Evaluation and removal efficiencies of a rural WWTP for metals and anions in Lufkin, East Texas (USA)

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Abstract The present study quantified element concentrations and evaluated the removal efficiencies of the Lufkin Wastewater Treatment Plant (LWWTP): a public municipal wastewater treatment plant in East Texas. Macroelements (Na, K, Mg, Ca, Al, Fe, Se, Zn, P, and S) and microelements (Ni, Pb, Mn, Cr, Mo, Cu, Co, V, As, B, Ba) were detected using ICP-OES and ICP-MS. In addition, the anion concentrations (Br⁻, NO₃⁻, NO₂⁻, PO₄³⁻, F⁻, Cl⁻, and SO₄²⁻) and their percent removal from the LWWTP were assessed by using ion chromatography. Whereas macroelements in the influent were above the maximum ceiling limits, the total metal concentrations in the effluent were found below the USEPA (below μg/L) guidelines. In general, the removal efficiencies for metals in LWWTP were ≥ 94%. The removal efficiencies of the anions were > 100% (Br⁻), 16.42% (Cl⁻), 78.89% (F⁻), 182.59% (NO₂⁻), > 100% (NO₃⁻), 51.81% (PO₄³⁻), and 67.01% (SO₄²⁻). In addition, Pierson correlation coefficients between the anions and cations, and implications for usage and suggested improvements of the treatment plants are proposed.

Keywords Water quality · Activated sludge · Lufkin · Ion chromatography · ICP-OES/ICP-MS · Element removal efficiency

Introduction

The continued increase in population dictate further demand for use and reclamation of and/or recirculation of water (Schmitz et al., 2018). Thus, sustainability of the environment poses many challenges needing to be resolved to be free of pollutants and bacterial pathogens hazardous to human health, plants, and/or other organisms. This is especially important in provision of water quality free of mainstream and emerging pollutants including microplastic contaminants (Garrido-Baserba et al., 2018; Park et al., 2020). The quality of water for all uses is therefore dependent on the treatment processes. For instance, in municipalities, wastewater treatment plants (WWTP) processes are critical to the removal of pollutants and maintain and/or improving the quality of wastewater that meets acceptable criteria. In the USA, various agencies in various states are mandated by the government to regulate and ensure water quality criteria are met. For this reason municipal wastewater treatment plants in many countries play central roles to remove the pollutants (Balogun et al., 2017).

Wastewater treatment plants (WWTP) are often designed to remove pollutants in a four-tiered wastewater treatment process for reduction of chemical and

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biological pollutant loads and chemical pollutants in the sewage to safe and acceptable levels. Municipal wastewater treatment plants (WWTPs) are valuable contributors to a circular economy by implementing the 3R principles (reduce, reuse, and recycle) (Shanmugam et al., 2022). The effluent urban sewage entering the WWTP first undergoes preliminary treatment to remove silt and grit. This is then followed by a series of primary and biologically active secondary treatment stages that remove suspended solids and biodegradable organics (Shanmugam et al., 2022). Several removal processes occur at each of the four-stage wastewater treatment plants, which includes a primary, secondary, tertiary (nutrient removal), and advanced tertiary (which remove contaminants of emerging concern) stages. The removal of pollutants continues to pose major challenges to municipalities around the globe. The increasing populations in municipalities generates large quantities of biosolids. The challenges are further compounded by the complexity of biosolids and the diverse emerging pollutants, together with limited financial support for the creation of new WWTPs. This often leads to large direct discharges of raw sewage into fresh water systems (Fekadu et al., 2019; Mushtaq et al., 2020; Sojobi & Zayed, 2022). In addition to these challenges, many municipalities are faced with the need to manage sewer overflow outbreaks that is linked to the transmission of food-chain pathogens via pathogen-laden wastewater (including coronaviruses), person-to-person transmission, and close contact with infected animals (Al-Omari et al., 2019; Han & He, 2021; Mackay & Arden, 2015).

Municipal wastewater effluent contains inorganic and organic contaminants that pose various health risks to man and the environment (Madadian & Simakov, 2022; Sojobi & Zayed, 2022). Wastewater treatment plants receive metal-laden influent water from industrial manufacturing and domestic processes (Giannakis et al., 2021). Inappropriate disposal and handling of untreated or treated wastewater may lead to discharge of a large amount of metallic waste into the environment (Maarof et al., 2017). For example, discharged wastewater may contain Hg, Cd, Pb, Zn, Cu, Ni, and Cr (Fu & Wang, 2011; Gorska et al., 2021). These metals tend to bioaccumulate in the environment and can harm living organisms (Basha et al., 2011; Lu et al., 2015; Mansoorian et al., 2014). Bioaccumulation of metals can ultimately end up in the human body where they pose health problems including carcinogenic, mutagenic, and teratogenic risks (Lee et al., 2012). It is therefore important that they are removed from wastewater matrices prior to discharge to the environment.

Wastewater is rich in organic matter and elements vital to plant nutrition, namely, N, P, and K as well as Na, Ca, Mg, S, Cl, Cu, Fe, B, and Zn (Sahay et al., 2016). Treated wastewater has been used in agriculture for crop irrigation (Tran et al., 2016). For this reason, the practice of reusing treated wastewater is a growing global practice. Studies show that using wastewater in irrigation is common in Europe, the USA, Mexico, Australia, China, Chile, Peru, Egypt, Lebanon, Morocco, Vietnam, and South Africa (Apostolidis et al., 2011; Jiménez & Asano, 2008; Lee et al., 2012). This leads to the constant disposal of the wastewater as a fertilizer and removes the need for the use of inorganic fertilizers. The advantage of using treated wastewater is that it reduces the demand for high-quality drinking water (Wyman, 2013) and increases the yield of field crops. This may lead to boosting the production of more food whenever this practice is employed (Ensink et al., 2004; Singh et al., 2012). On the other hand, there are risks of the presence of pathogens, pharmaceuticals, engineered or natural nanoparticulates, microplastics, and other emerging contaminants (Huang et al., 2021; Riemenschneider et al., 2016) that pose serious environmental issues if stringent measures are not enforced during the treatment process.

In the USA, the use of treated and untreated wastewater is regulated by the United States Environmental Pollution Agency (USEPA). In addition, many US states have enacted regulatory pollution laws for the use of wastewater. The Texas Commission on Environmental Quality (TCEQ, www.tceq.texas.gov) in concert with USEPA has set regulations for the use of the toxic and nontoxic elements (As, Cd, Cr, Cu, Pb, Hg, Mo, Ni, Se, Zn) (USEPA, 1993a, b). Although consistently monitored by TCEQC, no published assessment and evaluation of the LWWTP is reported. The metal and anion content of LWWTP wastewater over the various treatment stages were therefore analyzed and assessed.

The present study monitored and evaluated the performance of Lufkin Wastewater Treatment Plant (LWWTP), in East Texas. The removal efficiency of the WWTP was compared to the USEPA and WHO...
guideline standards (WHO, 2006). The removal efficiencies of metal and anion concentrations was assessed at various treatment stages. Thus, macroelements (Na, K, Mg, Ca, Al, Fe, P, S), microelements (Ni, Pb, Mn, Cr, Mo, Cu, As, B, Ba, Ag, Cd, Hg, Se, Zn, Co), and seven anions (Br\(^-\), NO\(_3^-\), NO\(_2^-\), PO\(_4^{3-}\), F\(^-\), Cl\(^-\), and SO\(_4^{2-}\)) were evaluated. This study is therefore important in providing baseline data useful for the evaluation and comparative studies for wastewater treatment plants in East Texas, and in the USA. The information is also important for assessment of possible risks posed to the environment prior to or after discharge to the environment. In addition, via Pierson correlation matrix, correlations between concentrations of anions and metals at each stage of the wastewater treatment stage and the possible improvements that may be needed in future were investigated. Thus, the results from the investigations relate to the efficiency of the current activated sludge treatment strategies for future municipalities in East Texas and the globe.

**Materials and methods**

**Site description, sampling and analysis, and techniques**

Figure 1a, b, and c depict the LWWTP, a conventional activated wastewater treatment system, along with its treatment stages, namely, influent, aeration, clarifier, chlorination, and sulfur dioxide chambers. LWWTP is in Lufkin City in Texas with a population of ~35,067 residents. The LWWTP has a treatment capacity of 11.3 million gallons per day (MGD). The LWWTP is located at latitude 31° 17′ 13.8804″ N and longitude 94° 44′ 56.2416″ W.

Wastewater grab samples were collected from LWWTP between June and September 2017 (on June 9, 16, 23, and 30, July 19, August 1, and August 17, 2017) from the raw influent, pre-aeration, primary clarifier, secondary clarifiers, primary-aeration and return-aeration basins, chlorine contact chamber (CCC), and effluent stages (Scheme 1). Clean polyethylene sampling bottles were thoroughly rinsed at least three times with 10% HNO\(_3\) acid and 18.2 MΩ water before filling with wastewater. Samples were transported to the laboratory and stored in a refrigerator at 4 °C until further analysis.

Raw wastewater sludge samples were collected from LWWTP on February 2, June 9, June 17, and June 23, 2017, from the primary clarifier and the anaerobic digester and on February 2nd and June 9th from the secondary clarifier and were stored in one-gallon plastic jugs. Raw wastewater sludge samples were stored at −80 °C until analysis.

**Field measurements and laboratory analysis**

The detailed protocols followed for sample collection and chemical analysis field measurements were previously reported (Onchoke et al., 2015). The Texas Commission on Environmental Quality (www.tceq.texas.gov) requires the assessment of dissolved oxygen, carbonaceous biological oxygen demand, and total settleable solids (DO, CBOD, and TSS). The CBOD were determined by the HACH 20101 analyzer manometric method (APHA, 2013; Çeçen & Yangın, 2000), respectively, at the Lufkin Wastewater Environmental Laboratory from January through May 2017. Samples were filtered with 0.45 μm filter following standard protocols (APHA, 2013).

Approximately 30 mL of wastewater sample were filtered with a 0.45 μm filter in a clean 50 mL DigiTube (DigiFILTER Field Filtration Kit (from SCP Science, http://www.scpscience.com/, Fig. 2)). Approximately ~25 mL filtered samples were then stored at < 4 °C until analysis. Detailed descriptions of anion analysis are presented elsewhere in published References (Onchoke et al., 2015, 2018). These protocols and instruments (Dionex Integrion HPIC ion chromatograph (Thermo Fisher Scientific Inc., USA) were adopted in this investigation.

The following protocols were used in the Analysis of Metal Concentrations in LWWTP. Element concentrations were analyzed by digesting wastewater samples following USEPA Method 3050B (USEPA, 1996). Fifty mL of wastewater sample was first transferred into clean 50 mL DigiTube. After adding 1.0 mL of HNO\(_3\) (1:1, v/v) and 0.5 mL of HCl (1:1, v/v) to each tube, samples were placed in a DigiPrep-MS digestion block. Polyethylene watch glasses were placed onto DigiTubes to minimize loss. The DigiPrep-MS block was heated to 95.0 °C and samples refluxed for 2 h. The samples were then allowed to cool and filtered with a 0.45-μm filter. The volume of filtered samples was then made up to 50 mL in
DigiTubes with 18.2 MΩ water and thereafter stored at 4 °C until analysis.

Wastewater sludge samples were analyzed by ICP-OES spectrometer (Agilent iCAP™ 7400, ICP-OES) or ICP-MS (Elan DRC-ICP-MS equipped with a dynamic reaction cell (DRCe)). ICP-OES operating parameters were as follows: gas flow, 0.5 mL min⁻¹; pump speed, 50 rpm; modes = axial or radial; RF power = 1150 W; uptake time of 70 s; argon, liquid. The detection limits for the instrument in ppm were Ag (0.01311), Al (0.02631), As (0.006583), B (0.00086), Ca (0.12498), Cd (0.00046), Co (0.00224), Cr (0.00983), Cu (0.01625), Fe (0.05053), Hg (0.01261), K (15.4327), Mg (0.0076), Mn (0.00034), Mo (0.07008), Na (1.20834), Ni (0.00221), P (0.02344), Pb (0.00966), S (0.18011), Se (0.02508), Zn (0.00109), and V (0.00399).

Quality assurance and quality control (QA/QC)

A standard reference material (NIST SRM 1515, apple leaves) was used to determine precision and limit of detection (LOD) of elements. A 0.5 g of the material was weighed and digested in a clean 50-mL DigiTube following USEPA method 3050 B (USEPA, 1996). The analysis was done using ICP-OES iCAP™ 7400 (Agilent) or ICP-MS (Perkin Elmer). Similarly, the SRM sample was digested via USEPA method.
200.7 as previously described (Onchoko et al., 2018) and analyzed alongside the wastewater samples. Comparison between measured and SRM metal values with ICP-OES shows good agreement (Table 1).

Further, reliability of anion concentration measurements was tested by using known anion concentrations (2 ppm, 4 ppm, Table 2) and spiked metal standard concentrations (5 ppm, 25 ppm, or 50 ppm, Table S1) and runs made through Ion chromatography C (IC, Table S1), ICP-OES, or ICP-MS (Table S1) instruments, respectively. The experimental results in Tables 2 (anions) and S1 (metals) show good recoveries of the measurements. The element analytes were detected within the range of 78.8–140% (Table 2), suggesting reliability of the prepared standards. Metal concentrations (Table S1) further show detectable analytes at > 80–120% for most elements.

Percent recoveries with use of ion chromatography

The reliability of measured anion concentrations at each stage of the LWWTP was determined by injecting standards of known amounts, along with the analyte samples, into the ion chromatograph. The recoveries of each analyte anion were calculated with the equation:

\[
\text{Recovery (\%)} = \frac{C_{\text{spi}} - C_{\text{raw}}}{C_{\text{std}}} \times 100
\]

where \(C_{\text{spi}}\), \(C_{\text{raw}}\), and \(C_{\text{std}}\) represent the concentrations in the spiked, raw, and standard, respectively. Table 2 shows reliable percent recoveries of seven anions, viz., 105.0% (F⁻), 99.5% (Cl⁻), 94.5% (NO\(_2\)^{-}), 105.0% (Br⁻), 60.2% (NO\(_3\)^{-}), 70.7% (SO\(_4\)^{2-}), and 100.0% (PO\(_4\)^{3-}).

Statistical data analysis

All statistical analysis of the data were performed with use of the software SigmaPlot 12.5 (Systat Software, San Jose, CA). Pearson regressions were used to test the correlations between all metal concentrations and anions. Pearson correlation matrices were calculated using MS Excel software (Microsoft Corporation, 2018. Microsoft Excel, Available at: https://office.microsoft.com/excel).
Results

Physical–chemical characteristics of wastewater

Average dissolved oxygen (DO), total settleable solids (TSS), and carbonaceous biological oxygen demand (CBOD) in influent and effluent were $1.9 \pm 0.4/7.1 \pm 0.2 \text{ mg O}_2/\text{L}$, $310.2 \pm 65.6/4.7 \pm 1.3 \text{ mg/L}$, and $297.6 \pm 38.3/3.4 \pm 0.5 \text{ mg O}_2/\text{L}$, respectively (Table 3). The DO, TSS, and CBOD measured values are comparable to values determined from the activated Nacogdoches WWTP, in East Texas (Onchoke et al., 2015), with similar sludge treatment process. The effluent NH$_3$-N values (Table 3) are well below reported WWTP values of 74–90 mg/L (Ma & Zhang, 2008).

Table 4 shows mean pH of samples at each of the treatment stages. The pH of the wastewater falls in the range 6.9–7.2. This is comparable to WHO or USEPA guideline standards in the range 6.5–8.5 (USEPA, 2000, 2014). The primary aeration showed the lowest pH which increased to 7.1 in the chlorine contact chamber due to removal of organic matter. As a result of the addition of SO$_2$, the pH decreased to 7.0 before flowing into the effluent stage and discharge into the Hurricane Creek.

Quantification and analysis of anions along the treatment stages

Table 5a and b shows F$^-$, Cl$^-$, NO$_2^-$, Br$^-$, NO$_3^-$, SO$_4^{2-}$, and PO$_4^{3-}$ concentrations of anions at each of the treatment stages in June 2017. Figures 3a–g and S1 depict changes in anion concentrations over the treatment stages. Notably, a spike in Cl$^-$ and SO$_4^{2-}$ concentrations (Table 5a and b, and Fig. 3b and g) is evident. The [Cl$^-$] increases by ~8 to 10 ppm in the chlorine contact chamber (CCC) stage, while the [SO$_4^{2-}$] increases by ~8–9 ppm in the effluent stage. The increase in [Cl$^-$] is attributed to the addition of NaOCl (sodium hypochlorite)
to disinfect any remaining bacteria in the chlorine contact chamber (CCC). The increase in \([\text{SO}_4^{2-}]\) is attributable to the addition of \(\text{SO}_2\) in the sulfur dioxide chamber (secondary clarifier). The \(\text{SO}_2\) then reacts with the hypochlorite (as shown in the equation \(\text{NaOCl(aq)} + \text{SO}_2 + \text{H}_2\text{O(l)} \rightleftharpoons \text{NaCl(aq)} + \text{H}_2\text{SO}_4(aq)\)) and is removed from the treated wastewater before discharge into the Hurricane Creek.

### Table 1

Comparison of average element concentrations (in ppm, average ± standard deviation) in certified reference material (SCP Science, SS-2 EnvironMAT contaminated soil) versus measured results via ICP-OES. NA, not available

| Element | Reference samples measured \((n)\) | SS-2 (average ± SD) | Measured\(^a\) (average ± SD) | Percent agreement |
|---------|-------------------------------------|---------------------|-------------------------------|-------------------|
| Al      | 6                                   | 13265 ± 1151        | 14219 ± 449                   | 107.19            |
| Ag      | 6                                   | 1.3                 | 1.09 ± 0.10                   | 83.85             |
| As      | 4                                   | 75 ± 10             | 88 ± 3                        | 117.33            |
| Ba      | 8                                   | 215 ± 13            | 223 ± 4                       | 103.63            |
| B       | 8                                   | 27 ± 2              | 27 ± 1                        | 99                |
| Ca      | 8                                   | 112861 ± 4872       | 1103730 ± 1548                | 91.91             |
| Cd      | 6                                   | 2                   | 1.70 ± 0.03                   | 85.15             |
| Co      | 6                                   | 12 ± 1              | 12.7 ± 0.1                    | 105.72            |
| Cr      | 6                                   | 33.8 ± 0.8          | 34 ± 1                        | 99.46             |
| Cu      | 6                                   | 191 ± 9             | 208 ± 8                       | 108.93            |
| Fe      | 6                                   | 21046 ± 1449        | 21093 ± 317                   | 100.22            |
| Hg      | 4                                   | 0.044 ± 0.004       | 0.115 ± 0.006                 | 161               |
| K       | 6                                   | 3418                | 4620 ± 190                    | 135.16            |
| Mg      | 6                                   | 11065 ± 606         | 11151 ± 171                   | 100.78            |
| Mn      | 6                                   | 457 ± 24            | 475 ± 7                       | 103.84            |
| Mo      | 6                                   | 0.094 ± 0.013       | 0.092 ± 0.040                 | 97.9              |
| Na      | 6                                   | 558 ± 102           | 503.67 ± 119.91               | 90.26             |
| Ni      | 6                                   | 54 ± 4              | 55 ± 2                        | 100.94            |
| P       | 12                                  | 752 ± 18            | 1494 ± 53                     | 94                |
| Pb      | 6                                   | 126 ± 10            | 115 ± 2                       | 91.09             |
| S       | 6                                   | 1800                | 1642.74 ± 56.93               | 91.26             |
| Se      | 4                                   | 0.050 ± 0.009       | 0.107 ± 0.200                 | 214.0             |
| Zn      | 6                                   | 467 ± 23            | 484 ± 6                       | 103.68            |
| V       | 6                                   | 34 ± 3              | 40.3 ± 0.9                    | 118.52            |

### Table 2

The percent recovery of anions measured via ion chromatography (IC); \(n = 42\)

| Anion          | Actual concentration (ppm) | Measured concentration (ppm); mean ± SD | % recovery |
|----------------|-----------------------------|-----------------------------------------|------------|
| Fluoride (F\(^-\)) | 0.4000                     | 0.42 ± 0.02                             | 105.0%     |
| Chloride (Cl\(^-\)) | 2.0000                     | 1.99 ± 0.08                             | 99.5%      |
| Nitrite (NO\(_2\)\(^-\)) | 2.0000         | 1.89 ± 0.04                             | 94.5%      |
| Bromide (Br\(^-\)) | 2.0000                     | 2.1 ± 0.5                               | 105%       |
| Nitrate (NO\(_3\)\(^-\)) | 2.0000         | 1.20 ± 0.00                             | 60.2%      |
| Sulfate (SO\(_4\)\(^2-\)) | 2.0000         | 1.413 ± 0.004                           | 70.7%      |
| Phosphate (PO\(_4\)\(^3-\)) | 4.0000             | 4.0 ± 0.2                               | 100.0%     |

**Nitrates**

Figure 3E show nitrate concentrations reach peak values in the primary-aeration basin and secondary clarifier for the samples collected on June 16 and 23, 2017, respectively, before decreasing to lower concentrations, in agreement with one previous study from the WWTP in East Texas (Onchoke et al., 2015). The nitrate
concentrations in the range 1.9 to 27.5 ppm are attributed to biological processes that breakdown organic matter or materials in the wastewater (Wang et al., 2021). Whereas \( \text{SO}_4^{2-} \) and \( \text{Cl}^- \) ions exhibit approximately the same concentrations in the effluent and influent stages, other anions (\( \text{NO}_3^- \), \( \text{NO}_2^- \), \( \text{PO}_4^{3-} \), \( \text{Br}^- \)) either increased or decreased. Notably, average initial \( \text{NO}_3^- \) concentrations (27.48 ppm) at the primary treatment stage are below WHO guideline of 50 mg/L (WHO, 2006).

**Bromide, nitrite, and phosphates**

The bromide, nitrite, and phosphate concentrations were determined below USEPA regulated levels of 6 mg/L for adults (for \( \text{Br}^- \)), 10, and 0.015 mg/L, respectively. Figures 3D and S1 show bromide concentrations are highest at the effluent stage (on 6/16/2017) and decrease in the order primary aeration (zero mg/L) < raw (1.34 mg/L) < pre-aeration (1.35 mg/L) < primary clarifier (1.34 mg/L) < secondary clarifier (103 mg/L) < CCC (116.51 mg/L) < effluent (117.62 mg/L) before discharge into the Hurricane Creek. It was however noted that subsequent determinations of \( \text{Br}^- \) were not detected on June 23, 2017. The \( \text{PO}_4^{3-} \) concentrations (Fig. 3F) decreases along the treatment stages and follow the order: 48 mg/L (Primary aeration) > 21 mg/L (raw) > pre-aeration (19.9 mg/L) ≈ primary clarifier (20 mg/L) > secondary clarifier (18.8 mg/L) > CCC (10.6 mg/L) > effluent (10.0 mg/L). Notably, the \( \text{PO}_4^{3-} \) stays nearly the same for the clarifiers before decreasing to half its original concentrations prior to discharge into the Hurricane Creek.

**Metal analysis in raw and liquid sludge**

Raw and liquid sewage samples from anaerobic, primary, and secondary sludge stages were collected. The raw activated sewage (RAS) samples from the anaerobic, primary, and secondary sludge were collected in May and June of 2016. Na, Mg, Ca, Ni, Pb, Mn, Cr, Mo, Cu, Al, As, B, Ba, Ag, Cd, Fe, Hg, K, Se, Zn, Co, P, and S concentrations were determined at each treatment stage.

**Microelement concentrations in raw sludge**

Figure 4A and Table 6 show microelement concentrations for the anaerobic sludge, primary sludge, and secondary sludge. The concentrations at the anaerobic treatment stage follow the order: Mn (21.31 ±

### Table 3

Influent and effluent characteristics (mean ± standard deviation) for CBOD in mg/L, TSS (mg/L), \( \text{NH}_3\-\text{N} \) (mg/L), and dissolved oxygen (DO, mg \( \text{O}_2 \)/L); \( n \) = 28–31 samples every month, approximately > 150 samples were analyzed in January 2017–May 2017

| Month     | Influent | Effluent |
|-----------|----------|----------|
|           | CBOD (mg \( \text{O}_2 \)/L) | TSS (mg/L) | \( \text{NH}_3\-\text{N} \) (mg/L) | DO (mg \( \text{O}_2 \)/L) | CzBOD (mg \( \text{O}_2 \)/L) | TSS (mg/L) | \( \text{NH}_3\-\text{N} \) (mg/L) | DO (mg \( \text{O}_2 \)/L) | % DO increase |
| January 2017 | 311.8 ± 111.3 | 226.9 ± 0.2 | 1.5 ± 0.2 | 3.2 ± 1.3 | 4.5 ± 2.1 | < 1.3 | 7.2 ± 1.0 | 480.0 |
| February 2017 | 332.7 ± 90.6 | 262.6 ± 88.2 | 2.3 ± 0.2 | 2.9 ± 0.5 | 3.5 ± 0.6 | < 1.15 | 7.3 ± 0.2 | 429.4 |
| March 2017 | 321.1 ± 81.1 | 308. ± 9.2 | 2.3 ± 0.2 | 4.1 ± 1.0 | 5.9 ± 1.8 | < 0.5 | 7.0 ± 0.2 | 304.3 |
| April 2017 | 285.8 ± 47.3 | 28.6 ± 3.6 | 1.8 ± 0.5 | 3.6 ± 0.6 | 6.2 ± 1.4 | < 0.5 | 7.1 ± 0.2 | 394.4 |
| May 2017 | 236.5 ± 48.1 | 309. ± 3.6 | 2.3 ± 0.6 | 3.2 ± 0.7 | 3.5 ± 0.6 | < 0.7 | 7.1 ± 0.2 | 308.7 |
| Average | 297.6 ± 38.3 | 310.2 ± 65.6 | 29.5 ± 1.9 | 1.9 ± 0.4 | 3.4 ± 0.5 | 4.7 ± 1.3 | < 0.85 | 7.1 ± 0.2 | 383.4 |

### Table 4

pH values at each stage of the WWTP (mean ± SD); SD, standard deviation; \( n \) = 24

| Treatment stage and parameter | Raw | Pre-aeration | Primary clarifier | Primary aeration | Secondary aeration | Return aeration | CCC | Effluent |
|-------------------------------|-----|--------------|------------------|------------------|-------------------|----------------|-----|---------|
| pH                            | 7.1 ± 0.03 | 7.20 ± 0.01 | 7.21 ± 0.01 | 6.87 ± 0.01 | 7.17 ± 0.02 | 7.06 ± 0.01 | 7.11 ± 0.01 | 7.00 ± 0.01 |
3.89 mg/kg) > Zn (16.56 ± 7.25 mg/kg) > Cu (10.73 ± 4.57 mg/kg) > B (0.78 ± 0.38 mg/kg) > Pb (0.74 ± 0.33 mg/kg) > Cr (0.605 ± 0.38 mg/kg) > Ag (0.45 ± 0.37 mg/kg) > Co (0.329 ± 0.130) > V (0.298 ± 0.122) > As (0.113 ± 0.130) > Hg (0.030 ± 0.089 mg/kg). Toxic elements (As, Cr, Cd, Hg, Se, Pb) were detected in anaerobic and primary treatment stages albeit below detection in the chlorine contact chamber before final effluent and prior to discharge (Fig. 5A). The observed trends are in agreement with results from other wastewater treatment plants in Onchoke et al. (2015) and Westerhoff et al. (2015). Except for the primary aeration stages, concentrations of Ag, As, Cd, Hg, Mo, and Se were determined below detection limits. Although toxic elements As, Cd, Hg, and Mo were detectable in raw sewage; they however were removed at the secondary stage. As the sewage reaches the tertiary treatment, the toxic metals were removed to between 80 and 95%.

**Macroelement concentrations in raw sewage**

Figure 4B depicts concentrations of macroelements in anaerobic sludge, primary sludge, and secondary sludge samples. The macroelement concentrations in the anaerobic sludge follow the order: P (1119.47 ± 112.34 mg/kg) > Na (691.19 ± 303.37) > Fe (355.73 ± 135.57) > Al (355.25 ± 145.06) > K (253.51 ± 21.13) > Ca (192.61 ± 145.06) > S (275.34 ± 112.34) > Mg (77.22 ± 28.50). Previous results from other WWTPs showed phosphorus accounts for the greater percentage of macro-elements in the influent wastewater (Cydzik-Kwiatkowska & Nosek, 2020; Kehrein et al., 2020; Li et al., 2019).
Fig. 3 Anion concentrations along the LWWTP stages; CCC, chlorine contact chamber
Phosphorus and sulfur analysis in liquid sludge

The average phosphorus and sulfur concentrations were in the range 349–1363 mg/L and 5000–6977 mg/L, respectively (Fig. 4B and Table 7). In general, the phosphorus and sulfur concentrations progressively decreased on passing from the raw sewage to the effluent wastewater (Figs. 4B and 7).

Micro- and macroelement analysis in wastewater

Microelements concentrations in wastewater

Figure 5a and b shows the concentrations of trace elements along the treatment stages. The observed trends are in line with reported research results from other wastewater treatment plants (Westerhoff et al.,
Table 6  Minor (trace) element concentrations (mg/L) at four stages measured via ICP-OES during treatment period for LWWTP (mean ± SD, n (number of samples analyzed) = 13). SD, standard deviation

| Element | Raw | Pre-aeration | Primary clarifier | Primary aeration | Secondary clarifier | Return | Chlorine contact chamber | Effluent | USEPA standard<sup>a</sup> (mg/L) | WHO standard<sup>b</sup>, (mg/L) | % mean removal |
|---------|-----|--------------|-------------------|------------------|---------------------|--------|--------------------------|----------|---------------------------|-----------------------------|-----------------|
| As      | 0.00 ± 0.0 | 0.00 ± 0.00 | 0.00 ± 0.00 | 0.00 ± 0.00 | 0.00 ± 0.00 | 0.00 ± 0.00 | 0.000 ± 0.00 | 0.01 | 0.01 | 100 |
| Ag      | 0.00 ± 0.0 | 0.00 ± 0.00 | 0.00 ± 0.00 | 0.82 ± 0.00 | bd | bd | bd | 0.10 | 0.10 | 100 |
| Ba      | 1.7 ± 0.8 | 5.95 ± 4.38 | 1.88 ± 1.16 | 73.86 ± 52.94 | 81.90 ± 75.06 | 120.93 ± 34.84 | 0.046 ± 0.039 | 10.45 ± 2.60 | 0.7 | 175.63 |
| B       | 10.6 ± 7.0 | 9.1 ± 6.6 | 9.1 ± 8.0 | 22.4 ± 4.5 | 25.1 ± 10.3 | 27.5 ± 9.2 | 13.0 ± 0.7 | 10.5 ± 2.6 | < 0.5 | - | 46.88 |
| Cd      | bd | bd | bd | 0.00 ± 0.00 | 0.00 ± 0.00 | 0.00 ± 0.00 | 0.000 ± 0.00 | 0.005 | 0.003 | - |
| Co      | bd | bd | bd | 2.80 ± 1.97 | 3.50 ± 1.89 | 3.14 ± 1.60 | bd | bd | - | 0.04 | 100 |
| Cr      | bd | bd | bd | 1.09 ± 0.43 | 1.52 ± 0.20 | 1.63 ± 0.74 | bd | bd | 0.1 | 0.05 | 100 |
| Cu      | 7.24 ± 1.19 | 9.95 ± 2.49 | 3.57 ± 2.31 | 152.78 ± 17.28 | 193.17 ± 11.32 | 173.38 ± 43.01 | bd | bd | 1.0 | 1.0 | 100 |
| Hg      | bd | bd | bd | bd | bd | bd | bd | bd | 0.002 | - | - |
| Mn      | 12.13 ± 4.95 | 16.81 ± 4.15 | 13.90 ± 0.96 | 668.49 ± 223.49 | 872.28 ± 107.00 | 771.80 ± 214.38 | 0.20 ± 0.14 | 0.31 ± 0.19 | 0.05 | 0.1 | > 100 |
| Mo      | 1.79 ± 0.00 | 0.00 ± 0.00 | bd | bd | bd | bd | bd | bd | - | 0.07 | 100 |
| Ni      | bd | bd | bd | 1.15 ± 0.38 | 2.25 ± 0.47 | 1.80 ± 1.22 | bd | bd | 1.0 | 0.07 | > 100 |
| Pb      | bd | bd | bd | 7.49 ± 2.60 | 10.09 ± 1.21 | 8.84 ± 2.66 | bd | bd | 0.015 | 0.01 | > 100 |
| Se      | bd | bd | bd | bd | bd | bd | bd | bd | 0.05 | 0.01 | - |
| V       | bd | bd | bd | 0.28 ± 0.23 | bd | 0.57 ± 0.35 | bd | bd | - | - | - |
| Zn      | 6.99 ± 2.75 | 20.63 ± 14.43 | 5.94 ± 3.30 | 123.20 ± 42.55 | 60.74 ± 80.89 | 140.46 ± 40.05 | 3.36 ± 1.00 | 3.08 ± 0.00 | 5.0 | 3.0 | 149.30 |
Except for the primary aeration stages, metal concentrations for Ag, As, Cd, Hg, Mo, Se, Se were determined below detection limits at all stages. Figure 5a depicts trace elements with < 5 ppm or below detectable levels for Cd, Cr, Se, Mo, Hg, Cd, Ni, As, Ag, and V. The metal concentrations for elements B (10.45 ± 2.57 ppm) > Mn (0.31 ± 0.19 ppm) > Zn (3.08 ± 0.00 ppm) > Ni (0.00 ppm) > V and Cu were detected at all treatment stages. There is notable decrease in metal concentrations along treatment stages with percent removals > 100% for most elements (Table 6). In the effluent the metals Pb, Co, Cr, Cu, Se, Mo, Hg, Cd, Ni, As, Ag, and V were found below detectable limits (Fig. 5a and b).

**Macrolelement concentrations in wastewater**

Figures 6 and 7 depict macrolelement concentrations Al, Ca, Fe, K, Mg, Na, P, and S along the treatment stages. The elements Al, Fe, and P were not detected at the effluent stage (Fig. 5, Table 7) and were removed to greater than 100%. The metal concentrations in the raw influent samples follow the order: Na (24124 ± 1790 ppm) > S (4105 ± 609 ppm) > K (3743 ± 839 ppm) > Ca (1267 ± 247 ppm) > P (1145 ± 295 ppm) > Mg (759 ± 317 ppm) > Fe (48.8 ± 17.5 ppm) > Al (6.6 ± 2.7 ppm). The effluent concentrations vis-a-vis influent stage (shown in Figs. 5 and 6) follow the order: Na (23840 ± 2512 ppm) > S (4848 ± 192 ppm) > K (3162 ± 1010 ppm) > Ca (1127 ± 125) > P (711 ± 173 ppm) > Mg (558 ± 90 ppm) > Al (below detection) ≈ Fe (below detection ppm). Figures 4, 5, and 6 show that the decreased concentrations to below detection for most elements occur in the effluent stage.

**Correlation analysis**

Correlation analyses are widely used in environmental studies to reveal relationships between multiple variables (Alum & Okoye, 2020; Okoro et al., 2017; Onchoke & Fateru, 2021; Sojobi, 2016). They are therefore useful in understanding the influencing factors as well as the of the chemical pollutants (Li et al., 2015). The Pearson correlation coefficients between analytes are shown in Tables 8 and 9. In this study, the following classifications were adopted from Sojobi (2016), namely, perfectly correlated ($R^2 = 1$), very strongly correlated ($±0.9 < R^2 < 1$), strongly correlated ($±0.7 < R^2 < ±0.9$), moderately correlated ($±0.5 < R^2 < ±0.9$), and poorly correlated ($R^2 < ±0.5$).

Table 8 shows Pierson’s correlation coefficients between the anions and the metals. In general, there is observed poor correlations between the metals and anions. However, $F^-$, $Cl^-$, $NO_2^-$, and $Br^-$ show moderately negative correlations to $K^+$ ($-0.511$, $-0.511$, $-0.507$, $-0.489$, respectively),
Table 7  Concentrations of macro elements (in ppm, mg/L) in samples collected from four treatment stages (mean ± SD); n (number of samples analyzed) = 12

| Elem | Raw | Pre-aeration | Primary clarifier | Primary aeration | Secondary clarifier | Return: aeration | Chlorine contact chamber (CCC) | Effluent | USEPA standarda (mg/L) | WHO standardb (mg/L) | % mean removal |
|------|-----|--------------|-------------------|------------------|---------------------|------------------|-------------------------------|----------|------------------------|-----------------------|---------------|
| Al   | 6.5 ± 2.6 | 210.9 ± 29.35 | 3.7 ± 1.7         | 1419.9 ± 445.0   | 1951.6 ± 219.0      | 1718.6 ± 552.9   | 0.00 ± 0.00                   | 0.00 ± 0.00 | 0.05                   | 0.2                   | 100           |
| Ca   | 1267.0 ± 247.2 | 1554.1 ± 373.7 | 1379.4 ± 197.7   | 3450.7 ± 1579.1  | 2529.7 ± 2076.1     | 4744.9 ± 1270.0  | 1170.2 ± 151.8                | 1172.7 ± 125.3 | 75                     | 0.10                  | 100           |
| K    | 3742.9 ± 839.0 | 3623.9 ± 886.5 | 3575.0 ± 1028.1  | 6093.9 ± 2930.0  | 5260.1 ± 3397.7     | 7615.9 ± 4293.6  | 3552.9 ± 915.7                | 3162.0 ± 1010.3 | 2.0                   | 0.7                   | 99.23         |
| Mg   | 759.25 ± 317.07 | 919.2 ± 283.3  | 872.4 ± 241.6    | 2006.9 ± 884.2   | 1969.6 ± 1709.3     | 2902.3 ± 1513.8  | 574.0 ± 105.4                 | 558.0 ± 90.1 | 50                     | -                     | 71.35         |
| Na   | 24124.1 ± 1790.0 | 24923.6 ± 557.0 | 25334.4 ± 497.9  | 24183.8 ± 1781.0 | 24396.6 ± 1851.7    | 22950.6 ± 2726.0 | 24047.4 ± 2555.3              | 23840.8 ± 251.8 | 200                    | 0.003                  | 100           |
| S    | 4105.4 ± 608.6 | 3976.1 ± 438.2 | 4540.5 ± 836.5   | 4901.3 ± 692.3   | 4339.6 ± 938.7      | 4085.7 ± 1253.4  | 4757.5 ± 1214                 | 4848.3 ± 191.5 | 0.04                   | 0.04                   | 100           |
| P    | 1144.6 ± 295.1 | 1296.1 ± 174.5 | 1192.2 ± 97.2    | 7147.3 ± 5174.2  | 4915.8 ± 7132.8     | 11431.3 ± 6753.8 | 754.4 ± 203.5                 | 710.9 ± 173.4 | 0.015                  | 0.05                   | 100           |
| Fe   | 48.8 ± 17.5  | 81.20 ± 18.99 | 35.98 ± 26.3     | 2803.7 ± 912.8   | 3896.5 ± 283.8      | 3372.1 ± 1047.8  | 0.00 ± 0.0                    | 0.00 ± 0.0 | 1.0                    | 1.0                    | 100           |
which suggests moderate dependency on each other and possible similar anthropogenic source (Sojobi, 2016). On the other hand, very strong correlations are observed between F\(^-\) and Cl\(^-\) (\(r = 0.9997\)), F\(^-\) and NO\(_2^-\) (\(r = 0.9996\)), F\(^-\) and Br\(^-\) (\(r = 0.9918\)), F\(^-\) and NO\(_3^-\) (\(r = 0.9548\)), and F\(^-\) and PO\(_4^{3-}\) (\(r = 0.9997\)). Similarly, NO\(_3^-\), NO\(_2^-\), SO\(_4^{2-}\), and Cl\(^-\) are very strongly and positively correlated with each other with \(r^2 \geq 0.94\). These positive correlations indicate the anions originate from the same sources.

Pearson’s correlation matrix for all metal concentrations in wastewater samples from LWWTP are collected in Table 9. The low concentrations of As, Cd, Hg, and Se gave indeterminate \(r\) values and are not included in this discussion. Significant positive correlations (\(p \leq 0.01\)) were observed between Ba and metals Cr, Co, Mn, Ni, Pb, Zn, Al, Ca, K, and Mg. Also noted are significant correlations between B and other elements: Co, Cr, Cu, Mn, Ni. Significant other correlations were also noted between Ba and Pb, Ba and Al, B and K, B and Mg, B and P, B and Fe, Co and Cr, Co and Cu, Co and Mn, Co and Ni, Co and Al Co and Mg, Cr and Cu, Cr and Mn, Cr and Ni, Cr and Al Cr, and K, Cr and Mg, Cr and Fe, Cu and Mn, Cu and Ni, Cu and Pb, Cu and Al, Cu and Mg, Cu and P, Cu and Fe, Mn and Ni, Mn and Pb, Mn and Al, Mn and Mg, Ni and Pb, Ni and Al, Mn and Mg, Mo and Fe, Ni and Pb, Ni and Al, Pb and Al, Pb and Mg, and Pb and Fe.

**Discussion**

Removal efficiencies of anions

The removal efficiencies were estimated by calculating comparative ratios between effluent concentrations versus influent and prior concentrations, especially the secondary clarifier. Table 5 show the removal efficiencies of anions; namely, 78.89 to 100% (F\(^-\)), 16–16.50% (Cl\(^-\)) > 51.81% (PO\(_4^{3-}\)), and > 2–67.01% (SO\(_4^{2-}\)). The removal efficiency was > 100% on June 16, 2017,
and increased on June 23, 2017. The removal efficiencies > 100% are attributed to the return activated sludge (RAS) that is returned to the aeration chamber. The removal efficiencies on June 23, 2017, were the lowest for NO$_3^-$ and SO$_4^{2-}$. The overall removal efficiencies for the grab samples were comparatively lower than in earlier studies assessed over an 18-month period (Onchoke et al., 2015) in Nacogdoches WWTP in East Texas, USA. Noticeably, the detected amounts are lower than the USEPA maximum contaminant levels (MCL). Thus, studies over longer time frames are envisaged in order to gain further insights into the operational efficiency of LWWTP.

Ring et al. (2015) reported that removal efficiencies of element concentrations of < 5 ppm from wastewater

Initially, Ag, Al, As, Ba, Co, Cr, Cu, Fe, Mn, Ni, P, Pb, Zn, and V concentrations display nearly similar trends (Fig. 5) and were low or below detection from the raw to primary clarifier treatment stages. Element concentrations then exhibited a spike at the primary-aeration stage. This is then followed by low or below detections at the secondary clarifier, chlorine contact chamber, and effluent stages. Except for Cd, Hg, Mo, Na, and Se, the primary-aeration stage shows the highest concentrations. This is reasonable as it is at the primary-aeration stage where wastewater and biosolid materials are introduced. This is the followed by biosolids settling in the primary clarifier bacterial breakdown, prior to transfer of sludge material and wastewater onto the secondary clarifier. Because the bulk of the elements are adsorbed or incorporated into the biosolid material, it is plausible that the primary-aeration stage contains the highest concentrations as biosolids concentrate the elements in this stage (Rauch & Harremoes, 1996).

Figure 5a shows concentrations of Mo and Se are highest in the raw stage and decrease to near or below detection the rest of the treatment stages. The Cd and Hg concentrations were below detection in all treatment stages. Thus, their removal efficiencies are 100% by the effluent stage.
Elemental analysis of macroelements (< 1000 ppm) in wastewater sludges

Figure 6 shows the secondary clarifier’s critical role in the removal of elements to low concentrations. This is feasible, given that sludge that settles in the secondary clarifier first after it passes through the aeration stages (Shivakoti et al., 2010). The majority of the element-containing biosolid material is either continually recycled in the return-aeration stage or sent to the anaerobic digester from the primary clarifier (Ferrar et al., 2013). Generally, the anaerobic sludge exhibits the highest elemental concentrations save for Al, Ca, Fe, Na, S, and Zn (Figs. 6 and 7) where the primary clarifier sludge exhibited higher concentrations. Notably Na (Fig. 7) concentration increases slightly from the raw to pre-aeration stages before continually decreasing over the stages to the effluent. Thus, Na is minimally removed at the effluent stage.

Wastewater treatment plants and climate change

The East Texas region is known to have humid subtropical climate typical of the Southeast and receives 35 to 60 in more rainfall than the rest of Texas (Kimmel et al., 2016). In this respect, the LWWTP plays a critical role in recycling and sustainability of water to the environment. Although few studies have been reported on the modulating effects of the Lufkin wastewater treatment plant, it is postulated that the role played by the plant is important in the conservation of water resources in the environment. In particular, the continual release of the treated water, and thus continual recycling, is important and especially
|       | Ag  | Ba  | B   | Co  | Cr  | Cu  | Mn  | Mo  | Ni  | Pb  | V   | Zn  | Al  | Ca  | K   | Mg  | Na  | S   | P   | Fe  |
|-------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| **Ag** | 1.000 |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| **Ba** | 0.592 | 1.000 |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| **B**  | 0.539 | 0.967 | 1.000 |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| **Co** | 0.540 | 0.993 | 0.980 | 1.000 |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| **Cr** | 0.487 | 0.987 | 0.978 | 0.998 | 1.000 |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| **Cu** | 0.532 | 0.991 | 0.974 | 0.999 | 0.998 | 1.000 |     |     |     |     |     |     |     |     |     |     |     |     |     |
| **Mn** | 0.518 | 0.991 | 0.977 | 1.000 | 0.999 | 0.999 | 1.000 |     |     |     |     |     |     |     |     |     |     |     |
| **Mo** | -0.167 | -0.285 | -0.241 | -0.256 | -0.253 | -0.239 | -0.251 | 1.000 |     |     |     |     |     |     |     |     |     |     |
| **Ni** | 0.330 | 0.951 | 0.951 | 0.973 | 0.985 | 0.974 | 0.978 | -0.241 | 1.000 |     |     |     |     |     |     |     |     |     |
| **Pb** | 0.504 | 0.990 | 0.979 | 0.999 | 1.000 | 0.999 | 1.000 | -0.254 | 0.982 | 1.000 |     |     |     |     |     |     |     |
| **V**  | 1.000 | 0.592 | 0.539 | 0.540 | 0.487 | 0.532 | 0.518 | -0.167 | 0.330 | 0.504 | 1.000 |     |     |     |     |     |     |
| **Zn** | 0.891 | 0.878 | 0.821 | 0.848 | 0.814 | 0.847 | 0.835 | -0.244 | 0.705 | 0.825 | 0.891 | 1.000 |     |     |     |     |     |     |
| **Al** | 0.488 | 0.986 | 0.964 | 0.994 | 0.996 | 0.997 | 0.996 | -0.273 | 0.980 | 0.996 | 0.488 | 0.824 | 1.000 |     |     |     |     |
| **Ca** | 0.838 | 0.913 | 0.856 | 0.892 | 0.864 | 0.893 | 0.883 | -0.259 | 0.769 | 0.873 | 0.838 | 0.992 | 0.874 | 1.000 |     |     |     |
| **K**  | 0.789 | 0.929 | 0.907 | 0.924 | 0.901 | 0.925 | 0.917 | -0.163 | 0.819 | 0.909 | 0.789 | 0.969 | 0.903 | 0.984 | 1.000 |     |     |
| **Mg** | 0.643 | 0.965 | 0.913 | 0.965 | 0.955 | 0.971 | 0.965 | -0.236 | 0.905 | 0.958 | 0.643 | 0.914 | 0.964 | 0.955 | 0.964 | 1.000 |     |
| **Na** | -0.185 | -0.163 | -0.272 | -0.134 | -0.125 | -0.117 | -0.234 | -0.099 | -0.128 | -0.185 | -0.117 | -0.087 | -0.048 | -0.104 | 0.038 | 1.000 |     |
| **S**  | 0.488 | 0.216 | 0.265 | 0.173 | 0.144 | 0.131 | 0.148 | -0.469 | 0.059 | 0.153 | 0.488 | 0.295 | 0.089 | 0.244 | 0.216 | 0.087 | -0.426 |
| **P**  | 0.816 | 0.939 | 0.895 | 0.922 | 0.897 | 0.921 | 0.913 | -0.227 | 0.809 | 0.905 | 0.816 | 0.984 | 0.899 | 0.995 | 0.992 | 0.963 | -0.107 |
| **Fe** | 0.487 | 0.987 | 0.975 | 0.998 | 1.000 | 0.998 | 0.999 | -0.249 | 0.985 | 1.000 | 0.487 | 0.816 | 0.997 | 0.867 | 0.903 | 0.958 | -0.115 |

Table 9 Pearson's correlation coefficients \((r)\) between macro- and microelements in all wastewater treatment stages \((n > 108)\)
during the hot summer where typical high temperatures are in the 90 s everywhere and spring months (Kimmel et al., 2016). The role played by the treatment plant is also important in controlling of pathogens, especially COVID-19 pandemic. Recent studies have shown that the need to reduce pathogens and the continuous usefulness of WWTPs mitigate the changes in climate change by recycling efforts (Wu et al., 2019). In this respect, more studies are needed to establish the role of the WWTPs in East Texas.

Environmental implications of study and current risks in usage of treated wastewater in the USA

The increased production of wastewater concomitantly rises with population growth. Thus, WWTPs form an important part in recycling water, and/or conservation, and management of the environment. The examination of LWWTP shows it efficiently removes most metals to below detection levels prior to discharge into water surfaces (in this case the Hurricane Creek). The noted high removal efficiency portends well for better engineering designs and further improvements for future wastewater management systems. Comparison to studies of other bioactive WWTPs in East Texas (Onchoke et al., 2015) and other areas (Agoro et al., 2020) is pertinent. In particular, there is noted similarity in design and operation between LWWTP and Nacogdoches wastewater treatment plant (NWWTP) and therefore comparable removal efficiencies (Onchoke et al., 2015). As observed, most anions and elements examined (except for P) were efficiently removed by the LWWTP as was that of the NWWTP (Onchoke et al., 2015). These results demonstrate the important role played by WWTPs in removing anions and metals from wastewater prior to release to the aquatic environment.

Although removal efficiencies and concentrations of the metals and anions are deemed within USEPA regulated concentration guidelines, the following risks should be carefully considered. Firstly, the unknown concentration of other emerging pollutants that have been recently found in wastewater were not investigated. For instance, perfluoroalkyl and polyfluoroalkyl substances (PFASs), pesticides, herbicides, pharmaceuticals, microplastics, and nano-particulates (Koutnik et al., 2021; Rodowa et al., 2020; Wu et al., 2021) are emerging as major analytes found in wastewater treatment facilities. Recent studies emphasize the need to quantify and determine their concentrations in wastewater treatment plants. It is also important that their health risks be determined as they pose challenges to the beneficial use of treated wastewater. The global ongoing research concern and in the LWWTP is needed to address this uncertainty. The ramifications of risks to man and the environment are further compounded by lack of unified analytical techniques and protocols for quick and easy quantification (Shin et al., 2019). Thus, WWTPs and globally may face this dilemma for some time. The public is thus to be educated on such risks.

Secondly, the concentration levels of microorganisms and pathogens present in wastewater are not comprehensively monitored in WWTPs. Though not reported in this article, the varied pathogens (Shin et al., 2019) pose special monitoring challenges (Liguori et al., 2022; Shin et al., 2019) before and after discharge into the course environment. In the current era, more concerns over the transmission of COVID-19 in wastewater and sewage pose health risks and hazards (Sojobi & Zayed, 2022). In this regard, several recent studies detected SARS-CoV-2 in wastewater and sewage (Dhama et al., 2021; Kitajima et al., 2020; Tran et al., 2021). Recent reports show SARS-CoV-2’s persistence for 3–14 days in wastewater and sewage. This poses serious public health risks (Dhama et al., 2021; Kitajima et al., 2020). Thus, there is caution being exercised and ongoing debate to limit recycling sewage and application of wastewater in irrigation and organic fertilizer. Thirdly, policy makers and engineering designers are faced with the constant need of upgrading WWTPs. The inability of WWTPs to remove SARS-CoV-2 and other emerging pollutants to low concentrations or undetectable levels is “supposedly due to their designs, having been constructed to pre-covid-19 times” (Sojobi & Zayed, 2022). Thus, risk of COVID-19 infection is further heightened by inefficient WWTPs, leaking sewer pipes, plumbing systems, and septic tanks (Oyegoke et al., 2012; Sojobi & Zayed, 2022). Several studies have therefore prompted a critical look on the use and recycling for irrigation and recreational facilities of sludge due (in part) to the emergence of the COVID-19 pandemic.
Conclusions

The present study evaluated the performance of an activated rural WWTP and its efficiency in removing metals and anions from both the raw sewage and along its treatment stages. The average anion concentrations showed that anions were removed by > 90%. Similarly macro- and microelements were successfully removed at the end of effluent stage by the LWWTP to levels below USEPA standards. The efficiency of metals is noted by the high percent removal at the effluent stage (especially of heavy metals) vis-a-vis influent stage and raw stage to below USEPA detectable limits. This is especially notable for toxic metals (As, Cd, Pb, Cu, and transition metals) that pose environmental and health risks. Notably, the primary and secondary clarifiers are essential to removing anion and metal ions and thus show highest removal efficiency prior to proceeding to chlorine contact chamber and effluent stages.

The outcome of this study informs WWTP designers in the following ways. First, despite the LWWTP wastewater treatment plant meeting its current regulated concentration levels for metals and anions, major designs are needed to meet future challenges of population increases. Further, there is the need to remove emerging pollutants that may be in low considerations (ng/L or less). This will be needed to accommodate demands for treated wastewater free of pathogens and the viruses.

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Author contribution Kefa K. Onchoke (KKO): project administration, conceptualization, resources, methodology, investigation, data curation, formal analysis, validation, writing—original and final draft, writing—reviews and editing, visualization, supervision, funding acquisition. Christopher M. Franclemont: investigation, methodology, writing—initial draft, data curation, formal analysis, validation.

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Declarations

Ethics approval This article does not contain any studies with human participants or animals performed by any of the authors.

Consent to participate All authors declare they have given consent to publish this article.

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References

Agoro, M. A., Adeniji, A. O., Adefisoye, M. A., & Okoh, O. O. (2020). Heavy metals in wastewater and sewage sludge from selected municipal treatment plants in Eastern Cape Province, South Africa. Water, 12(2746), 1–19. https://doi.org/10.3390/w12102746
Al-Omari, A., Rabaan, A. A., Salih, S., Al-Tawfiq, J. A., & Memish, Z. A. (2019). MERS coronavirus outbreak: Implications for emerging viral infections. Diagnostic Microbiology and Infectious Disease, 93(3), 265–285. https://doi.org/10.1016/j.diagmicrobio.2018.10.011
Alum, O. L., & Okoye, C. O. B. (2020). Pollution status of major rivers in an agricultural belt in Eastern Nigeria, Environmental Monitoring and Assessment, 192(6), 393. https://doi.org/10.1007/s10661-020-08366-3
APHA. (2013). Standard methods for the examination of water and wastewater. American Public Health Association(APHA), American Water Works Association, Water Environment Federation, Washington, DC, 2014 (22nd ed.). New York: American Public Health Association.
Apostolidis, N., Hertle, C., & Young, R. (2011). Water Recycling in Australia. Water, 3, 869–881. https://doi.org/10.3390/w3030869
Balogun, I. I., Sojobi, A. O., & Galkaye, E. (2017). Public water supply in Lagos State, Nigeria: Review of importance and challenges, status and concerns and pragmatic solutions. Cogent Engineering, 4(1), 1329776. https://doi.org/10.1080/23311916.2017.1329776
Basha, C. A., Somasundaram, M., Kannadasan, T., & Lee, C. W. (2011). Heavy metals removal from copper smelting effluent using electrochemical filter press cells. Chemical
Environ Monit Assess (2022) 194:920

Çeçen, F., & Yangın, Ç. (2000). Comparison of BOD results obtained by dilution and manometric methods in sanitary landfill leachates. Journal of Environmental Monitoring, 2, 628–633. https://doi.org/10.1039/B003244L

Cydzik-Kwiatkowska, A., & Nosek, D. (2020). Biological release of phosphorus is more efficient from activated than from aerobic granular sludge. Scientific Reports, 10, 11076. https://doi.org/10.1038/s41598-020-76796-5

Dhama, K., Patel, S. K., Yatoo, M. I., Tiwari, R., Sharan, K., Dhama, J., & Harapan, H. (2021). SARS-CoV-2 existence in sewage and wastewater: A global public health concern? Journal of Environmental Management, 280, 111825. https://doi.org/10.1016/j.jenvman.2020.111825

Ensink, J. H., Mahmod, T., Van der Hoek, W., Raschid-Sally, L., & Amerasinghe, F. P. (2004). A nationwide assessment of wastewater use in Pakistan: An obscure activity or a vitally important one? Water Policy, 6(3), 197–206. https://doi.org/10.2166/wp.2004.0013

Fekadu, S., Alemayehu, E., Dewil, R., & Van der Bruggen, B. (2019). Pharmaceuticals in freshwater aquatic environments: A comparison of the African and European challenge. Science of the Total Environment, 654, 324–337. https://doi.org/10.1016/j.scitotenv.2018.11.072

Ferrar, K. J., Michanowicz, D. R., Christen, C. L., Mulcahy, N., Malone, S. L., & Sharma, R. K. (2013). Assessment of effluent contaminants from three facilities discharging Marcellus Shale wastewater to surface waters in Pennsylvania. Environmental Science and Technology, 47, 3472–3481.

Fu, F., & Wang, Q. (2011). Removal of heavy metal ions from wastewaters: A review. Journal of Environmental Management, 92(3), 407–418. https://doi.org/10.1016/j.jenvman.2010.11.011

Garrido-Baserba, M., Vinardell, S., Molinos-Senante, M., Rosso, D., & Poch, M. (2018). The economics of wastewater treatment decentralization: A techno-economic evaluation. Environmental Science & Technology, 52(15), 8965–8976. https://doi.org/10.1021/acs.est.8b01623

Giannakis, I., Emmanouil, C., Mitrakas, M., Manakou, V., & Kungolos, A. (2021). Chemical and ecotoxicological assessment of sludge-based biosolids used for corn field fertilization. Environmental Science and Pollution Research, 28(4), 3797–3809. https://doi.org/10.1007/s11356-020-09165-6

Gorska, M., Greda, K., & Pohl, P. (2021). On the coupling of hydride generation (HG) with flowing liquid anode atmospheric pressure glow discharge (FLA-APGD) for determination of traces of As, Bi, Hg, Sb and Se by optical emission spectrometry (OES). Talanta, 222, 121510. https://doi.org/10.1016/j.talanta.2020.121510

Han, J., & He, S. (2021). Urban flooding events pose risks of virus spread during the novel coronavirus (COVID-19) pandemic. Science of the Total Environment, 755, 142491. https://doi.org/10.1016/j.scitotenv.2020.142491

Huang, Y., Keller, A. A., Cervantes-Avilés, P., & Nelson, J. (2021). Fast multielement quantification of nanoparticles in wastewater and sludge using single-particle ICP-MS. ACS Environmental Science & Technology Water, 1(1), 205–213. https://doi.org/10.1021/acswater.0c00083

Jiménez, B., & Asano, T. (2008). Water reuse, in an international survey of current practice, issues, and needs (Vol. 7). IWA Publishing.

Kehrein, P., Van Loosdrecht, M., Osseweijer, P., Garfi, M., Dewulf, J., & Posada, J. (2020). A critical review of resource recovery from municipal wastewater treatment plants – market supply potentials, technologies and bottlenecks. Environmental Science: Water Research & Technology, 6, 877–910. https://doi.org/10.1039/c9ew00905a

Kimmel, T. M., Nielsen-Gammon, J., Rose, B., & Mogil, H. M. (2016). The weather and climate of Texas: A big state with big extremes. Weatherwise, 69(5), 25–33. https://doi.org/10.1080/00431672.2016.1260446

Kitajima, M., Ahmed, W., Bibby, K., Carducci, A., Gerba, C. P., Hamilton, K. A., & Rose, J. B. (2020). SARS-CoV-2 in wastewater: State of the knowledge and research needs. Science of the Total Environment, 739, 139076. https://doi.org/10.1016/j.scitotenv.2020.139076

Koutnik, V. S., Alkidim, S., Leonard, J., DePrima, F., Cao, S., Koutnik, V. S., Alkidim, S., Leonard, J., DePrima, F., Cao, S., Kitajima, M., Ahmed, W., Bibby, K., Carducci, A., Gerba, C. P., Hamilton, K. A., & Rose, J. B. (2020). SARS-CoV-2 in wastewater: State of the knowledge and research needs. Science of the Total Environment, 739, 139076. https://doi.org/10.1016/j.scitotenv.2020.139076

Kungolos, A. (2021). Chemical and ecotoxicological assessment of sludge-based biosolids used for corn field fertilization. Environmental Science and Technology, 52(15), 8965–8976. https://doi.org/10.1021/acs.est.8b01623

Lee, J.-C., Son, Y.-O., Pratheekshumara, P., & Shi, X. (2012). Oxidative stress and metal carcinogenesis. Free Radical Biology and Medicine, 53(4), 742–757. https://doi.org/10.1016/j.freeradbiomed.2012.06.002

Li, J., Luo, G., Gao, J., Yuan, S., Du, J., & Wang, Z. (2015). Quantitative evaluation of potential ecological risk of heavy metals in sewage sludge from three different wastewater treatment plants in the main urban area of Wuxi, China. Chemistry and Ecology, 31(3), 235–251. https://doi.org/10.1080/02757540.2014.961439

Li, L., Pang, H., He, J., & Zhang, J. (2019). Characterization of phosphorus species distribution in waste activated sludge after anaerobic digestion and chemical precipitation with Fe3+ and Mg2+. Chemical Engineering Journal, 373, 1279–1285. https://doi.org/10.1016/j.cej.2019.05.146

Liguori, K., Keennum, I., Davis, B. C., Calarco, J., Milligan, E., Harwood, V. J., & Pruden, A. (2022). Antimicrobial Resistance monitoring of water environments: A framework for standardized methods and quality control. Environmental Science & Technology, 56(13), 9149–9160. https://doi.org/10.1021/acs.est.1c08918

Lu, J., Li, Y., Yin, M., Ma, X., & Lin, S. (2015). Removing heavy metal ions with continuous aluminum electrocoagulation: A study on back mixing and utilization rate of electro-generated Al ions. Chemical Engineering Journal, 267, 86–92. https://doi.org/10.1016/j.cej.2015.01.011

Ma, L., & Zhang, W.-X. (2008). Enhanced biological treatment of industrial wastewater with bimetallic zero-valent iron. Environmental Science and Technology, 42(15), 5384–5389. https://doi.org/10.1021/es801743s

Maoof, H. I., Daud, W. M. A. W., & Aroua, M. K. (2017). Recent trends in removal and recovery of heavy metals from wastewater by electrocoagulation technologies. Reviews in Chemical Engineering, 33(4), 359–386. https://doi.org/10.1015/reve-2016-00021

Mackay, I. M., & Arden, K. E. (2015). MERS coronavirus: Diagnostics, epidemiology and transmission. Virology Journal, 12(1), 222. https://doi.org/10.1186/s12985-015-0439-5

Madadian, E., & Simakov, D. S. A. (2022). Thermal degradation of emerging contaminants in municipal biosolids: The case of pharmaceuticals and personal care products.
vegetables irrigated with treated municipal wastewater. *Journal of Agricultural and Food Chemistry*, 64(29), 5784–5792. https://doi.org/10.1021/acs.jafc.6b01696

Rodowa, A. E., Christie, E., Sedlak, J., Peaslee, G. F., Bogдан, D., DiGiuseppe, B., & Field, J. A. (2020). Field sampling materials unlikely source of contamination for perfluoralkyl and polyfluoroalkyl substances in field samples. *Environmental Science & Technology Letters*, 7(3), 156–163. https://doi.org/10.1021/acs.estlett.0c00036

Sahay, S., Iqbal, S., Ashfaq, F., & Inam, A. (2016). Effect of water waste and fly ash application on physiological determinants, yield, and heavy metal contents of yellow mustard (B. campestris cv. P. Gold). *Journal of Plant Nutrition*, 40(12), 1710–1727. https://doi.org/10.1080/01904167.2017.1310892

Schmitz, B. W., Moriyama, H., Haramoto, E., Kitajima, M., Shcerban, S., Gerba, C. P., & Pepper, I. L. (2018). Reduction of cryptosporidium, giardia, and fecal indicators by bardenpho wastewater treatment. *Environmental Science & Technology*, 52(12), 7015–7023. https://doi.org/10.1021/acs.est.7b05876

Shanmugam, K., Gadhamshetty, V., Tysklind, M., Bhattacharyya, D., & Upadhyayula, V. K. K. (2022). A sustainable performance assessment framework for circular management of municipal wastewater treatment plants. *Journal of Cleaner Production*, 339, 130657. https://doi.org/10.1016/j.jclepro.2022.130657

Shin, D. J., Andini, N., Hsieh, K., Yang, S., & Wang, T.-H. (2019). Emerging analytical techniques for rapid pathogen identification and susceptibility testing. *Annual Review of Analytical Chemistry*, 12(1), 41–67. https://doi.org/10.1146/annurev-anchem-061318-115529

Shivakoti, B. R., Tanaka, S., Fujii, S., Kunacheva, C., Boontanon, S. K., Musirat, C., & Tanaka, H. (2010). Occurrences and behavior of perfluorinated compounds (PFCs) in several wastewater treatment plants (WWTPs) in Japan and Thailand. *Journal of Environmental Monitoring*, 12(6), 1255–1264. https://doi.org/10.1039/B927287A

Singh, P. K., Deshbhrrat, P. B., & Ramteke, D. S. (2012). Effects of sewage wastewater irrigation on soil properties, crop yield and environment. *Agricultural Water Management*, 103, 100–104. https://doi.org/10.1016/j.agwat.2011.10.022

Sojobi, A. O. (2016). Evaluation of groundwater quality in a rural community in North Central of Nigeria. *Environmental Monitoring and Assessment*, 188(3), 192. https://doi.org/10.1007/s10661-016-5149-y

Sojobi, A. O., & Zayed, T. (2022). Impact of sewer overflow on public health: A comprehensive scientoetric analysis and systematic review. *Environmental Research*, 203, 111609. https://doi.org/10.1016/j.envres.2021.111609

Tran, H. N., Le, G. T., Nguyen, D. T., Jiang, R.-S., Rinklebe, J., Bhatnagar, A., & Chao, H.-P. (2021). SARS-CoV-2 coronavirus in water and wastewater: A critical review about presence and concern. *Environmental Research*, 193, 110265. https://doi.org/10.1016/j.envres.2020.110265

USEPA. (1993a). 40CFR 257, Standards for the use or disposal of sewage sludge final rules. Retrieved from https://www.epa.gov/biosolids/biosolids-laws-and-regulations

USEPA. (1993b). 40 CFR Part 503, 503 biosolids management handbook 1 - Standards for the use or disposal of
sewage sludge, regulations. Biosolid Laws and Regulations. Retrieved December 22, 2021, from https://www.epa.gov/sites/production/files/documents/handbook1.pdf

USEPA. (1996). EPA method 3050B: Acid digestion of sediments, sludges, and soils. Retrieved December 22, 2021, from https://www.epa.gov/homeland-security-research/epa-method-3050b-acid-digestion-sediments-sludges-and-soils

USEPA. (2000). Risk-based concentration table. Washington, D.C.: Environmental Protection Agency. Retrieved December 8, 2014, from http://www.epa.gov/reg3hwmd/risk/human/index.htm

USEPA. (2014). Water: Industry Effluent Guidelines. Retrieved December 12, 2017, from http://water.epa.gov/scitech/wastetech/guide/contact.cfm#elg-list

Wang, X., Dalton, E. Z., Payne, Z. C., Perrier, S., Riva, M., Raff, J. D., & George, C. (2021). Superoxide and nitrous acid production from nitrate photolysis is enhanced by dissolved aliphatic organic matter. Environmental Science & Technology Letters, 8(1), 53–58. https://doi.org/10.1021/acs.estlett.0c00806

Westerhoff, P., Lee, S., Yang, Y., Gordon, G. W., Hristovski, K., Halden, R. U., & Herckes, P. (2015). Characterization, recovery opportunities, and valuation of metals in municipal sludges from U.S. wastewater treatment plants nationwide. Environmental Science & Technology, 49(16), 9479–9488. https://doi.org/10.1021/es505329q

WHO. (2006). Guidelines for the safe use of wastewater, excreta and greywater. Wastewater use in agriculture (Vol. 2). World Health Organization. Retrieved December 8, 2014, from http://www.who.int/water_sanitation_health/wastewater/gsuww/en/

Wu, L., Ning, D., Zhang, B., Li, Y., Zhang, P., Shan, X., & Global water microbiome, C. (2019). Global diversity and biogeography of bacterial communities in wastewater treatment plants. Nature Microbiology, 4(7), 1183–1195. https://doi.org/10.1038/s41564-019-0426-5

Wu, R., Ruan, Y., Lin, H., Yuen, C. N. T., Feng, H., & Lam, P. K. S. (2021). Occurrence and fate of psychiatric pharmaceuticals in wastewater treatment plants in Hong Kong: Enantiomeric profiling and preliminary risk assessment. ACS Environmental Science & Technology Water, 1(3), 542–552. https://doi.org/10.1021/acswat.0c00081

Wyman, R. J. (2013). The Effects of Population on the Depletion of Fresh Water. Population and Development Review, 39(4), 687–704. https://doi.org/10.1111/j.1728-4457.2013.00634.x

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