



# **PERCHLORATE – RISKS TO UK DRINKING WATER SOURCES**

**WRC Ref: Defra 7845  
MARCH 2009**



## PERCHLORATE – RISKS TO UK DRINKING WATER SOURCES

Report No.: DEFRA 7845 (DWI70/2/218)  
Date: March 2009  
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The research was funded by the Department for Environment, Food and Rural Affairs (Defra) under project DWI70/2/218. The views expressed here are those of the authors and not necessarily those of the Department.

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## SUMMARY

### I OBJECTIVES

The general objectives of this project were (a) to review and assess any monitoring data currently undertaken regarding perchlorate in drinking water and its sources in the UK, (b) to establish the usage of perchlorate within England and Wales to identify any activity that may give rise to high environmental contamination, (c) to conduct a risk assessment to identify high and low risk drinking water sources (both public and private supplies) based on the usage pattern studies identified, (d) to devise and perform a one-year monitoring study of perchlorate at 20 sites of water used for drinking water (both public and private) across England and Wales, and (e) to identify possible implications for water supplies.

### II REASONS

Perchlorate has a well known historical use as a rocket fuel propellant, however, other more widespread uses include in fireworks, medicinal treatments and car airbags. It is also reported to occur naturally in saltpetre in areas of Chile and other countries and have natural atmospheric origins. Perchlorate may suppress the function of the thyroid, which can lead to a variety of adverse effects. Sensitive sub-populations are neonates, infants and pregnant mothers. Recent work has shown that perchlorate is a widespread contaminant in the United States of America (USA) and it is also emerging that it may be an environmental contaminant in other countries such as Japan, China and Korea (where it has been detected in both environmental and drinking waters).

### III CONCLUSIONS

- The review of monitoring data for perchlorate in the UK indicated that only minimal information was available; from a single set of data in a rural setting, there was no evidence of perchlorate in the raw, untreated drinking water. There has been no comprehensive monitoring of environmental waters or drinking water abstraction points near industrial sites or sites of historical commercial activity.
- A sensitive method for perchlorate analysis based on ion chromatography and tandem mass spectrometry has been developed and performance tested.
- The survey of levels of perchlorate indicated that it appears to be a general low level background contaminant of raw and treated drinking water in England and Wales. No discrete significant sources of contamination, for example through the use of rocket propellant, were identified, and these low levels may be the result of natural processes.
- Perchlorate was detected at three of the control low risk sites and at every higher-risk site during at least one of the four sampling sessions. Concentrations were comparable in each session and showed no obvious increase or decrease over the period of this study. No English or Welsh drinking water standards currently exist for perchlorate, and based on the levels found, none of the health-based values set by authoritative bodies would be exceeded.

- From the limited data, no apparent trends exist in relation to the time of year, the type of perceived higher-risk, the method of chlorination, the type of treatment, or any of the associated parameters measured (pH, chloride, alkalinity and nitrate).
- The conventional drinking water treatment processes involved did not show any signs of being able to remove perchlorate, though there was evidence that ion exchange (for nitrate removal) was effective at one site. Limited laboratory work identified hypochlorite as a potential source of trace quantities of perchlorate.

#### **IV RECOMMENDATIONS**

- To ensure awareness of any ongoing perchlorate monitoring undertaken by the Water Companies and other National Bodies in the UK.
- To monitor the situation in the USA with regard to the possibility of the Environmental Protection Agency (EPA) setting a drinking water standard for perchlorate.
- To further investigate the removal of perchlorate.
- To undertake a risk assessment of perchlorate specifically in the UK to determine whether there is a need for a health-based standard.

## 1. INTRODUCTION

### 1.1 Objectives

The general objectives of this project were (a) to review and assess any monitoring data currently undertaken regarding perchlorate in drinking water and its sources in the UK, (b) to establish the usage of perchlorate within England and Wales to identify any activity that may give rise to high environmental contamination, (c) to conduct a risk assessment to identify high and low risk drinking water sources (both public and private supplies) based on the usage pattern studies identified, (d) to devise and perform a one-year monitoring study of perchlorate at 20 sites of water used for drinking water (both public and private) across England and Wales, and (e) to identify possible implications for water supplies.

The project was carried out in three phases: firstly the review and assessment of the literature and usage; secondly, to develop a robust method; and thirdly, a survey of perchlorate in drinking water and source water.

### 1.2 Background

Perchlorate has a well known historical use as a rocket fuel propellant, however, other more widespread uses include in fireworks, medicinal treatments and car airbags. It is also reported to occur naturally in saltpetre in areas of Chile and other countries and have natural atmospheric origins. Perchlorate may suppress the function of the thyroid, which can lead to a variety of adverse effects. Sensitive sub-populations are neonates, infants and pregnant mothers. Current work has shown that perchlorate is a widespread contaminant in the United States of America (USA) and it is also emerging that it may be an environmental contaminant in other countries such as Japan, China and Korea (where it has been detected in both environmental and drinking waters).

The data on perchlorate contamination came originally from the USA, but there is increasing information from other countries. From the literature review, it is clear that minimal monitoring for perchlorate has been performed in England and Wales. Therefore, the need for a geographically-spaced initial scoping study to assess both raw and final drinking water using an accurate and robust analytical method was required. This report includes the afore-mentioned literature review, the approved method that was developed, and then details the monitoring study undertaken. The report concludes with a brief discussion of further research needs.



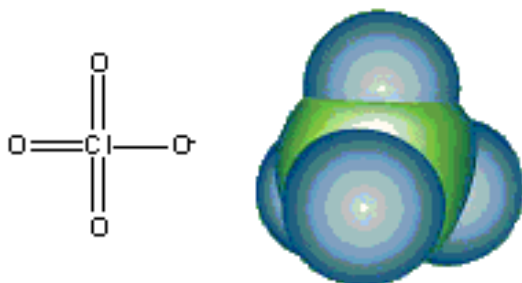
## 2. REVIEW OF CURRENTLY AVAILABLE MONITORING DATA FOR PERCHLORATE IN THE UK

This initial review was produced by Clare McLaughlin (née Atkinson), Simon Blake, Tom Hall and Paul Rumsby in February 2008, prior to the commencement of sampling, and has not been updated since. The findings of this review have been included in the broader conclusion of the overall work.

### 2.1 Introduction

#### 2.1.1 Background

Perchlorate is an anion which, when in the form of its various salts, has many uses. It is persistent in the environment due to its stable tetrahedral structure ([Figure 2.1](#) ~~Figure 2.1~~), and has high mobility in water (due to complete ionisation that occurs with the salts) (Crane *et al.*, 2005). Its long historical use (as ammonium and potassium perchlorate) in the USA as a rocket propellant and its physicochemical properties have led to severe contamination of surface and groundwaters, and subsequently contamination of drinking water.



**Figure 2.1** The 2D and 3D structures of perchlorate

Although the production of perchlorate salts started in the mid-1940s in the USA (US EPA, 2005a; SWRCB, 2005), it was not until 1997 that it was discovered to be a relatively widespread contaminant of US surface waters (Urbansky *et al.*, 2001). It has been detected in at least 35 states (Sturchio *et al.*, 2007). Therefore, it was subsequently added to the US Environmental Protection Agency (US EPA) Contaminant Candidate List (CCL) for drinking water.

Although it is a widespread contaminant, a preliminary risk assessment from the Environment Agency of England and Wales (EA) indicates that the perchlorate anion is unlikely to meet the screening criteria for a PBT (persistent, bioaccumulative and toxic) substance (EA, unknown).

## 2.1.2 Effects on Human Health

### Pharmacokinetics

Perchlorate is readily absorbed following oral and inhaled exposures (INM, 2006). It then remains in the blood and is distributed throughout the body, but primarily to the thyroid and mammary glands (INM, 2006). It is not metabolised (INM, 2006; Wolff, 1998). Rapid excretion via urine occurs; it has been detected in urine 10-15 minutes after oral dosing and it has been reported that 95% of an oral dose of 784 mg sodium perchlorate was excreted after 48 hours (INM, 2006; US EPA, 2002). A half-life of 8 hours for a dose of 0.5 mg/kg bw/day to healthy adults is also reported (INM, 2006).

### Thyroid Effects

The primary toxic effect of perchlorate is that it can lead to suppression of the functions of the thyroid – it competitively binds to the sodium iodide symporter (NIS) on the basolateral membrane of the thyroid (the NIS is also present in the mammary gland) (INM, 2006). This acts to inhibit the uptake of iodide, which is required for the synthesis of the thyroid hormones, of which the two predominant ones are thyroxine, T4, and triiodothyronine, T3 (Crane *et al.*, 2005; Wolff, 1998). This inhibition is relatively short-lived, as shown by daily dosing being required for its pharmaceutical use as a suppressor of thyroid hormones (Wolff, 1998). Although not currently fully understood, perchlorate also stimulates the expulsion of iodide from the thyroid (Crane *et al.*, 2005). The thyroid, via the thyroid hormones, has a vital role in controlling metabolism and has key roles in foetal and neonatal neurodevelopment (Dasgupta *et al.*, 2006; SWRCB, 2005). These hormones “regulate metabolic activity, affect the function of virtually every organ system and are required for normal central nervous system development and skeletal growth in foetuses and infants” (NRC, 2005). Therefore, particularly sensitive sub-populations to these effects include neonates, infants, women of child bearing age and pregnant mothers (Dasgupta *et al.*, 2006). This effect also occurs from exposure to other water contaminants, chlorate and nitrate, although they are less potent than perchlorate (Snyder *et al.*, 2006).

However, inhibition of iodide uptake by the thyroid is not necessarily considered to be an adverse effect. This is because the thyroid is regulated under a homeostatic mechanism and so can adjust to iodide fluctuations, especially in response to ingestion of nitrates and thiocyanates (from vegetables and meat, and vegetables and milk, respectively), which also inhibit iodide uptake (Snyder *et al.*, 2006). It has been reported that perchlorate can inhibit the uptake of iodine, but not affect the production of thyroid hormones (INM, 2006). In healthy individuals, it has been stated that the thyroid would have to be inhibited by 75% or more for months for adverse effects to occur (NRC, 2005).

### Other Toxic Effects

Perchlorate is of low to moderate acute oral toxicity to experimental animals; oral LD50s for ammonium perchlorate and sodium perchlorate range from 1900-4200 mg/kg bw in mice, rats, guinea pigs and rabbits (TERA, 2002). Symptoms in experimental animals from high acute exposure include respiratory difficulty, decreased body temperature, convulsions and coma (TERA, 2002). It is reported that experimental animal studies have identified few signs of

toxicity (Wolff, 1998). However, perchlorate can cross the placenta and can affect the thyroid of the foetus (Wolff, 1998).

Limited data are available on the acute toxicity in humans, however, symptoms are reported to be severe gastrointestinal pain, vomiting, diarrhoea and possible respiratory distress (INM, 2006). The lethal dose is approximately 15 g (250 mg/kg bw based on a 60 kg adult) (INM, 2006). Perchloric acid is corrosive to skin and mucous membranes (Clark *et al.*, 2004). Ammonium perchlorate is not genotoxic (US EPA, 2002).

Several chronic studies have been performed with perchlorate in healthy human volunteers owing to its clinical use. All effects observed are thyroid-related due to the inhibition of the NIS that occurs.

Side effects from its clinical use include nausea, gastritis, rashes, occasional thyroid enlargement and leukopenia, however, these only occurred in a small percentage of the volunteers (Wolff, 1998). For instance, "minor side effects" (rashes, fever, lymphadenopathy and nausea) are reported to have occurred in approximately 10% of cases, agranulocytosis (insufficient white blood cells) occurred in 1% of cases, and the most severe, aplastic anaemia (inability to produce red blood cells), occurred with a low incidence (Wolff, 1998). However, when doses increased to 1200-2000 mg/day (20-33 mg/kg bw/day based on a 60 kg adult), incidences of the minor side effects increased to 16-18% (Wolff, 1998). The cases of aplastic anaemia and agranulocytosis led to the use of perchlorate to treat hyperthyroidism/Graves disease being stopped in the 1960s (INM, 2006).

### Authoritative Evaluations

In 2003, the Toxicology Excellence for Risk Assessment (TERA) evaluated the epidemiological evidence for perchlorate exposure in humans. Based on a No-Observed-Adverse-Effect-Level (NOAEL)<sup>1</sup> of 6 µg/kg bw/day for decreases in the serum concentrations of the thyroid hormone, thyroxine (T<sub>4</sub>)<sup>2</sup> in children, an oral reference dose (RfD)<sup>3</sup> of 2 µg/kg bw/day was derived by application of an uncertainty factor of 3 to account for intraspecies variation (TERA, 2003).

In 2005, the US EPA Integrated Risk Information System (IRIS) set an oral RfD for perchlorate and perchlorate salts of 0.7 µg/kg bw/day (IRIS, 2005), which is also the RfD derived by the US National Academy of Science (NAS) (INM, 2006). This was based on a 2 week study in human volunteers who orally ingested 4 doses of 100 ml potassium perchlorate solutions at doses of 0, 7, 20, 100 or 500 µg perchlorate/kg bw/day. Thyroid uptake of radioactive iodide was examined at 8 and 24 hours after administration of the radioactive iodide, on days 2 and 14 of perchlorate administration and 15 days after cessation of the dosing. A No-Observed-

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<sup>1</sup> No-Observed-Adverse-Effect-Level (NOAEL): the highest dose of a material in a toxicity test that has no statistically significant adverse effects on the exposed population compared to the controls.

<sup>2</sup> Thyroxine, tetraiodothyronine (T<sub>4</sub>): the major hormone secreted by the follicular cells of the thyroid gland. It is involved in controlling the rate of metabolic processes in the body and influencing physical development.

<sup>3</sup> Oral reference dose (RfD): an estimate of the daily oral exposure to the human population that is likely to be without an appreciable risk of deleterious effect during a lifetime; derived from a NOAEL or Lowest-Observed-Adverse-Effect-Level (LOAEL).

Effect-Level (NOEL)<sup>4</sup> for inhibition of thyroid iodide uptake was identified to be 7 µg/kg bw/day. An uncertainty factor of 10 to account for intraspecies variation and to protect the most sensitive population (the foetuses of pregnant women, who might have hypothyroidism or iodide deficiency) was applied to the NOEL to derive the RfD. Using this RfD, a Drinking Water Equivalent Level (DWEL) of 24.5 µg/l was also derived (US EPA, 2005b). This was based on a 70 kg adult drinking 2 litres of water a day. The DWEL assumes all of the perchlorate comes from drinking water and is the concentration in drinking water that will have no adverse effects with a margin of safety included<sup>5</sup>.

Also in 2005, the US Agency for Toxic Substances and Disease Registry (ATSDR) derived a chronic (>365 days) Minimum Risk Level (MRL) for perchlorate of 0.7 µg/kg bw/day (ATSDR, 2005). This was based on the same derivation as the IRIS RfD described above.

No national drinking water standards currently exist for perchlorate in the European Union (EU), USA, Canada or Australia, nor is there a guideline set by the World Health Organization, however, various US states have set their own limits (see [Table 2.1](#) ~~Table 2.1~~). No information was located as to their derivations and it is not clear what analytical methods and Limit of Detections (LODs) are suggested to be used to maintain or enforce these limits. Although perchlorate features on the US Contaminant Candidate List (CCL), the US EPA are awaiting further characterisation of the amount of perchlorate in food before they set any drinking water standards (US EPA, 2006).

**Table 2.1 US state limits for perchlorate in drinking water (INM, 2006; MassDEP, 2007)**

State	Limit (µg/l)	Limit Type
Arizona	14	Health based guidance level
California	4	Action level
	6	Public health goal (MCL)
Massachusetts	2	MCL
Nevada	18	State provisional action level
New York	5	Drinking water planning level
	18	Public notification level
New Mexico	1	Interim groundwater screening level
Texas	4	Drinking water action level
	4	Residential groundwater cleanup level
	7 or 10	Industrial/Commercial groundwater cleanup level *

\* Depending on whether the site falls under the old or new Risk Reduction Program.

At the present time, perchlorate is not regulated by means of a standard, nor are there specific parameters for the purpose of routine monitoring of drinking water under the Water Supply (Water Quality) Regulations 2000 (2001 in Wales). However, the presence (if any) of perchlorate in drinking water is regulated in England and Wales through the catch-all

<sup>4</sup> No-Observed-Effect-Level (NOEL): the highest dose of a material in a toxicity test that has no statistically significant effects on the exposed population compared to the controls.

<sup>5</sup> This value was revised by the United States Environmental Protection Agency in January 2009 to give an interim sub-chronic Health Advisory value of 15 µg/l (see Section 6.3.5 for details).



requirement for drinking water to be wholesome, meaning that it may not contain any substance at a level that would constitute a potential danger to human health.

### **2.1.3 Health-Based Guidelines**

In light of the currently available data, it is apparent that use of the 2005 US EPA IRIS oral RfD of 0.7 µg/kg bw/day (IRIS, 2005) as a health-based guideline is appropriate. For water-specific incidents, the US EPA DWEL of 24.5 µg/l (US EPA, 2005b) can also be referred to.

However, conservative Suggested-No-Adverse-Response-Levels (SNARLs) can also be derived. These are unique to the National Centre of Environmental Toxicology (NCET) at WRc plc and are estimates of the concentration of a chemical in drinking water considered to be of no significant concern to human health with consumption over defined short-term exposure periods such as might be seen in a drinking water contamination incident. SNARLs are derived for the UK water industry as part of the UKWIR Toxicity Advisory Service. Based on the US EPA RfD of 0.7 µg/kg bw/day and assuming a 60 kg adult drinks 2 litres of water a day, health-based SNARLs can be derived as follows:

24 hour SNARL allocating 100% of the RfD to water = 21 µg/l

7 day SNARL allocating 50% of the RfD to water = 11 µg/l (rounded)

## **2.2 UK Data Collection Approach**

The possible presence of perchlorate in drinking water and its sources is due to its widespread use in explosive compounds (including fireworks), other industrial uses and its natural occurrence. Therefore, initial searches were performed using the standard publicly available data sources and search engines to gain an overview of any current data. The search was expanded by contacting all UK water companies to establish whether they had monitoring data available. In addition, owing to the potential threat of perchlorate to the environment, the Environment Agency may also have undertaken some monitoring; therefore they were also contacted. To gain an understanding of the analytical methods used, the laboratories that conducted any such analysis were also contacted to request details of their methods<sup>6</sup>.

### **2.2.1 Publicly-Available Sources**

Searches were performed in the following websites: PubMed; Science Direct; Environment Agency; and Google, using the keywords listed in [Figure 2.2](#)~~Figure 2.2~~.

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<sup>6</sup> Laboratory names are held in confidence.

Perchlorate	Groundwater	Concentration	Fireworks	UK
Monitoring data	Data	Borehole	Water	England
Northern Ireland	Wales	Scotland		

**Figure 2.2 Keywords used to search for publicly-available data**

### 2.2.2 Water Companies

Contact was made with UK and Channel Islands water companies to request monitoring data for perchlorate, as well as details of the analytical method employed. Monitoring data was available from 1 out of 30 organisations approached.

### 2.2.3 Environment Agency

The Environment Agency was contacted as to whether they had any information or monitoring data on perchlorate and its compounds.

### 2.2.4 Drinking Water Inspectorate

The Drinking Water Inspectorate were asked whether they had performed any monitoring of perchlorate or whether they had access to any other literature (information or monitoring data) not in the public domain on perchlorate and its compounds.

## 2.3 Consolidated UK Available Data

Only two sets of perchlorate data and details of the analytical methods used were identified from the publicly available data search, all UK water companies, the EA and the DWI. Data were available from a water undertaker and a Defence Science and Technology Laboratory (Dstl) study.

### 2.3.1 Publicly-Available Data

No drinking water concentrations (raw or finished waters from drinking water treatment plants, or indeed any surface water) of perchlorate were identified from the UK following the publicly available data search.

### 2.3.2 Water Undertaker 1

#### Data Available

Following a suggested link between perchlorate exposure from drinking water and adverse thyroid effects made by a local health officer in a rural area with a low population, 92 sites

within the catchment of Water Undertaker 1 were monitored for perchlorate. The sampled sites comprised treated drinking water distribution sites, as well as raw water samples from several drinking water treatment works (WTWs). There was no detection of any significant concentrations of perchlorate at any site.

The sampling period ranged from late November 2006 until mid January 2007. The majority of sites were only sampled once, however, the WTWs were sampled up to 16 different times. All, but two, samples were  $<1 \mu\text{g/l}$  (the Limit of Detection, LOD). The exceptions were raw water samples from two WTWs at concentrations of 1.1 and 1.0  $\mu\text{g/l}$ , respectively. However, as these values are very close to the LOD, it can be concluded that these results do not signify a local presence of perchlorate. Although it appears that no final waters from the WTWs were sampled, perchlorate was not identified from any of the drinking water sites within the two distribution networks.

### **Analysis Method**

The analysis used to obtain the results provided by Water Undertaker 1 was performed by Laboratory A<sup>7</sup>. The method provided uses direct sample injection LCMS - a variation of a recognised technique for the determination of perchlorate at low levels in waters. The LOD quoted (1  $\mu\text{g/l}$ ) seems better than would be anticipated for the procedure / equipment used, even though the method has not been fully validated having been specifically developed for this study.

The documented procedure provided by Laboratory A identifies key activities to be undertaken, but these primarily refer to additional documents not provided within this specification (e.g. the preparation of AQC standards is included, but the procedure for the recording / interpretation of the AQC data (control charts, etc.) is documented elsewhere). However, the laboratory has UKAS accreditation, but not for the determinand, and this would suggest these procedures are sound.

Minimal data are available on AQC and performance for method validation, although the summary table data provided indicates availability of further data.

Preservation procedures and times are documented, but no evidence is provided of sample stability.

### **Conclusion**

The very localised sampling undertaken by Water Undertaker 1 indicates that perchlorate is not present as a background contaminant in these rural areas; all but two of the levels were below the limit of detection of 1  $\mu\text{g/l}$ . The two exceptions (1.1 and 1.0  $\mu\text{g/l}$ ) were at, or very close to, the limit of detection, so are also considered to be of no concern.

It is understood that the analytical procedure was developed specifically for this study and not put through the routine method development procedure, and as such has not been fully validated. However, there appears to be some inconsistencies in the calibration standards and AQC solutions preparation.

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<sup>7</sup> Laboratory names have been held in confidence.

### 2.3.3 Environment Agency

No monitoring regarding perchlorate has been undertaken by the EA in the UK. However, a draft report entitled 'Priorisation of perchlorates for environmental risk assessment' has been released (EA, unknown). This details the uses of perchlorate compounds (see Section 2.5), but it does not include any UK monitoring data.

### 2.3.4 Drinking Water Inspectorate

The Drinking Water Inspectorate (DWI) has not performed any monitoring of perchlorate within the UK. However, they were able to provide copies of two reports that were in the 'grey' literature. The Institute of Naval Medicine report (INM, 2006) comprises a toxicology review of perchlorate, but does not contain any monitoring data. The Defence Science and Technology Laboratory (Dstl) (2007) report (prepared for the Ministry of Defence) includes information on uses of perchlorate and its environmental fate (including monitoring of ground and surface water) at one military range. These monitoring data are reviewed below, while other information is included elsewhere in this review.

## Defence Science and Technology Monitoring

### 1. Data Available

Although the UK has a number of weapons that use perchlorate, no monitoring of firing/disposal areas has previously been done, therefore, this work was undertaken to fill this data gap (Dstl, 2007). A literature review conducted before monitoring concluded that the demolition and disposal of munitions was the source most likely to result in perchlorate contamination of the environment. The primary UK site for this is at Foulness Island near Shoeburyness, off the coast of Essex. Therefore, the monitoring was focussed on this area. This site has been in operation for 140 years and is used to test, trial and dispose of weapons and munitions for the Ministry of Defence. Of the four disposal areas that were known to be used to dispose of rocket motors since 1993, the site 'X3' was chosen for monitoring. At this site, since 1993, 6 rocket motors have been destroyed employing both the open detonation and open burn methods. These equate to 14.5 tonnes of propellant containing ammonium perchlorate. It is not known when the last rocket motor was destroyed.

The area of land is flat and puddles of what were assumed to be rainwater were noted. The demolition pits were also reported to be filled with water (assumed by the authors to be rainwater). The site is underlain by quaternary marine and estuarine alluvial deposits, which are comprised of various sand and gravel units. The alluvial deposits are then directly underlain by the London Clay, which is a grey to dark brown, firm to stiff, fissured, slightly sandy-silty clay, with some gravel and thin laminations and pockets of grey silt. The London Clay is approximately 14 to 22 m below ground level and approximately 125 m thick. Owing to the nature of the alluvial deposits, and the fact that the London Clay is present underneath, any surface water present on the site would potentially leach into the groundwater and remain above the London Clay. Although the London Clay is stated to be fissured, it is unlikely that these will permeate the entire thickness of the clay.

Samples of surface water, groundwater, soil and ash were taken on 23<sup>rd</sup> February 2007. Locations included the demolition pits/cages, areas immediately adjacent to them and areas

at varying distances away. The analysis was undertaken at Laboratory B<sup>8</sup> using ion chromatography, which resulted in Limits of Detections (LODs) of 4 µg/l and 1 mg/kg for water and soil, respectively. The environmental background level of perchlorate was deemed to be less than the LODs. Soil concentrations ranged from <1.0 mg/kg (LOD) to a maximum value of 4.5 mg/kg, although the majority were below the LOD. Groundwater concentrations were 90-17 367 µg/l (only 4 samples were taken). It is interesting to note that the two sites furthest away from the cages/trays (approximately 30 m north west of the cages/trays) had greater concentrations (17000 and 5600 µg/l) than the two closer sites (approximately 15 m northwest of the cages/trays at 830 and 93 µg/l). This could indicate perhaps the flow of groundwater in a north-westerly direction, and also the fact that the cages/trays are not used continuously. However, the depths at which the samples were taken were not specified, which may also have some influence on concentrations. Surface water concentrations ranged from 4 µg/l (in a drainage ditch, the furthest point from the demolition/burning area, approximately 460 m away), to 2500 µg/l at a site approximately 280 m away, and to 150 000 µg/l (in one of the burning pits). Surface water samples were taken from around the cages/pits, but again showed contamination occurring in a north-westerly direction. Samples of ash were taken from inside the burning cages and trays and contained levels of 1.1-2.8 mg/kg and <1-1.1 mg/kg, respectively.

## **2. Analysis Method**

The analytical method used was based on the United States Environmental Protection Agency (US EPA) Method 314, using ion chromatography. Column and guard column set Dionex AS20, large volume injection of 900 µl, isocratic hydroxide based eluent and conductivity detection were used.

Water samples were cleaned up on an Ag/Ba/H cartridge to remove chloride and sulphate prior to injection. This had a reporting limit of 4 µg/l. In soil, a 25-50 µl injection of a 2:1 soil:water extract was used, which gave a reporting limit of 1 mg/kg.

## **3. Conclusion**

These results illustrate that perchlorate will migrate to groundwater, and because of this, the authors identified that it would be beneficial to monitor any drinking water abstraction points within the area. It is also apparent that disposal by detonation is more likely to cause significant release than disposal by burning. The authors state that they expect significantly less perchlorate to be released from firing ranges as compared to disposal areas. Levels found in groundwater on site are very high, but the level in the ditch furthest from the site of <LOD suggests that contamination is localised.

The US EPA Method 314 can be subject to matrix interferences, especially in the presence of high amounts of other anions, and claims (in the literature) an LOD of 4 µg/l. A modified version of the 314 method was published in 2005 (314.1), which uses preconcentration and cleanup prior to analysis, which reduces these effects and improves the method performance.

Method performance will be operator and equipment dependent and the LOD quoted by Dstl for the direct analysis with removal of major ions is not unreasonable if somewhat higher than the published version. The modified preconcentration approach yields an LOD in line with the best that can be expected for IC analysis. The EPA method 314 is a recognised standard procedure for perchlorate if now somewhat dated.

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<sup>8</sup> Laboratory names have been held in confidence.

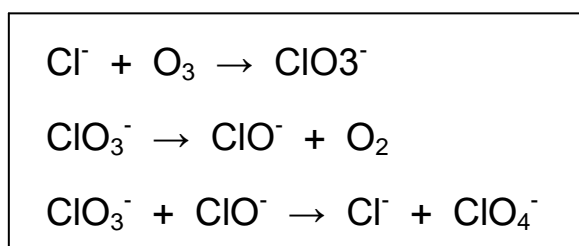
Newer methods using LCMSMS or ICMSMS are free from such interferences and can provide sub 0.1 µg/l detection limits, but are more costly both in terms of capital and running costs.

## 2.4 Discussion on Worldwide Occurrence and Uses

Perchlorate and its salts have a wide variety of uses (see [Table 2.4](#)) and have been detected across the world.

### 2.4.1 Occurrences

Three main sources of perchlorate in the environment have been stated, which relate to its use as an oxidiser (including rocket propellant), its presence in Chilean nitrate fertiliser (from saltpetre; imported into the USA for >100 years; no information was located as to whether they have ever been imported into the UK), and natural occurrence (it is thought to be formed in the atmosphere by the effect of ozone (see [Figure 2.3](#)), and lightning striking sodium chloride aerosols) (Dasgupta *et al.*, 2006). The source strengths for the latter two were estimated to be 0.75 and 0.13-0.64 Gg/year (approximately 750 and 130-640 tonnes/year), respectively, in the USA (Dasgupta *et al.*, 2006). Rajagopalan *et al.* (2006) have suggested that the widespread perchlorate contamination in groundwater from an area of 155 000 km<sup>2</sup> in northwest Texas and eastern New Mexico (typical levels are <4 µg/l, although some up to 200 µg/l have been reported) is due to long-term atmospheric deposition (and not Chilean nitrate fertiliser or industrial releases). They also report that perchlorate occurs in a nitrate deposit in California, potash minerals (impure form of potassium carbonate) and in other evaporates (mineral sediments resulting from evaporation) in California and New Mexico, and it has been detected in atmospheric aerosols and precipitation. Chilean nitrate, langbenite (a naturally occurring mineral), potash and phosphate rock contain perchlorate at 3.64%, 1.86%, <0.5% and <0.5%, respectively (INM, 2006).



**Figure 2.3 The presumed reaction pathway of the formation of perchlorate from the effect of ozone in the atmosphere**

Perchlorate in wet deposition (e.g. snow and rain) is reported to be <0.005 µg/l (LOD) - 0.105 µg/l (mean 0.015 µg/l) (Dasgupta *et al.*, 2006). It is emerging that analysis of the stable isotope ratios of oxygen and chlorine in perchlorate samples can be used to differentiate between natural and anthropogenic sources (Sturchio *et al.*, 2006), thereby strengthening the belief held by some that perchlorate can occur naturally. Additionally, Plummer *et al.* (2006) have detected perchlorate at levels of 0.12-1.8 µg/l in groundwater from remote parts of the Middle Rio Grande Basin in north-central New Mexico, which they conclude to be of natural sources, of which some might have atmospheric origins. Perchlorate formation in other arid geological ecosystems and in rain has also been reported (SWRCB, 2005). Natural occurrence of perchlorate in the atmosphere is thought to be due to reactions

of chloride in the atmosphere with ozone (Dstl, 2007; Dasgupta *et al.*, 2006). Whether this has any implications for drinking water treatment operations that employ ozone is unknown, but it is thought unlikely. Chloride may originate from the sodium chloride that has evaporated from the sea, or from chloride compounds that have been blown from the land (Dstl, 2007). Perchlorate may then be concentrated into geological formations following wet deposition and where it is left behind from evaporation (Dstl, 2007). The natural occurrence is supported by the widespread presence of microorganisms that can biodegrade it, which has been known about for >70 years (Dstl, 2007). Such bacteria are ubiquitous and have been detected in pristine and contaminated soils, sediments, sludge and lagoons (Dstl, 2007).

Perchlorate has been detected in some dietary supplements (non-detectable to 2.4 µg/g) and flavour enhancing ingredients in the USA (Snyder *et al.*, 2006). Of these, the source of perchlorate in dietary supplements is due to its occurrence in the seaweed, kelp, which is used as the source of iodine (Snyder *et al.*, 2006). Concentrations in kelp and seawater have been reported to be 77-3200 µg/kg and <0.07-0.345 µg/l, respectively (Snyder *et al.*, 2006). Concentrations in various types of US dietary supplements are as follows: prenatal <0.0032 (LOD)-2.420 µg/g; children <0.004 (LOD)-0.024 µg/g; women <0.0031 (LOD)-0.029 µg/g; and general <0.0035 (LOD)-0.320 µg/g (Snyder *et al.*, 2006). Out of the 31 tablet types, perchlorate was detected in 20, with concentrations of 0.010-2.420 µg/g, which (if recommendations on containers were followed) equates to daily oral doses of 0.03-18 µg/day. Of the four flavour enhancing ingredients analysed, only kelp granule product (the other three were salts) contained perchlorate, with a concentration of 0.725 µg/g. Again, if recommended servings were followed, this equates to 2.2 µg perchlorate/serving.

## 2.4.2 Uses

### Production

The methods used to produce perchlorate salts are based on the production of sodium perchlorate (EA, unknown):

- Sodium perchlorate: electrolysis of sodium chloride (the chloride ion (Cl<sup>-</sup>) is oxidised to hypochlorite (ClO<sup>-</sup>), chlorite (ClO<sub>2</sub><sup>-</sup>), chlorate (ClO<sub>3</sub><sup>-</sup>) and perchlorate (ClO<sub>4</sub><sup>-</sup>)), or the Merck process that electrochemically oxidises chlorine to produce perchloric acid.
- Ammonium perchlorate: reaction of sodium perchlorate with ammonia.
- Potassium perchlorate: reaction of sodium perchlorate with potassium chloride.

After all of the above reactions, crystals of perchlorate are then precipitated from the solutions and dried (CDTSC, 2007).

### UK/Europe

#### 1. General Uses

The primary uses of perchlorate and its compounds in the UK and EU are associated with their oxidising ability (they decompose on heating to form chlorine, chlorates and oxygen gases) (EA, unknown). Therefore, primary uses of ammonium and potassium perchlorate

include as oxidising agents in propellants for rocket motors and munitions, fuses, smoke generators, explosives, air bag gas generators, fireworks, flares and oxygen generating systems (INM, 2006; EA, unknown). Other uses of perchlorate are as follows: tanning, electroplating, aluminium refinishing; as a heat stabiliser during PVC processing (INM, 2006); in manufacturing processes; commercial blasting for construction; commercial manufacture of perchlorate salts or perchlorate containing items (e.g. pyrotechnics and flares) (Dstl, 2007); and drying agents, etching agents, temporary adhesives, and batteries (EA, unknown). However, as the majority of uses are industrial, any releases are thought to be very localised (EA, unknown).

Owing to the use of perchlorate as a heat stabiliser in PVC processing and subsequent migration from packaging into food, an EU limit of 50 µg/kg food has been reported by the Scientific Committee on Food for sodium perchlorate monohydrate (SCF, 2002).

From the EU ESIS (European chemical Substance Information System) database (which contains chemicals listed in EINECs, the European Inventory of Existing Commercial chemical Substances), it appears that out of the 112 'perchlorates' or 'perchloric' acid compounds listed, only four are used in large quantities in the UK or EU (EA, unknown):

**2. Ammonium perchlorate (CAS RN 7790-98-9):**

- A High Production Volume Chemical (HPVC), i.e. it is produced in the EU or imported into the EU by a company in amounts  $\geq 1000$  tonnes/year.
- Primary uses in the EU include as an oxidising agent in rocket and jet propellants and pyrotechnics, in analytical chemistry, and in etching and engraving.
- Named producers/importers in the EU are FiatAvio BPD in Italy and SNPE in France; for both of these companies it is not known whether there are any associated sites in the UK.

**3. Potassium perchlorate (CAS RN 7778-74-7):**

- A Low Production Volume Chemical (LPVC), i.e. it is produced in the EU or imported into the EU by a company in amounts  $>10$  tonnes/year, but  $<1000$  tonnes/year.
- Primary uses in the EU include as an oxidising agent in explosives, pyrotechnics, solid rocket propellants, photography, flares and chemical reagents.
- The named producer/importer in the EU is Deutsche Sinochem GMBH, Germany; it is not known whether there are any associated sites in the UK.

**4. Sodium perchlorate (CAS RN 7601-89-0):**

- A High Production Volume Chemical (HPVC), i.e. it is produced in the EU or imported into the EU by a company in amounts  $\geq 1000$  tonnes/year.
- Primary uses in the EU include as a starting material for the manufacture of other perchlorates (i.e. ammonium perchlorate and potassium perchlorate), as an oxidising agent in explosives, in rocket fuel/propellants, as an analytical reagent, in explosive emulsions, in slurries and in electrometallurgy.
- The named producer/importer in the EU is Arkema, France, which does not have any sites in the UK.

**5. Perchloric acid (CAS RN 7601-90-3):**

- A Low Production Volume Chemical (LPVC), i.e. it is produced in the EU or imported into the EU by a company in amounts  $>10$  tonnes/year, but  $<1000$  tonnes/year.
- Primary uses in the EU include as a laboratory chemical (especially an analytical reagent) (supplied in small amounts,  $\leq 22$  litres, but widespread), a catalyst, in the



manufacture of various esters, as an ingredient in bath deposition of lead, in electropolishing and in explosives.

- The named producer/importer in the EU is Merck KGaA, Germany; it is not known whether there are any associated sites in the UK.
- Merck supplies various grades and volumes of perchloric acid, which are available in 250 ml bottles, 1 litre bottles, 2.5 litre bottles and 22 litre bottles and carboys.

Merck also supplies other perchlorate salts in the following amounts (EA, unknown):

- Barium perchlorate in 250 g amounts, 1 kg amounts and 1 litre bottles.
- Holmium perchlorate in 100 ml bottles.
- Magnesium perchlorate hydrate in 100 g amounts and 500 g amounts.
- Potassium perchlorate in 250 g amounts and 1 kg amounts.
- Sodium perchlorate monohydrate in 100 g amounts, 500 g amounts and 50 kg drums.

The Environment Agency (EA) states that of the remaining 108 other 'perchlorates' or 'perchloric' acid compounds, most are supplied as laboratory scale chemicals for research purposes (supplied in packaging at <<1 kg), so their use and any subsequent release to the environment is probably negligible (EA, unknown). Main uses of these 108 compounds are, however, stated to be the following: metal perchlorate salts used as laboratory chemicals, e.g. in synthesis as analytical reagents; 'alkyl' perchlorate salts; and 'complex aromatic' perchlorate salts, used primarily as fluorescent dyes/laser dyes (EA, unknown). Some other perchlorate compounds have been identified as their uses are similar to those of the 'main' perchlorate compounds (see [Table 2.2](#) for their uses). However, uses for the full 112 compounds identified in ESIS are listed in the EA report (EA, unknown). Although the EA was contacted as to the quantities of perchlorate compound used in each of the uses specified above, no information was forthcoming.

Honda and the European Automobile Manufacturer's Association (ACEA) have been contacted to ascertain whether perchlorate is used in the airbags in vehicles, and if so, any further information (e.g. quantities, etc.), however, no information has been forthcoming.

**Table 2.2 Uses of perchlorate compounds (not HPV/LPV compounds)  
(EA, unknown)**

Compound	CAS RN	Uses
Lithium perchlorate	7791-03-9	Solid rocket propellant. As an electrolyte salt for lithium batteries.
Magnesium perchlorate	10034-81-8	Drying agent for gases (as anhydrous/dehydrate). Batteries.
Barium perchlorate	13465-95-7	Manufacture of explosives. Experimentally in rocket fuels.
Calcium perchlorate	13477-36-6	Present in some US products for chlorination treatment of swimming pool/spa water (e.g. Sani-clor shock treatment, classed as an inorganic hypochlorite, percentage of calcium perchlorate unspecified (Hasa, 2001)).
Caesium perchlorate	13454-84-7	Optics. Catalysts. Speciality glasses. Power generation (possibly nuclear power plants?).
Hydrazine perchlorate	Unknown	Rocket propellant.
Hydroxylammonium perchlorate	15588-62-2	Explosives.
Lead diperchlorate	13637-76-8	Batteries (not clear if current or historic). Accumulators (not clear if current or historic). Microelectronics (not clear if current or historic).
Nitronium perchlorate	Unknown	Rocket propellant oxidisers.
Silver perchlorate	7783-93-9	Manufacture explosive compositions.
Strontium perchlorate	13450-97-0	Pyrotechnics.
'Alkyl' perchlorates: tetrabutylammonium perchlorate tetraethylammonium perchlorate tetrahexylammonium perchlorate	1923-70-2 2567-83-1 4656-81-9	Primary uses as laboratory chemicals, but also electrolytes/electrochemical reagents for electroanalytical methods (i.e. polarographic and voltammetric methods) and other electrochemical methods.
'Aromatic' perchlorate dyes	-	Fluorescent dyes used in lasers, small quantities, they are supplied in amounts of a few hundred µg's to a few g's.

### Military Uses

Under the European Union Code of Conduct on Arms Export (EU, 2007), the following perchlorate compounds are listed, which would imply their use in Member States for various military uses:

1. BNCP (cis-bis (5-nitrotetrazolato) tetra amine-cobalt (III) perchlorate) as an 'explosive' under the 'energetic material and related substances' heading.
2. CP (2-(5-cyanotetrazolato) penta amine-cobalt (III) perchlorate) as an 'explosive' under the 'energetic material and related substances' heading.
3. Perchlorates composited with powdered metal or other high energy fuel components as a 'pyrotechnic, fuel and related substance' under the 'energetic material and related substances' heading.
4. Ammonium perchlorate as an 'oxidiser' under the 'energetic material and related substances' heading.
5. HAP (hydroxylammonium perchlorate) as an 'oxidiser' under the 'energetic material and related substances' heading.

6. Hydrazine perchlorate as an 'oxidiser' under the 'energetic material and related substances' heading.

Perchlorate use in military munitions and devices is likely to include the following: solid fuel rockets; mines; torpedo warheads; smoke generating compounds; illuminating and signal flares; thermite-type incendiaries; tracer rounds; incendiary bombs (fire bombs); fuzes (ignitors used to initiate the burning of a propellant); Jet-Assisted Take Off (JATO) devices; and simulators (Dstl, 2007). Specifically, several uses have been identified, which could potentially lead to perchlorate contamination in the environment, [Table 2.3](#) (Dstl, 2007).

**Table 2.3 Military activities with perchlorate compounds that are likely to lead to perchlorate contamination in the environment (Dstl, 2007)**

Activity	Primary sources	Release mechanism
Manufacturing	Wastewater impoundments	Leaching, surface water runoff.
	Storage areas	Spills, surface water runoff (outside storage).
	Wastewater outflow points	Spills, surface water runoff, leaching, septic systems.
	Open burn areas	Incomplete burning and associated leaching.
	Landfills	Precipitation and leaching of buried waste material.
Storage	Disposal facility for retrograde propellant/fuel	Discharge of washout for disposal operation.
	Open burn/open detonation facilities	Incomplete detonations, kickouts from open detonation, incomplete burning and associated leaching.
Research and development	Open burn/open detonation areas	Incomplete detonations, kickouts from open detonation, incomplete burning and associated leaching.
	Wastewater impoundments	Leaching, surface water runoff.
	Wastewater outflow points	Spills, surface water runoff, leaching septic systems.
	Landfills	Precipitation and leaching of buried waste material.
	Recycling operations	Mishandling and spills, washout.
Testing	Target area	Incomplete detonation or deflagration after deployment.
	Open burn/open detonation areas	Incomplete detonations, kickouts from open detonation, incomplete burning and associated leaching.
	Firing points	Burning of excess propellant, burial of excess munitions.
Training	Target areas	Incomplete detonation or deflagration after deployment.
	Open burn/open detonation areas	Incomplete detonations, kickouts from open detonation, incomplete burning and associated leaching.
	Firing points	Burning of excess propellant, burial of excess munitions.

Applicable military uses of perchlorate compounds in the UK are the following (Dstl, 2007):

1. Pyrotechnics: potassium perchlorate is used in flares, maroons, sound units and grenades.
2. Thermal batteries for missile systems: very small amounts (grams) of potassium perchlorate are used in Advanced Medium Range Air to Air Missile (AMRAAM) and Javelin.
3. Base bleed units for extended range shells: ammonium perchlorate is used in Shell 155 mm HEL20A1.
4. Ignitors: potassium perchlorate is widely used in small amounts (grams).
5. Torpedoes: hydroxylamine perchlorate is used in Spearfish torpedoes.

6. PBX (polymer bonded explosives): contain significant amounts of ammonium perchlorate (not used in the UK, but are likely to be used in the future).

However, the most significant use is in solid rocket fuel motors, where ammonium perchlorate is used as an oxidiser at tens of kg's (Dstl, 2007). Relatively close quarter battlefield weapons (i.e. infantry launched rockets or missiles) do not generally use ammonium perchlorate containing propellants, except the Rocket System 94 mm HEAT, but this is now withdrawn from service (Dstl, 2007). Generally, the munitions that contain significant amounts of ammonium perchlorate are sea or air launched ones, however, some land-based ones exist (i.e. the Rocket System 94 mm HEAT (as above) and Multiple Launch Rocket System, MLRS) (Dstl, 2007). Correct operation of these is not thought to release significant quantities of perchlorate into the environment, apart from small amounts of unreacted material. However, misfires could lead to contamination, i.e. areas near to fixed land-based firing points may prove to be contaminated (Dstl, 2007). The largest releases, however, are expected from munitions disposal, of which there are three methods (Dstl, 2007):

1. Static firing: rocket motor is anchored down and burnt while on the ground, almost complete combustion occurs, so low potential for release of perchlorate to the environment.
2. Burning with a cage: rocket motors are stacked together and all ignited, as above, so as long as each motor is ignited, low release is expected.
3. Demolition: each rocket motor is destroyed by use of high explosives, either on the surface or within a pit, not all the propellant (perchlorate) may be destroyed, some may be ejected from the pit, so high contamination is likely to result from this.

In the UK, demolition of munitions occurs in designated demolition areas (typically on firing ranges or attached to ammunition depots), however, these are infrequent occurrences and usually done on a small scale (Dstl, 2007). The primary UK site for this is on Foulness Island, near Shoeburyness, off the coast of Essex, of which the surface water, groundwater, soil and ash from the burning cages/pits have already been sampled by the Defence Science and Technology Laboratory, Dstl (Section 2.4.4; Dstl, 2007).

### **1. Pharmaceutical Uses**

In the UK, perchlorate is stated to have been used pharmaceutically to inhibit thyroid synthesis for many years (Crane *et al.*, 2005). However, it does not appear to be currently prescribed in the UK, as it does not feature in the British National Formulary (BNF, 2007). In Germany, perchlorate is identified as being used (with thionamides) for preventing excess iodine uptake during coronary angiographics (Wolff, 1988).

### **2. Aerospace Uses**

It is reported that, of the perchlorate produced in the USA since the 1950s ( $>3.95 \times 10^8$  kg,  $>8.7 \times 10^8$  lbs), some (quantity unspecified) was exported to Europe for use in European space exploration efforts (Dasgupta *et al.*, 2006). No known space launch sites in the European Union can be identified from the publicly available data and the European Space Authority operates out of French Guiana (ESA, 2007).

## North America

### 1. Rocket Propellant

Although it was first detected in California in 1985 (NRC, 2005), since 1997 when the limit of detection for perchlorate decreased from 100 µg/l to 4 µg/l, perchlorate contamination has been recorded throughout the USA (Motzer, 2001) in at least 35 states (Sturchio *et al.*, 2007). Ammonium perchlorate in rocket propellants has a limited shelf-life and so must be replaced periodically (Motzer, 2001; EA, unknown). This and the decommissioning of weapons may be responsible for the subsequent discharge to the environment (EA, unknown). To remove the spent perchlorate, high pressure jets of water are used to wash out the propellant, thereby potentially producing large quantities of contaminated wastewater (Dasgupta *et al.*, 2006). If this water is not disposed of appropriately, environmental contamination could occur. Perchlorate is extensively used as a propellant in rocket fuel, as it is a strong oxidiser and it is also very stable and safe to use (SWRCB, 2005). As it reacts, it releases gaseous products and therefore acts as a thrust booster (ACSH, 2002). It has been used for this application since the 1890s (NRC, 2005).

Ammonium perchlorate (via its use in solid propellant in rockets and missiles) has been reported to be responsible for the contamination of a significant number of ground and surface waters at concentrations of 8 – 3700 µg/l (up to 30 000 µg/l in surface water near the Longhorn Army Ammunition Plant in Texas) (Crane *et al.*, 2005). The majority of this source is released to the environment by discharge from rocket manufacturing plants, demilitarisation of weapons, and washing out and refuelling of rockets. Drinking water levels are reported to be 4-24 µg/l in Nevada, and 4-820 µg/l in California. In 2001-2003, under the US Unregulated Contaminant Monitoring Rule (UCMR), 4.1% and 1.6% of 3356 public water supplies contained perchlorate at >2 µg/l and >6 µg/l, respectively (Sturchio *et al.*, 2006). Perchlorate is known to have leached from US military dumpsites into drinking water sources (Sass, 2004), and perchlorate identified in south-western USA has been related to the use and release of ammonium perchlorate by defence contractors, military operations and aerospace programs (Urbansky, 2002). Atmospheric fallout, duds and misfires from firework displays are reported to be potential environmental pathways of perchlorate from its use in fireworks (SWRCB, 2005).

Ammonium perchlorate in combination with aluminium and a binder is used in solid fuel rockets that are used for launching space vehicles or armaments (Dasgupta *et al.*, 2006). Due to ammonium perchlorate being classed as a strategic chemical in the USA, it is considered that accurate data on production figures will not be available. The largest use of ammonium perchlorate is thought to be the solid rocket boosters of space shuttles. However, when plume samples were analysed from a launch on 26<sup>th</sup> July 2005, no excess perchlorate (greater than background levels) was identified. Additionally, only approximately 0.05% of the initial amount of perchlorate present in a road flare was detected when it was fully burnt down. Therefore, when perchlorate is used as it is intended, i.e. as an oxidiser, limited release of perchlorate to the environment occurs.

### 2. Pharmaceutical Uses

Perchlorate has been used pharmaceutically in the USA; it has been administered orally and rectally as a premedication to patients undergoing brain acintigraphy with pertechnetate (Turner *et al.*, 1977). Wolff (1998) reports that perchlorate is used to control amiodarone-induced thyroid dysfunction (amiodarone is an anti-arrhythmic agent, used to treat irregular heart beat (cardiac arrhythmia), but it can cause thyroid dysfunction due to excess iodine), and that it is also used to treat patients with total iodide organification defects in the thyroid

(TIOD), by increasing the expulsion of iodide from the thyroid. In fact its use as a treatment for toxicosis was started in the USA, although trials were done in the UK (Wolff, 1998). However, despite early work showing good results and the use of perchlorate in the 1950s for treatment of Grave's disease (excess production of thyroid hormone) (Synder *et al.*, 2006), in the 1960s seven cases of aplastic anaemia caused by perchlorate (4 in the UK, 1 in the USA, 1 in Norway and 1 in Israel) induced an almost complete cessation of its pharmaceutical use (Wolff, 1998). As well as the fact that the US Food & Drugs Administration (FDA) approved alternative anti-thyroid agents, which lasted longer and so were more effective (Synder *et al.*, 2006). Exceptions were for use in discharge tests (using single doses) and as an adjunct to pertechnetate screening (Wolff, 1998). However, its use is reported to be increasing again, due to the occurrence of amiodarone-induced thyrotoxicosis (Wolff, 1998). Since the 1960s no other cases of aplastic anaemia have been reported (Synder *et al.*, 2006). A minor use is in combination with thionamides to decrease sensitivity reactions; uses of this type include the treatment of iodide-induced thyrotoxicosis after angiography, in functioning metastatic thyroid carcinoma and in amiodarone-induced thyroid dysfunction (Wolff, 1998). Perchlorate is also used occasionally to treat drug-induced thyrotoxicosis (excessive production of thyroid hormones) or in combination with other anti-thyroid drugs (INM, 2006). It has been stated that doses up to 400 mg/day (6.7 mg/kg bw/day based on a 60 kg adult) are used clinically (ACSH, 2002).

### 3. Uses in Fireworks

The use of perchlorate in fireworks is to produce colour effects and as flash powder in 'salute' shells (to produce a loud bang/flash) (SWRCB, 2005). A Canadian study has detected perchlorate in the Great Lakes Basin at levels close to 0.2 µg/l (the limit of detection) (Backus *et al.*, 2005). The source of perchlorate was reportedly a nearby fireworks display and was in an area of high density livestock and crop farming. Wilkin *et al.* (2007) investigated the concentrations of perchlorate in a municipal lake before and after a firework display in 2006. The analysis method employed reported a lowest concentration minimum reporting level (LCMRL) of 0.011 µg/l and a method detection limit (MDL) of 0.003 µg/l. The mean perchlorate concentration before the display was 0.005-0.081 µg/l, however, 14 hours afterwards it had increased to 44.2 µg/l, which returned to background levels within 20-80 days. It has been reported that nearby fireworks have resulted in concentrations up to 10 µg/l in public drinking water supplies (SWRCB, 2005).

### 4. Other Uses

A US EPA review on emerging contaminants (US EPA, 2005a) has identified the following uses for ammonium perchlorate and its other salts: pyrotechnics, fireworks, blasting agents, safety matches, lubricating oils, textile dye fixing, nuclear reactors, electronic tubes, tanning and finishing leather, rubber manufacturing, electroplating, aluminium refinishing, automobile air bag inflators, paint and enamel production, and pharmaceuticals. Explosives and rocket propellant are stated to be the most common uses for ammonium perchlorate (US EPA, 2005a). Additional uses for perchlorate salts and perchloric acid include as model rocket engines, analytical testing agents, electropolishing operations, brass and copper etching, textile bleaching agent, hypochlorite/bleach solutions, photographic flash powder, oxygen generators, ejection seats, additive in polyvinyl chloride (PVC), and specialty industrial uses (SWRCB, 2005).

The use of perchlorate in explosive materials is stated to be in the form of water gels and emulsion blasting agents, as well as blasting caps (SWRCB, 2005). In the case of blasting operations, perchlorate has been detected at levels up to 1300 µg/l in public drinking water supplies within one mile of the blasting site (SWRCB, 2005).

Due to the fact that chlorate will break down over time and may result in perchlorate formation, perchlorate has also been found in hypochlorite/bleach solutions; levels of 260-4600 µg/l have been detected in various commercial hypochlorite solutions (SWRCB, 2005). Moreover, levels of 89-370 µg/l were detected in household bleach products, with an older product (approximately 2.5 years old) having a concentration of 8000 µg/l (SWRCB, 2005). Electrolytic chlorine products (ECP) are also reported to contain perchlorate (Dasgupta *et al.*, 2006).

Perchlorate is also used in road flares; typical compositions are (by weight) 75% strontium nitrate and <10% each of potassium perchlorate, sulphur and a binder. However, not all road flares contain perchlorate (Dasgupta *et al.*, 2006).

Perchlorate (as its salts and perchloric acid) is also reported to be widely used in analytical chemistry laboratories and for metal dissolution (Hodge *et al.*, 2003; Wolff, 1998), which has resulted in its presence at 1000s µg/l in the influent to the Radioactive Liquid Waste Treatment Facility at the Los Alamos National Laboratory (Hodge *et al.*, 2003). Specific uses of this type include the analysis of the potassium ion and its removal from biological materials (Wolff, 1998).

### **South America**

In northern Chile, perchlorate is stated to occur naturally in typically nitrate soil, or saltpetre, from areas such as the Atacama Desert (Hatzinger *et al.*, 2004, in US EPA, 2005a). This source of perchlorate is reported to have an unknown origin (Erickson, 2004, in US EPA, 2005a), however, natural formation may be involved. Saltpetre is a mineral source of sodium nitrate, which is mined for use in fertilisers (Urbansky, 2002; Urbansky *et al.*, 2001). Perchlorate levels in Chilean nitrate are reported to be 3.64% and groundwater levels in nearby areas have reported levels up to 10 000 µg/l (INM, 2006). Final drinking water has been analysed in three cities, Taltal, Chanaral and Antofagasta; with levels of 100-120, 5-7 and <4 (LOD) µg/l, respectively, being reported (INM, 2006). Similar areas of perchlorate-containing nitrate soil also occur in Peru and Bolivia (Dstl, 2007).

### **Asia**

A report by the Singapore Police Force states that owing to the increasing occurrence of terrorist attacks and the risks they pose, the local Government has increased their control of explosive precursors through the Arms and Explosives (Amendment) Bill 2006 (SPF, 2007). As such they have included in this list (which identifies compounds that are widely used in research, industrial and agricultural sectors) ammonium perchlorate (used in propellants, explosives and pyrotechnics), potassium perchlorate (photography, explosives and pyrotechnics), sodium perchlorate (explosives and matches) and perchloric acid (electropolishing and explosives). This document also states that Northern Ireland and New South Wales, Australia, have similar controls (although no details of these could be located from the publicly-available data).

In China, perchlorate has been detected in samples of sewage sludge (0.56-379.9 µg/kg, average 21.7 µg/kg), rice (0.16-4.88 µg/kg), bottled drinking water (0.037-2.013 µg/l) and milk (0.30-9.1 µg/l) from most regions (Shi *et al.*, 2007). The highest concentration in sewage sludge was from the Swchou sewage treatment works, which received 58% of its influent from the electronic industry and the remainder (42%) from domestic sewage. Three sewage treatment works that received 90% of their influent from domestic sewage were reported to

have perchlorate concentrations of 37.0, 30.5 and 16.3 µg/kg. No other conclusions regarding potential sources were made. Liu *et al.* (2004) have detected perchlorate in finished drinking water in Beijing, China, at levels of 0.1-6.8 µg/l. They state the source to be influenced by the local groundwater.

In Japan, perchlorate was detected at maximum concentrations of 340-2300 µg/l in the upper Tone River and the Usui River (its tributary) (Kosaka *et al.*, 2007). Industrial effluents (specifically one identified source was from a perchlorate and chlorate production industry, but the other was not related to perchlorate) were attributable to the cause, which suggests widespread use. Drinking water originating from the Tone River contained perchlorate at 0.06-37 µg/l. This study also examined perchlorate levels in the Hirose River just after and 5 days after a fireworks display that was performed on a barge in the river. The concentration immediately after the display was 79 µg/l, but it had dropped to 0.39 µg/l after the 5 days. A study into levels in drinking water was also undertaken, which found that maximum concentrations of 37 µg/l occurred, using source water from the rivers in the middle and lower Tone River basin. This basin receives the contaminated effluent as described above and although the water passed through drinking water treatment works, perchlorate was obviously not completely removed. The type of treatment used was not stated.



**Table 2.4 A summary of worldwide uses of perchlorate**

Country	Compound	CAS RN	Use	Ref.
UK	Perchlorate	14797-73-0	Pharmaceutical to inhibit thyroid synthesis.	Crane <i>et al.</i> , 2005
	Perchlorate	14797-73-0	Pyrotechnics: potassium perchlorate is used in flares, maroons, sound units and grenades. Thermal batteries for missile systems: very small amounts (grams) of potassium perchlorate are used in Advanced Medium Range Air to Air Missile (AMRAAM) and Javelin. Base bleed units for extended range shells: ammonium perchlorate is used in Shell 155 mm HEL20A1. Ignitors: potassium perchlorate is widely used in small amounts (grams). Torpedoes: hydroxylamine perchlorate is used in Spearfish torpedoes. PBX (polymer bonded explosives): contain significant amounts of ammonium perchlorate (not used in the UK, but are likely to be used in the future).	Dstl, 2007
Germany	Perchlorate	14797-73-0	Pharmaceutical (with thionamides) for preventing excess iodine uptake during coronary angiographics.	Wolff, 1988
Europe	BNCP (cis-bis (5-nitrotetrazolato) tetra amine-cobalt (III) perchlorate	117412-28-9	Explosive.	EU, 2007
	CP (2-(5-cyanotetrazolato) penta amine-cobalt (III) perchlorate)	70247-32-4	Explosive.	
	Perchlorates composited with powdered metal or other high energy fuel components	-	Pyrotechnic, fuel and related substance.	
	Ammonium perchlorate	7790-98-9	Oxidiser.	
	HAP (hydroxylammonium perchlorate)	15588-62-2	Oxidiser.	
	Hydrazine perchlorate	27978-54-7	Oxidiser.	
	Ammonium perchlorate	7790-98-9	Oxidising agents in propellants for rocket motors and munitions, fuses, smoke generators, explosives, air bag gas generators, fireworks, flares and oxygen generating systems.	INM, 2006; EA, unknown
	Potassium perchlorate	7778-74-7	Oxidising agents in propellants for rocket motors and munitions, fuses, smoke generators, explosives, air bag gas generators, fireworks, flares and oxygen generating systems.	INM, 2006; EA, unknown
	Perchlorate	14797-73-0	Tanning, electroplating, aluminium refinishing, and as a heat stabiliser during PVC processing. In manufacturing processes; commercial blasting for construction; in fertiliser; in sodium chlorate used as a herbicide (it is not known whether perchlorate is present in this as a contaminant); and commercial manufacture of perchlorate salts or perchlorate containing items (e.g. pyrotechnics and flares). Drying agents, etching agents, temporary adhesives, and batteries.	INM, 2006 Dstl, 2007
	Ammonium perchlorate	7790-98-9	Oxidising agent in rocket and jet propellants and pyrotechnics, in analytical chemistry, and in etching and engraving.	EA, unknown
Potassium perchlorate	7778-74-7	Oxidising agent in explosives, pyrotechnics, solid rocket propellants,	EA, unknown	

Country	Compound	CAS RN	Use	Ref.
			photography, flares and chemical reagents.	
	Sodium perchlorate	7601-89-0	Starting material for the manufacture of other perchlorates (i.e. ammonium perchlorate and potassium perchlorate), as an oxidising agent in explosives, in rocket fuel/propellants, as an analytical reagent, in explosive emulsions, in slurries and in electrometallurgy.	EA, unknown
	Perchloric acid	7601-90-3	Laboratory chemical (especially an analytical reagent), a catalyst, in the manufacture of various esters, as an ingredient in bath deposition of lead, in electropolishing and in explosives.	EA, unknown
	'Perchlorates' or 'perchloric' acid compounds	-	Laboratory scale chemicals for research purposes, but main uses are: metal perchlorate salts used as laboratory chemicals, e.g. in synthesis as analytical reagents; 'alkyl' perchlorate salts; and 'complex aromatic' perchlorate salts, used primarily as fluorescent dyes/laser dyes.	EA, unknown
	Lithium perchlorate	7791-03-9	Solid rocket propellant; as an electrolyte salt for lithium batteries.	EA, unknown
	Magnesium perchlorate	10034-81-8	Drying agent for gases (as anhydrous/dehydrate); batteries.	EA, unknown
	Barium perchlorate	13465-95-7	Manufacture of explosives; experimentally in rocket fuels.	EA, unknown
	Calcium perchlorate	13477-36-6	Present in some US products for chlorination treatment of swimming pool/spa water (e.g. Sani-clor shock treatment, classed as an inorganic hypochlorite, percentage of calcium perchlorate unspecified (Hasa, 2001)).	EA, unknown
	Caesium perchlorate	13454-84-7	Optics; catalysts; speciality glasses; power generation (possibly nuclear power plants?).	EA, unknown
	Hydrazine perchlorate	Unknown	Rocket propellant.	EA, unknown
	Hydroxylammonium perchlorate	15588-62-2	Explosives.	EA, unknown
	Lead diperchlorate	13637-76-8	Batteries (not clear if current or historic); accumulators (not clear if current or historic); microelectronics (not clear if current or historic).	EA, unknown
	Nitronium perchlorate	Unknown	Rocket propellant oxidisers.	EA, unknown
	Silver perchlorate	7783-93-9	Manufacture explosive compositions.	EA, unknown
	Strontium perchlorate	13450-97-0	Pyrotechnics.	EA, unknown
	'Alkyl' perchlorates: tetrabutylammonium perchlorate tetraethylammonium perchlorate tetrahexylammonium perchlorate	1923-70-2 2567-83-1 4656-81-9	Primary uses as laboratory chemicals, but also electrolytes/electrochemical reagents for electroanalytical methods (i.e. polarographic and voltammetric methods) and other electrochemical methods.	EA, unknown
	'Aromatic' perchlorate dyes	-	Fluorescent dyes used in lasers.	EA, unknown
	Perchlorate	14797-73-0	Military munitions and devices i.e.: solid fuel rockets, mines, torpedo warheads, smoke generating compounds, illuminating and signal flares, thermite-type incendiaries, tracer rounds, incendiary bombs (fire bombs), fuzes (igniters used to initiate the burning of a propellant), Jet-Assisted Take Off (JATO) devices and simulators.	Dstl, 2007
	Perchlorate	14797-73-0	European space exploration efforts	Dasgupta <i>et al.</i> , 2006
USA	Ammonium perchlorate and its other salts	-	Pyrotechnics, fireworks, blasting agents, matches, lubricating oils, textile dye fixing, nuclear reactors, electronic tubes, tanning and finishing leather, rubber manufacturing, electroplating, aluminium refining, automobile air bag	US EPA, 2005a

Country	Compound	CAS RN	Use	Ref.
			inflators, paint and enamel production, and pharmaceuticals.	
	Ammonium perchlorate	7790-98-9	Most common uses: explosives and solid propellant in rockets and missiles.	US EPA, 2005a; Crane <i>et al.</i> , 2005
	Perchlorate	14797-73-0	Fireworks.	Wilkin <i>et al.</i> , 2007
	Perchlorate salts	-	Air bag inflators, road flares, fireworks, electroplating, tanning and finishing leathers, mordant (fixes the dye) for fabric, and in producing paints and enamels.	Crane <i>et al.</i> , 2005
	Perchlorate	14797-73-0	Oxidiser (including rocket propellant), presence in Chilean nitrate fertiliser, used in fireworks, used in electrolytic chlorine products.	Dasgupta <i>et al.</i> , 2006
	Perchlorate	14797-73-0	Some dietary supplements and flavour enhancing ingredients.	Snyder <i>et al.</i> , 2006
	Perchlorate	14797-73-0	Analytical chemistry laboratories and for metal dissolution.	Hodge <i>et al.</i> , 2003
	Perchlorate	14797-73-0	Administered orally and rectally as a premedication to patients undergoing brain acintigraphy with pertechnetate.	Turner <i>et al.</i> , 1977
	Perchlorate salts and perchloric acid	-	Model rocket engines, analytical testing agents, electropolishing operations, brass and copper etching, textile bleaching agent, hypochlorite/bleach solutions, photographic flash powder, oxygen generators, ejection seats, additive in polyvinyl chloride (PVC), and specialty industrial uses.	SWRCB, 2005
	Perchlorate	14797-73-0	Pharmaceutical to control amiodarone-induced thyroid dysfunction; to treat patients with thyroids with iodide organification defects; discharge tests (using single doses); as an adjunct to pertechnetate screening; combination with thionamides to decrease sensitivity reactions (i.e. for iodide-induced thyrotoxicosis after angiography, in functioning metastatic thyroid carcinoma and in amiodarone-induced thyroid dysfunction). It is also used occasionally	Wolff, 1998
	Perchlorate	14797-73-0	Pharmaceutical to treat drug-induced thyrotoxicosis or in combination with other anti-thyroid drugs.	INM, 2006
Canada (Great Lakes Basin)	Perchlorate	14797-73-0	Fireworks	Backus <i>et al.</i> , 2005
Chile (Atacama Desert)	Perchlorate	14797-73-0	'Natural' occurrence in nitrate soil or saltpetre (mineral source of sodium nitrate, mined for use in fertilisers).	Hatzinger <i>et al.</i> , 2004 and Erickson, 2004, in US EPA, 2005a; Urbansky, 2002; Urbansky <i>et al.</i> , 2001
China	Perchlorate	14797-73-0	Electronic industry	Shi <i>et al.</i> , 2007
Japan	Perchlorate	14797-73-0	Fireworks and unspecified industry.	Kosaka <i>et al.</i> , 2007
Singapore	Ammonium perchlorate	7790-98-9	Propellants, explosives and pyrotechnics.	SPF, 2007
	Potassium perchlorate	7778-74-7	Photography, explosives and pyrotechnics.	
	Sodium perchlorate	7601-89-0	Explosives and matches.	
	Perchloric acid	7601-90-3	Electropolishing and explosives.	
Worldwide	Perchlorates	-	Drying agents, etching agents, temporary adhesives, batteries.	EA, unknown

In the Nakdong watershed in Korea, perchlorate was detected at maximum levels of 60 µg/l and up to 35 µg/l in local drinking water (Quinones *et al.*, 2007). The authors state that further work was required to identify potential sources.

## 2.5 Removal via Drinking Water Treatment

Inorganic perchlorate salts are extremely soluble and chemically stable in water. As a consequence, conventional treatment processes such as coagulation and sedimentation do not remove perchlorate.

Perchlorate can be removed using selective anion-exchange resins. As an example, more than 100 000 bed volumes of groundwater containing 50 µg perchlorate/l were treated before breakthrough occurred. Regeneration by conventional means requires large volumes of concentrated brine (12% sodium chloride). Laboratory experiments have shown that regeneration using tetrachloroferrate (formed in a solution of ferric chloride, hydrochloric acid and ethanol) is effective (Gu *et al.*, 2001), however, the practicality of using this regenerate is questionable.

Granular activated carbon (GAC) in the absence of biological activity has a limited capacity for perchlorate removal. Column tests using ROW 0.8 GAC to treat tap water spiked with 50 µg/l perchlorate resulted in detection of perchlorate in the treated water after treatment of 600 bed volumes (BV). After 1600 BV, the perchlorate concentration of the treated water was the same as that for the influent. The capacity was calculated as 0.17 mg perchlorate per gram of GAC. For an empty bed contact time (EBCT) of 15 minutes this equates to less than 7 days operation before breakthrough of perchlorate would occur (Brown *et al.*, 2002).

Studies on a full scale GAC plant with an empty bed contact time (EBCT) of 20 minutes and treated water containing 110 µg/l perchlorate, found that breakthrough started after treatment of 1800 BV and was essentially complete after 2200 BV. Laboratory tests showed that the removal capacity could be increased by 20-40% by pre-treatment of the GAC with ferric chloride and oxalic acid. The laboratory tests also showed that the GAC could be chemically regenerated using sodium borohydride solution (Na *et al.*, 2002). However, in terms of current water treatment, these pre-treatments may not be very practicable.

Laboratory tests have shown that perchlorate can be completely removed using GAC operated in biological mode. However, it was necessary to dose a carbon source (ethanol or acetic acid) at 1.6-2.8 mg/l as carbon. With an EBCT of 9 minutes, Biological Activated Carbon (BAC) filtration consistently removed perchlorate to below 2 µg/l, with influent perchlorate concentrations of 10 to 300 µg/l, sulphate concentrations from 0 to 200 mg/l, pH 6.5 to 9.0 and temperature of 5 to 22°C (Brown *et al.*, 2003).

Other studies have demonstrated effective perchlorate removal by biological processes (Kim & Logan, 2001; Min *et al.*, 2004; Nerenberg *et al.*, 2004). This suggests that biological denitrification processes would remove perchlorate.

Experiments showed approximately 80% removal from an initial perchlorate concentration of 100 µg/l in pure water by nanofiltration, but much poorer removals from natural waters. Removal could be improved by addition of a cationic surfactant (Yoon *et al.*, 2003).

Research is ongoing into the effectiveness of removal by nanofiltration and reverse osmosis (INM, 2006).

## **2.6 General Discussion**

### **2.6.1 Available Data**

The single small dataset supplied by Water Undertaker 1 of monitoring of water sources from non-contaminated rural sites indicated no background levels of perchlorate. There has been no systematic monitoring of drinking water abstraction points near UK industrial sites in general or sites specifically of commercial activity, which may have been associated with the production of fireworks or other perchlorate-containing products in the past. Such past or current uses might include, for example, fireworks, explosives and car airbag manufacturers, etc., but primarily include ordnance/munitions/firing sites.

Only one set of data was available regarding any specific incidents of perchlorate contamination in the environment. This was the localised sampling that occurred at Foulness Island in Shoeburyness, Essex and indicated that perchlorate contamination of soil and water in the immediate vicinity of demolition disposal of munitions does occur. Groundwater contamination did occur (at levels up to 17 367 µg/l), therefore levels at any nearby drinking water abstraction points were considered to be worth investigating.

### **2.6.2 Analytical Methods**

Only two sets of monitoring data were available regarding perchlorate in the UK: data from Water Undertaker 1 and the Defence Science and Technology Laboratory (Dstl) study. Although the principle of the analytical method used for the Water Undertaker 1 study (direct sample injection LCMS) is sound, it is understood that the analytical procedure was developed specifically for this study and not put through the routine method development procedure, and as such has not been fully validated. The Dstl results were based on the US EPA Method 314 (using ion chromatography), which although a recognised standard procedure for perchlorate, is now somewhat dated.

### **2.6.3 Uses/Occurrences**

Perchlorate is widespread in the USA as an environmental contaminant, most of which is explainable from the proximity to manufacturing sites or sites that use perchlorate as a rocket propellant, which appears to be the major use. Other occurrences are due to natural sources, such as the use of saltpetre in Chilean nitrate fertilisers, and atmospheric sources. However, a number of other industrial uses have also been identified; the presence of perchlorate in industrial effluent from sewage treatment works in the USA and Japan suggests more widespread industrial uses.

There has been some concern expressed over the possible presence of perchlorate as a contaminant in sodium hypochlorite solutions. If true in England and Wales, this would have implications in the use of such solutions in drinking water treatment. For this project, this could be tested by the choice of drinking water treatment works and their chlorination method in the monitoring stage.

## **2.7 Conclusions and Recommendations from the Review of Monitoring Data**

### **2.7.1 Conclusions**

- There has been no comprehensive monitoring of environmental or drinking waters in the UK for perchlorate.
- From a single set of data in a rural setting, there was no evidence of perchlorate in the raw drinking water.
- While the main use of perchlorate appears to be rocket propulsion, there are further industrial uses, including the manufacture of fireworks, car airbags, matches and as a laboratory reagent. Although perchlorate is a contaminant in Chilean nitrate fertilisers that have been imported into the USA, no information was located as to whether they have ever been imported into the UK.
- There is evidence that perchlorate arises naturally
- There has been no systematic monitoring of drinking water abstraction points near UK industrial sites or sites of historical commercial activity, which may have included the use of perchlorate; for example, perchlorate production, firework production/storage sites, car airbag manufacturers, etc., including areas where incidents (e.g. fires) may have occurred.

### **2.7.2 Recommendations**

- Targeted monitoring of perchlorate in England and Wales to ascertain whether perchlorate is found in UK drinking water. This monitoring should include drinking water abstraction points near sites where there is evidence for the use of perchlorate (current or historic) or, where possible, contamination incidents have taken place.
- Monitoring of perchlorate in raw and treated drinking water where different water treatment processes are in use to investigate any potential effect on the occurrence of perchlorate in final drinking water.
- Development and validation of a methodology for sampling and analysis for use in monitoring drinking water for perchlorate in England and Wales.

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### 3. DEVELOPMENT AND VALIDATION OF ANALYTICAL METHODOLOGY TO DETERMINE PERCHLORATE IN ENVIRONMENTAL AND POTABLE WATERS USING ION CHROMATOGRAPHY TANDEM MASS SPECTROMETRY

This Method Development Report was written by Rakesh Kanda, Theodore Sideris and Oliver Franklin (STL) in July 2008.

#### 3.1 Introduction

Ion Chromatography (IC) methods to determine perchlorate (US EPA, Method 314.0) (US EPA, 1999) allow perchlorate to be detected in the low  $\mu\text{g/l}$  range. Method 314 provides a reporting limit of  $4 \mu\text{g/l}$ , although a lower reporting limit of  $0.5 \mu\text{g/l}$  can be achieved for samples with low total dissolved solids (TDS). However, the analysis can be subject to false positives due to use of a non-specific conductivity detector.

Liquid Chromatography Mass Spectrometry (LCMS) can also be used for perchlorate analysis (US EPA Method 6850) (US EPA, 2007). The MS provides better selectivity and a lower limit of detection (LOD). US EPA method 6850 states an LOD of  $0.2 \mu\text{g/l}$  can be obtained. Another EPA method (US EPA 331.0) uses LCMS or LCMSMS to determine perchlorate with a reporting limit of  $0.02 \mu\text{g/l}$ . The MSMS method is highly selective (compared to single stage MS), however, the method can be prone to false positives unless adequate separation from common anions is achieved.

Ion Chromatography coupled with electrospray mass spectrometry (Dionex, application note 151) (Dionex Corporation, 2004) uses a 4 mm i.d. IonPac AS16 (ion exchange) column with large loop injection and eluent suppressor. The method uses an  $^{18}\text{O}_4$  labelled internal standard for quantification, a matrix diversion valve to eliminate the need for off-line pre-treatment and a mass spectrometer with an electrospray interface operated in selected ion monitoring mode (monitoring  $m/z$  99 and 101). The selectivity of the mass spectrometer allows low limits of detection ( $155 \text{ ng/l}$ ) to be achieved in high ionic strength matrices. The method requires the use of a suppressor to avoid inorganic salt build-up and uses the natural isotopic abundance of the ions  $^{35}\text{ClO}_4$  ( $m/z$  99) and  $^{37}\text{ClO}_4$  ( $m/z$  101) for peak confirmation.

The advantage of ICMS is the high selectivity of the technique compared with alternative techniques. However, one of the known interferences using this method is from bisulphate ( $\text{H}^{34}\text{SO}_4$ ), which also generates the ion  $m/z$  99 (due to the  $^{34}\text{S}$  isotope). High concentrations of bisulphate elevate the baseline and samples containing very high concentrations require a cleanup prior to analysis (Gandhi *et al.*, 2004).

Using tandem MS, interference caused by bisulphate can be completely eliminated. This report provides details of the development and validation of an ICMSMS method to determine perchlorate in raw and final drinking waters in the  $\text{ng/l}$  range.

## **3.2 Analytical Methodology**

### **3.2.1 Reagents, Materials and Instrumentation**

#### **Standards and reagents:**

Perchlorate of analytical grade (99% purity) was purchased from Sigma-Aldrich (Gillingham, Dorset, UK). Labelled sodium perchlorate ( $^{18}\text{O}_4$ ) was purchased from Dionex (P/N 062923). Acetonitrile (HPLC grade) was purchased from Rathburn Chemicals (Walkerburn, Scotland, UK). Deionised water (18 megaohm-cm resistance or better).

#### **Equipment:**

Dionex ICS1500 Ion Chromatograph with column heater and degasser

Dionex AS40 Autosampler with 100  $\mu\text{l}$  loop

Dionex IonPac AG16 Guard Column, 50 x 2 mm id P/N 055379

Dionex IonPac AS16 Analytical Column, 250 x 2 mm id P/N 055378

Dionex Suppressor for anions, ASRS 300, 2 mm

Agilent 1100 HPLC system with binary pump, degasser, column heater and valve

AppliedBiosystems LCMSMS with electrospray interface

### **3.2.2 Preparation of Standards and Samples for Method Validation**

#### **Preparation of Standards**

Perchlorate- $^{18}\text{O}_4$  (1 mg/l standard) was diluted using deionised water to a concentration of 0.1 mg/l.

A stock solution (1 mg/l) of perchlorate was prepared by dissolving sodium perchlorate in deionised water. Calibration solutions of perchlorate were prepared by dilution of the stock solution to generate concentrations of:

125 ng/l, 250 ng/l, 500 ng/l, 1000 ng/l, 2500 ng/l and 5000 ng/l perchlorate anion in deionised water.

#### **Preparation of Validation Samples**

The method was validated by the analysis of duplicate samples of river water (River Thames, Reading) and tap water. One set of duplicate samples was analysed at a low spiked concentration and another duplicate set were spiked at a high concentration.

River water (River Thames, Reading) samples were filtered sequentially through a Whatman GFF filter followed by filtration through a 0.22 µm Millipore Type GV filter prior to spiking. Tap water samples were unfiltered. All validation samples were spiked as follows:

**Low Spike (1000 ng/l):** Prepared by addition of 500 µl of sodium perchlorate spiking solution at 0.5 ng/µl.

**High Spike (4000 ng/l):** Prepared by addition of 2000 µl of sodium perchlorate spiking solution at 0.5 ng/µl.

**Blank:** Samples were unspiked.

### **Preparation of Stability Samples**

Samples to determine the stability of perchlorate in water were prepared in 100 ml Azlon polypropylene bottles. River and tap water were prepared as per the low spike (1000 ng/l) validation samples, which were spiked with 200 µl of sodium perchlorate spiking (0.5 ng/µl).

### **3.2.3 ICMSMS Analysis**

A 5 ml aliquot of each analytical standard and validation sample was transferred to an autosampler vial and 50 µl of the internal standard solution (0.1 mg/l) was added to each sample to give a sample concentration of 1 µg/l, prior to ICMSMS analysis.

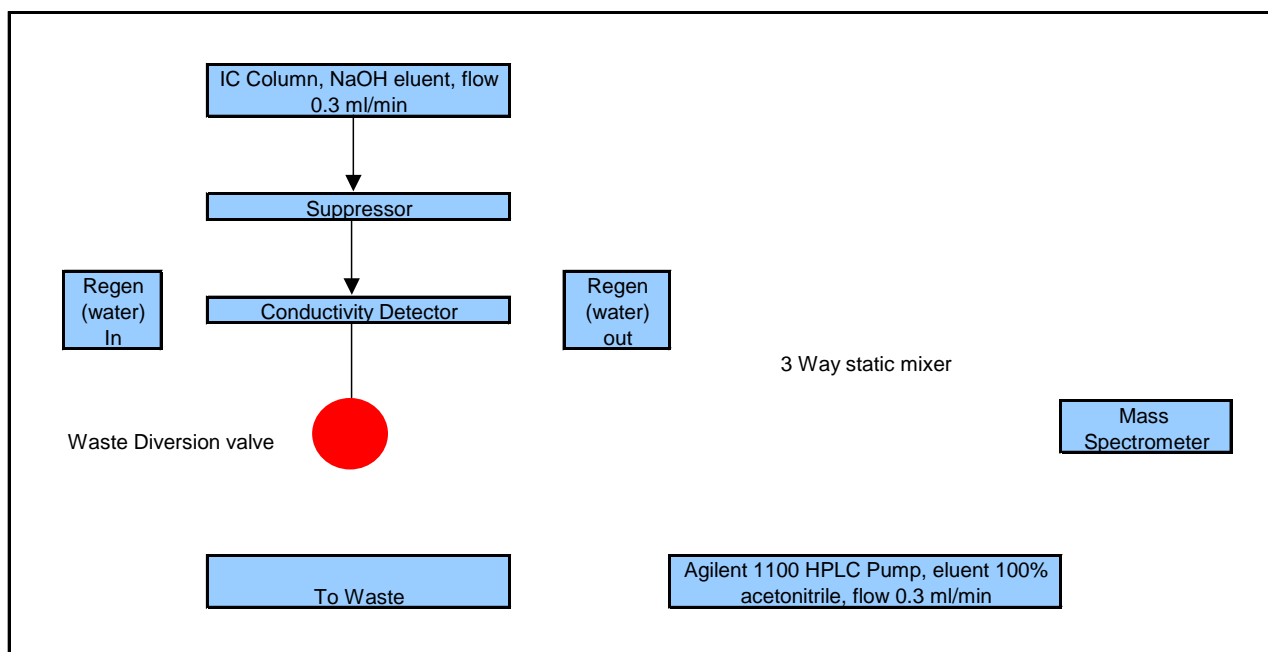
Table 3.1 details the ICMS/MS conditions used for analysis.

**Table 3.1 ICMS/MS Conditions for perchlorate analysis**

<b>IC Equipment:</b>	<b>Dionex IC1500</b>
Column	IonPac AS16, 250 x 2 mm i.d.
Suppressor	ASRS, 2 mm (65 mA)
Eluent	45 mM sodium hydroxide, flow rate 0.3 ml/minute
Injection volume	20 µl
Flow	0.3 ml/minute
Temperature	30°C
Run Time	15 minutes
Expected backpressure	1200 psi
Expected background conductance	<3 µS
<b>HPLC Equipment:</b>	<b>Agilent 1100</b>
Mobile phase	Acetonitrile 100%
Flow	0.3 ml/minute
Matrix diversion time	0-5 minutes and 14 to 15 minutes
<b>Mass Spectrometer:</b>	<b>API 5000</b>
Mode	Electrospray ionisation (negative ion)
Ion transitions monitored:	m/z
Perchlorate	101>85
<sup>18</sup> O <sub>4</sub> -Perchlorate	107>89
Dissociation Potential	70 V
Probe Temperature	450°C
Curtain gas	20.00
CAD Gas	5.00
GS1	50
GS2	60

The instrumentation is set-up as shown in Figure 3.1.

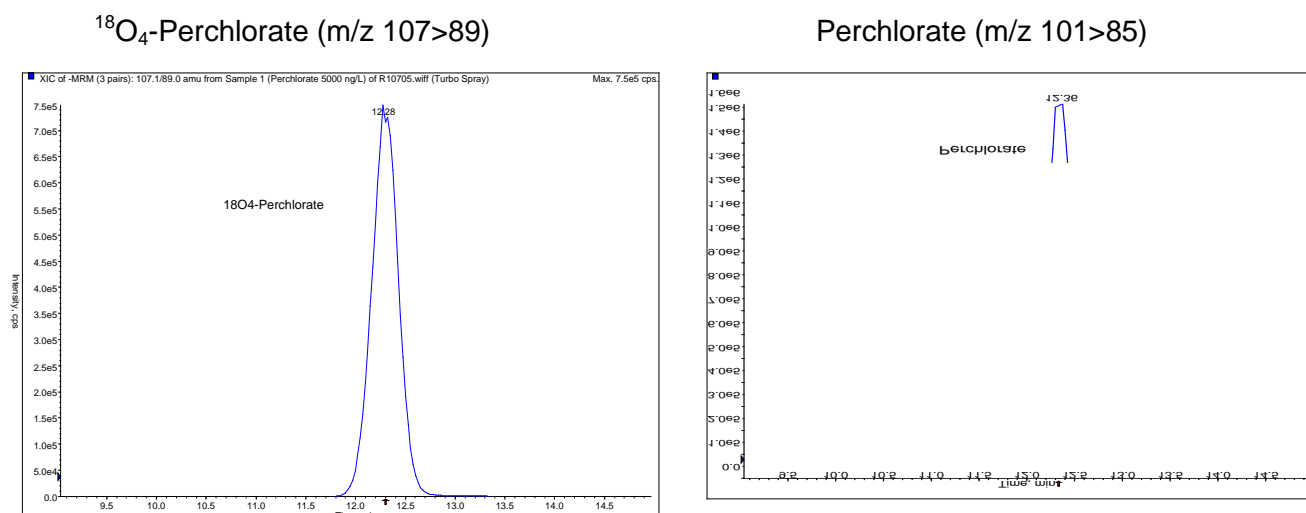
Helium or air pressurised water (15 psi) is used for the suppressor. Dionex (Application note 151) recommends that chemical regeneration of the suppressor is not used.



**Figure 3.1** Flow diagram showing ICMSMS set-up with anion suppression and matrix diversion valve

### 3.3 Results

The mass chromatograms of a 500 ng/l analytical standard of perchlorate and the labeled internal standard are shown in [Figure 3.2](#). While [Figure 3.4](#) shows the signal to noise of the bottom standard of 125 ng/l perchlorate, and [Figure 3.3](#) shows a typical calibration graph over the calibration range 125-5000 ng/l, using the internal standard method.



**Figure 3.2** ICMS/MS Mass chromatograms of an analytical standard perchlorate (500 ng/l) and labelled internal standard (1000 ng/l) using ion suppression and a matrix diversion valve

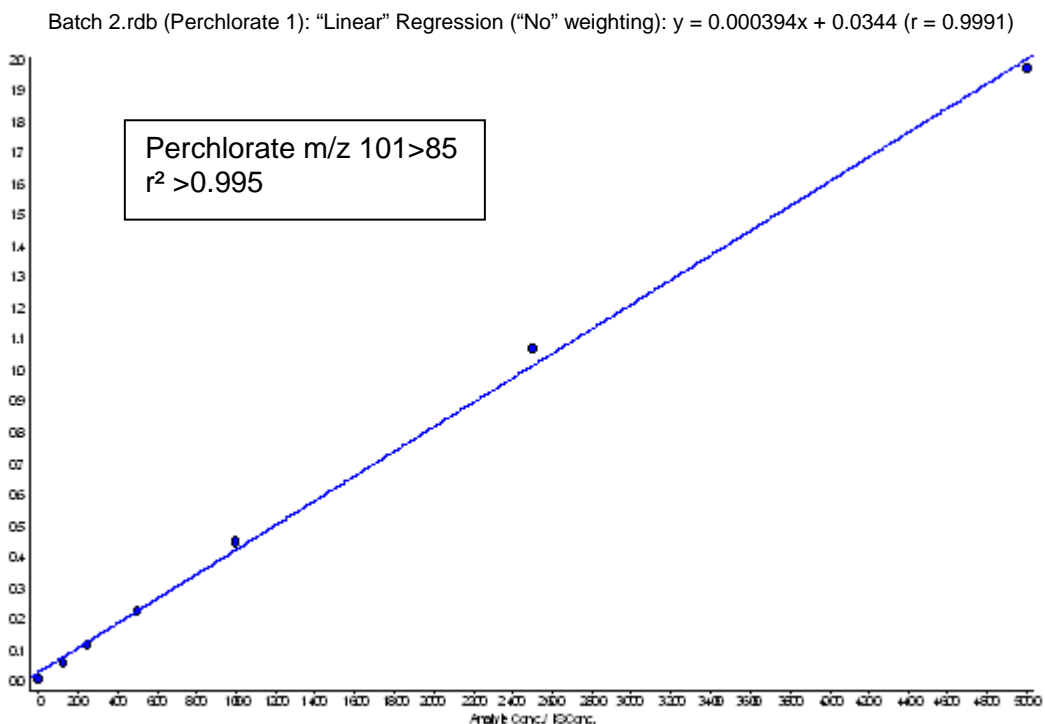


Figure 3.3 Calibration graph of perchlorate using  $^{18}\text{O}_4$ -perchlorate internal standardisation

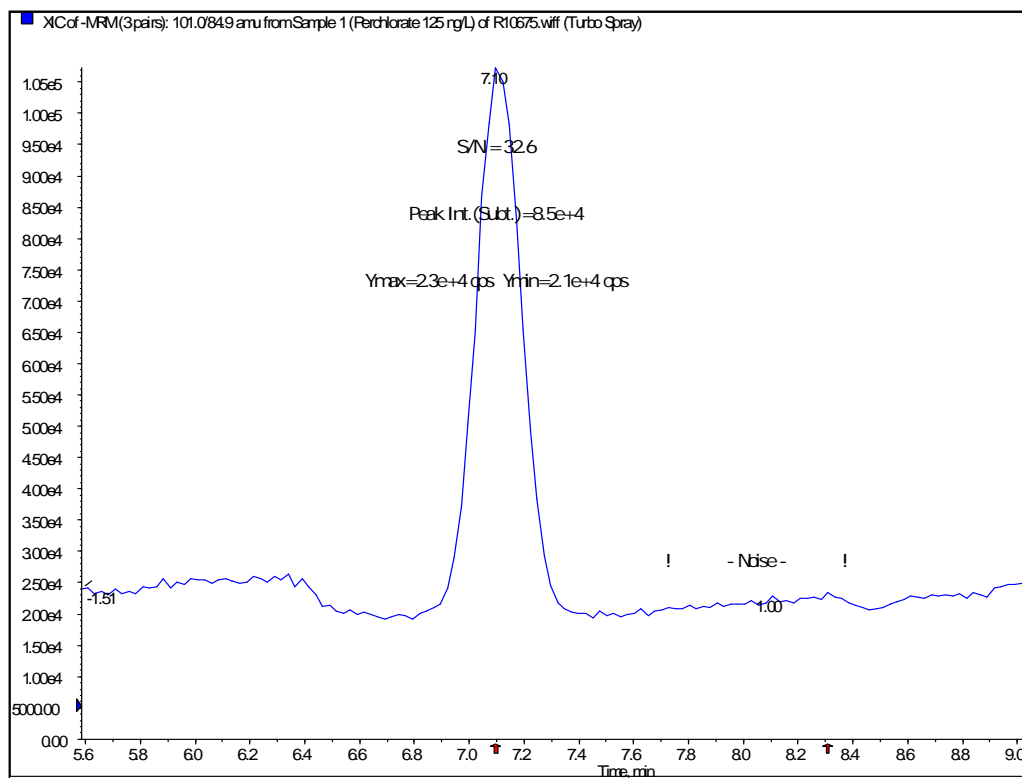


Figure 3.4 Mass chromatogram of a 125 ng/l standard showing typical signal to noise



## Recovery and Precision

The method was validated by the analysis of duplicate samples of raw and final water at a low spiked concentration and another duplicate set were spiked at a high concentration. Samples were analysed using the methodology described above (Section 3.2) on six occasions. The analysis of the unspiked and the low spike and high spike samples is shown in [Table 3.2](#) and the laboratory blank water analysis is in [Table 3.3](#).

All spiked samples show a standard deviation of less than 10% with % recovery 100+/- 10% in raw and treated waters.

Table 3.2 Perchlorate analysis by ICMSMS method performance data

## Perchlorate validation using ICMSMS

## Perchlorate in Drinking Water

Sample Name	Concentration (ng/l)
<i>Drinking Water unspiked</i>	
Batch 1 DWA	693
Batch 1 DWB	717
Batch 2 DWA	724
Batch 2 DWB	709
Batch 3 DWA	754
Batch 3 DWB	750
Batch 4 DWA	829
Batch 4 DWB	741
Batch 5 DWA	712
Batch 5 DWB	695
Batch 6 DWA	666
Batch 6 DWB	676
<b>Average</b>	<b>722.07</b>
<b>Total Standard Deviation</b>	<b>43.50</b>
<b>%RSD</b>	<b>6.0%</b>
<i>Drinking Water + 1000 ng/l spike</i>	
Batch 1 DWLSA	1890
Batch 1 DWLSB	1850
Batch 2 DWLSA	1840
Batch 2 DWLSB	1840
Batch 3 DWLSA	1735
Batch 3 DWLSB	1719
Batch 4 DWLSA	1525
Batch 4 DWLSB	1531
Batch 5 DWLSA	1702
Batch 5 DWLSB	1718
Batch 6 DWLSA	1692
Batch 6 DWLSB	1664
<b>Average</b>	<b>1725.57</b>
<b>Total Standard Deviation</b>	<b>117.69</b>
<b>%RSD</b>	<b>6.8%</b>
<b>% Recovery</b>	<b>100.4%</b>
<i>Drinking Water + 4000 ng/l spike</i>	
Batch 1 DWHSA	4920
Batch 1 DWHSB	4920
Batch 2 DWHSA	4790
Batch 2 DWHSB	4750
Batch 3 DWHSA	4771
Batch 3 DWHSB	4816
Batch 4 DWHSA	4838
Batch 4 DWHSB	4615
Batch 5 DWHSA	4756
Batch 5 DWHSB	4722
Batch 6 DWHSA	4916
Batch 6 DWHSB	5086
<b>Average</b>	<b>4825.01</b>
<b>Total Standard Deviation</b>	<b>122.05</b>
<b>%RSD</b>	<b>2.5%</b>
<b>% Recovery</b>	<b>102.6%</b>

## Perchlorate in River Water

Sample Name	Concentration (ng/l)
<i>River Water unspiked</i>	
Batch 1 RWA	342
Batch 1 RWB	340
Batch 2 RWA	315
Batch 2 RWB	334
Batch 3 RWA	320
Batch 3 RWB	312
Batch 4 RWA	325
Batch 4 RWB	347
Batch 5 RWA	311
Batch 5 RWB	311
Batch 6 RWA	244
Batch 6 RWB	252
<b>Average</b>	<b>312.87</b>
<b>Total Standard Deviation</b>	<b>32.86</b>
<b>%RSD</b>	<b>10.5%</b>
<i>River Water + 1000 ng/l spike</i>	
Batch 1 RWLSA	1480
Batch 1 RWLSB	1490
Batch 2 RWLSA	1450
Batch 2 RWLSB	1440
Batch 3 RWLSA	1467
Batch 3 RWLSB	1451
Batch 4 RWLSA	1383
Batch 4 RWLSB	1330
Batch 5 RWLSA	1383
Batch 5 RWLSB	1330
Batch 6 RWLSA	1328
Batch 6 RWLSB	1340
<b>Average</b>	<b>1406.05</b>
<b>Total Standard Deviation</b>	<b>63.43</b>
<b>%RSD</b>	<b>4.5%</b>
<b>% Recovery</b>	<b>109.3%</b>
<i>River Water + 4000 ng/l spike</i>	
Batch 1 RWHSA	4590
Batch 1 RWHSB	4650
Batch 2 RWHSA	4430
Batch 2 RWHSB	4480
Batch 3 RWHSA	4331
Batch 3 RWHSB	4376
Batch 4 RWHSA	4596
Batch 4 RWHSB	4487
Batch 5 RWHSA	4507
Batch 5 RWHSB	4459
Batch 6 RWHSA	4658
Batch 6 RWHSB	4703
<b>Average</b>	<b>4522.25</b>
<b>Total Standard Deviation</b>	<b>117.28</b>
<b>%RSD</b>	<b>2.6%</b>
<b>% Recovery</b>	<b>105.2%</b>

**Table 3.3 Laboratory Blank Water**

<i>Distilled Water Blank</i>	<i>Perchlorate (ng/l)</i>
Batch 1 DIA	5.565
Batch 1 DIB	6.815
Batch 2 DIA	2.244
Batch 2 DIB	2.688
Batch 3 DIA	2.358
Batch 3 DIB	2.704
Batch 4 DIA	4.708
Batch 4 DIB	3.095
Batch 5 DIA	3.469
Batch 5 DIB	2.952
Batch 6 DIA	1.962
Batch 6 DIB	2.362
<b>Average</b>	<b>3.41</b>
<b>Total Standard Deviation</b>	<b>1.51</b>
<b>%RSD</b>	<b>44.1%</b>

### Method Detection Limit

The method detection limit was calculated using unspiked tap and river water using the principles of Cheeseman and Wilson (NS30 1989) (Cheeseman & Wilson, 1989). However, the concentration of perchlorate in unspiked tap water samples (tap blank) was high, which resulted in a high limit of detection.

Analysis of six batches of tap water from another source, together with a fresh set of river water samples was repeated to derive the limit of detection.

A summary of these calculations is shown in Table 3.4 and Table 3.5.

**Table 3.4 Summary of calculation for limit of detection in river water**

<b>Batch</b>	<b>Concentration (ng/l)</b>	<b>Batch Mean Result</b>	<b>Estimate of within-batch SD</b>	<b>Estimate of within-batch variance</b>
<b>1</b>	496.2 501.4	498.809	3.69393	13.64509
<b>2</b>	476.8 477.7	477.2435	0.64842	0.42044
<b>3</b>	498.6 475.1	486.856	16.61984	276.21901
<b>4</b>	462.0 463.2	462.58	0.83439	0.69620
<b>5</b>	479.7 470.1	474.874	6.81227	46.40698
<b>6</b>	472.5 468.8	470.633	2.57811	6.64666
<b>Mean</b>	<b>478.4993</b>			
<b>M1</b>	<b>622.9748</b>			
<b>M0</b>	<b>57.3391</b>			
<b>F Value Observed</b>	<b>10.8648</b>			
<b>Sw</b>	<b>7.5723</b>			
<b>Sb</b>	<b>16.8172</b>			
<b>St</b>	<b>25.5273</b>			
<b>Rel SD(St)</b>	<b>0.0533</b>			
<b>F0.05</b>				
<b>Calculated F</b>				
<b>Est Deg F</b>	<b>19748.4495</b>			
<b>Limit of Detection</b>	<b>38.5838</b>	<b>ng/l</b>		

**Table 3.5 Summary of calculation for limit of detection in tap water**

Batch	Concentration (ng/l)	Batch Mean Result	Estimate of within-batch SD	Estimate of within-batch variance
1	294.3	295.8185	2.12061	4.49700
	297.3			
2	277.6	276.923	0.92065	0.84760
	276.3			
3	282.3	288.007	8.11759	65.89520
	293.7			
4	272.2	274.476	3.26683	10.67220
	276.8			
5	282.2	281.2285	1.32017	1.74284
	280.3			
6	280.3	282.7765	3.44715	11.88281
	285.2			
<b>Mean</b>	<b>283.2049</b>			
<b>M1</b>	<b>171.6983</b>			
<b>M0</b>	<b>15.9229</b>			
<b>F Value Observed</b>	<b>10.7831</b>			
<b>Sw</b>	<b>3.9904</b>			
<b>Sb</b>	<b>8.8254</b>			
<b>St</b>	<b>13.4037</b>			
<b>Rel SD(St)</b>	<b>0.0473</b>			
<b>F0.05</b>				
<b>Calculated F</b>				
<b>Est Deg F</b>	<b>1543.0955</b>			
<b>Limit of Detection</b>	<b>20.3325</b>	<b>ng/l</b>		

### Sample Stability

Stability of samples stored in plastic bottles over 7 days at ambient temperature is shown in [Table 3.6](#)~~Table 3.6~~. The results show that perchlorate is stable in plastic bottles stored at <25°C over 7 days.

**Table 3.6 Stability of perchlorate spiked samples stored at ambient temperature for 7 days**

<b>Stability of perchlorate stored for 7 days at &lt;25°C</b>				
<b>Perchlorate in river water</b>				
			day 0	day 7
			1335.505	1322.547
			1291.855	1368.618
			1304.473	1397.157
			1282.229	1314.829
			1317.346	1287.622
	counts	number	5.0	5.0
		Average each sample	1306.282	1338.2
		Stdev within sample	21.01	44.02
		pooled VAR	1189.61	
		<b>Mean difference</b>	<b>31.87</b>	
		pooled sd	34.491	
		<b>mean diff%</b>	<b>2</b>	
numbers samples	0.63	sigma d	21.814	
		t statistic	1.46	
df	8.0	t from tables	2.31	
		<b>Significance</b>	<b>NISG</b>	<b>(Not significant)</b>
<b>Perchlorate in tap water</b>				
			day 0	day 7
			1644.099	1650.724
			1683.287	1610.244
			1664.475	1701.997
			1638.592	1624.169
			1653.272	1669.635
	counts	number	5.0	5.0
		Average each sample	1656.745	1651.4
		Stdev within sample	17.79	36.50
		pooled VAR	824.26	
		<b>Mean difference</b>	<b>-5.39</b>	
		pooledsd	28.710	
		<b>mean diff%</b>	<b>0</b>	
numbers samples	0.63	sigma d	18.158	
		t statistic	-0.30	
df	8.0	t from tables	2.31	
		<b>Significance</b>	<b>NISG</b>	<b>(Not Significant)</b>

### **3.4 Conclusion**

An analytical method has been developed and validated to determine perchlorate in raw and final drinking water.

Limits of detection (LOD) in river water and tap water samples were calculated to be 0.039 µg/l and 0.020 µg/l, respectively. The % recovery (and % RSD) of low spiked (1000 ng/l) samples of river water and tap water were 100.4% (6.8% RSD) and 109.0% (4.5% RSD), respectively, and at a high spike, the recovery and % RSD were 102.6% (2.5% RSD) and 105.2% (2.6% RSD), respectively.

The samples were stable over a 7 day period stored at ambient temperature in plastic bottles.

### **3.5 References**

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## 4. EVALUATION OF PERCHLORATE IN COMMERCIAL HYPOCHLORITE AND AN INITIAL INVESTIGATION OF DRINKING WATER CONCENTRATIONS

Due to reports that perchlorate is formed during storage of hypochlorite solutions (Section 2; SWRCB, 2005), which is widely used in drinking water treatment (DWI, 2009), and in order to have an initial investigation into final drinking water levels of perchlorate, a mini-test was performed during the method validation phase (Section 3).

### 4.1 Sample Preparation

Treated samples consisted of either single distilled, deionised or cold tap water dosed with commercial sodium hypochlorite (NaOCl) of ultra low bromate grade obtained from Albion Chemicals, Thetford (manufactured on 26/09/07) ([Table 4.1](#)~~Table 4.1~~). Prior to use, the sodium hypochlorite had been stored in the laboratory at 4°C in the dark since the date of manufacture. Samples were then stored in the laboratory, in the dark and at ambient temperature. Sodium hypochlorite was diluted x1000 in distilled water to produce the stock solution, of which 30 ml was added to test water to make up to 1 litre. The chlorine concentration was measured using the palintest DPD method. Control samples did not have any sodium hypochlorite added.

**Table 4.1 Sample preparation of the mini-test and associated chlorine concentrations**

Test water	Chlorine dosed?	Free chlorine concentration (mg Cl <sub>2</sub> /l)	Total chlorine concentration (mg Cl <sub>2</sub> /l)
Single Distilled	Y	2.72 ***	2.84
Single Distilled	N	0	0
Deionised**	Y	2.84	2.84
Deionised**	N	0	0
Cold tap*	Y	2.84	2.84
Cold tap*	N	0	0

\* WRc Swindon laboratory tap water is not a direct feed from the mains, but stored in a header tank, hence there is no residual chlorine.

\*\* Deionised water is treated by activated carbon pre-filter, reverse osmosis, ion-exchange and UV.

\*\*\* This is considered unlikely to be significantly different from the other chlorine measurements, as it is equivalent to just 1% difference in transmittance.

### 4.2 Results

The results are presented in Table 4.2.

**Table 4.2 The results of the mini-test for perchlorate (the LOD is 0.020 µg/l)**

Sample	Perchlorate concentration (µg/l)
<i>Spikes for method validation:</i>	
Perchlorate 0 µg/l *	0.010
Perchlorate 0.125 µg/l *	0.128
Perchlorate 0.250 µg/l *	0.249
Perchlorate 0.500 µg/l *	0.489
Perchlorate 1.000 µg/l *	0.991
Perchlorate 2.500 µg/l *	2.510
Perchlorate 5.000 µg/l *	4.998
<i>Evaluation of commercial hypochlorite:</i>	
Distilled Water	< 0
Distilled Water & NaOCl	0.572
Tap Water	0.162
Tap water & NaOCl	0.685
Deionised Water	< 0
Deionised Water & NaOCl	0.545
<i>Spike for method validation:</i>	
Perchlorate 0.500 µg/l *	0.475
<i>Initial drinking water investigation:</i>	
Business 1 tap water **	0.794
Business 2 tap water **	0.776
Business 3 tap water **	0.794
<i>Spike for method validation:</i>	
Perchlorate 0.500 µg/l *	0.506

\* These are various validation samples included for completion.

\*\* These samples were included as concern was expressed over the concentration of perchlorate in the Reading tap water used in the method validation. All three locations are in the nearby vicinity of the STL Reading laboratory, which undertook the analysis.

### 4.3 Conclusion

The validation samples illustrate the method is functioning well and repeatability is good. Samples that were spiked with an old solution of commercial sodium hypochlorite that is widely used in drinking water treatment, had increased perchlorate levels. A spike of hypochlorite sufficient to generate approximately 3 mg/l free chlorine increased the perchlorate concentration by 0.520-0.560 µg/l. The original result noted for the laboratory tap water at the test laboratory in the Method Development Report (Section 3; 0.666-0.829 µg/l) is backed up in this repeat test and compares favourably with samples from the three nearby businesses. WRc Swindon tap water has a perchlorate concentration of 0.162 µg/l.

## 5. SELECTION OF SURVEY SITES

For the monitoring of perchlorate, it was agreed with Defra/DWI that 20 sites would be sampled, 5 control sites and 15 perceived higher-risk sites from England and Wales. These sites included lowland and upland surface waters and groundwater sources, covered both private and public supplies, and represented the geographical area. The control sites were chosen from rural areas, with no perceived higher-risk factors nearby.

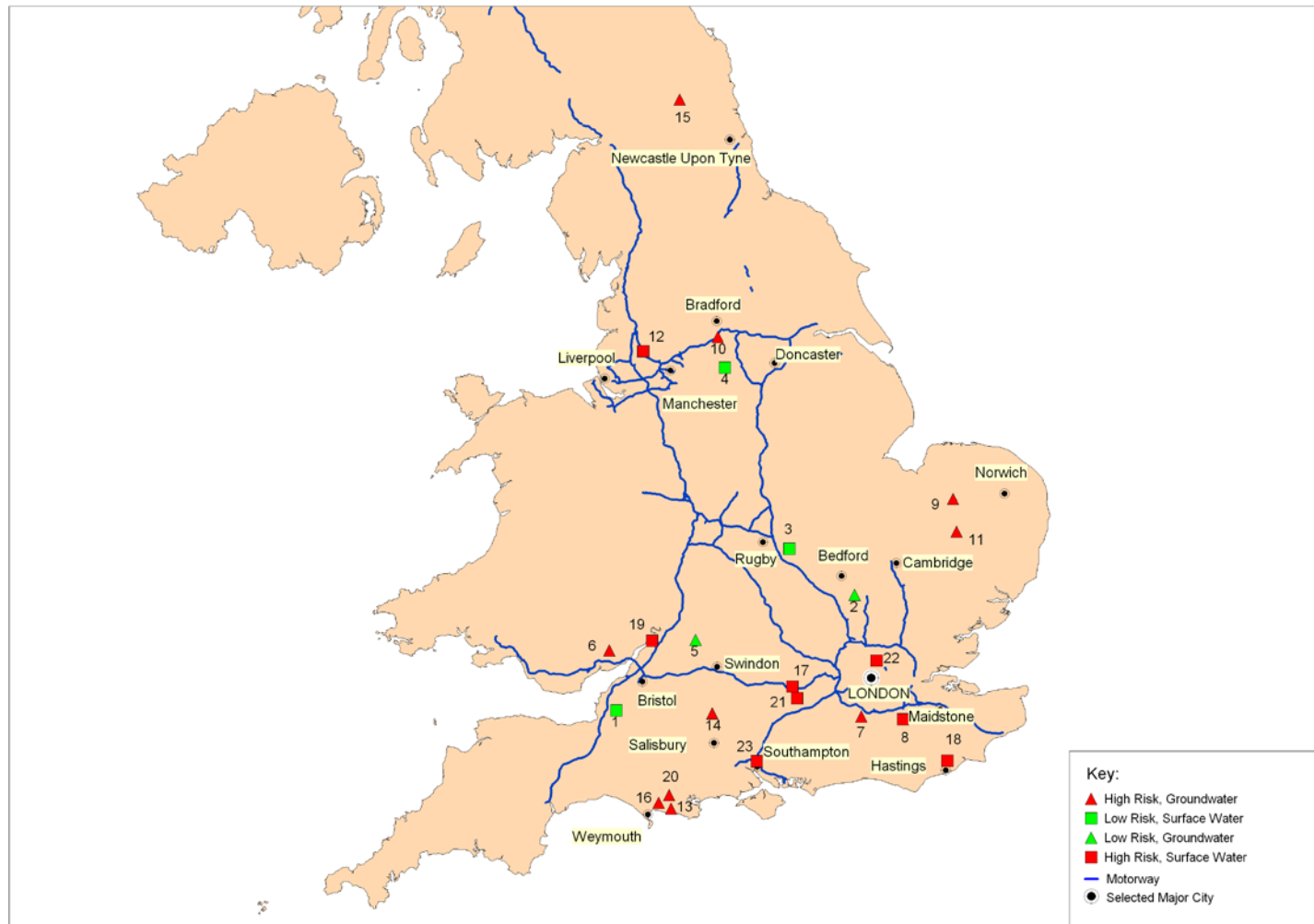
From the investigation into the usage of perchlorate it was apparent that main uses of potential relevance to the UK were fireworks, ammunition/military, with several others having minor relevance such as quarry blasting, drinking water treatments (e.g. hypochlorite, electrolytic chlorination, ozonation) and nuclear activity. All water companies were asked to nominate any sites that could be deemed as potentially higher-risk according to the risk factors noted above. Consultations with local councils and private organisations were also held to identify any private supplies at a higher risk of perchlorate. Regarding water sources, unconfined, shallow or adit sources were deemed to be at high risk following historical use of the compounds.

The Literature Review (Section 2) identified that minimal monitoring had been performed in England and Wales. That undertaken related to either the Dstl (Defence Science and Technology Laboratory) monitoring of the primary UK site for the demolition and disposal of munitions, or the rural monitoring undertaken by a Water Undertaker. The sites chosen in this study were selected such that they did not duplicate any of the areas already sampled for perchlorate.

The results from the Dstl study at Foulness Island, off the coast of Essex (Section 2.4.4) indicated that it would be beneficial to sample raw and treated drinking water from this area to elucidate whether perchlorate could enter any drinking water sources from the release of munitions demolition. However, consultations held with the local water company and council indicated that there were no public or private sites suitable.

In sampling session 3, which focussed on the impacts of firework displays held for Guy Fawkes Night / Bonfire Night (5<sup>th</sup> November), three additional sites were included (sites 21-23) to assess this effect.

The geographical distribution of the sites chosen is shown in [Figure 5.1](#)~~Figure 5.1~~.



**Figure 5.1 The geographical distribution of the sampling sites chosen**

## **6. MONITORING**

### **6.1 Sampling**

Samples were taken from prescribed sample points (usually taps); the sample being poured directly into the sample bottle (bottles were Azlon high density polyethylene, HDPE, with a volume of 125 ml). Although some samples were taken using a stainless steel jug lowered into position by nylon rope. All samples were kept in the dark in cool-boxes containing frozen ice-packs at between approximately 4°C to 8°C during transit, and either taken directly to the analysing laboratory, or kept overnight in a cold-room at approximately 4°C until submission to the analysing laboratory within approximately 48 hours of sampling.

#### **6.1.1 Sampling Survey 1**

The first sampling survey was carried out during the period 22/04/08 to 12/05/08. Raw samples only were taken from the 5 control sites, and raw and final waters were sampled from the majority of the 15 higher-risk sites. Site 13 was not sampled as it was not in operation at the time (i.e. off-line). No final water was sampled at site 6 as water is pumped elsewhere for treatment, and no final water was sampled at site 10 as it is a private supply with no treatment. At sites where the treatment method was being examined (i.e. site 17 for hypochlorite dosing, site 18 for electrolytic chlorination dosing and site 19 for ozonation), samples from within the treatment process were also taken.

#### **6.1.2 Sampling Survey 2**

The second sampling survey was carried out during the period 28/07/08 to 08/08/08. Raw samples only were taken from the 5 control sites, and raw and final waters were sampled from the majority of the 15 higher-risk sites. No final water was sampled at site 6 as water is pumped elsewhere for treatment, no final was sampled at site 10 as it is a private supply with no treatment, and no final water was sampled at site 13 as it was off-line. The choice of samples taken was the same as in session 1, but in addition, the effect of nitrate removal (using ion exchange) was assessed at site 17. Field blanks with distilled water from sites 1, 7 and 11 were also taken, which covered all of the samplers.

Field blanks were prepared using analytical grade laboratory water poured directly into 125 ml HDPE plastic bottles of the same type as those used for the analytical samples. At each site, a field blank was taken to one of the positions from which samples taken at the site were being transferred to the sample bottles. At each position, the analytical samples were taken from prescribed sample points (usually taps); the sample being poured directly into the sample bottle. To mimic this procedure, a field blank was manually transferred to a clean 125 ml HDPE plastic bottle taken at random from the same batch of bottles used for the samples. This field blank sample was then labelled and stored alongside the samples during transit and subsequent delivery to the analytical laboratory performing the analysis. Field blanks were included to determine whether the sampling procedure used introduced any perchlorate contamination into the process.

### 6.1.3 Sampling Survey 3

The third sampling survey was carried out during the period 06/11/08 to 19/11/08. In this round, the occurrence of Guy Fawkes Night / Bonfire Night (5<sup>th</sup> November) was used to examine whether perchlorate entered raw waters and environmental waters from the use of perchlorate-containing fireworks. Therefore the sites below were not sampled:

Site 2: this control site was considered suitable to exclude, as in the previous two sampling sessions, the Limit of Detection (LOD) of 0.039 µg/l had not been reached.

Site 7: although originally identified as a high risk site due to the impact of firework displays, when this was investigated further it was found that the displays were at least 8 km from the site, so was not considered a large enough risk to include as a site impacted by fireworks.

Site 8: although originally identified as a high risk site due to the impact of firework displays, when this was investigated further it was found that the displays were at least 5 km from the site, so was not considered a large enough risk to include as a site impacted by fireworks.

Site 12: the levels of perchlorate detected at this site in the previous two sampling sessions were relatively low, so it was considered suitable to exclude it.

Site 13: it had been identified that this site is typically off-line for the winter months, so only raw samples could be obtained, therefore, it was considered suitable to exclude.

At the other sites (15 of the original 20), raw samples were taken from the four remaining control sites, and raw and final waters were sampled from the majority of the 11 higher-risk sites. No final water was sampled at site 6 as water is pumped elsewhere for treatment, no final water was sampled at site 10 as it is a private supply with no treatment, and no raw water was sampled at site 16 as it was off-line.

In addition to the above sites, three extra sites were included to focus on the effects of the use of fireworks. Drinking water treatment works in the vicinity of firework displays were deemed to be the most suitable choices for these extra sites, however, only one could be identified. Therefore, the other two sites chosen were environmental surface waters. Samples at these sites were taken before and as close after the relevant firework display as possible.

Site 21: this is a private lake with a firework display held on an island within it. Samples were taken 1 day before and 1 day after the display, downstream of where the display site was located.

Site 22: this is a treatment works approximately 0.5 km from a large fireworks display. Samples of raw and treated water were taken 2 days before and 2 days after the display.

Site 23: this is a private lake with a firework display held on its edge. Samples were taken 1 day before and 1 day after the display, downwind of where the display site was located.

Field blanks with distilled water from sites 4, 11, 16 and 17 were also taken, which covered all of the samplers.

#### 6.1.4 Sampling Survey 4

The fourth and final sampling survey was carried out during the period 27/01/09 to 30/01/09. Raw water samples from the control sites 1, 3 and 5 were taken. Raw and final waters were sampled from sites 7, 8, 9, 11, 14 and 17. The remaining sites were excluded as they either showed levels of perchlorate below the LOD of 0.039 µg/l in previous sessions (sites 2, 4 and 15), or they showed relatively low levels and had been sampled at least twice before (sites 6, 10, 12, 16, 18, 19 and 20). Site 13 was not sampled as it was off-line. The additional sites that were included in session 3 (sites 21, 22 and 23) were excluded as the impact of firework displays was not the focus of this sampling session.

Field blanks with distilled water from sites 5 and 9 were also taken, which covered all of the samplers.

#### 6.2 Results

The results of all the field blanks were below the LOD for perchlorate.

The results from the control sites for all four sampling sessions are detailed in [Table 6.1](#)~~Table 6.1~~ [Table 6.4](#), and those from the perceived higher-risk sites in [Table 6.2](#)~~Table 6.2~~.

**Table 6.1 Perchlorate results of raw water sampling at the five control sites for all four sampling sessions**

Site No.	Water Type	Treatment	Typical Concentrations of...				Perchlorate Concentration ( $\mu\text{g/l}$ )			
			pH	Chloride (mg/l)	Alkalinity (mg/l)	Nitrate (mg/l)	Session 1 (22/04/08 - 12/05/08)	Session 2 (28/07/08 - 08/08/08)	Session 3 (06/11/08 - 19/11/08)	Session 4 (27/01/09 - 30/01/09)
1 (Pu)	SW (lowland)	Slow sand filtration, chlorination using chlorine gas.	8.17 (7.88-8.45) <sup>1</sup>	14.71 (13.60-16.00)	154.94 (115-205)	15.15 (4.80-28.40)	0.091	0.086	0.071	0.074
2 (Pu)	GW (C)	Iron/manganese removal, chlorination using chlorine gas.	7.09 (6.96-7.22) <sup>2</sup>	14.38 (11.00-19.90)	147.88 (124-163)	0.42 (0.03-0.76)	<0.039	<0.039	not sampled	not sampled
3 (Pu)	SW (lowland)	Primary filters, GAC, slow sand filtration, aeration to increase dissolved oxygen (DO) following degradation in slow sand stage, chlorination using chlorine gas, followed by ammonium sulphate addition to produce chloramine.	8.39 (7.46-9.98) <sup>3</sup>	27.69 (23.10-33.70)	83.44 (32.20-119)	13.02 (3.12-26.8)	0.118	0.058	0.065	0.113
4 (Pu)	SW (upland)	Rapid gravity filters, chlorination by gas.	5.61 (4.40-8.40) <sup>4</sup>	-	-	-	<0.039	<0.039	<0.039	not sampled
5 (Pu)	GW (C + UC) <sup>5</sup>	Chlorination using hypochlorite	6	6	6	6	0.173	0.188	0.170	0.170

Where, Cl: chlorine, groundwater (C): confined groundwater, groundwater (UC): unconfined groundwater, Pu: public water supply, Pr: private water supply, SW: surface water. 1: Associated parameters sampled from 03/01/07 - 19/12/07, from raw water. Alkalinity is as  $\text{CaCO}_3$ , and nitrate is as  $\text{NO}_3$  and from 04/01/06 to 03/07/08. 2: Associated parameters sampled from 01/01/07 - 01/01/08, from raw water. Alkalinity is as  $\text{CaCO}_3$ , nitrate is not specified. 3: Associated parameters sampled from 01/01/07 - 01/01/08, from raw water. Alkalinity is as  $\text{CaCO}_3$ , nitrate is not specified. 4: pH was sampled from 2007 from raw water. 5: At this site, boreholes draw from a confined aquifer, but the impact of the abstraction is considered to probably extend to an outcrop, so draws water from an unconfined aquifer. 6: No information has been provided by the relevant water undertaker.



**Table 6.2 Perchlorate results of sampling at the perceived higher-risk sites for all four sampling sessions**

Site No.	Water Type	Treatment	Risk type	Typical Concentrations of...				Sampled where	Perchlorate Concentration (µg/l)			
				pH	Chloride (mg/l)	Alkalinity (mg/l)	Nitrate (mg/l)		Session 1 (22/04/08 - 12/05/08)	Session 2 (28/07/08 - 08/08/08)	Session 3 (06/11/08 - 19/11/08)	Session 4 (27/01/09 - 30/01/09)
6 (Pu)	SW (upland)	No treatment here – water is pumped to another site for treatment after being blended with some other water.	Royal Ordnance site nearby	7.94 (7.58-8.58) <sup>1</sup>	-	-	2.36 (0.82-4)	Raw	0.052	0.071	0.078	not sampled
7 (Pu)	GW (UC, but surface is influenced by a local river)	Aeration and lime pellet softening of two thirds of the raw water and combined with the other third, which is prechlorinated. Then it is all coagulated with iron sulphate and polyelectrolyte is added, then rapid gravity filters (RGF), UV disinfection and chlorination by Cl gas. The Cl residual is reduced by sulphur dioxide, and ammonia is added to form monochloramine. Orthophosphoric acid is also dosed for plumbosolvency control.	Big fireworks display ~8 km away	8.04 (7.40-8.20) <sup>2</sup>	28.12 (24.10-31.20)	296.77 (256-322)	27.35 (24.29-31.19)	Raw	0.962	0.933	not sampled	0.991
				7.71 (7.5-8) <sup>3</sup>	29.93 (26.70-32.8)	156.87 (96-271)	29.90 (26.79-33.49)	Final	1.083	1.16	not sampled	not sampled
8 (Pu)	SW (lowland)	Prechlorination, coagulation with aluminium sulphate and polyelectrolyte addition before clarification, rapid gravity sand filtration, GAC, orthophosphoric acid addition, addition of caustic (if needed), aeration, Cl and ammonification. Cl is by Cl gas. Carbon in the GAC beds was replaced with new virgin carbon between Oct 07 and March 08.	Big fireworks display ~5.7 km away	8.13 (7.80-8.70) <sup>4</sup>	36.99 (29.10-42.80)	117.46 (90-143)	13.08 (4.50-19.13)	Raw	0.358	0.277	not sampled	0.374
				7.81 (7.5-8.1) <sup>5</sup>	44.11 (37.10-51.10)	87.36 (52-117)	14.34 (4.79-20.39)	Final	0.146	0.467	not sampled	not sampled
9 (Pu)	GW (UC at site and main catchment, but locally C to the east)	GAC, Cl gas, blended. GAC beds commissioned around December 1993, last regenerated in approx. 2006.	Fireworks (manufactured nearby)	7.2 <sup>6</sup>	30.2	246	74	Raw (BH 1 22/04/08)	2.992	off-line	not sampled	off-line
								Raw (BH 2 08/05/08)	2.853	off-line	3.194	3.235
								Raw (BH 3 08/08/08)	off-line	3.021	off-line	not sampled
								Final	1.701	1.596	1.927	0.319
				7.37 <sup>7</sup>	32.2	270	-					

Site No.	Water Type	Treatment	Risk type	Typical Concentrations of...				Sampled where	Perchlorate Concentration (µg/l)			
				pH	Chloride (mg/l)	Alkalinity (mg/l)	Nitrate (mg/l)		Session 1 (22/04/08 - 12/05/08)	Session 2 (28/07/08 - 08/08/08)	Session 3 (06/11/08 - 19/11/08)	Session 4 (27/01/09 - 30/01/09)
10 (Pr)	GW (UC)	None (UV unit if operational)	Fireworks (manufactured nearby + display 1 km away)	NA <sup>8</sup>	N/A	N/A	N/A	Raw	1.108	0.870	0.987	not sampled
11 (Pu)	GW (UC)	Raw 1 is a separate borehole in a different location to those (raw 2a and b) at the raw 2 location. Raw 1 may be regarded as a 'satellite' of the raw 2 facility about 1.2 km away. Raw 2 houses treatment for the raw 1 borehole input in a new building on the site, and treatment for the raw 2a and raw 2b is handled in other buildings on the raw 2 site. There is nitrate removal (using ion exchange) for the raw 1 water at the raw 2 site. The other processes are iron removal and manganese removal. Cl at the raw 2 site is by gas. The finals are blended approximately 40:60 for raw 1: raw 2.	Military (firing ranges nearby)	7.42 <sup>9</sup>	26.3	191	30.2	Raw 1 (22/04/08)	4.311	4.981	4.276	4.118
								Raw 1 (08/05/08)	3.978	not sampled	not sampled	not sampled
								Raw 2a	1.744	1.66	off-line	1.562
								Raw 2b	1.406	1.48	1.581	off-line
								After nitrate removal of raw 1 water	not sampled	0.314	0.409	0.515
				-	-	-	-	Final (raw 2 a + b only)	1.682	1.672	not sampled	not sampled
				-	-	-	-	Final (raw 1 and raw 2a and 2b combined)	1.980	2.073	1.891	1.922
12 (Pu)	SW (chain of impounding reservoirs)	Coagulation, clarification (DAF), first and second stage filtration, chlorination and plumbosolvency control. Chlorination is by gas.	Military (munitions found below water level in one of the reservoirs)	-	-	-	-	Raw	0.119	0.062	not sampled	not sampled
				7.37 (6.97-7.86) <sup>10</sup>	15.51 (14.10-24.10)	12.70 (8.2-15)	0.72 (0.38-0.99)	Final	0.089	0.065	not sampled	not sampled

Site No.	Water Type	Treatment	Risk type	Typical Concentrations of...				Sampled where	Perchlorate Concentration (µg/l)			
				pH	Chloride (mg/l)	Alkalinity (mg/l)	Nitrate (mg/l)		Session 1 (22/04/08 - 12/05/08)	Session 2 (28/07/08 - 08/08/08)	Session 3 (06/11/08 - 19/11/08)	Session 4 (27/01/09 - 30/01/09)
13 (Pu)	GW (UC)	Super and dechlorination only (the Cl method does not matter, as this site has never been on-line).	Military site (munitions) nearby	7.28 (7.10-7.60) <sup>11</sup>	31.21 (15-33.60)	-	6.79 (4.24-7.65)	Raw BH2	off-line	0.378	not sampled	off-line
				-	-	-	-	Final	off-line	off-line	not sampled	off-line
14 (Pu)	GW (UC)	Marginal chlorination by gas.	Military (next to site of military and tank testing)	7.52 (7.4-7.6) <sup>12</sup>	10.49 (9.9-11.6)	228 (180-320)	2.63 (2.35-3.15)	Raw BH1	off-line	1.642	off-line	1.796
				-	-	-	-	Raw BH3	1.949	off-line	1.741	not sampled
				-	-	-	-	Final	1.529	1.652	1.707	not sampled
15 (Pr)	GW (UC)	Chlorination (hypochlorite) to achieve residual of 0.3-0.5 mg Cl /l.	Military site nearby	N/A <sup>8</sup>	N/A	N/A	N/A	Raw	<0.039	<0.039	<0.039	not sampled
								Final	0.066	0.062	<0.020	not sampled
16 (Pu)	GW (UC)	Super and dechlorination only. Chlorination is by gas.	Other (quarry blasting nearby)	-	-	-	-	Raw BH3	0.228	0.251	off-line <sup>24</sup>	not sampled
				7.25 (7.1-7.8) <sup>13</sup>	26.76 (25.3-28.6)	236.75 (206-252)	8.79 (8.19-9.42)	Final	0.251	0.263	0.236 <sup>24</sup>	not sampled
17 (Pu)	SW (lowland)	Preozone, coagulation, Actiflow, RGF, slow sand filters, super and dechlorination. Chlorination is by hypochlorite.	Other (hypochlorite ; and it has ozone treatment with high chlorine in the water)	8.3 <sup>14</sup>	22	-	5.5	Raw	0.545	0.497	0.536	0.455
				-	-	-	-	After preozonation	0.546	0.513	not sampled	not sampled
				-	-	-	-	Final	0.542	0.543	0.577	not sampled

Site No.	Water Type	Treatment	Risk type	Typical Concentrations of...				Sampled where	Perchlorate Concentration (µg/l)			
				pH	Chloride (mg/l)	Alkalinity (mg/l)	Nitrate (mg/l)		Session 1 (22/04/08 - 12/05/08)	Session 2 (28/07/08 - 08/08/08)	Session 3 (06/11/08 - 19/11/08)	Session 4 (27/01/09 - 30/01/09)
18 (Pu)	GW (UC) & SW (2 impounding reservoirs)	The SW is blended, the GW is aerated, then blended with the SW. Dosing with polyaluminium chloride for coagulation, then DAF, then primary rapid gravity mixed media filters (RGF) (gravel, coarse sand, garnet, anthracite and finer sand), then dosed with sodium hypochlorite (manganese oxidation) and caustic soda (pH adjustment). Then secondary rapid gravity mixed media filters (sand and gravel) and dosed with sodium hypochlorite (from the OSEC plant). Then dosed with sodium bisulphite to reduce the free chlorine levels.	Other (electrolytic chlorination; and it has a high chlorine dose)	7.45 (6.6-8.48) <sup>15</sup>	65.07 (57.7-70.6)	-	0.66 (<0.097-2.23)	Raw 1	0.056	<0.039	off-line	not sampled
				7.03 (6.3-7.6) <sup>16</sup>	-	-	0.1 (<0.097-0.15)	Raw 2 (GW)	<0.039	<0.039	<0.039	not sampled
				7.25 (6.68-7.59) <sup>17</sup>	32	-	0.45 (0.27-0.58)	Raw 3 (SW)	0.078	0.055	0.069	not sampled
				7.34 (6.51-7.9) <sup>18</sup>	53.08 (37.4-66.2)	-	0.53 (<0.097-2.16)	Raw (combined)	0.062	not sampled	not sampled	not sampled
				-	-	79.22 (50.70-233) <sup>19</sup>	-	Final	0.078	0.053	not sampled	not sampled
19 (Pu)	SW (lowland)	Preozonation, coagulation, clarification, filtration, ozonation, GAC and chlorination with gas. GAC beds are <18 months old.	Other (ozone treatment with high chlorine in water)	7.00 (6.41-7.72) <sup>20</sup>	33.60 (24.5-49.3)	148.92 (112-185)	26.31 (10.6-47.8)	Raw	0.217	0.226	0.303	not sampled
				-	-	-	-	After main ozonation	0.221	0.233	not sampled	not sampled
				-	-	-	-	Final	0.266	0.249	0.244	not sampled
20 (Pu)	GW (UC)	Marginal chlorination by chlorine gas.	Other (nuclear facility nearby)	-	-	-	-	Raw BH 1	0.208	0.217	0.205	not sampled
				7.27 (7.1-8) <sup>21</sup>	22.2 (21.1-23.1)	232.75 (202-246)	7.16 (6.73-7.57)	Final	0.209	0.216	0.207	not sampled
21 (N/A)	SW (lowland)	None – it is a private lake not used for drinking water abstraction.	Firework display on island within it	N/A <sup>22</sup>	N/A	N/A	N/A	1 day before display	not included as part of the original sample regime	0.053	6.512	not included as part of the original sample regime
								1 day after display				

Site No.	Water Type	Treatment	Risk type	Typical Concentrations of...				Sampled where	Perchlorate Concentration (µg/l)			
				pH	Chloride (mg/l)	Alkalinity (mg/l)	Nitrate (mg/l)		Session 1 (22/04/08 - 12/05/08)	Session 2 (28/07/08 - 08/08/08)	Session 3 (06/11/08 - 19/11/08)	Session 4 (27/01/09 - 30/01/09)
22 (Pu)	SW (lowland)	This is not relevant as the site is off-line.	Firework display 0.5 km away	N/A <sup>23</sup>	N/A	N/A	N/A	2 days before display	not included as part of the original sample regime	1.432	not included as part of the original sample regime	
								2 days after display				1.531
23 (N/A)	SW (lowland)	None – it is a private lake not used for drinking water abstraction.	Firework display at its edge	N/A <sup>22</sup>	N/A	N/A	N/A	1 day before display	not included as part of the original sample regime	0.327	not included as part of the original sample regime	
								1 day after display				1.270

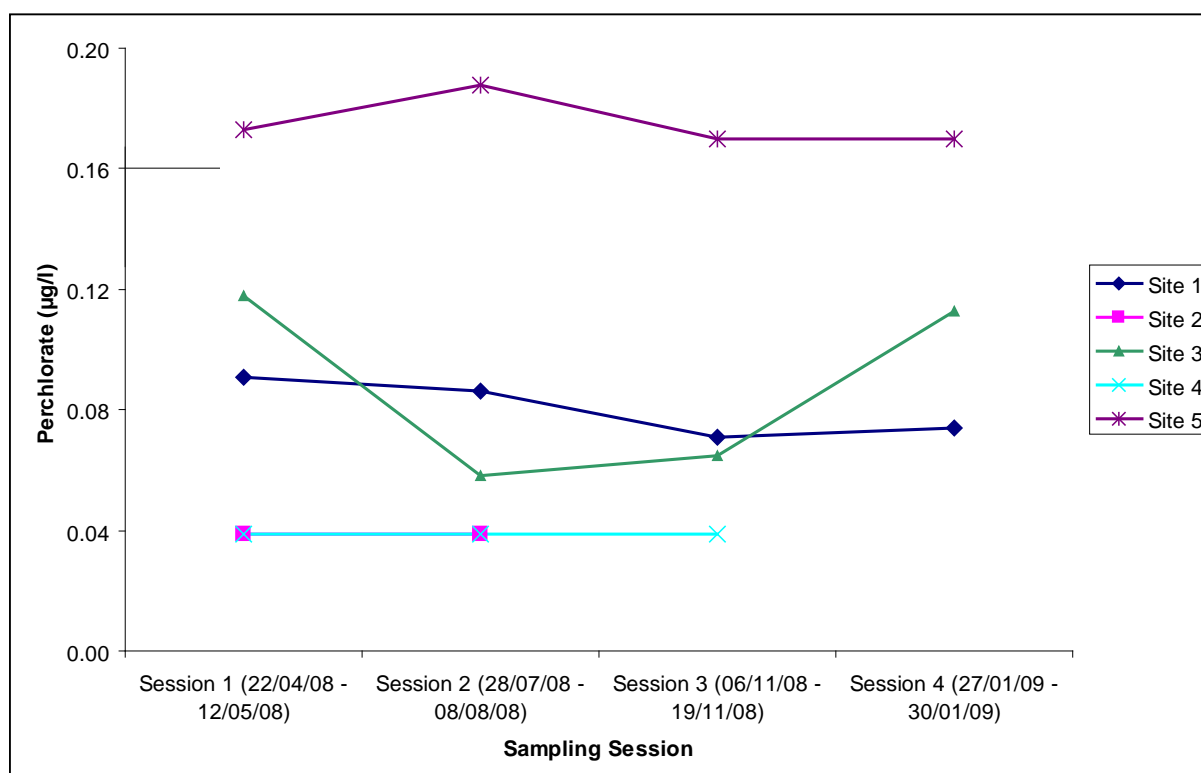
Where, Cl: chlorine, GW: groundwater, groundwater (C): confined groundwater, groundwater (UC): unconfined groundwater, Pu: public water supply, Pr: private water supply, SW: surface water, GAC: granular activated carbon, and HDPE: high-density polyethylene. 1: Associated parameters sampled from 03/09/05 – 11/01/08, from raw water. Nitrate is as N. 2: Associated parameters sampled from 02/01/07 - 02/02/08, from raw water. Nitrate is as NO<sub>3</sub>, alkalinity is unspecified, but stated to be total. 3: Associated parameters sampled from 01/01/07 - 03/07/08, from treated water. Nitrate is as NO<sub>3</sub>, alkalinity is unspecified, but stated to be total. 4: Associated parameters sampled from 03/01/07 - 02/07/08, from raw water. Nitrate is as NO<sub>3</sub>, alkalinity is unspecified. 5: Associated parameters sampled from 01/01/07 - 03/07/08, from treated water. Nitrate is as NO<sub>3</sub>, alkalinity is unspecified. 6: Associated parameters sampled from 2007 - 2008, from raw water. Nitrate is as NO<sub>3</sub>, alkalinity is as CaCO<sub>3</sub>. Nitrate is weighted mean of BH 1, 2 and 3. 7: Associated parameters sampled from unknown date, from treated water (a blend of this water and another water). Alkalinity is as CaCO<sub>3</sub>. 8: No associated parameters are available as this is a private supply. 9: Associated parameters were sampled from an unknown date from raw 2 water. Nitrate is as N and alkalinity is as CaCO<sub>3</sub>. 10: Associated parameters sampled from 02/01/08 - 02/07/08 from water in distribution. Not stated as to what alkalinity or nitrate is measured in. Chlorine data are from 03/01/06 - 21/12/06. 11: Associated parameters sampled from 06/01/06 - 03/10/06 from raw borehole 3 water. Nitrate is as N. 12: Associated parameters sampled from 11/01/06 - 03/12/06 from raw borehole 1 water. Nitrate is as N and alkalinity is as CaCO<sub>3</sub>. 13: Associated parameters sampled from 04/01/06 - 29/12/06 from treated water. Nitrate is as N and alkalinity is as CaCO<sub>3</sub>. 14: Associated parameters sampled from 01/03/08 - 22/08/08 from unspecified water. Nitrate is as N. 15: Associated parameters sampled from 02/01/07 - 28/12/07 from raw 1 water. Nitrate is as N. 16: Associated parameters sampled from 10/04/07 - 24/12/07 from raw 2 water. Nitrate is as N. 17: Associated parameters sampled from 21/11/07 - 28/12/07 from raw 3 water. Nitrate is as N. 18: Associated parameters sampled from 10/01/07 - 28/12/07 from raw (combined) water. Nitrate is as N. 19: Associated parameters sampled from 02/01/07 - 28/12/07 from final water. Alkalinity is as CaCO<sub>3</sub>. 20: Associated parameters sampled from 03/01/07 - 19/12/07 (chlorine and alkalinity only) from raw water. Nitrate is as N and from 03/01/06 - 03/07/08. Alkalinity is as CaCO<sub>3</sub>. pH is from 03/01/07 - 01/01/08. 21: Associated parameters sampled from 03/01/06 - 30/12/06 from treated water. Nitrate is as N and alkalinity is as CaCO<sub>3</sub>. 22: No associated parameters are available as this is a surface water not used for drinking water abstraction. 23: No associated parameters are available as the treatment at this site was not running. 24: The raw water at this site was not sampled as the borehole had shut down just as the sampler arrived at the site. There was, however, sufficient pressure and volume in the system to allow a final sample to be taken.

## 6.3 Discussion

### 6.3.1 General Overview

All the field blanks had non-detectable concentrations of perchlorate (below the Limit of Detection, LOD, of 0.020 µg/l for clean tap waters), indicating no observable faults in the sampling methodology or the analysis.

Perchlorate was not detected in the raw untreated water samples from two of the five control low-risk sites (LOD of 0.039 µg/l for raw untreated water), however, consistent levels (0.058 to 0.188 µg/l) were detected at three sites (sites 1, 3 and 5) (see [Table 6.1](#)). There seems to be no pattern for this occurrence; sites where no perchlorate was detected abstracted water from surface water and groundwater sources, and the sites with perchlorate were again a mixture of surface water and groundwater sources. The seasons seemed to have no effect either; levels were relatively consistent across all four sampling sessions (Figure 6.1). As no treated water samples were analysed, the effect of treatment at these sites could not be assessed. These data would indicate that perchlorate is present in raw untreated water throughout England, albeit at very low levels.



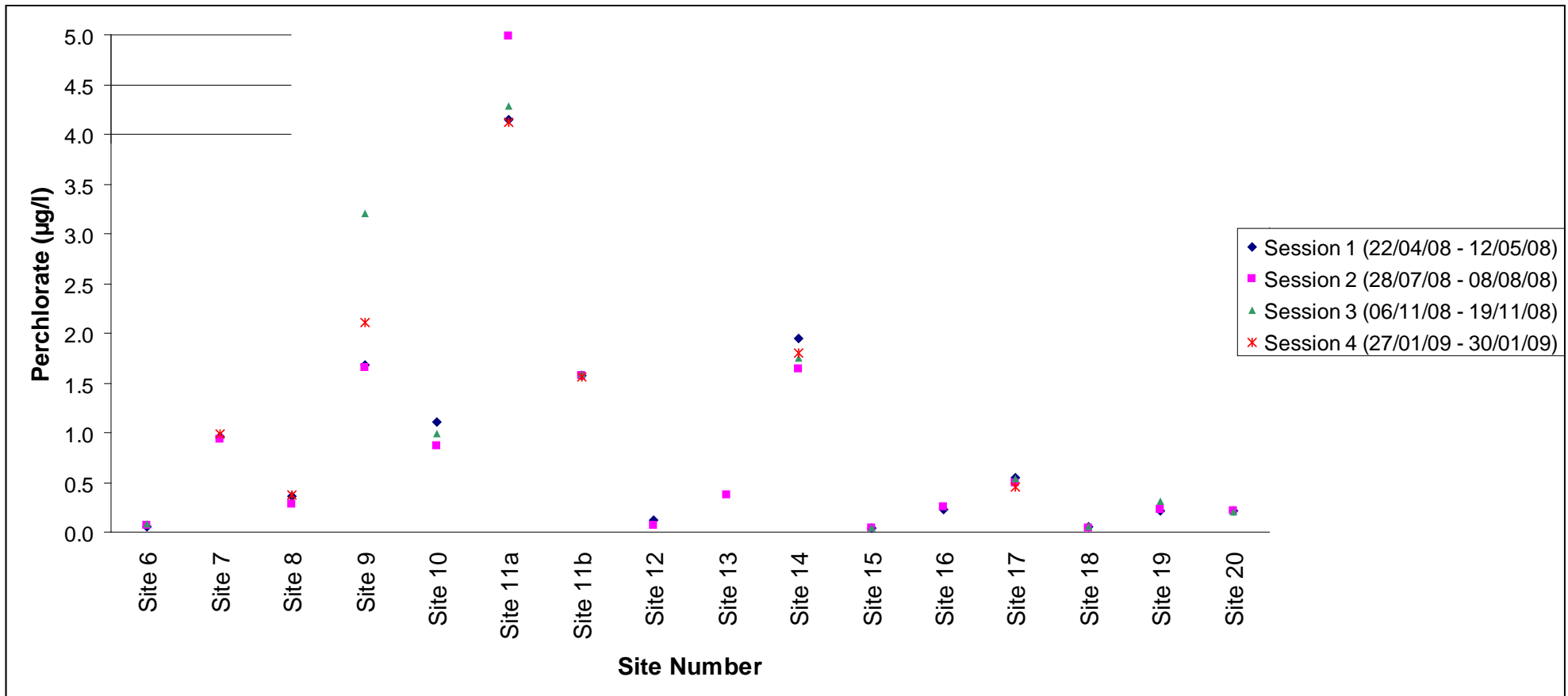
**Figure 6.1 Seasonal variation of perchlorate detected in raw water samples from the five control sites<sup>9</sup>**

<sup>9</sup> Where samples were less than the LOD (i.e. <0.039 µg/l for raw untreated drinking water), a level of 0.039 µg/l has been assumed as a worst case scenario.

Of the higher-risk sites, perchlorate was detected at all of them in either the raw untreated water samples or the final treated samples during at least one of the four sampling sessions ([Table 6.2](#)~~Table 6.2~~). There was no apparent correlation between the type of source water (e.g. surface water or groundwater) and the amount of perchlorate detected. Overall, concentrations were comparable in each session at each site and showed no obvious increase or decrease over the period of this study ([Figure 6.2](#)~~Figure 6.2~~). The maximum values for each session (excluding the level of 6.512 µg/l from site 21, as it is a private lake not used for drinking water abstraction) were all from the raw 1 samples at site 11. The highest treated drinking water samples in each session were 1.980, 2.073, 1.891 and 1.922 µg/l for the four sessions, respectively, and again were all from site 11.

All levels detected are in the lower range of concentrations detected elsewhere in the world, and are therefore comparable to other work (Section 2.5). No samples breached the United States Environmental Protection Agency interim Health Advisory of 15 µg/l (Section 6.3.5), although some do exceed the lowest limits set by some US states ([Table 2.1](#)~~Table 2.1~~). However, assuming a 60 kg adult drinking 2 litres of water a day with a perchlorate concentration of the maximum treated drinking water concentration detected of 2.073 µg/l, the equivalent intake (0.07 µg/kg bw/day) is at least 10-fold less than any of the health-based values set by authoritative bodies (Section 2.2.2). Therefore, no significant, if any, adverse health effects are anticipated following exposure to this water.

There are a number of factors that may influence the perchlorate concentrations detected in drinking water and its sources. To aid assessment of the detected levels, these factors are discussed in turn.



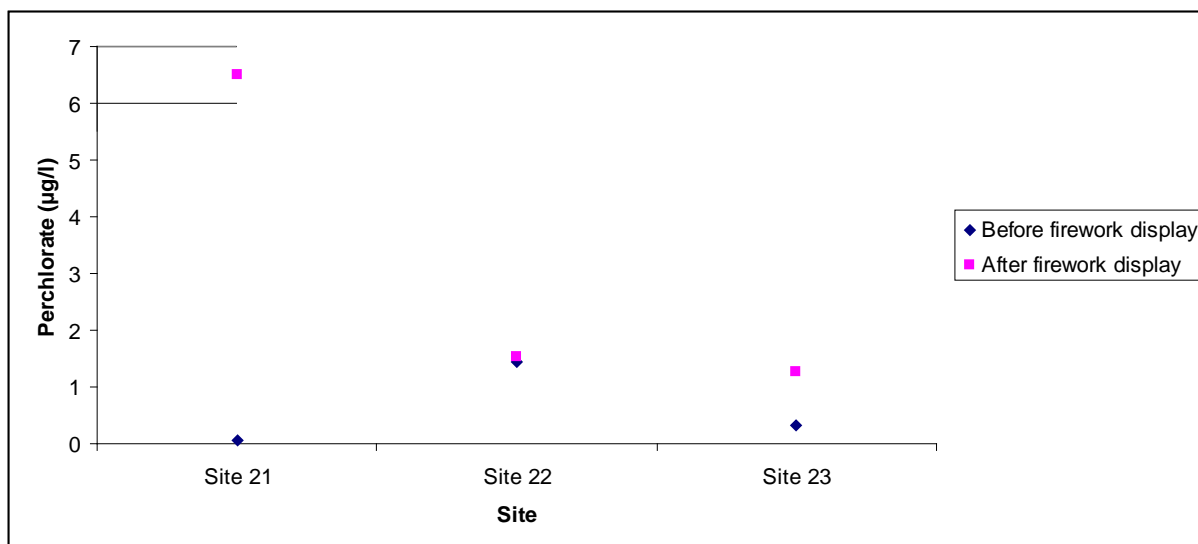
**Figure 6.2** Perchlorate results from raw water samples from the 15 'standard' higher risk sites (sites 21-23 have been excluded from this graph as they were only sampled once)



### 6.3.2 Risk Type

The risk factors associated with the potential presence of perchlorate in raw and treated drinking water were classified into three types when choosing the sites for inclusion in the sampling: fireworks (perchlorate is used as an explosive in fireworks); military (perchlorate is used in various explosives); and other. The latter included miscellaneous risks such as quarry blasting (perchlorate is used as an explosive), use of hypochlorite during treatment (perchlorate may be formed as a contaminant), use of on-site electrolytic chlorination (OSEC) during treatment (forms hypochlorite which may form perchlorate), use of ozonation during treatment (perchlorate may be formed from ozone in the atmosphere; Figure 2.3), and nuclear processes (perchlorate is formed from power generation and maybe from nuclear power).

Sites affected by fireworks were sites 7, 8, 9 and 10. However, in the third session that examined the effects of firework displays specifically, three additional sites were included for this round only (sites 21-23). All were thought to be impacted by nearby firework displays, however, only one was a drinking water treatment plant; the other two were private lakes not used for drinking water abstraction. From the results ([Figure 6.2](#)~~Figure 6-2~~), it is apparent that perchlorate concentrations in the raw samples from sites with nearby big firework displays or near firework manufacturers were greater than those of the controls. Also, when compared to the other risk factors they are slightly higher. Looking at the three additional sites ([Figure 6.3](#)~~Figure 6-3~~), it is clear that the two private lake sites (sites 21 and 23) were impacted by the firework displays, however, the drinking water treatment site (site 22) was not. Proximity to the firework displays and time after the displays are likely to be factors for this difference; sites 21 and 23 were located next to the display and sampled one day after, whereas site 22 was located further from the display and was sampled two days after. Additionally, site 22 abstracted water from a bankside storage reservoir that sourced water from a slow moving river that ran through a heavily populated area. It could be possible that firework displays were held in this area throughout the week before sampling, meaning that the 'before' sample had already been impacted by perchlorate exposure from fireworks. Additionally, weather conditions may have affected the results seen at these three sites. However, as the lakes at sites 21 and 23 are not used for drinking water abstraction, the increased levels of perchlorate are deemed to be of negligible relevance to possible exposure through drinking water in these areas. However, other drinking water sources elsewhere in the UK may be impacted by such firework displays. The increase seen at two of the sites is similar to previous observations from elsewhere in the world (Section 2.5).



**Figure 6.3 Perchlorate concentrations at the three additional sites used to assess the impact of firework displays**

The sites selected on the basis of being near to military site (e.g. explosives, etc.) were sites 6, 11, 12, 13, 14 and 15. Similarly to the firework risk sites, some of these also showed elevated levels when compared to the controls and other risk types (note sites 6, 12 and 15 have levels similar to the controls, 13 is low, and only 11 and 14 appear significantly higher than the controls). When compared to the UK Dstl study of the impact of demolition of munitions (Section 2.4.4), it can be seen that these concentrations are significantly lower than those reported from sites very close to the demolition areas. However, they are somewhat more comparable to the concentration of 4 µg/l that was reported from a drainage ditch approximately 460 m from the demolition area.

Perchlorate levels from the sites with 'other' risk types (sites 16-20) were similar to control levels, and have the lowest perchlorate concentrations of all the higher-risk sites. Therefore, it would appear that at these sites, quarry blasting, nuclear power and the use of hypochlorite, OSEC and ozonation during their treatment processes had minimal, if any, effects on background concentrations of perchlorate. However, only limited conclusions can be drawn from this due to the small number of sites included. The effect of treatment is discussed further in Section 6.3.3.

These results suggest that the low levels of perchlorate found are not exclusively linked to particular risk factors such as proximity of military sites. No discrete sources of contamination have been identified in this study and the levels found are within the range that may arise naturally.

### 6.3.3 Method of Treatment

#### Chlorination

As mentioned previously in the Literature Review and the results from the mini-test (Sections 2 and 4), perchlorate is reported to form in solutions of hypochlorite, therefore treatment that

uses hypochlorite or OSEC for disinfection may introduce perchlorate during the treatment process. Therefore an increase in perchlorate levels in the final samples should be seen when compared to the raw samples. The majority of the higher-risk sites use chlorine gas (sites 7, 8, 9, 11, 12, 14, 16, 19 and 20), two sites use hypochlorite (sites 15 and 17) and one uses OSEC (site 18). The remainder of the sites (6, 10, 13 and 22) did not have any treatment or the treatment processes were not running, so the effects of the chlorination method used could not be assessed. Site 15 showed a small increase in perchlorate concentration between the raw and treatment samples in sessions 1 and 2. However, consistent no trends associated with the chlorination method were identified.

### **Ozonation**

Perchlorate can be formed from ozone in the atmosphere; therefore it was postulated that it could be formed from ozonation during drinking water treatment. Two sites (sites 17 and 19) use ozonation, however, no significant effects were observed.

### **Other**

Some removal by GAC occurred at site 9 (particularly in session 4), however, the GAC at site 19 did not have any effects. No removal was observed by UV treatment (site 7). The effect of nitrate removal is discussed in Section 6.3.4.

#### **6.3.4 Associated Parameters**

It was postulated whether perchlorate would behave similarly to nitrate and so be removed where nitrate is also removed. Site 11 is the only site with nitrate removal (using ion exchange), however, data were collected from each site to identify those with relatively high levels of nitrate. The nitrate removal at site 11 was effective at decreasing perchlorate concentrations from about 5 µg/l (in raw borehole 1) to about 0.5 µg/l (after nitrate removal treatment). This effect is consistent with findings from the literature survey that anion exchange resin can remove perchlorate, see Section 2.6. However, as results are from only one site, caution should be used before concluding this effect is more widely applicable, and additional research would be required to assess this further. There were no consistent trends in perchlorate concentrations with any of the associated parameters (nitrate, pH, chloride and alkalinity).

#### **6.3.5 Potential Implications to Human Health**

Since the Literature Review (Section 2) was completed, further discussions have been undertaken in the USA on the necessity of deriving a standard for drinking water quality. In October 2008, following a review of the relevant data the US Environmental Protection Agency (EPA) stated that there is not a “meaningful opportunity for health risk reduction” through the introduction of a statutory standard for perchlorate in drinking water (US EPA, 2008a). However, in January 2009, the EPA issued an interim subchronic (30-365 days duration) Health Advisory (HA) of 15 µg/l, with pregnant women as their sensitive subpopulation (US EPA, 2009). This is a non-enforceable level of perchlorate in drinking water at which adverse health effects are not anticipated to occur for this duration of exposure. The HA was based on the NOEL of 7 µg/kg bw/day identified from the human study and used by the Integrated Risk Information System (IRIS) and the National Academy of

Science (NAS) to derive their oral Reference Doses (RfD) stated previously (Section 2.2.2) (US EPA, 2008b). A 70 kg adult drinking 2 litres of water a day, an uncertainty factor of 10 to account for intraspecies variation, and a relative source contribution of 0.62 were used. The relative source contamination was determined to be 0.62, due to analysis of urinary data for pregnant women, which illustrated that (at the 90<sup>th</sup> percentile), 38% of the reference dose came from food. No other exposures were considered, meaning the remainder (62%) was allocated to exposure from drinking water. A final regulatory standard has not yet been determined as the EPA is awaiting the views from NAS regarding the derivation of this interim guideline (US EPA, 2009).

In summary, no English or Welsh drinking water standards currently exist for perchlorate. The levels detected in this project do not breach the US EPA interim HA of 15 µg/l. However, some of these values do exceed the limits set by some US states ([Table 2.1](#)~~Table 2.1~~), for example, all of the highest treated drinking water samples in each session (1.980, 2.073, 1.891 and 1.922 µg/l for the four sessions, respectively) breach the New Mexico interim groundwater screening level of 1 µg/l, while one breaches the Massachusetts Maximum Contaminant Level (MCL) of 2 µg/l. The derivation of the New Mexico value is unclear, while the Massachusetts value of 2 µg/l and the Californian value of 6 µg/l are both derived from the NOEL from the annual study used by the US EPA to derive their oral Reference Dose (RfD). However, different allocations to water and sensitive subpopulation methodology was used (US EPA, 2009). However, assuming a 60 kg adult drinking 2 litres of water a day with a perchlorate concentration of the maximum treated drinking water concentration detected of 2.073 µg/l, the equivalent intake (0.07 µg/kg bw/day) is at least 10-fold less than any of the health-based values set by authoritative bodies (Section 2.2.2):

- 2003, US Toxicology Excellence for Risk Assessment (TERA), oral reference dose = 2 µg/kg bw/day
- 2005, US EPA, Integrated Risk Information System (IRIS) oral RfD = 0.7 µg/kg bw/day
- 2005, US Agency for Toxic Substances and Disease Registry (ATSDR), chronic Minimum Risk Level = 0.7 µg/kg bw/day
- 2006, US National Academy of Science (NAS), oral RfD = 0.7 µg/kg bw/day

Therefore, no significant, if any, adverse health effects are anticipated following exposure to this water.

## 7. CONCLUSIONS

### 7.1 Method

The method used for the analysis proved to be robust and was successfully validated. The results of the mini-test (Section 4) showed good repeatability. The sampling technique was deemed appropriate since all field blanks taken were below the LOD (0.020 µg/l). The LODs for river water and tap water (0.039 and 0.020 µg/l, respectively) meant that perchlorate could be detected at lower levels than previously reported for the UK and in most of the international studies.

### 7.2 Monitoring Survey

From the data obtained using this sensitive method of analysis generally very low levels in raw and treated water were found. No clear pattern for the presence of perchlorate in raw and treated drinking water in the England and Wales was apparent. Concentrations are consistent seasonally and are variable across the geographical location. The levels found in treated drinking water were up to approximately 2 µg/l – consistent with levels that have been considered to arise naturally in other studies. The levels found were not exclusively linked to particular risk factors such as the proximity to military sites. No discrete significant sources of contamination have been identified in this study.

Perchlorate was detected at three of the control low risk sites (0.058 to 0.188 µg/l) and at every higher-risk sites during at least one of the sampling sessions. Concentrations were comparable in each session and showed no obvious increase or decrease over the period of this study. The maximum values for each session (excluding the level of 6.512 µg/l from site 21, as it is a private lake not used for drinking water abstraction) were all from the raw 1 samples at site 11. The highest treated drinking water samples in each session were 1.980, 2.073, 1.891 and 1.922 µg/l for the four sessions, respectively, and again were from site 11. Although no English or Welsh drinking water standards currently exist for perchlorate, these values are well below the interim Health Advisory of 15 µg/l recently set by the United States Environmental Protection Agency (US EPA, 2009). Assuming a 60 kg adult drinking 2 litres of water a day with perchlorate concentrations at the maximum treated drinking water concentration of 2.073 µg/l (equivalent to 0.07 µg/kg bw/day) none of the health-based values set by authoritative bodies (>0.7 µg/kg bw/day; Section 2.2.2) are exceeded. Due to this, no significant, if any, adverse health effects are anticipated following exposure to this water.

All levels detected are in the lower range of concentrations detected elsewhere in the world (Section 2.5).

From the limited data, no apparent trends exist in relation to the time of year, the type of perceived higher-risk, the method of chlorination, the type of treatment, or any of the associated parameters (pH, chloride, alkalinity and nitrate). Though the laboratory studies did show the potential for hypochlorite to contain perchlorate. Additionally, the treatments involved did not show any consistent signs of being able to remove perchlorate, apart from the nitrate removal at site 11, which is supported by findings of the literature review (see Section 2.6) and the GAC at site 11 (but as these are both used at only one site, caution should be exercised about drawing conclusions as to their effectiveness at other sites). Additional

research is needed to investigate this further. A potential source of the presence of perchlorate could be the local geology at the sites involved.

## 8. RECOMMENDATIONS

Following completion of this project, the following recommendations are made:

- To ensure awareness of any ongoing perchlorate monitoring undertaken by the Water Companies and other National Bodies in the UK.

Limited monitoring prior to this work has been completed in the UK, and this work comprises a relatively small study. Further monitoring would be useful to confirm whether perchlorate is an indiscrete contaminant present throughout England and Wales at low levels, as suggested by the results obtained. Therefore to achieve this, it would be of benefit to either perform an extended monitoring study or to maintain an awareness of any monitoring and the possible presence of perchlorate in UK waters.

- To monitor the situation in the USA with regard to the Environmental Protection Agency (EPA) setting a statutory drinking water standard for perchlorate.

Due to the publication of an interim Health Advisory, the EPA appear to be in the process of considering setting a statutory standard for perchlorate in drinking water. If they do set a standard it would be of benefit to the UK and the rest of the world to understand the basis of the limit. A future US standard may promote the need for the UK and EU to assess the risk of perchlorate to drinking water and consider setting a standard.

- To monitor the work investigating how perchlorate is formed both naturally and in man-made situations.

Some literature exists to say that perchlorate can be formed from natural sources, however, the processes via which this occurs are not entirely clear. It would be of benefit to identify what these natural formation processes are to gain an understanding of the presence of perchlorate in certain environments. As there are significant man-made sources of perchlorate, it would also be useful to know how these differ from natural sources.

- To undertake a risk assessment of perchlorate specifically in the UK to determine whether there is a need for a health-based standard.

The results from this albeit small study suggest that perchlorate is an indiscrete low level background contaminant of drinking water and its sources. Due to the health-based guidelines and US limits that have been set (as low as 1 µg/l in some states), it would be of benefit to determine whether total exposure to perchlorate (not just from drinking water, but from the diet, environment, etc.) constitutes a potential health risk.





## REFERENCES

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## APPENDIX A SITE PROFILES

The information contained within this Appendix originates from the water companies involved and was not obtained from the public register.

### Site 1 – Public Water Supply

**Site Type:** Control.

**Water Type:** Lowland surface water.

**Treatment:** Slow sand filtration, chlorination using chlorine gas.

**Water Information:** Impounding reservoir water (considered good quality).

**Associated Parameters:**

Site	Statistical Parameter	Chloride (mg/l)	Hydrogen ion (pH units)	Nitrate (mg/l)	Total Alkalinity (mg/l)	Comments
Raw (combined microstrainer and reservoir outlets)	Mean	14.71	8.17	15.15	154.94	Alkalinity is as CaCO <sub>3</sub> ; Nitrate is as NO <sub>3</sub> and from 04/01/06 to 03/07/08
	Maximum	16.00	8.45	28.40	205.00	
	Minimum	13.60	7.88	4.80	115.00	
	Date range	03/01/07 to 19/12/07				

### Site 2 – Public Water Supply

**Site Type:** Control.

**Water Type:** Groundwater.

**Treatment:** Iron/manganese removal, chlorination using chlorine gas.

**Water Information:** It is classed as low risk, greensand (aquifer type) groundwater. It is on the Confined Lower Greensand aquifer, and is classified as low risk for crypto/bacti.

**Associated Parameters:**

Site	Statistical Parameter	Chloride (mg/l)	Hydrogen ion (pH units)	Nitrate (mg/l)	Total Alkalinity (mg/l)	Comments
Raw Combined	Mean	14.38	7.09	0.42	147.88	Not specified as to what nitrate is measured as; Alkalinity is as CaCO <sub>3</sub> .
	Maximum	19.90	7.22	0.76	163.00	
	Minimum	11.00	6.96	0.03	124.00	
	Date range	01/01/07 to 01/01/08				
Treated	Mean	-	-	0.86	-	Not specified as to what nitrate is measured as.
	Maximum	-	-	1.10	-	
	Minimum	-	-	0.43	-	
	Date range	01/01/07 to 01/01/08				

### Site 3 – Public Water Supply

**Site Type:** Control.

**Water Type:** Lowland surface water.

**Treatment:** Primary filters, GAC, slow sand filtration, aeration to increase dissolved oxygen (DO) following degradation in slow sand stage, chlorination using chlorine gas, followed by ammonium sulphate addition to produce chloramine.

**GAC Details:** Blending of the pre GAC water: it is supplied by two reservoirs, which are currently operating at an 80:20 ratio (ideally would be 50:50, but vary due to algal concentrations). Number of adsorbers: 4 (note that these are used as roughing filters upstream of the slow sand filters at the site. Regeneration regime (staggered/done all at the same time): each filter is regenerated annually, and the programme is staggered throughout the year. Ages of beds: dates that each was last regenerated are Filter 1 – 08.12.06, Filter 2 – 08.09.06, Filter 3 – 23.01.06 & 23.02.07, Filter 4 – 04.04.06 & 12.06.07.

**Water Information:** It is classed as low risk, with nothing significant in catchment. Both the reservoirs that supply it are naturally filled from streams.

#### Associated Parameters:

Site	Statistical Parameter	Chloride (mg/l)	Hydrogen ion (pH units)	Nitrate (mg/l)	Total Alkalinity (mg/l)	Comments
Raw 1 (primary)	Mean	27.69	8.39	13.02	83.44	Not specified as to what nitrate is measured as; Alkalinity is as CaCO <sub>3</sub> .
	Maximum	33.70	9.98	26.80	119.00	
	Minimum	23.10	7.46	3.12	32.20	
	Date range	01/01/07 to 01/01/08				
Raw 2 (secondary)	Mean	25.16	8.10	9.45	94.23	Not specified as to what nitrate is measured as; Alkalinity is as CaCO <sub>3</sub> .
	Maximum	29.70	9.08	17.80	119.00	
	Minimum	20.20	7.27	2.08	47.00	
	Date range	01/01/07 to 01/01/08				
Treated 1 (primary)	Mean	-	-	12.52	-	Not specified as to what nitrate is measured as.
	Maximum	-	-	24.80	-	
	Minimum	-	-	0.96	-	
	Date range	01/01/07 to 01/01/08				

**Site 4 – Public Water Supply****Site Type:** Control.**Water Type:** Upland surface water.**Treatment:** Rapid gravity filters, chlorination by gas.**Water Information:** Water is derived from two upland impounding reservoirs.**Associated Parameters:**

Site	Statistical Parameter	Chloride (mg/l)	Hydrogen ion (pH units)	Nitrate (mg/l)	Total Alkalinity (mg/l)	Comments
Raw	Mean	-	5.61	-	-	N/A
	Maximum	-	8.40	-	-	
	Minimum	-	4.40	-	-	
	Date range	2007				
Treated	Mean	11.90	8.33	0.61	9.73	Nitrate is as total N; Alkalinity as CaCO <sub>3</sub> .
	Maximum	14.80	10.50	0.68	13.53	
	Minimum	9.40	6.80	0.49	<10.74	
	Date range	2007				

**Site 5 – Public Water Supply****Site Type:** Control.**Water Type:** Groundwater.**Treatment:** Chlorination using hypochlorite.**Water Information:** At the site boreholes draw from a confined aquifer, but impact of abstraction probably extends to an outcrop so draws water from an unconfined aquifer.**Associated Parameters:** None have been provided by the water undertaker.**Site 6 – Public Water Supply****Site Type:** High risk.**Risk Factor:** A Royal Ordnance Site is nearby.**Water Type:** Surface water.**Treatment:** There is no treatment here – water is pumped to another site for treatment after being blended with some other surface water.**Water Information:** Upland.**Associated Parameters:**

Site	Statistical Parameter	Chloride (mg/l)	Hydrogen ion (pH units)	Nitrate (mg/l)	Total Alkalinity (mg/l)	Comments
Raw	Mean	-	7.94	2.36	-	N/A
	Maximum	-	8.58	4.00	-	
	Minimum	-	7.58	0.82	-	
	Date range	03/09/05 – 11/01/08				

## Site 7 – Public Water Supply

**Site Type:** Medium risk.

**Risk Factor:** A big firework display is ~8 km away.

**Water Type:** Groundwater.

**Treatment:** Aeration and lime pellet softening of two thirds of the raw water, and then combined with other third, which is prechlorinated. Then it is all coagulated with iron sulphate and polyelectrolyte is added, then rapid gravity filters (RGF), UV disinfection, then chlorination. Cl residual is removed by sulphur dioxide and ammonia is added to form monochloramine. Orthophosphoric acid is also dosed for plumbosolvency control. Chlorination is by Cl gas.

**Water Information:** The aquifer is unconfined, as the surface is influenced by a local River.

**Associated Parameters:**

Site	Statistical Parameter	Chloride (mg/l)	Hydrogen ion (pH units)	Nitrate (mg/l)	Total Alkalinity (mg/l)	Comments
Raw 4 inlet to pellet reactors (assumed to be the last raw in the treatment process of the 4 provided)	Mean	28.12	8.04	27.35	296.77	Nitrate is as NO <sub>3</sub> ; Alkalinity is unspecified, but stated to be total.
	Maximum	31.20	8.20	31.19	322.00	
	Minimum	24.10	7.40	24.29	256.00	
	Date range	02/01/07 to 2/02/08				
Treated	Mean	29.93	7.71	29.90	156.87	Nitrate is as NO <sub>3</sub> ; Alkalinity is unspecified, but stated to be total.
	Maximum	32.80	8.00	33.49	271.00	
	Minimum	26.70	7.50	26.79	96.00	
	Date range	01/01/07 to 03/07/08				

## Site 8 – Public Water Supply

**Site Type:** Medium risk.

**Risk Factor:** A big firework display is ~5.7 km away.

**Water Type:** Surface water.

**Treatment:** Prechlorination, coagulation with aluminium sulphate and polyelectrolyte addition before clarification, rapid gravity sand filtration, GAC, orthophosphoric acid addition, addition of caustic (if needed), aeration, chlorination and ammonication. Chlorination is by Cl gas.

**Water Information:** Lowland.

**Associated Parameters:**

Site	Statistical Parameter	Chloride (mg/l)	Hydrogen ion (pH units)	Nitrate (mg/l)	Total Alkalinity (mg/l)	Comments
Treated	Mean	44.11	7.81	14.34	87.36	Alkalinity is not specified as to what form it is in, nitrate is as NO <sub>3</sub> .
	Maximum	51.10	8.10	20.39	117.00	
	Minimum	37.10	7.50	4.79	52.00	
	Date range	01/01/07 to 03/07/08				
Raw	Mean	36.99	8.13	13.08	117.46	N/A
	Maximum	42.80	8.70	19.13	143.00	
	Minimum	29.10	7.80	4.50	90.00	
	Date range	03/01/07 to 02/07/08				

## Site 9 – Public Water Supply

**Site Type:** High risk.

**Risk Factor:** Fireworks are manufactured nearby.

**Water Type:** Groundwater.

**Treatment:** GAC, chlorination by gas, blended.

**Water Information:** The aquifer is unconfined at the site and main catchment, but is locally confined to the east.

**Associated Parameters:**

Site	Statistical Parameter	Chloride (mg/l)	Hydrogen ion (pH units)	Nitrate (mg/l)	Total Alkalinity (mg/l)	Comments
Raw	Mean	30.20	7.20	-	246.00	N/A
	Maximum	-	-	-	-	
	Minimum	-	-	-	-	
	Date range			-		
Treated	Mean	32.2	7.37	-	270	N/A
	Maximum	-	-	-	-	
	Minimum	-	-	-	-	
	Date range			-		

## Site 10 – Private Water Supply

**Site Type:** High risk.

**Risk Factor:** Fireworks are manufactured nearby and a display is held 1 km away.

**Water Type:** Groundwater.

**Treatment:** None – this is a private supply to one household.

**Water Information:** Unconfined aquifer.

**Associated Parameters:** This is N/A as it is a private supply, so they do not measure them.

## Site 11 – Public Water Supply

**Site Type:** High risk.

**Risk Factor:** Military firing ranges are located nearby.

**Water Type:** Groundwater.

**Treatment:** The primary site has two boreholes, but there is also a separate, secondary borehole about 1 km away. The primary site houses treatment for the secondary borehole input in a new building on the site, and treatment for the two primary boreholes is handled in other buildings on the primary site. All the available sources may be sampled individually from the primary site (i.e. without the need to visit the well-head at secondary site) and 'finals' for the primary and secondary boreholes may be sampled separately, as well as the mixed, combined final from the site. Raw 1 water undergoes nitrate removal (using ion exchange) at the raw 2 site. The other processes are iron and manganese removal. Chlorination is by gas.

**Water Information:** Unconfined aquifer.

**Associated Parameters:**

Site	Statistical Parameter	Chloride (mg/l)	Hydrogen ion (pH units)	Nitrate (mg/l)	Total Alkalinity (mg/l)	Comments
Raw	Mean	26.3	7.42	30.2	191	Alkalinity is as CaCO <sub>3</sub> . No dates specified.

### Site 12 – Public Water Supply

**Site Type:** High risk.

**Risk Factor:** Military munitions have been found at the bottom of one of the reservoirs.

**Water Type:** Surface water.

**Treatment:** Coagulation, clarification (DAF), first and second stage filtration, chlorination and plumbosolvency control. Chlorination is by gas.

**Water Information:** Chain of impounding reservoirs.

**Associated Parameters:**

Site	Statistical Parameter	Chloride (mg/l)	Hydrogen ion (pH units)	Nitrate (mg/l)	Total Alkalinity (mg/l)	Comments
Unspecified	Mean	15.51	7.37	0.72	12.70	Not stated as to what alkalinity or nitrate was measured in; Cl data are from 03/01/06 to 21/12/06.
	Maximum	24.10	7.86	0.99	15	
	Minimum	14.10	6.97	0.38	8.2	
	Date range	02/01/08 to 02/07/08				

### Site 13 – Public Water Supply

**Site Type:** High risk.

**Risk Factor:** Military site nearby.

**Water Type:** Groundwater.

**Treatment:** Super and dechlorination only. However, the site has been off-line for all four sampling sessions.

**Water Information:** Unconfined aquifer.

**Associated Parameters:**

Site	Statistical Parameter	Chloride (mg/l)	Hydrogen ion (pH units)	Nitrate (mg/l)	Total Alkalinity (mg/l)	Comments
Raw borehole 3	Mean	31.21	7.28	6.79	-	Nitrate is as N.
	Maximum	33.60	7.60	7.65	-	
	Minimum	15.00	7.10	4.24	-	
	Date range	06/01/06 to 03/10/06				

### Site 14 – Public Water Supply

**Site Type:** High risk.

**Risk Factor:** Is next to a military site, where tank testing occurs.

**Water Type:** Groundwater.

**Treatment:** Chlorination by gas (marginal).



**Water Information:** It is in the same geological strata as site 19, but it is a few valleys away, so it is not influenced by surface contamination in the same way as site 19 is. Crypto risk assessment - low risk; Lithology 1 - middle / lower chalk, Lithology 2 - upper greensand; unconfined aquifer.

**Associated Parameters:**

Site	Statistical Parameter	Chloride (mg/l)	Hydrogen ion (pH units)	Nitrate (mg/l)	Total Alkalinity (mg/l)	Comments
Raw Borehole 1	Mean	10.49	7.52	2.63	228.00	Nitrate is as N and alkalinity is as CaCO <sub>3</sub> .
	Maximum	11.60	7.60	3.15	320.00	
	Minimum	9.90	7.40	2.35	180.00	
	Date range	11/01/06 to 03/12/06				

### Site 15 – Private Water Supply

**Site Type:** High risk.

**Risk Factor:** Is a military site nearby.

**Water Type:** Groundwater.

**Treatment:** Chlorination (hypochlorite) to achieve residual of 0.3-0.5 mg Cl<sup>-</sup>/l.

**Water Information:** Unconfined. This is a large private water supply.

**Associated Parameters:** This is N/A as it is a private supply, so they do not measure them.

### Site 16 – Public Water Supply

**Site Type:** High risk.

**Risk Factor:** Quarry blasting occurs nearby.

**Water Type:** Groundwater.

**Treatment:** Super and dechlorination only. Chlorination is by gas.

**Water Information:** Unconfined aquifer.

**Associated Parameters:**

Site	Statistical Parameter	Chloride (mg/l)	Hydrogen ion (pH units)	Nitrate (mg/l)	Total Alkalinity (mg/l)	Comments
Treated	Mean	26.76	7.25	8.79	236.75	Nitrate is as N and alkalinity is as CaCO <sub>3</sub> .
	Maximum	28.60	7.80	9.42	252.00	
	Minimum	25.30	7.10	8.19	206.00	
	Date range	04/01/06 to 29/12/06				

### Site 17 – Public Water Supply

**Site Type:** High risk.

**Risk Factor:** Uses hypochlorite and ozonation.

**Water Type:** Surface water.

**Treatment:** Preozone, coagulation, Actiflow, RGF, slow sand filters, and super and dechlorination by hypochlorite.

**Water Information:** Lowland.

**Associated Parameters:**

Site	Statistical Parameter	Chloride (mg/l)	Hydrogen ion (pH units)	Nitrate (mg/l)	Total Alkalinity (mg/l)	Comments
Not specified	Mean	22	8.3	5.5	215	Raw water. Nitrate is as N; alkalinity is as CaCO <sub>3</sub> ; date not specified.

**Site 18 – Public Water Supply**

**Site Type:** High risk.

**Risk Factor:** Uses electrolytic chlorination for treatment, with high doses of chlorine (1-2 mg/l).

**Water Type:** Groundwater and surface water.

**Treatment:** Surface water is blended, groundwater is aerated then blended with the surface water. Dosing with polyaluminium chloride for coagulation, then DAF, then primary rapid gravity mixed media filters (RGF) (gravel, coarse sand, garnet, anthracite and finer sand), then dosed with sodium hypochlorite (manganese oxidation) and caustic soda (pH adjustment). Then secondary rapid gravity mixed media filters (sand and gravel) and dosed with sodium hypochlorite (from the OSEC plant). Then dosed with sodium bisulphite to reduce the free chlorine levels.

**Water Information:** Unconfined aquifer and surface water from two impounding reservoirs.

**Associated Parameters:**

Site	Statistical Parameter	Chloride (mg/l)	Hydrogen ion (pH units)	Nitrate (mg/l)	Total Alkalinity (mg/l)	Comments
Raw 1	Mean	65.07	7.451063 83	0.66	-	Nitrate is as N.
	Maximum	70.60	8.48	2.23	-	
	Minimum	57.70	6.6	<0.097	-	
	Date range	02/01/07 to 28/12/07				
Raw 2	Mean	-	7.03	0.10	-	N/A
	Maximum	-	7.60	0.15	-	
	Minimum	-	6.30	<0.097	-	
	Date range	10/04/07 to 24/12/07				
Raw 3	Mean	32.00	7.25	0.45	-	N/A
	Maximum	32.00	7.59	0.58	-	
	Minimum	32.00	6.68	0.27	-	
	Date range	21/11/07 to 28/12/07				
Raw Combined	Mean	53.08	7.34	0.53	-	N/A
	Maximum	66.20	7.90	2.16	-	
	Minimum	37.40	6.51	<0.097	-	
	Date range	10/01/07 to 28/12/07				
Final	Mean	-	-	-	79.22	Alkalinity as CaCO <sub>3</sub> .
	Maximum	-	-	-	233.00	
	Minimum	-	-	-	50.70	
	Date range	02/01/07 to 28/12/07				

**Site 19 – Public Water Supply****Site Type:** High risk.**Risk Factor:** Uses ozone treatment with high concentrations of chloride in the raw water.**Water Type:** Surface water.**Treatment:** Preozonation, coagulation, clarification, filtration, ozonation, GAC and chlorination with gas.**Water Information:** Lowland.**Associated Parameters:**

Site	Statistical Parameter	Chloride (mg/l)	Hydrogen ion (pH units)	Nitrate (mg/l)	Total Alkalinity (mg/l)	Comments
Unspecified	Mean	33.60	7.00	26.31	148.92	Nitrate is as mg N/l and from 03/01/06 to 03/07/08; Alkalinity is as CaCO <sub>3</sub> ; pH is from 03/01/07 to 01/01/08.
	Maximum	49.30	7.72	47.80	185.00	
	Minimum	24.50	6.41	10.60	112.00	
	Date range	03/01/07 to 19/12/07 (Cl and alkalinity only)				

**Site 20 – Public Water Supply****Site Type:** High risk.**Risk Factor:** Is near the nuclear facility Winfrith.**Water Type:** Groundwater.**Treatment:** Marginal chlorination by gas.**Water Information:** Unconfined aquifer.**Associated Parameters:**

Site	Statistical Parameter	Chloride (mg/l)	Hydrogen ion (pH units)	Nitrate (mg/l)	Total Alkalinity (mg/l)	Comments
Treated	Mean	22.20	7.27	7.16	232.75	Nitrate is as N and alkalinity is as CaCO <sub>3</sub> .
	Maximum	23.10	8.00	7.57	246.00	
	Minimum	21.10	7.10	6.73	202.00	
	Date range	03/01/06 to 30/12/06				

**Site 21 – Private Lowland Lake****Site Type:** High risk.**Risk Factor:** Firework display held on an island in the middle of the lake.**Water Type:** Surface water.**Treatment:** N/A.**Water Information:** Private lowland lake.**Associated Parameters:** N/A.

**Site 22 – Public Water Supply****Site Type:** High risk.**Risk Factor:** Approximately 0.5 km away from a big firework display.**Water Type:** Surface water.**Treatment:** N/A as not running.**Water Information:** Lowland.**Associated Parameters:**

Site	Statistical Parameter	Chloride (mg/l)	Hydrogen ion (pH units)	Nitrate (mg/l)	Total Alkalinity (mg/l)	Comments
Raw intake	Mean	42.29	7.86	6.63	217.26	Nitrate is as total N, alkalinity is as CaCO <sub>3</sub> .
	Maximum	58	8.3	8.1	256	
	Minimum	34	6.9	5.6	194	
	Date range	2008				

**Site 23 - Private Lowland Lake****Site Type:** High risk.**Risk Factor:** Firework display held on the edge of the lake.**Water Type:** Surface water.**Treatment:** N/A.**Water Information:** Private lowland lake.**Associated Parameters:** N/A.