The use of redox potential to estimate free chlorine in fresh produce washing operations: Possibilities and limitations

Sam Van Haute[a,b], Bin Zhou[a], Yaguang Luo[a], Imca Sampers[c], Martijn Vanhaverbeke[c], Patricia Millner[a,*]

[a] U. S. Department of Agriculture, Agricultural Research Service, Beltsville Agricultural Research Center, Environmental Microbiology and Food Safety Laboratory, 10300 Baltimore Ave, Beltsville, MD 20705, USA
[b] Ghent University Global Campus, Department of Molecular Biotechnology, Environmental Technology, and Food Technology, 119 Songdomunhwa-ro, Yeonsu-gu, Incheon, South Korea
[c] Laboratory of Food Microbiology and Biotechnology, Department of Food Technology, Safety and Health, Faculty of Bioscience Engineering, Ghent University Campus Kortrijk, Graaf Karel de Goedelaan 5, 8500 Kortrijk, Belgium

ABSTRACT

Maintaining free chlorine (FC) residual at appropriate pH values is a control approach used to prevent pathogen cross-contamination during tomato dump tank handling and fresh-cut produce washing operations. Oxidation reduction potential (ORP) is a rapid measurement of oxidant-based sanitizer strength, and has been used to estimate FC residual. However, factors, in addition to FC and pH, which influence ORP are not fully understood. This study examined the relationship between ORP and FC under chlorine demand (CLD) free conditions and during fresh produce washing. An equation predictive of FC was developed in the form logFC = f(ORP, ORP^2, ORP.pH). A good correlation between ORP and logFC was maintained when other variables changed, but the resulting ORP-logFC curve changed (slope, intercept). A decrease in pH or temperature led to an increase in ORP. Using tap water to wash the produce instead of distilled water significantly changed the ORP. For different types of tested produce, i.e., fresh-cut carrot, onion, romaine and iceberg lettuce, and for whole tomatoes, increasing the product-to-water ratio (i.e., increasing the organics transferred into the water) led to a decrease in ORP for a specific FC residual. The choice of acidulant during washing also influenced ORP. Overall, the correlation of ORP with logFC is more reliable at the lower end (5 mg/L FC) than at the higher end (100 mg/L FC) of the FC range used in fresh produce washing. However, since the ORP in fresh produce wash water is affected significantly in multiple ways by the wash water and process conditions, the predicted FC values with ORP under certain fresh-cut produce washing conditions cannot be generalized for other conditions.

1. Introduction

In fresh produce processing or packaging, washing is used for removal of dirt from, transport of, and disinfection of the produce. Disinfection is mostly done by adding chlorine (mostly dosed in the form of sodium hypochlorite) to the water that contacts the produce. This disinfection process can remove microorganisms from the produce surface to some degree, but disinfection is limited to about 1–2 log. In the water on the other hand, the microorganisms do not receive protection from the produce (although microbial clumping and particle association can provide some protection), which makes killing microorganisms in the water much more efficient. Even though elimination of pathogens from produce surfaces cannot be fully achieved with water disinfection, maintaining a sufficiently high water disinfectant concentration in the wash water is needed to limit or eliminate cross-contamination of pathogens among produce, and as such avoid spreading of the pathogen to more crops and potentially more consumers (Suslow, 2004; Gil et al., 2009; Van Haute et al., 2015; Gombas et al., 2017).

Chlorine over-dosing (in combination with a pH below 4.5) will lead to chlorine off-gassing in the work space as well as increased production of carcinogenic by-products in the presence of organics in the wash water (Van Haute et al., 2013). In addition, as chlorate is formed during storage of sodium hypochlorite, increased chlorine dosing during the washing process leads to accumulation of chlorate in the wash water (Stanford et al., 2011). As chlorate is no longer allowed as pesticide in the European Union, introduction of chlorate in the food chain due to excessive chlorination is considered a potential issue (Gil et al., 2016;

Nestlé, 2017). Chlorine under-dosing on the other hand can increase food safety risks due to insufficient protection from pathogen cross-contamination via the wash water. Chlorine is consumed by organics introduced into the water during produce washing (Nou and Luo, 2010; Luo et al., 2011; Van Haute et al., 2013). Ammonia reacts very rapidly with chlorine, but there is very little ammonia present in fresh produce wash water as degradation of N-containing organics has not yet set in during washing (Van Haute et al., 2013). Therefore, an easy-to-use technology for continuously measuring the FC residual is of great interest for the fresh produce processing industry.

The ORP is a measurement of the tendency of a chemical species to acquire electrons. The potential, measured using an ORP electrode, is influenced by all the redox reactions that occur at the electrode surface. As such, the ORP in a produce wash operation is a mixed potential that is usually impossible to relate to one particular redox reaction (White, 2010). However, in some systems the ORP is dominated by one reaction of interest, thereby providing useful information about that redox reaction, even though the signal is fundamentally semi-quantitative. Information about the presence of strong oxidants/reductants can be acquired in this way, because of the strong oxidizing/reducing properties of these chemicals. Thus, ORP has been used to estimate the presence of free chlorine in water (White, 2010). Limitations to the usage of ORP for chlorine measurement is the slow response time and the non-linear response of ORP to free chlorine (Hoorfar, 2014). The use of ORP for measuring free chlorine during the washing of fresh produce has been described in some tomato packing houses (Tomas-Callejas et al., 2012; Zhou et al., 2014b), and fresh-cut lettuce operations (Fu et al., 2018; López-Gálvez et al., 2019).

There are some clear practical benefits to using ORP. The probe can be put straight into the wash water. There is no need for tapping from the flow of water and passing it through a tubing system, adding reagents and doing a titrimetric or spectrophotometric analysis on the water sample, which is the case in automated N,N-diethyl-p-phenylenediamine (DPD) method devices. In addition, ORP is a voltage measurement and as such easy to be used as a signal for communicating with the pump of a dosing system in a feed-back loop.

In the early editions of the industry food safety guidelines in the US, 150 mg/L free chlorine at pH 6.5, or an ORP of 650 mV in wash tanks were used as control measures to prevent pathogen cross-contamination (FTEC, 2006; UFPA, 2008) based on scientific findings available then. With the advancement in science, the industry has recently updated their food safety standard, changing ORP requirement from previously 650 mV to 850 mV (UFPA, 2018). However, most of the scientific studies evaluating pathogen cross-contamination use only free chlorine and pH (Luo et al., 2011; Gereffi et al., 2015; Sreedharan et al., 2017), while many tomato packers and fresh-cut processors use ORP to gauge their sanitizer strength. Thus, a formula that allows the conversion between ORP, FC, and pH is highly desirable. Thus, this study was designed to address these critical data gaps. Specifically, the main objectives of this study are to i) evaluate the relationship between ORP and FC under ideal conditions, i.e., in chlorine demand (CLD) free water, ii) observe the changes that occur to the ORP-FC relationship under the conditions of tomato and fresh-cut leafy vegetable water (water source, organic matter, acidulant).

2. Materials and methods

2.1. Production of fresh produce wash water

Carrots (*Daucus carota* L. subsp. *sativus*), onions (*Allium cepa* L.), romaine and iceberg lettuce (*Lactuca sativa* L.) were purchased from a local wholesale market in Jessup, MD, USA, and stored at 4 °C for 24 h before processing. Root hairs of carrots were manually removed. Onions were peeled and de-cored in the packing house and were shredded without additional preparation. Lettuce was prepared by trimming the leaf edges and removing the stems (Luo, 2007). The vegetables were shredded into 0.32 cm width pieces at a rate of 1 kg min^{-1} using a commercial vegetable cutter (Nichimo Seven Chefs ECD-302, Tokyo, Japan). The lettuce wash water was made by consecutively washing 10 batches of 800 g in 10 L deionized (DI) water for 1 min and the carrot and onion wash water by washing 5 batches of 800 g in 10 L DI water for 1 min. The wash waters were stored at –80 °C until use.

Tomato (*Solanum lycopersicum*) wash water was made with tomatoes (including incidental leaf and stem debris), harvested in and shipped from Florida. Wash water was made by washing 20 kg of grape tomatoes plus debris in 20 L of tap water or DI water for 30 min. Additionally, sampling of tomato wash water was done in a tomato packinghouse in Florida.

2.2. Experimental design

The studied variables of influence were FC concentration, temperature, pH, used acidulant and the influence of the water source and the organics transferred to the water due to washing of produce.

Experiments in DI water were performed to assess the influence of FC, temperature (T), pH and acidulant on the ORP. The influence of pH on ORP was studied by measuring the ORP for FC residuals in the range 0.2–60 mg/L (0, 0.24, 0.47, 0.94, 1.88, 3.75, 7.5, 15, 30, 60 mg/L) and this in the pH range 3–9 (studied in half pH increments) in DI water at 25 ± 2 °C, for FC residuals in the range of 0–200 mg/L. The relationship between the FC residual and ORP, and the influence of T on that relationship, were studied at pH 6.5 in distilled water at 25 ± 2 °C and 4 ± 2 °C and for free chlorine residuals in the range 0.2–200 mg/L. The wash water was kept cool with an ice mantle around the reaction container. For the influence of acidulant on ORP during chlorination, HCl (Fluka, USA), phosphoric acid (Mallinckrodt Chemicals, USA), citric acid (VWR, USA), and T-128 (SmartWash® Systems) were compared at pH 6.5 in DI water at 25 ± 2 °C. The T-128 is mainly composed of phosphoric acid and propylene glycol (Lemons and Taylor Fresh Food, Inc., 2009; Shen et al., 2012). Even though citric acid is a regularly used acidulant in fresh produce washing, it cannot be recommended as it has inherent CLD and results in production of chlorinated organic disinfection by-products (Fan and Sokorai, 2015).

Experiments in fresh-cut produce wash waters (carrots, onions, romaine and iceberg lettuce) were performed to assess the influence of the organics, here expressed as CLD and chemical oxygen demand (COD). The fresh-cut produce wash water was produced with DI water, to only consider the influence of the added organics from the plant matter. The iceberg fresh-cut produce wash water was diluted in DI water by 2, 4 and 16 times in order to study the effect of CLD and COD on the ORP. The influence of the fresh-cut wash water on the ORP was studied at pH 6.5 for FC residuals in the range of 0 to 100 mg/L at 4 ± 2 °C.

Experiments in tomato wash water were performed as a case for whole produce washing. Tomato wash water was chosen because the tomato industry is interested in the use of ORP. In addition, tomatoes are a risk product for *Salmonella* in the USA since 15 multistate outbreaks are attributed to the consumption of raw tomatoes during 1990–2010, and all of the outbreaks were caused by *Salmonella enterica* serotypes (Bennett et al., 2015). Tomato wash water was made in tap water, to simulate the wash water as in industrial practice. In addition, the wash water was made in DI water to compare the effect of the water source (DI water or tap water) on the ORP. For tomato wash water experiments the water was kept at 25 ± 2 °C, because during industrial tomato washing, the water is kept warmer than the tomatoes to avoid possibility of infiltration of water into the tomato pores (UFPA, 2008). The influence of the organic load of the wash water was studied at pH 6.5 by diluting tomato wash water with tap water to 2/3, 1/3 and 1/8 of the original concentration of the wash water, and studying the ORP-FC relationship in the range of 10–150 mg/L FC. This high range was used because the tomato packaging industry tends to use higher FC residuals during washing than the fresh-cut produce industry, making

low chlorine residuals less relevant.

2.3. Setup of the experiments

The water (DI, tap or produce wash water), was transferred to a beaker and stirred magnetically (VMS-C7, VWR, USA). A larger beaker with ice water was used to keep the temperature of the prepared wash water at $4 \pm 2\,°C$ for those experiments that required it; other experiments were performed at $25 \pm 2\,°C$.

The pH, temperature (both with SevenEasy, Mettler Toledo, USA), and ORP were measured in the wash water, ORP was measured using two ORPTestr 10 devices (double junction Pt electrode, Oakton Instruments, IL, USA) and averaging the measurements of both meters (10 mV average difference between both the meters). The ORP meters were calibrated before each experiment using ORP standard solution (Orion, Thermo Fisher Scientific, USA, absolute value of 220 mV at 25 °C, 430 mV versus Standard Hydrogen Electrode). The CLD, i.e., the amount of free chlorine consumed by the water matrix constituents, was determined as described by Van Haute et al. (2018). To characterize the tap water, conductivity was determined with a conductivity meter (135A, Thermo Orion, Germany), as well as the pH, COD, and alkalinity. The alkalinity was determined with acid titration. COD was measured according to the small-scale sealed-tube method (HR COD digestion vials, Hach, CO).

Sodium hypochlorite (Clorox 8.25% sodium hypochlorite, Clorox Professional Products Company, USA) was added to chlorinate the wash water. The pH was maintained at the desired level by using HCl (1 mol/L or 0.1 mol/L) and NaOH (1 mol/L and 0.1 mol/L), except in experiments where the acidulant was studied, in which case phosphoric acid (1.5 mol/L or 0.15 mol/L), T-128 (10 v/v %), and citric acid (10 m/v %) were used as acidulant. The FC and total chlorine (TC) were measured by the DPD method (Eaton and Franson, 2005). Combined chlorine (CC) was calculated as the difference between TC and FC. The ORP, pH and temperature electrodes were immersed in the water during the experiment. The pH was continuously measured and data were recorded when pH stabilized. When chlorine was dosed and pH adjusted to the correct value, a 2 min period was allowed for stabilization of the ORP signal, after which the FC residual was measured and the ORP value at that moment was recorded, thus providing a measured linkage between ORP and FC at distinct pH values. Subsequently, additional sodium hypochlorite was dosed to increase the FC, pH was adjusted, and the above steps were repeated. Tomato packinghouse water was sampled during processing, a 2 min period was allowed for stabilization of the ORP signal, after which the FC residual was measured and the ORP value was recorded.

An exception to manual FC dosing was done when studying the formation of CC during chlorination of fresh produce wash water and the influence of CC on the ORP, where a membrane pump (IP31, Duramat Schutzart, Belgium) was used for dosing FC at a constant rate ($1.74\, mg\, L^{-1}\, min^{-1}$). FC, TC, ORP, pH and temperature were measured at set intervals and pH was continuously adjusted to 6.5 with HCl (0.1 mol/L). No 2 min waiting period for stabilization of the ORP signal was applied here because of the influx of FC at a constant rate and the continuous pH adjustment.

2.4. Statistics

Data was handled with Excel (Microsoft). Use of R-square change F-test and Analysis of Covariance (ANCOVA) were conducted with XLSTAT (Addinsoft) and R 3.4.4. (R-foundation) respectively. R-square change F-test was used to assess whether the relationship between ORP and the logarithm of FC (logarithm with base 10, i.e., logFC) or pH, was linear or rather quadratic. ANCOVA was used to assess whether the categorical variable 'acidulant' or 'type of wash water' had an impact on the relationship between ORP and FC. The Tukey post-hoc test was used on the least square means of the acidulant groups to assess differences

among groups. For assessing the impact of CLD and COD on the slope of the ORP-logFC relationship, multilinear regression was done, i.e., ORP as a function of logFC, CLD (or COD), and logFC x CLD. It could be assumed that the slope of the ORP-logFC relationship changed with CLD, if the ANOVA of the regression showed that the interaction term (logFC x CLD) was significant. Furthermore, ANOVA of the regression could indicate whether the influence of CLD (or COD) on the ORP was significant. A significance level of $p < 0.05$ was used for all the statistical tests.

The relationship between FC, pH and ORP was modeled using XLSTAT (Addinsoft). To predict FC, the variables pH, ORP, the second order terms and the interaction term were considered. Model selection was done based on stepwise entry of variables (probability for entry: 0.05; for removal: 0.1). Of the 260 collected observations, 210 were used for developing the model and 50 were randomly chosen for validating it.

3. Results & discussion

3.1. Log-linear relationship between FC and ORP with accounting for pH

A relationship between ORP and the logarithm of FC in CLD free water was observed (Fig. 1). This relationship was significantly affected by water temperature (ANCOVA: $p < 0.001$). At 4 °C, the ORP was higher than that at 25 °C (Fig. 1). The difference in ORP at 4 and 25 °C decreased with increasing FC, and at about 100 mg/L FC (logFC = 2), the ORP was virtually equal at both temperatures (Fig. 1). A quadratic equation was significantly better (R-square change F-test from linear to quadratic equation: $p < 10^{-4}$) suited to describe the relationship between ORP and logFC than a linear equation for both temperatures (Fig. 1).

This logFC-ORP relationship is a first major influence on the usability of ORP for estimating free chlorine. Because ORP is so sensitive to changes in very low FC concentrations, the ORP technology (in combination with ORP measurements) is effective for determining endpoints of breakpoint chlorination and quenching (i.e., dechlorination) of FC during wastewater treatment (Kim and Hensley, 1997; Yu and Cheng, 2003; Yu, 2004; Yu et al., 2009). On the other hand, because the sensitivity of the ORP signal for measuring FC decreases with increasing FC, the ORP technology will lose measuring accuracy when the applied FC residual increases.

The ORP value for a certain FC residual decreased with increasing pH (Fig. 2a). Notable is the large influence of pH on the ORP for a specific FC residual. In fact, the sensitivity of ORP for changes in pH is of similar order as the sensitivity for logarithmic changes in FC
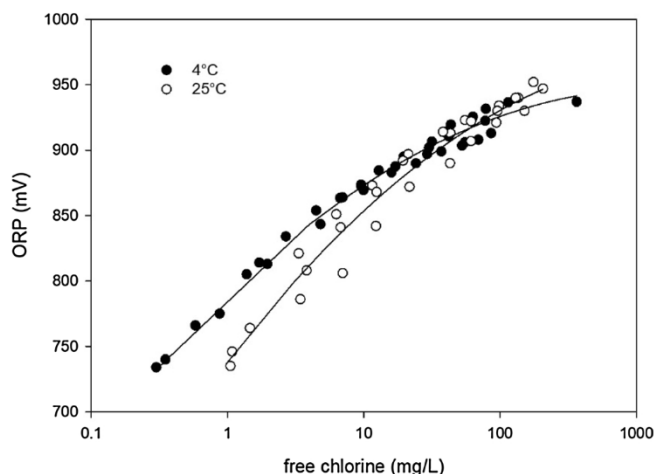

Fig. 1. ORP as a function of logFC (residual concentration) in deionized water at pH 6.5 and 4 °C or 25 °C.
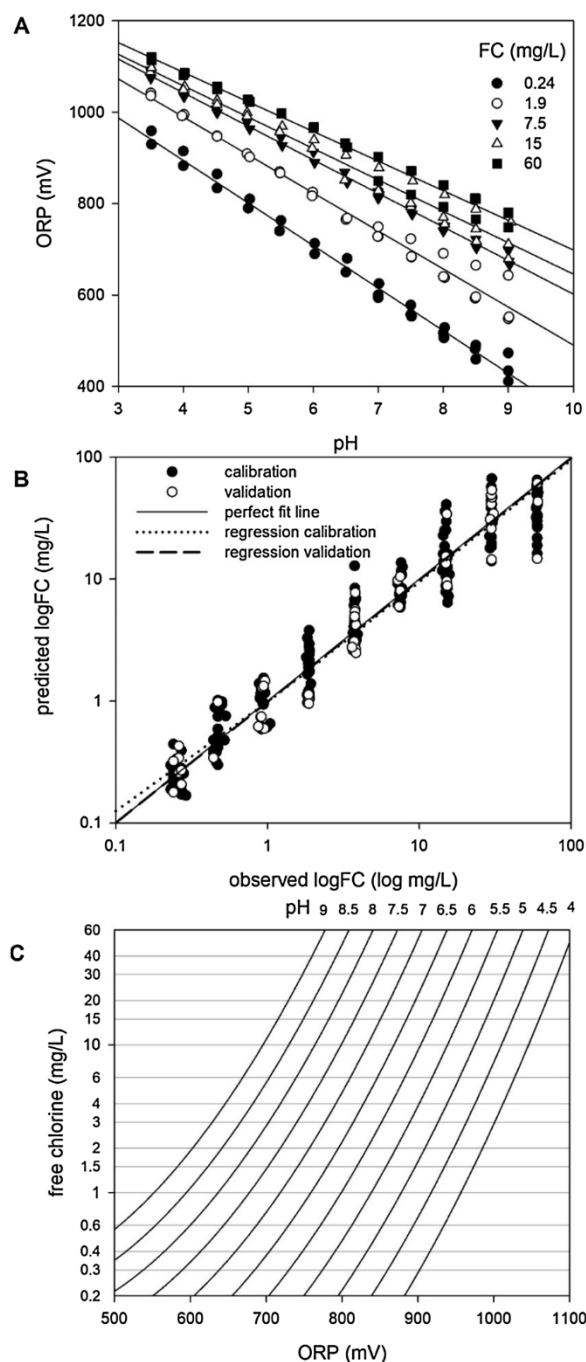
Fig. 2. A) ORP of DI water containing FC as a function of pH, at 25 °C, B) prediction quality of the model logFC = f(ORP, ORP², ORP.pH) in DI water at 25 °C, C) predicted FC residual as a function of ORP and pH, in DI water at 25 °C.

concentration (Table 1). The logarithmic relationships between ORP and FC and between ORP and the H^+ concentration (or otherwise stated linear relationship between ORP and pH) are predicted by the Nernst equation, as is the fact that the ORP increases with decreasing pH (Eqs. 1 and 2).

$$Eh = Eh0 - \frac{RT}{nF} \ln\left(\frac{red}{oxid}\right) \tag{1}$$

$$Eh = Eh0 - \frac{RT}{nF} \ln\left(\frac{[Cl-]}{[HOCl][H+]}\right) \tag{2}$$

Where:

Table 1
ORP change at different FC residuals in DI water at 25 °C when changing the FC residual or the pH.

FC (mg/L)	ORP change for increase in FC by 10 times (mV)[*]	ORP change for decrease in pH by 1 (mV)[**]
0.24	140	93
1.9	105	83
7.5	82	76
15	70	70
60	47	65

[*] Calculated with the equation as derived from the data in Fig. 1 (ORP = -19.4(logFC)² + 135logFC + 738), e.g. 10 times increase in ORP (FC = 0.24 mg/L) = ORP (FC = 2.4 mg/L) – ORP (FC = 0.24 mg/L).

[**] Using the slopes from the plotted curves in Fig. 2A.

Eh = the half-reaction potential, i.e. the ORP,
Eh_0 = standard half-reaction potential relative to the standard half-reaction for hydrogen,
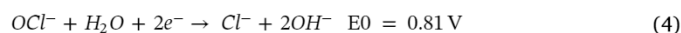R = universal gas constant (1.987 × 10-3 kcal/mol.K),
T = absolute temperature (K),
n = number (equivalent) of electrons transferred,
F = Faraday constant (23.061 kcal/equivalent.mol.V),
Red and *oxid* are the chemical species on the reduced and oxidized sides of the half-reaction (White, 2010).

The ORP of the protonated HOCl is considerably higher than that of OCl^- (Eqs. 3 and 4) and the pKa of HOCl is pH 7.5. Below pH 7.5, HOCl, causing a higher ORP, will be present in a larger abundance and above pH 7.5, OCl^-, causing a lower ORP will be more abundant (White, 2010).

$$HOCl + H^+ + 2e^- \rightarrow Cl^- + H_2O \quad E0 = 1.40\,V \tag{3}$$

$$OCl^- + H_2O + 2e^- \rightarrow Cl^- + 2OH^- \quad E0 = 0.81\,V \tag{4}$$

where E^0 is measured against standard hydrogen electrode at concentration of 1 mol/L, 1 atmosphere pressure, and 25 °C (White, 2010).

Considering both the relationship between ORP and logFC, and the influence of pH on the ORP, a model was constructed to predict logFC as a function of ORP and pH in DI water (Table 2). The model did not show a systematic bias or difference in slope from the perfect-fit line for both the calibration and validation observations; the fitted lines to both sets of observations almost coincided with the perfect-fit line (Fig. 2B). Using this model the prediction of free chlorine could be visualized, based on ORP and pH measurement (Fig. 2C).

The pH influence is a second major influence on the usability of ORP to measure FC. Zhou et al. (2014b) noted a stronger (negative) correlation of ORP with pH than the weak (positive) correlation with FC in tomato dump tank wash water. Murray et al. (2018) noted no significant correlation between the FC and the ORP in fresh-cut iceberg lettuce wash water. In both these cases, a linear correlation between the FC and ORP was made. A good linear correlation between FC and ORP cannot be expected, as the relationship is rather between ORP and the logarithm of FC. But also, a useful correlation between ORP and FC will not be found if the pH is not rigorously controlled or is not incorporated in the ORP terms of the FC model as shown in Table 2. From a practical standpoint it seems that very rigorous pH control would be of paramount importance for controlling FC residual based on ORP measurements.

The results shown so far in this manuscript depict the use of ORP for FC estimation in an ideal situation, i.e. when the water matrix is devoid of interfering water matrix constituents. In an actual commercial produce processing wash situation however, this is not the case.

3.2. ORP is a mixed potential; the water matrix constituents will influence it and limit its usability

Even though the ORP can be dominated by the presence of a strong

Table 2
Model for prediction of logFC as a function of ORP and pH at 25 °C in DI water.

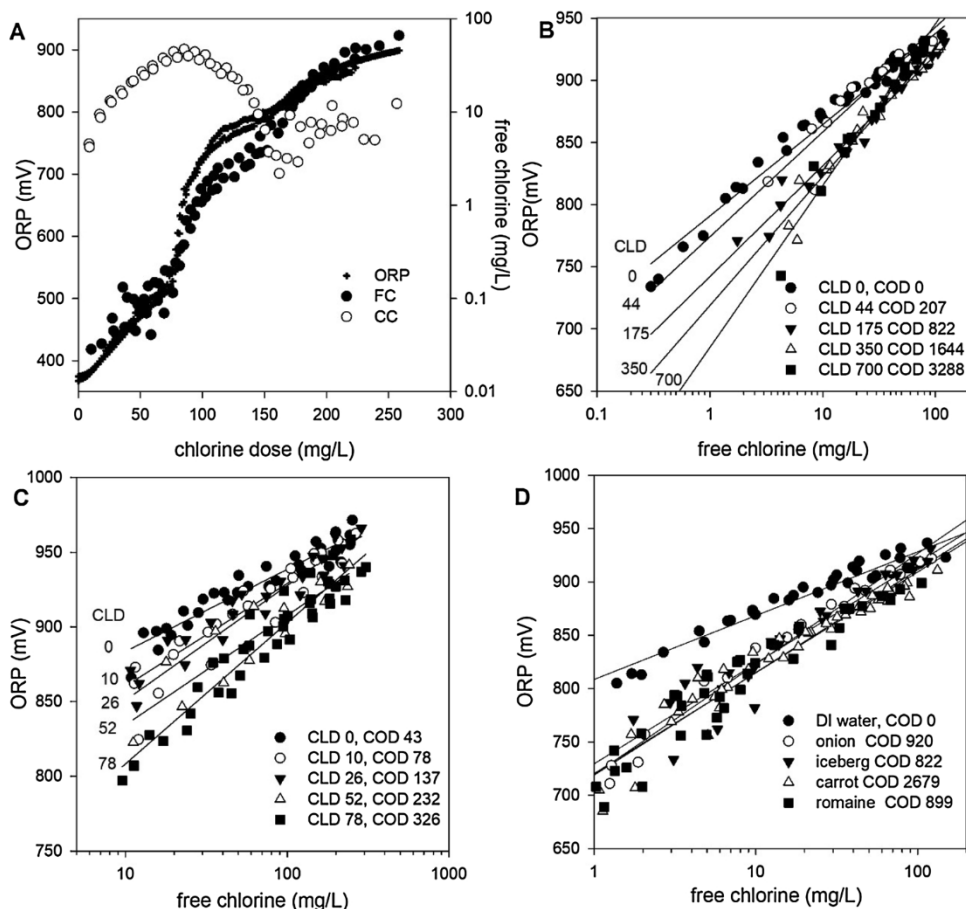| Intercept	ORP	ORP^2	ORP*pH	calibration		validation	
				R^2	RMSE	R^2	RMSE
0.44 ± 0.27	−0.015 ± 0.008	(1.1 ± 0.05)x10^{-5}	(8.4 ± 0.2)x10^{-4}	0.947	0.179	0.935	0.193

Fig. 3. A) Chlorination of iceberg lettuce wash water (CLD 175 mg/L, COD 822 mg/L) at pH 6.5 and 4 °C, B) ORP measured in iceberg wash water as a function of FC residual at pH 6.5 and 4 °C, for different levels of CLD and COD, C) ORP measured in tomato wash water as a function of FC residual at pH 6.5 and 25 °C, for different levels of CLD and COD, D) ORP measured in different fresh-cut wash waters with 175 mg/L CLD as a function of FC residual at pH 6.5 and 4 °C, (n = 3), lines denote log-linear regression curves with numbers representing CLD values.

oxidizer, the presence of other substances can shift the ORP to some degree. Three relevant possible influential factors were studied: i) organics washed from the produce; ii) the influence of the water source; iii) the used acidulant during processing.

3.2.1. Influence of materials washed from the produce on the ORP

When dosing FC in DI water, no CC is formed because insignificant amounts of organics or ammonia are present for reaction. On the other hand, when chlorinating iceberg lettuce wash water, initially there was a build-up of CC without considerable formation of FC, due to the consumption of the FC by the wash water organics, more specifically organic amines (Fig. 3a). When additional FC was dosed, the CC decreased because of further oxidation of the chloramines by FC (Donnermair and Blatchley, 2003; White, 2010; Zhou et al., 2014a). Fig. 3a shows that the increase in ORP closely followed the increase in logFC, whereas the changes in CC were not strongly reflected in the ORP changes. FC has a higher ORP than chloramines formed from ammonia or organic nitrogen (Singer and Reckhow, 1999; White, 2010). The correlation between ORP and FC (R = 0.63), CC (R = -0.25), TC (R = 0.45), and the log of these variables, logFC (R = 0.97), logCC (R = -0.01), and logTC (R = 0.41) indicated that only logFC had a strong correlation with the ORP in the wash water, which corroborates with the findings in CLDfree water.

Iceberg lettuce wash water was used to assess the relationship between ORP and the wash water organics in more detail. Two effects were observed that are clear with log-linear curves fitted to the data (Fig. 3b). First, the intercept in the curves (i.e., the ORP for log(FC) = 0 or FC = 1 mg/L) decreased with increasing CLD and COD. In other words, increasing CLD and COD decreased the ORP. Secondly, the slope of the ORP versus logFC curves increased with increasing CLD and COD (ANOVA interaction between logFC and CLD: p < 10^{-10}). The influence of CLD or COD on the ORP seemed to decrease with increasing FC, and the curves converged at around 100 mg/L FC (logFC = 2). In short, increasing COD or CLD lowered the observed ORP at a certain FC residual, but this effect decreased with increasing FC residual. Similarly, for whole produce, i.e., for whole tomatoes washing, a higher CLD resulted in a steeper ORP/FC slope (ANOVA interaction between logFC and CLD: p = 0.001), yet lower ORP (Fig. 3c). The CLD in wash water from tomato packing houses is lower than that in the wash water of fresh-cut produce washing operations, mainly because the amount of exudate is limited to that leaching from damaged tomatoes compared to leaching from cut surfaces in fresh-cut produce (Zhou et al., 2014b; Luo et al., 2018).

In all the fresh-cut wash waters (standardized to a CLD of 175 mg/L for each wash water, made with DI water), the ORP at a certain FC concentration was lower than in DI water (ANCOVA (Tukey): p < 10^{-4}
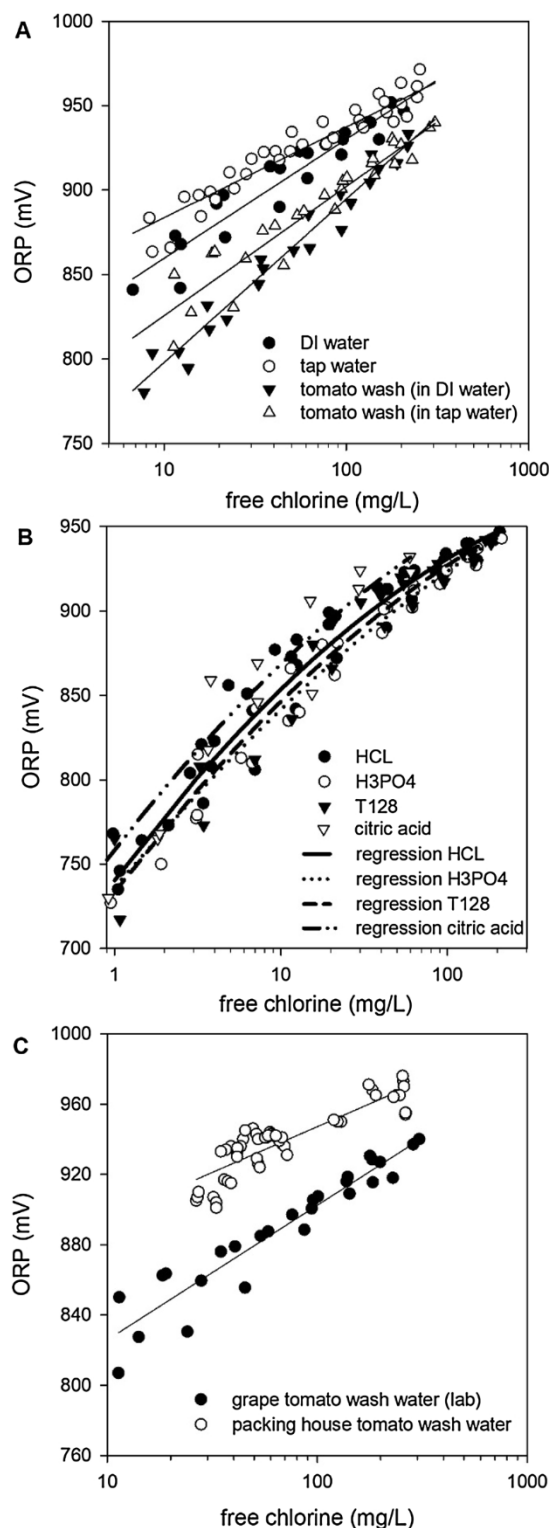
Fig. 4. A) ORP as a function of FC residual at pH 6.5 and 25 °C in DI water, tap water, tomato wash water from tomatoes washed in DI water and from tomatoes washed in tap water, B) influence of acidulant on the ORP of FC in DI water at pH 6.5 and 25 °C, C) comparison of ORP as a function of FC residual between grape tomato wash water (COD = 326 ± 6 mg/L, pH 6.5 ± 0.1, 25 ± 2 °C) and packing house tomato wash water (COD = 439 ± 130 mg/L, pH 6.4 ± 0.1, 40 ± 1 °C).

for all waters) (Fig. 3d). At lower FC residuals, the difference in ORP between DI water and wash water was considerably higher than at higher FC residuals (approaching 100 mg/L). There were no significant differences in ORP among the different fresh-cut produce wash waters with equal CLD (ANCOVA (Tukey): p > 0.05 for all waters), despite some differences in COD, mainly the much higher COD of carrot wash water.

3.2.2. Water source influences the ORP-logFC relationship

Not only do the materials that are introduced during washing influence the ORP, but also the chemical constituents in the source water (e.g., tap water or groundwater) that is used during food processing. The used tap water had a FC residual of 1.8 ± 0.1 mg/L, an alkalinity of 0.052 ± 0.003 mmol/L carbonate and 0.247 ± 0.006 mmol/L bicarbonate, conductivity of 79.8 ± 0.9 μS, pH of 9.3 ± 0.1, and COD of 43 ± 9 mg/L. When chlorinating at pH 6.5, 25 °C, the ORP in tap water was greater than that in DI water (ANCOVA: Tukey: $p = 10^{-3}$), but convergence occurred with increasing FC residual and both waters converged at around 150 mg/L FC residual (Fig. 4a). A water source has a certain "poising intensity", which is the baseline ORP of the water source, determined by the interaction of various water constituents with the electrodes. Consequently, an ORP set point will be dependent on the water source (White, 2010). This translates into a "water source dependent" shift of the ORP. A difference was observed between the ORP in tomato wash water from tomatoes washed in DI water, and tomato wash water from tomatoes washed in tap water (Fig. 4a), very similar to the difference between the ORP in tap water and in DI water. In other words, the water matrix constituents in the water source (here tap water) have an effect on the ORP in the chlorinated wash water. Softening of the water (tap or ground) before use in the washing process could help reduce the variation in ORP by removing inorganics in the water source.

3.2.3. The influence of acidulant on the ORP

Several acidulants can be used during fresh produce washing for controlling pH. The acidulant (HCl, phosphoric acid, T-128 and citric acid) had a significant effect (ANCOVA: $p = 3.10^{-6}$) on the ORP of the FC solution (Fig. 4b). When using citric acid, the ORP was higher than with phosphoric acid and T-128 (Tukey: p < 0.002 in both cases), and when using HCl, the ORP was higher than with the use of phosphoric acid (Tukey: p < 0.004), while the other comparisons between acidulants did not result in significant differences. Though significant, based on the trendlines (Fig. 4b), the difference in ORP due to usage of HCl instead of H_3PO_4 as acidulant was between 4 and 8 mV in the range 0–100 mg/L FC, which is limited considering the variation observed in the ORP signal in the present study. On the other hand, the difference between the citric acid and the other acidulants was 15–20 mV in the range 0–70 mg/L FC, which can be considered problematic.

3.3. Is predicting FC using ORP reliable for produce washing?

Short answer: no. A general target ORP value for all commodities and situations, or one prediction curve for all commodities to estimate FC based on ORP and pH is unrealistic. To illustrate this, the ORP was measured during washing of whole tomatoes in a tomato packing house. Citric acid was used as acidulant. A collection of data points from the packinghouse wash water were chosen so that the COD and pH (COD = 438 ± 122, pH = 6.4 ± 0.1, 40 ± 1 °C) were similar to that in the grape tomato wash water (COD = 326 ± 6 mg/L, pH 6.5 ± 0.1, 25 ± 2 °C). The variable CLD could not be used for the packing house wash water because CLD cannot be measured directly during a washing process (Van Haute et al., 2018), and as such was not measured at that time. The ORP in the packing house tomato wash water was at least 30 mV higher than the ORP in the grape tomato wash water (Fig. 4c). Differences between the wash waters that could have an influence include: the water source composition, the slightly higher average COD, the type of tomato, the acidulant (HCl was used in the lab trials, citric acid in the company), and the water temperature. In addition, because tomato washing is done with high FC residuals, the sensitivity of ORP to

changes in FC is low, and as such, the 30 mV or more offset in ORP observed, has a huge influence. For example, at 920 mV, the grape tomato wash water had 170 mg/L FC, but the packing house wash water had 30 mg/L. In both wash waters however, a trend was observable, and as such, a relationship between ORP and FC could be made. It is a different relationship in both wash waters however. Thus, to make the prediction more accurate, these additional processing conditions that impact water quality must be considered.

4. Conclusion

During a produce washing process with FC as the water sanitizer, the ORP is at least dependent on four major variables: FC, T, pH and water matrix constituents. The water matrix constituents include the mineral and organic chemical composition of the tap water or ground water (water source), along with the constitution and amount of substances introduced with the produce. The ORP increases with the logarithm of the FC residual. This implies high changes at very low FC and low changes at higher FC residual, decreasing the sensitivity with increasing FC. The influence of pH on ORP is quantitatively similar to the influence of the logarithm of FC, with the ORP increasing when pH decreases. The water source influences ORP as do the constituents that enter the water during the washing. In general, for a certain wash water, an increasing CLD, or amount of COD in the wash water, decreased the ORP. As more produce is washed, increasing amounts of materials are transferred from produce to the wash water, and the increase of some of those compounds further decreases the ORP. The influence of these factors complicates the relationship between ORP and FC, and thus limits the usability of the ORP technology for estimating FC in produce wash water. Even as technologies for on-line direct measurement of FC by DPD methods advance for commercial produce wash, the extent to which ORP could still be used for certain operations to reliably predict and meet FC target concentrations will need to be validated.

Acknowledgements

References

Bennett, S.D., Littrell, K.W., Hill, T.A., Mahovic, M., Behravesh, C.B., 2015. Multistate foodborne disease outbreaks associated with raw tomatoes, United States, 1990-2010: a recurring public health problem. Epidemiol. Infect. 143, 1352–1359. https://doi.org/10.1017/S0950268814002167.

Donnermair, M.M., Blatchley 3rd, E.R., 2003. Disinfection efficacy of organic chloramines. Water Res. 37, 1557–1570. https://doi.org/10.1016/S0043-1354(02)00522-5.

Eaton, A.D., Franson, M., 2005. Standard Methods for Examination of Water and Wastewater, 21th ed. APHA, AWWA., Washington.

Fan, X., Sokorai, K.J., 2015. Formation of trichloromethane in chlorinated water and fresh-cut produce and as a result of reaction with citric acid. Postharvest Biol. Technol. 109, 65–72. https://doi.org/10.1016/j.postharvbio.2015.06.009.

FTEC (Florida Tomato Exchange Committee), 2006. . Tomato Good Agricultural Practices (T-GAP) & Tomato Best Management Practices (T-BMP). available at https://www.floridatomatoes.org/wp-content/uploads/2013/01/TOMATO_QA_on_T-GAP_and_T-BMP11-8-06.pdf (Accessed 6 July 2019). .

Fu, T.-J., Li, Y., Awad, D., Zhou, T.-Y., Liu, L., 2018. Factors affecting the performance and monitoring of a chlorine wash in preventing Escherichia coli O157:H7 cross-contamination during postharvest washing of cut lettuce. Food Control 94, 212–221. https://doi.org/10.1016/j.foodcont.2018.06.035.

Gereffi, S., Sreedharan, A., Schneider, K.R., 2015. Control of Salmonella cross-contamination between green round tomatoes in a model flume system. J. Food Protect. 78, 1280–1287. https://doi.org/10.4315/0362-028X.JFP-14-524.

Gil, M.I., Selma, M.V., López-Gálvez, F., Allende, A., 2009. Fresh-cut product sanitation and wash water disinfection: problems and solutions. Int. J. Food Microbiol. 134, 37–45. https://doi.org/10.1016/j.ijfoodmicro.2009.05.021.

Gil, M.I., Marín, A., Andujar, S., Allende, A., 2016. Should chlorate residues be of concern in fresh-cut salads? Food Control 60, 416–421. https://doi.org/10.1016/j.foodcont.2015.08.023.

Gombas, D., Luo, Y., Brennan, J., Shergill, G., Petran, R., Walsh, R., Hau, H., Khurana, K., Zomorodi, B., Rosen, J., Varley, R., Deng, K., 2017. Guidelines to validate control of cross-contamination during washing of fresh-cut leafy vegetables. J. Food Protect. 80, 312–330. https://doi.org/10.4315/0362-028X.JFP-16-258.

Hoorfar, J., 2014. Global Safety of Fresh Produce: A Handbook of Best Practice, Innovative Commercial Solutions and Case Studies, 1st ed. Woodhead Publishing Limited, Cambridge.

Kim, Y.H., Hensley, R., 1997. Effective control of chlorination and dechlorination at wastewater treatment plants using redox potential. Water Environ. Res. 69, 1008–1014. https://doi.org/10.2175/106143097X125704.

Lemons, K.E., Taylor Fresh Food, Inc., assignee, 2009. Antimicrobial compositions and methods of use thereof. United States Patent #20,090,192,231.

López-Gálvez, F., Tudela, J.A., Allende, A., Gil, M.I., 2019. Microbial and chemical characterization of commercial washing lines of fresh produce highlights the need for process water control. Innov. Food Sci. Emerg. Technol. 51, 211–219. https://doi.org/10.1016/j.ifset.2018.05.002.

Luo, Y., 2007. Fresh-cut produce wash water reuse affects water quality and packaged product quality and microbial growth in romaine lettuce. HortScience 42, 1413–1419. https://doi.org/10.21273/HORTSCI.42.6.1413.

Luo, Y., Nou, X., Yang, Y., Alegre, I., Turner, E., Feng, H., Abadias, M., Conway, W., 2011. Determination of free chlorine concentrations needed to prevent Escherichia coli O157: H7 cross-contamination during fresh-cut produce wash. J. Food Protect. 74, 352–358. https://doi.org/10.4315/0362-028X.JFP-10-429.

Luo, Y., Zhou, B., Van Haute, S., Nou, X., Zhang, B., Teng, Z., Turner, E.R., Wang, Q., Millner, P.D., 2018. Association between bacterial survival and free chlorine concentration during commercial fresh-cut produce wash operation. Food Microbiol. 70, 120–128. https://doi.org/10.1016/j.fm.2017.09.013.

Murray, K., Aldossari, H., Wu, F., Warriner, K., 2018. Dynamic changes in free-chlorine levels within a commercial post-harvest wash and prevention of cross-contamination between shredded lettuce batches. Food Control 85, 127–134. https://doi.org/10.1016/j.foodcont.2017.09.029.

Nestlé, 2017. Washing of Produce: Guidance to Minimize the Microbiological Risk. (Accessed 11 October 2018). https://profel-europe.eu/news/washing-of-produce-guidance-to-minimize-the-microbiological-risk/.

Nou, X.W., Luo, Y.G., 2010. Whole-leaf wash improves chlorine efficacy for microbial reduction and prevents pathogen cross-contamination during fresh-cut lettuce processing. J. Food Sci. 75, M283–M290. https://doi.org/10.1111/j.1750-3841.2010.01630.x.

Shen, C., Luo, Y., Nou, X., Bauchan, G., Zhou, B., Wang, Q., Millner, P., 2012. Enhanced inactivation of Salmonella and Pseudomonas biofilms on stainless steel by use of T-128, a fresh-produce washing aid, in chlorinated wash solutions. Appl. Environ. Microbiol. 78, 6789–6798. https://doi.org/10.1128/AEM.01094-12.

Singer, P., Reckhow, D., 1999. Chemical Oxidation. Water Quality and Treatment, 5th ed. McGraw-Hill, New York.

Sreedharan, A., Li, Y., De, J., Gutierrez, A., Silverberg, R., Schneider, K.R., 2017. Determination of optimum sanitizer levels for prevention of Salmonella cross-contamination of mature round tomatoes in a laboratory model flume system. J. Food Protect. 80, 1436–1442. https://doi.org/10.4315/0362-028X.JFP-17-032.

Stanford, B.D., Pisarenko, A.N., Snyder, S.A., Gordon, G., 2011. Perchlorate, bromate, and chlorate in hypochlorite solutions: guidelines for utilities. J. Am. Water Works Assoc. 103, 71–83. https://doi.org/10.1002/j.1551-8833.2011.tb11474.x.

Suslow, T.V., 2004. Oxidation-reduction Potential (ORP) for Water Disinfection Monitoring, Control, and Documentation. ANR Catalog Publ. no. 8149. Univ. Of California, Davis, CA.

Tomas-Callejas, A., Lopez-Velasco, G., Valadez, A.M., Sbodio, A., Artes-Hernandez, F., Danyluk, M.D., Suslow, T.V., 2012. Evaluation of current operating standards for chlorine dioxide in disinfection of dump tank and flume for fresh tomatoes. J. Food Protect. 75, 304–313. https://doi.org/10.4315/0362-028X.JFP-11-347.

UFPA (United Fresh Produce Association), 2008. Commodity Specific Food Safety Guidelines for the Fresh Tomato Supply Chain, 2nd edition. (Accessed 10 August 2018). https://www.fda.gov/downloads/food/guidanceregulation/ucm171708.pdf.

UFPA (United Fresh Produce Association), 2018. Commodity Specific Food Safety Guidelines for the Fresh Tomato Supply Chain, 3rd edition. (Accessed 10 August 2018). https://www2.unitedfresh.org/forms/store/ProductFormPublic/commodity-specific-food-safety-guidelines-for-the-fresh-tomato-supply-chain-3rd.

Van Haute, S., Luo, Y., Sampers, I., Mei, L., Teng, Z., Zhou, B., Bornhorst, E.R., Wang, Q., Millner, P., 2018. Can UV absorbance rapidly estimate the chlorine demand in wash water during fresh-cut produce washing processes? Postharvest Biol. Technol. 142, 19–27. https://doi.org/10.1016/j.postharvbio.2018.02.002.

Van Haute, S., Sampers, I., Holvoet, K., Uyttendaele, M., 2013. Physicochemical quality and chemical safety of chlorine as a reconditioning agent and wash water disinfectant for fresh-cut lettuce washing. Appl. Environ. Microbiol. 79, 2850–2861. https://doi.org/10.1128/AEM.03283-12.

Van Haute, S., Sampers, I., Jacxsens, L., Uyttendaele, M., 2015. Selection criteria for water disinfection techniques in agricultural practices. Crit. Rev. Food Sci. Nutr. 55, 1529–1551. https://doi.org/10.1080/10408398.2012.705360.

White, G.C., 2010. White's Handbook of Chlorination and Alternative Disinfectants, 5th ed. John Wiley & Sons, Inc., Hoboken, New Jersey ISBN: 978-0-470-18098-3.

Yu, R.-F., 2004. Feed-forward dose control of wastewater chlorination using on-line pH and ORP titration. Chemosphere 56, 973–980. https://doi.org/10.1016/j.chemosphere.2004.03.015.

Yu, R.-F., Chen, H.-W., Cheng, W.-P., Shen, Y.-C., 2009. Application of pH-ORP titration to dynamically control the chlorination and dechlorination for wastewater reclamation. Desalination 244, 164–176. https://doi.org/10.1016/j.desal.2008.05.021.

Yu, R.F., Cheng, W.P., 2003. Determination of chlorine demand in water and wastewater chlorination by oxidation-reduction potential. Water Sci. Technol.: Water Supply 3, 313–320. https://doi.org/10.2166/ws.2003.0119.

Zhou, B., Luo, Y., Nou, X., Millner, P., 2014a. Development of an algorithm for feed-forward chlorine dosing of lettuce wash operations and correlation of chlorine profile with *Escherichia coli* O157:H7 inactivation. J. Food Protect. 77, 558–566. https://doi.org/10.4315/0362-028X.JFP-13-352.

Zhou, B., Luo, Y., Turner, E.R., Wang, Q., Schneider, K.R., 2014b. Evaluation of current industry practices for maintaining tomato dump tank water quality during packinghouse operations. J. Food Process. Preserv. 38, 2201–2208. https://doi.org/10.1111/jfpp.12200.