

original article

Investigation of chlorine decay of water resource in Khanbebein city, Golestan, Iran

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ABSTRACT

Aims: The object of the study was to identify chlorine demand factors in water and chlorine in Khanbebein City water and eliminating of them.

Materials and Methods: Concentration of free and combined residual chlorine with the methods presented in the book "Standard Methods for Water and Wastewater Examination" were measured. Other parameters such as: Temperature, TOC, TDS, pH, EC, nitrate, ammonia, total hardness, alkalinity, iron and manganese were also examined before and after of chlorination.

Results: The Highest chlorine decay constant in the short time were in water well was $0.895 \text{ mgL}^{-1}\text{h}^{-1}$ and the least amount of it was $0.0097 \text{ mgL}^{-1}\text{h}^{-1}$ and the Highest chlorine decay constant in the long time were in water well was $-0.092 \text{ Lmg}^{-1}\text{h}^{-1}$ and the least amount of it was $-0.0017 \text{ Lmg}^{-1}\text{h}^{-1}$ that correlated with nitrite, ammonia and iron concentration.

Conclusion: The factors that affected short-time chlorine decay constant (k_2) were nitrite, ammonia and iron and The factors that affected on long-time chlorine decay constant (k_2) were Nitrite, ammonia and iron. The material removal techniques for them were the use of natural resins, zeolite, ion exchange, membrane and aeration methods, oxidation and sedimentation, and filtration.

Key words: Chlorination, Disinfection, Khanbebein City, water

INTRODUCTION

Obviously, the quality and safety of drinking water is one of the most important public health issues. Pollution

of water source with pathogen microorganisms result in transferring infectious diseases and other related diseases.^[1] Microbiological safety of drinking water is generally achieved by treating the water through a chemical disinfectant, usually a powerful oxidizing agent such as chlorine, chlorine dioxide or ozone. Chlorine, added to water in the form of either as hypochlorous acid/hypochlorite ion or as chlorine gas, is still the most widely applied and most cost-effective disinfectant worldwide, despite the well-known problems of disinfection by-product (DBP) formation.^[2] Before treated water leaves the water treatment plant, there's chlorination unit to maintain

Access this article online	
Quick Response Code: 	Website: www.ijehe.org
	DOI: 10.4103/2277-9183.110137

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This article may be cited as:
Rahmani K, Khademi SS, Rahmani A, Godini K, Shahamat YD. Investigation of chlorine decay of water resource in Khanbebein city, Golestan, Iran. *Int J Env Health Eng* 2013;2:11.

certain chlorine residual in the distribution system. All that does is prevent microbiological regrowth. Free chlorines (HClO and ClO^-) are the most commonly employed disinfectants because of its remaining property in water.^[3] Nevertheless, chlorine decays occurs in long distribution systems, and in areas where the chlorine concentration drops below a minimum desired level (0.2-0.8 mg/L); therefore, booster chlorination has to be installed so as to protect an enough chlorine level in the water.^[4,5]

Despite the effective use of chlorine over many decades as a disinfectant for potable water supplies, there are still regulatory failures in the quality of drinking water, which cause concern to the water utilities.^[6,7] Chlorine is a non-selective oxidant; therefore, it reacts with both organic and inorganic chemical materials in water and it also is an antimicrobial agent. Generally, in natural water bodies, the species that are most reactive with chlorine are inorganic substances in a reduced valence state such as iron (II), manganese, sulfide, bromide and ammonia.^[8,9] The presence of free chlorine residual in drinking water indicates that: A sufficient amount of chlorine is added to the water to inactivate most of the bacteria and viruses that cause diarrheal disease. The water is protected against recontamination when it is transported in the distribution system, and during storage of water in the household. Because the presence of free residual chlorine in drinking water indicates the possible absence of disease-causing organisms; therefore, it is used as one measure of the potability of drinking water.^[10] Previous research has assumed first-order chlorine wall decay^[11-15] and found to be characterized by first-order kinetics.^[5] Vasconcelos *et al.*^[5] found that a zero-order wall decay kinetic reaction was effective for characterizing the wall decay, but he also indicated that the first-order model might be better. Thus, the aim of this study was to identify and resolve problems over the use of chlorine in drinking water of Khanbbyn City.

MATERIALS AND METHODS

All the water samples were collected from the drinking water resources of City of Khanbebein in June 2010 [Figure 1]. The research method is in accordance with the most recent methods of determining of the chlorine demand in developed by the experts in the field.^[6] The sampling process and chemical measurements of the drinking water was according to the standard book of the water and wastewater experiments.

Four sources of the drinking water with the names (All names here are local names for water resources) Ohadi Reservoir, Klukan Reservoir, Well Number 3, and Aludarreh Reservoir as well as a resource of drinking water of Gorgan (a well in the Alimohammadi Water and Wastewater Office) were collected for comparison and investigation. Based on the experiment type, different sample volumes included 200 samples of free chlorine and 200 samples of combined chlorine, 110 samples of chemical experiments and 15 samples of TOC experiments.

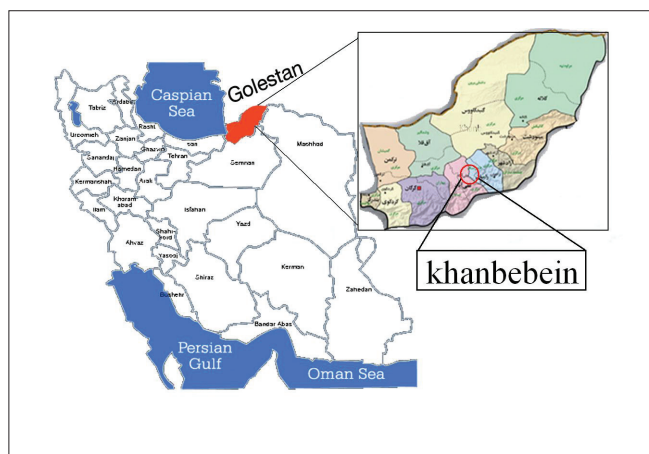


Figure 1: The Zone of study that wells located in there

The hypochlorinators, installed on the concrete reservoir of the water, did the chlorination of the water. The pumps injected calcium hypochlorite powder into the reservoir, after preparation of the stock solution. The research method was in accordance with the most recent methods of determining of the chlorine developed by the experts in the field. Different concentrations of chlorine including 1, 3, 4, 5, and 7 mg/lit were solved in the water of four resources. Other parameters such as temperature, TOC, TDS, pH, EC, nitrate, ammonium nitrogen, total hardness, alkalinity, iron and manganese were measured before and after addition of chlorine in the concentration of 3 mg/lit and 30 minutes as contact time. In order to recognize the chlorine behavior in the sample, control waters in short (0 to 4 hours), and long (0 to 7 days) periods, the free and combined chlorines were measured. After the drawing, the related graphs and the calculation of the formulation of chlorine degeneration in water, optimum concentration and the causes of degeneration were determined.

The chlorine demand of each sample and the concentration of materials such as ammonia, EC, TDS, pH, Temperature, Alkalinity, Hardness, Nitrite, Nitrate, Iron and Manganese along the examination were analyzed in ANOVA statistical test and effectiveness each of them was determined.

Before addition of chlorine into water samples were added, the test of chlorine purity was carried out. To do this, first adds specific volumes of perchlorine to distilled water. Dividing the volume measured by the spectrophotometric apparatus (DR 2500) in the concentration of less than 3 mg/L into the expected concentration will give the purity degree of chlorine in different samples.

RESULTS

In order to recognize the chlorophilic factors, the chemical components of the drinking water of the city such as measuring the chlorine and chlorination of the samples were examined. The results are presented in Table 1.

Water and Wastewater Office carried all tests of chlorination of the samples out using the stock solution prepared using per chlorine powder provided. Table 2 gives the degree of purity of chlorine of the samples. Table 3 shows the amount of the water consumption of the city during the period between 2008 and 2010; the total consumption of the city was calculated in m³ and L/s. The inlet flow of each resource was measured and is shown in Table 4.

The graphs of the free chlorine in the water resources of the city are given below [Figures 2-13].

According to the experimental method, a series of chemical tests were carried out in the concentration of 3 mg/L at 30 minutes before and after adding the chlorinated solution to the water samples and paired *t*-test for determining the level of significance of the changes in the values of

chemicals after chlorination, the results of which are shown in Table 5.

The nonparametric Spearman correlation test was carried out to determine the possible link between chemical components and chlorine demand of the water and synthetic coefficients due to the lack of normality of the data; the result of this test is given in Table 6.

DISCUSSION

Because of the high correlation coefficients for all resources, the chlorine decomposition follows the second-degree kinetic constant in short-time whereas in long it follows the first-degree kinetic constant term. However, in some research, long term chlorine demand and

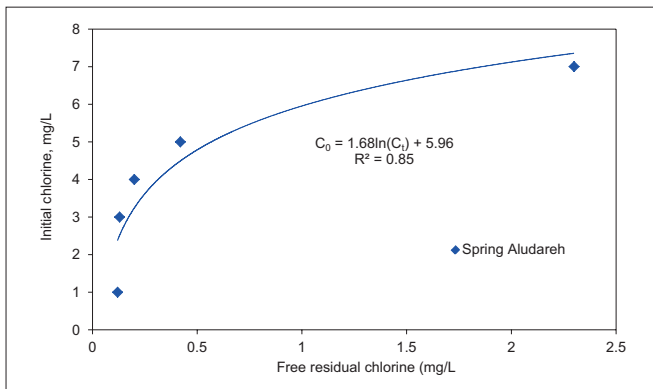


Figure 2: Free residual chlorine of Spring Aludareh after 24 hours

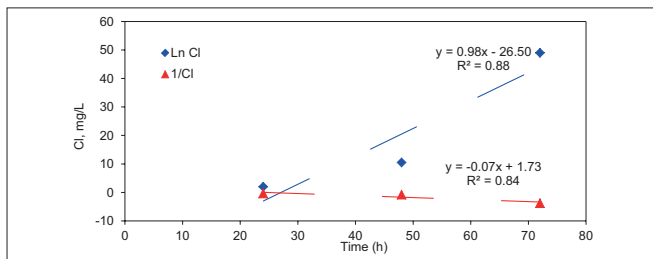


Figure 4: Kinetics of long term decay chlorine in samples from spring water Aludareh

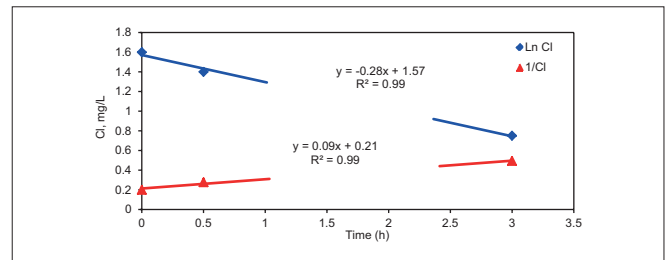


Figure 3: Kinetics of Short-term decay chlorine in spring water samples from Aludareh

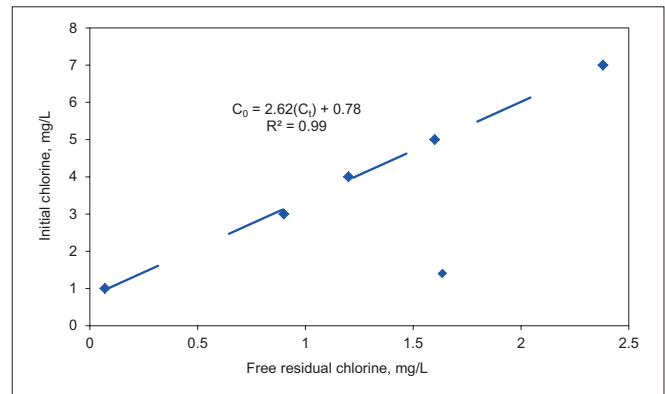


Figure 5: Free residual chlorine of Kalukon well after 24 hours

Table 1: Chemical testing of water before the chlorine Debate

Chemical parameters	Well of the water organization of Gorgan	Aludareh Springs	Kalukon well (No. 4)	Surface area (No. 3)	Ohadi well (No. 2)	The well shaft and sheath area
EC	1000	509	772	834	950	807
TDS	499	244	362	404	463	387
PH	7.12	7.08	7.39	7.48	7.79	7.53
Temperature	26	28	27	27.4	28.6	25
Alkalinity (as CaCO3)	298	170	184	178	165	172
Total hardness (as CaCO3)	440	240	260	200	220	240
Nitrite	0.0198	0.0132	0.08	0.0132	0.132	0.0066
Nitrate	36.52	8.8	7.48	4.4	21.56	3.96
Ammonia	0.04	0.024	0.01	0.471	0.09	0.06
Iron	0.04	0.01	0.1	0.15	0.1	0.23
Manganese	0.05	0.01	0.022	0.09	0.097	0.09

the formation of halomethanes follow the second-degree kinetic constant.^[16]

The maximum value of chlorine decomposition coefficient in long term was related to Well N.3 (-0.092 h⁻¹) and its minimum was related to Alimohammadi Well in the Water and Wastewater Office (-0.0017 h⁻¹) and Ohadi Well (-0.019 h⁻¹).

According to Table 5 indicating the effect of chemical components on the chlorine demand of water, due to the lack of normality in data, the Spearman nonparametric correlation test was carried out, which was found that the factors with high chlorine demand were nitrite, ammonia, iron, manganese, and TOC and factors under the effect of chlorination were EC and TDS.

According to Table, effectiveness of factors on the chlorine degeneration was recognized for Short-term degeneration (k₂): nitrite, ammonia, iron, EC, and TDS; and Long-term degeneration (k₁): nitrite, ammonia, iron, EC, and TDS [Table 6]. The high concentrations in the study was owing to the existing compounds such as ammonia, and nitrate, because the water drainage of manure to the wells and as well as minerals containing iron compounds in the area. In view of the fact that high concentrations of chlorine results in hygienic and economic issues; therefore, these materials should be removed from the wells.

The solution for the problem is deletion of factors affecting chlorine demand. The common method for deletion of ammonia is the use of the natural resins, zeolite, ion

exchange, membrane methods, and aeration. In order to remove iron and manganese, the most common methods includes oxidation, sedimentation, and infiltration. For lower

Table 2: Purity percentage of chlorine in used perchlorin

Row	Months of 2010	Puritychlorine (percent)
1	August	61
2	September	59
3	October	56
4	November	57
5	December	60
Average purity (percentage)		58.6
Standard deviation(%)		2.07

Table 3: Water consumption of khanbebein City in various years

Year	Consumption (m ³)	Averagedaily (L/s)
2008	563672	17.9
2009	596672	18.9
2010	616301	18.9
Meanconsumption	592215	18.78

Table 4: Choice kinetic model for water resources

Source ofdrinking water	Short-term		Long-term	
	k ₁ h ⁻¹	r ²	k ₂ Lmg ⁻¹ h ⁻¹	r ²
AludarehSpring	0.091	0.99	-0.063	1
Wellouhadi	0.895	0.89	-0.019	0.86
Wellkalukon	0.080	0.93	-0.051	0.95
No. 3 Well	0.186	0.84	-0.092	0.92
Alimohamadiwell	0.0097	0.75	-0.0017	0.99

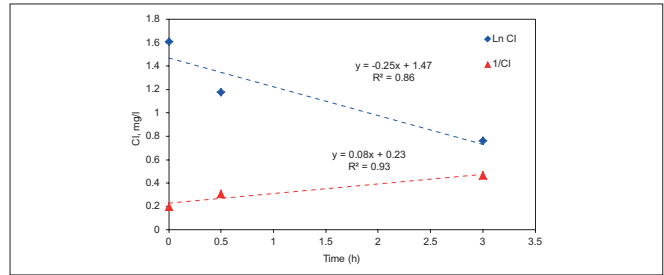


Figure 6: Kinetics of Short-term decay chlorine in samples from well water kalukon

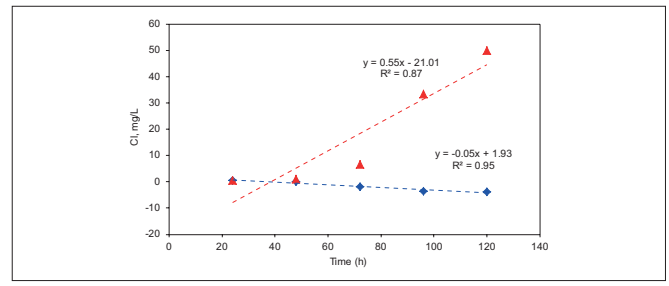


Figure 7: Kinetics of long term decay chlorine from samples in well water Kalukon

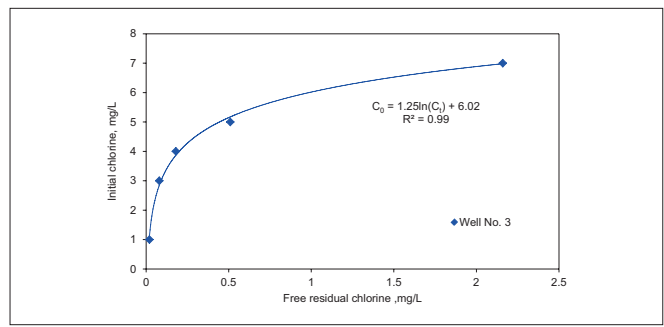


Figure 8: Free residual chlorine of well No.3 after 24 hours

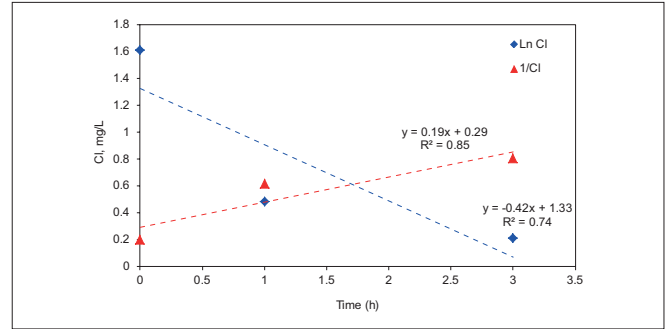


Figure 9: Kinetics of Short-term decay chlorine in samples of well water from area No. 3

Table 5: Table paired T test chemical parameters before and after chlorination

Chemical parameters	Situation	Mean	Std. Deviation	N	t	Correlation coefficient	Sig	Significant
Ammonia	Before	0.19	0.29	10	2.48	0.89	0.03	*
	After	0.08	0.20	10				
EC	Before	812.00	172.22	6	-4.56	1.00	0.01	*
	After	836.33	167.50	6				
TDS	Before	393.17	88.83	6	-5.92	1.00	0.002	*
	After	403.50	86.16	6				
pH	Before	7.40	0.27	6	-1.30	0.64	0.25	
	After	7.52	0.27	6				
Temperature	Before	27.00	1.32	6	-1.29	0.81	0.25	
	After	27.45	1.43	6				
Alkalinity (as CaCO3)	Before	194.50	51.13	6	4.79	1.00	0.00	*
	After	189.33	52.23	6				
Total hardness (as CaCO3)	Before	266.67	87.33	6	-1.38	1.00	0.23	
	After	270.83	87.17	6				
Nitrite	Before	0.04	0.01	6	3.60	0.24	0.02	*
	After	0.01	0.02	6				
Nitrate	Before	13.80	12.85	6	-0.69	1.00	0.52	
	After	14.12	12.35	6				
Iron	Before	0.12	0.07	6	3.86	0.58	0.01	*
	After	0.03	0.01	6				
Manganese	Before	0.07	0.03	6	5.34	0.32	0.003	*
	After	0.01	0.01	6				

*The correlation is significant

Table 6: Correlation between required chlorine to establish residual (0.5 mg/L) and chemical parameters

		EC	TDS	PH	Temperature	Alkalinity	Hardness	NO ₂ ⁻	NO ₃ ⁻	NH ₄	Fe	Mn	TOC
required Chlorine	Spearman correlation coefficient	-0.900	-0.900	-0.600	-0.600	0.600	-0.600	0.949	-0.700	1.000	1.000	0.900	0.900
k ₁	Sig. (2-tailed)	0.037	0.037	0.285	0.285	0.285	0.285	0.014	0.188	.	.	0.037	0.037
k ₂	The number of samples	5	5	5	5	5	5	5	5	5	5	5	5
required Chlorine	Spearman correlation coefficient	-1.000	-1.000	-0.500	-0.500	0.800	-0.500	0.949	-0.400	0.900	0.900	0.700	0.800
k ₁	Sig. (2-tailed)	0.000	0.000	0.391	0.391	0.104	0.391	0.014	0.505	0.037	0.037	0.188	0.104
k ₂	The number of samples	5	5	5	5	5	5	5	5	5	5	5	5
required Chlorine	Spearman correlation coefficient	-1.000	-1.000	-0.500	-0.500	0.800	-0.500	0.949	-0.400	0.900	0.900	0.700	0.800
k ₁	Sig. (2-tailed)	0.000	0.000	0.391	0.391	0.104	0.391	0.014	0.505	0.037	0.037	0.188	0.104
k ₂	The number of samples	5	5	5	5	5	5	5	5	5	5	5	5

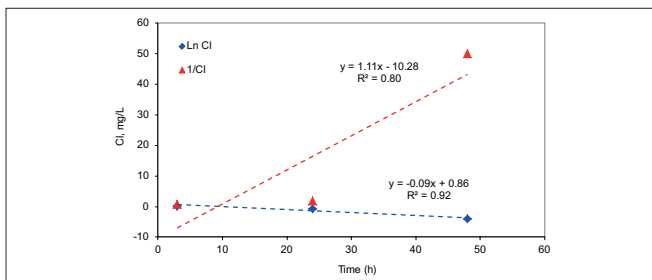


Figure 10: Kinetic of long term decay chlorine in samples of well water from area No.3

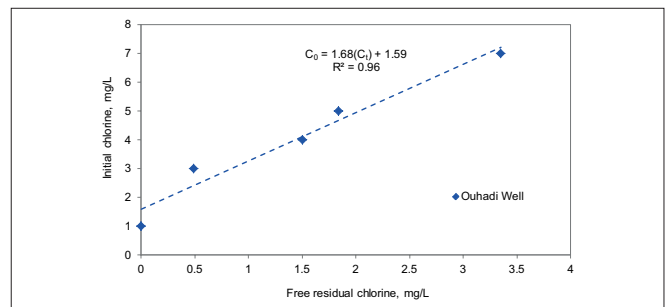


Figure 11: Free chlorine remaining of wells Ouhadi after 24 hours

inlets, the ion exchange method is also used. Among these methods to remove organic materials aeration or remove with air, oxidation, advanced coagulation, adsorption, biologically active carbon, ion exchange, and membrane methods.^[17] This

study is unprecedented in its own category across the country. Nothing has been published of the kind in the literature of the field. The present study can act as a milestone for other

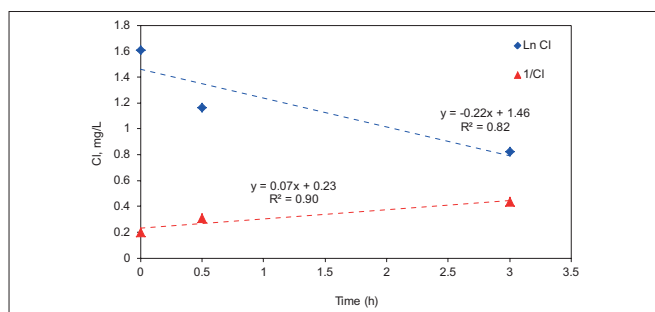


Figure 12: Kinetics graph of short-term decay of chlorine in samples from well water Ouhadi

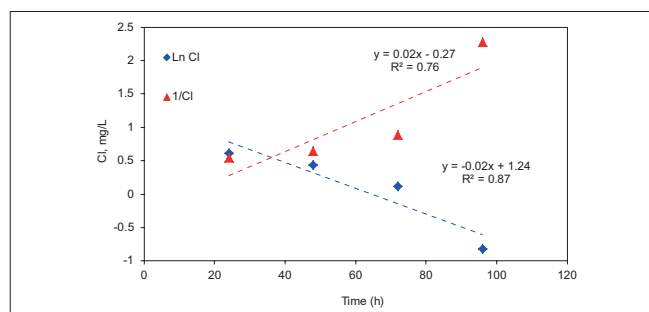


Figure 13: Kinetics graph of long term decay of chlorine in samples from well water Ouhadi

research and provide a useful manual of addition of chlorine into drinking water of the cities, and thus prevent the high consumption of chlorine in the water.

ACKNOWLEDGMENTS

The authors are grateful for the financial and technical support of Golestan Water and Wastewater Company.

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Source of Support: Golestan Water and Wastewater Company, **Conflict of Interest:** None declared.