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Bench scale investigation of the effects of a magnetic water treatment device in pool systems on chlorine demand

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ABSTRACT

Chlorination is the most common form of water disinfection for recreational swimming pools and represents a major cost for many large-scale operations. Reducing the chlorine demand in a system may alleviate these costs by decreasing the amount of chlorine required to maintain a target disinfection residual. While magnetic water treatment is common for removal of pipe scale, impacts on chlorine demand have not been evaluated. The application of a commercial magnetic treatment device significantly ($p < 0.05$) reduced the chlorine demand by 13.8 % within 24 h, due to a reduction of monochloramine (NH_2Cl), when applied to a simulated pool system. Subsequent breakpoint chlorination through the addition of calcium hypochlorite ($CaOCl_2$) resulted in a 30.8 % increase in free chlorine concentration. Additionally, a 1-h exposure to the magnetic field resulted in a 6.1 % reduction in monochloramine compared to the control, demonstrating that transient flow-through treatment can yield a reduced yet still significant effect. Mechanistically this effect could be due to the magnetic field effects (MFE) influencing the electron configuration of compounds in the system, thus altering reaction equilibria to favor more volatile chloramine species. This treatment is potentially a cost-effective method to improve the efficiency of chlorination via the demonstrated reduction of chlorine demand.

1. Introduction

Chlorination is one of the most common forms of water treatment, especially in swimming pools, due to its effectiveness and low costs. However, in large-scale systems the cost of chlorination can quickly increase as a greater chlorine demand is introduced into the system. Therefore, technologies are desirable that can reduce the chlorine demand and/or improve the efficiency of chlorine usage while still maintaining the target disinfection residual. There have been anecdotal claims of improvements to water quality in both cooling tower and pool systems as well as reduced chlorination costs of ~$40,000 USD annually in resort-style swimming pools through the use of magnetic technologies (P. Basha, Personal Communication). This prompted an investigation into the potential effects of such devices. While not commonly used in pool systems, magnetic treatment of water may hold promise due to the influence of magnetic fields on chemical reactions with charged or polar intermediates [1–4], including the chloramine forming reactions involving $HOCl^-$ or OCl^- with NH_3 or with organic molecules.

Many water treatment applications, such as the disinfection of pool waters, utilize free chlorine in the form of hypochlorite ions (OCl^-) or hypochlorous acid (HOCl) because of their reactivity with both inorganic and organic contaminants [5–7]. The amount of chlorine that is consumed by these reactions is termed the “chlorine demand”, which also dictates the amount of chlorine that must be added to the water to maintain the target disinfection residual. When the molar ratio of the Cl:N is <1:1, chloramines are formed as the free chlorine reacts with NH_3 or organic molecules. These chloramines have a much weaker oxidative potential than free chlorine and are therefore less desirable as a disinfectant in these systems. The sum of all the chlorine species in the system (free chlorine, chloramines, organic chloramines, etc.) can be described as the total chlorine. The relationship between the total chlorine as the free chlorine dose is increased in a system with nitrogenous compounds is described in Fig. 1. As free chlorine is added and the ratio of Cl:N increases to >1:1, chloramines are oxidized to various nitrogen species (N_2, NO_3, NCl_3) [8]. The point at which this occurs is termed the “breakpoint” (Fig. 1). When the breakpoint occurs, all organic and inorganic contaminants are degraded. For swimming pools, a Cl:N ratio > 1 along with a sufficient free chlorine residual are maintained such that should any contaminant be introduced into the pool it will be degraded while retaining a safe chlorine residual. Any further addition

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of free chlorine will remain as free chlorine as there is no chlorine demand remaining in the system. The magnitude of available free chlorine that is lost due to the breakpoint is related to the amount of chloramines in the system that are imparting a chlorine demand. Thus, by reducing the amount of chloramines present in the water the free chlorine consumed during the breakpoint is also reduced. Therefore, one possible way in which the final free chlorine is increased under the presence of a magnetic field is to reduce the chlorine demand prior to the breakpoint by influencing these chloramine forming reactions.

The use of magnetic treatment in water systems is not a new concept. Magnetic treatment has been utilized across various industrial applications for removal of pipe scale by altering the formation of calcium carbonate crystals [9–12]. Tai et al. [12] documented a change in $CaCO_3$ formation under various saturation and pH conditions, but noted recirculation was necessary for these effects to manifest owing to the magnetic effect needing time to develop. While many of these studies document the removal of scale resulting from magnetic field effects (MFE) interfering with $CaCO_3$ crystals formation, it remains unclear as to the exact mechanism that causes this, highlighting the difficulty of elucidating MFE at a mechanistic level in real world scenarios.

The objective of this study was to evaluate the potential for magnetic water treatment to improve chlorination practices by documenting the MFE on chlorine demand in a simulated pool system. This was achieved through a batch study by evaluating the effects of magnetic water treatment on chlorine demand through the addition of NH_3 to a simulated pool system containing free chlorine, and the resulting impact on chloramine formation and removal. The chloramine forming reactions have been well studied and shown to have polar compounds (OCl^- and NH_3), which may be influenced by a magnetic field [4,13]. While the use of organic compounds would mimic inputs of bathers entering the pool (via deposition of bacteria, sweat, dirt, etc.), ammonia (which may be deposited by bathers [14–16]) was used to simplify the system and limit the number of reactions occurring. Evaluation of this technology on chlorine chemistry may provide a unique tool for industries to utilize to reduce costs or improve water treatment in this and other water systems.

2. Materials and methods

2.1. Description of the magnetic treatment device

The magnetic treatment device, designed for placement directly into the water, was obtained from Vodaa Technologies. The unit is 100 cm × 20 cm × 18 cm (L × W × H) (Fig. 2). The magnetic treatment device was operated at the maximum power for the given power supply (3.87 A, 55.5 watts and utilizing 0.055 kW·h). Magnetic field strength was measured by DC Gaussmeter Model GM-1 HS (AlphaLab Inc., USA), and produced a maximum magnetic field of 210 gauss. Average cost usage ~0.644 cents US$ per hour based on the average kW·h in the United States [17]

2.2. Preparation of chlorine stock solutions

Industrial grade calcium hypochlorite (70 % free available chlorine) (LPM Manufacturing Inc. Phoenix, AZ) was dissolved in deionized water to achieve a concentration of 300 mg/L free chlorine. Industrial grade sodium hypochlorite (10 % NaOCl by weight) (Apex Chemical Corporation, Scottsdale, AZ) was also prepared at 300 mg/L free chlorine, and used to assess any potential differences due to chlorine source.

2.3. Analytical methods

Free and total chlorine were analyzed by Hach DPD free chlorine or Hach DPD total chlorine using a Hach Pocket Colorimeter II (Loveland, CO) following the manufacturers recommended protocol. In brief, cuvettes were washed 3 times with sample water to remove any contaminants. After rinsing, 5 mL of sample was added to the cuvette and two DPD powder pillows for either free chlorine or total chlorine were added and dissolved by shaking. The color was allowed to develop for 30 s or 3 min respectively and measured with the spectrophotometer.

Free ammonia and monochloramine were analyzed by Hach Monochlor F using a Hach DR-3900 Spectrophotometer as per the manufacturers protocol. In brief, cuvettes were rinsed with sample water 3 times before finally filling with 10 mL of sample water. Samples analyzed for free ammonia were treated with Hach Free Ammonia Chlorinating Solution, inverted to mix, and allowed to react with the sample for 1 min. One Hach Monochlor F Reagent DPD powder pillow was added to each sample and color developed for 5 min before measuring. Monochloramine was measured following the sample protocol as free ammonia without the addition of the ammonia chlorination solution. Requisite dilutions for free ammonia and monochloramine were made using deionized water prior to performing the assay. pH was measured using a Corning pH meter 445 and Fisherbrand™ Accument™ pH probe. All analytical assays were performed within 30 min of sample collection.

2.4. Preparation of bench scale batch experiments

Bench scale batch experiments were carried out in 208.2 L polypropylene bins (Home Depot, USA) containing a magnetic treatment device, a submersible water heater, and a submersible pump (Kedsum-1500). Chambers and all components were cleaned by soaking in acidified water for 30 min to remove calcium residue, rinsed twice with dH_2O, and wiped down with 70 % EtOH.

Each chamber was filled with 151 L of tap water, chlorine stabilizer as 4.53 g of industrial grade cyanuric acid (LPM Manufacturing Inc. Phoenix, AZ) and chlorinated with $Ca(OCl)_2$ stock solution in excess to remove any residual chlorine demand. The magnetic treatment device

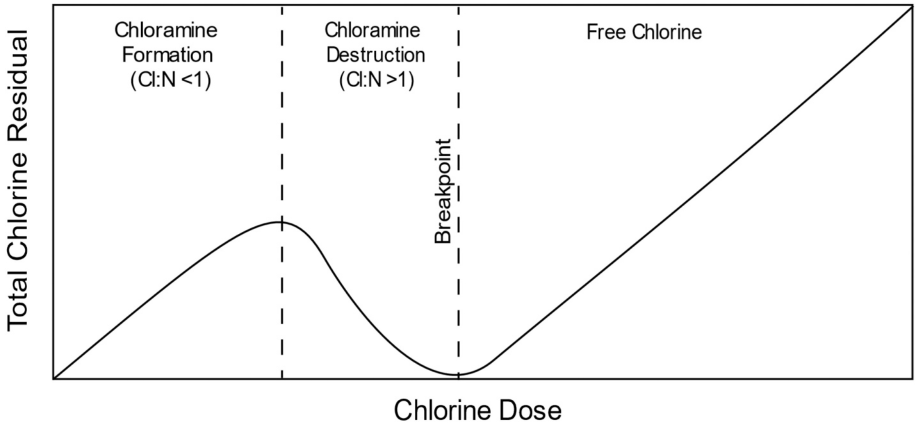

Fig. 1. Breakpoint chlorination curve.
At chlorine to nitrogen molar ratios of <1, chloramines are formed which contribute to the total chlorine residual. As the chlorine to nitrogen ratio increase to >1 chloramine destruction by free chlorine occurs. The point in which all chloramines have been degraded is called the breakpoint, the magnitude of which is equal to the demand caused by the chloramines. After the breakpoint no chlorine demand remains thus, all additional chlorine added remains as free chlorine.

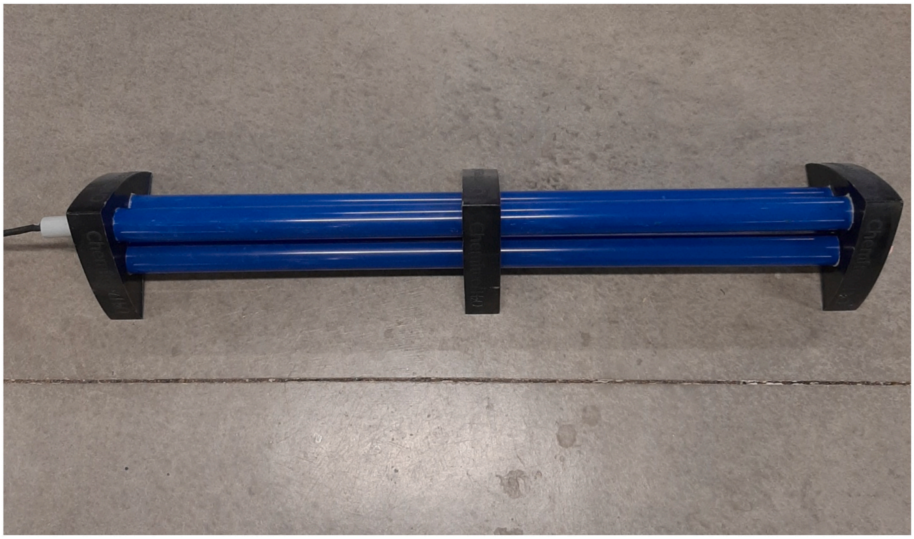

Fig. 2. Magnetic treatment device.
The magnetic unit dimensions are 100 cm × 20 cm × 18 cm (L × W × H) and is designed to be in direct contact with the water. The magnet produces a maximum field strength of 210 gauss when run at 3.87 A.

was submerged directly in the water along with the water heater and the pump (Fig. 3). The water heaters and the magnetic treatment device (test chamber only) were turned on and the system was allowed to equilibrate overnight to 25 °C. This temperature was maintained throughout the duration of experimentation through the ambient heat produced by the magnetic treatment device or a water heater. No magnetic treatment device was present in the control system unless otherwise stated. The pump flow was set to the maximum flow rate (1500 L/h) and directed along the length of the bin to facilitate recirculation of the water in the container. The container was covered with a plastic pool cover to reduce contamination and light.

2.5. *Experiment 1: evaluation of 24 h constant exposure to magnetic field on chlorine demand*

The chlorine demand under continuous exposure to the magnetic field was evaluated by the generation of chloramines, followed by subsequent breakpoint chlorination in a 151 L batch study. Each system was adjusted to an average free chlorine concentration of 5.3 ± 0.2 mg/L as measured by Hach Free Chlorine DPD though the addition of $Ca(OCl)_2$ stock solution. The magnetic field was applied to the system and an ammonium "contaminant" was added to both test and control systems by addition of NH_4NO_3 (Sigma-Aldrich, St. Louis, Mo) to achieve a 0.8:1 Cl to N molar ratio to produce a "chloramination phase". Each system was subsequently allowed to mix for 24 h, with the test system under constant exposure to the magnetic field. Additional $Ca(OCl)_2$ was then added in excess to achieve "breakpoint chlorination". Free chlorine, total chlorine, monochloramine, free ammonia, pH, and temperature were measured at three time points: before the addition of NH_4NO_3, 24 h after the addition of NH_4NO_3, and 3 h post breakpoint chlorination. This experiment was repeated four times.

2.6. *Experiment 2: effectiveness of brief exposure to magnetic field on chlorine demand compared to constant exposure*

Depending on the design of a pool system, the water may only momentarily pass-through a given point and be exposed to the magnetic treatment device for only a brief period. To mimic the transient nature of exposure in these systems, NH_4NO_3 was added as described previously to achieve the chloramination phase however, samples were collected shortly after the addition of NH_4NO_3 to assess "MFE from Brief Exposure" on chlorine demand. For brief exposure assessments NH_4NO_3 was added, while under magnetic treatment, and 100 mL samples were collected 0.5 and 1 h in 125 mL chlorine demand free bottles, sealed, and

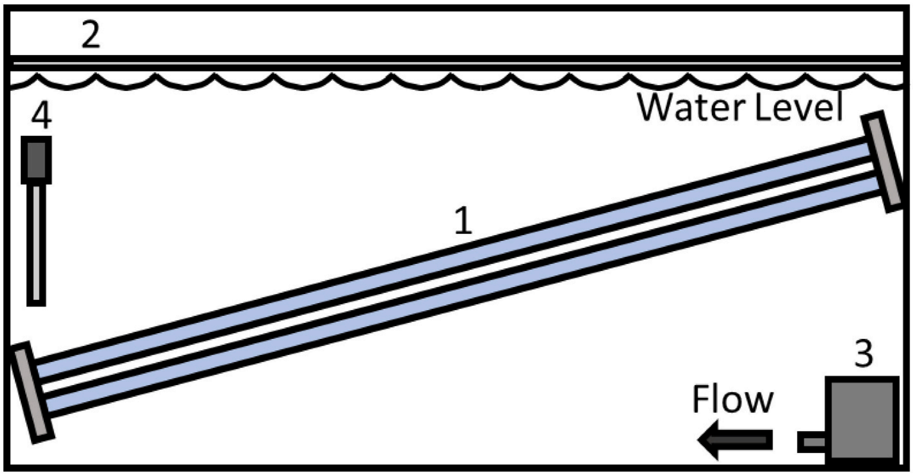

Fig. 3. Bench scale reactor.
The magnetic treatment device (1) was placed in a polypropylene container and completely submerged in 151.4 L of tap water. The surface of the water was covered with a plastic pool cover (2) to reduce light and contaminants from entering the system. A submersible pump (3) was placed in the container and the flow was directed lengthwise across the system to ensure adequate water mixing. A submersible water heater (4) was placed in the system to maintain the target temperature.

incubated at 25 °C in the dark, outside of the influence of the magnetic field. These stored MFE from Brief Exposure samples were assayed 24 h post collection along with samples that remained under constant exposure to the magnetic field. The "MFE from Constant Exposure" was also evaluated by following the previous protocol of exposing the water to the magnetic field for the duration of the experiment and assaying at concurrent timepoints with the MFE from Brief Exposure samples to serve as a comparison.

Both the MFE from Brief Exposure and the MFE from Constant Exposure water samples were assayed for free chlorine, total chlorine, monochloramine, free ammonia, pH, and temperature. This experiment was repeated three times.

2.7. Experiment 3: evaluation of experimental variables on chlorine demand

To begin to elucidate a possible explanation for any effects demonstrated in the previous studies, key variables (Table S1) were systematically altered to evaluate their potential influence on changes in chlorine demand. The reactors were prepared as previously described. After initial chlorination and the 24 h equilibration of the system the ammonia source was added achieve a Cl:N molar ratio of <1 to achieve the chloramination phase. During this experiment, a magnetic treatment device was placed into the control system, but turned off, to alleviate concerns of reactions being altered due to the physical presence of the device. These parameters include hypochlorite source, ammonia source, presence of cyanuric acid, and pH. Each experiment was repeated three times.

2.8. Statistical analysis

Statistical significance ($p < 0.05$) was evaluated using Paired Student's *t*-tests to compare the effects of the magnetically treated systems and their corresponding controls at each time point for each measured variable.

3. Results

3.1. Experiment 1: evaluation of 24 h constant exposure to magnetic field on chlorine demand

Exposure to a static magnetic field (test) during the introduction of a NH_4NO_3 contaminant in a 151 L batch study resulted in a significant reduction in total chlorine by 11.4 % and monochloramine by 13.8 % over the control after 24 h of treatment (Tables 1, 2, 3). The initial pH decreased from 7.8 ± 0.17 to 7.7 ± 0.12 and 8.0 ± 0.11 to 7.9 ± 0.04 in the test and control respectively following ammonia addition. Subsequent breakpoint chlorination resulted in a significant increase of 30.8 % in final free chlorine concentration and 20.0 % in total chlorine concentration when exposed to the magnetic field, compared to the control, after the second addition of chlorine. Final pH of the test and control waters were 7.4 ± 0.03 and 7.5 ± 0.06 respectively, with a small but significant difference between the two. Results are the average of four repeated experiments.

Table 2

Stoichiometric analysis of Cl and N after magnetic treatment and subsequent breakpoint chlorination.

Time (hours)	Test		Control	
	mmol Cl	mmol N	mmol Cl	mmol N
0	22.66	0.35	22.66	0.23
24	15.46	19.77	17.92	19.75
27	7.42	0.26	5.84	0.19

Table 3

Effects of magnetic treatment and subsequent breakpoint chlorination on the % change of free chlorine, total chlorine, and monochloramine.[a]

Time (hours)	Magnetically treated samples compared to the corresponding control at each time		
	Free chlorine (% change)	Total chlorine (% change)	Monochloramine (% change)
0	0 %	3.7 %	−28.6 %
24	–	−11.4 %	−13.8 %
27	30.8 %	20.0 %	33.3 %

[a] $\%Change = \left(\frac{Treatment - Control}{Control}\right) \times 100.$

3.2. Experiment 2: effectiveness of brief exposure to magnetic field on chlorine demand compared to constant exposure

Brief exposure to the static magnetic field followed by removal from the field resulted in a lower reduction in chlorine demand when compared to the longer constant exposure. However, average total chlorine in MFE from Brief Exposure samples were still reduced by 7.5 % and 7.3 % in samples exposed for 0.5 and 1 h respectively, when measured 24 h after collection, and compared to their corresponding controls (Fig. 4, Table 4.). In contrast, reductions of 12.8 % and 10.5 % in total chlorine were seen in MFE from Constant Exposure samples when compared to their corresponding controls. Average monochloramine concentrations were reduced by 5.9 % and 6.1 % in MFE from Brief Exposure samples collected after 0.5 and 1 h respectively and

Table 1

Evaluation of 24 h constant exposure to a magnetic field on chlorine demand.[a,b,c,*].

Location on the breakpoint curve	Time (hr)	Free Cl		Total Cl		Combined Cl		Free NH_3		Monochloramine		pH	
		(mg/L)		(mg/L)		(mg/L)		(mg/L)		(mg/L)			
		Test	Control	Test	Control	Test	Control	Test	Control	Test	Control	Test	Control
Breakpoint[c]	0	5.3	5.3	5.6	5.4	0.3	0.2	0.02	0.01	0.05	0.04	7.8	8.0
Standard error		5.3 ± 0.042	5.3 ± 0.067	5.6 ± 0.076	5.4 ± 0.057	0.3 ± 0.062	0.2 ± 0.035	0.02 ± 0.0056	0.01 ± 0.0016	0.05 ± 0.0078	0.04 ± 0.0037	7.8 ± 0.056	8.0 ± 0.036
Chloramination[b]	24	N/A	N/A	3.9*	4.4*	3.9*	4.4*	0.85*	0.69*	3.63*	4.21*	7.7*	7.9*
Standard Error		–	–	3.9 ± 0.011	4.4 ± 0.053	3.9 ± 0.011	4.4 ± 0.053	0.85 ± 0.1565	0.69 ± 0.1663	3.63 ± 0.0276	4.21 ± 0.0498	7.7 ± 0.038	7.9 ± 0.012
Breakpoint[c]	27	1.7*	1.3*	1.8*	1.5*	0.1	0.1	0.01	0.01	0.04	0.03	7.4*	7.5*
Standard error		1.7 ± 0.043	1.3 ± 0.070	1.8 ± 0.056	1.5 ± 0.079	0.1 ± 0.017	0.1 ± 0.019	0.01 ± 0.0017	0.01 ± 0.0014	0.04 ± 0.0108	0.03 ± 0.0074	7.4 ± 0.011	7.5 ± 0.019

[a] All experiments repeated four times ($n = 4$).

[b] Chloramines are present. No free available chlorine is present.

[c] Free available chlorine is present. All chloramines are destroyed.

[*] Significant at $\alpha = 0.05$.

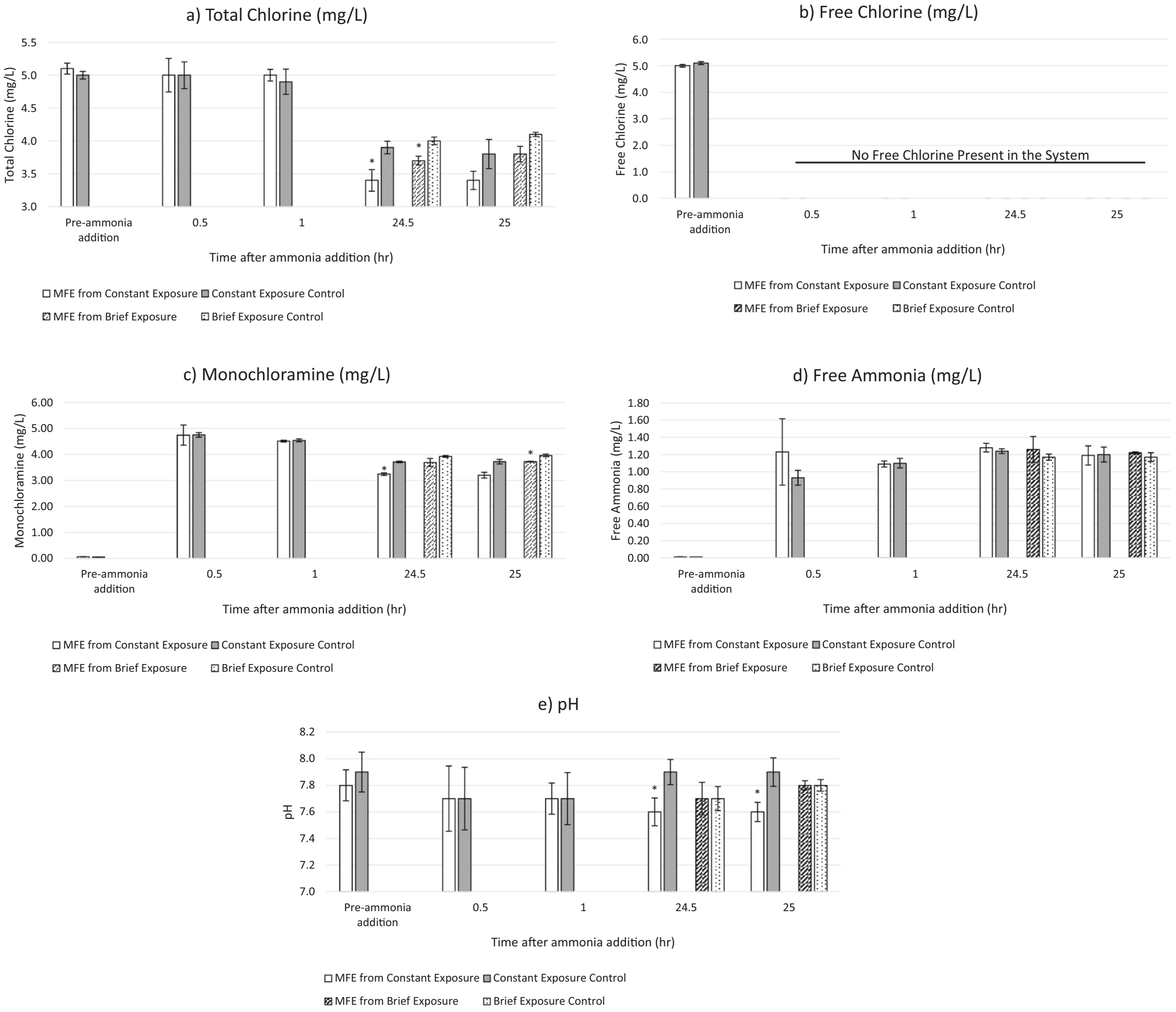

Fig. 4. Effectiveness of brief exposure to magnetic field on chlorine demand compared to constant exposure.
Prior to the addition of ammonia all chlorine is present as free chlorine, following the addition of ammonia, all other time points describe a chloraminated system where the presence of total chlorine is primarily as monochloramine and represents a potential chlorine demand in the system. MFE from Brief Exposure samples were collected at 0.5 and 1 h and removed from the magnetic field, samples were then assayed 24 h after collection concurrently with water that was constantly exposed. * = Significant ($p < 0.05$).

Table 4
Effects of constant and brief magnetic treatment on the % change of total chlorine and monochloramine.[a]

	MFE constant exposure compared to MFE constant exposure control		MFE brief exposure compared to MFE brief exposure control	
Time (hours)	Total chlorine (% change)	Monochloramine (% change)	Total chlorine (% change)	Monochloramine (% change)
0.5	0 %	−0.2 %	–	–
1	2.0 %	−0.7 %	–	–
24.5	−12.8 %	−12.7 %	−7.5 %	−5.9 %
25	−10.5 %	−14.0 %	−7.3 %	−6.1 %

[a] $\%Change = \left(\frac{Treatment - Control}{Control}\right) \times 100.$

subsequently measured 24 h after collection. In contrast, reductions of 12.7 % and 14.0 % monochloramine were seen in MFE from Constant Exposure samples at their respective timepoints (24.5 and 25 h) when compared to their corresponding controls. The pH of briefly exposed samples did not vary significantly after each timepoint. In contrast, the pH in waters under constant magnetic field exposure resulted in a significant difference of 7.6 ± 0.10 and 7.6 ± 0.07 in the test compared to 7.9 ± 0.10 and 7.9 ± 0.11 for the controls, at both 24.5 and 25 h respectively after the addition of NH_4NO_3. Results are the averages of three replicates.

3.3. *Experiment 3: evaluation of experimental variables on chlorine demand*

To assess each variable's contribution to any effect on the chlorine demand of the system; each variable was substituted or removed to determine which constituents altered any potential effects. Similar trends were seen when using NaOCl as the source of chlorine as when $Ca(OCl)_2$ was used in previous studies (Fig. 5b); as well as when NH_4Cl was substituted for NH_4NO_3 (Fig. 5c). However, no discernible effect was seen when the pH was buffered to 7.1 (Fig. 5d) or when cyanuric acid was removed from the system (Fig. 5e). The effects of different variables on the % increase in total chlorine and monochloramine are found in Table 5. Effects on parameters other than total chlorine are found in the supplementary materials (Tables S2–S5).

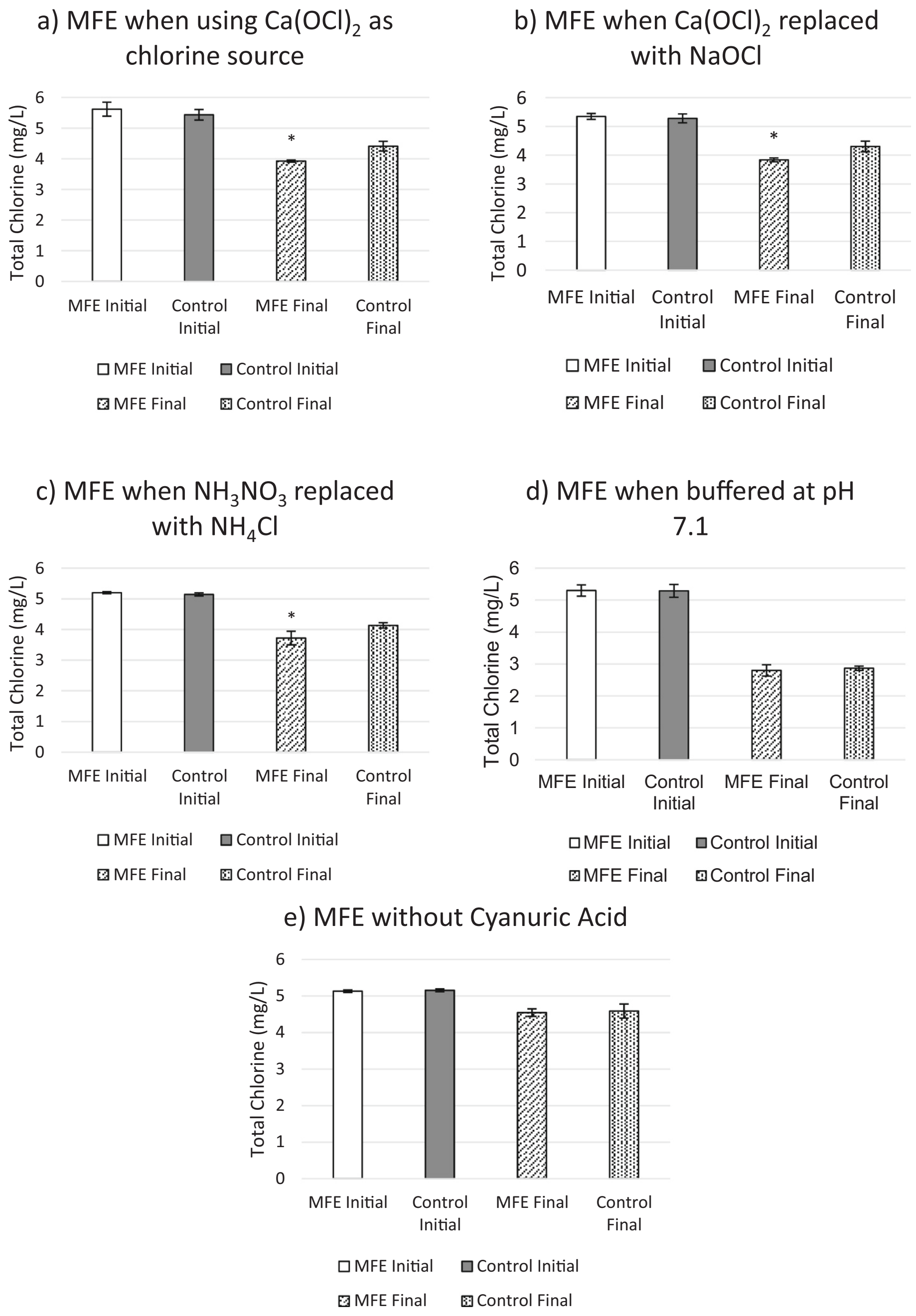

Fig. 5. Magnetic field effects (MFE) of different variables on chlorine demand.
A comparison of chlorine demand to magnetically treated systems caused by changing a single experimental variable, experimental conditions are found in Table S1. a) Trials using $Ca(OCl)_2$ from Table 1 are shown from 0 to 24 h, prior to the second addition of chlorine, to provide a visual comparison. b) Source of chlorine changed from $Ca(OCl)_2$ to NaOCl. c) Source of ammonia changed from NH_4NO_3 to NH_4Cl. d) System was buffered at pH 7.1 using sodium phosphate buffer solution. e) No cyanuric acid was added to the system. A significant difference between the magnetically treated system and the control were still seen when the source of chlorine and ammonia were changed. The results of the other variables are provided in Tables 2–5. * = significant ($p < 0.05$).

Table 5
Effect of different variables on the % change in total chlorine and monochloramine after 24 h of magnetic treatment.[a]

Variable changed	Time (hours)	Magnetically treated samples compared to the control 24 h after chloramine formation	
		Total chlorine (% change)	Monochloramine (% change)
$Ca(OCl)_2$ to NaOCl	24	−11.6 %	−9.6 %
NH_3NO_3 to NH_3Cl	24	−9.8 %	−12.7 %
No Cyanuric Acid	24	−2.2 %	1.1 %
pH buffered to 7.1	24	−3.4 %	2.3 %

[a] $\%Change = \left(\frac{Treatment\ at\ 24\ hours - Control\ at\ 24\ hours}{Control\ at\ 24\ hours}\right) \times 100.$

4. Discussion

This proof-of-concept study demonstrates MFE on chlorine demand in simulated pool systems through the reduction in monochloramine and also documents the key constraints required for the manifestation of this phenomenon. Few studies have evaluated magnetic field effects in chlorinated waters however, with chlorination being one of the most common water treatment methods for pool systems, improvements to either the disinfection capabilities, or minimizing chlorine loss may prove to be a valuable advancement in water treatment. While these results cannot perfectly mimic the complexity of a full-scale pool system, it was possible to demonstrate that the chloramine forming reactions were influenced by this technology in a manner that reduced chlorine demand. It is surmised that the effects of magnetic treatment may stem from influencing the chloramine forming reactions that could occur if the magnetic field altered the electron configuration of compounds in the system. This study also successfully demonstrated conditions where this effect was and was not observed, highlighting the importance of certain water parameters, such as cyanuric acid and pH (Fig. 5d and e, Table 5), in the system. These results demonstrate that under certain conditions the chlorine demand in a simulated pool system can be reduced by the presence of a static magnetic field.

In Experiment 1, chlorinated water which had undergone magnetic treatment was exposed to a chlorine demand (NH_3), and subsequently breakpoint chlorinated to remove that demand (Tables 1, 2, 3). This strategy was chosen because it was expected to mimic the conditions that would be experienced in real-world swimming pool systems. When a bather enters a pool a chlorine demand will be imparted due to the addition of organic and inorganic compounds. Typically, the chlorine residual in a pool is then sufficient to satisfy the chlorine demand while maintaining a free chlorine residual for continued disinfection. Initial experiments (data not shown) showed no measurable difference between magnetic treatment and the control when a free chlorine residual was maintained for the entirety of the experiment. It is possible that the magnetic treatment does affect this system, but the sensitivity of the assay relative to the amount of reactant used was not sufficient to yield a measurable difference. However, when the chlorine demand exceeded the free chlorine residual for extended periods of time, the monochloramine concentration decreased more rapidly in the magnetically treated system (Tables 1, 2, 3). The reduction in monochloramine concentration resulted in a lower chlorine demand after 24 h and ultimately resulted in a 30.8 % increase, on average, of free chlorine residual after subsequent breakpoint chlorination.

It is unrealistic to assume that in most recreational water systems that the water will remain under constant exposure to a magnetic treatment. To mimic a short exposure period, NH_3 was added to chlorinated water in the presence of the magnetic field, and a sample subsequently collected in chlorine demand free bottles and removed from the magnetic field after 30 min and 1 h. At the time of sampling, no significant difference in monochloramine was observed between waters under treatment and the control (Fig. 4, Table 4.). Interestingly, 24 h after collection and removal of the sample from the magnetic field, it was found that the monochloramine concentration was lower in samples that experienced even a brief exposure to the magnetic field. The monochloramine concentration was once again reduced after 24 h post sample collection in the waters under constant exposure (12.7 % and 14.0 %), and to a lesser extent in the samples removed from the field at 0.5 and 1 h (5.9 % and 6.1 % respectively) compared to their controls at the equivalent times (Section 3.2).

The importance of various water parameters was systematically evaluated to understand what conditions are required for the reduction of chlorine demand under magnetic treatment. This evaluation included changing: the chlorine source (NaOCl), ammonia source (NH_4Cl), pH (buffered at 7.1) and the presence of cyanuric acid (Fig. 5, Table 5, Tables S2–S5). These data demonstrate that the initial source of chlorine or ammonia did not appear to influence the reduction of the chlorine demand in a magnetic field, however both the pH and the presence of cyanuric acid did influence this reduction. This indicates that both the pH and cyanuric acid potentially play a role in the reduction of chlorine demand. In the previous experiments (Table 1), it was seen that the pH significantly changed between the treated and non-treated water. When the pH was buffered the chlorine demand was not reduced. These results, coupled with the previously described smaller magnitude of pH shift in samples under brief exposure resulting in a lower reduction in monochloramine, indicate that the change in pH may not be a result of the change in chlorine demand but rather a driver for that change.

These experiments highlight four key findings that may point to how chlorine demand could be reduced in the system: the mass balance difference (Section 3.1), the time required after the chloramine formation that result in a reduced chlorine demand (Section 3.2), the necessity on cyanuric acid (Section 3.3), and the effects of pH. A difference in mass balance can be observed when the magnetic treatment, yielded a reduction on monochloramine, and was subsequently breakpoint chlorinated (Table 1). This would imply that chlorine demand was removed from the system. A possible explanation for this reduction of monochloramine is that the yield of the reaction may be shifted to favor di- or trichloramine, which are more volatile, resulting in the removal of chloramines through degassing [18]. Stoichiometric analysis of the results in section 3.1 indicate that the amount Cl (mmol) is lower in the treated system than the control (Table 2). However, the amount of N (mmol) is the same, this is likely due to losses primarily as dichloramine which is more volatile than monochloramine. This would, in part, explain the relatively slow reduction in chlorine demand as degassing would likely occur on the scale of hours to days, as noted by Schmalz et, al [19]. The hypothesis that the removal of chlorine demand is due to a secondary process is further supported in Experiment 2 (Fig. 4, Table 4.), evaluating the effects of brief exposure to the magnetic field, which at ≤1 h show no difference in the measured water parameters but do show a difference at ≥24.5 h in both briefly exposed and constantly exposed samples.

Determining the mechanism of how a magnetic field could produce such effects are beyond the scope of this study. However, the most obvious drivers of this effect are likely to be pH and the reactant concentration, due to chloramine forming reactions being dependent on both. Yamashita et al. [20] noted that a magnetic field may subtly affect the local pH of the system, which could subsequently favor di- or trichloramine formation. A multitude of mechanisms have also been described in which a magnetic field may influence the spin of electrons, changing the yield of the reaction [3]. The change in electron configuration could be facilitated by the mixing of the system as compounds cross the static magnetic field, which in turn could increase the yield of di- or trichloramine at a higher pH than what would normally be expected.

Another consideration is the necessity of cyanuric acid which helps prevent the loss of free chlorine by UV light through the complexion between the two molecules [21]. It is possible that the presence of cyanuric acid slows down the chloramine forming reactions by reducing the amount of available chlorine that may initially react with the addition of ammonia. Cyanuric acid may also impact the effective concentration of chlorine in solution. This equilibria between bound chlorine and chlorine in solution could be impacted by aromatic ring shielding. Due to isocyanuric acid, the predominant cyanuric acid species in water, having weakly aromatic characteristics [22] it could be possible for an external magnetic field to deshield electrons the outer electrons and slightly shift the equilibria of bound and unbound chlorine should the molecule cross the magnetic field due to mixing [23].

Determining on a mechanistic level how magnetic technologies produce various outcomes in water systems remains contested to this day, even in the most well documented magnetic field effect of scale removal [24,25]. Differences in results between studies can, in part, be attributed to subtle differences in experimental design ranging from different magnetic fields [26], pipe material [27], flow rates [28] and water characteristics. It is likely that a multitude of factors contribute to the reduction of chlorine demand, as seen throughout this study, and many more may potentially contribute or hinder these effects.

These experiments address two key issues regarding the applicability of this method to reduce chlorine inputs necessary for recreational pool waters. First, it demonstrates that the chlorine demand is reduced over time showing how less chlorine could be used to maintain the desired free chlorine residual. Additionally, the Experiment 2 (Fig. 4, Table 4) demonstrates how a localized effect has the capacity to affect a much larger recirculating system in that a brief exposure to the magnetic field is sufficient to produce an effect on the chlorine demand. This experiment showed that so long as the reaction occurred in the presence of the magnetic field the reduction of chlorine demand could still manifest, albeit at a reduced level.

Given the complexity of real-world systems, future work should be conducted to evaluate the translatability of this research to full-scale systems. Real-world pool systems contain a variety of organic and inorganic compounds that may react synergistically or antagonistically with this treatment. Additionally, it is possible that the presence of organic nitrogen from bathers [14] (urea and creatinine) may yield different results than inorganic chloramines and should be the focus of further investigations. Although these factors will likely influence the efficacy of magnetic water treatment, this study has demonstrated that it is possible to alter reactions found in swimming pools in a manner that could reduce chlorine consumption in these systems.

5. Conclusion

Magnetic treatment of water has the potential to reduce chlorine demand in simulated pool water systems resulting in net savings for chlorine costs under real world applications. This magnetic treatment device provides an energy and cost-effective method of reducing chlorination costs in swimming pools. A significant reduction in chlorine demand, in the form of reduced monochloramine, was observed under certain experimental conditions. This phenomenon was apparent in non-buffered pool waters containing cyanuric acid regardless of the source of chlorine or ammonia that was supplied into the system. Interestingly the reduction in chlorine demand appears to be based on the presence of the magnetic field during the formation of the chloramines, which provides the potential for unique applications even when waters are treated only briefly. The reduction in chlorine demand may be due to magnetic field effects on the pH of the system or the electron configuration of the reactants resulting in an increased yield of the more volatile di- or trichloramine which may ultimately gas out of the system.

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Declaration of competing interest

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Data availability

Data will be made available on request.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jwpe.2022.103198.

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