

Removal of Herbicide Glyphosate in a Drinking Water Treatment System

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ABSTRACT: The removal efficiency of herbicide glyphosate in a drinking water treatment system was investigated. Four major processes of a drinking water treatment system were selected and experiments were performed separately including; treatments by sodium hypochlorite (NaOCl), a sedimentation process by PAC (polyaluminum chloride), ozonation and a GAC (granular activated carbon) treatment. In the sodium hypochlorite experiment, about 50% of the glyphosate was removed by 2 mg/L of hypochlorite and more than 90% was eliminated when 5 mg/L of NaOCl was applied. Also, AMPA, the main metabolite of glyphosate, was treated with hypochlorite. More than 30% of the AMPA was removed by 2 mg/L of hypochlorite and 50% by 5 mg/L. In the PAC experiment, it was determined that more than 60% could be removed. Further experiments were performed and the results indicated that the removed amount was dependent upon the amount of soil and upon the properties of the soil especially that of clay minerals. Ozonation could oxidize glyphosate to its byproducts at about a level of 50%. In contrast, when 1 mg/L of glyphosate was treated with GAC, the amount removed was negligible. The results of this experiment were conclusive. We confirmed that drinking water, which has been contaminated with water polluted with glyphosate can be effectively purified by the application of the drinking water treatment processes currently used

Key Words: Glyphosate, Removal efficiency, Sodium hypochlorite, PAC, Ozonation, GAC

Introduction

Glyphosate, *N*-(phosphonomethyl) glycine, is a widely popular herbicide known for its extensive non-selective spectrum, and rapid deactivation in soil¹⁾. Glyphosate, which is the active ingredient in the trade names Roundup[®] and Rodeo[®] produced by Monsanto, is often used in various applications for broadleaf weeds and grasses²⁾.

Glyphosate is one of the most widely used pesticides by volume. Usage in 1990 was estimated to be 11,595,000 pounds³⁾. Due to the frequency of its usage, its effects on humans and other living organisms have been investigated. Glyphosate and its

technical formulation Roundup[®] (Active ingredient isopropylamine salt of glyphosate) have been found to be genotoxic. Damage to the DNA in kidney and liver tissue and in chromosomes has been reported in mice⁴⁾. According to reports on human exposure to glyphosate there have not been any acute effects when the doses were small and of short duration. The maximum contaminants level (MCL) allowed in drinking water is 0.7 mg/L in the United State^{2,3)}.

Glyphosate is believed to be strongly adsorbed by soil. Therefore, after applying glyphosate to soil including forests and field, it is believed that the probability of glyphosate leaching is low. Due to its high solubility in water (about 12 g/L), however, reports indicate that glyphosate has the potential for leaching to groundwater and to surface run-off water^{1,2,5)}. Moreover, its application has not been

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limited to soil, glyphosate has been used in aquatic ecosystems for weed control in some countries including the United State³).

Since almost all drinking water consumed in the US and many other countries comes from a surface water system and because it is possible that glyphosate can be found in surface water, testing the removal efficiency of glyphosate by the available drinking water treatment processes is an essential and valuable water purification factor to study. The objective of this paper was to assess the removal efficiency of glyphosate in each processes of the present drinking water treatment system including; sodium hypochlorite treatment, coagulation by poly-aluminum chloride, ozonation and adsorption by granular activated carbon.

MATERIALS AND METHODS

Chemicals

Glyphosate, analytical grade, and its main metabolite in soil, AMPA (aminophosphonic acid), were obtained from Monsanto, USA. Sodium hypochlorite (12% NaClO) was purchased from Yakuri Pure Chemicals (Kyoto, Japan). Polyaluminum chloride solution (13% Al₂O₃) was procured from the Daegu Water Treatment Institute (Korea). Two kinds of soil used in the coagulation experiment were collected from the Bokhyun and Ansim areas (Daegu, Korea), respectively. A laboratory research ozone generator (Ho-Dong Electric Company, Korea) was used. GAC (granular activated carbon) was purchased from Pica Corp., Japan.

Treatment by sodium hypochlorite

Five hundred mL of 1 mg/L of glyphosate and AMPA solution were prepared (the concentration of glyphosate used in all experiments was higher than MCL). The hypochlorite stock solution was added to beakers and altered to obtain the following hypochlorite concentration levels, 0.5, 2 and 5 mg/L, respectively. The mixing speed was fixed at 100 rpm. The solutions were sampled at 30 min, 1 h, 2 h and 4 h. Twenty-five mL of 1 mg/L glyphosate was prepared in a 40 mL vial with HPLC-grade water as the solvent, buffer solutions of pH 5, pH 7 and pH 9, respectively, were created. The hypochlorite stock

solution was prepared and added to each vial to make 0.5 mg/L concentrations. The vials were capped, put in a 25°C water bath and shaken at the rate of 75 rpm. After 2 h, the samples were transferred for analysis.

Treatment by PAC

Two kinds of soil colloid were prepared as follows: 10 g of each soil and 1 L of water were mixed together by a mixer. Then, supernatant and soil colloid was obtained by filtering the two soil suspensions individually through a 250 µm sieve. The total suspended solid (TSS) of soil suspensions was determined at a temperature of about 105°C⁷. In order to simulate a real system, 10% and 50% of the prepared soil colloid, which consists of both soil types, were mixed with a glyphosate solution to make an overall volume of 500 mL. The soil suspension was mixed by a propeller at 120 rpm for 5 minute, after that PAC was added to the system. After the addition of PAC, the propeller speed was increased to 200 rpm for 1 min to increase the coagulation rate. Then, the speed was decreased to 50 rpm for an additional 10 min. The suspension was sampled and the amount of glyphosate was analyzed in the supernatant after 30 min of settling time.

Adsorption by clay minerals

Forty mg of kaolinite and 40 mg of montmorillonite, were weighed and prepared separately in 40 mL vials. Then 25 ml of glyphosate solution was added. The concentration levels of glyphosate used in this experiment were 0.5, 1, 5, 10, and 20 mg/L. The vials were capped, kept in a water bath at 25°C and shaken at 80 rpm. After 8 h, the samples were centrifuged at 15,000 rpm for 15 min⁸. Then, the supernatants were taken for analysis.

The adsorption experiment data was examined by using the Freundlich or Langmuir equations. Those equations can be described as follows;

$$X = KC_{eq}^{1/n} \quad \text{Freundlich equation}$$

$$X = X_m KC_{eq} / (1 + KC_{eq}) \quad \text{Langmuir equation}$$

Where X is the amount of pesticide adsorbed per unit weight of the soil (mg/kg), X_m is the maximum

amount of pesticide adsorbed (mg/kg), C_{eq} is the equilibrium concentration of the pesticides (mg/L), K is an affinity parameter, and $1/n$ is an empirical parameter.

Ozonation

Ozone was bubbled into 4,000 mL of 1 mg/L of glyphosate at the ambient temperature. The samples were collected at 5, 15, 30, 60, 120, and 240 min, and then analyzed the concentration of glyphosate. The ozone was analyzed on the basis of a ozone demand semi-batch method⁷.

Removal by GAC treatment

Five-hundred mL of a 1 mg/L glyphosate solution was prepared and added to a beaker. GAC was weighed, added to beakers and mixed by a jar-test machine (Shin Seang Instrument Co., Korea). The weight percentages of GAC were 0.5% (w/v) and 1% (w/v), respectively. The propeller speed was fixed at 100 rpm in this experiment. The supernatant was sampled at 5 min, 15 min, 30 min, 1 h and 2 h, respectively to determine the remaining glyphosate.

Analytical procedure

Before being analyzed by high performance liquid chromatography (HPLC) with a fluorescence detector, the supernatants of glyphosate and AMPA were derivatized with 9-fluorenylmethylchloroformate to yield the highly fluorescent derivatives of the analytes, which were sensitive to a fluorescence detector^{9,10}. The analytical procedure was as follows: First, 1 mL of each sample was added to a test tube containing 2 mL of 0.075 M sodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7$) to adjust the pH. Then, 3 mL of 0.015 M 9-fluorenylmethyl chloroformate was added for a derivatization reaction. After shaking and standing for 30 min, 5 mL of pure dichloromethane was added for partition. The water layer (2 mL) was collected and analyzed by HPLC using a fluorescence detector. A Shimadzu-10A high performance liquid chromatography system (Shimadzu Co., Kyoto, Japan) was equipped with a fluorescence detector (Gmbh, Eresing, Germany). A fluorescence detector was used at the excitation and emission wavelengths of 265 nm and 315 nm, respectively. A 250 mm x 4 mm column (NH_2 5 μm , Merck, Germany) was used. The mobile

phase was composed of acetonitrile and 0.1 M of KH_2PO_4 (5 : 5 for analysis of glyphosate and 3 : 7 for analysis of AMPA).

RESULTS AND DISCUSSION

About 50% of the glyphosate was removed with a 2 mg/L hypochlorite treatment and more than 90% was eliminated when 5 mg/L of hypochlorite was applied as shown in Fig. 1. When AMPA, the main metabolite of glyphosate was treated with hypochlorite more than 30% of the AMPA was removed with a 2 mg/L hypochlorite treatment and 50% at 5 mg/L as shown in Fig. 2.

It is well known that hypochlorite can react readily with nitrogenated compounds¹¹. The reaction between the nitrogenated compounds and sodium hypochlorite was found to follow an overall second order rate law, the first order was relative to the

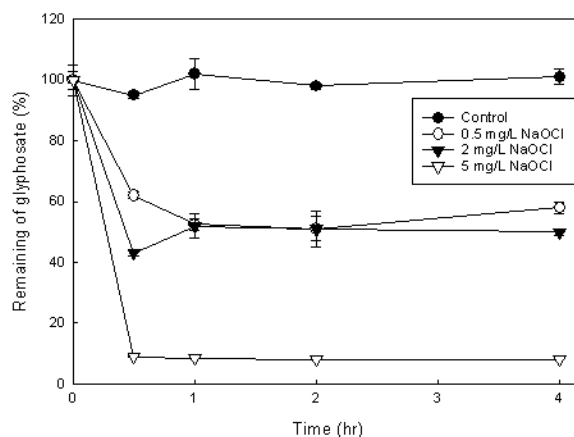


Fig. 1. Removal efficiency of glyphosate by NaOCl.

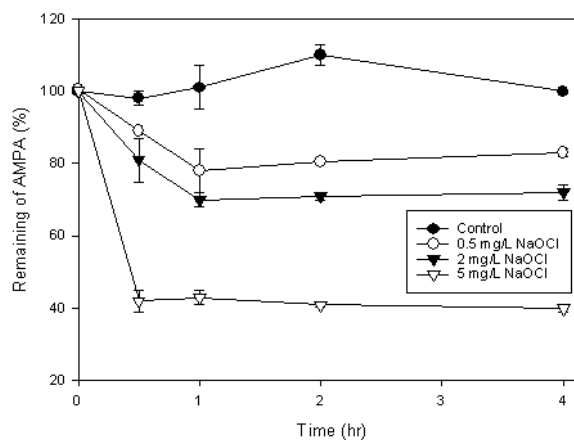


Fig. 2. Removal efficiency of AMPA by NaOCl.

amine and the first order was relative to the sodium hypochlorite:

$$R = k[\text{NaOCl}][\text{amine}]$$

The rate constants of reactions between sodium hypochlorite and many nitrogenated compounds have been calculated before by researchers. Glycine, the basic compound of glyphosate, was found to react with hypochlorite effectively exhibiting a high rate constant k of about $11.3 \times 10^7 \text{ mol}^{-1}\text{dm}^{-3}\text{s}^{-1}$ ¹¹⁾.

AMPA, which is the main metabolite of glyphosate in soil, was not found to be a byproduct of the reaction between glyphosate and hypochlorite.

Generally, products between nitrogenous compounds and sodium hypochlorite are chloramines. Chlorine can substitute the H atom in an amine group to form monochloramine. The substitution of chlorine can continue to form dichloramine and trichloramine if there are more hydrogen atoms attached to the amine group. Initial chlorine-to-nitrogen (Cl : N) ratio, pH, temperature, and contact time are all important factors in determining which kinds of chloramines will be predominant ¹²⁾. The reactions between organic amino compounds and hypochlorite should in theory be the same as the reactions between ammonia and hypochlorite ^{11,13,14)}. Therefore, the production of glyphosate and AMPA, when resulting from a reaction with hypochlorite, might be chloramine compounds. It is monochloramine in the case of glyphosate and mono and dichloramine in the case of AMPA.

When the results were considered, it was clear that AMPA was more difficult to oxidize with NaOCl than glyphosate. The reason may have been the disappearance of the carboxylic group in AMPA. In a glyphosate structure, both the phosphonic and carboxylic groups are electrophilic groups and try to attract non-paired electrons of nitrogen atoms to them. Since the electronegativity of both groups do not differ a great deal, the net of the dipole moment around the nitrogen atom is small. As a result, NaOCl can oxidize the N atom easily. On the other hand in AMPA, the disappearance of the carboxylic group results in the higher dipole moment. The non-paired electrons of nitrogen are attracted pretty strongly by the phosphonic group resulting in the inhibition of the oxidation of the N atom by NaOCl.

The glyphosate removal experiments, that tested the effects of various pH were performed because the pH level of the inlet water, normally, is not adjusted during sodium hypochlorite treatment (pH is controlled before the sedimentation process which follows the hypochlorite treatment). From the results, it was apparent that the pH level can affect the reaction between glyphosate and NaClO. When the pH is increased, the removal efficiency of glyphosate by NaClO also increased. A pH level of 9 was more effective than that of 7 and 5. The results were similar to that of other research in that the rate of reaction between the nitrogenous compounds and hypochlorite was pH dependent. Abia et al ¹¹⁾ determined the relationship between K (rate constant) and pH as follows :

$$K = \frac{a[\text{H}^+]}{(b + [\text{H}^+])(c + [\text{H}^+])}$$

where, a , b , and c are constants to be optimized.

At the lower pH level, HOCl can react with H^+ and form H_2O and Cl_2 . As a result, when the amount of oxidizing agent (NaOCl) was decreased, the removal efficiency of glyphosate decreased.

In the coagulation process, it was apparent that glyphosate can be removed by adsorption. When there was no addition of the coagulant, PAC, the adsorbed amount of glyphosate increased when the TSS (total suspended solid) in the soil suspension increased both in soil 1 and soil 2 (Fig. 3, 4). After the evaluation of the TSS and the soil properties of both soils (Table 1), even though the TSS and the amount of organic matter in soil 2 used in the experiment were greater than those of soil 1, it seemed that soil 1 could adsorb glyphosate more effectively than soil 2. Therefore, the amounts of clay minerals in soil 1 were determined to be the main factor, which caused greater adsorption. These results parallel those of existing research ¹⁵⁻¹⁸⁾, which has determined that the binding of glyphosate to soil was attributed to the reaction between the phosphonic group and the polyvalent cations adsorbed on clay.

With the addition of 50 mg/L of PAC, the removal efficiency of glyphosate increased to about 20-40%. PAC is generally used to decrease the zeta

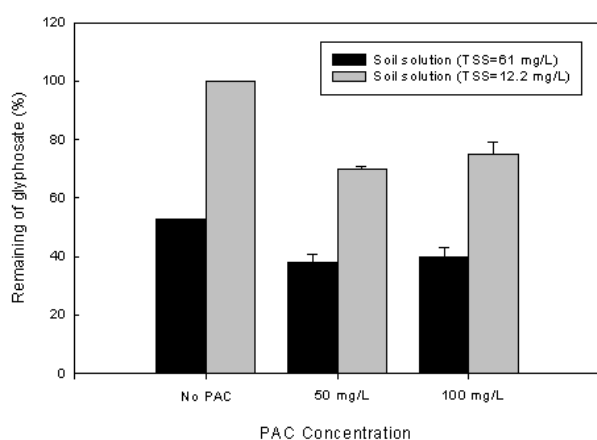


Fig. 3. Removal efficiency of glyphosate by PAC in soil 1.

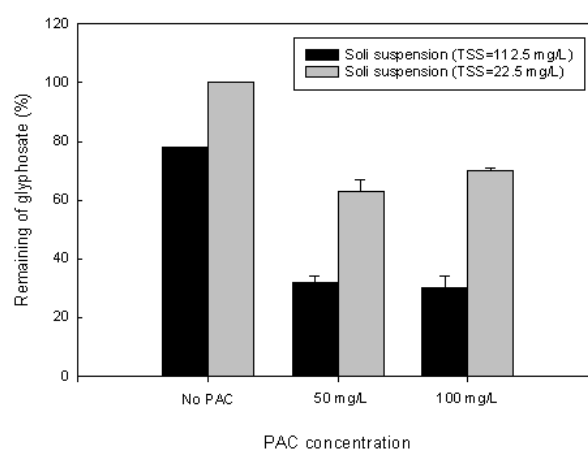


Fig. 4. Removal efficiency of glyphosate by PAC in soil 2.

Table 1. Physico-chemical properties of soils used in PAC treatment

Soil	Texture(a)	Particle size dist. (%)			pH 1:5(b)	O.M.(%)	CEC (cmol/kg)
		Clay	Silt	Sand			
Soil 1	LiC	33.0	42.0	25.0	7.3	1.0	13.2
Soil 2	SiCL	16.0	70.6	13.4	7.4	3.8	13.9

a) LiC : light clay, SiCL : silty clay loam b) Soil : Deionized water

potential on the surface of colloids, thus inducing rapid sedimentation. The availability of aluminum ions in PAC is the predominant factor responsible for sinking suspended colloids. When aluminum ions enter the water, the aluminum ions become hydrated, meaning that the water molecules attach themselves to the aluminum ions. Also, anions present in water can attach themselves to these aluminum ions. These reactions result in large, positively charged molecules that have aluminum ions at their center. These particles may have charges as high as +4. Since glyphosate has functional carboxyl and phosphate groups which are negatively charged, it can react with aluminum ions easily. However, when the concentration of PAC increased from 50 to 100 mg/L, the removal efficiency did not increase in both kinds of soil. This result may have been due to the amount of clay present. Aluminum ions attached to the functional groups of glyphosate need a greater amount of colloids in order to attach and settle down.

It appeared that the addition of PAC could increase the removal efficiency in the system containing soil 2 more than in a system that has soil 1. Following the addition of 100 ppm of PAC, soil 2 could adsorb

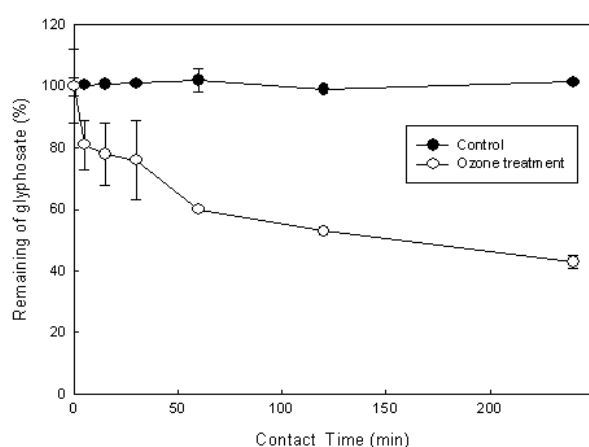
about 70% of the glyphosate and about 62% in soil 1. This could have been due to the higher amount of organic matter in soil 2. Without the addition of PAC, more glyphosate was adsorbed in soil 1 because it had more clay minerals. However, when an excessive amount of PAC, which also had polyvalent cations similar to those found in clay minerals, was added the clay mineral content of the soil was not estimated to be a major factor. Humic substances were then determined to have been the major factor for the adsorption. The adsorption of glyphosate was found to be directly proportional to the humic content of the soil. The greater the humic content the greater the degree of adsorption. Related studies concluded that glyphosate was found to be more easily and reactively adsorbed by humic substances, even more so than clay minerals. Adsorption between humic substances and glyphosate has been explained as multiple hydrogen bondings which can occur among the various acidic and oxygen-containing groups of both molecules¹⁹.

The results in Table 2 indicate that not only the amount of clay minerals present but also the kinds of clay can affect the adsorption of glyphosate.

Montmorillonite, which has a higher specific

Table 2. Freundlich and Langmuir constants for the adsorption of glyphosate on kaolinite and montmorillonite

Clay	Freundlich equation			Langmuir equation		
	K	1/n	r	X _m	K	r
Kaolinite	712	0.5353	0.95	1132.95	2.28	0.90
Montmorillonite	1085.42	0.5521	0.96	4155	0.6825	0.99

**Fig. 5. Removal efficiency of glyphosate by ozonation.**

surface area (about 700-800 m²/g) and higher cation exchange capacity (about 70-100 cmol/kg), has shown a very high adsorption property compared to kaolinite (specific surface area about 7-30 m²/g, CEC about 1-10 cmol/kg)²⁰. A higher K (in Freundlich isotherm) and higher X_m (in Langmuir isotherm) could be observed when glyphosate was adsorbed by the montmorillonite.

About 50% of the glyphosate was removed by ozonation after 4 hr as shown in

Fig.5. The ozone dose used in this experiment (375 mg/min) was much greater than solubility of ozone in water, which has been generally estimated to be less than 40 mg/L. The rate limiting step of the reaction was found to be the dissolving of ozone into water. The solubility of ozone in water has been found to obey Henry's Law and is a function of the temperature and the pH level.

The ozone can decompose into OH. (hydroxyl radicals) which are the strongest oxidants in water²¹. Ozone is a very selective oxidant, whereas OH radicals are not selective and react quickly with many dissolved compounds. Under the conditions of this experiment, however, where the pH was not high nor was there the addition of hydrogen peroxide, the amount of OH radicals should have been less.

Therefore, it may be concluded that glyphosate was oxidized predominantly by ozone.

Even though the products were not investigated in this experiment, research was performed to identify the products of some amino compounds including glycine, the basic component of glyphosate and AMPA²². In those experiments after excessive ozonation, glycine decomposed into ammonium ions as the major inorganic nitrogen species (about 60%) and also nitrite (20%) and nitrate ions (20%). Also, organic products were found which included oxalic and oxamic acid. These products are not known to be harmful to human health. Currently, the only form of ozonation regulated in drinking water treatment is bromate, which is formed during the ozonation of water containing bromide²³. Hence, the by-products of glyphosate formed during ozonation may be less harmful than those of glycine.

Futhermore, a batch experiment was also performed (spiking the glyphosate in the saturated ozone) but because the half-life of ozone in water is very short (ranging from a minute to 1 h depending on water characteristics), the removal efficiency was found to be low (about 10%, data not shown)²⁴.

Even though the results from this experiment did not provide much definitive information, at least it confirmed that more glyphosate will be removed (>50%) in a real drinking water treatment system in which ozone solubility can be increased to a greater degree than it was than in this experiment. This can be achieved by simple methods, for example pressurizing ozone gas, decreasing the temperature, increasing the flow rate of ozone gas, etcetera.

The removal efficiency of glyphosate by GAC was the least effective among water treatment process as shown in Fig. 6. Actually, it was not surprising that glyphosate, a polar compound, was not readily adsorbed by GAC which is commonly used to adsorb non-polar compounds. A portion of the glyphosate adsorption by GAC may have resulted from weak physical adsorption. This is visibly evident in the

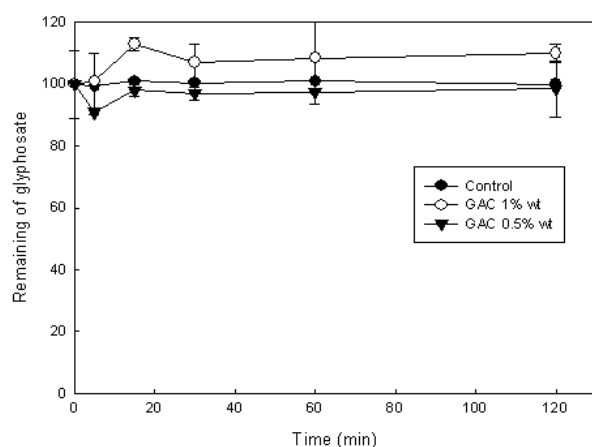


Fig. 6. Removal efficiency of glyphosate by GAC.

graph lines rising up and falling down over the duration of the experiment.

CONCLUSIONS

The sodium hypochlorite treatment was very effective with respect to the removal of glyphosate. In the coagulation process, the amount and kinds of clay minerals were determined to be important factors accountable for the removal of glyphosate. It was also determined that ozone could transform glyphosate into other compounds but its low solubility in water limited the rate of reaction. The adsorbed amount of glyphosate, which is a polar compound, by GAC was found to be negligible. However, it can be reasoned that even though glyphosate can contaminate surface water and enter the drinking water processing system, it is apparent that glyphosate can be effectively removed from the drinking water treatment system.

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