



**EPA DRINKING WATER GUIDANCE
ON DISINFECTION BY-PRODUCTS
Advice Note No. 4. Version 2.
Disinfection By-Products in Drinking Water**

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1.0 INTRODUCTION

Disinfection by-products are formed by the reaction of chemical disinfectants with by-product precursors. Natural organic matter (usually measured as Total Organic Carbon (TOC)) and inorganic matter (bromide) are the most significant disinfection by-product precursors. All commonly used chemical disinfectants (e.g. chlorine, chlorine dioxide, chloramines and ozone) react with organic matter and/or bromide to varying degrees to form different disinfection by-products (DBPs). Trihalomethanes (THMs) are one of the most common disinfection by-product in Ireland.

The *European Communities (Drinking Water) Regulations (No. 2), 2007* set a parametric value of 100 µg/l for Total Trihalomethanes (TTHMs) (i.e. a group of four disinfection by-products, namely chloroform, bromoform, dibromochloromethane and bromodichloromethane), with chloroform tending to be present in the greatest concentrations. The parametric value for bromate is 10 µg/l.

While no parametric values have been set for disinfection by-products other than THMs and bromate, there is a requirement under Regulation 13 of the Drinking Water Regulations that “any contamination from disinfection by-products is kept as low as possible without compromising the disinfection, in accordance with any such directions as the supervisory authority may give”. Furthermore, Regulation 4 states that for water to be considered wholesome and clean it must be “free from any micro-organisms and parasites and from any substances which in numbers or concentrations, constitute a potential danger to human health”. While there may not be specific parametric values for DBPs, other than THMs or bromate, they must not be present in concentrations that constitute a potential danger to human health.

The World Health Organisation (WHO) states that efficient disinfection must never be compromised in attempt to meet the guidelines for disinfection by-products and that the microbiological quality of the water must always take precedence.

The EPA report “*The Provision and Quality of Drinking Water in Ireland: A Report for the Years 2009 – 2010*” (EPA, 2011) indicates that there has been a reduction in the number, from 96 (16.1%) in 2009 to 79 (13.5%) in 2010, of public water supplies where the detection of trihalomethanes was notified to the EPA. This drop is due to the on-going improvements made by WSAs under the Remedial Action Program.

There has also been a drop in the number of Public Group Water Schemes (PuGWS) and Private Group Water Schemes (PrGWS) that failed to meet the 100 µg/l parametric value. PuGWS THM failures decreased from 31.6% in 2009 to 25.3% in 2010 and PrGWS THM failures decreased from 9.7% in 2009 to 6.9% in 2010 (EPA, 2011).

Other disinfection by-products include haloacetic acids, haloaldehydes, haloketones, chloral hydrate, haloacetonitriles, halogenated hydroxyfuranone derivatives, chlorite and chlorate (WHO, 2000).

The purpose of this advice note is to provide guidance to operators to ensure that the levels of disinfection by-products, especially THMs, are kept as low as possible.

This advice note is not a legal document and the *European Communities (Drinking Water) (No. 2) Regulations, 2007 (S.I. 278 of 2007)* takes precedence in all cases of doubt. The information contained within this advice note supplements the EPA ‘A Handbook on the *Implementation of the Regulations for Water Services Authorities for Public Water Supplies*’ (EPA, 2010) (hereafter referred to as the Handbook).

1.1 FORMATION OF DISINFECTION BY-PRODUCTS

While the most common form of chemical disinfection in Ireland is chlorination, other methods of disinfection are increasingly being used. Some of the more common methods, other than chlorination, are chloramination, chlorine dioxide and ozone. Alternative disinfection methods also have the potential to produce disinfection by-products.

Factors which influence DBP formation include:

- ▼ Type of disinfectant used;
- ▼ Concentration of disinfectant used;
- ▼ Concentrations of organic matter and other DBP precursors in water to be disinfected;
- ▼ Water temperature;
- ▼ pH;
- ▼ Contact time;
- ▼ Length of the distribution network.

The most commonly used disinfectants and their associated disinfection by-products are outlined in Table 1 below. Appendix 1 outlines Drinking Water Regulations, World Health Organisation Guideline Values and US EPA Maximum Contaminant Levels for the DBPs listed on Table 1 (where such standards exist).

Table 1. Disinfectants and Associated Disinfection By-products

Disinfectant	Disinfectant By-product
Chlorine (e.g. gas, sodium hypochlorite, tablets, OSEC)	Trihalomethanes, Haloacetic Acids, Chloramines ¹ , Chlorinated Acetic Acids, Halogenated Acetonitriles, Chloral Hydrate, Chlorophenols, MX ² , bromate ³ , chloropicrin, halofurans, bromohydrins.
Chlorine Dioxide	Chlorite, Chlorate and Chloride.
Ozone	Bromate, Formaldehyde, Aldehydes, Hydrogen Peroxides, Bromomethanes.
Chloramines	Dichloramines, Trichloramines, Cyanogen Chloride, Chloral Hydrate.

The levels of bromate formed where ozone is used and chlorite/chlorate where chlorine dioxide is used will need to be closely monitored by WSAs to ensure that the levels do not exceed the parametric value of the *European Communities (Drinking Water) (No.2) Regulations 2007* or the World Health Organisation guideline values.

A further group of chlorine disinfection by-products is haloacetic acids (HAAs), which are of increasing concern but there is no parametric limit specified in the *European Communities (Drinking Water) (No.2) Regulations, 2007*.

As THMs are the most common disinfection by-product, they are dealt with in more detail in the following sections.

In 2011 the EPA undertook a study of THM issues on a national basis, the findings of which form the basis for this advice note.

¹ If ammonium present in disinfected water.

² 3-chloro-dichlormethyl-5-hydroxy-2(5H)-furanone.

³ Bromate is not formed where gas is used.

2.0 TRIHALOMETHANES HEALTH EFFECTS

People can be exposed to THMs in drinking water in a number of ways; ingestion of drinking water, inhalation of indoor air largely due to volatilisation from drinking-water, inhalation and dermal exposure during showering and bathing.

Acute effects of THMs in drinking water are rare. The International Agency for Research on Cancer (IARC) classified both Chloroform and Bromodichloromethane, two individual THMs, as possibly carcinogenic to humans (Group 2B). This category is used where there is inadequate evidence of carcinogenicity in humans and sufficient evidence of carcinogenicity in experimental animals. Bromoform or Chlorodibromomethane were not classified as to their carcinogenicity (Group 3).

2.1 THM FORMATION FACTORS

THMs are formed when chlorine reacts with organic matter in water. THMs are prevalent in Irish Public Water Supplies, because 81.9% Irish supplies are sourced from surface waters (EPA, 2011). Surface water sources contain higher levels of organic matter, compared to ground water sources, therefore surface waters have a greater THM formation potential. Also surface waters, in comparison with ground waters, vary in seasonal temperature which can also result in an increase in THMs.

2.2 CHLORINE DISINFECTANT

Chlorine is the most widely used disinfectant in Ireland because it is an effective disinfectant which provides a stable residual throughout the network. There is a potential to form THMs when sufficient levels of chlorine are in contact with organic matter if this organic matter is not removed during the treatment process.

The concentration of chlorine dose can affect THM formation. Changes in the chlorine dose are typically more significant at primary disinfection stage than at secondary stage, due to the higher chlorine doses required at primary stage to achieve appropriate disinfection.

THM formation can be minimised by avoiding the use of pre-chlorination.

The use of booster chlorination, to maintain an adequate residual in the distribution system, can also increase the formation process, as THMs can continue to form within the network where organic matter has not been removed or organic sediments exist within the reservoirs and pipelines. THM formation becomes disinfectant limited, within the network, when the free chlorine residual typically drops to 0.3mg/l (Ryan Hanley, 2012).

2.3 REACTIVITY OF NOM

The organic matter in surface and ground waters is predominantly natural organic matter (NOM). NOM is derived from living or decayed vegetation. It is present in particulate, dissolved and colloidal forms. NOM fractions can also be described in terms of those which are water repelling (hydrophobic) or water absorbing (hydrophilic).

The water repelling or hydrophobic fractions are aromatic compounds and are composed of primarily humic material. Humic material is formed by decaying vegetative matter, such as lignin. Lignin is found in plants and is quite resistant to biodegradation yet it is reactive to oxidants, such as chlorine. These characteristics of the aromatic hydrophobic humic material tend to form higher THM levels.

The water absorbing or hydrophilic fraction of organic matter is composed of primarily fulvic material, carbohydrates and sugars, and is a relatively poor THM precursor.

The EPA National THM project found that the highest reactive Total Organic Carbon (TOC) readings were from source waters downstream of upland forestry catchments and lowland lakes (Ryan Hanley, 2012).

2.4

THM INDICATOR

The concentration and type of NOM and its propensity to form THMs are often assessed using surrogate parameters. The most frequently used surrogate parameters are total and dissolved organic carbon (TOC and DOC) and UV absorbance at 254nm wavelength (UVA_{254}).

While UV absorbance reflects the bulk concentration of precursors in water, the nature and reactivity of the precursor is best assessed using a parameter called specific UV absorbance (SUVA). SUVA correlates well with the aromaticity and the hydrophobicity of the organic carbon and hence its potential to form THMs (Ryan Hanley, 2012).

$$SUVA \text{ as L/mg-m} = \frac{(UVA_{254} \text{ in cm}^{-1}) \times 100}{DOC \text{ in mg/L}}$$

SUVA values less than 2 generally indicate a high fraction of hydrophilic non-humic matter with low UV absorbance, a low chlorine demand and low THM formation potential.

SUVA values between 2 and 4 are indicative of a mixture of hydrophobic humic and hydrophilic non-humic matter, with medium UV absorbance a higher chlorine demand and higher THM formation potential.

SUVA values in excess of 4 are indicative of the presence of humic highly aromatic hydrophobic matter associated with high UV absorbance, high chlorine demand and a high THM formation potential.

2.5

THE EFFECTIVENESS OF THE TREATMENT PROCESS

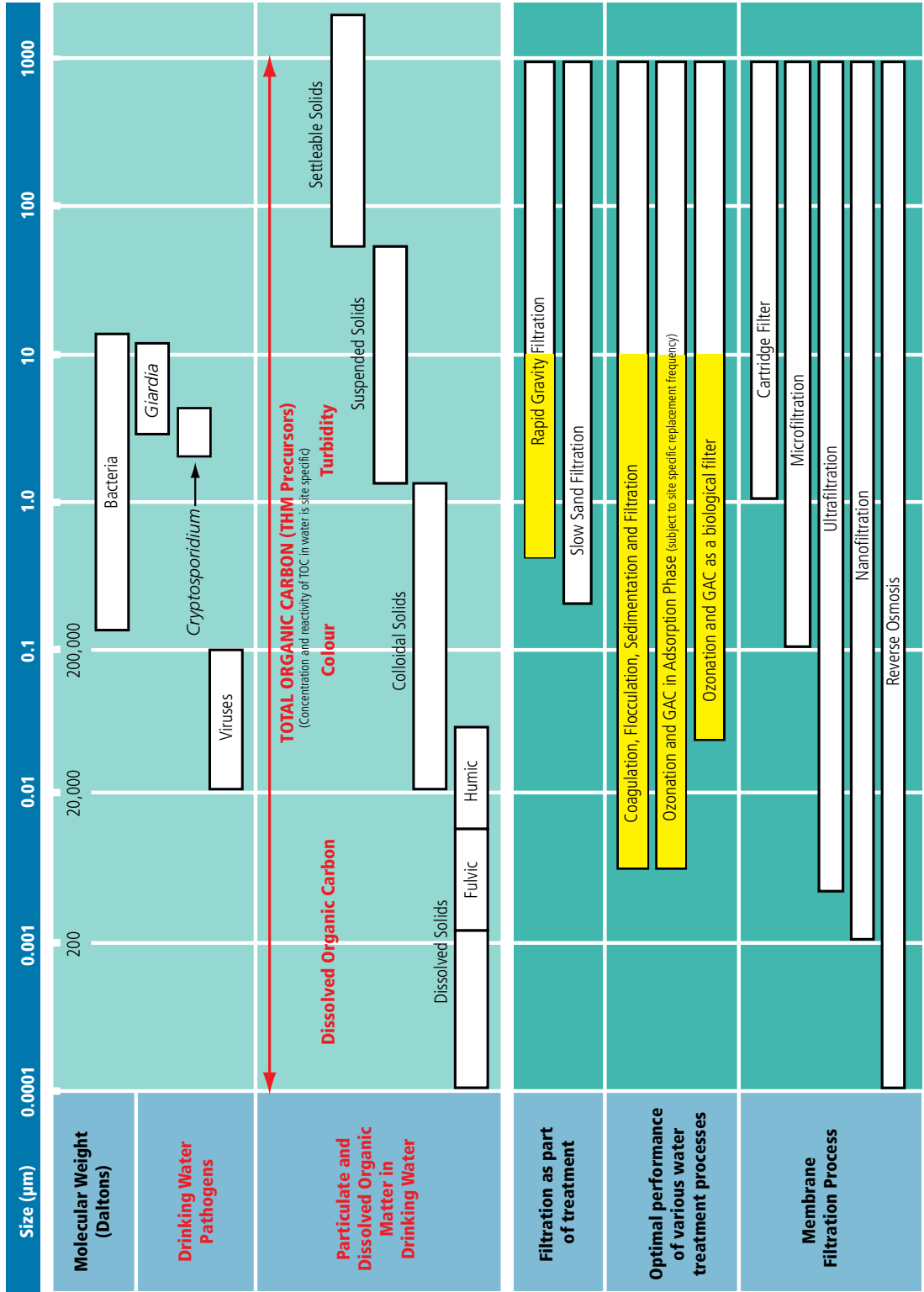
The effectiveness and efficiency of the treatment plant is directly related to the concentration of disinfection by-products formed, such as THMs. The efficiency of different treatment systems, when operated optimally, in removing levels of TOC and its constituents can be estimated from Figure 2.1. The formation of THMs can be minimised by effective coagulation, sedimentation and filtration by removing organic precursors prior to final disinfection or by additional treatment to slow sand filters (e.g. installation of a GAC layer).

Figure 2.1 shows that rapid gravity filtration or slow sand filtration on their own are unable to fully remove the THM precursor. Oxidation processes, such as ozonation, used upstream of disinfection, do not remove organic matter but instead break it down to smaller, more bio-degradable compounds which can lead to an increase in disinfection by-products, such as THMs if there is no subsequent removal stage. These more reactive forms of organic carbon can be effectively removed / reduced using granular activated carbon (GAC) or biological filtration. However, early exhaustion of the GAC layer, in its adsorption phase, may occur where high TOC levels exist in the water prior to the GAC layer. This may make the GAC layer uneconomical as frequent replacement may be required.

Suitable treatments for the reduction of the THM precursor include the following;

- ▼ Conventional treatments, such as coagulation and sedimentation or variations such as DAFF, adsorption clarification, etc.;
- ▼ Ozonation used in conjunction with GAC in adsorption phase, where suitable;
- ▼ Membrane filtration in the ultrafiltration and nanofiltration range, which may be more suitable than conventional treatment when used in water with low background alkalinity.

Figure 2.1 Removal Capabilities of optimised treatment processes (Ryan Hanley, 2012)



2.6 CONTACT TIMES

THMs continue to form in drinking water as long as sufficient disinfectant residuals and reactive precursors are present in the water. THMs have high chemical stability and persist in the water following formation.

Generally the longer the contact times between chlorine and NOM, the greater the amount of THMs that can be formed. High THM values usually occur at points in the distribution system with the longest residence time or water age, such as reservoirs, oversized pipes and network dead ends.

2.7 SEASONAL VARIABILITY OF THM FORMATION

In Ireland water temperature usually ranges from 3-18°C with the highest temperature typically recorded in late September/ early October. The rate of THM formation in water increases with increasing temperature. Therefore, warmer water temperatures result in higher levels of TTHM and HAAs (Haloacetic acids) unless adequate precursor removal is achieved.

High water temperature in the distribution system also promotes accelerated depletion of free residual chlorine. Thus higher chlorine doses are required to maintain residual free chlorine levels.

Conversely, water demands on certain schemes are often higher in summer months, resulting in lower water age within the distribution system thus helping to control THM formation during the peak summer months.

From the EPA's National THM study it was found that peak THM formation in Ireland occurs in late summer/ autumn. This period corresponds with peak loads of dying vegetation and high water temperatures. Levels also peak in spring following heavy rainfall events.

2.8 pH OF WATER TO BE DISINFECTED

When chlorine in gaseous or liquid form is added to water hypochlorous acid (HOCl) is formed below a pH of 7. Above a pH of 7, hypochlorous acid (HOCl) disassociates into H⁺ and hypochlorite ion (OCl⁻). As the hypochlorite ion (OCl⁻) is a much weaker oxidant/disinfectant than hypochlorous acid (HOCl), the chlorine dose required to achieve the same level of disinfection is usually greater as the pH rises above 7.5 – 8.

2.9 BROMIDE ION CONCENTRATION

Free chlorine and ozone oxidise the bromide ion, where it occurs in water, to form hypobromite ion (OBr⁻)/ hypobromous acid (HOBr), which in turn can react with NOM to form brominated THMs (e.g bromoform). As the ratio of bromide to the remaining NOM in water increases, the percentage of brominated THM also increases. The reaction time for formation of brominated THM is faster than for chloroform due to the higher chemical reactivity of hypobromous acid/hypobromous ion.

Waters with bromide typically form more TTHM and HAA5⁴ than waters without bromide.

⁴ HAA5 = Sum of Monochloroacetic Acid (MCAA), Dichloroacetic Acid (DCAA), Trichloroacetic Acid (TCAA), Monobromoacetic Acid (MBAA) and Dibromoacetic Acid (DBAA).

3.0 INVESTIGATIONS INTO THE CAUSE OF DISINFECTION BY-PRODUCT EXCEEDANCES

The Regulations require that any failure to meet the THM or Bromate parametric values as specified in Table B of Part 1 of the Schedule of the Regulations be notified to the EPA. The WSA is required to identify the cause of the failure. While the primary reason for the formation of THMs is the reaction of organic matter with chlorine, WSA should identify the specific cause of the failure rather than reporting the generic cause.

The main causes of failures are most likely to be one of the following, (this list is not exhaustive);

- ▼ No treatment stage capable of removing organic matter (e.g. no filters, rapid gravity filters with no coagulation or slow sand filters on a highly coloured water);
- ▼ Coagulation or filtration stage bypassed;
- ▼ Filtration rate too high (i.e. overloaded filters);
- ▼ Breakthrough of filters (due to poor media quality);
- ▼ Poor filter management (e.g. filters not being run to waste);
- ▼ An extreme weather event (such as flooding or an exceptional storm);
- ▼ Accumulation of sediments in the network or reservoirs;
- ▼ Ingress into reservoirs or distribution network (more likely to be the former);
- ▼ Long residence time in the distribution network.

The cause should be investigated and identified by the operator and this information should be used to determine appropriate measures to reduce the concentrations of disinfection by-product.

It is proposed that investigations should involve the following;

- ▼ Develop a monitoring program for each stage of the process to evaluate critical parameters in THM formation. A monitoring program will help identify areas of THM formation and help in the implementation of effective corrective actions.
- ▼ Evaluate operational practices of the treatment process and the distribution system.

Investigations should be conducted as per Figure 3.1 and Appendix 2, where each stage of the process should be examined as follows;

- ▼ Stage 1 – Efficacy of treatment plant.
 - 1a Determine the TOC removal efficiency upstream of disinfection process by analysing raw and treated water sampling results.
 - 1b Determine the nature and reactivity of the THM precursor in the treated water by determining the SUVA (see section 2.4).
- ▼ Stage 2 – Storage.

Evaluate the potential for THM formation in the storage facilities following disinfection. The Water Service Authority (WSA) should establish operational limits for TTHM and HAA5 after storage, such as < 80 µg/L and <60 µg/L⁵ respectively. This should ensure that the parametric value for THM will not be exceeded prior to distribution.

⁵ At present there is no standard or parameter set for HAAs, while in the USA there is a standard of 60 µg/L for 5 HAAs. The recent review of potential revisions to the European Drinking Water Directive suggested that a parameter value of 80 µg/L for a total of 9 HAAs should be considered if they were identified by a Drinking Water Safety Plan or needed to be controlled by product specification.

▼ Stage 3 – Distribution System.

Identify specific areas where THMs are formed by carrying out monitoring at various locations within the distribution system, as per Figure 3.1. TTHM for drinking water in the distribution system should not exceed 100 µg/and 80 µg/L for HAA5.

Using this staged approach evaluates the performance of the entire water supply system, and the contribution of each stage to DBP formation. This will help WSAs to identify issues at various locations and will allow for the appropriate proactive steps to be taken.

Figure 3.1 Recommended sampling data to be collated following the incident of a THM exceedance (Ryan Hanley, 2012)

Source	Treatment Process	Storage	Distribution System
Stage 1a		Stage 2	Stage 3
Parameters to be monitored (Monthly) 1) FW TOC (mg/L) 2) RW TOC (mg/L) 3) RW Alkalinity (mg/L as CaCO ₃)		Parameters to be monitored (Monthly) 8) TW TTHM (mg/L) 9) FW total chlorine (mg/l) 10) TW chlorite (mg/l) 11) TW Bromate (mg/l) 12) TW free chlorine residual (mg/L) 13) FW pH 14) TW Temperature (OC) 15) Storage water age (hrs)	Parameters to be monitored (Locations within the network) 16) DW TTHM (mg/L) 17) DW free chlorine residual (mg/L) 18) Monitoring location water age
Stage 1b			
Parameters to be monitored (Monthly) 4) RW DOC (mg/L) 5) RW UV254 (l/cm) 6) FW DOC (mg/L) 7) FW UV254 (l/cm)			

Legend

RW = raw water (prior to any treatment)
 FW = filtered water (combined, prior to clear water tank)
 TW = treated water (outlet of clear water tank or first reservoir on distribution system)
 DW = drinking water (consumer’s tap)
 TOC = total organic carbon

DOC = dissolved organic carbon
 TTHM = total trihalomethanes
 HAA5 = sum of five haloacetic acid species
 SUVA = specific UV absorption
 UV₍₂₅₄₎ = amount of UV light absorbed by sample

3.1 STAGE – 1A: EVALUATION OF THE TREATMENT PROCESS

While monitoring data on colour and turbidity may indicate the efficiency of the treatment process, Total Organic Carbon (TOC) is a key indicator of the propensity of THMs to form following chlorination. As part of the investigation the operator should measure the TOC levels in the untreated and treated water to determine the efficiency of the treatment process. This should be done under different raw water conditions (e.g. for different alkalinity, weather and raw water quality conditions) for an appropriate period of time. Where the removal is insufficient it may indicate that the treatment processes is inadequate or not being operated optimally.

At TOC >4.0 mg/l it is likely that THM levels will exceed 100 µg/l if the residence time in the network is 2-3 days and if a free residual chlorine is to be maintained at the tap (UKWIR, 2000). However, notifications to the EPA indicate that THM formation can occur at levels below this in some circumstances (>2.0 mg/l). Therefore, if the levels of TOC are greater than 4.0 mg/l remedial works will likely be necessary, whereas if the level is between 2 and 4 mg/l a more detailed assessment will need to be carried out to determine if these levels of TOC are leading to the formation of THMs.

TOC monitoring results for treated water prior to primary disinfection using chlorine should generally not exceed 2.0 mg/L.

Conventional coagulant based treatment processes can also be evaluated using the TOC performance ratio. This ratio can be determined using the actual TOC percentage removed and the required TOC percentage to be removed. TOC monthly performance ratio (TOC removal) should be greater or equal to 1.0.

$$\text{TOC Monthly Performance Ratio} = \frac{\text{Actual TOC removal percentage}}{\text{Required TOC removal percentage}}$$

The actual TOC removal percentage upstream of the disinfection is determined by the following equation;

$$\text{Actual TOC removal percentage} = 1 - [\text{FW TOC} \div \text{RW TOC}] \times 100$$

The required TOC percentage to be removed for coagulation based treatments can be estimated using the USEPA Stage 1 Disinfectants and Disinfection By-products Rule, see Table 3.1. The removal percentages are based on raw water characteristics such as alkalinity and TOC.

Table 3.1 Required TOC removal percentage based on the TOC and Alkalinity of the raw water (US EPA, 1998)

RW TOC (mg/L)	RW Alkalinity (mg/L as CaCO ₃)		
	0 to 60	> 60 to 120	> 120
> 2.0 to 4.0	35%	25%	15%
> 4.0 to 8.0	45%	35%	25%
> 8.0	50%	40%	30%

This method can to be used as a guide to evaluate the performance of the treatment process. Monitoring for THMs still needs to be undertaken and if THMs are found after treatment, even though the TOC removal percentages and the required performance ratios are being achieved. WSA should undertake investigations to establish where THMs are being formed.

3.2 STAGE – 1B: ALTERNATE EVALUATION OF THM PRECURSOR REMOVAL

As an alternative to sampling for TOC, a WSA may also monitor specific ultraviolet absorption (SUVA). Reactions between chlorine and DOC with a high hydrophobic (aromatic) content generally result in higher levels of THMs. UV_{254} is generally linked to the hydrophobic (aromatic) and reactive DOC components of NOM, and is considered a good indicator of the potential of water to form THMs.

SUVA is an indicator of the humic content of water which is generally amenable to removal by chemical coagulation process.

In general SUVA monitoring results for treated water prior to disinfection should generally not exceed 2.0 L/mg-m.

3.3 STAGE 2: THM FORMATION EVALUATION IN STORAGE (FOLLOWING CHLORINE DISINFECTION)

The configuration and operation of storage facilities has a significant impact on water age. Same day testing and measurement, as per Figure 3.1 and Appendix 2, at the reservoir inlet and outlet will give WSA an indication of:

- ▼ Factors affecting THM formation such as pH, residence times and temperature.
- ▼ The existence of a chlorine demand, which will give an indication of the presence of organic matter deposits within the reservoir and the THM formation potential.

3.4 STAGE 3: THM FORMATION EVALUATION IN THE DISTRIBUTION NETWORK (DOWNSTREAM OF STORAGE)

The objective of Stage 3 monitoring, (see Figure 3.1 and Appendix 2), is to identify appropriate monitoring locations within the network so as to determine where THMs are formed and where consumers are exposed to THMs.

For THM investigative purposes only, the number of monitoring sites on a distribution network should be based on the population size served by the water supply systems, (see Table 3.2). This monitoring procedure does not apply to compliance monitoring, which should be carried out as per Section 3 of the EPA Drinking Water Handbook.

Table 3.2 Recommended number of TTHM monitoring locations v Population (Ryan Hanley, 2012)

Population Size	No. of Monitoring Locations within network
< 3,000	2
≥ 3,000 to < 10,000	4
≥ 10,000 to < 50,000	8
≥ 50,000 to < 100,000	10
≥ 100,000 to < 200,000	14

The selection of these monitoring sites should take account of historical THM exceedance data, high water age, and the disinfectant residual gradient and geographic coverage of distribution system.

The WSA will need to increase THM monitoring frequency if there are exceedances in order to assess the extent and frequency of the exceedances.

4.0 MEASURES TO REDUCE DISINFECTION BY-PRODUCTS IN DRINKING WATER

Consequent to investigating THM formation factors one or more of the following measures will be required to mitigate THM formation:

- Improvements to raw water management;
- Modification of treatment process up stream of disinfection to improve the efficiency of THM precursor removal;
- Optimisation of the disinfection process;
- The use of alternative disinfectants for primary and secondary disinfection; and/or
- Regular flushing and cleaning of storage reservoirs and distribution pipelines.

4.1 RAW WATER

Some mitigation measures that the WSA could employ are listed below;

- ▼ Examine the option of using an alternative source such as a ground water source;
- ▼ Improve raw water management; including storage, intake management and monitoring and control (e.g. raw water turbidity monitors or automation of coagulant dosing based on raw water conditions);
- ▼ Install automatic shut off when raw water quality is poor.

4.2 TREATMENT PROCESS

The principal reason for THM formation in drinking water supplies is the absence or ineffectiveness of existing treatment processes in removing the THM precursor (reactive humic organic matter as TOC/DOC). The removal of THMs after their formation is difficult and involves resource-intensive processes such as activated carbon adsorption or air stripping. Therefore, operators should strive to optimise the operation of existing water treatment plants to minimise THM formation.

Figure 2.1 shows that direct filtration or slow sand filtration on their own may not adequately remove THM precursors. Although, the gradation of sand and a functioning smutzchdecke layer in a slow sand filter may remove some colloidal solids, the reactive THM precursors are not adequately removed, especially during times of seasonal peak humic NOM generation.

Figure 2.1 also shows that coagulant based clarification treatment processes, ozonation with GAC adsorption, where suitable, and membrane filtration are treatment processes that can reduce the THM precursors in the treated water prior to chlorination.

Where there is a need for process modification, the WSA should undertake a feasibility study, using Stage 1 sampling data, to ensure that;

- ▼ The most efficient and effective treatment methods are being used to consistently remove the THM precursor. WSAs need also take into account seasonality factors and water quality parameters which may affect treatment such as alkalinity.
- ▼ Any modification to the treatment process or disinfection strategies must comply with the WHO guidelines and EPA requirements.

Some potential mitigation measures to the treatment process are listed below;

- ▼ Increase the design capacity of the plant to prevent bypassing of treatment stages and to reduce pressure on the existing treatment stages;
- ▼ Install appropriate treatment, where there is no treatment other than disinfection, or where the level of treatment is inadequate (e.g. rapid gravity filtration with no coagulation or slow sand filtration of a coloured water);
- ▼ Assess and optimise the coagulation and clarification stages;
- ▼ Introduce a coagulation phase prior to rapid gravity filtration;
- ▼ Optimise coagulation pH;
- ▼ Optimise the coagulant dosage for particulate removal for DBP removal;
- ▼ Review the type of coagulant to ensure optimum precursor removal.
- ▼ Assess and optimise the filtration stage. Include an assessment of media quantity and quality, as well as operational practices (e.g. use turbidity monitors to improve filtered water quality);
- ▼ Ensure filters in operation are not overloaded during backwashing;
- ▼ Introduce a colour removal phase to slow sand filtration (e.g. GAC layer);

4.3 OPTIMISATION OF THE EXISTING DISINFECTION PROCESS

WSAs have no control over the temperature variations in surface sources and its effects on THM formation. However, control can be exercised over the chlorine dose and the reaction time of chlorine following primary and secondary disinfection.

The WSAs should note that the chlorine dose as recommended by WHO (≥ 0.5 mg/litre for at least 30 min contact time at pH < 8.0) for effective disinfection, must not be compromised in an attempt to meet the THM parametric value as set out in the Drinking Water Regulations.

In general, in treated water containing residual organics following treatment, the impact of chlorine dose concentration, on the formation of THMs, is greater following primary chlorination rather than secondary chlorination.

High primary doses may be needed to maintain free chlorine residual within the network or as far as the nearest chlorination booster station. This can result in THM formation (depending on the level of reactive THM precursors remaining in the water following treatment).

Secondary chlorination dose rates are generally less than primary dosage. They are determined by trying to achieve a free chlorine residual of > 0.1 mg/l at the network extremities. As discussed previously THM formation is generally disinfectant limited at free chlorine residual levels below 0.3mg/l.

When chlorine is used as a secondary disinfectant the WSA should consider dosing post rather than prior to the reservoir, as secondary chlorination does not require a contact time, unless the reservoir is uncovered. Secondary dosing post the reservoir will ensure that chlorine levels within the reservoirs are reduced and THM formation reduced.

A large proportion of THM formation in drinking water occurs within 6-10 hours of the initial chlorine dose. Many schemes in Ireland have considerably greater downstream storage, some in excess of 2-3 days. Long storage times can lead to high levels of THM formation. As free residual chlorine is depleted upon entry into and during storage within reservoirs, the chlorine dose may have to be increased to counter act long retention times, again promoting THM formation.

In addition, an important factor in reducing the chlorine dose is to maximise the effectiveness of chlorine. This can be achieved by ensuring that the pH of the water to be treated is less than 7.5⁶, where plumbosolvency is not an issue, as chlorine is a more effective disinfectant at this pH.

The EPA National THM study showed that many of the supplies in Ireland with frequent THM exceedances are chlorinated at pH levels in excess of 7.5. This necessitates higher chlorine doses which in turn facilitates THM formation. Proper pH control of the final water following treatment may play a role in reducing THM formation.

Some potential mitigation measures to optimise the disinfection process are listed below;

- ▼ Improve disinfection control systems, including linking the chlorine dose to chlorine demand, installing chlorine monitors and alarms and carrying out improvements to dosing arrangements.
- ▼ Maximise the effectiveness of chlorine by ensuring that chlorine is being dosed at pH <7.5 wherever possible.
- ▼ Use booster disinfection to ensure disinfectant residuals are maintained within the network. This may help in reducing the initial primary dose.

4.4

ALTERNATIVE PRIMARY DISINFECTION STRATEGIES

ClO₂, ozone and UV disinfection are viable alternative primary disinfectants to chlorine which don't form chlorinated or brominated THMs. However for surface waters, these primary disinfectants must be supplemented with a chemical secondary disinfectant to produce a lasting residual in the distribution system which should be greater than 0.1 mg/l at all points in the network.

A. ClO₂

Pilot-scale testing of chlorine dioxide (ClO₂) as an alternative non-THM forming primary disinfectant has been undertaken in Ireland. Generally, the use of this technology on treated waters with a high organic content has been problematic, due to the high ClO₂ dose required to meet the demand required when disinfecting waters with high levels of natural organic matter. This necessary high ClO₂ dose has resulted in excessive formation of chlorites and chlorates which like THMs are undesirable disinfection by-products. Nonetheless, ClO₂ may have alternative uses as a pre-oxidant.

B. Ozonation

In addition to its use as an oxidant to remove colour from raw water, ozonation is a viable alternative primary disinfection system. Ozonation breaks down organic matter into smaller, more bio degradable compounds. Some of these compounds react more readily with chlorine leading to an increase rather than a decrease in the formation of disinfection by-products. These organic by-products can provide nutrients for biological growth and thus promote after growth in the distribution system as well. The addition of GAC adsorption media after ozonation can remove a high portion of the organic by-products, but not the inorganic by-products such as bromate. Various pilot projects, undertaken in Ireland, have shown that where GAC adsorption media is used after ozonation, in surface waters with high organic matter content, regular GAC media replacement is required, making it uneconomical and unviable.

C. UV disinfection

The validated and verified delivery of a 40 mJ/cm² UV dose followed by secondary chlorination would provide a full spectrum of primary disinfection of bacteria, protozoa and viruses. It is also an acceptable barrier to *Cryptosporidium*.

⁶ The WHO state that the pH of water in the distribution system is often between 6.5-9.5 but should preferably be less than 8.0.

UVA_{254} and UV Transmissivity (UVT) can be used as surrogate parameters for the measurement of TOC/DOC levels in water. As high TOC/DOC levels correspond to low UVT levels, the presence of high TOC/DOC in final treated water would render UV disinfection ineffective. UV disinfection is unsuitable on sources that have a UVT of less than 75%.

To ensure viable UVT levels are achieved for UV disinfection, adequate clarification to reduce colour, turbidity, DOC and iron levels is a prerequisite.

D. Chloramines

The use of chloramines for secondary disinfection has the advantage over chlorination in that it does not form THMs and it has a longer residual time than chlorine.

The reaction of ammonia and chlorine in the chloramination process is designed to produce monochloramine. Monochloramine is a less effective disinfectant than free-residual chlorine but has a long lasting residual. Therefore, as chloramines require a higher dose and longer contact time than free-residual chlorine for the same degree of primary disinfection, they are only suitable for secondary disinfection.

The use of chloramines as a secondary non THM forming disinfectant is a viable alternative to chlorine. However, a risk assessment of consumer usage on the proposed distribution system should be carried out, as chloramines can pose a risk for haemodialysis patients and fish, due to the fact that chloramines can easily enter the bloodstream through dialysis membranes and fish gills.

When considering using chloramination further consideration should also be given to the following;

- ▼ Water quality issues for chloramines such as the formation of other currently unregulated DPBs, nitrification, corrosion and taste and odour issues;
- ▼ Whether to switch all or only a portion of the distribution system to chloramines; and
- ▼ The cost of handling and safety issues.

4.5 STORAGE

Configuration and operation of storage facilities has a significant impact on water age in the areas “downstream” of the storage tank. In general, storage facilities can impact on TTHM and HAAs formation by increasing residence time and chlorine contact time.

If the storage facility is operated such that water level fluctuations are small and water turnover is infrequent, water age can be high. Some storage facilities are oversized to provide water under emergency circumstances. One disadvantage of this is that normally much smaller volumes of water are needed, which leads to higher contact times within the reservoir. The longer the water is in contact with a disinfectant, the more likely TTHM and HAAs will form.

Storage tank configuration and operation can significantly affect DBP levels. Tanks are impacted by the inlet/outlet piping configuration, inlet momentum, temperature, and duration of drain/fill cycles. For example, oversized inlet piping can result in low inlet velocity causing poor mixing and stagnant areas within storage facilities. In poorly mixed storage tanks, water age may actually be higher.

Thermal stratification in a tank, where colder denser water remains in the lower portion of the tank and warmer less dense water remains at the top, can also cause poor mixing conditions.

During periods of higher than normal water demand and where there is poor mixing and/or thermal stratification, water from the upper regions of the tank may be discharged, which can have a substantially higher water age (e.g., several days or weeks) and higher DBP concentrations.

Lack of proper maintenance in conjunction with poor mixing within reservoirs can lead to sediment accumulation at the bottom of the tank resulting in loss of disinfection residual and increased DPB formation.

Some potential mitigation measures for storage facilities are listed below;

- ▼ Implement a regular program of cleaning out of any clear water tanks and/or service reservoirs.
- ▼ Decrease overall hydraulic residence time within reservoirs by managing reservoir turnover.
- ▼ Reduce areas of stagnant water and areas of thermal stratification within storage reservoirs by ensuring that there is proper mixing within the reservoir.

4.6 DISTRIBUTION

A WSA should seek to target areas within the distribution system where there is the potential for TTHM formation. This can be determined by analysis of same day water quality and other collated data, see (Figure 3.1 and Appendix 2).

The regular cleaning out of reservoirs and the flushing of mains using unidirectional flushing techniques will help to mitigate additional THM formation with the network. Aging pipes such as cast iron pipes can also exert high disinfectant demand because of the presence of corrosion by-products, biofilms and sediment deposits. Overall disinfection demand can be reduced by replacing or lining pipes and or by conducting periodic flushing.

As water travels through the distribution system, chlorine continues to react with NOM to form DBPs. The longer the travel time or water age, the more likely it is that water quality will degrade, chlorine residual effectiveness will be reduced and TTHM and HAA concentrations will be increased. Because of this WSA should endeavour to manage water age within the distribution system.

Some methods to reduce water age within the distribution system include (US EPA, 2008);

Eliminating dead ends

Excessive hydraulic residence time at dead ends can provide for long contact times for DPB formation.

Managing valves

Intentionally or unintentionally closed valves in a distribution system may create areas of stagnant water. A comprehensive valve inventory and maintenance program can help determine the status of valves and find improperly positioned and broken valves.

Bypassing or replacing oversized pipes

In oversized pipes water velocity is lower and water residence times are longer than is necessary. WSA should evaluate if oversized pipes exist within the distribution system and whether these can be replaced without impacting on downstream areas.

Improving tank mixture and turnover

Improving mixing within tanks can reduce the average water age and minimise stagnant zones within a tank.

Eliminating excess storage

Oversized tanks may have inadequate turnover or poor mixing. WSA should examine the option of increasing hydraulic turnover, mixing or where possible decommission oversized tanks.

5.0 NOTIFICATION OF EXCEEDANCES

Where the parametric value for THMs has been exceeded, the WSA must notify the EPA in accordance with *Section 6 of the EPA Handbook* and should prepare an action program to return the supply to compliance with the TTHM parametric value. Total THMs are monitored under the Regulations but a specific breakdown of the individual THM chemical groups may also be requested.

Supplies where intermittent or persistent THM exceedances have been reported will be included on the EPA Remedial Action List. These supplies will remain on the RAL until appropriate actions have been taken (as outlined in *Section 6 of the EPA Handbook*) to return the supply to compliance.

The action programme, to ensure compliance with the THM parametric value, should be prepared as soon as possible following the initial failure. The program should be implemented within one year if there is a risk to public health or two years where there is no risk to public health. If a Direction has been issued to the WSA, then the works should be carried out within the timeframe as stipulated in the Direction.

Operators of water treatment plants should ensure that where the method of disinfection is to be replaced or supplemented with an alternative method, none of the relevant standards in Appendix 1 are exceeded and that disinfection is never compromised in an attempt to meet the guideline values for disinfection by-products.

APPENDIX 1. RELEVANT STANDARDS FOR DISINFECTION BY-PRODUCTS IN DRINKING WATER

Disinfection By-product	Drinking Water Regulations Parametric Value	World Health Organisation Guideline Value	US EPA Maximum Contaminant Level
Aldehydes			
Bromate	10 µg/l	10 µg/l	10 µg/l
Brominated Acetic Acids		Note 1	
Bromohydrins			
Bromomethanes			
Chloral Hydrate		Note 2	
Chloramines		3 mg/l (Note 3)	4 mg/l (Note 4)
Chlorate		0.7 mg/l	
Chlorite		0.7 mg/l	1.0 mg/l
Chloroacetones		Note 1	
Chloride	250 mg/l		
Chlorophenols		0.2 mg/l (Note 5)	
Chloropicrin		Note 1	
Cyanogen Chloride		0.6 mg/l (Note 2 and 6)	
Dichloramines			
Dichloroacetic Acid		0.05 mg/l	
Formaldehyde		Note 2	
Haloacetic acids	80 µg/l (Note 7)		60 mg/l
Halofurans			
Halogenated Acetonitriles		Note 8	
Iodine		Note 1	
Monochloroacetic Acids		0.02 mg/l	
MX		Note 2	
N-Nitrosodimethylamine (NDMA)		0.1 µg/l	
Trichloroacetic Acid		0.2 mg/l	
Trichloramines			
Trihalomethanes (total)	100 µg/l	Note 9	80 µg/l

Note 1: Available data inadequate to permit derivation of health based guideline values.

Note 2: Occurs in drinking-water at concentrations well below those of health concern.

Note 3: This WHO guideline value relates to monochloramine.

Note 4: This standard is a Maximum Residual Disinfection Level Goal and the Maximum Residual Disinfectant level, expressed as (Cl₂).

Note 5: This WHO guideline value is for 2,4,6-Trichlorophenol.

Note 6: This is a WHO health based value for long term exposure.

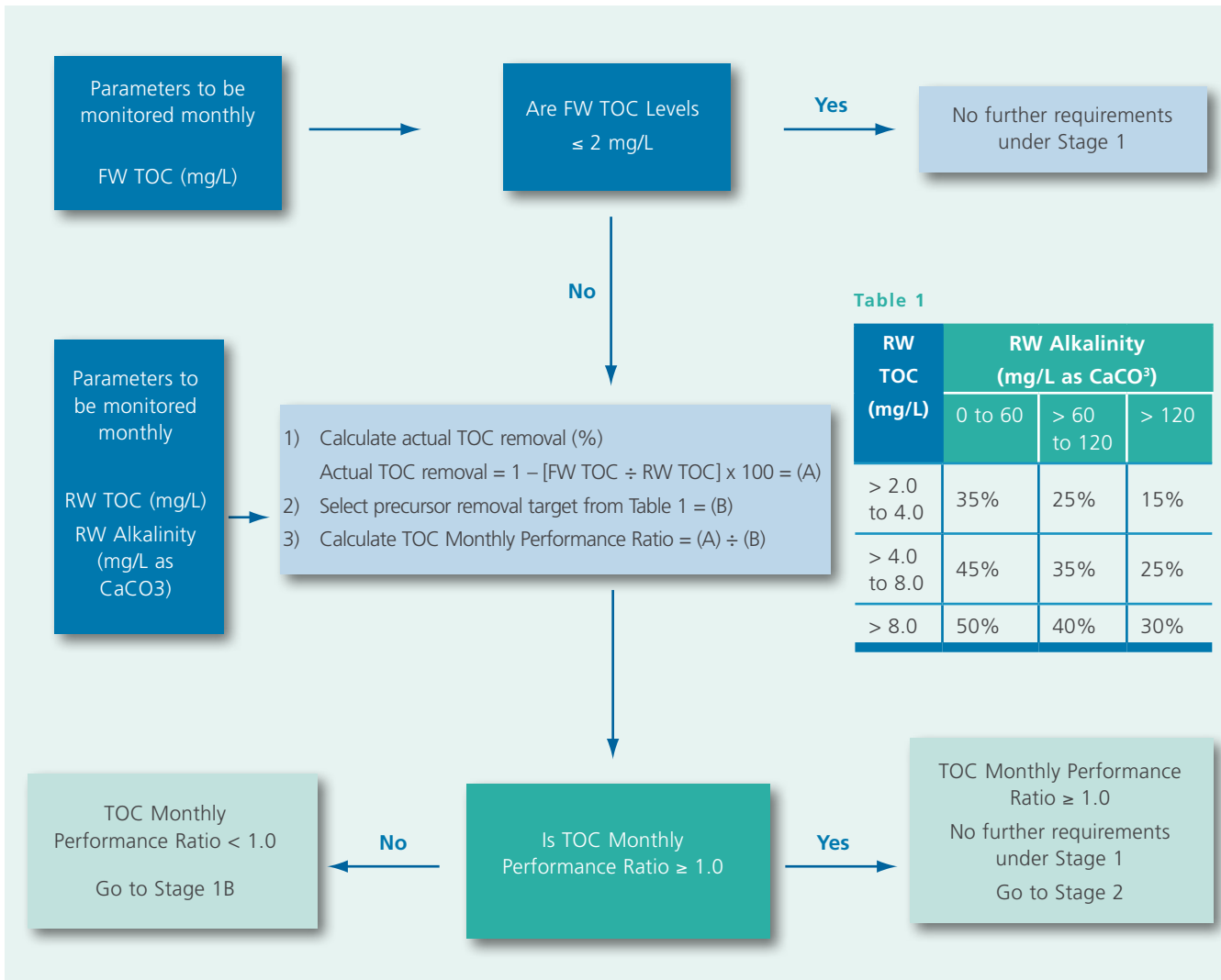
Note 7: No guideline value currently exists but this is a value proposed by the European Commission.

Note 8: There are WHO Guideline Values for 2 of the 4 individual acetonitriles – Dibromoacetonitrile (70 µg/l), Dichloroacetonitrile (20 µg/l).

Note 9: There are WHO Guideline Values for the 4 individual trihalomethanes – Chloroform (0.3 mg/l), bromoform (0.1 mg/l), dibromochloromethane (0.1 mg/l) and bromodichloromethane (0.06 mg/l).

APPENDIX 2. DBP INVESTIGATION FLOWCHARTS AND MONITORING PROGRAMME SHEETS

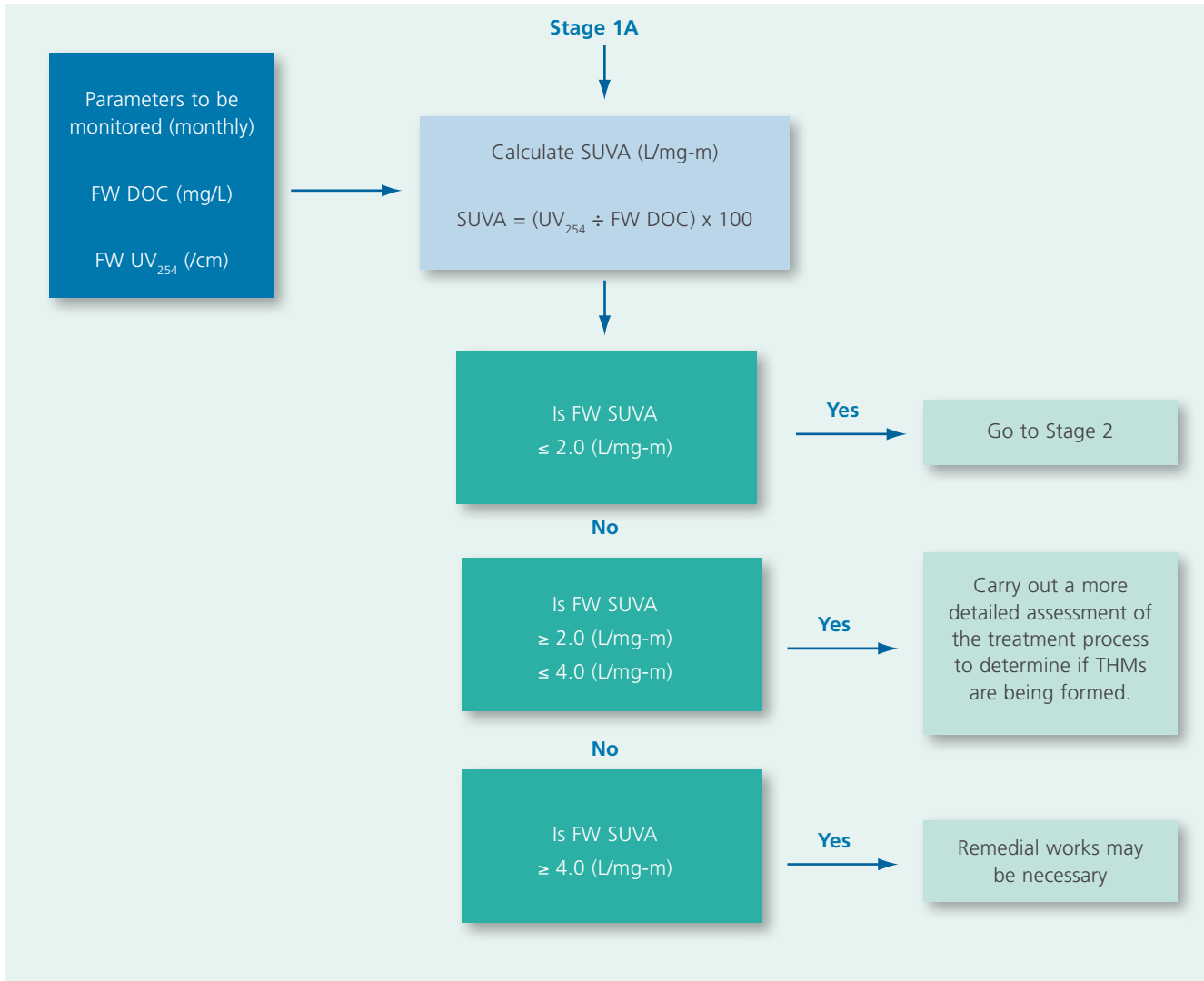
STAGE 1A RAW WATER AND TREATMENT PLANT MONITORING PROGRAMME FOR COAGULATION BASED TREATMENT PLANTS



Legend

- RW = raw water (prior to any treatment)
- FW = filtered water (combined, prior to clear water tank)
- TW = treated water (outlet of clear water tank or first reservoir on distribution system)
- DW = drinking water (consumer’s tap)
- TOC = total organic carbon
- DOC = dissolved organic carbon
- TTHM = total trihalomethanes
- HAA5 = sum of five haloacetic acid species
- SUVA = specific UV absorption
- UV₍₂₅₄₎ = amount of UV light absorbed by sample

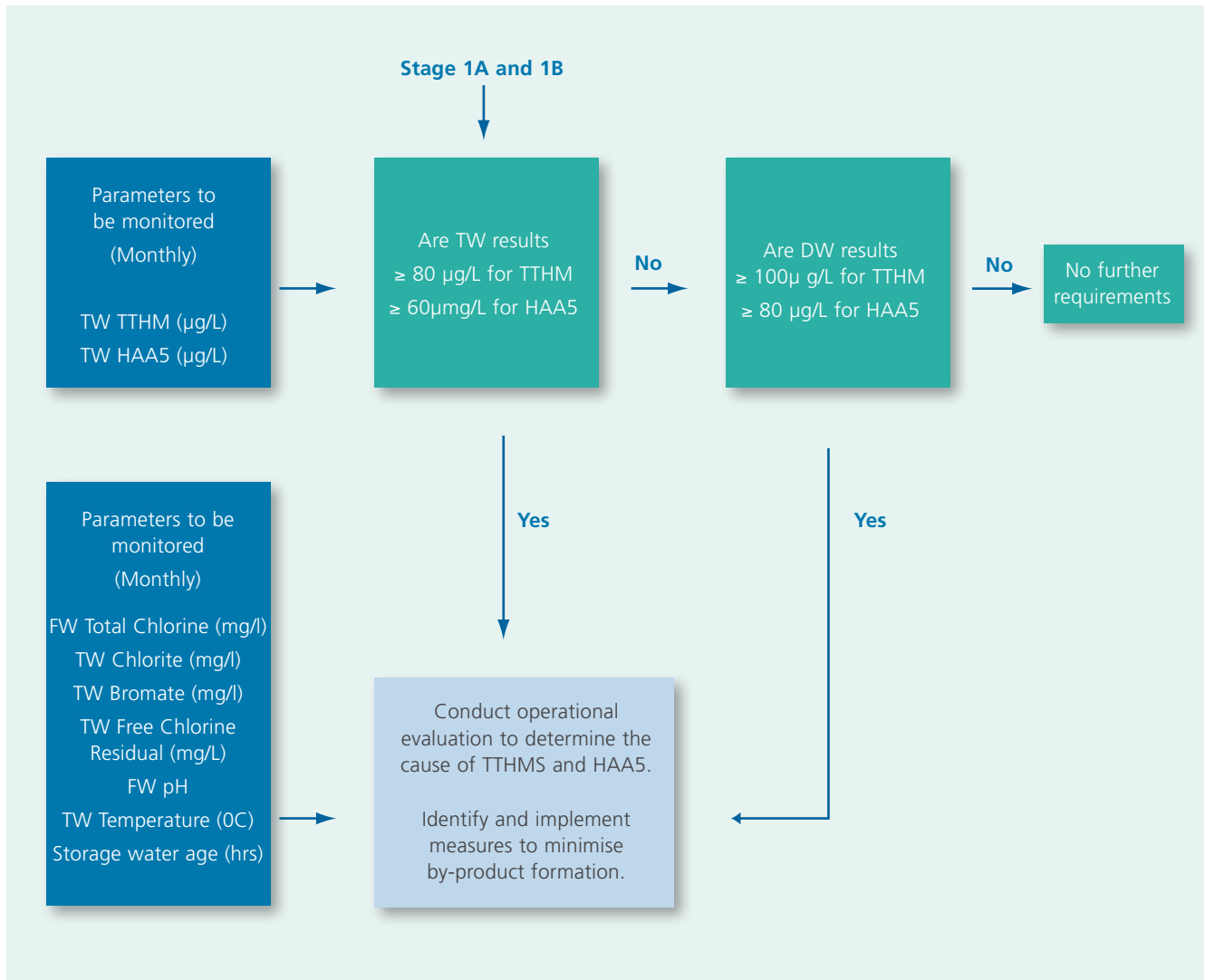
STAGE 1B ALTERNATIVE TREATMENT MONITORING PROGRAMME



Legend

- RW = raw water (prior to any treatment)
- FW = filtered water (combined, prior to clear water tank)
- TW = treated water (outlet of clear water tank or first reservoir on distribution system)
- DW = drinking water (consumer's tap)
- TOC = total organic carbon
- DOC = dissolved organic carbon
- TTHM = total trihalomethanes
- HAA5 = sum of five haloacetic acid species
- SUVA = specific UV absorption
- UV₍₂₅₄₎ = amount of UV light absorbed by sample

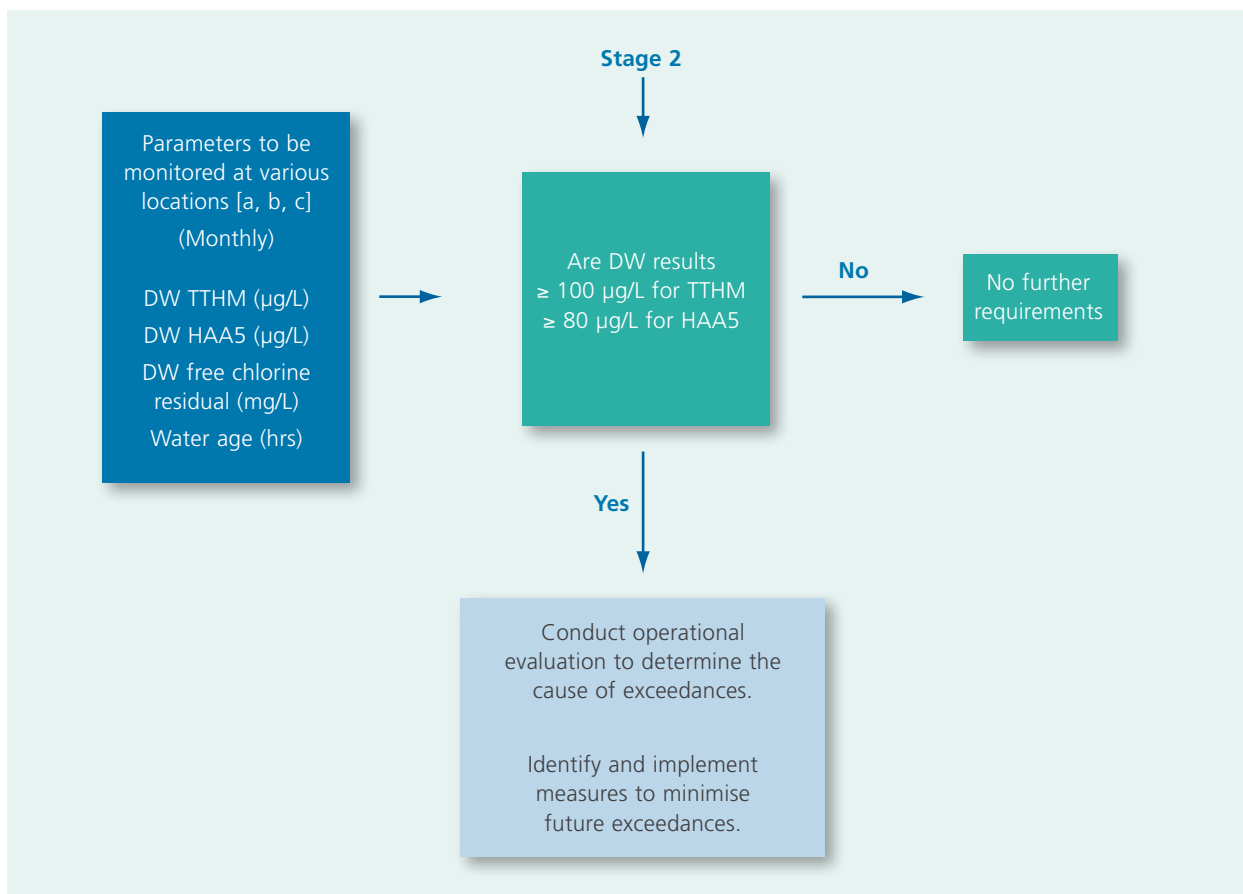
STAGE 2 STORAGE SYSTEM MONITORING PROGRAMME



Legend

- RW = raw water (prior to any treatment)
- FW = filtered water (combined, prior to clear water tank)
- TW = treated water (outlet of clear water tank or first reservoir on distribution system)
- DW = drinking water (consumer’s tap) TOC = total organic carbon
- DOC = dissolved organic carbon
- TTHM = total trihalomethanes
- HAA5 = sum of five haloacetic acid species
- SUVA = specific UV absorption
- UV₍₂₅₄₎ = amount of UV light absorbed by sample

STAGE 3 DISTRIBUTION SYSTEM MONITORING PROGRAMME



Legend

RW = raw water (prior to any treatment)

FW = filtered water (combined, prior to clear water tank)

TW = treated water (outlet of clear water tank or first reservoir on distribution system)

DW = drinking water (consumer's tap) TOC = total organic carbon

DOC = dissolved organic carbon

TTHM = total trihalomethanes

HAA5 = sum of five haloacetic acid species

SUVA = specific UV absorption

UV₍₂₅₄₎ = amount of UV light absorbed by sample

STAGE 1 TREATMENT DISINFECTION BY-PRODUCTS FORMATION MONITORING PROGRAMME REPORT

Local Authority
 Public Water System Name:
 Water Supply Zone Code:
 Source Name:
 Water Treatment Plant Name:

Stage 1A							Stage 1B		
Date	FW TOC (mg/L)	RW TOC (mg/l)	RW Alkalinity (mg/l CaCO ₃)	Actual TOC Removal (A)%	Required TOC Removal (B)%	TOC Removal Performance Ratio (A) ÷ (B) >1.0	FW DOC (mg/l)	FW UV ₂₅₄ (/cm)	FW SUVA (L/mg-m)

FW = filtered water (combined, prior to clear water tank)
 RW = raw water (prior to any treatment)
 UV₍₂₅₄₎ = amount of UV light absorbed by sample
 SUVA = specific UV absorption

STAGE 2 STORAGE DISINFECTION BY-PRODUCTS FORMATION MONITORING PROGRAMME REPORT

Local Authority
 Public Water System Name:
 Water Supply Zone Code:
 Source Name:
 Water Treatment Plant Name:

Stage 2

Date	TW TTHM (µg/L) ≤80	TW HAA5 (µg/l) ≤60	FW TChlorine (mg/l)	TW FCR (mg/l)	TW Temp °C	TW Water Age (hrs)	pH	Chlorite (mg/l)	Bromate (mg/l)

TW = treated water (outlet of clear water tank or first reservoir on distribution system)
 TTHM = total trihalomethanes
 HAA5 = sum of five haloacetic acid species
 FW = filtered water (combined, prior to clear water tank)
 TChlorine = Total Chlorine
 FCR = Free chlorine residual

STAGE 3 NETWORK DISINFECTION BY-PRODUCTS FORMATION MONITORING PROGRAMME REPORT

Local Authority
Public Water System Name:
Water Supply Zone Code:
Source Name:
Water Treatment Plant Name:

Date	Stage 3 Location a				Stage 3 Location b				Stage 3 Location c			
	DW (a) TTHM (µg/L) <100	DW (a) HAA5 (mg/l) <80	DW (a) FCR (mg/l)	DW (a) Water Age	DW (b) TTHM (µg/L) <100	TW (b) HAA5 (mg/l) <80	DW (b) FCR (mg/l)	DW (b) Water Age	DW (c) TTHM (µg/L) <100	DW (c) HAA5 (mg/l) <80	DW (c) FCR (mg/l)	DW (c) Water Age

DW = Drinking water (consumer's tap)
TTHM = total trihalomethanes
HAA5 = sum of five haloacetic acid species
FCR= Free chlorine residual

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