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Furfural and its biochar improve the general properties of a saline soil

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Abstract. Organic materials (e.g., furfural residue) are generally believed to improve the physical and chemical properties of saline soils with low fertility. Recently, biochar has been received more attention as a possible measure to improve the carbon balance and improve soil quality in some degraded soils. However, little is known about their different amelioration of a sandy saline soil. In this study, 56 d incubation experiment was conducted to evaluate the influence of furfural and its biochar on the properties of saline soil. The results showed that both furfural and biochar greatly reduced pH, increased soil organic carbon (SOC) content and cation exchange capacity (CEC), and enhanced the available phosphorus (P) in the soil. Furfural is more efficient than biochar in reducing pH: 5 % furfural lowered the soil pH by 0.5–0.8 (soil pH: 8.3–8.6), while 5 % biochar decreased by 0.25–0.4 due to the loss of acidity in pyrolysis process. With respect to available P, furfural addition at a rate of 5 % increased available P content by 4–6 times in comparison to 2–5 times with biochar application. In reducing soil exchangeable sodium percentage (ESP), biochar is slightly superior to furfural because soil ESP reduced by 51 % and 43 % with 5% furfural and 5 % biochar at the end of incubation. In addition, no significant differences were observed between furfural and biochar about their capacity to retain N, P in leaching solution and to increase CEC in soil. These facts may be caused by the relatively short incubation time. In general, furfural and biochar exhibited a different effect depending on the property: furfural was more effective in decreasing pH and increasing available P, whereas biochar played a more important role in increasing SOC and reducing ESP of saline soil.

1 Introduction

A large saline soil reserve has been explored in the Yellow River delta. Seasonal accumulation of salt in the surface soil caused by high soil salinity and water shortage restricts the germination of plants, while poor physical and chemical properties of soil are the major obstacles of plant growth. Few categories and small amount of active substances like soil enzyme and microorganisms are important influencing factors of circulation of materials and plants' sustainable utilization of soil resources (Angst and Sohi, 2012). The low productivity of soil and soil environment deterioration in the Yellow River delta further aggravate the soil salinity (Bai et al., 2005; Wang et al., 2010), thus restricting the growth of crops. Amendment with organic materials can improve the soil salinity and increase crop yield significantly (Luo et al., 2008).

As a kind of inexpensive acid organic substance with rich resources, furfural is effective in improving the saline soil. Furfural is the corncob after industrial distillation. It is dark brown and belongs to strong acid organic materials with pH around 2. Furfural contains N(0.5 %–0.6%), P2O5(0.2–0.15 %), K2O(0.15 %), humic acid substances(36%), and the content of organic materials is above 98 % (Yang, 2008; Li et al., 2008). Cai et al. (1997) and Li et al. (2008) reported that furfural can lower the soil pH and salinity and increase crop yield. In recent years, incorporation of biochar into low fertility soils has attracted interest because biochar application increases C sequestration while also increasing soil water or nutrient availability, thereby improving plant growth (Lehmann, 2007; Marris, 2006; Renner, 2007; Zhang, 2010). Although there is some research about the influence of

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furfural on alkaline soils (Li, 2008), no comparative research on the impact of furfural on the physicochemical properties of saline soil before and after its carbonization has been reported yet. Therefore, based on the indoor constant temperature incubation and leaching test, this paper evaluated the effect of furfural in improving saline soil according to the variation trend of acid-base property, water-soluble salt, basic nutrients in soil and cation exchange performance, aiming to provide theoretical basis for the application of furfural and biochar in saline soil improvement.

2 Materials and method

2.1 Materials

In October 2012, the testing soil samples were collected at 0–10 cm depth of saline soil at Yellow River delta (37°45′50 N–118°59′24 E), which is located in the northeast of Shandong province of China. The sampling site has a warm continental monsoon climate with distinctive seasons and a rainy summer. The soil is typical saline alluvial soil (Fluvisols, FAO) developed on loess material of the Quaternary period, which was carried by water from the Loess Plateau. The collected soil samples were air-dried under room temperature and then sieved in a mesh to 2 mm. The proportion of clay, silt, and sand was 8.4 %, 6.2 %, and 85.4 %, respectively. The physicochemical properties of testing soils are shown in Table 1. The soil showed a pH of 8.3 and an ESP as high as 27 %, known as strong alkaline soil (Lu, 1999).

The involved furfural is the corncob after industrial distillation. It is in dark brown. The furfural biochar (hereinafter referred to as biochar) is made from furfural through 4 h carbonization under 300 °C under the completely or partly anoxic condition. Biochar in association with porous characteristics and high surface area is favorable to accumulating soil moisture, increasing the porosity and reducing bulk density (Wu et al., 2014). The physicochemical properties of furfural and its biochar are listed in Table 1.

2.2 Incubation method

A soil incubation test was conducted to investigate the similarities and differences of furfural and biochar in influencing the physicochemical properties of saline soil. The test involved five test treatments: (1) CK, soil without furfural and biochar; (2) T_1, added with 2.5 % furfural; (3) C_1, added with 2.5 % biochar; (4) T_2, added with 5 % furfural; and (5) C_2, added with 5 % biochar. Each group was repeated four times. In the test, each soil incubation container was filled with 500 g saline soil from the Yellow River delta with a maximum water content of 30 % (evaporated water was replenished every day by weighing method). Soil samples were incubated under constant 25 °C. We took soil samples at 1 d, 3 d, 7 d, 14 d, 21 d, 28 d, 42 d and 56 d of the incubation, respectively, for measuring pH, conductivity, available P, total carbon (TC), NO_3^--N and NH_4^+-N content. Artificial rainfall was given to the incubated soil at 4 d and 38 d by using distilled water of 200 mL. The leachate was used for measuring the P, NO_3^--N and NH_4^+-N content.

2.3 Measuring method

The physicochemical properties of the testing materials were measured by soil agricultural chemical analysis method (Lu, 1999). pH (soil/water = 1 : 2.5), electrical conductivity (EC) (water/soil = 1 : 5), total carbon (TC) and total nitrogen (TN) were measured by Elementar, Vario Micro cube. Total organic carbon (TOC) was measured by potassium dichromate oxidation/colorimetric method. Exchangeable K^+ / Ca^{2+} / Na^+ / Mg^{2+} was measured by an ammonium-acetate–flame atomic-absorption spectrophotometer. Cation exchange capacity (CEC) was measured by sodium acetate–flame atomic absorption spectrophotometer. Total phosphorus (TP) and available phosphorus (AP) were measured by molybdenum antimony colorimetric method. NO_3^--N and NH_4^+-N were measured by continuous flow analyzer (Seal, AutoAnalyzer III).

2.4 Data analysis

ESP is a key parameter of saline soil evaluation. ESP=15 is the critical value of soil structural deterioration (So and Aylmore, 1993).

$$\text{ESP } (\%) = \frac{\text{Na}^+}{\text{CEC}} \times 100, \quad (1)$$

where Na^+ is the content of exchange sodium (cmol kg^{-1}), and CEC is the cation exchange capacity (cmol kg^{-1}).

Excel 2010 and SPSS 13.0 were used for data statistical analysis. The significant differences among different groups used the one-way ANOVA. The significance level was 0.05.

3 Results and discussion

3.1 Impact of furfural and biochar on the physicochemical properties of soil

3.1.1 pH

According to Fig. 1, furfural and biochar added into soil can lower the soil pH, and the more furfural and biochar added into soil, the lower soil pH. This is mainly caused by the far lower pH of furfural and biochar compared with the soil pH. Compared with same dosage of biochar, furfural can lower the soil pH more significantly, which is mainly caused by its stronger acidity. More evenly, 2.5 % furfural lowered the soil pH more than 5 % biochar. During the incubation period, 5 % furfural lowered the soil pH by 0.5–0.8 (soil pH: 8.3–8.6), while 5 % biochar only lowered the soil pH by 0.3–0.4. Lower soil pH is beneficial for the dissolution and activation

Table 1. The physical and chemical properties of materials in this study.

	pH	EC ($ms\ cm^{-1}$)	TC	TN	Ash	CEC ($cmol\ g^{-1}$)	ESP	Fixed carbon	Volatile matter	TP	AP	NO_3^--N	NH_4^+-N	Exchange cations ($mg\ kg^{-1}$)			
			($g\ kg^{-1}$)				(%)			($mg\ kg^{-1}$)				K^+	Na^{2+}	Mg^{2+}	Ca^{2+}
Soil	8.3	0.5	16.9	1.0	ND*	7.2	26.9	ND	ND	550	5	52.2	15.4	120	446	557	3007
Furfural	2.9	3.9	394.9	9.8	112.7	37.4	13.8	ND	34.8	903	196	1.4	44.4	1132	759.5	1252	4373
Biochar	4.5	2.7	506.4	11.5	287.9	41.8	12.4	51.6	19.6	1222	139	0.8	1.7	11 616	1190	1377	9156

ND*, not determined.

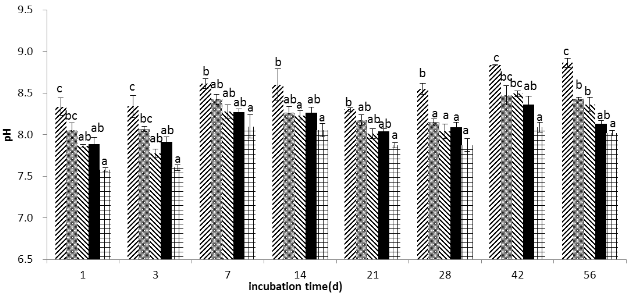

Figure 1. Effects of the added furfural and biochar on soil pH. CK; C1: soil added with 2.5 % biochar; T1: soil added with 2.5 % furfural; C2: soil added with 5 % biochar; T2: soil added with 5 % furfural. The vertical lines are means ($n = 3$) ± standard error; different letters represent significant differences (Tukey post hoc test, $p < 0.05$).

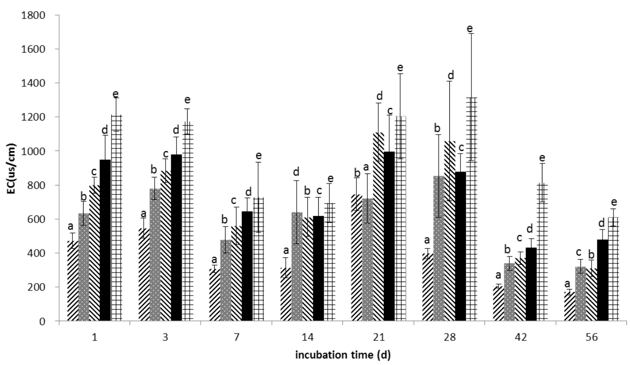

Figure 2. Effects of the added furfural and biochar on soil EC. CK; C1: soil added with 2.5 % biochar; T1: soil added with 2.5 % furfural; C2: soil added with 5 % biochar; T2: soil added with 5 % furfural. The vertical lines are means ($n = 3$) ± standard error; different letters represent significant differences (Tukey post hoc test, $p < 0.05$).

of some difficult soluble elements, thus increasing the ionic concentration of soil solution (Yuan and Xu, 2011; Nelson, et al, 2011).

3.1.2 Variation of EC

Soluble salts in the soil are proportional to the electrical conductivity, so the variation of soluble salt can be shown by the

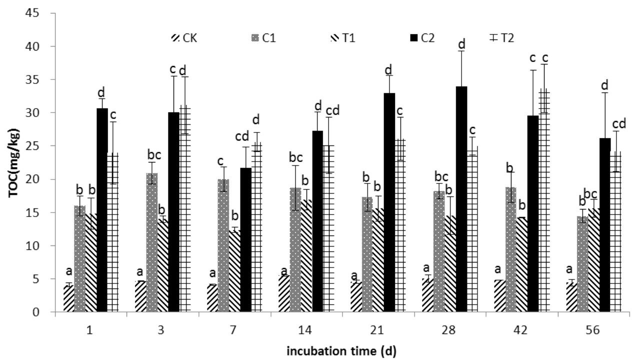

Figure 3. Effects of the added furfural and biochar on soil organic matter contents. CK; C1: soil added with 2.5 % biochar; T1: soil added with 2.5 % furfural; C2: soil added with 5 % biochar; T2: soil added with 5 % furfural. The vertical lines are means ($n = 3$) ± standard error; different letters represent significant differences (Tukey post hoc test, $p < 0.05$).

CE of the leaching liquid. In Fig. 2, EC of all five treatments decreased firstly and then increased, and it finally showed a downtrend. This reflected the great impact of artificial rainfall on the EC. Leaching carried away abundant soluble salt in soil. After the first artificial rainfall, EC of all five groups decreased. Subsequently, soil EC increased with the addition of furfural and biochar. This is possibly because soil organic matter (SOM) losses or gains in a short time are difficult to be measured directly because of (1) the large amount of organic matter in soils and (2) the low magnitude of changes compared to the total organic carbon stored in the soils (Glaser et al., 2002).

3.1.3 Variation of TOC

No significant difference of TOC change with time was discovered among all five treatments ($P > 0.05$) in Fig. 3. This may be related to the lower organic content in soil and organic losses during the leaching (Deenik et al., 2010; Keith et al., 2011). Both furfural and biochar can increase the TOC content in soil significantly, especially the biochar. Treatments with biochar showed a TOC content increase up to 8 times compared to CK, which is mainly caused by the higher organic content of biochar. The TOC content of biochar is 89 times that of soil, and the TOC content of furfural is 67

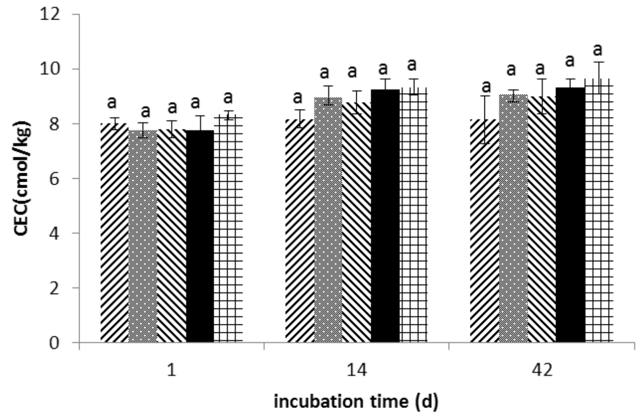

Figure 4. Effects of the added furfural and biochar on soil CEC. CK; C1: soil added with 2.5 % biochar; T1: soil added with 2.5 % furfural; C2: soil added with 5 % biochar; T2: soil added with 5 % furfural. The vertical lines are means ($n = 3$) ± standard error; different letters represent significant differences (Tukey post hoc test, $p < 0.05$).

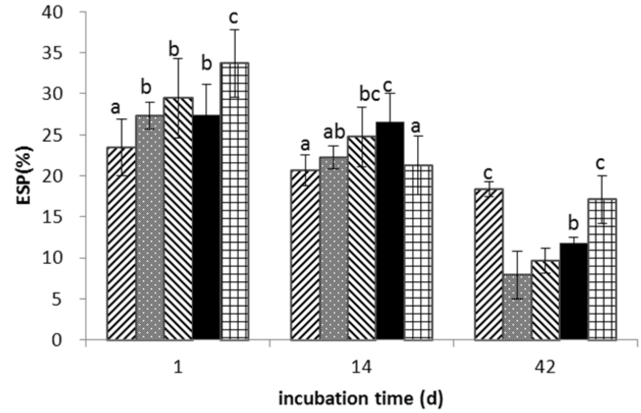

Figure 5. Effects of the added furfural and biochar on soil exchange ESP. CK; C1: soil added with 2.5 % biochar; T1: soil added with 2.5 % furfural; C2: soil added with 5 % biochar; T2: soil added with 5 % furfural. The vertical lines are means ($n = 3$) ± standard error; different letters represent significant differences (Tukey post hoc test, $p < 0.05$).

times that of soil. Chan et al. (2011) and Uzoma et al. (2012) also reported a significance increase of TOC in soil by adding biochar, which is important for soil quality improvement.

3.1.4 Variation of CEC and ESP

In Fig. 4, biochar (compared with furfural) failed to increase the soil CEC significantly as the incubation time went on, which may be related to the short incubation period (Liang et al., 2006). As the incubation time went on, surface groups of biochar were oxidized, which increased the surface charge density and thereby increased the CEC significantly (Cheng et al., 2008). Both furfural and biochar can increase the soil CEC ($P < 0.05$) and 5 % biochar increased the soil CEC by 15 %, indicating the involvement of furfural and biochar can increase the buffer performance of soil (Liang et al., 2006). This is because the large specific surface area of organic matter and negatively charged functional groups increased the exchange point of soil colloids, thus increasing the CEC (Lehmann, 2009).

In Fig. 5, ESP decreased more significantly when adding biochar compared with the furfural as the incubation time went on. But at the beginning of the experiment, ESP is increased. At the end of the test, ESP of T_2 and C_2 decreased to 51 % and 43 % of their initial ESP, respectively. On one hand, biochar has a high concentration of exchange Ca^{2+} / Mg^{2+} to replace Na^{+} for soil colloidal absorption (Hu and Wang, 1987; Lashari et al., 2013), thus decreasing the exchange Na^{+} in the soil. Table 1 represents that biochar contains 3 times higher exchange Ca^{2+} than soil. On the other hand, biochar with loose and porous texture can increase the total porosity of soil (Lehmann and Joseph, 2009), thus losing more exchange Na^{+} during rainfall and reducing the ESP.

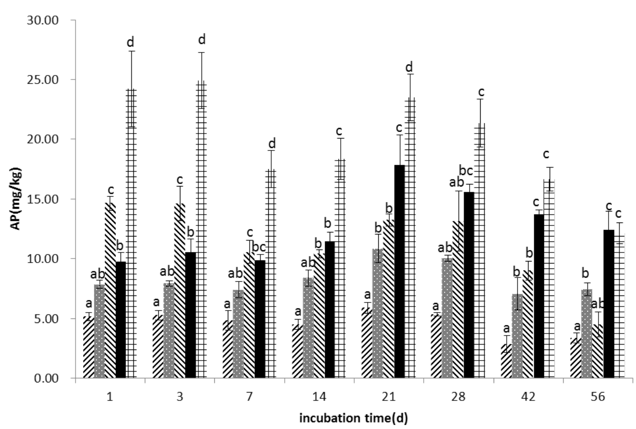

Figure 6. Effects of the added furfural and biochar on soil available P contents. CK; C1: soil added with 2.5 % biochar; T1: soil added with 2.5 % furfural; C2: soil added with 5 % biochar; T2: soil added with 5 % furfural. The vertical lines are means ($n = 3$) ± standard error, different letters represent significant differences (Tukey post hoc test, $p < 0.05$).

3.1.5 Variation of AP

A significant increase of AP content in alkaline soil was observed by adding furfural and biochar (Fig. 6). On one hand, both furfural and biochar can lower the soil acidity due to their lower pH value, which is accompanied by a significant increase of AP (Devau et al., 2011). On the other hand, furfural and biochar have higher AP content. The AP content in furfural is about 40 times that in soil (Table 1). Therefore, the application of furfural can increase the AP content in soil directly. The AP content was increased by 2–5 times by adding 5 % biochar and 4–6 times by adding 5 % furfural. This indicated the better performance of furfural compared

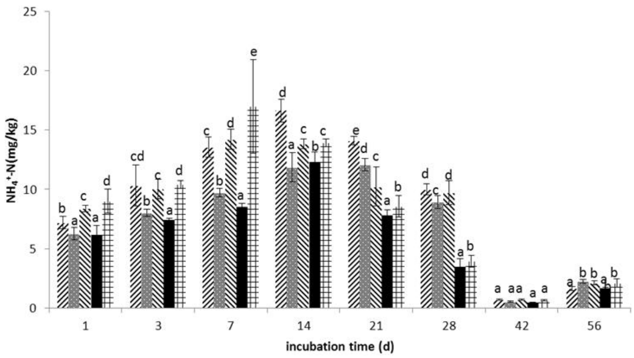

Figure 7. Effects of the added furfural and biochar on soil NH_4^+-N contents. CK; C1: soil added with 2.5 % biochar; T1: soil added with 2.5 % furfural; C2: soil added with 5 % biochar; T2: soil added with 5 % furfural. The vertical lines are means (n = 3) ± standard error; different letters represent significant differences (Tukey post hoc test, $p < 0.05$).

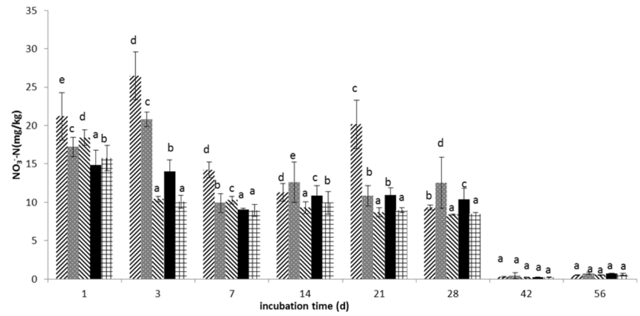

Figure 8. Effects of the added furfural and biochar on soil NO_3^--N contents. CK; C1: soil added with 2.5 % biochar; T1: soil added with 2.5 % furfural; C2: soil added with 5 % biochar; T2: soil added with 5 % furfural. The vertical lines are means (n = 3) ± standard error; different letters represent significant differences (Tukey post hoc test, $p < 0.05$).

with biochar in AP growth. According to Table 1, during the carbonization of furfural, the AP content decreased although TP content increased, indicating the occurrence of phosphorus immobilization during the carbonization of furfural (Parvage et al., 2013). This corresponds to the significant increase of exchange Ca^{2+} during the carbonization. Therefore, the significant increase of exchange Ca^{2+} during the carbonization leads to the reduction of AP content (Tunesi et al., 1999).

3.1.6 Variation of NO_3^--N and NH_4^+-N

In Fig. 7, NH_4^+-N in all five treatments increased firstly and then decreased. It reached the peak at 14 d and then decreased gradually. At the end of the test, NH_4^+-N decreased to less than 2 mg kg^{-1}. This may be caused by the gradual decrease of organic nitrogen that is easy to be mineralized (Stanford and Epstein, 1974; Powers, 1990; Wennman and Kätterer, 2006), increased ammonia volatilization in soil due to the increased soil pH value (Dancer et al., 1973; Xu, 2012, 2013) and NH_4^+-N losses caused by leaching. Significant decrease of NO_3^--N concentration was observed after two artificial rainfall events (Fig. 8). Particularly, NO_3^--N concentration of five groups decreased by more than 95 %, indicating the easy leaching losses of NO_3^-N (Delgado, 2002).

It can be seen from Figs. 7 and 8 that furfural and biochar did not increase the inorganic nitrogen in soil ($P > 0.05$). Singh (2010) also reported similar results which may be caused by lower inorganic nitrogen content in biochar.

3.2 Impact of furfural and biochar on soil leachate

It can be known from Table 2 that, during the first leaching process, leachate from groups with biochar and furfural showed an obvious increase of NH_4^+-N concentration. The NH_4^+-N concentration in the leachate increased with the increase of furfural and biochar dosages. During the second leaching process, no significant difference of NH_4^+-N concentration in all five treatments was observed. With the increase of leaching processes, the NH_4^+-N and NO_3^--N concentrations in leachate from all treatments decreased significantly. The NO_3^--N concentrations in leachate from C_1 decreased from 14.85 mg L^{-1} of the first leaching process to 0.6 mg L^{-1}. The involvement of furfural and biochar did not reduce the leaching losses of inorganic nitrogen. Soluble salts, such as NO_3^--N and NH_4^+-N, will become dissolved and lost during rainfall or irrigation.

During the two leaching processes in this test, AP concentration in leachate from C_1 and C_2 increased, which goes on continuously with the enhanced biochar dosage. This may be caused by the poor AP retaining capacity of biochar, thus making AP easy to lose through leaching. However, the AP concentration in leachate from T_1 and T_2 decreased with the increase of furfural dosage, indicating its better retaining capacity of AP compared to biochar.

4 Conclusions

A short-term (56 d) incubation experiment was conducted to compare the amendments of furfural and its biochar on the properties of saline soil. The results showed that both furfural and biochar can improve the fertility of studied soil because the reduced pH, increased soil organic carbon (SOC) content and cation exchange capacity (CEC), and enhanced the available phosphorus (AP) will increase plant growth in this soil. Compared with biochar, furfural was more pronounced in decreasing soil pH and improving phosphorus availability; 5 % biochar can increase the AP content by 2–5 times, while 5 % furfural can increase the AP content by 4–6 times. This is possibly related to the lower pH value of furfural. In addition, biochar increases more SOC content and greatly decreases exchangeable sodium percentage (ESP) of the soil.

Table 2. Change of inorganic N and available P in leaching solution. CK (control); C1 (soil added with 2.5 % biochar); T_1 (soil added with 2.5 % furfural); C2 (soil added with 5 % biochar); T_2 (soil added with 5 % furfural).

Treatment	Leaching first incubation for 3 d			Leaching second incubation for 38 d		
	NH_4^+-N (mg L^{-1})	NO_3^--N (mg L^{-1})	AP (µg L^{-1})	NH_4^+-N (mg L^{-1})	NO_3^--N (mg L^{-1})	AP (µg L^{-1})
CK	0.41 ± 0.15a	28.93 ± 5.05a	65.25 ± 6.21a	0.18 ± 0.07a	2.22 ± 1.92a	27.62 ± 10.5a
C1	2.68 ± 0.96bc	14.85 ± 3.75b	73.45 ± 3.59a	0.49 ± 0.17b	0.6 ± 0.37a	36.06 ± 11.06a
T1	1.02 ± 0.01a	61.13 ± 3.69c	61.98 ± 5.11a	0.26 ± 0.09a	0.15 ± 0.02a	25.58 ± 7.66a
C2	2.94 ± 0.28c	40.97 ± 6.88d	88.47 ± 7.51b	0.18 ± 0.003a	0.54 ± 0.57a	64.53 ± 8.66b
T2	1.97 ± 0.31b	80.34 ± 9.08e	59.24 ± 6.89a	0.2 ± 0.09a	0.47 ± 0.31a	18.66 ± 3.71a

This is possibly related to the porous structure of biochar and its higher exchange Ca^{2+} content. In general, furfural and biochar exhibited a different effect depending on the property: furfural was more effective in decreasing pH and increasing available P, whereas biochar played a more important role in increasing SOC and reducing ESP of saline soil.

Nomenclature.

EC:	electrical conductivity
TC:	total carbon
TN:	total nitrogen
TP:	total phosphorus
AP:	available phosphorus
SOC:	soil organic carbon
CEC:	cation exchange capacity
ESP:	exchangeable sodium percentage

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