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Contrasting effects of untreated textile wastewater onto the soil available nitrogen-phosphorus and enzymatic activities in aridisol

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Abstract Water shortage and soil qualitative degradation are significant environmental problems in arid and semi-arid regions of the world. The increasing demand for water in agriculture and industry has resulted in the emergence of wastewater use as an alternative in these areas. Textile wastewater is produced in surplus amounts which poses threat to the environment as well as associated flora and fauna. A 60-day incubation study was performed to assess the effects of untreated textile wastewater at 0, 25, 50, 75, and 100 % dilution levels on the physico-chemical and some microbial and enzymatic properties of an aridisol soil. The addition of textile wastewater provoked a significant change in soil pH and electrical conductivity and soil dehydrogenase and urease activities compared to the distilled-water treated control soil. Moreover, compared to the control treatment, soil phosphomonoesterase activity was significantly increased from 25 to 75 % application rates, but decreased at 100 % textile wastewater application rate. Total and available soil N contents increased significantly in response to application of textile wastewater. Despite significant increases in the soil total P contents after the addition of textile wastewater, soil available P content decreased with increasing concentration of wastewater. Changes in soil nutrient contents and related enzymatic activities suggested a dynamic match between substrate availability and soil N and P contents. Aridisols have high fixation and low P availability, application of textile wastewater to such soils should be considered only after careful assessment.

Keywords Textile wastewater · Soil nitrogen · Soil phosphorus · Soil enzymes · Aridisol

Introduction

Overexploitation of water resources for agriculture, industrial, and domestic use have made fresh water

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availability a limiting factor in arid and semi-arid regions of the world (Rodríguez-Liébana et al. 2014). Therefore, finding alternate sources of water for irrigation has been emerging a big challenge for the agriculture sector. Reuse of wastewater in agriculture is gaining popularity as a low cost and useful alternative for irrigation (Thapliyal et al. 2013; Bame et al. 2014).

Textile wastewater constitutes a major part of the total industrial effluents on global scale (Ghaly et al. 2014). An estimated 1000–3000 m^3 of wastewater is produced for processing of 12–20 tons textile product which depends on the type of textile processing operation (Al-Kdasi et al. 2004). The textile sector is the mainstay of the economic development in Pakistan. Textile wastewater generally has higher chemical oxygen demand (COD), biological oxygen demand (BOD), dissolved solids, macro- and micronutrients (Garg and Kaushik 2008).

In Pakistan, about 30 % of wastewater is directly utilized to fertigate 32,500 ha of land (Ensink et al. 2004), while 64 % is discharged into rivers without any treatment (UN WWAP 2009). It has been estimated that out of the total wastewater produced in Pakistan, <8 % is treated only at primary level through sedimentation (Pak-SCEA 2006). Wastewater use for irrigation has the benefits to reduce pollution pressure on freshwater resources and conserving the useful nutrients in wastewater for agriculture production (Mekki et al. 2006; Rhee et al. 2011).

Nitrogen (N) and phosphorus (P) are essential nutrients for plant growth, and their adequate supply is necessary to optimize plant growth which has both economic and environmental implications. (Grant et al. 2001; Tilman et al. 2002). Aridisol are characterized for low organic matter content and low soil N and P pools supporting the use of nutrient-rich industrial wastewater to enhance soil fertility to considerable extent (Garg and Kaushik 2006).

Activities of soil enzymes are good indicators of changes in soil quality, and they represent integrated status of soil fertility and nutrient transformations (Bergstrom et al. 1998; Zhao et al. 2012). Dehydrogenase occurs in all intact and viable microbial cells, so its activity is usually related to the presence of viable microorganisms and their oxidative capability, hence reflects general metabolic and microbial activity of soil (Nannipieri et al. 2002). Urease and phosphomonoesterase are important extracellular hydrolases that convert urea and orthophosphate monoester into ammonium and orthophosphate, thus regulate both N and P cycles, respectively (Zhang et al. 2015). Some previous studies have reported the positive (Mosse et al. 2012), negative (Kayikcioglu 2012), and neutral (Morugán-Coronado et al. 2011) effects of wastewater on soil biochemical and microbiological properties. In contrast, on a relative basis, a large number of researchers have reported the effect of textile wastewater application on food crops (e.g., Kaushik et al. 2005; Garg and Kaushik 2008; Khalid et al. 2013). Therefore, there exists a significant need to study how application of untreated textile wastewater affect soil physiochemical and biological properties, especially by keeping in view of the increasing number of textile industry and resultant increase in the discharge of wastewater in Pakistan.

The objective of this study, therefore, was to characterize changes in soil physiochemical and biochemical properties including soil nitrogen (N) and phosphorus (P) concentrations and related enzymatic activities after application of untreated textile wastewater at different dilution levels in an agricultural aridisol by using a 60-day laboratory incubation study.

Materials and methods

Wastewater sampling and analysis

Textile wastewater was sampled from an industrial textile unit located at Khurianwala, Faisalabad, Pakistan (31° 29′ N, 73° 17′ E). Sampling location represents a typical textile industry of the main hub of textile industrial estate at Faisalabad. Textile wastewater samples were collected in triplicate in pre-cleaned plastic bottles, and sample volume was ca. 2.5 L for each replicate sufficient for the analysis and experimentation. No rain event had taken place in the previous week or on the sampling day. Samples were transported in an ice-cooler to the laboratory and kept at 4 °C until used for further experimentation. pH and electrical conductivity (EC) were measured with a handheld water quality meter

(WTW multi 350i, Weilheim, Germany). Chemical oxygen demand (COD) was determined according to the method of Knechtel (1978). Biochemical oxygen demand (BOD) was measured according to the respirometric method. Other analyses of textile wastewater were performed using standard methods for examination of water and wastewater (APHA 1995).

Soil sampling and pre-incubation analysis

The soil used in this study was sandy clay loam and belonged to Lyallpur soil series (aridisol-fine-silty, mixed, hyperthermic Ustalfic, Haplarged; in Haplic Yerrmosols in FAO Classification). Soil samples were collected from a wheat field at Nuclear Institute for Agriculture and Biology (NIAB) Faisalabad, Pakistan. The site is located (31° 23′ N, 73° 20′ E) in the Sandal Bar region, north-east (Punjab) Pakistan and in subtropical monsoon climate. Soil samples were passed through a 2-mm sieve to remove stones and/or any live or dead plant parts. One part was air-dried at room temperature for initial physical and chemical analysis using standard methods described below (Table 2). Water holding capacity of the soil was measured as the experiment was conducted at 70 % of the water holding capacity of the soil.

Construction of microcosm and experimental setup

Microcosms were constructed using the method described by Riaz et al. (2012) involving PVC pipes of 3-cm diameter and 10-cm length with a fine-sealed mesh at bottom. Experiment consisted of five treatments: 0 (distilled-treated control), 25, 50, 75, and 100 % textile wastewater. Each treatment was replicated five times, and experiment was laid in completely randomized design (CRD) under laboratory conditions. Different dilution levels for these treatments were achieved by mixing untreated wastewater with distilled water. Twenty-five microcosms were filled with 400 g of homogenized soil at appropriate bulk density and brought to moisture levels equivalent to 70 % water holding capacity with respective treatment solutions. The treatment solutions were gently sprayed in small amounts at the surface of the soils in the microcosms so that soils were least disturbed. After the treatment application, microcosms were incubated at 25 °C in an incubator for 3 days so that soil microbial activity was stabilized. When the pre-conditioning/incubation period was over, the microcosms were placed in loosely capped plastic containers and placed in the incubator for 60 days. During the course of experiment, each microcosm was, periodically, checked for any loss of moisture which was subsequently replenished with corresponding treatment solution. In addition, each microcosm was vented twice per week to remove the CO_2 from the headspace so that proper aeration was provided for optimum microbiological activities. After 60 days, microcosms were removed from the containers, and soil was transferred to plastic bags for physico-chemical and enzymatic analysis. Soil samples were always kept at 4 °C when not required for analysis.

Soil analysis

Soil pH and EC were determined at 1:5 soil-water ratio (*w/v*) on moist samples. Fifty milliliter distilled water was added to 10 g moist soil samples. The suspension was shaken for 30 min on an orbital shaker and was allowed to settle for 1 hour before measuring the pH and EC (WTW multi 350i, Weilheim, Germany). In terms of soil textural analysis, soil samples were characterized for particle size distribution at the start of the experiment using Bouyoucos hydrometer method of Gee and Bauder (1986). Total organic carbon (TOC) content was analyzed by dichromate oxidation and titration with acidified ferrous ammonium sulfate without external heat (Walkley and Black 1934). Soil total N was determined by the method of Bremner and Tabatabai (1972) following Kjeldahl's digestion and distillation procedure. Total soil P was determined by alkaline extraction followed by molybdate colorimetric measurement (Murphy and Riley 1962). Soil available N was measured by the method of Subbiah and Asija (1956) using methyl red indicator and titration of distillate to a colorless end point with 0.02 M NaOH. Soil available P was estimated using the method of Olsen et al. (1954).

Soil enzymatic activities

Dehydrogenase activity was determined using the method of Casida et al. (1964). Briefly, 6 g moist soil was incubated with 3 % triphenyl tetrazolium chloride (TTC) in a test tube at 37 °C. After 24 h, 10 ml methanol was added to extract the triphenyl formazan. The content in each tube was mixed thoroughly, and supernatant was filtered by methanol washing. The absorbance of the filtrate was measured at 485 nm, and dehydrogenase activity was expressed as microgram triphenyl formazan (TPF) g^{-1} soil h^{-1}.

Urease activity in the soil sample was measured by following the method of Kandeler and Gerber (1988). Five grams of fresh soil sample was mixed with 2.5 ml 80 mM urea and 20 ml 0.1 M borate buffer (pH 10.0). The mixture was shaken vigorously and incubated for 2 h at 37 °C. After incubation, 30 ml 2.0 M KCl was added and shaken for 30 min followed by centrifugation at 10,000 rpm for 2 min. The supernatant was filtered through a Whatman no. 42 filter paper, and NH_4^+ concentration was analyzed by measuring the absorbance at 690 nm. Urease activity was reported as microgram NH_4^+-N g^{-1} soil h^{-1}.

Phosphomonoesterase activity was assayed following the method of Tabatabai and Bremner (1969). One-gram moist soil was suspended in 4 ml modified universal buffer of pH 11. Soil was incubated after addition of 1 ml 0.025 M p-nitrophenyl phosphate at 37 °C for 1 h; the enzyme reaction was stopped by addition of 4 ml 0.5 M NaOH. The suspension, then, was filtered through a Whatman no. 42 filter paper. Absorbance of supernatant was measured at 440 nm. Phosphomonoesterase activity was presented as microgram p-nitrophenol g^{-1} soil h^{-1}.

Statistical analysis

Data were subjected to analysis of variance test (ANOVA) to identify significance of textile effluent treatment effects on soil chemical and biological properties. Tukey's HSD post hoc test was used for multiple mean comparison technique for those parameters where significant treatments effects were found. Nature and strength of relationships described in 3D figures were based on linear regression analysis. Figures and tables contain means of five replicates followed by standard errors of means unless otherwise stated. All statistical analysis was performed using SPSS 21 for Windows Software.

Results

Characteristics of textile wastewater

The textile wastewater pH was 10.1 and the EC was 7.3 dS m^{-1} (Table 1). Total dissolved solids (TDS), BOD, and COD values were 4830, 351, and 800 mg L^{-1}, respectively. Concentrations of total C, total inorganic C, and total dissolved C in the textile wastewater were 394.2, 159.9, and 234.3 mg L^{-1}, respectively. The textile wastewater also contained considerable concentrations of total dissolved N dominated by dissolved organic N (79.15 mg L^{-1}).

Table 1 Physico-chemical characteristics of textile wastewater used in the study

Physical/chemical property	Value
pH	10.1
EC (dS m^{-1})	7.3
Chemical oxygen demand (COD; mg O_2 L^{-1})	800
Biological oxygen demand (BOD; mg O_2 L^{-1})	351
Total dissolved solids (TDS, mg L^{-1})	4830
Total carbon (TC, mg L^{-1})	394.2
Total inorganic carbon (TIC, mg L^{-1})	159.9
Dissolved organic carbon (DOC; mg L^{-1})	234.3
Total dissolved nitrogen (TDN; mg L^{-1})	86.05
NH_4^+-N (mg N kg^{-1} soil)	6.5
NO_3^--N (mg N kg^{-1} soil)	0.4
Dissolved inorganic nitrogen (DIN; mg L^{-1})	6.9
Dissolved organic nitrogen (DON; mg L^{-1})	79.15
Na^+ (mg L^{-1})	1300
K^+ (mg L^{-1})	19.5
PO_4^{-1} (mg L^{-1})	17.2

Initial physicochemical soil properties

The soil, used in this study, was a sand clay loam typic haplocambids of aridisol soil order (Table 2). The soil was slightly alkaline with pH 7.6 and EC 2.04 dS m^{-1}. Soil nutrient analysis showed that it had 3.26 g kg^{-1} total N, 0.63 g kg^{-1} available mineral N, 160 mg kg^{-1} total P, and 6.3 mg kg^{-1} available P. Total organic C contents of the soil was 69.2 g kg^{-1}.

Effects of wastewater on soil pH and EC

Soil pH and EC were increased consistently with the increase in the concentration of wastewater; however, treatment effects were not always significant (Table 3). pH increased from 7.60 for the control treatment to 8.06 for the 100 % wastewater treatment. However, change

Table 2 Physico-chemical properties of agricultural soil used in the study

Analysis	Value	Reference
Sand (g kg^{-1})	468	Gee and Bauder (1986)
Silt (g kg^{-1})	146	
Clay (g kg^{-1})	386	
Textural class	Sandy clay loam	
pH$_{1:5}$ (H_2O)	7.60	Gee and Bauder (1986)
EC (dS m^{-1})	2.04	
Soil organic matter (g kg^{-1})	11.93	Walkley and Black (1934)
Total soil C (g kg^{-1})	6.92	
Total soil N (g kg^{-1})	3.26	Bremner and Tabatabai (1972)
Soil available N (g kg^{-1})	0.63	Subbiah and Asija (1956)
Total soil P (mg kg^{-1})	160	Murphy and Riley (1962)
Soil available P (mg kg^{-1})	6.3	Olsen et al. (1954)

in pH for the treatments containing 75 and 100 % wastewater was significantly higher compared to the control treatment. Change in soil pH in response to application of 25 and 50 % wastewater was not significantly different to the other treatments. Changes in soil EC followed similar trend to that of the pH; increase in EC for the 50, 75, and 100 % wastewater receiving treatments was significant compared to the control and 25 % wastewater treatments (Table 3). Both the control and 25 % wastewater treatments were not resulted in a substantial change in EC. However, increase in EC of soil treated with 50, 75, and 100 % wastewater was significant, and the highest EC of 2.76 d Sm^{-1} was noted for the soils received 100 % wastewater.

Table 3 Effect of textile wastewater application on soil pH and EC treated with 0–100 % effluent concentrations after 60 days of incubation.

Treatment (% Effluent)	pH	EC (d Sm^{-1})
0	7.60 ± 0.07 a	2.04 ± 0.05 a
25	7.90 ± 0.07 ab	2.19 ± 0.05 a
50	8.00 ± 0.07 ab	2.54 ± 0.05 b
75	8.02 ± 0.12 b	2.62 ± 0.04 bc
100	8.06 ± 0.14 b	2.76 ± 0.02 c

Values are means of five replicates followed by standard errors of means. Means in a column with different letters differ significantly from each other at $p < 0.05$ (one-way ANOVA; Tukey's HSD post hoc test)

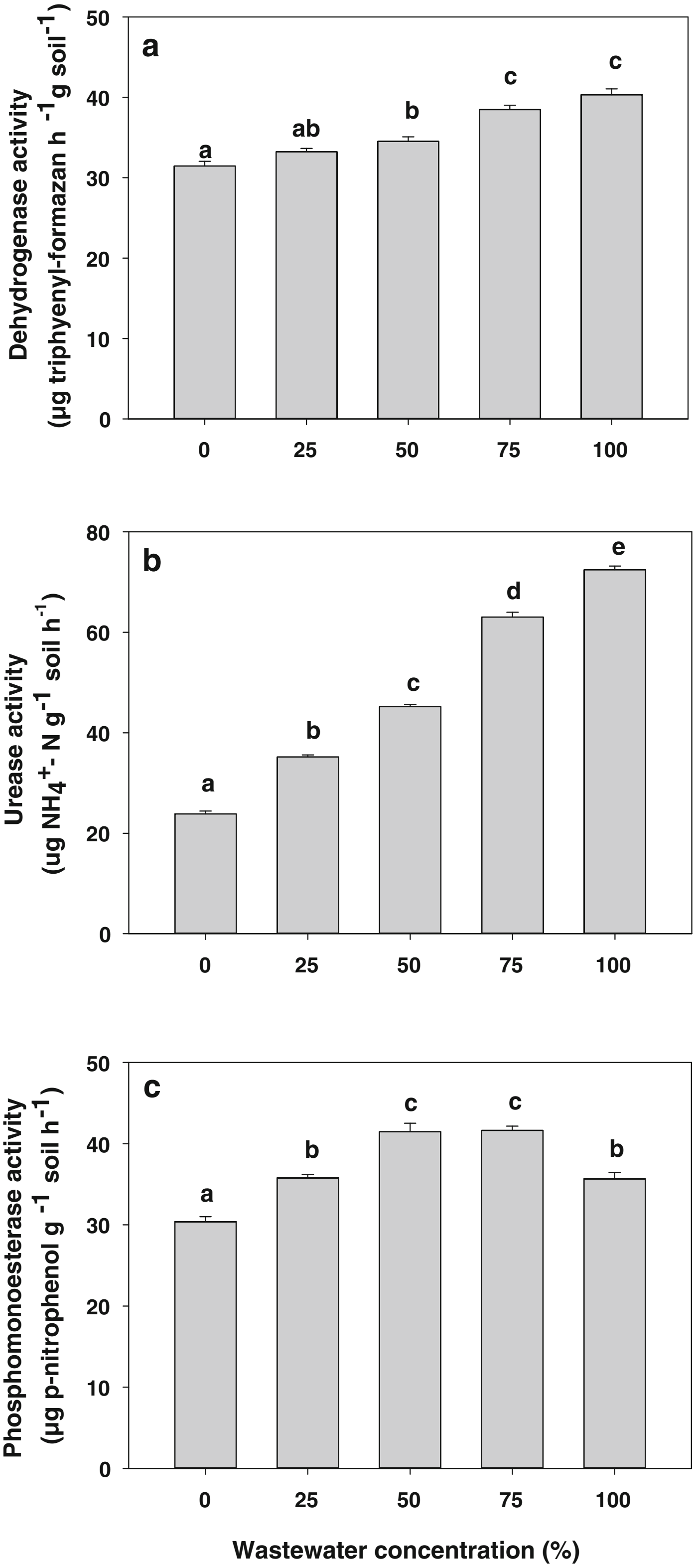
Effects of textile wastewater on activities of soil enzymes

Textile wastewater application altered soil dehydrogenase activity in the soils incubated for 60 days (Fig. 1a). There was no significant change in dehydrogenase activity of soil treated with distilled water and 25 % wastewater. A significant increase in soil dehydrogenase activity was recorded when wastewater was applied at 50, 75, and 100 % wastewater application rates. Dehydrogenase activity of the soils incubated with 75 and 100 % wastewater was significantly higher compared to that in the 0, 25, and 50 % wastewater treatments. However, dehydrogenase activity in the 75 and 100 % wastewater treatments was not significantly different from each other. Increase in dehydrogenase activity was linear but less sharp (Fig. 1a; $y = 2.298x + 28.71$, $R^2 = 0.97$).

Increase in the soil urease activity in response to wastewater treatments was clearer, significant, and followed a sharp linear increase (Fig. 1b; $y = 12.512x + 10.404$, $R^2 = 0.99$). Urease activity of soils at 75 and 100 % wastewater application rate was more than three-fold higher compared to the distilled water-treated control soil. Moreover, the highest soil urease activity of 72 mg NH_4^+-N 100 g^{-1} was found in soil supplied with undiluted wastewater.

Phosphomonoesterase activity varied in soil receiving textile wastewater at different dilution concentrations and followed a non-linear trend (Fig. 1c; $y = -2.0214x^2 + 13.771x + 17.912$, $R^2 = 0.95$). A significantly higher phosphomonoesterase activity was observed in soils treated with 25 % wastewater than that for the distilled water-treated control. Increase in phosphomonoesterase activity was also observed in soil treated with 50 and 75 % wastewater; however, these treatments were not significantly different from each other. However, application of 100 % wastewater reduced phosphomonoesterase activity compared to the soil treated with 50 and 75 % wastewater. Phosphomonoesterase activity for soils treated with 25 and 100 % wastewater was non-significant and similar.

Fig. 1 Effect of textile wastewater on **a** dehydrogenase activity (μg triphyenyl-formazan h^{-1} g $soil^{-1}$) **b** soil urease activity (μg NH_4^+-N g^{-1} soil h^{-1}) and **c** soil phosphomonoesterase activity (μg p-nitrophenol g^{-1} soil h^{-1}) in soils incubated for 60 days. *Bars* represent mean values of five replicates and contain ± standard error of means. *Bars with different letters* differ significantly from each other at $p < 0.05$ (one-way ANOVA; Tukey's post-hoc test).



Effects of wastewater on soil nutrient contents

Total N concentration in soil increased in response to wastewater applied at different dilution levels (Fig. 2a). For the distilled water-treated control and 25 % diluted wastewater applied soil, the change in total soil N contents was not significant. However, increase in total N contents of soils treated with 50, 75, and 100 % textile wastewater was significantly higher. The highest total N contents of 6.08 g kg soil^{-1} were noted for soil treated with undiluted wastewater. Increase in total P contents of soil treated with wastewater was more consistent than the increase in total soil N contents; however, the treatment effects were not always significant (Fig. 2b). Total P contents increased from 154.27 mg kg soil^{-1} for the distilled water-treated soil to 228.58 mg kg soil^{-1} for the soil supplied with textile wastewater at 100 % dilution level. However, treatments of 75 and 100 % wastewater resulted in significantly higher total soil P contents compared to the distilled water control treatment.

Concentrations of available N were generally similar to total N contents of the soil for the all treatments (compare Figs. 2a and 3a). However, in contrast, there was a mismatch between the total and available P contents of the soil treated with wastewater at 75 and 100 % concentrations (Figs. 2b and 3b). Soil available N contents varied from 0.62 g kg soil^{-1} to 1.21 g kg soil^{-1} (Fig. 3a). Treatments of 75 and

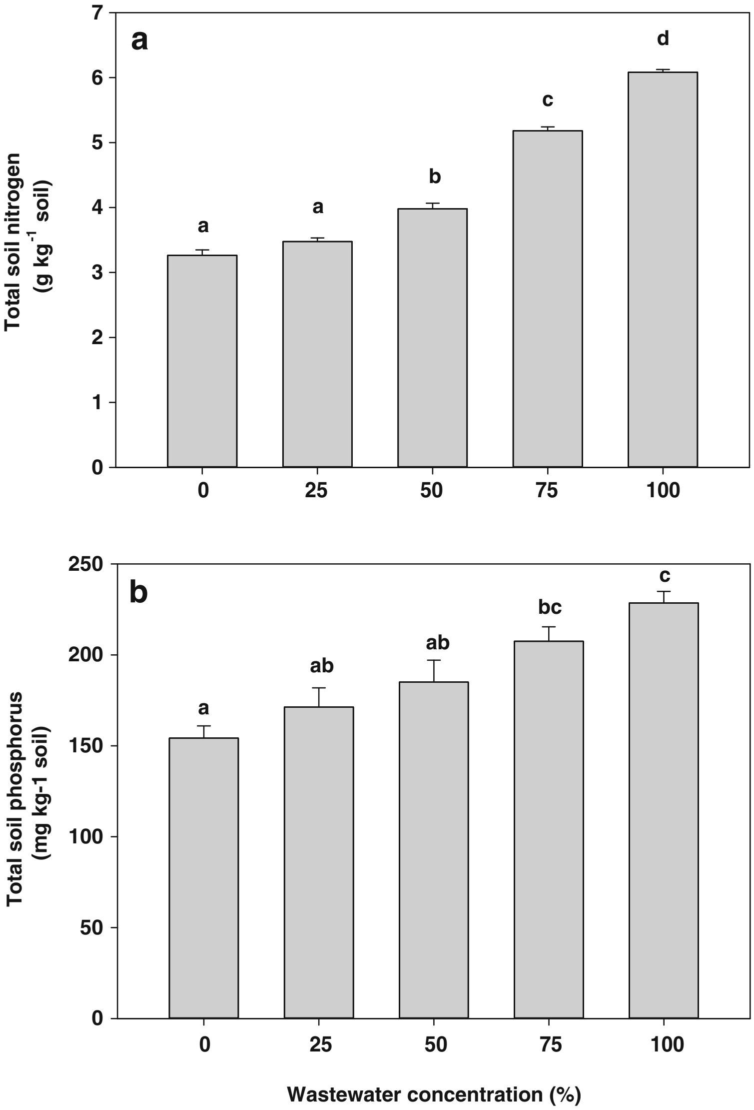


Fig. 2 Effect of textile wastewater on **a** total soil N (g kg^{-1} soil) and **b** total soil P (mg kg^{-1} soil) in soils incubated for 60 days. *Bars* represent mean values of five replicates and contain ± standard error of means. *Bars with different letters* differ significantly from each other at $p < 0.05$ (one way ANOVA; Tukey's post hoc test).

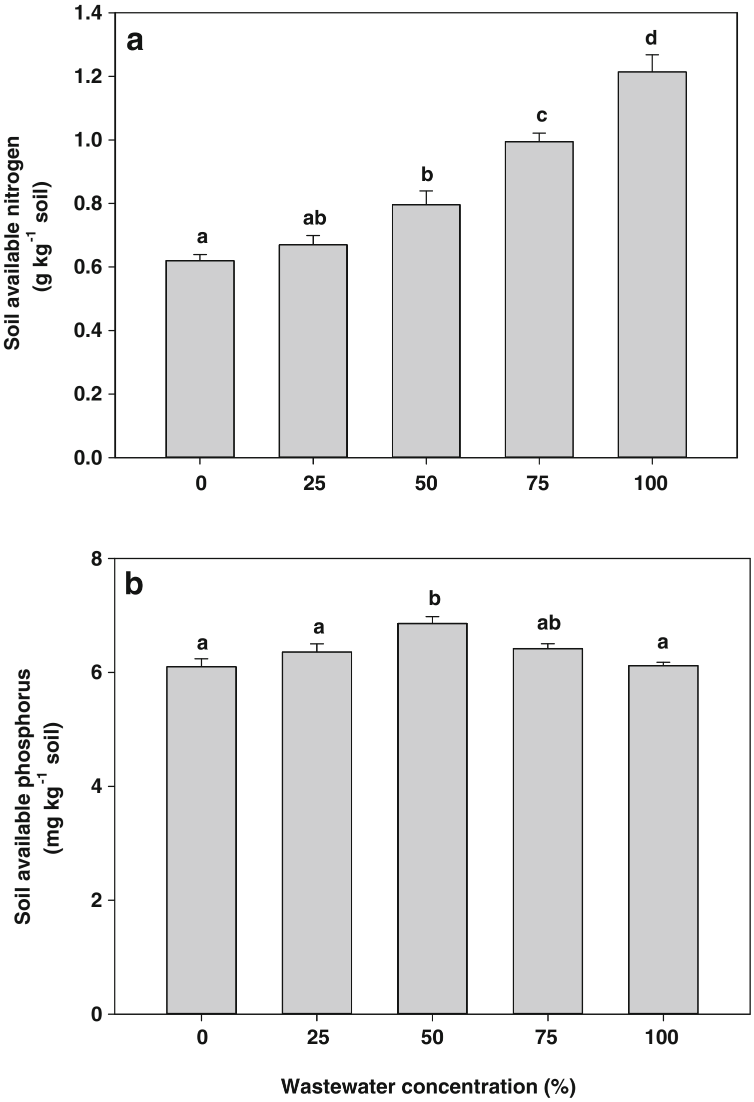


Fig. 3 Effect of textile wastewater on **a** soil available N (g kg^{-1} soil) and **b** soil available P (mg kg^{-1} soil) in soils incubated for 60 days. *Bars* represent mean values of five replicates and contain ± standard error of means. *Bars with different letters* differ significantly from each other at $p < 0.05$ (one way ANOVA; Tukey's post-hoc test).

100 % wastewater had significantly higher soil available N contents compared to the soil received 0–50 % wastewater. Contrary to the increase in soil available N contents for the 75 and 100 % wastewater-treated soil, soil available P contents were decreased for the same treatments (Fig. 3). However, this decrease was significantly different from the treatment of 50 % wastewater application only. Consequently, the treatment consisting of 100 % wastewater resulted in the lowest soil available P contents of 6.12 mg kg soil^{-1} among the wastewater-treated soil. The highest soil available P contents (6.86 mg kg soil^{-1}) were found in soil treated with 50 % wastewater.

Stoichiometric relationships of total and available NP contents with enzymatic activities

The stoichiometric relationships between soil total NP, soil available NP, and their associated soil enzymatic activities were explored by using 3D surface hatch dot plots. Linear regression analysis was performed to study the relationship between every two parameters on alternative basis. There was a dynamic and positive interaction between soil total and available N contents and soil urease activity in wastewater-treated soil (Fig. 4). We found a significant positive relationship between total soil N and soil urease activity ($R^2 = 0.94$, $p < 0.001$, $n = 25$), whereas the soil urease activity and soil

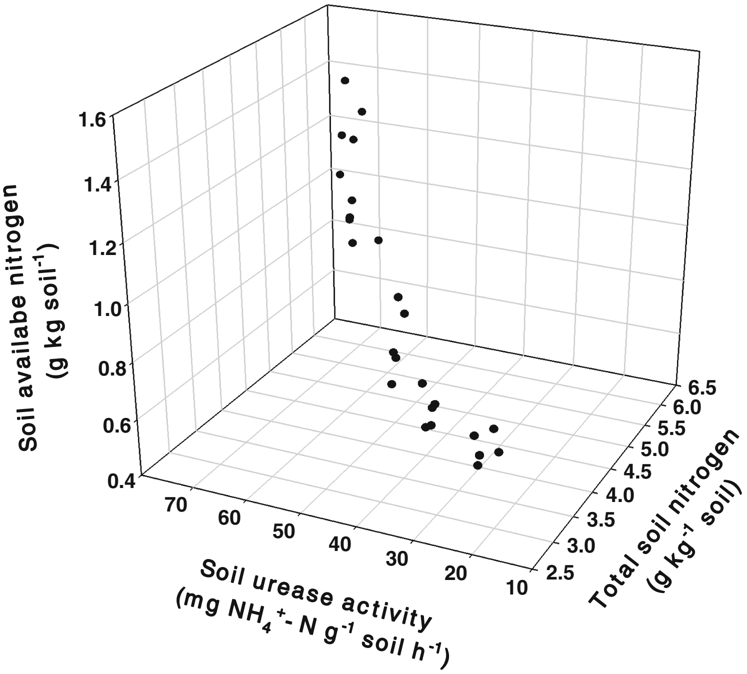


Fig. 4 3D relationship between total soil N (g kg^{-1} soil), soil urease activity (μg NH_4^+-N g^{-1} soil h^{-1}), and soil available N (g kg^{-1} soil). 3D stoichiometric relationships = total soil N and soil urease activity: $R^2 = 0.94$, $p < 0.001$, $n = 25$; Soil urease activity and soil available N: $R^2 = 0.86$, $p < 0.001$, $n = 25$, soil available N and total soil N $R^2 = 0.90$, $p < 0.001$, $n = 25$)

available N contents were also correlated significantly and positively ($R^2 = 0.86$, $p < 0.001$, $n = 25$). The 3D relationship between total soil P, phosphomonoesterase activity, and soil available P is shown in Fig. 5. Soil total P content had non-significant but positive relationship with activity ($R^2 = 0.15$, $\underline{p} = 0.06$, $n = 25$). However, soil phosphomonoesterase activity was weakly correlated with soil-available P ($R^2 = 0.34$, $p = 0.06$, $n = 25$). When relationship between urease, phosphomonoesterase, and dehydrogenase activities was investigated, we found a highly significant and positive relationship between urease and dehydrogenase activities (Fig. 6,

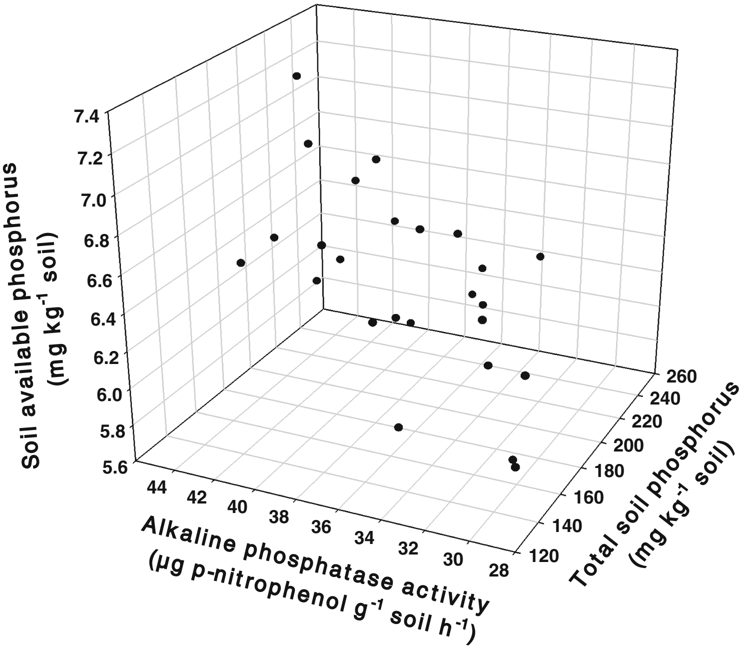


Fig. 5 3D relationship between total soil P (mg kg^{-1} soil), soil phosphomonoesterase activity (μg p-nitrophenol g^{-1} soil h^{-1}), and soil available P (mg kg^{-1} soil). 3D stoichiometric relationships = total soil P and phosphomonoesterase activity: $R^2 = 0.15$, $p = 0.06$, $n = 25$, phosphomonoesterase activity and soil available P: $R^2 = 0.34$, $p < 0.01$, $n = 25$, soil available P and total soil P: $R^2 = 0.02$, $p = 0.487$, $n = 25$).

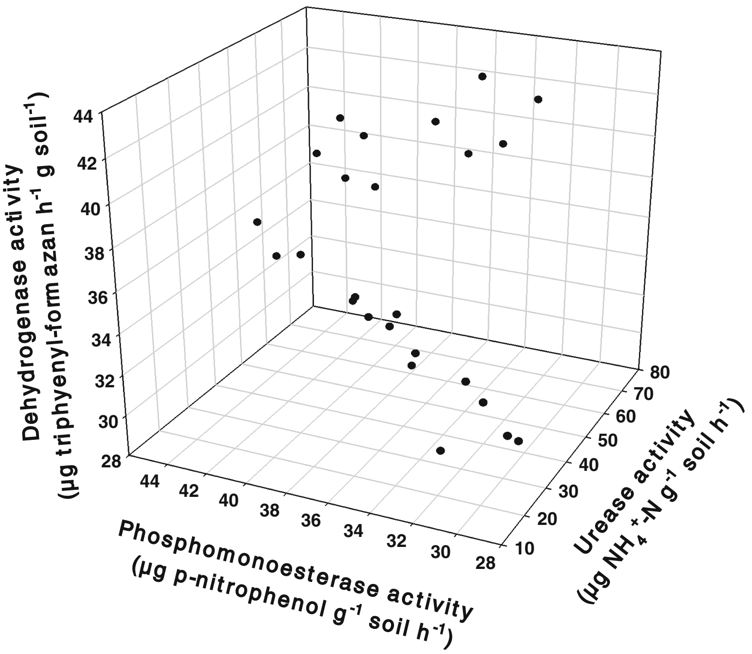


Fig. 6 3D relationship between soil urease activity (µg NH_4^+-N g^{-1} soil h^{-1}), soil phosphomonoesterase activity (µg p-nitrophenol g^{-1} soil h^{-1}), and dehydrogenase activity (µg triphyenyl-formazan h^{-1} g $soil^{-1}$). 3D stoichiometric relationships = urease and phosphomonoesterase activities: $R^2 = 0.25$, $p < 0.05$, $n = 25$, phosphomonoesterase and dehydrogenase activities: $R^2 = 0.20$, $p < 0.05$, n = 25; Dehydrogenase and urease activities: $R^2 = 0.89$, $p < 0.001$, $n = 25$).

$R^2 = 0.89$, $p < 0.001$, $n = 25$). However, the intercorrelations between urease and phosphomonoesterase as well as phosphomonoesterase and dehydrogenase activities were rather less strong but positive and significant (Fig. 6).

Discussion

Changes in soil pH and EC

The application of textile wastewater significantly increased soil pH and EC. Increase in soil pH could be related to alkaline nature of the textile wastewater used in the study. There were considerable concentrations of Na^+ and K^+ in undiluted wastewater and, in addition, the presence of basic cations such as Ca and Mg might also had increased soil pH. An increase in the pH of a sandy loam soil irrigated with alkaline industrial effluents was observed due to accumulation of sodium and bicarbonate in soil resulting structural destabilization (Dakouré et al. 2013). There was a consistent and significant increase in soil EC, especially for the soil treated with wastewater at higher concentrations, primarily due to high level of total dissolved solids (4830 mg L^{-1}) in wastewater that could have accumulated in soil after wastewater application. In addition, release of ions from mineralization of organic fractions in waste effluent might also have increased the EC of soil (Kiziloglu et al. 2008).

Changes in soil enzymatic activities

Soil enzymes are considered the potential indicators of soil quality in stressed and polluted environments (Badiane et al. 2001). The results of this study revealed that application of untreated textile wastewater had significant effect on soil dehydrogenase activity, especially at higher concentrations. However, lower dehydrogenase activity in distilled water-treated control soil may be linked to the low indigenous organic C contents of soil as is the case of the soil used in this study and those reported from the arid regions (Bastida et al. 2006). Wastewater applied at higher concentrations (50, 75, and 100 %) significantly increased dehydrogenase activity compared to the control soil. This difference in dehydrogenase activity could be related to varied concentrations of nutrients supplied with respective treatment solutions. Increase in soil dehydrogenase activity also suggested microbial utilization of the readily available nutrients from the wastewater for C, N, and energy source. Positive effects of higher labile organic C containing waste effluent on soil enzymatic activities have been reported earlier (e.g. Marín-Benito et al. 2012; Liang et al. 2014).

Soil urease activity catalyzes the hydrolysis of urea and is a good measure of soil N transformations. In general, treatment of wastewater resulted in significant and consistent increase in soil urease activity. Decomposition of nitrogenous compounds from organic matter is a major process of urea production in soil under natural conditions. Textile wastewater generally contains Azo dyes which are rich nitrogenous aromatic compounds consisting of one or more azo bonds (R_1-N=N-R_2). Higher soil dehydrogenase and urease activities might have worked concurrently to cleavage N-N bond of the textile wastewater to produce higher N contents of soil received more concentrated wastewater. Moreover, availability of substrate as total dissolved organic N (79.15 mg L^{-1}) and dissolved organic C (234.3 mg L^{-1}) could also have fueled soil dehydrogenase and urease activities. Previously, Khorsandi and Nourbakhsh (2007) observed organic manure (substrate) application induced stimulation of soil urease activity.

Application of textile wastewater at 25, 50, and 75 % concentrations resulted in significantly higher soil phosphomonoesterase activity compared to the distilled water-treated control soil. Reduction in phosphomonoesterase activity at 100 % wastewater application suggested that nutrient loading from wastewater favored the synthesis of phosphomonoesterase up to certain concentrations of wastewater. It could also be due to lack of substrate accessibility than its availability at more concentrated wastewater application rate that might have reduced the activity of P hydrolyzing microbial communities. There are some studies reporting negative effects of heavy metals on phosphomonoesterase activity in soils; however, the degree of inhibitory effect was generally related to dose of applied wastewater, soil type, and background concentration of heavy metals (Kandeler et al. 1996; Yim and Tam 1999). Our results show partial collinearity to those reported by Brzezinska et al. (2006) for wastewater dose dependent decrease in soil phosphomonoesterase activities. We also realize that soil phosphomonoesterase activity in wastewater-irrigated soil could be highly time-dependent, and length of incubation period could have strong influence on enzyme activity (Seshadri et al. 2014). Results presented here could be argued to represent the cumulative treatment effects after the 60-day incubation period. However, quantification of soil phosphomonoesterase activity at multiple incubation times would have been more advantageous. Nevertheless, changes in soil enzymatic activities after incubating the soil with wastewater for 60 days still provide useful insights into the behavior of the soil under wastewater application.

Changes in total and available NP pools

Soil total N contents were significantly higher in soil received 50–100 % wastewater compared to the 25 % wastewater and distilled water-treated soil. Our results show general increase in soil total N contents with the increase in concentration of wastewater. A study conducted by Mohawesh et al. (2014) also found increase in soil CN contents after application of wastewater containing higher concentrations of CN. In our study, total soil P contents of soil treated with 25 and 50 % wastewater were higher but not significantly different from the control treatment. However, addition of wastewater at higher (75 and 100 %) concentrations resulted in significantly higher total soil P content than the control treatment. These results could be related to P substrate (PO_4^{-1}; 17 mg L^{-1}) availability in the textile wastewater, and results of this study are supported by Sierra et al. (2007) who also found increased soil P contents after application of wastewater in a short-term incubation study. In addition, Bame et al. (2014) also reported the significance of P input from the wastewater and found considerably higher soil P contents in wastewater-irrigated soil.

Soil available N contents followed trend similar to that of total soil N contents in the wastewater-treated soil. These results signify the role of wastewater N compounds, especially dissolved inorganic and organic N in improving soil N status as argued by Cordovil et al. (2011) and Motta and Maggiore (2013). In addition, breakdown of azo dyes, N rich organic compounds present in textile wastewater, might have contributed to increase soil N availability and enhanced microbial activity. Almeida et al. (2012) also found evidence of NH_4^+ and NO_3^- release from mineralization of azo dyes present in textile wastewater.

In addition to N, availability of P is a major growth-limiting factor in aridisol having high pH and low P solubility of added phosphatic fertilizer. In our study, P availability in soil treated with 25 % wastewater was not significantly different from that of the control soil. However, wastewater application at 50 % concentration resulted in significantly increased soil P. When wastewater was applied at 75 and 100 % concentrations, soil-available P was reduced to the level noted for the distilled water and 25 % treated soil. These results suggested the possible adsorption or immobilization of P which is a common problem in aridisol. Soil P availability is influenced by microbiological activities, distribution-precipitation reactions, and formation of organic and/or inorganic complexes (DeLuca et al. 2015). In addition, phosphate anions are highly reactive and can be immobilized through sorption and/or precipitation with basic cations (Arias et al. 2002).

Soil NP nutrient and enzymatic activities

There was significant positive relationship between soil urease activity and soil total N content suggesting N limitation of the soil microbes when wastewater was applied. Wastewater application also resulted in higher soil metabolic activity, the dehydrogenase activity, and N cycling, the urease activity. Turner et al. (2014) also discussed the N regulation of soil urease activity, in addition to enzyme activity responsiveness to N limitation.

Soil urease activity was positively and significantly correlated with soil-available N, which could indicate the possible involvement of soil urease in the mineralization of organic compound, thus increasing N availability. Our results are in contrast to some studies which reported a decrease in urease activity in wastewater treated soils and related it to depletion of organic compounds and low soil N contents (e.g. Henriksen and Breland 1999; Geisseler et al. 2009); however, these studies involved the use of industrial wastewater compared to the textile wastewater which generally contain higher concentrations of N rich compounds. Strong positive relationship between soil total and available N contents in our study agrees with that reported by Hernández et al. (2002) for soil incubated with sewage sludge.

Phosphomonoesterase is synthesized by soil microorganisms by releasing free phosphate and regulate P cycling, and therefore, theoretically, phosphomonoesterase activity correlates positively with soil total soil P contents (Dawei et al. 2011). However, no such relationship was observed in our study. Moreover, there was also positive but non-significant relationship between total and available soil P contents. These observations might show a dynamic mismatch between P cycling in wastewater-irrigated soil, especially if more concentrated wastewater was applied which led to increase in soil total P contents but soil-available P contents followed opposite pattern. As discussed earlier, the decrease in soil-available P at high wastewater concentrations could be due to adsorption, precipitation with low solubility compound of Fe, Al, and Ca (Khan and Joergensen 2009). A weak relationship between phosphomonoesterase activity and soil available P suggested the P cycling microbial flora and hydrolytic enzyme activities are negating stressful condition to a certain limit.

A strong positive relationship was found between the urease and dehydrogenase enzyme activities in this study. This reflects a revitalization of the soil microbial activities provoked by the input of fresh bioavailable substrates from wastewater application, ultimately leading to a higher metabolic activity and nutrient turnover. Measure of the soil dehydrogenase activity provides qualitative and quantitative overview of the soil microbial community dominance to their metabolic nutrient requirements and, hence, the available nutrients. Therefore, study of enzymatic activities gives a better and comprehensive understanding about some key processes linking microbial activities and nutrient dynamics (Sinsabaugh and Moorhead 1994; Schimel and Weintraub 2003). We found a significant positive relationship between soil urease and phosphomonoesterase activities and could draw an inference that N and P transformations were tightly coupled for the total soil NP contents. However, at higher wastewater concentrations, soil available NP contents showed contrasting trends; this observation warrants careful consideration of using wastewater in aridisol soils where P fixation and phosphatic fertilizer use efficiency is a problem.

Conclusions

We performed a 60-day laboratory soil incubation study to investigate the effects of untreated textile wastewater at 0–100 % dilutions on soil NP nutrient dynamics and activities of associated soil enzymes. Significant changes in soil pH and EC were observed when wastewater was applied at high concentrations. Activities of urease, phosphomonoesterase, and dehydrogenase enzymes increased with increase in wastewater concentration. Soil total NP contents also followed ascending trend after application of wastewater from 0 to 100 % concentration. Soil available N also increased with application of more concentrated wastewater; however, soil available P contents were the highest in soil treated with 50 % wastewater and decreased considerably at 75 to 100 % wastewater application rate. Use of industrial wastewater has been emerging as an attractive and alternative irrigation water source in arid and semi-arid regions of the world including Pakistan. Results of this study suggest foreseeing the effects of wastewater application on nutrient availability, especially, dynamics of P since P is prone to fixation and precipitation losses in aridisol. Therefore, use of nutrient rich wastewater in such soil may be considered but only after assessing the short- and long-term effects on soil nutrient status and biochemical changes.

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