

DISINFECTION BY-PRODUCTS FROM DRINKING WATER TREATMENT
Final Report to the Drinking Water Inspectorate

Disinfection By-Products from Drinking Water

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DISINFECTION BY-PRODUCTS FROM DRINKING WATER TREATMENT

EXECUTIVE SUMMARY

The broad objective of the contract was to provide the Department of the Environment/Department of the Environment, Transport and the Regions with information on the identity and concentrations of disinfection by-products (DBPs) generated in water treatment and on concentration changes occurring within distribution systems.

To meet this overall objective, and its associated sub-objectives, a series of research and review studies were carried out.

A review of the modelling of the formation of trihalomethanes (THMs) in distribution showed that there are a number of models which can predict the formation of THMs in distribution to some degree. They appear to perform well under the reported conditions. However, they do have potential weaknesses which include not having been tested over a broad range of water and distribution system types, and/or not taking into account the concentration of certain potentially-important variables, such as bromide ion, ammonia or Total Organic Carbon (TOC).

Following on from the review of modelling, a study of the factors influencing changes in THM concentrations in four distribution systems was carried out. A number of conclusions could be drawn from the results.

Unquenched ex-works waters showed the potential to form more THMs within a 24 hour period. If the water was spiked with further chlorine then the formation of THMs was greater. The magnitude of the chlorine residual in the water as it leaves the works, the fraction of chlorine demand satisfied at the works, and any booster chlorination will play an important role in determining the increase in THM concentrations in distribution.

Where works operated to target minimum chlorine residuals leaving the works then a rise in THM precursors in the works did not necessarily lead to higher concentrations of THMs in the distribution. As the precursor level, and hence the chlorine demand, rises then the chlorine residual leaving the works falls. As long as the residual remains above the target minimum then the chlorine dose remains constant. Thus, whilst the THM concentration leaving the works will have risen, the formation in distribution will have been limited by the fall in chlorine residual. Therefore there may not be an appreciable rise in the concentration at the tap. However, if the THM precursor level rises such that the chlorine dose has to be increased to maintain the residual leaving the works then it is likely that the THM concentration at the tap will rise appreciably.

- For works C the difference between the maximum and minimum residuals is 0.45 mg l^{-1} . The experiments where 0.5 mg l^{-1} chlorine was added to the samples on their return to the laboratory showed increases of $10 - 25 \text{ } \mu\text{g l}^{-1}$ in THM concentrations over 24 hours. Given that the range of concentrations reported for tap THM concentrations in 1996 was $40 - 118 \text{ } \mu\text{g l}^{-1}$, the variation allowed by the residual limits appears to cover a small, but appreciable, portion of the annual variation in precursor levels.
- There did not appear to be any evidence of THMs arising due to reactions of chlorine with pipe materials, sediments or biofilms in the distribution system.

An investigation of the influence of UV disinfection on the formation of disinfection by-products was carried out, with emphasis on any operational implications. It was demonstrated that, if UV units are operated at a dose of around 100 mJ cm^{-2} , then at high nitrate levels (i.e. close to the 50 mg l^{-1} drinking water limit) the concentration of nitrite may approach or exceed the regulatory limit of $100 \text{ } \mu\text{g l}^{-1}$. In this case some monitoring for nitrite should be undertaken, and if necessary, adjustments made to the UV dose applied to allow an operational safety margin. If the UV units are operated in the range $25 - 30 \text{ mJ cm}^{-2}$ then, even for waters with high nitrate levels, the concentration of nitrite formed is unlikely to approach the regulatory limit.

If UV units are operated at a dose of around 100 mJ cm^{-2} , then if tetrachloroethene (PCE) is present in high concentrations, i.e. at, or above, 1 mg l^{-1} , then the concentrations of dichloroacetic acid (DCA) produced may approach the WHO Drinking Water Guideline value of $50 \text{ } \mu\text{g l}^{-1}$. Therefore, if PCE is found to be present at high concentrations in the source water then monitoring should be applied to ensure that significant concentrations of DCA are not being formed.

The study found no firm evidence, within the scope of the Gas Chromatography - Nitrogen Phosphorus detection (GC-NPD) and Gas Chromatography-Mass Spectrometry (GC-MS) methods applied, that the UV irradiation of water resulted in the formation of any nitrogen-containing organic compounds.

An analysis of the potential for the development of surrogate measurements for DBPs was carried out using data collected for a previous DoE study. The implication of the analysis is that any relationship that can be drawn between an individual by-product and a surrogate varies from works to works. At each works the relationship will depend in some degree on the nature and extent of the treatment applied. Thus it does not appear likely that surrogate relationships can be established covering a wide range of works/water types. However, it may be possible to construct works-specific relationships. For such relationships to be a useful monitoring tool then it would have to be determined whether a relationship which holds at the works also holds throughout the distribution system.

A review was conducted of the state of knowledge with regard to the balance between the formation of bromate and the removal of pesticides by ozonation. There have been a

number of studies which have specifically examined this balance. Whilst these studies are not extensive enough to be able to apply the results to different treatment situations, and to a wide range of pesticides, a number of useful pointers can be drawn.

- There appears to be a law of diminishing returns for pesticide removal, i.e. the degree of removal tails off as the ozone dose increases.
- Some of the measures which can be taken to limit bromate formation include lowering of pH and the addition of hydrogen peroxide. For most pesticides these measures will tend to increase the degree of removal.
- The addition of hydrogen peroxide to limit bromate formation is most effective when the ozone dose is kept constant. However, in some cases a reduction in bromate has been observed where the final ozone residual has been kept constant. These latter conditions are the better option for pesticide removal.

In principle, it should be feasible to extend the models of bromate formation such as those produced by Von Gunten (e.g. Von Gunten and Hoigné 1992) to take account of the requirements to remove specific contaminants. However, this is likely to take a significant degree of effort to generate sufficient data on the kinetics of reaction of individual pesticides. For some frequently studied pesticides, such as atrazine, sufficient data may already exist.

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1. INTRODUCTION

The Department of the Environment has supported a substantial research programme on disinfection by-products (DBPs) since October 1984. The work carried out on behalf of the Department by WRc between 1984 and 1995 has been summarised in an earlier report, 'Effects of disinfectants on organic substances in water: Final report to the Department of the Environment' DWI 3898/1, August 1995.

The main areas of research were:

- the chlorination and ozonation of selected organic chemicals;
- the use of chlorine demand to assess reactivity of organic chemicals;
- the reactions of pesticides with disinfectants/oxidants;
- the reactions of water treatment chemicals with disinfectants/oxidants;
- the occurrence and formation of haloacetic acids;
- mutagenicity arising from ozonation;
- the formation and occurrence of bromate;
- balancing chemical and microbial risks; and
- disinfection by-product indicators.

The Department placed a further contract with WRc in May 1995 with the following objectives:

- to provide the Department with information on the identity and concentrations of disinfection by-products (DBPs) generated in water treatment and on concentration changes occurring during distribution or within distribution systems;
- to develop and inform the Department's negotiating position on the proposed standards for the revised Directive;
- to inform the Department about world-wide regulatory developments which might have a bearing on water treatment and the quality of drinking water in England and Wales;
- to review and critically appraise new and emerging scientific knowledge in the field of DBPs; and
- to undertake prospective studies on the formation and significance of DBPs, including the assessment of reactions between disinfectants and substances and products used in the provision of drinking water supplies.

The following section summarises the work carried out, and indicates the reports where more detailed descriptions of the work can be found.

2. RESEARCH AND REVIEW TOPICS COVERED DURING THE CONTRACT PERIOD

2.1 Review of modelling of formation of trihalomethanes (THMs) in distribution (Report no. DWI 4045/1)

The acquisition of the capability to model the formation and behaviour of water quality parameters in general, and disinfection by-products in particular, has long been regarded as desirable. From the point of view of disinfection by-products, the areas of interest include:

- regulatory procedures. A predictive model of formation could be used as an aid in a standards-setting procedure, as has occurred, to a degree, in the United States through the derivation of the Disinfection/Disinfection By-Products Rule. One particular area of interest would be in a model which predicted the formation and behaviour of by-products in distribution systems, given the setting of EC standards based on concentrations at the consumer's tap. This could lead to scope for a shift in the approach to monitoring programmes;
- operational procedures. A model could provide the potential for process control directly-related to specific, regulated, by-products. For example, if the model related the formation of a given by-product to process and water quality parameters which are amenable to on-line monitoring, then an interactive control procedure could be established.

There are two approaches to the construction of a predictive model that could be envisaged:

1. an explicit approach, which is based on the chemical kinetics. This would require detailed knowledge of all, or at least of a significant proportion, of the reactions involved. Given the range and complexity of the reactions involved in, for example, the formation of chlorination by-products during water treatment this is unlikely to form a practical approach;
2. an empirical, or semi-empirical approach. This is the most commonly-adopted approach in attempts to generate formation models. They are based on deriving relationships, from observed data, between by-product concentrations, treatment conditions and water quality parameters.

The range of empirical approaches adopted for modelling THMs can be summarised as follows:

1. predicting the THM formation potential (THMFP). The THMFP is a measure of the maximum THM concentration that can be formed in a water. This parameter has proved useful for assessing the control of THM formation by precursor removal in treatment, where a change in THMFP will reflect a likely change in the THM concentration produced by treatment. However, since water treatment will rarely, if ever, cause the THMFP to be attained, it is less useful in predicting the actual THM concentrations either in water leaving the works, or in the distribution system;
2. predicting the total THM concentration. Some authors have developed so-called 'bromine incorporation factors' to convert total THM values into individual THM concentrations for a given water;
3. predicting individual THM concentrations directly.

2.1.1 Summary

There are a number of models established which can predict the formation of THMs in distribution to some degree, and they appear to perform well, at least under the reported conditions. However, they do have potential weaknesses which include some, or all, of the following:

- not having been tested over a broad range of water and distribution system types,
- not taking into account the concentration of certain potentially-important variables, such as bromide ion, ammonia or Total Organic Carbon (TOC).

Assessment of Water Undertaker's data for trihalomethanes (THMs) and bromate (Report no. DWI 4242)

Assessments were carried out on UK water undertakers' THM and bromate monitoring data, as collected on behalf of the DoE for a separate study into the cost implications of the proposed revision to the EC Drinking Water Directive.

The purpose of the assessment of the THM data was to establish whether there exists a relationship between THM concentrations at the consumer's tap and those leaving the treatment works, particularly in terms of ancillary parameters such as pH or chlorine residual. Whilst the database contained much THM data, detailed examination showed that only a limited amount was suitable for the derivation of the desired type of relationships. From the limited data available, no significant relationship could be established to explain the change in THM concentration in distribution. The only statistically significant relationship that could be drawn indicated that the speciation of THMs shifted more towards chloroform in distribution as the raw water pH decreased.

To derive useful relationships between trihalomethanes at tap and ex-works then a larger and more systematic dataset is required. The dataset needs to cover a broader range of potentially influential parameters measured at appropriate points. Thus, for example, TOC values immediately prior to chlorination and in the treated water would be more useful than the TOC values for the raw water. Where possible, a better defined time relationship between the measurement of the various parameters would be beneficial.

The purpose of the assessment of the bromate data was to investigate the potential impact of a range of limits on the concentration bromate. The database contained bromate data from 46 works supplying a total population of about 13 500 000. A limit of $10 \mu\text{g I}^{-1}$ was included in the proposed revision to the EC Drinking Water Directive. If this limit were based on an annual mean then 7 works covered in the database, supplying about 1.5 million people and all using ozone, would give exceedences. By contrast, if the limit were based on total compliance with a Maximum Allowable

Concentration (MAC) then 24 works supplying about 10 million people would give exceedences. This would include some works not using ozone. The assessment was based on monitoring data for water leaving the works, since there was virtually no data available from the distribution system. In general the concentration of bromate would not be expected to increase in distribution, the main exception being if booster chlorination with hypochlorite solutions was used.

2.3 Factors influencing changes in trihalomethane (THM) concentrations in distribution systems (Report nos. DWI 4331 and DWI 4460/1)

Following on from the assessment of UK water undertakers' THM monitoring data which is described in Section 2.2, a study was conducted into the factors influencing changes in THM concentrations in distribution systems.

This investigation was carried out on four distribution systems. This was done in two stages, with two systems being studied in early 1997 (reported in DWI 4331) and a further two being studied in late summer 1997 (reported in DWI 4460/1). Of the first two systems, one was supplied by a works (Works A) using ozone/Granular Activated Carbon treated water derived from a lowland river water impounded in a reservoir. The other system was supplied by a works (Works B) using conventionally-treated water derived from an upland river water impounded in a reservoir. These works were selected on the basis of their historic THM data, with Works A having little change in THM concentration during distribution and Works B having an approximate doubling in THM concentration.

The initial study was extended to include upland works where there were difficulties achieving compliance with the $100 \mu\text{g l}^{-1}$ limit for total THMs. In consultation with DWI and the water company concerned two upland works were selected, one (Works C) which provides only basic treatment (i.e. simple filtration and chlorination) and one (Works D) which uses coagulation/filtration before chlorination. It was further agreed that the sampling programme should take place in late summer. At this time it was likely that a combination of lower water flows, leading to higher TOC concentrations, and higher temperatures would give rise to the greatest difficulty in achieving compliance.

2.3.1 Survey of works variability

One key factor in interpreting the results of sampling for disinfection by-products from distribution systems is the degree of short-term variation in the concentrations of the by-products of interest in the water leaving the treatment works. This is particularly the case for distribution systems where the times of travel are ill-defined. This was investigated for the selected treatment works by sampling the ex-works water over a period of 48 hours for THMs, adsorbable organic halides (AOX), dichloroacetic acid (DCA), trichloroacetic acid (TCA), Total Organic Carbon (TOC) and chlorine residuals. Ex-works were taken at each works over a three day period to monitor variation in disinfection by-products in the ex-works water. The samples were taken morning and afternoon on consecutive days and morning on the third day. Samples for THMs and AOX were taken in duplicate, with the average of the analytical results being reported.

In summary the evidence suggests that the short-term variation in THM concentrations and chlorine residual leaving the works is sufficiently small (relative to the uncertainty in the information relating to time of travel) that the changes in distribution could be investigated without seeking to accurately track a plug of water.

2.3.2 Survey of changes in distribution

Each works and distribution system was sampled on three days, with three sampling points being used for each distribution system. The distribution points were chosen so as to be representative of the distribution system being studied, i.e. short, medium and long residence times.

On each sampling day, duplicate samples from each point were taken, quenched with sodium thiosulphate and stored on ice. These were analysed for TOC, THMs, AOX, bromide and UV absorbance at 254 nm on return to the laboratory (for Works C and D, DCA and TCA were also analysed). Further duplicate samples were taken at each point and the temperature, residual free and total chlorine immediately measured.

On each sampling day, further samples were taken to allow the study of the effect of contact time and increased chlorination on THM formation. Samples of ex-works water and water from the distribution point furthest from the works were collected on each of the three sampling days for these storage experiments. Samples were left quenched (with sodium thiosulphate), and unquenched at ambient temperature and in the dark for 24 and 48 hour periods prior to analysis. Further samples were also dosed with extra chlorine in the laboratory (0.5 mg l^{-1} or 10 mg l^{-1}) and left at ambient temperature and in the dark for a 24 hour period before being analysed. The chlorine boosting experiment was done to see to assess the degree to which the potential of the water to form THMs had changed during distribution.

The sampling programme for Works A and B took place in February and March 1997. The sampling programme for Works C and D took place in August and September 1997.

2.3.3 Results and discussion

The detailed results for the four works are reported separately (DWI 4331 and DWI 4460/1). A summary of the change in THM concentration observed in distribution for all four works is given in Table 2.1.

Table 2.1 Comparison of THM formation in distribution

Works Code	Type of treatment	Mean THM ratio (Tap/Works)	Mean CHCl ₃ ratio (Tap/Works)	Mean BDCM ratio (Tap/works)
A	Ozone/GAC treated water from a lowland river source	1.38 +/- 0.24	1.32 +/- 0.18	1.44 +/- 0.30
B	Conventionally treated water from an upland river	1.22 +/- 0.24	1.17 +/- 0.26	1.48 +/- 0.12
C	Upland water source with basic treatment	1.27 +/- 0.10	1.26 +/- 0.15	1.26 +/- 0.09
D	Upland water source with conventional treatment	1.11 +/- 0.11	1.11 +/- 0.13	1.13 +/- 0.10

At the time of sampling, Works A water showed only a small increase in THM formation in distribution. This is reasonably consistent with the historical data available for the works. Works B water showed a much smaller increase in THM concentration in distribution than was expected from the historical data, i.e. a doubling was expected. Since the ex-works water contained double the expected concentration of THMs, it is conceivable that a higher proportion of the THM potential has been satisfied at the works hence reducing the increase in their level in the distribution water.

Neither Works C or D approached the 100 µg l⁻¹ limit for total THMs in any of the samples taken from the works or in distribution, despite the sampling programme being targeted on the time when exceedences were thought most probable. This was also the case for the unquenched samples stored for up to an additional 48 hours. However, the addition of a further 0.5 mg l⁻¹ free chlorine to water from Works C and its distribution system caused the THM concentration to approach, and in one case exceed, 100 µg l⁻¹. For Works D, the only sample exceeding 100 µg l⁻¹ was one which had been dosed with an additional 10 mg l⁻¹ free chlorine.

There is no large difference in the tap:works ratio for THMs between any of the works. The tap:works ratio was below 2.0 in all cases. This held even in the case of Works C, when temperatures and chlorine residual were high. Given the historic difficulty Works C has had in meeting the THM limit (and hence the current programme of upgrading) this suggests that the problem is primarily one of formation at the works. However, since the sampling programme covered hot late summer conditions it would have been expected that THM concentrations would have been higher.

The overall pattern of results for Works C and D fits with that for A and B. Specifically, the concentration of THMs leaving the works is highest when the chlorine residual leaving the works is lowest. This observation was made for both Works B and C. These works received the simplest treatment of the four studied, i.e. were likely to have the lowest degree of precursor removal. The observation is consistent with the chlorine dose only being adjusted when the final residual is outside the relatively broad operating limits. Thus an increase in THM precursor concentration, and hence chlorine demand, in the works will be reflected in an increase in THMs and a decrease in the chlorine residual leaving the works.

2.3.4 Conclusions

Based on the results obtained from all four works studied the following conclusions can be drawn:

1. The unquenched ex-works waters showed the potential to form more THMs within a 24 hour period. If the water was spiked with further chlorine then the formation of THMs was greater. The magnitude of the chlorine residual in the water as it leaves the works, the fraction of chlorine demand satisfied at the works, and any booster chlorination will play an important role in determining the increase in THM concentrations in distribution.
2. Where works operate to target minimum chlorine residuals leaving the works then a rise in THM precursors in the works does not necessarily lead to higher concentrations of THMs in the distribution. As the precursor level, and hence the chlorine demand, rises then the chlorine residual leaving the works falls. As long as the residual remains above the target minimum then the chlorine dose remains constant. Thus, whilst the THM concentration leaving the works will have risen, the formation in distribution will have been limited by the fall in chlorine residual. Therefore there may not be an appreciable rise in the concentration at the tap. However, if the THM precursor level rises such that the chlorine dose has to be increased to maintain the residual leaving the works then it is likely that the THM concentration at the tap will rise appreciably.
3. For works C the difference between the maximum and minimum residuals is 0.45 mg l^{-1} . The experiments where 0.5 mg l^{-1} chlorine was added to the samples on their return to the laboratory showed increases of $10 - 25 \text{ } \mu\text{g l}^{-1}$ in THM concentrations over 24 hours. Given that the range of concentrations reported for tap THM concentrations in 1996 was $40 - 118 \text{ } \mu\text{g l}^{-1}$, the variation allowed by the residual limits appears to cover a small, but appreciable, portion of the annual variation in precursor levels.
4. There did not appear to be any evidence of THM levels increasing due to reactions of chlorine with pipe materials, sediments or biofilms in the distribution system. This is demonstrated by the fact that the samples taken from the distribution system had concentrations lower than those found in the stored unquenched ex-works samples.
5. For the other by-products investigated (AOX, DCA and TCA), whilst there is evidence of variations in concentrations, there is no evidence of any consistent patterns.

2.4 Influence of UV treatment (Report no. DWI 4237/1)

An investigation was carried out into the influence of UV disinfection on the formation of disinfection by-products. This investigation included:

1. the formation of by-products directly by the action of UV irradiation on components of the water matrix; and
2. the influence of UV irradiation on the formation of by-products when disinfectants such as chlorine are subsequently added.

The findings can be summarised as follows:

- the irradiation of solutions of nitrate with high UV doses (high relative to the levels recommended for achieving adequate disinfection, 16 mJ cm^{-2}) produces concentrations of nitrite well in excess of the $100 \text{ } \mu\text{g l}^{-1}$ regulatory limit. The concentration formed appears to be

directly dependent on the UV dose applied and the nitrate concentration present. At low UV doses, pH values typical of UK water sources, and nitrate concentrations within the regulatory limit, the formation of nitrite is rarely, if ever, likely to exceed $100 \mu\text{g l}^{-1}$;

- aldehydes, in particular formaldehyde and acetaldehyde, are formed as a result of the UV irradiation of solutions of humic acid and of Thames river water. However, they do not appear to be formed at levels that would be of concern;
- UV irradiation may reduce the chlorination by-product formation potential (trihalomethanes {THMs} and trichloroacetic acid {TCA}) of humic acid solutions and Thames river water, but the changes observed are too small to be categorical. Under some conditions there may be a slight increase in formation potential;
- UV irradiation will remove brominated THMs, but has little, or no, effect on chloroform. There is insufficient information to whether an analogous observation would be true for haloacetic acids;
- the use of UV irradiation to treat water contaminated with tetrachloroethene (PCE) can give rise to significant concentrations of dichloroacetic acid (DCA). TCA can also be formed but generally at lower concentrations. This may also be a consideration where UV-based advanced oxidation processes are used to remove PCE;
- UV irradiation of nitrate-containing river water results in the apparent formation of nitrogen- or phosphorus-containing compounds. However, Gas Chromatography - Mass Spectrometry (GC-MS) experiments failed to confirm the formation of any compounds of interest. Some unsaturated long-chain amides were tentatively identified in some samples but these were not confirmed;
- GC-MS analysis of river water spiked with dimethylamine (DMA) and nitrite did not detect the presence of any identifiable nitrosamine under the limited set of conditions used (the estimated detection limit being of the order of a few $\mu\text{g l}^{-1}$).

While the main aim of the use of UV disinfection is to achieve adequate disinfection, the formation of by-products may, in some circumstances, influence the mode of operation. A number of potential implications for the operation of UV disinfection systems were identified and these can be summarised as follows:

- the prime controlling factor in by-product formation will be the overall energy input. However, the formation of by-products will be affected by the wavelength (i.e. photon energy) of the UV radiation to some degree, but the extent is hard to quantify and will be compound specific. In general, the longer wavelengths (i.e. those with lower photon energy) will be less likely to produce by-products. Thus, the conservative approach would be to base any controls on overall energy input using results obtained with the narrow-band, low pressure lamps, since this would tend to overestimate the extent of by-product formation for the same energy input from the broad-band, medium pressure lamp.
- if UV units are operated at a dose of around 100 mJ cm^{-2} , then at high nitrate levels the concentration of nitrite may approach or exceed the regulatory limit of $100 \mu\text{g l}^{-1}$. In this case then some monitoring for nitrite should be undertaken, and if necessary, adjustments made to the UV dose applied to allow an operational safety margin. If the UV units are operated in the range $25 - 30 \text{ mJ cm}^{-2}$ then, even for waters with high nitrate levels, the concentration of nitrite formed is unlikely to approach the regulatory limit.
- if UV units are operated at a dose of around 100 mJ cm^{-2} , then if PCE is present in high concentrations, i.e. at, or above, 1 mg l^{-1} , then the concentrations of DCA produced may

approach the WHO Drinking Water Guideline value of $50 \mu\text{g l}^{-1}$. Therefore, if PCE is found to be present at high concentrations in the source water then monitoring should be applied to ensure that significant concentrations of DCA are not being formed.

- this study found no firm evidence, within the scope of the Gas Chromatography - Nitrogen Phosphorus detection (GC-NPD) and GC-MS methods applied, that the UV irradiation of water resulted in the formation of any nitrogen-containing organic compounds.

2.5 Disinfection By-Product (DBP) dossiers (Report no. DWI 4279)

The Drinking Water Inspectorate (DWI) identified a need for a compendium of information on disinfection by-products to act as a support to:

1. the efforts of Department of the Environment (DoE) representatives negotiating the revisions to the EC Drinking Water Directive; and
2. the ability of the DWI to respond rapidly to queries raised relating to DBPs.

To this end a series of dossiers were compiled on the main (21 in all) by-products which were considered by the World Health Organisation (WHO) during their revision of the Drinking Water Guidelines. The revised WHO guidelines were published in 1993.

Two versions of the dossiers were produced, one giving single-page summaries and the other giving detailed versions.

2.6 Nitrosamines in drinking water (Report no. DWI 4168)

There has been much study of the formation and occurrence of N-nitroso compounds in food, particularly in cured meats, in certain beverages such as beer and whisky, in tobacco smoke, and in pesticide formulations. N-nitroso compounds are the subject of an International Agency for Research on Cancer (IARC) Monograph (IARC 1978). The purpose of this assessment is to examine the evidence for the formation and occurrence of N-nitroso compounds in drinking water, and to evaluate whether the evidence indicates cause for concern.

There is a reasonable amount of data on the occurrence of nitrosamines in water, but little for drinking water. Much of that which does exist relates to N-nitrosodimethylamine (NDMA). The available data is restricted to some degree due to the difficulties involved in the analysis. There are no US or EC drinking water standards for nitrosamines. There is a recommended US Water Quality Standard for NDMA in water supplies intended for human consumption of 0.69 ng l^{-1} (based on an excess cancer risk of 10^{-6}), but the basis for its derivation is regarded as weak and is currently under review.

In 1987, the Ministry of Agriculture, Fisheries and Food produced a report 'Nitrate, nitrite and N-nitroso compounds in food'. This report contained a consideration of the report by the Committee on Toxicity of Chemicals in Food, Consumer Products and the Environment. They stated that 'the available data on the likely dietary intake of those nitrosamines whose carcinogenic potency is known suggest that for these compounds the magnitude of any adverse health effects is likely to be small, and we do not consider that there are adequate grounds to advise any dietary modification to reduce their intake'. The available evidence suggests that the intake of nitrosamines from drinking water will be small in comparison to those from food, alcoholic beverages and tobacco smoke.

One of the controlling factors in the formation of nitrosamines is the concentration of nitrite. If the concentrations of nitrosamines in drinking water should be demonstrated to be of greater concern, then adjustments to treatment to minimise nitrite concentrations should be considered. These considerations should cover both the treatment plant and the distribution system.

2.7 Potential for contamination from use of modified starches and alginates (Report no. DWI 4133)

There have been concerns raised with regard to the possible significance of contamination arising from the use of modified starches and alginates in drinking water treatment. In part, these concerns are being addressed through the CEN process. A brief assessment of the potential problem has been carried out, covering the contaminants thought likely to be of most concern and the scale of usage within the UK water industry.

2.7.1 Modified starches

Anionic and cationic starches may contain traces of the reagents used during manufacture to generate charged sites. The reagents most commonly-used are sodium monochloroacetate (SMCA) and 3-chloro-2-hydroxypropyl trimethylammonium chloride (CHPT).

SMCA is a salt of monochloroacetic acid. Haloacetic acids are the subject of concern as disinfection by-products, and monochloroacetic acid is regulated in US drinking water under the Disinfectant/Disinfection By-Products Rule total haloacetic acids standard. There are no publicly-available data on the residual levels of the reagents in commercial products. However, from contacts made with suppliers of modified starch products which are approved for use in drinking water treatment, it can be said that:

- only relatively small quantities of modified starches are sold for use in water treatment in the UK. Goldcrest sold 400 tonnes of all products last year, Fospur have sold none in the last 2-3 years, Allied Colloids were less definite but thought the sales were minor.
- SMCA was not used as the modifying agent in the manufacturing processes for any of the products identified as having been supplied last year.

Therefore, it does not appear that the use of modified starches in the UK will give rise to significant additional concentrations of monochloroacetate in drinking water.

There is no publicly-available data on the residual concentrations of CHPT in modified starch products. However, a Tentative 24 hour Suggested No Adverse Response Level (SNARL) for CHPT has been derived from rat LD₅₀ data, and this can be used to calculate a product specification limit. If this calculation is based on a reference dose of 10 mg l⁻¹, then the limit for CHPT is about 100 g per kg product. Based on confidential data, this is at least an order of magnitude higher than that which may occur in the product. This, in combination with the low usage of modified starches, indicates that contamination of drinking water by CHPT should not present a problem.

2.7.2 Alginates

Sodium alginate is obtained by the treatment of brown seaweed with dilute alkali followed by purification. No evidence has been found in the literature of impurities in alginate products, other than trace levels of simple inorganic salts. There are no reported studies on organic impurities in alginates, but it is difficult to envisage anything of concern being present.

The supplier of the sole approved alginate product was contacted, and it was established that only 4-5 tonnes were sold to water companies last year. Hence, the use of alginates in drinking water treatment does not appear to be of any current, or likely future concern.

2.8 Bromate from the use of chlorine dioxide (Report no. DWI 4133)

One possible route by which bromate could enter drinking water is via contamination of the raw materials used during the production of chlorine dioxide, namely sodium chlorite and hydrochloric

acid. This possibility was investigated by contacting UK-based suppliers and obtaining samples, which were then analysed for bromate.

For the products tested and for a chlorine dioxide dose of 1 mg l^{-1} , the concentration of bromate arising from:

sodium chlorite is $<0.34 \text{ } \mu\text{g l}^{-1}$

hydrochloric acid is $<0.1 \text{ } \mu\text{g l}^{-1}$

This suggests that the raw materials of chlorine dioxide production are not likely to give rise to significant concentrations of bromide in drinking water. This should be qualified by noting that a researcher (Magnin 1996) has reported finding 700 mg l^{-1} of bromate in a commercial sodium chlorite solution with nominal concentration of 350 g l^{-1} . For a 1 mg l^{-1} dose of chlorine dioxide this would give about $3.4 \text{ } \mu\text{g l}^{-1}$ of bromate in the treated water.

2.9 Analytical methods for DBPs (Report no. DWI 4274/1)

A review was carried out of the available analytical methods for disinfection by-products (DBPs), using the Standing Committee of Analysts (SCA) methods as the starting point. Whilst many DBPs are not covered by an SCA method, the main need is identified as a method for haloacetic acids. There exists a well-established United States Environmental Protection Agency (USEPA) method (Method 552) for haloacetic acids. There also exists a USEPA method (Method 551) which covers a broad range of DBPs of interest, including trihalomethanes (THMs), haloacetonitriles, chloral hydrate and chloropicrin. Both of these methods have the potential to be readily incorporated into the SCA style. However, it should be noted that the reported performance of the USEPA methods for some of the DBPs (e.g. brominated haloacetic acids, chlorophenols) places some qualifications on their suitability for producing good quality monitoring data.

2.10 Formation and removal of aldehydes and ketoacids in treatment plants utilising ozone (Report no. DWI 4331)

A survey of treatment works using ozone was carried out to investigate the formation of aldehydes and keto/aldo acids. This demonstrated that ozonation can produce appreciable concentrations of the keto/aldo acids glyoxylic acid, pyruvic acid and keto-malonic acid (up to $30 \text{ } \mu\text{g l}^{-1}$), supporting the findings of other workers. In general Granular Activated Carbon (GAC) filtration gives good removal, in some cases better than 80%. Furthermore there is evidence that other types of filtration such as anthracite/sand/garnet have the potential to give similar degrees of removal. In the cases studied the formation of aldehydes was generally low (typically $<40 \text{ } \mu\text{g l}^{-1}$ in total).

2.11 The potential for the development of surrogate measurements for Disinfection By-Products (Report no. DWI 4331)

As part of a previous Department of the Environment (DoE) contract 'Effects of disinfectants on organic substances in water' (PECD 7/7/137), the feasibility of using selected disinfection by-products (DBPs) or classes of DBPs as indicators (or surrogates) of a range of DBPs was investigated. The findings were included in the report, DWI 3967, July 1995.

The study was conducted by collecting samples of raw and final waters from two treatment works on alternate weeks over a period of twelve weeks. One works treated water from a lowland river source and the other water from an upland source. The raw and final waters were analysed for the following:

- Free chlorine residual
- Total Organic Carbon (TOC)
- Bromide
- Trihalomethanes (THMs)
- Dichloroacetic acid (DCA)
- Trichloroacetic acid (TCA)
- Trichloroacetaldehyde (TCAL)
- Dichloroacetonitrile (DCAN)
- Trichloroacetonitrile (TCAN)
- Adsorbable Organic halide (AOX)

In addition, an aliquot of raw water was treated in the laboratory by coagulation in a jar tester using aluminium sulphate (3 mg l^{-1}), followed by filtration under vacuum through a 540 GF/F filter. This, and an aliquot of untreated raw water, were then chlorinated (10 mg l^{-1} , 17 hours, 20°C in the dark). The chlorinated raw and coagulated water were also analysed for the range of DBPs.

The data obtained was only subjected to a preliminary evaluation, consisting of the calculation of linear correlation coefficients. This evaluation indicated that relationships may exist between individual DBPs and classes of DBPs (e.g. THMs). The correlation coefficients quoted in the original report were calculated for the data covering both sites and the three 'types' of treatment. This approach did not allow a proper determination as to how good any relationships were, or whether there existed significant differences between water from the two sites or between the different treatment regimes.

The possible relationships were analysed in more detail by use of a stepwise regression approach, which tested the percentage of variance explained by a series of models and also tested the degree of significance which could be attached to a given model. The procedure started with the most complex model, i.e. allowing full variation due to differing treatment and site, and calculated the

accountable percentage of variance. The model was then sequentially simplified by restricting the degree of variation and then removing terms entirely. If any given step resulted in a large change in the accountable percentage of variation then clearly the restricted or removed term was of importance to the model.

The relationships tested were those between each individual by-product and the broader parameters of total THMs, AOX and TOC. In general, in order that a model has a chance of proving viable then at least 90% of the variance should be explained. In most cases the highest percentage variance was explained by a model which allowed for variation between treatments and between sites.

The implication of the analysis is that any relationship that can be drawn between an individual by-product and a surrogate varies from works to works. At each works the relationship will depend in some degree on the nature and extent of the treatment applied. Thus it does not appear likely that surrogate relationships can be established covering a wide range of works/water types. However, it may be possible to construct works-specific relationships. For such relationships to be a useful monitoring tool then it would have to be determined whether a relationship which holds at the works also holds throughout the distribution system.

2.12 Balance between the formation of bromate and the removal of pesticides by ozonation (Report no. DWI 4460/1)

2.12.1 Background

The use of ozonation in water treatment as an oxidant and/or disinfectant is well established world-wide. It has become increasingly common in the UK over the last 10 years, particularly for the treatment of lowland surface waters. In the UK the motivation for introducing ozone has been manifold. The introduction of regulations governing the levels of chlorinated disinfection by-products led to a desire to reduce the usage of chlorine - primarily by using ozone as an oxidant, e.g. for plant hygiene, for iron and manganese removal, for organics removal. Furthermore, under the EC Drinking Water Directive (Directive 80/778/EEC) limits were introduced on the concentrations of pesticides permitted in water supplied for human consumption, with a limit of $0.1 \mu\text{g l}^{-1}$ for any individual pesticide, and a limit of $0.5 \mu\text{g l}^{-1}$ for the total of all pesticides. In many cases the control of pesticides to comply with these limits could be achieved by the using of Granular Activated Carbon (GAC) filters. Ozone is also effective at removing a number of pesticides, and pesticide removal has been the motivation in introducing ozonation in some cases.

However, there are disadvantages associated with the use of ozone, with especial concern surrounding the ability of ozone to oxidise bromide to form bromate. The World Health Organisation set a provisional drinking water guideline value for bromate of $25 \mu\text{g l}^{-1}$ (WHO, 1993). If WHO had used their standard approach, based on an excess lifetime cancer risk of 10^{-5} , then the guideline value would have been $3 \mu\text{g l}^{-1}$. The higher valued was proposed in recognition of the limitations of the analytical methods for bromate available at the time. In the United States, under Stage 1 of the Disinfectant/Disinfection By-Product Rule, a limit of $10 \mu\text{g l}^{-1}$ has been proposed. Under the current revisions to the EC Drinking Water Directive it is proposed that there should be a limit of $10 \mu\text{g l}^{-1}$ for bromate.

Therefore there is a potential conflict between the use of ozone to reduce pesticide concentrations and minimising the formation of bromate. A review of the current state of knowledge was carried out, and reported in DWI 4460/1. The summary and conclusions drawn are reproduced below.

In the context of pesticides, 'the degree of removal' or 'the degree of oxidation' refers to the

conversion of the original pesticide into a different compound. It does not necessarily imply the complete mineralisation of the original molecule. In some cases the by-product will not differ greatly from the original pesticide, and its properties are unlikely to be known, i.e. it will not be known whether or not it retains pesticidal properties.

2.12.2 Summary and conclusions

There have been a number of studies which have specifically examined the balance during ozonation between pesticide removal and bromate formation. Whilst these studies are not extensive enough to be able to apply the results to different treatment situations, and to a wide range of pesticides, a number of useful pointers can be drawn.

- there appears to be a law of diminishing returns for pesticide removal, i.e. the degree of removal tails off as the ozone dose increases. Also a threshold ozone dose for bromate formation has been found, and this may mirror this tailing off of pesticide removal.
- some of the measures which can be taken to limit bromate formation include lowering of pH and the addition of hydrogen peroxide. Both lead to the formation of hydroxyl radicals at the expense of molecular ozone. For most pesticides these measures will tend to increase the degree of removal.
- the addition of hydrogen peroxide to limit bromate formation is most effective when the ozone dose is kept constant. However, in some cases a reduction in bromate has been observed where the final ozone residual has been kept constant. These latter conditions are the better option for pesticide removal.
- other measures which can be taken to limit bromate formation will also tend to have no effect or reduce the degree of pesticide removal, such as addition of ammonia, limiting the applied ozone dose and decreasing temperature (were such a thing practicable).

In principle, it should be feasible to extend the models of bromate formation such as those produced by Von Gunten (e.g. Von Gunten and Hoigné 1992) to take account of the requirements to remove specific contaminants. However, this is likely to take a significant degree of effort to generate sufficient data on the kinetics of reaction of individual pesticides. For some frequently studied pesticides, such as atrazine, sufficient data may already exist.

3. STAND-ALONE REPORTS AND CONFERENCE PAPERS

The following stand-alone reports have been produced as part of this contract:

- N-Nitrosodimethylamine in drinking water: an assessment of its potential significance (DWI 4168).
- Analytical methods for disinfection by-products (DWI 4274/1).
- Influence of UV disinfection on by-product formation and the operational implications (DWI 4237/1).
- Disinfection by-product dossiers (DWI 4279).

The following conference papers have been produced as part of this contract:

- 'Disinfection by-products' presented by Mike Fielding to 'Drinking Water 2000'. Held at the University of Warwick, March 1998.
- 'The influence of UV disinfection on by-product formation' presented by Nicholas Mole to 'The International Conference on Disinfection by-products: the way forward'. Held at Robinson College, Cambridge, March 1998.

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