Biochar and manure influences tomato fruit yield, heavy metal accumulation and concentration of soil nutrients under wastewater irrigation in arid climatic conditions

Hameeda¹, Shamim Gul¹*, Gul Bano², Misbah Manzoor¹,³, Tasawar Ali Chandio⁴ and Adnan A. Awan⁵

Abstract: Balochistan produces more than 40% of the total tomato production of Pakistan. The climate of this province is mostly arid, and agriculture around urban areas commonly depends on wastewater irrigation. This study evaluated under groundwater and wastewater irrigation the influence of wood-derived biochar, cow manure and their co-amendment (as 1:1 biochar:manure ratio) at 0.5 kg m⁻² (or 5 t ha⁻¹) and 1 kg m⁻² (or 10 t ha⁻¹) rate on fruit yield production of tomato, concentration of heavy metals (lead (Pb), copper (Cu), zinc (Zn), nickel (Ni) and chromium (Cr)), nutrient use efficiency (NUE) of heavy metals (calculated as fruit yield/concentration of a given heavy metal in fruits) and the pH, concentration of mineral nitrogen (N) and soluble inorganic phosphorus (P) of tomato-grown soil. As compared to groundwater irrigation, the biomass and yield production was higher under wastewater irrigation. Organic amendments significantly
improved yield production and tended to increase soil pH than control under both irrigation treatments. Wood-derived biochar applied at 1 kg m\(^{-2}\) caused the highest yield under both irrigation treatments. Organic amendments tended to reduce the concentration of Pb, Cu and Cr and increased the NUE of tomato fruits, indicating that fruits require less acquisition of heavy metals per unit yield production. Organic amendments increased the concentration of soluble inorganic P under wastewater irrigation. Our findings suggest that amendment of biochar, manure and their mixture promoted tomato fruit yield under both irrigation treatments, increased NUE of fruits for heavy metals and increased the concentration of soluble P under wastewater irrigation.

**Subjects:** Agriculture & Environmental Sciences; Botany; Soil Sciences

**Keywords:** wastewater irrigation; biochar-manure mixture; tomato fruit yield; soil soluble inorganic phosphorus; soil pH

1. **Introduction**

Tomato (*Solanum lycopersicum* L.) is one of the important food crop worldwide, and due to its availability both as a fresh and a processed fruit, it is also commercially important all over the world (Giuliani, Nardella, Gagliardi, & Gatta, 2017; Shah et al., 2015). In Pakistan, tomato was grown on 52.3 thousand hectares area during 2011, and during the last decade, its production was 9.5–10.5 tons per hectare (Anonymous, 2011). Currently, Pakistan exports tomatoes to Sri Lanka, Afghanistan, U.A.E., Iran, Saudi Arabia and India (Shah et al., 2015). This crop is cultivated in almost all provinces of the country (Imran et al., 2012), and the major contribution in its production is from the Balochistan province, which accounts for >40% of the total production in Pakistan (Government of Pakistan [GOP], 2015). The climate of this province is semi-arid to arid, and wastewater irrigation of agricultural lands around urban areas is a common practice due to water limitation and farmers irrigate their lands mostly with wastewater. Furthermore, wastewater irrigation is also an inexpensive alternative to inorganic fertilizer in urban agriculture in Balochistan, which minimizes the need for manure or inorganic fertilizer.

In developing countries, especially arid and semi-arid regions, wastewater irrigation of agricultural lands is a common practice (Elgallal, Fletcher, & Evans, 2016; Libutti et al., 2018). It reduces the need of freshwater irrigation and is used as an alternative to inorganic fertilizer (Gatta et al., 2016; Khan, Malik, & Muhammad, 2013; Murtaza et al., 2010). Wastewater irrigation not only save the fresh water for human consumption, it also prevents the loss of wastewater and its mixing with waterbodies, which affects aquatic life and human health (due to pathogens and access nutrients such as nitrate). However, wastewater irrigation results in the high accumulation of heavy metals in the edible parts of vegetables (Haider et al., 2018; Tahir et al., 2018).

The quality of soil and crop growth performance under wastewater irrigation can be improved if the soil is amended with organic wastes such as manure, compost, biochars or their mixture (Gul & Whalen, 2016; Gul, Winans, Leila, & Whalen, 2014; Murtaza et al., 2010). Biochar is a highly porous black material produced from pyrolysis of biomass under oxygen-deficient condition (Brewer & Brown, 2012). Besides playing role in soil carbon sequestration, biochar serves as a soil conditioner. It increases soil pH (as in general it has an alkaline pH); promotes soil aggregation, air and water infiltration; enhances water-holding capacity and serves as a slow-release fertilizer because it captures nutrients and prevents their leaching from soil (Brewer & Brown, 2012; Cornelissen et al., 2013; GOP, 2015; Gul and Wheln, 2016; Haider et al., 2018; Kammann et al., 2015; Lehman, 2007). Therefore, amendment of biochar in agricultural lands generally promotes crop yield. Biochar properties vary with respect to its production temperature (e.g. slow versus fast pyrolysis or gasification or hydrothermal carbonization and high versus low production temperature under slow pyrolysis conditions) and source of production. For instance, biochar produced from manure
has many times higher concentration of nutrients than the biochar produced from wood (Gul, Whalen, Thomas, Sachdeva, & Deng, 2015). Therefore, being generally low in nutrients, if wood-derived biochar is co-applied with organic (e.g. manure, compost or wastewater) or inorganic fertilizer in the soil, it brings more positive results compared to when it is applied alone (Gul & Whalen, 2016; Gul et al., 2015).

Nitrogen (N) and phosphorus (P) are major nutrients required for the growth and metabolism of living organisms and are the limiting factors for crop production around the world. Besides that, inorganic fertilizers are getting expensive with time due to sudden hike in the prices of fossil fuel and diminishing reserve of rock phosphate, which is the source of inorganic P production (Ziadi, Whalen, Messiga, & Morel, 2014). Amendment of biochar in soil generally increases the concentration of these two nutrients via (1) adsorption (thus help prevent their loss), (2) mineralization of organic N and P via increasing microbial activities and (3) promoting root growth, which in return causes P solubilization through organic acid production by roots and rhizosphere microorganisms (Gul & Whalen, 2016; Gul et al., 2015).

The information about the influence of amendment of biochar, manure and their mixture on the yield of tomato irrigated with groundwater or wastewater under arid climatic conditions, as well as their influence on the concentration of mineral N and soluble inorganic P in soil has not been well established. The main objectives of this study are to assess the influence of biochar, cow manure and their mixture on (1) biomass and yield production; (2) concentration of Pb, Cu, Zn, Ni and Cr in tomato fruits and the NUE for these metals of tomato fruits and (3) the concentration of mineral nitrogen and soluble phosphorus in soil cultivated with tomato under groundwater and wastewater irrigation. Our hypotheses are as follows: amendment of biochar manure and their mixture improves (1) biomass and yield production of tomato, (2) enhances the NUE of fruits for heavy metals and (3) increases the concentration of mineral N and soluble mineral P in soil.

2. Materials and methods

2.1. Study site

This study was conducted in a private farm in Satellite Town, Quetta city (30°10′52″N 67°01′59″E) in April 2017. The experimental land was not cultivated before. The climate of Quetta city is arid and is of Mediterranean type (Gul, Ahmad, Achakzai, & Islam, 2007). This region receives <250 mm precipitation per annum (Gul et al., 2007) and winter receives snowfall, in 2017, total precipitation was 164.5 mm, mean annual minimum night temperature was 16.6 and mean annual maximum day temperature was 23.9 (data source: World Weather Online https://www.worldweatheronline.com/). Soil was sandy loam (sand 57.5%, silt 32.5%, clay 10%) with organic matter 5.5 g kg⁻¹ soil and total nitrogen 0.2 g kg⁻¹ soil.

2.2. Biochar, manure and wastewater

Slow-pyrolysis biochar made from wood was purchased from local timber market. Since the biochar was produced by burning wood in kilns under oxygen-deficient conditions, such biochar is slow pyrolysis with a production temperature between 350°C and 500°C (Deal, Brewer, Brown, & Okure, 2012; Mia et al., 2015; Spokas et al., 2011). Manure was collected from a dairy farm in Quetta city and air-dried prior to amendment in soil or mixing with biochar. The municipal wastewater of the colony was used for irrigation purpose. The properties of biochar, manure, groundwater and wastewater are provided in Table 1. The data of Cu, Zn, Ni and Cr in biochar, manure and water samples used in this study are reported in Tahir et al. (2018) and provided in Ghori et al. (in preparation) and are presented in Table 1.

2.3. Experimental design

Twenty-one 1 x 1 m plots were established along two transect lines for groundwater irrigation and the same number and size of plots were established for wastewater irrigation. The plots of groundwater irrigation treatment were at the distance of 1 m from the plots of wastewater irrigation treatment. The treatments were (1) control, 2) wood-derived biochar amended at the
rate of 0.5 kg m$^{-2}$ soil (abbreviated as B 0.5), *3) wood-derived biochar amended at the rate of 1 kg m$^{-2}$ in soil (abbreviated as B 1), (4) air-dried cow manure amended at 0.5 kg m$^{-2}$ rate in soil (abbreviated as M 0.5), 5) air-dried cow manure amended at 1 kg m$^{-2}$ rate in soil (abbreviated as M 1), (6) mixture of cow manure and biochar at 1:1 ratio amended at the rate of 0.5 kg m$^{-2}$ soil (abbreviated as BM 0.5) and (7) mixture of cow manure and biochar at 1:1 ratio amended at the rate of 1 kg m$^{-2}$ soil (abbreviated as BM 1). All treatments had three replications and were assigned randomly in plots by using a random number table. The total number of plots were 42. The amendment rates as 0.5 and 1 kg m$^{-2}$ were selected because these amendment rates are (1) frequently reported to have a positive influence on crop yield (Gul & Whalen, 2016) and (2) more affordable for local farmers than higher application rates. Biochar, manure and biochar–manure mixture was surface-applied followed by shallow mixing the mixture in soil up to 3–5 cm depth because the density of lateral roots is highest at 0–5 cm along the main root and also to prevent soil disturbance to the greater depth. Inorganic fertilizers were not applied to soil.

2.4. Tomato growth and field irrigation
The seedlings of locally grown tomato variety were purchased from local market of Quetta city. Five tomato seedlings were planted per plot in the second week of April. After two weeks of growth, seedlings were thinned to three per plot for the feasible collection of tomato fruits and to allow plants to grow with less disturbance during fruit collection. During first two weeks of growth, the plots of wastewater irrigation treatments received groundwater and wastewater at alternate days (to avoid mortality as was observed with continuous wastewater irrigation), thereafter wastewater was applied at alternate days for the rest of experiment. Both groundwater and wastewater irrigation were rendered at the same time. The water was applied to the field to gravitational water content level.

2.5. Assessment of plant growth performance
Fruits were collected when they ripened from early June to late September and air-dried (moisture contents of air-dried plant tissues are less than 2% (personal observation) due to very low humidity, e.g. 0% most of the time in summer and autumn); fruits of a given plot were pooled and weighed. After last fruit harvest, plants were removed with roots from each plot, roots were washed and separated from aboveground plant biomass (stover), plant biomass was air-dried and weight of the pooled sample of stover biomass and root biomass of a given plot was recorded.

2.6. Assessment of heavy metals in tomato fruits, manure, biochar and water samples
Plant tissues, biochar and manure (1g of each sample) were burned to ash at 500°C, and the ash was dissolved in 0.302 M HCl (diluted from 37% HCl, calculated from [link to https://www.sig-maaldrich]).

| Table 1. Electrical conductivity (EC), pH, organic matter, phosphorus (P), lead (Pb), copper (Cu), zinc (Zn), nickel (Ni) and chromium (Cr) |
|-----------------|-----------------|-----------------|-----------------|-----------------|
|                | Biochar         | Cow manure      | Groundwater     | Wastewater      |
| EC (µS cm$^{-1}$) | 2.38            | nd              | 732 (µS cm$^{-1}$) | 1720 (µS cm$^{-1}$) |
| pH              | 8.2             | nd              | nd              | nd              |
| Organic matter (%) | 71 (%)         | 35 (%)         | nd              | nd              |
| P (mg g$^{-1}$)   | 3.46            | 1.47            | nd              | nd              |
| Pb (mg g$^{-1}$)  | nd              | 2.54            | 0.05 (ppm)     | 0.05 (ppm)     |
| Cu (mg g$^{-1}$)  | nd              | nd              | nd              | nd              |
| Zn (mg g$^{-1}$)  | 0.09            | 0.32            | 0.73 (ppm)     | 4.88 (ppm)     |
| Ni (mg g$^{-1}$)  | 0.006           | 0.039           | 0.48 (ppm)     | 0.33 (ppm)     |
| Cr (mg g$^{-1}$)  | 0.02            | 0.02            | nd              | 0.13 (ppm)     |

*Data from Tahir et al. (2018) and Ghori et al. (in preparation).
*Concentration below the detectable limit by atomic absorption spectrophotometer.
nd, no data.
com/chemistry/stockroom-reagents/learning-center/technical-library/molarity-calculator.html) (Rechcigl & Payne, 1989). The samples of wastewater and groundwater were filtered using Whatman filter paper grade 42 (Estefan, Sommer, & Ryan, 2013). The concentrations of heavy metals in samples of plant tissues, biochar, manure and water were measured using Atomic Absorption Spectrophotometer (AA-7000 Shimadzu) (Haider et al., 2018; Tahir et al., 2018). Due to limited funding, for fruit tissues, the pool of three samples from only wastewater irrigation treatment were analysed. The NUE of tomato fruits for heavy metals was measured following the formula of Baligar, Fageria, and He (2001);

\[
\text{NUE} = \frac{\text{Tomato fruit yield}}{\text{Concentration of a given nutrient tomato fruit}}
\]

2.7. Assessment of pH, mineral nitrogen and soluble phosphorus and in soil

After harvest of tomato plants, soil samples from 0 to 5 cm depth were collected from the centre of each plot by using 10 cm diameter and 5 cm height soil corer as described in Gul et al. (2007). The 0–5 cm depth for soil collection was considered because the soil at this depth has higher concentration of nutrients, root biomass and microbial activities than deeper soil layer (Gul et al., 2016; Islam et al., 2018). Soil samples were air-dried, crushed with hands and passed through 2 mm mesh sieve to remove pebbles and residues (leaf litter, stems and roots). Soil samples were extracted with 2 M KCl solution. Soil pH was determined by mixing soil in distilled water by 1:2 w/v ratio as described in Estephan et al. (2013). Mineral N as nitrate (NO$_3^-$) and ammonium (NH$_4^+$) were assessed following the protocol of Sims, Ellsworth, & Mulvaney (1995), and soluble phosphorus (P) was assessed by the method of D’Angelo, Crutchfield, & Vendivere (2001) as described in Qasim et al. (2017).

2.8. Statistical analysis

Prior to analysis of variance (ANOVA), data were subjected to normal distribution assessment by using D’Agostino-Pearson $K^2$ test. The data of stover biomass, root biomass, fruit yield, soil pH mineral nitrogen and soluble mineral phosphorus were subjected to three-way ANOVA to assess the differences between (1) irrigation treatments (factor 1), (2) biochar and manure amendments (factor 2) and (3) the application rate of biochar and manure amendments (factor 3). The differences between treatment means were assessed by least significance difference test. All the data were analysed with CoStat software (version 6.311) and Microsoft excel.

3. Results

3.1. Plant growth performance and concentration of heavy metals in tomato fruits

Plant growth performance was higher under wastewater than groundwater irrigation ($P < 0.05$; Figure 1; Table 2). Organic amendments significantly increased stover biomass, root biomass and fruit yield of tomato under both irrigation treatments ($P < 0.05$; Figure 1). The interaction between organic amendments and application rate was significant for all plant growth performance parameters ($P < 0.05$; Table 2). The interaction between irrigation treatment × organic amendment and between irrigation treatment and application rate of organic amendment was not significant (Table 2). Likewise, the interaction between irrigation treatment × organic amendment × application rate was not significant except for root biomass (Table 2). The highest stover, root biomass and fruit yield were observed for biochar amendment at 1 kg m$^{-2}$ (Figure 1).

Amendment of biochar, manure and their mixture tended to reduce the concentration of heavy metals in tomato fruits and increased nutrient use efficiency (NUE) for heavy metals (Table 3). Soil gets contaminated of heavy metals through wastewater and manure amendment as they contain heavy metals in high concentrations (Murtaza et al., 2010) (Table 1).
Figure 1. Stover biomass, root biomass and fruit yield (dry mass) of tomato under groundwater and wastewater irrigation (mean ± SD). Bars with different letters represent a significant difference between treatments under given irrigation treatment (P < 0.05). Bars with * indicate significant differences between groundwater and wastewater irrigation for a given organic amendment treatment (P < 0.05). B: biochar, M: manure, BM: biochar–manure mixture, 0.5: amendment at 0.5 kg m$^{-2}$, 1: amendment at 1 kg m$^{-2}$.
### Table 2. Three-way ANOVA results for F- and P-values

|                              | F     | P       |
|------------------------------|-------|---------|
| **Aboveground plant biomass**|       |         |
| Irrigation treatment         | 78.25 | 0.0000  |
| Organic amendment (biochar, manure and mixture of biochar and manure) | 122.41 | 0.0000  |
| Application rate             | 81.65 | 0.0000  |
| Irrigation treatment × organic amendment | 0.79  | 0.5065  |
| Irrigation treatment × application rate | 0.036 | 0.8508  |
| Organic amendment × application rate | 184.47 | 0.0000  |
| Irrigation treatment × organic amendment × application rate | 2.947 | 0.0689  |
| **Root biomass**             |       |         |
| Irrigation treatment         | 143.53| 0.0000  |
| Organic amendment            | 77.78 | 0.0000  |
| Application rate             | 10.42 | 0.0032  |
| Irrigation treatment × organic amendment | 2.26  | 0.1028  |
| Irrigation treatment × application rate | 7.51  | 0.0105  |
| Organic amendment × application rate | 18.83 | 0.0000  |
| Irrigation treatment × organic amendment × application rate | 17.33 | 0.0000  |
| **Fruit yield (g dry weight)**|       |         |
| Irrigation treatment         | 41.85 | 0.0000  |
| Organic amendment            | 51.81 | 0.0000  |
| Application rate             | 11.06 | 0.0025  |
| Irrigation treatment × organic amendment | 2.64  | 0.0689  |
| Irrigation treatment × application rate | 1.22  | 0.2779  |
| Organic amendment × application rate | 14.63 | 0.0000  |
| Irrigation treatment × organic amendment × application rate | 2.91  | 0.0708  |
| **Soil pH**                  |       |         |
| Irrigation treatment         | 71.11 | 0.0000  |
| Organic amendment            | 21.46 | 0.0000  |
| Application rate             | 43.20 | 0.0000  |
| Irrigation treatment × organic amendment | 30.70 | 0.0000  |
| Irrigation treatment × application rate | 0.25  | 0.6207  |
| Organic amendment × application rate | 8.36  | 0.0041  |
| Irrigation treatment × organic amendment × application rate | 11.63 | 0.0002  |
| **Mineral nitrogen of soil** |       |         |
| Irrigation treatment         | 0.48  | 0.4930  |
| Organic amendment            | 16.82 | 0.0000  |
| Application rate             | 25.81 | 0.0000  |
| Irrigation treatment × organic amendment | 0.303 | 0.8224  |
| Irrigation treatment × application rate | 0.93  | 0.5132  |
| Organic amendment × application rate | 23.37 | 0.0000  |

(Continued)
3.2. Soil pH, mineral N and soluble inorganic P

Soil pH was higher for wastewater than groundwater irrigation for control and biochar-amended treatments while manure amendment at 0.5 kg m\(^{-2}\) rate significantly increased pH under groundwater than wastewater irrigation (\(P < 0.05\); Table 4). Amendment of biochar significantly increased soil pH under both irrigation treatments (\(P < 0.05\); Table 4). The interaction between organic amendment \(\times\) application rate was significant (\(P < 0.05\); Table 2) and showed positive relation with soil pH (e.g. by increasing application rate, soil pH also increased). The interaction between irrigation treatment \(\times\) organic amendment \(\times\) application rate was also significant (Table 2).

There was no difference in the concentration of mineral N in soil between irrigation treatments (Table 4). Except for amendment of manure at 0.5 kg m\(^{-2}\) application rate, all other organic amendment treatments did not cause a significant increase in the concentration of mineral N in soil under both irrigation treatments. The interaction between organic amendment \(\times\) application rate was significant (\(P < 0.05\); Table 2).

The concentration of soluble inorganic P was also higher in soil amended with manure at 0.5 kg m\(^{-2}\) rate under groundwater irrigation. Under wastewater irrigation, all amendments increased significantly the concentration of soluble inorganic P (Table 4). All the interactions, i.e. irrigation treatment \(\times\) organic amendment, irrigation treatment \(\times\) application rate of organic amendment, organic amendment \(\times\) application rate of organic amendment and irrigation treatment \(\times\) organic amendment \(\times\) application rate of organic amendment, were significant (Table 2).

4. Discussion

4.1. Plant growth performance and concentration of heavy metals in tomato fruits

The experimental land of this study was not cultivated before. One year wastewater irrigation showed an improved tomato growth performance in almost all treatments than groundwater irrigation. Our findings show that wastewater has the potential to enhance tomato yield in this arid region as the yield and biomass production of wastewater control treatment were approximately two-fold higher than groundwater control treatment. Moreover, a further significant increase in biomass production and fruit yield was observed when biochar, manure or their mixture as 1:1 ratio were added to soil under wastewater irrigation. Our findings are consistent with previously published reports that wastewater irrigation in arid environment improves crop yield when the soil is amended with biochar, manure or their mixture (Haider et al., 2018).
### Table 3. Concentration (µg g⁻¹) and NUE (calculated as average yield/concentration of a given heavy metal) of Pb, Cu, Zn, Ni and Cr in tomato fruits irrigated with wastewater (n = 1, pool of three samples)

| Treatment | Pb  | NUE for Pb | Cu  | NUE for Cu | Zn  | NUE for Zn | Ni  | NUE for Ni | Cr  | NUE for Cr |
|-----------|-----|------------|-----|------------|-----|------------|-----|------------|-----|------------|
| Control   | 3.89| 23.6       | 10.3| 8.89       | 28.27| 3.25       | -   | nd         | 0.79| 116.3      |
| B 0.5     | 3.19| 66.3       | -   | nd         | 27.64| 7.65       | 0.43| 491.9      | -   | nd         |
| B 1       | 2.50| 144.9      | -   | nd         | 30.45| 11.8       | 1.46| 248.1      | -   | nd         |
| M 0.5     | -   | nd¹        | -   | nd         | 27.72| 9.38       | 6.37| 40.84      | -   | nd         |
| M 1       | 2.94| 101.5      | -   | nd         | 28.23| 10.5       | 1.54| 193.7      | -   | nd         |
| BM 0.5    | 4.82| 39.9       | 1.18| 163.3      | 36.47| 5.28       | -   | nd         | -   | nd         |
| BM 1      | 4.20| 37.2       | 0.79| 198.0      | 30.61| 5.11       | -   | nd         | -   | nd         |

*Concentration below detectable limits, by atomic absorption spectrophotometer. ^No data.
An exception to our hypothesis is that biochar–manure mixture had lower yield production than other organic amendments under wastewater irrigation. Wood-derived biochar generally has low nutrient contents and brings a positive yield response when it is co-amended with inorganic or organic (e.g. compost, manure or stover) fertilizers (Gul & Whalen, 2016). Our findings are not in agreement with published reports in this regard. The possible reason for these results may be the high adsorption capacity of biochar; when it was mixed with manure, it might have adsorbed nutrients from manure and reduced nutrient availability to plants, thus resulting in lower yield as compared to when biochar and manure were amended alone at 1 kg m$^{-2}$ rates under wastewater irrigation. Autumn amendment of biochar–manure mixture when there is no crop in field can bring higher yield for the plants grown following spring as it will allow sufficient time for such amendments to enhance the soil physico-chemical and biological properties and in return nutrient availability to the plants (Gul & Whalen, 2016; Gul et al., 2014) versus when these amendments are done in spring at the time the tomato plants are grown in field (as in our case).

Contrary to that, the maximum yield was observed for biochar amendment at higher application rates (1 kg m$^{-2}$) where it resulted in approximately six-fold and four-fold increases in the yield of tomato fruit under groundwater and wastewater irrigation, respectively, as compared to control and also caused significantly higher yield (34.5%–55.4% under groundwater and 18%–57% under wastewater irrigation) than other amendments. The amendment of biochar or manure at higher application rates (i.e. 1 kg m$^{-2}$) might have improved the physico-chemical properties of soil, thus allowing higher root growth, leading to higher mineralization of nutrients and their availability to plants under groundwater (for biochar amendment) and wastewater irrigation (for biochar and manure amendments). Bruun et al. (2014) reported that application of slow pyrolysis wood-derived biochar and straw biochar produced from gasification improved soil water retention capacity and root growth of barley resulting in higher yield than control. It is quite likely that application of biochar and manure to soil at higher amendment rates improved the yield of tomato via promoting soil properties such as water retention capacity and pH, which in return may have enhanced

| Groundwater irrigation | Treatment | pH | Total mineral N (mg g$^{-1}$ soil) | Soluble mineral P (mg g$^{-1}$ soil) |
|------------------------|-----------|----|-----------------------------------|-------------------------------------|
| Control                | 7.58 ± 0.005$^a$ | 1.66 ± 0.61$^b$ | 0.89 ± 0.49$^a$ |
| B 0.5                  | 7.85 ± 0.087$^{bc}$ | 1.28 ± 0.14$^b$ | 1.52 ± 1.14$^b$ |
| B 1                    | 7.65 ± 0.040$^d$ | 0.78 ± 0.03$^b$ | 4.06 ± 3.69$^{ab}$ |
| M 0.5                  | 7.82 ± 0.032$^{bc}$ | 13.1 ± 1.84$^a$ | 4.93 ± 1.45$^a$ |
| M 1                    | 7.91 ± 0.065$^a$ | 0.96 ± 0.23$^b$ | 1.45 ± 0.32$^b$ |
| BM 0.5                 | 7.75 ± 0.042$^d$ | 1.42 ± 0.35$^b$ | 1.99 ± 1.50$^b$ |
| BM 1                   | 7.77 ± 0.050$^c$ | 0.84 ± 0.48$^b$ | 1.63 ± 1.04$^b$ |

| Wastewater irrigations | Treatment | pH | Total mineral N (mg g$^{-1}$ soil) | Soluble mineral P (mg g$^{-1}$ soil) |
|------------------------|-----------|----|-----------------------------------|-------------------------------------|
| Control                | 7.83 ± 0.017$^{****}$ | 1.63 ± 0.17$^a$ | 0.17 ± 0.12$^a$ |
| B 0.5                  | 8.06 ± 0.032$^{a***}$ | 1.03 ± 0.21$^b$ | 2.51 ± 1.92$^c$ |
| B 1                    | 8.04 ± 0.020$^{a**}$ | 0.98 ± 0.29$^b$ | 4.75 ± 2.36$^b$ |
| M 0.5                  | 7.65 ± 0.045$^a$ | 10.0 ± 7.71$^c$ | 15.1 ± 3.25$^{ab**}$ |
| M 1                    | 7.95 ± 0.055$^b$ | 1.21 ± 0.52$^a$ | 1.77 ± 0.06$^c$ |
| BM 0.5                 | 7.84 ± 0.066$^a$ | 1.37 ± 0.40$^b$ | 3.28 ± 0.58$^b$ |
| BM 1                   | 7.88 ± 0.070$^{bc}$ | 0.66 ± 0.12$^b$ | 2.53 ± 1.66$^{bc}$ |

Values within the column of a given irrigation treatment followed by different letters are significantly different at $P < 0.05$. **Significantly higher values between wastewater and groundwater irrigation for a given amendment treatment.
the root growth and associated nutrient cycling in the rhizosphere. Furthermore, the influence of wood-derived biochar on crop yield may vary for different crops (Gul & Whalen, 2016). The influence of wood-derived biochar at higher application rates may be more favourable for tomato than other crops.

The interaction of irrigation treatment with organic amendments and their application rates for biomass production and fruit yield of tomato was however not significant, which indicates that the degree of impact of organic amendments on growth performance of tomato is not influence by irrigation type. As this research was carried out in the land which was not previously cultivated, first-year application of wastewater with organic amendments may have possibly affected growth yield the same way as did groundwater. The similar trend of biochar and manure in groundwater versus wastewater in the soil previously not cultivated before was reported for turnip (Haider et al., 2018).

Amendment of biochar, manure and their mixture tended to reduce the concentration of heavy metals in tomato fruits. Wastewater and manure amendment contain heavy metals in high concentrations (Murtaza et al., 2010). Our results are in agreement with previous findings that biochar and manure amendments reduce accumulation of heavy metals in the edible parts of vegetables (Nawab, Ghani, Khan, & Xiaoping, 2018; Nzediegwu et al., 2019). However, as compared to the other treatments, the concentrations of Zn, Ni and Pb were consistently higher in tomato fruits in response to the amendment of biochar–manure mixture at both application rates. Tahir et al. (2018) also observed a significantly higher concentration of Cu in the leaves of spinach, amended with manure-derived biochar under wastewater irrigation treatment. This and the results of the present study show that biochar and manure if applied as a mixture or separately may not always reduce the concentration of heavy metals in plants grown in heavy metal-contaminated soil. However, since these results are based on the pooled sample (n = 1) and the values are not very different, the differences may be marginal and non-significant. Moreover, as compared to other amendment treatments, biochar amendment at both application rates tend to reduce accumulation of heavy metals. Wood-derived biochar is highly porous and has a low concentration of trace elements; when applied to soil, its high adsorption capacity reduces heavy metal uptake by plants (Nzediegwu et al., 2019). Furthermore, the NUE of fruits measured as yield/concentration of a given heavy metal in fruits was consistently higher in response to amendment of biochar, manure and their mixture than control. This suggests that these organic amendments enhance the ability of plants to acquire less heavy metal per unit biomass production. Furthermore, as observed highest yield response of tomato fruits for biochar amendment at 1 kg m$^{-2}$ rate than all the other treatments, plants also showed consistently higher NUE at this amendment rate as compared to other treatments. Plants with high growth rates show high NUE for nutrients (Baligar et al., 2001). Organic amendments that enhance plant growth also improve their NUE (Gul & Whalen, 2016).

4.2. Soil pH, mineral N and soluble inorganic P
Soil pH was higher for wastewater than groundwater irrigation for control and biochar-amended treatments while organic amendments tend to significantly increase pH especially under groundwater irrigation. Our results are consistent with previous reports that manure and biochar increase the pH of soil (Gul et al., 2015; Liu, Rong, Wei, & Liang, 2017; Zhu et al., 2018) and may have substantial implications for farmers regarding attenuating soil acidity in drylands caused by inorganic N fertilizer application and for the soils that have low organic matter contents (Brown, Koenig, Higgins, Harsh, & Rossi, 2008; Taghizadeh Toosi et al., 2012). The application of biochar at both application rates as well as manure at high application rate tend to enhance soil pH more than when they were amended together. From our findings, it appears that type of amendment (i.e. biochar, manure or their co-amendment) and its application rate have influenced plant yield and soil pH with a similar trend. For instance, manure and wood biochar amendment at high
application rates caused higher biomass production and higher fruit yield and also caused higher soil pH especially under wastewater irrigation than when they were co-amended in the soil.

In organic amendment-related treatments, a negative relation can be seen between the concentration of mineral N in soil and stover biomass and yield production of tomato plants. The possible reason for higher mineral N in soil in response to the amendment of manure at 0.5 kg m$^{-2}$ rate can be that except for biochar amendment at 1 kg m$^{-2}$ rate, as compared to other organic amendments, this amendment had no difference in yield whereas the root biomass was higher than for wood biochar amended at 0.5 kg m$^{-2}$ rate and for co-amendment of manure and biochar at 0.5 kg m$^{-2}$ rate, this may have resulted in higher N concentration in soil probably due to root-induced high mineralization of organic N but no difference in N uptake by plants. Biochar and manure reduce N losses such as denitrification, ammonia volatilization and nitrate leaching and act as a slow-release fertilizer for plant growth (Gul & Whalen, 2016; Kammann et al., 2015; Taghizadeh et al., 2012).

The concentration of soluble inorganic P was higher in soil only for the treatment of manure amendment at 0.5 kg m$^{-2}$ rate as compared to all other amendments under groundwater irrigation, while under wastewater irrigation, all amendments increased significantly the concentration of soluble inorganic P than control, whereas as compared to all other treatments, the highest P concentration was found for the treatment of manure amendment at 0.5 kg m$^{-2}$ rate followed by amendment of biochar applied at 1 kg m$^{-2}$ rate. The amendment of manure at 0.5 kg m$^{-2}$ rate resulted in an approximately five-fold increase in the concentration of soluble inorganic P as compared to all other treatments under groundwater irrigation, while under wastewater irrigation, all organic amendments increased many-fold the concentration of P than control. We anticipate similar possible reason for the highest concentration for soluble inorganic P concentration in response to the amendment of manure at 0.5 kg m$^{-2}$ as for its influence on mineral N in soil. Except for the treatment of biochar amendment at 1 kg m$^{-2}$ rate, high root production for this treatment as compared to amendment of biochar at 0.5 kg m$^{-2}$ rate and co-amendment of biochar and manure at 0.5 kg m$^{-2}$ might have played a role in high solubilization of inorganic P and high mineralization of organic P in soil (Gul & Whalen, 2016) and comparatively a possible lower uptake by plants than the plants of the treatment of manure amendment at 1 kg m$^{-2}$ rate, which might result in higher P concentration in soil. Phosphorus is an important nutrient for plant growth and is commonly applied to soil as an inorganic fertilizer (Ziadi et al., 2014). As P fertilizer is been produced from rock phosphate, prices of this fertilizer are envisaged to become high in future because of diminishing of rock phosphate (Ziadi et al., 2014). Management actions that involve the organic P hydrolysis and solubilization of precipitated/inorganic P into ortho-phosphate in soil and reduction in its leaching can reduce the need of inorganic P fertilizer (Gul, Whalen 2016; Ziadi et al., 2014). Organic amendments such as manure, biochar and their mixture increase the concentration of inorganic P in soil via promoting root growth as roots harbour P solubilizing and organic P hydrolyzing microorganisms and also secrete acids that solubilize precipitated P (Gul & Whalen, 2016; Ziadi et al., 2014). As amendment of biochar, manure and their mixture promoted root growth, this may explain significantly high concentration of soluble inorganic P in the soil in our study. Our findings suggest that we can increase the yield of tomato plants under groundwater and wastewater irrigation by applying biochar, manure or their mixture. Furthermore, our results suggest that wastewater irrigation has a significant positive influence on tomato fruit yield and concentration of soluble mineral P of soil as compared to groundwater irrigation.

4.3. Insights for the local farmers of Balochistan

Our findings have substantial implications for the local farmers of Balochistan to use these amendments as an alternative to inorganic fertilizer to get a high agronomic output of this economically important crop for the region. Farmers of urban agriculture generally do not use manure and biochar as fertilizer, while in rural areas, the use of manure as a fertilizer is a common practice because the system for wastewater irrigation does not exist and manure costs much less than inorganic fertilizer. The price of inorganic NP (nitrogen and phosphorus) fertilizer is around US$ 0.65 per “one kg” while the cost of air-dried cow manure is approximately US$ 35 per “1000 kg”. The amendment of the mixture of wood-derived biochar and manure is a rare practice in rural areas. Wood-derived biochar is available
for Bar-B-Q purpose, and its cost is approximately US$ “0.45”, while the junk of this biochar (leftover small broken pieces) is around US$ “20”. The common source of wood is pruned twigs from orchards of Balochistan. Therefore, the use of biochar, manure and their mixture as organic fertilizer in agricultural lands irrigated either with groundwater or with wastewater have the potential to bring many-folds higher yield at very low cost as compared to when the soil is not amended with any fertilizer.

The urban agriculture in this dry region depends on wastewater for irrigation. As biochar, manure and their mixture improve soil quality, and our one-year study also showed their positive influence on crop yield, and it merits further study to investigate on special and temporal scales, which of these organic fertilizers (i.e. biochar, manure or their mixture) bring the most promising result regarding yield improvement and soil quality (e.g. soil aggregate stability, nutrient contents, microbial abundance, etc.).

5. Conclusions
This study aimed to evaluate the influence of biochar, manure and their mixture as a soil amendment on the biomass and yield of tomato; concentration of Pb, Cu, Zn, Ni and Cr in fruits and pH and concentration of mineral N and soluble P in soil under groundwater and wastewater irrigation. Our findings suggest that wastewater irrigation improved the biomass and yield production of tomato. Organic amendments further significantly improved tomato biomass and yield production and increased soil pH and concentration of inorganic soluble phosphorus in soil under wastewater irrigation. Furthermore, organic amendments reduced the concentration of Pb, Cu and Cr in fruits and improved the NUE of fruits for these heavy metals under wastewater irrigation. Our findings suggest that we can enhance the output of wastewater irrigation by using manure, biochar or their mixture and enhance production of tomato under groundwater irrigation with these amendments. Since the highest yield under both irrigation types was observed when biochar alone was amended at 1 kg m$^{-2}$ rate, it warrants future investigation to evaluate if this response was due to the positive influence of biochar on water retention capacity of soil, which in return promoted root growth and related rhizosphere processes (e.g. nutrient cycling) during early stages of plant growth and in return caused high biomass production and fruit yield. Furthermore, it merits future investigation to evaluate if the influence of wood-derived biochar on crop yield when it is not co-amendment with organic and inorganic fertilizer (as was the case for present study) is also positive on temporal scales for tomato as well as for other crops under arid environmental conditions, and whether this response is due to its positive influence on root growth during its initial growth stages. Our results have implications for tomato production in urban agriculture of Balochistan where wastewater irrigation is practised and for rural agriculture where farmers rely on groundwater and surface water for irrigation. Manure and biochar are much less expensive than inorganic fertilizers. Their use in agricultural lands have the potential for enhanced crop production and this will be a means of proper disposal of manure as waste.

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Competing interests
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Author details
Hameeda¹
E-mail: hameedakhan62@yahoo.com
Shamim Gul¹
E-mail: shamim_babar@yahoo.com
Gul Bano²
E-mail: gulbano_rehman@yahoo.co.uk
Misbah Manzoor¹,³
E-mail: alfa_botany@yahoo.com
Tasawar Ali Chandio⁴
E-mail: alfa_botany@yahoo.com
Adnan A. Awan⁴
E-mail: adnan.gsp@yahoo.com

¹ Department of Botany, Faculty of life sciences, University of Balochistan, Address: Saryab Road, postal code, 87300, Quetta, Pakistan.
² Department of Natural Resource Sciences, McGill University, 21,111 Lakeshore Road Ste. Anne de Bellevue, Quebec, H9X 3V9, QC, Canada.
³ Department of Botany, Faculty of life sciences, Sardar Bahadur Khan Women’s University, Address: Brewery Road, postal code, 87300, Quetta, Pakistan.
⁴ Department of Analytical Chemistry, Geological Survey of Pakistan, Quetta, 87300, Pakistan.
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