



## **Pilot Study Report**

for

## **Z-88<sup>®</sup> Radium Removal System**



conducted for

**Lower Colorado River Authority  
Tow Village, Texas**

**April 1, 2014**

## Executive Summary

A radium removal pilot study was conducted for the Lower Colorado River Authority (LCRA) at the Tow Village, Texas water system. Before the pilot study commenced, naturally occurring radionuclides in Tow Village's raw water source exceeded the current Maximum Contaminant Level (MCL) for gross alpha and radium.

LCRA selected Water Remediation Technology's (WRT) Z-88<sup>®</sup> Radium Treatment Process as a cost effective solution to their radium problem. WRT provided a Modular Component treatment system, which was delivered in September 2013 and installed in early October 2013.

The purpose of this pilot study is to document the effectiveness of the WRT system on high radium water and to provide information necessary to meet regulatory compliance.

The treatment system has successfully met radium compliance at all times during the pilot study. The system was placed into operation on October 17, 2013 and remains in full scale operation. The treatment system continues to effectively reduce the level of radium (Figure 1) and adjusted gross alpha (Figure 2) to less than the MCL at all times (see gross alpha discussion later in this report)

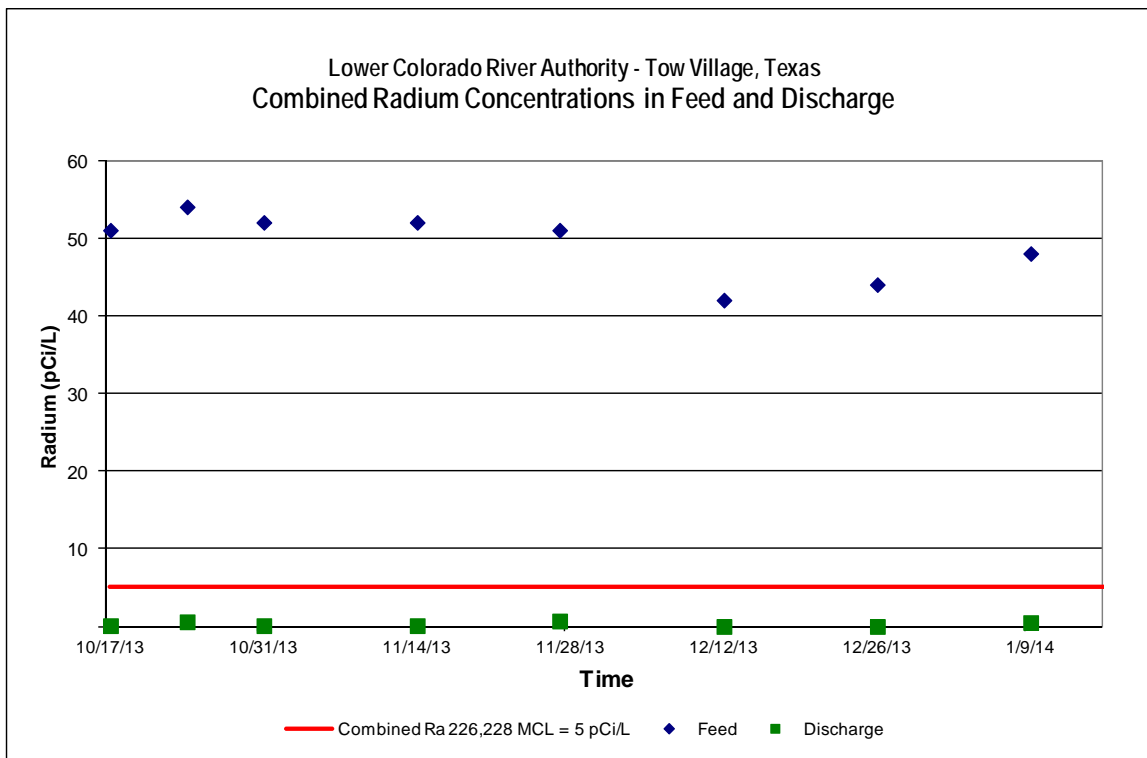


Figure 1

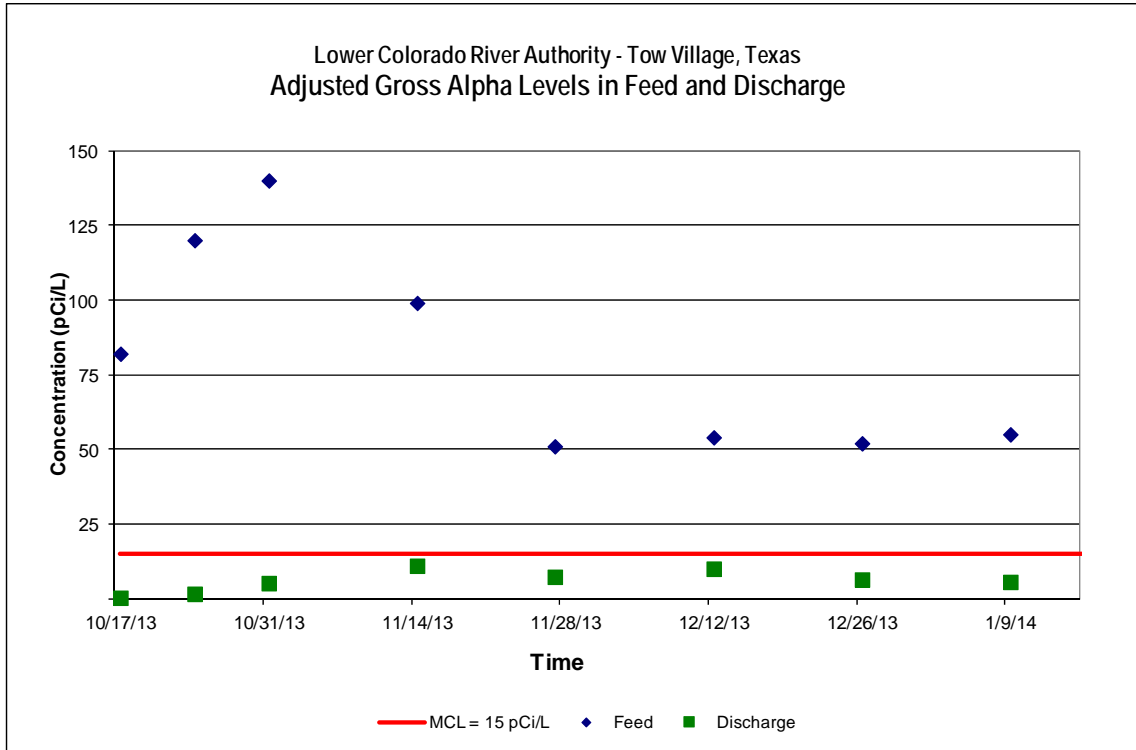


Figure 2

The results are also shown in Table 1. The average feed concentration of combined radium, 49.3 pCi/L, was reduced to an average of 0.3 pCi/L; well below the MCL of 5 pCi/L. The average feed concentration of adjusted gross alpha, 81.0 pCi/L, was reduced to an average of 5.0 pCi/L; also well below the MCL of 15 pCi/L.

**Table 1. Radium and Adjusted Gross Alpha levels in feed and discharge water.**

Combined Radium	Feed (pCi/L)	Discharge (pCi/L)
<b>Combined Ra 226, 228 MCL</b>	—	<b>5.0</b>
Average	49.3	0.3
Highest value	54	0.7
Lowest Value	42	0.0

Adjusted Gross Alpha	Feed (pCi/L)	Discharge (pCi/L)
<b>Gross Alpha MCL</b>	—	<b>15.0</b>
Average	81	5
Highest value	140	11
Lowest Value	46	0.1



### Application Information

Tow Village is located approximately 61 miles northwest of Austin in Llano County. The water source for the system's approximately 40 connections is a single well withdrawing from the Hickory aquifer.

### Technology Overview

WRT's Z-88<sup>®</sup> Radium Treatment Process utilizes proprietary adsorptive media in a series of treatment vessels to remove radium from drinking water. Radium laden water is passed through columns of Z-88<sup>®</sup> media in a down-flow manner, insuring that each particle is in intimate contact with the water. Z-88<sup>®</sup> is suitable for radium removal due to its extremely high surface area (30 square meters / gram) and its affinity for capturing select cations.

Z-88<sup>®</sup> is placed in vertical columns, or stages, with sufficient depth of media to achieve the required EBCT (Empty Bed Contact Time), typically 5 to 15 minutes per stage. Depending on the radium and other contaminant content of the feed water, multiple stages (typically 2 to 6) can be used for treatment.

Because of the large quantity of media in the system, no media exchanges are typically required during the course of a pilot study.

No chemicals are added to the water for the treatment process and there is no change of water chemistry, except for the removal of radium, barium, and gross alpha, through the treatment process.

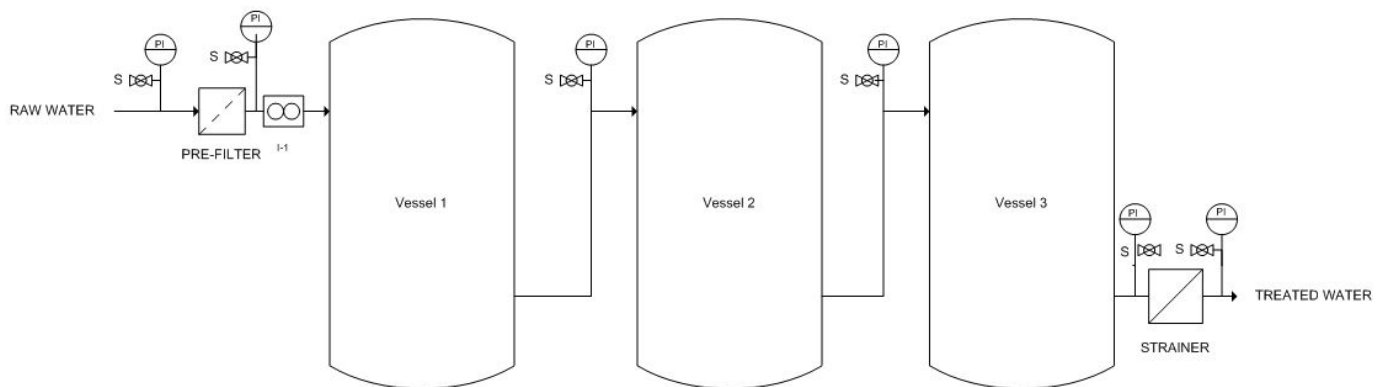
After the media is loaded with radium, it is removed from the circuit and permanently disposed of in a licensed facility. The anticipated media exchange frequency based on the pilot study is estimated to be once every 1 to 2 years. This estimate is not definitive. The results of the pilot test suggest that the Z-88<sup>®</sup> media is removing materials exhibiting alpha activity in addition to radium-226 isotope. Therefore specific removal efficiency or longevity of gross alpha activity removal from the raw water, not affiliated with radium-226 is not known. Gross alpha and combined radium-226 and -228 will be analyzed quarterly in order to monitor removal and anticipate media exchanges.

WRT designs, manufactures and provides the equipment and media used in the facility. The handling and exchange of new media to replace spent media, as well as the shipping and disposal into licensed disposal sites, will be handled by WRT in compliance with all license conditions. WRT is licensed to remove and dispose of the radioactive media (See Texas Department of State Health Services Radioactive Material License L06316). The treatment media is ANSI/NSF Standard 61 certified for use in drinking water. Certification indicates the Z-88<sup>®</sup> media exceeds established NSF 61 contaminant leaching requirements for media materials used in the treatment of drinking water.

Based on the variability of media exchanges necessary to maintain compliance, LCRA does not have an executed agreement for media replacement. If a contract were signed, LCRA anticipates that over the course of the life of the media, prices would change and the contract would need to be updated. When the results of the finished water begin to show an increase in the level of radionuclides, LCRA will execute a contract with WRT in anticipation of a media replacement. LCRA will allow ample time to ensure the system will remain in compliance with the relevant MCLs.

### Equipment Overview

The WRT Modular Component System (MCS) was installed for the Lower Colorado River Authority at the Tow Village water treatment site. The full scale treatment equipment used for this pilot study consists of three treatment vessels arranged in series. The treatment vessels are 42" diameter by 72" vertical height vessels, each containing approximately 49" or 37 cu. ft. (approximately 2,100 lbs) of Z-88<sup>®</sup> granular media. All vessels operate in a down-flow configuration; with the flow exiting the bottom of the first vessel, then following the same flow path through vessel 2 and vessel 3. The last component in the system is a safety strainer. Sample ports are located prior to the first vessel, and after each treatment vessel in the series. All sample valves and pressure indicators are arranged on a central sampling station to facilitate monitoring operations.



**Figure 3. Simplified Process Drawing**



Tow Village's Z-88<sup>®</sup> Radium Removal treatment system



Face piping and sampling station



Tow Village radium removal system treatment building



### Statement of Purpose

The combined radium levels in the raw water during the pilot study were as high as 54.0 pCi/L, exceeding the Environmental Protection Agency (EPA) mandated combined radium MCL of 5 pCi/L. The raw water's highest adjusted gross alpha result of 140 pCi/L measured much higher than the EPA MCL of 15 pCi/L. Both parameters are not in compliance with the EPA mandated MCL values.

The purposes of this pilot study are to:

- Demonstrate the ability of the WRT Z-88<sup>®</sup> Radium Treatment Process to consistently and effectively reduce the radium content to below the MCL on this specific water.
- Demonstrate the reliability and ease of operation of the WRT Process.
- Comply with regulatory requirements.

### Delivery and Installation of the Modular Component System

The Z-88<sup>®</sup> treatment system was delivered to the Lower Colorado River Authority's Tow Village water treatment site and subsequently installed and placed into operation. The pilot study began the same day on October 17, 2013.

Operator training for system operation, monitoring and sampling was conducted on the final day of installation and a schedule for sampling was established. Samples were collected by the Lower Colorado River Authority's operator and Environmental Laboratory Services personnel from sample valves located in the feed line and on the discharge from Vessel 2 and 3, at pre-determined sample intervals. Four samples taken at:

- Feed (prior to Vessel 1);
- Discharge from Vessel 2;
- Discharge from Vessel 3; and
- Final treated water.

### Analytical

The samples for radium and gross alpha analysis were delivered to Hazen Research, Inc. (TCEQ Certificate No.: T 104704256-13-4) in Golden, Colorado. Samples for water quality analysis including metals were delivered to Environmental Laboratory Services in Austin, Texas. Both laboratories are National Environmental Laboratory Accreditation Program certified laboratories. Methods for analysis were:

Radium 226

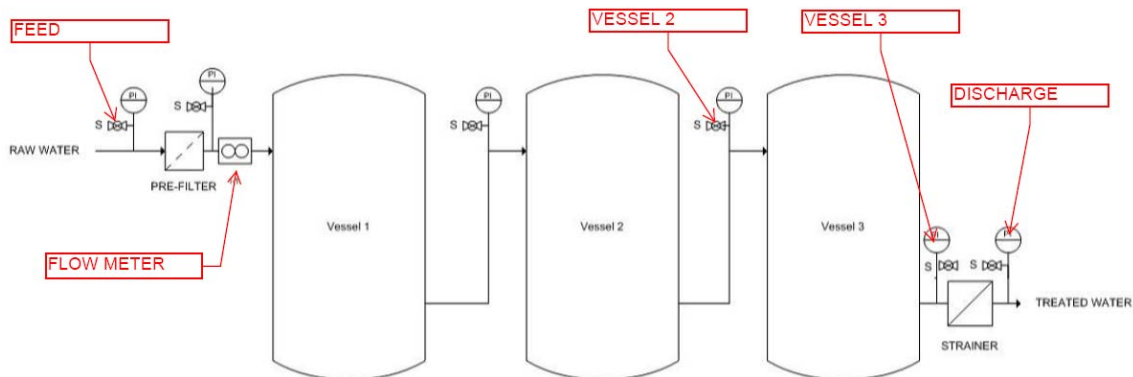
7500-Ra B

Radium 228	EPA Ra-05
Gross Alpha	SM 7110 B and SM 7500-U B*
Uranium	ASTM D2907-97
Metals	M200.7
ICP-MS	M200.8
Anions	E300.0

\*SM 7500-U B was only used for the 11/27/13 sample to compare gross alpha measurements (see Gross Alpha discussion on page 12).

### Results and Discussion

The sampling results are shown in Tables 2 and 3. Feed samples were collected immediately prior to the first treatment vessel. Samples were then taken immediately after the second vessel (V-2) and the third vessel (V-3) at their discharge point (see Figure 4 below). Final treated water was taken after the strainer. Effectively results from V-3 and discharge are the same. Analytical laboratory certificates are attached as Appendix A. Figures 5 and 6 show combined radium 226 and 228 and adjusted gross alpha levels in the feed water entering the treatment system, and treated water exiting the treatment system. The graphs show that the treatment system successfully reduced combined radium and adjusted gross alpha in the treated water to significantly below the required MCL.



**Figure 4. Sample Locations**

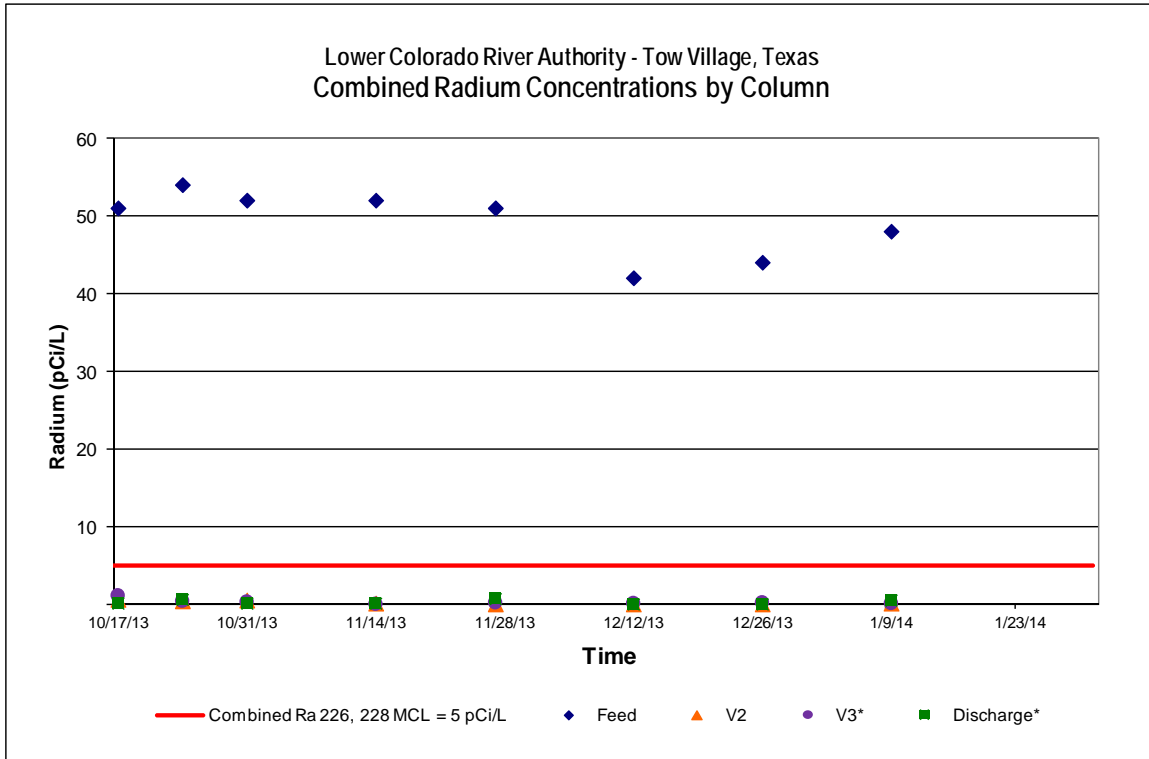


**Table 2. Radium Test Results**

Radium 226		Column Concentrations (pCi/L)			
Date	Feed	V-2	V-3*	Discharge*	MCL
10/17/13	21	0.1	0.2	0.1	—
10/24/13	21	0.1	0.1	0.1	—
10/31/13	22	0.1	0.1	0.1	—
11/14/13	20	0.1	0.0	0.1	—
11/27/13	22	0.0	0.2	0.1	—
12/12/13	19	0.0	0.1	0.0	—
12/26/13	18	0.0	0.2	0.0	—
1/9/14	20	0.1	0.1	0.3	—
Radium 228		Column Concentrations (pCi/L)			
Date	Feed	V-2	V-3*	Discharge*	MCL
10/17/13	30	0.5	0.9	0.0	—
10/24/13	33	0.3	0.3	0.5	—
10/31/13	30	0.4	0.2	0.0	—
11/14/13	32	0.0	0.0	0.0	—
11/27/13	29	0.0	0.0	0.6	—
12/12/13	23	0.0	0.0	0.0	—
12/26/13	26	0.0	0.0	0.0	—
01/09/14	28	0.0	0.0	0.2	—
Combined Radium		Column Concentrations (pCi/L)			
Date	Feed	V-2	V-3*	Discharge*	MCL
10/17/13	51	0.6	1.1	0.1	5.0
10/24/13	54	0.4	0.4	0.6	5.0
10/31/13	52	0.5	0.3	0.1	5.0
11/14/13	52	0.1	0.0	0.1	5.0
11/27/13	51	0.0	0.2	0.7	5.0
12/12/13	42	0.0	0.1	0.0	5.0
12/26/13	44	0.0	0.2	0.0	5.0
01/09/14	48	0.1	0.1	0.5	5.0

\* Samples taken after no further treatment.

Figure 5 below, presents in graph format, the data in Table 2.



\* Samples were taken from the same sample stream

Figure 5

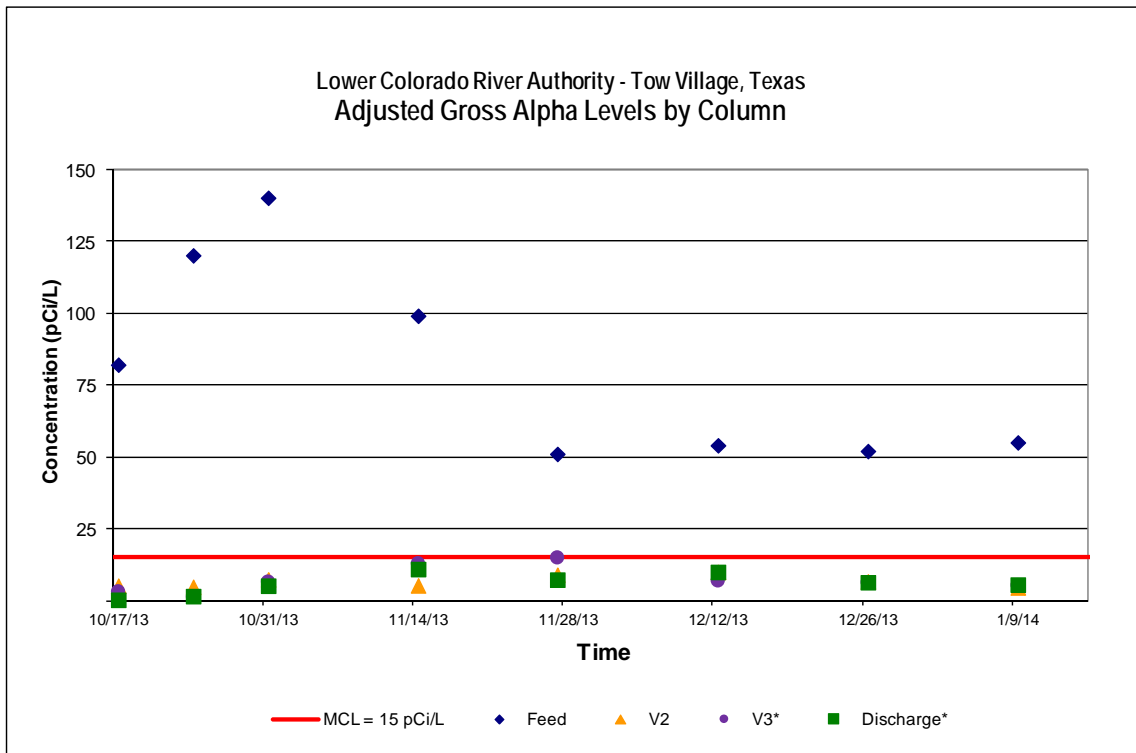
**Table 3. Adjusted Gross Alpha Test Results (using method SM 7110 B)**

Adjusted Gross Alpha Date	Column Concentrations (pCi/L)				
	Feed	V-2	V-3*	Discharge*	MCL
10/17/13	82	5.2	3.2	0.3	15.0
10/24/13	120	4.8	1.4	1.6	15.0
10/31/13	140	7.4	6.6	5.2	15.0
11/14/13	99	5.3	13	11	15.0
11/27/13	51	9	15	7.3	15.0
12/12/13	54	10	7	10	15.0
12/26/13	52	6.7	6.4	6.4	15.0
01/09/14	55	4.6	5.4	5.6	15.0

\* Samples taken after no further treatment.

NOTE: 11/27/13 adjusted gross alpha results were calculated using ASTM D2907-97 values versus SM 7500-UB

Figure 6 below, presents in graph format, the data in Table 3.



\* Samples were taken from the same sample stream

Figure 6

## Gross Alpha

Under the EPA Radionuclide Rule, gross alpha measurements initially measuring above the MCL value of 15 pCi/L should be reported with a revised figure referred to as the “adjusted gross alpha.” The adjusted gross alpha is defined as the gross alpha activity less than the contribution of uranium and radon alpha activities. Adjusted gross alpha activity in the treated water at Tow Village was reduced to below the EPA MCL of 15 pCi/L in all treated water measurements.

The Z-88<sup>®</sup> process is not designed to remove all alpha activity generating isotopes that may be present in the water but specifically targets and is selective to radium. For this pilot study, Z-88<sup>®</sup> showed effective radium removal. Since the majority of alpha activity seen in most waters is due to the radium-226 isotope, removing this from the water should reduce the overall alpha activity.

In general, this pilot showed this to be true. In two instances adjusted gross alpha discharge samples were reported at 11.0 and 10.0 pCi/L. Due to these elevated results, WRT had a secondary uranium analysis performed. In the ASTM D 2907-97 method (used predominantly in this pilot study), the adjusted gross alpha contribution from uranium is estimated by gravimetrically measuring the uranium concentration in the sample and converting this measurement to an activity using a recognized natural uranium activity ratio of  $6.77 \times 10^{-7}$  Ci/gram. On occasion, natural ground water samples do not adhere to this ratio. This is most likely due to a sample’s uranium isotopic mixture not consistent with the majority of natural uranium in secular equilibrium or similar to that found in most uranium bearing waters.

To assure the validity of this recognized ratio for use with Tow Village’s water supply, WRT asked the testing laboratory to separately test for the actual uranium alpha activity using EPA method SM 7500-U B. This value is then compared to the estimated or assumed activity for natural uranium using the standard ratio. This separate uranium activity test was performed on the November 27, 2013 sample. The results of our request are provided below in Table 4.

**Table 4. Adjusted Gross Alpha Measurement Adjusted Variability**

Sample Date	Sample Identification	Gross Alpha (pCi/L)	Gross Alpha (pCi/L) by ASTM D2907-97 & National Uranium Ratio	Gross Alpha (pCi/L) by SM Method SM-7500-UB
11/27/13	Raw Water	52	51	46
11/27/13	Vessel 2	10	9	3
11/27/13	Vessel 3	17	15	11
11/27/13	Discharge	8.9	7.3	0.1

The results of these tests reveal that the majority of gross alpha activity remaining in the treated water is attributed to uranium. And that this activity is in all cases greater than the recognized natural uranium activity ratio.

Therefore adjusted gross alpha results in this study are elevated and it can be surmised that a commensurate reduction in adjusted gross alpha values would be realized had the actual uranium activity test been performed on earlier samples. It is suggested that for any future sampling, Tow Village should measure using EPA method SM 7500-U B and not estimate from a gravimetric determination using the natural uranium activity ratio.

## Uranium

Samples were collected during this study to evaluate the general level of uranium in the product water. Table 5 contains the uranium test results taken during the pilot study. The WRT Z-88<sup>®</sup> process is not designed to remove uranium. Supporting documentation for Table 5 is attached as Appendix A.

Because the uranium levels in the initial water analysis were well below the MCL, uranium removal was precluded as a target contaminant in reducing gross alpha. Uranium levels remained below detection limits in the feed water and discharge throughout the pilot testing.

**Table 5. Uranium Test Results**

Uranium Date	Column Concentrations (µg/L)				
	Feed	V-2	V-3*	Discharge*	MCL
10/17/13	2.6	1.8	2.0	1.4	30.0
10/24/13	2.7	2.7	1.5	1.9	30.0
10/31/13	1.9	2.1	1.6	1.6	30.0
11/14/13	1.9	2.0	2.4	2.0	30.0
11/27/13	1.9	2.1	2.6	2.3	30.0
12/12/13	1.2	1.1	1.2	1.8	30.0
12/26/13	1.5	1.6	1.7	1.6	30.0
01/09/14	3.9	1.7	1.6	1.6	30.0

\* Samples taken after no further treatment.

## Gross Alpha and Uranium Result Discussion

In a few instances, specifically 11/14/13 and 11/27/13 samples predominantly, uranium and adjusted gross alpha values increased with further treatment (i.e. activity or concentrations increased from Vessel 2 to 3). Results listed and graphically depicted above do not show the variability of the radioactive decay process (counting error) as shown on the results sheets (see Appendix A). For instance, the 11/27/2013 adjusted gross alpha measurement for Vessel 3 of 11 pCi/L has a counting error of plus or minus 5 pCi/L. With this precision realized, the measured value is within the measured GA values obtained in other sampling dates. It should be noted that gross alpha measurements in water are inherently variable and carry a high degree of imprecision and therefore no conclusions can be definitively made on the discrepancy with these two sample points.





## Water Quality

A water quality analysis was performed on the feed water to the treatment system and on the treated water exiting the WRT system to document any changes in water quality through the treatment process. The results of those tests are shown in Table 6 and 7. Other than the reduction of radium, barium and gross alpha, there is no significant change to the water quality. The reduction in barium is consistent with Z-88<sup>®</sup> media performance. The media will irreversibly remove barium from the raw water to trace level. The barium results in the raw water quality analysis are significant but not detrimental to the radium removal performance of the Z-88<sup>®</sup> media. Support documentation for Table 6 and 7 are attached as Appendix B.

**Table 6. Water Quality Test Results**

Lower Colorado River Authority - Tow Village, Texas							
WATER QUALITY DATA							
Item	units	October 17, 2013		October 31, 2013		November 14, 2013	
		Pre WRT Process	Post WRT Process	Pre WRT Process	Post WRT Process	Pre WRT Process	Post WRT Process
Alkalinity	mg/L	316	332	320	325	319	318
Antimony	mg/L	<0.00100	<0.00100	<0.00100	<0.00100	<0.00100	<0.00100
Arsenic	mg/L	<0.00200	<0.00200	<0.00200	<0.00200	<0.00200	<0.00200
Barium	mg/L	0.222	<0.00200	0.206	<0.00200	0.217	<0.00200
Beryllium	mg/L	<0.00100	<0.00100	<0.00100	<0.00100	<0.00100	<0.00100
Calcium	mg/L	74.9	0.799	71.3	0.739	72.4	1.07
Chloride	mg/L	5.30	5.3	5.93	6.09	5.92	5.95
Chromium	mg/L	<0.00100	<0.00100	0.0100	0.00891	0.0138	0.0152
Copper	mg/L	<0.00100	<0.00100	<0.00100	0.00157	<0.00100	0.00168
Fluoride	mg/L	0.300	0.280	0.270	0.253	0.260	0.242
Hardness	mg/L	335	3.26	324	118	328	151
Iron	mg/L	0.223	<0.500	0.245	<0.0500	0.233	<0.0500
Lead	mg/L	<0.00100	<0.00100	<0.00100	<0.00100	<0.00100	<0.00100
Magnesium	mg/L	36.0	0.308	35.5	28.1	35.8	36.1
Manganese	mg/L	0.0197	<0.00100	0.0210	0.00828	0.0230	0.0167
Mercury	mg/L	<0.0700	<0.0700	<0.0700	<0.0700	<0.0700	<0.0700
Nickel	mg/L	<0.00100	<0.00100	<0.00100	<0.00100	<0.00100	0.00116
Nitrate as N	mg/L	<0.0500	<0.0500	<0.0500	0.0645	<0.0500	0.0530
Nitrite as N	mg/L	<0.0500	<0.0500	<0.0500	<0.0500	<0.0500	<0.0500
Phosphorus	mg/L	<0.0200	<0.0200	<0.0200	<0.0200	<0.0200	<0.0200
Potassium	mg/L	4.32	4.30	4.27	4.08	4.18	3.58
Selenium	mg/L	<0.00400	<0.00400	<0.00400	<0.00400	<0.00400	<0.00400
Silica	mg/L	13.6	17.2	13.2	15.1	13.3	14.6
Sodium	mg/L	5.60	162	5.15	98.2	5.32	78.4
Sulfate	mg/L	13.3	13.4	14.0	13.9	13.8	13.5
Thallium	mg/L	<0.00100	<0.00100	<0.00100	<0.00100	<0.00100	<0.00100
Total Dissolved Solids	mg/L	350	405	341	362	344	354
Total Organic Carbon	mg/L	<0.500	<0.500	0.617	0.696	<0.500	<0.500
Uranium	µg/L	2.44	1.78	2.15	1.93	2.26	2.82
Zinc	mg/L	<0.00400	<0.00400	<0.00400	<0.00400	<0.00400	<0.00400

**Table 7. Volatiles and Haloacetic Acids Test Results**

<b>Volatiles</b>	<b>Column Concentrations (µg/L)</b>
<b>November 7, 2013</b>	<b>Discharge</b>
Bromodichloromethane	<1.00
Bromoform	<1.00
Chloroform	<1.00
Dibromochloromethane	<1.00
Total Trihalomethanes	<1.00
1,2-Dichlorobenzene-d4 (S)	97%
4-Bromofluorobenzene (S)	93.5%

<b>Haloacetic Acids</b>	<b>Column Concentrations (µg/L)</b>
<b>November 7, 2013</b>	<b>Discharge</b>
Bromochloroacetic Acid	<1.00
Dibromoacetic Acid	<1.00
Dichloroacetic Acid	<1.00
Monobromoacetic Acid	<1.00
Monochloroacetic Acid	<2.00
Total Regulated HAA	<1.00
Trichloroacetic Acid	<1.00
2,3-Dibromopropionic Acid (S)	94.6%

Tow Water System uses chlorine for disinfection. The chlorine is added after the water passes through the Z-88® Radium Removal System. The Operator Daily Sample Logs in Appendix include the chlorine dosage (noted as Chlorine Feed), which is measured in pounds per day and the chlorine residual levels (noted as Chlorine Tank), which is measured in parts per million (ppm).

### Hydraulic Loading Rate (HLR) and Empty Bed Contact Time (EBCT)

The treatment unit operates only when the well is providing water to the distribution system. The Z-88<sup>®</sup> treatment system was designed to operate at a nominal 45 GPM which is an equivalent of 4.7 GPM per square foot of treatment vessel cross-sectional area. Nominal flow conditions from 5 to 12 GPM per square foot are within the standard design operating range of the Z-88<sup>®</sup> media. However, flow conditions as low as 4 GPM per square foot are acceptable and have shown the ability to provide nominal radium removal. During pilot test operation discharge radium was between 0.0 – 0.7 pCi/L.

The average flow rate through the treatment units varied from a low of 34.7 GPM to 44.5 GPM equivalent to 3.7 to 4.7 GPM per square foot. Radium removal performance throughout the variable flow rate operation remained consistent and satisfactory. This demonstrates that any Hydraulic Loading Rate (HLR) variations within the range of the full-scale pilot test notably had negligible effect upon the Z-88<sup>®</sup> media radium removal performance. The total gallons treated during the pilot study are summarized in Table 8 and Appendix C.

The Empty Bed Contact Time (EBCT) at the design HLR through three (3) treatment vessels, each containing 49 inches of media, is 6.2 minutes each, for a cumulative EBCT of 18.5 minutes. The average EBCT through the treatment system during the pilot testing varied between 18 and 24 minutes as a result of the flow variations described above.

**Table 8. Cumulative treated flow in gallons**

Sample Data	Cumulative Treated Flow in Gallons
10/17/13	0
10/24/13	11,056
10/31/13	24,080
11/27/13	73,040
12/13/13	111,777

## Radiation Safety

The Modular Component System is designed to collect naturally occurring radioactive material while in operation and concentrates radioactive material on the solid phase of the media. Because of this action, the Z-88<sup>®</sup> media gradually becomes radioactive during normal operation. WRT both predicts and monitors the level of radiation present in the treatment system.

The total amount of radiation that members of the public can be exposed to is 2 mrem per hour and 100 mrem over the course of a year. WRT's maximum measured activity is less than half of the hourly exposure limit. Due to the limited amount of operator attention necessary for the pilot test, the annual exposure limit is also readily met.

WRT has prepared a safety plan for its treatment systems that includes radiation level monitoring, logging time spent in proximity to a unit, emergency procedures to be followed and an introduction to radiation safety for operators. Operators are instructed in radiation safety before the pilot test is started.

The Modular Component System includes appropriate equipment, radiation level monitoring, and a corresponding safety plan approved by regulatory authorities.

## Operational Results

An operation log was maintained during the pilot study, and is attached as Appendix C. The treatment system operated throughout the course of this test without any operational problems. No backwash event occurred during the pilot test operation period. No media loss events occurred during the pilot test operation period and no media was detected on the exit strainer.

## Conclusion

The WRT Z-88<sup>®</sup> Radium Treatment Process consistently reduced the radium and gross alpha in the system discharge to levels well below the required MCLs. The flow ranges seen during actual pilot testing were appropriate and no changes are recommended. The treatment system operated easily and reliably during the study.

WRT would like to thank the personnel and staff of the Lower Colorado River Authority and Tow Village for their assistance, cooperation and participation in this study.



Appendices available upon request