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Radiological Characteritics of Raw and Treated Industrial Wastewater

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Abstract: Traditionally, wastewater has been treated to remove certain contaminants in order to redeem a reusable effluent and to protect human health and environment. Recently, new contaminants are becoming of concern due to industrialization and their concentrations are increasing in different types of wastewater especially industrial wastewater. This paper addresses the presence of radioactivity and radionuclides in the raw influent and effluent from an industrial wastewater treatment plant. Although the levels of radioactivity and radionuclides were below thresholds and close to background levels but ^{224}Ra, ^{210}Po, and ^{40}K levels were elevated. The findings also confirmed the accumulation of radionuclides within the secondary biological wastewater treatment process leading to an increase in the effluent concentrations. Most importantly, different types of wastewater have different concentrations of radioactivity and radionuclides. The findings of the study are of importance to further examine radionuclides removal from wastewater and their recovery as resources.

Keywords: *wastewater, treatment, radioactivity, Gross alpha activity, Gross beta activity, radionuclides, industrial, Resource recovery*

1. Introduction (font size 12)

In many parts of the world and particularly in arid regions, wastewater reclamation is becoming a common alternative to augment water sources. Wastewater traditionally is treated to meet the thresholds for certain parameters however, recently, many emerging pollutants exist in wastewater that needs to be monitored and removed for safe wastewater reuse. One of these contaminants of emerging concern are radioactivity and radionuclides.

More frequently, wastewater treatment plants are producing effluents containing significant amounts of radionuclides and radioactivity [1-3]. These radionuclides may originate from radionuclides present in the original source of water or from industrial wastewater. Martinez et al. [4] found some levels of radionuclides in potable water treatment plants (PWTP) which is transformed to wastewater at the end. The effluent from the wastewater treatment and the and produced sludge, ultimately, end up in the environment before or after reuse. Therefore, evaluation of radioactivity and radionuclides is an essential element in wastewater managment to protect the human and environmental health [2,5]. Additionally, as a resource, recovery of radionuclides from wastewater could be an additional opportunity [6].

After entering the treatment facilities, radionuclides will fractionate between liquid and solids phases based on their physical and chemical characteristics and the type of treatment process. Some of them may even decay before being discharged from the treatment plant due to their short half-lives. Several radionuclides from different sources with different concentrations have been observed in treatment plants. The goal is to keep these concentrations under the assigned limits for each of these radionuclides [7].

Many research studies have reported on the radioactivity and radionuclides in wastewater treatment plants [1-4]. Ahmed et al. [1] reported the presence of 40K, total 210Pb, 137Cs, 226Ra, 228Ra, 238U, and 235U in the wastewater and effluents in Kuwait, and found that they would likely

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partition onto sludge and biosolids than be discharged in the liquid effluents. Also Montana et al. [2] and Camacho et al. [3] reported the presence of some radionuclides in Spain). They reported that gross beta activities were not influenced by treatment in the studied WWTPs however, gross alpha activities behave differently and an increase was detected in the effluent values compared with influent wastewater. This behavior was due to the increase in the total dissolved uranium produced during secondary treatment. Cosenza et al. [8] confirmed this finding during a long-term sampling campaign where the results revealed a relationship between the concentrations of radionuclides and the sludge residence time (SRT). Furthermore, Cosenza et al. results indicate that the radiological characteristics of the effluents do not present a significant radiological risk and make them suitable for future applications [1,3].

This paper presents the findings of a one-year monitoring campaign of radioactivity and radionuclides in an industrial wastewater treatment plant in Kuwait. This subject is important since industrial wastewater may have elevated levels of radionuclides as opposed to municipal wastewater presented in previous studies. Although specific to the surveyed industrial wastewater treatment plant, the results are of international value as it fills a gap in the field of radioactivity and radionuclides in wastewater.

2. Materials and Methods

Within a larger one-year sampling campaign, quarterly composite samples were collected from the influent and effluent of an industrial wastewater treatment plant in Kuwait. The samples were collected from Jun-2021 to June-2022, were 5l each, and were preserved using 10% nitric acid. Then the radioactivity analysis has been performed to determine the concentration of radionuclides in wastewater collected from Jun-2021 to June-2022. The four batches of samples included three representatives coded as (lagoon1, lagoon2, and effluent). Lagoon 1 is the influent from petrochemical industry and lagoon 2 were food and beverage industry wastewater. Both lagoons are primary treated separately and then combined before the biological treatment to yield one effluent.

The radioactivity concentration of the uranium and thorium series', natural radionuclides 40K, and the fission radionuclide 131I were determined by alpha and gamma spectrometry methods. Also, gross alpha and beta activities have been determined using the gross alpha and beta counting method.

The determination methods applied had been validated at radiological materials laboratories (RML) and also quality assured through the external assessment program of the ALMERA network (Analytical Laboratories for the Measurement of Environmental Radioactivity) established by the International Atomic Energy Agency (IAEA). The measurement procedure is further described following.

Sample preparation and measurements

Determination of gamma emitters

Two preparation methods were applied; the direct measurement method of the water sample using a large Marnelle beaker (3 liters) for determining 40K and 131I, and the co-precipitation method by KMnO4 for determining the radium isotopes (224Ra, 226Ra, and 228Ra). The co-precipitation method is selective for the radium and uranium isotopes but not for the other radionuclides.

Determination of 40K and 131I

The 12 samples were prepared in a large volume Marnelle Beaker (3000 ml) geometry. Gamma spectrometry system, equipped with High Purity Germanium detectors (Ortec Coaxial GMX40-83-LB-C, relative efficiency 40%, FWHM @ 1332 keV is 1.95 keV), has been used to measure 131I, 40K. The detector was shielded with low background lead. The spectrometer was calibrated using a mixed nuclide standardized solutions QCYB41 (Eckert & Ziegler Nuclitec GmbH). The efficiency calibration curve of the Marnelle Beaker counting geometry (3000 ml) is shown in figure (1).

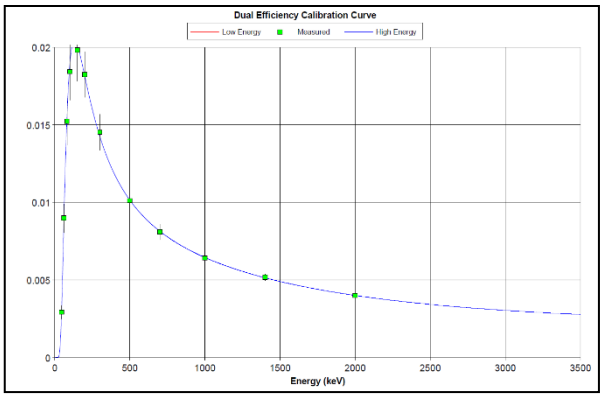
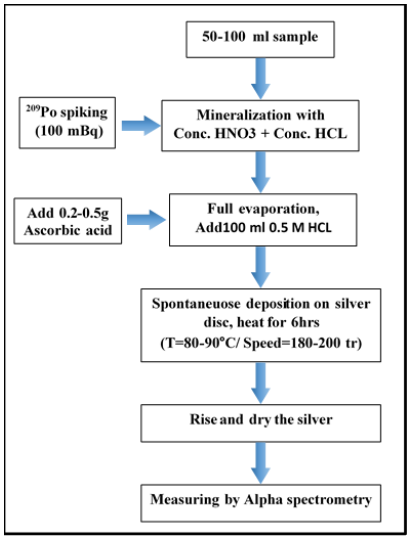


Figure1: Efficiency for gamma detector, geometry of 3L water.

2.1.1 Determination of Radium isotopes



The co-precipitation method by KMnO4 was performed for Radium isotope determination (224Ra, 226Ra, and 228Ra). A blank spiked sample was prepared and measured along with each sample for quality control and co-precipitation

recovery correction. The schismatic diagram of the method is shown in Fig. 2. The MnO2 precipitate was dissolved in 30 ml, bottled in a calibrated counting geometry (G3), and then counted on the gamma spectrometry system (Fig. 2 step 1). The gamma spectrometry system is equipped with a Canberra Broad Energy Germanium (BEGe) detector, with excellent low energy resolution (i.e., FWHM @ 122 keV is 750 eV). The spectrometer was calibrated using mixed nuclide standardized solutions from (Eckert & Ziegler Nuclitec GmbH) and LabSOCS simulation software. The efficiency calibration curve of the 2cm solution in the Cone container used is shown in figure (3). And the collected gamma spectra were analyzed by Canberra Genie-2000 gamma acquisition and analysis software.

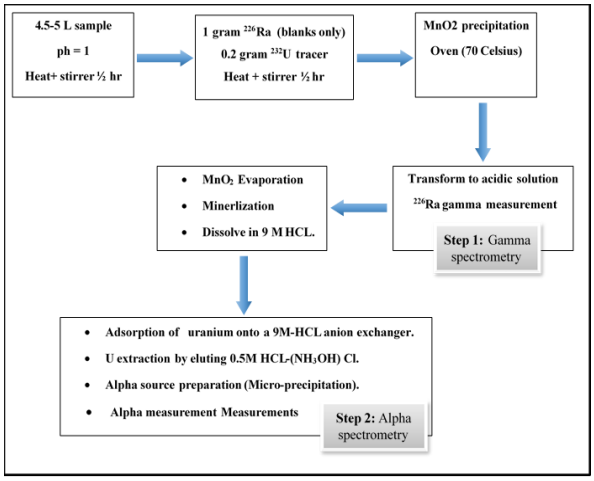


Figure 2: The schematic diagram of the co-precipitation by $KMnO_4$ method.

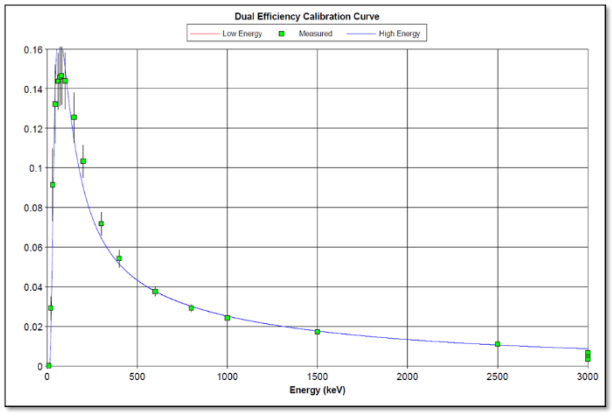


Figure3: Efficiency for gamma detector, geometry of 2cm water in 220 ml cone container.

Figure 4: The schismatic diagram of 210Po separation method.

1.2 Determination of ^{210}Po concentration

A duplicate sample was prepared for 210Po determination by the radiochemistry separation method present in Fig. 4. The prepared alpha sources were measured by an alpha spectrometry system (Apex, Canberra) that is equipped with 450-mm2 passive implanted planar silicon (PIPS) detectors with excellent resolution (20–24 keV at 4586 keV). The detector efficiency is about 15% on a chamber's second shelf at a 5 mm distance. Blank and 209Po spiked blank samples were prepared along with each batch of samples for quality control and radioactivity correction. The alpha sources were counted for three days to determine 210Po at 5310 keV.

1.3 Determination of uranium isotopes

The MnO_2 precipitation samples was used for uranium determination by radiochemistry method and alpha spectrometry as presented in Fig.2, step 2. Blank and 232U spiked blank samples for quality control and radioactivity correction.

The prepared sources were counted for 3-4 days to obtain less statistical error of the net peak areas of 238U at 4147 keV, ^{234}U at 4777 keV.

1.4 Determination the gross alpha and beta activity

A set of triplicate samples were prepared for gross alpha and beta radioactivity determination. About 50 ml of each sample was transferred to a 250 ml beaker, mineralized with aqua regia acid solution (1:3 mixture of concentrated nitric and hydrochloric acids). The solution was evaporated on a hot plate at temperature less than water boiling point and then diluted to 15 ml. The solution was transferred drop by drop using plastic dropper into planchet and dried under IR lamp until residue was almost dried, and left for cooling. A blank sample was prepared following the same procedure and using high purity distilled water.

The blank and the triplicate sample set were counted for three hours by an Extra Low Background (XLB) counting system equipped with a pancake proportional counter shielded with a heavy low background lead castle as shown in figure 5 (10cm od custom molded lead). The XLB was calibrated, and the discrimination window was adjusted to detect alpha and beta counts and apply the slipover correction. The gross counts of the measured samples were corrected to blank samples, and the detection efficiency for the activity determination. The average activity concentration of the triplicate sample and the associated uncertainty were calculated and presented in Bq/l.

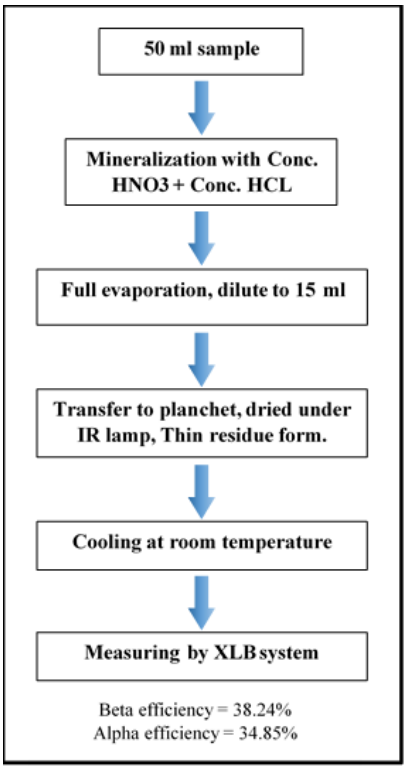


Figure 5: The schismatic diagram of Sample preparation for the gross alpha and beta analysis.

3. Results

The activity concentrations and the associated uncertainties of the four batches were calculated and presented in Table 1 and Table 2.

Table 1 presents the gross alpha and gross beta concentrations in the three sampling locations while the gross beta has shown some variation in the two lagoons, however, it was below thresholds and thus not harmful to operators. Gross alpha activity was below detection limits in raw wastewater at both lagoons. Both gross alpha and gross beta was not detected in the plant's effluent.

Table 1. Gross alpha and Gross Beta concentration in samples (Bq/l)

Radionuclide	Lagoon1			
	Batch 1	Batch 2	Batch 3	Batch 4
Gross Beta	BDL (1)	2.4 ± 0.7	2.44 ± 0.47	2.13 ± 1.4
Gross Alpha	BDL (2)	BDL (2)	BDL (2)	BDL (2)
	Lagoon 2			
Gross Beta	BDL (7)	2.82 ± 1.4	2.35 ± 0.4	2.12 ± 0.5
Gross Alpha	BDL (2)	BDL (2)	BDL (2)	BDL (2)
	Effluent			
Gross Beta	BDL (1)	BDL (1)	BDL (1)	BDL (1)
Gross Alpha	BDL (2)	BDL (2)	BDL (2)	BDL (2)

BDL: Below the Detection Limit

(1) 2 Bq/l (7200 secs measurements time, beta detection efficiency 38%, sample size 5 ml)
(2) 0.4 Bq/l (10800 secs, XLB, alpha counting efficiency 35%, sample size 5 ml.

Table 2 presents the results of radionuclides concentrations in mBq/l. ^{224}Ra, ^{210}Po, and ^{40}K were detected at significant levels in the raw wastewater and to a lesser degree in the effluent while ^{210}Pb was only detected once in lagoon 1 but was not detected in the other samples. This could be attributed to a slug dose in the wastewater.

The low concentrations of radioactivity reported in Table 1 and 2 does not eliminate potential accumulation within the plant various equipment in the future and therefore continuous monitoring is required and has been the focus of this paper.

Table 2. Radioactive concentration in samples (mBq/l)

Radionuclide	Lagoon1			
	Batch 1	Batch 2	Batch 3	Batch 4
^{224}Ra	119.3 ± 6.7	87.09 ± 5.7	117.39 ± 7.0	111.09 ± 6.8
^{226}Ra	BDL(1)	BDL(1)	BDL(1)	BDL(1)
^{228}Ra	34.4 ± 4.0	BDL(2)	BDL(2)	BDL(2)
^{210}Pb	112.6 ± 19.5	BDL(3)	BDL(3)	BDL(3)
^{210}Po	72.5 ± 48	127.3 ± 40	15.1 ± 3.6	406.0 ± 37.0
^{40}K	1420.8 ± 288.9	1740.6 ± 223.3	621.5 ± 92.4	2565.7 ± 162.2
^{131}I	BDL(5)	BDL(5)	BDL(5)	BDL(5)
^{234}U	4.0 ± 0.66	BDL(6)	2.44 ± 0.33	1.65 ± 0.1
^{235}U	BDL(6)	BDL(6)	BDL(6)	BDL(6)
^{238}U	BDL(6)	BDL(6)	2.58 ± 0.3	1.14 ± 0.1
	Lagoon 2			
^{224}Ra	47.95 ± 3.59	87.18 ± 5.2	95.05 ± 6.14	90.71 ± 5.9
^{226}Ra	BDL(1)	BDL(1)	BDL(1)	BDL(1)
^{228}Ra	BDL(2)	BDL(2)	BDL(2)	BDL(2)
^{210}Pb	BDL(3)	BDL(3)	BDL(3)	BDL(3)
^{210}Po	19.0 ± 5.0	BDL(4)	12.67 ± 2.0	48.8 ± 2.0
^{40}K	1156.7 ± 136.9	1113.6 ± 214.6	331.6 ± 90.9	779 ± 102
^{131}I	BDL(5)	BDL(5)	BDL(5)	BDL(5)
^{234}U	7.0 ± 0.3	5.04 ± 1.22	2.15 ± 0.3	2.0 ± 0.12
^{235}U	BDL(6)	BDL(6)	BDL(6)	BDL(6)
^{238}U	6.0 ± 0.4	4.39 ± 1.1	2.47 ± 0.22	1.24 ± 0.13
	Effluent			
^{224}Ra	86.99 ± 4.69	98.95 ± 4.5	93.79 ± 6.53	93.28 ± 6.01
^{226}Ra	BDL(1)	BDL(1)	BDL(1)	BDL(1)
^{228}Ra	BDL(2)	BDL(2)	BDL(2)	BDL(2)
^{210}Pb	BDL(3)	BDL(3)	BDL(3)	BDL(3)
^{210}Po	BDL(4)	BDL(4)	14.43 ± 4	21.8 ± 3.0
^{40}K	1139 ± 217	1308 ± 280	598 ± 113	2306 ± 174
^{131}I	BDL(5)	BDL(5)	BDL(5)	BDL(5)
^{234}U	BDL(6)	1.6 ± 0.4	1.72 ± 0.18	8.5 ± 0.5
^{235}U	BDL(6)	BDL(6)	BDL(6)	BDL(6)
^{238}U	BDL(6)	BDL(6)	2.18 ± 0.4	8.4 ± 0.65

BDL: Below the Detection Limit

(1) 14.40 mBq/l (100,000 secs. ULB detector, 2cm in 220 ml cone container)

(2) 25.1 mBq/l (100,000 secs. ULB detector, 2cm in 220 ml cone container)

(3) 61.7 mBq/l (100,000 secs. ULB detector, 2cm in 220 ml cone container)

(4) 10 mBq/l (100,000 secs measurement time, alpha detection efficiency 14%, sample size 0.1 l)

(5) 20 mBq/l (100,000 secs, GMX detector, Marinelli Beaker 3 l)

(6) 1.2 mBq/l (100,000 secs measurement time, alpha detection efficiency 14%, sample size 5 l)

4. Discussion

As can be clearly seen from table 1 and 2 there is a difference in the radioactivity and radionuclides concentration depending on type of wastewater (food and beverage versus petroleum wastewater). These differences are expected since the origins of the two types of wastewater are different. For example, the water used in the food and beverage comes from potable supplies while the petroleum wastewater is predominantly of geological origin.

Radionuclides like 40K, total 210Pb, 226Ra, 228Ra, 238U, and 235U, would likely partition onto sludge and biosolids rather than be discharged in the liquid effluents [1,2]. In contrast, 131I would more likely remain in the liquid effluent than partition onto the sludge [7]. For example, 131I short half-life of 8 days would, however, mean that it would have limited effects even if the treated wastewater is widely used. However, ^{224}Ra, ^{210}Po, and ^{40}K which were detected at elevated levels in the raw wastewater and the treated effluent (Table 1 and 2) require some attention since storage to segregate these radionuclides may not be feasible because it will require long periods due to the long half-lives of some of them [7].

Mathuthu and Olobatoke [9] Gamma spectroscopy revealed very high concentrations of 235U and 226Ra in water samples. Pereira et al. [5] confirmed that among the radionuclides studied, ^{210}Pb and ^{228}Ra were the major contributors to both dose rate and cancer risk. These results confirm the findings of this study.

As evident from Figure 6, ^{224}Ra did not exhibit significant difference between raw wastewater and effluent, however its concentrations in lagoon 1 (petrochemical wastewater) was slightly higher than it concentrations in the food and beverage wastewater. The same applies to ^{210}Po (Figure 7), however its concentrations in the effluent were much lower than the raw wastewater implying that it has been removed by partitioning into sludge and biosolids in the activated sludge process [2,5,9].

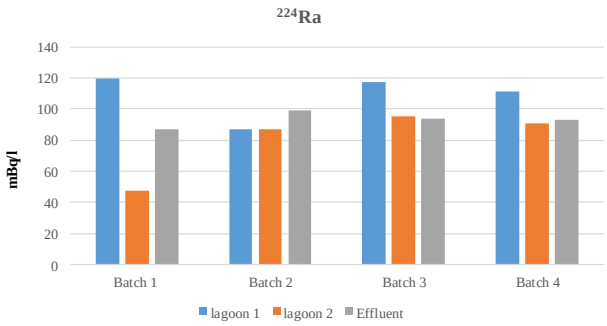


Figure 6. ^{224}Ra concentration in different samples.

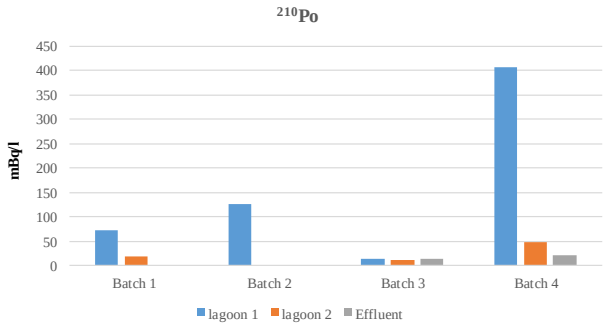


Figure 7. ^{210}Po concentration in different samples.

^{40}K was an exception (Figure 8) since its concentrations did not differ significantly between raw wastewater or effluent. As a matter of fact, in some cases its concentration has increased in the effluent. This could be explained by the fact that recycling of the sludge in the activated sludge process contributes to the accumulation of 40K within the wastewater. This is could also be seen clearly from ^{238}U and ^{235U} concentrations since radioactive potassium and uranium are the main contributors to alpha radiation [1].

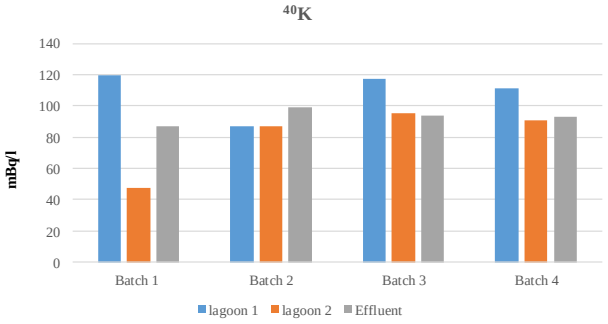


Figure 8. ^{40}K concentration in different samples.

Few treatment technologies exist for treatment of radionuclides in wastewaters at low concentrations [10-12]. Enhancing coagulation-precipitation in treatment plants, such as chemically assisted primary clarification, is one possible treatment improvement. Segregation of contaminated waters and using volume reduction by evaporation or reverse osmosis is also a possibility [7]. These technologies could be identified as research areas which need to be investigated in order to develop short-term treatment technologies.

In summary, radioactivity is not well eliminated by existing wastewater treatment plants' technology regardless of its sources. This contributes to higher risk of exposure within the plant and poor effluent quality. Recovery processes for radioactive materials needs to be considered in wastewater

treatment to ensure reasonable effluent quality and to recover these valuable resources.

3. Conclusion

This paper investigated the levels of concentrations of radionuclides and radioactivity in an industrial wastewater treatment plant. The levels were below background levels, however:

1. The type of wastewater affects the levels of radioactivity and radionuclides concentrations.
2. There is a risk of exposure due to long term accumulation of radionuclides within the plant components.
3. Radionuclides are not necessarily reduced in the treated effluent and their increased concentration is likely to happen in the secondary biological treatment stage due to recycling of biosolids.

4. Acknowledgements

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