

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 study¹ (“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 $<1 \mu\text{g/l}$ and close to the limit of detection of $0.48 \mu\text{g/l}$; it is probable that many of these results were false positives. In six coagulants higher concentrations (up to $19 \mu\text{g/l}$) 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.