



Grower Summary

CP 154a

Chlorine and its Oxides:
Chlorate and Perchlorate
Review

Final 2016

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Use of pesticides

Only officially approved pesticides may be used in the UK. Approvals are normally granted only in relation to individual products and for specified uses. It is an offence to use non-approved products or to use approved products in a manner that does not comply with the statutory conditions of use, except where the crop or situation is the subject of an off-label extension of use.

Before using all pesticides check the approval status and conditions of use.

Read the label before use: use pesticides safely.

Further information

If you would like a copy of the full report, please email the AHDB Horticulture office (hort.info.@ahdb.org.uk), quoting your AHDB Horticulture number, alternatively contact AHDB Horticulture at the address below.

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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>.

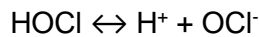
Chlorate exceedance in UK fresh produce is thought mostly to arise from the use of chlorine dioxide treated water or otherwise chlorinated water that is used for crop irrigation and produce post-harvest washing. The use of such water reduces the risk of microbial contamination in fresh produce.

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_2), sodium hypochlorite (NaClO), calcium hypochlorite ($\text{Ca}(\text{ClO})_2$) and sometimes chlorine gas (Cl_2), 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^-). In the case of sodium hypochlorite in solution:



HOCl is a stronger oxidising agent than OCl^- , and is more effective as a disinfectant.

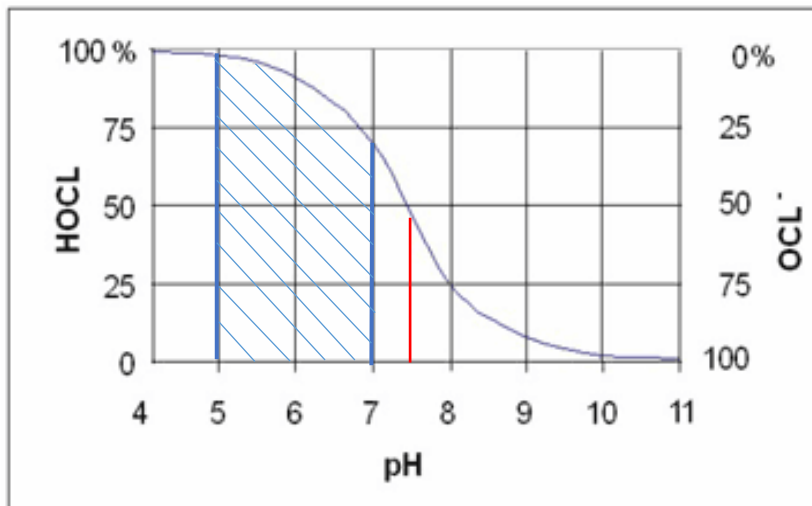
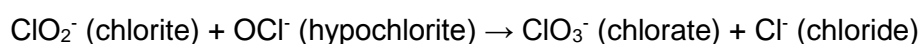


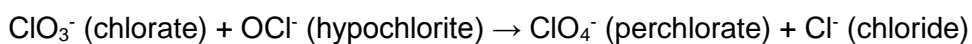
Figure 1. Ratio of a solution of hypochlorous acid and hypochlorite ions showing 50% HOCl and 50% OCl^- achieved at pH 7.5 (red line), with HOCl being the more effective disinfectant below this point (between 5 and 7 pH) (shaded area).

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 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 (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). Seasonal flushing of the lines to clear out algae and other foreign bodies would reduce the need for higher concentrations of chlorine disinfectant.

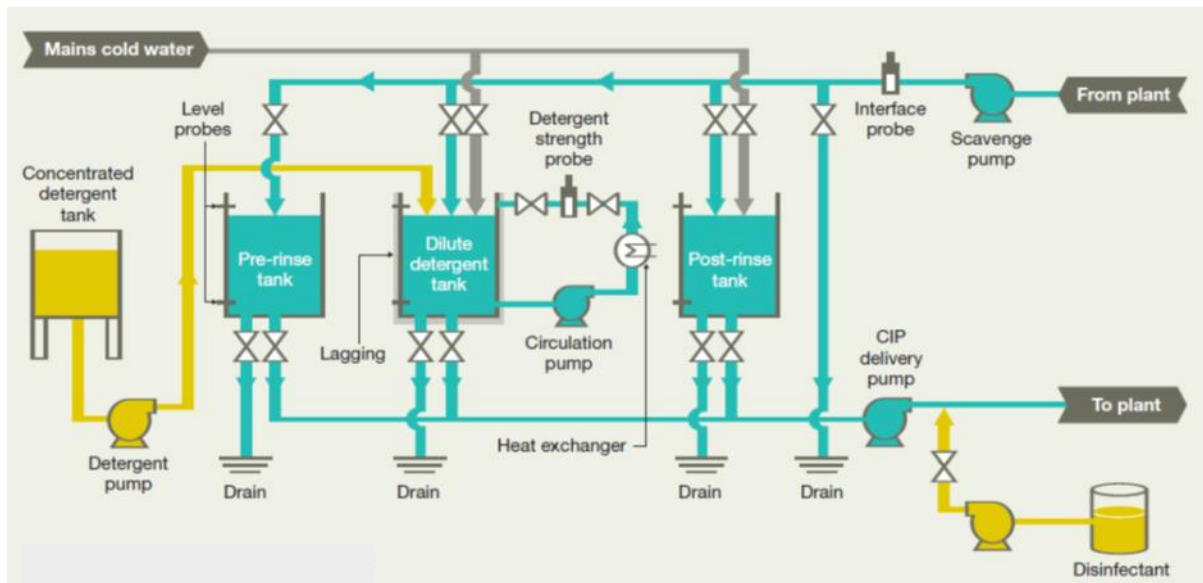


Figure 2. Schematic of a soil cleaning system in a food manufacturing plant recycling water, showing where detergents are added to the system and strength monitored. Source: <http://www.wrap.org.uk/>

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.

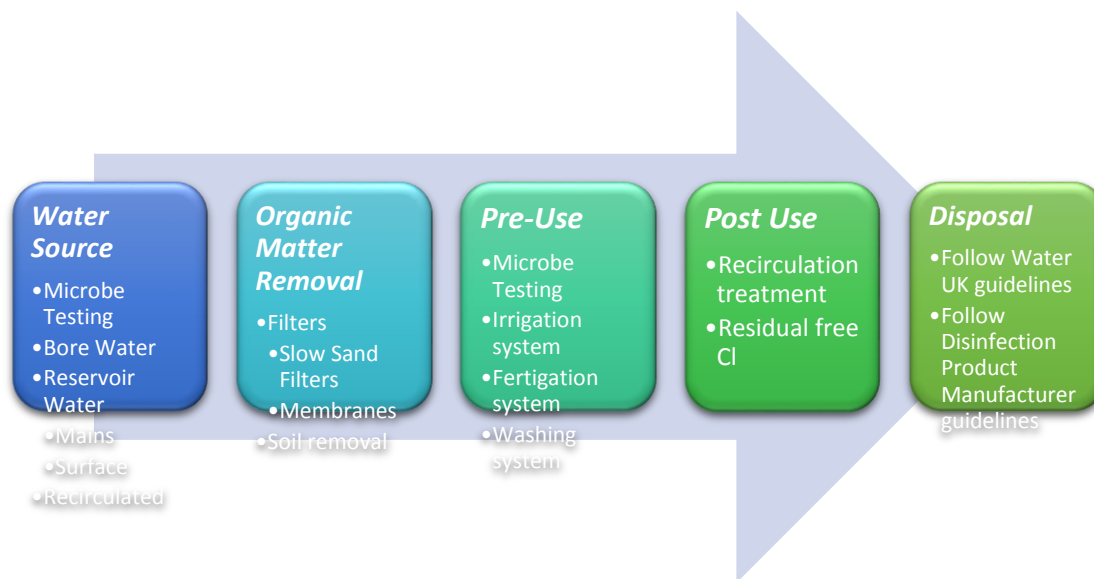


Figure 3. Example control point system based on the HACCP principle. Used to monitor water quality from the source, to point of use to disposal. This is a generalised diagram and not representative of a specific growing system (see Section 10 for further details).

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/) 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 (H₂O₂)

Hydrogen peroxide (H₂O₂) 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. H₂O₂ breaks down to water and oxygen in solution, giving it the advantage of leaving no residues. H₂O₂ 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 H₂O₂ is combined with organic acids such as acetic acid (to form peracetic acid) to increase stability.

The mechanism of H₂O₂ 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_2O_2 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_2O_2 must be transported in polyethylene, stainless steel or aluminium containers because when H_2O_2 comes into contact with flammable substances there is a risk of explosion. Due to the oxidising capacity of H_2O_2 , 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_2O_2 . 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.