid preservative and transported in ice-packed cool boxes. On receipt into the laboratory, samples were stored in the dark at 4 °C ± 2 °C prior to extraction. Once extracted, the extracts were stored in the dark at -15 °C ± 5 °C and analysed by STS using the procedure described in Section 3.

In addition to sampling for NDMA, factors contributing to its possible formation and/or removal were recorded, e.g. water temperature and quality (TOC, NH_3, NO_2, NO_3), chemical type and dose (coagulant, polyelectrolyte, disinfectant), distribution retention time, etc.

5.2 Seasonal Survey

The seasonal variation in NDMA detected at the six selected treatment works and in distribution is summarised in Sections 5.2.1-5.2.6 for each of the works; full details are shown in Appendix D.

Following the 2008 Defra/DWI study, the manufacturer of Coagulant A1 altered its manufacturing process to reduce the concentration of NDMA in the ferric coagulant. It was expected that NDMA would not be detected (as a result of dosing the coagulant) at the six treatment works with the exception of the 'Recycled Water 2' sample at Works C12. Generally this was observed until about September 2009 when the NDMA in Coagulant A1 increased substantially. There were more incidences of NDMA detected in raw water, particularly at Works H5 where NDMA was generally detected throughout treatment and in distribution.

As a result of the substantial increase in NDMA in Coagulant A1 in September, the data are summarised separately for the six works for the periods November 2008-August 2009 (Surveys 1-9) and September-November 2009 (Surveys 10-12).

5.2.1 Works C11

In the 2008 Defra/DWI study, NDMA was detected at Works C11 throughout treatment and in distribution, attributed principally to the NDMA contamination of Coagulant A1 used in treatment.

In the present study, NDMA was not detected in the raw water but was detected in treatment and distribution as illustrated in Figures 5.1 and 5.2.

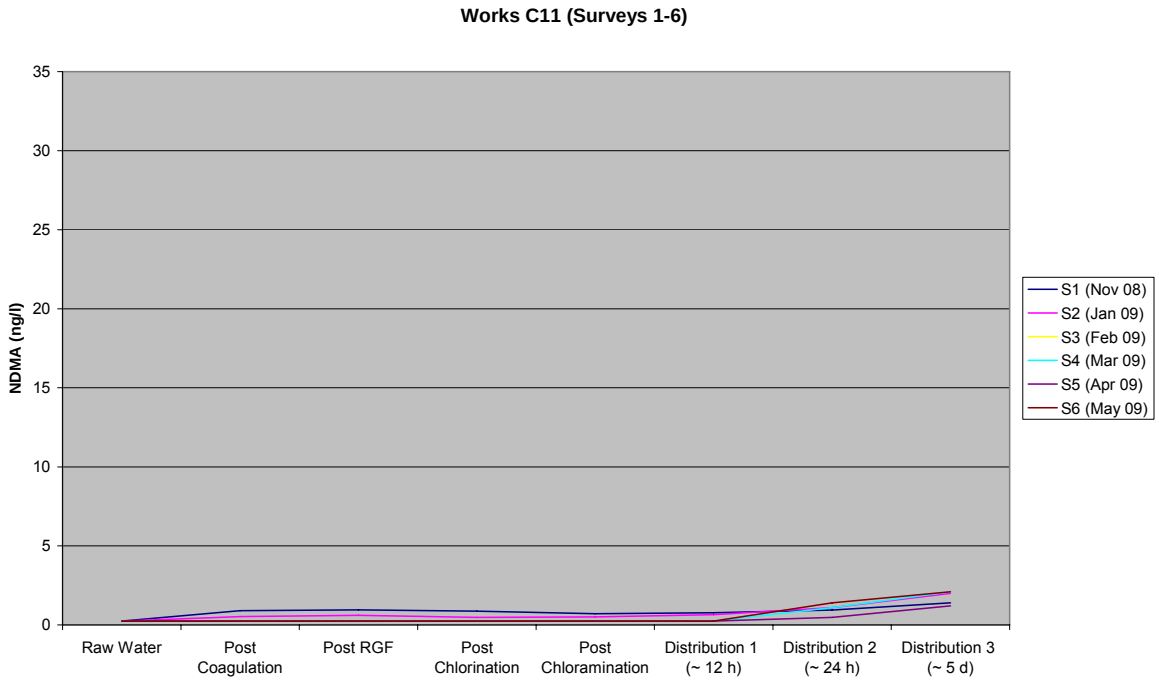

Figure 5.1 NDMA in treatment and distribution (Works C11, Surveys 1-6)

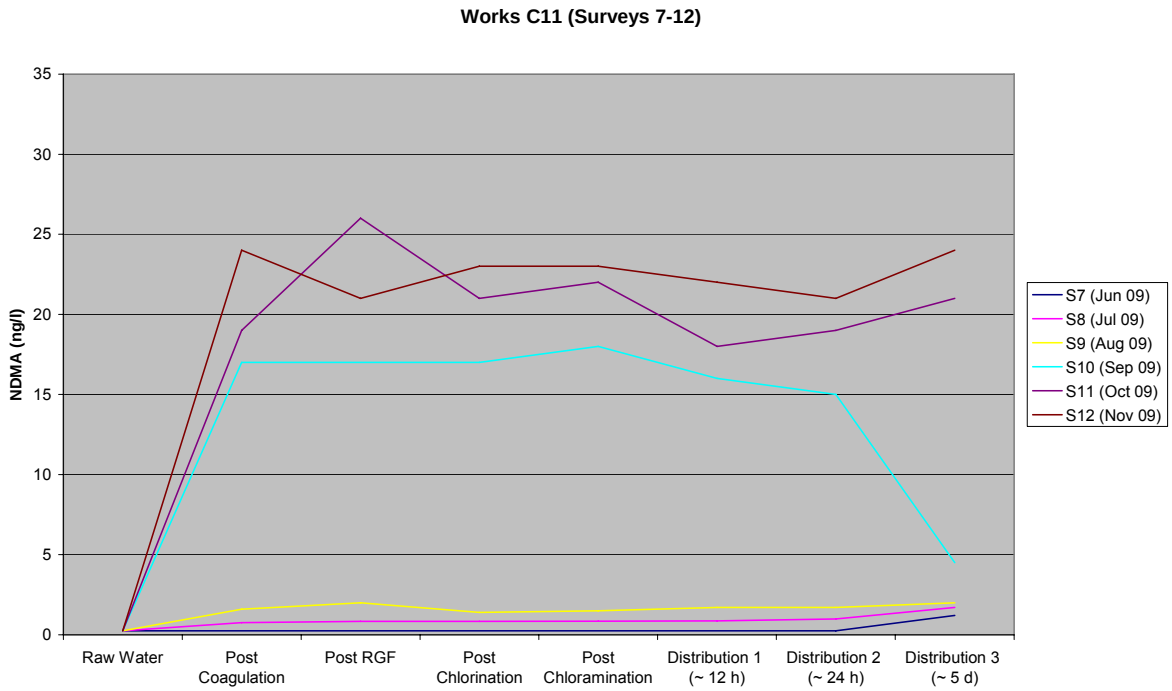

Figure 5.2 NDMA in treatment and distribution (Works C11, Surveys 7-12)

NDMA concentrations measured throughout the survey are summarised in Table 5.1.

Table 5.1 Summary of NDMA concentrations (ng/l): Works C11

Sample	Surveys 1-9: Range (mean)	Surveys 10-12: Range (mean)
Raw water	<0.48 (<0.48)	<0.48 (<0.48)
Post-coagulation	<0.48-1.6 (0.64)	17-24 (20)
Post-RGF	<0.48-2.0 (0.67)	17-26 (21)
Post-chlorination	<0.48-1.4 (0.57)	17-23 (20)
Post-chloramination	<0.48-1.5 (0.60)	18-23 (21)
Distribution 1 (Retention ~12 h)	<0.48-1.7 (0.67)	17-22 (19)
Distribution 2 (Retention ~24 h)	<0.48-1.7 (0.97)	15-21 (18)
Distribution 3 (Retention ~120 h)	1.2-2.1 (1.69)	4.7-24 (17)

Note:
1. In calculating the mean NDMA concentration, data values less than the analytical limit of detection (0.48 ng/l) have been treated as 0.24 ng/l. Where the calculated mean was less than 0.48 ng/l, the result has been reported as <0.48 ng/l.

- From November 2008 to August 2009 (Surveys 1-9), NDMA was detected in treatment up to 2.0 ng/l. This concentration of NDMA could be associated with levels of NDMA in the coagulant of up to about 15 µg/l (assuming a coagulant dose of about 13 mg Fe/l). NDMA in distribution increased with retention time, up to 2.1 ng/l after 5 days, possibly indicating a slow rate of NDMA formation or formation enhanced by factors in distribution.

- From September to November 2009 (Surveys 10-12), NDMA concentrations in treatment and distribution increased dramatically, up to 26 ng/l and 24 ng/l, respectively.

- The ferric coagulant sampled from this works in October 2009 contained 386 µg NDMA/l (see Table 4.5), equivalent to 1.91 ng NDMA/mg Fe. The coagulant dose used in September to November (11.0-12.0 mg Fe/l) would have increased the concentration of NDMA by 21-23 ng/l, comparable to the measured concentration in the post-coagulation samples.

- The reduction in the concentration of NDMA in the coagulant subsequent to the treatment works survey is described in Section 4.

- Works C11 switched from Coagulant A1 to Coagulant B2 during 2010/2011.

5.2.2 Works C12

In the 2008 Defra/DWI study, low concentrations of NDMA were detected throughout treatment and in distribution. This was as a result of a relatively high concentration of NDMA in recovered water (30-40 ng/l) being recycled to the head of the works. The water recovery process included dosing of Coagulant A1 in excess of 100 mg Fe/l.

In the present study, NDMA was not detected in raw water but was detected in treatment and distribution as illustrated in Figures 5.3 and 5.4.

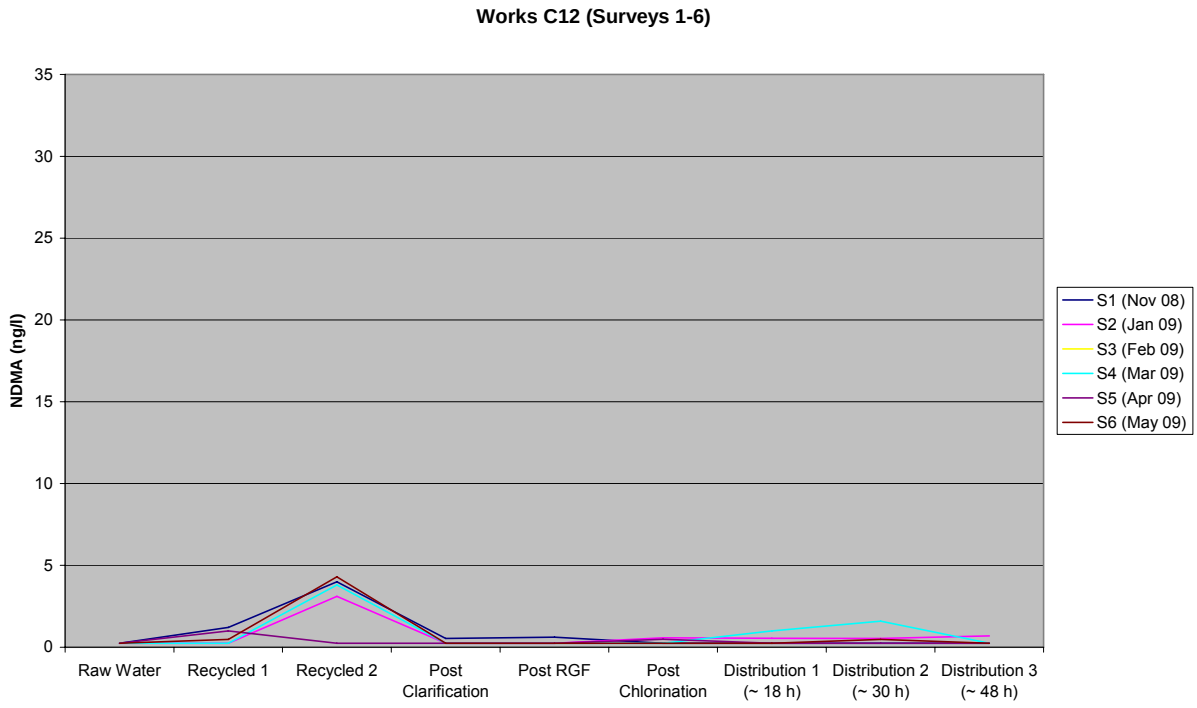

Figure 5.3 NDMA in treatment and distribution (Works C12, Surveys 1-6)

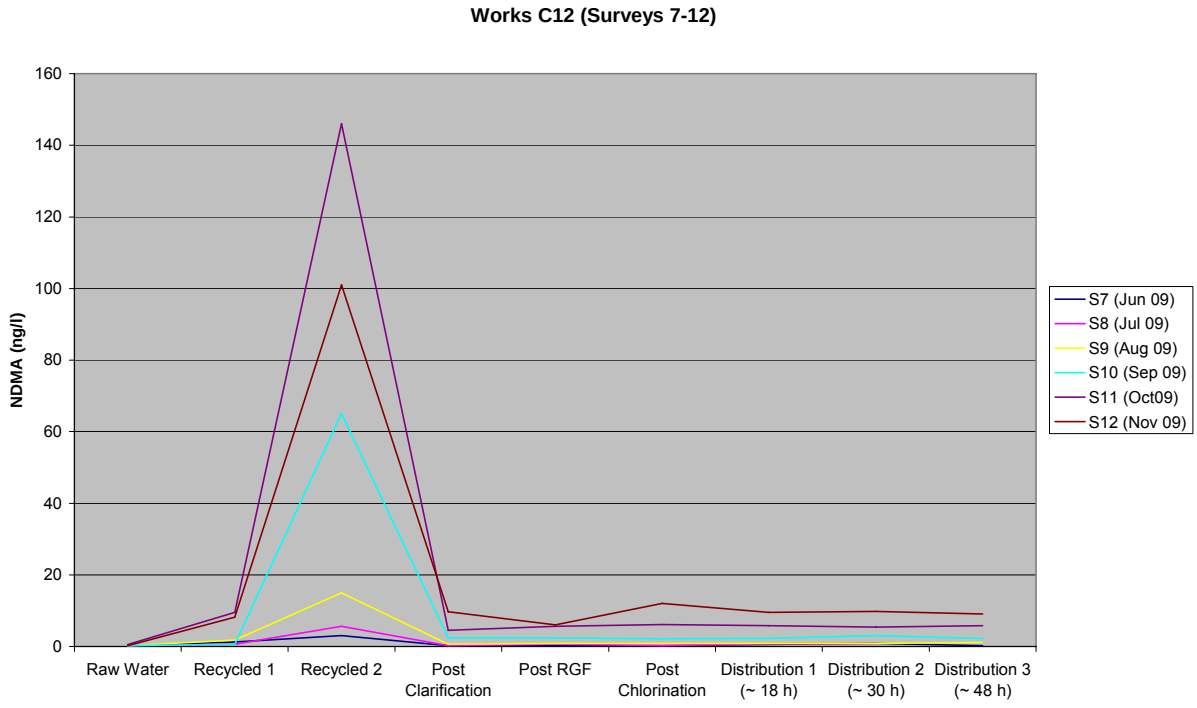

Figure 5.4 NDMA in treatment and distribution (Works C12, Surveys 7-12)

NDMA concentrations measured throughout the survey are summarised in Table 5.2.

Table 5.2 Summary of NDMA concentrations (ng/l): Works C12

Sample	Surveys 1-9: Range (mean)	Surveys 10-12: Range (mean)
Raw water	<0.48 (<0.48)	<0.48 (<0.48)
Recycled water 1	<0.48-1.8 (0.93)	2.97-9.5 (6.89)
Recycled water 2	<0.48-15 (4.83)	68-146 (105)
Post-clarification	<0.48-0.59 (<0.48)	2.25-9.7 (5.48)
Post-RGF	<0.48-0.84 (<0.48)	2.55-6.0 (4.72)
Post-chlorination	<0.48-0.82 (<0.48)	2.25-12 (6.78)
Distribution 1 (Retention ~18 h)	<0.48-0.82 (0.50)	2.9-9.5 (6.07)
Distribution 2 (Retention ~30 h)	<0.48-1.1 (0.64)	3.0-9.8 (6.07)
Distribution 3 (Retention ~48 h)	<0.48-1.1 (<0.48)	2.2-9.1 (5.70)

Note:
1. In calculating the mean NDMA concentration, data values less than the analytical limit of detection (0.48 ng/l) have been treated as 0.24 ng/l. Where the calculated mean was less than 0.48 ng/l, the result has been reported as <0.48 ng/l.

- From November 2008 to August 2009 (Surveys 1-9), NDMA was detected in the recycled water at concentrations up to 15 ng/l. This observation was not unexpected as the dose of ferric coagulant used in the water recovery process exceeded 100 mg Fe/l. Concentrations in water treatment downstream of the recycle point measured up to 0.84 ng/l as a result of the dilution of the recycled water. Concentrations in distribution were generally comparable with concentrations measured in treatment and showed no significant increase with retention time.

- From September to November 2009 (Surveys 10-12), NDMA concentrations in the recycled water increased dramatically, up to 146 ng/l. Concentrations in treatment and distribution showed corresponding increases, up to 12 ng/l and 9.8 ng/l, respectively.

- The ferric coagulant sampled from this works in November 2009 contained 245 µg NDMA/l (see Table 4.5), equivalent to 1.22 ng NDMA/mg Fe. Assuming a dose in the water recovery process of 100 mg Fe/l, the resultant increase in the concentration of NDMA in recycled water would be 122 ng/l, comparable to the measured concentrations.

- The reduction in the concentration of NDMA in the coagulant subsequent to the treatment works survey is described in Section 4. By July 2010, concentrations of NDMA in post-clarification water had reduced to 1 ng/l or less (see Table 4.6).

- Works C12 switched from Coagulant A1 to Coagulant B2 in May 2010.

5.2.3 Works C16

In the 2008 Defra/DWI study, NDMA was detected in one post-coagulation sample but not in two earlier final water samples.

In the present study, NDMA was detected in treatment as illustrated in Figures 5.5 and 5.6.

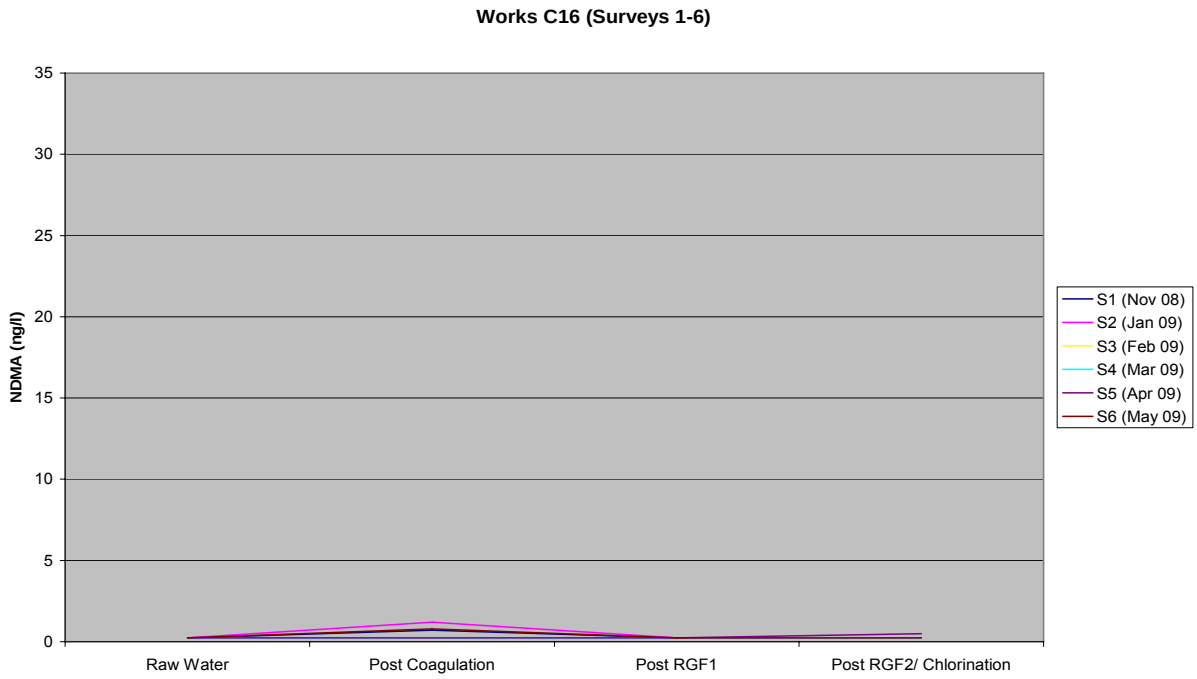

Figure 5.5 NDMA in treatment and distribution (Works C16, Surveys 1-6)

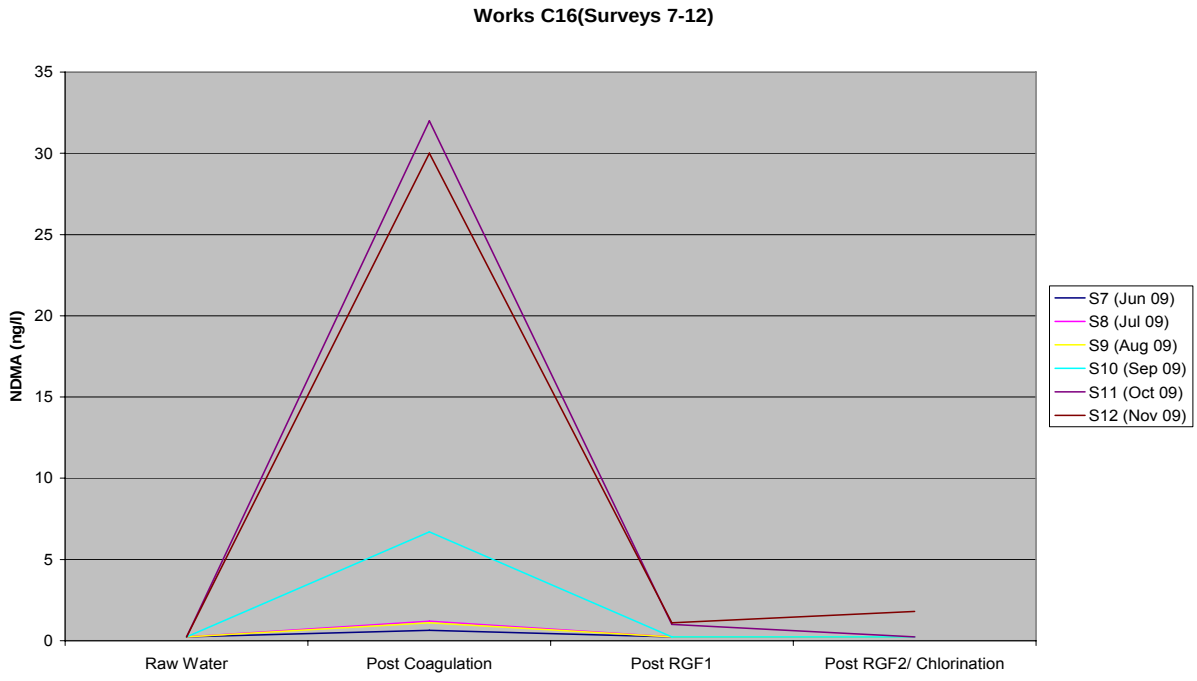

Figure 5.6 NDMA in treatment and distribution (Works C16, Surveys 7-12)

NDMA concentrations measured throughout the survey are summarised in Table 5.3.

Table 5.3 Summary of NDMA concentrations (ng/l): Works C16

Sample	Surveys 1-9: Range (mean)	Surveys 10-12: Range (mean)
Raw water	<0.48 (<0.48)	<0.48 (<0.48)
Post-coagulation	<0.48-1.2 (0.82)	6.7-32 (22.9)
Post-RGF1	<0.48-0.54 (<0.48)	<0.48-1.1 (0.78)
Post-RGF2 / final water	<0.48 (<0.48)	<0.48-1.8 (0.76)

Note:
1. In calculating the mean NDMA concentration, data values less than the analytical limit of detection (0.48 ng/l) have been treated as 0.24 ng/l. Where the calculated mean was less than 0.48 ng/l, the result has been reported as <0.48 ng/l.

- From November 2008 to August 2009 (Surveys 1-9), NDMA was not detected in raw water but in post-coagulation and post-RGF1 samples up to 1.2 ng/l and 0.54 ng/l, respectively.
- From September to November 2009 (Surveys 10-12), NDMA concentrations in post-coagulation samples increased dramatically up to 32 ng/l. Coagulant A1 used at this works was not analysed for NDMA at this time but it is highly probable that the increase in concentration of NDMA in Surveys 10-12 was attributed to this source.
- From September to November 2009 (Surveys 10-12), NDMA concentrations in post-RGF1 samples were reduced to 1.1 ng/l or less, indicating significant removal across the rapid gravity filters. This observation suggested the possibility of a biological removal mechanism (see Section 6.2.1).
- Assuming a ferric coagulant containing 316 µg NDMA/l (the mean of values for Works C11 and C12 in October/November 2009 (see Table 4.5)), equivalent to 1.56 ng NDMA/mg Fe, the dose in September to November (14.0-15.7 mg Fe/l) would have increased the concentration of NDMA by 21.8-24.5 ng/l, comparable to the measured post-coagulation samples.
- The reduction in the concentration of NDMA in the coagulant subsequent to the treatment works survey is described in Section 4.
- Works C16 switched from Coagulant A1 to Coagulant B2 during 2010/2011.

5.2.4 Works D17

NDMA was not detected at Works D17 in the 2008 Defra/DWI study.

In the present study, NDMA was detected at low concentrations in some raw water and post-coagulation samples, increasing as a result of subsequent ozonation but then decreasing as a result of RGF and GAC, as illustrated in Figures 5.7 and 5.8.

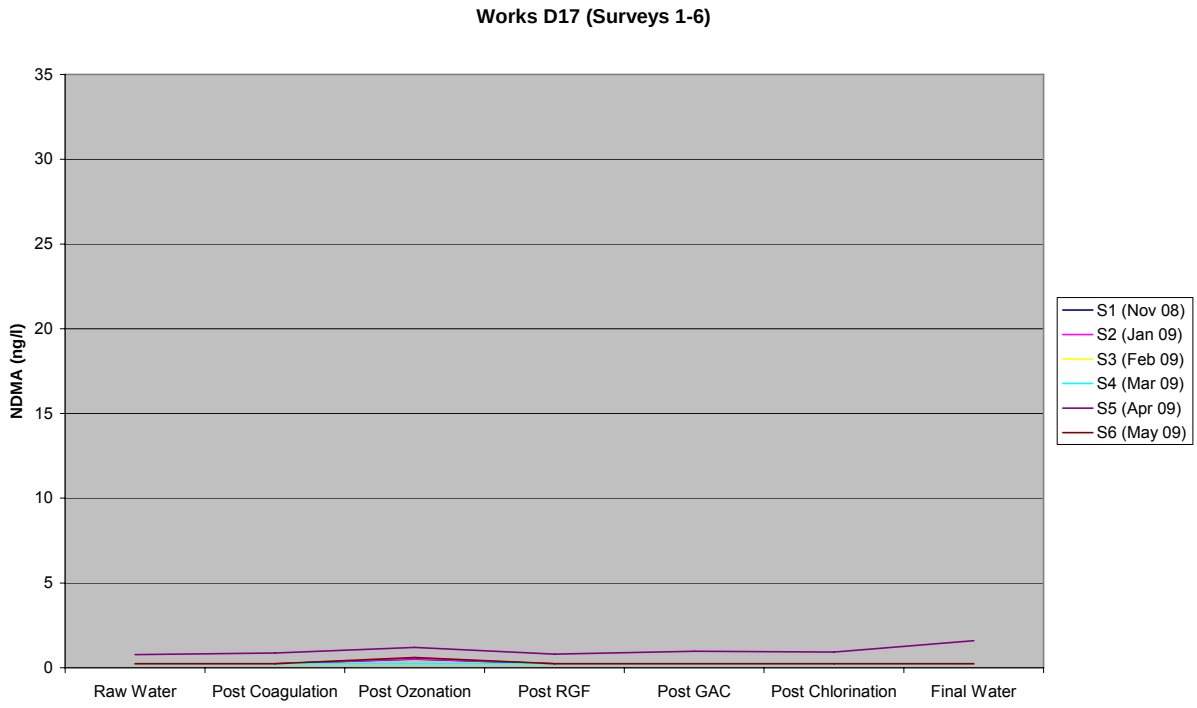

Figure 5.7 NDMA in treatment and distribution (Works D17, Surveys 1-6)

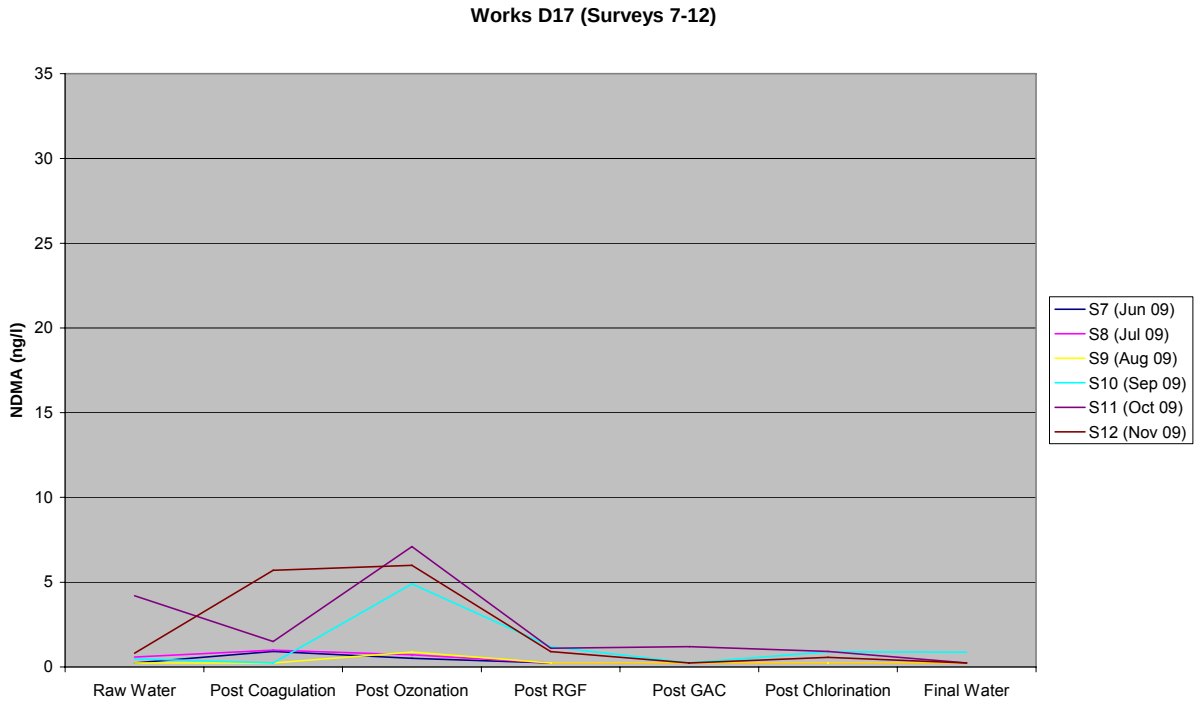

Figure 5.8 NDMA in treatment and distribution (Works D17, Surveys 7-12)

NDMA concentrations measured throughout the survey are summarised in Table 5.4.

Table 5.4 Summary of NDMA concentrations (ng/l): Works D17

Sample	Surveys 1-9: Range (mean)	Surveys 10-12: Range (mean)
Raw water	<0.48-0.78 (<0.48)	0.48-4.2 (1.83)
Post-coagulation	<0.48-0.99 (0.50)	<0.48-5.7 (2.48)
Post-ozonation	<0.48-1.2 (0.65)	4.9-7.1 (6.00)
Post-RGF	<0.48-0.80 (<0.48)	0.91-1.2 (1.07)
Post-GAC	<0.48-0.98 (<0.48)	<0.48-1.2 (0.56)
Post-chlorination	<0.48-0.93 (<0.48)	0.57-0.92 (0.79)
Final water	<0.48-1.6 (<0.48)	<0.48-0.87 (<0.48)

Note:
1. In calculating the mean NDMA concentration, data values less than the analytical limit of detection (0.48 ng/l) have been treated as 0.24 ng/l. Where the calculated mean was less than 0.48 ng/l, the result has been reported as <0.48 ng/l.

- From November 2008 to August 2009 (Surveys 1-9), NDMA was detected in two raw water samples (up to 0.78 ng/l), in three post-coagulation samples (up to 0.99 ng/l) and in seven post-ozonation samples (up to 1.2 ng/l). Generally, NDMA was not detected in samples taken downstream of the subsequent RGF stage.

- From September 2009 to November 2009 (Surveys 10-12), NDMA concentrations in post-coagulation and post-ozonation samples increased, up to 5.7 and 7.1 ng/l, respectively. Again there was a significant reduction in concentration in samples taken downstream of the subsequent RGF stage (1.2 ng/l or less). Analysis of the ferric coagulant used at this works (see Table 4.5) showed an NDMA concentration of 283 µg/l and the increase in concentration of NDMA was again principally attributed to this source.

- The ferric coagulant sampled from this works in November 2009 contained a mean concentration of 258 µg NDMA/l (see Table 4.5), equivalent to 1.28 ng NDMA/mg Fe. The coagulant dosed in September to November (5.5 mg Fe/l) would have increased the concentration of NDMA by 7 ng/l, comparable to the measured post-coagulation samples.

5.2.5 Works D18

In the 2008 Defra/DWI study, NDMA was detected at Works D18 throughout treatment and in distribution.

In the present study, NDMA was detected at low concentrations in some raw water and post-coagulation samples, and in fewer samples and at lower concentrations following RGF, as illustrated in Figures 5.9 and 5.10.

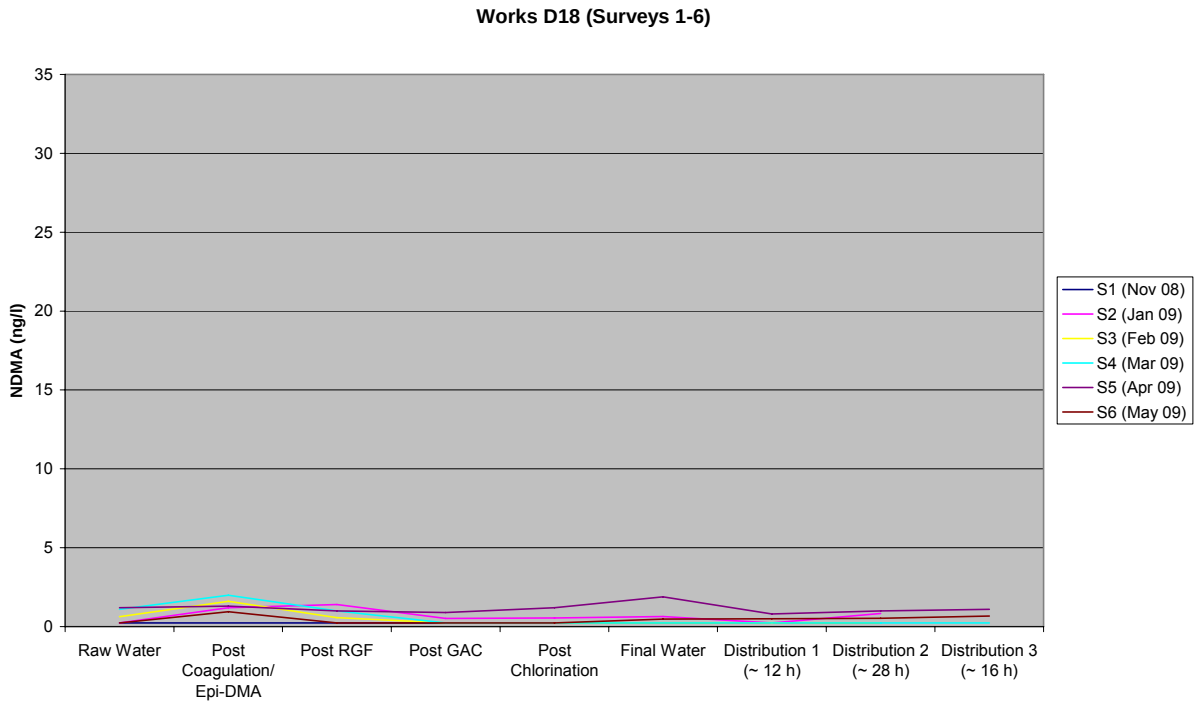

Figure 5.9 NDMA in treatment and distribution (Works D18, Surveys 1-6)

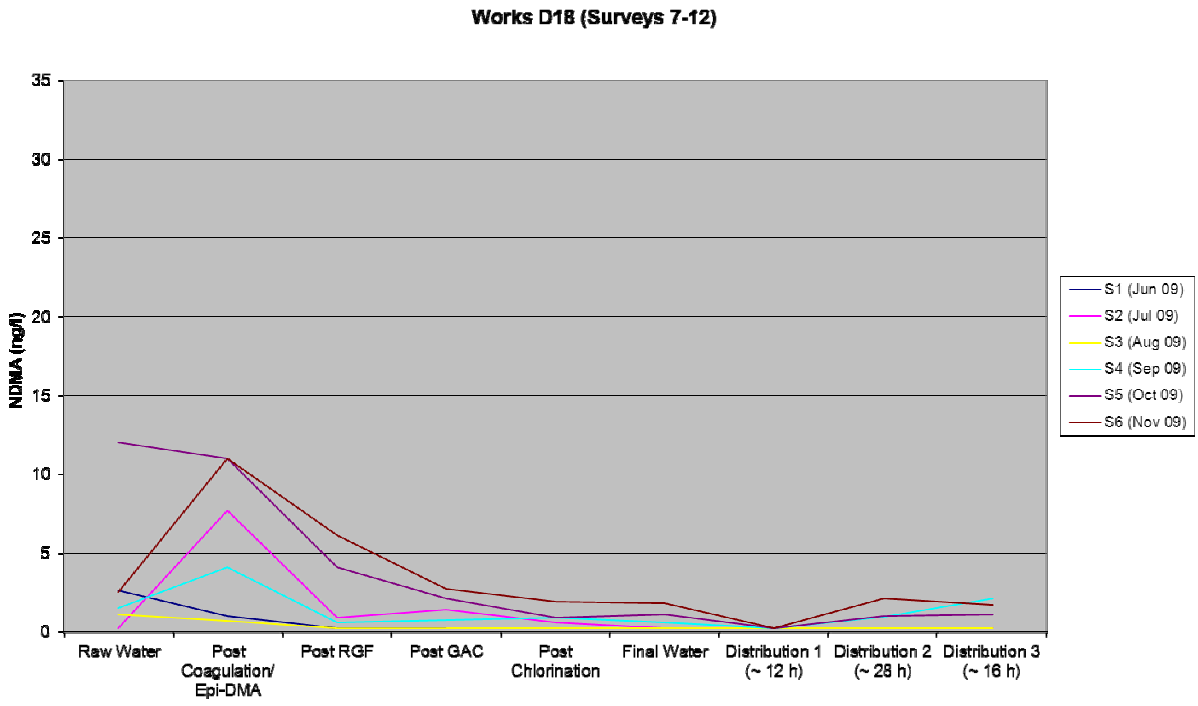

Figure 5.10 NDMA in treatment and distribution (Works D18, Surveys 7-12)

NDMA concentrations measured throughout the survey are summarised in Table 5.5.

Table 5.5 Summary of NDMA concentrations (ng/l): Works D18

Sample	Surveys 1-9: Range (mean)	Surveys 10-12: Range (mean)
Raw water	<0.48-2.6 (0.81)	1.5-12 (5.33)
Post-coagulation / epi-DMA	<0.48-7.7 (1.84)	4.1-11 (8.70)
Post-RGF	<0.48-1.4 (0.61)	0.58-6.1 (3.59)
Post-GAC	<0.48-1.4 (0.50)	0.74-2.7 (1.85)
Post-chlorination	<0.48-1.2 (<0.48)	0.88-1.9 (1.23)
Final water	<0.48-1.9 (0.53)	0.58-1.8 (1.16)
Distribution 1 (Retention ~12 h)	<0.48-0.81 (<0.48)	<0.48 (<0.48)
Distribution 2 (Retention ~28 h)	<0.48-1.0 (<0.48)	0.96-2.1 (1.34)
Distribution 3 (Retention ~16 h)	<0.48-1.1 (0.50)	1.1-2.1 (1.63)

Note:
1. In calculating the mean NDMA concentration, data values less than the analytical limit of detection (0.48 ng/l) have been treated as 0.24 ng/l. Where the calculated mean was less than 0.48 ng/l, the result has been reported as <0.48 ng/l.

- From November 2008-August 2009 (Surveys 1-9), NDMA was detected in five raw water samples (up to 2.6 ng/l), in eight post-coagulation samples (up to 7.7 ng/l) and in five post-RGF samples (up to 1.4 ng/l). NDMA was detected in a small number of samples taken downstream of the RGF stage but at concentrations typically less than 1 ng/l.

- From September 2009 to November 2009 (Surveys 10-12), NDMA concentrations in the raw water increased up to 12 ng/l and in post-coagulation samples up to 11 ng/l. Although this increase in NDMA in the raw water coincided with the increase in NDMA in the coagulant, there was no recycling of recovered water at this works nor any known use of the coagulant in the water source. There was a significant reduction in NDMA concentrations in post-RGF (0.58-6.1 ng/l) and post-GAC (0.74-2.7 ng/l) samples. NDMA was detected in most samples following GAC and in distribution at lower concentrations. There was an indication that NDMA increased in distribution (with a retention time up to 28 h) up to 2.1 ng/l. Analysis of the ferric coagulant used at this works (see Table 4.5) showed up to 312 µg NDMA/l and the increase in concentration of NDMA in water samples was again principally attributed to this source, although the frequent occurrence in the raw water was unexplained.

- The ferric coagulant sampled from this works in November 2009 contained a mean concentration of 300 µg NDMA/l (see Table 4.5), equivalent to 1.49 ng NDMA/mg Fe. The coagulant dosed in September-November (7.5-8.0 mg Fe/l) would have increased the concentration of NDMA by about 11.2-11.9 ng/l, generally comparable to the measured post-coagulation samples.

5.2.6 Works H5

In the 2008 Defra/DWI study, NDMA was not detected at Works H5.

In the present study, NDMA was detected at low concentrations in most raw water samples and generally throughout water treatment and in distribution.

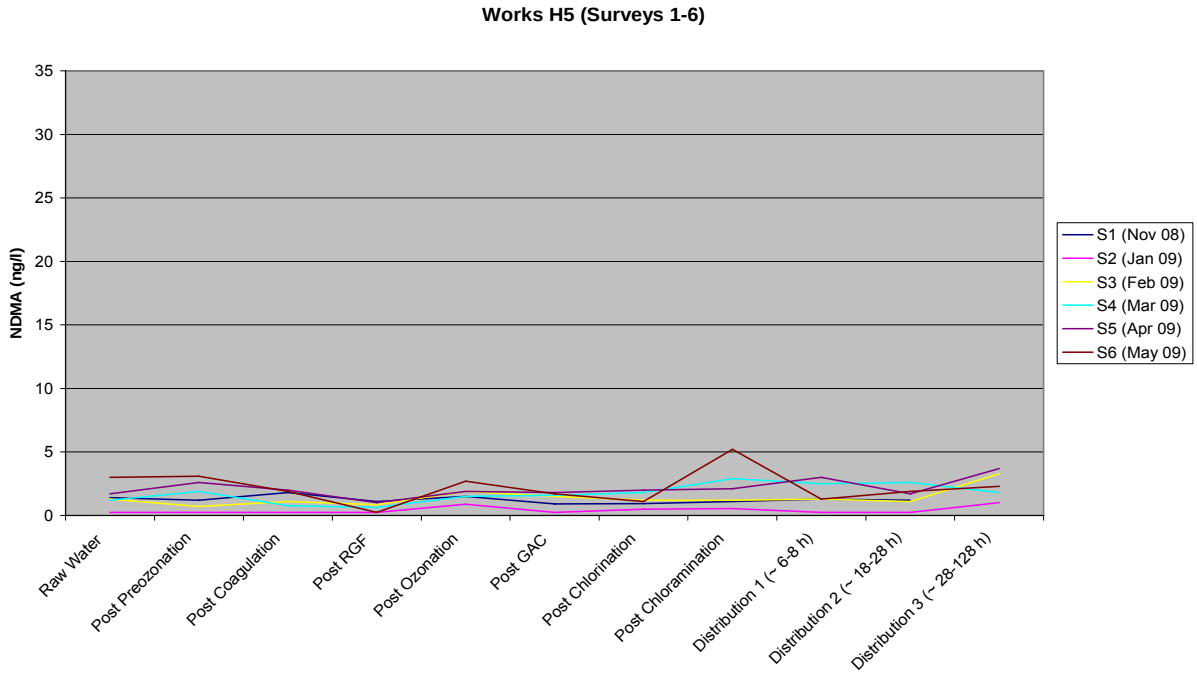

Figure 5.11 NDMA in treatment and distribution (Works H5, Surveys 1-6)

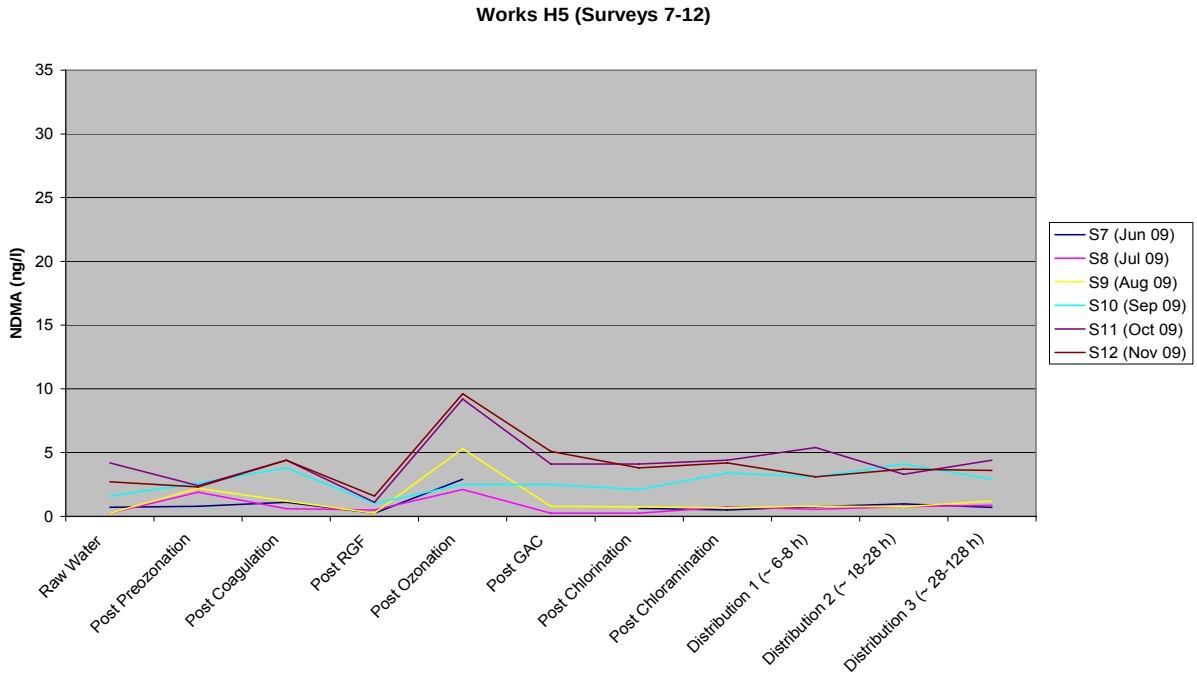

Figure 5.12 NDMA in treatment and distribution (Works H5, Surveys 7-12)

NDMA concentrations measured throughout the survey are summarised in Table 5.6.

Table 5.6 Summary of NDMA concentrations (ng/l): Works H5

Sample	Surveys 1-9: Range (mean)	Surveys 10-12: Range (mean)
Raw water	<0.48-3.0 (1.11)	1.6-4.2 (2.83)
Post-pre-ozonation	<0.48-3.1 (1.63)	2.3-2.6 (2.43)
Post-coagulation	<0.48-2.0 (1.19)	3.8-4.4 (4.20)
Post-RGF	<0.48-1.1 (0.56)	1.0-1.6 (1.23)
Post-ozonation	0.89-5.3 (2.30)	2.5-9.6 (7.10)
Post-GAC	<0.48-1.8 (1.10)	2.5-5.1 (3.90)
Post-chlorination	<0.48-2.0 (1.01)	2.1-4.1 (3.33)
Post-chloramination	0.50-5.2 (1.66)	3.4-4.4 (4.00)
Distribution 1 Retention time ~6-8 h	<0.48-3.0 (1.31)	3.1-5.4 (3.87)
Distribution 2 Retention time ~18-28 h	<0.48-2.6 (1.25)	3.3-4.1 (3.70)
Distribution 3 Retention time ~28-128 h	0.69-3.7 (1.86)	2.9-4.4 (3.63)

Note:
1. In calculating the mean NDMA concentration, data values less than the analytical limit of detection (0.48 ng/l) have been treated as 0.24 ng/l. Where the calculated mean was less than 0.48 ng/l, the result has been reported as <0.48 ng/l.

- From November 2008 to August 2009 (Surveys 1-9), NDMA was detected in six raw water samples (up to 3.0 ng/l) and in eight samples taken after pre-ozonation (up to 3.1 ng/l) and post-coagulation (up to 2.0 ng/l). NDMA appeared to be removed across RGF and was detected in only five samples (up to 1.1 ng/l) but was detected after ozonation in all samples (up to 5.3 ng/l). NDMA appeared to be removed by GAC and was detected in six (out of eight) samples (up to 1.8 ng/l), post-chlorination (8 samples, up to 2.0 ng/l), post-chloramination (9 samples, up to 5.2 ng/l). NDMA was generally detected in distribution (up to 3.7 ng/l) but showed no real evidence that concentration increased with retention time.

- From September to November 2009 (Surveys 10-12), NDMA was detected in all samples; in the raw water (up to 4.2 ng/l), post pre-ozonation (up to 2.6 ng/l), post-coagulation (up to 4.4 ng/l), post-RGF (up to 1.6 ng/l), post-ozonation (up to 9.6 ng/l), post-GAC (up to 5.1 ng/l), post-chlorination (up to 4.1 ng/l), post-chloramination (up to 4.4 ng/l), and in distribution (up to 5.4 ng/l).

- The ferric coagulant sampled from this works in November and December 2009 contained a mean concentration of 326 µg NDMA/l (see Table 4.5), equivalent to 1.61 ng NDMA/mg Fe. The coagulant dosed in September to November (3.4 mg Fe/l) would have increased the concentration of NDMA by about 5.5 ng/l, generally comparable to the measured post-coagulation samples.

5.3 Operating Data

Key operating data measured at each works during the water treatment surveys are shown in Appendix D.

5.4 Raw Water Quality

The seasonal variation in raw water quality at the six selected treatment works is shown in Appendix D.

6. LABORATORY STUDIES

6.1 Introduction

Laboratory studies were carried out to investigate formation and removal mechanisms of NDMA and nitrosamines. The results of the various studies are summarised below; full details are presented in Appendix E.

6.2 NDMA Formation and Removal

6.2.1 NDMA removal by biological filtration

It was noted at several works throughout the treatment works survey that NDMA concentrations were reduced across RGFs following coagulation. This was particularly evident at Works C16 in Surveys 10-12 (September-November 2009) when the NDMA concentration in post-coagulated water was reduced from 6.7-32.0 ng/l to less than 1.1 ng/l in post-RGF1 water.

In order to confirm this possible biological removal mechanism, samples of media were taken from both stages of RGFs at Works C16 (RGF1 and RGF2 (manganese contactors)) and mixed with samples of Works C16 post-coagulated clarified water and nitrosamine-spiked tap water.

Due to difficulties with the analytical method for nitrosamines at the time, only indicative results were available for this test. Indicative results of the tests showed 35.1% and 94.6% removals of NDMA from Works C16 clarified water due to contact with RGF1 and RGF2 media, respectively. Indicative results of the tests on spiked tap water showed 32.3% (RGF1) and 82.5% (RGF2) removal of NDMA, assuming 10 ng NDMA/l in the spiked water (as calculated). However, analysis of the spiked tap water indicated only 5.11 ng NDMA/l, in which case the results indicate an increase in NDMA concentration due to contact with RGF1 media and a smaller removal (65.8%) due to contact with RGF2 media.

6.2.2 NDMA formation in distribution (I): Chloraminated water

Results from the treatment works survey at Works C11 indicated the possible formation of NDMA in distribution, increasing with nominal retention times up to 5 days. A simple test was devised to simulate retention in distribution. A sample of chloraminated water from Works C11 was stored in the dark at temperatures of 5, 10 and 20°C, and sampled for NDMA analysis after 5, 10, 15 and 25 days.

NDMA was not detected in chloraminated water sampled from Works C11 but was present in distribution samples taken at the same time at 1.4 ng/l and 2.1 ng/l (nominal retention times of 24 hours and 5 days, respectively (see Table D6)).

Results of the laboratory test (see Table E2) showed that this observation was not replicated in the laboratory simulation, although there was an indication that NDMA was formed after 10-

15 days storage (0.50-0.78 ng/l) but was then degraded. There was no noticeable effect of temperature.

6.2.3 NDMA formation in distribution (II): Chlorinated and chloraminated waters

A second test was devised to further simulate retention in distribution of chloraminated water (see Section 6.2.2) and also to simulate retention of chlorinated water for comparison. The test with chlorinated water acted as a control as to whether formation of NDMA was enhanced or promoted by chloramination. Samples of chlorinated water (sampled before dosing of ammonium sulphate) and chloraminated water from Works C11 were stored in the dark at 10°C and sampled for NDMA analysis after 5 and 10 days.

NDMA was not detected in either of the chlorinated or chloraminated samples from Works C11 but was present at the time of sampling at 1.2 ng/l in a distribution sample with a nominal retention time of 5 days (see Table D7):

Results of the laboratory test (see Table E3) showed that this observation was not replicated in the laboratory simulation and NDMA was not detected in any sample of stored water.

6.2.4 NDMA formation in distribution (III): Chlorinated and chloraminated waters

A third test was devised to further simulate retention in distribution of chlorinated and chloraminated waters (see Section 6.2.3), and also to simulate the extended retention of samples of water taken from distribution (with nominal retention times of 24 h and 5 days). The test with the samples from distribution allowed a comparison between disinfected waters taken from the works and subsequently stored, with waters that had been exposed to conditions in a real distribution network. Samples of chlorinated and chloraminated waters from Works C11 and from the distribution network were stored in the dark at 10°C and sampled for NDMA analysis after 5 and 10 days.

NDMA was detected in all samples from Works C11 and distribution (see Table D8):

Results of the laboratory test (see Table E4) showed that NDMA increased (up to 1.4 ng/l) when both the chlorinated and chloraminated samples were stored for 10 days. There was no significant change in NDMA concentration in the 24-h distribution sample whereas the 5-day distribution sample showed a reduction in NDMA concentration after 5-10 days storage.

6.3 Nitrosamine Formation and Removal

6.3.1 Tests on upland water

A series of tests was carried out to investigate the formation and removal of a range of nitrosamine compounds by water treatment processes simulated at laboratory scale:

- Pre-ozonation
- Sedimentation/dissolved air flotation (of water coagulated with ferric sulphate /polyDADMAC)

- Ozonation (of coagulated water)
- GAC adsorption (of coagulated water)
- Chlorination/chloramination (of coagulated water)

Tests were carried out on highly coloured upland surface water (ex. Works C12) as indicated by the flow schematic shown in Figure 6.1. Analysis was carried out for nine nitrosamines: NDMA, NMEA, NDEA, NPYR, NDPA, NPIP, NDBA, NMOR and NDPHA (N-nitrosodiphenylamine).

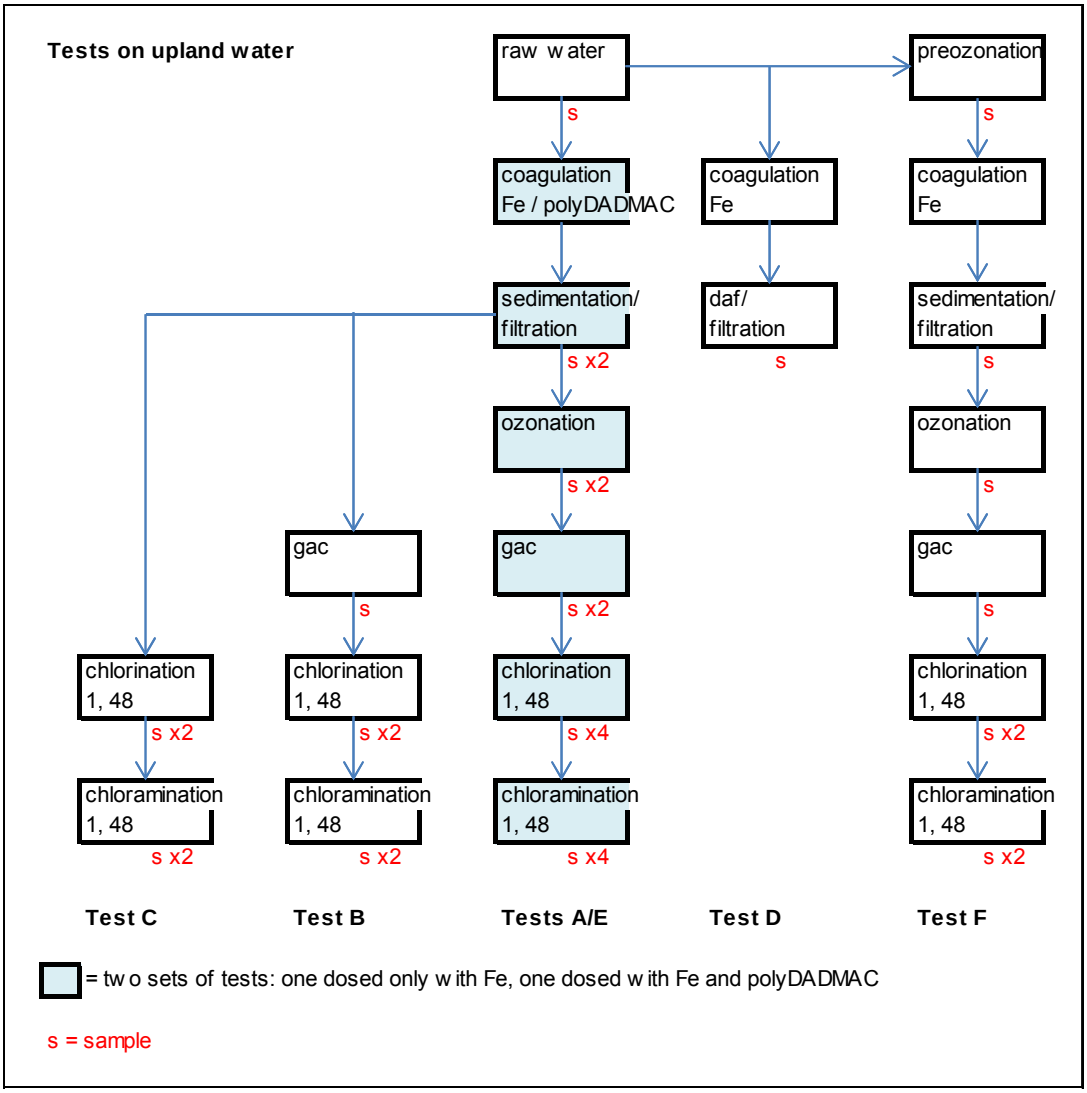

Figure 6.1 Nitrosamine laboratory tests: Tests on upland water

The analysis for nitrosamines proved problematic and the method required considerable development. NDMA and NMEA were subsequently measured by GCMS and the other nitrosamines by LCMSMS (see Appendix B).

Results

Samples of the ferric sulphate (Coagulant B2) and polyDADMAC (Floquat® FL4440) used in the tests were analysed for nitrosamines. For comparison to Coagulant B2, ferric coagulants known to contain high and low concentrations of NDMA - Coagulant A1 and Coagulant C2, respectively - were also analysed. Results are shown in Table 6.1.

Table 6.1 Nitrosamine analysis: Diluted coagulants and polyDADMAC

Chemical[1]	Nitrosamine (ng/l)								
	NDMA	NMEA	NDEA	NPYR	NDPA	NPIP	NDBA	NMOR	NDPHA
Coagulant B2[2]	-	-	<3.1	<2.3	<0.8	<2.6	<2.6	45.8	<3.3
Coagulant C2	1.52	<0.5	<3.1	<2.3	<0.8	<2.6	<2.6	<1.5	<3.3
Coagulant A1	351	<0.5	<3.1	<2.3	<0.8	<2.6	<2.6	189	<3.3
PolyDADMAC[2]	-	-	<3.1	<2.3	0.86	<2.6	<2.6	<1.5	<3.3

Notes:
1. All chemicals diluted 1:1000 with distilled water.
2. Coagulant B2 and polyDADMAC indicative results only; data from method development trials.

Table 6.1 shows that the Coagulant B2 used in the tests contained a significant concentration of NMOR (45.8 µg/l). Due to a failure of the analytical equipment, NDMA and NMEA were not determined but it is highly probable that the coagulant was also contaminated with NDMA (the previous samples of Coagulant B2, ex. Works C12, contained 27-29 µg NDMA/l and a value in this order is consistent with the concentrations of NMOR measured in the coagulant and in the coagulation/sedimentation/filtration (Test A) sample). The polyDADMAC contained no significant concentrations of nitrosamines, although again NDMA and NMEA were not determined.

Coagulant A1 contained high concentrations of NDMA (351 µg/l) and NMOR (189 µg/l) but no other nitrosamines. Waters dosed with this coagulant would contain measurable concentrations of both NDMA and NMOR, unless removed in treatment. Coagulant C2 contained only 1.52 µg NDMA/l which would not produce a measurable concentration in dosed water.

Results for the laboratory tests on the upland water are presented in full in Appendix E. Only NDMA and NMOR were detected in samples and these results are shown in Table 6.2.

Table 6.2 Nitrosamine (NDMA and NMOR) analysis: Upland water ex. Works C12

Treatment / sample	Nitrosamine (ng/l)	
	NDMA	NMOR
Raw water	<0.48	2.89
Test A		
Coagulation(Fe)/Sedimentation/Filtration	2.53	6.49
Coagulation(Fe)/Sedimentation/Filtration/Ozonation	0.95	1.69
Coagulation(Fe)/Sedimentation/Filtration/Ozonation/GAC	0.93	<1.5
Coagulation(Fe)/Sedimentation/Filtration/Ozonation/GAC/Chlorination 1 h	<0.48	<1.5
Coagulation(Fe)/Sedimentation/Filtration/Ozonation/GAC/Chlorination 48 h	0.54	<1.5
Coagulation(Fe)/Sedimentation/Filtration/Ozonation/GAC/Chloramination 1 h	<0.48	<1.5
Coagulation(Fe)/Sedimentation/Filtration/Ozonation/GAC/Chloramination 48 h	0.54	<1.5
Test B		
Coagulation(Fe)/Sedimentation/Filtration/GAC	0.51	<1.5
Coagulation(Fe)/Sedimentation/Filtration/GAC/Chlorination 1 h	0.65	<1.5
Coagulation(Fe)/Sedimentation/Filtration/GAC/Chlorination 48 h	1.01	<1.5
Coagulation(Fe)/Sedimentation/Filtration/GAC/Chloramination 1 h	0.77	<1.5
Coagulation(Fe)/Sedimentation/Filtration/GAC/Chloramination 48 h	1.13	<1.5
Test C		
Coagulation(Fe)/Sedimentation/Filtration/Chlorination 1 h	2.31	4.19
Coagulation(Fe)/Sedimentation/Filtration/Chlorination 48 h	2.11	4.85
Coagulation(Fe)/Sedimentation/Filtration/Chloramination 1 h	1.73	4.09
Coagulation(Fe)/Sedimentation/Filtration/Chloramination 48 h	2.18	4.12
Test D		
Coagulation(Fe)/DAF/Filtration	6.31	25.9
Test E		
Coagulation(Fe+polyDADMAC)/Sedimentation/Filtration	1.27	3.04
Coagulation(Fe+polyDADMAC)/Sedimentation/Filtration/Ozonation	1.51	3.17
Coagulation(Fe+polyDADMAC)/Sedimentation/Filtration/Ozonation/GAC	<0.48	<1.5
Coagulation(Fe+polyDADMAC)/Sedimentation/Filtration/Ozonation/GAC/ Chlorination 1 h	<0.48	<1.5
Coagulation(Fe+polyDADMAC)/Sedimentation/Filtration/Ozonation/GAC/ Chlorination 48 h	0.53	<1.5
Coagulation(Fe+polyDADMAC)/Sedimentation/Filtration/Ozonation/GAC/ Chloramination 1 h	<0.48	<1.5
Coagulation(Fe+polyDADMAC)/Sedimentation/Filtration/Ozonation/GAC/ Chloramination 48 h	0.48	<1.5
Test F		
Preozonated raw water	<0.48	<1.5
Preozonation/Coagulation(Fe)/Sedimentation/Filtration	2.13	2.94
Preozonation/Coagulation(Fe)/Sedimentation/Filtration/Ozonation	1.18	3.07
Preozonation/Coagulation(Fe)/Sedimentation/Filtration/Ozonation/GAC	<0.48	<1.5
Preozonation/Coagulation(Fe)/Sedimentation/Filtration/Ozonation/GAC/ Chlorination 1 h	<0.48	<1.5
Preozonation/Coagulation(Fe)/Sedimentation/Filtration/Ozonation/GAC/ Chlorination 48 h	0.72	<1.5
Preozonation/Coagulation(Fe)/Sedimentation/Filtration/Ozonation/GAC/ Chloramination 1 h	<0.48	<1.5
Preozonation/Coagulation(Fe)/Sedimentation/Filtration/Ozonation/GAC/ Chloramination 48 h	0.71	<1.5

Table 6.2 shows that NDMA was not detected in the raw water but that NMOR was detected at 2.89 ng/l. NDMA and NMOR were detected in various treated water samples derived from sedimentation (up to 2.53 ng/l and 6.49 ng/l, respectively) and from DAF (6.31 ng/l and 25.9 ng/l, respectively).The concentrations measured for the samples derived from DAF in particular were higher than expected. Based on the coagulant dose and concentration of NMOR in the coagulant, the expected concentration in the dosed water would be 3.8 ng/l. The NDMA concentration is also higher than measured in any sample derived from sedimentation although the coagulant dose was the same (9.0 mg Fe/l). The reason for the higher values of NDMA and NMOR is unclear but contamination from the equipment used in the DAF test is a possibility.

The following observations can be made from the tests:

- Pre-ozonation (Test F) reduced the concentration of NMOR in the raw water.
- Coagulation increased the concentrations of NDMA and NMOR generally in proportion to dose for coagulation/sedimentation/filtration (Test A).
- Coagulation/DAF/filtration (Test D) gave the highest concentrations of both NDMA (6.31 ng/l) and NMOR (25.9 ng/l) although the coagulant dose was the same as used for coagulation/sedimentation/filtration (Test A). The reason for the higher values is unexplained but contamination from the equipment used in the test is a possibility.
- Ozonation reduced concentrations of NDMA and NMOR following coagulation with Coagulant B2 (Test A) but not following coagulation with Coagulant B2/polyDADMAC (Test E).
- GAC removed both NDMA and NMOR, the latter consistently to below its limit of detection.
- Storage of chlorinated or chloraminated water for 48 hours – simulating retention in distribution - generally showed a small increase in concentrations of NDMA and NMOR.

6.3.2 Tests on nitrosamine-spiked tap water

A shorter series of tests was carried out on nitrosamine-spiked tap water to determine if ozone, GAC or a combination of the two removed any preformed nitrosamines, as indicated by the flow schematic shown in Figure 6.2.

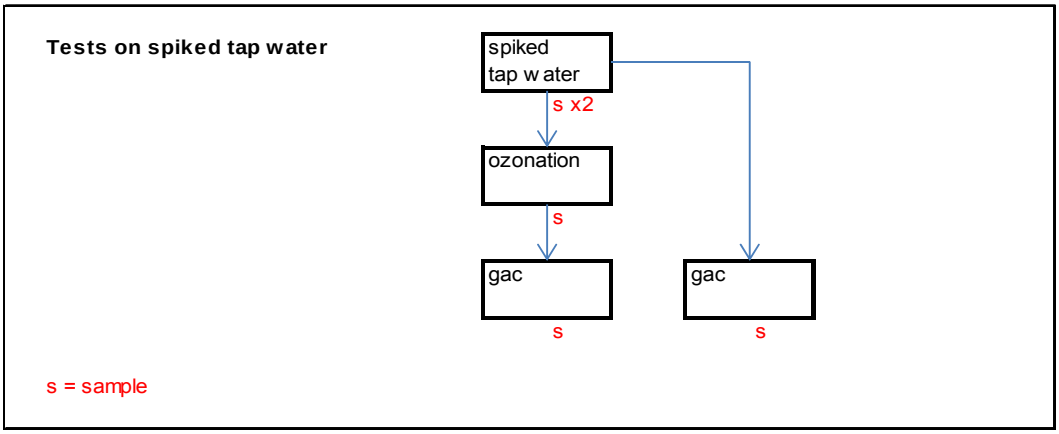

Figure 6.2 Nitrosamine laboratory tests: Tests on spiked tap water

Results

Results are shown in Table 6.3.

Table 6.3 Nitrosamine analysis: Spiked tap water

Treatment	Nitrosamine (ng/l)								
	NDMA	NMEA	NDEA	NPYR	NDPA	NPIP	NDBA	NMOR	NDPHA
Spiked[1] tap water	19.32/ 19.69	19.4/ 20.7	22.6/ 21.9	22.3/ 18.0	17.0/ 19.6	22.8/ 19.4	22.8/ 21.3	17.7/ 20.5	14.8/ 10.5
Spiked tap water/Ozonation	21.2	20.8	28.2	17.6	17.5	22.2	18.6	16.2	7.09
Spiked tap water/Ozonation/GAC	1.35	<0.5	<3.1	<2.3	<0.8	<2.6	<2.6	<1.5	<3.3
Spiked tap water/GAC	0.64	<0.5	<3.1	<2.3	<0.8	<2.6	<2.6	<1.5	<3.3

Note:
1. Nitrosamines spiked at 20 ng/l.

Analysis of the spiked tap water showed a good recovery of each of the nitrosamines with the exception of NDPHA (52.5-74.0%).

The following observations can be made from the tests:

- Ozonation generally had little effect on the concentration of the nitrosamines.
- Virgin GAC (Chemviron F400) significantly reduced the concentration of the nitrosamines, most to below their limits of detection; the concentration of NDMA was reduced by 93-97%.

7. CONCLUSIONS

7.1 Literature Review

The International Agency for Research on Cancer (IARC) has classified several nitrosamines as either Group 2A ("probably carcinogenic to humans") or Group 2B ("possibly carcinogenic to humans"); NDMA, the most widely reported nitrosamine, is classified as Group 2A. WHO has issued a Guideline Value for NDMA in drinking water of 100 ng/l based on an upper bound excess lifetime cancer risk of 10^{-5}.

NDMA has been found at treatment works and in distribution at concentrations up to 100 ng/l in North America, although usually at concentrations less than 10 ng/l. In the UK, NDMA has been detected in final waters from a small number of treatment works at concentrations up to 5.8 ng/l. Reports of other nitrosamines in drinking water suggest that their concentrations are considerably less: NDEA has been detected in the US at up to 0.7 ng/l, NPYR and NMOR have been detected in Canada following chloramination, and NDBA has been detected in one distribution system in the UK.

Prevention of contamination of drinking water by nitrosamines can be achieved by removal of formation precursors or removal of nitrosamines once formed. Some removal of precursors may be achieved by biodegradation, adsorption on activated carbon and pre-chlorination. Once formed, nitrosamines may be removed to varying degrees and efficacies by biofiltration, adsorption on carbonaceous resins (claimed to be more effective than activated carbon), advanced oxidation processes and UV irradiation.

7.2 Coagulant Survey

7.2.1 Coagulant usage

A survey of water companies in England and Wales identified the use of twenty-eight ferric- and aluminium-based coagulants supplied by seven manufacturers/suppliers.

In the initial survey carried out in 2009, NDMA was either not detected or detected only as a trace contaminant in 22 coagulants. Allowing for dilution in the tests, NDMA concentrations in these coagulants were typically <1.0 µg/l and close to the limit of detection of 0.48 µg/l; it is probable that many of these results were false positives. In six coagulants higher concentrations (up to 19 µg/l) were detected but these were well below the concentrations detected during the 2008 Defra/DWI study. The six contaminated coagulants were all ferric sulphates produced by three manufacturers using similar processes.

7.2.2 Contract Extension 1 (2010)

Towards the end of the 2008-2009 water treatment works survey (see below), significantly increased NDMA concentrations were detected in treated waters and distribution. Investigation revealed the NDMA concentration in Coagulant A1 had increased considerably, believed as a result of an NDMA precursor contained in a raw material used in the manufacturing process.

A subsequent 5-month analytical survey (June-October 2010) monitored NDMA concentrations in Coagulant A1 and Coagulant B2 (manufactured by a similar process to Coagulant A1).

NDMA concentrations in Coagulant A1 were reduced following a partial replacement of the affected raw material in the manufacturing process. NDMA concentrations in coagulant samples taken during delivery ('ex. delivery') to Works D20 reduced from 195 µg/l to 67 µg/l. NDMA concentrations in coagulant samples supplied directly to WRc by the manufacturer ('ex. production') were generally lower and reduced to 18 µg/l by mid-October. The NDMA concentration in the final 'ex. production' coagulant sample submitted at the end of October increased to 325 µg/l. The reason for the substantial increase was unexplained.

NDMA concentrations in samples of Coagulant B2 taken from Works C12 ('ex. Works') were initially high due to contamination from residual Coagulant A1 in the coagulant holding tanks. By the end of the 5-month survey, NDMA concentrations in 'ex. works' samples reduced to 27 µg/l, comparable to 'ex. production' samples supplied directly to WRc by the manufacturer.

At both Works C12 and D20, NDMA concentrations in water samples taken throughout treatment generally decreased in proportion to the reduction in NDMA in the coagulant.

7.2.3 Contract Extension 2 (2011)

As a result of the unexplained increase in NDMA in Coagulant A1 at the end of October 2010, a second survey was carried out to confirm that NDMA concentrations had been subsequently reduced.

It was not possible to obtain samples of Coagulant A1 because production had ceased and no residual stock of coagulant could be sourced from water treatment works. The survey therefore investigated NDMA concentrations in Coagulant B2.

A five-month analytical survey (June-October 2011) showed that NDMA concentrations in Coagulant B2 sampled from Works C12 measured 26-36 µg/l. If dosed at typical values used in water treatment, Coagulant B2 would increase the NDMA concentration in coagulated water by 0.4-2.7 ng/l. NDMA was detected in only one sample of final water, at 0.9 ng/l.

NDMA concentrations in the 'ex. works' coagulant samples were consistently higher than in 'ex. production' samples (3.8-9.2 µg/l) supplied directly to WRc by the manufacturer.

NMOR concentrations measured in Coagulant B2 sampled from Works C12 measured 4.3-28 µg/l, potentially giving rise to NMOR concentrations in coagulated water between 0.03-2.12 ng/l. NMOR was not detected in any samples of final water from this works.

NMOR concentrations in the 'ex. works' coagulant samples were consistently lower than in 'ex. production' samples (22-143 µg/l) supplied directly to WRc by the manufacturer.

7.3 Water Treatment Works Survey

A 12-month survey measuring NDMA concentrations in water from six selected water treatment works was carried out between November 2008 and November 2009. Towards the end of the survey, results were affected by a large increase in NDMA concentration in Coagulant A1 used at the works. In Surveys 1-9 (November 2008-August 2009), NDMA

concentrations detected in final waters and distribution were generally not detectable and occasionally low ng/l. Surveys 10-12 (September 2009-November 2009) showed significantly increased levels, typically low ng/l levels but up to 24 ng/l. No samples of treated water were found to exceed the WHO guideline value of 100 ng/l. Reduction in NDMA concentrations in coagulants (described above) lead to corresponding reductions in final water NDMA concentrations.

Conclusions from the treatment works are shown below:

- Works C11: NDMA was not detected in the raw water. NDMA was detected in some samples within treatment and distribution at concentrations up to 2.1 ng/l in Surveys 1-9 and up to 26 ng/l in Surveys 10-12. There was an indication that NDMA concentrations in distribution increased with retention time.

- Works C12: NDMA was not detected in the raw water. NDMA concentrations in water from the recovery process measured up to 15 ng/l during Surveys 1-9 and up 146 ng/l during Surveys 10-12. Following recycle of the recovered water, NDMA was detected in some samples within treatment and distribution at concentrations up to 1.1 ng/l in Surveys 1-9 and up to 12 ng/l in Surveys 10-12.

- Works C16: NDMA was not detected in the raw water. In Surveys 1-9, NDMA was detected in post-coagulation samples up to 1.2 ng/l but not in post-RGF or final water samples. In Surveys 10-12, NDMA in post-coagulation samples increased up to 32 ng/l but this was substantially removed within treatment, with concentrations in post-RGF and final water samples reduced to 1.0-1.1 ng/l and 1.8 ng/l, respectively. The removal of NDMA across the RGFs (observed also to a smaller extent at other works) suggested a possible biological removal mechanism.

- Works D17: NDMA was detected in some raw water samples up to 4.2 ng/l. In Surveys 1-9, NDMA was detected in three post-coagulation samples up to 0.99 ng/l and in seven post-ozonation samples up to 1.2 ng/l. NDMA was generally not detected in samples taken downstream of the subsequent RGFs. In Surveys 10-12, NDMA in post-coagulation and post-ozonation samples increased up to 5.7 and 7.1 ng/l, respectively, but again was largely removed across the RGFs, with concentrations in post-RGF samples measuring 1.2 ng/l or less. NDMA in the final water measured less than 1 ng/l.

- Works D18: NDMA was detected in most raw water samples up to 12 ng/l but this frequent occurrence was unexplained. In Surveys 1-9, NDMA was detected in eight post-coagulation samples (up to 7.7 ng/l) but in only five post-RGF samples (up to 1.4 ng/l) and in a small number of downstream samples at concentrations typically <1 ng/l. In Surveys 10-12, NDMA increased in post-coagulation samples up to 11 ng/l, in post-RGF samples up to 6.1 ng/l and in post-GAC samples up to 2.7 ng/l. Removal across the GAC suggested a possible adsorptive/biological removal mechanism. NDMA was detected in final water and distribution at low concentrations, and there was an indication that NDMA formed in distribution with increased residence time.

- Works H5: NDMA was detected in most raw water samples up to 4.2 ng/l but this frequent occurrence was unexplained. In Surveys 1-9, NDMA was generally detected throughout treatment (with some removal across RGFs and GAC, and formation across ozonation) and in distribution (up to 3.7 ng/l). In Surveys 10-12, NDMA was detected in all samples throughout treatment (with similar removal across RGFs and GAC, and formation across ozonation) and in distribution (up to 5.4 ng/l).

During September to November 2009, the coagulant doses at Works D17 (5.5 mg Fe/l), D18 (7.5-8.0 mg Fe/l) and H5 (3.4 mg Fe/l) were lower than those at Works C11 (11.0-12.0 mg Fe/l), C12 (>100 mg Fe/l in the water recovery process) and C16 (14.0-15.7 mg Fe/l), thus the effect of the contaminated coagulant was not as significant.

7.4 Laboratory Studies

7.4.1 NDMA formation and removal

Observations from the treatment works survey at several works indicated that NDMA was removed across RGFs. A laboratory trial carried out using RGF media from Works C16 confirmed removal of NDMA from post-coagulated clarified water and nitrosamine-spiked tap water, indicating a possible biological removal mechanism.

Observations from the treatment works survey indicated the possible formation of NDMA in distribution with increased residence times. Laboratory trials carried out investigating the effects of temperature and storage time on chlorinated and chloraminated waters sampled from Works C11 proved inconclusive; in one test there was no NDMA formation, whilst in two other tests NDMA increased up to 1.4 ng/l. In all cases, concentrations of NDMA measured in actual samples from distribution were greater than in simulated samples.

7.4.2 Nitrosamine formation and removal

The formation and removal of a range of nitrosamines by water treatment processes was investigated in laboratory tests.

In trials dosing Coagulant B2 to highly coloured upland water from Works C12, NDMA and NMOR were detected in the various post-coagulated water samples; NMOR was also detected in the raw water. Increases in NDMA and NMOR in post-coagulated water samples were almost certainly due to contamination of the coagulant used in the tests and, in the investigation of DAF, possible contamination from the equipment used.

Ozonation and/or GAC generally reduced concentrations of NDMA and NMOR. Storage of chlorinated or chloraminated water for 48 hours – simulating retention in distribution - generally showed a small increase in concentration of both nitrosamines.

In trials on pre-formed nitrosamines spiked to tap water, all the spiked nitrosamines were removed effectively by GAC or ozonation/GAC. Ozonation alone had little effect on nitrosamine concentrations.

8. SUGGESTIONS

The principal source – or potential source - of nitrosamines (NDMA and NMOR) in drinking water appears to be contaminated ferric coagulants. It is suggested that manufacturers be required to analyse coagulants for nitrosamines and provide results to water companies to ensure that this contamination route is controlled.

Should nitrosamines in drinking water continue to be a concern, removal by GAC adsorption may be particularly effective based on the results of laboratory tests with virgin GAC (Chemviron F400). If appropriate, further tests should be carried out on GAC to fully investigate the process, including optimum GAC type, EBCT, bed life, etc.

APPENDIX A LITERATURE REVIEW

A1 INTRODUCTION

In 2006, Defra commissioned a survey to investigate the formation and occurrence of N-nitrosodimethylamine (NDMA) in drinking water in England and Wales. NDMA is classified by the US Environmental Protection Agency (USEPA) as a 'probable human carcinogen'. The survey, carried out during 2006-2008, examined water from 43 treatment works (Dillon *et al.*, 2008). NDMA was detected in final water at three works at concentrations less than 10 ng/l, with the probable source being a contaminated ferric coagulant. Subsequent to this survey, the DWI issued guidance to the water industry in England and Wales regarding NDMA in drinking water (DWI, 2008).

NDMA is the most prominent of a group of chemicals known as nitrosamines, others of which also present health concerns. It is possible that other nitrosamines might be formed within water treatment and be present in final water. Accordingly, Defra commissioned WRc to investigate the potential formation and removal of nitrosamines in drinking water treatment.

This literature review presents a brief summary of the formation, occurrence, toxicity and removal of several nitrosamines that might be formed during drinking water treatment, as listed below:

Nitrosamine	Abbreviation	Structure
N-Nitrosodimethylamine	NDMA	$O=N\text{-}N(CH_3)_2$
N-Nitrosomethylethylamine	NMEA	$O=N\text{-}N(CH_2CH_3)CH_3$
N-Nitrosodiethylamine	NDEA	$O=N\text{-}N(CH_2CH_3)_2$
N-Nitrosopyrrolidine	NPYR	$(C_4H_8)N\text{-}N=O$
N-Nitrosodipropylamine	NDPA	$O=N\text{-}N(C_3H_7)_2$
N-Nitrosopiperidine	NPIP	$(C_5H_{10})N\text{-}N=O$
N-Nitrosodibutylamine	NDBA	$O=N\text{-}N(C_4H_9)_2$
N-Nitrosomorpholine	NMOR	$O=N\text{-}N(C_4H_8O)$

A2 FORMATION AND OCCURRENCE

A2.1 Overview

The formation of nitrosamines is complex and depends on many factors including concentrations of reactants, catalysts and inhibitors, and other competing reactions. Most published work focuses on the formation of NDMA. However, most of the principles directing NDMA formation should be valid (at least on a qualitative basis) to the formation of other nitrosamines.

The three major pathways by which nitrosamines might be formed are:

- Nitrosation of nitrogen-containing compounds by nitrosating agents.

- Reaction of monochloramine with aliphatic amines (e.g. dimethylamine (DMA)) to unsymmetrical dimethylhydrazine (UDMH) and subsequent oxidation to nitrosamines.

- Reaction of dichloramine with aliphatic amines to chlorinated UDMH and subsequent oxidation to nitrosamines by either monochoramine or dissolved oxygen.

A2.1.1 Nitrosamine formation by nitrosation of nitrogen-containing compounds

Nitrosamines may be formed by the nitrosation, i.e. the introduction of a nitroso group (-NO), of nitrogen-containing organic compounds. Possible nitrosating agents include nitrous acid (HNO_2), some nitrogen oxides (N_2O_3, N_2O_4), nitrosyl halides and thiocyanates (NOCl, NOBr and NCSNO) (Mirvish 1975; Wainright 1986). Nitrates do not form nitrosamines directly, but might be transformed to nitrites by micro-organisms present in the environment.

Under acidic conditions, nitrite (NO_2^-) is transformed to nitrous acid (HNO_2) which decomposes to the nitrosyl cation NO^+ or to dinitrogen trioxide N_2O_3, both being capable of reacting with nitrogen-containing compounds to form nitrosamines.

$$HNO_2 + H^+ \Leftrightarrow NO^+ + H_2O$$

$$2HNO_2 \Leftrightarrow N_2O_3 + H_2O$$

In addition to the aliphatic and aromatic amines, there are a number of other possible nitrogen-containing precursors for N-nitrosamine formation: N,N-dialkylhydrazides, N-alskylamides, N-alkylureas, 1,3-dialkylureas and N-alkylcarbamates for the monoalkylnitrosamines, and 1,1-dialkylureas, 1,3-dialkylphenylureas, tetraalkylureas, and 1,1-dialkylthioureas for the dialkylnitrosamines (Mirvish 1975; Fishbein 1979). Other organic compounds containing these structural elements can also act as precursors, including various pesticides, cosmetics, sunscreen agents, pharmaceuticals (Loeppky *et al*., 1994) or even natural organic matter (NOM).

Tertiary and quaternary amines are also able to form nitrosamines but are generally regarded as less important precursors.

A2.1.2 Nitrosamine formation by reaction of monochloramine with aliphatic amines to UDMH

A reaction pathway for nitrosamine formation particularly relevant to chloramination of drinking waters involves the reaction of monochloramine ($NHCl_2$) with DMA to UDMH followed by oxidation to NDMA. The proposed mechanism accounts for the fact that NDMA formation has been observed during disinfection with chlorine and chloramine even in the absence of nitrite. For example, Choi and Valentine (2002a) found that NDMA was formed when only chlorine was added to an aqueous solution of DMA. After addition of ammonia, the amount of NDMA formed was much higher. Najm and Trussell (2001) found that nitrosamine formation during disinfection with chlorine required the presence of ammonia (i.e. chloramination). These workers also found that ozonation alone did not cause nitrosamine formation.

The formation of NDMA by reaction of monochloramine with aliphatic amines during chlorination or chloramination was studied in more detail by several workers. The simplified

reaction of the multi-step mechanism proposed by Choi and Valentine (2002a, 2002b) is given below:

$$(CH_3)_2NH + NH_2Cl \xleftrightarrow{OH^-} (CH_3)_2N - NH_2 \xleftrightarrow{oxidation} (CH_3)_2N - N = O$$

Several workers have reported that the formation of NDMA during chloramination from tertiary amines with a DMA functional group, e.g. trimethylamine (Mitch and Sedlak 2004). Amines without the DMA functional group did not form significant amounts of NDMA.

Mitch and Sedlak (2002b) also investigated the formation of nitrosamines during chloramination of wastewater effluents. They were able to detect NDMA as well as NDEA, NPYR and NPIP. NDMA concentrations were one order of magnitude greater than NDEA and NPYR and two orders of magnitude greater than NPIP.

A2.1.3 Nitrosamine formation by reaction of dichloramine with aliphatic amines to chlorinated UDMH

An alternative reaction pathway to the formation of nitrosamines based on the reaction between secondary amines (e.g. DMA) and dichloramine has been proposed by Schreiber and Mitch (2006). DMA and dichloramine react to form chlorinated unsymmetrical dialkylhydrazine intermediates (e.g. chlorinated UDMH for DMA), rather than unsymmetrical dialkylhydrazine intermediates (e.g. UDMH). These intermediates can then be oxidised to the respective nitrosamine by chloramines or dissolved oxygen.

$$(CH_3)_2NH + HNCl_2 \Leftrightarrow (CH_3)_2N - NHCl + HCl$$

$$(CH_3)_2N - NHCl \xrightarrow{oxidation} (CH_3)_2N - N = O$$

This reaction pathway is proposed based on two experimental facts: firstly, the rate constant for the formation of chlorinated UDMH is three orders of magnitude faster than the rate constant for the formation of UDMH from monochloramine and DMA; and secondly, chlorinated UDMH can be oxidised to NDMA by dissolved oxygen. As a consequence, NDMA formation by this pathway could be reduced by reducing the concentration of dissolved oxygen.

A2.2 Formation and Occurrence of Specific Nitrosamines

A2.2.1 Nitrosodimethylamine (NDMA)

The principal formation mechanism for NDMA is chloramination of organic precursors, particularly secondary and tertiary amines (Dillon *et al*., 2008). The most common precursor is dimethylamine (DMA), which is ubiquitous in water. In a laboratory study investigating the ozonation of DMA-containing waters, Andrzejewski *et al.,* (2008) reported the formation of NDMA (yield <0.4% in relation to DMA) and suggested nitrosation of DMA as the reaction pathway, and further suggested the potential importance of this reaction in treatment for waters containing “reasonable” µg/l DMA concentrations. It has been suggested that NDMA can also be formed via reactions with bromamines. Bromamines are generally more reactive than chloramines and therefore would be expected to react more readily with DMA.

Templeton and Chen (2010) reported a survey of NDMA and seven other nitrosamines in six UK drinking water supply systems. Five of the six systems were selected as likely to have elevated nitrosamine concentrations because of known source water characteristics and/or treatment practices; the sixth system had no such factors and was included as a control. NDMA was measured barely above the analytical limit of detection (0.9 ng/l) in a few isolated samples in one distribution system; the majority of samples contained no detectable NDMA. NDBA was also detected in one distribution system.

Asami *et al.,* (2009) reported the results of a nationwide survey of NDMA in raw and final waters in Japan. NDMA was detected in 15 of 31 raw water samples collected in the summer at concentrations up to 2.6 ng/l, and in 9 of 28 raw water samples collected in the winter at concentrations up to 4.3 ng/l. NDMA concentrations were higher in samples collected from more highly populated catchment areas. NDMA was detected at concentrations up to 2.2 ng/l in 10 of 31 final water samples collected in summer and up to 10 ng/l in 5 of 28 samples collected in winter. The highest NDMA concentrations (up to 20 ng/l) were measured after ozonation but then decreased following subsequent biological activated carbon.

Park *et al*., (2009) investigated the NDMA formation from four amine-based water treatment polymers using different oxidants directly with solutions of the polymer. The NDMA formation potential for the polymers was aminomethylated polyacrylamide (Mannich polymer) >> polyamine > polyDADMAC > cationic polyacrylamide copolymer (PAM). The high formation potential of the Mannich polymer was due to a large amount of DMA residue in the polymer solution. For the other polymers the DMA concentration increased after oxidation, indicating polymer degradation. Among the oxidants, NDMA formation followed the order monochloramine > chlorine > chlorine dioxide, although the DMA release from the polymers caused by the oxidants followed the opposite order. Nitrate and nitrite were suggested to have little influence at concentrations that can be expected in water supply. Coagulation jar tests showed small contributions from polyamine and polyDADMAC to the overall NDMA formation.

Morran *et al.,* (2009) reported the contamination of drinking water with NDMA as a result of contact with rubber seals and other rubber components of water supply pipelines. NDMA is used as a plasticiser in the manufacture of rubber and polymers, and in a range of other manufacturing processes. High NDMA concentrations were detected in water samples following the commissioning of a new branch main in South Australia. Subsequent laboratory tests confirmed detectable levels of NDMA in samples of milli-Q (de-ionised) and chloraminated water in contact with rubber sealing rings and rubber inserts from gate valves.

In 2008, NDMA was detected in drinking water at concentrations of 0-53 ng/l (location not stated in the abstract) (Zhao *et al*., 2008).

In 2008 in England and Wales, NDMA was detected in final waters from three of 43 drinking water treatment works at concentrations up to 5.8 ng/l (Dillon *et al*., 2008).

In 2007, Charrois *et al*., reported the results of a survey of 20 drinking water distribution systems in Alberta, Canada; NDMA, NPYR and NMOR were detected. NDMA was detected in six distribution systems, with two at concentrations above the Ontario Drinking Water Quality Standard (ODWQS) of 9 ng/l; one at 100 ng/l. Five of the six systems were fed chloraminated water.

Zhao *et al.,* (2006) described the development of a liquid chromatography tandem mass spectrometry (LCMSMS) method for the detection of nitrosamines in drinking water. NDMA, NPYR, NPIP and NDPHA were detected in subsequent analysis of samples from a single

distribution system fed from a works treating surface water by chloramination and UV irradiation. Concentrations of NDMA ranged from zero to 108.2 ng/l, with the higher values associated with samples with higher residence times in distribution.

In 2005 in the USA and Canada, results of an extensive study on the occurrence of NDMA were published. NDMA was detected in 28 of 81 final water samples at concentrations ranging from 0.7 to 30.0 ng/l and was detected in the majority of drinking water distribution samples at concentrations ranging from 0.6 to 24.0 ng/l (AWWARF/WERF, 2005).

Charrois *et al.,* (2004) found NDMA, NPYR and NMOR in drinking water supplied to two cities in Canada, at the treatment works that used chloramination and in distribution. NDMA concentrations ranged from 2-180 ng/l.

A2.2.2 Nitrosomethylethylamine (NMEA)

No data were located during the literature search.

NMEA has been detected in river water in the USA at a concentration range of <1-2.2 ng/l (NFP) (AWWARF, 2007).

A2.2.3 Nitrosodiethylamine (NDEA)

It has been suggested that NDEA may be formed naturally in some plants, however, no details have been reported (IPCS, 1978). NDEA may be formed in drinking water through the reaction of diethylamine with chloramine. Approximately 0.53% (based on molar concentrations) of an initial concentration of diethylamine of 1000 ng/l spiked with 7.4 ng/l chloramine was reported to be converted to NDEA (AWWARF, 2007).

In 1981, NDEA was detected in tap water in Philadelphia, USA, at a concentration range of <0.1-0.7 ng/l (HSDB, 2008).

A2.2.4 Nitrosopyrrolidine (NPYR)

In 2007, Charrois *et al*., reported the results of a survey of 20 drinking water distribution systems in Alberta, Canada; NDMA, NPYR and NMOR were detected. NPYR was detected in one chloraminating distribution system at a concentration of 4 ng/l. NPYR was detected only at the extreme end of the distribution system (high residence time) possibly indicating residence time as an important variable in its formation.

NPYR may be formed in drinking water through the reaction of pyrrolidine with chloramine. Approximately 1.84% (based on molar concentrations) of an initial concentration of pyrrolidine of 1000 ng/l spiked with 26 ng/l chloramine was reported to be converted to NPYR (AWWARF, 2007).

NPYR has been detected in river water in the USA at a concentration range of <1-35 ng/l (NFP) (AWWARF, 2007).

Zhao *et al.,* (2006) described the development of a liquid chromatography tandem mass spectrometry (LCMSMS) method for the detection of nitrosamines in drinking water. NDMA, NPYR, NPIP and NDPHA were detected in subsequent analysis of samples from a single

distribution system fed from a works treating surface water by chloramination and UV irradiation. Concentrations of NPYR ranged from 18.0-70.5 ng/l, with the higher values associated with samples with higher residence times in distribution.

Charrois *et al.,* (2004) found NDMA, NPYR and NMOR in drinking water supplied to two cities in Canada, at the treatment works that used chloramination and in distribution. This was the first report of NPYR in drinking water, at concentrations from 2-4 ng/l.

A2.2.5 Nitrosodipropylamine (NDPA)

NDPA may be formed by the reaction of di-n-propylamine with nitrogen oxide, nitrous acid, nitrite salts and other nitro- and nitroso- compounds (ATSDR, 1989). NDPA may be formed in drinking water through the reaction of dipropylamine with chloramine. Approximately 0.02% (based on molar concentrations) of an initial concentration of dipropylamine concentration of 1000 ng/l spiked with 0.2 ng/l chloramine was reported to be converted to NDPA (AWWARF, 2007).

NDPA was detected in 2 of 32 secondary effluents from textile plants in the USA, at a concentration range of 2-20 µg/l. No NDPA was detectable in the raw wastewater, suggesting it was formed during the treatment process (ATSDR, 1989).

A2.2.6 Nitrosopiperidine (NPIP)

NPIP may be formed in drinking water through the reaction of piperidine with chloramine. Approximately 1.35% (based on molar concentrations) of an initial concentration of piperidine of 1000 ng/l spiked with 18 ng chloramine/l was reported to be converted to NDBA (AWWARF, 2007).

NPIP has been detected in river water in the USA at a concentration range of <1-28 ng/l (NFP) (AWWARF, 2007).

Zhao *et al.,* (2006) described the development of a liquid chromatography tandem mass spectrometry (LCMSMS) method for the detection of nitrosamines in drinking water. NDMA, NPYR, NPIP and NDPHA were detected in subsequent analysis of samples from a single distribution system fed from a works treating surface water by chloramination and UV irradiation. Concentrations of NPIP ranged from 33.1 to 117.8 ng/l, with the higher values associated with samples with higher residence times in distribution. NPIP had not been reported previously in drinking water systems.

A2.2.7 Nitrosodibutylamine (NDBA)

NDBA may be formed in drinking water through the reaction of dibutylamine with chloramine. Approximately 0.69% (based on molar concentrations) of an initial concentration of dibutylamine concentration of 1000 ng/l spiked with 8.4 ng/l chloramine was reported to be converted to NDBA (AWWARF, 2007).

Templeton and Chen (2010) reported a survey of NDMA and seven other nitrosamines in six UK drinking water supply systems. The majority of samples contained no detectable NDMA or other nitrosamines. An exception was NDBA that was consistently detected in one distribution system, up to a maximum concentration of 6.4 ng/l.

NDBA has been detected in river water in the USA at a concentration range of <1-2.5 ng/l (NFP) (AWWARF, 2007).

A2.2.8 Nitrosomorpholine (NMOR)

NMOR is formed via the nitrosation of n-morpholine by nitric oxide or nitrogen dioxide. An aqueous solution of 10 mM n-morpholine (approximately 1161 mg/l) nitric oxide at a concentration of 0-100 mg/l was reported to proceed at a first order rate. The rate of reaction was also approximately first-order for nitrogen dioxide at concentrations below 20 mg/l (Cooney *et al*., 1992). Nitrosation is reported to increase at pH 4-7, reaching a plateau between pH 9-12. The addition of iodine ions was reported to increase the rate of NMOR formation, while fluoride ions had no effect (Cooney *et al*., 1987). NMOR may also be formed via bacterial nitrosation of morpholine. Bacterial nitrosation is reported to be optimal at neutral or slightly alkaline pH, and is generally associated with the ability of bacteria to reduce nitrate (IPCS, 1996).

In 2007, Charrois *et al*., reported the results of a survey of 20 drinking water distribution systems in Alberta, Canada; NDMA, NPYR and NMOR were detected. NMOR was detected in two chloraminating distribution system, at a concentration up to 3 ng/l. NMOR was detected only at the extreme end of one of the distribution systems (high residence time) possibly indicating residence time as an important variable in its formation.

NMOR has been detected in river water in the USA at a concentration range of <1-6.8 ng/l (NFP) (AWWARF, 2007).

Charrois *et al.,* (2004) found NDMA, NPYR and NMOR in drinking water supplied to two cities in Canada, at the treatment works that used chloramination and in distribution. This was the first report of NMOR in drinking water, at a concentration of 1 ng/l.

A2.2.9 Nitrosodiphenylamine (NDPHA)

Zhao *et al.,* (2006) described the development of a liquid chromatography tandem mass spectrometry (LCMSMS) method for the detection of nitrosamines in drinking water. NDMA, NPYR, NPIP and NDPHA were detected in subsequent analysis of samples from a single distribution system fed from a works treating surface water by chloramination and UV irradiation. Concentrations of NDPHA ranged from zero to 1.86 ng/l, with the higher values associated with samples with higher residence times in distribution. NDPHA had not been reported previously in drinking water systems.

A3 TOXICITY

A3.1 Overview

The International Agency for Research on Cancer (IARC) evaluated several nitrosamines and classified them as either Group 2A (“probably carcinogenic to humans on the basis that there is evidence of carcinogenicity in experimental animals”) or Group 2B (“possibly carcinogenic to humans on the basis that there is evidence of carcinogenicity in experimental animals”) (IARC 1974, 1978, 1987, 2000). NDMA, the most widely reported nitrosamine, is classified by IARC as Group 2A and by the US Environmental Protection Agency (EPA) as a ‘probable

human carcinogen' with an estimated 10^{-5} cancer risk level at 7 ng/l (EPA 1997). WHO (WHO, 2008) has issued a Guideline Value for NDMA in drinking water of 100 ng/l based on an upper bound excess lifetime cancer risk of 10^{-5}. The US EPA IRIS database includes eight other aliphatic nitrosamines with significant health concerns and derived estimated 10^{-5} cancer risk levels (see Table A1).

Table A1 Cancer risk estimates for nitrosamines

Nitrosamine	Abbreviation	10^{-5} Cancer Risk (ng/l)
N-Nitrosodimethylamine	NDMA	7
N-Nitrosomethylethylamine	NMEA	20
N-Nitrosodiethylamine	NDEA	2
N-Nitrosopyrrolidine	NPYR	160
N-Nitrosodipropylamine	NDPA	50
N-Nitrosopiperidine	NPIP	8
N-Nitrosodibutylamine	NDBA	60
N-Nitrosodiethanolamine	NDELA	100
N-Nitrosomorpholine	NMOR	8

Source: US Department of Health and Human Services (2005)

Both the WHO guideline value and the US EPA IRIS 10^{-5} cancer risk estimate level for NDMA are derived from large studies showing increased liver tumours in rats. Different methods and defaults have then been used to derive cancer risk estimates for humans. The IRIS estimates have not been used by US EPA to derive drinking water standards for NDMA.

The California Department of Health Services (CDHS) established a notification level in 1998 for NDMA of 10 ng/l (AWWARF 2007). In 2004 and 2005, notification levels of 10 ng/l for NDEA and NDPA were also established.

In 2002, CDHS requested a Public Health Goal (PHG) from the Office of Environmental Health Hazard Assessment (OEHHA). In December 2006, OEHHA developed a PHG for NDMA in drinking water of 3 ng/l (OEHHA 2006), based on a cancer risk of 10^{-6} for lifetime exposure to NDMA in drinking water.

A3.2 Toxicity of Specific Nitrosamines

A3.2.1 Nitrosodimethylamine (NDMA)

NDMA is of moderate to high acute oral toxicity to experimental animals; oral LD50s of 23-40, 20 and 28 mg/kg body weight (bw) have been reported in rats, dogs and hamsters, respectively (WHO, 2002).

In a life-time study, Colworth-Wistar rats (60/sex/dose) were administered NDMA at 15 different doses between 0.001-1.224 mg/kg bw/day in drinking water. Increased incidences of

liver tumours (hepatocellular carcinoma and biliary cystadenoma) were observed at >0.02 mg/kg bw/day for both males and females (WHO, 2002).

In 1987, the International Agency for Research on Cancer (IARC) evaluated NDMA and classified it as Group 2A, i.e. probably carcinogenic to humans on the basis that there is evidence of carcinogenicity in experimental animals (IARC, 1987).

The US National Toxicology Program (NTP) evaluated NDMA and considered it is 'reasonably anticipated to be a human carcinogen' based on evidence of carcinogenicity in experimental animals (NTP, year unknown[a]).

A3.2.2 Nitrosomethylethylamine (NMEA)

In a limited carcinogenesis study, 16 F344 rats were administered NMEA at doses of 0.2 ml twice/week (approximately 1.5 mg/kg bw/day) via oral gavage for 60 weeks. One rat died after 30 weeks, four rats died after 35 weeks, three died after 40 weeks, 3 died after 45 weeks, two died after 50 weeks and all rats had died after 60 weeks. NMEA induced hepatocellular and cholangiocellular tumours (Lijinsky *et al.,* 1987).

In 1978, the International Agency for Research on Cancer (IARC) evaluated NMEA and classified it as Group 2B, i.e. possibly carcinogenic to humans on the basis that there is evidence of carcinogenicity in experimental animals (IARC, 1978a).

A3.2.3 Nitrosodiethylamine (NDEA)

Oral administration of NDEA at a dose of 50 mg/day (approximately 0.025 mg/kg bw/day) to rabbits on a hypercholesterolemic diet was reported to result in significant increases in osmotic fragility of erythrocytes and marginal changes in hepatic cholesterol levels. Unspecified histological changes to the heart and liver were noted to be more severe in rabbits administered NDEA than those administered the hyperchloesterolemic diet alone. *In vitro* lipid peroxidation of erythrocytes was increased in rabbits administered NDEA (Mittal *et al*., 2008).

In a carcinogenic study, 129Sv wt mice, IFN-α/β receptor knockout and IFN-γ receptor knockout mice were administered 50 µg NDEA/l (approximately 6 mg/kg bw/day) for 5 months. Liver tumours were apparent in 46% of mice after three months and in all mice after 4 months. Numbers and diameters of tumours increased with exposure time. Tumours were identified as hepatocellular carcinoma (HCC) expressing glutathione-S-transferase-p (GST-p) and the surrounding hepatic parenchyma displayed infiltration of inflammatory cells. Analysis of mRNA expression revealed increased expression of intrahepatic cytokines following exposure for 1 month or greater. IFN-γ receptor knockout mice displayed fewer tumours than other mice, however, the diameter of the tumours were not significantly different and CYP2E1 activities were similar between groups. Numbers of infiltrating mononuclear cells were similar between groups (Matsuda *et al*., 2005).

In another carcinogenicity study, inbred male Wistar rats were administered either control drinking water for 130 days (Group A), NDEA in drinking water at a concentration of 100 µg/l (approximately 9.5 mg/kg bw/day) for 100 days, followed by control water from Day 101 onwards (Group B) or NDEA at a concentration of 100 µg/l (approximately 9.5 mg/kg bw/day) for 30 days, followed by control water from day 31 to 61, and followed with 100 µg NDEA/l (approximately 9.5 mg/kg bw/day) for 70 days (Group C). All rats in Groups A and C survived

until the end of the study, 6 rats (20%) in Group B died. Rats in Group B appeared to be in poorer condition than those in Groups A and C. Bodyweight was significantly decreased in Group B. All surviving rats in Group B and all rats in Group C displayed diffuse hepatocellular carcinoma and cirrhosis of the liver (Yang *et al*., 2004).

In a limited carcinogenicity study, male Sprague-Dawley rats were administered NDEA in drinking water at a dose of 0 or 1 mg/l (approximately 0 and 0.1 mg/kg bw/day). Administration of the test substance was terminated 4 weeks prior to sacrifice. Four to twelve rats were sacrificed after 10, 15, 20, 25, 30, 35, 40, 50 55, and 65 weeks. Macroscopic analysis revealed gross alterations of the liver from Week 35. These changes consisted of small, multicentric whitish spots on the liver surface. These spots increased in size and frequency with time, giving rise to protuberant tumours from Week 40. These tumours were solid masses of nodular appearance and grayish colour with haemorrhagic areas. Histological examinations of the liver revealed basophilic and glycogenic areas, which increased in size and frequency with time. A high number of rats sacrificed after Week 40 displayed multiple papillomas of the oesophagus (Cortinovis *et al*., 1991).

It has been suggested that activation of NDEA by the cytochrome P450 enzyme CYP2E1 may contribute to its carcinogenicity. In a carcinogenicity study, wild-type and Cyp2e1-null mice were administered NDEA at a dose of 10 mg/kg bw/day (duration of exposure not stated). Incidences of liver tumours (hepatocellular adenomas and carcinomas) were significantly lower in Cyp2e1-null mice than wild-type mice (Kang *et al*., 2007), thus supporting the hypothesis.

NDEA has been reported to produce positive results in *in vitro* SOS chromotests at concentrations of 0.75-36.46 µg/ml. Positive results have also been reported in *in vitro* Ames studies at concentrations of 1.01 $x10^{-3}$ to 50.64 $x10^{-3}$ µg/plate (Aiub *et al*., 2003). These results suggest NDEA has mutagenic potential *in vitro*.

In 1978, the International Agency for Research on Cancer (IARC) evaluated NDEA and classified it as Group 2A, i.e. probably carcinogenic to humans on the basis that there is sufficient evidence of carcinogenicity in experimental animals (IARC, 1978b).

The US NTP evaluated NDEA and considered it is ‘reasonably anticipated to be a human carcinogen’ based on evidence of carcinogenicity in experimental animals (NTP, year unknown[b]).

A3.2.4 Nitrosopyrrolidine (NPYR)

NPYR is of low acute oral toxicity; an oral LD50 of 900 mg/kg bw has been reported in rats (HSDB, 2008).

Overall, the evidence for genotoxicity of NPYR *in vitro* and *in vivo* is equivocal. Results of genotoxicity studies conducted in *Salmonella typhimurium* have been mixed. Positive results have been reported in strains TA102, TA104 and TA1975 Positive and negative results have been reported in strains TA100 and TA1535, and negative results have been reported in strains TA97, TA98, TA2410 and TA2678 (CCRIS, 2008).

NPYR was reported to be severely clastogenic to Chinese hamster lung cells at a concentration of 0.5 mM (approximately 50 mg/l) and irradiated with near-UV radiation for 3 hours (Yamashita *et al*., 1995).

In a limited carcinogenicity study, Swiss mice (20/sex/dose) were administered NPYR in drinking water at doses of 0 or 0.01% 5 days/week (approximately 0 and 17 mg/kg bw/day, respectively, adjusting for 7 day/week exposure). Most treated mice died early in the study (mean survival time 12 weeks). Surviving mice displayed unspecified hepatic injury and four mice displayed a total of 51 lung adenomas, compared to a total of 8 adenomas observed in the controls (IARC, 1978f).

In another limited carcinogenicity study, BD rats were administered NPYR in drinking water at doses of 5 or 10 mg/kg bw/day. Doses were doubled after 150 days of treatment. Average tumour induction times were 470 and 290 days at the low and high dose, respectively, with tumours consisting of hepatocellular carcinomas (IARC, 1978f).

In a carcinogenicity study, Sprague-Dawley rats were administered NPYR in drinking water at doses of 0 or 0.02% for 5 days/week (approximately 0 and 35 mg/kg bw/day, respectively, adjusting for 7 day/week exposure) for 50 weeks, followed by observation for 55 weeks. All treated animals died during weeks 45-105. Twenty-six of 29 rats had developed hepatocellular carcinomas, 4 developed cholangiocarcinomas and 2 developed olfactory carcinomas (IARC, 1978f).

In another carcinogenicity study, Sprague-Dawley rats were administered NPYR in drinking water at doses of 0, 0.3, 1, 3 or 10 mg/kg bw/day over a lifetime. Hepatocellular carcinomas were noted in 13/62, 30/38 and 9/24 rats at 1, 3 and 10 mg/kg bw/day, respectively. Hepatocellular adenomas and a slight increase in overall incidences of malignant tumours were noted at all doses. The mean time of death in tumour-bearing rats was 664, 685, 533 and 444 days at 0.3, 1, 3 and 10 mg/kg bw/day, respectively (IARC, 1978f).

In 1978, the International Agency for Research on Cancer (IARC) evaluated NPYR and classified it as Group 2B, i.e. possibly carcinogenic to humans on the basis that there is sufficient evidence of carcinogenicity in experimental animals (IARC, 1978g).

A3.2.5 Nitrosodipropylamine (NDPA)

NDPA is of low acute oral toxicity; and oral LD50 of 480 mg/kg bw was reported in rats (ATSDR, 1989).

In a 1-week study, mice were administered NDPA in drinking water at a dose of 9.5 mg/kg bw/day. No effects on liver histology or activity of the enzymes, aspartate aminotransferase (SGOT), lactate dehydrogenase or γ-glutamyl-transferase. Unspecified esterase alterations were noted (ATSDR, 1989).

The available data indicate that NDPA is genotoxic *in vitro* following metabolic activation. Positive results were reported in *in vitro* Ames studies conducted in *Salmonella typhimurium* strain TA100, TA1530 and TA1535 with metabolic activation. Positive results have also been reported in reverse mutation assays in *Escherichia coli* with metabolic activation and in genotoxicity assays with Chinese hamster V79 cells (IARC, 1978f).

In a 30 week study, rats were administered NDPA via gavage at doses of 2.6-12.6 mg/kg bw/day for 2 days/week (approximately 0.7-3.6 mg/kg bw/day, adjusting for 7 day/week exposure). Mortality was increased in females administered 6.3 mg/kg bw/day (approximately 1.8 mg/kg bw/day, adjusting for 7 days/week exposure) and in males administered 12.6 mg/kg bw/day (approximately 3.6 mg/kg bw/day, adjusting for 7 day/week

exposure). High incidences of liver carcinomas, nasal cavity carcinomas, oesophageal carcinomas and papillomas, forestomach tumours and tongue tumours were reported at 6.3-12.6 mg/kg bw/day (approximately 1.8-3.6 mg/kg bw/day, adjusting for 7 day/week exposure) (ATSDR, 1989).

In a similar 30 week study, rats were administered NDPA via gavage at doses of 2.6-12.6 mg/kg bw/day for 5 days/week (approximately 1.8-9 mg/kg bw/day, adjusting for 7 day/week exposure). Mortality was increased at 5.1 mg/kg bw/day (approximately 3.6 mg/kg bw/day, adjusting for 7 day/week exposure) High incidences of liver carcinomas, nasal cavity carcinomas, oesophageal carcinomas and papillomas, forestomach tumours and tongue tumours were noted at all doses (ATSDR, 1989).

In a carcinogenicity study, BD rats (48/dose) were administered NDPA in drinking water at doses of 0, 4, 8, 15 or 30 mg/kg bw/day. Forty-five rats from each dose developed liver carcinomas after average induction times of 300, 202, 155 and 120 days at doses of 4, 8, 18 and 30 mg/kg bw/day, respectively. Eight rats at doses of 8 or 15 mg/kg bw/day also developed papillomas or carcinomas of the oesophagus, and 6 rats developed carcinomas of the tongue (IARC, 1978f).

In 1978, the International Agency for Research on Cancer (IARC) evaluated NDPA and classified it as Group 2B, i.e. possibly carcinogenic to humans on the basis that there is sufficient evidence of carcinogenicity in experimental animals (IARC, 1978e).

The US NTP evaluated NDPA and considered it is 'reasonably anticipated to be a human carcinogen' based on evidence of carcinogenicity in experimental animals (NTP, year unknown[e]).

A3.2.6 Nitrosopiperidine (NPIP)

In 1978, the International Agency for Research on Cancer (IARC) evaluated NPIP and classified it as Group 2B, i.e. possibly carcinogenic to humans on the basis that there is sufficient evidence of carcinogenicity in experimental animals (IARC, 1978d).

A3.2.7 Nitrosodibutylamine (NDBA)

NDBA is genotoxic *in vitro* following metabolic activation. Positive results were reported in have been reported in Ames studies with *Salmonella typhimurium* strains TA100, TA104, TA1535, TA1975 with metabolic activation. However, negative results have been reported in *Salmonella typhimurium* TA1535 without metabolic activation (CCRIS, 2008). Positive results have also been reported in *in vitro* mutagenicity assays conducted in Chinese hamster V79 cells at a concentration range of 500-1000 µmol (approximately 79 125-158 250 mg/l) (CCRIS, 2008).

In a carcinogenicity study, F344 rats were administered NDBA via gavage at doses of 1 or 2 mmol (approximately 158 and 317 mg/l, respectively) for 30 weeks followed by observation for 53 weeks. Approximately 80% of rats at the top dose survived until the end of the study. Approximately 60% of animals displayed liver carcinomas, 50% displayed forestomach carcinomas and 35% displayed transitional cell carcinomas of the urinary bladder (Lijinsky & Reuber, 1983).

The US NTP evaluated NDBA and considered it is 'reasonably anticipated to be a human carcinogen' based on evidence of carcinogenicity in experimental animals (NTP, year unknown[c]).

A3.2.8 NItrosomorpholine (NMOR)

NMOR is of low acute oral toxicity; an oral LD50 of 282 mg/kg bw has been reported in rats (HSDB, 2008).

Data on the genotoxicity of NMOR indicate that it is genotoxic *in vitro* with metabolic activation. Positive results were reported in *in vitro* Ames studies conducted in *Salmonella typhimurium* strains TA100, TA104, TA1530, TA1535 and TA1975 with metabolic activation, however, negative results were reported without metabolic activation (CCRIS, 2008). Negative results were reported in *Salmonella typhimurium* TA98 with and without metabolic activation (CCRIS, 2008). Positive results have also been reported in *in vitro* genotoxicity studies conducted in Chinese hamster V79 cells and rodent hepatocyte cells (CCRIS, 2008).

In a limited carcinogenicity study, male Sprague-Dawley rats were administered NMOR in drinking water at a dose of 0 or 10 mg/l (approximately 0 and 0.95 mg/kg bw/day). Administration of the test substance was terminated 4 week prior to sacrifice. Four to twelve rats were sacrificed after 20, 25, 30, 35, 40, 50, 55, 60 and 65 weeks. Macroscopic analysis revealed gross alterations of the liver from week 35. These changes consisted of small, multicentric whitish spots on the liver surface. These spots increased in size and frequency with time, giving rise to protuberant tumours from week 40. These tumours were solid masses of nodular appearance and grayish colour with haemorrhagic areas. Histological examinations of the liver revealed basophilic and glycogenic areas, which increased in size and frequency with time. One rat died at week 60 and one rat died at week 61. Examination of the lungs of these rats revealed lung metastases from hepatocellular carcinomas (Cortinovis *et al*., 1991).

In a carcinogenicity study, F344 rats were administered NMOR via drinking water at doses of 0, 0.07, 0.18, 0.45, 1.1, 2.6, 6.4, 16, 40 or 100 mg/l for 5 days week (approximately 0, 5, 12, 30, 75, 177, 434, 1086, 2714 and 6786 µg/kg bw/day, adjusting to a 7 day/week exposure). The exposure regime for the rats is reported in Table A2.

Table A2 Exposure regime in rats administered NMOR via drinking water

Dose (mg/l)	Dose (µg/kg bw/day)	Number of rats	Exposure duration
0	0	80	100
0.07	5	100	100
0.18	12	100	100
0.45	30	48	50
0.45	30	48	100
1.1	75	48	50
1.1	75	48	100
2.6	177	48	50
2.6	177	48	100
6.4	434	24	50
6.4	434	24	100

Dose (mg/l)	Dose (µg/kg bw/day)	Number of rats	Exposure duration
16	1086	24	50
40	2714	24	40
100	6786	24	25

Source: Lijinsky *et al.* (1988)

Survival was significantly lower than controls at the top four doses, at 1.1 mg/l (approximately 75 µg/kg bw/day) following 50 weeks exposure and 2.6 mg/l (approximately 177 µg/kg bw/day) following 100 weeks exposure. Most of the rats that died in the study, including the controls, displayed mononuclear cell leukaemia, pituitary neoplasms and neoplasms of the adrenal and mammary glands. These tumours were particularly present at the lowest doses and the controls, which lived the longest and therefore may be related to age, rather than treatment. At the higher doses, rats displayed neoplasms of the liver. Hepatocellular carcinomas were apparent following administration of 1.1 mg/l (approximately 75 µg/kg bw/day) and above, and haemagiosarcomas were apparent following administration of 2.6 mg/l (approximately 177 µg/kg bw/day) and above Lijinsky *et al.,* (1988).

In 1978, the International Agency for Research on Cancer (IARC) evaluated NMOR and classified it as Group 2B, i.e. possibly carcinogenic to humans on the basis that there is sufficient evidence of carcinogenicity in experimental animals (IARC, 1978c).

The US NTP evaluated NMOR and considered it is 'reasonably anticipated to be a human carcinogen' based on evidence of carcinogenicity in experimental animals (NTP, year unknown[d]).

A4 REMOVAL

A4.1 Overview

Prevention of contamination of drinking water by nitrosamines can be achieved by removal of precursors, i.e. prevention of formation, or actual removal once formed. Both approaches are reviewed below.

A4.2 Removal of Precursors

According to literature and laboratory studies reported by AWWARF (2007), nitrosamine precursors were removed according to Table A3.

Table A3 Nitrosamine precursor removal

Process	Comment
Biodegradation (e.g. during underground passage)	Good removal of some nitrogen-containing precursors. Most of the aliphatic amines seem to be removed efficiently.
Biofiltration (laboratory test)	Poor removal of NDMA precursors (10-30% removal after one month).
Flocculation and sedimentation	Poor removal of dissolved organic nitrogen (DON) as well as single aliphatic amines (<10% removal of precursors for NDMA, NDEA and NPYR).
Activated carbon	Removal dependent on chemical structure, e.g. approximately 50% adsorption of DON but poor removal of aliphatic amines; good removal of precursors for nitrosamine formation (e.g. PAC dose of 5 mg/l reduced formation potential of NDMA, NMOR and NPYR by a factor of at least two.
Oxidation	DMA possibly produced as a result of oxidation of tertiary amines with a DMA functional group.
Ozonation	Oxidation of NDMA precursors yielded a lower concentration of DMA than oxidation with chlorine dioxide. Aliphatic amines are not effectively oxidised by ozone, although significant reduction in NDMA formation potential.
Chlorination	Aliphatic amines react 'rather fast' with chlorine. Pre-chlorination can lower NDMA formation potential substantially.
Chlorine dioxide	Oxidation of NDMA precursors yielded a higher concentration of DMA than oxidation with ozone, although significant reduction in NDMA formation potential.

A4.3 Removal of Nitrosamines

According to literature and laboratory studies reported by AWWARF (2007), nitrosamines were removed according to Table A4.

Table A4 Nitrosamine removal

Process	Comment
Biodegradation (e.g. during underground passage)	Relatively slow process and dependent on levels of nutrients and other factors. Reported half-lives for nitrosamine biodegradation range from days to years.
Biofiltration (laboratory test under aerobic conditions)	Good microbial degradation of NDMA. Aerobic biodegradability decreased in the order: NDMA>>NDBA>NDcHxA>NDEA>NPIP> NDPA>NEMA>NPYR>NMOR
Air stripping (volatilisation)	Poor removal of NDMA and other nitrosamines.
Activated carbon	Poor adsorption of nitrosamines.

Process	Comment
Carbonaceous resins	Adsorption of nitrosamines better than for GAC, particularly for zeolites, but still low compared to other organic substances.
Oxidation	Dependent on pH; increased reaction rate under acidic conditions (pH<4.5) but value still low.
Ozonation	No effect on NDMA concentration.
AOPs	Fenton-type reactions efficient for removal of NDMA, but generally reaction rates are well below most other organic compounds.
UV irradiation (photolysis)	Effective for NDMA removal but at high dosage, e.g. one order of magnitude NDMA reduction requires about 10 times the dose for virus removal.

A4.4 Removal of Specific Nitrosamines

A4.4.1 Nitrosodimethylamine (NDMA)

In a nationwide survey of NDMA in raw and final waters in Japan, Asami *et al.* (2009) reported the reduction of NDMA concentrations (up to 20 ng/l following ozonation) as a result of biological activated carbon treatment.

It has been reported that nitrosamines may be slowly mineralised by microbial communities, however, half-lives have been estimated to range from days to years (AWWARF, 2007). However, AWWARF (2007) have reported that NMDA degradation rapidly occurred using a test filter to simulate biodegradation under aerobic conditions. Air stripping and ozonation are reported not to be effective at removing NDMA (AWWARF, 2007). Photolysis of NDMA by UV irradiation in some pilot-scale and industrial-scale experiments has been reported to remove NDMA. Removal of NDMA by 1 order of magnitude was reported to require a UV dose of 1000 mJ/cm² (AWWARF, 2007). GAC is reported to be poor at NDMA removal, however, carbonaceous resins and zeolite displayed some adsorption (AWWARF, 2007).

A4.4.2 Nitrosomethylethylamine (NMEA)

In an aqueous photolysis experiment, several nitrosamines, including NMEA, were irradiated at an energy level of 765 W/m², equivalent to Southern California midsummer midday sun. A half-life of 12-15 minutes was calculated (Plumlee & Reinhard, 2007). NMEA is expected to volatilise slowly from water surfaces, based on an experimental Henry's Law constant of 1.44×10^{-6} atm.m³/mole (SRC, 2008). It is not expected to adsorb to sediment or suspended solids, based on an experimental Log K_{ow} of 0.04 (SRC, 2008).

A4.4.3 Nitrosodiethylamine (NDEA)

In an aqueous photolysis experiment, several nitrosamines, including NDEA, were irradiated at an energy level of 765 W/m², equivalent to Southern California midsummer midday sun. A half-life of 12-15 minutes was calculated (Plumlee & Reinhard, 2007). NDEA is expected to volatilise slowly from water surfaces, based on an experimental Henry's Law constant of

3.63 x10^{-6} atm.m³/mole (SRC, 2008). It is not expected to adsorb to sediment or suspended solids, based on an experimental Log K_{ow} of 0.48 (SRC, 2008).

A4.4.4 Nitrosopyrrolidine (NPYR)

In an aqueous photolysis experiment, several nitrosamines, including NPYR, were irradiated at an energy level of 765 W/m², equivalent to Southern California midsummer midday sun. A half-life of 12-15 minutes was calculated (Plumlee & Reinhard, 2007). NPYR is not expected to adsorb to sediment or suspended solids, based on an experimental log K_{ow} of -0.19 (SRC, 2008). NPYR is not expected volatilise from water surfaces, based on an experimental Henry's Law constant of 4.89 x10^{-8} atm.m³/mole (SRC, 2008).

A4.4.5 Nitrosodipropylamine (NDPA)

NDPA is not expected to adsorb to sediment or suspended solids, based on an experimental log K_{ow} of 1.36 (SRC, 2008). NDPA may volatilise slowly from water surfaces, based on an experimental Henry's Law constant of 5.38 x10^{-6} atm.m³/mole (SRC, 2008). NDPA is expected to undergo photolysis; a photolytic half-life of 2.5 hours has been reported in lake water. The degradation products were identified as n-propylamine and di-n-propylamine (ATSDR, 1989).

A4.4.6 Nitrosopiperidine (NPIP)

In an aqueous photolysis experiment, several nitrosamines, including NPIP were irradiated at an energy level of 765 W/m², equivalent to Southern California midsummer midday sun. A half-life of 12-15 minutes was calculated (Plumlee & Reinhard, 2007). NPIP is not expected to adsorb to sediment or suspended solids, based on an experimental log K_{ow} of 0.36 (SRC, 2008). Volatilisation from water surfaces is not expected to be an important fate process, based on an experimental Henry's Law constant of 8.44 x10^{-7} atm.m³/mole (SRC, 2008).

A4.4.7 Nitrosodibutylamine (NDBA)

No data were located during the literature search.

A4.4.8 Nitrosomorpholine (NMOR)

NMOR is not expected to adsorb to sediment or suspended solids, based on an experimental log K_{ow} of -0.44 (SRC, 2008). It is not expected to undergo volatilisation from surface waters, based on an experimental Henry's Law constant of 2.45 x10^{-8} atm.m³/mole (SRC, 2008). It is reported to be rapidly photolysed in sunlight to the amino radical and nitric oxide, however, in the absence of free radical scavengers, reformation to NMOR is also expected to rapidly occur (HSDB, 2008).

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APPENDIX B DETERMINATION OF NDMA AND OTHER NITROSAMINES IN DRINKING WATER

B1 INTRODUCTION

An objective of the project was to develop an analytical method to determine NDMA in water with a limit of detection close to 1 ng/l. A method was developed with a limit of detection for NDMA of 0.48 ng/l, which was determined from the within batch standard deviation of tap water samples using the procedure described in NS30 (a manual on analytical quality control for the water industry). All results reported within the report have been blank corrected unless stated otherwise.

The method describes a procedure for the determination of NDMA in drinking water using a solid phase extraction (SPE) cartridge containing 2 g of 80-120 mesh coconut charcoal analysed using gas chromatography mass spectrometry (GCMS).

The method described has been shown to be suitable for the determination of NDMA in drinking water samples.

The method described was also used to determine NDMA in diluted samples of coagulants.

The method may be applicable to untreated source waters (with suitable adaptation) and to other types of water samples, but it has not been evaluated for these uses.

An analytical method to determine other nitrosamines in drinking water based on liquid chromatography tandem mass spectrometry (LCMSMS) is also described (Section B3).

B2 NDMA ANALYSIS – METHOD DEVELOPMENT AND VALIDATION

B2.1 Overview

B2.1.1 Substances determined

N-nitrosodimethylamine (NDMA) CAS Number: 62-75-9.

B2.1.2 Type of sample

Drinking water.

B2.1.3 Basis of method

The aqueous sample is spiked with the labelled internal standard d_6-N-nitrosodimethylamine (d_6-NDMA) and extracted using solid phase extraction cartridges by passing a 1-litre water sample through a cartridge containing 2 g of 80-120 mesh coconut charcoal. NDMA is eluted from the solid phase with dichloromethane (DCM), the extract is dried and concentrated using a nitrogen blow-down apparatus prior to analysis.

The extracts are analysed by injecting an aliquot of the concentrated extract onto a fused silica capillary column (two columns in series) of a GCMS system operated in positive ion electron ionisation (EI) mode.

The concentration of NDMA is measured by internal standardisation.

B2.1.4 Range of application

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

B2.1.5 Calibration curve

Calibration is linear over the range of application of the method.

B2.1.6 Interferences

Any substance which is co-extracted under the conditions used, is not removed by the clean-up methods used, which exhibits similar chromatographic behaviour to NDMA, which produces the same mass fragments and has the same retention time as NDMA.

B2.1.7 Standard deviation

See Section B2.13.

B2.1.8 Limit of detection

NDMA 0.48 ng l^{-1}.

B2.1.9 Sensitivity

This is instrument dependent.

B2.1.10 Bias

See Section B2.13.

B2.2 Principle

Samples are collected in 1-litre plastic PET bottles containing 40 mg of ascorbic acid. The aqueous sample is spiked with the labelled internal standard d_6-N-nitrosodimethylamine (d_6-NDMA) and extracted using solid phase extraction cartridges by passing the water sample through a cartridge containing 2 g of 80-120 mesh coconut charcoal. NDMA is eluted from the solid phase with dichloromethane (DCM), the extract is dried and concentrated using a nitrogen blow-down apparatus prior to analysis.

The extracts are analysed by injecting an aliquot of the concentrated extract onto a fused silica capillary column (two columns in series) of a GCMS system operated in positive ion electron ionisation (EI) mode.

The concentration of NDMA is measured by internal standardisation.

B2.3 Terms, Definitions and Symbols

For the purposes of this standard operating procedure, the following terms, definitions and symbols apply:

B2.3.1 Analyte

N-nitrosodimethylamine (NDMA).

B2.3.2 Calibration standard

A solution prepared from a secondary standard and/or stock solutions and used to calibrate the response of the instrument with respect to the analyte concentration.

B2.3.3 Calibration verification standard or continuing calibration check

A mid-point calibration standard that is used to verify calibration.

B2.3.4 Internal standard spiking

The addition of d_6-NDMA. The recovery of d_6-NDMA is used to correct values of native NDMA.

B2.3.5 Statistical performance characteristics

Quantification for measured values of the possible deviations resulting from the random part of the measuring process, e.g. repeatability or instability [ISO 6879:1995].

B2.3.6 Method blank

A blank water sample that has been treated exactly as a sample through the complete analytical procedure including extraction, clean-up, identification and quantification, including all the relevant reagents and materials.

B2.3.7 GCMS

Gas Chromatography Mass Spectrometry.

B2.4 Hazards Warning and Safety Precautions

Hazard assessments should be carried out for all of the chemicals and procedures used and should be consulted prior to carrying out any work with the chemicals involved.

Appropriate precautions should be taken when handling pure compounds and standard solutions of these compounds.

Several of the reagents used are potentially hazardous. Dichloromethane (DCM) is harmful if swallowed or inhaled. DCM may be harmful by skin contact, it is an eye and skin irritant.

B2.5 Reagents

All reagents must be of sufficient purity such that they do not give rise to significant interfering peaks in the analysis. Purity must be checked for each batch of materials by the running of procedural blanks with each batch of samples analysed. Solvents suitable for high performance liquid chromatography (HPLC) or pesticide analysis use and analytical grade materials are normally suitable unless otherwise stated and details of preparation are given where appropriate.

To avoid excessive evaporation of solvent, standard solutions should be stored in a refrigerator. However, prior to use, all solutions and solvents should be allowed to reach ambient room temperature before volumetric measurements are made.

B2.5.1 Standards, internal standards and reagents

N-nitrosodimethylamine (Greyhound Chromatography, Part No. N-8270 JM)

d_6-N-nitrosodimethylamine (QMx Laboratories, Part No. D2937)

L-Ascorbic acid 99+% ACS Reagent (Sigma-Aldrich, Part No. 255564-100).

B2.5.2 Solvents

Dichloromethane, water - Rathburns HPLC grade or equivalent.

B2.5.3 Solid phase cartridges

Solid phase extraction (SPE) cartridge containing 2 g of 80-120 mesh coconut charcoal – 6 ml Resprep EPA 521 (Thames Restek, Part No. 26032).

B2.6 Standard Solutions

B2.6.1 Internal standard stock solution, 1 mg/ml

Into a 10-ml volumetric flask, dissolve an accurately weighed amount of approximately 10 mg of d_6-NDMA in approximately 9 ml of dichloromethane. Make to 10 ml with dichloromethane and mix well.

This solution is stable for 1 year when stored in a freezer at -18 °C.

B2.6.2 Internal standard intermediate solution, 100 μg/ml

Add 1 ml of stock solution (see B2.6.1) into a 10 ml volumetric flask containing dichloromethane, and then make up to the mark.

This solution is stable for 1 year when stored in a freezer at -18 °C.

B2.6.3 Internal standard spiking solution, 0.4 μg/ml

Add 40 µl of the intermediate solution (see B2.6.2) into a 10 ml volumetric flask containing methanol, and then make up to the mark.

This solution is stable for 1 year when stored in a freezer at -18 °C.

B2.6.4 NDMA standard intermediate solution, 10 μg/ml

Add 50 µl of commercial stock solution (see B2.5.1) into a 10 ml volumetric flask containing dichloromethane, and then make up to the mark.

This solution is stable for 1 year when stored in a freezer at -18 °C.

B2.6.5 Standard spiking solution, 0.1 μg/ml

Add 100 µl of the intermediate solution (see B2.6.4) into a 10 ml volumetric flask containing methanol, and then make up to the mark.

This solution is stable for 1 year when stored in a freezer at -18 °C.

B2.6.6 Calibration standards

Calibration standard solutions should be prepared. Each calibration solution should contain NDMA and the deuterated internal standard d_6-NDMA as follows:

Each flask should be made up to 10 ml with dichloromethane.

Description	Concentration of NDMA ng ml^{-1}	Concentration of internal standard μg ml^{-1}
Cal-40	400	0.4
Cal-20	200	0.4
Cal-10	100	0.4
Cal-5	50	0.4
Cal-2	20	0.4
Cal-1	10	0.4
Cal-0	0	0.4

B2.7 Apparatus

In addition to general laboratory glassware, the following are required.

B2.7.1 Analytical balance

Analytical balance capable of weighing to 0.0001 g.

B2.7.2 Solid phase extraction apparatus

The manifold should be capable of handling several solid phase extraction cartridges. The flow rate through each individual cartridge should be controlled by adjusting the vacuum applied to each one, or by the application of air or nitrogen.

B2.7.3 Extract concentration equipment

Any suitable proprietary concentrator with thermostatically controlled water bath or equivalent system.

B2.7.4 Nitrogen or air blow-down apparatus or equivalent system

Nitrogen or air blow-down apparatus or equivalent system.

B2.7.5 GCMS equipment

Any capillary GCMS with an electron ionization (EI) source. The suitability of the equipment would need to be evaluated.

The following conditions have been used in the performance testing of NDMA by this method:

- Agilent GC-MS (6890GC, 5973 MS, 7683 injector).
- DB625 and Rtx5-amine columns attached in series with deactivated pre-column.

1) Rtx5: 30 m × 0.25 mm i.d. fused silica capillary column coated with a 1.0 micron bonded film of polyphenylmethylsilicone (Restek Rtx 5SIL MS or equivalent)

2) DB625: 30 m × 0.25 mm i.d. fused silica capillary column coated with a 1.4 micron bonded film of polyphenylmethylsilicone (J&W DB625 or equivalent)

3) Base deactivated gooseneck splitless liner (Thames Restek, Part No. 20785-210.5).

- Helium carrier gas, constant pressure mode.
- Split-splitless injector - 2 µl injection.
- Oven ramp - 35 °C up to 250 °C.
- Transfer line heated to 260 °C.
- Positive ion Electron Ionisation (EI) mode.
- SIM Mode - NDMA ions: 74, 42, 43 and d_6-NDMA Ion: 80.

B2.8 Sample Collection and Storage

Samples from a water tap should be taken after allowing the system to flush until the water temperature has stabilized (usually about 2 min). Adjust the flow to about 500 ml min^{-1} and collect samples from the flowing stream in 1-litre PET bottles containing 40 mg of ascorbic acid. Take care not to rinse out the dechlorination agent during sample collection. When sampling from an open body of water ensure that sampling equipment is free of plastic or rubber tubing, gaskets and other parts that may leach interfering analytes into the water sample.

Samples should be shipped to the laboratory within 48 hours of collection. The samples should be kept cool during transportation (below 10 °C). On receipt into the laboratory, samples are stored in the dark at 4 °C ± 2 °C prior to extraction. Samples are stable for up to 3 weeks when stored in the dark at 4 °C ± 2 °C and extracts for 3 weeks when stored in the dark at -15 °C ± 5 °C.

B2.9 Analytical Procedure

B2.9.1 Extraction procedure

Sample pre-treatment

One litre of sample is spiked with internal standard at 40 ng l^{-1}.

Sample extraction

SPE conditioning

SPE cartridges are washed with methanol (15 ml), dichloromethane (15 ml) and methanol (6 ml), dichloromethane (6 ml) before being conditioned with methanol (6 ml) and ultrapure water (15 ml).

Ensure that the cartridge does not dry out during this process or prior to passage of a sample through the cartridge.

Sample extraction

Attach the sample lines, apply vacuum and extract the sample at a flow rate of less than 10 ml per minute. After extraction, remove the lines and add distilled water to the reservoir (5 ml).

SPE cartridge drying

Dry the cartridge under nitrogen, ensure that the cartridge is thoroughly dry.

Elution of NDMA

A collection vessel is placed inside the extraction manifold prior to sample elution. NDMA is eluted with 100% dichloromethane, which is added to the SPE cartridge (8 ml). Soak the cartridge with DCM for 1 minute. The vacuum is then applied and DCM is pulled through the cartridge.

The procedure is repeated with further aliquots of DCM (4 x 3 ml). The collection vessel is removed and the contents concentrated to a final volume of 1 ml using a TurboVap concentrator and then to 100 μl using a nitrogen-blow down apparatus in an autosampler vial.

B2.9.2 Drying extract

Prepare a glass column packed with 5 g of anhydrous sodium sulfate. Pre-wet with a small volume of dichloromethane prior to passing the extract through it. Collect the dried extract in a clean centrifuge tube.

After passing the extract through the drying column, wash the sodium sulfate with at least 3 ml DCM and collect the solvent wash in the same collection tube as the sample extract.

B2.9.3 Extract concentration

Concentrate the extract to approximately 1 ml in using a TurboVap concentrator and transfer to a vial. Concentrate the extract to a final volume of 100 μl under a gentle stream of nitrogen.

B2.9.4 Quality control

With each extraction batch, a laboratory blank and a blank spiked AQC sample should be prepared as described below and taken through the complete analytical procedure described.

Laboratory blank

One litre of ultrapure water is dechlorinated with ascorbic acid and extracted using the procedure given in Section B2.9.1.

AQC spike

One litre of ultrapure water is dechlorinated with ascorbic acid and spiked with NDMA at 10 ng l^{-1} and extracted using the procedure given in Section B2.9.1.

B2.9.5 GCMS analysis procedure

Following manufacturer's instructions, optimise the operating conditions of the GCMS system.

Analyse the calibration standard solutions, blank, AQC spike and sample extract. Determine the concentration of NDMA in the sample extracts (Section B2.10).

B2.10 Calculation of Results

A calibration graph of the ratio of the peak area of NDMA to the corresponding labelled internal standard against the mass of internal standard injected is constructed either manually or via the data handling system. The original sample concentration is calculated from the graph taking into account the sample volume extracted, the sample volume injected and any dilutions that may have been used.

Using the mass spectrometer software, the area of each specific peak can be measured. For each determinand the response ratio is then calculated:

$$\text{Response} = [\text{Pk Area (D)}] / [\text{Pk Area (I.S.)}]$$

where:

Pk Area (D) is the peak area of the determinand

Pk Area (I.S.) is the peak area of the d_6-NDMA internal standard

Using the data system attached to the analytical instrument (or manually), plot the response ratio against the concentration for the standards. From the plotted calibration curve, calculate the slope and intercept using linear regression.

By determining the response ratio in the unknown samples, AQC blanks and controls, described above, this can then be applied to the following equation and the concentration of each determinand calculated:

$$\text{Concentration} = [\text{Response} - \text{Intercept}] / [\text{Slope}]$$

B2.11 Quality Control

The quality of the analysis is assured through reproducible calibration and testing of the extraction and GCMS system. A series of quality control samples should be analysed with each batch of samples and monitored through control charting and other quality review procedures. It is recommended that with every batch of samples extracted, a blank and a spiked control sample (spiked with NDMA) are produced.

B2.12 References

1. 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).

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B2.13 Appendices

B2.13.1 Chemical structures of N-nitrosodimethylamine and d6-N-nitrosodimethylamine

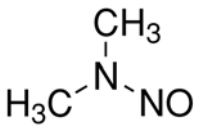


Figure B1 Structure of N-nitrosodimethylamine (NDMA)

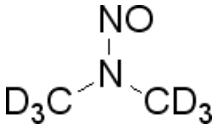
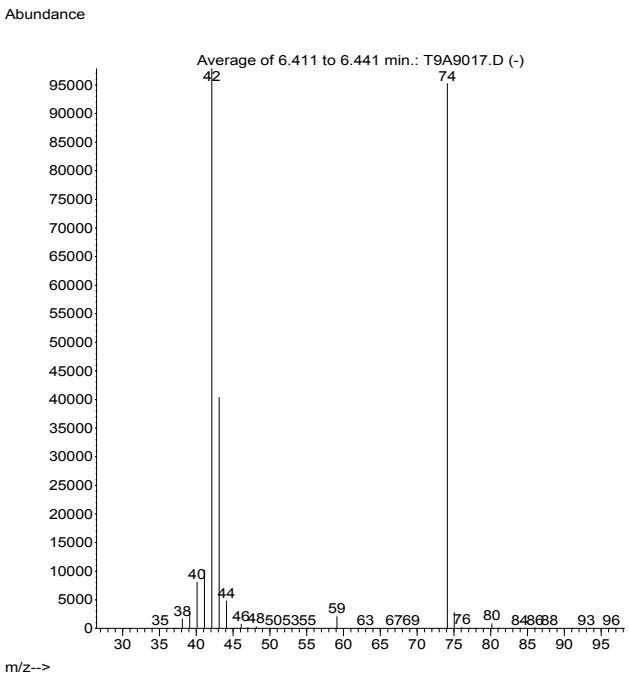


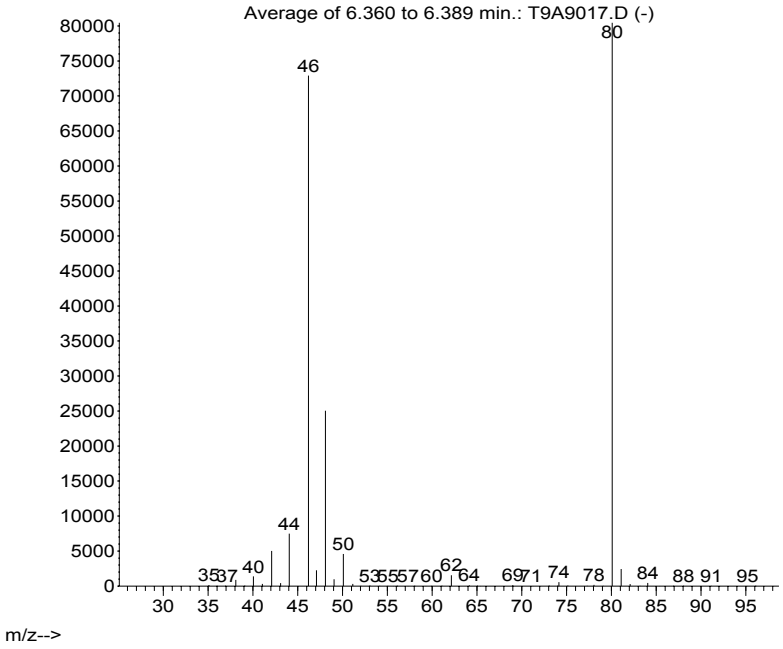
Figure B2 Structure of d_6-N-nitrosodimethylamine (d_6-NDMA)

B2.13.2 Electron Ionisation (EI) Mass Spectra of N-nitrosodimethylamine and d6- N-nitrosodimethylamine

NDMA Mass Spectrum

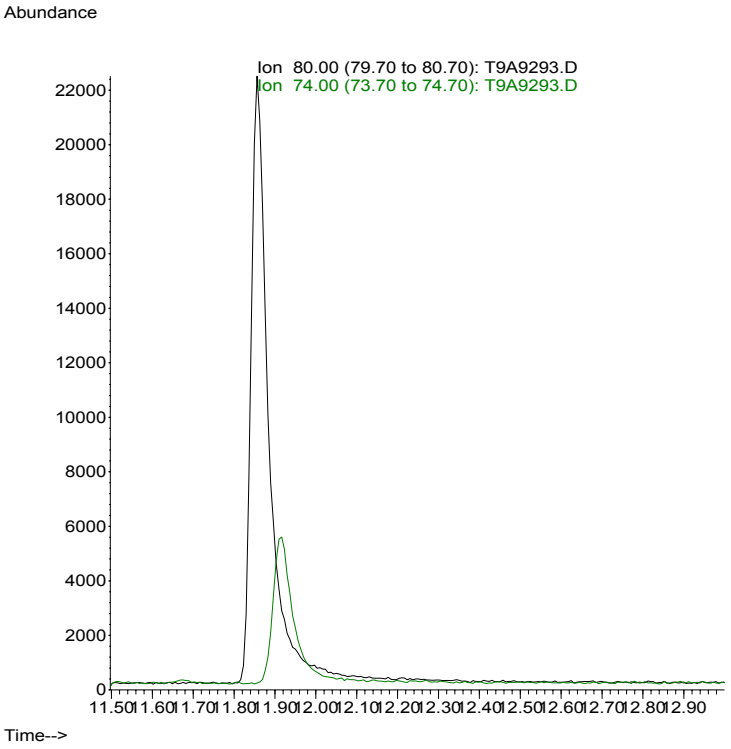


d_6 NDMA Mass Spectrum

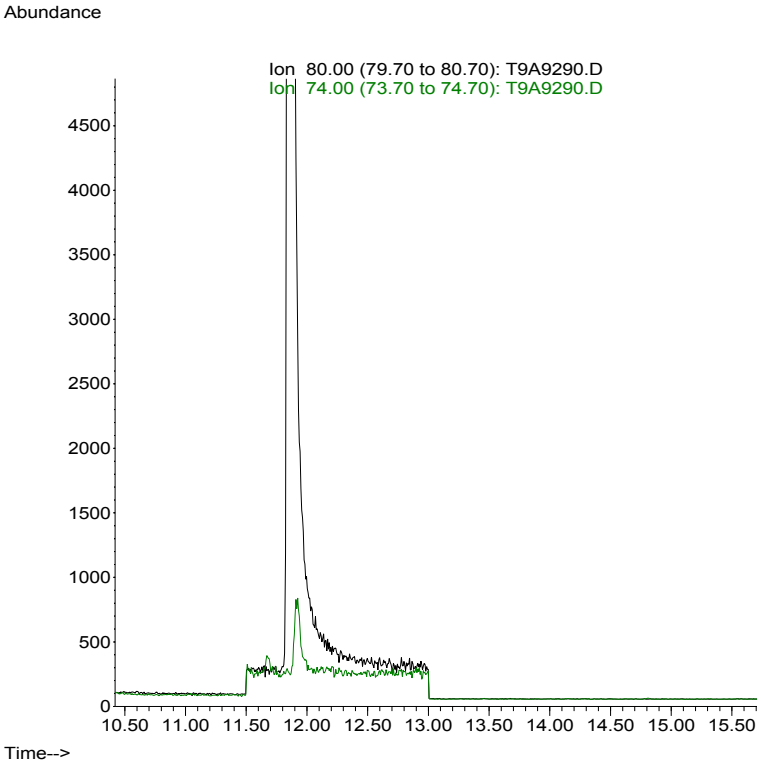


B2.13.3 Mass Chromatograms

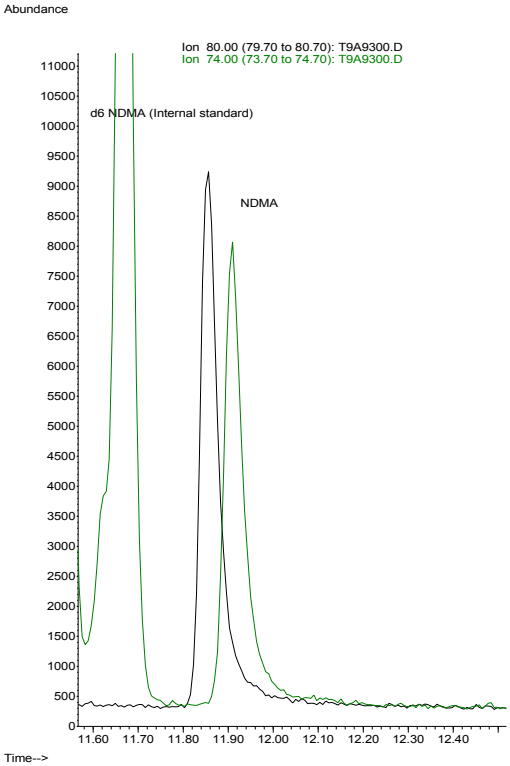
Calibration standard 10ng/l NDMA (40ng/l d_6-NDMA)



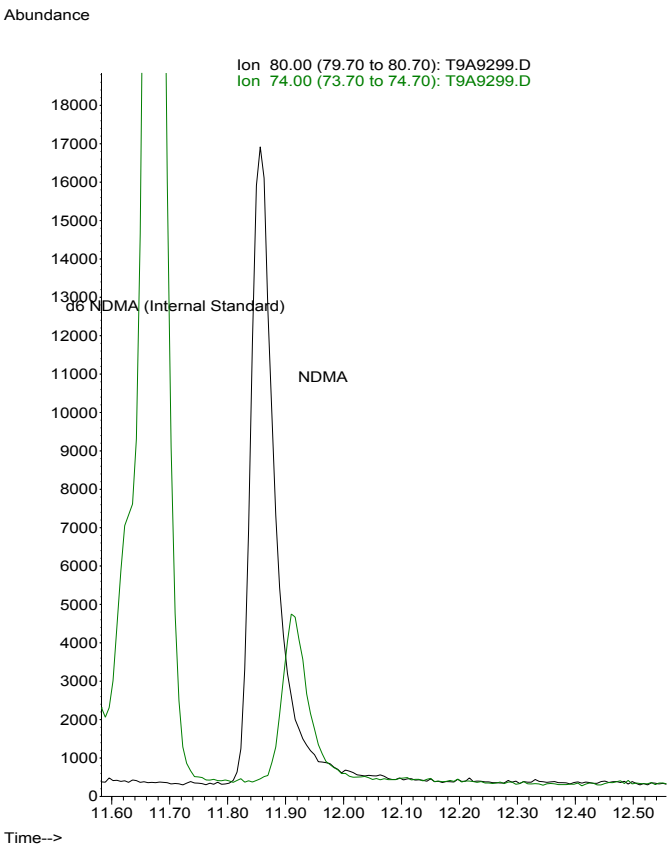
Calibration standard 1ng/l NDMA (40ng/l d_6 NDMA)



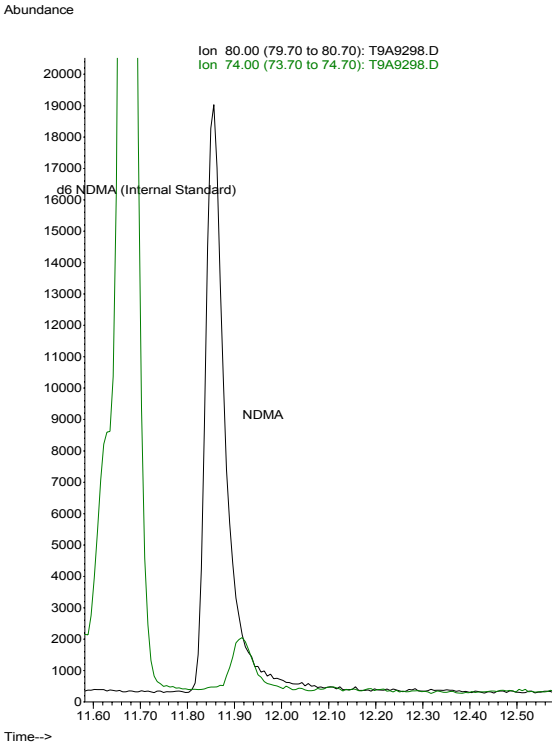
Validation Tap Water High Spike (32 ng/l)



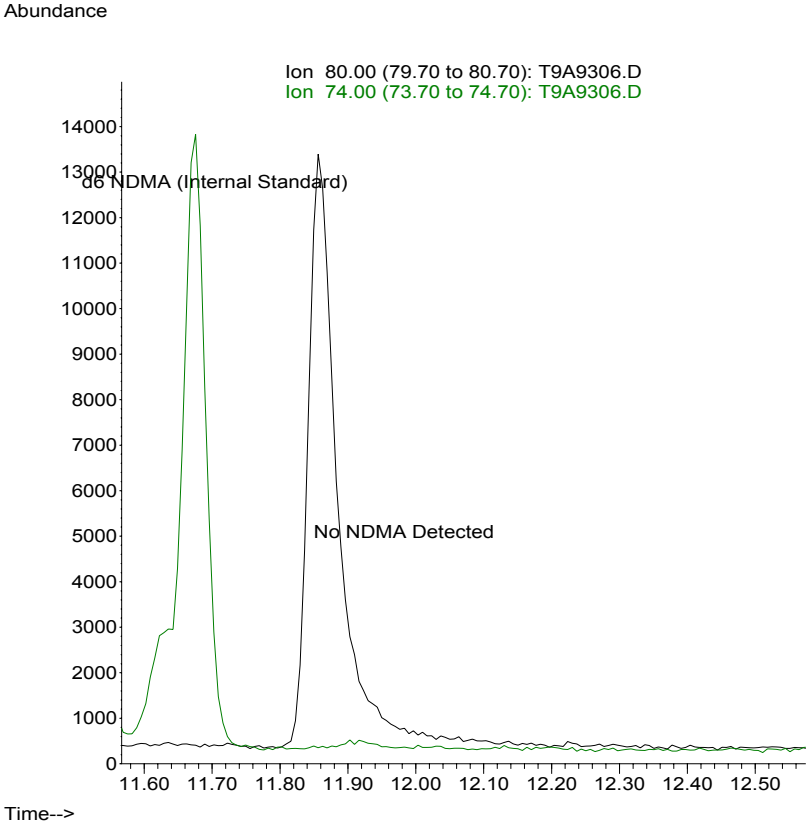
Validation Tap water Low Spike (8ng/l)



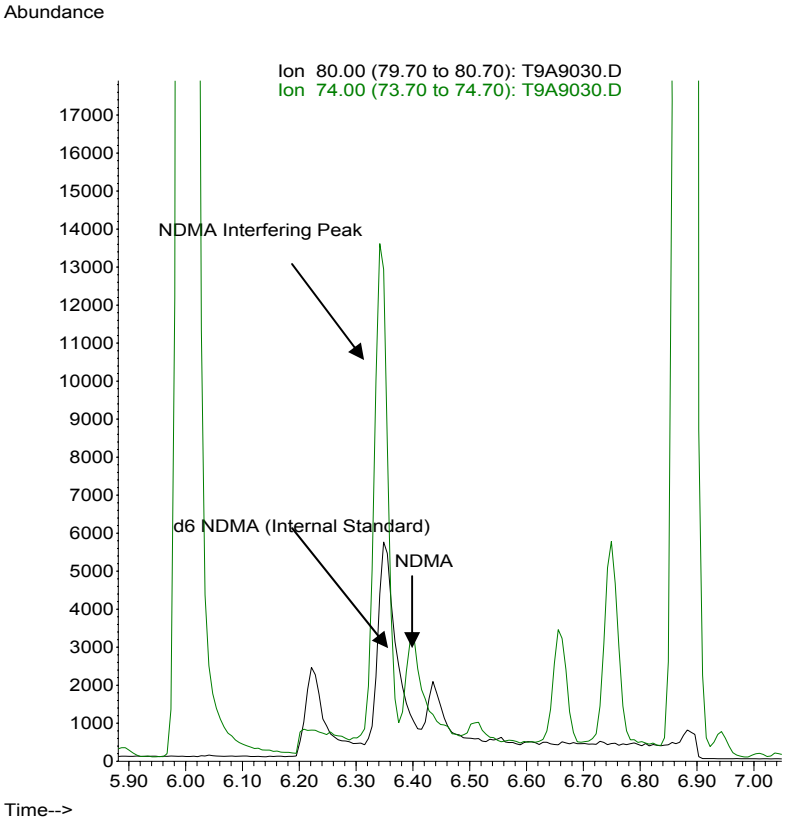
Validation Tap Water MDL Spike (2 ng/l)



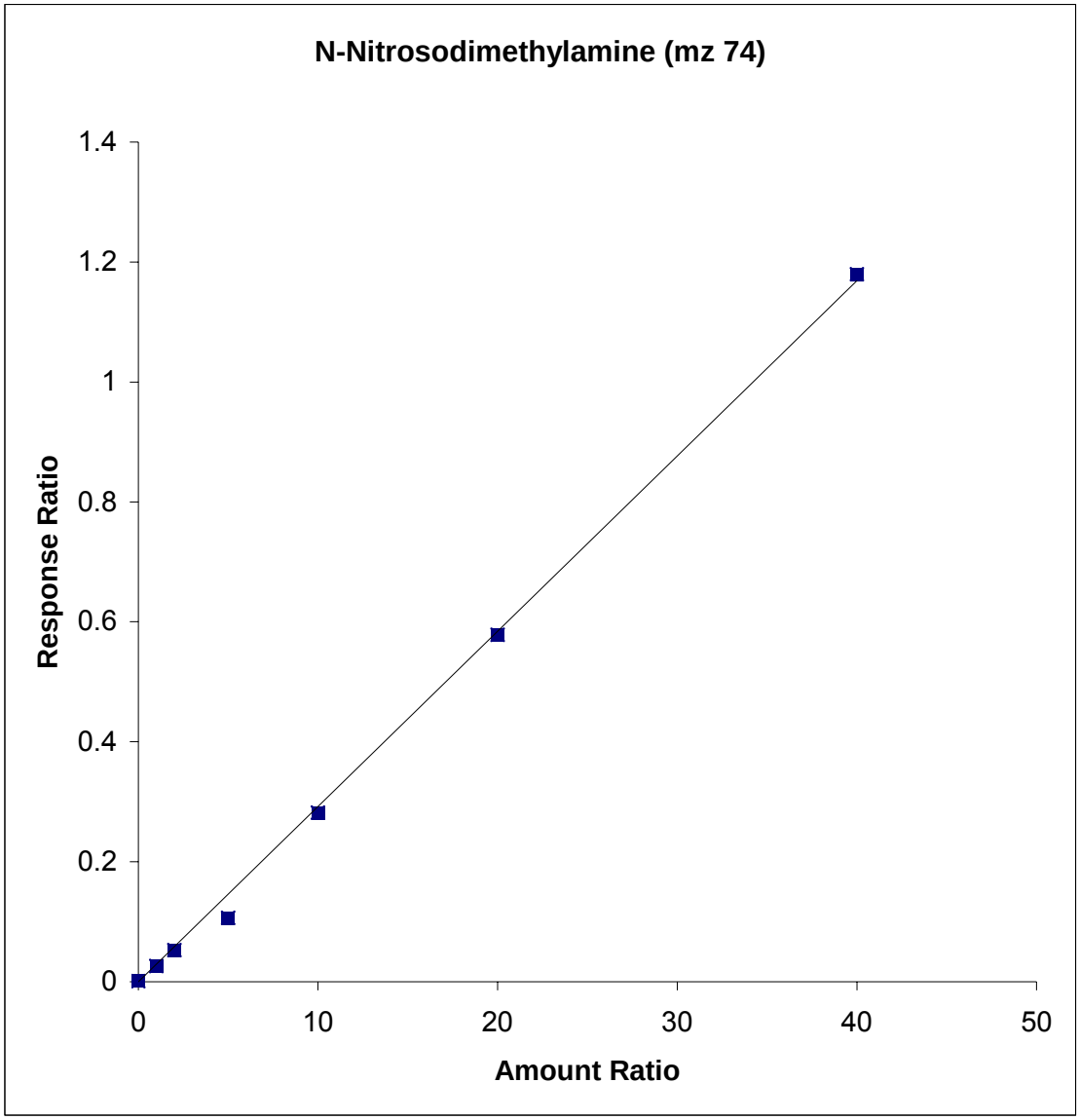
Ultrapure Water Blank (Rathburns)



Tap Water spiked with NDMA (10 ng/l) extracted using original EPA method 521



B2.13.4 NDMA Typical Calibration Curve



Response Ratio = 2.92e-002 * Amount
Coeff of Det (r^2) 0.9983 Curve Fit : Linear / (0,0)

B2.13.5 Method Performance

Batch	Replicate	Standards	Tap Water			
		Blank	Tap Blank	LOD	Low spike	High Spike
1	1	0.44	0.78	2.9	8.23	33.99
	2	0.42	0.43	2.4	8.07	33.34
2	1	0.5	0.31	2.49	8.44	33.17
	2	0.36	0.39	2.36	8.05	33.89
3	1	0.18	0.62	2.23	8.11	33.86
	2	0.28	0.47	2.23	8.59	34.2
4	1	0.2	0.3	2.33	8.1	36.8
	2	0.19	0.24	2.21	8.18	33.45
5	1	0.27	0.22	2.19	8.32	35.52
	2	0.16	0.25	2.31	8.8	34.66
6	1	0.13	0.37	2.24	8.31	35.84
	2	0.22	0.49	2.17	8.72	36.51
7	1	0.21	0.21	2.33	8.53	35.99
	2	0.42	0.36	2.39	8.26	35.87
8	1	0.27	0.27	2.22	7.91	34.48
	2	0.46	0.28	2.2	7.75	33.89
9	1	0.23	0.38	2.24	8.34	34.69
	2	0.3	0.29	2.07	7.98	34.43
10	1	1.32	0.79	2.55	8.73	34.19
	2	0.9	1.45	2.87	8.9	34.03
11	1	0.76	0.82	2.48	9.07	38.02
	2	1.05	0.82	2.84	9.41	36.97
	Mean	**0.421**	**0.479**	**2.375**	**8.400**	**34.900**
	M1	**0.188**	**0.154**	**0.085**	**0.291**	**2.983**
	M0	**0.018**	**0.029**	**0.026**	**0.054**	**0.683**
	F value	**10.429**	**5.320**	**3.299**	**5.403**	**4.368**
	Signif.	**	**	*	**	*
	Sw	**0.13414714**	**0.170**	**0.160**	**0.232**	**0.826**
	Sb	**0.29126917**	**0.250**	**0.172**	**0.344**	**1.072**
	St	**0.32067613**	**0.302**	**0.235**	**0.415**	**1.354**
	Rel SD (St)	**76.10%**	**63.11%**	**9.90%**	**4.94%**	**3.88%**
	F 0.05	**1.75**	**1.69**	**1.64**	**1.69**	**1.69**
	Calc. F	**0.411**	**0.366**	**0.221**	**0.061**	**0.038**
	Est Degs F	**12**	**14**	**16**	**14**	**14**
	OK ?		**Pass**	**Pass**	**Pass**	**Pass**
	L.O.D	****	****	**0.481**	****	****

L.O.D calculated as 3 * Sw of "low spiked tap water blank"
Uncertainty calculated as bias + (2*SD)

Key:

N.S	Not Significant
*	Significant at the 0.05 level
**	Significant at the 0.01 level

B2.13.6 NDMA Stability

Replicate	Day 0	Day 21
1	9.7	9.9
2	10.0	10.3
3	9.8	10.8
4	10.0	10.3
5	10.1	10.3
6	10.0	10.1
7	9.9	10.4
8	10.0	10.3
9	10.1	10.1
10	9.9	10.3
Number	**10.0**	**10.0**
Average each sample	**9.950**	**10.3**
Stdev within sample	0.13	0.23
pooled VAR	0.04	
Mean difference	0.33	
Pooled sd	0.19	
Mean diff%	3.32	
sigma d	0.08	
t statistic	3.91	
t from tables	2.10	
Significance	**SIG**	**(Not significant)**

Conclusion: The sample is stable at ambient temperature, preserved with ascorbic acid, stored over 21 days.

B3 NITROSAMINE ANALYSIS - METHOD DEVELOPMENT AND VALIDATION

B3.1 Overview

B3.1.1 Scope

The method is used to determine the following determinands using LCMSMS analysis.

N-Nitrosodimethylamine (NDMA)*
N-Nitrosopyrrolidine (NPYR)
N-Nitrosodipropylamine (NDPA)
N-Nitrosomethylethylamine (NMEA)
N-Nitrosodiethylamine (NDEA)*
N-Nitrosopiperidine (NPIP)
N-Nitrosodibutylamine (NDBA)
N-Nitrosomorpholine (NMOR)

*NDMA and NDEA are also determined using GCMS.

B3.1.2 Principle

This method is for the determination of nitrosamines in waters. Samples are spiked with a known concentration of deuterated internal standard (d_6-NDMA) and extracted by passing the sample through a solid phase extraction (SPE) cartridge containing coconut charcoal. The cartridge is dried under vacuum and nitrosamines are eluted from the cartridge with dichloromethane (DCM). The DCM extract is dried and concentrated down to incipient dryness and reconstituted into methanol (200 µl). The extract is analysed by LCMSMS using positive ion electrospray ionisation.

B3.1.3 Range of application and reporting limits

The range of application is up to 40 ng/l of each determinand. Concentrations above the range of application can be determined by dilution.

B3.2 Sampling and Preservation

Samples are collected in 1-litre plastic PET bottles containing 40 mg of ascorbic acid. On receipt into the laboratory, samples are stored in the dark at 4°C ± 2°C prior to extraction.

B3.3 Extraction Procedure

B3.3.1 Conditioning SPE cartridges

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

B3.3.2 Preparation of standards and AQC

One litre of ultrapure water is dechlorinated with ascorbic acid and spiked up with internal standard / standard / AQC as appropriate. The calibration range is as follows: 0, 4, 10, 20 and 40 ng/l of each determinand with an AQC at 10 ng/l. The internal standard used is D_6-NDMA at 40 ng/l.

B3.3.3 Preparation of samples

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

B3.3.4 Extraction

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

B3.3.5 Drying, elution and concentration

The cartridges are dried under vacuum and eluted with DCM. The DCM extract is dried with sodium sulphate to remove any residual water and concentrated using a stream of nitrogen to incipient dryness and reconstituted into methanol (200 µl).The extract is transferred to an amber vial with insert and analysed by LC-MSMS.

B3.4 Instrumental Procedure

B3.4.1 LCMS conditions

HPLC

Pump: Agilent 1100 Quatanary Pump

Injection volume used: 20.00 µl

Column temperature: 30 °C

Column: Phenomenex Polar-RP 80A 150mm x 4.6 mm

LC Gradient:

Step	Total Time(min)	Flow Rate(µl/min)	A (%)	B (%)
0	0.00	1000	5.0	95.0
1	2.00	1000	5.0	95.0
2	5.00	1000	80.0	20.0
3	7.00	1000	95.0	5.0
4	8.00	1000	5.0	95.0
5	12.00	1000	5.0	95.0

Agilent autosampler: Agilent 1100 Thermo Autosampler

Syringe size (µl): 100

Injection volume (µl): 20.00

Draw speed (µl/min): 200.0

Eject speed (µl/min): 200.0

Mass spectrometer

Mass Spectrometer: Applied Biosystems API 5000 Triple Quadrupole LC/MS/MS

Source temperature (at setpoint): 600.0 °C

MRM Transitions monitored:

Compound	Q1 Mass (Da)	Q3 Mass (Da)	Dwell(msec)	CE	CXP
NDMA	75	43	250	25	6
NDMA-D6	81	46	100	25	6
NMEA	89	61	250	15	8
NPYR	101	55	100	25	8
NDEA	103	75	250	15	12
NPIP	115	69	100	25	10
NMOR	117	87	100	15	14
NDPA	131	89	100	15	14
NDPA-D14	145	97	100	15	14
NDBA	159	103	100	25	8
NDPHA	199	169	100	15	10

B3.5 Validation

The limit of detection was determined using US EPA 40 CFR Part 136 Appendix B, for calculating method detection limit (MDL).

Sample[1]	NDMA[2]	NMEA[2]	NPYR	NDEA	NPIP	NMOR	NDPA	NDBA	NDPHA[3]
MDL1	N/A	4.96	5.39	5.55	5.53	5.18	4.76	6.65	2.97
MDL2	N/A	4.74	3.88	5.05	5.74	5.05	5.12	5.23	1.30
MDL3	N/A	4.81	5.97	3.83	7.88	5.53	5.33	7.02	3.72
MDL4	N/A	4.76	5.11	4.67	5.54	4.90	4.83	7.46	2.38
MDL5	N/A	4.99	5.41	7.18	5.74	4.49	5.07	7.05	4.41
MDL6	N/A	4.89	5.29	4.84	5.35	5.63	5.17	8.09	[3]
MDL7	N/A	4.54	6.33	4.56	6.23	6.03	4.64	6.83	2.35
Mean	N/A	4.813	5.340	5.097	6.001	5.259	4.989	6.904	2.855
Std	N/A	0.154	0.772	1.056	0.873	0.512	0.249	0.878	1.103
LOD(3s)	0.48[4]	0.46	2.31	3.17	2.62	1.54	0.75	2.63	3.31

Notes:
1. MDL samples spiked @ 5 ng/l.
2. Analysis by GCMS.
3. Excludes one sample due to interference.
4. NDMA calculated using NS30.

Method detection limit (MDL) was calculated using the following formula:

$$MDL = T_{(n-1,\ 1-\alpha=0.99)} \times SD$$

where:

$T_{(n-1,\ 1-\alpha=0.99)}$ = Student's t value appropriate for 99% confidence level and a standard deviation estimate with n-1 degrees of freedom

n = Number of replicates (=7)

SD = Standard deviation

APPENDIX C COAGULANT NDMA: CONTRACT EXTENSIONS

C1 INTRODUCTION

Towards the end of the 2008-2009 water treatment works survey, NDMA concentrations up to 386 µg/l in Coagulant A1 resulted in significantly increased NDMA levels in distribution, typically low ng/l levels but up to 24 ng/l. No samples of treated water were found to exceed the WHO Guideline Value of 100 ng/l.

A 5-month survey ('Contract Extension 1') was carried out subsequently to investigate and monitor NDMA concentrations in Coagulant A1 and Coagulant B2 (a ferric coagulant manufactured by a similar process).

This 5-month survey was subsequently extended, and a second survey ('Contract Extension 2') was carried out to further investigate and monitor NDMA concentrations in the coagulants.

C2 CONTRACT EXTENSION 1 (2010)

Between September and November 2009, NDMA concentrations measured in distribution increased up to 24 ng/l. Analysis of Coagulant A1 sampled from the affected works revealed NDMA concentrations up to 386 µg/l, considerably greater than measured in the 2008 Defra/DWI study.

The contamination was believed to be caused by an NDMA precursor contained in a raw material used in the coagulant manufacturing process. Subsequent to this discovery, the manufacturer switched to an alternative source of the raw material and concentrations of NDMA in the coagulant were expected to reduce.

Analysis of other samples of aluminium- and ferric-based coagulants used in England and Wales at this time generally showed negligible concentrations of NDMA with the exception of Coagulant A2 and Coagulants B1, B2, B3 and C4 manufactured by a similar process.

To ensure that NDMA in Coagulant A1 was reduced, and to monitor concentrations in Coagulant B2, a 5-month survey was carried out between June and October 2010 measuring NDMA concentrations in the coagulants and in samples from two treatment works using these coagulants.

C2.1 Procedure

C2.1.1 Manufacturers' coagulant samples

Coagulant samples were submitted direct to WRc by the manufacturers from their production sites ('ex. production'). Samples of Coagulant A1 were submitted every two weeks and Coagulant B2 every four weeks. In addition to the samples, the manufacturers were requested to provide information that identified the coagulant and the raw material used in manufacture, e.g. production date, batch number and import date.

C2.1.2 Treatment samples

Samples of coagulant and water from different stages of treatment were collected every four weeks from Works C12 and Works D20. At Works C12, Coagulant B2 ('ex. works') was sampled from the coagulant pumps when the works was visited to take samples from water treatment. At Works D20, Coagulant A1 ('ex. delivery') was sampled from the road tanker prior to the site visits to sample from water treatment. In addition to the samples, information was collected identifying coagulant deliveries, e.g. delivery date or batch number, and ongoing coagulant usage.

C2.2 Results

C2.2.1 Works C12

Samples were collected from Works C12 monthly between June and October 2010. The results of NDMA analysis are shown in Table C1. NDMA analyses of coagulant samples obtained directly from the manufacturer are shown for comparison.

Table C1 Contract Extension 1: NDMA (ng/l unless stated) measured at Works C12

Sample Point	Works C12 Sample Date				
	24/06/10	**26/07/10**	**25/08/10**	**20/09/10**	**25/10/10**
Raw water	<0.48	<0.48	<0.48	<0.48	<0.48
Recycled water 2	60	42	21	16	15.1
Post-clarification	2.2	1.0	0.78	1.0	0.53
Coagulant B2[1] (ex. works)	125	92	39	29	27.3
Coagulant B2[1] (ex. production)	26 (12/06/10)[2]	27 (14/07/10)[2]	31 (09/08/10)[2]	25 (04/09/10)[2]	5.8 (21/10/10)[2]

Notes:
1. Coagulant samples µg NDMA/l.
2. Coagulant production date.

Works C12 switched from using Coagulant A1 to Coagulant B2 in May 2010, with the first delivery of Coagulant B2 made on 17/05/10.

Data identifying the production of the samples of Coagulant B2 submitted by the manufacturer, including details of the raw material used in production, are shown in Table C2.

Table C2 Contract Extension 1: Coagulant B2 production data (Survey 1, Works C12)

Works C12 Sample Date	Raw Material		Coagulant B2		
	Batch ID	**Import Date**	**Batch ID**	**Production Date**	**Sample Date**
June 2010	Shipment 'K'	06/2010	1344	12/06/2010	12/06/2010
July 2010	Shipment 'K'	06/2010	1621	14/07/2010	14/07/2010

Works C12 Sample Date	Raw Material		Coagulant B2		
	Batch ID	Import Date	Batch ID	Production Date	Sample Date
August 2010	Shipment 'K'	02/08/2010	1812	09/08/2010	18/08/2010
September 2010	Shipment 'SG'	18/08/2010	1993	04/09/2010	04/09/2010
October 2010	-	20/09/2010	2456	21/10/2010	25/10/2010

Coagulant deliveries and stock levels are shown in Table C3 and illustrated in Figure C1.

Table C3 Contract Extension 1: Coagulant deliveries and stock levels - Works C12

Date	Tank 1 (tonne)	Tank 2 (tonne)
25/05/10	55.0 (delivery 17/05)	52.0
27/05/10	55.0	48.0
28/05/10	55.0	47.0
01/06/10	55.0	42.0
04/06/10	55.0	38.0
06/06/10	55.0	34.0
07/06/10	55.0	32.0
11/06/10	51.0	55.0 (Delivery 10/06)
14/06/10	48.0	55.0
16/06/10	45.0	55.0
17/06/10	43.0	55.0
21/06/10	37.0	55.0
24/06/10	34.0	53.0
26/06/10	33.0	48.0
06/07/10	61.0 (Delivery 29/06)	33.0
16/07/10	46.0	60.0 (Delivery 08/07)
26/07/10	40.0	47.0
05/08/10	40.0	31.0
15/08/10	60.0 (Delivery 10/08)	39.0 (Delivery 07/08)
25/08/10	60.0	43.0 (Delivery 19/08)
02/09/10	60.0	27.0
03/09/10	60.0	53.0 (Delivery 03/09)
10/09/10	60.0	33.0
11/09/10	60.0	59.0 (Delivery 11/09)
22/09/10	60.0	26.0
23/09/10	60.0	55.0 (Delivery 23/09)
07/10/10	60.0	22.0
08/10/10	60.0	47.0 (Delivery 08/10)
14/10/10	60.0	29.0
15/10/10	60.0	55.0 (Delivery 15/10)

Date	Tank 1 (tonne)	Tank 2 (tonne)
20/10/10	60.0	40.0
25/10/10	60.0	28.0

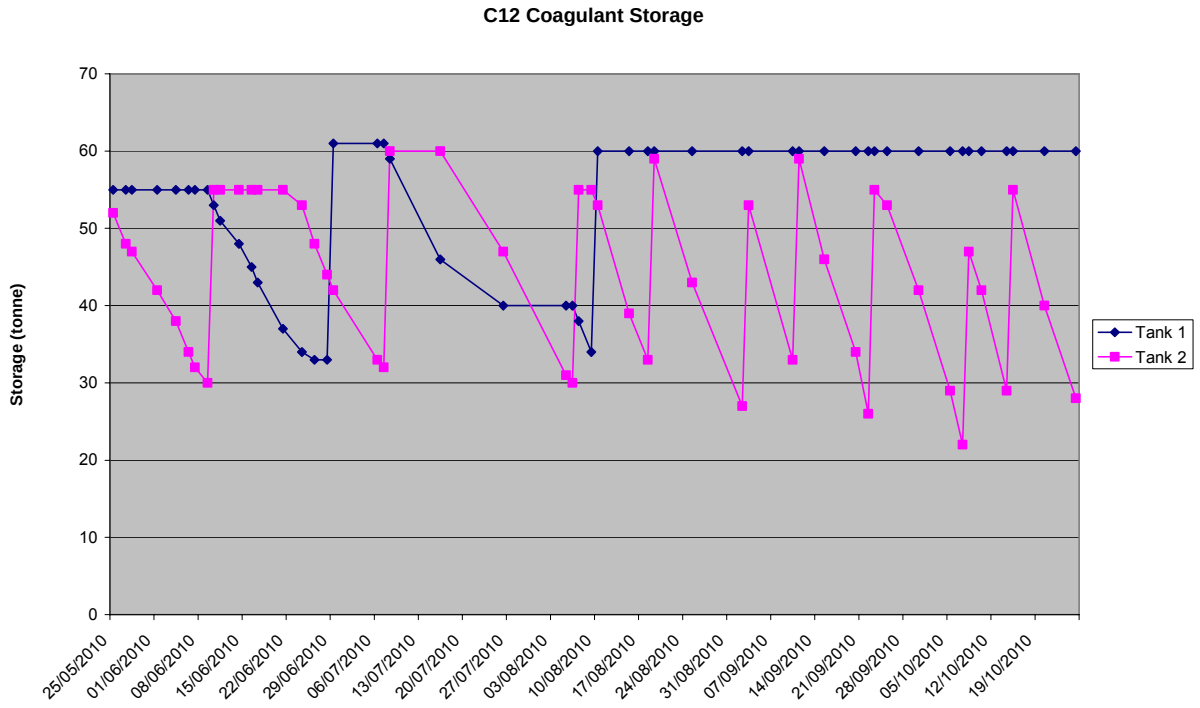


Figure C1 Contract Extension 1: Coagulant stock levels - Works C12

The coagulant samples taken from the works in June and July contained significantly greater concentrations of NDMA (125 µg/l, 92 µg/l) than samples supplied directly by the manufacturer (26 µg/l, 27 µg/l). It is believed that this was a result of mixing Coagulant B2 with residual Coagulant A1 contained in the holding tanks. Practice at this works allowed coagulant holding tanks to reduce to approximately half operating capacity before receiving a delivery, with deliveries made to each tank approximately monthly. The measured NDMA concentrations corresponded to this practice (assuming the residual Coagulant A1 contained about 300 µg NDMA/l and the Coagulant B2 contained about 20 µg NDMA/l). Concentrations of NDMA in subsequent coagulant samples taken from the works decreased to values similar to those measured in samples supplied directly to WRc by the manufacturer.

Concentrations of NDMA detected in the recycled water and clarified water were consistent with the concentration of NDMA detected in the works coagulant. NDMA concentrations in the recycled water reduced from 60 ng/l in June to 15 ng/l in October, whilst concentrations in the clarified water reduced from 2.2 ng/l to 0.53 ng/l over the same period.

C2.2.2 Works D20

Samples were collected from Works D20 monthly between June and October 2010. The results of NDMA analysis are shown in Table C4. NDMA analyses of coagulant samples obtained directly from the manufacturer are shown for comparison.

Table C4 Contract Extension 1: NDMA (ng/l unless stated) measured at Works D20

Sample Point	Works D20 Sample Date				
	24/06/10	**26/07/10**	**25/08/10**	**20/09/10**	**25/10/10**
Raw water	< 0.48	3.0	< 0.48	< 0.48	< 0.48
Post-coagulation	8.5	3.5	1.9	2.5	0.83
Final water	< 0.48	< 0.48	< 0.48	1.7	< 0.48
Coagulant A1[1] (ex. delivery)	149 (16/06/10)[2]	195 (30/06/10)[2]	75 (24/08/10)[2]	67 (22/09/10)[2]	76 (11/10/10)[2]
Coagulant A1[1] (ex. production)	140 (25/06)[3] 31 (05/07)[3]	132 (21/07)[3] 22 (04/08)[3]	22 (18/08)[3,4] 19 (30/08)[3]	24 (16/09)[3] 23 (28/09)[3]	18 (13/10)[3,5] 325 (28/10)[3]

Notes:
1. Coagulant samples µg NDMA/l.
2. Coagulant delivery date.
3. Coagulant production date.
4. A 'non-blended' coagulant sample produced using only 'Raw Material 2' was also submitted to WRc by the manufacturer. The NDMA content of this sample measured 16 µg/l (production date 18/08/10).
5. A 'non-blended' coagulant sample produced using only 'Raw Material 2' was also submitted to WRc by the manufacturer. The NDMA content of this sample measured 12 µg/l (production date 10/10/10).

Data identifying the production of the samples of Coagulant A1 submitted by the manufacturer, including details of the raw material used in production, are shown in Table C5.

Table C5 Contract Extension 1: Coagulant A1 production data (Works D20)

Works D20 Sample Date	Raw Material 1		Raw Material 2		Coagulant A1		
	Batch ID	**Import Date**	**Batch ID**	**Import Date**	**Batch ID**	**Production Date**	**Sample Date**
June 2010	Shipment 'N'	20/02/10	Shipment 'P'	08/04/10	49191	25/06/10	25/06/10
	Shipment 'N'	20/02/10	Shipment 'C'	03/06/10	49234	05/07/10	05/07/10
July 2010	Shipment 'N'	20/02/10	Shipment 'C'	03/06/10	49349	21/07/10	21/07/10
	Shipment 'N'	20/02/10	Shipment 'CN'	12/07/10	49414	04/08/10	04/08/10
August 2010	Shipment 'N'	20/02/10	Shipment 'CN'	12/07/10	49465	18/08/10	18/08/10
	Shipment	20/02/10	Shipment	12/07/10	49534	30/08/10	31/08/10

Works D20 Sample Date	Raw Material 1		Raw Material 2		Coagulant A1		
	Batch ID	Import Date	Batch ID	Import Date	Batch ID	Production Date	Sample Date
	'N'		'CN'				
September 2010	Shipment 'N'	20/02/10	Shipment 'CN'	12/07/10	49607	16/09/10	16/09/10
	Shipment 'N'	20/02/10	Shipment 'CN'	12/07/10	49662	28/09/10	28/09/10
October 2010	Shipment 'N'	20/02/10	Shipment 'AA'	25/08/10	49732 RV1	13/10/10	13/10/10
	Shipment 'N'	20/02/10	Shipment 'AA'	25/08/10	49804 RV4	28/10/10	28/10/10

Coagulant deliveries and stock levels are shown in Table C6 and illustrated in Figure C2.

Table C6 Contract Extension 1: Coagulant deliveries and stock levels - Works D20

Date	Tank A (tonne)	Tank B (tonne)	Tank C (tonne)	Tank D (tonne)
10/06/10	9.70	0.99	77.42	97.81
11/06/10	39.60 (Delivery)	0.79	70.69	97.61
13/06/10	39.40	0.79	57.42	97.81
14/06/10	68.31 (Delivery)	0.20	50.69	97.61
15/06/10	68.11	0.20	44.35	97.81
16/06/10	97.22 (Delivery)	0.20	37.82	97.81
29/06/10	97.02	0.00	10.10	32.67
30/06/10	97.22	0.00	40.00 (Delivery)	25.74
04/07/10	81.97	0.00	39.80	9.90
05/07/10	74.45	0.00	39.20	39.20 (Delivery)
06/07/10	66.33	0.00	39.01	39.20
07/07/10	58.61	0.00	39.20	68.31 (Delivery)
08/07/10	50.89	0.00	39.20	68.11
09/07/10	43.56	0.00	68.71 (Delivery)	68.11
11/07/10	27.92	0.00	68.71	68.11
12/07/10	20.00	0.00	97.02 (Delivery)	67.52
13/07/10	12.28	0.00	97.02	67.52
14/07/10	9.90	0.00	92.07	96.43 (Delivery)
15/07/10	9.90	0.00	85.14	96.23
16/07/10	39.20 (Delivery)	0.00	78.41	96.23
18/07/10	39.01	0.00	64.35	96.03
19/07/10	67.52 (Delivery)	0.00	58.41	96.03
20/07/10	67.52	0.00	52.07	96.03
21/07/10	96.43 (Delivery)	0.00	45.54	96.03
27/07/10	96.03	0.00	9.90	90.29

Date	Tank A (tonne)	Tank B (tonne)	Tank C (tonne)	Tank D (tonne)
28/07/10	96.03	0.00	38.61 (Delivery)	83.56
29/07/10	96.03	0.00	66.73 (Delivery)	76.82
30/07/10	96.03	0.00	95.44 (Delivery)	70.49
03/08/10	96.03	0.00	95.24	46.13
04/08/10	92.27	0.00	95.24	72.67 (Delivery)
23/08/10	9.50	0.00	68.51	72.27
24/08/10	38.61 (Delivery)	0.00	63.36	72.27
25/08/10	67.32	0.00	58.01	72.27
26/08/10	67.32	0.00	52.87	72.07
27/08/10	96.23 (Delivery)	0.00	48.11	72.07
02/09/10	96.23	0.00	20.00	72.07
03/09/10	96.03	27.13 (Delivery)	14.85	72.27
05/09/10	96.23	26.73	9.90	66.92
06/09/10	96.03	26.53	38.81 (Delivery)	61.78
07/09/10	96.03	26.53	38.61	57.02
08/09/10	96.03	56.03 (Delivery)	38.61	52.47
19/09/10	83.95	55.44	38.41	9.90
20/09/10	78.01	84.55 (Delivery)	38.41	9.90
21/09/10	71.87	84.55	39.20	10.10
22/09/10	66.33	84.55	67.91 (Delivery)	10.10
26/09/10	44.75	84.55	67.91	10.10
27/09/10	39.40	84.55	96.62 (Delivery)	38.81 (Delivery)
28/09/10	34.06	84.55	96.62	39.01
29/09/10	29.11	84.55	96.62	68.51 (Delivery)
30/09/10	23.96	84.55	96.62	68.51
01/10/10	19.01	84.55	96.62	97.81 (Delivery)
07/10/10	9.90	84.55	73.66	97.81
08/10/10	39.40 (Delivery)	84.55	66.53	97.81
10/10/10	39.40	84.55	52.07	97.81
11/10/10	68.51 (Delivery)	84.55	44.15	97.81

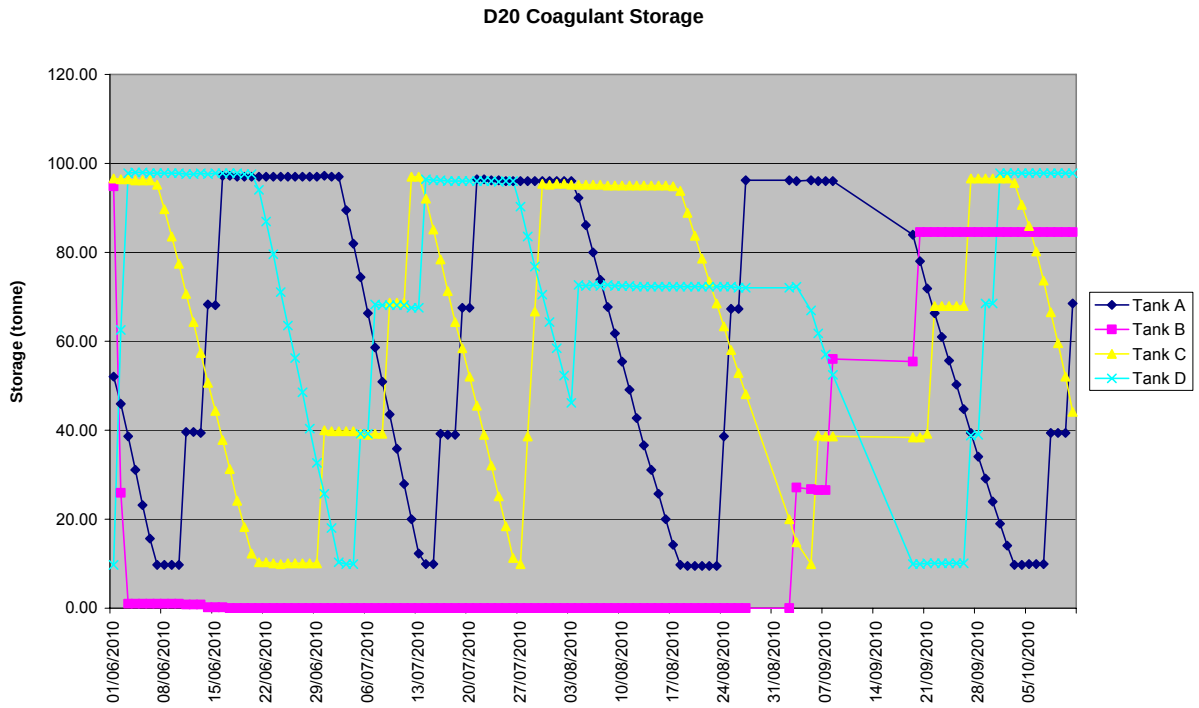


Figure C2 Contract Extension 1: Coagulant stock levels - Works D20

The coagulant samples taken from deliveries to the works in June and July contained high concentrations of NDMA (149-195 µg/l), but lower than measured in this coagulant towards the end of 2009. Concentrations of NDMA in subsequent coagulant samples taken from deliveries to the works decreased (67-76 µg/l) but were still high.

The concentrations of NDMA in coagulant samples delivered to the works were generally greater than measured in samples supplied directly to WRc by the manufacturer, particularly from August to early October (18-24 µg/l). The NDMA concentration in the final sample submitted by the manufacturer in late October increased substantially to 325 µg/l. The samples supplied by the manufacturer were 'ex. production' samples and were expected to show no significant difference to the 'ex. delivery' samples. The manufacturer also supplied two 'test' coagulant samples (see below) with NDMA concentrations (18-22 µg/l) comparable to the ex. production samples.

The manufacture of Coagulant A1 includes chemical oxidation of a specific raw material. The raw material used in the manufacturing process included an older stock containing an elevated concentration of an NDMA precursor, ('Raw Material 1') and a newer, uncontaminated stock ('Raw Material 2'). These stocks were blended in a 1:4 ratio (Raw Material 1:Raw Material 2). The manufacturer also produced 'test' coagulant samples using only Raw Material 2 to gauge the likely concentration of NDMA in coagulant following the depletion of Raw Material 1 (and also to confirm that any new deliveries of the raw material remained free of contamination). The two 'test' samples submitted to WRc contained 18-22 µg NDMA/l, less than the 'ex. delivery' samples but comparable to the 'ex. production' samples analysed from late July to early October.

The reason for this discrepancy between the 'ex. delivery' and 'ex. production' samples is unexplained.

Concentrations of NDMA detected in the post-coagulation water samples were generally consistent with the concentration of NDMA detected in the works coagulant. With the exception of the September measurement (1.7 ng/l), NDMA was not detected in the final water, possibly as a result of removal by treatment (possibly RGF or GAC).

It was noted that NDMA was detected in the raw water on one occasion (July, 3.0 ng/l).

C3 Contract Extension 2 (2011)

The final 'ex. production' sample of Coagulant A1 submitted in Survey 1 in late October 2010 contained 325 µg/l NDMA (see Table C4). This was considerably higher than measured in previous 'ex. production' samples or in 'ex. delivery' samples. As discussed above, the source of the contamination was believed to be an NDMA precursor in the raw material used in the manufacturing process.

It was decided to continue analysing samples of Coagulant A1 to monitor the concentration of NDMA. However, before sampling commenced, production of Coagulant A1 ceased and no residual stock of the coagulant could be sourced from water treatment works.

As Coagulant B2 was manufactured by a similar process to Coagulant A1 and used the same raw material, it was decided to carry out a 5-month survey between June and October 2011 measuring concentrations of NDMA and NMOR (which had been detected in the laboratory tests; see Section 6.3) in this coagulant. Samples of Coagulant B2 were obtained from Works C12 ('ex. works') and supplied directly to WRc by the manufacturer ('ex. production').

The manufacture of Coagulant B2 used raw material from three distinct sources: Source F, Source N/G and Source S. The manufacturing process used a raw material from a single source in production, thus it was possible to sample and analyse coagulants produced specifically with raw material from any of the three sources.

C3.1 Procedure

C3.1.1 Manufacturer's coagulant samples

Samples of Coagulant B2 were submitted to WRc by the manufacturer from its production site ('ex. production'). Samples were sent at intervals corresponding to the use of raw material from Source F, Source N/G or Source S. In addition to the samples, the manufacturer was requested to provide information that identified the coagulant and the raw material used in manufacture, e.g. source, production date, batch number and import date.

C3.1.2 Treatment samples

Samples of Coagulant B2 were collected every four weeks from Works C12 ('ex. works'), sampled from the coagulant pumps. In addition to the coagulant samples, information was collected identifying coagulant deliveries, e.g. delivery date or batch number, and indicating ongoing coagulant usage. Samples of final water were also taken and analysed for NDMA and NMOR.

C3.2 Results

Samples were collected from Works C12 monthly between June and October 2011. The results of NDMA and NMOR analysis are shown in Tables C7 and C8, respectively. NDMA analysis of coagulant samples obtained directly from the manufacturer are shown for comparison.

Table C7 Contract Extension 2: NDMA (ng/l unless stated) measured at Works C12

Sample Point	Works C12 Sample Date				
	15/06/11	**13/07/11**	**24/08/11**	**21/09/11**	**12/10/11**
Final water	-	-	<0.48	<0.48	0.90
Coagulant B2[1] (ex. works)	34	36	27.4	26.1	27.5
Coagulant B2[1] (ex. production): Raw material = Source F					
	7.0 (03/05/11)[2]	7.7 (19/07/11)[2]	-	-	-
Coagulant B2[1] (ex. production): Raw material = Source N/G					
	5.1 (28/05/11)[2]	-	-	-	3.8 (30/10/11)[2]
Coagulant B2[1] (ex. production): Raw material = Source S					
	-	7.9 (07/07/11)[2]	9.2 (26/08/11)[2]	-	-

Notes:
1. Coagulant samples µg NDMA/l.
2. Coagulant production date.

Table C8 Contract Extension 2: NMOR (ng/l unless stated) measured at Works C12

Sample Point	Works C12 Sample Date				
	15/06/11	**13/07/11**	**24/08/11**	**21/09/11**	**12/10/11**
Final water	-	-	<1.54	<1.54	<1.54
Coagulant B2[1] (ex. works)	12	4.3	2.04	7.06	28.3
Coagulant B2[1] (ex. production): Raw material = Source F					
	143 (03/05/11)[2]	85.7 (19/07/11)[2]	-	-	-
Coagulant B2[1] (ex. production): Raw material = Source N/G					
	68 (28/05/11)[2]	-	-	-	22.4 (30/10/11)[2]

Coagulant B2[1] (ex. production): Raw material = Source S					
	-	35 (07/07/11)[2]	49.1 (26/08/11)[2]	-	-

Notes:
1. Coagulant samples µg NMOR/l.
2. Coagulant production date.

Data identifying the production of the samples of Coagulant B2 submitted by the manufacturer, including details of the raw material used in production are shown in Table C9.

Table C9 Contract Extension 2: Coagulant B2 production data (Works C12)

Works C12 Sample Date	Raw Material		Coagulant B2		
	Batch ID (Source)	Import Date	Batch ID	Production Date	Sample Date
June 2011	Shipment 'F' (Source F)	15/04/11	839	03/05/11	10/06/11
June 2011	Shipment 'AS' (Source N/G)	21/04/11	1039	28/05/11	10/06/11
July 2011	Shipment 'WH' (Source S)	29/06/11	1353	07/07/11	07/07/11
July 2011	(Source F)	-	1440	19/07/11	19/07/11
August 2011	(Source S)	-	1762	26/08/11	26/08/11
October 2011	(Source N/G)	-	2354	30/10/11	31/10/11

Coagulant deliveries and stock levels at Works C12 are shown in Table C10 and illustrated in Figure C3.

Table C10 Contract Extension 2: Coagulant deliveries and stock levels - Works C12

Date	Tank 1 (tonne)	Tank 2 (tonne)
19/05/11	Out of Service	35.0
20/05/11		62.0 (Delivery 20/05)
05/06/11		36.0
06/06/11		63.0 (Delivery 20/05)
26/06/11		34.5
27/06/11		61.0 (Delivery 27/06)
17/07/11		32.0
18/07/11		59.0 (Delivery 18/07)
02/08/11		35.8
03/08/11		62.5 (Delivery 03/08)
17/08/11		18.3
18/08/11		43.4 (Delivery 18/08)
22/08/11		36.0
23/08/11[1]		61.0

Date	Tank 1 (tonne)	Tank 2 (tonne)
30/08/11		45
31/08/11[1]		54
11/09/11		32.5
12/09/11		57.4 (Delivery 12/09)
28/09/11		29.0
29/09/11		56.8 (Delivery 29/09)
12/10/11		32.0

Note:
1. Transfer of coagulant from Tank 1.

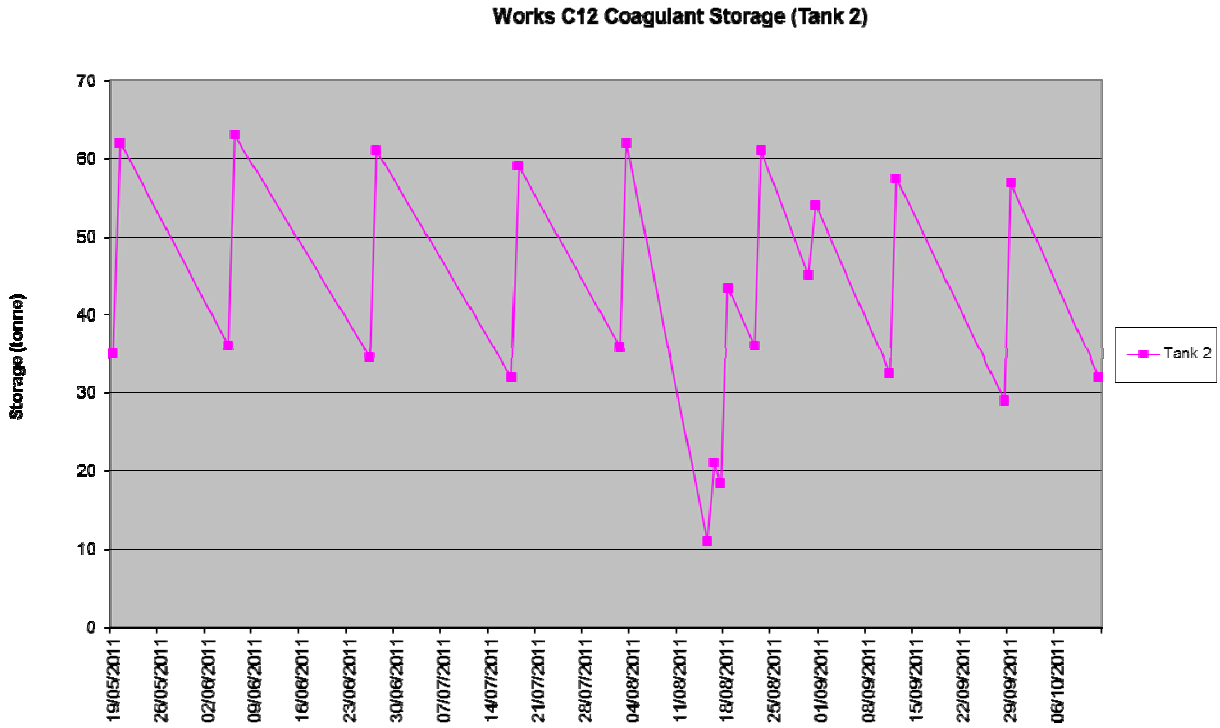


Figure C3 Contract Extension 2: Coagulant stock levels - Works C12

The coagulant samples taken from Works C12 from June to October 2011 contained 26-36 µg NDMA/l and 4.3-28 µg NMOR/l. The 'ex. works' NDMA concentrations were higher than the concentrations measured in the 'ex. production' samples (3.8-9.2 µg/l). The NDMA concentrations in the 'ex. production' samples were similar irrespective of the source of the raw material. The NMOR concentrations in the 'ex. works' samples were significantly lower than the concentrations measured in the 'ex. production' samples (22-143 µg/l). NMOR concentrations were highest in the coagulants produced with raw material from Source F.

At the NDMA and NMOR concentrations measured in the coagulant sampled from Works C12, concentrations in water treatment following dosing of the coagulant at typical doses (3-15 mg Fe/l) could measure about 0.4-2.7 ng NDMA/l and 0.03-2.12 ng NMOR/l. Actual concentrations measured in final waters would depend on the extent of any removal in water treatment.

NDMA was detected in only one sample of final water (0.9 ng/l) whilst NMOR was not detected above its limit of detection (<1.54 ng/l).

APPENDIX D WATER TREATMENT WORKS SURVEY

D1 INTRODUCTION

A water treatment works survey was conducted over a period of one year (November 2008 - November 2009) with samples taken monthly from sampling points throughout treatment and in distribution. The selection of works and sample points were discussed and agreed with DWI prior to the sampling survey. The works were selected to provide a wide and representative range of treatment processes and treatment chemicals.

Samples were collected in 1-litre plastic PET bottles, containing 40 mg of ascorbic acid preservative, in ice-packed cool boxes. On receipt into the laboratory, samples were stored in the dark at 4 °C ± 2 °C prior to extraction. Once extracted, the extracts were stored in the dark at -15 °C ± 5 °C and analysed according to the procedure described in Section 3.

In addition to sampling for NDMA, factors contributing to its possible formation and/or removal were recorded, e.g. water temperature and quality (TOC, NH_3, NO_2, NO_3), chemical types and dose (coagulant, polyelectrolyte, disinfectant), distribution retention time, etc.

D2 SELECTION OF TREATMENT WORKS

The treatment works selected included the three works where NDMA was detected consistently in the final water in the 2008 Defra/DWI study: Works C11, Works C12 and Works D18. Samples were taken throughout treatment and in distribution at points representing different retention times.

Samples were also taken from three works where NDMA was not detected in the final water in the previous study but where the NDMA-contaminated coagulant (Coagulant A1) was used. In addition, the selection of works was guided by the presence of other factors associated with the formation of NDMA. After discussion with DWI, Works C16, Works D17 and Works H5 were selected for sampling.

D3 TREATMENT WORKS SURVEYS

NDMA analysis of the samples from the six treatment works are shown in Sections D3.1 to D3.12.

Key operating data collected from the works at the time of sampling for NDMA are shown in Section D4.

Analyses of raw water samples taken from the works at the time of sampling for NDMA are shown in Section D5.

D3.1 Survey 1 (November 2008)

The six works were each sampled during w/b 24 November 2008.

Table D1 Treatment works Survey 1: November 2008

Sample point	Sample code	NDMA (ng/l)	Comment
Works C11			
Raw water	C11/A	< 0.48	
Post-coagulation	C11/B	0.90	
Post-RGF	C11/C	0.95	
Post-chlorination	C11/D	0.88	
Post-chloramination / Final water	C11/E	0.71	
Distribution 1	C11/F	0.77	Retention ~12 h
Distribution 2	C11/G	0.94	Retention ~24 h
Distribution 3	C11/H	1.4	Retention ~120 h
Works C12			
Raw water	C12/A	< 0.48	
Recycled water 1	C12/B	1.2	Pre-coagulant dose
Recycled water 2	C12/C	4.0	Post-coagulant dose
Post-clarification	C12/D	0.54	
Post-RGF	C12/E	0.61	
Post-chlorination / Final water	C12/F	< 0.48	
Distribution 1	C12/G	< 0.48	Retention ~18 h
Distribution 2	C12/H	< 0.48	Retention ~24-36 h
Distribution 3	C12/I	< 0.48	Retention ~48 h
Works C16			
Raw water	C16/A	< 0.48	
Post-coagulation	C16/B	0.70	
Post-RGF1	C16/C	< 0.48	
Post-RGF2	C16/D	< 0.48	
Post-chlorination / Final water	C16/E	< 0.48	
Works D17			
Raw water	D17/A	< 0.48	
Post-coagulation	D17/B	< 0.48	
Post-ozonation	D17/C	0.51	
Post-RGF	D17/D	< 0.48	
Post-GAC	D17/E	< 0.48	
Post-chlorination	D17/F	< 0.48	
Final water	D17/G	< 0.48	
Works D18			
Raw water	D18/A	< 0.48	
Post-coagulation / epi-DMA	D18/B	< 0.48	
Post-RGF	D18/D	< 0.48	
Post-GAC	D18/E	< 0.48	
Post-chlorination	D18/F	< 0.48	
Final water	D18/G	< 0.48	
Distribution 1	D18/H	< 0.48	Retention ~12 h
Distribution 2	D18/I	< 0.48	Retention ~28 h
Works H5			
Raw water	H5/A	1.4	
Post pre-ozonation	H5/B	1.2	
Post-coagulation	H5/C	1.8	
Post-RGF	H5/D	1.1	
Post-ozonation	H5/E	1.5	
Post-GAC	H5/F	0.91	
Post-chlorination	H5/G	0.93	
Post-chloramination / Final water	H5/H	1.1	
Distribution 1	H5/I	1.3	Retention ~6-8 h
Distribution 2	H5/J	1.2	Retention ~18-28 h

Note:
1. Works D18 distribution samples blended, typically 3.8-4.5 parts Works D18 to 1.0 part other Works.

- Works C11: NDMA was detected in seven samples between 0.71-1.4 ng/l, but above 1.0 ng/l in only the 5-day distribution sample (1.4 ng/l). NDMA was not detected in the raw water. In the 2008 Defra/DWI study, NDMA was detected throughout water treatment and in distribution at this works.

- Works C12: NDMA was detected in four samples between 0.54-4.0 ng/l, but above 1.0 ng/l in samples of recovered water recycled to water treatment (C12/B, 1.2 ng/l; C12/C, 4.0 ng/l). Sample C12/B was taken before dosing of coagulant in the water recovery process and Sample C12/C was taken after dosing; it is probable that the sample taken before dosing of coagulant was affected by backmixing. NDMA was not detected in the raw water, the final water or in distribution. In the 2008 Defra/DWI study, NDMA was detected throughout water treatment and in distribution at this works, although it was probable that these measurements resulted from the relatively high concentration of NDMA in the recycled water.

- Works C16: NDMA was detected in only the post-coagulation sample (0.70 ng/l). In the 2008 Defra/DWI study, NDMA was also detected following coagulation at this works.

- Works D17: NDMA was detected in only the post-ozonation sample (0.51 ng/l). In the 2008 Defra/DWI study, NDMA was not detected at this works.

- Works D18: NDMA was not detected in any samples. In the 2008 Defra/DWI study, NDMA was detected throughout treatment and in distribution at this works.

- Works H5: NDMA was detected in all samples between 0.91-1.8 ng/l. NDMA was detected in the raw water (1.4 ng/l), post-coagulation (1.8 ng/l), post-ozonation (1.5 ng/l) and final water (1.1 ng/) samples, and in distribution (1.1-1.3 ng/l). The raw water was a significant source of NDMA. In the 2008 Defra/DWI study, NDMA was not detected in the raw water or in final water from this works.

D3.2 Survey 2 (January 2009)

The six works were each sampled during w/b 5 January 2009.

Table D2 Treatment works Survey 2: January 2009

Sample point	Sample code	NDMA (ng/l)	Comment
Works C11			
Raw water	C11/A	< 0.48	
Post-coagulation	C11/B	0.52	
Post-RGF	C11/C	0.61	
Post-chlorination	C11/D	0.48	
Post-chloramination / Final water	C11/E	0.51	
Distribution 1	C11/F	0.64	Retention ~12 h
Distribution 2	C11/G	1.1	Retention ~24 h
Distribution 3	C11/H	2.0	Retention ~120 h
Works C12			
Raw water	C12/A	< 0.48	
Recycled water 1	C12/B	< 0.48	Pre-coagulant dose
Recycled water 2	C12/C	3.1	Post-coagulant dose
Post-clarification	C12/D	< 0.48	
Post-RGF	C12/E	< 0.48	

Sample point	Sample code	NDMA (ng/l)	Comment
Post-chlorination / Final water	C12/F	0.57	
Distribution 1	C12/G	0.55	Retention ~18 h
Distribution 2	C12/H	0.54	Retention ~24-36 h
Distribution 3	C12/I	0.69	Retention ~48 h
Works C16			
Raw water	C16/A	< 0.48	
Post-coagulation	C16/B	1.2	
Post-RGF1	C16/C	< 0.48	
Post-RGF2 / Final water	C16/D	< 0.48	
Works D17			
Raw water	D17/A	< 0.48	
Post-coagulation	D17/B	< 0.48	
Post-ozonation	D17/C	0.53	
Post-RGF	D17/D	< 0.48	
Post-GAC	D17/E	< 0.48	
Post-chlorination	D17/F	< 0.48	
Final water	D17/G	< 0.48	
Works D18			
Raw water	D18/A	< 0.48	
Post-coagulation / epi-DMA	D18/B	1.2	
Post-RGF	D18/D	1.4	
Post-GAC	D18/E	0.52	
Post-chlorination	D18/F	0.56	
Final water	D18/G	0.65	
Distribution 1	D18/H	< 0.48	Retention ~12 h
Distribution 2	D18/I	0.83	Retention ~28 h
Works H5			
Raw water	H5/A	< 0.48	
Post pre-ozonation	H5/B	< 0.48	
Post-coagulation	H5/C	< 0.48	
Post-RGF	H5/D	< 0.48	
Post-ozonation	H5/E	0.89	
Post-GAC	H5/F	< 0.48	
Post-chlorination	H5/G	0.50	
Post-chloramination / Final water	H5/H	0.54	
Distribution 1	H5/I	< 0.48	Retention ~6-8 h
Distribution 2	H5/J	< 0.48	Retention ~18-28 h
Distribution 3	H5/K	1.0	Retention ~28-98 h (summer) ~52-128 h (winter)

Note:
1. Works D18 distribution samples blended, typically 3.8-4.5 parts Works D18 to 1.0 part other Works.

- Works C11: NDMA was detected in seven samples between 0.48-2.0 ng/l, but above 1.0 ng/l in only the 24-hour and 5-day distribution samples (1.1 ng/l; 2.0 ng/l). NDMA was not detected in the raw water. These results suggest that where conditions for NDMA formation are favourable, formation in distribution may be a function of time.

- Works C12: NDMA was detected in five samples between 0.54-3.1 ng/l, but above 1.0 ng/l in only the post-coagulant dosed recycled water sample (3.1 ng/l). NDMA was not detected in the raw water.

- Works C16: NDMA was detected in only the post-coagulation sample (1.2 ng/l).

- Works D17: NDMA was detected in only the post-ozonation sample (0.53 ng/l).

- Works D18: NDMA was detected in six samples between 0.52-1.4 ng/l, but above 1.0 ng/l in the post-coagulation (1.2 ng/l) and post-RGF (1.4 ng/l) samples. NDMA was not detected in the raw water.

- Works H5: NDMA was detected in four samples between 0.50-1.0 ng/l. NDMA was not detected in the raw water or post-coagulation sample.

D3.3 Survey 3 (February 2009)

Works D17 and D18 were sampled during w/b 2 February 2009. Sampling of the other works that week was disrupted by adverse weather conditions. Works H5 was sampled subsequently during w/b 16 February but it was not possible to reschedule sampling of Works C11, C12 or C16.

Table D3 Treatment works Survey 3: February 2009

Sample point	Sample code	NDMA (ng/l)	Comment
Works D17			
Raw water	D17/A	< 0.48	
Post-coagulation	D17/B	< 0.48	
Post-ozonation	D17/C	< 0.48	
Post-RGF	D17/D	< 0.48	
Post-GAC	D17/E	< 0.48	
Post-chlorination	D17/F	< 0.48	
Final water	D17/G	< 0.48	
Works D18			
Raw water	D18/A	0.63	
Post-coagulation / epi-DMA	D18/B	1.6	
Post-RGF	D18/D	0.57	
Post-GAC	D18/E	< 0.48	
Post-chlorination	D18/F	< 0.48	
Final water	D18/G	< 0.48	
Distribution 1	D18/H	< 0.48	Retention ~12 h
Distribution 2	D18/I	< 0.48	Retention ~28 h
Works H5			
Raw water	H5/A	1.3	
Post pre-ozonation	H5/B	0.71	
Post-coagulation	H5/C	1.1	
Post-RGF	H5/D	0.84	
Post-ozonation	H5/E	1.9	
Post-GAC	H5/F	1.5	
Post-chlorination	H5/G	1.2	
Post-chloramination / Final water	H5/H	1.2	
Distribution 1	H5/I	1.3	Retention ~6-8 h
Distribution 2	H5/J	1.1	Retention ~18-28 h
Distribution 3	H5/K	3.3	Retention ~28-98 h (summer) ~52-128 h (winter)

Notes:
1. Works D18 distribution samples blended, typically 3.8-4.5 parts Works D18 to 1.0 part other Works.
2. Works C11, C12 and C16 not sampled due to adverse weather conditions.

- Works D17: NDMA was not detected in any sample.

- Works D18: NDMA was detected in three samples between 0.57-1.6 ng/l, but above 1.0 ng/l in only the post-coagulation sample (1.6 ng/l). NDMA was not detected in the final water or in distribution.

- Works H5: NDMA was detected in all samples between 0.71-3.3 ng/l. NDMA was detected in the raw water (1.3 ng/l), post-coagulation (1.1 ng/l), post-ozonation (1.9 ng/l) and final water (1.2 ng/) samples, and in distribution (1.3-3.3 ng/l).

D3.4 Survey 4 (March 2009)

Works C11, C12, C16, D17 and D18 were sampled during w/b 2 March 2009; Works H5 was sampled during w/b 9 March.

Table D4 Treatment works Survey 4: March 2009

Sample point	Sample code	NDMA (ng/l)	Comment
Works C11			
Raw water	C11/A	< 0.48	
Post-coagulation	C11/B	0.60	
Post-RGF	C11/C	< 0.48	
Post-chlorination	C11/D	< 0.48	
Post-chloramination / Final water	C11/E	0.49	
Distribution 1	C11/F	0.68	Retention ~12 h
Distribution 2	C11/G	0.92	Retention ~24 h
Distribution 3	C11/H	1.9	Retention ~120 h
Works C12			
Raw water	C12/A	< 0.48	
Recycled water 1	C12/B	< 0.48	Pre-coagulant dose
Recycled water 2	C12/C	3.4	Post-coagulant dose
Post-clarification	C12/D	< 0.48	
Post-RGF	C12/E	< 0.48	
Post-chlorination / Final water	C12/F	< 0.48	
Distribution 1	C12/G	0.59	Retention ~18 h
Distribution 2	C12/H	1.1	Retention ~24-36 h
Distribution 3	C12/I	< 0.48	Retention ~48 h
Works C16			
Raw water	C16/A	< 0.48	
Post-coagulation	C16/B	0.68	
Post-RGF1	C16/C	0.54	
Post-RGF2 / Final water	C16/D	< 0.48	
Works D17[1]			
Raw water	D17/A	< 1.0	
Post-coagulation	D17/B	< 1.0	
Post-ozonation	D17/C	< 1.0	
Post-RGF	D17/D	< 1.0	
Post-GAC	D17/E	< 1.0	
Post-chlorination	D17/F	< 1.0	
Final water	D17/G	< 1.0	
Works D18[1,2]			
Raw water	D18/A	1.1	
Post-coagulation / epi-DMA	D18/B	2.0	
Post-RGF	D18/D	1.0	
Post-GAC	D18/E	< 1.0	
Post-chlorination	D18/F	< 1.0	
Final water	D18/G	< 1.0	
Distribution 1	D18/H	< 1.0	Retention ~12 h
Distribution 2	D18/I	< 1.0	Retention ~28 h
Distribution 3	D18/J	< 1.0	Retention ~16 h

Sample point	Sample code	NDMA (ng/l)	Comment
Works H5			
Raw water	H5/A	1.2	
Post pre-ozonation	H5/B	1.9	
Post-coagulation	H5/C	0.77	
Post-RGF	H5/D	0.63	
Post-ozonation	H5/E	1.5	
Post-GAC	H5/F	1.6	
Post-chlorination	H5/G	1.8	
Post-chloramination / Final water	H5/H	2.9	
Distribution 1	H5/I	2.5	Retention ~6-8 h
Distribution 2	H5/J	2.6	Retention ~18-28 h
Distribution 3	H5/K	1.8	Retention ~28-98 h (summer) ~52-128 h (winter)

Notes:
1. Data not blank corrected.
2. Works D18 distribution samples blended, typically 3.8-4.5 parts Works D18 to 1.0 part other works.

- Works C11: NDMA was detected in five samples between 0.49-1.9 ng/l, but above 1.0 ng/l in only the 5-day distribution sample (1.9 ng/l). NDMA in distribution increased with retention time. NDMA was not detected in the raw water.

- Works C12: NDMA was detected in three samples between 0.59-3.4 ng/l, but above 1.0 ng/l in the post-coagulant (3.4 ng/l) and 24-36 hour distribution (1.1 ng/l) samples. NDMA was not detected in the raw water or final water.

- Works C16: NDMA was detected in two samples between 0.54-0.68 ng/l but not in the raw water or final water.

- Works D17: NDMA was not detected in any sample.

- Works D18: NDMA was detected in three samples between 1.0-2.0 ng/l, but above 1.0 ng/l in the raw water (1.1 ng/l) and post-coagulation (2.0 ng/l) samples. NDMA was not detected in the final water or in distribution.

- Works H5: NDMA was detected in all samples between 0.63-2.9 ng/l. NDMA was detected in the raw water (1.2 ng/l), post-ozonation (1.5 ng/l) and final water (2.9 ng/) samples, and in distribution (1.8-2.6 ng/l).

D3.5 Survey 5 (April 2009)

Works D17 and D18 were sampled during w/b 31 March; Works C11, C12, C16 and H5 were sampled during w/b 6 April 2009.

Table D5 Treatment works Survey 5: April 2009

Sample point	Sample code	NDMA (ng/l)	Comment
Works C11			
Raw water	C11/A	< 0.48	
Post-coagulation	C11/B	< 0.48	
Post-RGF	C11/C	< 0.48	
Post-chlorination	C11/D	< 0.48	
Post-chloramination / Final water	C11/E	< 0.48	
Distribution 1	C11/F	< 0.48	Retention ~12 h
Distribution 2	C11/G	0.48	Retention ~24 h
Distribution 3	C11/H	1.2	Retention ~120 h
Works C12			
Raw water	C12/A	< 0.48	
Recycled water 1	C12/B	< 0.48	Pre-coagulant dose
Recycled water 2	C12/C	1.0	Post-coagulant dose
Post-clarification	C12/D	< 0.48	
Post-RGF	C12/E	< 0.48	
Post-chlorination / Final water	C12/F	0.49	
Distribution 1	C12/G	< 0.48	Retention ~18 h
Distribution 2	C12/H	< 0.48	Retention ~24-36 h
Distribution 3	C12/I	< 0.48	Retention ~48 h
Works C16			
Raw water	C16/A	< 0.48	
Post-coagulation	C16/B	< 0.48	
Post-RGF1	C16/C	< 0.48	
Post-RGF2 / Final water	C16/D	< 0.48	
Works D17			
Raw water	D17/A	0.78	
Post-coagulation	D17/B	0.87	
Post-ozonation	D17/C	1.2	
Post-RGF	D17/D	0.80	
Post-GAC	D17/E	0.98	
Post-chlorination	D17/F	0.93	
Final water	D17/G	1.6	
Works D18			
Raw water	D18/A	1.2	
Post-coagulation / epi-DMA	D18/B	1.3	
Post-RGF	D18/D	1.0	
Post-GAC	D18/E	0.90	
Post-chlorination	D18/F	1.2	
Final water	D18/G	1.9	
Distribution 1	D18/H	0.81	Retention ~12 h
Distribution 2	D18/I	1.0	Retention ~28 h
Distribution 3	D18/J	1.1	Retention ~16 h
Works H5			
Raw water	H5/A	1.7	
Post pre-ozonation	H5/B	2.6	
Post-coagulation	H5/C	2.0	
Post-RGF	H5/D	1.0	
Post-ozonation	H5/E	1.9	
Post-GAC	H5/F	1.8	
Post-chlorination	H5/G	2.0	
Post-chloramination / Final water	H5/H	2.1	
Distribution 1	H5/I	3.0	Retention ~6-8 h
Distribution 2	H5/J	1.7	Retention ~18-28 h
Distribution 3	H5/K	3.7	Retention ~28-98 h (summer) ~52-128 h (winter)

Note:
1. Works D18 distribution samples blended, typically 3.8-4.5 parts Works D18 to 1.0 part other Works.

- Works C11: NDMA was detected in two samples between 0.48-1.2 ng/l, but above 1.0 ng/l in only the 5-day distribution sample (1.2 ng/l). NDMA in distribution increased with retention time. NDMA was not detected in the raw water or final water.

- Works C12: NDMA was detected in two samples between 0.49-1.0 ng/l. NDMA was not detected in the raw water or in distribution.

- Works C16: NDMA was not detected in any sample.

- Works D17: NDMA was detected in all samples between 0.78-1.6 ng/l, but above 1.0 ng/l in the post-ozonation (1.2 ng/l) and final water (1.6 ng/l) samples. NDMA had not been previously detected in the raw water at this works and in few samples from water treatment.

- Works D18: NDMA was detected in all samples between 0.81-1.9 ng/l, including above 1.0 ng/l in the raw water (1.2 ng/l), post-coagulation (1.3 ng/l), final water (1.9 ng/l) and 16-hour distribution (1.1 ng/l) samples.

- Works H5: NDMA was detected in all samples between 1.0-3.7 ng/l, including above 1.0 ng/l in the raw water (1.7 ng/l), post-coagulation (2.0 ng/l), final water (2.1 ng/l) samples and in distribution (1.7-3.7 ng/l).

D3.6 Survey 6 (May 2009)

Works C11 was sampled w/b 27 April; Works C12, C16, D17, D18 and H5 were sampled during w/b 4 May 2009.

Table D6 Treatment works Survey 6: May 2009

Sample point	Sample code	NDMA (ng/l)	Comment
Works C11			
Raw water	C11/A	< 0.48	
Post-coagulation	C11/B	< 0.48	
Post-RGF	C11/C	< 0.48	
Post-chlorination	C11/D	< 0.48	
Post-chloramination / Final water	C11/E	< 0.48	
Distribution 1	C11/F	< 0.48	Retention ~12 h
Distribution 2	C11/G	1.4	Retention ~24 h
Distribution 3	C11/H	2.1	Retention ~120 h
Works C12			
Raw water	C12/A	< 0.48	
Recycled water 1	C12/B	0.48	Pre-coagulant dose
Recycled water 2	C12/C	4.3	Post-coagulant dose
Post-clarification	C12/D	< 0.48	
Post-RGF	C12/E	< 0.48	
Post-chlorination / Final water	C12/F	< 0.48	
Distribution 1	C12/G	< 0.48	Retention ~18 h
Distribution 2	C12/H	0.49	Retention ~24-36 h
Distribution 3	C12/I	< 0.48	Retention ~48 h
Works C16			
Raw water	C16/A	< 0.48	
Post-coagulation	C16/B	0.79	
Post-RGF1	C16/C	< 0.48	
Post-RGF2 / Final water	C16/D	< 0.48	

Sample point	Sample code	NDMA (ng/l)	Comment
Works D17			
Raw water	D17/A	< 0.48	
Post-coagulation	D17/B	< 0.48	
Post-ozonation	D17/C	0.60	
Post-RGF	D17/D	< 0.48	
Post-GAC	D17/E	< 0.48	
Post-chlorination	D17/F	< 0.48	
Final water	D17/G	< 0.48	
Works D18			
Raw water	D18/A	< 0.48	
Post-coagulation / epi-DMA	D18/B	0.95	
Post-RGF	D18/D	< 0.48	
Post-GAC	D18/E	< 0.48	
Post-chlorination	D18/F	< 0.48	
Final water	D18/G	0.48	
Distribution 1	D18/H	0.51	Retention ~12 h
Distribution 2	D18/I	0.53	Retention ~28 h
Distribution 3	D18/J	0.67	Retention ~16 h
Works H5			
Raw water	H5/A	3.0	
Post pre-ozonation	H5/B	3.1	
Post-coagulation	H5/C	1.9	
Post-RGF	H5/D	< 0.48	
Post-ozonation	H5/E	2.7	
Post-GAC	H5/F	1.7	
Post-chlorination	H5/G	1.1	
Post-chloramination / Final water	H5/H	5.2	
Distribution 1	H5/I	1.3	Retention ~6-8 h
Distribution 2	H5/J	1.9	Retention ~18-28 h
Distribution 3	H5/K	2.3	Retention ~28-98 h (summer) ~52-128 h (winter)

Note:
1. Works D18 distribution samples blended, typically 3.8-4.5 parts Works D18 to 1.0 part other works.

- Works C11: NDMA was detected in two samples between 1.4-2.1 ng/l; the 24-hour and 5-day distribution samples (1.4 ng/l; 2.1 ng/l). NDMA in distribution increased with retention time.

- Works C12: NDMA was detected in three samples between 0.48-4.3 ng/l, but above 1.0 ng/l in only the post-coagulant recycled water (4.3 ng/l). NDMA was not detected in the raw water or final water.

- Works C16: NDMA was detected in only the post-coagulation sample (0.79 ng/l).

- Works D17: NDMA was detected in only the post-ozonation sample (0.60 ng/l).

- Works D18: NDMA was detected in five samples between 0.48-0.95 ng/l. NDMA was not detected in the raw water.

- Works H5: NDMA was detected in ten samples between 1.1-5.2 ng/l, including above 1.0 ng/l in the raw water (3.0 ng/l), post-coagulation (1.9 ng/l), post-ozonation (2.7 ng/l) and final water (5.2 ng/l) samples and in distribution (1.3-2.3 ng/l).

D3.7 Survey 7 (June 2009)

All treatment works were sampled during w/b 1 June 2009.

Table D7 Treatment works Survey 7: June 2009

Sample point	Sample code	NDMA (ng/l)	Comment
Works C11			
Raw water	C11/A	< 0.48	
Post-coagulation	C11/B	< 0.48	
Post-RGFPost-RGF	C11/C	< 0.48	
Post-chlorination	C11/D	< 0.48	
Post-chloramination / Final water	C11/E	< 0.48	
Distribution 1	C11/F	< 0.48	Retention ~12 h
Distribution 2	C11/G	< 0.48	Retention ~24 h
Distribution 3	C11/H	1.2	Retention ~120 h
Works C12			
Raw water	C12/A	< 0.48	
Recycled water 1	C12/B	1.2	Pre-coagulant dose
Recycled water 2	C12/C	3.0	Post-coagulant dose
Post-clarification	C12/D	< 0.48	
Post-RGF	C12/E	< 0.48	
Post-chlorination / Final water	C12/F	< 0.48	
Distribution 1	C12/G	0.56	Retention ~18 h
Distribution 2	C12/H	0.85	Retention ~24-36 h
Distribution 3	C12/I	< 0.48	Retention ~48 h
Works C16			
Raw water	C16/A	< 0.48	
Post-coagulation	C16/B	0.63	
Post-RGF1	C16/C	< 0.48	
Post-RGF2 / Final water	C16/E	< 0.48	
Works D17			
Raw water	D17/A	< 0.48	
Post-coagulation	D17/B	0.92	
Post-ozonation	D17/C	0.50	
Post-RGF	D17/D	< 0.48	
Post-GAC	D17/E	< 0.48	
Post-chlorination	D17/F	< 0.48	
Final water	D17/G	< 0.48	
Works D18			
Raw water	D18/A	2.6	
Post-coagulation / epi-DMA	D18/B	1.0	
Post-RGF	D18/D	< 0.48	
Post-GAC	D18/E	< 0.48	
Post-chlorination	D18/F	< 0.48	
Final water	D18/G	< 0.48	
Distribution 1	D18/H	< 0.48	Retention ~12 h
Distribution 2	D18/I	< 0.48	Retention ~28 h
Distribution 3	D18/J	< 0.48	Retention ~16 h
Works H5			
Raw water	H5/A	0.70	
Post pre-ozonation	H5/B	0.78	
Post-coagulation	H5/C	1.1	
Post-RGF	H5/D	< 0.48	
Post-ozonation	H5/E	2.9	
Post-GAC	H5/F	-	
Post-chlorination	H5/G	0.62	
Post-chloramination / Final water	H5/H	0.50	
Distribution 1	H5/I	0.77	Retention ~6-8 h
Distribution 2	H5/J	0.98	Retention ~18-28 h

Sample point	Sample code	NDMA (ng/l)	Comment
Distribution 3	H5/K	0.69	Retention ~28-98 h (summer) ~52-128 h (winter)

Note:
1. Works D18 distribution samples blended, typically 3.8-4.5 parts Works D18 to 1.0 part other Works.

- Works C11: NDMA was detected in only the 5-day distribution sample (1.2 ng/l).
- Works C12: NDMA was detected in four samples between 0.56-3.0 ng/l, but only above 1.0 ng/l in the pre-coagulant and post-coagulant recycled water samples (1.2 ng/l; 3.0 ng/l). NDMA was not detected in the raw water or final water.
- Works C16: NDMA was detected in only the post-coagulation sample (0.63 ng/l).
- Works D17: NDMA was detected. NDMA was not detected in the raw water or final water.
- Works D18: NDMA was detected in two samples between 1.0-2.6 ng/l, including above 1.0 ng/l in the raw water (2.6 ng/l). NDMA was not detected in the final water or in distribution.
- Works H5: NDMA was detected in nine samples between 0.50-2.9 ng/l, but above 1.0 ng/l in the post-coagulation (1.1 ng/l) and post-ozonation (2.9 ng/l) samples.

D3.8 Survey 8 (July 2009)

All treatment works were sampled during w/b 6 July 2009.

Table D8 Treatment works Survey 8: July 2009

Sample point	Sample code	NDMA (ng/l)	Comment
Works C11			
Raw water	C11/A	< 0.48	
Post-coagulation	C11/B	0.75	
Post-RGF	C11/C	0.84	
Post-chlorination	C11/D	0.84	
Post-chloramination / Final water	C11/E	0.85	
Distribution 1	C11/F	0.87	Retention ~12 h
Distribution 2	C11/G	0.99	Retention ~24 h
Distribution 3	C11/H	1.7	Retention ~120 h
Works C12			
Raw water	C12/A	< 0.48	
Recycled water 1	C12/B	0.60	Pre-coagulant dose
Recycled water 2	C12/C	5.6	Post-coagulant dose
Post-clarification	C12/D	< 0.48	
Post-RGF	C12/E	0.67	
Post-chlorination / Final water	C12/F	< 0.48	
Distribution 1	C12/G	0.73	Retention ~18 h
Distribution 2	C12/H	0.81	Retention ~24-36 h
Distribution 3	C12/I	-	Retention ~48 h

Sample point	Sample code	NDMA (ng/l)	Comment
Works C16			
Raw water	C16/A	< 0.48	
Post-coagulation	C16/B	1.2	
Post-RGF1	C16/C	< 0.48	
Post-RGF2 / Final water	C16/E	< 0.48	
Works D17			
Raw water	D17/A	0.59	
Post-coagulation	D17/B	0.99	
Post-ozonation	D17/C	0.72	
Post-RGF	D17/D	< 0.48	
Post-GAC	D17/E	< 0.48	
Post-chlorination	D17/F	< 0.48	
Final water	D17/G	< 0.48	
Works D18			
Raw water	D18/A	< 0.48	
Post-coagulation / epi-DMA	D18/B	7.7	
Post-RGF	D18/D	0.91	
Post-GAC	D18/E	1.4	
Post-chlorination	D18/F	0.59	
Final water	D18/G	< 0.48	
Distribution 1	D18/H	< 0.48	Retention ~12 h
Distribution 2	D18/I	< 0.48	Retention ~28 h
Distribution 3	D18/J	< 0.48	Retention ~16 h
Works H5			
Raw water	H5/A	< 0.48	
Post pre-ozonation	H5/B	1.9	
Post-coagulation	H5/C	0.60	
Post-RGF	H5/D	0.50	
Post-ozonation	H5/E	2.1	
Post-GAC	H5/F	< 0.48	
Post-chlorination	H5/G	< 0.48	
Post-chloramination / Final water	H5/H	0.73	
Distribution 1	H5/I	0.54	Retention ~6-8 h
Distribution 2	H5/J	0.77	Retention ~18-28 h
Distribution 3	H5/K	0.86	Retention ~28-98 h (summer) ~52-128 h (winter)

Note:
1. Works D18 distribution samples blended, typically 3.8-4.5 parts Works D18 to 1.0 part other Works.

- Works C11: NDMA was detected in seven samples between 0.75-1.7 ng/l, but above 1.0 ng/l in only the 5-day distribution sample (1.7 ng/l). NDMA in distribution increased with retention time. NDMA was not detected in the raw water.

- Works C12: NDMA was detected in five samples between 0.60-5.6 ng/l, but only above 1.0 ng/l in the post-coagulant recycled water sample (5.6 ng/l). NDMA was not detected in the raw water or final water.

- Works C16: NDMA was detected in only the post-coagulation sample (1.2 ng/l).

- Works D17: NDMA was detected in three samples between 0.59-0.99 ng/l. NDMA was not detected in the final water.

- Works D18: NDMA was detected in four samples between 0.59-7.7 ng/l, but only above 1.0 ng/l in the post-coagulation (7.7 ng/l) and post-GAC (1.4 ng/l) samples. NDMA was not detected in the raw water, final water or in distribution.

- Works H5: NDMA was detected in eight samples between 0.50-2.1 ng/l, but above 1.0 ng/l in the post pre-ozonation (1.9 ng/l) and post-ozonation (2.1 ng/l) samples. NDMA was not detected in the raw water.

D3.9 Survey 9 (August 2009)

All treatment works were sampled during w/b 3 August 2009.

Table D9 Treatment works Survey 9: August 2009

Sample point	Sample code	NDMA (ng/l)	Comment
Works C11			
Raw water	C11/A	< 0.48	
Post-coagulation	C11/B	1.6	
Post-RGF	C11/C	2.0	
Post-chlorination	C11/D	1.4	
Post-chloramination / Final water	C11/E	1.5	
Distribution 1	C11/F	1.7	Retention ~12 h
Distribution 2	C11/G	1.7	Retention ~24 h
Distribution 3	C11/H	2.0	Retention ~120 h
Works C12			
Raw water	C12/A	< 0.48	
Recycled water 1	C12/B	1.8	Pre-coagulant dose
Recycled water 2	C12/C	15.0	Post-coagulant dose
Post-clarification	C12/D	0.59	
Post-RGF	C12/E	0.84	
Post-chlorination / Final water	C12/F	0.82	
Distribution 1	C12/G	0.82	Retention ~18 h
Distribution 2	C12/H	0.85	Retention ~24-36 h
Distribution 3	C12/I	1.1	Retention ~48 h
Works C16			
Raw water	C16/A	< 0.48	
Post-coagulation	C16/B	1.1	
Post-RGF1	C16/C	< 0.48	
Post-RGF2 / Final water	C16/E	< 0.48	
Works D17			
Raw water	D17/A	< 0.48	
Post-coagulation	D17/B	< 0.48	
Post-ozonation	D17/C	0.88	
Post-RGF	D17/D	< 0.48	
Post-GAC	D17/E	< 0.48	
Post-chlorination	D17/F	< 0.48	
Final water	D17/G	< 0.48	
Works D18			
Raw water	D18/A	1.1	
Post-coagulation / epi-DMA	D18/B	0.70	
Post-RGF	D18/D	< 0.48	
Post-GAC	D18/E	< 0.48	
Post-chlorination	D18/F	< 0.48	
Final water	D18/G	< 0.48	
Distribution 1	D18/H	< 0.48	Retention ~12 h
Distribution 2	D18/I	< 0.48	Retention ~28 h
Distribution 3	D18/J	< 0.48	Retention ~16 h
Works H5			
Raw water	H5/A	< 0.48	
Post pre-ozonation	H5/B	2.2	
Post-coagulation	H5/C	1.2	
Post-RGF	H5/D	< 0.48	
Post-ozonation	H5/E	5.3	

Sample point	Sample code	NDMA (ng/l)	Comment
Post-GAC	H5/F	0.78	
Post-chlorination	H5/G	0.74	
Post-chloramination / Final water	H5/H	0.68	
Distribution 1	H5/I	0.80	Retention ~6-8 h
Distribution 2	H5/J	0.75	Retention ~18-28 h
Distribution 3	H5/K	1.2	Retention ~28-98 h (summer) ~52-128 h (winter)
Lagoon 1		0.74	
Lagoon 2 inlet		< 0.48	
Lagoon 2 outlet		< 0.48	
Offord PS inlet		0.92	
Long intake		0.74	
Short intake		< 0.48	

Note:
1. Works D18 distribution samples blended, typically 3.8-4.5 parts Works D18 to 1.0 part other Works.

- Works C11: NDMA was detected in seven samples between 1.4-2.0 ng/l, including the post-coagulation (1.6 ng/l) and final water (1.7 ng/l) samples and in distribution (1.7-2.0 ng/l). NDMA was not detected in the raw water.

- Works C12: NDMA was detected in eight samples between 0.59-15 ng/l, but above 1.0 ng/l in the pre-coagulant and post-coagulant recycled water (1.8 ng/l; 15.0 ng/l) and 48-hour distribution (1.1 ng/l) samples. NDMA was not detected in the raw water.

- Works C16: NDMA was detected in only the post-coagulation sample (1.1 ng/l).

- Works D17: NDMA was detected in only the post-ozonation sample (0.88 ng/l).

- Works D18: NDMA was detected in two samples between 0.7-1.1 ng/l, but above 1.0 ng/l in only the raw water (1.1 ng/l). NDMA was not detected in the final water or distribution.

- Works H5: NDMA was detected in nine samples between 0.68-5.3 ng/l, including above 1.0 ng/l in the post-coagulation (1.2 ng/l), post-ozonation (5.3 ng/l) and 28-98 hour distribution (1.2 ng/l) samples. NDMA was not detected in the raw water.

Additional samples were taken from Works H5 to investigate possible sources of NDMA but none indicated significant concentrations. A sample taken from a pumping station that transferred water from the river source to the supply reservoir measured 0.92 ng/l; samples taken in the reservoir close to the draw-off ("short intake") and at the far end of the reservoir ("long intake") measured <0.48 ng/l and 0.74 ng/l, respectively; while samples from two sludge lagoons also measured up to 0.74 ng/l.

D3.10 Survey 10 (September 2009)

Works H5 was sampled during w/b 7 September; Works D17 and D18 during w/b 14 September; and Works C11, C12 and C16 during w/b 21 September.

Table D10 Treatment works Survey 10: September 2009

Sample point	Sample code	NDMA (ng/l)	Comment
Works C11			
Raw water	C11/A	< 0.48 / < 0.48	
Post-coagulation	C11/B	17 / 17	
Post-RGF	C11/C	17 / 17	
Post-chlorination	C11/D	17 / 17	
Post-chloramination / Final water	C11/E	18 / 18	
Distribution 1	C11/F	17 / 16	Retention ~12 h
Distribution 2	C11/G	14 / 15	Retention ~24 h
Distribution 3	C11/H	4.9 / 4.5	Retention ~120 h
Works C12			
Raw water	C12/A	- / < 0.48	
Recycled water 1	C12/B	5.3 / 0.64	Pre-coagulant dose
Recycled water 2	C12/C	71 / 65	Post-coagulant dose
Post-clarification	C12/D	2.1 / 2.4	
Post-RGF	C12/E	2.7 / 2.4	
Post-chlorination / Final water	C12/F	2.4 / 2.1	
Distribution 1	C12/G	3.5 / 2.3	Retention ~18 h
Distribution 2	C12/H	3.0 / 3.0	Retention ~24-36 h
Distribution 3	C12/I	2.2 / 2.2	Retention ~48 h
Works C16			
Raw water	C16/A	< 0.48	
Post-coagulation	C16/B	6.7	
Post-RGF1	C16/C	< 0.48	
Post-RGF2 / Final water	C16/E	< 0.48	
Works D17			
Raw water	D17/A	0.48	
Post-coagulation	D17/B	< 0.48	
Post-ozonation	D17/C	4.9	
Post-RGF	D17/D	1.2	
Post-GAC	D17/E	< 0.48	
Post-chlorination	D17/F	0.89	
Final water	D17/G	0.87	
Works D18			
Raw water	D18/A	1.5	
Post-coagulation / epi-DMA	D18/B	4.1	
Post-RGF	D18/D	0.58	
Post-GAC	D18/E	0.74	
Post-chlorination	D18/F	0.90	
Final water	D18/G	0.58	
Distribution 1	D18/H	< 0.48	Retention ~12 h
Distribution 2	D18/I	0.96	Retention ~28 h
Distribution 3	D18/J	2.1	Retention ~16 h
Works H5			
Raw water	H5/A	1.6	
Post pre-ozonation	H5/B	2.6	
Post-coagulation	H5/C	3.8	
Post-RGF	H5/D	1.0	
Post-ozonation	H5/E	2.5	
Post-GAC	H5/F	2.5	
Post-chlorination	H5/G	2.1	
Post-chloramination / Final water	H5/H	3.4	
Distribution 1	H5/I	3.1	Retention ~6-8 h
Distribution 2	H5/J	4.1	Retention ~18-28 h
Distribution 3	H5/K	2.9	Retention ~28-98 h (summer) ~52-128 h (winter)

Note:
1. Works D18 distribution samples blended, typically 3.8-4.5 parts Works D18 to 1.0 part other Works.

The results from Survey 10 showed some significant increases in NDMA concentrations across all of the works, mostly in samples taken after coagulation suggesting elevated NDMA concentrations in the coagulant. The increased concentrations were greatest for Works C11, C12 and H5, and persisted throughout treatment and distribution.

- Works C11: NDMA was detected in seven samples between 4.5-18 ng/l, including the post-coagulation (17 ng/l) and final water (18 ng/l) samples and in distribution (4.5-17 ng/l). The NDMA concentration in the post-coagulation sample suggested that the coagulant was the source of the elevated concentrations and that the NDMA concentration in the coagulant had increased considerably. NDMA was not detected in the raw water.

- Works C12: NDMA was detected in eight samples between 0.64-71 ng/l, including above 1.0 ng/l in the post-coagulant recycled water sample (65/71 ng/l). This NDMA concentration was significantly greater than measured in Surveys 1-9, suggesting that the coagulant was the source and that the NDMA concentration in the coagulant had increased considerably. NDMA was not detected in the raw water.

- Works C16: NDMA was detected in only the post-coagulation sample (6.7 ng/l).

- Works D17: NDMA was detected in five samples between 0.48-4.9 ng/l, but only above 1.0 ng/l in the post-ozonation (4.9 ng/l) and post-RGF (1.2 ng/l) samples. NDMA was detected in the raw water at 0.48 ng/l.

- Works D18: NDMA was detected in eight samples between 0.58-4.1 ng/l, but only above 1.0 ng/l in the raw water (1.5 ng/l), post-coagulation (4.1 ng/l) and 16-hour distribution (2.1 ng/l) samples.

- Works H5: NDMA was detected in all samples between 1.0-4.1 ng/l, including above 1.0 ng/l in the raw water (1.6 ng/l), post-coagulation (3.8 ng/l), post-ozonation (2.5 ng/l) and final water (3.4 ng/l) samples, and in distribution (2.9-4.1 ng/l).

D3.11 Survey 11 (October 2009)

Works D17, D18 and H5 were sampled during w/b 5 October; and Works C11, C12 and C16 during w/b 12 October.

Table D11 Treatment works Survey 11: October 2009

Sample point	Sample code	NDMA conc. (ng/l)	Comment
Works C11			
Raw water	C11/A	< 0.48	
Post-coagulation	C11/B	19	
Post-RGF	C11/C	26	
Post-chlorination	C11/D	21	
Post-chloramination / Final water	C11/E	22	
Distribution 1	C11/F	18	Retention ~12 h
Distribution 2	C11/G	19	Retention ~24 h
Distribution 3	C11/H	21	Retention ~120 h

Sample point	Sample code	NDMA conc. (ng/l)	Comment
Works C12			
Raw water	C12/A	< 0.48	
Recycled water 1	C12/B	9.5	Pre-coagulant dose
Recycled water 2	C12/C	146	Post-coagulant dose
Post-clarification	C12/D	4.5	
Post-RGF	C12/E	5.6	
Post-chlorination / Final water	C12/F	6.1	
Distribution 1	C12/G	5.8	Retention ~18 h
Distribution 2	C12/H	5.4	Retention ~24-36 h
Distribution 3	C12/I	5.8	Retention ~48 h
Works C16			
Raw water	C16/A	< 0.48	
Post-coagulation	C16/B	32	
Post-RGF1	C16/C	1.0	
Post-RGF2 / Final water	C16/E	< 0.48	
Works D17			
Raw water	D17/A	4.2	
Post-coagulation	D17/B	1.5	
Post-ozonation	D17/C	7.1	
Post-RGF	D17/D	1.1	
Post-GAC	D17/E	1.2	
Post-chlorination	D17/F	0.92	
Final water	D17/G	< 0.48	
Works D18			
Raw water	D18/A	12	
Post-coagulation / epi-DMA	D18/B	11	
Post-RGF	D18/D	4.1	
Post-GAC	D18/E	2.1	
Post-chlorination	D18/F	0.88	
Final water	D18/G	1.1	
Distribution 1	D18/H	< 0.48	Retention ~12 h
Distribution 2	D18/I	0.97	Retention ~28 h
Distribution 3	D18/J	1.1	Retention ~16 h
Works H5			
Raw water	H5/A	4.2	
Post pre-ozonation	H5/B	2.4	
Post-coagulation	H5/C	4.4	
Post-RGF	H5/D	1.1	
Post-ozonation	H5/E	9.2	
Post-GAC	H5/F	4.1	
Post-chlorination	H5/G	4.1	
Post-chloramination / Final water	H5/H	4.4	
Distribution 1	H5/I	5.4	Retention ~6-8 h
Distribution 2	H5/J	3.3	Retention ~18-28 h
Distribution 3	H5/K	4.4	Retention ~28-98 h (summer) ~52-128 h (winter)

Notes:
1. Works D18 distribution samples blended, typically 3.8-4.5 parts Works D18 to 1.0 part other Works.
2. Works C11 coagulant - 247 µg NDMA/l; Works C12 coagulant - 201 µg NDMA/l.

The increased NDMA concentrations seen in Survey 10 were repeated to a generally greater degree in the October survey across all works. Large increases were associated with coagulation for works C11, C12 and C16. However, for works D17, D18 and H5, levels were also high in the raw water, with no significant increase associated with coagulation.

- Works C11: NDMA was detected in seven samples between 18-26 ng/l, including the post-coagulation (19 ng/l) and final water (22 ng/l) samples and in distribution (18-21

ng/l). The elevated concentration in the post-coagulation sample suggested that the coagulant was the source of the NDMA. NDMA was not detected in the raw water.

- Works C12: NDMA was detected in eight samples between 4.5-146 ng/l, including in the post-coagulant recycled water sample (146 ng/l). This elevated concentration suggested that the coagulant was the source of the NDMA. NDMA was not detected in the raw water.

- Works C16: NDMA was detected in the post-coagulation (32 ng/l) and post-RGF (1.0 ng/l) samples, but not in the raw water or final water. The large difference in NDMA concentration across the RGFs suggested removal by a possible biological and/or adsorptive mechanism.

- Works D17: NDMA was detected in six samples between 0.92-7.1 ng/l, including above 1.0 ng/l in the raw water (4.2 ng/l), post-coagulation (1.5 ng/l), post-ozonation (7.1 ng/l) and post-RGF (1.1 ng/l) samples. NDMA was not detected in the final water.

- Works D18: NDMA was detected in eight samples between 0.88-12 ng/l, including above 1.0 ng/l in the raw water (12 ng/l), post-coagulation (11 ng/l) and final water (1.1 ng/l) samples, and in distribution (0.97-1.1 ng/l).

- Works H5: NDMA was detected in all samples between 1.1-9.2 ng/l, including the raw water (4.2 ng/l), post-coagulation (4.4 ng/l), post-ozonation (9.2 ng/l) and final water (4.4 ng/l) samples, and in distribution (3.3-5.4 ng/l).

D3.12 Survey 12 (November 2009)

Works C11, C12, C16 and H5 were sampled during w/b 2 November; and Works D17 and D18 during w/b 9 November.

Table D12 Treatment works Survey 12: November 2009

Sample point	Sample code	NDMA conc. (ng/l)	Comment
Works C11			
Raw water	C11/A	< 0.48	
Post-coagulation	C11/B	24	
Post-RGF	C11/C	21	
Post-chlorination	C11/D	23	
Post-chloramination / Final water	C11/E	23	
Distribution 1	C11/F	22	Retention ~12 h
Distribution 2	C11/G	21	Retention ~24 h
Distribution 3	C11/H	24	Retention ~120 h
Works C12			
Raw water	C12/A	< 0.48	
Recycled water 1	C12/B	8.2	Pre-coagulant dose
Recycled water 2	C12/C	101	Post-coagulant dose
Post-clarification	C12/D	9.7	
Post-RGF	C12/E	6.0	
Post-chlorination / Final water	C12/F	12	
Distribution 1	C12/G	9.5	Retention ~18 h
Distribution 2	C12/H	9.8	Retention ~24-36 h
Distribution 3	C12/I	9.1	Retention ~48 h

Sample point	Sample code	NDMA conc. (ng/l)	Comment
Works C16			
Raw water	C16/A	< 0.48	
Post-coagulation	C16/B	30	
Post-RGF1	C16/C	1.1	
Post-RGF2 / Final water	C16/E	1.8	
Works D17			
Raw water	D17/A	0.81	
Post-coagulation	D17/B	5.7	
Post-ozonation	D17/C	6.0	
Post-RGF	D17/D	0.91	
Post-GAC	D17/E	< 0.48	
Post-chlorination	D17/F	0.57	
Final water	D17/G	< 0.48	
Works D18			
Raw water	D18/A	2.5	
Post-coagulation / epi-DMA	D18/B	11	
Post-RGF	D18/D	6.1	
Post-GAC	D18/E	2.7	
Post-chlorination	D18/F	1.9	
Final water	D18/G	1.8	
Distribution 1	D18/H	< 0.48	Retention ~12 h
Distribution 2	D18/I	2.1	Retention ~28 h
Distribution 3	D18/J	1.7	Retention ~16 h
Works H5			
Raw water	H5/A	2.7	
Post pre-ozonation	H5/B	2.3	
Post-coagulation	H5/C	4.4	
Post-RGF	H5/D	1.6	
Post-ozonation	H5/E	9.6	
Post-GAC	H5/F	5.1	
Post-chlorination	H5/G	3.8	
Post-chloramination / Final water	H5/H	4.2	
Distribution 1	H5/I	3.1	Retention ~6-8 h
Distribution 2	H5/J	3.7	Retention ~18-28 h
Distribution 3	H5/K	3.6	Retention ~28-98 h (summer) ~52-128 h (winter)

Note:
1. Works D18 distribution samples blended, typically 3.8-4.5 parts Works D18 to 1.0 part other Works.

Results for Survey 12 were consistent with those for the previous two months, with high levels of NDMA usually associated with coagulant dosing. Removal by subsequent treatment was apparent at Works C16, D17 and D18. Works D18 and H5 had measurable concentrations of NDMA in the raw water.

- Works C11: NDMA was detected in all samples except the raw water at concentrations between 21-24 ng/l.

- Works C12: NDMA was detected in all samples except the raw water at concentrations between 6.0-101 ng/l. NDMA in the post-coagulant recycled water (101 ng/l) was lower than measured in the previous survey, possibly suggesting a reduced concentration of NDMA in the coagulant.

- Works C16: NDMA was detected in the post-coagulation (30 ng/l), post-RGF (1.1 ng/l) and final water (1.8 ng/l) samples, but not in the raw water. As observed previously, the large difference in NDMA concentration across the RGFs suggested a possible biological and/or adsorptive removal mechanism.

- Works D17: NDMA was detected in five samples between 0.57-6.0 ng/l, but above 1.0 ng/l in the post-coagulation (5.7 ng/l) and post-ozonation (6.0 ng/l) samples. NDMA was not detected in the final water.

- Works D18: NDMA was detected in eight samples between 1.7-11 ng/l, including in the raw water (2.5 ng/l), post-coagulation (11 ng/l) and final water (1.8 ng/l) samples, and in distribution (1.7-2.1 ng/l).

- Works H5: NDMA was detected in all samples between 1.6-9.6 ng/l, including in the raw water (2.7 ng/l), post-coagulation (4.4 ng/l), post-ozonation (9.6 ng/l) and final water (4.2 ng/l) samples, and in distribution (3.1-3.7 ng/l).

D3.13 Additional survey: Works C16 (March 2010)

Because of the apparent substantial removal of NDMA over the first-stage RGFs at Works C16, the sample point was examined at the beginning of March 2010 to ensure the integrity of the sample. It was discovered that the RGF1 sample was taken following passage through an online UV absorbance monitor. To confirm whether UV was affecting the measured NDMA concentration, a sample was taken as usual following the UV monitor and a second sample prior to the UV monitor.

At this time, NDMA was being analysed using the method for nitrosamines (GCMSMS). Due to difficulties with this method of analysis, the analytical results for these samples can only be considered as indicative (see Table D13).

Table D13 Effect of UV on NDMA measurements (- indicative results only)

Sample / Treatment	NDMA (ng/l)
Works C16 clarified water	4.05
Works C16 post-RGF1 (UV exposure)	2.42
Works C16 post-RGF1 (no UV exposure)	2.41

The indicative results in Table D13 show that the NDMA concentrations in the samples following RGF1 were reduced by about 40%, from 4.05 ng/l to 2.41-2.42 ng/l. Although the removal was not as extensive as noted previously, there was no significant difference between the two samples.

In addition, during the site visit it was noted that UV absorbance was not measured after the second-stage RGFs, thus the RGF2 sample was not affected in this way. Throughout the treatment works survey, the RGF2 NDMA concentrations were in the same order as the RGF1 NDMA concentrations, further suggesting that the UV absorbance monitor was having negligible, if any, affect on the concentration of NDMA in the RGF1 sample.

D4 TREATMENT WORKS SURVEY: SUMMARY OF KEY OPERATING DATA

Parameter	Survey No.					
	1 (11/2008)	2 (01/2009)	3 (02/2009)	4 (03/2009)	5 (04/2009)	6 (05/2009)
Works C11						
Raw water pH	5.7	-	Not sampled	4.3-4.4	7.04	7.09
Raw water temp (°C)	6.5	4.1-4.3		4.9-5.1	7.4	8.7
Coagulation dose (mgFe/l)	12.1	10.2		9.1	8.1	7.7
Coagulation pH	4.2-4.3	4.3-4.5		4.2-4.3	4.3-4.4	4.2-4.3
Post contact tank chlorine residual (mgCl/l)[1]	0.5	0.5		0.5	0.5	0.5
Ammonium dose ($mgNH_4/l$)[2]	0.125	0.125		0.125	0.125	0.125
Final water chlorine residual (mgCl/l)[3]	0.05-0.10	0.05-0.10		0.05-0.10	0.05-0.10	0.05-0.10
Final water pH	8.2-8.3	8.2		8.2	8.1-8.2	8.2
Final water temp (°C)[4]	7.5-8.1	3.8-4.0		5.5-5.7	8.4-8.7	10.0-10.2
Works C12						
Raw water pH	6.6-6.7	6.7	Not sampled	6.3-6.4	6.3-6.4	6.4
Raw water temp (°C)	6.0-7.5	2.8		5.6	-	9.6
Coagulation dose (mgFe/l)[5]	> 100	> 100		> 100	> 100	> 100
Coagulation pH	> 10	> 10		> 10	> 10	> 10
PolyDADMAC dose (mg/l)	3.49	3.49		3.49	3.49	3.49
Final water chlorine residual (mgCl/l)[6]	1.00-1.59 / 0.64-0.69	1.59 / 0.60		0.82 / 0.46	0.81 / 0.61	- / 0.40
Final water pH	8.1	8.6		8.4	8.7 / 8.6	8.8
Final water temp (°C)	7.7	4.8-5.0		6.0-6.8	7.4	10.1
Works C16						
Raw water pH	5.5	5.6	Not sampled	5.7	6.0	5.91
Raw water temp (°C)	7.4-7.7	2.8		4.0	6.6	9.9
Coagulation dose (mgFe/l)	14.2	14.6		11.9	11.9	13.0
Coagulation pH	3.7-3.9	3.9		3.9-4.0	4.0	3.9
Final water chlorine residual (mgCl/l)[7]	0.89-1.14 / 0.50	0.72-0.77 / 0.50		0.68	0.76	0.80 / 0.40
Final water pH	8.3-8.5	8.4		8.5	8.7	8.6 / 8.7
Final water temp (°C)	8.3-8.6	4.8-5.0		5.9-6.2	8.7	11.1-11.6
Works D17						
Raw water pH	8.03	8.09	7.86	8.10	8.31	8.27
Raw water temp (°C)	8.0	4.5	8.0	8.0	10.0	13.2
Coagulation dose (mgFe/l)	6.61	5.14	6.61	6.61	5.4	5.55
Coagulation pH	7.1	7.74	7.13	7.13	-	7.8
Ozonation dose (mgO_3/l)	2.0	2.0	2.0	2.0	1.2	1.0
Final water chlorine residual (mgCl/l)	0.76	0.82	0.76	0.76	0.85	0.90
Final water pH	-	-	-	-	-	-
Final water temp (°C)	8.0	4.5	8.0	8.0	10.1	13.4
Works D18						
Raw water pH	7.98	8.01	7.86	8.10	8.69	8.08
Raw water temp (°C)	8.6	2.8	8.6	8.6	9.9	14.1
Coagulation dose (mgFe/l)	8.00	9.0	8.0	8.0	7.5	9.5
Coagulation pH	7.8	7.55	7.8	7.8	8.3	8.13
Epi-DMA dose (mg/l)	1.0	1.0	1.0	1.0	0.8	1.0
Final water chlorine residual (mgCl/l)	1.50	1.60	1.50	1.50	0.61	0.60
Final water pH	-	-	-	-	-	-
Final water temp (°C)	7.8	2.7	7.8	7.8	9.9	14.1

Parameter	Survey No.					
	1 (11/2008)	2 (01/2009)	3 (02/2009)	4 (03/2009)	5 (04/2009)	6 (05/2009)
Works H5						
Raw water pH	8.4	8.4	8.3	8.5	8.5	8.5
Raw water temp (°C)	7.0	7.0	3.0	5.5	8.5	12.5
Pre ozonation dose (mgO_3/l)	2.2	2.5	-	2.4	s/d	-
Coagulation dose (mgFe/l)	3.0	3.0	3.0	3.5	4.0	3.8
Coagulation pH	7.7-7.9	7.69-7.90	7.6	7.53	-	7.41
Ozonation dose (mgO_3/l)	0.5	0.5	0.6	1.21	s/d	-
Post contact tank chlorine residual (mgCl/l)	0.9	0.9	1.20	0.91	0.88	0.90
Ammonium dose ($mgNH_4/l$)[8]	0.225	0.225	0.38	0.23	0.22	0.225
Final water chlorine residual (mgCl/l)[9]	1.29 / 0.05	0.05	1.11 / 0.05	1.20 / 0.05	1.32 / 0.07	1.18 / 0.09
Final water pH	7.2	7.12	7.34	7.59	7.49	7.65
Final water temp (°C)	-	-	-	-	-	-

Notes:
1. Post-contact tank chlorine residual reduced with sodium bisulphite to approximately 0.5 mg/l prior to ammoniation.
2. Ammonium dosed in proportion (~ 5:1) to free chlorine residual.
3. Target free chlorine residual.
4. Measured pre-RGFs.
5. Coagulant dosed in water recovery stage prior to recycle to water treatment.
6. Free chlorine residual measured to Clear Water Tank / into supply.
7. Free chlorine residual measured to Service Reservoir / into supply.
8. Ammonium dosed in proportion (~ 3.8-4.0:1) to free chlorine residual.
9. Total / free chlorine residual.

Parameter	Survey No.					
	7 (06/2009)	8 (07/2009)	9 (08/2009)	10 (09/2009)	11 (10/2009)	12 (11/2009)
Works C11						
Raw water pH	-	6.92	-	-	-	7.12
Raw water temp (°C)	-	15.1	14.8-15.6	13.0	10.0-11.3	9.3-10.4
Coagulation dose (mgFe/l)	-	9.4	10.3	11.7	11.0	11.0-12.0
Coagulation pH	-	4.32	4.35-4.38	4.28	4.20-4.37	4.28-4.30
Post contact tank chlorine residual (mgCl/l)[1]	-	0.69-0.70	0.68-0.72	0.72	0.71	0.73
Ammonium dose ($mgNH_4/l$)[2]	-	0.17-0.18	0.13	0.18	0.18	0.18
Final water chlorine residual (mgCl/l)[3]	-	0.05-0.10	0.05-0.10	0.05-0.10	0.05-0.10	0.05-0.10
Final water pH	-	8.18-8.21	8.21-8.27	8.17	8.28	8.15-8.17
Final water temp (°C)[4]	-	16.0-16.2	-	14.6	11.9	11.0-11.2
Works C12						
Raw water pH	-	6.5-6.6	6.31-6.45	6.5	6.5-6.7	6.6-6.7
Raw water temp (°C)	-	14.3	-	13.8	-	-
Coagulation dose (mgFe/l)[5]	-	>100	>100	>100	>100	>100
Coagulation pH	-	>10	>10	>10	>10	>10
PolyDADMAC dose (mg/l)	-	2.2	3.49	3.49	3.49	3.49
Final water chlorine residual (mgCl/l)[6]	-	0.72	0.75	0.95 / 0.35	0.90 / 0.30	0.90 / 0.50
Final water pH	-	8.8	8.8	8.35	8.5	8.31-8.37
Final water temp (°C)	-	15.3	15.0	13.8	12.3	-
Works C16						
Raw water pH	-	5.94	6.03	6.31	6.5	6.0
Raw water temp (°C)	-	14.3	16.1	13.7	12.0	10.3
Coagulation dose (mgFe/l)	-	11.8	14.0	14.0	15.6	15.7
Coagulation pH	-	3.9	3.9	3.9	4.0	4.0

Parameter	Survey No.					
	7 (06/2009)	8 (07/2009)	9 (08/2009)	10 (09/2009)	11 (10/2009)	12 (11/2009)
Final water chlorine residual (mgCl/l)[7]	-	0.90	1.12	1.14 / 0.52	1.30 / 0.50	1.0 / 0.74
Final water pH	-	8.75	8.7	8.6	8.6	8.6-7.75
Final water temp (°C)	-	14.3	18.7	-	14.0	-
Works D17						
Raw water pH	8.32	-	-	-	-	-
Raw water temp (°C)	17.5	18.5	16.2	15.0	13.2	10.1
Coagulation dose (mgFe/l)	5.54	6.6	5.20	5.5	5.5	5.5
Coagulation pH	7.70	7.80	7.80	7.66	7.8	7.3
Ozonation dose (mgO_3/l)	2.0	2.0	2.0	1.0	1.0	1.5
Final water chlorine residual (mgCl/l)	0.85	0.74	0.86	0.86	0.82	0.74
Final water pH	-	-	-	-	-	-
Final water temp (°C)	17.6	20.0	17.8	15.4	12.8	10.1
Works D18						
Raw water pH	7.89	-	-	-	-	-
Raw water temp (°C)	18.8	21.3	16.6	15.7	14.8	8.9
Coagulation dose (mgFe/l)	7.5	8.5	9.0	8.0	7.5	8.0
Coagulation pH	8.13	7.90	8.0	8.03	7.8	7.92
Epi-DMA dose (mg/l)	1.0	1.0	1.0	0.9	1.0	0.8
Final water chlorine residual (mgCl/l)	0.56	0.67	0.42	0.50	0.65	0.52
Final water pH	-	-	-	-	-	-
Final water temp (°C)	19.7	21.0	17.1	15.8	14.4	9.1
Works H5						
Raw water pH	8.30	8.3	8.4	8.54	8.56	8.32-8.44
Raw water temp (°C)	16.0	18.0	18.0	17.0	15.6	10.0-11.3
Pre ozonation dose (mgO_3/l)	(4.79)	0.8	0.8	0.7	0.7	0.7
Coagulation dose (mgFe/l)	3.8	3.4	3.4	3.4	3.4	3.4
Coagulation pH	7.44	8.4	8.4	8.56	8.47	8.22
Ozonation dose (mgO_3/l)	0.48	1.0	1.15	1.2	1.13	0.96
Post contact tank chlorine residual (mgCl/l)	0.90	1.0	1.2	0.89	0.79	0.79
Ammonium dose ($mgNH_4$/l)[8]	0.29	0.15	0.28-0.34	0.20	0.19	0.19
Final water chlorine residual (mgCl/l)[9]	1.20 / 0.10	0.55	1.28	0.08	0.09	0.09
Final water pH	7.71	7.6	7.7	7.4	7.4	7.2
Final water temp (°C)	-	-	-	-	-	-

Notes:
1. Post-contact tank chlorine residual reduced with sodium bisulphite to approximately 0.5 mg/l prior to ammoniation.
2. Ammonium dosed in proportion (~ 5:1) to free chlorine residual.
3. Target free chlorine residual.
4. Measured pre-RGFs.
5. Coagulant dosed in water recovery stage prior to recycle to water treatment.
6. Free chlorine residual measured to Clear Water Tank / into supply.
7. Free chlorine residual measured to Service Reservoir / into supply.
8. Ammonium dosed in proportion (~ 3.8-4.0:1) to free chlorine residual.
9. Total / free chlorine residual.

D5 TREATMENT WORKS SURVEY: SUMMARY OF RAW WATER QUALITY

Parameter	Survey No.					
	1 (12/2008)	2 (01/2009)	3 (02/2009)	4 (03/2009)	5 (04/2009)	6 (05/2009)
Works C11						
pH	7.19	6.78	Not sampled	6.57	6.38	6.46
Turbidity (NTU)	2.23	3.76		1.44	2.02	2.03
True colour (°H)	108.5	78.4		130.4	69.4	61.9
True UV254 (AU/m)	67.3	50.0		69.5	38.3	41.2
TOC (mg/l as C)	13.2	8.49		6.97	7.25	6.59
NH_3 (mg/l as N)	< 0.3	0.046		0.022	0.019	0.024
NO_2 (mg/l as N)	< 0.1	0.014		0.021	0.013	< 0.003
NO_3 (mg/l as N)	< 0.3	1.80		1.32	1.58	1.78
Works C12						
pH	6.80	6.72	Not sampled	7.10	6.46	6.30
Turbidity (NTU)	2.62	2.29		2.42	2.09	1.54
True colour (°H)	101.6	88.3		69.3	56.6	56.5
True UV254 (AU/m)	57.0	49.8		39.7	37.0	34.3
TOC (mg/l as C)	10.6	7.84		5.99	6.11	5.77
NH_3 (mg/l as N)	< 0.3	< 0.009		0.010	0.015	0.036
NO_2 (mg/l as N)	< 0.1	0.015		0.017	0.014	< 0.003
NO_3 (mg/l as N)	0.6	2.49		2.64	3.06	3.11
Works C16						
pH	6.30	6.29	Not sampled	6.57	6.06	5.98
Turbidity (NTU)	2.04	2.02		1.44	1.27	2.16
True colour (°H)	193.1	159.2		130.4	123.9	116.3
True UV254 (AU/m)	102.0	84.8		69.5	63.7	63.5
TOC (mg/l as C)	18.1	12.9		10.1	10.8	10.0
NH_3 (mg/l as N)	< 0.3	< 0.009		< 0.009	0.009	0.024
NO_2 (mg/l as N)	< 0.1	0.028		0.025	0.021	< 0.003
NO_3 (mg/l as N)	0.6	3.09		3.16	3.36	3.90
Works D17						
pH	8.03	8.09	7.86	8.10	8.31	8.27
Turbidity (NTU)	12.1	4.25	7.01	4.42	8.76	7.83
True colour (°H)	19.7	10.4	17.3	11.2	15.0	7.2
True UV254 (AU/m)	20.1	13.2	19.0	13.9	12.3	1.2
TOC (mg/l as C)	9.8	5.08	6.63	5.08	4.81	4.67
NH_3 (mg/l as N)	< 0.3	0.043	0.040	0.024	0.025	0.055
NO_2 (mg/l as N)	< 0.1	0.067	0.085	0.060	0.049	0.089
NO_3 (mg/l as N)	3.7	22.0	11.5	16.2	18.1	18.3
Works D18						
pH	7.98	8.01	7.86	7.97	8.69	8.08
Turbidity (NTU)	14.9	3.48	4.74	3.55	3.63	1.47
True colour (°H)	25.1	14.7	21.9	14.7	12.8	13.1
True UV254 (AU/m)	23.1	15.9	20.8	15.9	13.9	15.7
TOC (mg/l as C)	8.1	5.56	6.14	4.77	5.67	5.95
NH_3 (mg/l as N)	< 0.3	0.117	0.041	0.029	0.273	0.086
NO_2 (mg/l as N)	< 0.1	0.192	0.083	0.057	0.110	0.156
NO_3 (mg/l as N)	5.7	39.7	28.8	36.9	32.6	33.7
Works H5						
pH	8.35	8.25	8.28	8.26	8.75	8.50
Turbidity (NTU)	2.54	0.80	7.50	15.30	2.11	3.04
True colour (°H)	7.7	6.9	8.3	8.8	8.8	5.6
True UV254 (AU/m)	11.6	11.3	12.1	11.8	11.6	10.3
TOC (mg/l as C)	6.4	5.02	4.93	4.94	5.34	5.07
NH_3 (mg/l as N)	< 0.3	0.057	0.068	0.156	0.058	0.133
NO_2 (mg/l as N)	< 0.1	0.066	0.147	0.089	0.102	0.161
NO_3 (mg/l as N)	3.4	18.1	23.3	22.2	19.1	19.7

Parameter	Survey No.					
	7 (06/2009)	8 (07/2009)	9 (08/2009)	10 (09/2009)	11 (10/2009)	12 (11/2009)
Works C11						
pH	6.61	6.50	6.54	6.47	6.54	6.51
Turbidity (NTU)	2.00	4.55	1.84	1.87	1.75	2.36
True colour (°H)	60.5	65.6	78.4	110.4	100.4	106.9
True UV254 (AU/m)	40.4	42.4	51.6	69.4	67.5	68.8
TOC (mg/l as C)	6.44	7.55	9.4	11.3	10.9	11.6
NH_3 (mg/l as N)	0.029	< 0.009	0.033	<0.3	<0.3	0.014
NO_2 (mg/l as N)	< 0.003	< 0.003	0.004	<0.01	<0.01	<0.003
NO_3 (mg/l as N)	3.52	2.11	1.71	<2.5	<2.5	1.86
Works C12						
pH	6.62	6.73	6.73	6.63	6.49	6.64
Turbidity (NTU)	1.08	1.57	1.14	1.44	1.84	2.48
True colour (°H)	56.8	58.4	94.4	89.7	98.3	94.1
True UV254 (AU/m)	35.1	35.8	55.6	53.4	58.1	55.2
TOC (mg/l as C)	5.51	5.85	-	9.74	8.95	8.79
NH_3 (mg/l as N)	0.020	0.013	-	<0.3	<0.3	0.012
NO_2 (mg/l as N)	0.004	< 0.003	-	<0.01	<0.01	<0.003
NO_3 (mg/l as N)	3.00	3.28	-	2.6	2.8	2.64
Works C16						
pH	6.60	6.15	6.33	6.18	6.30	6.08
Turbidity (NTU)	2.88	1.61	2.22	3.33	1.9	5.1
True colour (°H)	116.8	115.2	171	262.7	166.6	180.8
True UV254 (AU/m)	64.0	64.0	92.4	98.5	89.2	97.8
TOC (mg/l as C)	9.94	10.1	-	16.6	13.6	15.0
NH_3 (mg/l as N)	0.019	< 0.009	-	<0.3	<0.3	0.016
NO_2 (mg/l as N)	< 0.003	< 0.003	-	<0.01	<0.01	<0.003
NO_3 (mg/l as N)	3.87	4.31	-	3.2	3.3	3.33
Works D17						
pH	8.32	7.95	7.98	8.22	8.05	7.90
Turbidity (NTU)	3.10	2.44	7.81	4.04	3.07	9.68
True colour (°H)	8.8	9.9	13.1	9.1	8.5	9.6
True UV254 (AU/m)	12.1	12.0	15.5	12.0	10.7	11.1
TOC (mg/l as C)	5.07	5.07	6.69	5.39	5.25	4.72
NH_3 (mg/l as N)	0.030	0.034	0.036	0.056	0.067	0.043
NO_2 (mg/l as N)	0.075	0.22	0.089	0.066	0.063	0.055
NO_3 (mg/l as N)	13.0	15.9	11.3	11.8	18.7	15.5
Works D18						
pH	7.89	7.70	7.56	-	7.91	7.87
Turbidity (NTU)	0.85	0.51	3.39	0.7	1.41	1.1
True colour (°H)	11.2	12.0	34.7	13.6	11.2	14.9
True UV254 (AU/m)	12.6	13.4	30.9	14.3	12.1	15.2
TOC (mg/l as C)	4.83	4.67	9.31	5.55	5.19	5.19
NH_3 (mg/l as N)	0.073	0.047	0.047	0.033	0.032	0.033
NO_2 (mg/l as N)	0.297	0.301	0.154	0.065	0.082	0.045
NO_3 (mg/l as N)	39.9	26.4	19.6	37.7	39.7	26.8
Works H5						
pH	8.32	8.41	8.38	8.75	8.71	8.33
Turbidity (NTU)	3.30	0.63	5.61	3.40	6.06	9.50
True colour (°H)	5.9	5.6	5.9	6.7	6.1	6.1
True UV254 (AU/m)	11.5	9.7	9.7	10.2	9.7	9.6
TOC (mg/l as C)	4.65	5.1	5.27	5.25	5.43	4.84
NH_3 (mg/l as N)	0.055	0.054	0.043	0.082	0.077	0.079
NO_2 (mg/l as N)	0.093	0.133	0.082	0.056	0.08	0.165
NO_3 (mg/l as N)	21.6	18.5	17.6	13.6	15.2	14.3

APPENDIX E LABORATORY STUDIES

E1 INTRODUCTION

Laboratory studies were carried out in parallel with the treatment works survey to try to elucidate the removal of NDMA across the RGFs at Works C16 and the formation of NDMA in distribution at Works C11, where concentrations appeared to increase with retention time. These studies are reported in Sections E2 and E3, respectively.

Following the completion of the treatment works survey, a series of laboratory studies was carried out to investigate the formation and removal of nitrosamines. These studies are reported in Section E4.

E2 NDMA REMOVAL BY BIOLOGICAL FILTRATION

It was noted at several works throughout the treatment works survey that NDMA concentrations were reduced across RGFs following coagulation. This was particularly evident at Works C16 in Surveys 10-12 (September-November 2009) when the NDMA concentration in post-coagulated water was reduced from 6.7-32.0 ng/l to less than 1.1 ng/l in post-RGF1 water.

In order to confirm this possible biological removal mechanism, samples of media were taken from both RGF stages at Works C16 (RGF1 and RGF2 (manganese contactors)) and mixed with samples of post-coagulated clarified water and nitrosamine-spiked tap water (nitrosamines spiked at 10 ng/l) in stirred one-litre glass beakers. Following the contact period, the samples were settled and filtered to remove the media and analysed for NDMA.

At this time, NDMA was being analysed using the method for nitrosamines (GCMSMS). Due to difficulties with this method of analysis, the analytical results for these samples (see Table E1) can only be considered as indicative.

Table E1 NDMA (ng/l) measured before and after contact with RGF media (- indicative results only)

Sample / Treatment	NDMA (ng/l)
Works C16 post-coagulated clarified water	4.05
Works C16 clarified water contacted with RGF1 media	2.63
Works C16 clarified water contacted with RGF2 media	0.22
Nitrosamine-spiked tap water[1]	5.11
Nitrosamine-spiked tap water contacted with RGF1 media	6.77
Nitrosamine-spiked tap water contacted with RGF2 media	1.75

Note:
1. Tap water spiked with 10 ng NDMA/l.

Results of the tests, based on the indicative results, showed removals of NDMA from the Works C16 clarified water contacted with RGF1 and RGF2 media of 35.1% and 94.6%, respectively. The analysis of the tap water spiked with 10 ng NDMA/l indicated only 5.11 ng/l:

based on the spike of 10 ng NDMA/l, removals due to contact with RGF1 and RGF2 media measured 32.3% and 82.5%, respectively; based on the measured value of 5.11 ng NDMA/l, contact with RGF1 media showed an apparent increase in NDMA concentration, whilst removal due to contact with RGF2 media measured 65.8%.

E3 NDMA FORMATION IN DISTRIBUTION

E3.1 Works C11: Simulation of Retention in Distribution (Chloraminated Water)

Results from the treatment works surveys indicated that formation of NDMA in distribution may be related to retention time. NDMA was not detected in the raw water or within treatment at Works C11 at concentrations much above the limit of detection (0.48 ng/l). However, concentrations measured in distribution consistently increased with nominal retention times up to 5 days. A simple test was devised to simulate retention in distribution to investigate NDMA formation with retention time at temperatures up to 20°C.

Twenty-five litres of chloraminated final water was taken from the Works C11 Service Reservoir (Distribution 1). This sample was sub-divided into three aliquots, with each stored in the dark at 5°C, 10°C and 20°C, respectively. Two 1-litre samples were taken from each aliquot for NDMA analysis after 5, 10, 15 and 25 days. Results of the test are shown in Table E2.

Table E2 NDMA (ng/l) measured in simulated distribution samples (chloraminated water)

Day	Temperature (°C)		
	5	**10**	**20**
0	-	< 0.48	-
5	< 0.48	< 0.48	< 0.48
10	0.58	0.50	0.60
15	0.78	0.59	0.52
25	< 0.48	0.54	< 0.48

NDMA was not detected in the sample taken from the Service Reservoir (12-hour retention; see Table D6, Sample C11/F) but was subsequently detected in distribution at 1.4 ng/l (after 24-hour retention) and 2.1 ng/l (5-day retention). The magnitude of this observation was not replicated in the laboratory simulation, although there was an indication that NDMA was formed after 10-15 days retention but was then degraded, although it is noted that the concentrations measured were comparable to the limit of detection. Temperature within the range 5-20°C appeared to have negligible affect on NDMA formation.

E3.2 Works C11: Simulation of Retention in Distribution (Chlorinated and Chloraminated Waters)

To further clarify the formation of NDMA in the distribution network of Works C11 (see Section E3.1), a simple test was devised to simulate the retention in distribution of chlorinated and chloraminated water samples.

Twenty-five litres each of chlorinated water (ex. Contact Tank) and chloraminated final water (ex. Service Reservoir) were taken from Works C11. Both samples were stored in the dark at 10°C for up to 10 days. Two 1-litre samples were taken from each water type for NDMA analysis after 5 and 10 days. Results of the test are shown in Table E3.

Table E3 NDMA (ng/l) measured in simulated distribution samples (chlorinated and chloraminated waters)

Day	Chlorinated Water	Chloraminated Water
0	< 0.48	< 0.48
5	< 0.48	< 0.48
10	< 0.48	< 0.48

NDMA was not detected in either of the samples of chlorinated or chloraminated water (see Table D7, Samples C11/D and C11/E), whereas the 5-day distribution sample (C11/H) contained 1.2 ng/l NDMA. In the laboratory simulation, NDMA was not detected in any sample.

E3.3 Works C11: Further Investigation of Simulation of Retention in Distribution (Chlorinated and Chloraminated Waters)

A similar study to that described in E3.2 was carried out to further investigate the formation of NDMA in distribution. Samples of works chlorinated water (ex. Contact Tank), chloraminated water (ex. Service Reservoir) and samples from the distribution system were stored in the dark at 10°C for 5 and 10 days. The results are shown in Table E4.

Table E4 NDMA (ng/l) measured in stored chlorinated, chloraminated and distribution samples

Sample	NDMA (ng/l) after storage		
	0 days	5 days	10 days
Chlorinated (ex. Contact Tank)	0.84	0.96	1.4
Chloraminated (ex. Service Reservoir)	0.85	0.80	1.3
Distribution 2 : ~ 24 h retention	0.99	0.93	0.96
Distribution 3: ~ 5 d retention	1.7	0.60	1.4

NDMA was detected in all the samples of water taken from Works C11 (see Table D8): in the chlorinated and chloraminated samples (C11/D, 0.84 ng/l; C11/E, 0.85 ng/l) and in the 24-hour and 5-day distribution samples (C11/G, 0.99 ng/l; C11/H, 1.7 ng/l). Results of the

laboratory simulation were inconclusive: both chlorinated and chloraminated samples showed increased NDMA after 10 days, but there was no significant change in the 24-hour distribution sample, whilst the 5-day distribution sample decreased.

Whilst the concentrations measured in this investigation were low, there is no indication that the chloraminated samples from the works or distribution produced higher levels of NDMA on storage than the works chlorinated sample.

E3 NITROSAMINE FORMATION AND REMOVAL

E3.1 Laboratory Study

E3.1.1 Introduction

As a result of the more comprehensive analysis of coagulants for NDMA contamination - and the tests carried out in parallel with the treatment works study to investigate and simulate the formation of NDMA in distribution and possible removal by biological filtration - the scope of the laboratory study to investigate nitrosamine formation and removal was reduced. The programme described below was discussed and agreed with DWI.

The objective of the laboratory study was to identify the formation and removal of a range of nitrosamine compounds by water treatment processes simulated in the laboratory. Specifically, the study addressed the following processes for upland surface water (ex. Works C12):

- Pre-ozonation
- Coagulation (ferric sulphate/polyDADMAC)
- Sedimentation / Dissolved air flotation
- Ozonation
- GAC
- Chlorination / Chloramination

Tests were also carried out with nitrosamine-spiked tap water (each at 20 ng/l) to determine if ozone, GAC or a combination of the two remove any preformed nitrosamines.

Analysis was carried out for nine nitrosamines: NDMA, NMEA, NDEA, NPYR, NDPA, NPIP, NDBA, NMOR and NDPHA.

E3.1.2 Methods

Jar tests

Jar tests were conducted on the raw water from Works C12 to identify optimal coagulation conditions (dose and pH). A ferric sulphate coagulant was used (Coagulant B2) and pH was

adjusted using either NaOH or H_2SO_4. The effect of a polyDADMAC polyelectrolyte (Floquat® FL4440) was additionally investigated in a number of tests.

The optimum coagulation conditions are summarised in Table E5.

Table E5 Coagulation conditions

Water	pH	Coagulant dose mg Fe/l	polyDADMAC dose mg FL4440/l
Upland ex. Works C12	5.5	9.0	2.0

After 30 minutes coagulation and flocculation, the samples were settled for 10 minutes and then filtered through Whatman 113 filter papers.

Dissolved air flotation

The effect of dissolved air flotation (DAF) was investigated using a DAF jar tester and the coagulation conditions shown in Table E5. After 30 minutes coagulation and flocculation, approximately 12% air-saturated tap water was injected at the bottom of the sample. After 5 minutes flotation of the flocs, clarified samples were collected and filtered.

Pre-ozonation

Aliquots of the raw water were pre-ozonated for 10 s, resulting in initial ozone concentrations of 0.04 mg O_3/l. For comparison, tap water ozonated for 10 s had an ozone residual of approximately 0.6 mg O_3/l.

Ozonation

Aliquots of the coagulated/filtered waters were ozonated for 30 s using the same ozonator settings as for the pre-ozonation tests. The initial ozone concentration for the coagulated/filtered waters was 1.05 mg O_3/l. After 10 minutes, ozone concentration had decreased to 0.47 mg O_3/l.

Tap water spiked with nitrosamines was ozonated for 10 s. The initial residual of 0.41 mg O_3/l decreased to 0.16 mg/l after 15 min. The initial residual was lower than measured on unspiked tap water, possibly due to an ozone demand exerted by methanol contained in the nitrosamine spiking solution.

Chlorination

Sodium hypochlorite (NaOCl) was dosed to selected samples, aiming for a residual of 0.5 mg Cl_2/l. Free and total chlorine were measured after 1 h or 48 h - to simulate retention in distribution - using a portable Palintest spectrometer (DPD method).

Chloramination

Sodium hypochlorite (NaOCl) was dosed to selected samples, aiming for a residual of 0.5 mgCl_2/l. Free and total chlorine were measured after 1 h and ammonium sulphate ($(NH_4)_2SO_4$) was dosed at a Cl_2/NH_3 ratio of 5:1 on a weight basis (1:1 on a molar basis). Free

and total chlorine were measured after a further 1 h or 48 h - to simulate retention in distribution - using a portable Palintest spectrometer (DPD method).

GAC

Virgin GAC (Chemviron F400) was placed in a 1-litre glass cylinder with a glass frit bottom and backwashed to remove finer particles. The flow through the GAC was adjusted to achieve an empty bed contact time (EBCT) of 15 minutes. The first 1-2 bed volumes of treated water were discharged to waste and the sample collected thereafter.

E3.1.4 Analytical results

Difficulties were encountered with the analysis of nitrosamines and method development required substantial effort. NDMA and NMEA were subsequently analysed by GCMS and the remaining nitrosamines (NDEA, NPYR, NDPA, NPIP, NDBA, NMOR, NDPHA) by LCMSMS.

The results of the tests on coloured upland water and on nitrosamine-spiked tap water are shown in Tables E6 and E7, respectively.

Table E6 Nitrosamine analysis: Upland water ex. Works C12

Treatment	Nitrosamine (ng/l)								
	NDMA	NMEA	NDEA	NPYR	NDPA	NPIP	NDBA	NMOR	NDPHA
Raw water	<0.48	<0.5	<3.1	<2.3	<0.8	<2.6	<2.6	2.89	<3.3
Test A									
Coagulation/Filtration	2.53	<0.5	<3.1	<2.3	<0.8	<2.6	<2.6	6.49	<3.3
Coagulation/Filtration/Ozonation	0.95	<0.5	<3.1	<2.3	<0.8	<2.6	<2.6	1.69	<3.3
Coagulation/Filtration/Ozonation/GAC	0.93	<0.5	<3.1	<2.3	<0.8	<2.6	<2.6	<1.5	<3.3
Coagulation/Filtration/Ozonation/GAC/Chlorination 1 h	<0.48	<0.5	<3.1	<2.3	<0.8	<2.6	<2.6	<1.5	<3.3
Coagulation/Filtration/Ozonation/GAC/Chlorination 48 h	0.54	<0.5	<3.1	<2.3	<0.8	<2.6	<2.6	<1.5	<3.3
Coagulation/Filtration/Ozonation/GAC/Chloramination 1 h	<0.48	<0.5	<3.1	<2.3	<0.8	<2.6	<2.6	<1.5	<3.3
Coagulation/Filtration/Ozonation/GAC/Chloramination 48 h	0.54	<0.5	<3.1	<2.3	<0.8	<2.6	<2.6	<1.5	<3.3
Test B									
Coagulation/Filtration/GAC	0.51	<0.5	<3.1	<2.3	<0.8	<2.6	<2.6	<1.5	<3.3
Coagulation/Filtration/GAC/Chlorination 1 h	0.65	<0.5	<3.1	<2.3	<0.8	<2.6	<2.6	<1.5	<3.3
Coagulation/Filtration/GAC/Chlorination 48 h	1.01	<0.5	<3.1	<2.3	<0.8	<2.6	<2.6	<1.5	<3.3
Coagulation/Filtration/GAC/Chloramination 1 h	0.77	<0.5	<3.1	<2.3	<0.8	<2.6	<2.6	<1.5	<3.3
Coagulation/Filtration/GAC/Chloramination 48 h	1.13	<0.5	<3.1	<2.3	<0.8	<2.6	<2.6	<1.5	<3.3
Coagulation/Filtration/Chlorination 1 h	2.31	<0.5	<3.1	<2.3	<0.8	<2.6	<2.6	4.19	<3.3
Coagulation/Filtration/Chlorination 48 h	2.11	<0.5	<3.1	<2.3	<0.8	<2.6	<2.6	4.85	<3.3
Coagulation/Filtration/Chloramination 1 h	1.73	<0.5	<3.1	<2.3	<0.8	<2.6	<2.6	4.09	<3.3
Coagulation/Filtration/Chloramination 48 h	2.18	<0.5	<3.1	<2.3	<0.8	<2.6	<2.6	4.12	<3.3
Test C									
Coagulation/DAF/Filtration	6.31	<0.5	<3.1	<2.3	<0.8	<2.6	<2.6	25.9	<3.3
Test D									
Preozonated raw water	<0.48	<0.5	<3.1	<2.3	<0.8	<2.6	<2.6	<1.5	<3.3
Preozonation/Coagulation/Filtration	2.13	<0.5	<3.1	<2.3	<0.8	<2.6	<2.6	2.94	<3.3
Preozonation/Coagulation/Filtration/Ozonation	1.18	<0.5	<3.1	<2.3	<0.8	<2.6	<2.6	3.07	<3.3
Preozonation/Coagulation/Filtration/Ozonation/GAC	<0.48	<0.5	<3.1	<2.3	<0.8	<2.6	<2.6	<1.5	<3.3
Preozonation/Coagulation/Filtration/Ozonation/GAC/ Chlorination 1 h	<0.48	<0.5	<3.1	<2.3	<0.8	<2.6	<2.6	<1.5	<3.3
Preozonation/Coagulation/Filtration/Ozonation/GAC/ Chlorination 48 h	0.72	<0.5	<3.1	<2.3	<0.8	<2.6	<2.6	<1.5	<3.3

Treatment	Nitrosamine (ng/l)								
	NDMA	**NMEA**	**NDEA**	**NPYR**	**NDPA**	**NPIP**	**NDBA**	**NMOR**	**NDPHA**
Preozonation/Coagulation/Filtration/Ozonation/GAC/ Chloramination 1 h	<0.48	<0.5	<3.1	<2.3	<0.8	<2.6	<2.6	<1.5	<3.3
Preozonation/Coagulation/Filtration/Ozonation/GAC/ Chloramination 48 h	0.71	<0.5	<3.1	<2.3	<0.8	<2.6	<2.6	<1.5	<3.3
Test E									
Coagulation(+polyDADMAC)/Filtration	1.27	<0.5	<3.1	<2.3	<0.8	<2.6	<2.6	3.04	<3.3
Coagulation(+polyDADMAC)/Filtration/Ozonation	1.51	<0.5	<3.1	<2.3	<0.8	<2.6	<2.6	3.17	<3.3
Coagulation(+polyDADMAC)/Filtration/Ozonation/GAC	<0.48	<0.5	<3.1	<2.3	<0.8	<2.6	<2.6	<1.5	<3.3
Coagulation(+polyDADMAC)/Filtration/Ozonation/GAC/ Chlorination 1 h	<0.48	<0.5	<3.1	<2.3	<0.8	<2.6	<2.6	<1.5	<3.3
Coagulation(+polyDADMAC)/Filtration/Ozonation/GAC/ Chlorination 48 h	0.53	<0.5	<3.1	<2.3	<0.8	<2.6	<2.6	<1.5	<3.3
Coagulation(+polyDADMAC)/Filtration/Ozonation/GAC/ Chloramination 1 h	<0.48	<0.5	<3.1	<2.3	<0.8	<2.6	<2.6	<1.5	<3.3
Coagulation(+polyDADMAC)/Filtration/Ozonation/GAC/ Chloramination 48 h	0.48	<0.5	<3.1	<2.3	<0.8	<2.6	<2.6	<1.5	<3.3

Table E7 Nitrosamine analysis: Spiked tap water

Treatment	Nitrosamine (ng/l)								
	NDMA	NMEA	NDEA	NPYR	NDPA	NPIP	NDBA	NMOR	NDPHA
Spiked tap water	19.32/ 19.69	19.4/ 20.7	22.6/ 21.9	22.3/ 18.0	17.0/ 19.6	22.8/ 19.4	22.8/ 21.3	17.7/ 20.5	14.8/ 10.5
Spiked tap water/Ozonation	21.2	20.8	28.2	17.6	17.5	22.2	18.6	16.2	7.09
Spiked tap water/Ozonation/GAC	1.35	<0.5	<3.1	<2.3	<0.8	<2.6	<2.6	<1.5	<3.3
Spiked tap water/GAC	0.64	<0.5	<3.1	<2.3	<0.8	<2.6	<2.6	<1.5	<3.3

Note:
1. Tap water spiked with 20 ng/l of each nitrosamine.