Environmental Risks from Bulk Chlorine Storage Installations used in the Water Industry

Celia Figueira, PhD, CEnv, MIEEM, Mott MacDonald Ltd, Ecologist, Mott MacDonald Ltd, 22 Station Road, Cambridge, CB1 2JD.
Nigel Harrison, F I Chem E, Professional Process Safety Engineer, Principle Safety and Reliability Consultant, Mott MacDonald Ltd, Spring Bank House, 33 Stamford Street, Altrincham, WA14 1ES.
Roisin Ni Mhathuna, MSc, Ecologist, Mott MacDonald Ltd, 22 Station Road, Cambridge, CB1 2JD.

Anglian Water Services Limited (Anglian Water) is required under the Control of Major Accident- Hazards (COMAH) Regulations to conduct a periodic review the Safety Reports for their water works that use large quantities of chlorine. The latest review determined that consideration of potential Major Accidents to the Environment (MATTEs) needed updating as the water works are located close to sensitive receptors, improvements to the chlorination system had been made and new good practice guidance for assessment of the environmental risks had just been published. Anglian Water decided to commission Mott MacDonald to undertake this package of work to support the new Safety Report submissions in September 2014. This was followed with interest by the COMAH Competent Authority, as we understood from the Environment Agency that Anglian Water is one of the first COMAH site operators to have applied the good practice guidance published by the Chemical and Downstream Oil Industries Forum (CDOIF, 2013).

Our study included bulk chlorine storage toxic gas accidental release consequence modelling and assessments of the on-site and wider area impacts on people and the environment. The Safety Reports aim to demonstrate compliance with the COMAH Regulations (2015) and that the major accident risks are kept as low as reasonably practicable. As part of this demonstration a Major Accident to the Environment (MATTE) assessment was carried out to investigate the potential effects from an accident to the environment within the estimated zone of influence.

The assessment focuses on the potential effects on the environment, particularly the impacts on designated sites located within the range of the worst case scenario as defined in the chlorine release consequence modelling , as well as sensitive environmental receptors such as protected habitats and species, surrounding habitats, and running water and freshwater bodies (ironically the reservoirs Anglian Water had created to supply the water treatment works which have since become SSSI and Ramsar designated sites).

Six potential unmitigated accident scenarios with potential to result in a significant chlorine spill from storage were investigated and assessed as 'Sub-MATTE' category, and are therefore not considered Major Accidents to the Environment. The accident scenarios identified are therefore 'Broadly Acceptable' in terms of MATTE and were screened out from further assessment. It was not deemed necessary to consider what forms of mitigation need to be in place to further reduce the risk of the accident scenarios to be Tolerable if As Low As Reasonably Possible (TifALARP), as this is the lowest risk category.

Keywords: Chlorine, MATTE, Environmental Risk Assessment; Air dispersion modelling;

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Introduction

Anglian Water Services Limited (Anglian Water) operates 3 water treatment works (WTWs) that store sufficient quantities of Chlorine[1] to come under the COMAH regulations [SI 743 1999[2]].

Two of the WTWs are upper tier COMAH sites operating bulk chlorination systems and which are located close to large reservoirs.

The third WTW is a lower tier COMAH site that operates a drum chlorination system.

Anglian Water is required under the Control of Major Accident- Hazards (COMAH) Regulations to conduct a periodic review the Safety Reports for their top tier COMAH sites. This review determined that:

- Consideration of potential Major Accidents to the Environment (MATTEs) needed updating as the water works are located close to sensitive receptors.
- New good practice guidance for assessment of the environmental risks had just been published.
- Improvements to the chlorination system had been made which weren't reflected in the current safety reports.

Anglian Water decided to appoint consultants to undertake packages of work to support the revision to the safety reports. Black & Veatch were appointed to undertake HAZard and OPerability (HAZOP) studies and to conduct a Layers of

[1] Chlorine is a named substance in Schedule 1 of the COMAH regulations. Its lower tier limit is 10 tonnes and upper tier limit 25 tonnes
[2] Now superseded by Statutory Instrument 2015 No. 483, The Control of Major Accident Hazards (COMAH) Regulations 2015

Protection Analysis (LOPA) of the chlorination system. Mott MacDonald were appointed to provide a Literature Review of relevant information on Chlorine, dispersion modelling of major chlorine release accidents, individual and societal risk assessments and occupied building risk assessments for all the sites.

Mott MacDonald also produced the Environmental Risk Assessments (ERA) for the 3 sites. This paper focuses on the ERA for one of the upper tier COMAH sites, designated as WTW "A".

Assessment of a Major Accident to the Environment

This assessment uses a source-pathway-receptor methodology to determine if, when a pollutant linkage appears to be present, there is potential for a MATTE. The severity of any MATTE is then considered and suitable clean up and recovery measures are assessed to demonstrate that the risk associated with the adopted measures is As Low as Reasonably Possible (ALARP).

In general terms, major accident hazards to the environment will be those where events have the potential to:

- Pose knock-on threats to human health;
- Affect large areas of land designated for conservation, amenity or planning purposes;
- Be long-term or inhibit natural regeneration; and/or
- Cause significant, permanent or long-term damage to the ecosystem (DETR, 1999).

Only major accidents resulting in serious danger to the environment are addressed in this study. A major accident is defined in Regulation 2 of the COMAH Regulations (1999) as "an occurrence (including in particular, a major emission, fire or explosion) resulting from uncontrolled developments in the course of the operation of any establishment and leading to serious danger to human health or the environment, immediate or delayed, inside or outside the establishment, and involving one or more dangerous substances".

Potential pathways to environmental receptors

We identified the potential pathways between the source and vulnerable environmental receptors including designated sites, habitats and sensitive species. Pathways can include the following:

- Infiltration through underlying ground;
- Infiltration along pipes, drainage or effluent systems;
- Surface water run-off;
- Surface water including lakes, streams , rivers, estuaries and coastal waters;
- Air with associated washout and deposition of particles; and
- Through the food chain (bioaccumulation).

In this specific study for the investigated sites, in the case of a major accident in the chlorine bulk storage at WTW "A", the two main pathways through which chlorine could affect ecological receptors are considered to be:

- Through air dispersion – due to the formation of a dispersion cloud. Chlorine dispersed through this pathway has the potential to mainly affect terrestrial receptors. However, depending on weather conditions at the time of the accident some chlorine could disperse to the freshwater habitats nearby and affect freshwater ecological receptors. There is also potential for dispersion of chlorine to the soil.
- Through direct discharge into freshwater receptors. A small proportion of liberated chlorine would remain in liquid form after it is released and there is a potential for this to enter the surface water drainage system at the WTW, which discharges directly into a local stream, therefore the possibility of this liquid chlorine being discharged to the watercourse cannot be discounted.

Identifying environmental receptors and impacts

In a MATTE assessment, vulnerable environmental receptors in the vicinity of the facility might include protected and designated sites, specific land and/or water features, habitats or particular species. Assessment of MATTEs requires knowledge of these receptors and the potential impact of the hazard in terms of extent, severity and duration. These impacts can include the following:

- Loss of habitat and/or populations of fauna or flora;
- Long term contamination of protected land;
- Pollution of water bodies leading to the deaths of vertebrates and invertebrates;
- Contamination of surface waters and reduction in the chemical and biological quality of the water for a period of time in excess of a few days;
- Mutagenic and teregenetic effects;

- Damage to buildings and structures; and
- Loss of amenity use of land.

This paper does not aim to include all receptors identified at the site, rather a summary with examples of the different receptors groups are provided to exemplify the process followed.

Determining the level of severity

The assessment of MATTE in the case of this study will be based on the thresholds as they are listed in the Guidance on Environmental Risk Tolerability for COMAH Establishments (CDOIF, 2013). These criteria have been developed with regard to the Major Accident EC reporting thresholds in the Seveso Directive (Sch.7 of the COMAH Regulations) and the Guidance on the Interpretation of Major Accident to the Environment for the Purposes of the COMAH Regulations (DETR, 1999) which the new CDOIF (2013) guidance provides a framework and screening methodology by which regulators can build on. For each major accident scenario and receptor affected, a level of severity is assigned to four categories:1) Significant (This level is not considered a MATTE); 2) Severe; 3) Major and 4) Catastrophic. Each level of severity is described in CDOIF (2013).

Assigning a duration/recovery category

Once a MATTE is predicted and a severity category assigned based on the matrix presented in **Table 1**, a duration/recovery category associated with unmitigated consequences is then assigned based on the natural recovery time of the environment and in this case the effects and persistence of chlorine in natural environments. Examples of duration descriptors relevant to the environmental receptors at WTW “A” are provided in **Table 1**.

Table 1- Duration/recovery criteria for environmental receptors, based on unmitigated accident scenarios

Receptor	Duration of Harm			
	Short term	**Medium Term**	**Long term**	**Very long term**
Harm duration category →	**1**	**2**	**3**	**4**
Land	≤3 years	>3 years or >2 growing seasons for agricultural land	>20 years	>50 years
Surface water (all except private/public drinking water sources)	≤1 year	>1 year	>10 years	>20 years

Source: CDOIF (2013)

Determining tolerability boundaries

Using the harm/severity level and the harm-duration categories calculated for each accident scenario, an overall unmitigated consequence level is assigned according to each accident scenario, based on **Table 5**.

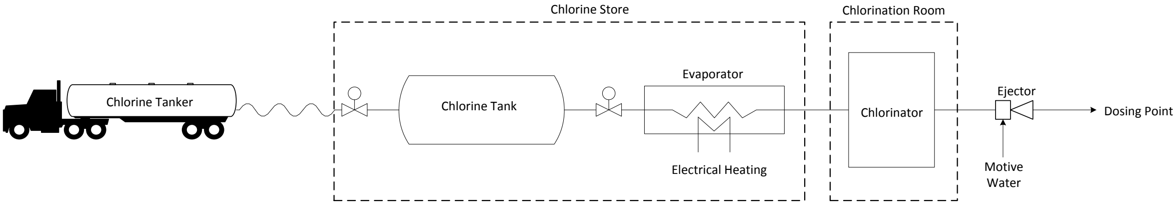
Each consequence level A-D is then assigned a tolerability threshold to define the As Low As Reasonably Possible (ALARP) band, i.e. ‘intolerable’ or ‘broadly acceptable’ frequencies based on the probability of the accident occurring per receptor, per establishment, per year. Probability thresholds are detailed in **Table 6**.

Chlorine Release Accidents

Chlorination systems principles

The chlorination system used at WTW “A” is of a standard design. The chlorine tank is located in a chlorine building which is heated to maintain at least 15 degrees Celsius. Liquid chlorine is supplied from the tank through an evaporator and a chlorinator located in a separate room. The chlorinator room is maintained at a temperature of at least 20 degrees Celsius to prevent re-liquefaction of the chlorine. The chlorinator controls the flow of chlorine and requires a below atmospheric down-stream pressure, supplied by an ejector to operate. If vacuum is lost the flow from the ejector the chlorinator stops the flow of chlorine and thus limits the potential chlorine release in the event of a leak downstream of the chlorinators.

Figure 1 Simplified Flow Diagram of WTW "A" Chlorination System



Accidents selected for modelling

The accidents for modelling and their frequencies were derived from a review of the Black & Veatch LOPA analysis. We were primarily concerned with releases with the potential to have environmental affects outside the site boundary so only the significant leaks of liquid chlorine were analysed. A comparison with the frequencies of accidents predicted from the LOPA with those derived from HSE guidance (HSE 2012) showed reasonable agreement. **Table 2** shows an example of the potential major accidents for a bulk chlorination system.

Table 2 – Major Chlorine Release Accidents for WTW "A"

Reference	Accident	Accident Frequency/yr.	Leak Size
B1	Catastrophic failure of the bulk tank.	2.0E-06	-
B2	Uncontrolled leak from tank or associated connections (assumed to be 25mm diameter)	2.7E-06	25mm
B3	Slow rate uncontrolled leak (assumed to be up to 6mm diameter) from tank or associated connections.	2.6E-04	6mm
B4	Release of chlorine in the event of failure downstream of the remote isolation valves (in conjunction with remote isolation failure)	3.7E-05	25mm
B5	Tanker discharge pipework failure outside the building, 25mm diameter leak.	4.0E-06	25mm

Note: Accidents B1 and B2 were considered to be of sufficiently low frequency as not to require further analysis as no environmental receptor would be subject to a risk from these accidents greater than 10^{-6} per year.

Air Dispersion Modelling

End Points

The effects of toxic exposure depend on both the concentration of the toxic substance and the time of exposure.

Values for the Specified Level of Toxicity (SLOT) and Significant Likelihood of Death (SLOD) applicable to Chlorine are recommended by the HSE [HSE 1990] and are reproduced below (equations 1 and 2):

- SLOT - 1.08×10^5 ppm^n.min (1)
- SLOD - 4.84×10^5 ppm^n.min (2)

For chlorine the value of the constant 'n' is equal to 2, and therefore a relationship between time (t) and concentration (c) required to produce a given level of toxicity can be established.

Using the above equations the SLOT and SLOD figures for 30 minutes exposure are:

- (3)
- (4)

Environmental receptors have different sensitivities to chlorine than humans. Animals appear to be generally less sensitive to chlorine. Thus the human exposure SLOD and SLOT figures could be used as a slightly pessimistic estimate of the potential impact on animals.

Environmental receptors that have particular significance for WTWs "A" are birds, particularly water birds. The SLOD and SLOT values for birds are not known, although birds are well known to be more sensitive to toxins than humans, as illustrated by the historic use of canaries as gas detection in coal mines. Following advice received from the Environment Agency (EA) birds have been assumed to be approximately six times more sensitive to chlorine than humans based on the approximate relationship between body weights. Therefore the SLOD figure for birds would be of the order of 127ppm/6, i.e. approximately 20ppm. By similar logic the lower limit of death from chlorine toxicity, based on the human SLOT value would be about 60ppm/6, i.e. 10ppm.

Therefore, for large mammals such as grazing farmstock, human LC50 values will be used for large mammals such as livestock (grazing farmstock) and wildstock (including badgers). For smaller mammals such as rodents and bats, the LC50 values for small mammals reported in the literature are far higher than expected when compared to LC50 values for humans consequently the LC50 values estimated for birds will be used. Thus the following end points were used for the modelling the effects on environmental receptors of chlorine release accidents:

- 127ppm (50% mortality of large mammals)
- 60ppm (1% mortality of large mammals)
- 20ppm (50% mortality of birds and small mammals)
- 10ppm (1% mortality of birds and small mammals)

Release Modelling Method

The chlorine release accidents were modelled using the DNV (Det Norsk Veritas) PHAST modelling software version 7.01. This is a widely used standard accident consequence software package.

The key parameters used in the modelling were as follows:

Wind speed and Pasquill atmospheric stability

The following standard modelling conditions were used (**Table 3**).

Table 3– Windspeed and Atmospheric Stability

Wind speed (m/s)	Pasquill (Atmospheric) Stability Category	Definition
5 m/s	D	Neutral
1.5 m/s	D	Neutral
1.5 m/s	F	Stable

Temperature and Pressure

The liquid chlorine pressure assumed to be at the saturated vapour pressure at 25 degrees Celsius.

Chlorine Store and Ventilation

The PHAST program allows modelling of releases within a building to be modelled. The chlorine/air mixture is assumed to be released to the environment at the building ventilation rate.

The Chlorine store dimensions were entered and a minimum ventilation rate of 2 air changes per hour was used. PHAST calculates the rate of the vapour release and will not allow a ventilation rate less than the rate of vapour release (i.e. the building will not become pressurised, so in the case of the larger leaks the ventilation rate had to be increased. This is pessimistic as chlorination room ventilation systems are design to stop in the event of serious chlorine leak so in the later stages of a release the dispersion rate of chlorine is over estimated. In the case of catastrophic tank failure the release rate of vapour was so great that the accident had to be modelled as occurring outdoors. This is not unduly pessimistic as it is very likely that doors or windows in the chlorine store would fail in these circumstances.

Terrain Roughness

PHAST allows different surface roughness to be entered to take account of buildings and vegetation. The areas around the WTWs sites are fairly rural so the default surface roughness as used. A sensitivity study was carried out to confirm that the dispersion over water was not significantly under estimated.

Site Topography

PHAST does not specifically model site topography. In the areas around the WTWs are fairly flat so that is not a major issue. If the sites had very hilly topography physical modelling may have been required.

Two examples of the Phast model outputs are presented in Figure 2 and Figure 3 for scenario B3. Outputs were generated for all scenarios and for 10ppm, 20ppm, 60ppm and 127ppm plumes.

Figure 2 Maximum dispersion of cloud of 127ppm after Scenario B3

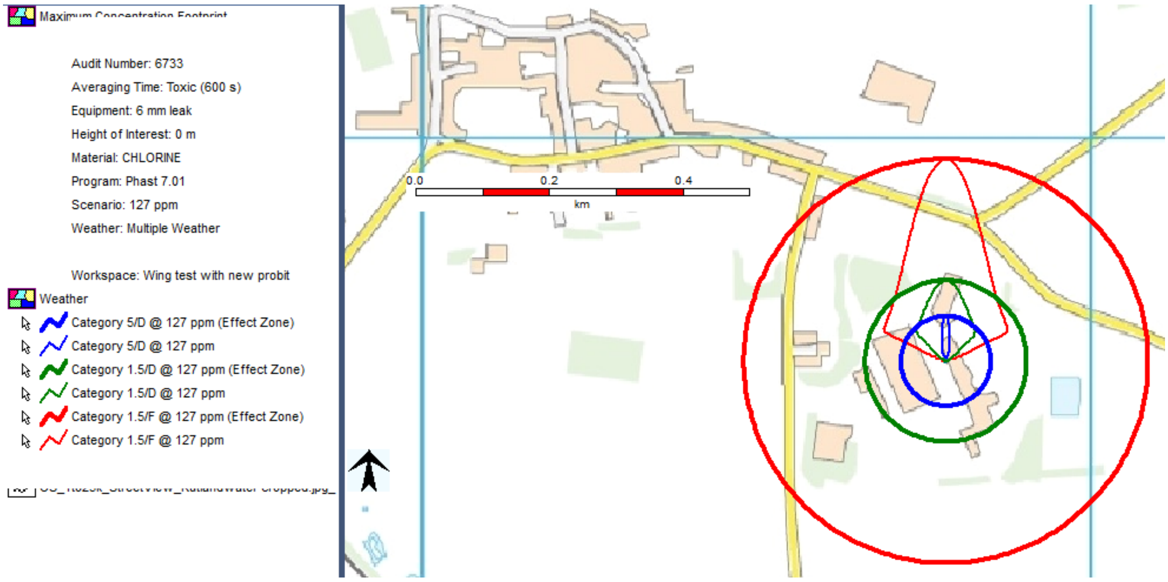
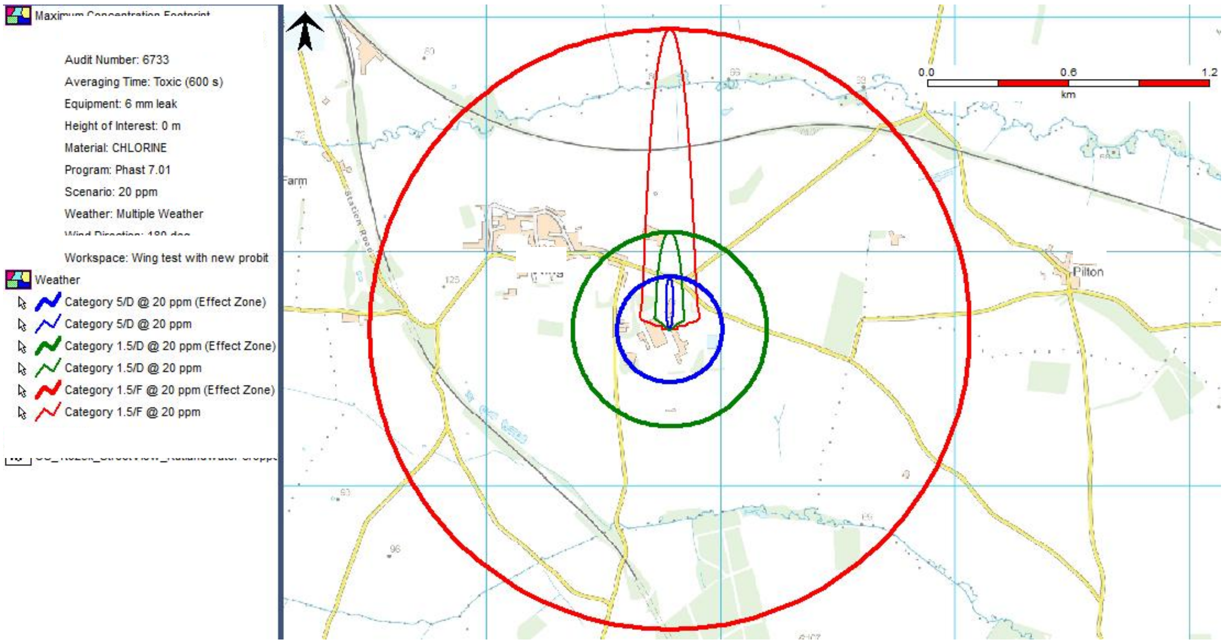


Figure 3 Maximum dispersion of cloud of 20ppm after Scenario B3



Environmental Risk Assessment

Potential hazards to the environment

In the case of an accidental chlorine release under different scenarios, the potential hazards to the environment are discussed in the following sections. For the three sites all scenarios were considered together and the worst-case accident used for the assessment of each environmental receptor – designated sites, terrestrial and aquatic receptors.

International designated site

The modelling predicted that for some scenarios of the potential unmitigated accidents in the bulk chlorine storage facility at WTW “A” have the potential to affect the reservoir SPA/Ramsar site which lies approximately 2.9km north of WTW “A”.

The reservoir SPA/Ramsar site is the closest designated site to WTW “A” and in both accident scenarios the 10ppm and 20ppm chlorine plumes modelled have dispersed as far as the reservoir under 1.5F weather conditions only. 1.5F weather conditions are the worst-case conditions used by the chlorine plume model. The reservoir is designated for its bird assemblage and it is expected that all birds that are unable to escape the area affected by 20ppm of chlorine gas will be killed. Potentially, 50ha and 9 ha within the protected site boundary could be affected by the 20ppm plume, depending on the scenario considered.

Terrestrial environment

In mammals, exposure to chlorine leads to degeneration of olfactory sensory cells in the olfactory mucosa, loss of the respiratory epithelium and cellular exfoliation. However, this is reported to be from exposure to the gas between 1 to 5 days.

In the case of an accidental release of chlorine, it is conservatively assumed that all large mammals would be killed within the predicted 127ppm plume (SLOD value for humans) of chlorine and there would be substantial distress to all mammals with the 60ppm plume (SLOT value for humans). Small mammals such as bats and rodents are likely to be killed within the 20ppm plume field (extrapolated LC50 value for birds) and there would be substantial distress to all small mammals with the 10ppm plume (extrapolated SLOT value for birds).

Habitats and plants

Information on the effects of chlorine on terrestrial species particularly plant species is scarce. This might be due to the very reactive nature of chlorine and therefore it is not expected to remain in the environment very long after it is released, or the fact that it naturally has a negligible presence in the atmosphere. Chlorine is phytotoxic but also essential to plant growth. Acute toxicity to plants is characterized by defoliation with no leaf symptoms and in higher plants by spotting of the leaves (at 1.5mg/m3) and marginal and interveinal injury (at 150-300 mg/m3) (U.S. EPA, 1994). However, these values are likely to be due to long term exposure. Minor damage to plants through exposure to low levels of chlorine may take up to eight days to manifest itself and 3-4 weeks to recover. Exposure to higher levels can cause more permanent damage to woody tissue and recovery would take longer.

Chlorine does not appear to effect the germination of seeds and there is no known impact on soils other than the formation of chlorides which may reduce soil fertility in high concentrations.

The modelled results presented the 127ppm, and the 60ppm modelled plumes for all scenarios for the four sites. The land use within this range is mostly agricultural. As chlorine does not appear to affect the germination of seeds and does not appear to persist in soils but rather binds covalently to soil organics within the first few millimetres of the soil surface, it can be assumed that chlorine gas released from accidental spill will only affect the current growing season of crop or arable land, therefore the time of year of the spill is important to its determination as a major accident to the environment. If crop is growing in the field, concentrations of up to 300ppm are only likely to cause marginal or interveinal injury to plants over long-term exposure (US EPA, 1994).

Large mammals

The agricultural land surrounding WTW “A”, for example, includes arable land which may contain livestock such as sheep and cattle at the time of the hypothetical chlorine spill, and agricultural land in general provides habitat suitable for larger wild stock such as badgers who may use the scrub and woodland habitat around WTW “A” and the field margin hedgerows for foraging and commuting. In other sites badgers could also be present.

To account for the worst case scenario where large mammals could be affected from an accidental chlorine leak, the area affected by the 127ppm modelled plume was calculated for all sites and although reliable estimates of populations’ numbers do not exist, it was deemed unlikely that the size of affected area would be populated by 1% of the population of these species; the threshold suggested by the CDOIF (2013) guidance.

Small mammals and birds

Concentrations of chlorine gas of 20ppm and 10ppm will reach a further distance from the point of release than high concentrations of the chemical. At optimum weather conditions for wind dispersion (i.e. 1.5F weather conditions) 20ppm would be detectable at distances as great as approximately 2.4km away and cover an area of 75ha if Scenario B4 or Scenario B5 were to occur; 10ppm would be detectable up to 4km away covering an area of approximately 150ha. By common standards, it is expected that all birds, bats and small mammals such as those from the order Rodentia that are unable to escape the area affected by 20ppm of chlorine gas will be killed. At WTW “A” suitable habitat for the following protected terrestrial species which have been recorded within 12km of the site in previous records is present in the 10ppm and 20ppm concentration zone include for example: hazel dormouse *Muscardinus avellanarius* (European Annex II protected species) and bat species (all European protected species), brown long-eared bat *Plecotus auritus*, noctule bat *Nyctalus noctula*, soprano pipistrelle *Pipistrellus pygmaeus*, western barbastelle *Barbastella barbastellus* (listed as near-threatened on the IUCN Red List).

All the protected bird species previously recorded that have the potential to be present in the 20ppm and 10ppm affected zone of chlorine gas could be affected should the accident in this scenario occur. There will be a certain level of avoidance of the plume by mobile animals, and given that both diurnal and nocturnal species will be present, i.e. bats that are active by night, and birds who are active by day, a high incidence of avoidance is likely.

Aquatic Environment

Liquid chlorine and drainage systems at the WTWs

Chlorine is stored as a liquid under pressure inside the bulk chlorine facility at WTW “A”. If failure of a chlorine drum causes a chlorine leak, the internal pressure of the chlorine drum will push the liquid chlorine out as a thin stream at about 30 kg/min (FESA, 2008). Most of the chlorine will flash boil and vaporise into the atmosphere creating a dense mist of entrained air and chlorine vapour (approximately 17% initially, FESA (2008)), but some escaping liquid chlorine may initially remain. The chlorine delivery area at the WTW has a collection pit dug underneath it, designed to collect and retain any liquid chlorine remaining after a spill. Therefore it is not likely that any liquid chlorine will enter the surface water drainage system at the WTW after an accidental drum spill outside. The underground pit will eventually be emptied as controlled waste under operational procedures at the WTW, but it is likely that the remaining chlorine liquid will continue to boil off at a rate at which heat can be drawn into it from surrounding heat sources (such as the air and the ground) and full vaporisation will occur before the pit is emptied.

Chlorine gas and the surrounding aquatic environment

Chlorine is a highly reactive gas that dissolves readily in water. Solubility decreases with salt strength and temperature (above 10°C). When chlorine is added to fresh water, partial hydrolysis will occur with the formation of hypochlorous acid (HOCl) and hydrochloric acid (HCl), i.e. equation (5)

$Cl_2 + H_20 \rightarrow HCl + HOCl.$ (5)

Hypochlorous acid can ionize to hydrogen ion (H+) and hypochlorite ion (OCl-), in ratios dependant on the pH of the water. Across the pH range typically found in freshwaters (6.5-7.2), the chlorine gas will hydrolyse after which hypochlorite will predominate and hypochlorous acid will also be present (US EPA, 1994). The ratio of these chemicals in water is also dependent on temperature, although this has a less pronounced impact than pH. Hypochlorous acid is more toxic than the hypochlorite ion. Consequently, across the pH range expected in the affected running waterbodies, chlorine is likely to be in its most toxic form.

Probability of freshwater habitat being affected

Three waterbodies have the potential to be affected by chlorine gas should any of the three scenario accidents in the bulk chlorine storage facility were to occur; the local stream to the south of the WTW, the local river and the reservoir to the north.

The model results suggest that an accidental chlorine release from the bulk chlorine storage facility at WTW “A” could result in clouds of chlorine of maximum 60ppm reaching both the local stream and the local river and 20ppm reaching the reservoir if Scenario B4 or Scenario B5 were to occur, given 1.5F weather conditions and optimum wind condition in the direction of these receptors. Approximately 500m of both water courses would be directly affected by the plume and a maximum area of 500m^2 of aquatic habitat at the reservoir. Under 1.5D or 5D conditions the chlorine gas will have dissipated before it reaches these freshwater habitats.

The chlorine plume reaching these rivers also depends on a given wind direction – in the case of the local river north of the WTW. We have looked at the probabilities for wind directions to occur to estimate the probability of the plumes affected the water bodies.

Adverse impacts on freshwater waterbodies

Zillich (1972) established that chlorine and the chemicals produced by its reaction with freshwater (i.e. hypochlorous acid, hypochlorite ion) are toxic to fish at a few hundredths of a milligram per litre (or a few micrograms per litre), which corresponds approximately to a few thousandths of a part per million. Other literature where laboratory tests have been conducted on the effect of chlorine products on freshwater organisms have all shown high mortality rates in concentrations no higher than 1ppm of chlorine (Sorokin et al., 2007). The predicted no-effect concentrations (PNEC) of chlorine in freshwater proposed under the Water Framework Directive is 0.04-0.05µg/l for long and short-term exposure (i.e. 0.008-0.01ppm).

Therefore it might be assumed that for concentrations of at least 60ppm to reach the watercourses, or 20ppm to reach the reservoir freshwater habitats as proposed by the model, a major accident is to be expected as this concentration is 100s of times higher than the proposed PNEC value and much higher than the toxicity levels in the laboratory tests. But it is not known at this stage what concentrations of hypochlorous acid and hypochlorite will be present in the water after the reaction with chlorine gas occurs at the water surface as the rates at which the products of the chemical reaction are produced at the water–air interface are unknown. There is no data available in current literature on this topic, although it is realistic to assume it will be lower than the concentration of the chlorine gas plume as products can reduce significantly after chemical reactions, and the products will continue to be diluted in the water column at the same time as it is transported downstream. It is also safe to assume that fish and small mammals are likely to employ some level of avoidance of toxic water should toxic compounds be present, so even at the worst case scenario, it is not expected that all aquatic biodiversity will be killed. This includes the following protected species which have been identified in the local river in previous records which have the potential to be present in the affected area: European eel *Anguilla anguilla* and brown trout *Salmo trutta* as well as the protected mammals water vole *Arvicola amphibious* and European otter *Lutra lutra*. Brown trout is present in the local stream also. Twenty-three fish species are listed for the reservoir including European eel, pike *Perca fluviatilis*, brown trout and common carp *Cyprinus carpio* -, water vole and European otter are also present.

Some mortality is expected amongst the smaller groups (such as plankton and macroinvertebrates) and small fish. But the effects of the toxic products resulting from the chlorine reactions in the water is considered to be temporary and short term and recolonisation from upstream reaches is expected to occur rapidly.

Table 4 provides a summary of the assessment for the different receptors under different scenarios. Table 5 - provides the different Harm severity levels (following CDOIF (2013) guidance) based on the severity level and duration categories assigned for each accident scenario.

Conclusions

This study constituted one of the first applying the new guidance issued by CDOIF in 2013. Following this approach, of the six potential unmitigated accidents which may result in a significant chlorine spill from storage at WTW "A", all have fallen into the 'Sub-MATTE' category, and are therefore not considered Major Accidents to the Environment.

The accident scenarios are therefore 'Broadly Acceptable' in terms of MATTE and can be screened out from further assessment at this stage. It is not necessary to consider what forms of mitigation are in place to further reduce the risk of the accident scenarios to be Tolerable if As Low As Reasonably Possible (TifALARP). This is the lowest risk category.

The study demonstrated the importance of designing, operating and maintaining sound tertiary and secondary containment as critical mitigation barriers for protection of the environment in the event of a loss of primary containment of chlorine.

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Table 4 - MATTE assessment for environmental receptors at WTW "A".

Receptor type	Example Receptor description	Accident scenario under which receptor will be affected	Accident scenario probability of occurrence[1]	Description of chlorine plume predicted effect	Significance[2]	Severity of Harm[2]	Duration term[2]	Harm/ duration category[2]	Tolerability Assessment[4] (Band)
Designated land/water sites (internationally important)	Reservoir SPA/Ramsar site	B4	3.7E-05	20ppm affecting ~50ha of the SPA/Ramsar	Severe (~50ha <10%)	2	Short-term (≤1 yr)	1	Sub-MATTE Harm (Sub-MATTE tolerability not considered by guidance)
		B5	4.0E-05	20ppm affecting ~9ha of the SPA/Ramsar	Severe (~9ha <10%)	2	Short-term (≤1 yr)	1	Sub-MATTE Harm (Sub-MATTE tolerability not considered by guidance)
Designated land/water sites (nationally important)	4 x SSSI: all designated for botanical interest.	B4 and B5	7.7E-05	10ppm	Significant (<0.5ha)	1	Short-term (≤1 yr)	1	Sub-MATTE Harm (Sub-MATTE tolerability not considered by guidance)
Widespread habitat – non-designated land (land/water)	Agricultural land surrounding the site	All scenarios	4.37E-04	10/20ppm	Not applicable due to low concentration of chlorine causing little effect				
		worst case B4 and B5	7.7E-05	worst case S2/S3 127ppm reaching 900m and 60ppm reaching 1500m)	Severe (contamination of 10-100ha of land preventing growing of crops/grazing of animals)	2	Short-term (≤3 yrs)	1	Sub-MATTE Harm (Sub-MATTE tolerability not considered by guidance)
Particular species	Large mammals surrounding the site - farming livestock and wildstock	All scenarios	4.37E-04	worst case S2 127ppm affecting 500m2 and 60ppm affecting 1km2.	Significant (<1% national population)	1	Short-term (≤3 yrs)	1	Sub-MATTE Harm (Sub-MATTE tolerability not considered by guidance)
		Worst case B4.	3.7E-05						
	Small mammals and birds	All scenarios	4.37E-04	worst case S2/S3 20ppm covering	Significant (<1% of	1	Short-term	1	Sub-MATTE Harm (Sub-MATTE tolerability not

Receptor type	Example Receptor description	Accident scenario under which receptor will be affected	Accident scenario probability of occurrence[1]	Description of chlorine plume predicted effect	Significance[2]	Severity of Harm[2]	Duration term[2]	Harm/ duration category[2]	Tolerability Assessment[4] (Band)
		Worst case B4 and B5	7.7E-05	0.75km2 and 10ppm 1.5km2	national population of 1 species affected)		(≤3 yrs)		considered by guidance)
Fresh and estuarine water habitats	Local stream and river	All scenarios	4.37E-04	Lesser effect S4/S5/S6 20ppm	Significant (no chemical or ecological long-term change to WFD status of the waterbody expected)	1	Short-term (≤1 yr)	1	Sub-MATTE Harm (Sub-MATTE tolerability not considered by guidance)
		Lesser effect D3/D4/D5	8.0E-04						
		Worst case B4 and B5	7.7E-05	Worst case S2/S3 60ppm					

1. Where more than one scenario has the potential to cause a MATTE the probability of occurrence is the cumulative frequency of these scenarios

2 - Following CDOIF (2013) Guidance (refer to tables 5 and 6)

Table 5 - Harm severity levels based on the severity level and duration categories assigned for each accident scenario

Severity of harm				
4	Sub-MATTE	C	D	D
3	Sub-MATTE	B	C	D
2	Sub-MATTE	A	B	C
1	Sub-MATTE	Sub-MATTE	Sub-MATTE	Sub-MATTE
Harm duration category	**1**	**2**	**3**	**4**

Source: CDOIF (2013) Guidance

Table 6 - Frequency at which the accident scenario is likely to occur

Harm severity level	**Frequency per receptor per establishment per year**	
	Intolerable	Broadly Acceptable
A	>1.0 E-02	<1.0 E-04
B	>1.0 E-03	<1.0 E-05
C	>1.0 E-04	<1.0 E-06
D	>1.0 E-05	<1.0 E-07

Source: CDOIF (2013) Guidance