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# Summary

## i Reasons

Due to the introduction of the EU Drinking Water Directive (98/83) (implemented in England through regulation 26(2)(a) of the Water Supply (Water Quality) Regulations 2016) there is a legal requirement to minimise disinfection by-product (DBP) formation. The regulatory focus has primarily been on DBPs arising from chlorine (notably trihalomethanes, THMs) and ozone (bromate). Concern about chlorinated by-products has contributed to the adoption of alternative oxidants in water treatment, notably ozone, and the wider application of UV disinfection. Advanced oxidation processes (AOPs) have also been introduced to degrade micropollutants such as pesticides. Advanced oxidation processes generate highly reactive hydroxyl radicals ( $\text{OH}\cdot$ ), which are potent, but non-selective, oxidants that react orders of magnitude faster than molecular ozone. Advanced oxidation processes that have application in drinking water treatment utilise combinations of ozone ( $\text{O}_3$ ), hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and ultraviolet (UV) light to generate the free radicals. Alternative approaches are available in other industrial sectors, for example UV in combination with titanium dioxide ( $\text{TiO}_2$ ). In practice, AOPs mineralise only a small proportion of organic material such that a wide range of organic and potentially inorganic disinfection by-products are formed.

Previous studies have been carried out by the Drinking Water Inspectorate (DWI) regarding the formation of DBPs produced following ozonation. There is, however, less knowledge of the types of DBPs produced following AOPs. Therefore the aim of this project is to identify potential DBPs that may be formed as a consequence of AOPs, identify potential hazard posed by the DBPs and to carry out a risk assessment to estimate the risk they may pose to public health.

## ii Objectives

This project has been divided into seven objectives:

- Objective 1. Define the range of advanced oxidation techniques that are or may soon be in use in England and Wales.
- Objective 2. Review of chemical reactions and potential formation of Disinfection by-products (DBPs).
- Objective 3. Conduct a systematic review of the published and grey literature issued since 1990 on the formation of by-products from the advanced oxidation processes identified under objective 1 and their potential removal by subsequent treatment processes.

- Objective 4. Review existing knowledge of toxicity of the DBPs identified under objective 3 above.
- Objective 5. Conduct a high level risk assessment based on the outcome of objectives 3 and 4.
- Objective 6. Review the availability of methods of analysis for the DBPs identified.
- Objective 7. Devise a sampling and analysis strategy that could be employed as part of a future research project to investigate any issues arising.

### iii Conclusions

#### Objective 1

A scoping study identified 14 AOPs with actual or potential application for drinking water treatment. Of these, one is currently used in England and Wales, and seven were judged as being realistic options for use within 10 years. The review of DBPs in subsequent objectives focussed on these eight AOPs.

AOP	Overview	Status
UV / H <sub>2</sub> O <sub>2</sub>	Worldwide applications for potable water and water re-use. Currently used in the UK.	In use in the UK
O <sub>3</sub> / H <sub>2</sub> O <sub>2</sub>	Worldwide applications for potable water. Has been trialled in UK at pilot scale.	Possible use in the UK in the near future
O <sub>3</sub> / UV	Available commercially, has been used in US for groundwater treatment and remediation. UK experience as individual processes. Including O <sub>3</sub> and UV is potentially expensive.	Possible use in the UK in the near future
O <sub>3</sub> / UV / H <sub>2</sub> O <sub>2</sub>	Available for industrial wastewater applications, with potential use for potable water. May offer improved treatment efficacy than a two-component AOP. Including O <sub>3</sub> and UV is potentially expensive.	Possible use in the UK in the near future
UV / Cl <sub>2</sub>	Potential users may have DBP concerns because of Cl <sub>2</sub> . No trials identified in UK. However, available commercially in US. May have operational cost benefits relative to UV / H <sub>2</sub> O <sub>2</sub> .	Possible use in the UK in the near future

AOP	Overview	Status
UV / S <sub>2</sub> O <sub>8</sub>	Available commercially for industrial wastewater treatment. Tested at bench-scale for odour treatment but no trials identified in UK, but has potential due to high oxidation level.	Possible use in the UK in the near future
UV / TiO <sub>2</sub>	Commercially available outside of UK, used for wastewater, groundwater remediation and water treatment applications. Has only been investigated at laboratory scale in UK. An AOP with no chemical addition may be of particular interest as would represent lower costs.	Possible use in the UK in the near future
UV / TiO <sub>2</sub> / H <sub>2</sub> O <sub>2</sub>	No commercial applications found. Data from pilot and bench-scale research in wastewater. Process has been researched for over 10 years. No trials identified in UK. Conceptually straightforward extension of UV / TiO <sub>2</sub> , to potentially enhance treatment efficiency.	Possible use in the UK in the near future

## Objective 2

The radicals formed by AOPs are strong oxidising agents that will react with organic and inorganic constituents of water to produce various DBPs. Oxidation by molecular ozone, or photolysis by UV, can also contribute to the formation of DBPs. Types of DBPs identified in treated water are therefore dependent on the nature of the water being treated and the AOP applied. The formation of DBPs by each of the eight AOPs identified in Objective 1, were reviewed in Objective 3.

## Objective 3

Systematic literature reviews of each of the eight AOPs from Objective 1 identified a total of 78 DBPs.

## Objective 4

A 5-step prioritisation process was applied to the 78 DBPs identified in Objective 3, to exclude those which had already been assessed for potential risk by WHO or DWI, or for which UKWIR/WRc Toxicity datasheets already exist; or are not likely to be formed under conditions of relevance to UK treatment processes. By this approach, nine DBPs were prioritised for high level risk assessment in Objective 5.

DBP
2-Hydroxy-5-nitrobenzoic acid
2-Methoxy-4,6-dinitrophenol
2-Nitrohydroquinone
3,5-Dinitrosalicylic acid
4-Hydroxy-3-nitrobenzoic acid
4-Nitrobenzene-sulfonic acid
4-Nitrocatechol
4-Nitrophthalic acid
5-Nitrovanillin

## Objective 5

A summary of the risk characterisation of the nine DBPs prioritised in Objective 4 is given below.

DBP	TDI (µg/kg bw/day)	TTC (µg/kg bw/day)	Estimated Daily Intake (TDI)			Estimated Daily Intake (TTC)		
			Adult	Child	Adult	Adult	Child	Infant
2-Hydroxy-5-nitrobenzoic acid	-	0.0025	-	-	-	Below	Above	Above
2-Methoxy-4,6-dinitrophenol	90.6	0.0025	Below	Below	Below	Below	Above	Above
2-Nitrohydroquinone	-	0.0025	-	-	-	Below	Below	Below
3,5-Dinitrosalicylic acid	29.6	0.0025	Below	Below	Below	Below	Below	Below
4-Hydroxy-3-nitrobenzoic acid	-	0.0025	-	-	-	Below	Above	Above
4-Nitrobenzene-sulfonic acid	871	1.5	Below	Below	Below	Below	Below	Below
4-Nitrocatechol	1472	0.0025	Below	Below	Below	Below	Above	Above
4-Nitrophthalic acid	-	0.0025	-	-	-	Below	Below	Below
5-Nitrovanillin	166	0.0025	Below	Below	Below	Below	Below	Below

- No data; modelled NO(A)EL/LO(A)EL could not be derived

Below; estimated daily intake is below the proposed TDI/TTC value, adverse health effects are not anticipated

Above; estimated daily intake is above the proposed TDI/TTC value, adverse health effects cannot be excluded

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## Objective 6

Analytical methods for the prioritised nine DBPs that were potentially formed in water following AOP processes and for which a human health risk assessment was carried out have been investigated. Some methods are well developed such as nitrobenzene diols and dinitrophenols whereas other methods for compounds such as the hydroxynitrobenzoic acids, 4-nitrobenzene sulfonic acid, 4-nitrophthalic acid and 5-nitrovanillin will need further development to ensure they are robust and reliable. Additionally problems with limits of detection for these methods may not be low enough to detect the concentrations of these compounds in drinking water. Advances in chromatography during the past twenty years has allowed for better quantification of hydroxynitrobenzoic acids without the need to use less accurate colorimetric spectrophotometry. However these methods are yet to be verified as industry standards.

## Objective 7

A range of potential DBPs may arise as a result of the use of AOP treatment. However, the identified DBPs went through a prioritisation process as part of Objective 4. Nine DBPs were identified requiring further consideration.

As part of Objective 1 it was identified that currently only two plants are using AOP within England and Wales. The research undertaken has identified that both of these plants currently employ the use of GAC.

Based on the data currently available, it may be a reasonable expectation that, following formation of these potential DBPs via AOP treatment, their concentrations in drinking water will subsequently be reduced by GAC adsorption, assuming effective operation of the GAC. This conclusion is based on limited data and further monitoring may be required to validate it.

Prior to instigating a full sampling programme, a number of preliminary steps are required to ensure that the sampling programme is fit-for-purpose. Further analytical method development is required using 'spiked' water samples to optimise detection limits in UK drinking water and ensure that results are repeatable. This includes optimisation of calibration curves and further refinement of LODs.

There is also a lack of understanding as to the conditions that may favour the formation of these DBPs. Prior to full-scale sampling, bench-scale analysis should be conducted with different water conditions to determine these conditions. This information can then be used to determine sites where, should AOPs be employed, there is a reasonable expectation that these DBPs will be formed. These sites should be the primary focus of the sampling survey.

Once the survey sites have been identified, a number of approaches can be taken. A one-year, bimonthly sampling strategy is proposed, and has been broadly described in this report.

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However, due to a number of unresolved questions, this approach may need to be adjusted once bench-scale results are known. The approach of sampling over the course of one year allows for the determination of any seasonal variability of the surface water quality that may influence the formation of these DBPs.

Within this sampling programme, sampling at each water treatment works will be conducted over a range of times of the day (morning, afternoon, evening) to address this question. To fully understand the effects of changes in water conditions that may potentially affect DBP formation (such as high rainfall events), a sampling programme has also been recommended to determine the influence of these events.

Sampling in this manner allows for the majority of samples being collected immediately after AOP treatment. Assuming this represents the highest concentration of DBPs in water this represents a 'worst-case' by which to estimate exposure to the consumer. Sampling after GAC has also been proposed to confirm the effectiveness of this treatment in reducing DBP concentrations.