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Analysis of nutrient loads, heavy metals and physicochemical properties of wastewater, wetland grass, and papaya samples: Gondar Malt factory, Ethiopia with global implication

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ABSTRACT

Robust attention was brought to researchers due to deterioration of wastewater quality of lakes and reservoirs as major global concerns by industrial release. The uncontrolled releases of effluents impose serious impacts for both aquatic and terrestrial environments. In the current study, many parameters like nutrient loads, heavy metals and physicochemical properties of wastewater, wetland grass, and papaya samples were analysed. The investigated nutrients, alkalinity, and total hardness in fresh water samples were within the allowable limits except for phosphate in fresh wastewater and alkalinity in wastewater. The detected levels of heavy metals (mg/L) in wastewater samples were:- Cd (0.386–0.905), Cr (ND-0.074), Cu (0.064–0.096), Mn (0.184–1.528), Fe (0.167–4.636), Zn (0.175–0.333), and Pb (0.044–0.892) (mg/L). The studied metals in the wastewater sample, except Cd, Fe, and Pb were lower than the allowable limit. The level of heavy metals in the grass and papaya samples ranged from Cd (37.14–147.62), Cr (ND-8.82), Cu (3.14–8.33), Mn (2.89–85.46), Fe(5.0–65.15), Zn (3.44–36.84), and Pb (ND-60.36) (mg/kg). The detected metals were below the permissible limits, except Cd, Cr, and Pb. The findings of the physicochemical characteristics in wastewater samples were computed: pH (6.61–8.54), temperatures (21.63–26.57 °C), TDS (205.9–1896 mg/L), EC (359.9–3226.67 μs/cm), BOD (12.0–732.67 mg/L), COD (3.67–1691.33 mg/L). Except for temperature and pH, all levels in the wastewater were above the recommended limit for wastewater discharge by USEPA.

1. Introduction

Industries released their major wastewater into the receiving environment [5,23,26,42]. Anthropogenic activities coupled with rapid urbanization and industrialization have brought about ecological pressure on the aquatic environment which directly or indirectly affects human health [4,6]. There is a serious problem of wastewater pollution around the world due to the discharge of dissolved and suspended substances into ground water, streams, rivers, and oceans [19,31,37]. The major source of pollution, in developing countries, is industrial activities and this has gradually increased the problem of waste disposal. Most breweries discharge 70% of their incoming wastewater as effluent [2,10]. Sources of industrial wastes may vary widely depending on the size of the industry [27,31,37,42].

The use of wastewater for irrigation increases organic carbon (OC), nitrogen (N), phosphorus (P) [24], potassium (K), and magnesium (Mg) contents of the soil as compared to clean surface wastewater irrigation, but it may lead to adverse health implications by heavy-metal contaminants like; Cd, Cr, Fe, Cu, Zn, Mn, Ni, Pb, etc. in agricultural production systems [15,16,32].

The strength of wastewater is normally expressed in terms of pollution load [34], which is determined from the concentrations of significant physical, chemical, and biological contents of the wastewater [20]. Wastes from industries could be discharged as liquids, dust particles, and smoke without being treated [12].The effluents could be characterized by abnormalities in turbidity, conductivity, chemical oxygen demand (COD), alkalinity, and hardness [21].

Heavy metals enter in the human body through ingestion of food [8,

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17]; breathing in air and drinking wastewater [3,29,39]. The heavy metals are very harmful because of their non-biodegradable nature, long biological half-lives, and their potential to accumulate in different body parts even at low concentration. Crops and plants accumulate these heavy metals of wastewater in their tissues at concentrations ranging above acceptable levels, which is considered harmful to the ecosystem and aquatic organisms ([11,38]; Ma et. al., 2020). Therefore, the aim of this study was to assess the nutrient loads, heavy metals and physicochemical properties of wastewater, wetland grass, and papaya samples grown in the wetland of Gondar malt factory, Gondar, Ethiopia.

2. Material and methods

2.1. Description of study area

The study area is found in central Gondar zone, Gondar town which is located in Northern part of Ethiopia mainly in the Amhara regional state at about 738 km from Addis Ababa, Ethiopia. Geographically Gondar is bounded by 12° 35' 07'' North latitude and 37° 26' 08'' East longitudes and it has a narrow range of altitude. It is 2000 – 2200 m above sea level with annual rainfall reaching 1172 mm and mean annual average temperature of 20 °C. The River Shinta, which contributed to the Angereb river part of the wastewater shed of Lake Tana, is located near the factory and serves as natural sewerage lines for domestic and industrial wastes of Gondar malt factory.

2.2. Chemicals and reagents

All reagents and chemicals: were analytical graded. HNO_3 (69–70%, Blulux laboratories, (p) Ltd 121001, India) and $HClO_4$ (70%, Blulux fine chem., India) were used for the digestion of wastewater, grass, and fruit samples. Diluted HCl (37% Aldrich, A.C.S. Reagent, Germany) used for washing plastic bottles. Mix of H_2SO_4 (98% Blulux laboratories (p) Ltd 121001, India) and $K_2Cr_2O_7$ was used for preparing chromic acid for soaking and washing digestion flasks and other glasswares before starting digestion to remove metals and other contaminants left on the surface of the apparatuses. Stock standard solutions (1000 mg/L) of the metals Cd, Cr, Cu, Mn, Fe, Zn, and Pb were used for preparation of calibration standards and in the spiking experiments. Distilled wastewater was used for rinsing glassware and sample bottles; deionized wastewater was used for dilution of sample and intermediate metal standard solutions prior to analysis.

2.3. Instruments and apparatus

A refrigerator (LR1602, Lec Refrigeration PLC England), ICP-OES, Polyethylene bottles, Palin test photometer 7100 (UK), micro 800 multi-parameter, BOD Trak ™ II (HACH), DRB 200 (HACH) and HACH DR 900, Digital electric precision balance (Citizone, CTG 1200–1200, India), Conical flasks (100 mL), fume-cupboard (envair Ltd, England), Filtration funnels, Whatman filter paper No.1,volumetric flasks, Measuring cylinders, and micropipettes were used.

2.4. Sample collection, preparation, and analysis

2.4.1. Wastewater sampling

Wastewater samples for analyses were collected at Gondar malt Factory in polyethylene bottles acidified with 3 mL of concentrated HNO_3 per liter of wastewater. All wastewater samples were transported to the laboratory and immediately filtered through acid-treated Millipore filters (0.45 µm mesh) within 24 hours of collection and stored under a refrigerator at 4 °C. The wastewater sample was digested following the American Public Health Association (APHA) protocol.

2.4.2. Grass and papaya sampling

The grass and papaya samples were collected by using stainless steel sickle in different representative sampling points (wetland and control site) and washed several times with tap wastewater followed by distilled wastewater to remove any dust particles on it. The collected samples were dried under room temperature with aluminum foil for 5 days in a clean laboratory room. After air dried, the samples were further dried in an oven at 105 °C until it gives a fixed mass. Samples were ground by an electrical grinder, passed through 250 µm, sieve, and stored in polyethylene plastic bags for digestion with Kjeldahl digestion block (Gallenhamp, England) for analysis by ICP-OES.

2.5. Physicochemical characteristics of wastewater samples

2.5.1. In-situ measurements

The pH, Temperature, Electrical Conductivity (EC), and Total Dissolved Solid (TDS) of wastewater effluents were measured by calibrated micro 800 multi-parameter following the standard protocols and methods of APHA.

2.5.2. BOD measurement

Measured 95 mL of wastewater samples were added to amber bottles having a magnetic stirrer and then one BOD nutrient buffer pillow was added to each bottle for optimum bacterial growth and applied stopcock to the seal lip of each bottle and two KOH pellets were added to each seal cup. The bottle was placed on the chassis of the BOD track and connected to the sample bottle and then the cup was firmly tightened and placed in the incubator, after 5 days, the reading of the BOD directly from the BOD track was displayed following the standard protocols and methods.

2.5.3. COD measurement

2 mL of wastewater sample and blank were added to the different reagent bottles mixed well, then put to the COD DRB 200 reactor and turned on the power. Temperature and time were adjusted to 150 °C and 2 h, respectively. After cooling, the sample and the blank were put into the sample holder of the HACH DR 900, and the reading was made following the standard protocols and method.

2.5.4. Total alkalinity, hardness, and nutrients

The Palin test tube was filled with a filtered wastewater sample to the 10 mL mark except for nitrate analysis; the respective tablet was added and mixed to ensure that all particles were dissolved. After calibration by blank, sample of the portable 7100 photometer triplicate reading was recorded.

2.6. Optimization of working procedure and instrument calibration

The optimization procedures for the determination of heavy metal contents in wastewater, grass, and papaya samples were made by wet digestion method in Kjeldahl. Different digestion procedures were optimized using the HNO_3 and $HClO_4$ acid mixtures by varying one parameter at a time. A combination of optimum conditions was chosen based on the clarity of digests, minimum reagent volume consumption, minimum digestion time, simplicity, and minimum temperature applied for the entire digestion process. Instruments were calibrated prior to measurements and the correlation coefficients (R^2) of the calibration curves were determined. As a result, several working standard solutions from 1000 mg/L were prepared and the concentration of metals in the sample solution was determined using calibration curves.

2.7. Validation of the analytical method

Precision was expressed as the relative standard deviation (%RSD) of the triplicate results and the spiked samples were then subjected to the same Kjeldahl digestion procedure like the actual sample [17,39].

Table 1
Recovery result for water, grass, and papaya samples.

Metals	Concentration of metals in Water				Concentration of metals in wetland grass				Concentration of metals in Papaya			
	Unspiked (mg/L)	Added (mg/L)	Spiked (mg/L)	Recovery (%)	Unspiked (mg/L)	Added (mg/L)	Spiked (mg/L)	Recovery (%)	Unspiked (mg/L)	Added (mg/L)	Spiked (mg/L)	Recovery (%)
Cd	0.905 ±0.4	0.680	1.567 ±1.5	97.34±3	1.476 ±0.02	1.107	2.540 ±0.2	96.46±2	1.095±1.1	0.800	1.820 ±0.5	95.67±6
Cr	0.074 ±0.0	0.060	0.128 ±0.3	96.23±5	0.088 ±0.21	0.060	0.158 ±0.4	106.41±4	0.053 ±0.05	0.042	0.980 ±0.5	105.78±3
Cu	0.096 ±0.5	0.08	0.166 ±1.2	96.63±1	0.083 ±0.04	0.060	0.148 ±1.2	104.19±3	0.072 ±0.42	0.060	0.131 ±0.1	102.64±4
Mn	1.528 ±1.2	1.140	2.656 ±2.1	98.40±2	0.855 ±0.11	0.640	1.290 ±1.5	101.61±1.2	0.110 ±0.00	0.080	0.195 ±0.1	103.16±5
Fe	4.636 ±2.0	3.480	8.250 ±3.2	103.93±2	0.576±0.6	0.440	1.031 ±0.3	105.22±0.8	0.100±0.1	0.072	0.165 ±0.0	90.91±2.4
Zn	0.333 ±0.3	0.260	0.577 ±1.7	97.47±3	0.368 ±0.25	0.280	0.582 ±0.7	100.11±0.5	0.069 ±0.03	0.060	0.126 ±0.1	103.82±0.7
Pb	0.892 ±0.4	0.680	1.642 ±0.8	99.99±4	0.171 ±0.32	0.120	0.306 ±0.1	105.37±5	1.207±1.4	0.900	2.044 ±1.6	92.55±3

Water Sample (WS), Grass Sample (GS), Papaya Sample (PS).

$$\%RSD = \frac{\text{standard deviation}}{\text{mean value}} X100 \quad (1)$$

LOD and LOQ for each metal were determined from the analysis of triplicates of method blanks which were digested in the same digestion procedure as the actual samples and calculated as ([18]; Mulu et. al., 2022).

$$LOD = \frac{3xSD}{\text{mean value}} \quad (2)$$

$$LOQ = \frac{10xSD}{\text{mean value}} \quad (3)$$

Recovery is another parameter used to detect the accuracy of the method and it was performed by spiking the wastewater, grass, and papaya samples with standard solutions of heavy metals due to the absence of certified reference materials. The spiked sample were digested and analyzed following the same analytical procedure as the white lupine and soil samples. In recovery-spiking, the known amount of analyte was added into the natural test sample matrix, and the recovered amount was determined ([13,22], Mulu et. al., 2022).

A 50 mL of wastewater spiked with 34 μL of Cd, 3 μL of Cr, 4 μL of Cu, 57 μL of Mn, 174 μL of Fe, 13 μL of Zn, and 34 μL of Pb form 1000 mg/L of standard solution. The spiked wastewater samples were digested with 3 mL of HNO_3 and 3 mL of $HClO_4$ at 120°C for 65 min. Similarly, 0.5 g of wetland grass and 1.0 g of papaya samples were spiked with 55 and 40 μL of Cd, 4 and 2 μL of Cr, 3 and 3 μL of Cu, 32 and 4 μL Mn, 22 and 4 μL of Fe, 14 and 3 μL Zn, and 6 and 45 μL of Pb, respectively. The spiked grass samples were digested with 6 mL of HNO and 4 mL of $HClO_4$ at 125°C for 45 min. The spiked papaya samples were also digested with 5 mL of HNO_3 and 4 mL of $HClO_4$ at 120 °C for 25 min. All measurements were performed in triplicates and recovery was calculated using equ. 4.

$$\%R = \frac{\text{CM in the spiked sample} - \text{CM in the none spiked sample}}{\text{CM added for spiking}} x100 \quad (4)$$

Where, CM = concentration of metal of interest.

Table 3
LOD, and LOQ for water, grass, and fruit samples (n=3).

Elements	LOD			LOQ		
	WS	GS	PS	WS	GS	PS
Cd	0.086	0.429	0.857	0.286	1.429	2.857
Cr	0.054	0.027	0.082	0.182	0.091	0.273
Cu	0.014	0.283	0.142	0.047	0.943	0.472
Mn	0.032	0.064	0.032	0.106	0.213	0.106
Fe	0.109	0.818	0.273	0.364	0.273	0.909
Zn	0.039	0.026	0.053	0.132	0.088	0.175
Pb	0.016	0.081	0.162	0.054	0.270	0.540

Water Sample (WS), Grass Sample (GS), Papaya Sample (PS).

2.8. *Statistical analysis of variance (ANOVA)*

The variation in the sample mean of the analyte was tested by using analysis of variance (ANOVA), whether the source for variation was from the experimental procedure or heterogeneity among the samples. ANOVA used the t-test to compare whether the difference between sample means are significant or not. In the present study, one-way ANOVA was used to compare the means between all the samples, and the calculations were made as only one factor being considered in the triplicate data for changing the level of the factor.

3. Results and discussion

3.1. *Method validations*

The mean percentage recovery (%R) of metals in the wastewater, grass, and papaya samples were found to be in the range of 96.23–103.93%; 96.46–106.41%; and 90.91–105.78%, respectively (Table 1). All the recovery values were within the acceptable range of 80–120% for metal analysis [1]. %RSD values obtained for wastewater, grass, and papaya fruit samples were ranged from 0.00% to 9.8%; 0.00–9.12%; and 0.00–9.0%, respectively (Table 2). The values were

Table 2
%RSD, T-test (p-value), and R2 of water, grass, and fruit sample.

Sample	Cd	Cr	Cu	Mn	Fe	Zn	Pb	P value
Water	9.12–9.78	0.00–9.35	4.23–7.87	3.33–5.08	5.19–8.33	1.45–8.66	5.97–9.35	<0.05
Grass	5.59–8.67	0.00–1.03	3.27–8.45	3.85–7.19	4.03–9.12	2.38–9.12	3.10–9.12	<0.05 except Fe
Papaya	6.66–7.53	0.00–4.95	3.77–4.33	5.59–6.97	3.15–9.09	2.79–3.69	0.00–2.59	<0.05
R2	0.9997	0.9990	0.9995	0.9991	0.9994	0.9990	0.9994	

Table 4
Mean ± SD values of the physicochemical characteristics of raw and wastewater of malt factory.

Physico-chemical parameters	Water Samples				Permissible Limit		
	RW	WD	WAW	p-value	USEPA[a]	EEPA[b]	GEG/EQIER[c]
pH	8.54±0.01	6.69±0.01	6.61±0.01	< 0.001	6–9	6–9	6–9
Temp (°C)	26.57±0.06	23.17±0.06	21.63±0.06	< 0.001	37		≤30/40
TDS (ppm)	205.90±0.20	1896.00±3.00	1835.00±2.00	< 0.001	1000	-	-
EC(μs/cm)	359.90±3.56	3226.67±57.74	3160.00±23.8	< 0.001	1500	1000	
BOD (mg/L)	12.00±1.00	732.67±8.02	552.67±4.73	< 0.001	50	≤5	≤30/20
COD (mg/L)	3.67±0.29	1691.33±12.66	1277.33±6.66	< 0.001	250	-	-
Total hardness	70.00±3.00	178.67±7.70	56.67±0.58	< 0.001	300	-	-
Alkalinity-M	183.0±2.00	1197.67±4.04	331.67±2.89	< 0.001	200	-	-
CO_3	110.0±1.00	718.67±2.31	199.0±1.73	< 0.001			
HCO_3	223.67±2,52	1464.0±4.43	406.0±3.46	< 0.001			
Alkalinity-P	52.0±2.65	822.33±9.62	107.0±2.00	< 0.001			
OH	18.13±0.81	285.33±2.70	37.17±0.76	< 0.001			

Raw water (RW), wastewater at discharged point (WD), wastewater after wetland (WAW),
([a][36],
[b][14],
[c]U[36]; Lau, and Le, 2023).

under the limit of ≤ 15%. These indicated that the method has good precision and accuracy. The correlation coefficients (R^2) of the calibration curves were ≥ 0.999 (Table 2), suggesting the presence of good linearity of the calibration curve for the measured parameters.

The LOD and LOQ for each metal analysis were also determined from three samples of blank analysis in order to evaluate whether method had been validated. Then, the mean and standard deviation of the blanks were computed and the following results of wastewater, grass, and fruit samples were obtained (Table 3). As shown in Table 3, the values of IDL were less than LOD and that the all the parameters were quantified as per the values of LOQ in the same Table 3. The method employed was found to be acceptable.

3.2. Physicochemical analysis of wastewater samples

The solubility of many toxic and nutritive chemicals is affected by the pH of wastewater. In this study, the pH values of wastewater samples ranged from 6.61 to 8.54. The mean pH values found in RW, WD, and WAW were 8.54±0.01, 6.69±0.01, and 6.61±0.01, respectively (Table 4). The pH values of wastewater were within the range of 6–9 [40,43].

Temperature (°C) is one of the most important characteristics that determine the trends and tendencies of changes in wastewater quality. Increased wastewater temperature increases physiological processes in the aquatic system and the decomposition of organic pollutants that deplete the amount of dissolved oxygen. Above 32 °C, it would also be suitable for public use [7]. In our study, the temperatures of wastewater samples were in the range of 21.63–26.57 °C. The measured mean temperature values (°C) for RW, WD, and WAW were 26.57±0.06, 23.17 ±0.06, and 21.63±0.06, respectively. The measured temperature values of wastewater samples were in the permissible threshold value of 37 °C. The pattern of temperature was profiled as follows: RW > WD > WAW.

Total dissolved solids (TDS):

TDS denotes mainly the various kinds of minerals present in the wastewater in the dissolved state. In this study, the measured values of TDS ranged from 205.9 to 1896 mg/L. The values of TDS were 205.9 ±0.20, 1896±3.00, and 1835±2.00 mg/L for RW, WD, and WAW, respectively. The higher and lower values of TDS were recorded for WD (1896±3.0 mg/L) for RW (205.9± 0.2 mg/L), respectively. The recorded value of TDS for the RW sample was lower than the USEPA recommended limit of 1000 mg/L; however, TDS values were recorded above the permissible limits of 1000 mg/Lin WD and WAW. The possible reason might be due to their soluble salts in barley of malt and dust particles of the raw material. The dissolved solids in natural wastewater are mostly calcium carbonates, magnesium carbonates, sodium carbonates, potassium carbonates, iron carbonates, manganese carbonates, etc [9].

Electrical conductivity (EC):the values ranged from 359.9 to 3226.67 μs/cm for the analysed samples. The EC values in RW, WD, and WAW were 359.9±3.56 and 3226.67±57.76, 3160.0±23.8 μs/cm, respectively. The higher and lower EC values were recorded within WD and RW samples, respectively. The EC value, recorded in raw water, was found below the allowable limits of 1000 μs/cm while in WD and WAW, the values were above the permissible limits of USEPA (2003). The high values of EC might be accounted for by high amounts of dissolved salts and the dust parts of the barley.

Biological oxygen demand (BOD_5):

The **BOD_5** of wastewater samples ranged from 12.0 to 732.67 mg/L. the BOD_5 values in RW, WD and WAW were 12.00±1.0 and 732.67 ±8.02, 552.67±4.73 mg/L, respectively. The maximum and minimum values of BOD were recorded within WD and RW, respectively. The BOD found in the RW sample was lower than the maximum permissible limits, while in WD and WAW; its values were above the permissible limit [25,36]. A high level of BOD_5 is an indication of contamination and there could be low oxygen available for living organisms in the wastewater. The high BOD_5 also creates septic conditions, generating foul-smelling hydrogen sulphide, which in turn could precipitate iron and any dissolved salts, turning the wastewater black and highly toxic for aquatic life [14].

Chemical oxygen demand (COD):

The COD values were highly detected in wastewater and less detected in the raw water samples. COD was ranged from 3.67 to 1691.33 mg/L. The COD values were 3.67±0.29, 1691.33±12.66, and 1277.33±6.66 mg/L in RW, WD, and WAW, respectively. The maximum value of COD was recorded in WD and the minimum value was found in RW. The COD found in wastewater was higher than the maximum allowable limit [36]. The possible reason might be due to the presence of large amounts of biologically resistant organic substances in the wastewater of industry. The high levels of COD in the wastewater sample might indicate the toxicity of the effluents and the presence of large amounts of biologically resistant organic substances.

Total hardness is a measure of the total content of calcium (Ca^{2+}) and magnesium (Mg^{2+}) in wastewater and it is the most popular indicator of wastewater quality. The levels in raw and wastewater were ranged from 70.0 to 178.67 mg/L $CaCO_3$. The mean values were 70.00 ±3.00, 178.67±7.70, and 56.67±0.58 mg/L $CaCO_3$ in RW, WD, and WAW, respectively. The maximum value was detected for the WD sample which might be due to untreated wastewater discharged into the receiving environment. The overall values were found within the range of soft wastewater between 100 and 200 mg/L $CaCO_3$ and a permissible limit of 300 mg/L $CaCO_3$ [36]. However, the value of raw water was found within the ranges of soft wastewater below 100 mg/L $CaCO_3$.

Table 5
Mean ± SD concentration values of Metals in RW, WD, WAW.

Analyzed Metals	Conc. Water sample (mg/L)			Permissible Limit			
	RW	WD	WAW	WHO[d]	USEPA[a]	EEPA[b]	GEG/EQIER[c]
Cd	0.800±0.076	0.905±0.082	0.386±0.038	0.003	0.005	0.005	≤ 0.01
Cr	ND	0.074±0.006	ND	0.05	-	0.05	≤ 0.1
Cu	0.064±0.003	0.096±0.007	0.069±0.005	2.1	1.3	0.112	≤ 0.25
Mn	0.184±0.006	1.528±0.061	1.209±0.061	5.0	-	0.3	0.2
Fe	0.167±0.014	4.636±0.241	2.030±0.139	1.0	-	1.0	1.0
Zn	0.303±0.004	0.333±0.023	0.175±0.015	1.5	-	0.5	≤ 1.0
Pb	0.044±0.002	0.051±0.001	0.892±0.072	0.01	0.015	0.05	≤ 0.1

P-values at 95% was ($p < 0.05$) for heavy metals in all water sampling sites [33].

Based on the total hardness values of wastewater samples, the profiling order was as WD > RW > WAW.

Alkalinity:

The ionic concentration, which can neutralize the hydrogen ions of wastewater. Carbonates, bicarbonates, phosphates, nitrates, borax, silicates, etc., together with free hydroxyl ions, impart alkalinity [36].

Alkalinity-M:

The mean values of alkalinity-M recorded in RW, WD, and WAW were 183.0±2.0, 1197.67±4.04, and 331.67±2.89 mg/L $CaCO_3$, respectively. The detected values of alkalinity in WD and WAW were above the permissible limits. This might be due to the use of T-cera detergent for cleaning purposes in the factory. However, the alkalinity values of raw water were lower than the allowable limit of 200 mg/L [36]. In this study, the high overall mean values of alkalinity could be the presence of carbonate-containing compounds. The pattern could be displayed as WD > WAW > RW.

Alkalinity-P:

The overall mean values of alkalinity-P were 52.0±2.65, 822.33 ±9.62, and 107.0±2.0 mg/L $CaCO_3$ found in RW, WD, and WAW, respectively. The detected values of alkalinity in WD and WAW were above the permissible limits of 200 mg/L [36]. This might also be due to the presence of T-cera detergent for cleaning purposes. However, the alkalinity values of RW were lower than the allowable limit of 200 mg/L. In the absence of an alternate wastewater source, an acceptable alkalinity level of up to 600 mg/L for drinking wastewater could be tolerated [7]. In this study, the high overall mean values of alkalinity could be the presence of -carbonate-containing compounds. The pattern was as follows: WD > WAW > RW.

3.3. Concentration of metals in wastewater, grass, and papaya samples

3.3.1. Concentration of metals in wastewater samples

The concentration of essential metals (Cr, Cu, Mn, Fe, and Zn) and non-essential metals (Cd and Pb) were analyzed by ICP-OES. All essential and non-essential metals in raw and wastewater samples were detected (Table 5).

Cadmium (Cd):

The levels of Cd from raw water and wastewater samples were ranged from 0.386 to 0.905 mg/L. The detected concentrations of Cd in RW, WD, and WAW were 0.800±0.08, 0.91±0.08, and 0.39±0.04 mg/L, respectively. The minimum concentrations were found in WAW; the possible reason might be due to the effectiveness of the factory wetland in removing the metal. The maximum concentrations were found in WD, which might be due to accumulated Cd in the soil as the sources of heavy metals for the barley and raw water. The toxicity of Cd in wastewater is influenced by wastewater hardness. This value is much higher than the maximum allowed limit (Rezaei et. al., 2019; Awual, et. al., 2019). This indicated that, the wastewater is not safe for irrigation and domestic purposes after discharged by Cd content. The distribution of Cd in all sampling sites could be profiled as follows: WD > RW > WAW.

Chromium (Cr):

The Cr was detected in WD but not in RW and WAW. Therefore, its concentration was ranged from ND to 0.074 mg/L. The concentration (0.074±0.006 mg/L) of Cr at WD was lower than the values of the GEG 2007 and EQIER2009 recommended limit of 0.1 mg/L (Hao et. al., 2023). However, its concentration was higher than World Health Organization [41], and EEPA [14] in drinking wastewater. The possible sources of Cr may be barley or the dust particles of the barley used for malting. So in terms of Cr, the wastewater samples were safe for irrigation. Continuous exposure to high Cr levels causes lung cancer in men, liver and kidney damage in animals, and skin irritation. However, Cr supplementation lowers glucose, and lipid levels in elderly diabetics [35].

Copper (Cu):

The levels of Cu were ranged from 0.064 to 0.096 mg/L. The concentrations of Cu in RW, WD, and WAW were 0.064±0.003, 0.096 ±0.007, and 0.069±0.005 mg/L, respectively. The minimum and maximum concentrations of Cu were found in RW and WD, respectively. The maximum concentration of Cu in WD might be due to its accumulation in barley as well as raw water transferred from the soil, as it was also detected in fresh water samples. However, the levels of Cu were lower than the maximum allowed limits [14,36,41]. This indicated that in terms of Cu content, the wastewater is safe for irrigation and domestic purposes. The distribution of Cu in all samples could also be profiled as follows: WD > WAW > RW.

Manganese (Mn):

The levels of Mn from wastewater samples were ranged from 0.184 to 1.528 mg/L. The concentrations of Mn were 0.184±0.006, 1.528 ±0.061, and 1.209±0.061 mg/L from wastewater samples of RW, WD, and WAW, respectively. The minimum and maximum concentrations of Mn were found in RW and WD, respectively. Mn was highly detected within WD; this might be due to its accumulation capacity in soil that could transfer the metal to barley and raw water [30]. The concentrations of Mn in all wastewater samples were found to be lower than the health-based standard guideline given by World Health Organization [41]. The level of Mn found in RW was lower than ([14]; Hart et. al., 1956; Titchou et. al., 2021). However, the levels of Mn detected in WD and WAW were normally higher. **Mn** is an essential element for growth, reproduction, and skeletal development. The major sources of manganese are fertilizer, ores, rocks, and pesticides. Mn has not been particular toxicological issue, but its concentration in a particular spot may vary the taste and yet causes turbidity [7,30]. The distribution of Mn in wastewater samples was as follows: - WD > WAW > RW.

Iron (Fe):

The mean concentrations of Fe in RW, WD, and WAW were 0.167 ±0.014, 4.636±0.241, and 2.030±0.139 mg/L, respectively. The minimum and maximum concentrations of Fe were found in RW and WD, respectively. The maximum concentration of Fe in WD might be due to the accumulation capacity of Fe in the soil in which barley has grown. The minimum concentration of Fe was found in RW and the value was lower than the maximum permissible limits of 1.0 mg/L for drinking water and domestic purpose. This value shows that the raw water is safe for malting of barley, drinking, and other domestic purposes. The amounts of Fe in WD and WAW were much higher than the maximum allowed limit [14,41]; Hart et. al., 1956; Titchou et. al., 2021). This indicated that, in terms of Fe content, the wastewater is not safe for irrigation and domestic purposes. The distribution of Fe in all wastewater samples is as follows: WD > WAW > RW.

Zinc (Zn):

The concentration of Zn from raw and wastewater samples were ranged from 0.175 to 0.333 mg/L. The detected concentrations of Zn were 0.030±0.004, 0.333±0.023, and 0.175±0.015 mg/L in RW, WD, and WAW, respectively. The minimum and maximum concentrations of Zn were found in WAW and WD, respectively. The maximum concentration of Zn was found in WD; this might be due to the accumulation capacity of Zn in soil later transferred to barley. The levels of Zn were lower than the maximum allowed limit (Gao et. al., 2021). The distribution patterns of Zn in wastewater samples were as follows: WD > RW > WAW.

Lead (Pb):

The detected levels of Pb from raw and wastewater samples ranged from 0.044 to 0.892 mg/L. The concentrations of Pb were 0.044±0.002, 0.051±0.001, and 0.892±0.072 mg/Lin RW, WD, and WAW, respectively. The minimum and maximum concentrations of Pb were found in RW and WAW, respectively. The maximum concentrations of Pb were found in WAW, which might be due to the previous restoration or accumulation of Pb in the soil matrix of the industry wetland zone. This value is much higher than the maximum allowed limit (Casso-Hartmann et. al., 2022). This indicated that the wastewater is not safe for irrigation and domestic purposes. The distribution patterns of Pb in wastewater samples were as follows: WD > RW > WAW.

3.3.2. *Concentration of metals in grass and papaya samples*

Cadmium (Cd):

The detected levels of Cd ranged from 95.24 to 147.62 mg/kg and 37.14–54.76 mg/kg for grass and papaya samples, respectively. The concentrations of Cd in WG, CG, WP, and CP were 147.62±8.25, 95.24 ±8.25, 54.76±4.12, and 37.14±2.47 mg/kg, respectively. The concentrations of Cd found in wetland grass and papaya samples were higher than the control grass and papaya samples, the possible reason might be due to the raw materials of the factory. The minimum and maximum concentrations of Cd were found in papaya and grass samples, respectively. These might be due to the malt industry wastewater being directly discharged to the wetland area for grass than papaya. The detected concentrations of Cd were much higher than the allowable limit (Rezaei et. al., 2019; Awual et. al., 2019). The possible reason might be due to the accumulation properties of Cd within soil and food matrix.

Chromium (Cr):

The Cr was detected from wetland grass and papaya samples but not at the control point. The levels of Cr were ranged from ND to 8.82 mg/kg for grass and papaya samples. The concentrations of Cr in WG, CG, WP, and CP were 8.82±0.09, ND, 2.65±0.13, and ND mg/kg, respectively. The levels of Cr were found in wetland grass and papaya samples, while it was not detected in the control grass and papaya samples. The plausible reason might be due to the contaminated raw materials with Cr from the soil. The detected concentrations of Cr were higher than the permissible limit [14,41]. This might be accounted for by the accumulation properties of Cr within the soil and food matrix.

Copper (Cu):

The source of Cu in raw water and crops are suspected to be fertilizers and industrial and municipal wastes released to wastewater bodies. In the present study, the levels of Cu were ranged from 3.14 to 8.33 mg/kg from factory control papaya and wetland grass samples. The mean concentration of Cu with maximum (8.33±0.27) and minimum (6.45 ±0.54) mg/kgs values in wetland and control grass samples were found, respectively. It was detected as the maximum (3.62±0.14) and minimum (3.14±0.14) concentration from wetland and control papaya samples, respectively. In the overall analyzed data, Cu was detected in all grass and fruit samples. These concentrations (mg/kg) were 8.33 ±0.276, 45±0.54, 3.62±0.14, and 3.14±0.14 for the wetland grass, control grass, wetland papaya, and control papaya, respectively. All the detected concentrations of Cu were found below the permissible limits ([14,41]; Hart et. al., 1956; Titchou et. al., 2021).

Manganese (Mn):

Mn was detected in all grass and fruit samples. In our study, the levels of Mn were ranged from 2.89 to 85.46 mg/kg from factory control papaya and wetland grass samples. The concentrations (mg/kg) of Mn were 85.46±6.14, 27.66±1.06, 5.50±0.31, and 2.89±0.20 for the WG, CG, WP, and CP, respectively. In all analyzed samples, the maximum concentration of Mn was found in WG and WP samples, while the minimum was found in CG and CP samples. This might be ascribed to the directly discharged wastewater to wetland areas without pretreatment. The mean concentrations of Mn in grass and papaya samples were above the permissible limits, while the concentration of Mn from control papaya was lower than the permissible limit; however the concentrations of Mn from the rest samples were above the permissible limit [41]. The contamination of grass and papaya samples might be due to contamination of wastewater from malted barley, dust, and raw water that were discharged into their areas of growth. It is in line with the detection of Mn in raw and wastewater samples in the present study.

Iron (Fe):

The detected mean concentrations (mg/kg) of Fe in this study was 57.58±5.25, 65.15±2.62, 5.00±0.45, and 8.33±0.26 from wetland grass, control grass, wetland papaya, and control papaya samples collected from Gondar malt factory, respectively. The concentration of Fe found in wetland grass was higher than in the control grass samples. This indicated that the malt factory wastewater could be polluted with excess Fe. The concentration of Fe found in wetland papaya was lower than in control papaya, this might be due to the accumulation of Fe in the soil matrix. All the mean concentrations of Fe were below the permissible limits (Lau, and Le, 2023).

Zinc (Zn):

The detected Zn was ranged from 3.44 to 36.84 mg/kg. The mean concentrations (mg/kg) of Zn in WG, CG, WP, and CP samples were 36.84±0.88, 8.33±0.76, 3.44±0.13, and 4.53±0.13, respectively. In this study, Zn was highly detected in wetland grass samples which might be due to the untreated wastewater discharged to wetland areas of the malt factory. The minimum concentration of Zn was recorded in wetland papaya samples compared to the controlled grass and papaya samples. The levels of Zn found in all analyzed grass and papaya samples were below recommended limits (WHO/FAO, 2015).

Lead (Pb):

Pb was detected in most analyzed samples except the control papaya sample. The detected levels of Pb in grass and papaya samples were ranged from ND to 60.36 mg/kg. The maximum concentration (60.36 mg/kg) was found in wetland papaya samples, which might be caused by Pb accumulated from barley and dust (soil) during the cultivation of the crop in the presence of fertilizer and discharged directly to the wetland areas. The levels (mg/kg) of Pb from wetland and control grass, wetland, and control papaya samples were 28.02±0.87, 17.12 ±1.56, 60.36±1.56, and ND, respectively. In both matrices, Pb was highly detected from wetland samples than control samples. The mean concentrations of Pb found in all analyzed grass and papaya samples were above recommended limits (Lau, and Le, 2023). The distribution patterns of Pb were as follows; WP > WG > CG > CP.

Table 6
Mean ± SD concentration (mg/kg) values of Metals in WG, CG, WP, and CP.

Analyzed Metals	Conc. Grass sample		Conc. fruit sample		Permissible Limit			
	WG	CG	WP	CP	WHO[d]	USEPA[a]	EEPA[b]	GEG/EQIER[c]
Cd	147.62±8.25	95.24±8.25	54.76±4.12	37.14±2.47	0.2	0.005	0.005	≤ 0.01
Cr	8.82±0.09	ND	2.65±0.13	ND	2.3	-	0.05	≤ 0.1
Cu	8.33±0.27	6.45±0.54	3.62±0.14	3.14±0.14	73.3	1.3	0.112	≤ 0.25
Mn	85.46±6.14	27.66±1.06	5.50±0.31	2.89±0.20	5.0	-	0.3	0.2
Fe	57.58±5.25	65.15±2.62	5.00±0.45	8.33±0.26	425.5	-	1.0	1.0
Zn	36.84±0.88	8.33±0.76	3.44±0.13	4.53±0.13	99.4	-	0.5	≤ 1.0
Pb	28.02±0.87	17.12±1.56	60.36±1.56	ND	0.03	0.015	0.05	≤ 0.1

WG = wetland grass, CG = control grass, WP = wetland papaya & CP = control papaya.

3.4. Nutrient analysis in wastewater samples

Phosphate (PO_4^{3-}):

The levels of PO_4^{3-} ranged from 3.40 to 34.33 mg/L in wastewater samples and the overall mean phosphate concentration were 3.40±0.10, 29.33±0.58, and 34.33±1.15 mg/ L in fresh water, wastewater at discharged point, and wastewater after wetland. All recorded values of PO_4^{3-} from the wastewater sample were higher than the permissible limit [36]. This indicated that in terms of the phosphate content the raw water used for the malt factory was not safe for malting purposes. The distribution patterns of phosphate in wastewater samples were as follows: WAW > WD > RW. In our study, available phosphorus and elemental phosphorous were detected in all wastewater samples collected from Gondar malt factory.

Nitrate (NO_3^-):

The presence of NO_3^- in drinking wastewater is undesirable since it can lead to a number of health problems, including methemoglobinemia in infants, gastric cancer, goiter, birth defects, and hypertension. As a result of agricultural activities, domestic effluent, and septic tank effluent discharge, NO_3^- concentrations are generally low in ground water, but are usually increased by several anthropogenic activities [28]. In this study, the concentrations of NO_3^-in analyzed wastewater samples ranged from 0.23 to 8.27 mg/L. The mean determined values of NO_3^- from raw water, wastewater at discharged point, and wastewater after the wetland were 0.23 ± 0.03, 8.27 ± 0.03, and 2.03 ± 0.06 mg/L, respectively. The maximum values of NO_3^- were found in wastewater at the discharged point than others; this might be due to untreated wastewater of factory discharged to our environment. However, the levels of NO_3^-in raw and wastewater samples were below the maximum permissible limit [14,41]. The distribution patterns of NO_3^- in wastewater samples were as follows: WD > WAW > RW.

Sulphate (SO_4^{2-}):

Natural wastewater contains SO_4^{2-} ions and most of these ions are also soluble in wastewater. Many SO_4^{2-} ions are produced by the oxidation process of their ores. They are also present in industrial wastes. It is another important chemical parameter for wastewater quality and influences the taste and odor of drinking wastewater. Wastewater containing higher levels of SO_4^{2-}often caused noticeable taste that would have laxative effect for unfamiliarly drinking sulphate rich wastewater. SO_4^{2-} in the aquifer system is derived primarily from weathering of two major forms of SO_4^{2-}containing rocks, namely pyrite, and gypsum, in addition to the inputs from anthropogenic activities. The mean values of sulphate in our study were ranged from26.2to 126.0 mg/L. The overall levels of SO_4^{2-}were 26.2 ± 0.42, 126.0 ± 2.0, and 73.18 ± 17.0 mg/L from raw water, wastewater at discharged point, and wastewater after the wetland, respectively. In terms of total and elemental sulphate; they were detected in all wastewater samples. However, these values were lower than the maximum recommended limit (Chen, 2023; [22]). So in the case of sulphate all wastewater samples were safe for irrigation and domestic purpose. The distribution patterns of sulphate in wastewater samples were as follows: WD > WAW > RW.

Sulphite (SO_3^{2-}):

The levels of SO_3^{2-}, in this study, were ranged from4.52 to 6.63 mg/L. The mean values of sulphite were 4.52 ± 0.16, 6.63 ± 0.35, and 5.66 ± 0.50 mg/L from fresh wastewater, wastewater at discharged point, and wastewater after the wetland, respectively. The recorded values of SO_3^{2-} in all wastewater samples collected from Gondar malt factory were lower than sulphate found in all analyzed wastewater samples, this is because sulphate was stable than SO_3^{2-}. While the cause of oxidation-reduction reaction occurred in the wastewater system sulphite might be changed to sulphate compounds. The distribution patterns were as follows: WD > WAW > RW.

3.5. Pearson correlation analysis

Pearson's correlation was used to identify the factors contributing to the spread and transport of pollutants in wastewater bodies, wetland grasses, and papaya. In addition, it identified the interrelationships between the variables affecting wastewater quality to identify the most likely common sources. The values −1 and +1 represent strong, positive connections. There may be a common source or similar behavior between parameters if there is a significant positive correlation between

Table 7
Nutrients Mean ± SD value in fresh water, discharge water (mg/L).

Nutrients		Samples				Permissible Limit		
		RW	WD	WAW	P-value	WHO[d]	USEPA[b]	EEPA[c]
Phosphate	PO_4	3.40±0.10	29.33±0.58	34.33±1.15	< 0.05	-	0.4	-
	P	1.08±0.03	9.34±0.18	10.94±0.37	< 0.05	-	-	-
Nitrate	NO_3	0.23±0.03	8.27±0.03	2.03±0.06	< 0.05	50	50	50
	N	0.06±0.01	1.86±0.01	0.46±0.01	< 0.05	-	10	-
Sulphate	SO_4	26.20±0.42	126.00±2	73.18±1.17	< 0.05	250	-	200
	S	8.59±0.14	41.10±1.01	24.32±0.92	< 0.05	-	-	-
Sulphite	SO_3	4.52±0.16	6.63±0.35	5.66±0.50	< 0.05	-	-	-

P-value was (p < 0.05) for nutrients in all water sampling sites.
Raw water (FW), wastewater at discharged point (WD), wastewater after wetland (WAW).
[b][36],
[c][14],
[d](WHO, 2017).

Table 8
Pearson correlation of between phytochemical properties and nutrients of water samples.

Parameters	pH	Temp	TDS	EC	BOD	COD	TH	Alk-M	CO_3^{2-}	HCO_3	Alk-P	OH	PO_4^{3-}	P	NO_3^-	N	SO_4^{2-}	S	SO_3^{2-}
pH	1																		
Temp	0.96*	1																	
TDS	-0.99*	-0.94	1																
EC	-0.99*	-0.94	1.00**	1															
BOD	-0.96*	-0.85	0.978*	0.975*	1														
COD	-0.96*	-0.85	0.979*	0.977*	1.00**	1													
TH	-0.37	-0.11	0.440	0.430	0.618	0.614	1												
Alk-M	-0.58	-0.34	0.638	0.629	0.785	0.782	0.972*	1											
CO_3^{2-}	-0.58	-0.34	0.637	0.629	0.784	0.781	0.972*	1.00**	1										
HCO_3	-0.58	-0.34	0.638	0.629	0.785	0.782	0.972*	1.00**	1.00**	1									
Alk-P	-0.52	-0.27	0.581	0.571	0.738	0.735	0.987*	0.997*	0.997*	0.997*	1								
OH	-0.52	-0.27	0.580	0.571	0.738	0.735	0.987*	0.997*	0.997*	0.997*	1.00**	1							
PO_4^{3-}	-0.99*	-0.98*	0.983*	0.985*	0.924	0.925	0.269	0.487	0.487	0.487	0.423	0.42	1						
P	-0.99*	-0.99*	0.983*	0.985*	0.923	0.925	0.269	0.486	0.486	0.487	0.422	0.42	1.00**	1					
NO_3^-	-0.64	-0.42	0.696	0.688	0.831	0.828	0.951*	0.997*	0.997*	0.997*	0.989*	0.98*	0.554	0.55	1				
N	-0.64	-0.41	0.695	0.687	0.830	0.827	0.951*	0.997*	0.997*	0.997*	0.989*	0.98*	0.553	0.55	1.00**	1			
SO_4^{2-}	-0.82	-0.65	0.865	0.859	0.951	0.949	0.831	0.938	0.938	0.938	0.911	0.91	0.759	0.75	0.96*	0.962*	1		
S	-0.83	-0.66	0.873	0.867	0.955*	0.954	0.823	0.933	0.933	0.933	0.904	0.90	0.769	0.76	0.958*	0.958*	1.00**	1	
SO3	-0.87	-0.70	0.902	0.897	0.973*	0.971*	0.784	0.907	0.907	0.907	0.875	0.87	0.809	0.81	0.938	0.930	0.997*	0.99*	1

*Correlation is significant at the 0.05 level (2-tailed).
**Correlation is significant at the 0.01 level (2-tailed). Alk-M = Alkalinity-M, Alk-P = Alkalinity-P.

them (Akoto et al., 2021).

The results of Pearson correlation analysis between the physicochemical properties and nutrients of wastewater samples were presented in Table 8. There is a significant strong positive correlation at 0.01 level between TDS and EC; BOD and COD; alkalinity-M with CO_3^{2-} and HCO_3; alkalinity-P and OH^-; PO_4^{3-} and P; NO_3^- and N; and SO_4^{2-} and S. Furthermore, the results of Pearson correlation revealed that significant positive correlations the physicochemical properties and nutrients at of wastewater at 0.05 level (Table 8) between BOD-TDS and EC; COD-TDS and EC; alkalinity-M-TH; CO_3^{2-}-TH; HCO_3-TH; alkalinity-P-TH, alkalinity-M, CO_3^{2-}, and HCO_3; OH^--TH, alkalinity-M, CO_3^{2-}, and HCO_3; PO_4^{3-}-TDS and EC; P-TDS and EC; NO_3^- and N- TH, alkalinity-M, alkalinity-P, CO_3^{2-}, $OH^-$and HCO_3; SO_4^{2-}-P and NO_3^-; S-BOD, P, and NO_3^-; and SO_3^{2-}-BOD, COD, N, and SO_4^{2-} (Tables 6, 7 and 9).

4. Conclusion

In this study, the levels of heavy metals (Cd, Cr, Cu, Mn, Fe, Zn, and Pb), nutrient loads (PO_4^{3-}, NO_3^-, SO_4^{2-}, SO_3^{2-}) and physico-chemical parameters (pH, Temp, EC, TDS, BOD, COD, Alkalinity M & P, and total hardness) were analysed by using ICP-OES and palin test photometer based on EPA Guideline, respectively, for three matrix (wastewater, grass, and papaya) collected from Gondar malt factory. The wet digestion method was also employed for matrix removal before heavy metal analysis.

The physicochemical characteristics of raw water were found within the ranges of permissible limits stated by WHO, USEPA, EEPA, GEG, and EQIER, however, the levels of most parameter in wastewater samples were found above the permissible limits except pH and Temperature. The investigated nutrients in the wastewater sample were found under the allowable limits except for phosphate. The influx of phosphorus/nutrient loads into the wetland was found to elevate its accumulation in the papaya fruit with time and causes calcium depletion from the bones of the consumers particularly children. Thus, the environmental and food safety authority should force the factory either to ban cultivating papaya on the wastewater receiving wetland or advise to treat the wastes before discharging. The alkalinity of raw water samples was also found below the accepted limit but detected in wastewater samples exceeding the limit set by USEPA.

All heavy metals analyzed in wastewater, grass, and papaya samples were detected, except Cr in (raw water, wastewater, control wetland grass, and papaya) and Pb in papaya samples taken at the control point. The detected concentration of heavy metals in raw water was lower than the allowable limit set by WHO, USEPA & EEPA except for Cd while most analyzed metals in wastewater were detected below the limit. However, the levels of the Cd and Fe were found above the permissible limits which might pollute the wetland environment and pose health impacts to consumers of fruits grown on the wastewater receiving wetland. In wetland grass and papaya samples, most of the studied metals were detected below the permissible limit except Cd, Cr, Mn, and Pb. The levels of Cd, Cr, Mn, and Pb were found unsafe for papaya consumers exceeding the allowable limit set by WHO, USEPA, EEPA & GEG/EQIER, and their health impact should be discerned. The bioaccumulation of the trace metals may pose human health risks to the long term papaya consumers of occupational workers. The environmental pollution control and food safety authority bodies of Ethiopia should enforce the wise discharges of the wastewater after treatments from the factory. (Fig. 1).

CRediT authorship contribution statement

Tesfamariam Gezahegn: Formal analysis. **Meseret Dereje**: Writing – review & editing; Visualization; Methodology. **Molla Tefera**: Writing – original draft; Methodology; Data curation. **Tamene Beshaw**: Writing – review & editing; Writing – original draft; Methodology. **Mengstu Mulu**: Writing – review & editing; Methodology; Data curation;

Table 9
Pearson correlation matrix of heavy metals in water, grass, and papaya samples.

	Metals	Cd	Cr	Cu	Mn	Fe	Zn	Pb
Water Sample	Cd	1						
	Cr	0.656	1					
	Cu	0.540	0.989*	1				
	Mn	-0.102	0.684	0.782	1			
	Fe	0.284	0.910	0.960*	0.925	1		
	Zn	1.000**	0.647	0.529	-0.114	0.272	1	
	Pb	-0.980	-0.494	-0.362	0.297	-0.088	-0.983*	1
	Metals	Cd	Cr	Cu	Mn	Fe	Zn	Pb
Grass Sample	Cd	1						
	Cr	0.866	1					
	Cu	0.863	0.494	1				
	Mn	0.932	0.989*	0.620	1			
	Fe	0.484	-0.019	0.860	0.132	1		
	Zn	0.724	0.972*	0.276	0.925	-0.253	1	
	Pb	0.975	0.956*	0.728	0.989*	0.275	0.860	1
	Metals	Cd	Cr	Cu	Mn	Fe	Zn	Pb
Papaya Sample	Cd	1						
	Cr	0.456	1					
	Cu	0.998*	0.505	1				
	Mn	0.997*	0.386	0.991*	1			
	Fe	-0.833	-0.872	-0.863	-0.788	1		
	Zn	-0.851	-0.855	-0.879	-0.808	0.999**	1	
	Pb	0.997*	0.380	0.990*	1.000**	-0.784	-0.804	1

*. Correlation is significant at the 0.05 level (2-tailed).
**. Correlation is significant at the 0.01 level (2-tailed).

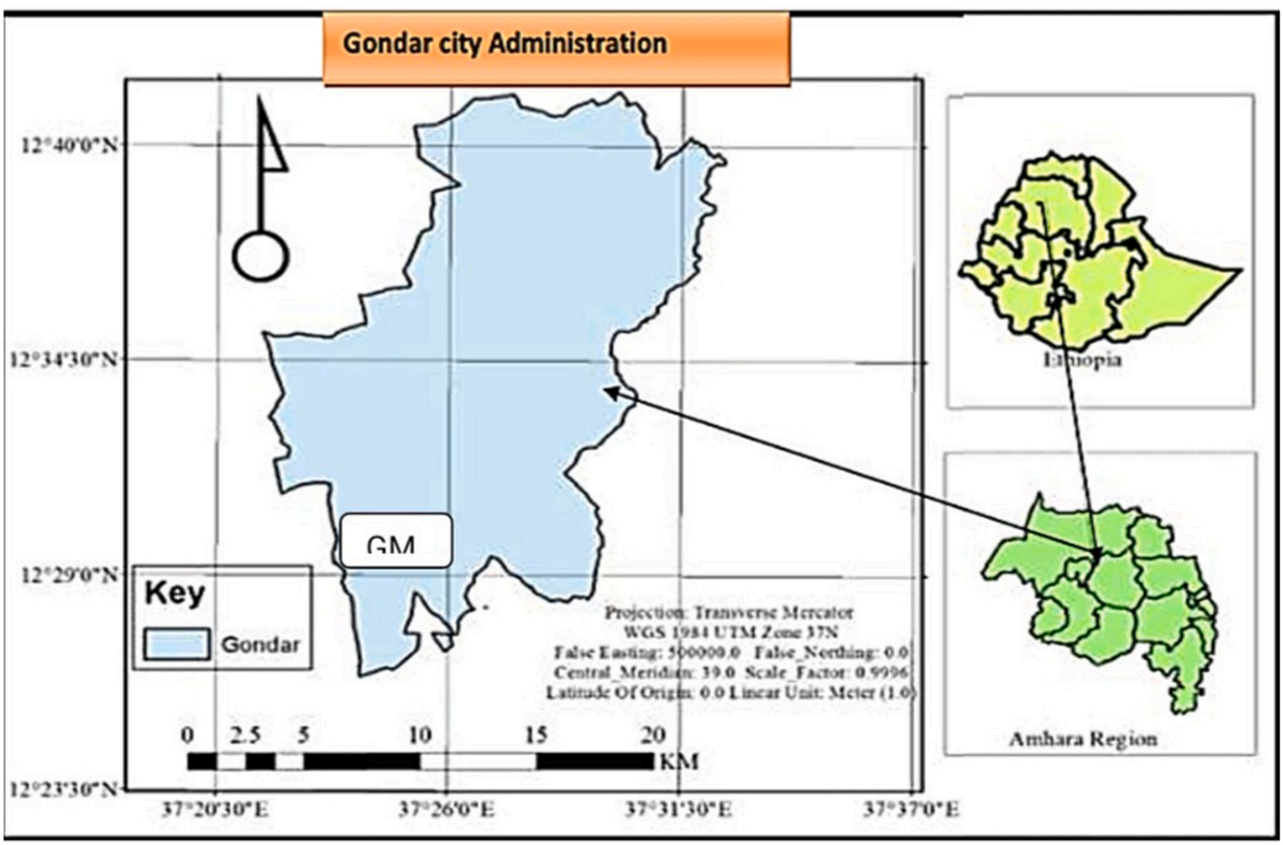

Fig. 1. Map of Gondar city malt factor.

Conceptualization. **Mulugeta Legesse**: Resources; Data curation; Conceptualization. **Addis Kokeb**: Writing – review & editing; Resources; Methodology. **Tsegu Lijalem**: Writing – review & editing; Software; Resources. **Tarekegn Fentie**: Writing – original draft; Data curation; Conceptualization. **Ayal Adugna**: Writing – review & editing; Data curation. **Atnafu Guadie**: Data curation; Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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