

THE CHLORINE DEMAND CHARACTERISTICS OF IRISH WATER SUPPLIES

Process design implications for disinfection and THM formation

Tom Casey Pat Kearney Hugh Kerr

INTRODUCTION

Chlorine has been the drinking water disinfectant of choice in Ireland and worldwide for many years and as a result there is a well-established underlying process design methodology coupled with an operational focus on the delivery of process reliability. In this regard, the recent publication of an updated version of the EPA Water Treatment Manual on Disinfection (EPA, 2011), providing comprehensive design and operational disinfection guidelines, is a welcome source of up-to-date information for technical personnel engaged in water supply practice in Ireland. However, despite these facts there remains a significant degree of non-compliance with the current Irish Drinking Water Regulations (S.I. No. 278, 2007) associated with disinfection/chlorination. According to the EPA Report on the Provision and Quality of Drinking Water in Ireland (EPA, 2011) the number of Public Water Supplies reporting water quality parametric non-compliance to the EPA in 2009 and 2010 predominantly related to E.coli and total trihalomethanes (TTHMs) transgressions. The presence of E.coli in drinking water indicates a failure of the disinfection process while the presence of excessive THMs reflects the reaction between the added chlorine and natural organic matter (NOM) in the treated water. It is therefore opportune to review chlorination practice both in relation to its efficacy in providing primary disinfection and its role in the generation of THMs.

PRIMARY DISINFECTION

The term primary disinfection, as used here, refers to the disinfection process as applied at a water treatment works (WTW), where the process design requirement is to ensure that the water leaving the process is hygienically safe and meets regulatory disinfection standards. The disinfection effectiveness of chlorine depends on the chlorine dose and chlorine contact time. Added chlorine reacts with various constituents in the water to which it is dosed resulting in a progressive reduction in the residual free chlorine (RFC) with contact time. The product of RFC concentration and contact time gives the process CT-value (mg.min/l) which is a key measure of the disinfection potential of the disinfection process and hence is a key process design variable. Hence, the RFC decay profile over time has a very significant influence on the CT value achieved in a given contact time. It is commonly observed that the decay rate of chlorine is rapid immediately after dosing and then experiences a decreasing rate of reduction with increasing contact time. Chlorine reacts rapidly with inorganic substances in a reduced valence state such as iron, manganese, ammonia and bromide. In general, the concentration of these inorganic reactants in Irish surface waters is very low. Chlorine also reacts with natural organic matter (NOM) at varying rates to form a range of organochloride compounds, some of which may pose a potential threat to the health of consumers (Hrudey & Charrois, 2012). Of these resulting disinfection by-products (DBPs), only the THMs are currently regulated by EU and Irish drinking water standards.

NOM is the ill-defined complex matrix of organic material found in natural waters, derived mainly from living or decayed vegetation and microbial decomposition processes. While the overall NOM amount in water is conventionally quantified by its total organic carbon (TOC) content or dissolved organic carbon (DOC) content, these parameters reveal little about its detailed chemical composition or the reactivity of component constituents with chlorine.

There is no universally accepted design chlorination CT value for drinking water production. The EPA Disinfection Manual (EPA, 2011) cites the original WHO recommendations for the use of chlorine as a disinfectant, which stipulated a minimum free chlorine concentration of 0.5 mg/l (C) after 30 minutes contact time (T) at a pH of less than 8, provided that the turbidity is less than 1 NTU, which it took to be equivalent to a CT of $30 \times 0.5 = 15$ mg.min/l. The same CT value could be achieved by having a longer contact time at a lower RFC, for example an RFC of 0.3 mg/l for a contact time of 50 minutes. While extending the contact time allows the RFC to be reduced, it should not be set below 0.2 mg/l.

As protozoan pathogens such as Giardia and Cryptosporidium are effectively resistant to disinfection by chlorine, the primary disinfection targets of chlorination are pathogenic bacteria and viruses, the latter being significantly more resistant than the former. Table 1 contains virus inactivation recommendations given in Annex 1 of the WHO Guidelines for Drinking Water Quality, 4th Edition, 2011:

Table 1
Disinfection CT for 99% Virus Inactivation (WHO, 2011)

pH range	CT in mg.min/l	
	0-5 °C	10 °C
7.0-7.5	12	8
7.5-8.0	20	15
8.0-8.5	30	20
8.5-9.0	35	22

TREATED WATER CHLORINE DEMAND SURVEY

The *Chlorine Demand* parameter, as used in this presentation, is defined as the reduction in RFC with contact time due to its reaction with various constituents in the water. Hence, its value increases with contact time. Also, the term *Treated Water*, as used here, refers to surface water that has been WTW-processed to the pre-chlorination stage.

For the purposes of this presentation, a survey of the immediate chlorine demand of treated waters from 13 WTWs was undertaken. The WTWs were selected to provide a broadly representative sample of Irish water supplies, both in terms of source type (all were surface water sources) and treatment technology. The survey was limited to one-off grab samples, taken during August 2012. Thus, while the resulting data set presents a useful overall estimate of the potential range and profile of chlorine demand of WTW-treated surface water, it provides no information on the temporal or seasonal variation in chlorine demand that would be experienced at any of the WTWs sampled.

Two chlorine decay tests were carried out on each water sample, one at an applied dose of ca. 2 mg/l and a second test at a lower applied dose of 1.5 mg/l. Test sample volumes of 5 litre or 10 litre were used. The test vessels were incubated in an insulated water bath at about 15 °C. The free chlorine was measured by the DPD colourimetric method using Hach instrumentation. The RFC was generally measured at 15 minute intervals for the first hour of contact and at 30 minute intervals for the second hour of contact.

The measured chlorine demand profile of a representative set of the tested waters is illustrated graphically in Fig 1a through 1f, inclusive. Figs 1a and 1b relate to low chlorine demand waters; Figs 1c and 1d relate to intermediate demand waters, while Figs 1e and 1f relate to high chlorine demand waters. The 15-min and 120-min measured chlorine demands for all samples tested are set out in Table 2, which also includes the water pH and test temperature.

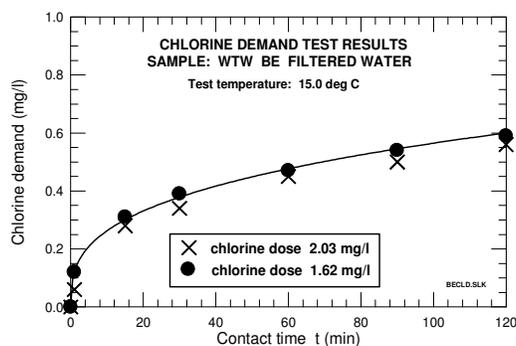


Fig 1a

Chlorine demand of WTW BE treated water

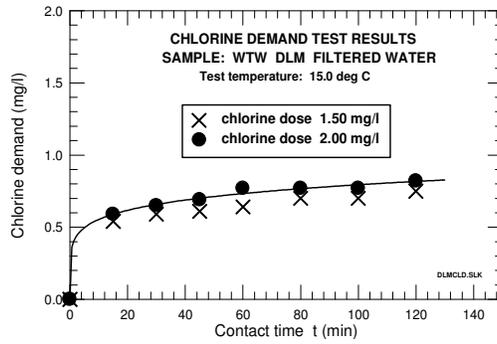


Fig 1b Chlorine demand of WTW DLM treated water

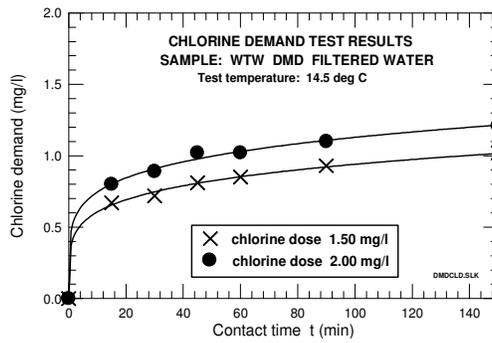


Fig 1c Chlorine demand of WTW DMD treated water

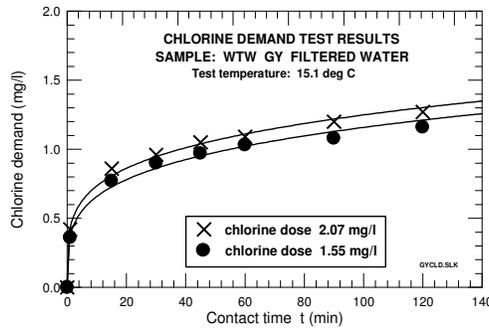


Fig 1d Chlorine demand of WTW GY treated water

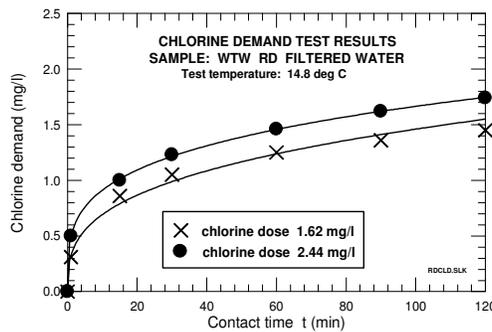


Fig 1e Chlorine demand of WTW RD treated water

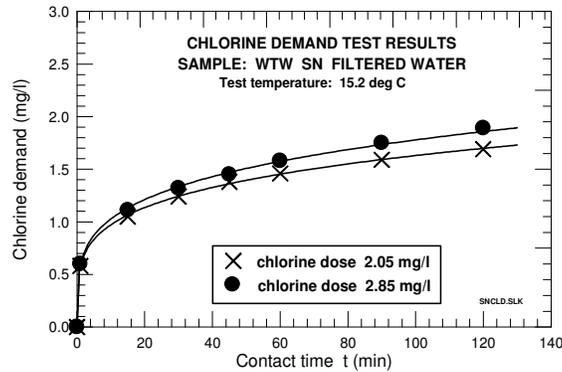


Fig 1f Chlorine demand of WTW SN treated water

Table 2
Primary chlorine demand test data summary

Sample ID	Treatment category*	pH	Test temp. (°C)	Cl ₂ dose (mg/l)	15-min. Cl ₂ demand (mg/l)	120-min. Cl ₂ demand (mg/l)
BE	C	6.19	15.0	1.62	0.28	0.56
				2.03	0.31	0.59
DEE	C	6.33	12.0	1.50	0.33	0.61
				2.00	0.41	0.66
DLM	C	5.88	15.0	1.50	0.54	0.75
				2.00	0.59	0.82
DEI	C	6.47	15.0	1.48	0.57	0.84
				1.97	0.57	0.91
LP	C	7.44	15.1	1.55	0.62	1.02
				2.07	0.69	1.10
DMD	SSF	7.10	14.5	1.5	0.67	0.97
				2.0	0.80	1.16
GY	C	7.21	15.1	1.55	0.77	1.16
				2.07	0.86	1.27
CE	C	6.73	15.0	1.51	0.72	1.17
				2.01	0.75	1.30
KN	C	7.08	15.0	1.68	0.90	1.44
				1.93	0.85	1.44
DPD	C	5.90	15.0	1.50	0.99	1.19
				2.00	1.26	1.48
LG	N	7.35	15.1	1.51	0.91	1.39
				2.01	1.07	1.66
RD	SSF	6.38	14.8	1.62	0.86	1.45
				2.44	1.00	1.74
SN	C	7.13	15.2	2.05	1.05	1.69
				2.85	1.11	1.89

C: indicates conventional treatment i.e. chemical coagulation/clarification/filtration

SSF: indicates slow sand filtration

N: indicates no pre-treatment

The chlorine demand plots exhibit a common free chlorine reactivity profile in which there is an initial very high reaction rate that very rapidly decreases with contact time. The sample set covers a wide range of chlorine demand as reflected in the fact that the largest 120-minute demand measured is approximately three times the smallest measured value. In the case of high chlorine demand waters up to one third of the 120-minute chlorine demand is exerted in the first minute of contact time, while between 50% and 70% of the 120-minute chlorine demand is exerted in the first 15 minutes of contact time.

Analysis of the measured chlorine demand data has shown that the demand time profile can be accurately represented by a power-type correlation of the following form:

$$D_t = k_D t^n \quad (1)$$

where D_t is the chlorine demand (mg/l) at time t (min), k_D and n are empirical coefficients. The coefficient k_D corresponds to the fitted model 1-minute chlorine demand value.

In all cases the chlorine demand was measured at two chlorine dose rates, the larger dose rate (ca. 2 mg/l) exceeding the lower dose rate (ca. 1.5 mg/l) by about 33%. However, while the 120-minute chlorine demand at the higher chlorine dose equalled or exceeded that for the lower dose in all samples tested, the increase in all cases was considerably less than 33%, indicating that the free chlorine reaction rate was not a first-order reaction in respect of chlorine. In the case of the low and medium demand waters, the increase in demand at the higher dose rate was found to be marginal. The slow-sand filtered waters exhibited the largest dose-related differential demand at about 20%.

The treated water chlorine demand profiles reflected in the foregoing plots are not unique to Irish waters. The USEPA (1992) proposed division of the chlorine reaction process into three sequential time periods (1) zero-order reaction for contact time $t = 0$ to 5 min, second order for 5 min to 5 h, and (3) first-order for $t > 5$ h. A variety of mathematical models of the chlorine decay process are to be found in the research literature (Bocelli et al., 2003; Powell et al., 2000; Warton et al., 2000). However, their application as a predictive tool, under primary chlorination conditions, is problematical due to the catchment-specific and heterogeneous nature of the water constituents that consume chlorine. As the measured chlorine decay data presented in Figs 1(a) – 1(f) indicate, the reaction rate is partly chlorine concentration-dependent for some waters but not others. It would appear that the primary decay rate is very significantly influenced by the organic content of the water, which is conventionally measured as undifferentiated TOC. A correlation of chlorine demand and TOC for a range of Irish treated surface waters is presented in Fig 2. While there is the expected positive correlation between chlorine demand and TOC, the dependency varies from one catchment to another. This is not an unexpected finding considering that TOC is an umbrella parameter, embracing a range of unidentified organic constituents of natural origin and reflecting the organic profile of the source catchment. Thus, there is no universal model that can be applied to quantify the primary chlorine decay rate of treated surface waters. Hence, the importance of its experimental measurement to disinfection process design.

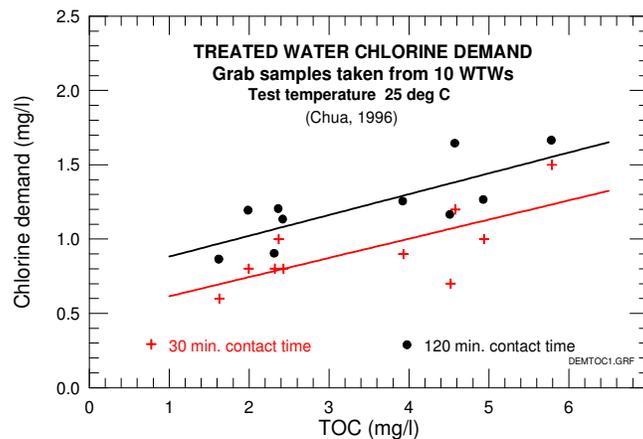


Fig 2 Chlorine demand/TOC relationship

CHLORINE DISINFECTION PROCESS DESIGN

The objective in drinking water chlorine disinfection process design is to ensure that the entire outflow from the chlorine contact tank has been in contact with free chlorine at a concentration and for a sufficient time period to ensure compliance with the selected design CT-value. The CT-value is calculated as the product of RFC and contact time, integrated over the period of contact, taking into account the decreasing RFC concentration with

time. This product is illustrated graphically in Fig 3 as the hatched area bounded by the chlorine dose line and the chlorine demand curve. The CT value is calculated by integration as follows:

$$CT = \int_0^{t_c} [C_0 - k_D t^n] dt = C_0 t_c - \frac{k_D t_c^{1+n}}{(1+n)} \quad (2)$$

For a given contact time t_c , the CT value may be usefully considered as being made up of two parts (a) the product of the outflow RFC by the contact time (upper hatched area in Fig 3), and (b) the contribution of the reacted free chlorine at contact time t_c (lower hatched area in Fig 3). The latter, designated CT^R for discussion purposes, is given by:

$$CT^R = k_D t_c^{1+n} \left(1 - \frac{1}{1+n}\right) \quad (3)$$

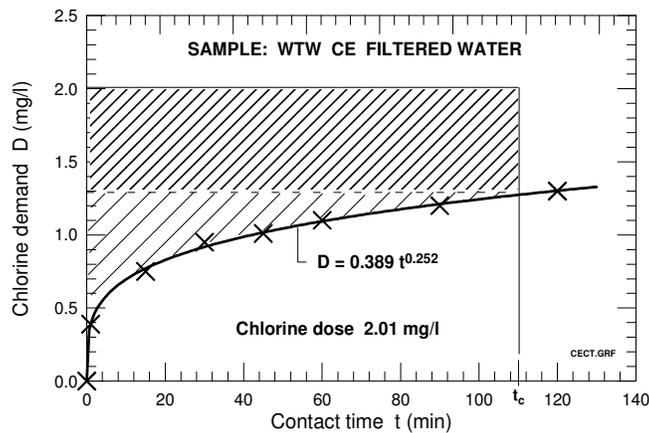


Fig 3 CT computation using chlorine demand curve

The selection of a process CT value is a primary design consideration. The original WHO recommendation of an RFC of 0.5 mg/l after 30 minute contact has long been used as an authoritative design guideline. It is therefore of interest to examine the CT-value range it would provide for the set of treated surface waters in the survey outlined above. Inserting the calculated chlorine demand coefficients k_D and n for a chlorine dose of 2 mg/l in the relevant equations, as outlined above, produced the following value ranges:

Chlorine dose range required to generate a 30-min. RFC of 0.5 mg/l: 0.9 – 1.8 mg/l
 Corresponding CT-value range (30 x 0.5 + CT^R): 18 – 23 mg.min/l

Thus, the calculated required chlorine dose for the water with the highest chlorine demand was twice that required for the water with the lowest chlorine demand. However, the CT-value delivered by the higher dose only exceeded that delivered by the lower dose by only 28%. Thus, at a short contact time of 30 minutes, the CT^R contribution of the higher chlorine dose is diminished by the initial high chlorine demand rate.

The required chlorine residual (C_t) and corresponding chlorine dose (C_0) required to deliver the selected process design CT value are calculated as follows:

$$C_t = \frac{CT}{t} - k_D t \left(1 - \frac{1}{1+n}\right) \quad (4)$$

$$C_0 = C_t + k_D t^n \quad (5)$$

The more recent (2011) WHO recommendations, as set out in Table 1, suggest a CT value of 35 mg.min/l for a 99% virus inactivation under adverse pH and temperature conditions. Adopting a design CT value of 35 mg.min/l and a 60 minute contact time, the calculated required chlorine dose and corresponding effluent RFC values for the tested treated waters are plotted in Fig 4. The required dose varied from 0.94 mg/l for the water with the lowest chlorine demand to 1.85 mg/l for the water with the highest chlorine demand. The outflow RFC,

which is the more important parameter from a process control viewpoint, varied from 0.28 mg/l for the highest chlorine demand water to 0.46 mg/l for the lowest chlorine demand water. It is also noteworthy that the CT^R fraction of the total CT varied from 20% in the lowest chlorine demand water to 52% in the highest chlorine demand water.

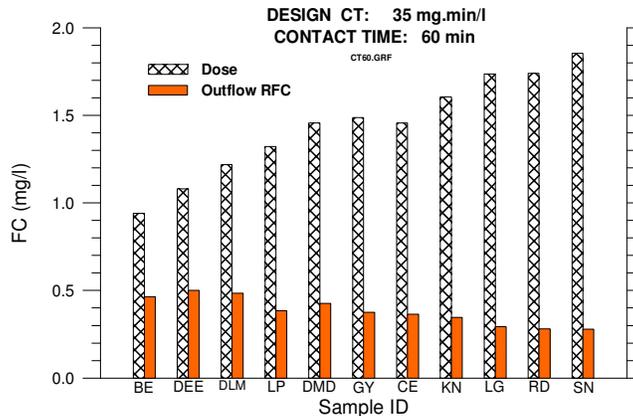


Fig 4 Chlorine dose and outflow RFC required for CT of 35 mg.min/l

Contact tank design

The ideal contact tank has plug-flow characteristics i.e. all elements of the flowing water mass have the same residence time, providing equal exposure to chlorine and a common CT, which can be calculated as indicated in the previous section. In practice, ideal plug-flow conditions are not achievable and instead of a common residence time the flow-through characteristics are quantified by a residence time distribution about the nominal or average residence time as defined by V/Q , where V is the tank volume and Q is the flow rate. The key design objective is the contraction of the residence time spread by the elimination of short-circuiting. The extent of short-circuiting is mainly influenced by the inlet and outlet arrangements and the internal geometry of the contact tank.

Selection of retention time is an important process design decision as it determines the tank volume. While it would be feasible to achieve the WHO disinfection criterion of an RFC of 0.5 mg/l at a retention time of 0.5h, a somewhat longer retention time, say 1-2h, provides a more stable design basis. The longer retention time ensures that the immediate rapid chlorine demand is satisfied within the contact tank and ensures that the RFC in the tank outflow will not be dissipated very rapidly.

In practice, the mixing characteristics of contact tanks fall between being fully mixed and plug flow, resulting in a residence time distribution about the average value. This can be taken into account in contact tank sizing by applying a correction factor to the mean residence time. The residence time distribution can be determined by tracer testing (EPA Manual, 2011). US EPA contact tank design guidance (USEPA, 1999) for disinfection proposes a residence time correction factor based on the t_{10} value which is defined as the time for 10% of the injected tracer to be discharged from a contact tank. The recommended contact time correction factor F_m is taken as the ratio of the t_{10} value to the nominal average residence time $RT = V/Q$. Guidance design F_m values are given in Table 2.

In some water supply developments treated water is pumped from the WTW to a remote elevated service reservoir. Where the rising main has an adequate residence time, it has the potential to provide the ideal contact tank. However, the use of a rising main in this way is only feasible where there are no branch supplies off the rising main or local supplies in the environs of the WTW.

The principles of good contact tank design are illustrated in Fig 5, which shows the plan layout of a rectangular contact tank. The tank features that are designed to reduce short-circuiting include:

- Flow path length large relative to flow cross-sectional dimensions, further enhanced by internal baffle wall arrangement.

- Inflow kinetic energy dissipated over full water depth by use of a vertical standpipe with multiple orifices
- Perforated baffles used to generate flow over full cross-section of tank
- Outflow collected over water depth by vertical standpipe with multiple orifices and discharged over a fixed weir that defines the contact water surface elevation and hence defines the contact tank volume.

Table 2
Guidance values for t_{10}/RT for indicated baffling
(USEPA, 1999; EPA Manual, 2011)

Condition	t_{10}/RT	Description*
Unbaffled	0.1	None, agitated basin, very low length to width ratio, high inlet and outlet velocities
Poor	0.3	Single or multiple unbaffled inlets and outlets, no intra-basin baffles
Average	0.5	Baffled inlet and outlet with some intra-basin baffles
Superior	0.7	Perforated inlet baffle, serpentine or perforated intra-basin baffles, outlet weir or perforated launders.
Perfect	1.0	Very high length to width ratio (pipeline flow)

*Refer EPA manual, 2011 for additional details

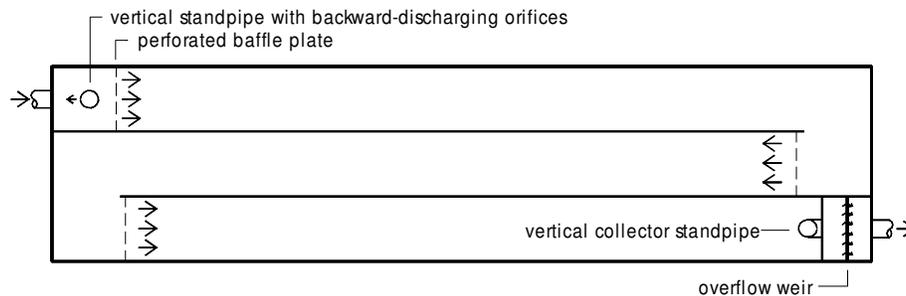


Fig 5 Plan layout of chlorine contact tank

INFLUENCE OF TEMPERATURE ON CHLORINE DEMAND.

As the data in Table 1 indicate, the CT requirement for disinfection is strongly influenced by temperature, as reflected in the fact that the recommended 99% Virus inactivation value at 5 °C is approximately 1.5 times that at 10 °C. As a consequence, the influence of temperature on primary chlorine demand is an important consideration in disinfection process design, since for a given chlorine dose and contact time, the demand rate affects the resultant CT value.

A frequently used approximate rule, enunciated by van't Hoff (Fair et al., 1968), is that aqueous reaction rates typically double for a rise in temperature of 10 °C, corresponding to about 8.4% per degree rise in temperature. Research findings (Powell et al., 2000) have shown a 1.8- to 3.2-fold increase in chlorine decay rate in distribution pipework for a temperature rise from 10 °C to 20 °C. However, in a limited series of chlorine decay tests carried out as part of this study, a temperature rise of 10 °C (from 5 to 15 °C) was found to result in only about a 10% rise in the 120-minute primary chlorine demand value. The significant difference between these findings may indicate that primary chlorine demand is less influenced by temperature than is the ongoing subsequent distribution system chlorine demand. However, this indication should be regarded as tentative and would need to be verified by further testing. Thus, while it is clearly the case that a given chlorine dose would deliver a greater CT value at 5 °C than it would at 15 °C, the difference is most reliably obtained by chlorine demand measurements at both temperatures.

There is anecdotal evidence that public water supplies using surface water sources experience a seasonal variation in chlorine usage, with increased demand in the summer and early autumn periods. While this increase is very probably temperature-related it may also be caused by a seasonal NOM variation both in composition and concentration.

ONGOING CHLORINE DEMAND

The primary chlorine demand data reported above is limited to a contact duration of 120 minutes. There is obviously a continued growth in chlorine demand beyond this terminal point. While the empirical model that has been used to quantify the primary chlorine demand is not necessarily valid outside the contact time period for which it has been verified, the slope of the demand graph at its terminal point measures the ongoing rate of increase in chlorine demand at this point. Analysis of the graph slopes shows the rate of increase varied within the range 0.06 - 0.24 mg/l per hour, the lower end of the range relating to the low chlorine demand waters and the upper end of the range relating to the high chlorine demand waters. This points to the fact that waters with a high primary chlorine demand are also likely to have a much greater ongoing chlorine demand than waters with a low primary chlorine demand.

THM FORMATION

Although chlorine has been in use for drinking water disinfection for over 100 years (USEPA, 2000), its reaction with NOM leading to the generation of undesirable haloform byproducts was not established until 1974, when Rook published the findings of an investigation at the Rotterdam Water Utility, which showed that haloforms formed at significant levels immediately following chlorination. Later that year, Bellar et al. reported significant levels of organochlorides in some US drinking waters. These findings prompted the US Environmental Protection Agency (USEPA) to initiate a national survey to determine to what extent organochlorides were present in waters nationwide and especially the effect of chlorination on the formation of chlorinated organics. The results of the survey (Symon et al.) indicated that four trihalomethanes – chloroform, bromodichloromethane, dibromochloromethane and bromoform – were present in a large number of the 80 city water supplies surveyed.

Bromide ions, the precursors of brominated THMs, are to be found in natural waters at low concentrations. Bromide is a conservative constituent in natural water and takes part in very few chemical reactions (Hutton & Chung, 1994). In the process of chlorination, bromide ions are oxidized to hypobromous acid (HOBr), which reacts more readily with organic matter than chlorine to form brominated THMs. It is noteworthy that water sources in coastal areas that are influenced by seawater intrusion may have elevated bromide levels.

Because of the suspected causative link between these chlorination-disinfection byproducts and various cancer forms, mandatory limit values have been set for their concentration in drinking water. The current EU and Irish drinking water limit value for total THM (TTHM) is 100 µg/l. The TTHM drinking water limit concentration in the United States is 80 µg/l.

The complexity of THM precursor species makes it impossible to measure their exact concentration in natural water. Not all NOM will react with free chlorine to form THM. The general term “DBP precursor” is used to represent the culprit fraction. The most widely used surrogate parameter is total organic carbon (TOC). TOC is a collective measure of organic matter in water. However, it provides no information on the composition and distribution of the wide array of organic constituents. Most groundwaters contain less than 2 mg/l TOC. The TOC of raw water grab samples collected from 12 Irish WTWs, using surface water sources, was found (Chua, 1996) to vary in the range 3.5-14.0 mg/l.

Another parameter frequently used is ultraviolet absorbance (UVA, l/cm) at 254 nm. Organic compounds that are aromatic or that have conjugated double bonds absorb light in the ultraviolet region. UVA is considered a good potential surrogate parameter because humic substances contain aromatic moieties. Specific ultraviolet absorbance i.e. UVA/TOC (SUVA, l/cm.mg) is also used in the characterization of NOM in water with reference to its potential for THM production in reaction with chlorine.

THM formation potential

The THM formation potential (THMFP) of water is measured in a standard test procedure, which allows ample time and chlorine availability for the reaction between chlorine and NOM. In the results reported here (Chua, 1996), the THMFP test involved 7 days incubation at 25 °C, pH of 7.0, an applied chlorine dose of ca. 3 times the TOC concentration, resulting in an RFC at the end of the 7-day incubation period in the range 2 – 5 mg/l. The test environmental conditions are important as THM formation is observed to increase with temperature, pH and available free chlorine. Fig 6 presents the results of THMFP measurements for a set of raw and treated water grab samples taken from Irish WTWs. The plotted data illustrate the extent of THMFP removal by alum coagulation/filtration without pH adjustment for optimal TOC removal.

Since the data plotted in Fig 6 relate to grab samples, a wide value range is to be expected, reflecting both the temporal variability of the individual water sources as well as variability between sources. The measured raw water THMFP varied within the range 234-1058 µg/l, while the measured treated water THMFP varied within the range 87-295 µg/l. Only two of the 13 treated waters had a THMFP ≤ 100 µg/l while four had a THMFP ≥ 200 µg/l. The extent of THMFP removal by chemical coagulation/filtration was found to vary within the range 17 – 80%.

Sample LT, which had the highest raw water THMFP at 1058 µg/l, may be regarded as typical of a soft highly coloured peaty surface water (colour: 170 HU; TOC 13.9 mg/l). Sample LK, which had the second highest raw water THMFP at 641 µg/l, may be regarded as typical of a lowland river reach with a hard alkaline water of

moderate colour and high TOC (colour: 50 HU; TOC 8.9 mg/l). Sample CI, which had the lowest raw water THMFP, may be regarded as typical of a good quality upland impounded water of low colour (colour: 29 HU, TOC: 3.6 mg/l).

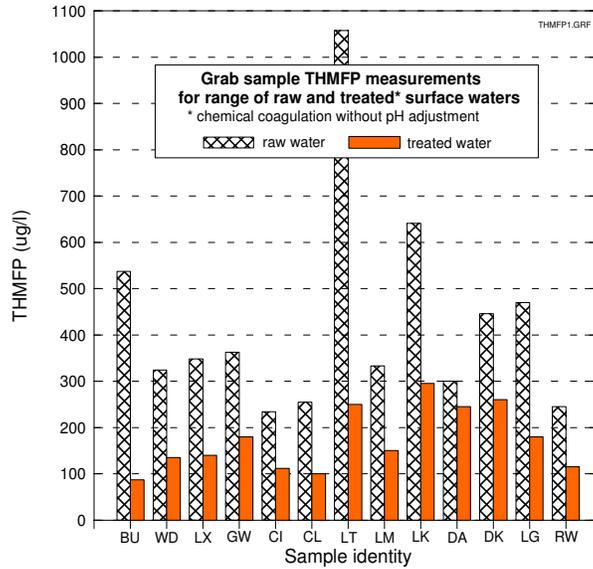


Fig 6
THMFP for selected Irish surface waters
(Chua, 1996)

As THM formation is a consequence of the reaction between chlorine and NOM in water, it is of interest to examine the correlation between THMFP and TOC and THMFP and UVA, the surrogate parameters commonly used as an indices of the predisposition of waters to form THMs. Fig 7 plots a correlation of THMFP and TOC for a set of grab samples taken from 14 Irish WTWs. Fig 8 presents a correlation of THMFP and UVA for the same sample set. While THMFP exhibits a positive correlation with TOC, it is clear that there is a significant variation in dependency, particularly in the commonly prevailing surface water TOC range of 3-6 mg/l. This is not surprising as only a relatively small fraction of the TOC reacts with chlorine to form THM species, as demonstrated in Fig 9, which plots the fraction of TOC incorporated in THM species under THMFP testing conditions. The carbon incorporation in TTHM was found to vary from 0.3% to 0.6% of TOC for treated surface waters and from about 0.4% to 1% of TOC for raw surface waters. Hence, it is not surprising that TOC on its own is not a very precise predictive parameter for THMFP. The data plotted in Fig 8 indicate a reasonably linear correlation between UVA and THMFP for the raw waters examined but a more scattered relation for the treated waters.

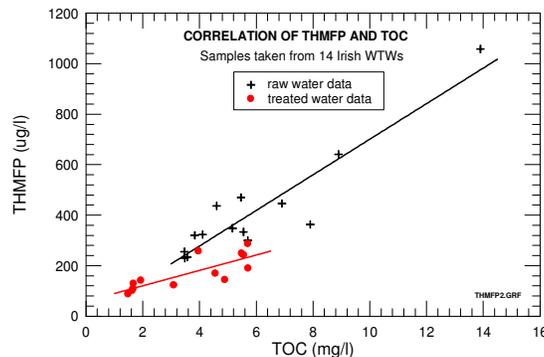


Fig 7
Correlation of THMFP and TOC
(Chua, 1996)

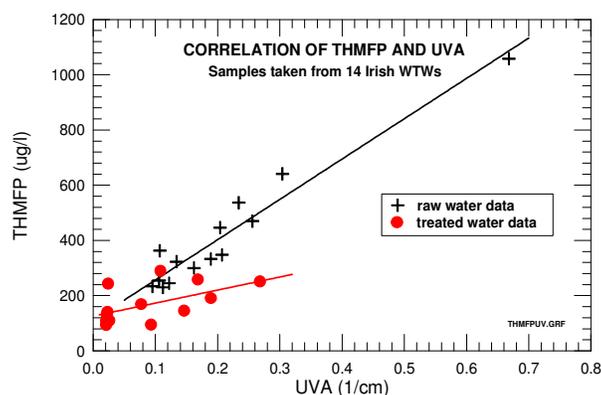


Fig 8 Correlation of THMFP and UVA (Chua, 1996)

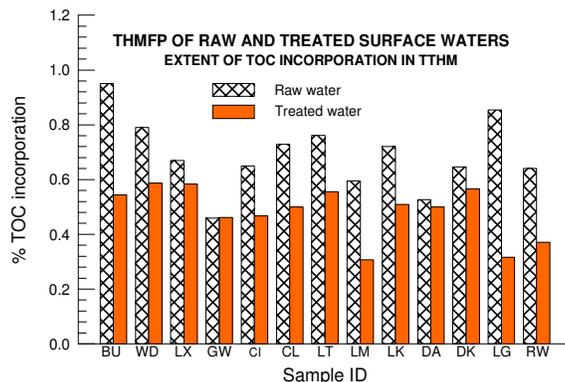


Fig 9 Extent of TOC incorporation in TTHM

THM speciation

Potential THM species comprise chloroform (CHCl_3), bromodichloromethane (CHBrCl_2), chlorodibromomethane (CHBr_2Cl) and bromoform (CHBr_3). The measured individual concentrations of these organochlorine species in a set of grab samples taken from Irish WTWs are plotted in Fig 10. Chloroform was found to be the dominant THM species formed in 11 of the 14 test samples, accounting for some 60% to 80% of the TTHM expressed on a $\mu\text{g/l}$ concentration basis. Bromodichloromethane was found in all samples in concentrations ranging from 2 to 21 $\mu\text{g/l}$. Chlorodibromomethane was detected in 9 of the 14 samples with a significant level in samples CL and WD. Bromoform was not detected in any of the samples.

THM formation kinetics

The rate of THM formation following chlorination typically exhibits a decreasing growth rate profile similar to that of primary chlorine demand, albeit at a somewhat slower rate. A typical example is illustrated in Fig 11, which plots both TTHM formation and chlorine decay over time in a grab sample taken from WTW DA. The sample was found to have an RFC of 0.9 mg/l after a 2h contact period; as shown in Fig 10, the RFC effectively decreased to zero after a contact period of ca. 9h. The TTHM concentration grew rapidly initially, reaching half its maximum value in about 2.5 h while further TTHM development was found to negligible after 24h.

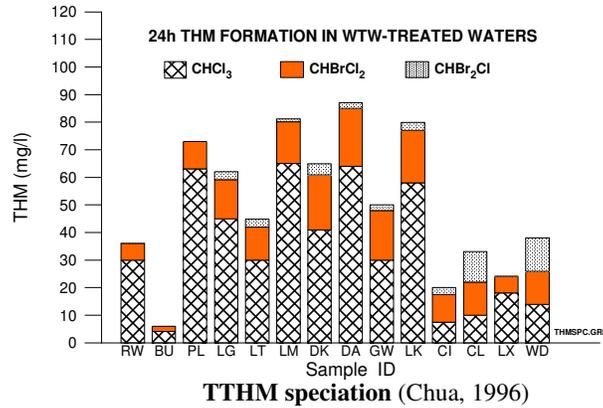


Fig 10 TTHM speciation (Chua, 1996)

The typical TTHM decreasing growth rate pattern illustrated in Fig 11 can be modeled as a hyperbolic function having the form:

$$TTHM_t = TTHM_{max} \frac{t}{t_{50} + t} \tag{6}$$

- where
- $TTHM_t$ = TTHM concentration at time t, $\mu\text{g/l}$
 - $TTHM_{max}$ = maximum TTHM concentration, $\mu\text{g/l}$
 - t = reaction time (h)
 - t_{50} = time taken to reach 50% of TTHMmax (h)

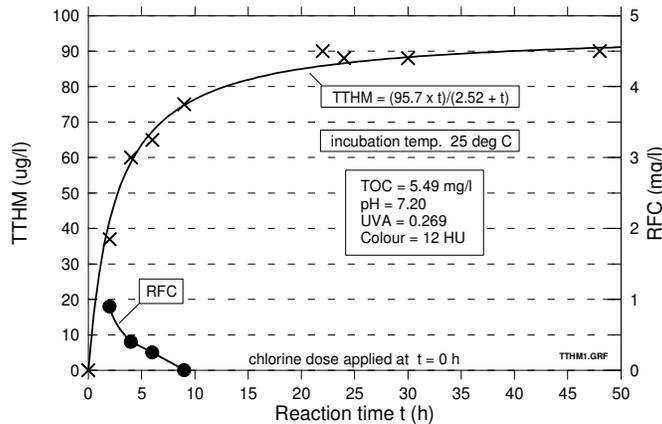


Fig 11 TTHM formation and RFC decay in water sample (grab sample taken from WTW DA (Chua, 1996))

The hyperbolic model growth rate is defined by two parameters, namely $TTHM_{max}$ and t_{50} . In the example illustrated in Fig 11, the $TTHM_{max}$ is $95.7 \mu\text{g/l}$ and the t_{50} value is 2.52h. The values of these parameters are not constants for a given treated water, increasing with increasing chlorine dose.

Environmental factors influencing THM formation

The rate of THM formation is influenced by both temperature and pH.

As with most chemical reactions, THM formation is found to increase with increasing temperature. Chua (1996) found that THMFP formation increased approximately linearly with temperature, resulting in an increase in the range 50-60% per 10°C rise in temperature. Engerholm and Amy (1983) reported the increase in THM formation per 10°C rise in temperature to be within the range 25-50%. As the Irish surface water seasonal

temperature variation is at least 10 °C, a significant seasonal variation in THM formation is to be expected with higher values in summer than in winter. Seasonal variation in NOM also contributes to the variation in THM formation.

THM formation has been found to increase with increase in pH (Kim et al., 2002; Oliver & Lawrence, 1979). Chowdhury & Champagne (2008) found that THM production increased by about 40% when the pH was changed from 6.5 to 8.0 for one source and increased by about 25% when the pH was changed from 6.2 to 7.4 for a second source.

Influence of chlorine demand on THM formation

It has been found (Clarke, 1998; Bocelli et al., 2003) that TTHM production in a chlorinated drinking water at an RFC contact time t can be linearly related to the chlorine demand exerted at that time:

$$TTHM_t = F.D_t + M \tag{7}$$

where D_t is the total chlorine demand at time t, F is a parameter relating THM formation to chlorine demand, and M is the TTHM present at t = 0 (typically M = 0 for primary chlorination, and M > 0 for booster chlorination).

Fig 12 plots TTHM as a function of chlorine dose for water samples taken from 10 Irish WTWs (Chua, 1996). The raw water grab samples (all of surface water origin) were treated in the laboratory by chemical coagulation/clarification/filtration for colour and turbidity removal and were chlorinated at the dose level required to generate an RFC of 0.5 mg/l at 25 °C. The TTHM concentration was measured after 48h contact. The RFC decay time varied from 4 to 10h; hence the chlorine dose may also be regarded as the chlorine demand in this case. The parameter F varied within the range 22-33 µg/mg for the 10 waters tested, with a mean value of 26 µg/mg (i.e. µg TTHM per mg chlorine demand). Bocelli et al. (2003) reported F-values in the range 29-59 µg/mg for a similar set of treated water test samples. Thus, while TTHM may be linearly related to chlorine demand for a given water source, there is clearly a considerable variation in this correlation between waters derived from different catchments.

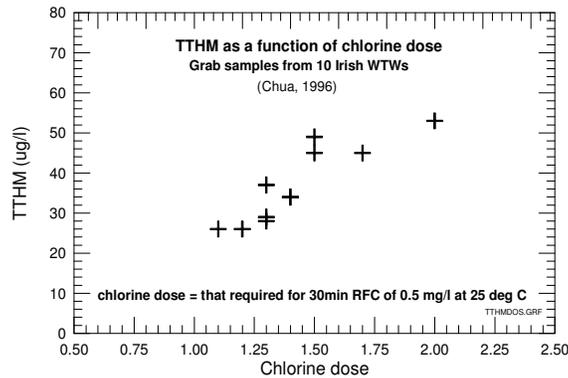


Fig 12 Influence of chlorine demand on TTHM

The practice of maintaining an RFC of at least 0.1 mg/l throughout water distribution systems means that drinking water is in contact with free chlorine from the time of primary chlorination to the time of consumption. This means that chlorine demand, and hence also THM formation, increases with the water age, as measured from the time of primary chlorination. Thus, the risk of THM non-compliance is greatest for waters that have a high NOM/chlorine reactivity combined with a high age. The NOM/chlorine reactivity of treated surface waters can vary over a wide range as illustrated by the survey results presented in Table 2, which found that the maximum 2h chlorine demand was about three times the minimum 2h chlorine demand. While a high 2h chlorine demand is a good indicator of longer-term chlorine demand, this is not always the case. A better indicator is the differential between the 2h demand and the 30min. demand, which for the set of samples in Table 2 varied in the range 0.14 mg/l for sample DEE to a high of 0.51 for sample RD.

REDUCTION OF CHLORINE DEMAND

Surface waters are conventionally treated by a process combination of chemical coagulation/clarification/sand filtration to produce a treated water that meets drinking water standards as measured by control parameters, notably colour, turbidity and residual coagulant chemical. Where the raw water is of exceptional quality, such as impounded waters of low colour and turbidity, slow sand filtration (SSF) may provide an adequate treatment to deliver drinking water quality in respect of colour and turbidity levels.

Chemical coagulation

Chemical coagulation based on aluminium sulphate (alum), followed by clarification and rapid gravity filtration is by far the most widely used process combination for the production of drinking water from surface water sources in Ireland. Its effectiveness in reduction of THMFP (hence, also chlorine demand) has been illustrated in Fig 6, which presents the results of THMFP measurements for a set of raw water grab samples taken from 13 Irish WTWs. As is evident from examination of Fig 6, the removal percentage in THMFP across the sample set was found to be quite variable, falling within the range 40-80% for most samples. Perhaps of more significance is the residual THMFP, which was found to be highest for the hard alkaline raw waters, such as samples DA and LK. This reflects the fact that the effectiveness of alum coagulation in chlorine demand reduction is generally found to be pH-sensitive. Hence, process performance with low and medium alkalinity waters, where alum addition results in coagulation at an acid pH in the range 6-7, is more effective than with hard alkaline waters where the alkalinity is sufficient to maintain a coagulation pH in the range 7-8. The influence of coagulation pH on chlorine demand and THM production for raw water sample LK is illustrated in Fig 13. The upper curve relates to coagulation at an alum dose of 7 mg Al³⁺/l and a coagulation pH of 7.22. The lower curve relates to coagulation at an alum dose of 4 mg Al³⁺/l and a pH of 5.51. The applied chlorine dose in both cases was that required to generate a residual of 0.5 mg/l at 30 minute contact time. Since the RFC reduced to zero in less than 6h the applied dose is also the chlorine demand in this case. The results show that the reduction in coagulation pH effected a ca. 20% reduction in chlorine demand and ca. 30% reduction in TTHM. It is also noteworthy that reduction in the coagulation pH resulted in a significant reduction in the required alum dose.

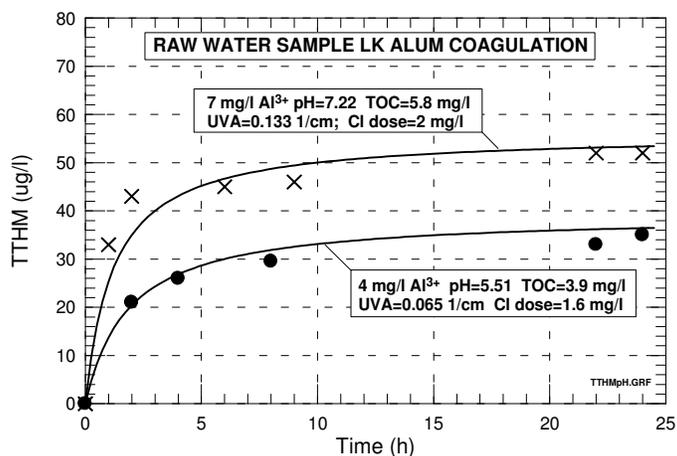


Fig 13

Influence of coagulation pH on chlorine demand and THM formation

Thus, for hard alkaline surface waters, such as are found in the lower reaches of a number of Irish rivers, optimization of the coagulation pH to maximize TOC and chlorine demand removal is essential to avoid excessive THM production in water supplies derived from these sources. The THM reduction impact of improved chemical coagulation is confined to the CHCl₃ species, as chemical coagulation does not effect removal of bromide ion.

Slow sand filtration

Slow sand filtration (SSF) has traditionally been used to treat surface waters of a high quality that may be marginally outside drinking water standards in terms of colour and turbidity. Such sources are typically upland artificial impoundments or natural lakes derived from catchments that are free of peat cover.

The SSF process effects a marginal removal of colour, turbidity, TOC and chlorine demand. Chua (1996) reported a THMFP removal in the range 14-21% for an SSF pilot plant treating an impounded raw water that already was being successfully treated by a plant-scale SSF process over a long period. Collins & Eighmy (1988) reported a similar level of SSF performance with a THMFP removal in the range 9-27% and a TOC removal in the range 13-33%.

While it is probably the case that raw waters, that meet the quality requirements for treatment by SSF, are unlikely to have high TOC and chlorine demand levels, nevertheless the related issues of chlorine demand and THM formation should be included in the set of criteria used for assessment of SSF suitability in a particular application.

Activated carbon

NOM removal by granulated activated carbon (GAC) generally requires a minimum empty bed contact time (EBCT=Vol/Q) of 10-20 minutes to achieve significant removal (Cummings & Summers, 1994). The effectiveness of a GAC contactor decreases with increasing operating duration. GAC adsorption capacity could be exhausted in as short as 41 days or as long as 182 days (Jacangelo et al., 1995). For example, a summary of the precursor removal performance of a GAC pilot plant, treating SSF filtrate (Chua, 1996) is presented in Table 3. The pilot plant was operated over a 260d period at an EBCT of 20 minutes.

Table 3
GAC contactor performance

Parameter	Percentage removal	
	Start	End
TOC	64	23
UVA	64	14
THMFP	72	29

While GAC adsorption is an excellent process for TOC/THMFP removal, the requirement for its regeneration/replacement is a major obstacle to its adoption as a viable process in water treatment practice.

DISCUSSION

Disinfection

The test results and analysis presented above point to the fact that chlorine demand is a key process variable in the production of drinking water from surface water sources, affecting both the disinfection process and the potential for undesirable THM formation. It is obviously an hygienic imperative that water leaving a WTW should be fully disinfected. In this regard, the primary chlorine demand of a treated water is a key design variable as it determines the minimum required chlorine dose that would provide the necessary CT for disinfection. For current discussion purposes, the primary chlorine demand is taken to mean the immediate demand as reflected in the free chlorine decay rate over a 2h period following chlorination.

It has been shown by an analysis of primary chlorine demand test results for a range of treated water grab samples taken from Irish WTWs that the primary demand could be reliably quantified by a simple power function of contact time. The tested sample set was representative of Irish surface waters in water treatment terms in that it included surface waters of varying colour, turbidity and alkalinity/hardness. All waters tested exhibited the same general primary chlorine demand/time profile, characterized by an initial rapid decrease in RFC over the initial few minutes of contact, followed by a decreasing rate that could be accurately represented as a simple power function of time. While all samples exhibited the same general chlorine demand/time profile,

the 2-h chlorine demand varied in magnitude by a factor of about 3:1 between the treated water of lowest demand and the treated water of highest demand.

The primary chlorine demand of treated surface waters was found to be partially influenced by the prevailing free chlorine concentration but not to the extent inferred by a first-order reaction rate, as commonly assumed in chlorine decay rate modeling. However, it is important that this partial dependence on chlorine concentration is taken into account in measuring primary chlorine demand by selecting a chlorine dose \geq the disinfection dose when experimentally determining the primary demand profile. Indeed, it would be useful to relate primary chlorine demand to a standard chlorine dose of 2 mg/l (disinfection dose unlikely to exceed 2 mg/l) and a standard temperature to provide an additional useful comparative index of treated water quality.

Water temperature is a significant variable in chlorine disinfection process design. Irish surface waters experience a seasonal temperature fluctuation of up to about 15 °C. As indicated in Table 1, the required disinfection CT-value increases as the water temperature decreases. In water treatment practice, the chlorination process is normally controlled by regulating the applied dose to achieve a set RFC in the outflow from the contact tank. However a fixed outflow RFC would deliver a reducing CT-value as the water temperature drops. Hence, it is important that the target outflow residual is modified as the water temperature changes.

The importance of having a properly designed contact tank at all WTWs cannot be overstated as it plays a key role in delivering safe drinking water. The key characteristics of the ideal contact tank are (a) fixed volume that provides a retention time $RT = V/Q$, and (b) near-to plug-flow hydraulic behavior, thus minimizing short-circuiting. A fixed volume is easily provided by a fixed level overflow outlet weir or similar control to maintain a fixed water level. There is flexibility in selecting a design retention time, which would generally be in the range 0.5-2h. As outlined in the text, knowledge of the empirically determined chlorine demand coefficients k_D and n enables calculation of the required chlorine dose and corresponding contact tank outflow RFC to achieve a selected design CT value. The chlorine dose required to achieve a target CT is inversely related to the retention time as is the outflow residual. Thus a larger chlorine dose is required where the contact time is short. In general, this may not prove to be wasteful of chlorine since a residual has to be maintained in the distribution system.

THM formation

The foregoing presentation has outlined the factors that influence THM formation in water supplies. THMFP data for a range of surface water types indicate that precursor organics are only partially removed by conventional water treatment process technology. The chlorine demand/time profile of treated waters provides a good index of the effectiveness of the applied treatment, particularly in relation to NOM removal. The requirement of maintaining an RFC of at least 0.1 mg/l in water distribution systems means that the total chlorine dose must marginally exceed the demand of the water over its lifetime. Thus, the required total chlorine dose and THM generation both increase with water age.

In water supplies where chlorination is confined to a single upfront chlorine dose, the requirement to maintain an RFC of at least 0.1 mg/l in the distribution system rather than disinfection considerations may be the determinant of the dose magnitude. Where the chlorine dose applied at the WTW exceeds that required for disinfection purposes, the provision of a purpose-designed contact tank may be deemed to be not necessary. In such circumstances, service reservoirs serve a dual purpose of contact tank and water demand buffer. In general, this is not best process design practice as service reservoirs tend to have a variable volume and uncertain residence time distribution, resulting in a low effective CT yield per unit of chlorine dose.

THM formation is primarily minimized by the production of treated water having a low chlorine demand, following by a chlorination regime designed to minimize the total chlorine dose required for both disinfection and maintenance of a residual in the distribution system. For example, a chlorination regime relying on a single large dose inevitably results in a greater system chlorine demand than a regime where an initial disinfection dose is followed one or more booster doses. This arises from the fact that the chlorine decay rate is partly concentration-dependent. Maintaining unnecessarily high RFC levels in service reservoirs can add greatly to system chlorine demand and hence THM production.

CONCLUSIONS

1. Chlorine demand has been shown to be a key parameter in disinfection process design and in the formation of THMs in water supply systems.
2. Quantification of the initial short-term chlorine demand (contact time ≤ 2 h) is essential for reliable design of primary disinfection processes. The initial 2h chlorine demand for a set of treated Irish surface water grab samples was found to vary in the range 0.6-1.9 mg/l.
3. It has been shown that the initial short-term chlorine demand of treated Irish surface waters could be accurately represented by a simple power function of contact time: $D_t = k_D \cdot t^n$ where D_t is the chlorine demand (mg/l) at time t (min), k_D and n are empirical coefficients. The coefficient k_D corresponds to the fitted model 1-minute chlorine demand value.
4. The initial short-term chlorine demand was found to be partially chlorine concentration-dependent, but not to the extent that the decay rate could be represented as a first-order reaction with respect to RFC.
5. As demonstrated in the text, the use of the derived model equation for short-term chlorine demand enables an accurate calculation of the CT-value generated in a contact tank, based on either the outflow RFC or the applied chlorine dose.
6. It is highly desirable that all WTWs have a purpose-designed chlorine contact tank, having a fixed water volume, hydraulically configured to eliminate short-circuiting and sized to deliver the required CT to achieve primary disinfection.
7. As with all chemical reactions, chlorine demand has been found to be influenced by water temperature as is the CT value required for primary disinfection. Since Irish surface waters may undergo a seasonal temperature fluctuation of up to 15 °C, treated water temperature is an important primary chlorination process operational parameter, requiring a higher contact tank outflow RFC in winter than in summer.
8. THMs are generated in all treated surface waters to which chlorine has been added, the resulting TTHM being directly related to the total chlorine added, which in turn is determined by the chlorine demand of the water.
9. The total chlorine demand of treated surface water is related to its residual NOM content, which is conventionally measured as TOC. Only a very small fraction of TOC is incorporated into THMs. Hence, while THMFP is found to have a positive correlation with parameters such as TOC and UVA, the correlation is not sufficiently tight for general predictive use in the process design context.
10. Conventional surface water treatment technology, incorporating chemical coagulation/clarification/filtration has a variable effectiveness in reducing THMFP, performing best with soft low-alkalinity waters and poorest with hard high-alkalinity waters. With the latter category of surface water, coagulation pH regulation by acid addition may be necessary to achieve the required THMFP and chlorine demand reductions necessary to ensure that the supplied water TTHM remains below the regulatory limit of 100 $\mu\text{g/l}$.
11. Slow sand filtration is found to effect a marginal reduction of chlorine demand and THMFP. Hence chlorine demand and THM formation should be included in the set of criteria used for evaluation of the suitability of SSF treatment.
12. GAC adsorption has been found to be an excellent process for TOC/THMFP removal. However, the requirement for its regeneration/replacement is a major obstacle to its adoption as a viable process in water treatment practice.
13. Chlorine demand has been shown to be a very useful and informative parameter in characterizing treated surface water quality. The fact that it is easily measured using equipment available at all WTWs makes its more widespread use as a comparative treated water quality parameter readily feasible.

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REFERENCES

- Bellar et al. (1974) The Occurrence of Organohalides In Finished Drinking Waters, J. AWWA, 66:12:703.
- Boccelli, D., Tryby, M. E., Uber, J. G., and Summers, R. S. (2003): A reactive species model for chlorine decay and THM formation under rechlorination conditions, Water Research, 37, 2654-2666.
- Brezonik, P. L. (1994) Chemical Kinetics and Process Dynamics in Aquatic Systems, CRC Press, Boca Raton.
- Chowdhury, S. and Champagne, P. (2008): An investigation on parameters for modelling THM formation, Global NEST Jour., Vol. 10, No. 1, pp80-91.
- Chua, K. H. (1996): THM Formation in Drinking Water, Ph.D Thesis, Department of Civil Engineering, UCD.
- Clark, R. M. (1998): Chlorine demand and TTHM kinetics: a second order model. J. Environ Eng ASCE, 124(1), pp16-24.
- Collins, M. R. and Eighmy, T.T. (1988): Modification to the slow sand filtration process for improved trihalomethane removal; Sect. 4.4, pp281-304 in Slow Sand Filtration: Recent developments in water treatment technology, Ed. N.J.D. Graham, Ellis Horwood.
- Engerholm, B. A. and AMY G. L. (1983): A predictive model for chloroform formation from humic acid, JAWWA, 75(8), 418-423.
- EPA(Irl) (2011) Water Treatment Manual: Disinfection, Environmental Protection Agency, Johnstown Castle, Co. Wexford.
- EPA(Irl) (2011) The Provision and Quality of Drinking Water in Ireland, A Report for the Year 2010, Environmental Protection Agency, Johnstown Castle, Co. Wexford.
- Fair, G. M., Geyer, J. C. and Okun, D. A. (1968) Water and Wastewater Engineering, Vol. 2, John Wiley & Sons, Inc.
- Hrudey, S. E., Charrois, J. W. A. (2012): Disinfection By-products and Human Health, IWA Publishing, London.
- Hutton, P. L. and Chung, F. I. (1994): Bromide distribution factors in THM formation. Jour. Water Resource, Planning and Management ASCE, Vol. 120, No. 1.
- Kim, J., Chung, Y., Shin., D., Kim, M., Lee, Y., Lim, Y. and Lee, D. (2002): Chlorination by-products in surface water treatment process, Desalination, 151, 1-9.
- Oliver, B. G. and Lawrence, S. (1979): Haloforms in drinking water: A study of precursors and precursor removal, JAWWA, 71(3),161-163.
- Powell, J. C., Hallam, N. B., West, J. R., Forster, C. F. and Simms, J. (2000): Factors which control bulk chlorine decay rates, Wat. Res. Vol. 34, No. 1 pp. 117-126.
- Rook, J. J. (1976) Haloform in Drinking Water, J. AWWA 68:3:168
- Snoeyink, V. L. and Jenkins, D. (1980) Water Chemistry, John Wiley & Sons, Inc.
- USEPA (1992) Water Treatment Simulation Program User's Manual Version 1.21, EPA No. 811B92001.
- USEPA (1999) Enhanced Coagulation and Enhanced Precipitative Softening Guidance Manual, EPA 815-R-99-012
- USEPA (1999) EPA Guidance Manual, Alternative Disinfectants and Oxidants, EPA 815-R-99-0.14.
- Warton, B., Heitz, A., Joll, C. and Kagi, R. (2006): A new method for calculation of the chlorine demand of natural and treated waters, Water Research, 40, 2877-2884.
- WHO (1992) Guidelines for Drinking Water Quality: Vol. 2: Health Criteria and Other Supporting Information, Geneva.
- WHO (2011) Guidelines for Drinking Water Quality, 4th. Edition, Annex 1: Water treatment and pathogen control: Process efficiency in achieving safe drinking water, Geneva.