

**Project title:** Chlorine and its Oxides: Chlorate and Perchlorate Review

**Project number:** CP 154a

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**Report:** Final report, September 2016

**Previous report:** None

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**Date project commenced:** 14 July 2016

**Date project completed** 16 September 2016

**(or expected completion date):**

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We declare that this work was done under our supervision according to the procedures described herein and that the report represents a true and accurate record of the results obtained.

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## GROWER SUMMARY

### Headline

Action points given in this Grower Summary may help growers to mitigate against high levels of chlorate and perchlorate in fresh produce.

### Introduction

Growers, packers and processors in the horticulture and potato industries require supplies of clean water that is free of human and plant pathogens for irrigation, fertigation and postharvest washing. Clean and/or disinfected water is also needed for transporting delicate produce; for use in hydrocoolers, and for surface and equipment cleaning.

Sources of water used by growers of edible produce include borehole, reservoir, mains and surface/rain water. The extent of disinfection required for the water depends on its organic matter and microbial loading, and where it has come from (i.e. reservoir and surface water are commonly treated, whereas borehole and mains water are not often treated by users depending on water quality). Not all produce is washed however, with harvested produce from soft fruit, protected edibles, whole head lettuces and the majority of Brassica crops being picked and sent directly to customers. Processed produce destined for the 'ready to eat' category are mostly washed in disinfected water.

Chlorine and chlorine compounds are mostly used to disinfect the water. *This practice of disinfecting water will be termed 'chlorination' in this review.* Moreover, even where chlorine is not used to treat water for irrigation, chlorine-based disinfectants are sometimes added to the water to flush irrigation lines and prevent blockages from algae build-up in irrigation lines and to kill water-borne pathogens because plant pathogens like *Phytophthora spp.* can be carried in untreated water and infect plants. Some fresh produce is washed or transported in flotation systems, and without treatment, the water can spread pathogens responsible for storage rots.

Without the proper disinfection of water, consumers are put at risk of succumbing to human pathogens such as *Escherichia coli*, *Salmonella*, *Shigella spp.* and *Listeria monocytogenes* (Bermúdez-Aguirre and Barbosa-Cánovas, 2013) which result in food-borne illnesses. Mains water, which is chlorinated by water supply companies to kill microorganisms, contains a certain level of free chlorine (hypochlorous acid or

hypochlorite ions) in solution at the point of use for agricultural/horticultural practices or for drinking.

Chlorate and perchlorate (which result from chlorinating water) are competitive inhibitors of iodine uptake in the thyroid, and their residues in water and foods have come to the attention of the European Food Safety Authority (EFSA) as a health concern for humans, particularly for infants, the young and elderly demographic, as well as for pregnant women.

This project, AHDB Horticulture project CP 154a, was commissioned to review the sources and fate of chlorine and chlorine compounds that are taken up by edible horticultural plants and potatoes during crop production and at postharvest washing, with aims to recommend actions that growers could take, to mitigate against chlorate and perchlorate exceedances.

## **Background**

The review is the output of the Call that was published by AHDB Horticulture in early 2016. This call is available on the AHDB Horticulture website:

<https://horticulture.ahdb.org.uk/chlorine-and-its-oxides-chlorate-perchlorate-review>.

Chlorate exceedance in UK fresh produce is thought mostly to arise from the use of chlorine dioxide treated water or otherwise chlorinated water that is used for crop irrigation and produce post-harvest washing. The use of such water reduces the risk of microbial contamination in fresh produce.

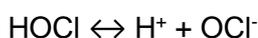
Chlorate, in the form of sodium chlorate, was also used as an herbicide and was a cheap method of non-selective/total weed control in amenity/industrial situations. It was not used in the UK on land intended for cropping. It was effective due to its action on the roots and vascular parts in the plant, as well as being persistent in soil for up to five years, depending on several edaphic factors such as soil type and soil moisture. Sodium chlorate lost UK pesticide approval status in 2009, but its previous listing as a pesticide has resulted in the need for a MRL in produce to be set. In the absence of information of what an appropriate level might be, a default MRL of 0.01 mg chlorate/kg, the minimum level of detection for chlorate, has been set for all foods.

An MRL for chlorate at this default limit would be virtually unachievable for most growers and the processing industry to comply with. The EC have released a series of proposed MRLs for chlorate (See Appendix 1). There has been no decision so far (accurate at the submission date of this report) as to when these proposed levels will

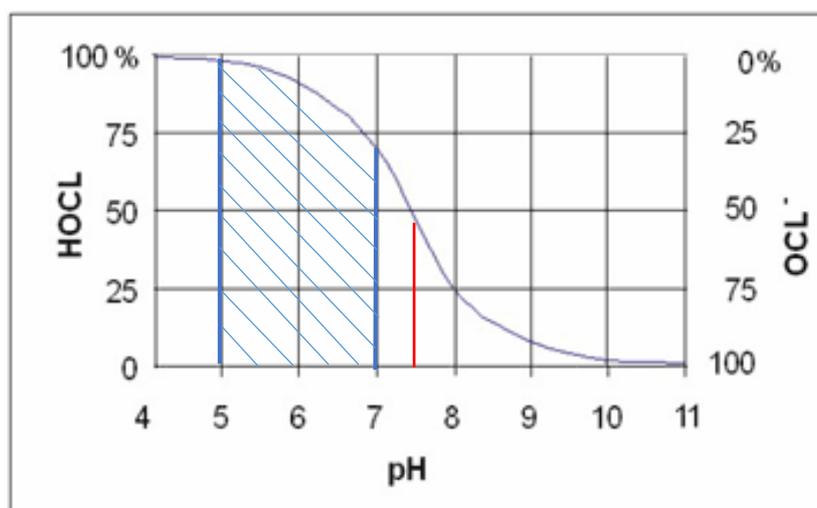
be made official. There are no statutory MRLs for perchlorate. However, there are reference values for perchlorate set by the Commission and endorsed by the EC directorate-general for health and food safety Standing Committee on Plants, Animals, Food and Feed (PAFF Committee) in March and June 2015. Due to perchlorate being regarded as an environmental contaminant, the regulating authority is the Food Standards Agency (FSA) and not the Chemicals Regulation Directorate (CRD). The reference values for the different produce can be found on page 3 of [this document](#). These values have no legal status to date, therefore, any action to be taken for any food found to be exceeding these levels is at the discretion of the individual Member States.

### Chlorine chemistry

The chlorine disinfectant, in the form of chlorine dioxide (ClO<sub>2</sub>), sodium hypochlorite (NaClO), calcium hypochlorite (Ca(ClO)<sub>2</sub>) and sometimes chlorine gas (Cl<sub>2</sub>), will eventually break down to by-products chlorate and perchlorate. In solution, the disinfectant will breakdown to form active (free) chlorine: hypochlorous acid (HOCl) and hypochlorite ions (OCl<sup>-</sup>). In the case of sodium hypochlorite in solution:



HOCl is a stronger oxidising agent than OCl<sup>-</sup>, and is more effective as a disinfectant.

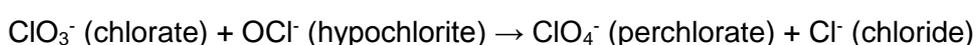


**Figure 1.** Ratio of a solution of hypochlorous acid and hypochlorite ions showing 50% HOCL and 50% OCl<sup>-</sup> achieved at pH 7.5 (red line), with HOCl being the more effective disinfectant below this point (between 5 and 7 pH) (shaded area).

Source: adapted from <http://www.hach.com/DisinfectionSeries02>

Therefore, a lower pH is favourable to achieving a more effective disinfection (Figure 1). The actual pH range is contradictory, with a source from Oregon State University stating a pH between 5 and 7 is more effective (OSU, 2011) and another states that neutral pH of about 6.5 to 7.5 is best.

The degradation of  $\text{OCl}^-$  results in the formation of chlorate and then perchlorate via a chlorite intermediate stage (Gordon and Tachiyashiki, 1991):



The degradation of a chlorine disinfectant to chlorate is influenced by a number of factors including the concentration of the solution, the pH, the presence of organic and inorganic contaminants and the temperature. More information on this is found in Section 4 of the Science Section.

### **Chlorate and Perchlorate uptake in the plant: pre- and post-harvest**

It is unclear as to the mechanism of how chlorate and perchlorate is taken up by the plant, as there is limited information available, but it is thought to follow a similar mechanism to nitrate (Seyfferth and Parker, 2007; Seyfferth and Parker, 2008). In preliminary data of chlorate and perchlorate residues detected in various horticultural crops from the UK gathered by AHDB Horticulture from 2014 to 2016, it was shown that there was more chlorate present in the leaves of edible-crop plants, rather than the roots or fruit. This is also the case for perchlorate. From this limited data, it was also shown that most crops are able to comply with the proposed MRLs for chlorate. With this in mind, while legislation of chlorate and perchlorate MRLs are pending a decision, it is advised that growers and processors continue to monitor chlorate and perchlorate levels in their water and produce if they continue to use chlorine-based disinfectant.

Chlorate and perchlorate are both analogues of nitrate and can negatively influence the uptake of nitrate in the plant. However, it has been noted that the transpiration pathway alone cannot predict the extent of chlorate and perchlorate uptake in the plant (Seyfferth and Parker, 2008). There is also a theory that perchlorate and chlorate are most probably assimilated by root cell membranes against an electrochemical

gradient. This is the most generally accepted model for plant uptake of anions (Marschner, 2011).

There is a theory discussed by Seyfferth and Parker (2008) that plants are capable of degrading perchlorate once it has been assimilated (phytodegradation), as well as that of degradation in the roots (rhizodegradation). The latter would occur at a higher rate than phytodegradation and is facilitated by anaerobic conditions. Occurrence of perchlorate in nature is found to be aligned with deposits of sodium nitrate in Chile (Chilean nitrate), but such deposits are not found in the UK, and when industrially produced nitrogen fertilisers became common in the 1940's they substituted for Chilean nitrate. Another occurrence of perchlorate has been postulated to develop from thermodynamic reactions of chloride ( $\text{Cl}^-$ ) in the atmosphere from ozonated seawater (Srinivasan and Viraraghavan, 2009). However, due to the energy required for this reaction, and the fact that the resulting perchlorate would become dissolved in precipitation as it travels to Earth, the wide distribution of the dissolved perchlorate would make the amount negligible (Srinivasan and Viraraghavan, 2009). More information in the uptake and occurrence of chlorate and perchlorate in plants pre- and post-harvest can be found in Section 5.

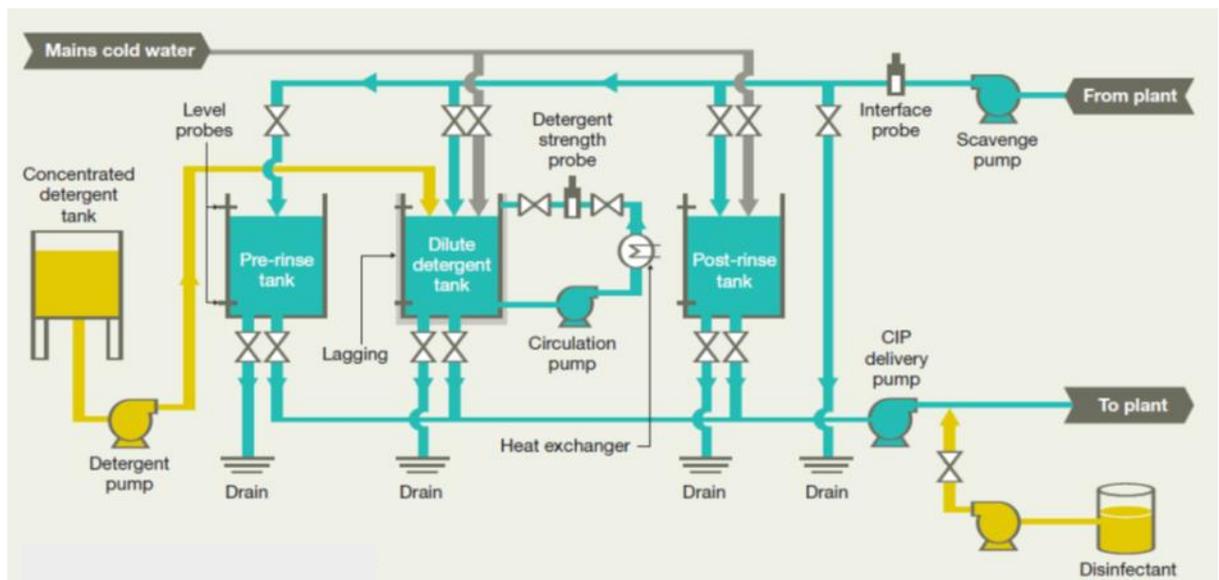
### **Testing and diagnosis of chlorate and perchlorate in plant tissue and water**

Accurate testing of chlorate and perchlorate in plant tissue is an area of controversy requiring review. It is currently recommended that growers submit produce for regular testing of these residues via suitably qualified laboratories. However, UKAS accreditation (ISO 17025) for a single test for perchlorate and chlorate is not totally reliable, as admitted by UKAS. Another issue is the difficulty of obtaining accurate chlorate and perchlorate detection with the presence of chlorophyll from green tissue in the sample. Low levels of perchlorate are difficult to analyse in most food matrices and waters with a high electro-conductivity (EC), particularly in the presence of organic matter. There is a high level of uncertainty with significant variation in results between laboratories.

More investigation into the variation of analyses between laboratories and the possible standardisation of analysis for chlorate and perchlorate residues in fresh produce is required to ensure that accurate levels are known for compliance.

## Chlorination management and residue mitigation

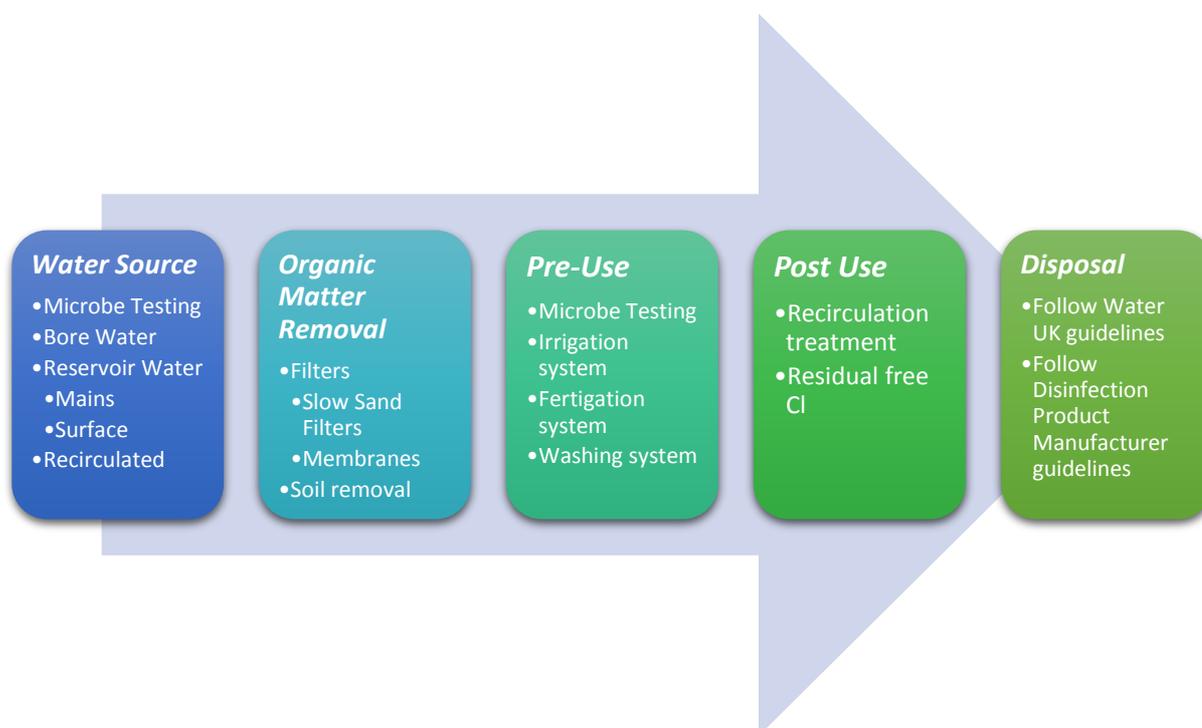
With regards to chlorination and managing chlorate and perchlorate residues in water and fresh produce, physical methods have been suggested in the literature including pre-washing produce with filtered water to remove organic particles (soil, plant exudates, insects, etc.) prior to disinfection. For recirculation systems, it is suggested that a pre-wash with clean mains or borehole water is done to remove soil particles and plant exudates prior to moving into an aerated and sanitised washing tank. The produce would then be rinsed with clean water. WRAP released guidance to the food manufacturing industry for the removal of 'soil' from processing equipment and machinery (See Figure 2 and Section 8 of the Science Section). A programme such as this could be one of measures undertaken by growers and processors as part of Good Agricultural Practice and Good Manufacturing Practice (GMP) ([www.chilledfood.org](http://www.chilledfood.org)). Seasonal flushing of the lines to clear out algae and other foreign bodies would reduce the need for higher concentrations of chlorine disinfectant.



**Figure 2.** Schematic of a soil cleaning system in a food manufacturing plant recycling water, showing where detergents are added to the system and strength monitored. Source: <http://www.wrap.org.uk/>

Another option to manage a lower level of microbial and organic matter loading (which influences the amount of chlorine required) that growers and processors could employ is a Hazard Analysis Critical Control Point (HACCP) based programme to monitor the effectiveness of their water supply system for irrigation and post-harvest washing (Figure 3). Growers whose edible produce is at risk of exceeding the proposed chlorate MRLs (such as leafy-salads) could also consider using an alternative to chlorine, such

as hydrogen peroxide that has the same or similar effect without the risk of contamination from chlorine by-products.



**Figure 3.** Example control point system based on the HACCP principle. Used to monitor water quality from the source, to point of use to disposal. This is a generalised diagram and not representative of a specific growing system (see Section 10 for further details).

Food-borne pathogens causing illness are a continual cause for public concern and growers need to have processes in place to mitigate the risk of contamination. Typically, chlorine has successfully been used as a disinfectant for plant produce, surfaces and water.

The Food and Biocides Industry Group ([www.chilledfood.org/fbig/](http://www.chilledfood.org/fbig/)) has produced best practice guidelines on NaOCl to minimise chlorate build-up:

1. Buy NaOCl with low as possible levels of chlorate (<1.5 mg/l)
2. Store correctly:
  - In the dark
  - In the cool (at 5°C degradation to chlorate in the absence of heavy metal contamination is very limited. Every 10°C increase increases degradation rate three to four-fold)

Note degradation is increased when the initial solution is more concentrated (at 20°C 12.5% solution degrades to 10% in 100 days).

- Store in UPVC reinforced with glass fibre reinforced polymer (GRP) resin or a full post cured vinylester GRP laminate.
3. Do not add new NaOCl to old - this promotes chlorate formation.
  4. Reduce the level of suspended solids to nearly undetectable levels to significantly reduce degradation.

By products of chlorine disinfectants such as sodium hypochlorite can form during storage. As mentioned previously, factors that affect the formation of chlorate and perchlorate are pH, temperature and the concentration of the solution. Section 4.3 of the Science Section provides guidance on how to reduce the likelihood of chlorate and perchlorate forming during storage. To summarise:

- Upon delivery, dilute hypochlorite solutions for storage prior to use
- Store the hypochlorite solutions at 5°C or below in the dark
- Control the pH of stored hypochlorite solutions at pH 11-13, even after dilution (consult the product supplier for instructions)
- Control the exposure to transition metal ions by reducing contact with copper and iron in rusty or old pipework and pumps
- Store in UPVC reinforced with glass fibre reinforced polymer (GRP) resin or a full post cured vinyl ester GRP laminate
- Use fresh hypochlorite solutions where possible rather than using or adding to older solutions. Ensure the use-by date on the container has not passed.

### **Disposal of chlorinated water**

- Chlorinated water must also be disposed of in a responsible way to ensure that it does not adversely affect biodiversity in waterways and catchments. Water UK provides some guidance on how chlorinated water may be disposed of, including advice on dechlorinating and who to contact (See Section 8 of the Science Section).

#### *Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>)*

Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) has been suggested as an alternative to chlorination for disinfection during food production and processing. It derives its antimicrobial capacity from its potency as an oxidiser. H<sub>2</sub>O<sub>2</sub> breaks down to water and oxygen in solution, giving it the advantage of leaving no residues. H<sub>2</sub>O<sub>2</sub> can be used directly in treatment (often with a stabilising component such as silver), or as an active ingredient in an

'activated peroxygen', a class of products where H<sub>2</sub>O<sub>2</sub> is combined with organic acids such as acetic acid (to form peracetic acid) to increase stability.

The mechanism of H<sub>2</sub>O<sub>2</sub> against bacteria and fungi is believed to involve damaging DNA through oxidative stress (Brul and Coote, 1999; Baureder *et al.*, 2012). Resistance in some bacteria and fungi due to the continued use of hydrogen peroxide involves the catalase enzyme, which is relied upon to degrade the toxic levels in microbial cells. Damage still occurs, as H<sub>2</sub>O<sub>2</sub> has a high diffusion rate into the cell. However, effectiveness can depend on the size and extent of the microbial population as dense populations of *E. coli*, can produce enough catalase to protect most of the population.

H<sub>2</sub>O<sub>2</sub> must be transported in polyethylene, stainless steel or aluminium containers because when H<sub>2</sub>O<sub>2</sub> comes into contact with flammable substances there is a risk of explosion. Due to the oxidising capacity of H<sub>2</sub>O<sub>2</sub>, it can be phytotoxic to some plants and damage plant tissue. There is also some inconsistency in the literature as to its efficacy on removing biofilms. There are those in industry that have found chlorination to have a better efficacy on disinfection after trialling H<sub>2</sub>O<sub>2</sub>. Hence, more work is needed to evaluate this product against other disinfection products/systems. See Section 9 for further details.

### **Action Points**

- Build up a record of produce samples that are sent for chlorate/perchlorate residue testing and link results to records of crop husbandry, processing and the use of mains water and chlorine-based disinfectants to determine where and how contaminant residues are arising.
- Implement a HACCP based system (such as within Good Agricultural Practice (GAP) and Good Manufacturing Practice (GMP) to help identify key control points for removing microbial contamination from the water source through to the point of use.
- Test treated water regularly to ensure that levels of free chlorine created are not in excess of needs (the breakpoint) and ensure that manual dosing is done to meet agreed criteria. Free chlorine levels required for microbial control are given by manufacturers together with the ration of product to water to be used to achieve these levels.

- Ensure that as much organic matter is removed as possible from produce and surfaces before the use of chlorine-based disinfectants so that lower concentrations are effective.
- If using sodium hypochlorite do not store for longer than given on the product batch as chlorate and perchlorate are produced on decomposition. Factors such as light, dilution and initial chlorine levels impact on levels produced and the length of storage time and temperature should be used to determine the strength of sodium hypochlorite purchased.
- If exceedances of chlorate MRLs are unable to be stopped by modifying current procedures, then explore alternative treatment procedures such as using hydrogen peroxide, UV, pasteurisation or organic acids or investigate other and novel disinfection technologies.
- Provide information on your use of water, disinfection systems and concerns about MRLs to your producer organisation and/or the AHDB so that more-detailed information can be gathered to aid recommendations on best practice relevant to your sector.

## SCIENCE SECTION

### 1. Introduction

Residues of chlorate and perchlorate can arise in foods following the use of chlorinated water for irrigated and hydroponic crops, chlorine washes of fresh produce and the use of chlorine-bearing biocides to wash down and disinfect surfaces, machinery and food processing equipment. The source of the water used for these practices differs between growers, in some cases pre-chlorinated mains water is used for either irrigation, fertigation, hydroponics or post-harvest produce washing. Growers of field crops normally use untreated surface water and filtered borehole water for irrigation, whereas growers that have access to other sources of water for irrigation may choose to treat it with disinfectant. In the leafy-salad growing sector, it is commonplace for growers to abstract from surface or harvested rain water into a reservoir or storage tank and let it stand for a known period of time (between days and weeks depending on the farm, weather and reliability of the water source) (PDM Produce, pers. comm. 2016) (Figure 4). If water was abstracted from a river or catchment, it would usually



**Figure 4.** Lettuce grown in the field can be irrigated with either treated or non-treated water. Photograph source: ADAS UK Ltd

stand for about 3 to 6 months. In some cases, it may still be disinfected prior to use.

If water from any of these sources was to be used directly onto the crop without it standing, it will be disinfected, with the treatment type depending on the grower. Leaving water to stand may not have the intended benefits and treatment of water with a disinfectant can sometimes be carried out to ensure that when it is used it is free from soil borne and water borne pathogens. However, low risk water is specific for high risk (RTE) crops in guidance used by the Chilled Food Association (CFA) and in their

retailers' guidance (Kaarin Goodburn, CFA, pers. comm.). Leafy-salads sold washed and ready to eat will wash with water that is often either chlorinated or treated with fruit acids (CFA website). Chlorates can also be present in soil and ground water as a legacy from sodium chlorate use as an herbicide for pathways, but typically residues are at low levels in the UK.

The EC is currently reviewing the Maximum Residue Level (MRL) for chlorate and investigating the implementation of a MRL for perchlorate for food produce, including horticultural fresh produce and potatoes. Chlorate is a by-product of chlorine disinfection. It was on the pesticides register based on its use as a non-selective herbicide until approval was withdrawn in 2009. Under Commission Decision No. 2008/865/EC it hence requires a MRL to be set, however, no MRL for chlorates has been established and so the default 0.01 mg/kg (the minimum level of detection for chlorate) that applies to all plant protection products for which the safe level is unclear has been set. However according to the FSA: "both the European Commission and Member States acknowledge that this MRL does not reflect the levels arising in foods from contact with water legitimately treated with chlorine or from legitimate biocide applications. All parties agree that the default level should be replaced by higher substantive levels, but as matters stand the EU Standing Committee on Plant Animals Food and Feed have been unable to agree on what those levels should be."

The reason for the review on the residues of chlorate and perchlorate in food is due to the concern of the human health effect on the iodine uptake by the thyroid, particularly in infants and young children and those with iodine deficiencies. Perchlorate (as potassium perchlorate) has been used to treat hypothyroidism at dose rates much higher than the proposed MRLs (e.g. 1 g potassium perchlorate/day for an adult (Connell, 1981; Ferner, 1996). Potassium chlorate has even been used as a gargle for sore throats (Alstead, 2013).

The World Health Organization (WHO) have provided the guideline level of 0.7 mg chlorate/l (a rounded figure) for drinking water. This is based on the total daily intake (TDI) of 30 µg/kg of body weight, given a typical human body weight of 60 kg, the assumption that drinking-water contributes 80% of the total exposure and a typical consumption of 2 litres of water per day (World Health Organization, 2004). This guideline level is provisional and is not officially enforced.

The [AHDB Horticulture Contaminants Update](#), released in March 2016, provides a link to a list of MRLs proposed by the EC, specified by crop group and crop type (Appendix

1). In the update, AHDB Horticulture note that there were a number of concerns raised by the Member States. They stated that:

- For some foods, the proposed MRLs were likely to be lower than, or variable from, the residues currently found in produce (from UK and non-UK sources).
- That if the proposed MRLs were to be implemented, any exceedances would seriously disrupt food trade.
- The cost of adjusting practices would be considerable, likewise applying new and potentially unproven systems, could impact on the efficacy of microbial control in fresh produce. As such, further work is required to properly assess the effect of the changes in MRLs for chlorate.

For perchlorate, the AHDB Horticulture Contaminants Update cites a comment by David Mortimer of the UK Food Standards Agency (FSA), which in summary reads: Perchlorate is not currently regulated in the EU. It has never been used as a Plant Protection Product and is not subject to the default MRL in 396/2005 (if a pesticide is not specifically mentioned, it carries the default MRL of 0.01 mg/kg, as in the case for chlorate). As perchlorate is listed as a health concern, it is being monitored with the possibility that a limit will eventually be set.

The FSA have monitored for perchlorate in fruit and vegetable produce from November 2013 to December 2015. No results have yet been disclosed. Perchlorate levels in food are to be considered again by the Commission in the second half of 2016. Therefore growers are recommended to continue monitoring crops by having their produce tested for chlorate and perchlorate residues. It is also suggested that growers monitor the water sources, filters and pipework, since changes in organic matter and microbial loading from these areas can influence the efficacy of the disinfectant and the amount used. Further information on reference MRLs for perchlorate can be found here:

<http://horticulture.ahdb.org.uk/sites/default/files/Perchlorate%20reference%20values%202015.pdf>.

An alternative to chlorine disinfectants that has been suggested is hydrogen peroxide ( $H_2O_2$ ). It is a strong oxidiser and disinfection with  $H_2O_2$  can be very selective with different pollutants or contaminants able to be targeted by changing the conditions and form of the  $H_2O_2$  solution.  $H_2O_2$  is commonly stabilised with silver nitrate to prevent it from degrading too rapidly. Though the danger of  $H_2O_2$  leaving residues is reduced (as

it breaks down to water and oxygen in solution), it can result in some phytotoxic damage to sensitive plant tissue such as leaves and petals. There has been discussion in the literature concerning the viability of H<sub>2</sub>O<sub>2</sub> applied as a vapour to surfaces, a method pioneered in the 1980's by Wang and Toledo. They showed that antimicrobial efficacy of H<sub>2</sub>O<sub>2</sub> was greatly enhanced over the liquid form (Wang and Toledo, 1986). However, there is the concern that it may not be completely effective in removing biofilm from surfaces (Araújo *et al.*, 2011). Further work is required to investigate where hydrogen peroxide is most effective for the disinfection of fresh produce or surfaces, and whether it can be used in combination with other methods. New products and systems are constantly being evolved to provide safe and easy to use products that provide sufficient efficacy against pathogens and microbes in the horticultural and potato producing industries.

The purpose of this review is to:

- Investigate the sources and fate of chlorate and perchlorate residues occurring pre-harvest (during crop production), at harvest and post-harvest.
- Provide an overview of chlorine chemistry relating to chlorine-based disinfectants used in horticulture and potato systems.
- Provide guidance on practices to mitigate the occurrence of chlorate and perchlorate residues in horticulture and potato systems.
- Provide recommendations for further work.

## **2. Disinfection requirement of fresh produce and the occurrence of residues of chlorate and perchlorate**

The activity of microorganisms in the production of horticultural crops can lead to pre and post-harvest losses in yield and quality, from both plant pathogens and secondary decay-causing organisms. Additionally, food, such as salads, which may be consumed without further processing or cooking can become contaminated with human pathogens such as *Escherichia coli* (especially Shiga toxin-producing *E. coli* (STEC)), *Salmonella spp.* and *Listeria monocytogenes*. Transfer of these pathogens onto produce can occur via contaminated garden compost, irrigation water, or workers handling the produce on farm (De Roever, 1998; Oliveira *et al.*, 2011; Pan and Nakano, 2014). In an attempt to minimise the negative impact of microorganisms on horticultural produce, numerous hygiene measures are utilised, including the widespread disinfection of irrigation and process water, and of contaminated surfaces. Not all fresh produce is washed, however, with harvested produce from, for example, soft fruit,

protected edibles, whole-head lettuce and brassica crops, picked and sent direct to consumers. Some produce, such as apples, can be moved in water flotation systems to minimise bruising, root vegetables such as carrots and potatoes can be washed to remove soil and bagged salads sold “ready-to-eat” require the contents to have been cleaned and according to UK/EEU law subject to a limit of 100cfu/g for *Listeria monocytogenes* in ready to eat pre-cut produce. There is an implied requirement for absence of other pathogens such as Shiga toxin-producing *Escherichia coli*. Salmonella must be absent from ready to eat produce.

A wide range of work has been carried out on the subject of plant pathogens and their association with irrigation systems/water (Pettitt, 2003; Hong and Moorman, 2005; Stewart-Wade, 2011; FDA, 2014; Raudales *et al.*, 2014; Zappia *et al.*, 2014; Pettitt, 2015). CP 126, a review of oomycetes causing root-rot (Pettitt, 2015), provided an overview of a selection of irrigation water treatment techniques and assessed the risk of different irrigation water sources. FV 248 assessed the risks of contamination posed to fresh salad leaf production by irrigation water sources and their potential implications to human health whilst also considering the concerns of retailers (Tyrell, 2004). Project FV 292 (Monaghan, 2008), which aimed to quantify the risk of pathogen contamination of fresh salads through irrigation water, showed that although pathogen persistence on the crop surface is limited, water quality needs to be high in the three week period prior to harvest.

AHDB Horticulture have funded numerous projects focussed on improving hygiene in horticultural production systems by utilising disinfection. PE 001a (McPherson, 2014) identified numerous disinfectants with different actives (including a chlorine based treatment) effective at reducing the contamination of apparatus with *Mycosphaerella melonis*, the cause of gummy stem blight on cucumber. PC 181 (O'Neill, 2003) assessed the viability of different disinfectants at effectively removing contamination with Pepino Mosaic Virus (PepMV) from numerous surfaces; a sodium hypochlorite solution was found to be effective. PC 212 (Spence, 2004) showed that effective disinfection of surfaces from Potato Spindle Tuber Viroid (PSTVd) could be still be achieved with sodium hypochlorite treatment for five minutes at concentrations as low as 0.5% m/m (5000 mg/kg) free chlorine, no information on the pH level of the solution was given. FV 314 (McPherson, 2007) evaluated the use of various biocides for the control of *Xanthomonas campestris* pv. *campestris* in-vitro and chlorine dioxide (ClO<sub>2</sub>) was found to be the most effective.

## **2.1. Residue occurrence of chlorate and perchlorate**

### *2.1.1. Chlorate*

No specific MRLs have been established for chlorate, the default MRL of 0.01 mg/kg of chlorate applying across all crop types in lieu of further information on chlorate and perchlorate residues in food (EFSA, 2014; EFSA, 2015). In November 2015, the European Commission released a list of produce categorised by crop type with associated proposed MRLs (Appendix 1). It has been found by AHDB Horticulture that, from the anonymised preliminary data gathered from growers in the UK during 2014-2016, around 70% of the crop groups for which results were received by the AHDB would comply with the proposed MRLs. All of these crops, for which such information was given, used various forms of irrigation. It must be noted, however, that for the crop groups where exceedances did occur, the data sample was limited, with only up to five samples obtained for that particular crop type. Exceedances occurred mainly in crops grown either in pots, hydroponically or under protection. From the laboratory residue determination method used, it cannot be known whether the residues arose from contamination only on the surface of the produce or whether it includes residue from within crop tissue.

From data held by AHDB to July 2016, between half and a third of the fruit that was irrigated with chlorinated water was showed to exceed the 0.01 mg/kg MRL for chlorate. The crops with the lowest risk of MRL exceedance were root crops. This data, although preliminary, could give the first indication of the target crops that are most likely to exceed the associated proposed MRLs. However, more data is required.

Though the issue concerning EFSA is the prolonged exposure to chlorate and perchlorate, EFSA have admitted that there is a need for more information on chronic exposure to chlorate and perchlorate in humans. It has been noted that the fatal dose for chlorate has been estimated to be ~30 g (30,000 mg) of sodium chlorate (equivalent to 23,517 mg chlorate) (Ferner, 1996). This would mean that, for a product with the chlorate residual level at 0.01 mg/kg, one would have to ingest 2500 tonnes of the product in one day before death as a result of the total chlorate intake. It must be noted that this is only in reference to the default MRL.

Information to AHDB was also provided by growers on the water source used, and is assumed to be referring to irrigation (rather than produce washing). Water sources principally included mains (pre-chlorinated) water and borehole water. Chlorinated water is a potential source of chlorate and perchlorate residues, more information on this is given in Section 3.2. Out of 295 samples, for 10 crop categories it was stated that mains water was the primary water source. These crops were basil (soil grown), basil (hydroponic/pot grown; See Figure 5), coriander, parsley, lettuce (hydroponic), protected curly lettuce, protected round lettuce, protected lettuce trio, soil grown lettuce). Only four crop categories were reported by the growers who replied to the



survey to be washed in water chlorinated themselves (predominantly using chlorine dioxide dosing). More information on other sources of chlorate and perchlorate are found in Section 5.2.

**Figure 5.** Basil grown in pots under a glasshouse in a hydroponic system. Source: Thinkstock Photos

### 2.1.2. Perchlorate

For the perchlorate residue data from the UK horticulture industry to date, there have been fewer than 30% of crop samples exceeding the intra-Union trade reference value 0.2 mg/kg perchlorate (EFSA, 2014) (see Table 1). Again, more data from the industry is required in order to make a judgement on the extent of the likelihood that crops in the UK that will exceed this level.

Harmonised reference values have been implemented for intra-Union trade, and the principal of setting the values as low as reasonably achievable by applying best practice was utilised. There are no EU imposed MRLs for perchlorate in drinking water or food. However, the intra-Union trade reference values range from 0.1mg/kg in most fruit and veg to 0.75 mg/kg in herbs, lettuce and salads and 1.0 mg/kg for herbal and fruit infusions (dried) (EFSA, 2014).

**Table 1.** Table adapted from the 2014 EFSA Scientific Opinion on Perchlorate, depicting the reference perchlorate levels for intra-Union Trade in fresh produce.

Food <sup>(a)</sup>	Level (mg/kg perchlorate)
Fruits and vegetables, <b>with the exception of:</b>	0.1
<i>Cucurbitaceae</i> and leafy vegetables, <b>with the exception of:</b>	0.2
Protected (glasshouse/polytunnel) grown celery and spinach	0.5
Protected (glasshouse/polytunnel) grown herbs, lettuce and salad plants, including rucola	1.0

<sup>(a)</sup>: the levels as reference values for intra-Union trade applies, insofar not specified, to the unprocessed food. For dried, diluted, processed and compound foodstuffs, Article 2 of Regulation (EC) 1881/2006 is of application.

The proportion of produce and economic cost as a result of exceeding the proposed MRLs, should they be implemented, is difficult to predict, but is likely to be significant if produce is deemed unmarketable. Also of consideration is the potential increase in microbial contamination stemming from a reduced use of chlorine based disinfectants from growers attempting to meet the new MRLs, if proven and effective alternatives to chlorine are not used. There has been no time span given as to when or if revised MRLs will be instated. It has been noted in correspondence with some of UK growers that alternatives to chlorine disinfectants are often already under trial.

### 3. Use of chlorine for disinfection

#### 3.1. Horticulture and potatoes

One class of widely used disinfectants in horticulture is based around chlorine (Gil *et al.*, 2016), and include hypochlorite solutions (primarily from sodium hypochlorite (NaClO) and calcium hypochlorite (Ca(ClO)<sub>2</sub>)), chlorine dioxide (ClO<sub>2</sub>) and, to a much lesser extent, chlorine gas (Cl<sub>2</sub>). A few well-known brands of these products include [Dejex](#), [Klenzan](#) (sodium hypochlorite), and [International Water Solutions](#) (chlorine dioxide) (information on some suppliers of disinfection products and systems can be found Appendix 2; an example of a chlorine dioxide generator is shown in Figure 6).



**Figure 6.** An example of a chlorine dioxide generator and injection unit.

These disinfectants play a significant role pre-, during, and post-harvest, in the treating of water for irrigation and hydroponics, to keep clean the water that is used for washing of harvested produce (not to have a cleaning/disinfectant effect on the produce itself) and for hydro-cooling and in the sterilisation of harvesting and processing equipment. The estimated costs of chlorine dioxide and hydrogen peroxide disinfectants can be seen in Appendix 5. The targets for water disinfection include plant pathogens and secondary decay organisms (to reduce losses and improve quality), as well as human pathogens (for example *Salmonella enterica* in relation to fresh-cut salads (Sagoo *et al.*, 2003)).

The use of chlorination for wash-water disinfection of fresh-cut operations was

evaluated as being less expensive than using UV, ozone or peroxyacetic acid treatments for the same purpose (Garrett *et al.*, 2003). It is used widely in fresh packing systems for washing potatoes and other root vegetables. Chlorine derived disinfectants have been identified as a significant source of chlorate and perchlorate in produce by EFSA during their assessments, as well as identifying that mains drinking water was also a major source of chlorate and perchlorate.

### **3.2. Mains / Drinking Water**

Chlorine (in the form of NaClO, Ca(ClO)<sub>2</sub> or Cl<sub>2</sub>) is widely used in mains-water disinfection and has been a component in a multi-barrier approach to preventing pathogens entering mains water (Gil *et al.*, 2009). In some cropping systems, the primary source of water is mains water which is already treated with chlorine by the water supply companies. Chlorine is typically added to the mains water, resulting in 0.1 to 0.5 mg/L of free chlorine in the water network ([Severn Trent networks](#)). A chlorine disinfectant is first added at the water treatment works, but to ensure that the water quality is maintained as it travels underground to the end user, low doses of chlorine are added where necessary. All along this system, the water quality is monitored by the water company. There have been some questions raised by the horticulture and potato industry concerning the level of free chlorine in the mains water network in relation to geography. Different water treatment companies would add differing concentrations of chlorine disinfectant according to the microbial load on the water source. Any extra free chlorine added by the grower at the point of use would result in a higher free chlorine concentration in the water and a greater likelihood of chlorate and perchlorate formation.

## **4. An overview of chlorine chemistry as relevant to disinfection in horticulture (including potatoes): pre-, during, and post-harvest**

### **4.1. Production of active chlorine from hypochlorites, chlorine dioxide and elemental chlorine (Cl<sub>2</sub>)**

Solutions derived from hypochlorites such as NaClO or Ca(ClO)<sub>2</sub>, or from chlorine gas, contain hypochlorous acid (HOCl) which is an effective disinfectant. Hypochlorous acid is highly antimicrobial while the hypochlorite ion (OCl<sup>-</sup>) has a relatively poor antimicrobial efficacy. Such solutions are used extensively in the post-harvest treatment of produce as well as in treating irrigation water, surfaces, and apparatus. HOCl is able to rapidly, and non-specifically oxidise organic (including components of microorganisms) and oxidisable inorganic material in solution, giving it its strong

antimicrobial properties. Once active chlorine (HOCl and ClO<sup>-</sup>) has oxidised a target (e.g. various components of microbes) it becomes locked up and/or reduced to harmless chloride ions and the active chlorine concentration of the solution drops. The chemical reactions involved are as follows:

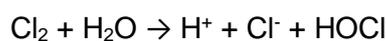
*Sodium and Calcium Hypochlorite (NaClO and Ca(ClO)<sub>2</sub>)*

When a hypochlorite is added to water it hydrolyses, forming a hydroxide salt along with hypochlorous acid and the final solution has a slightly raised pH:

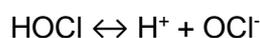


*Chlorine Gas (Cl<sub>2</sub>)*

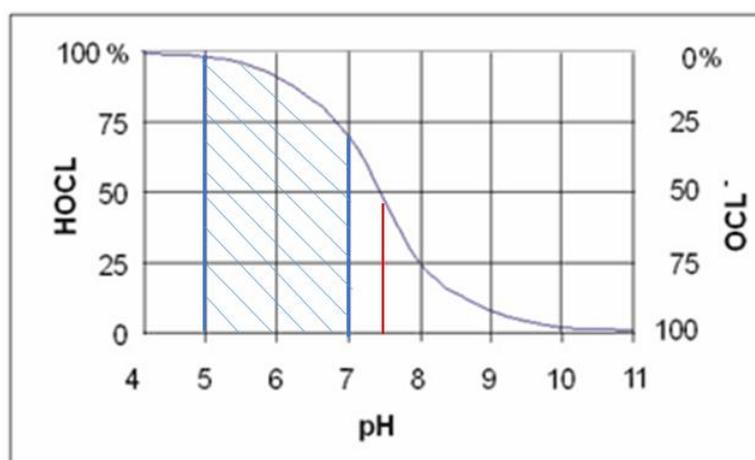
When Cl<sub>2</sub> is added to water it hydrolyses, forming hydrogen and chloride ions along with hypochlorous acid. The final solution has a slightly lowered pH:



On formation, hypochlorous acid exists in equilibrium with its constituent ions:



The position of the equilibrium is determined by numerous factors, including temperature, but mainly by pH, and it is the concentration of active chlorine which dictates the oxidising potential of the solution and ultimately its potency as an antimicrobial agent. It is suggested that HOCl<sup>-</sup> is the more potent, and thus favourable, of the two ions. At a pH of below 6, the equilibrium approaches 100% HOCl; at a pH



of above 9, the equilibrium approaches 100% OCl<sup>-</sup>. A ratio of 50% hypochlorous acid and 50% hypochlorite is reached at a pH of 7.5. (Figure 7).

**Figure 7.** Ratio of a solution of hypochlorous acid and hypochlorite ions showing 50% HOCL and 50% OCl<sup>-</sup> achieved at pH 7.5 (red line). Lower pH is to be preferred, from pH 5 to pH 7 (shaded area).

Source: <http://www.hach.com/DisinfectionSeries02>

### Chlorine Dioxide (ClO<sub>2</sub>)

Though chlorine dioxide leads to the formation of chlorate and perchlorate in solution, the chemical process is not the same as chlorination. However, for the purposes of this review, chlorine dioxide will be included under the term of ‘chlorination’. Chlorine dioxide does not hydrolyse in water but instead remains a dissolved gas in solution. Like other chlorine antimicrobials, it reacts with organic matter, including components of microorganisms. As an antimicrobial, chlorine dioxide has been reported to be more effective than solutions made from chlorine gas and is commonly used as a shock treatment to remove biofilms (Zheng *et al.*, 2013). Chlorine dioxide can also lead to the production of both chlorite (ClO<sub>2</sub><sup>-</sup>) and chlorate via a disproportionation reaction as follows, and is favoured by alkaline conditions:



Further information is available in the downloadable document;

<http://www.ncbi.nlm.nih.gov/pmc/articles/PMC1569028/pdf/envhper00463-0101.pdf>

Chlorine dioxide use is via a dosing system. According to Zheng *et al.* (2013), the optimum chlorine dioxide range to treat biofilms and common plant pathogens is 0.25 to 3.3 ppm (mg/l). The table below (Table 2) is adapted from Zheng *et al.* (2013) to show, from a range of resources, the critical level of chlorine dioxide and the contact time required to control particular microorganisms, including when present as conidia (spores).

**Table 2.** Adapted from Zheng *et al.* (2013), the concentration of chlorine dioxide and contact time required to control the listed microorganisms, as found in a review of various studies.

Microorganism	Critical Level (mg/l or ppm)	Contact time (minutes)

Algae*	0.25 - 2.0	5 - 10
<i>Alternaria zinnia</i> (spores)	2.0 - 3.1	8 - 12
<i>Botrytis cinerea</i> (conidia)	3.0	1
Biofilm (unspecified)	0.25 – 1.55**	Continuous
<i>Colletotrichum capsici</i> (conidia)	0.7 - 1.8	2
<i>Cryptosporiopsis perennans</i> (conidia)	1.0	0.5
<i>Cylindrocladium</i> spp. (conidia)	10.0	0.5
<i>Erwinia chysanthermi</i> (bacteria)	20.0	20 - 40
<i>Fusarium oxysporum</i> (conidia)	0.4 – 5.0	2 - 20
<i>Mucor piriformis</i> (conidia)	1.0	2
<i>Phytophthora cinnamomi</i> (spores)	1.0 - 2.9	2 - 8
<i>Rhizoctonia</i> spp. (mycelia)	Ineffective	Not applicable
<i>Xanthomonas campestris</i> (bacteria)	0.2	Daily

\*No further information on the type of algae stated\*\*From Gagnon *et al.* (2005). Chlorine dioxide at 1.55 mg/l on polycarbonate surfaces showed the greatest efficacy in this study against biofilms.

#### **4.2. The production of unwanted by-products, chlorate and perchlorate**

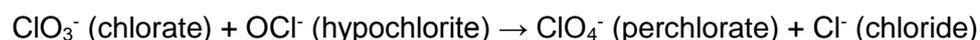
Chlorates and perchlorates are formed in chlorinated water and on produce coming into contact with chlorine based disinfectant. There is currently limited data regarding

how chlorate is taken up and stored in fresh produce when hypochlorite or chlorine dioxide is used during plant production or post-harvest for water disinfection (see Section 5). Uptake, or absorption, of chlorate is likely to depend on the type of contact with the chlorine disinfectant. For example:

- Overhead irrigation (from pre-chlorinated mains water) causing direct contact on leaves and fruit during crop production.
- Direct contact between the harvested produce and chlorinated wash-water.
- Direct contact between the harvest produce and a surface that was previously disinfected with chlorine.

Exposure time to the disinfection treatment, concentration of the chlorine in solution and how the chlorine-treated water is applied will affect how much chlorate residue is present.

It has been noted (Section 4.1) that HOCl is a stronger oxidiser than OCl<sup>-</sup>, and so is more effective a disinfectant. The degradation of OCl<sup>-</sup> results in the formation of chlorate and then perchlorate via a chlorite intermediate stage (Gordon and Tachiyashiki, 1991):



The degradation to chlorate is influenced by a number of factors, including the concentration of the solution, the pH and the temperature. The amount of chlorate produced can be controlled by limiting the final strength of the solution, maintaining cool temperatures for storage, and maintaining a high pH until use is required (i.e. use acid injection at time of use to facilitate the formation of HOCl).

### **4.3. Reducing by-product formation in chlorine disinfectants during their storage**

Guidance from the literature on how chlorate and perchlorate formation from sodium hypochlorite (referred to here as hypochlorite) may be reduced is listed as follows (Stanford *et al.*, 2011). These recommendations would benefit from further experimental investigation as to how they may be implemented on a practical level as a method to help reduce the incidence of chlorate and perchlorate residues:

- *Upon delivery, dilute stored hypochlorite solutions with soft water for storage prior to use as this will decrease the rate of perchlorate formation*

By diluting a 2 molar (~15% m/m) hypochlorite solution by a factor of 2, the rate of perchlorate formation decreases by a factor of 7. This is due to a combination of concentration and ionic strength effects. A four-fold dilution of hypochlorite will decrease the rate of perchlorate formation by 36. A ten-fold dilution of hypochlorite will decrease the rate of perchlorate formation by 270.

- *Store the hypochlorite solutions at a lower temperature, e.g. storage at 5°C or below will minimise its decomposition*

The higher the temperature, the faster the decomposition of hypochlorite to chlorate and perchlorate. For every 5°C decrease in storage temperature, perchlorate formation rate reduces by a factor of 2.

- *Control the pH of stored hypochlorite solutions at pH 11-13, even after dilution (consult the supplier for instructions)*

Storing hypochlorite solutions at a pH value lower than 11 increases the rate of decomposition of hypochlorite ion/hypochlorous acid to chlorate, even though this reduces the amount of perchlorate formed. When the pH is higher than 13, perchlorate formation is enhanced due to the ionic strength effect. Manufacturer specifications of hypochlorite should include pH control in the range of 11 to 13.

- *Control the exposure to transition metal ions by avoiding contact with copper and iron in rusty or old pipework and pumps*
- *Store in UPVC reinforced with glass fibre reinforced polymer (GRP) resin or a full post cured vinyl ester GRP laminate*

The presence of transition metals such as iron (Fe<sup>3+</sup>) and copper (Cu<sup>2+</sup>) in the hypochlorite solution (e.g. from old piping on a tank or pump) can result in its increased degradation rate ([Hill Brothers Chemical Co.](#)). While the degradation is associated with reduce perchlorate formation, the free chlorine concentration is also reduced. This results in the requirement for additional hypochlorite solution which leads to a higher mass loading of contaminants such as perchlorate, chlorate and bromate.

- *Use freshly delivered or new hypochlorite solutions where possible*

Over time, hypochlorite will naturally decompose to produce oxygen, chlorate and perchlorate. Reducing storage time will result in a lower rate for formation of these contaminants in the hypochlorite solution. Using fresh hypochlorite solution, which has

a higher concentration of hypochlorite, will reduce the amount of solution required to obtain the target free chlorine concentration. Do not add new to old hypochlorite solutions. Take care not to over order hypochlorite and ensure use-by dates are complied with.

#### **4.4. The effect of contaminants and breakpoint for available free (active) chlorine**

An additional factor which influences the active chlorine content of the solution is the presence of organic and inorganic contaminants, including for example; flotation salts used in the top fruit industry, plant exudates that are produced after cutting (such as from lettuce butts after harvest), soil particles and fertiliser. Nitrogenous compounds, such as ammonia and amino acids (from fertigation or growing media), can result in the formation of 'combined chlorine' (e.g. in the form of chloramines). Combined chlorine is a poor antimicrobial agent compared to HOCl and can be produced in situations such as when washing dirt off potatoes or when cleaning an irrigation system containing nitrogen compounds.

A 'breakpoint' is reached once all organic matter has been oxidised after which further chlorination only results in an increase in free available chlorine (as HOCl or OCl<sup>-</sup>). For effective disinfection, it is recommended in the literature that chlorination should continue until the point of establishing free chlorine. This results in a situation where more highly contaminated water requires treating with higher levels of chlorine to reach the breakpoint, which increases the chlorate/perchlorate content of the water. This can be the case with recirculated water, or water from highly contaminated water source (Gil *et al.*, 2016).

For disinfection of produce and equipment, target free chlorine levels to achieve are typically recommended by the disinfectant manufacturer. From discussion with a limited number of grower contacts, it is common practice for growers and packers to follow a manufacturer protocol on the ratio of product to water, to maximise microbial control by achieving a certain free chlorine level. The concentration of the disinfectant dosed or applied manually in solution should reflect the chemical oxygen demand (COD), the indirect measure of organic compounds in solution) of the water used and the surfaces being disinfected. Further work is needed to assess what levels of free chlorine are being obtained and how they can be managed. For example, Gomez-Lopez *et al.* (2014) found that a minimum of 7 mg/l free chlorine was required to completely control *E coli* O157:H7 at a level of 5 log CFU/ml in a solution of process

water.

With this information in mind, growers must assess the presence of microbial and organic contaminants from the water source used for their practices, whether it is for irrigation, fertigation, hydroponics or post-harvest washing. There are many factors that could lead to contamination in the water, such as the use of surface and reservoir water, cracked piping and blocked or inadequate filters. Mitigation methods must then be implemented to reduce contaminants occurring, and hence, lessen requirement for additional chlorine (see Sections 8 and 10).

## **5. Uptake and fate of chlorate and perchlorate in the plant**

There is limited information available from academic and grey literature as to a definitive uptake mechanism and rate of chlorate and perchlorate by plants pre- and post-harvest. What is ascertained from literature are potential uptake mechanisms and fate of chlorate and perchlorate based on associated factors. For example:

- The relationship between nitrate and chlorate uptake in plants
- The utilisation of the xylem and transpiration pathway as a means for chlorate/perchlorate uptake and accumulation in plant tissue

Therefore, further investigation through practical experimentation is recommended on the following:

- How and where chlorate and perchlorate are assimilated (including the rate of uptake) and metabolised within the plant,
- How it is then partitioned into different types of tissue in the plant
- The differences in accumulation rate between crop species
- Chlorate/perchlorate contamination of fresh produce exterior or tissue from disinfected surfaces
- How much chlorate/perchlorate can be attributed to a particular chlorination method (irrigation, fertigation, produce washing)
- The percentage of input of free chlorine is converted to chlorate/perchlorate in the final horticultural product that is ready for harvest and processing.

### **5.1. *During crop production (pre-harvest) and in the environment***

Concerns about residues and presence of chlorate and perchlorate in food, water and soil led to the withdrawal of the herbicide sodium chlorate. It was used as a non-

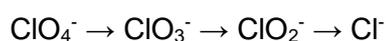
selective herbicide from 1910 until its withdrawal in the UK in 2009. It is unlikely to have been used by horticultural growers in the UK, but mainly on non-cropped industrial sites and amateur use on paths (John Atwood, weed specialist, pers. comm.). A colourless powder, it is absorbed through the roots and foliage of plants, killing the phloem tissue. It has been used worldwide as a desiccant and defoliant in cotton, safflowers, clover, lupins and other crops (Tomlin, 1994). According to the Pesticide Properties Database (supported and maintained by the University of Hertfordshire), chlorate (in the form of the herbicide 'sodium chlorate') is classed as persistent in soil, and can remain so for between six months to five years depending on the rate, soil type, organic matter content, soil moisture and weather conditions (Tomlin, 1994; Hertfordshire, 2016).

High levels of chlorate and perchlorate accumulation by plants can occur over a relatively short period with some plants accumulating high levels within a week (Yu *et al.*, 2004), and evidence suggests that external nutrient levels available to the roots may influence the rate of chlorate and perchlorate uptake by plants (Tan *et al.*, 2004). The mechanism of uptake of these contaminants by plant roots is understood to be via a similar pathway to nitrate accumulation, utilising the same ion transporter and with storage mainly in the leaf tissue as driven by transpiration (Seyfferth and Parker, 2007). The varying transpiration rates between different plant tissues is likely to be the reason why chlorate/perchlorate levels are higher in leaves than in fruit (Jackson *et al.*, 2005; Sanchez *et al.*, 2006). This agrees with observations from the chlorate and perchlorate residue data (anonymised) from UK horticulture growers collected by AHDB Horticulture, where more chlorate was found in the tomato leaf than in the fruit. The use and uptake of nitrate as a fertiliser in hydroponics fertigation and solid dressings could also be another source of information to aid understanding of how chlorate and perchlorate might become present in crops grown in the UK (Jenkins and Sudakin, 2006).

It has been observed that plants tend to take up more perchlorate during the day than at night, when the plant is transpiring at a higher rate (Seyfferth and Parker, 2008). It is unclear if this is also the case for chlorate. However, the authors state that transpiration alone cannot be used to predict the uptake of chlorate and perchlorate in higher plants. There is also a theory that perchlorate and chlorate are most probably assimilated by root cell membranes against an electrochemical gradient. This is the most generally accepted model for plant uptake of anions like chlorate and perchlorate

(Marschner, 2011).

An alternate explanation is that as certain plants are capable of degrading perchlorate once assimilated (phytodegradation), and that this may occur at a higher rate in fruit than leaves (Seyfferth and Parker, 2008). *Ex situ*, degradation can also occur in the root zone via microbial activity (rhizodegradation) (Seyfferth and Parker, 2008). This process occurs at a higher rate than phytodegradation, and is facilitated by anaerobic conditions (Shrout *et al.*, 2006). Perchlorate is reduced to chloride via chlorate and chlorite intermediates through a stepwise reaction:



In terms of perchlorate breakdown, a study by Nozawa-Inoue *et al.* (2005) found that under arid conditions (favourable for perchlorate accumulation) perchlorate was found to be broken down by indigenous microbial populations such as *Dechloromonas* sp., *Bacillus cereus* and *Azospirillum* sp.

Perchlorate also occurs naturally in the environment, particularly in arid environments where annual rainfall is limiting. The concentration in geographical deposits tends to be low, except for in areas such as the Chilean caliches, nitrate deposits, brines and some potash ores. A theory described by Srinivasan and Viraraghavan (2009) speculates that perchlorate may be formed through an atmospheric process, though the exact mechanism is unknown. However, the theory suggests that chloride (Cl<sup>-</sup>), possibly from sea water or land based chloride compounds, reacts with atmospheric ozone. Photolysis of ozone in the presence of chlorine (Cl<sub>2</sub>) and HOCL may occur in the marine environment. During such reactions, chlorate formation has been proposed in the stratosphere. These reactions were re-examined in studies on the surface of sodium chloride (NaCl) particles, which resulted in oxygenated products forming on dry salt surfaces. Chlorate has been observed to form during the ozonation of natural waters containing chloride, and the dissolution of chlorine in water can result in hypochlorite radicals (OCL<sup>-</sup>). The addition of oxygen to chlorate may result in the formation of perchlorate. These reactions are thermodynamically favourable and the amounts of perchlorate formed are kinetically dependant. Due to the energy that may be required to form perchlorate in the atmosphere, there is the possibility that lightning may play a role, though the perchlorate would become diluted in the precipitation as it falls to earth. As such, the amount of perchlorate that forms in the atmosphere is likely to be relatively small compared to the amounts produced by man-made enterprises

such as fireworks, rocket fuel and explosives manufacturing (Trumpolt *et al.*, 2005; Srinivasan and Viraraghavan, 2009).

Chlorate can persist in soil for long periods, and can be subject to run-off into water courses. It appears that, according to Urbansky and Brown (2003) that perchlorate behaves differently, but it depends on the soil type. It was found by Urbansky and Brown (2003) that perchlorate does not effectively adsorb to soils and that its mobility and fate are largely influenced by hydrologic and biological factors. Depending on the soil type, the intra-soil perchlorate content is depositional rather than adsorptive. For soils and substrates that had a higher anionic exchange capacity, there was a greater degree of perchlorate sorption (e.g. perlite). Therefore, the authors recommend that analysis of perchlorate in soils must take in account ionic exchange and that leaching water alone may give inaccurate results.

Tan *et al.* (2004) showed that perchlorate levels in the plant correlated with chlorate levels in the primary water source. It is worth noting that most work focussing on plant chlorate/perchlorate uptake is tailored towards phytoremediation options for contaminated soil, rather than in edible produce. This is the case in Sundberg *et al.* (2003), where they explored the use of tobacco plants for remediation of land from perchlorate contamination. Perchlorate was found to accumulate in the leaf tissue. Work done on phytoremediation is done mainly in response to the previous use of sodium chlorate as an herbicide prior to its withdrawal from use.

Alternative sources where chlorate and perchlorate may be present, other than irrigation water, include disinfected surfaces, hydrocooling and post-harvest washing. Following this review, there is still an unresolved question of whether or not an accumulation of chlorate (and subsequently perchlorate) resulting from the use of chlorinated water (e.g. mains water) for irrigation may possibly occur in substrates or soil. More investigation is required in order to make a judgement on the correlation between irrigation with chlorinated water (either pre-treated mains water or treated borehole water) and the potential subsequent accumulation of chlorate in plant tissue. Also to be explored is the potential extent of chlorate contamination on the surface of fresh produce that has been in contact with a surface that has been disinfected with chlorine and not been rinsed.

More information is needed in relation to perchlorate laboratory analysis in different horticultural growing-media and soil types as well as different tissue portions of plants.

## 5.2. Post-harvest

It is unclear as to whether there is any phytodegradation of chlorate and perchlorate post-harvest (Seyfferth and Parker, 2008). Process water can become contaminated during (but not limited to) the washing process and hydrocooling, which can subsequently lead to the large-scale microbiological contamination of produce. Chlorination is often utilised to control microbial contamination and as such leads to the presence of chlorate and perchlorate in the water. By chlorinating the water, the system's oxidation-reduction potential (ORP) is increased. This means that a point is reached where the oxidising chemical pulls electrons away from the cell membrane of the microbe, destabilising the cell and causing it to become leaky (Suslow, 2004). An ORP of 650mV in solution is recommended by the WHO to provide instantaneous disinfection (McPherson, 1993).

Process water can contain high levels of organic matter, giving rise to a high chemical oxygen demand (COD) which locks up a large amount of the added chlorine due to the ease at which it is oxidised. Therefore, chlorine levels need continuously topping up to maintain the concentration of free active chlorine (HOCl and ClO<sup>-</sup>) (Gil *et al.*, 2016). This will increase the overall chlorine content of the system if water replenishment is not at a high enough rate to maintain the dilution factor, facilitating the build-up of increased chlorate and perchlorate levels (Gil *et al.*, 2016). Evidence suggests that chlorate levels in fresh produce after washing are about 10% of the levels found in the wash-water and that rinsing with clean water only reduces contamination of produce by about 10%. The author cites that the Health and Consumers Directorate General of the European Commission recently reported that the chlorate levels found in fresh produce appear to be inversely related to the rate at which the wash-water is replenished by addition of fresh water. Therefore, it is suggested that if water is to be reused during post-harvest washing, the reused water must be replenished with clean water and chlorinated to achieve sufficient free chlorine and then disposed of a short period after use, as chlorate is formed over time (Gil, *et al.* 2016).

Adding sodium hypochlorite to process wash-water leads to an increase in pH, promoting conversion of HOCl to the less active ClO<sup>-</sup>. Maintaining the pH at an optimal level that will favour HOCl may reduce the amount of chlorine required to maintain microbial integrity due to the higher antimicrobial activity of HOCl compared to ClO<sup>-</sup>. Acid injection into the system can effectively reduce the pH, driving the equilibrium towards the more antimicrobial HOCl.

There appear to be some methods growers can employ to mitigate the level of residues present in fresh produce post-harvest. Steps to take during the post-harvest washing stage are further explored in Section 8.

Information on the use of chlorine-based disinfectants and alternatives such as hydrogen peroxide was sought from the potato processing and fresh packing sectors of the potato industry. A questionnaire was sent to the stakeholder associations (Potato Processors Association and Fresh Potatoes Suppliers Association), who then distributed it to members (the questionnaire for the potato industry can be found in Appendix 7). Information was either sent directly back to the author via email or the information was collated and summarised in a single overview. Although this feedback from the industry was a useful insight into the issue of chlorate and perchlorate in the post-harvest potato industry, more information is required to qualify the statements that were made.

An overview of the answers and feedback from the potato processing and fresh packing sectors is as follows: Potato growers would tend to use borehole, surface or reservoir water for irrigation and almost all UK grown potatoes arrive at the plant dirty from the field. In some fresh potato packer companies a spray-bar system is used to wash potatoes ready for consumption. Most of the water used in fresh packing comes from mains (potable) water. Only some of the companies that replied to the questionnaire routinely check the chlorate levels in produce and wash water and chlorate residues in UK potatoes were found to be below the MRL of 0.01 mg/kg. One reply stated that produce they have received from abroad had residues for chlorate up to 0.03 mg/kg. More data is required. It has been stated in the information received so far that it is not common practice to request that suppliers (i.e. growers) test for chlorate and perchlorate in their produce and water sources. Chlorination, or use of chlorine-based disinfectants, is reported to be used widely in the fresh potato packer sector (according to industry feedback for this review), though alternatives are being sought and trialled. All respondents of the questionnaire believe it would be highly problematic if the residue level for chlorate was to be set at 0.01 mg/kg for potatoes.

The potato processing sector generally uses neither chlorination nor hydrogen peroxide as a method of disinfection, as mains water is used for washing the potatoes supplied to them direct from the field. As some of the packers and processors in both the vegetable and potato processing sectors tend to use mains water for their systems, the varying levels of free chlorine and chlorate in the mains water in relation to

geography is an area to be reviewed. It was recommended by both the fresh packers and processing industries that the results from this would contribute to chlorate management in the horticulture and potato supply chain.

Limited information is found in literature, including grey literature, on the contamination of chlorate on fresh produce from disinfected surfaces. Where cross contamination of chlorate to fresh produce may have occurred, an alternative method of disinfection may be suggested, such the use of hydrogen peroxide. This is an area that requires further investigation.

### **5.3. Bioaccumulation rate differences between crop species (pre- and post-harvest)**

Different species of plants accumulate different amounts of chlorate and perchlorate (Tan *et al.*, 2004) with evidence showing that lettuce accumulates higher levels of perchlorate than cucumber and soybean (Yu *et al.*, 2004). Dicotyledonous plants are able to accumulate markedly higher levels than monocotyledons (Smith *et al.*, 2004). In addition, it appears that different cultivars of the same plant species accumulate chlorate/perchlorate at different rates (Sanchez *et al.*, 2005).

Chlorate is a structural analogue of nitrate, inhibiting its uptake by plant roots (Bose and Srivastava, 2001). An AHDB Horticulture funded project, PC 297, found that lettuce varieties such as butterhead and curly lettuce tend to accumulate nitrate in the 'ribby' parts of the head (Davies, 2009). The analysis occurred over the winter period, when crops are more likely to exceed the nitrate MRL (nitrate MRLs range from 2000 to 4500 mg/kg depending on protected or outdoor grown lettuce or spinach and whether the crop is harvested in summer or winter, due to growing conditions and fluctuating growth rates (Alexander *et al.*, 2008). However, it remains unclear as to the extent that chlorate and perchlorate is taken up by plants by the same mechanism as nitrate due to the limited literature available concerning edible crops and different crop species (i.e. tomatoes, potatoes, carrots, etc.). Theories concerning the uptake mechanisms of chlorate and perchlorate in plants is found in Sections 5.1 and 5.2. Another consideration is the accuracy of the chlorate and perchlorate residue analysis results from fresh produce, particularly those where the leafy part of a crop is that to be eaten (e.g. lettuce, fresh herbs). Currently, there is no standard analytical method and a review of laboratories and their methods of chlorate and perchlorate analysis is required (see Appendix 4).

Perchlorate is also found as a contaminant in waterways, particularly near industrial areas. Tan *et al.* (2004) evaluated the uptake of perchlorate by Bulrush (*Scirpus* sp.) from the vertical up flow of wetlands in the presence and absence of nitrate in the sediment and water. Where perchlorate was present near the root zone, there was greater uptake of perchlorate in the plant regardless of the presence of nitrate. The study concluded that for remediation of waterways, planting a plant species such as Bulrush reduced perchlorate in the waterways to below the level of detection (4 µg/L perchlorate). A greater concentration of perchlorate was found in the Bulrush stems and leaves than in the roots (Tan *et al.*, 2004), which follows the theory by Sundberg *et al* (2003), who devised a kinetic model to show the flow of perchlorate from the soil/water to the leaves via the roots.

## **6. Diagnostic testing of chlorate and perchlorate in plant tissue and water**

The accuracy of diagnostic methods of chlorate and perchlorate residues are an area to be reviewed by the horticulture industry. A brief evaluation of analyses for chlorate and perchlorate has been made (Appendix 4). In summary:

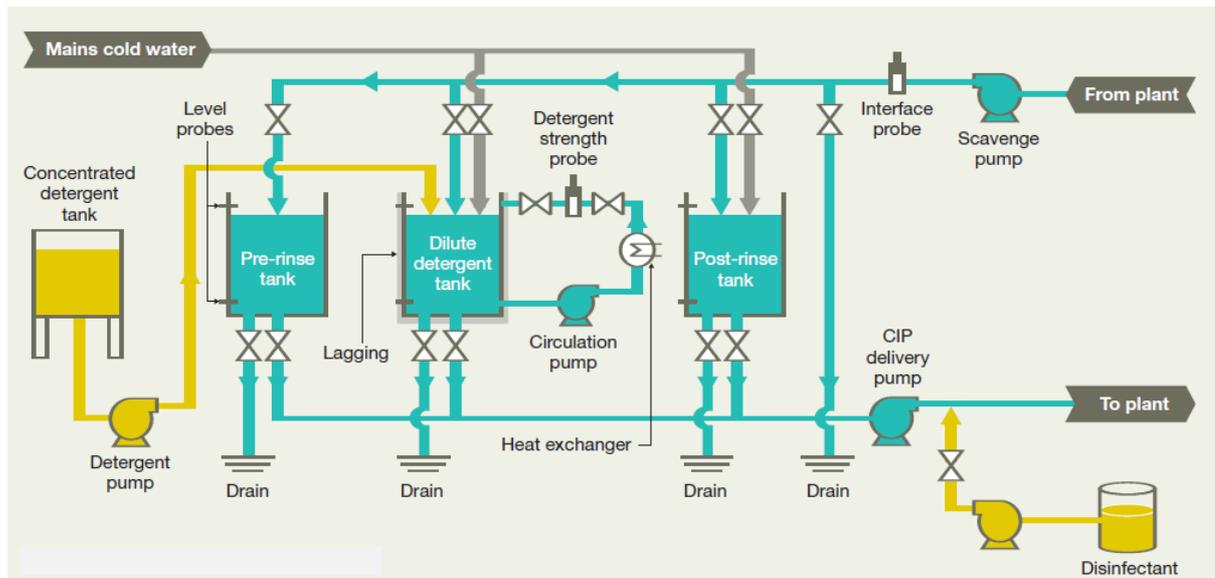
It is necessary to submit produce for regular testing to suitably qualified analytical laboratories for chlorate and perchlorate residues. However, it appears that no UK laboratories are cited as ISO 17025 (UKAS) accredited for perchlorate analysis in food and water matrices. A method for perchlorate analysis is currently awaiting accreditation. UKAS acknowledges that the UKAS single test search for chlorate is not totally reliable. When submitting the produce for a fit-for-purpose analysis, it is important that the specimen is placed in appropriate sample receptacles (especially those provided by the laboratory) with a suitable preservative (if required) to ensure that no significant sample deterioration occurs. Another question raised involves the difficulty of obtaining accurate chlorate and perchlorate detection with the presence of chlorophyll from green tissue in the sample. Low levels of perchlorate are difficult to analyse in most food matrices and waters with a high electro-conductivity (EC), particularly in the presence of organic matter. There is a high level of uncertainty with significant variation in results between laboratories. This problem will also apply to chlorate analysis.

With many outbreaks of human pathogens occurring from fresh produce, disinfection is an important aspect to food safety. More investigation into the variation of analyses between laboratories and the possible standardisation of analysis for chlorate and perchlorate residues in fresh produce is required.

## 7. Reducing chlorate and perchlorate residues

It may be possible to manipulate certain chemical and physical parameters such as pH, temperature, storage concentration and storage duration in order to reduce the build-up of chlorate and perchlorate in solution prior to application. Additionally, pre-washing of produce/apparatus in untreated water to remove any bulk contamination (soil etc.) prior to disinfection will facilitate the use of solutions with lower concentrations of active chlorine, shorter exposure times, or both, reducing chlorate/perchlorate accumulation in the produce. For recirculation systems, there are many challenges with maintaining sufficient control of pathogens in the wash or irrigation water and preventing contamination of fresh produce as a result (Gil *et al.*, 2009). The authors suggest a recirculation system where input water, such as mains or borehole water, is used to pre-wash the harvested produce in order to remove soil particles and plant-cell exudates from the cut areas of the crop. Then the produce would move to an aerated washing tank which is sanitised, before the produce is moved on to be rinsed with clean water such as mains water.

Information provided by [WRAP](#) to the food manufacturing industry for the removal of “soil” from processing equipment and machinery should be utilised (see Figure 8). Although the cleaning method does not include the use of disinfectants, it does implement the principle of a pre-wash to remove soil from the water source and pipes (which is a factor for chlorate and perchlorate formation). Similarly, if possible, beginning-of-season / between crop flushing of fertigation lines through with clean water prior to treatment with a chlorine solution would again likely reduce the required concentration of active chlorine to achieve the desired results by removing (or at least reducing) additional oxidation targets such as soil or components of fertiliser.



**Figure 8.** Schematic of an example cleaning protocol in a food manufacturing plant, detailing where rinsing and detergent is used in a recirculating system. Disinfection could follow detergent use. Source: <http://www.wrap.org.uk/>

It has been shown that utilising various physical techniques in conjunction with chlorination can enhance disinfection efficacy (Inatsu *et al.*, 2005; Klaiber *et al.*, 2005; Pan and Nakano, 2014). Pan and Nakano (2014) found micro-bubbling and ultra-sonication to be ineffective, but that using a mild heat treatment (50°C), either prior or simultaneously with treatment of ClO<sub>2</sub> or NaClO, significantly increased the log reductions of recovered bacteria from the surfaces of leafy vegetables, including of *E. coli* strain O157:H7. That being said, introduced *E. coli* strain O157:H7 was shown to be more persistent than the naturally occurring microflora. However, the fact that any bacteria were able to be recovered is of concern as it illustrates the issues with attempting to disinfect contaminated produce surfaces as opposed to contaminated planktonic suspensions of bacteria, for which similar treatments are relatively efficacious (López-Gálvez *et al.*, 2010). One explanation for this could be that the surface structure of various produce is able to provide some degree of protection to microorganisms (suggesting certain products are harder to decontaminate than others), or that biofilms may be formed which also shelter bacteria from chlorine treatment (López-Gálvez *et al.*, 2010; Durak *et al.*, 2012; Pan and Nakano, 2014). It must be noted, therefore, that planktonic (suspended in water) bacteria are much easier to control than bacteria residing in biofilm.

It has been reported that increasing exposure time of produce to the disinfectant solution enhances their decontamination. However, it is also reported that after a

certain exposure (or contact) time, little additional control is achieved and therefore exposing produce for longer than this time period is likely to provide an unnecessarily lengthened window for the uptake of residues. For example, (Rahman *et al.*, 2011) found three minutes contact time to have a better antimicrobial effect than one minute exposure, but not significantly lower than a five minutes extended exposure.

Washing produce prior to chlorine treatment and/or treating water to remove reducing substances (organic substances,  $\text{Fe}^{2+}$  etc.) before it is chlorinated will reduce the amount of contaminants which could mop up active (free) chlorine, reducing the amount of chlorine required to reach the breakpoint of the system. Consequently, this would lead to lower levels of chlorate and perchlorate being exposed to fresh produce. Additionally, replacing wash/process water frequently will facilitate lower levels of chlorate and perchlorate and maintain the systems disinfecting capacity by lowering the breakpoint. (Pan and Nakano, 2014) found that *E. coli* cells on inoculated leaf surfaces were able to survive numerous (over 10) wash cycles in recycled water with an initial  $\text{NaClO}$  concentration of 10 mg/l and 20 mg/l and showed that *E. coli* cells were not able to survive where the initial wash water had higher concentrations of  $\text{NaClO}$  (50 and 100 mg/l as free chlorine). These levels were achieved under laboratory conditions on inoculated leaf surfaces. Further evaluation into the desired minimum free chlorine achievable to control the main plant and human pathogens in fresh produce washing, irrigation and surface/equipment cleaning is required under industrial conditions.

## **8. Disposal of chlorinated wash water**

"Water UK" provides guidance on how to dispose of chlorine solutions and chlorinated water. Since chlorine can be toxic to flora and fauna in the environment, care must be taken when disposing on chlorinated wash water. There are a series of methods to follow, which are summarised in Appendix 3, but in summary: a risk assessment should always be performed, do not dispose of chlorinated water near water courses without prior consent from the Environment Agency, and ensure water drains from the out-pipes from the wash systems are not discharging into water courses. It may be necessary to dechlorinate the water prior to disposal. The most commonly used compounds are sodium thiosulphate and sodium bisulphite (powders and tablets of these compounds are not to be used after their expiry date) (WaterUK, 2015).

It is also suggested that the manufacturer of the chlorine-based disinfection product being used is consulted on their protocol for disposing of chlorinated water and disinfection products that have reached their use-by-date.

## 9. Hydrogen peroxide disinfection

Hydrogen peroxide, like the chlorination approaches described above, derives its antimicrobial capacity from its potency as an oxidiser. The exact biocidal mechanism is not fully understood and will vary based on physical state (solution or gas) and formulation (or mixture with other chemicals), but likely involves targeting various components of proteins, cell walls, cell membranes, and DNA.

H<sub>2</sub>O<sub>2</sub> is completely miscible with water and concentrations greater than 30% m/m are typically used in water treatment for a swimming pool, and approximately 3% is used for medicinal purposes, although for washing, vaporised forms have been shown to have greater efficacy perhaps due to increased penetration (Wang and Toledo, 1986; USPTechnologies, 2016). Disinfection with H<sub>2</sub>O<sub>2</sub> can be very selective and different pollutants can be targeted by varying pH, temperature, dose and catalyst (USPTechnologies, 2016). H<sub>2</sub>O<sub>2</sub> can be used directly in treatment (often with a stabilising component such as silver), or as an active ingredient in an 'activated peroxygen', a class of products where H<sub>2</sub>O<sub>2</sub> is combined with organic acids such as acetic acid (to form peracetic acid) to increase stability.

### *How hydrogen peroxide is transported and stored*

Hydrogen peroxide must be transported in polyethylene, stainless steel or aluminium containers. When hydrogen peroxide comes in contact with flammable substances (such as wood, paper, oil or cotton i.e. cellulose), iron, copper, chromium, lead, silver, manganese, sodium, potassium, magnesium, nickel, gold, platinum, metalloids, metal oxides or metal salts, the result will be at risk of explosion or spontaneous ignition. Likewise, when hydrogen peroxide is mixed with organic matter, such as alcohols, acetone and other ketones, aldehydes and glycerol, severe explosions may occur. Therefore, hydrogen peroxide is usually transported in diluted form as a safety measure. The compound can decompose during transport to produce O<sub>2</sub> water and heat; the heat facilitates further breakdown in a positive feedback loop. Alkalinity and the presence of pollutants also accelerate the decomposition of H<sub>2</sub>O<sub>2</sub>.

### Applications of Hydrogen Peroxide

In agricultural irrigation systems, the H<sub>2</sub>O<sub>2</sub> is injected into flowing water; the suitability of a system for disinfection by H<sub>2</sub>O<sub>2</sub> is determined largely by pH, temperature, and size. For the cleaning of systems (e.g. biofilm removal) high concentration shock treatments are typically used. The mechanism of H<sub>2</sub>O<sub>2</sub> against bacteria and fungi is believed to involve damaging DNA through oxidative stress. Resistance in some bacteria and

fungi due to the continued use of hydrogen peroxide involves the catalase enzyme, which is relied upon to degrade the toxic levels in microbial cells (Brul and Coote, 1999; Baureder *et al.*, 2012). Damage still occurs, as H<sub>2</sub>O<sub>2</sub> has a high diffusion rate into the cell. However, effectiveness can depend on the size and extent of the microbial population. For example, individual *E. coli* cells are not active enough against H<sub>2</sub>O<sub>2</sub>, as they have weak endogenous catalase. However, in dense populations of *E. coli*, enough catalase is produced to protect most of the population.

For control of pathogens, continuous treatment at a low concentration is usually employed. Information for critical levels required for pathogen control vary between non-peracid hydrogen peroxide based disinfectants and activated peroxygen products, with most information being available for the latter.

Phytotoxicity also needs to be taken into account as due to its oxidising capacity, H<sub>2</sub>O<sub>2</sub> can also damage plant tissue (Ölmez and Kretzschmar, 2009). There also appears to be discontinuity within the wider literature with regards to the efficacy of H<sub>2</sub>O<sub>2</sub> as a disinfectant in varying systems. Much more work is needed, specifically targeting applications of H<sub>2</sub>O<sub>2</sub> within horticultural production systems, especially in the presence of natural biofilms.

#### Health effects of hydrogen peroxide

Exposure to hydrogen peroxide takes place through inhalation of damp air or mist, through food uptake and through skin or eye contact (Lenntech, 2016). Hydrogen peroxide can irritate the eyes, skin and mucous membranes. When humans inhale hydrogen peroxide, it causes lung irritation. Exposure to skin can cause painful blisters, burns and skin whitening. Lungs, intestines, thymus the liver and kidneys are organs that are extra susceptible to hydrogen peroxide exposure. Hydrogen peroxide, as with potassium chlorate, can also be used as a gargle with a 1-3% solution, though it is considered not safe for children and caution must be considered as swallowing H<sub>2</sub>O<sub>2</sub> can result in adverse digestion related effects (<http://www.using-hydrogen-peroxide.com/hydrogen-peroxide-as-mouthwash.html>; <http://www.newhealthadvisor.com/Gargling-with-Peroxide.html>). The effects of chronic exposure on humans are to date unknown. Therefore, always follow manufacturer protocol when handling hydrogen peroxide, or any chemical that is used.

#### *Legislation concerning hydrogen peroxide*

Hydrogen peroxide is not mentioned in the [European Drinking Water Standard 98/83/EC](#). In the USA, hydrogen peroxide was registered as a pesticide by the EPA in 1977.

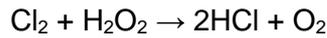
### **9.1. Hydrogen peroxide versus chlorine**

Ferrari *et al.* (2015) carried out a study in a healthcare environment looking at the efficacy of a 5-8% m/m (50,000-80,000 mg/l) hydrogen peroxide (with silver) based solution versus a disinfectant with 5 mg/l active chlorine at killing multidrug resistant bacteria on surfaces. The hydrogen peroxide system proved equally as effective at reducing colony forming units (CFU) immediately after disinfection. The intricacies of the study were not given so no further comment can be made.

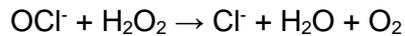
Bacterial 'inactivation' by water treatment utilising H<sub>2</sub>O<sub>2</sub> (in combination with silver) was shown in general to be slow compared to inactivation by activated chlorine. The same H<sub>2</sub>O<sub>2</sub> formulation was also shown to be considerably less effective at preventing biofilm formation than 1 mg/l chlorine. In addition, it was observed that in response to continuous treatment with a combined disinfectant of 30 mg/l H<sub>2</sub>O<sub>2</sub> and 30 µg/litre silver, bacterial cells had increased catalase activity (an enzyme that very rapidly breaks down H<sub>2</sub>O<sub>2</sub>). That being said, when used in combination with a halogen based disinfectant, treatment with H<sub>2</sub>O<sub>2</sub> lead to a reduction in unwanted by-products, including halate ion formation (XO<sub>3</sub><sup>-</sup>, where X represents a halogen). A study carried out on a municipal treatment plant highlighted the potential for H<sub>2</sub>O<sub>2</sub> use to kill 99% of pathogens (total coliform, faecal coliform, and *E. coli*) at 336mg/L (Rizvi *et al.*, 2013). Peracetic acid (1 mg/l solution prepared from a 15% m/m solution) has been shown to achieve a 99.9% reduction in microorganisms (Wagner *et al.*, 2002; Rizvi *et al.*, 2013).

Reports from some growers in the UK state that they have tried hydrogen peroxide to reduce the microbial load in their water but it was not as effective as the chlorine disinfectant they used, but details such as doses for comparison are not available. However, there are now hydrogen peroxide products in industry that are reputed to be as or more effective than chlorination. See the list of suppliers in Appendix 2.

It has been noted in correspondence with [EndoSan](#) (manufacturers of a hydrogen peroxide disinfectant) that hydrogen peroxide combines with elemental chlorine to create hydrogen chloride and oxygen:



It also neutralises free chlorine in solution (e.g. hypochlorite ion):

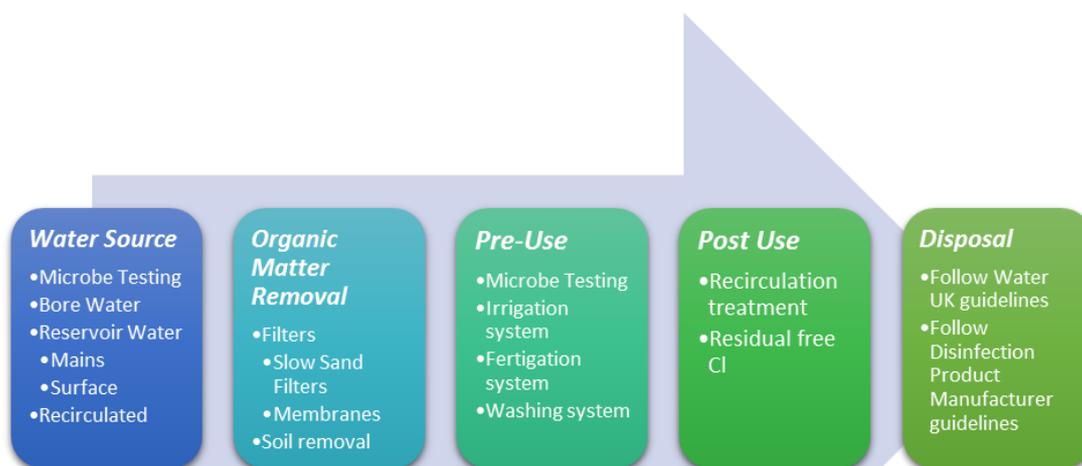


As such, it would be inadvisable to add hydrogen peroxide to an already established chlorine-disinfection system. An area to investigate further is whether one could use hydrogen peroxide to dechlorinate water that is due for disposal. Information on the disposal of chlorinated water is found in Appendix 3.

Communication with H<sub>2</sub>O<sub>2</sub> product and system manufacturers have stated that, for engineering reasons, it should not be overly difficult to convert from a chlorination system to that of H<sub>2</sub>O<sub>2</sub>. Suppliers such as [ProMinent](#) advise that anyone who wishes to convert systems should contact either themselves or another disinfection systems supplier/manufacturer to get a quote. The conversion could be a matter of changes to probes and other parts, but as each sector has a differing disinfection system, this should be discussed with relevant manufacturers and suppliers, the details of which are found in Appendix 2.

## 10. Control points for mitigating chlorate residues

As a preliminary suggestion to mitigate chlorate and/or perchlorate residues in fresh produce, based on the available literature and information gathered, a control points system could be implemented (Figure 9). Based on the HACCP principle, this can help growers identify key points in a water-use pathway where microbial load may be high, and subsequent chlorination may also be high. As an example, if a microbial test at



**Figure 9.** A Control Point System, based on HACCP principles, provide a guide to identify the key points for microbial load and free chlorine testing within a water use pathway. This is a generalised diagram and not representative of a specific growing system.

the water source and after filtration is found to be high, this can affect the required amount of chlorination (or other disinfectant product/system) due to the high chemical oxygen demand (COD). The same can be said if there is a high quantity of soil particles such as silt in the water source. Removal of soil and some organic matter and microorganisms, which contribute to chlorate and perchlorate formation, can be done by implementing a slow sand filter. A system devised by Francis Richardson called [‘The Manchester System’](#) utilises the principle of filtering water through sand and encouraging beneficial organisms to assist with the filtering process. This has been found to speed up the throughput of water through the sand and minimise the number of water borne pathogens and soil in the irrigation water. The extent of microbial loading in a water source can depend on the time of year, so regular testing is recommended.

This model can also be used for recirculated water systems, as the water can pick up organic matter such as exudates from roots and cut areas from harvested produce (e.g. lettuce butts, petioles). With the above in mind, it is important that, given the possibility of MRLs being set to the proposed MRLs for chlorate, experiments on the extent of how chlorination can be optimised to achieve these levels must take place. This should be in conjunction with alternative disinfection products that are available in the industry, such as hydrogen peroxide and other novel products. Physical treatment to remove chlorite ions that are present in treated water, as a result of the breakdown of active chlorine, can be removed using granulated activated carbon filters or iron and sulphur reducing agents (HealthCanada, 2008).

To provide an idea of costings involved in chlorine dioxide and sodium hypochlorite water disinfection systems, a table adapted from the Soft Fruit Grower Guide on Water Recirculation (Atwood, 2014), can be found in Appendix 5.

## **11. Conclusions and proposals for future research targets**

This review has made it evident that more work into various areas of chlorate and perchlorate uptake and analysis is required, particularly if the proposed MRL levels for chlorate in fresh produce and potatoes are set. Discussion with some growers in the horticulture industry has identified the concerns they have regarding the possibility and cost implications of changing from a very effective disinfectant (chlorination) to an alternative that has not been broadly advertised or proven in the wider horticulture industry.

However it has not been proven that alternative disinfectant methods and systems are not as good as or better than using chlorine based disinfectants. Experimentation of methods to manage these residues, comparing chlorine based disinfectants (such as sodium or calcium hypochlorite, chlorine dioxide or chlorine gas) in conjunction with the use of alternative disinfection methods (e.g. UV, pasteurisation, hydrogen peroxide, ozone, etc.) that are currently available or in the industry research and development pipeline is thus required.

Another area of research that can be pursued is the implementation of an auditing benchmarking initiative across the UK to assess where in a grower's water use (e.g. irrigation, post-harvest washing) the likely areas of contamination from microorganisms and organic particles are likely to occur, as this will be contributing to the chlorine (or other disinfectant) dosing requirement. This initiative would be voluntary and anonymised to protect grower integrity if data were to be circulated, but where issues do arise in a water use system, that individual grower would be notified and advised. Additionally, it is unclear what effect Brexit will have on the industry where chlorate residues are concerned. There has been no information to date relating to its impact on MRLs and trade. The key objective areas this report has met and critically evaluated according to the tender can be summarised as follows:

- An overview was provided of chlorine chemistry relevant to its use as a disinfectant in horticultural and potato systems, including factors that influence the production of un-wanted by-products, chlorate and perchlorate.
- The source and mechanism of chlorate/perchlorate uptake by horticultural plants was evaluated.
- The fate, bioaccumulation and assimilation of chlorate/perchlorate in different horticultural plants was touched upon, but due to limited data and information in literature and grey literature, it was advised that further work was to be carried out.
- The amount of chlorate/perchlorate assimilation by fresh produce and potatoes through contaminated process and wash water was evaluated. Most sources state the fact that chlorate and perchlorate was indeed assimilated, but the amount (percentage) assimilated is unclear relative to the amount of free chlorine/chlorate/perchlorate present in the wash water.
- Opportunities for levy payers were identified to manipulate existing chlorination systems to reduce chlorate/perchlorate residues whilst maintaining product quality and consumer safety. This was in the form of a HACCP-like programme

(Cleaning-In-Place) implementation ensuring that the factors that influence the formation of chlorate and perchlorate in the wash/irrigation water are managed, rather than reducing the amount of chlorine disinfectant in the system and risking microbial contamination in the water and produce. Other disinfection systems that can be evaluated by growers can be found in Appendix 2.

- The advantages and disadvantages of using hydrogen peroxide as an alternative disinfection method were evaluated, including the comparison with chlorination and the conversion from chlorination to a hydrogen peroxide system.

A summary of action points to pursue for further work in research and development are as follows:

- To understand better how residues of chlorate and perchlorate may be occurring in produce by setting up monitoring experiments across a range of commercial crop production and food processing systems. Case studies were not able to be undertaken within the remit of the current review.
- Scientific investigation into the mechanism of chlorate and perchlorate uptake in plant tissue, as well as the extent of contamination transfer from surfaces disinfected with chlorine.
- Whether contamination is on the surface and/or inside different produce, and if only the former, whether it can be removed.
- Whether there is any decrease in residues on surfaces with time, in particular between irrigation over produce before harvest (if not subsequently washed before sale) and between produce washing during processing and its sale and consumption.
- Perform a survey of laboratories in the UK in relation to the accuracy of chlorate and perchlorate analysis in plant tissue, as per the considerations raised in Appendix 4.
- Explore alternative disinfection methods to chlorination (e.g. hydrogen peroxide, UV, pasteurisation, organic acids, etc.) through experimentation in laboratory and field conditions where sufficiently detailed information cannot be obtained from on-site studies on existing alternative systems already in use by growers and packers.
- Identify treatments to reduce perchlorate and chlorate in mains water.
- Implement a HACCP based system to help identify key control points along the water use pathway from source (i.e. reservoir, borehole, etc.) to the point of

use where disinfection would occur. This would include filters and pumps. See Section 10 for further details.

- Explore agronomic factors by which chlorate and perchlorate may occur. For example, the use of salt to improve asparagus crops that have been damaged by fusarium; Use of nitrate fertilisers in hydroponic production and fertigation to observe how it affects chlorate and perchlorate residues in plants.

Further considerations for work in this area related to the chemistry as raised by Professor K. Clive Thompson, Chief Scientist at [ALcontrol Laboratories](#) are given in Appendix 6.

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## Appendix 1. Proposed MRLs as Advised by the EC for Fresh Produce and Derivatives

<p><b>WORKING DOCUMENT</b></p> <p>SANTE 10684/2015 Rev0</p> <p><b>[Annex IIIA]</b></p> <p>Pesticide residues and maximum residue levels (mg/kg)</p>		
<b>Code number</b>	<b>Groups and examples of individual products to which the MRLs apply (a)</b>	Chlorate (chlorates (including Mg, Na and K chlorates), expressed as chlorate)
0100000	<b>FRUITS, FRESH or FROZEN; TREE NUTS</b>	
0110000	<b>Citrus fruits</b>	<b>0.015</b>
0110010	Grapefruits	
0110020	Oranges	
0110030	Lemons	
0110040	Limes	
0110050	Mandarins	
0110990	Others	
0120000	<b>Tree nuts</b>	<b>0.01*</b>
0120010	Almonds	
0120020	Brazil nuts	
0120030	Cashew nuts	
0120040	Chestnuts	
0120050	Coconuts	
0120060	Hazelnuts/cobnuts	
0120070	Macadamias	
0120080	Pecans	

0120090	Pine nut kernels	
0120100	Pistachios	
0120110	Walnuts	
0120990	Others	
0130000	<b>Pome fruits</b>	<b>0.02</b>
0130010	Apples	
0130020	Pears	
0130030	Quinces	
0130040	Medlars	
0130050	Loquats/Japanese medlars	
0130990	Others	
0140000	<b>Stone fruits</b>	<b>0.015</b>
0140010	Apricots	
0140020	Cherries (sweet)	
0140030	Peaches	
0140040	Plums	
0140990	Others	
0150000	<b>Berries and small fruits</b>	<b>0.015</b>
0151000	<b>(a) grapes</b>	
0151010	Table grapes	
0151020	Wine grapes	
0152000	<b>(b) strawberries</b>	
0153000	<b>(c) cane fruits</b>	
0153010	Blackberries	
0153020	Dewberries	
0153030	Raspberries (red and yellow)	
0153990	Others	
0154000	<b>(d) other small fruits and berries</b>	

0154010	Blueberries	
0154020	Cranberries	
0154030	Currants (black, red and white)	
0154040	Gooseberries (green, red and yellow)	
0154050	Rose hips	
0154060	Mulberries (black and white)	
0154070	Azaroles/Mediterranean medlars	
0154080	Elderberries	
0154990	Others	
0160000	<b>Miscellaneous fruits with</b>	<b>0.03</b>
0161000	<b>(a) edible peel</b>	
0161010	Dates	
0161020	Figs	
0161030	Table olives	
0161040	Kumquats	
0161050	Carambolas	
0161060	Kaki/Japanese persimmons	
0161070	Jambuls/jambolans	
0161990	Others	
0162000	<b>(b) inedible peel, small</b>	
0162010	Kiwi fruits (green, red, yellow)	
0162020	Litchis/lychees	
0162030	Passionfruits/maracujas	
0162040	Prickly pears/cactus fruits	
0162050	Star apples/cainitos	
0162060	American persimmons/Virginia kaki	
0162990	Others	
0163000	<b>(c) inedible peel, large</b>	

0163010	Avocados	
0163020	Bananas	
0163030	Mangoes	
0163040	Papayas	
0163050	Granate apples/pomegranates	
0163060	Cherimoyas	
0163070	Guavas	
0163080	Pineapples	
0163090	Breadfruits	
0163100	Durians	
0163110	Soursops/guanabanas	
0163990	Others	
<b>0200000</b>	<b>VEGETABLES, FRESH or FROZEN</b>	
0210000	<b>Root and tuber vegetables</b>	
0211000	<b>(a) potatoes</b>	<b>0.01*</b>
0212000	<b>(b) tropical root and tuber vegetables</b>	<b>0.03</b>
0212010	Cassava roots/manioc	
0212020	Sweet potatoes	
0212030	Yams	
0212040	Arrowroots	
0212990	Others	
0213000	<b>(c) other root and tuber vegetables except sugar beets</b>	
0213010	Beetroots	<b>0.01*</b>
0213020	Carrots	<b>0.1</b>
0213030	Celeriacs/turnip rooted celeries	<b>0.01*</b>
0213040	Horseradishes	<b>0.01*</b>
0213050	Jerusalem artichokes	<b>0.01*</b>
0213060	Parsnips	<b>0.01*</b>

0213070	Parsley roots/Hamburg roots parsley	<b>0.01*</b>
0213080	Radishes	<b>0.01*</b>
0213090	Salsifis	<b>0.01*</b>
0213100	Swedes/rutabagas	<b>0.01*</b>
0213110	Turnips	<b>0.01*</b>
0213990	Others	<b>0.01*</b>
0220000	<b>Bulb vegetables</b>	<b>0.015</b>
0220010	Garlic	
0220020	Onions	
0220030	Shallots	
0220040	Spring onions/green onions and Welsh onions	
0220990	Others	
0230000	<b>Fruiting vegetables</b>	
0231000	<b>(a) solanacea</b>	
0231010	Tomatoes	<b>0.07</b>
0231020	Sweet peppers/bell peppers	<b>0.15</b>
0231030	Aubergines/eggplants	<b>0.4</b>
0231040	Okra/lady's fingers	<b>0.07</b>
0231990	Others	<b>0.07</b>
0232000	<b>(b) cucurbits with edible peel</b>	<b>0.07</b>
0232010	Cucumbers	
0232020	Gherkins	
0232030	Courgettes	
0232990	Others	
0233000	<b>(c) cucurbits with inedible peel</b>	<b>0.04</b>
0233010	Melons	
0233020	Pumpkins	
0233030	Watermelons	

0233990	Others	
0234000	<b>(d) sweet corn</b>	<b>0.07</b>
0239000	<b>(e) other fruiting vegetables</b>	<b>0.07</b>
0240000	<b>Brassica vegetables (excluding brassica roots and brassica baby leaf crops)</b>	
0241000	<b>(a) flowering brassica</b>	
0241010	Broccoli	<b>0.7</b>
0241020	Cauliflowers	<b>0.03</b>
0241990	Others	<b>0.03</b>
0242000	<b>(b) head brassica</b>	<b>0.03</b>
0242010	Brussels sprouts	
0242020	Head cabbages	
0242990	Others	
0243000	<b>(c) leafy brassica</b>	<b>0.03</b>
0243010	Chinese cabbages/pe-tsai	
0243020	Kales	
0243990	Others	
0244000	<b>(d) kohlrabies</b>	<b>0.03</b>
0250000	<b>Leaf vegetables, herbs and edible flowers</b>	
0251000	<b>(a) lettuces and salad plants</b>	
0251010	Lamb's lettuces/corn salads	<b>0.06</b>
0251020	Lettuces	<b>0.3</b>
0251030	Escaroles/broad-leaved endives	<b>0.06</b>
0251040	Cresses and other sprouts and shoots	<b>0.06</b>
0251050	Land cresses	<b>0.06</b>
0251060	Roman rocket/rucola	<b>0.06</b>
0251070	Red mustards	<b>0.06</b>

0251080	Baby leaf crops (including brassica species)	<b>0.06</b>
0251990	Others	<b>0.06</b>
0252000	<b>(b) spinaches and similar leaves</b>	
0252010	Spinaches	<b>0.2</b>
0252020	Purslanes	<b>0.06</b>
0252030	Chards/beet leaves	<b>0.06</b>
0252990	Others	<b>0.06</b>
0253000	<b>(c) grape leaves and similar species</b>	<b>0.06</b>
0254000	<b>(d) watercresses</b>	<b>0.06</b>
0255000	<b>(e) witloofs/Belgian endives</b>	<b>0.06</b>
0256000	<b>(f) herbs and edible flowers</b>	<b>0.6</b>
0256010	Chervil	
0256020	Chives	
0256030	Celery leaves	
0256040	Parsley	
0256050	Sage	
0256060	Rosemary	
0256070	Thyme	
0256080	Basil and edible flowers	
0256090	Laurel/bay leave	
0256100	Tarragon	
0256990	Others	
0260000	<b>Legume vegetables</b>	
0260010	Beans (with pods)	<b>0.15</b>
0260020	Beans (without pods)	<b>0.7</b>
0260030	Peas (with pods)	<b>0.15</b>
0260040	Peas (without pods)	<b>0.15</b>
0260050	Lentils	<b>0.15</b>

0260990	Others	<b>0.15</b>
0270000	<b>Stem vegetables</b>	
0270010	Asparagus	<b>0.03</b>
0270020	Cardoons	<b>0.03</b>
0270030	Celeries	<b>0.1</b>
0270040	Florence fennels	<b>0.03</b>
0270050	Globe artichokes	<b>0.03</b>
0270060	Leeks	<b>0.03</b>
0270070	Rhubarbs	<b>0.03</b>
0270080	Bamboo shoots	<b>0.03</b>
0270090	Palm hearts	<b>0.03</b>
0270990	Others	<b>0.03</b>
0280000	<b>Fungi, mosses and lichens</b>	<b>0.1</b>
0280010	Cultivated fungi	
0280020	Wild fungi	
0280990	Mosses and lichens	
0290000	<b>Algae and prokaryotes organisms</b>	<b>0.01*</b>
<b>0300000</b>	<b>PULSES</b>	<b>0.07</b>
0300010	Beans	
0300020	Lentils	
0300030	Peas	
0300040	Lupins/lupini beans	
0300990	Others	
<b>0400000</b>	<b>OILSEEDS AND OIL FRUITS</b>	<b>0.07</b>
0401000	<b>Oilseeds</b>	
0401010	Linseeds	
0401020	Peanuts/groundnuts	
0401030	Poppy seeds	

0401040	Sesame seeds	
0401050	Sunflower seeds	
0401060	Rapeseeds/canola seeds	
0401070	Soyabeans	
0401080	Mustard seeds	
0401090	Cotton seeds	
0401100	Pumpkin seeds	
0401110	Safflower seeds	
0401120	Borage seeds	
0401130	Gold of pleasure seeds	
0401140	Hemp seeds	
0401150	Castor beans	
0401990	Others	
0402000	<b>Oil fruits</b>	
0402010	Olives for oil production	
0402020	Oil palms kernels	
0402030	Oil palms fruits	
0402040	Kapok	
0402990	Others	
<b>0500000</b>	<b>CEREALS</b>	<b>0.04</b>
0500010	Barley	
0500020	Buckwheat and other pseudo-cereals	
0500030	Maize/corn	
0500040	Common millet/proso millet	
0500050	Oat	
0500060	Rice	
0500070	Rye	
0500080	Sorghum	

0500090	Wheat	
0500990	Others	
<b>0600000</b>	<b>TEAS, COFFEE, HERBAL INFUSIONS, COCOA AND CAROBS</b>	<b>0.15</b>
0610000	<b>Teas</b>	
0620000	<b>Coffee beans</b>	
0630000	<b>Herbal infusions from</b>	
0631000	<b>(a) flowers</b>	
0631010	Chamomile	
0631020	Hibiscus/roselle	
0631030	Rose	
0631040	Jasmine	
0631050	Lime/linden	
0631990	Others	
0632000	<b>(b) leaves and herbs</b>	
0632010	Strawberry	
0632020	Rooibos	
0632030	Mate/maté	
0632990	Others	
0633000	<b>(c) roots</b>	
0633010	Valerian	
0633020	Ginseng	
0633990	Others	
0639000	<b>(d) any other parts of the plant</b>	
0640000	<b>Cocoa beans</b>	
0650000	<b>Carobs/Saint John's breads</b>	
<b>0700000</b>	<b>HOPS</b>	<b>0.05*</b>
<b>0800000</b>	<b>SPICES</b>	
0810000	<b>Seed spices</b>	<b>0.08</b>

0810010	Anise/aniseed	
0810020	Black caraway/black cumin	
0810030	Celery	
0810040	Coriander	
0810050	Cumin	
0810060	Dill	
0810070	Fennel	
0810080	Fenugreek	
0810090	Nutmeg	
0810990	Others	
0820000	<b>Fruit spices</b>	<b>0.08</b>
0820010	Allspice/pimento	
0820020	Sichuan pepper	
0820030	Caraway	
0820040	Cardamom	
0820050	Juniper berry	
0820060	Peppercorn (black, green and white)	
0820070	Vanilla	
0820080	Tamarind	
0820990	Others	
0830000	<b>Bark spices</b>	<b>0.08</b>
0830010	Cinnamon	
0830990	Others	
0840000	<b>Root and rhizome spices</b>	
0840010	Liquorice	<b>0.08</b>
0840020	Ginger	<b>0.08</b>
0840030	Turmeric/curcuma	<b>0.08</b>
0840040	Horseradish	(+)

0840990	Others	<b>0.08</b>
0850000	<b>Bud spices</b>	<b>0.08</b>
0850010	Cloves	
0850020	Capers	
0850990	Others	
0860000	<b>Flower pistil spices</b>	<b>0.08</b>
0860010	Saffron	
0860990	Others	
0870000	<b>Aril spices</b>	<b>0.08</b>
0870010	Mace	
0870990	Others	
<b>0900000</b>	<b>SUGAR PLANTS</b>	<b>0.015</b>
0900010	Sugar beet roots	
0900020	Sugar canes	
0900030	Chicory roots	
0900990	Others	
	(*) Indicates lower limit of analytical determination	
	(a) For the complete list of products of plant and animal origin to which MRLs apply, reference should be made to Annex I.	
<b>Chlorate (chlorates (including Mg, Na and K chlorates), expressed as chlorate)</b>		
(+)	The applicable maximum residue level for horseradish ( <i>Armoracia rusticana</i> ) in the spice group (code 0840040) is the one set for horseradish ( <i>Armoracia rusticana</i> ) in the Vegetables category, root and tuber vegetables group (code 0213040) taking	

	into account changes in the levels by processing (drying) according to Art. 20 (1) of Regulation (EC) No 396/2005.	
	<b>0840040 Horseradish</b>	

## Appendix 2. Suppliers of Disinfection Products and List of Alternative Disinfectant Products

Company Name	Product	Website	Phone	Address
<b>Ximax Environmental Solutions PLC</b>	XzioX (Chlorine Dioxide)	<a href="http://ximaxes.com/">http://ximaxes.com/</a>	+44 (0) 1277 849 988	1A Bates Industrial Estate, Church Road, Romford, Essex RM3 0HU
<b>Scotmas Group</b>	chlorine dioxide dosing system	<a href="http://www.scotmas.com/industries/agriculture/horticulture.aspx">http://www.scotmas.com/industries/agriculture/horticulture.aspx</a>	+44 (0) 1573 226 901	Spylaw Road, Kelso, Borders, Scotland TD5 8DL
<b>Klenzan Ltd</b>	Sodium hypochlorite	<a href="http://www.klenzan.co.uk/">http://www.klenzan.co.uk/</a>	01925 234 696	Klenzan Ltd., 2 Cameron Court, Winwick Quay, Warrington, Cheshire WA2 8RE
<b>Endo Enterprises</b>	EndoSan	<a href="http://endoenterprises.com/">http://endoenterprises.com/</a>	+44(0)19 45747101	Unit 231, Europa Boulevard, Gemini Business Park, Warrington, Cheshire, WA5 7TN United Kingdom
<b>Priva UK</b>	UV Water Disinfection	<a href="http://www.priva.co.uk/solutions-products/horticulture/water-management/">http://www.priva.co.uk/solutions-products/horticulture/water-management/</a>	+44 (0)1923 813 480	34 Clarendon Road WD17 1JJ Watford United Kingdom
<b>PeroxyChem</b>	Hydrogen Peroxide Peracetic Acid Persulphates	<a href="http://www.peroxychem.com/markets/food-beverage/fruit-and-vegetable-processing">http://www.peroxychem.com/markets/food-beverage/fruit-and-vegetable-processing</a>	+1 609 870 6016 +49 40 3250 95-0	Rhein Per Chemie GmbH Kattrepel 2 20095 Hamburg
<b>Drywite</b>	Organic Acids	<a href="http://www.drywite.co.uk/">http://www.drywite.co.uk/</a>	+44(0) 1384 569556	The House of Lee, Park Lane, Halesowen, West Midlands, B63 2RA
<b>Aqualution Systems Ltd</b>	Solosan (electronically activated water)	<a href="http://www.aqualution.co.uk/products/solosan/">http://www.aqualution.co.uk/products/solosan/</a>	+44 (0)1223 236088	Aqualution Systems Ltd (England) Finance, Sales & Marketing – Europe Cambridge United Kingdom
<b>OZO Innovations</b>	Ozone (gaseous) Electrolysed water	<a href="https://ozoinnovations.com/">https://ozoinnovations.com/</a>	+44 (0) 18658 91012	1 Drayton House Court, Drayton St Leonard, Wallingford, OX10 7BG
<b>Airedale Chemical</b>	Peracetic acid (PAA)	<a href="https://www.airedalechemical.com/product/peracetic-acid/">https://www.airedalechemical.com/product/peracetic-acid/</a>	+44 (0) 15356 37876	Airedale Chemical Company Ltd, Airedale Mills, Skipton Road, Cross Hills, Keighly, West Yorkshire BD20 7BX

**Alternative disinfection products in laboratory conditions or not yet available to commercial use:**

Cold Plasma (Dublin Institute of Technology);

Grape Seed Extract

Citric acid

Carvacrol (oregano oil)

Heat treatment (foam, steam)

Electrolysis and ionisation (copper, silver)

Ecological Water Treatment Methods

Constructed wetlands and bio-beds using crops with phytoremediation qualities (to be investigated)

(Raudales *et al.*, 2014)

***'AHDB are a public body, providing evidence to levy payers on a range of technical issues. Reference to specific novel technologies in this report relates to interest from our members. These technologies have not been independently assessed in AHDB funded work and inclusion does not imply AHDB endorsement. Readers are reminded to investigate the full range of technologies available on the market and the suitability of these to their own production systems'***

## AQUALUTIONS

AHDB Horticulture are aware that some of our members have adapted the Aqualutions technology to treat water. Nick Meakins (Aqualutions) provided the following:

### A brief description of the product and how it works

The system is based on electrolysed water (active chlorine as hypochlorous acid) and uses salt (sodium chloride) to generate the hypochlorous acid as the decontamination agent instead of the conventional sodium hypochlorite acidified with citric acid. At pH 7 which is typically where most companies run their flumes, this converts approximately 50% of the sodium hypochlorite into hypochlorous acid.

This has a number of benefits, but the most significant is that in producing pure hypochlorous acid through the electro-dialysis process you can immediately reduce the chemical required to decontaminate by 50% as the technology only produces the chlor-oxy species required to provide disinfection.

In addition the biocide supports the recycling of the produce wash water which also further enhances the physical cleaning of the produce permitting even further reductions in the concentration required to deliver the necessary log reductions. Typically our integrated decontamination and water recycling technology runs at 20ppm compared to a hypochlorite system at 100ppm. Water and energy consumption reductions are in the region of 80 to 90% compared to a conventional flume system.

On the chlorate issue, the system produces very low levels of chlorate impurities, typically around 0.5 - 4 ppm in the concentrate which at the point of dilution and application in the flume gives a level of 0.05 to 0.4ppm in the wash water. Depending on the age of the sodium hypochlorite in use in conventional washing (it is not very stable and one of the first degradation products is Sodium Chlorate) the level of chlorate is likely to be between 10 to 100 times greater than this, and with the lower dilution rate possible to deliver the same level of hypochlorous acid in the flume, the level of chlorates in the flume water will be between 20 to 200 times greater.

Our analysis on product is ongoing but to date with UK standard potable water to produce the hypochlorous acid, even on diced beans which are notoriously chlorine hungry we get none detected results when samples are presented for analysis.

### The evidence that it works

The system is an approved technology listed in the new M&S code of practice, the efficacy of the biocide has been validated at Campden BRI and the €3m EU funded SusClean project (the UK feedback to which was presented at Campden BRI in December 2015) validated the technology at commercial scale and it was the only commercially viable system of all the technologies that they investigated as part of the study to find ways to reduce chemical and water consumption in produce washing.

### Is the product registered?

The product is registered as a biocide, Aqualution Systems Ltd are listed on article 95 as review programme participants as we are the owners of the regulatory dossier under EU 528/2012 (biocidal products regulations). We are currently listed under product types 1, 2, 3, 4 and 5 and are in the process of extending the scope to PT 11 and 12 and are listed on the compliant notifications document in this regard as well.

Contact details Nick Meakins at [nick.meakin@aqualution.com](mailto:nick.meakin@aqualution.com) or on 07725 860507 or Dr Michelle Lewis (technical director) on 07768 507919 or [michelle.lewis@aqualution.co.uk](mailto:michelle.lewis@aqualution.co.uk).



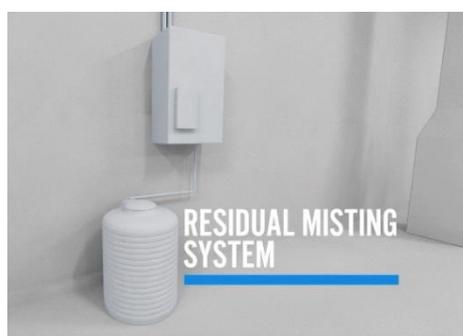
## RBT247

AHDB are also aware that some members are interested in RBT247 technology as an option for disinfecting surfaces. Tony Shawcross provided the following information:

### The misting system

The RBT residual whole room misting system is a unique and patented system designed to cover large areas with the ProtectUs Viridis disinfectant mist. Its patented nozzle design creates a dry mist with droplet sizes between 4-20 µm which reaches all surfaces including vertical panels, ceilings, hard abrasion surfaces, equipment and air conditioning units with coverage of 1,500sqm in 15 minutes. The mist is immediately effective against pathogens such as Listeria, Swine Flu H1N1 and E.Coli and leaves behind no toxic chemicals.

Each installation is tailored to suit site requirements and is operated by a single button operation at the end of a shift. In comparison to traditional disinfection protocols, the RBT misting system can reduce water usage by up to 80% and be up to 90% faster than manual labour.



### The disinfectant

ProtectUs Viridis is the world's first disinfectant that is 100% green, 99.9999% effective and leaves 24hr residual barrier protection when dry. Viridis is free of harmful residues such as Quats, chlorites and chlorate and is safe for use in food and food processing environments. Used at 0.25-1% dilution, Viridis gives a kill of log 5 even when tested at 10°C and is currently going through Biocide registration.

Viridis has been tested at the following accredited independent laboratories: Campden BRI; Blutest Laboratories Ltd and Dr Brill and Dr Steinmann laboratory (Germany) for EN1276, EN13697, EN1650, residual efficacy, residue testing, taint testing, EN14476 viruses, biofilm removal (in process) and Halal approval. It is effective against a range of microorganisms including *Staphylococcus aureus*, *Salmonella typhimurium*, *Listeria monocytogenes* and *Escherichia coli* 0157:H7.

For more information, please contact [tony.shawcross@rbt247.com](mailto:tony.shawcross@rbt247.com) or call 07792 020973

## **Appendix 3. Disposal of Chlorine Solutions and Chlorinated Water – WATER UK Guidelines**

### **Introduction**

Chlorine is toxic to aquatic flora and fauna. Care should be taken when disposing of water containing chlorine, particularly strong solutions used for the disinfection of water mains and fittings and, in this case, horticultural practices. Chlorine may also inactivate the biological process necessary for effective sewage treatment.

### **Good Practice**

1. Chlorine solutions and chlorinated water should not be discharged to water courses, without prior consultation and consent from the [Environment Agency](#). Care should also be taken to ensure that surface and land drains do not discharge to water courses.
2. A risk assessment should be carried out prior to discharging chlorine solutions to foul drainage systems and the results to be notified to the sewage treatment works. This is to confirm that the receiving sewage treatment works will not be adversely affected.
3. It may be necessary to dechlorinate water prior to disposal. Dechlorination can be achieved using a number of different chemical compounds, the most commonly used of which are sodium thiosulphate and sodium bisulphite.
4. Only materials which are approved under Regulation 31 of the Water Supply (Water Quality) Regulations 2000 England (as amended) and their equivalents in Scotland and Wales should be used for the dechlorination of water that will be subsequently used for supply.
5. Dechlorination solutions, powders and tablets should not be used after the stated “expiry date”.
6. Chlorine-based solutions must only be stored in dedicated and clearly marked containers. Containers previously used for the storage of petroleum products must not be used (see TGN13)
7. The following information is provided as a guide to the relative concentration of sodium thiosulphate and sodium bisulphite solutions required to neutralise a specific chlorine

solution. Advice from technical and scientific staff should be sought in order to calculate the required amount of dechlorination chemical in other circumstances.

- 1ml of 1.8% (w/v) solution of sodium thiosulphate pentahydrate will neutralise 1L of water containing 5mg/L (ppm) of free available chlorine.
- 18g of sodium thiosulphate pentahydrate (w/w) crystals will neutralise 1,000L of water containing 5mg/L (ppm) free available chlorine.
- 15ml of 23% (w/v) sodium bisulphite will neutralise 1000L of water containing 5mg/L of free available chlorine

## Appendix 4. Analysis Considerations of Chlorate and Perchlorate in Food and Water

### Analysis considerations for perchlorate and chlorate

1. It is important to appreciate that there are no robust and fit for purpose on-site testing methods for perchlorate and chlorate in water and foods
2. It is necessary to submit any samples for analysis to suitably qualified laboratories for this type of analysis. The only UK laboratory with ISO 17025 (UKAS) accreditation for chlorate and perchlorate analysis in food or water matrices is SAL Cambridge Ltd., 2 Links Ind Pk/Trafalgar Way, Cambridge CB23 8UD. [www.salltd.co.uk](http://www.salltd.co.uk). However the UKAS single test search is acknowledged by UKAS not to be totally reliable. <http://www.ukas.org/testing/singlesearch.asp>
3. It is essential to take fit for purpose samples in appropriate sample bottles with a suitable preservative (if required) and to ensure that no significant sample deterioration takes place prior to analysis.
4. **Annex A** of this Appendix summarises the current ISO perchlorate and chlorate methods for waters. The chlorate method is a 1997 method and only applicable to “water with low contamination”. The working range is 0.03 to 10 mg/litre chlorate.
5. The ISO 19340 provisional (CD) water analysis method for perchlorate utilises ion chromatography with detection by suppressed electrical conductivity. Methods with or without matrix elimination and with or without pre-concentration are described depending upon the complexity of the relevant water matrix. The scope covers drinking water, mineral water, raw water, surface water, partially treated water or swimming pool water, waste water from drinking/swimming pool water treatment plants. Appropriate pre-treatment of the sample (e.g. matrix elimination) allows a direct determination of perchlorate  $\geq 1 \mu\text{g/l}$ .
6. For more complex (higher conductivity) matrices consideration is being given to including an Informative Annex using two dimensional chromatography to improve specificity and reduce interference from other ions present at much higher concentrations than perchlorate. It is felt unlikely that a process water containing a significant amount of plant organic matter could be reliably analysed for perchlorate

using ion chromatography with detection by suppressed electrical conductivity at the concentration levels required.

7. No ISO perchlorate or chlorate methods for food matrices could be found.
8. **Annex B** (below) is entitled "*Background Information and a harmonised provisional enforcement approach for intra-Union trade*"  
It is taken from - "*Statement as regards the presence of perchlorate in food endorsed by the standing Committee on Plants, Animals, Food and Feed on 10 March 2015, updated on 23 June 2015*". See: -  
[http://ec.europa.eu/food/safety/docs/cs\\_contaminants\\_catalogue\\_perchlorate\\_statement\\_food\\_update\\_en.pdf](http://ec.europa.eu/food/safety/docs/cs_contaminants_catalogue_perchlorate_statement_food_update_en.pdf)
9. **Annex C** (below) is entitled "*Details of an EFSA Identified Method for Analysis of Perchlorate of Food that has been identified to provide reliable results*"  
It is taken from : - "*Statement as regards the presence of perchlorate in food endorsed by the standing Committee on Plants, Animals, Food and Feed on 10 March 2015, updated on 23 June 2015*". See: -  
[http://ec.europa.eu/food/safety/docs/cs\\_contaminants\\_catalogue\\_perchlorate\\_statement\\_food\\_update\\_en.pdf](http://ec.europa.eu/food/safety/docs/cs_contaminants_catalogue_perchlorate_statement_food_update_en.pdf)
10. *Low level perchlorate is a difficult analysis to carry out in most food matrices and also in waters with a high electrical conductivity especially in the presence of organic matter. E.g. (total organic carbon [TOC]). As outlined in **Annex B**, the Limit of Quantification (LOQ) should be targeted not to be higher than 2 µg/kg for the analysis of perchlorate in foods for infants and young children, 10 µg/kg in other foods and 20 µg/kg in dried herbs and spices and dried herbs and tea for infusion. This is a challenging task and it is to be expected that the level of result uncertainty could be high with significant variation in results between different laboratories. Until sufficient third party proficiency scheme data is available, it will be difficult to estimate the typical perchlorate result uncertainty. This problem will also apply to chlorate analysis*
11. EFSA EC (See **Annex C**) has recommended the following method of analysis should be employed to provide reliable results: - "*Quick Method for the Analysis of*

*Residues of numerous Highly Polar Pesticides in Foods of Plant Origin involving Simultaneous Extraction with Methanol and LC-MS/MS.* In addition the article "Analysis of Perchlorate in Food Samples of Plant Origin Applying the Quick Polar Pesticides (QuPPE) Method and LC-MS/MS" has to be consulted in which it is reported how to integrate the environmental contaminant perchlorate into the above mentioned QuPPE multiresidue method. The article can be downloaded from <http://www.analytic-news.com/papers/pdf/cvuase2.pdf> . See also: - <http://guppe.eu/>. This is a very complex method and it would appear that few commercial labs currently offer it.

12. Dionex (part of Thermo Fisher Scientific) has developed an ion chromatographic method perchlorate method with some preliminary data for melon, milk, alfalfa, corn and spinach [http://www.dionex.com/en-us/webdocs/114729-PN70743\\_HPLC13.pdf](http://www.dionex.com/en-us/webdocs/114729-PN70743_HPLC13.pdf)

and a drinking water method based upon U.S. EPA Method 314.1 using ion chromatography : -[https://tools.thermofisher.com/content/sfs/brochures/AN176-IC-Sub-ppb-Perchlorate-Drinking-Water-Matrix-Elimination-AN70398\\_E.pdf](https://tools.thermofisher.com/content/sfs/brochures/AN176-IC-Sub-ppb-Perchlorate-Drinking-Water-Matrix-Elimination-AN70398_E.pdf)

and another with pre-concentration and two-dimensional ion chromatography for more complex water matrices.: -

<https://tools.thermofisher.com/content/sfs/brochures/AN-178-IC-Trace-Perchlorate-Drinking-Water-2D-IC-AN70396-EN.pdf>

However multi-lab validation trials are needed to demonstrate the fitness for purpose of these food and water methods in relation to matrices relevant to this report

13. For a summary of USA methods for food and water (up to 2009) see: - <https://www.atsdr.cdc.gov/ToxProfiles/tp162-c7.pdf> Perchlorate contamination has been much more widespread in the US than in the UK.
14. For the background to the analysis requirements for perchlorate in foods, it is necessary to consult the authoritative EFSA (117 pages) document entitled "*Scientific Opinion on the risks to public health related to the presence of perchlorate in food, in particular fruits and vegetables*" by the EFSA Panel on Contaminants in the Food Chain (Panel, #466), European Food Safety Authority

(EFSA), Parma, Italy, 26 May 2015. See: -

<http://onlinelibrary.wiley.com/doi/10.2903/j.efsa.2014.3869/epdf>

15. For the background to the analysis requirements for chlorate in foods, it is necessary to consult the authoritative EFSA (103 pages) document entitled “Risks for public health related to the presence of chlorate in food”  
<http://onlinelibrary.wiley.com/doi/10.2903/j.efsa.2015.4135/epdf>
16. Chlorate and perchlorate ions can usually be determined together and the many of the problems of analysis outlined for perchlorate are likely to also be relevant for chlorate.
- 17. Risk Considerations**
  - 17.1. The levels of perchlorate as reference for intra-Union trade of Foods varies from: - 0.02 mg/kg for “infants and young children - ready-to-eat products “to 1.0 mg/kg for herbs, lettuce and salad plants, including rucola, grown in glasshouse/under cover.” This represents a safety factor of 50 times lower for the former category.  
(See **Annex B**)
  - 17.2. It is felt unlikely that adult consumers will ever consume more than an average 500 g per day of food products likely to be significantly contaminated with perchlorate
  - 17.3. It is generally accepted that ingested perchlorate is eliminated (unmetabolised) by the kidneys within 3 - 48 hours. (EFSA report cited in Para 14, Para 5.1.3 (page 37) in the web link). Thus, at the highest permitted level of 1 mg/kg, for ingestion of 500 g of perchlorate tainted food would correspond to ingestion of 0.5 mg of perchlorate per day. This is considered to be a worst case situation
  - 17.4. Yet there are reports in the past of people with hyperthyroidism being dosed with up to 2,000 mg of potassium perchlorate (equivalent to 1,436 mg of perchlorate/day) See: - M. E. Morgans and W. R. Trotter, Potassium Perchlorate in Thyrotoxicosis, Br Med J. 1960 Oct 8; 2(5205): 1086–1087. See; -  
<http://www.ncbi.nlm.nih.gov/pmc/articles/PMC2097927/?page=1> It was stated that a reasonable compromise would therefore seem to be to use doses in the region of 800 mg of potassium perchlorate daily. (equivalent to 575 mg of perchlorate/day)

- 17.5. Another, later report cites information on a patient who was initially dosed with 1 g/day of potassium perchlorate by mouth for one month, and maintained thereafter on 200 mg/day (equivalent to 144 mg of perchlorate/day), with good control of symptoms for 22 years without adverse effect.
- J. M. C. Connell, Postgraduate Medical Journal (August 1981) 57, 516-517. See: - <http://www.ncbi.nlm.nih.gov/pmc/articles/PMC2426142/pdf/postmedj00224-0047.pdf> .

This perchlorate level corresponds to 288 times above worst case situation estimated in Para 17.3 above. For young children there is a further factor of 50 (See Para 17.1 above), giving a total factor of 14,400.

- 17.6.** With respect to risk, see the NHS Choices website: - <http://www.nhs.uk/news/2013/07July/Pages/Food-poisoning-warning-over-fruit-and-veg.aspx> cites the following information relating to a decade-long US study of the sources of foodborne illnesses in the US: -

17.6.1. ***Causes of foodborne illness***

- plant commodities – fruits, nuts and vegetables – accounted for 46% of foodborne illnesses
- meat and poultry accounted for 22% of illnesses
- among all 17 commodities, more illnesses were attributable to leafy vegetables (2.2 million or 22%) than any other commodity
- After leafy vegetables, commodities linked to the most illnesses were dairy (1.3 million 14%), fruits and nuts (1.1 million, 12%), and poultry (900,000, 10%)

***Hospitalisations for food poisoning***

- 46% (26,000) of annual hospitalisations were attributed to meat and dairy (land animals)
- 41% (24,000) were attributed to plant foods
- 6% (3,000) were attributed to fish and other seafood (aquatic animals)
- dairy foods accounted for the most hospitalisations, followed by leafy vegetables, poultry and vine stalk vegetables

### ***Deaths from food poisoning***

- an estimated 43% (629) deaths each year were attributed to meat (land animals), 363 (25%) to plant foods and 94 (6%) to fish and other seafood (aquatic animals)
- Poultry accounted for the most deaths (19%) followed by dairy (10%), vine stalk vegetables (7%), fruit-nuts (6%) and leafy vegetables (6%)
- They also say that plant foods accounted for 66% of viral illness, 32% of bacterial, 25% of chemical and 30% of parasitic illness.

### **How did the researchers interpret the results?**

The researchers point out that more illnesses were attributed to leafy vegetables (22%) than to any other commodity. In addition, illnesses associated with leafy vegetables were the second most frequent cause of hospitalisations (14%) and the fifth most frequent cause of death (6%). Efforts are particularly needed to prevent contamination of plant foods and poultry, they argue.

- ***Potential sequel from food poisoning***

The risk from removing existing proven chlorine disinfection practices by unproven non-chlorine disinfection practices, especially for biofilms on salad leaves could result in a significant increase in pathogenic bacterial infections (e.g. *Listeria*, *Salmonella* and Shiga toxin-producing *E. coli* (STEC)). Many such infections can lead to long-term adverse health sequelae with a significant reduction of “Quality Life Years”

- See: - <http://www.scientificamerican.com/article/food-poisonings-hidden-legacy/> and <http://www.howlongdoesfoodpoisoninglast.net/>

### 17.7. ***Final comment***

Chlorine disinfection has been shown to be a simple, safe, robust and well understood disinfection technique and has been in use for over 100 years, and it is felt that the relative microbiological risks from non-chlorinated poorly disinfected horticultural produce and potatoes needs to be balanced against those of the toxic effects arising from perchlorate and chlorate contamination resulting from chlorine use for disinfection purposes

**Prof. K. Clive Thompson, ALcontrol Laboratories**

**8<sup>th</sup> Aug 2016**

**Note:** - All web links in this Annex were accessed on 8<sup>th</sup> Aug 2016

## **Annex A**

### **ISO Standard Methods for Chlorate and Perchlorate determination in water**

<b>Standard / Project</b>	<b>Scope</b>
ISO 10304-4:1997	Determination of dissolved anions by liquid chromatography of ions - Part 4: Determination of chlorate, chloride and chlorite in water with low contamination  <a href="https://www.iso.org/obp/ui/#iso:std:iso:10304:-4:ed-1:v1:en">https://www.iso.org/obp/ui/#iso:std:iso:10304:-4:ed-1:v1:en</a> and  <a href="http://www.iso.org/iso/catalogue_detail.htm?csnumber=22573">http://www.iso.org/iso/catalogue_detail.htm?csnumber=22573</a>
ISO/CD 19340:2016	Determination of dissolved perchlorate - Method using ion chromatography (IC)  This document should be published in late 2016 after the validation trial study has been finalised  <a href="http://www.iso.org/iso/catalogue_detail.htm?csnumber=64654">http://www.iso.org/iso/catalogue_detail.htm?csnumber=64654</a>

## **Annex B**

### **Background information and a harmonised provisional enforcement approach for intra-Union trade**

Taken from “Statement as regards the presence of perchlorate in food endorsed by the standing Committee on Plants, Animals, Food and Feed on 10 March 2015, updated on 23 June 2015”.

See:

[http://ec.europa.eu/food/safety/docs/cs\\_contaminants\\_catalogue\\_perchlorate\\_statement\\_food\\_update\\_en.pdf](http://ec.europa.eu/food/safety/docs/cs_contaminants_catalogue_perchlorate_statement_food_update_en.pdf)

#### *Background information*

The perchlorate ion ( $\text{ClO}_4^-$ ) is very stable in water, and its salts are highly soluble in water. Perchlorate occurs naturally in the environment, in deposits of nitrate and potash, and can be formed in the atmosphere and precipitate into soil and groundwater. It also occurs as an environmental contaminant arising from the use of nitrate fertilizers and from the manufacture, use and disposal of ammonium perchlorate used in rocket propellants, explosives, fireworks, flares and air-bag inflators and in other industrial processes. Perchlorate can also be formed during the degradation of sodium hypochlorite used to disinfect water and can contaminate the water supply. Water, soil and fertilizers are considered to be potential sources of perchlorate contamination in food.

#### *Need for more monitoring data*

There is a need for having more data on the presence of perchlorate in food. In particular, there are not sufficient occurrence data on the presence of perchlorate in food sampled after 1<sup>st</sup> September 2013 as it is considered that then mitigation measures were from then onwards put in place and these data might reflect the principle “as low as reasonable achievable” following good practices. More occurrence data on the presence of perchlorate are also needed to enable a more accurate exposure assessment.

So therefore Member States, with the active involvement of food business operators, are requested to monitor the presence of perchlorate in food and this in accordance with Commission Recommendation (EU) 2015/682 of 29 April 2015 on the monitoring of the presence of perchlorate in food (<http://eur-lex.europa.eu/legal-content/EN/TXT/?qid=1434527808532&uri=CELEX:32015H0682>)

The following method of analysis has been identified to provide reliable results:

"Quick Method for the Analysis of Residues of numerous Highly Polar Pesticides in Foods of Plant Origin involving Simultaneous Extraction with Methanol and LC-MS/MS Determination (QuPPE-Method) - Version 7.1" The method can be downloaded from: [http://www.crl-pesticides.eu/library/docs/srm/meth\\_QuPPE.pdf](http://www.crl-pesticides.eu/library/docs/srm/meth_QuPPE.pdf)

In addition the article "Analysis of Perchlorate in Food Samples of Plant Origin Applying the QuPPE-Method and LC-MS/MS" has to be consulted in which it is reported how to integrate the environmental contaminant perchlorate into the abovementioned QuPPE multiresidue method. The article can be downloaded from <http://www.analytic-news.com/papers/pdf/cvuase2.pdf>

The Limit of Quantification (LOQ) should be targeted not to be higher than 2 µg/kg for the analysis of perchlorate in foods for infants and young children, 10 µg/kg in other foods and 20 µg/kg in dried herbs and spices and dried herbs and tea for infusion.

Sampling is to be performed in accordance with current sampling procedures in place to control the level of nitrates in leafy vegetables and pesticide residues in food.

#### *Investigations on the sources of contamination and related mitigation measures*

Member States, with the active involvement of the food business operators, should perform investigations to identify the factors resulting in the presence of perchlorate in food. In particular, the analysis of the presence of perchlorate in fertilizer, soil, irrigation and processing water is appropriate in situations where these factors are relevant.

#### *A harmonised provisional enforcement approach for intra-Union trade*

Divergent approaches as regards the issue of perchlorate in fruits and vegetables have resulted in problems/tensions in intra-Union trade and therefore a harmonised enforcement approach was appropriate. This harmonised enforcement approach should take into account the consumer health protection and what is feasible and achievable taking also into account good practices and regional differences.

The provisional enforcement approach is to address problems and possible tensions in intra-Union trade. Competent authorities of Member States can determine to which extent they enforce the levels of perchlorate as reference for intra-Union trade for their domestic production / products placed on their domestic market. The competent authorities of the

Member States agreed not to take action below these levels. For taking action, measurement uncertainty has to be taken into account and the level as reference has to be beyond reasonable doubt exceeded, taking into account the correction for recovery and measurement uncertainty.

The revised levels as reference for intra-Union trade, provided in the table hereafter, are based upon available occurrence data obtained after September 2013. The provisional enforcement approach is provisional awaiting the availability of more data on the occurrence of perchlorate in food, following the recommendation to monitor the presence of perchlorate in food (see above)

These revised levels as reference for intra-Union trade are of application as from 16 March 2015, except for herbal and fruit infusions which are of application as from 1 July 2015, and the levels agreed at the Committee on 16 July 2013 are no longer valid.

**Levels of perchlorate as reference for intra-Union trade**

<b>FOOD (*)</b>	<b>level (mg/kg)</b>
	(*)
Fruits and vegetables	0.1
with the exception of	
- <i>Cucurbitaceae</i> and leafy vegetables except	0.2
- - celery and spinach grown in glasshouse/undercover	0.5
- - herbs, lettuce and salad plants, including rucola, grown in glasshouse/under cover	1.0
Dried spices (except dried herbs and paprika), dried hops	0.5
Tea ( <i>Camellia sinensis</i> ), dried	0.75
Herbal and fruit infusions, dried	0.75
Foods for infants and young children - ready-to-eat	0.02
Other food	0.05

(\*) - The levels as reference values for intra-Union trade applies, insofar not specified, to the unprocessed food. For dried, diluted, processed and compound foodstuffs, Article 2 of Regulation (EC) 1881/2006 is of application.

- The levels as reference values shall apply to the edible part of the food concerned.

- The leafy vegetables grown in glasshouse/under cover have to be labelled as such (or be reasonably demonstrated as being from such production in case of non-compliance with the specific level for open air production) for the application of the specific level as reference value established for the leafy vegetables grown in glasshouse/ under cover. In the absence of such a labelling (or subsequent proof of origin), the levels as reference values for intra-Union trade established for leafy vegetables grown in the open air shall apply.

Statement as regards the presence of perchlorate in food endorsed by the Standing Committee on Plants, Animals, Food and Feed on 10 March 2015, updated on 23 June 2015

## Annex C

### Details of an EFSA Identified Method for Analysis of Perchlorate of Food that has been identified to provide reliable results

Taken from "Statement as regards the presence of perchlorate in food endorsed by the standing Committee on Plants, Animals, Food and Feed on 10 March 2015, updated on 23 June 2015".

See:

[http://ec.europa.eu/food/safety/docs/cs\\_contaminants\\_catalogue\\_perchlorate\\_statement\\_food\\_update\\_en.pdf](http://ec.europa.eu/food/safety/docs/cs_contaminants_catalogue_perchlorate_statement_food_update_en.pdf)

Member States, with the active involvement of food business operators, are requested to monitor the presence of perchlorate in food and this in accordance with Commission Recommendation (EU) 2015/682 of 29 April 2015 on the monitoring of the presence of perchlorate in food (<http://eur-lex.europa.eu/legalcontent/EN/TXT/?qid=1434527808532&uri=CELEX:32015H0682>)

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Determination (QuPPE-Method) - Version 7.1" The method can be downloaded from:

[http://www.crl-pesticides.eu/library/docs/srm/meth\\_QuPPE.pdf](http://www.crl-pesticides.eu/library/docs/srm/meth_QuPPE.pdf)

In addition the article "Analysis of Perchlorate in Food Samples of Plant Origin Applying the QuPPE-Method and LC-MS/MS" has to be consulted in which it is reported how to integrate the environmental contaminant perchlorate into the abovementioned QuPPE multiresidue method. The article can be downloaded from <http://www.analytic-news.com/papers/pdf/cvuase2.pdf>

The Limit of Quantification (LOQ) should be targeted not be higher than 2 µg/kg for the analysis of perchlorate in foods for infants and young children, 10 µg/kg in other foods and 20 µg/kg in dried herbs and spices and dried herbs and tea for infusion.

Sampling is to be performed in accordance with current sampling procedures in place to control the level of nitrates in leafy vegetables and pesticide residues in food.

## Appendix 5. Estimated Costs for Disinfection Products and Systems: Chlorine Dioxide, Sodium Hypochlorite and Hydrogen Peroxide

### Chlorine Dioxide and Sodium Hypochlorite

	Chlorine Dioxide	Sodium Hypochlorite
<b>10 m<sup>3</sup>/hr</b>		
<b>Equipment</b>	£2,350	£1973
<b>Running Costs/year</b>	£1090	£14.74
<b>Running Costs/m<sup>3</sup></b>	£0.18	£0.025
<b>25 m<sup>3</sup>/hr</b>		
<b>Equipment</b>	£3000	£2812
<b>Running Costs/year</b>	£1090	£30.87
<b>Running Costs/m<sup>3</sup></b>	£0.08	£0.015
<b>50 m<sup>3</sup>/hr</b>		
<b>Equipment</b>	£4150	£4912
<b>Running Costs/year</b>	£1090	£40.55
<b>Running Costs/m<sup>3</sup></b>	£0.04	£0.025
<b>100 m<sup>3</sup>/hr</b>		
<b>Equipment</b>	£5550	£8187
<b>Running Costs/year</b>	£1090	£60.82
<b>Running Costs/m<sup>3</sup></b>	£0.02	£0.041

### Assumptions

**Equipment costs** – these costs do not include installation

**Electricity** – Electricity costs assume a charge of £0.128/kWh

**Chlorine dioxide** – the costs incurred in this form of treatment assume a cost of £0.25/l for sodium hypochlorite and £1.00/l for hydrochloric acid.

**Sodium hypochlorite** is normally supplied in a 1,000 l intermediate bulk container (IBC), which must be stored in a bund to protect the soil from accidental leakage. It is assumed that bulk sodium hypochlorite is injected at a rate of 10 ppm and costs £0.26/l.

### Hydrogen Peroxide – Example: EndoSan50 General Costing

<b>Price per Litre (£/l)</b>	<b>Dose rates</b> (constant dosing)	<b>Shock Rate</b> ( <i>based on well-maintained system. For heavy biofilm load, please double</i> )
£8-10/l EndoSan50	10-20 ppm ( <i>equivalent to 20-40 ml/1000 l water</i> )	200 ppm over 12-24 hours (400 ml/m <sup>3</sup> )

### **GUARDIAN PULSE PLUS DOSING SYSTEM – Approximately £ 1500-1600.00 (excluding water meter)**

This is an example of a pulse fed, proportional dosing system with additional inbuilt traffic light chemical indicator system, lance, cable, bund, pump and associated ancillary equipment.

This dosing system is a true ‘plug and play’ system which doses proportionally to the water used via direct injection. It has the added ability to monitor the EndoSan levels in the drum and to warn on low readings. This is achieved using a traffic light system, cable and lance which is placed inside the EndoSan drum. The beta 4 pump is manufactured to a very high standard and comes with de-gassing head at the rear. The system is all mounted on a bespoke designed bund, stress tested and palletised ready for delivery to site.

For an online dosing calculator click [here](#).

## **Appendix 6. Additional Recommendations for Further Work**

1. Review of long-term medical uses of potassium chlorate and potassium perchlorate in relation to proposed horticultural chlorate and perchlorate limit values and adverse effects on thyroid function
2. Review of thiocyanate, iodide and nitrate, based on potency per moles in relation to inhibiting iodide uptake. Look at typical diets.
3. Risk assessment of current levels of chlorate and perchlorate in various food horticultural products versus the short and long term risks from microbial infections resulting from avoidance of the use of existing simple and relatively inexpensive chlorine-based disinfectants.
4. Review of inducing pathogen catalase generation when using hydrogen peroxide (there is little evidence of generating free chlorine resistance in pathogens when using free chlorine.)
5. The justification for the precautionary principle factors used for the generation chlorate and perchlorate horticultural limits.
6. Improving the precision and accuracy of chlorate and perchlorate testing in horticultural products
7. Optimising the required specification for sodium and calcium hypochlorite; the optimum method of use and associated storage conditions
8. Expanding the review on the use of chlorine dioxide and hydrogen peroxide.
9. Alternative potential disinfectants (e.g. ozone; cold plasmas etc.)

**Prof. K. Clive Thompson, ALcontrol Laboratories**

**4<sup>th</sup> Sept 2016**

## Appendix 7. Questionnaire for the Potato Industry

1. What will it mean for the industry if MRLs for chlorate and perchlorate are made official at the current default 0.01 mg/kg? There is currently a hypothetical MRL of 0.7 mg/kg for all food stuffs and drinking water
2. What are the sources of water that are mainly used in growing, processing and/or packing and is it treated further for disinfection? (i.e. mains water, bore water, reservoir/surface water)
3. Have any problems ever arisen from chlorate/perchlorate residues in potatoes before and/or after washing?
4. Is there a pre-wash treatment to remove soil and other larger particles prior to washing?
5. How widely is chlorine used as a disinfectant in the potato industry?
6. Is chlorine used at any other stage of the growing season apart from post-harvest produce washing?
7. What kind of systems are used? Do you follow manufacturer protocol?
8. Has H2O2 ever been used in potato washing or hygiene practices in the potato industry?
9. Do you think that 0.01 mg/kg is an achievable residue target?

10. Are residues for chlorate (and its derivatives) tested for? If so, how often?
11. Do potatoes arrive at your factory washed or unwashed? What percentage are washed?
<p>12.If potatoes are washed before they are delivered to your factories, do you:</p> <ul style="list-style-type: none"> <li>● Instruct suppliers not to use chlorinated water or disinfectants that contain chlorine in the wash water they use?</li> <li>● Ask them to monitor or measure the level of chlorate in the water they use?</li> <li>● Ask them to only use potable water? If using potable water, do you ask them to measure the level of chlorate in that water?</li> </ul>
13.If you are sourcing washed potatoes from merchants, have you agreed a protocol to avoid chlorate residues on the potatoes that are delivered to your factory? Are the merchants monitoring Chlorate residue levels?