Llovet Martin, Alba; Vidal Durà, Andrea; Alcañiz, Josep M; [et al.]. «Biochar addition to organo-mineral fertilisers delays nutrient leaching and enhances barley nutrient content». Archives of Agronomy and Soil Science, Vol. 69, issue 13 (2023), p. 2537-2551. 15 pàg. DOI 10.1080/03650340.2022.2161092

Biochar addition to organo-mineral fertilisers delays nutrient leaching and enhances barley nutrient content

Alba Llovet[1,2,3] . Andrea Vidal-Durà[1,2] . Josep Maria Alcañiz[1,2] . Angela Ribas[1,2,3] . Xavier Domene[1,2]

[1] BABVE, Edifici C, Universitat Autònoma de Barcelona, 08193 Bellaterra, Spain

[2] CREAF, Cerdanyola del Vallès 08193, Spain

[3]Centre Tecnològic Forestal de Catalunya (CTFC), 25280 Solsona, Spain

* Corresponding author at: UAB, 08193 Cerdanyola del Vallès, Spain. E-mail address: a.llovet@creaf.uab.cat (A. Llovet).

This is an original manuscript of an article published by Taylor & Francis in Archives of Agronomy and Soil Science on December 2022, available at: http://www.tandfonline.com/10.1080/03650340.2022.2161092

Abstract

Biochar, a carbon-rich solid produced from biomass pyrolysis, has attracted growing interest as a fertiliser ingredient due to its ability to non-permanently retain nutrients. A greenhouse pot experiment was set up to compare three commercial organo-mineral fertiliser formulations (NPK, NP and K) with the corresponding formulations containing a slow-pyrolysis wood biochar (NPK+B, NP+B and K+B). Nutrient leaching as well as crop growth and crop nutrient uptake were monitored using barley as model species. Nutrient leaching was slowed down in the NPK+B compared to the NPK fertiliser. The most responsive ions were nitrate and potassium, whose leaching during the two first weeks was reduced by 28 % and 22%, respectively, while this trend reversed from the third week on. One plausible explanation would be a microbial nutrient immobilisation mediated by the concurrent NPK and biochar habitat provision. NPK+B significantly enhanced barley straw biomass (23.43 % increase respect to NPK), whereas all the biochar-based fertilisers showed increases in nutrient content and export (involving potassium, sulphur, calcium and manganese), possibly indicating that biochar acted as a nutrient source. These results provide some evidence of the potential use of the studied biochar in biochar-based fertilisers to meet nutrient availability with plant demands.

Keywords: biochar-based fertilisers; nutrient leaching; barley; crop growth; nutrient content

Introduction

Nitrogen (N), phosphorus (P), and potassium (K) are the main limiting nutrients for crop growth, but due to the high solubility of traditional mineral fertiliser formulations, there is a poor synchrony between N, P, and K release rate and crop uptake needs (Pang et al. 2018). Apart from solubilisation and subsequent leaching losses, other processes such as NH_3 volatilisation and denitrification, in the case of N (Cameron et al. 2013), or P retrogradation (Vanderdeelen 1995), also contribute to low nutrient use efficiency by plants. As a matter of fact, plant nutrient uptake from mineral fertilisers has been reported to be as low as 33-50% for N (Raun and Johnson 1999; Hirel et al. 2011) and 10- 25% for P (Syers et al. 2008), which results in economic costs for farmers and has environmental risks associated. Namely, N and P leaching and runoff to water bodies provokes eutrophication (Vitousek et al. 1997) and have been linked to human health risks, such as the carcinogenic effect of N-nitroso compounds formation after nitrate-polluted drinking water exposure (Ward et al. 2018).

Furthermore, conventional NPK fertiliser production involves a high amount of fossil fuels and energy for N industrial fixation (Haber-Bosch process), and exploitation of non-renewable resources (phosphate rock and potash) in the case of P and K (Blanco 2011). This is why there is an urgent need to develop fertiliser formulations able to increase nutrient availability without further compromising natural resources. Strategies which might be used for this purpose include: preventing nutrient losses, e.g. by using slow-release fertilisers (Calabi-Floody et al. 2018); promoting waste's nutrient recycling, either by using organic waste combinations, hybrid fertilisers that combine organic wastes enriched with mineral components (Kominko et al. 2017), or by adding nutrient–solubilising microorganisms (Das and Pradhan 2016); and using new nutrient sources such as struvite (Talboys et al. 2016). The use of biochar as fertiliser ingredient would mostly fit with the first strategy, for its known nutrient retention capacity.

Biochar, the solid co-product of pyrolysis, has been widely proposed as an effective tool to increase the refractory C pool in soils but also to enhance nutrient retention and reduce nutrient leaching out of the root zone (Lehmann et al. 2003; Laird 2010a). Different mechanisms have been put forward to explain biochar's retentive capabilities, such as: (1) electrostatic adsorption of nutrients onto biochar due to its micropore structure (physisorption) (Nguyen et al. 2017) or surface charge (chemisorption), the latter including both negative functional groups (Liang et al. 2006), and, although less commonly reported, positively charged functional groups (Lawrinenko and Larid 2015); (2) the retention of nutrient-enriched water in biochar's pores (Brockhoff et al. 2010; Lehmann et al. 2003); (3) biochar-induced pH alterations which can affect solubility and leachability of nutrients (Laird and Rogovska 2015); (4) redox status alteration (Chacón et al. 2017); and (5) by influencing nutrient cycling through biochar's interaction with soil microbes, e.g., by nutrient immobilisation in microbial biomass (Novak et al. 2010; Ippolito et al. 2012).

Despite the beneficial effects of some biochars when applied on its own, a great deal of research has demonstrated that the co-application of biochar with inorganic or organic fertilisers could exert synergistic effects on crop yields, and indeed, it is sometimes required to achieve any agronomic benefits (Alburquerque et al. 2013; Mete et al. 2015; Oladele et al. 2019; Pandit et al. 2019). Consequently, the importance of optimising biochar application in the form of new-generation fertilisers, i.e. being able to reduce biochar application rates and concomitantly improve nutrient use efficiency, has been highlighted (Joseph et al. 2013). Although the development of biochar-based fertilisers is still in its infancy, there are some examples with promising results (Chen et al. 2018; Chew et al. 2020; Liao et al. 2020; Luo et al. 2021). In this direction, the use of biochar in organic farming as a fertiliser or soil conditioner was approved in Europe in 2019, by amending the Annex I of Regulation (European Commission) No 889/2008 (European Parliament 2019).

The main aim of this study was to elucidate if biochar inclusion in fertiliser formulation of three organo-mineral fertilisers could enhance nutrient retention and thus act as slow-release fertilisers, by reducing or by at least delaying nutrient leaching losses, coupled to an improved crop nutrient uptake and growth. For this purpose, a pot experiment using barley as model crop was used to compare three conventional organo-mineral fertilisers (NPK, NP, and K) with the corresponding biochar-based fertilisers (NPK+B, NP+B, and K+B). Nutrient dynamics shifts and plant use efficiency were assessed by leachate nutrient content monitoring, plant nutrient uptake and biomass quantification.

Materials and methods

Experimental setup

The greenhouse pot experiment was conducted at the IRTA Torre Marimón experimental station in Caldes de Montbui (Barcelona, NE Spain)). Six organo-mineral fertilisers produced by Desarrollos Agroquímicos S.A. DASA-ELFER (Menàrguens, Lleida, Spain) were tested in a fully randomised design with six-fold replication. Fertilisers were produced in a tablet form (see **Supplementary Fig. S1**), all of them contained maize flour in their formulation and differed in their macronutrient content (NPK, NP and K), and in the presence of biochar (+B). The six resulting combinations were designated as NPK, NP, K, NPK+B, NP+B, and K+B. The exact formulation is not shown for being subject to business confidentiality but it should be noted that N was provided as a mixture of ammonium and organic sources while P and K were supplemented in an inorganic form (carbon (C) content, and C/N ratio of fertilisers are shown in **Table 1**).

Table 1 Carbon content (%); C/N ratio; dosing of fertiliser (g pot^{-1}) and application rates of N, P, K, and biochar (mg kg^{-1} soil) for each fertiliser

			Application rate				
Fertiliser	**C (%)**	**C/N ratio**	**g fertiliser pot $^{-1}$**	**mg N kg^{-1}**	**mg P kg^{-1}**	**mg K kg^{-1}**	**mg biochar kg^{-1}**
NPK	40.44	15.67	4.74	66.67 [a]	171.28	108.04	0
NPK+B	43.78	15.89	4.38	66.67	160.83	99.76	1046.23
NP	41.58	10.12	2.96	66.67	110.02	0	0
NP+B	44.29	10.41	2.84	66.67	106.07	0	551.62
K	38.62	-	1.31	0	0	108.04	0
K+B	41.12	-	1.31	0	0	108.04	217.52

[a] 66.67mg N kg^{-1} = 173.3 kg N ha^{-1}

The biochar used for NPK+B, NP+B, and K+B formulations was produced by slow pyrolysis (400-550 ºC, 120 min) from a mixed feedstock of *Quercus ilex*, *Quercus suber*, and *Eucalyptus* sp., and obtained by Corchos Oliva S.L. (Oliva de la Frontera, Badajoz, Spain). A detailed characterisation of the biochar is presented in **Table 2**.

Table 2 Characteristics of the biochar used in the experiment

Parameter	**Unit**	**Value**	**Method**
C	g kg^{-1}	632.3	elemental analysis
N	g kg^{-1}	4.5	elemental analysis
H	g kg^{-1}	21.7	elemental analysis
S	g kg^{-1}	0.8	elemental analysis
O	g kg^{-1}	94.3	difference of sum of elemental analysis and ash
O/C_{org}	%	0.14	
H/C_{org}	%	0.41	
Ash (540 ºC)	%	24.64	
Volatile matter	%	22.69	
P	g kg^{-1}	1.02	
Na	g kg^{-1}	0.48	
K	g kg^{-1}	4.90	
Ca	g kg^{-1}	41.00	
Mg	g kg^{-1}	3.16	
pH (H_2O, 1:20)	-	8.5 ± 0.63	
EC (25ºC, 1:20)	dS m^{-1}	0.4 ± 0.003	
CEC	$mmol_c$ kg^{-1}	4.23 ± 0.27	ISO 23470, 2007
Surface area (BET)	m^2 g^{-1}	135.73	N_2 adsorption isotherm, 77K
Porosity	%	56.69	Hg porosimetry
Mean porus size	nm	180.6	Hg porosimetry

The top soil layer (0–20 cm depth) of a deep calcareous sandy-loam alluvial soil (a Fluventic Haploxerept, according to Soil Survey Staff, 2010), was collected from the IRTA Torre Marimón experimental farm (41º36’47” N, 2º10’16” E) and used as soil matrix for the experiment. The soil had a 0.74 % of organic carbon (Walkley-Black), presented an alkaline pH ($pH_{1:2.5} = 8.2$) and corresponded to a sandy loam textural class (56.4% sand, 24.9% silt, and 18.7% clay) (see Marks et al. 2016 for a detailed soil description).

Pots with a height of 20 cm were filled with 1.8 kg of soil sieved to 5 mm. On the onset of the experiment, the amount of fertiliser tablets to provide 66.67 mg N kg^{-1} (equivalent to 173.3 kg N ha^{-1}) for N-containing fertilisers, and equivalent K contents for K-containing fertilisers (**Table 1**) were added to each pot at a 5 cm depth. Biochar addition rates were not possible to even out (**Table 1**) since each fertiliser formulation differed in its biochar proportion for stability purposes. Aside from fertilisation, pots were watered to field capacity (around a 20 % moisture content) and fifteen barley seeds (*Hordeum vulgare* L. Graphic variety) were sown (thinned to three plants after a fortnight period). Plants were grown under a photoperiod of 14 h light:10h dark.

Leaching assay

Pots contained a 2 mm mesh gauze at the bottom to allow proper drainage while preventing soil losses. Soil water content was determined gravimetrically before the leachate sampling and used for the estimation of the water to be added to achieve a target leaching volume of 100 ml per pot. Distilled water was used for leaching, and, to simulate natural rainfall, water was slowly added to the pots using perforated bottles. The leachate was collected by placing each pot on a glass tray but raised 1.3 cm to ensure drainage. A total of nine leaching events were carried out. Leachates were collected once per week during the first five leaching events; then, the sampling frequency was extended to two weeks and, finally, to three weeks (see sampling schedule in **Fig. 1**). The collected leachate was then filtered (using Whatman no. 42 filters) under laboratory conditions and stored at -20°C until analysis.

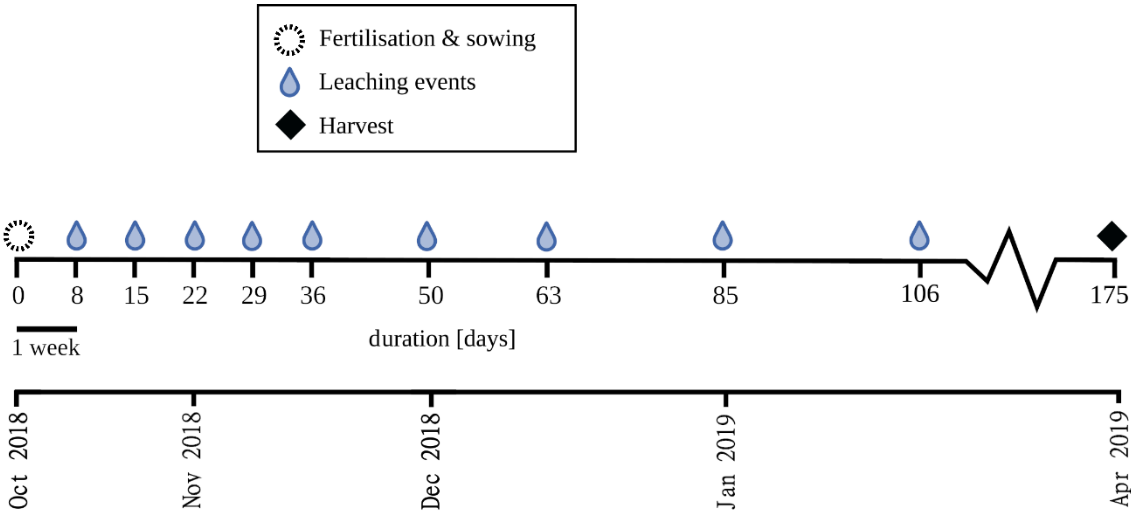

Fig. 1 Experimental schedule showing fertilisation and sowing, leaching events, and harvest.

Water-soluble ions in leachates were measured as proxy for nutrient availability. Although Na^+ is not generally considered an essential element for plant nutrition it was ascribed under the 'plant nutrient' category for being a beneficial element (sensu Brown et al 2021). Liquid chromatography was carried out to determine leachate inorganic ions content on a Dionex ICS-1100 ion chromatograph (Dionex, Sunnyvale, USA) using a AS4A-SC Dionex anion column for the quantification of Cl^-, NO_2^-, NO_3^-, HPO_4^{2-} and SO_4^{2-}, and a CS12A Dionex cation column for Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+} determination. All the ion concentrations were estimated using linear calibration except for SO_4^{2-}, NH_4^+, Mg^{2+}, and Ca^{2+}, in which quadratic regression substantially increased the fitting (R^2). Detection limit (LOD) estimation was set as three times the standard deviation of five blank values. NO_2^- concentration values were not considered in this study for being almost always below detection limits (i.e. < 0.10 mg NO_2^- L^{-1}). Additionally, HPO_4^{2-} was also discarded from analysis since its signal-to-noise ratio in the chromatogram did not exceed the set value of 3. Leachate ionic concentration was quantified both as absolute and cumulative leaching and was expressed as mg per dry weight (kg) of soil, according to the following equation (Eq. (a)):

$$LIC_{soil}\ (mg\ kg^{-1}) = \frac{[LIC_{LC}\ mg\ L^{-1}]\ x\ [water\ added\ for\ leaching + water\ in\ soil\ (L)]}{kg\ soil\ dry\ weight} \qquad (a)$$

Where LIC_{soil} stands for leachate ionic concentration expressed on a soil dry weight basis, and LIC_{LC} for leachate ionic concentration as obtained from liquid chromatography.

Plant measurements

Above-ground barley biomass was harvested after plants were fully grown and senescent (after a 6-month growth period) and dried at 60ºC for 48 h. The total number of ears and the number of grains per ear were quantified. Then, straw and grain were weighed separately to determine their biomass. After straw and grain were ground in a ball-mill, nutrient content (N, P, K, Ca, Mg, S, Fe, Mn, and Zn) was determined through near infrared spectrometry (NIRS) by scanning the grounded samples from 1100 to 2500 nm in a NIRSystems 5000 scanning monochromator (FOSS, Hilleröd, Denmark). The calibrations used were developed in a previous study (see the Supplementary Materials in Martos et al. 2020 for more details). P content in straw presented some negative values that were set to 0. Finally, nutrient export was calculated by multiplying each nutrient concentration measurement by its corresponding biomass.

Statistical analyses

Since the objective of this research is to compare fertilisers with and without biochar inclusion in its formulation, statistical tests involved comparisons between each organo-mineral fertiliser (without biochar) and its counterpart with biochar (i.e. NPK vs NPK+B; NP vs NP+B, and K vs K+B). Longitudinal data, i.e. variables for which exist a between-subjects factor (biochar inclusion in the fertiliser), and a within-subjects factor (sampling dates) were analysed using two-way mixed ANOVAs, which were computed with the *rstatix* package v0.2.0 (Kassambara 2019b). Before, Shapiro-Wilk and Levene tests were used to ensure that data had a normal distribution and homogeneous variances, respectively. When these assumptions were not met, the test was run on the $\log_{10}$-transformed variable. The assumption of sphericity was checked using the Mauchly's test, and when violated, the Greenhouse-Geisser correction was applied. Finally, homogeneity of covariances was tested by Box's M. Statistical results of the mixed ANOVA are shown in **Supplementary Table S1** (**S1.1.-S1.48.**). Pairwise comparisons were tested with t-test with Bonferroni adjustment, and the significance level was set at $p < 0.05$. These statistical analyses and results visualisation were performed using R software v. 3.6.1 (R Core Team 2021) using the packages *ggplot2* (Wickham 2016) and *ggpubr* v 0.2.3 (Kassambara 2019a).

For absolute nutrient leaching data the Principal Response Curves (PRC) method (Van den Brink and Ter Braak 1999), developed for biological community data, was conducted using the CANOCO software version 5.12 (Ter Braak and Šmilauer 2012). The PRC describe the trajectory over time of the community response (nutrients in this study) in each treatment group, expressed as coefficient of community response, i.e. the canonical coefficient C_{dt}, relative to the control (which response is set to 0); whereas the weight (b_k) indicates the affinity of the response of each attribute (here ions in leachates) to the overall community response. Positive b_k values indicate attributes whose response pattern follows the PRC, by contrast, negative values indicate attributes whose response pattern is in the opposite fashion to the overall PRC pattern. Near zero b_k values represent weak responses or response patterns unrelated to the PRC. Given the disparity of nutrient concentration ranges, data was standardised to zero-mean and unit-variance prior analysis. Significance of the first axis was checked with a Monte Carlo permutation test while significances at each time point were evaluated by performing redundancy analysis (RDA) on subsets of different sampling dates.

Finally, those parameters analysed at a single sampling date (plant measurements) were assessed by means of Student t-test, Welch's t-test (if homoscedasticity assumption was not met) or the Mann-Whitney-U test (if normality assumption was not met), all of them with Bonferroni correction (*rstatix* package v 0.2.0 (Kassambara 2019b)). When mixed ANOVA analysis of longitudinal data was not significant, differences at each sampling date were also checked with this approach.

Results

Nutrient leaching

The pair of fertilisers NPK vs NPK+B (**Fig. 2a**) was the only one showing significant results on nutrient leaching patterns as measured by the PRC analysis (**Fig. 2**), with 80.18% of the total variance being explained by time and 5.78% by biochar treatment. A significant proportion of the variance (52.21%) was captured by the first canonical axis of the PRC (Monte Carlo permutation test, 499 permutations, $F = 1.8$, $p = 0.018$). The RDA analyses at each sampling time showed contrasted and significant temporal effects associated to biochar inclusion in the formulation. At the first leaching events (days 8 and 15 since experimental onset) the NPK+B leached less nutrients in contrast to the NPK. However, at the third leaching event (day 22) this trend was inverted, and from that moment onwards, NPK+B leached more nutrients than NPK (significantly at days 22, 36, 85 and 106). As shown by b_k values of the PRC, the most responsive nutrients were NO_3^--N ($b_k = 1.50$) followed by K^+ ($b_k = 1.26$), whereas NH_4^+ was the only ion showing an inverse pattern with respect to the PRC ($b_k = -0.53$).

Regarding the absolute leaching of each ion plotted separately (**Supplementary Figs. S2 and S3**), the results of mixed ANOVA showed significant interactions between biochar treatment and time for NO_3^--N, NH_4^+-N, Na^+, K^+, and Ca^{2+} (**Supplementary Tables S1.1-4** and **S6**) in the NPK vs NPK+B fertiliser pair. In addition, Mg^{2+}, Cl^- and SO_4^{2-} also showed significant effects at some sampling dates for the same pair of fertiliser (**Supplementary Figs. S2 and S3**). These ions mostly followed the same trend explained in the PRC analysis, i.e. more leaching in the NPK fertiliser at the first weeks and the inverse trend in the subsequent weeks. As an example, in the NPK+B treatment, NO_3^--N and K^+, decreased their leaching at the two first weeks by a 27.99 % and a 22.01 %, respectively. That was not the case for ammonium, whose leaching was slightly higher (0.5 mg kg^{-1}) in the NPK+B compared to NPK at the first sampling time. Concerning the NP and K fertiliser pairs, only sparse significant results were found and thus there was no clear pattern on nutrient leaching as mediated by biochar.

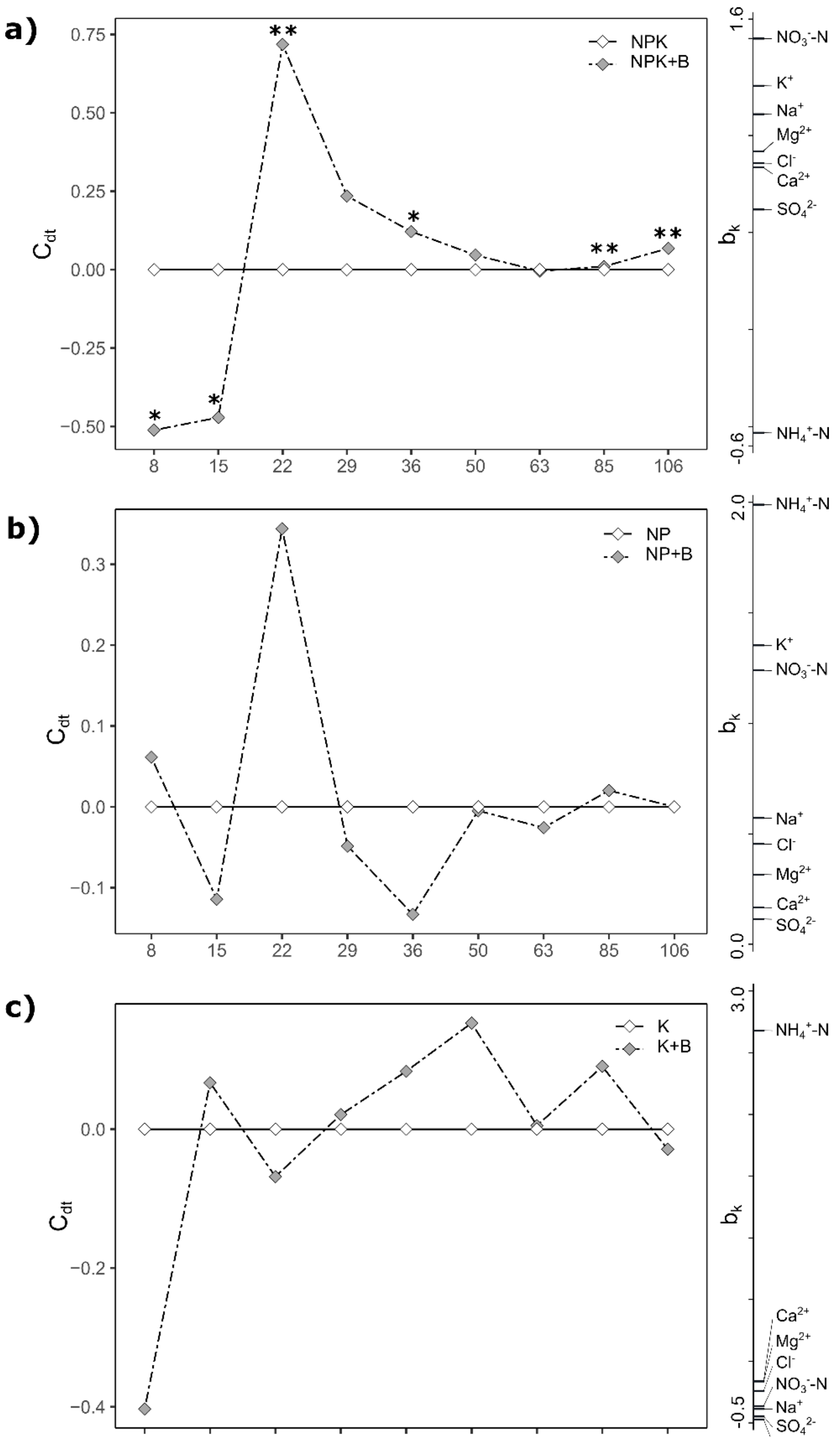

Fig. 2 PRC diagram (left) and weight (bk) (right), for the first principal component of nutrient leaching in the fertiliser pairs NPK vs NPK+B (a); NP vs NP+B (b); and K vs K+B (c) showing shifts caused by biochar inclusion in fertiliser formulation in comparison to the conventional (without biochar) fertiliser along nine sampling dates. *,** indicate significant differences at p values comprised between 0.05 and 0.01, and between 0.01 and 0.001, respectively.

The results of mixed ANOVA evidenced time effects always being significant (**Supplementary Tables S1.1-24**), i.e. there was a generalised plunge in all ions for every fertiliser pair at about the fifth leaching event. Concerning the nitrogen forms, it should be noted that, NO_3^--N content was about two orders of magnitude larger than that of NH_4^+-N at the first samplings, while from the fifth leaching event ionic content was similar (and lower) for the two ions (**Supplementary Figs. S2 and S3**).

Finally, in the matter of cumulative nutrient leaching, whereas sparse significant differences were found at the first sampling dates, there were no significant differences on the final cumulative amount of nutrients leached associated to biochar inclusion in fertiliser formulation (**Supplementary Figs. S4 and S5**).

Barley growth parameters

Barley straw weight was significantly enhanced in the NPK+B fertiliser (23.43 % increase) in contrast with NPK according to Welch's t-test, *t* (5.68) = -2.61, p = 0.04. However, the higher straw biomass in the NPK+B fertiliser did not concur with significantly higher grain yield on this same treatment, although it was marginally improved (Welch's t-test, *t* (6.0) = -2.25, p = 0.065) (**Fig. 3a** and **b**). Ear number and grain number per ear were not significantly different within any pair of fertilisers (**Fig. 3c** and **d**).

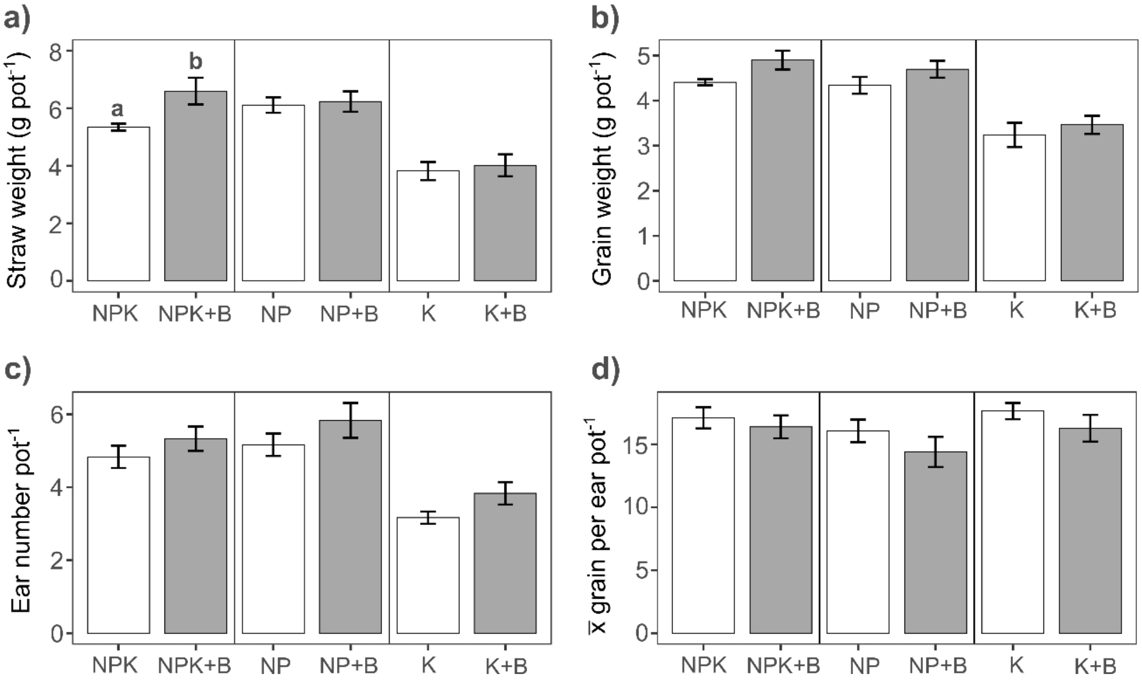

Fig. 3 Mean (± SE) (n = 6) straw weight (g pot^{-1}) (a); grain weight (g pot^{-1}) (b); ear number per pot (c); and grain number per ear averaged per pot. Different letters indicate statistically significant differences within a fertiliser pair (NPK vs NPK+B, NP vs NP+B, and K vs K+B).

Barley nutrient content and export

Grain nutrient content was unaffected by any of the treatments within any fertiliser pair (**Table 3**). However, the NP+B fertiliser did increase Ca (t-test, *t* (10) = -2.59, p = 0.03) and Mn export in grain (Mann-Whitney test, *U* = 5, z = -2.04, p = 0.04) compared to the NP fertiliser (**Table 4**). Concerning straw nutrient content and export, some beneficial effects were found for the biochar-based fertilisers. Precisely, K content (Welch's t-test, *t* (5.33) = -2.53, p = 0.049) and export (Welch's t-test, *t* (5.43) = -3.11, p = 0.02), together with S export (Welch's t-test, *t* (5.69) = -4.39, p = 0.01) were higher at the NPK+B in contrast with the NPK fertiliser (**Tables 3** and **4**). In addition, Mn content (t-test, *t* (10) = -2.53, p = 0.03) and both Ca content (**Table 3**) (Mann-Whitney test, *U* = 4, z = -2.17, p = 0.03) and export (**Table 4**) (Mann-Whitney test, *U* = 5, z = -2.04, p = 0.04) were improved at the K+B compared to the K fertiliser.

Table 3 Nutrient content in grain and straw of harvested barley for the six organo-mineral fertilisers. Reported values are mean ± standard errors (n = 6). Different letters indicate statistically significant differences within a fertiliser pair (NPK vs NPK+B, NP vs NP+B, and K vs K+B)

	NPK	**NPK+B**	**NP**	**NP+B**	**K**	**K+B**
Grain						
N (g kg^{-1})	8.68 ± 0.2	8.84 ± 0.2	9.00 ± 0.2	8.97 ± 0.3	9.23 ± 0.1	9.28 ± 0.2
P (g kg^{-1})	6.18 ± 0.1	6.08 ± 0.1	6.25 ± 0.1	6.13 ± 0.3	6.56 ± 0.1	6.45 ± 0.1
K (g kg^{-1})	5.60 ± 0.1	5.53 ± 0.3	5.87 ± 0.2	5.84 ± 0.2	6.00 ± 0.1	5.77 ± 0.1
S (g kg^{-1})	0.40 ± 0.0	0.38 ± 0.0	0.43 ± 0.0	0.43 ± 0.1	0.47 ± 0.0	0.38 ± 0.0
Ca (g kg^{-1})	1.34 ± 0.0	1.30 ± 0.1	1.32 ± 0.1	1.39 ± 0.0	1.20 ± 0.1	1.17 ± 0.0
Mg (g kg^{-1})	1.26 ± 0.0	1.25 ± 0.0	1.30 ± 0.0	1.27 ± 0.0	1.32 ± 0.0	1.30 ± 0.0
Mn (mg kg^{-1})	1.41 ± 0.0	1.28 ± 0.1	1.37 ± 0.0	1.38 ± 0.0	1.51 ± 0.1	1.51 ± 0.0
Zn (mg kg^{-1})	4.84 ± 0.0	4.94 ± 0.1	4.95 ± 0.1	4.90 ± 0.1	4.86 ± 0.0	4.81 ± 0.0
Straw						
N (g kg^{-1})	1.38 ± 0.1	2.22 ± 0.5	2.42 ± 0.5	2.65 ± 0.4	1.19 ± 0.4	1.18 ± 0.3
P (g kg^{-1})	0.00 ± 0.0	1.27 ± 0.6	0.00 ± 0.0	1.07 ± 0.7	1.14 ± 0.5	0.00 ± 0.0
K (g kg^{-1})	5.52 ± 0.5 **a**	12.54 ± 2.7 **b**	6.05 ± 0.6	11.33 ± 3.4	14.04 ± 2.9	7.25 ± 0.5
S (g kg^{-1})	2.10 ± 0.0	2.47 ± 0.2	2.02 ± 0.0	2.39 ± 0.2	2.49 ± 0.2	2.19 ± 0.1
Ca (g kg^{-1})	11.32 ± 0.2	7.35 ± 1.7	10.66 ± 0.2	8.66 ± 1.6	6.85 ± 1.7 **a**	11.04 ± 0.2 **b**
Mg (g kg^{-1})	2.07 ± 0.1	1.84 ± 0.2	2.12 ± 0.1	2.10 ± 0.1	1.69 ± 0.1	1.94 ± 0.1
Mn (mg kg^{-1})	3.43 ± 0.1	3.07 ± 0.2	3.26 ± 0.1	3.35 ± 0.1	2.91 ± 0.1 **a**	3.36 ± 0.1 **b**
Zn (mg kg^{-1})	3.12 ± 0.1	3.22 ± 0.1	3.30 ± 0.1	3.32 ± 0.1	2.85 ± 0.1	2.82 ± 0.1

Table 4 Nutrient export (nutrient content*biomass) in grain and straw of harvested barley for the six organo-mineral fertilisers. Reported values are mean ± standard errors (n = 6). Different letters indicate statistically significant differences within a fertiliser pair (NPK vs NPK+B, NP vs NP+B, and K vs K+B)

	NPK	**NPK+B**	**NP**	**NP+B**	**K**	**K+B**
Grain						
N (g)	3.82 ± 0.1	4.34 ± 0.2	3.90 ± 0.2	4.20 ± 0.2	2.98 ± 0.2	3.22 ± 0.2
P (g)	2.72 ± 0.1	2.97 ± 0.1	2.70 ± 0.1	2.86 ± 0.1	2.11 ± 0.1	2.23 ± 0.1
K (g)	2.47 ± 0.0	2.70 ± 0.2	2.54 ± 0.1	2.74 ± 0.1	1.93 ± 0.1	2.00 ± 0.2
S (g)	0.18 ± 0.0	0.19 ± 0.0	0.18 ± 0.0	0.20 ± 0.0	0.15 ± 0.0	0.13 ± 0.0
Ca (g)	0.59 ± 0.0	0.64 ± 0.1	0.57 ± 0.0 **a**	0.65 ± 0.0 **b**	0.39 ± 0.0	0.40 ± 0.0
Mg (g)	0.55 ± 0.0	0.61 ± 0.0	0.56 ± 0.0	0.59 ± 0.0	0.42 ± 0.0	0.45 ± 0.0
Mn (mg)	0.62 ± 0.0	0.62 ± 0.0	0.59 ± 0.0 **a**	0.64 ± 0.0 **b**	0.48 ± 0.0	0.52 ± 0.0
Zn (mg)	2.13 ± 0.0	2.42 ± 0.1	2.14 ± 0.1	2.30 ± 0.1	1.57 ± 0.1	1.67 ± 0.1
Straw						
N (g)	0.74 ± 0.1	1.55 ± 0.5	1.51 ± 0.3	1.68 ± 0.3	0.46 ± 0.2	0.51 ± 0.2
P (g)	0.00 ± 0.0	0.76 ± 0.3	0.00 ± 0.0	0.69 ± 0.4	0.41 ± 0.2	0.00 ± 0.0
K (g)	2.97 ± 0.3 **a**	8.00 ± 1.6 **b**	3.75 ± 0.4	7.15 ± 2.3	5.21 ± 1.0	3.00 ± 0.5
S (g)	1.12 ± 0.0 **a**	1.61 ± 0.1 **b**	1.24 ± 0.1	1.49 ± 0.2	0.94 ± 0.1	0.89 ± 0.1
Ca (g)	6.04 ± 0.1	5.01 ± 1.3	6.52 ± 0.4	5.35 ± 1.0	2.72 ± 0.8 **a**	4.43 ± 0.4 **b**
Mg (g)	1.11 ± 0.1	1.24 ± 0.2	1.30 ± 0.1	1.31 ± 0.1	0.65 ± 0.1	0.79 ± 0.1
Mn (mg)	1.83 ± 0.1	2.04 ± 0.2	2.00 ± 0.1	2.09 ± 0.1	1.12 ± 0.1	1.35 ± 0.1
Zn (mg)	1.67 ± 0.1	2.14 ± 0.2	2.02 ± 0.1	2.07 ± 0.1	1.10 ± 0.1	1.14 ± 0.1

Discussion

NPK+B formulation delayed most of the nutrients release

The fact that nutrient release was only delayed in the NPK+B fertiliser and not in the other biochar-based fertilisers plausibly discards any biochar direct nutrient retention mechanisms such as chemisorption, physisorption or water-pore retention. Namely, despite the higher rate of biochar applied in the NPK+B formulation in relation to NP+B and K+B, we would have expected some kind of effect (albeit weaker) also in the other two biochar fertilisers. Although biochar could also have altered leaching patterns by shifting pH (Laird and Rogovska 2015), it seems unlikely in the current study, where both the soil ($pH_{1:2.5}$ 8.2; Marks et al. 2016) and biochar ($pH_{1:20}$ 8.5) had an alkaline pH, and this same soil has been proved to resist biochar-induced pH shifts (Marks et al. 2016). On the other hand, redox status alterations that could drive nutrient availability are less common at alkaline pH (Chacón et al. 2017).

By contrast, as both biochar and macronutrients in NPK+B could influence the microbial potential to grow and store nutrients, microbial nutrient immobilisation could be behind the observed temporary nutrient retention. Concretely, microbial biomass can grow and store nutrients while C and nutrient provision is available, but when microbes are devoid of such resources, nutrients immobilised within them are returned to the soil phase via decomposition of dead cells, which can, in turn, contribute to the pool of available nutrients for plants (Anderson and Domsch 1980). Regarding the causative mechanisms of the potential microbial nutrient immobilisation, different drivers could have played a role. Since microorganisms in agricultural soils are usually C limited (Schimel 1986), biochar labile C provision could be one explanatory factor. In particular, low-temperature biochars (< 500 ºC), thus akin to our biochar produced at

400-550 ºC, are more likely to induce net nutrient immobilisation, because they contain higher concentrations of bioavailable C and residual bio-oils (DeLuca et al. 2015). Nevertheless, all fertilisers contained labile C in the form of maize flour, so this mechanism could be mostly disregarded. In this regard, the effect of biochar providing suitable habitat for microorganisms could have played a role, i.e. the porous structure of biochar could have protected microbes from grazers, increased the water retention (and thus meet microbial moisture requirements), or prevented microbes from leaching as they adsorb on biochar surfaces (Lehmann et al. 2011; Ennis et al. 2012). Although microbial colonisation is not expected to be a substantial process in the short-term, biochar blending in a powdered form could have promoted such an effect (Quilliam et al. 2013). This biochar habitat effect in combination with commensurate nutrient supply (NPK instead of reduced nutrient combinations) could fulfil the microbial stoichiometric requirements (Ashraf et al. 2020) and thus allow for microbial growth and retention of nutrients within their biomass. Interestingly, in the meta-analysis of Melo et al (2022), significant increases in crop productivity were found for biochar-based fertilisers when combined with NPK but not for those with NP. This could fit with the hypothesis that the concurrent provision of both biochar and the three macronutrients is determinant for biochar to show effects.

Furthermore, the timing of nutrient release in the NPK+B fertiliser, i.e. retaining nutrients the first two weeks and releasing them from the third week onwards, may support the microbial immobilisation mechanism. Specifically, and although microbial turnover time can vary greatly (normally in the range of days to months; Schmidt et al. 2007), similar values of microbial turnover have been found in cultivated soils (Cheng 2009).

Additionally, the microbial immobilisation mechanism could also explain the nutrient release delay found for multiple ions (NO_3^--N, K^+, Na^+, Ca^{2+}, Mg^{2+}, Cl^-, and SO_4^{2-}) since although microbial immobilisation mainly provokes N and P retention (Malik et al. 2013) other nutrients such as K, S, and Ca are also substantially stored in microbial biomass (Anderson and Domsch 1980; Brookes 2001; Yamashita et al. 2014). In accordance with this, PRC results of the NPK+B vs NPK pair of fertilisers pointed to major effects on NO_3^--N and K^+ retention, both plausibly as a result of their high relative abundance in microbial biomass or by their direct addition with fertiliser application.

On the other hand, the low recovery in leachates of added P in both NPK+B and NPK, is not surprising as phosphate is immobile in most soils because of precipitation reactions and adsorption to mineral surfaces (Haygarth et al. 2013). In our experiment, the negligible P release is mainly attributed to P precipitation with Ca due to the high Ca content and high soil pH (Hopkins and Ellsworth 2005) found in the soil used for this experiment. Regarding the Cl^- leaching delay, it is less straightforward to understand because its retention in microbial biomass is not expected (Kanwar et al. 1997). As a possible explanation, nitrification of the ammoniacal N provided in fertilisers is known to cause acidification and therefore to displace basic cations from the cation exchange complex (Poss and Saragoni 1992; Bouman 1995), but this process can also affect anion availability and leaching. In detail, when cations like Ca^{2+} or Mg^{2+} are displaced by H^+ resulting from nitrification, anions (as Cl^-) could be concurrently released (i.e. they can be directly bounded to these polyvalent cations by bridging or be present in the diffuse double layer around the cation exchange complex). Then, if microbial immobilisation was promoted in the NPK+B fertiliser, less NH_4^+ would have been available for nitrification and, as a result, acidification and leaching of ions (including Cl^-) could have been prevented to some extent at this treatment. It is worth mentioning that if this process occurred, it could imply complex interactions between microbial immobilisation, nitrification and nutrient leaching, making difficult to discern why NH_4^+ was the only ion whose release was not delayed by the NPK+B formulation, with its leaching indeed being higher at the NPK+B than in NPK at the first sampling date. However, the low quantities found for soluble NH_4^+ even at the first sampling date, especially in comparison with NO_3^-, make us disregard NH_4^+ release as an important process for understanding nutrient dynamics.

All biochar-based fertilisers enhanced barley nutrient status and NPK+B increased straw biomass

As expected given the more gradual nutrient release achieved in the NPK+B fertiliser, thus potentially improving plant uptake, this fertiliser was the only one significantly enhancing barley straw biomass, whereas grain biomass was only marginally improved. However, it should be noted that the high number of leaching events performed in this experiment, which led to a soluble nutrient shortage at about the fifth sampling, could have diluted the possible NPK+B beneficial effects on grain biomass.

Regarding barley nutrient content and export, all biochar-based fertilisers exerted some beneficial effects compared to the corresponding non-biochar formulations. The majority of effects became apparent in straw nutrient and export, i.e. the NPK+B fertiliser enhanced K content and export, and S export in contrast with NPK, while K+B improved Ca content and export and Mn content compared to the K fertiliser. On the other hand, the NP+B fertiliser provoked effects on grain export, i.e. enhanced Ca and Mn export in comparison with the NP fertiliser. Nutrient content and export improvement caused by the NPK+B fertiliser might result from its more gradual nutrient release pattern, by directly providing nutrients, i.e. biochar acting as a source of nutrients itself (Chan and Xu 2009), or a combination of these two mechanisms. On the other hand, regarding the NP+B and K+B fertilisers, since nutrient leaching patterns were not found to improve in relation to its conventional counterpart, the beneficial effects on plant nutrient status would mostly fit the direct nutrient provision hypothesis. In support of this, the studied biochar has been proven to release K in water extracts (unpublished results). In addition K, Ca, and S are nutrients commonly reported to be released after biochar application (Lehmann et al. 2003; Laird et al. 2010b; Marks et al. 2016). Finally, although less commonly reported, biochar could also have released Mn (Elmer and Pignatello 2011), alternatively, soil Mn solubilisation due to redox properties of biochar has also been reported (Graber et al. 2014), but only at pH levels below 8, and therefore this mechanism is not likely in our alkaline system.

Our results could be in line with those of Güereña et al. (2013), who reported not significant biochar effects on grain yield whereas N leaching was reduced in biochar treatments, this result being potentially attributable to a three-fold increase in microbial biomass. However, if the microbial immobilisation mechanism is confirmed, caution must be laid on fertiliser development and application, since this positive effect might be soil-specific and highly dependent on the native microbial activity, biochar dosing and biochar composition. For instance, no microbial immobilisation might be observed in soils with already high soil organic carbon contents and microbial biomass (Subedi et al. 2016; Yanardağ et al. 2017). On the other hand, excessive microbial immobilisation on larger time frames could cause competition for nutrients between plants and soil microorganisms (Anderson and Domsch 1980).

Despite these potential constraints, biochar-based fertilisers are of high interest for being able to provide immediate benefits for soil fertility by supplying and, more importantly, by retaining nutrients. Additionally, biochar-based fertilisers can also provide multiple environmental benefits widely proposed in the literature, such as a higher C sequestration (Shackley et al. 2013), greenhouse gas mitigation (Kammann et al. 2017), or water retention (Omondi et al. 2016). Further research is needed to avoid unintended effects and to maximise the number of services which biochar can deliver as a fertiliser ingredient.

Conclusions

The inclusion of biochar in fertiliser formulation did not alter the final cumulative amount of nutrients leached, nevertheless, there were distinct temporal patterns of nutrient release in the NPK+B fertiliser. While most fertilisers contributed to a large flush of available nutrients upon application, the NPK+B biochar-based fertiliser caused a delayed and more sustained release of nutrients throughout the growing season. Microbial nutrient immobilisation could be behind this response since the effects were only found in the biochar fertiliser which supplied simultaneously the three macronutrients (reduced nutrient combinations could have limited microbial growth). Although there were no significant differences on grain production, straw biomass was indeed increased in the NPK+B treatment, potentially indicating that this fertiliser might aid in the synchronisation of nutrient availability and crop requirements. Furthermore, nutrient content and export were enhanced in all biochar-based fertilisers, likely as a result of biochar acting as a direct nutrient source. To conclude, the slow nutrient release of NPK+B might facilitate the gradual provision of nutrients for plants and holds promise for the development of new generation biochar-based fertilisers.

Funding

This work was funded by the project FERTICHAR (AGL2015-70393-R) of the Spanish Ministry of Economy and Competitiveness and is supported by a Margarita Salas grant under the European Union-NextGenerationEU funds.

Disclosure statement

On behalf of all authors, the corresponding author reports there are no competing interests to declare.

Data availability statement

Data will be available upon request.

References

Alburquerque JA, Salazar P, Barrón V, Torrent J, del Campillo MDC, Gallardo A, Villar R. 2013. Enhanced wheat yield by biochar addition under different mineral fertilization levels. Agron Sustain Dev. 33(3):475–484. http://doi.org/10.1007/s13593-012-0128-3

Anderson JPE, Domsch KH. 1980. Quantities of plant nutrients in the microbial biomass of selected soils. Soil Sci. 130(4):211–216. http://doi.org/10.1097/00010694-198010000-00008

Ashraf MN, Hu C, Wu L, Duan Y, Zhang W, Aziz T, Cai A, Abrar MM, Xu M. 2020. Soil and microbial biomass stoichiometry regulate soil organic carbon and nitrogen mineralization in rice-wheat rotation subjected to long-term fertilization. J Soils Sediments. 20:3103–3113. https://doi.org/10.1007/s11368-020-02642-y

Blanco M. 2011. Supply of and access to key nutrients NPK for fertilizers for feeding the world in 2050. UPM, Madrid.

Bouman OT, Curtin D, Campbell CA, Biederbeck VO, Ukrainetz H. 1995. Soil acidification from long-term use of anhydrous ammonia and urea. Soil Sci Soc Am J. 59(5):1488–1494. http://doi.org/10.2136/sssaj1995.03615995005900050039x

Brockhoff SR, Christians NE, Killorn RJ, Horton R, Davis DD. 2010. Physical and mineral-nutrition properties of sand-based turfgrass root zones amended with biochar. Agron J. 102(6):1627–1631. http://doi.org/10.2134/agronj2010.0188

Brookes P. 2001. The soil microbial biomass: concept, measurement and applications in soil ecosystem research. Microbes Environ 16(3):131–140. http://doi.org/10.1264/jsme2.2001.131

Brown PH, Zhao FJ, Dobermann A. 2021. What is a plant nutrient? Changing definitions to advance science and innovation in plant nutrition. Plant Soil. 476:1–13. https://doi.org/10.1007/s11104-021-05171-w

Cameron KC, Di HJ, Moir JL. 2013. Nitrogen losses from the soil/plant system: A review. Ann Appl Biol. 162(2):145–173. https://doi.org/10.1111/aab.12014

Calabi-Floody M, Medina J, Rumpel C, Condron LM, Hernandez M, Dumont, M, de la Luz Mora M. 2018. Smart fertilizers as a strategy for sustainable agriculture. Adv Agron. 147:119–157. http://doi.org/10.1016/bs.agron.2017.10.003

Chacón FJ, Cayuela ML, Roig A, Sánchez-Monedero MA. 2017. Understanding, measuring and tuning the electrochemical properties of biochar for environmental applications. Rev Environ Sci Biotechnol. 16(4):695–715. https://doi.org/10.1007/s11157-017-9450-1

Chan KY, Xu Z. 2009. Biochar: nutrient properties and their enhancement. In: Lehmann J, Joseph S, editors. Biochar for environmental management: Science, Technology and Implementation. London: Earthscan; p. 67–84.

Chen L, Chen Q, Rao P, Yan L, Shakib A, Shen G. 2018. Formulating and optimizing a novel biochar-based fertilizer for simultaneous slow-release of nitrogen and immobilization of cadmium. Sustainability. 10(8):2740. http://doi.org/10.3390/su10082740

Cheng W. 2009. Rhizosphere priming effect: its functional relationships with microbial turnover, evapotranspiration, and C–N budgets. Soil Biol Biochem. 41(9):1795–1801. http://doi.org/10.1016/j.soilbio.2008.04.018

Chew J, Zhu L, Nielsen S, Graber E, Mitchell DR, Horvat J, Mohammed M, Liu M, Zwieten L, Donne S, et al. 2020. Biochar-based fertilizer: Supercharging root membrane potential and biomass yield of rice. Sci Total Environ. 713:136431. https://doi.org/10.1016/j.scitotenv.2019.136431

Das I, Pradhan M. 2016. Potassium-Solubilizing Microorganisms and Their Role in Enhancing Soil Fertility and Health. In: Meena V, Maurya B, Verma J, Meena R, editors. Potassium Solubilizing Microorganisms for Sustainable Agriculture. New Delhi : Springer; p. 281–291. https://doi.org/10.1007/978-81-322-2776-2_20

DeLuca TH, Gundale MJ, MacKenzie MD, Jones DL. 2015. Biochar effects on soil nutrient transformations. In: Lehmann J, Joseph S, editors. Biochar for environmental management: Science, Technology and Implementation. 2nd ed. London: Earthscan; p. 421–454.

Elmer WH, Pignatello JJ. 2011. Effect of biochar amendments on mycorrhizal associations and *Fusarium* crown and root rot of asparagus in replant soils. Plant Dis. 95(8):960–966. http://doi.org/10.1094/PDIS-10-10-0741

Ennis CJ, Evans AG, Islam M, Ralebitso-Senior TK, Senior E. 2012. Biochar: carbon sequestration, land remediation, and impacts on soil microbiology. Crit Rev

Environ Sci Technol. 42(22):2311–2364. http://doi.org/10.1080/10643389.2011.574115

European Parliament. 2019. *Commission Implementing Regulation (EU) 2019/2164 of 17 December 2019 amending Regulation (European Commission) No 889/2008 laying down detailed rules for the implementation of Council Regulation (European Commission) No 834/2007 on organic production and labelling of organic products with regard to organic production, labelling and control*. Brussels: European Parliament.

Graber ER, Tsechansky L, Lew B, Cohen E. 2014. Reducing capacity of water extracts of biochars and their solubilization of soil Mn and Fe. Eur J Soil Sci. 65(1):162–172. http://doi.org/10.1111/ejss.12071

Güereña D, Lehmann J, Hanley K, Enders A, Hyland C, Riha S. 2013. Nitrogen dynamics following field application of biochar in a temperate North American maize-based production system. Plant Soil. 365(1):239–254. http://doi.org/10.1007/s11104-012-1383-4

Haygarth PM, Bardgett RD, Condron LM. 2013. Nitrogen and phosphorus cycles and their management. In: Gregory PJ, Nortcliff S, editors. Soil conditions and plant growth. Chichester: Wiley-Blackwell; p. 132-159. http://doi.org/10.1002/9781118337295

Hirel B, Tétu T, Lea PJ, Dubois F. 2011. Improving nitrogen use efficiency in crops for sustainable agriculture. Sustainability. 3(9):1452–1485. http://doi.org/10.3390/su3091452

Hopkins B, Ellsworth J. 2005. Phosphorus availability with alkaline/calcareous soil. Western Nutrient Management Conference. 6:88–93.

Ippolito JA, Novak JM, Busscher WJ, Ahmedna M, Rehrah D, Watts DW. 2012. Switchgrass Biochar Affects Two Aridisols. J Environ Qual. 41(4):1123–1130. https://doi.org/10.2134/jeq2011.0100

Joseph S, Graber ER, Chia C, Munroe P, Donne S, Thomas T, Nielsen S, Marjo C, Rutlidge H, Pan GX, et al. 2013. Shifting paradigms: development of high-efficiency biochar fertilizers based on nano-structures and soluble components. Carbon Manag. 4(3):323–343. http://doi.org/10.4155/cmt.13.23

Kammann C, Ippolito J, Hagemann N, Borchard N, Cayuela ML, Estavillo JM, Fuertes-Mendizabal T, Jeffery S, Kern J, Novak J, Rasse D, et al. 2017. Biochar as a tool to reduce the agricultural greenhouse-gas burden–knowns, unknowns and future research needs. J Environ Eng Landsc. 25(2):114–139. https://doi.org/10.3846/16486897.2017.1319375

Kanwar RS, Baker JL, Singh P. 1997. Use of chloride and fluorescent dye as tracers in measuring nitrate and atrazine transport through soil profile under laboratory conditions. J Environ Sci Health A Tox Hazard Subst Environ Eng. 32(7):1907–1919. http://doi.org/10.1080/10934529709376654

Kassambara A. 2019a. Ggpubr: ‘ggplot2’ based publication ready plots. [accessed 6 June 2022]. https://github.com/kassambara/ggpubr.

Kassambara A. 2019b. Rstatix: Pipe-friendly framework for basic statistical tests in R. [accessed 6 June 2022]. https://github.com/kassambara/rstatix.

Kominko H, Gorazda K, Wzorek Z. 2017. The possibility of organo-mineral fertilizer production from sewage sludge. Waste Biomass Valorization. 8(5):1781–1791. http://doi.org/10.1007/s12649-016-9805-9

Laird DA, Fleming P, Wang B, Horton R, Karlen DL. 2010a. Biochar impact on nutrient leaching from a Midwestern agricultural soil. Geoderma. 158(3–4):436–442. http://doi.org/10.1016/j.geoderma.2010.05.012

Laird DA, Fleming P, Davis DD, Wang B, Horton R, Karlen DL. 2010b. Impact of biochar amendments on the quality of a typical Midwestern agricultural soil. Geoderma. 158(3–4):443–449 http://doi.org/10.1016/j.geoderma.2010.05.013

Laird D, Rogovska N. 2015. Biochar effects on nutrient leaching. In: Lehmann J, Joseph S, editors. Biochar for environmental management: Science, Technology and Implementation. 2nd ed. London: Earthscan; p. 553–574.

Lawrinenko M, Laird DA. 2015. Anion exchange capacity of biochar. Green Chem. 17(9):4628–4636. https://doi.org/10.1039/C5GC00828J

Lehmann J, da Silva JP, Steiner C, Nehls T, Zech W, Glaser B. 2003. Nutrient availability and leaching in an archaeological Anthrosol and a Ferralsol of the Central Amazon basin: fertilizer, manure and charcoal amendments. Plant Soil. 249(2):343–357. http://doi.org/10.1023/A:1022833116184

Lehmann J, Rillig MC, Thies J, Masiello CA, Hockaday WC, Crowley D. 2011. Biochar effects on soil biota–a review. Soil Biol Biochem. 43(9):1812–1836. https://doi.org/10.1016/j.soilbio.2011.04.022

Liang B, Lehmann J, Solomon D, Kinyangi J, Grossman J, O'Neill B, Skjemstad JO, Thies J, Luizao FJ, Petersen J, et al. 2006. Black carbon increases cation exchange capacity in soils. Soil Sci Soc Am J. 70(5):1719–1730. https://doi.org/10.2136/sssaj2005.0383

Liao J, Liu X, Hu A, Song H, Chen X, Zhang Z. 2020. Effects of biochar-based controlled release nitrogen fertilizer on nitrogen-use efficiency of oilseed rape

(*Brassica napus* L.). Sci Rep. 10(1):1–14. http://doi.org/10.1038/s41598-020-67528-y

Luo W, Qian L, Liu W, Zhang X, Wang Q, Jiang H, Cheng B, Ma H, Wu Z. 2021. A potential Mg-enriched biochar fertilizer: Excellent slow-release performance and release mechanism of nutrients. Sci Total Environ. 768:144454. https://doi.org/10.1016/j.scitotenv.2020.144454

Malik MA, Khan KS, Marschner P, Hassan, F. 2013. Microbial biomass, nutrient availability and nutrient uptake by wheat in two soils with organic amendments. J Soil Sci Plant Nutr. 13(4):955–966. http://doi.org/10.4067/S0718-95162013005000075

Marks EAN, Mattana S, Alcañiz JM, Pérez-Herrero E, Domene X. 2016. Gasifier biochar effects on nutrient availability, organic matter mineralization, and soil fauna activity in a multi-year Mediterranean trial. Agric Ecosyst Environ. 215:30–39. http://doi.org/10.1016/j.agee.2015.09.004

Martos S, Mattana S, Ribas A, Albanell E, Domene X. 2020. Biochar application as a win-win strategy to mitigate soil nitrate pollution without compromising crop yields: a case study in a Mediterranean calcareous soil. J Soils Sediments. 20:220–233. http://doi.org/10.1007/s11368-019-02400-9

Melo LCA, Lehmann J, Carneiro JSDS, Camps-Arbestain M. 2022. Biochar-based fertilizer effects on crop productivity: a meta-analysis. Plant Soil. 472:45–58. https://doi.org/10.1007/s11104-021-05276-2

Mete FZ, Mia S, Dijkstra FA, Abuyusuf Md, Hossain ASMI. 2015. Synergistic effects of biochar and NPK fertilizer on soybean yield in an alkaline soil. Pedosphere. 25:713–719. https://doi.org/10.1016/S1002-0160(15)30052-7

Nguyen TTN, Xu CY, Tahmasbian I, Che R, Xu Z, Zhou X, Wallace HM, Bai SH. 2017. Effects of biochar on soil available inorganic nitrogen: A review and meta-analysis. Geoderma. 288:79–96. https://doi.org/10.1016/j.geoderma.2016.11.004

Novak, J M, Busscher WJ, Watts DW, Laird DA, Ahmedna MA, Niandou MA. 2010. Short-term CO_2 mineralization after additions of biochar and switchgrass to a Typic Kandiudult. Geoderma. 154(3-4):281–288. http://doi.org/10.1016/j.geoderma.2009.10.014

Pang W, Hou D, Wang H, Sai S, Wang B, Ke J, Wu G, Li Q, Holtzapple MT. 2018. Preparation of microcapsules of slow-release NPK compound fertilizer and the release characteristics. J Braz Chem Soc. 29(11):2397–2404. http://doi.org/10.21577/0103-5053.20180117

Oladele S, Adeyemo A, Awodun M, Ajayi A, Fasina A. 2019. Effects of biochar and nitrogen fertilizer on soil physicochemical properties, nitrogen use efficiency and upland rice (*Oryza sativa*) yield grown on an Alfisol in Southwestern Nigeria. Int J Recycl Org Waste Agric. 8(3):295–308. http://doi.org/10.1007/s40093-019-0251-0

Omondi MO, Xia X, Nahayo A, Liu X, Korai PK, Pan G. 2016. Quantification of biochar effects on soil hydrological properties using meta-analysis of literature data. Geoderma. 274:28–34. http://doi.org/10.1016/j.geoderma.2016.03.029

Pandit NR, Schmidt HP, Mulder J, Hale SE, Husson O, Cornelissen G. 2019. Nutrient effect of various composting methods with and without biochar on soil fertility and maize growth. Arch Agron Soil Sci. 66(2):250–265. http://doi.org/10.1080/03650340.2019.1610168

Poss R, Saragoni H. 1992. Leaching of nitrate, calcium and magnesium under maize cultivation on an oxisol in Togo. Fertil Res. 33(2):123–133.

Quilliam RS, Glanville HC, Wade SC, Jones DL. 2013. Life in the 'charosphere'–Does biochar in agricultural soil provide a significant habitat for microorganisms?. Soil Biol Biochem. 65:287–293. https://doi.org/10.1016/j.soilbio.2013.06.004

Raun WR, Johnson GV. 1999. Improving nitrogen use efficiency for cereal production. Agron J 91(3):357–363. http://doi.org/10.2134/agronj1999.00021962009100030001x

R Core Team. 2021. R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria. [accessed 24 March 2021]. https://www.R-project.org/.

Shackley S, Sohi S, Ibarrola R, Hammond J, Mašek O, Brownsort P, Haszeldine S. 2013. Biochar, tool for climate change mitigation and soil management. In: Lenton T, Vaughan N, editors. Geoengineering Responses to Climate Change. New York (NY): Springer; p. 73–140. http://doi.org/10.1007/978-1-4614-5770-1_6

Schimel DS. 1986. Carbon and nitrogen turnover in adjacent grassland and cropland ecosystems. Biogeochemistry. 2(4):345–357. http://doi.org/10.1007/BF02180325

Schmidt SK, Costello EK, Nemergut DR, Cleveland CC, Reed SC, Weintraub MN, Meyer AF, Martin AM. 2007. Biogeochemical consequences of rapid microbial turnover and seasonal succession in soil. Ecology. 88(6):1379–1385. http://doi.org/10.1890/06-0164

Soil Survey Staff. 2010. Keys to Soil Taxonomy, 11th ed. USDA—Natural Resources Conservation Service.

Subedi R, Taupe N, Ikoyi I, Bertora C, Zavattaro L, Schmalenberger A, Leahy JJ, Grignani C. 2016. Chemically and biologically-mediated fertilizing value of manure-derived biochar. Sci Total Environ. 550:924–933. http://doi.org/10.1016/j.scitotenv.2016.01.160

Syers JK, Johnston AE, Curtin D. 2008. Efficiency of soil and fertilizer phosphorus use: reconciling changing concepts of soil phosphorus behaviour with agronomic information. FAO Fertilizer and Plant Nutrition Bulletin 18, Food and Agriculture Organization of the United Nations, Rome

Talboys PJ, Heppell J, Roose T, Healey JR, Jones DL, Withers PJ. 2016. Struvite: a slow-release fertiliser for sustainable phosphorus management?. Plant Soil. 401(1–2):109–123. http://doi.org/10.1007/s11104-015-2747-3

Ter Braak CJF, Šmilauer P. 2012. Canoco reference manual and user's guide: software for ordination, version 5.0. Microcomputer Power, Ithaca, USA.

Van den Brink P J and Braak C J. 1999. Principal response curves: Analysis of time-dependent multivariate responses of biological community to stress. Environ Toxicol Chem. 18(2):138–148. doi: 10.1002/etc.5620180207.

Vanderdeelen J. 1995. Phosphate immobilisation in an uncropped field experiment on a calcareous soil. Plant Soil. 171(2):209–215. https://doi.org/10.1007/BF00010274

Vitousek PM, Aber JD, Howarth RW, Likens GE, Matson PA, Schindler DW, Schlesinger WH, Tilman DG. 1997. Human alteration of the global nitrogen cycle: sources and consequences. Ecol Appl. 7:737–750. https://doi.org/10.1890/1051-0761(1997)007[0737:HAOTGN]2.0.CO;2

Ward MH, Jones RR, Brender JD, de Kok TM, Weyer PJ, Nolan BT, Villanueva CM, van Breda SG. 2018. Drinking water nitrate and human health: An updated review. Int J Environ Res Public Health. 15(7):1557. https://doi.org/10.3390/ijerph15071557

Wickham H. 2016. ggplot2: Elegant Graphics for Data Analysis: Springer Verlag New York. doi:10.1007/978-3-319-24277-4.

Yamashita K, Honjo H, Nishida M, Kimura M, Asakawa S. 2014. Estimation of microbial biomass potassium in paddy field soil. Soil Sci Plant Nutr. 60(4):512–519. http://doi.org/10.1080/00380768.2014.919237

Yanardağ IH, Zornoza R, Bastida F, Büyükkiliç-Yanardağ A, García C, Faz A, Mermut AR. 2017. Native soil organic matter conditions the response of microbial communities to organic inputs with different stability. Geoderma. 295:1–9. http://doi.org/10.1016/j.geoderma.2017.02.008

Supplementary material

Table S1 Summary of the results of two-way mixed ANOVAs on different variables, with treatment (control fertiliser without biochar vs biochar-based fertiliser) as between-subjects factor, and time (sampling dates) as within-subjects factor. Degrees of freedom (df) are shown as: (degrees of freedom numerator, degrees of freedom denominator); the effect size is reported as generalised eta squared (η_G^2), and significant p-values ($p < .05$) are marked in bold

Table S1.1 NO_3^--N absolute leaching (NPK vs NPK+B)

Source	**df**	**F**	**p**	η_G^2
treatment	(1, 10)	0.04	0.840	0.00
time	(2.07, 20.74)	73.77	< **.001**	0.87
treatment x time	(2.07, 20.74)	6.30	**0.007**	0.37

Table S1.2 NH_4^+-N absolute leaching (NPK vs NPK+B)

Source	**df**	**F**	**p**	η_G^2
treatment	(1, 10)	0.04	0.847	0.00
time	(2.24, 22.39)	17.26	< **.001**	0.61
treatment x time	(2.24, 22.39)	6.20	**0.006**	0.36

Table S1.3 Na^+ absolute leaching (NPK vs NPK+B)

Source	**df**	**F**	**p**	η_G^2
treatment	(1, 10)	1.79	0.211	0.03
time	(3.06, 30.56)	99.96	< **.001**	0.89
treatment x time	(3.06, 30.56)	4.92	**0.006**	0.29

Table S1.4 K^+ absolute leaching (NPK vs NPK+B)

Source	**df**	**F**	**p**	η_G^2
treatment	(1, 10)	0.42	0.532	0.01
time	(8, 80)	126.11	< **.001**	0.91
treatment x time	(8, 80)	4.04	< **.001**	0.24

Table S1.5 Mg^{2+} absolute leaching (NPK vs NPK+B)

Source	**df**	**F**	**p**	η_G^2
treatment	(1, 10)	0.48	0.503	0.00
time	(2.05, 20.55)	110.57	< **.001**	0.91
treatment x time	(2.05, 20.55)	3.41	0.052	0.24

Table S1.6 Ca^{2+} absolute leaching (NPK vs NPK+B)

Source	df	F	p	η_G^2
treatment	(1, 10)	0.18	0.681	0.00
time	(3.44, 34.38)	360.53	**< .001**	0.97
treatment x time	(3.44, 34.38)	6.19	**0.001**	0.36

Table S1.7 Cl^- absolute leaching (NPK vs NPK+B)

Source	df	F	p	η_G^2
treatment	(1, 10)	2.75	0.128	0.03
time	(1.83, 18.28)	87.96	**< .001**	0.89
treatment x time	(1.83, 18.28)	2.69	0.099	0.20

Table S1.8 SO_4^{2-} absolute leaching (NPK vs NPK+B)

Source	df	F	p	η_G^2
treatment	(1, 10)	0.48	0.505	0.00
time	(2.26, 22.6)	126.93	**< .001**	0.92
treatment x time	(2.26, 22.6)	2.82	0.075	0.21

Table S1.9 NO_3^--N absolute leaching (NP vs NP+B)

Source	df	F	p	η_G^2
treatment	(1, 10)	0.17	0.685	0.00
time	(2.08, 20.76)	41.78	**< .001**	0.80
treatment x time	(2.08, 20.76)	0.50	0.623	0.04

Table S1.10 NH_4^+-N absolute leaching (NP vs NP+B)

Source	df	F	p	η_G^2
treatment	(1, 10)	0.20	0.661	0.00
time	(2.75, 27.54)	21.43	**< .001**	0.66
treatment x time	(2.75, 27.54)	0.67	0.568	0.06

Table S1.11 Na^+ absolute leaching (NP vs NP+B)

Source	**df**	**F**	**p**	η_G^2
treatment	(1, 10)	0.05	0.823	0.00
time	(2.31, 23.07)	70.38	**< .001**	0.86
treatment x time	(2.31, 23.07)	0.26	0.807	0.02

Table S1.12 K^+ absolute leaching (NP vs NP+B)

Source	**df**	**F**	**p**	η_G^2
treatment	(1, 10)	0.00	0.956	0.00
time	(2.46, 24.57)	57.16	**< .001**	0.83
treatment x time	(2.46, 24.57)	0.75	0.508	0.06

Table S1.13 Mg^{2+} absolute leaching (NP vs NP+B)

Source	**df**	**F**	**p**	η_G^2
treatment	(1, 10)	0.16	0.702	0.00
time	(1.67, 16.68)	52.54	**< .001**	0.83
treatment x time	(1.67, 16.68)	0.09	0.881	0.01

Table S1.14 Ca^{2+} absolute leaching (NP vs NP+B)

Source	**df**	**F**	**p**	η_G^2
treatment	(1, 10)	0.08	0.784	0.00
time	(1.28, 12.84)	41.34	**< .001**	0.79
treatment x time	(1.28, 12.84)	0.03	0.920	0.00

Table S1.15 Cl^- absolute leaching (NP vs NP+B)

Source	**df**	**F**	**p**	η_G^2
treatment	(1, 10)	0.95	0.353	0.01
time	(2.85, 28.49)	92.79	**< .001**	0.89
treatment x time	(2.85, 28.49)	0.83	0.481	0.07

Table S1.16 SO_4^{2-} absolute leaching (NP vs NP+B)

Source	**df**	**F**	**p**	η_G^2
treatment	(1, 10)	0.00	0.948	0.00
time	(1.65, 16.48)	88.47	**< .001**	0.89
treatment x time	(1.65, 16.48)	0.43	0.620	0.04

Table S1.17 NO_3^--N absolute leaching (K vs K+B)

Source	**df**	**F**	**p**	η_G^2
treatment	(1, 10)	0.37	0.558	0.01
time	(8, 80)	216.83	**< .001**	0.95
treatment x time	(8, 80)	0.76	0.637	0.06

Table S1.18 NH_4^+-N absolute leaching (K vs K+B)

Source	**df**	**F**	**p**	η_G^2
treatment	(1, 10)	0.09	0.773	0.00
time	(2.85, 28.54)	21.84	**< .001**	0.67
treatment x time	(2.85, 28.54)	1.47	0.245	0.12

Table S1.19 Na^+ absolute leaching (K vs K+B)

Source	**df**	**F**	**p**	η_G^2
treatment	(1, 10)	0.68	0.429	0.01
time	(2.2, 22.04)	46.95	**< .001**	0.81
treatment x time	(2.2, 22.04)	0.20	0.839	0.02

Table S1.20 K^+ absolute leaching (K vs K+B)

Source	**df**	**F**	**p**	η_G^2
treatment	(1, 10)	0.32	0.585	0.01
time	(2.3, 23)	31.13	**< .001**	0.71
treatment x time	(2.3, 23)	0.29	0.781	0.02

Table S1.21 Mg^{2+} absolute leaching (K vs K+B)

Source	**df**	**F**	**p**	η_G^2
treatment	(1, 10)	0.00	0.983	0.00
time	(1.64, 16.44)	42.35	**< .001**	0.79
treatment x time	(1.64, 16.44)	0.02	0.967	0.02

Table S1.22 Ca^{2+} absolute leaching (K vs K+B)

Source	**df**	**F**	**p**	η_G^2
treatment	(1, 10)	0.07	0.796	0.00
time	(1.27, 12.69)	47.24	**< .001**	0.81
treatment x time	(1.27, 12.69)	0.09	0.824	0.01

Table S1.23 Cl^- absolute leaching (K vs K+B)

Source	**df**	**F**	**p**	η_G^2
treatment	(1, 10)	0.03	0.870	0.00
time	(1.87, 18.68)	28.56	**< .001**	0.73
treatment x time	(1.87, 18.68)	0.07	0.926	0.01

Table S1.24 SO_4^{2-} absolute leaching (K vs K+B)

Source	**df**	**F**	**p**	η_G^2
treatment	(1, 10)	0.02	0.887	0.00
time	(2.49, 24.9)	174.20	**< .001**	0.93
treatment x time	(2.49, 24.9)	0.10	0.942	0.01

Table S1.25 NO_3^--N cumulative leaching (NPK vs NPK+B)

Source	**df**	**F**	**p**	η_G^2
treatment	(1, 10)	0.13	0.725	0.01
time	(1.16, 11.6)	101.03	**< .001**	0.60
treatment x time	(1.16, 11.6)	5.40	**0.035**	0.08

Table S1.26 NH_4^+-N cumulative leaching (NPK vs NPK+B)

Source	**df**	**F**	**p**	η_G^2
treatment	(1, 10)	0.79	0.394	0.06
time	(1.75, 17.49)	529.49	**< .001**	0.88
treatment x time	(1.75, 17.49)	2.03	0.165	0.03

Table S1.27 Na^+ cumulative leaching (NPK vs NPK+B)

Source	**df**	**F**	**p**	η_G^2
treatment	(1, 10)	0.48	0.506	0.04
time	(1.39, 13.88)	618.10	**< .001**	0.89
treatment x time	(1.39, 13.88)	5.42	**0.027**	0.07

Table S1.28 K^+ cumulative leaching (NPK vs NPK+B)

Source	**df**	**F**	**p**	η_G^2
treatment	(1, 10)	0.04	0.845	0.00
time	(1.25, 12.49)	276.34	**< .001**	0.89
treatment x time	(1.25, 12.49)	2.06	0.176	0.06

Table S1.29 Mg^{2+} cumulative leaching (NPK vs NPK+B)

Source	**df**	**F**	**p**	η_G^2
treatment	(1, 10)	1.10	0.320	0.09
time	(1.32, 13.18)	316.93	**< .001**	0.71
treatment x time	(1.32, 13.18)	2.71	0.117	0.02

Table S1.30 Ca^{2+} cumulative leaching (NPK vs NPK+B)

Source	**df**	**F**	**p**	η_G^2
treatment	(1, 10)	2.25	0.165	0.18
time	(1.5, 15)	362.74	**< .001**	0.55
treatment x time	(1.5, 15)	3.27	0.077	0.01

Table S1.31 Cl^- cumulative leaching (NPK vs NPK+B)

Source	**df**	**F**	**p**	η_G^2
treatment	(1, 10)	0.00	0.969	0.00
time	(1.12, 11.21)	72.56	**< .001**	0.70
treatment x time	(1.12, 11.21)	2.74	0.124	0.08

Table S1.32 SO_4^{2-} cumulative leaching (NPK vs NPK+B)

Source	**df**	**F**	**p**	η_G^2
treatment	(1, 10)	0.00	0.954	0.00
time	(1.17, 11.66)	229.72	**< .001**	0.87
treatment x time	(1.17, 11.66)	1.39	0.269	0.04

Table S1.33 NO_3^--N cumulative leaching (NP vs NP+B)

Source	**df**	**F**	**p**	η_G^2
treatment	(1, 10)	0.06	0.813	0.01
time	(1.56, 15.61)	157.95	**< .001**	0.61
treatment x time	(1.56, 15.61)	0.99	0.373	0.01

Table S1.34 NH_4^+-N cumulative leaching (NP vs NP+B)

Source	**df**	**F**	**p**	η_G^2
treatment	(1, 10)	0.27	0.616	0.02
time	(2.42, 24.23)	486.08	**< .001**	0.87
treatment x time	(2.42, 24.23)	0.22	0.846	0.00

Table S1.35 Na^+ cumulative leaching (NP vs NP+B)

Source	**df**	**F**	**p**	η_G^2
treatment	(1, 10)	0.17	0.691	0.02
time	(2.13, 21.33)	923.31	**< .001**	0.90
treatment x time	(2.13, 21.33)	0.52	0.615	0.00

Table S1.36 K^+ cumulative leaching (NP vs NP+B)

Source	**df**	**F**	**p**	η_G^2
treatment	(1, 10)	0.00	0.988	0.00
time	(1.44, 14.36)	406.77	**< .001**	0.91
treatment x time	(1.44, 14.36)	0.32	0.662	0.01

Table S1.37 Mg^{2+} cumulative leaching (NP vs NP+B)

Source	**df**	**F**	**p**	η_G^2
treatment	(1, 10)	0.11	0.743	0.01
time	(1.62, 16.23)	446.93	**< .001**	0.58
treatment x time	(1.62, 16.23)	0.25	0.740	0.00

Table S1.38 Ca^{2+} cumulative leaching (NP vs NP+B)

Source	**df**	**F**	**p**	η_G^2
treatment	(1, 10)	0.06	0.813	0.01
time	(1.53, 15.32)	425.49	**< .001**	0.46
treatment x time	(1.53, 15.32)	0.14	0.812	0.00

Table S1.39 Cl^- cumulative leaching (NP vs NP+B)

Source	**df**	**F**	**p**	η_G^2
treatment	(1, 10)	1.25	0.290	0.08
time	(1.33, 13.3)	58.05	**< .001**	0.61
treatment x time	(1.33, 13.3)	1.47	0.257	0.04

Table S1.40 SO_4^{2-} cumulative leaching (NP vs NP+B)

Source	**df**	**F**	**p**	η_G^2
treatment	(1, 10)	0.11	0.746	0.01
time	(2.19, 21.85)	459.53	**< .001**	0.77
treatment x time	(2.19, 21.85)	0.85	0.452	0.01

Table S1.41 NO_3^--N cumulative leaching (K vs K+B)

Source	**df**	**F**	**p**	η_G^2
treatment	(1, 10)	0.02	0.885	0.00
time	(1.3, 13.04)	67.02	**< .001**	0.35
treatment x time	(1.3, 13.04)	0.06	0.875	0.00

Table S1.42 NH_4^+-N cumulative leaching (K vs K+B)

Source	**df**	**F**	**p**	η_G^2
treatment	(1, 10)	0.66	0.434	0.06
time	(2.15, 21.5)	792.21	**< .001**	0.90
treatment x time	(2.15, 21.5)	1.42	0.265	0.02

Table S1.43 Na^+ cumulative leaching (K vs K+B)

Source	**df**	**F**	**p**	η_G^2
treatment	(1, 10)	0.69	0.425	0.06
time	(1.64, 16.42)	698.25	**< .001**	0.88
treatment x time	(1.64, 16.42)	0.33	0.681	0.00

Table S1.44 K^+ cumulative leaching (K vs K+B)

Source	**df**	**F**	**p**	η_G^2
treatment	(1, 10)	0.16	0.700	0.01
time	(1.25, 12.51)	241.11	**< .001**	0.80
treatment x time	(1.25, 12.51)	0.53	0.520	0.01

Table S1.45 Mg^{2+} cumulative leaching (K vs K+B)

Source	**df**	**F**	**p**	η_G^2
treatment	(1, 10)	0.00	0.966	0.00
time	(1.18, 11.79)	138.83	**< .001**	0.41
treatment x time	(1.18, 11.79)	0.02	0.915	0.00

Table S1.46 Ca^{2+} cumulative leaching (K vs K+B)

Source	**df**	**F**	**p**	η_G^2
treatment	(1, 10)	0.17	0.690	0.02
time	(1.19, 11.95)	151.64	**< .001**	0.34
treatment x time	(1.19, 11.95)	0.30	0.634	0.00

Table S1.47 Cl^- cumulative leaching (K vs K+B)

Source	**df**	**F**	**p**	η_G^2
treatment	(1, 10)	0.02	0.882	0.00
time	(1.47, 14.68)	61.01	**< .001**	0.38
treatment x time	(1.47, 14.68)	0.13	0.812	0.00

Table S1.48 SO_4^{2-} cumulative leaching (K vs K+B)

Source	**df**	**F**	**p**	η_G^2
treatment	(1, 10)	0.24	0.637	0.02
time	(2.17, 21.74)	480.96	**< .001**	0.84
treatment x time	(2.17, 21.74)	0.06	0.953	0.00

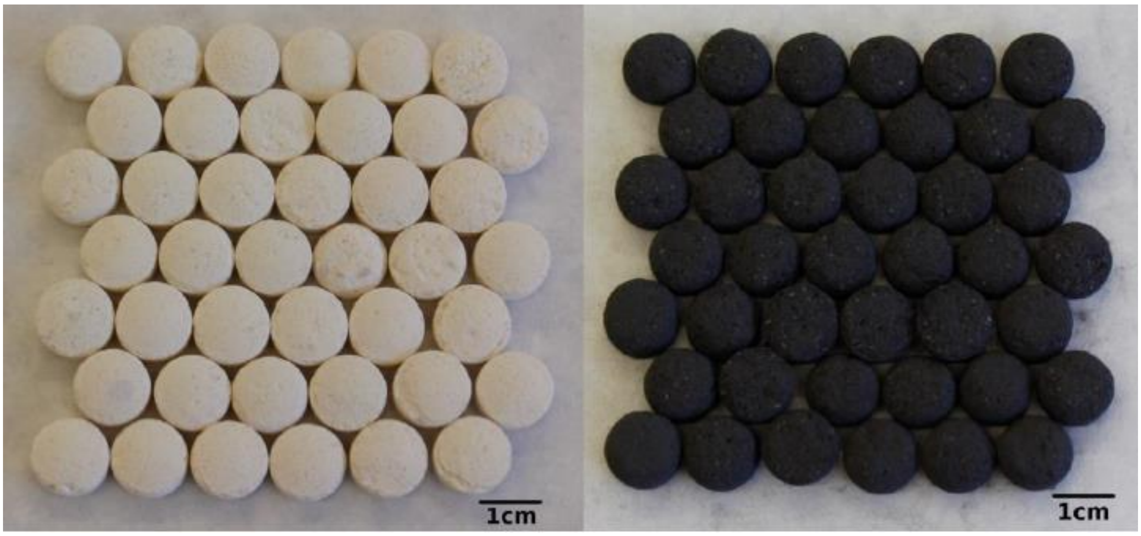

Fig. S1 Fertiliser tablets without (left) and with biochar (right)

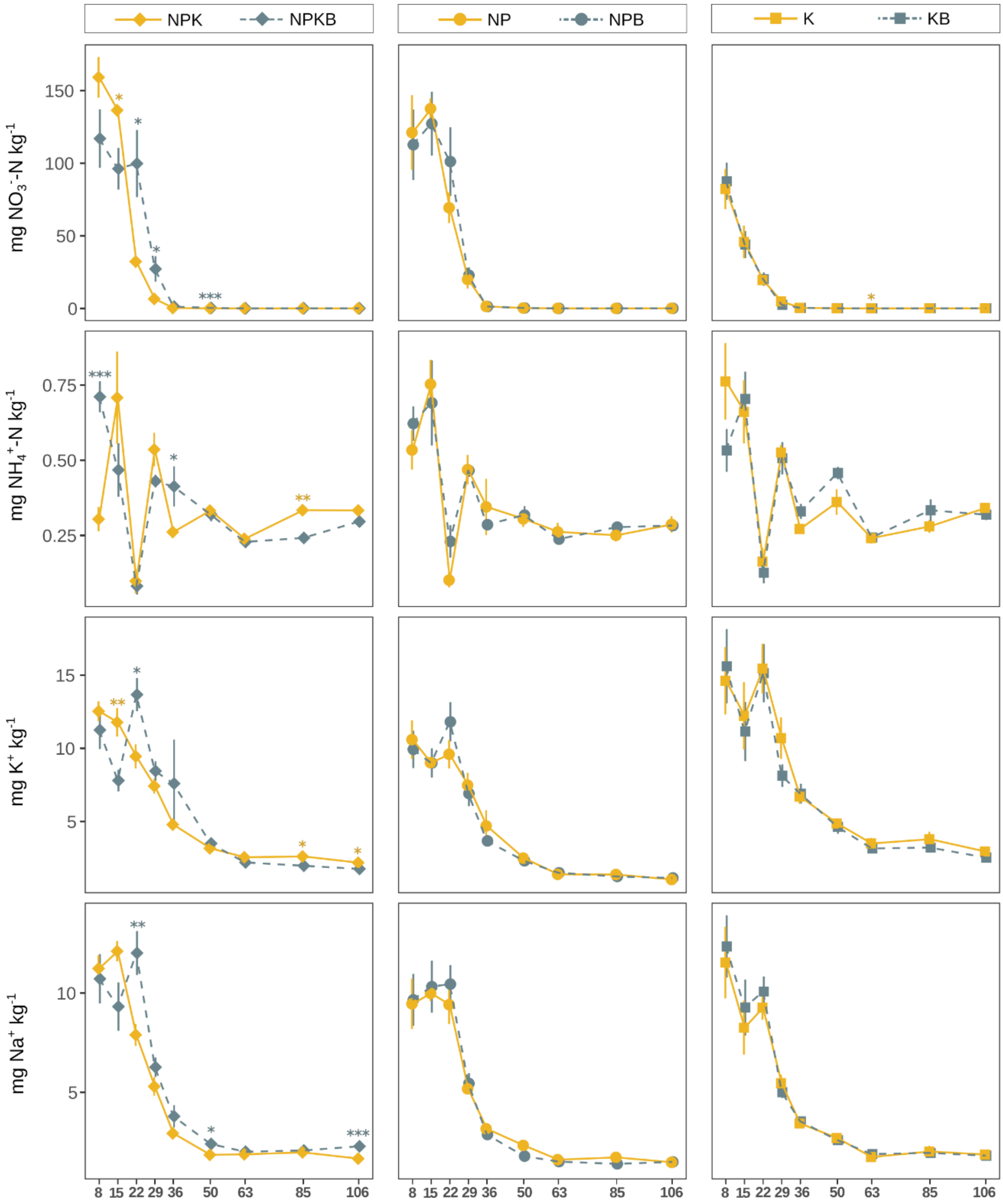

Fig. S2 Absolute leaching of NO$_3^-$-N, NH$_4^+$-N, K$^+$, and Na$^+$ (mg kg^{-1} dry soil) for the three pairs of organo-mineral fertilisers (NPK vs NPK+B, NP vs NP+B, and K vs K+B) along nine leaching events. *,**,*** indicate significant differences at p values comprised between 0.05 and 0.01, between 0.01 and 0.001, and <0.001, respectively. The colour of the asterisk matches the colour of the treatment with higher leached amount

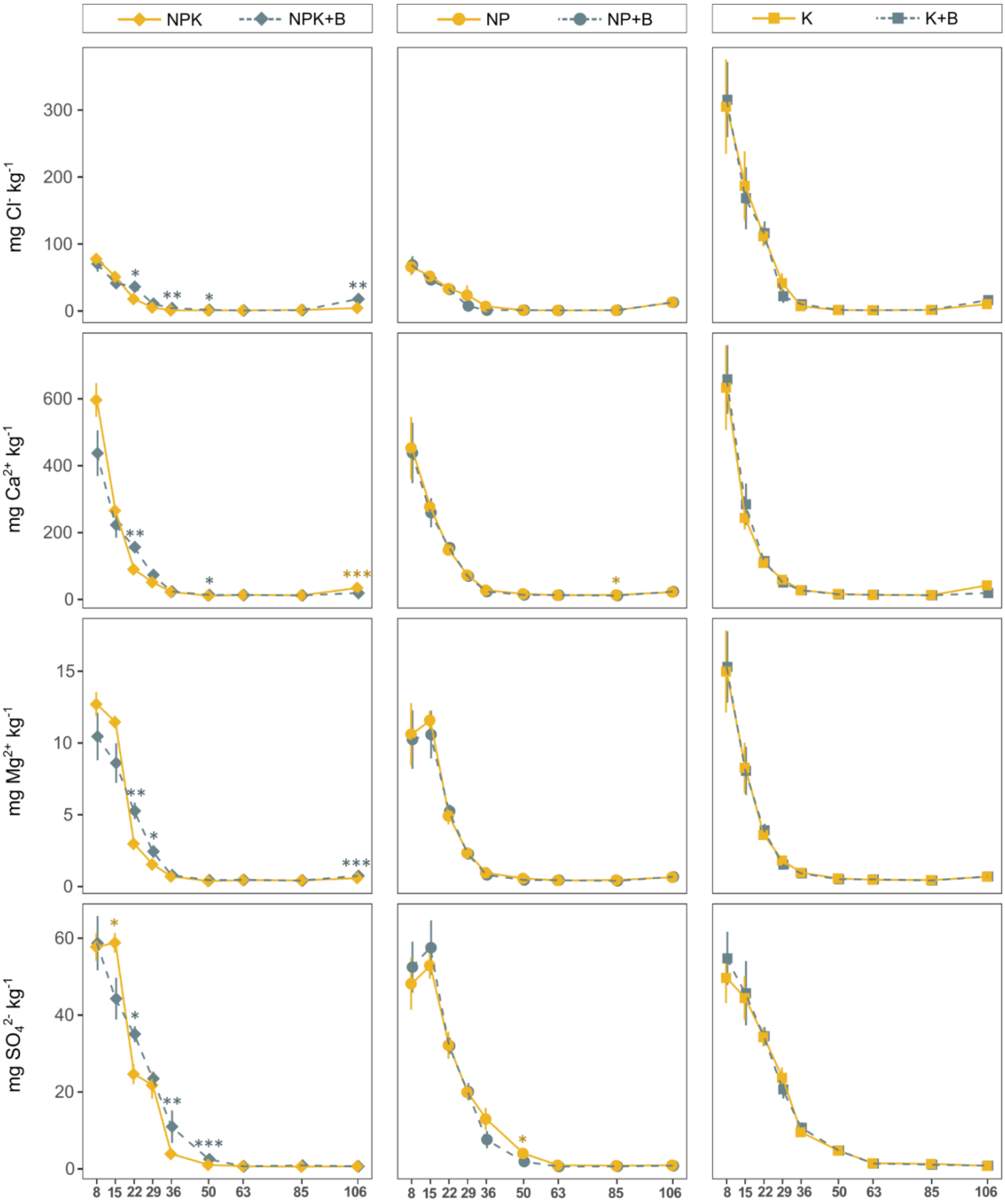

Fig. S3 Absolute leaching of Cl^-, Ca^{2+}, Mg^{2+}, and SO_4^{2-} (mg kg^{-1} dry soil) for the three pairs of organo-mineral fertilisers (NPK vs NPK+B, NP vs NP+B, and K vs K+B) along nine leaching events. *,**,*** indicate significant differences at p values comprised between 0.05 and 0.01, between 0.01 and 0.001, and <0.001, respectively. The colour of the asterisk matches the colour of the treatment with higher leached amount

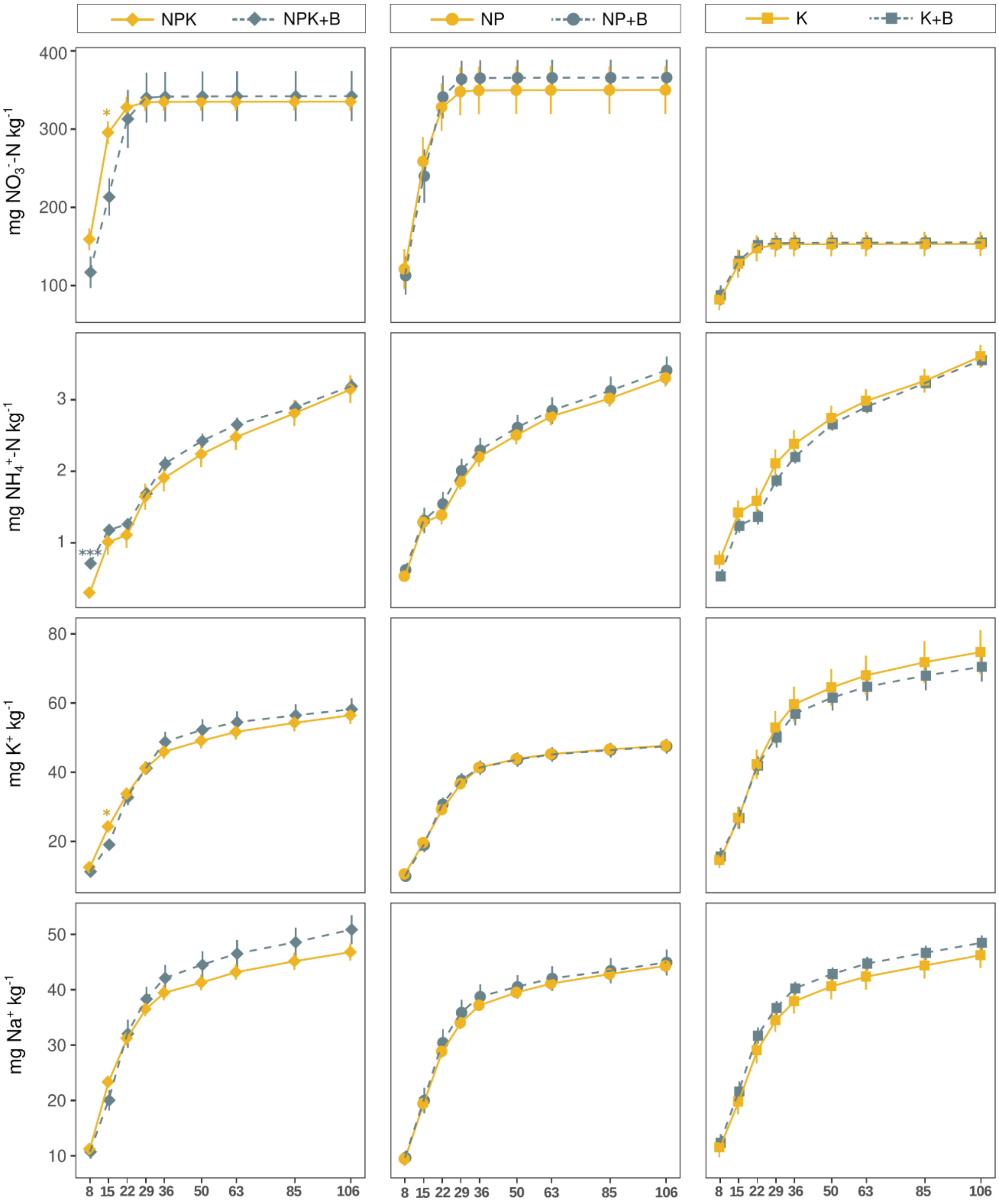

Fig. S4 Cumulative leaching of NO_3^--N, NH_4^+-N, K^+, and Na^+ (mg kg^{-1} dry soil) for the three pairs of organo-mineral fertilisers (NPK vs NPK+B, NP vs NP+B, and K vs K+B) along nine leaching events. *,**,*** indicate significant differences at p values comprised between 0.05 and 0.01, between 0.01 and 0.001, and <0.001, respectively. The colour of the asterisk matches the colour of the treatment with higher leached amount

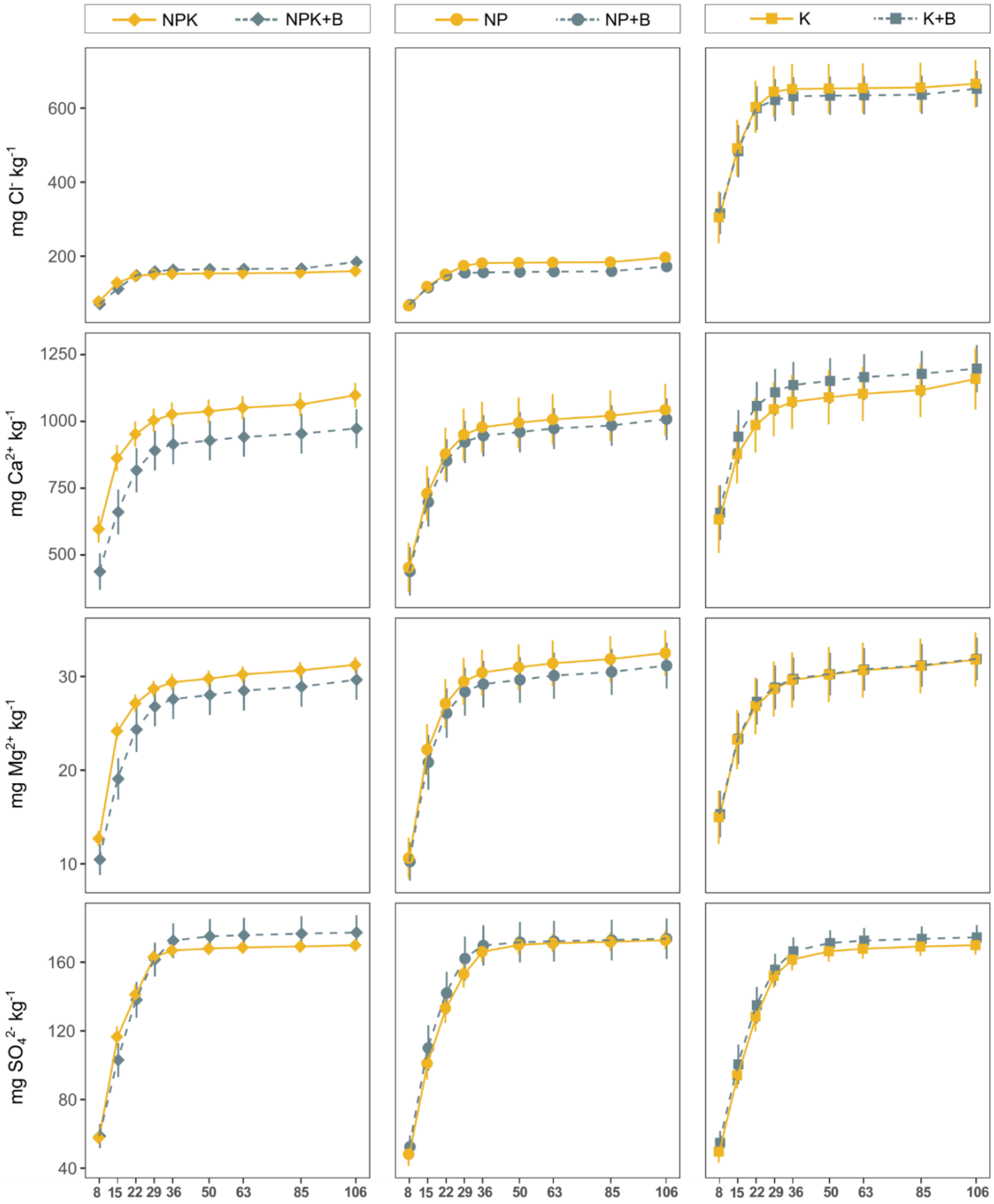

Fig. S5 Cumulative leaching of Cl^-, Ca^{2+}, Mg^{2+}, and SO_4^{2-} (mg kg^{-1} dry soil) for the three pairs of organo-mineral fertilisers (NPK vs NPK+B, NP vs NP+B, and K vs K+B) along nine leaching events. There were no significant statistical differences between each pair of fertilisers at each sampling date