HAND-HELD OXIDATION-REDUCTION POTENTIAL METER FOR USE AS AN INDICATOR OF SWIMMING POOL WATER QUALITY

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DEDICATION

I would like to dedicate this work to my wife Laura Peña-Cameon whose patience and support have been exceptional. Thank you Laura, through challenges and achievement you have stood by me.

ABSTRACT OF THE THESIS

Hand-Held Oxidation-Reduction Potential Meter for Use as an Indicator of Swimming Pool Water Quality
by
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The use of Oxidation-Reduction Potential (ORP) meters to assess recreation pool water quality is becoming more common. Traditional chemical based kits have been used for decades. Currently in the United States DPD (diethyl-paraphenylenediamine) chemical based test kits have become the standard. Other jurisdictions have established standards for ORP and many are either accepting ORP values exclusively or suggesting such testing as an adjunct to traditional chemical tests. We evaluated two hand-held ORP testers currently commercially available, to determine if ORP measurements might be an acceptable method for evaluating swimming pool and spa water quality. One-Hundred and Seventy-seven permitted commercial "pools" were tested with both traditional chemical tests and ORP measurements. Oxidation-Reduction Potential was evaluated by both the Oakton ORPtestr and Extech model 300 hand-held ORP testers. Both the Oakton ORPtestr (p-value <0.05) and the Extech model 300 (p-value<0.05) demonstrated a statistically significant correlation with traditional chemical measures of total and free chlorine residual. Cyanuric acid is used as a conditioner in pools to protect the loss of chlorine to the effects of the sun. Tests conducted in the present study correlating cyanuric acid levels to ORP did not show a significant correlation using either with the ORPtestr (p-value 0.437) or those collected with the Extech model tester (p-value 0.884) .

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CHAPTER 1

INTRODUCTION

Availability and use of recreational swimming pools and spas is widespread. The U.S. Census Bureau (2009) estimated that 339 million visits to such venues takes place yearly. The County of San Diego has a climate that contributes to an extended swimming season. With an excess of 4,000 permitted recreational swimming pool venues at any given time, as well as many more private swimming pools, there is a significant potential for a recreational waterborne illness. The Centers for Disease Control and Prevention (CDC; 2008) reports 78 waterborne disease outbreaks associated with recreational waters during the years 2005-2006 represents an increase of 25% over the previous reporting period of 2003-2004 when 62 such outbreaks were reported (CDC, 2006). The 78 outbreaks reported in 2005- 2006 is the largest number ever reported in a two year period. Fifty-eight (74%) of these reports were related to treated water venues (CDC, 2006). The prevalence of Recreational Water Illnesses (RWI) has been shown to be increasing in recent years (Lee, Levy, Craun, Beach, & Calderon, 2002). In other data compiled by the CDC between the years of 1997 and 2006, bacteria and viruses including giardia spp., E. coli, Shigella ssp., norovirus, salmonella, and camplobacter among others, which are known to be susceptible to preferred swimming pool sanitizers, chlorine, and bromine, were responsible for 23% of RWIs (CDC, 2008). As with any disease that depends heavily on self-reporting, the true number of illnesses caused by swimming venues is unknown and likely much larger than the number of documented cases.

Current methods used to assess water quality in treated water venues are largely based upon chemical colorometric test kits. These kits measure a surrogate, free chlorine for example, to evaluate water quality. The effectiveness of free chlorine as an indicator of water quality has been shown to be related to many factors that are inherent in a recreation swimming environment. Such factors need not be taken into account with ORP testing as the tests register the actual potential present in the water tested.

BACKGROUND

An understanding of the relationship between bacterial contaminants, sanitizers and Oxidation reduction potential is essential in evaluating the potential effectiveness of an ORP based testing regimen. The actual process of the destruction of bacteria cells is beyond the scope of this paper. In basic terms, sulphydryl enzymes within the bacteria as well as other enzymes sensitive to oxidation, are inhibited by the oxidative effect of the chlorine (Knox, Stumph, Green, & Auerbach, 1948). Unfortunately, this compound begins to disassociate in water and becomes hypochlorite (OCl-) and a hydrogen ion. As the pH is increased the relative proportion of the hypochlorite ion also increases.

The oxidation of bacteriological compounds has been shown to occur as a result of the presence of HOCl. The relative ease at which HOCl provides antimicrobial activity is due to its neutral characteristic. Different disinfectant forms have electrical charges that affect their ability to disinfect. The outer surface of bacterium cells have a negative charge and therefore the ability of neutral hypochlorous acid to enter the cell wall is greater than that of the hypochorite ion, the related dissociation product which has a negative charge. The negative charge of the OCl- ion and the negative charge on the cell wall repel one another and hinder the effectiveness of the chlorine (Connell, 1996).

The inability of chlorine to kill harmful organisms in recreational water is only part of the challenge as it relates to the disinfection of recreation water quality. Cyanuric acid $(CNOH)_3$ is more commonly known as water conditioner or chlorine stabilizer and is often used to prevent the loss of chlorine to the effects of the sun. It exists in recreational swimming venues as a compound with chlorine. In aqueous solutions chlorinated cyanurates form cyanuric acid and a salt of cyanuric acid in equilibrium as Potassium dichlorocyanurate and potassium cyanurate respectively (Kowalski & Hilton, 1966). In studies conducted in recreational swimming pools in St. Louis County, Missouri, data showed that pools treated with cyanuric acid demonstrated better disinfection rates than pools without (Robinson, 1967). It was supposed that the consistent levels of cyanuric acid that could be obtained provided more effective sanitation. In contrast to Kowalski and Hilton (1966) the evaluation of effectiveness of chlorine against viruses and bacteria, cyanuric acid was shown to inhibit the effect of chlorine (Shields, Arrowood, Hill, & Beach, 2009; Steininger, 1991; Yamashita, 1988). One early study of the effect of cyanuric acid on the ability of chlorine to act as an oxidizer showed that it had a greater effect than pH on the effectiveness of chlorine to sanitize and that in the presence of cyanuric acid, free available chlorine did not exhibit the same bactericidal properties as without (Andersen, 1965).

As stated earlier HOCl is very often in some form of disassociation and it is in this form that if forms weak bonds with cyanuric acid protecting the chlorine from loss to the destructive effects of the sun, but also diminishing chlorine's ability to oxidize organic material. Of significant concern is the observation of decreased chlorine activity when cyanuric acid was in use in swimming waters (Fitzgerald & Dervartanian, 1969). This was noted specifically during periods when the use of the pool by an increased number of swimmers was observed. Significant levels of chlorine present in water, was markedly less effective against Cryptosporidium parvum, when cyanuric acid was also present (Shields et al., 2009). Swimming pool water is a complex mix of impurities, chemicals and factors. Because of this, it is difficult to consistently monitor chemical levels in water when depending on chemical parameters.

In a comprehensive study conducted on 11 recreation pools in Greece, the compliance with chlorination and pH standards were noted in only 27% and 64% of inspections respectively. The bacterial load noted in this investigation showed as low as 45% (*S aureus*) met suggested requirements, while none met requirements for Oxidation-Reduction-potential (Rigas, Mavridou, & Zacharopoulos, 1998).This would suggest that compliance with accepted standards for some parameters including chlorine and pH levels does not necessarily indicate safe levels of bacteria.

Acceptable chemical sanitation as well as pH levels, as defined by the local jurisdiction, in another survey conducted in Australia also demonstrated a consistent difficulty in maintaining adequate chlorine levels. In this study 41% failed to meet minimum chlorine levels. Furthermore, 37% did not meet acceptable levels for pH (Esterman et al., 1984). Although acceptable levels of specific species of interest, P. *auriginosa* and Naegleria*spp.*, were maintained, 29% of pools with adequate sanitizer level continued to demonstrate the presence of some unnamed species of amoeba.

In a study of 85 swimming pools in Amman, Jordan in which several samples were taken for sanitizer and bacteriological testing, results were similar to those obtained by Esterman et al. (1984). Thirty-eight percent of Jordanian pools tested failed to meet chemical requirements while 43.5% had unacceptable total coliform counts (Rabi, Khader, Alkafajei, & Abu-Agoulah, 2008).

The availability of chlorine at acceptable values has also been shown to not be a good predictor of the presence of microorganisms including Cryptosporidium *ssp* and Giardia (Maida, Benedetto, & Firenze, 2008). Since these studies did not include any pools which demonstrated acceptable ORP levels it is unclear if it would directly support a suggestion of superior value in terms of assessing pool water quality. It does however lead to further questions as to the value of chlorine dependent standards.

Oxidation Reduction Potential (ORP) is a direct reading of the potential of chemicals present in water to destroy viral and bacterial pathogens (McPherson, 1993). These levels are measured directly and therefore they must not be viewed in the context of other factors, such as cyanuric acid and pH that are affecting the pool. Oxidation-Reduction is a process by which electrons are transferred from one substance to another, one agent is said to be oxidized as it loses electrons while another complimentary agent is reduced as it gains electrons. Oxidized atoms no longer contain an electrochemical potential and becomes disassociated with the potentially harmful organism. In terms of oxidizing agents, its oxidation-reduction potential has appropriately been described as “a measure of its readiness to seize electrons” (Schmelkes, 1933). This effected organism is no longer viable and does not represent a potential threat to the health of recreation water users.

Chlorine is the most widely used oxidizing agent used as a sanitizer in recreational bathing venues (Black, Kinman, Keirn, Smith, & Harlan, 1970; Carpenter, Fayer, Troute, & Beach, 1999). The addition of chlorine under favorable conditions results in the development of an excellent bactericidal agent which can also be described as a strong oxidizer. The reaction that takes place in an aqueous solution with adequate chlorination is as follows:

$$Cl_2 + H_2O = HOCl + HCl$$

where HOCl is Hypochlorous Acid and HCl is Hydrochloric Acid

As it relates to swimming pool chlorination, HOCl as well as OCl-, hypochlorite ion is commonly described as free chlorine. Both of these compounds provide some bactericidal effect but HOCl is the more effective form. The penetrating efficiency of chlorine in this form is due to its modest size and its absence of an electrical charge, in fact its penetration into the cell wall is comparable to that of water. In contrast hypochlorite ion OCl- is relatively less effective due to its charged nature (White, 1986). Theoretically, the addition of chlorine as a sanitizer will proportionately effect ORP levels. In traditional colorimetric testing the presence of chlorine is demonstrated by color change, a product of the action of chlorine, an oxidizing agent, resulting in either the predominance of a purple colored product or a colorless one. More chlorine will result in more of the clear product known as imine. The relative amount of the colored vs. colorless product is then compared to a standard value. This is not necessarily the case primarily due to the many factors that affect chlorine values that can be obtained with current testing methods. The relationship between ORP and chlorine is a fundamental one. In contrast to chemical testing, the measurement of ORP is not limited by its inability to distinguish “active” and “inactive” forms of chlorine. It is a direct measure of electrical potential that is present in the water. The chemical test is susceptible to the effects of many factors including pH and dissolved solids in the water to name just a few.

The connection between chemicals, bactericidal properties, and electrical potentials has been studied for some time. In an early laboratory study this relationship was demonstrated (Schmelkes, Horning, & Campbell, 1939). In referring to chlorinated solutions the authors state: “The bactericidal effect of chlorine residuals can be correlated to potential measured in such solutions” (Schmelkes et al., 1939, p. 1538). The County of San Diego currently utilizes testing methods that are dependent upon chemical testing tools. These chemical tests are subject to error related to subjective reading of colorimetric tests. Because, the chlorine value is demonstrated in a gradient of color it is often difficult to distinguish the level of color with certainty. These testing methods also require chemicals to be purchased and stored. Such elements are susceptible to damage caused by improper storage and handling that may vary wildly from one jurisdiction to another. Additionally this equipment is subject to a date of expiration established by the manufacturer. Evaluating these factors is not necessary when ORP is used.

The measurement of ORP, has been shown to be a reliable determinant for assessing water sanitation (Carlson, Hasselbarth, & Mecke, 1968; Lund, 1961; Lund, 1965; Victorin, Hellstrom, & Rylander, 1972). In fact, several jurisdictions already have requirements for ORP. As early as 1936 when researchers at Harvard University studied the relationship between ORP and bactericidal properties there has been an effort to determine a standard value for acceptable Oxidation Reduction Potential. These requirements are included in the

Ohio administrative code 3701-31-07 (650mv), World Health Organization (2006, 680-720mv), Oregon Ideal Pool and Spa Parameters (750-800mv), and the Codes of the German Federal Health office (DeutschesInstitutfürNormung, DIN19643, 700-750mv), while the Colorado State Board of Health lists an ideal level at 650-850mv. Several other districts and organizations have established acceptable level of ORP in recreational bathing waters. The evaluation of oxidation potential with hand held meters is not subjective but is based on a numerical value, the actual oxidation-reduction potential measure in millivolts.

OBJECTIVES

The overall aim of this study for 177 pools and spas in San Diego County was to determine if the measurement of ORP could be shown to be a reliable determinant for assessing pool/spa sanitation.

The specific objectives were:

1. Is there a statistically significant relationship between ORP (mV) and levels of free chlorine residual (ppm)?
2. Is there a statistically significant relationship between ORP (mV) and levels of total chlorine residual (ppm)?
3. Is there a statistically significant relationship between ORP (mV) and levels of the chlorine stabilizer, cyanuric acid?
4. For pools/spas that comply with San Diego County chlorine residual level, what is the frequency of compliance with and accepted ORP limit of 650 mv?

CHAPTER 2

METHODS AND MATERIALS

We evaluated the correlation between ORP and current testing methods to determine if ORP values obtained from hand held devises are a reliable indicator of pool water quality, in comparison to results obtained through the uses of currently accepted chemical based testing methods. Most similar tests to assess ORP values were based upon laboratory test equipment or In-line meters (Erdinger, Kirsch, Gabrio, & Kühn, n.d.; Kimbrough, Kouame, & Moheban, 2006). Our investigation tested two available hand-held units. Previous attempts to assess hand held equipment are limited.

DATA COLLECTION

One hundred and seventy-seven public pool venues were tested with chemical tests currently accepted for use in the County of San Diego by the County of San Diego Department of Environmental Health. All bodies of water tested were located within the county of San Diego in the cities of Oceanside and Vista (Figure 1). The limited sample area was due to the nature of the tests and the limited availability of the data collections.

All venues tested were located within the County of San Diego (Figure 1). All testing with the exception of ORP testing was done with currently accepted testing techniques. Un-announced inspections were completed by a single environmental health specialist from the County of San Diego Environmental Health Department, in an effort to ensure consistency. Tested “pools” were public bathing venues and included pools, spas, waders, and commercial water park features (Figure 2).

All testing was done on-site at the time of the inspection. If possible all testing was done at the deep end of the pool away from return lines and in conjunction with manufactures suggested methods. Samples were taken for testing with the Taylor kit from Taylor Technologies, as well as the 4-in-1 DPD kit from Chemtura Corporation were taken at a depth and distance from the pool side of approximately 0.5 meters. Additional testing including those completed with Aquacheck test strip from Hach Company. ORP testing was

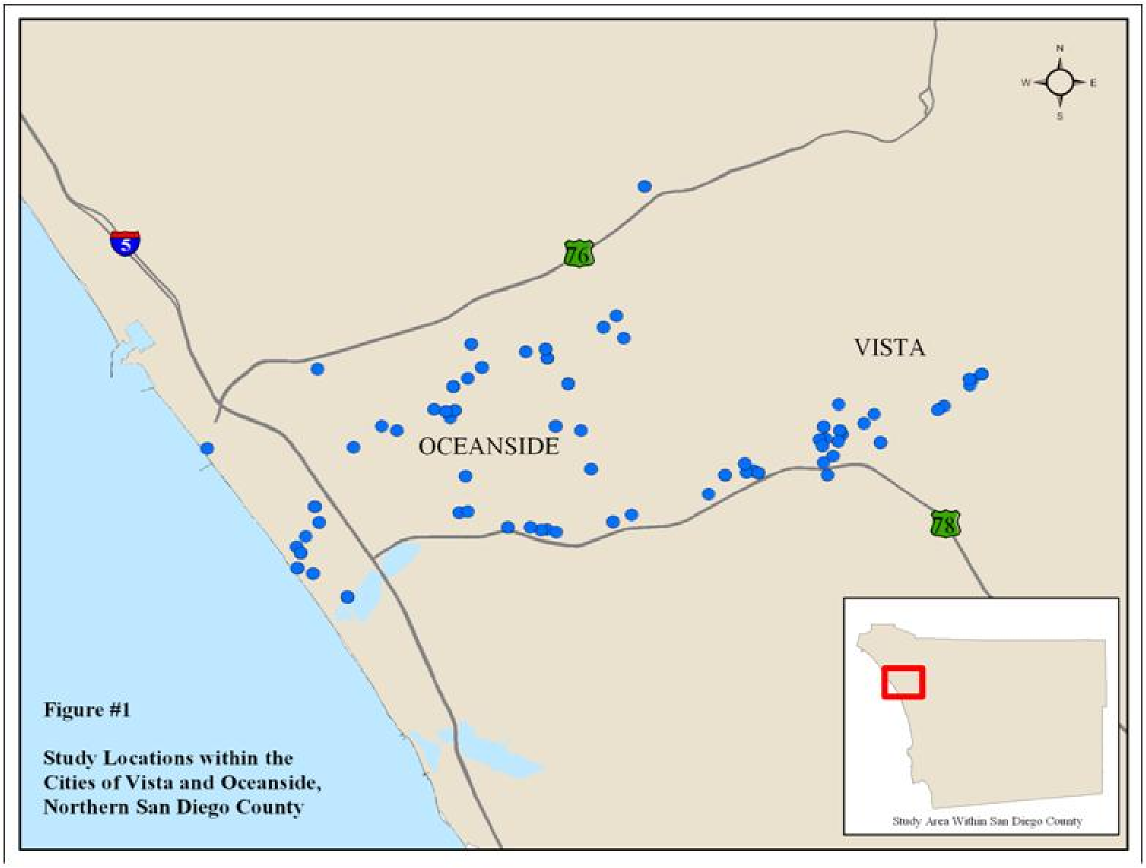

Figure 1. Location of test (GPS data from County of San Diego database).

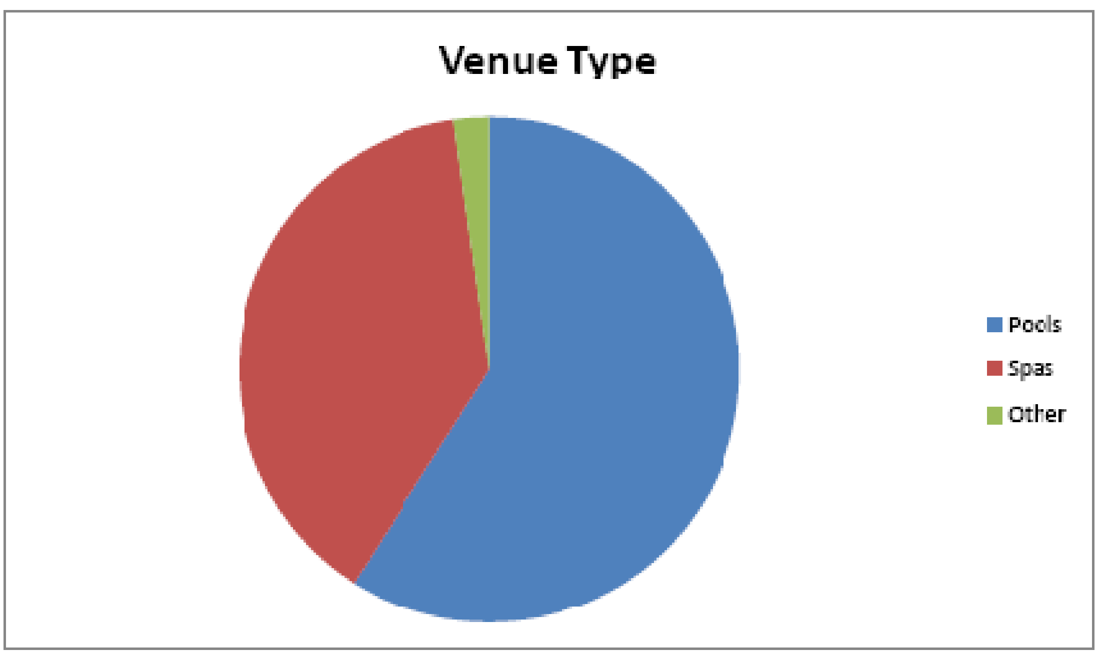

Figure 2. Venue type (Pool / spa / waterpark feature).

completed at a depth of no more than 25 cm due to characteristics inherent to those testing methods Aquacheck chemical testing was completed to assess: Chlorine sanitizer level, both available and total chlorine, pH, cyanuric acid, total hardness and alkalinity. Sanitizer levels were tested with both the 4-in-1 DPD kit and Taylor kits as well as with the Aquachek strips. pH was assessed with the 4-in-1 DPD kit and the Aquachek stip. The balance of testing with the exception of ORP testing was completed with the Aquachek strips. ORP testing results were obtained with Extech, Exstik model and Oakton ORPtestr10 both devices use a platinum electrode and an inert reference electrode. Water temperature was collected through use of a thermocouple manufactured by Cooper Atkins. Attempts were made to maintain certainty of testing by subjecting both meters to a 600 mV at 25°C standard, from Ricca.

Statistical analysis including p-values and Spearman Rho were calculated on SPSS statistical programs. Testing was done in a non-parametric manner as the values are likely to be a more conservative estimate of correlation. Because of the limitations of non-parametric testing it is less able to make assumptions about the data and is therefore considered to provide a more robust result. Non-numeric or values that were not consistent with the balance of data, i.e., greater than or not observed, were excluded from statistical analysis. Statistical analysis was completed to assess the relationship between the chlorine level and the ORP tester reading. Similar statistical analysis was completed to assess correlation between chlorine level and values obtained with the Extect meter. Comparative statistics were also used in an attempt to assess the relationship between ORP and cyanuric acid.

RESULTS

Hand-held Oxidation Reduction Meters were evaluated to assess their relationship to results obtained through traditional chemical based testing procedures. In a comparison performed with the ORPtestr vs. free chlorine chemical testing a statistically significant relationship was observed (p-value <0.05) between oxidation reduction potential and the level of free chlorine (see Figure 1). An evaluation of the ORptestr vs. total chlorine showed a similar significant relationship (p-value <0.05) (see Figure 2). Similarly, the hand-held Extech ORP meter also demonstrated a statistically significant (p-value <0.05) relationship between measured oxidation reduction potential and free chlorine (Figure 3) and ORP vs. total chlorine (p-value<0.05) (Figure 4).

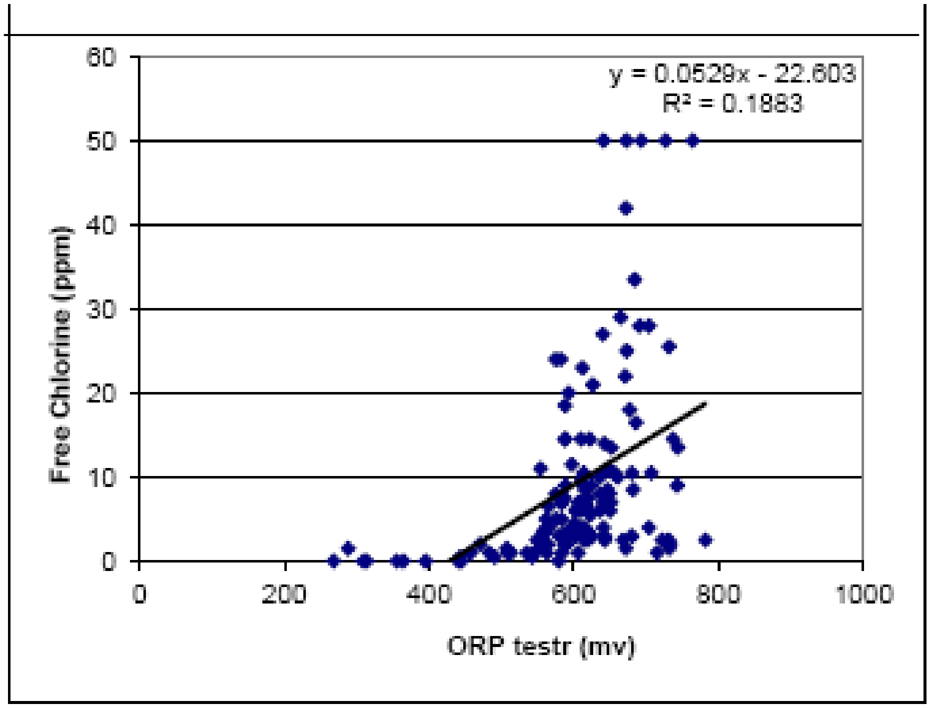

Figure 3. Free Chlorine vs. ORPtestr (p-value <0.05).

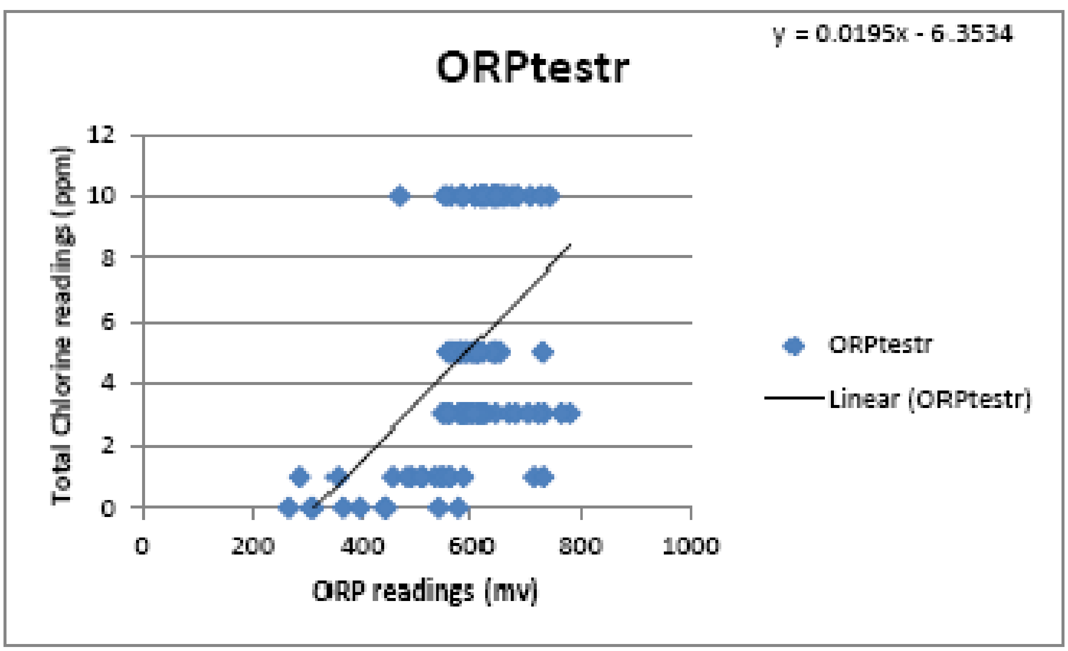

Figure 4. Total Chlorine vs. ORPtestr (p-value <0.05).

Cyanuric acid is a chemical that is used to protect chlorine from the destructive effects of sun light, and has been shown to effect chlorine values (Fitzgerald & Dervartanian, 1969) . Therefore an evaluation of the relationship between levels of cyanuric acid and ORP was evaluated. There was no significant relationship shown between the ORP measurements taken with either the ORPtestr, and Cyanuric Acid (Figure 5 and Table 1) or the Extech meter and Cyanuric acid (Figure 6 and Table 2) with p-values of 0.437 and 0.884 respectively.

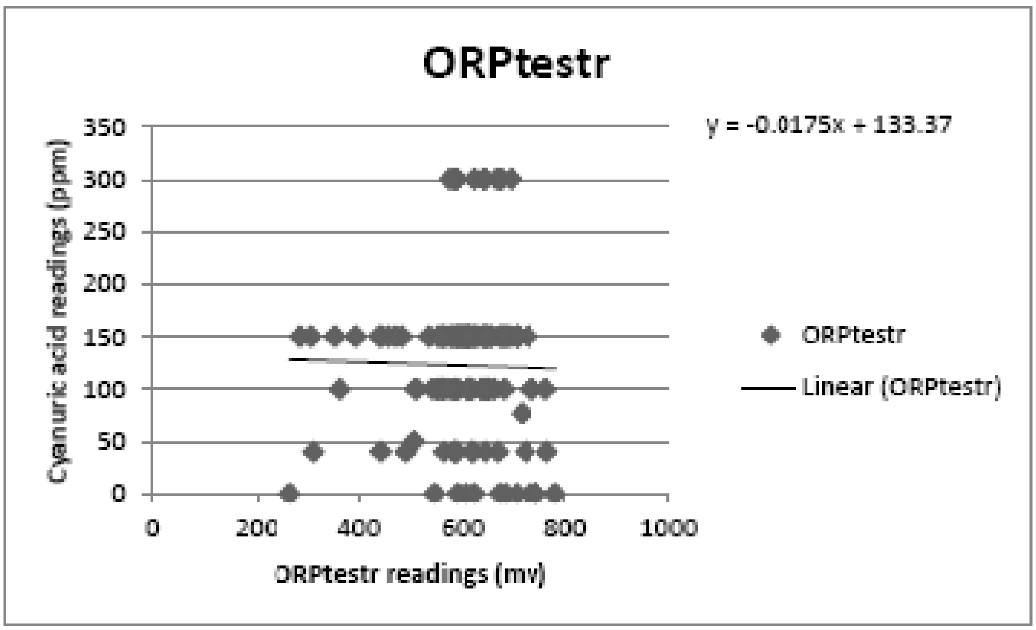

Figure 5. Cyanuric acid vs. ORPtestr.

Table 1. Cyanuric Acid Vs. ORPtestr

Correlations (Cyanuric acid reading vs. ORPtestr)	ORP Reading
Cyanuric acid reading Spearman's rho correlation coefficient	-0.066
Sig (2-tailed) ,p-value	0.437
N	142

The average chlorine value observed with the Taylor test kit when an ORP value of =/> 650mv was observed with the ORPtestr was 11.9ppm while the average of those that did not have a minimum ORP of 650mv had an average of 6.2 ppm chlorine as measured with the Taylor test kit.

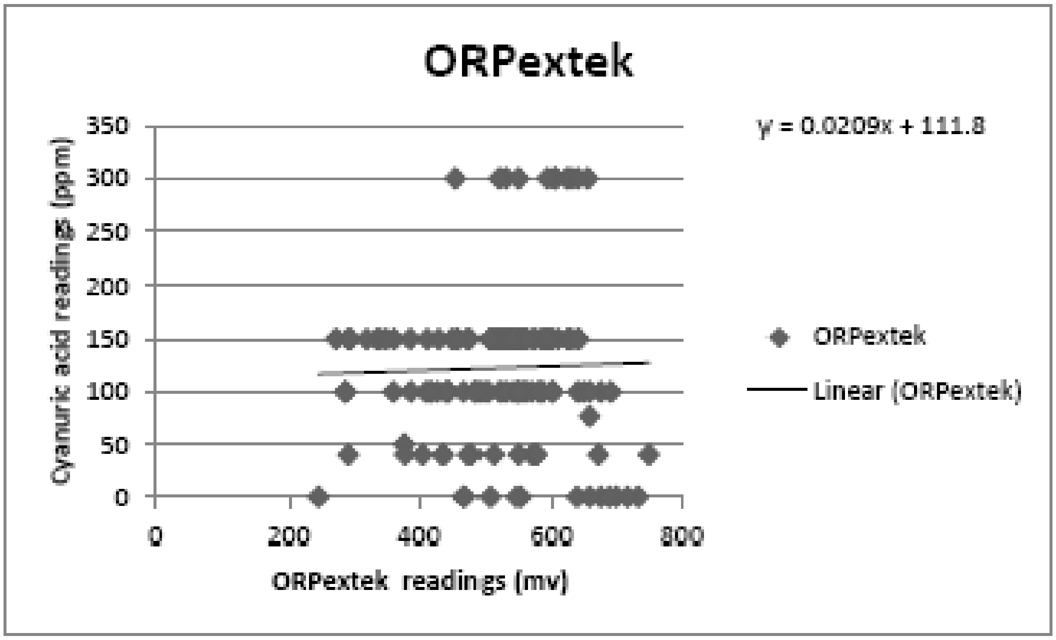

Figure 6. Cyanuric acid vs. ORPextek.

Table 2. Cyanuric Acid Vs. ORPextek

Correlations (Cyanuric acid reading vs. ORPextek)	**ORP Reading**
Cyanuric acid reading Spearman's rho correlation coefficient	0.012
Sig (2-tailed) ,p-value	0.884
N	142

An evaluation of the hand held equipment used in this study found no significant loss of sensitivity or accuracy of either meter due to regular use (Table 3).

Characterization of the data observed in this study (Table 4) demonstrated a high level of pools that did not meet standards for chlorine 23.5% and pH 27.9.

Table 3. Standardization (600mv Standard)

Test Date	**ORPtstr mv (Average of three)**	**Percent of Standard (600mv)**	**Extech mv (Average of three)**	**Percent of Standard (600mv)**
8/19/09	571.33	-4.8	591.00	-1.5
10/5/09	588.33	-2.0	595.33	-.7
5/5/10	591.00	-1.5	595.66	-.7
9/28/10	590.00	-1.7	592.33	-1.3

Table 4. Water Chemistry Parameters

Parameter	Mean*	High/Low	Percent Meeting Standard**
Pool			
Temperature	77.2° F	99 – 54° F	n/a
Total Chlorine (Taylor)	n/a	n/a	n/a
Free Chlorine (Taylor)	5.7 ppm	24-0 ppm	67.9
Total Chlorine (Aquachek)	4.55	10-0	n/a
Free Chlorine (Aquachek)	4.81	20-0	76.5
Cyanuric acid (Aquachek)	104.4	0-300	59.8 (100 ppm or less)
pH (Aquachek)	7.5	8.4-6.2	72.1
ORPtestr	600	782-314	18.4 (>or=650)
ORPextech	508	750-273	6.8 (>or=650)
Spa			
Temperature	103.2° F	106-100° F	77.7 (<or=104° F)
Total Chlorine (Taylor)	n/a	n/a	n/a
Free Chlorine (Taylor)	14.6	50-0 ppm	40.4
Total Chlorine (Aquachek)	5.76	10-0	54
Free Chlorine (Aquachek)	9.3	20-0	41.8
Cyanuric acid (Aquachek)	149.39	0-300	30.8 (100 ppm or less)
pH (Aquachek)	7.8	8.4-6.2	50
ORPtestr	610.7	764-268	39.3 (>or=650)
ORPextech	551.1	717-246	12.5 (>or=650)

*Mean may be affected by test limitations / categorical nature of data.

**San Diego County; 650mv standard based on published data as no standard in place in San Diego County.

Failures to meet required limits of chlorine and pH were more prevalent in spas. Only 59.6% met requirements for chlorine and 50% of values were acceptable when compared with pH values required by San Diego County Code (Table 4).

When ORP values gathered in my evaluation were compared to all Minnesota “pool” requirements (Pool Water Conditions, 2009) for water quality including Free chlorine, pH, alkalinity, combined chlorine and cyanuric acid an equal number demonstrated a value less than 650mv (9 of 18), fifty percent of the time. The exteck meter demonstrated a value of 650mv or higher 5 of 18 (28%) and less than 650mv 13 of 18 (72%) of the time under the same comparison.

CHAPTER 3

DISCUSSION

In this study, data showed a large proportion of pools that did not meet the requirements of the San Diego Department of Environmental Health (Table 4, p. 13). Of the pools tested, 23.5% did not have the regulatory value of 1-10 ppm for free chlorine. When spas were tested 59.6% did not fall within the desired free chlorine limits. The pH values that were obtained (using aquacheck) were also frequently out of the desired range of 7.2 - 8.0 with 27.9% of pools and 50% of spas having a value outside of the required limits. For cyanuric acid, values (using aquachek) in pools (40.2%) and Spas (69.2%) also did not fall within the desired range of 0-100 ppm.

An ORP value of 650mv has been shown for provide adequate antibacterial and antiviral activity (Carlson et al., 1968). ORP values that met this 650mv limit were surprisingly infrequent for both the ORPtestr and the Exteck meter. Pools and spas tested with the ORPtestr failed to demonstrate the 650mv value in 81.6% of pools and 60.6% of spas, while the Extech meter was less likely to demonstrate the desired value 93.2% and 87.5% of the time, respectively. This relatively low frequency of compliant pools would suggest the need to look at other methods for assuring compliance, including more frequent testing and increased pool operator education in an effort to increase the number of pools that meet required values.

This evaluation of ORP value as a tool to assess water quality was mixed. Sufficient evidence was found (Figures 1- 4, pp. 8-10), to consider the use of hand-held ORP meters for evaluating the safety of recreational pool waters. Indeed, a statistically significant relationship between ORP was found for both free and total chlorine for both ORP meters tested (Figures 1-4). Despite this, the future of these testing devices for measuring recreational water quality is still controversial. Some studies, such as the present one, have concluded that satisfactory disinfectant test results can be correlated to ORP readings. Indeed, an ORP value of 650mv has been shown for provide adequate antibacterial and antiviral activity (Carlson et al., 1968; Lund, 1961) and has been adopted by a number of jurisdictions including the State of Ohio and the Colorado Board of Health (650-850mv). Another recent study by Bastian (2009) of 162 pools and spas measured chlorine levels with traditional chemical testing methods and compared these with ORP values obtained with ORP testing equipment. Bastian (2009) also showed a direct and statistically significant (p-value, 0.001) correlation between free chlorine and ORP; however, Bastian could not find a correlation between compliance with the Minnesota Pool Code (§4717.1750) and an ORP of 650mv or greater. This author concluded that 40% of code-compliant pools had ORP values <650 and also found that 80% of the 65 non-code compliant pools had an adequate ORP. In a similar way, the percentage of pools that the present study found to be code compliant (by free chlorine level alone) with an ORP less than 650 mv was 78.2% (86/110). The similar ORP testing device the Extech Exstik in the present study, failed to produce an ORP of at least 650 in 81% (89/110) of free chlorine compliant pools.

Pools and spas were similar in their results when evaluated individually with the ORPtstr, 80% (64/80) and 78% (21/27) respectively, did not have the minimum ORP value of 650 mv when they were compliant for free chlorine as determined by traditional measures. Similar results were observed when the Exteck model was evaluated, with 92.5% of pools and 88% of spas not having an ORP of 650 mv or greater when they were free chlorine code compliant. When ORP values from San Diego County “pools” were evaluated against all requirements of the Minnesota pool rules which include pH, alkalinity, combined chlorine and cyanuric acid a similar result to that of Bastian (2009) was observed, with 9 of 18 (50%) having an ORP of 650 mv or less (ORPtstr). When the Extech meter was evaluated against Minnesota compliant “pools,” thirteen of 18 (72%) had ORP values of <650 and 5 of 18 (28%) had ORP values of =>650mv. Neither the results observed by Bastian (2009) nor those of the present study showed a high percentage of pools/spas that both met MPC compliance and had adequate ORP levels. The San Diego pool requirements include accepted ranges for pH, free chlorine and cyanuric acid. Similar results to those above were obtained when the compliance with San Diego pool rules were compared with ORP values. Of 55 “pools” that were compliant for pH, free chlorine and cyanuric acid, only 14 (25.4%) had an ORP value of 650 mv or greater. It remains unclear why this ORP level of 650 mv was not clearly associated with compliance for both the Minnesota and San Diego pool requirements, especially since there was a strong statistical correlation observed between ORP and free chlorine levels in both datasets. However, the fact that a relatively high frequency of chlorine-compliant pools/spas were not compliant with the accepted 650 mv OPR level, suggests that OPR might represent a more conservative measure of pool/spa sanitation.

The number and scope of previous analyses of ORP as a means of assessing pool water quality is rather limited. As explained in the introduction, several and varied factors can affect the overall quality of swimming pool water. They include bactericidal factors which may evaluated in terms of ORP, but also include many physical characteristics including type of filtration and frequency of backwashing. Tests performed on pools do suggest some value in the use of ORP (as opposed to chlorine levels), to assess water quality. Victorin (1974) found that although neither oxidation-reduction potential nor chlorine demonstrated a strong correlation with heterotrophic plate count (HPC) levels of bacteria, the ORP reading provided more accurate results. Victorin (1974) fell short of advocating for the use of ORP alone as an indicator of water quality stating [redox is not an] "absolutely sure yardstick, but the error is less than with free chlorine." The Victorin (1974) study further concluded that much of the effect that any sanitizer may have is based upon physical factors. The author concluded that the efficiency of the filtering system (ie., the frequency of backwashing), is probably critical for the disinfecting effect of the available chlorine. Victorin (1974) also found that in baths that exhibited a relatively high bacteria count, fecal coliforms were not observed. This observation highlights a criticism of the use of fecal coliforms to assess water quality, but this latter subject is a much bigger question that can be addressed here.

Testing conducted by Rigas et al. (1998), showed that compliance with ORP standards was lacking in all instances they measured in recreational pools, including those displaying acceptable values for chlorine (obtained with traditional chemical based testing techniques). Other investigators (Lund, 1965), suggested that oxidation potential allows a better method to evaluate water quality than residual chlorine. Inactivation of poliovirus was found to be more related to ORP than the level of chlorine residual. Lund (1965) also pointed to a technical limitation of ORP testing stating, "Drawbacks connected with the potential measurements seem to be first of all the technical ones, i.e., how to find a way of maintaining clean electrodes." A similar concern was raised by Kim and Hensley (1997) who stated "contamination of the electrode surfaces or internal electrolyte can lead to poor electrode response." Both Lund (1965) and Kim and Hensley (1997) go on to suggest that technological advances and a regular cleaning regimen, may serve to address such concerns. From the work and quality control conducted in this study, it appears that regular assessment of accuracy through the use of a predetermined standard is both easily accomplished, and acceptably accurate. In fact, in the present evaluation, little maintenance of the equipment was performed beyond regular rinsing with tap water. Measurements taken periodically against a known standard at three different times during our data collection failed to show a significant deterioration on the equipment's ability to detect the ORP standard's value (see Table 3, p. 12).

Other characteristics of the meters to be used to calculate ORP may contribute to concerns related to such meters. The relationship between potential as measured by ORP meters and other factors in the measured medium in this case, recreational pool water, can be represented by the Nernst equation. This equation can be used to determine reduction potential in a system. The equation requires the inclusion of factors such as temperature and natural log (ln) of the concentration of the chemical of interest to determine the potential of the media. An evaluation of the ln of the chlorine levels collected in swimming pools compared to both meters resulted in significant p-values, ORPtester (p-value = < 0.05) and the Extech (p-value = < 0.05). These results were not different than statistical results demonstrating a significant correlation between ORP readings and chemical chlorine levels measured in ppm. A low R^2 (coefficient of determination) was observed in all data sets comparing ORP and chlorine levels measured in ppm.

Comparing ORP readings with the ln of collected chlorine values made only a marginal difference in the R^2 values, ($R^2 = 0.106$) for the ORPtestr (Figure 7) and ($R^2 = 0.078$) for the Extech meter (Figure 8). Though it is unlikely that the temperature range observed in data collected would result in large calculated ORP differences, an attempt to statistically evaluate this characteristic was conducted. Because there is a difference in average temperature between pools (77.2° F) and spas (103.2° F) the R^2 values were calculated separately. Spa R^2 values were observed to be higher when measured with the ORPtstr ($R^2 = 0.265$) (Figure 9) and with the Extech meter ($R^2 = 0.265$) (Figure 10) than values measured in all venues including pools and spas ($R^2 = 0.188$) (Figure 1, p. 8) and ($R^2 = 0.2$) (Figure 3, p.10) respectively. The slight increase in these values cannot be

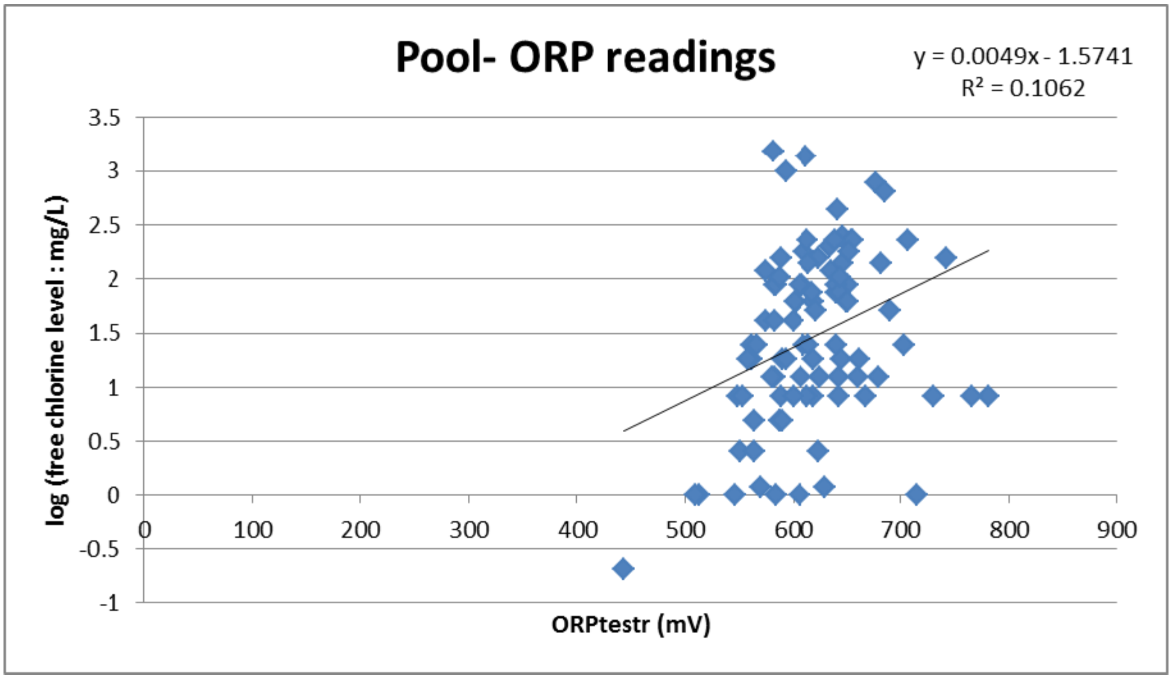

Figure 7. Pool – ORPtestr vs. chlorine ppm (log).

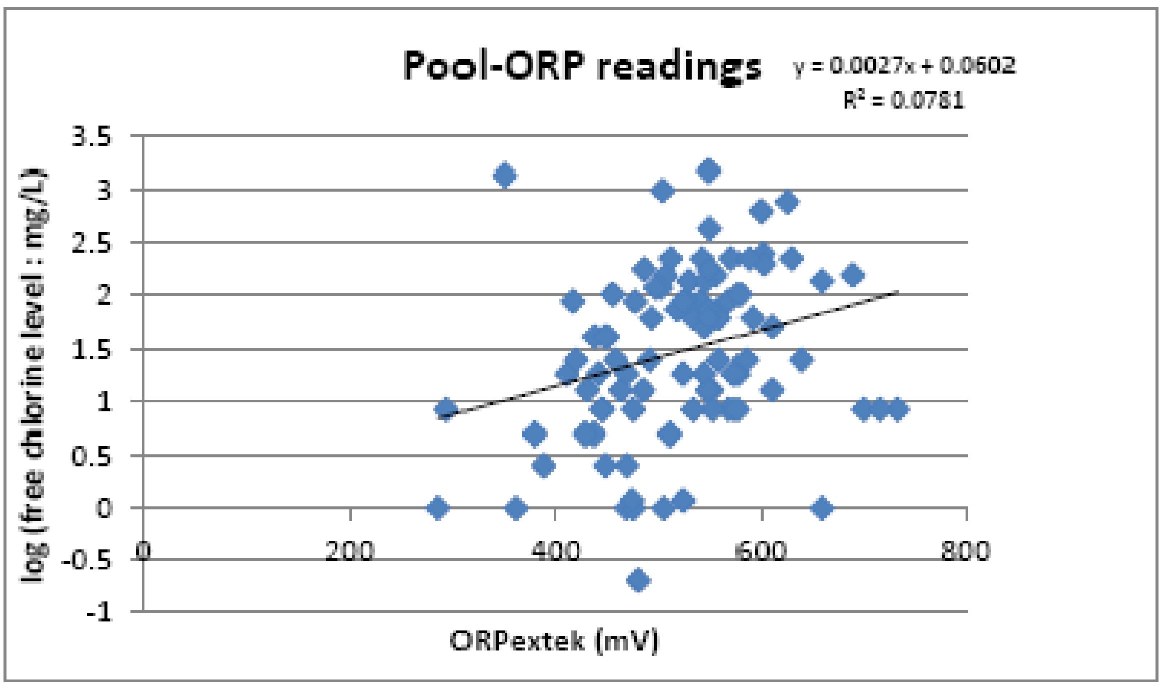

Figure 8. Pool - ORPextech vs. chlorine ppm (log).

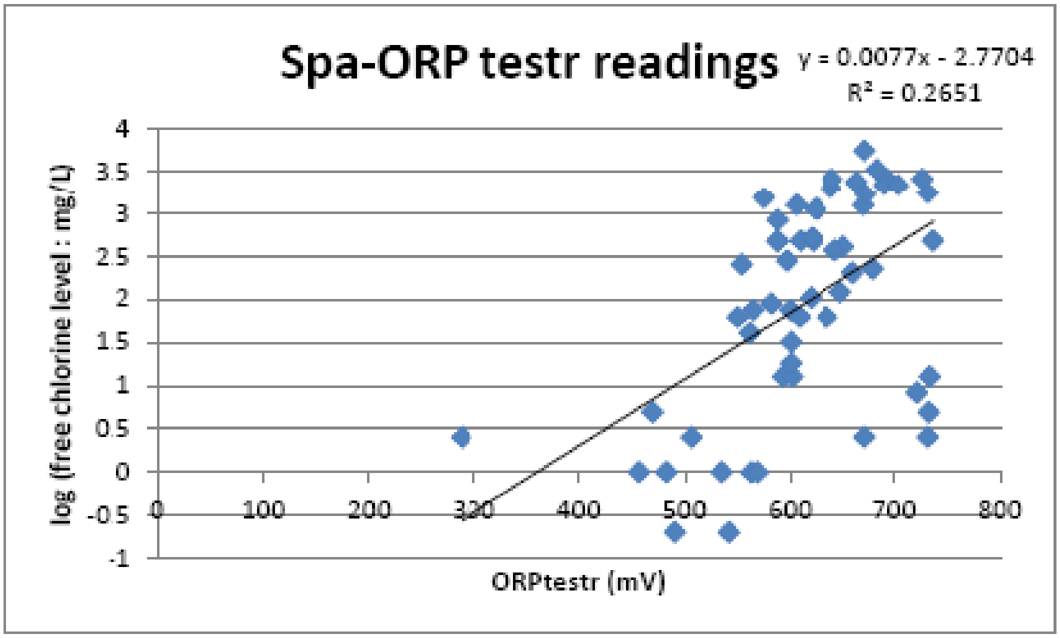

Figure 9. Spa - ORPtestr vs. chlorine ppm (log).

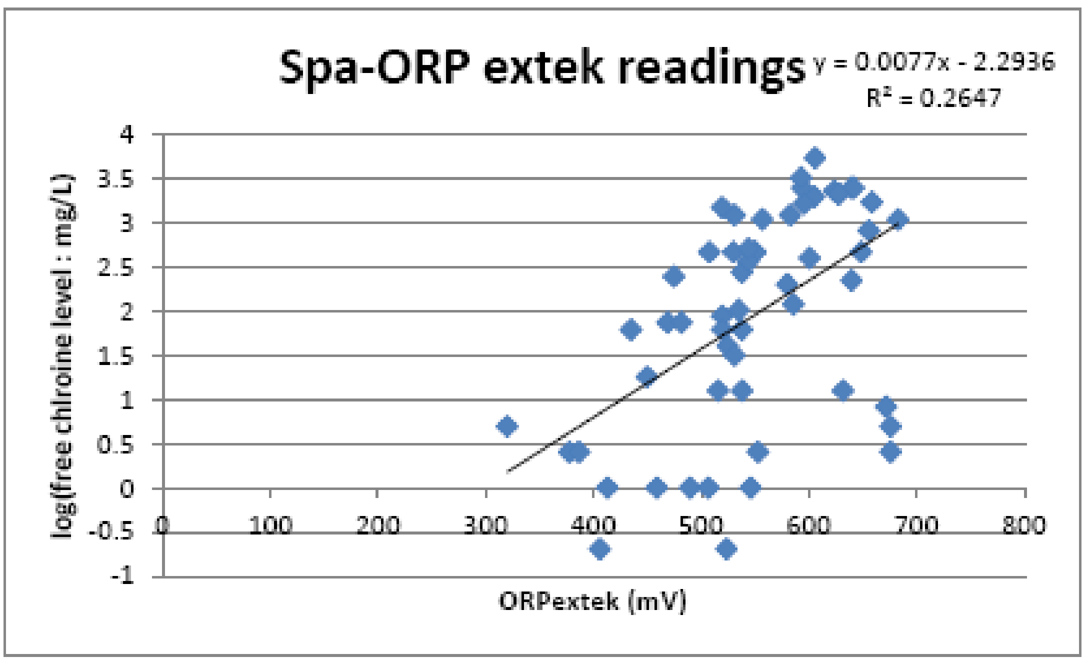

Figure 10. Spa - ORPextek vs. chlorine ppm (log).

attributed to the temperature alone because other variables, most notably, chlorine levels are not included in this comparison. Furthermore, the increased R^2 values observed in spas are still relatively small.

Though the geographic location of venues tested in our research was limited in size, two cities (Oceanside and Vista) in the northern portion of San Diego County, there is little reason to conclude that a larger sampling area would necessarily provide a stronger sample set. The case for the use of ORP devices to assist in the evaluation of recreational water quality is strengthened by the fact that in the present investigation, ORP values obtained consistently produced more conservative results when compared with traditional testing equipment. Only 24 of the 125 (19.2%) pools/spas that were chlorine code compliant also had an ORP reading of at least 650 mV. Because readings obtained for chlorine residual with traditional equipment, are highly dependent upon the values of other chemicals such as cyanuric acid and ambient conditions (e.g., pH), accepting chlorine readings as a primary indicator of water quality is also not without risk. Any evaluation of recreational waters must be based upon several factors. The use of ORP measurements in conjunction with other testing methods can provide a more robust indication of recreational water quality and safety.

ORP testing equipment will continue to evolve, and greater understanding of the factors relating to recreational water as a complete system will assist in this evolution. Many conventional limitations exist that could result in poor maintenance of water quality beyond the limits related to chemical testing equipment. It has been reported that in an investigation of 120,975 swimming pools, inspections identified violations related to disinfection in as many as 10.7% of the total, and additionally, 21.4% showed other water quality deficiencies that included violations of pH levels, algae presence, bacterial quality, total alkalinity, and dissolved solids, among others. An additional 3.3% had violations directly related to improper test kit use (Hendrix, 2010). These numbers would suggest that current testing methods do not produce adequate compliance. Hendrix (2010) acknowledges that pool inspectors do minimize the risk related to recreational water infections through the use of traditional testing methods such as chlorine residual. One concern is the infrequent nature of their inspections. The minimal number of physical inspections completed by government inspectors, usually 2-3 per year, could contribute to the lack of maintenance of proper sanitation levels. Because the number of days on which testing is actually done is minimal, it was suggested that current testing methods do not provide adequate assurance that recreational water quality is maintained as required by local jurisdictions(Hendrix, 2010). More consistent and simpler testing equipment such as ORP testers could encourage more self-testing by pool operators. Easily readable and maintained equipment which does not require purchase and storage of chemical components could encourage more frequent testing. Furthermore, ORP testing by either hand-held or in-line equipment would allow much easier access to test data than that which is possible with current chemical based equipment. Direct downloading of ORP data by in-line equipment or a process by which data from ORP devices are downloaded manually would give jurisdictions the ability to monitor data more often and share data to better document trends between jurisdictions. This capability would also provide a tool to help in the investigation of illnesses and outbreaks related to recreation swimming waters.

CHAPTER 4

CONCLUSION

In this study of Pools and Spas in San Diego County, there was a statistically significant relationship between ORP (mv), measured with the ORPtestr, and levels (ppm) of both total (p-value <0.05) and free chlorine residual (p-value < 0.05). The comparison between ORP (mv) was also found to be statistically significant when the ORP values were measured with the Extech model ORP meter. There was no statistically significant relationship found however between ORP (mV) and levels of the chlorine stabilizer, cyanuric acid (p-value 0.437) when ORP was measured with the ORPtestr and (p-value 0.884) when measured with the Extech model.

Despite the findings above, the research to this point, including the results obtained through the efforts here, there remains some obstacles to using ORP to evaluate recreation pools water sanitation.

As demonstrated by my results and those of a similar study (Bastian, 2009), the presence of free chlorine at sufficient levels according to local requirements does not ensure adequate oxidation-reduction potential values (> 650 mv). The observation that adequate free chlorine levels do not provide code compliance (although they correlate with ORP) was observed in this study and has been noted by other observers.

Furthermore, the relatively low coefficient of determination (R^2) between free chlorine and ORP as measured with the ORPtestr (R^2=0.1883) as well as free chlorine and ORP measured with the Extech meter (R^2=0.2) would suggest that much of the variation that is observed with both meters cannot be explained exclusively by this relationship. As previously noted, comparing the natural log of the concentration of chlorine values did not change the calculated R^2 to a meaningful extent.

A finding of significance does not mean that there is a strong relationship, and the low variance would suggest that there is not a strong relationship between ORP and total chlorine. The imposition of the relative importance of significance versus variability is largely determined by the goal of the investigation. Though the relatively low coefficient may not be sufficient to forecast of predict future outcomes, a statistically significant result with a low coefficient of determination may be accepted for the purpose of identifying relationships. Until the relationship between oxidation-reduction potential, free chlorine and the potential presence of harmful bacteria is better understood, oxidation-reduction potential should only be used in conjunction with other methods to assess water quality.

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