Sustainable soil amendments to improve nature-based wastewater treatment through vegetation filters: nutrients transformation and recovery

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Abstract

Urban wastewater effluents contain important amounts of nutrients that, in small and scattered populations, can be recovered using vegetation filters (VFs). However, an excess of nutrients entering into the environment has become a global threat causing negative effects such as eutrophication of water bodies. The addition of two sustainable soil amendments, woodchips and biochar, has been tested as a strategy to improve nutrient attenuation in VFs increasing sorption sites and microbial activity.

To this end, unsaturated infiltration and batch experiments have been carried out at laboratory scale. A stock solution of synthetic wastewater was produced mimicking the real wastewater used to irrigate a pilot scale VF. The systems for infiltration experiments contain natural soil, natural soil amended with woodchips and natural soil amended with biochar. To determine the sorption capacity of NH_4^+, batch tests were performed using an amendment/SWW ratio of 1:20 and an NH_4^+ initial concentration ranging from 30 to 600 mg L^{-1}.

Results from the infiltration experiments show a high attenuation (~ 95%) of total phosphorous (TP) independently of the amendments. Different behaviour is observed for total nitrogen (TN). The removal of this species is obtained only in the soil amended with woodchips (> 85%) whereas the natural soil alone and the soil with biochar have no impact on TN attenuation. In these two porous media, all the NH_4^+ input concentration is transformed to NO_3^- that infiltrates without further reactions. According to our batch experiment results, the potential role of biochar in the nutrient attenuation is limited to sorption processes (K_d (NH_4^+)= 21.37-193.18 L kg^{-1}). Woodchips act primarily as a labile source of carbon promoting biodegradation, being more effective for nutrient attenuation than the sorption capacity of biochar.

1. Introduction

An excess of nutrients entering into the environment has become a global threat causing negative effects such as eutrophication of water bodies. However, nutrient concentrations in soil are necessary for the vegetation to grow. Urban wastewater effluents contain important amounts of nutrients. Water and nutrients are important resources that can be recovered from wastewater changing the paradigm of seeing wastewater as a source of contaminants into a source of valuable compounds (Neczaj and Grosser, 2018).

In small municipalities and scattered populations, the application of nature-based treatment systems usually entails a favourable integration into the environment, minimizing the consumption of energy (Miloš Rozkošný et al., 2014). The use of Vegetation Filters (VFs) to treat wastewater can be a sustainable solution for these cases. A VF, as a type of Land Application System, is a non-conventional water treatment technology where wastewater and/or treated water is applied for the irrigation of a forestry plantation. The treatment is carried out by the mutual action of soil, microorganisms and plants. In this system, nutrients are recovered from wastewater by plant uptake to generate biomass. The main advantages are: i) the low maintenance costs; ii) the production of biomass as an extra economic value; iii) the low energy consumption; iv) the contribution to mitigate climate change as CO_2 sink; v) the increase of groundwater resources by irrigation returns and vi) the creation of an ecologic niche that fosters biodiversity.

Part of the nutrients, such as phosphorous and nitrogen, present in wastewater are retained in soil. Phosphorous is removed from the water and remain in the soil phase due to mineral precipitation with calcium, iron and aluminium. Part of the nitrogen, present in wastewater in form of NH_4^+, is sorbed onto the soil by cation exchange prior to its transformation to NO_3^-. In these forms, nutrients can be stored in the soil and used by plants when necessary. Although the plants recover part of the nutrients, there is the possibility of their leaching towards deeper levels. For example, when NH_4^+ is transformed to NO_3^- it becomes very mobile in the subsurface and, therefore it can reach the aquifer and contaminate groundwater resources. Different studies have demonstrated that VFs highly reduce total nitrogen (NT) concentrations in water during infiltration (Aronsson and Perttu, 2011; de Miguel et al., 2014; Holm and Heinsoo, 2013) but the transformation to NO_3^- also occurs and is the main disadvantage of the system (de Miguel et al., 2014).

The removal of NO_3^- from water can be performed using ion-exchange, reverse osmosis and electrodialysis but they are expensive and displace NO_3^- into a concentrated waste brine that may pose a disposal problem afterwards (Shrimali and Singh, 2001). Denitrifying bacteria that use bound oxygen in NO_3^- as electron acceptor carries out biological denitrification. This process presents an advantage since it reduces NO_3^- to innocuous nitrogen gas. Woodchips have been used to treat high NO_3^- content waters in denitrifying bioreactors with promising results (Nordström and Herbert, 2018; Schipper et al., 2010). Indeed, woodchips act as electron donors for denitrification due to their high content of carbon. Denitrifying bacteria are found in soils and their activity can be promoted by incorporating woodchips as a source of organic matter (OM) reducing oxygen and favouring anoxic conditions (Meffe et al., 2016).

On the other hand, biochar is a potential sorbent for inorganic and organic ions by chemical and physical sorption. Its sorption capacity as soil amendment has been tested to immobilize different type of contaminants such as trace metals (Rechberger et al., 2019), CO_2 and nutrients (Pokharel and Chang, 2019) and organic compounds such as pesticides (Ghani et al., 2018; Yang et al., 2010). Its addition to the soil increases the sorption capacity and also can change pore structure and aeration, improving the physico-chemical conditions for plants and microbes (Ajayi and Horn, 2017) to retain and remove nutrients and OM.

The sorption capacity of the soil together with the microbial activity able to degrade OM are essential factors to be addressed in order to maximize contaminant attenuation using VFs. In this sense, the addition of two soil amendments, biochar and woodchips, has been tested as a strategy to improve nutrient attenuation in VFs by increasing sorption sites and promoting microbial activity. We expect that woodchips increase sorption sites and, especially, stimulate microbial activity due to the addition of extra organic carbon. We hypothesise that the addition of biochar as a soil amendment considerably increases sorption sites and favours the establishment of the soil microbial community due to its high surface area. Besides their properties, both amendments have the advantage of being provided from the VF itself following therefore a sustainable and resource recovery approach.

Laboratory scale experiments represent a valid and efficient methodology to determine reactive transport parameters and to monitor environmental variables. The hydrodynamic and redox conditions occurring during infiltration through the subsurface affect nutrient cycles. Therefore, it is very important to accurately reproduce the field conditions with specific experiments that enable to reproduce unsaturated conditions and that overcome the limitation of this finite system.

The objectives of this work are: i) to determine the sorption capacity of woodchips and biochar to retain NH_4^+; ii) to evaluate the effects of the two amendment addition in the hydrodynamic of the soil; iii) to assess the removal capacity of nutrients and OM from wastewater during infiltration when adding woodchips or biochar to the soil. To this end, infiltration under unsaturated conditions and batch experiments have been carried out at laboratory scale.

2. Methods

2.1. Soil, synthetic wastewater and amendments

The soil used in the experimental tests comes from a pilot scale VF that treats wastewater from an office building. Consequently, soil had been in contact with pretreated wastewater for one year allowing biological and chemical equilibration. The VF is divided in 5 furrows but only the 3 central furrows were sampled to avoid border effects. During the sampling campaign, 9 sample units of soil (approximately 2 kg each unit) were collected from the first 30 cm (3 units per furrow sampled). The soil was air-dried, mixed, gently crushed and passed through a 2 mm sieve. Quartering method was applied to form a composite sample. Soil was maintained refrigerated (4ºC) until the experimental set-up.

The collected soil is a sandy clay loam soil (50.9% sand, 22.5% silt and 26.6% clay), contains 1.69% of OM and its cation exchange capacity is 11.1 $cmol_c\ kg^{-1}$.

A stock solution of synthetic wastewater (SWW) mimicking the real composition of the wastewater used to irrigate the pilot scale VF was produced in the laboratory using the following reagents (purity > 95.0%) in tap water: $(NH_4)_2CO_3$ (0.08 g L^{-1}), $KHCO_3$ (0.04 g L^{-1}), NH_4Cl (0.09 g L^{-1}), $MgSO_4$ (0.02 g L^{-1}), $CaCl_2$ (0.03 g L^{-1}), K_2HPO_4 (0.015 g L^{-1}), $NaHCO_3$ (0.18 g L^{-1}), peptone (0.03 g L^{-1}), and meat extract (0.08 g L^{-1}) (all purchased from Scharlab, Spain). Such a recipe provides the concentrations given in Table 1. The software PHREEQC-2 (Parkhurst and Appelo, 1999) was used to check the thermodynamic stability of the solution, confirming the absence of mineral precipitation. Periodic analyses of the SWW were also performed to exclude both mineral precipitation and microbial degradation. Results proved that the SWW could be stored at 4ºC during approximately two weeks without changes in chemical composition.

Table 1. Mean concentrations and standard deviations in terms of OM, nutrients and other ion concentrations in SWW, reproducing the concentrations measured in real wastewater.

		SWW
Total carbon (mg L^{-1})	TC	69.61±4.96
Total organic carbon (mg L^{-1})	TOC	32.79±8.09
Chemical Oxygen Demand (mg L^{-1})	COD	107.67±8.48
Total Nitrogen (mg L^{-1})	TN	50.75±10.60
Nitrogen in nitrate form (mg L^{-1})	$N\text{-}NO_3$	0.16±0.04
Nitrogen in ammonia form (mg L^{-1})	$N\text{-}NH_4$	38.72±4.24
Total Phosphorous (mg L^{-1})	TP	4.96±0.33
Phosphorous in phosphate form (mg L^{-1})	$P\text{-}PO_4$	4.04±0.17
Carbonates (mg L^{-1} $CaCO_3$)	CO_3^{2-}	0.56±1.24
Bicarbonates (mg L^{-1} $CaCO_3$)	HCO_3^{2-}	167.29±16.84
Sulphate (mg L^{-1})	SO_4^{2-}	29.37±3.80
Chlorine (mg L^{-1})	Cl^-	146.37±7.30
Sodium (mg L^{-1})	Na^+	61.31±0.85
Potassium (mg L^{-1})	K^+	27.45±1.60
Calcium (mg L^{-1})	Ca^{2+}	29.78±1.76
Magnesium (mg L^{-1})	Mg^{2+}	6.73±0.36

Woodchips were obtained for the pilot scale VF. Poplars were pruned after 2 years of experiment and the wood was chipped in situ and let dry under environmental conditions. Biochar was obtained by pyrolysis of poplar woodchips and it was carried out in a Microsynth Microwave oven (Batch) from Milestone following the methodology described in Martín et al. (2017).

2.2. Infiltration experiments

To investigate the attenuation of nutrients during vadose zone infiltration, three unsaturated infiltration experiments were performed. A detailed sketch of the experimental set-up is reported in Fig. 1.
The systems contain natural soil (Column S), natural soil amended with 3% w/w of woodchips (Column S+W) and natural soil amended with 3% w/w of biochar (Column S+B). The porous materials were packed with increments of 2 cm in stainless steel columns (L 30.0 cm, Ø 8.49 cm) avoiding the formation of stratified layers and preferential flow paths. In the case of the column S, the obtained bulk density resembles that measured in the soil of the pilot scale FV (1.57 g cm^{-3}).

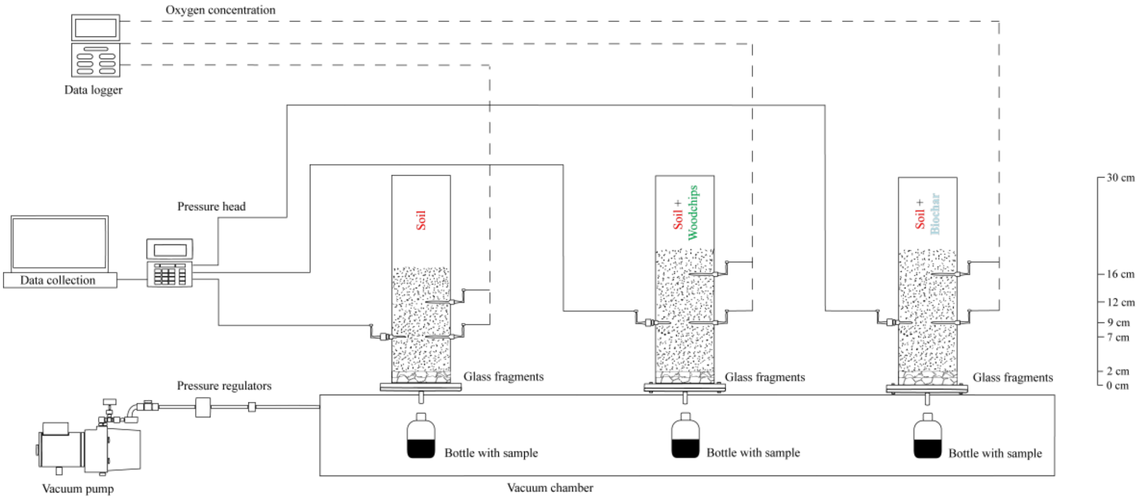

Fig. 1. A schematic representation of the experimental set-up. Pressure heads and oxygen concentrations were measured by two tensiometers and one oxygen probe, respectively installed along the columns. Most of the devices and instruments of the experimental set-up were purchased from Soil Measurements Systems (SMS, Tucson, AZ)

A teflon membrane with a bubbling pressure of 600 mbar was placed at the lower end of the columns. Between the membrane and the porous material (soil or soil+amendments), a 2 cm layer of glass fragments (Ø 0.6-1.2 mm) was also located to prevent membrane clogging. Once assembled, the columns were saturated with SWW by an upward flow of 0.1 ml min^{-1} using a peristaltic pump. The upward flow ensures the absence of entrapped air. Once saturated, the columns were weighted to obtain the saturated water content and total porosity (Table 2).

Table 2. Column set-up parameters

	S	S+W	S+B
Total porosity	0.33	0.43	0.43
Bulk density (g cm^{-3})	1.55	1.36	1.36
Saturated water content (ml)	283.05	433.90	433.45

S: Soil; S+W: Soil + Woodchips; S+B: Soil + Biochar

The columns were then let to drain under atmospheric pressure and when water flow ceased the outlets were connected to a vacuum chamber where a constant pressure of 250 mbar was applied by a vacuum pump and recorded by a manual manometer. During 5 weeks, hydraulic adjustments of the columns using SWW were performed to adapt the drainage of the experimental set-up to that observed at field conditions. Once a reasonable match between the two scales was obtained, experiments began and lasted for 10-12 weeks. The irrigation of wastewater occurring at the pilot scale by flooding the furrows of the VF was simulated in the laboratory by manually applying 500 ml of SWW at the upper end of the columns once per week. The simulated irrigation occurred in a dual pulse of 250 ml each, in the following referred to as irrigation event, with a difference of 4 hours between the first and the second one. SWW was generated and preserved under dark at each irrigation event to keep organic and inorganic input concentrations constant. During the experiment, unsaturated conditions were ensured by the suction pressure applied at the vacuum chamber and water contents were monitored weekly by weighting the columns shortly before each irrigation event. The average saturation degree was 82.6±3.2%, 77.3±6.9% and 72.1±2.7% for S, S+W and S+B, respectively. To monitor redox conditions inside the columns, two calibrated oxygen minisensors (optodes)

(Presens, Fibox 3, 2 mm cable) were placed along the column profile at 5 and 10 cm depth for S and at 4 and 11 cm depth for S+W and S+B. The optical oxygen measurement is based on the fluorescence-quenching effect of oxygen. Modulated blue light is fed into an optical fibre with a fluorescent dye glued to its tip. The fluorescent light is returned by the optical fibre and detected in the measuring device. In the presence of oxygen fluorescence is quenched, and on the basis of the intensity and lifetime of the fluorescence the oxygen concentration can be detected (Hecht and Kölling, 2002). To study the hydrodynamic during wetting and drying cycles, a tensiometer was installed at a depth of 10 cm in the column S and of 11 cm in column S+W and column S+B. The tensiometer is provided with a pressure transducer that convert a pressure differential into a voltage recorded on a datalogger every 2 min. The voltage is then converted to units of pressure using the calibration curve developed prior to tensiometer installation.

2.3. Batch experiments

Nitrogen is present in the wastewater in form of NH_4^+ and to determine the capacity of biochar and woodchips to sorb this species, batch tests were performed.

<u>2.3.1. Sorption experimental design</u>

The sorption isotherms were determined in parallel batch experiments following OECD guideline 106 (OECD, 2000). SWW (50 mL) in 100 ml plastic vessels containing 2.5 g amendment was spiked with NH_4Cl at different NH_4^+ concentrations (30, 60, 100, 300 y 600 mg L^{-1}). The OECD guidelines recommend a 1:5 sediment/water ratio for batch experiments, but a 1:20 amendment/SWW ratio was selected to better mimic unsaturated water conditions and to have enough volume of the liquid phase to be analysed. The vessels were shaken at 180 rpm for 24 h until sorption equilibrium was reached. All preparations were made in triplicate per each amendment (woodchips and biochar). To measure the current NH_4^+ concentration in the amendments, and to exclude the possibility of NH_4^+ sorption onto the vessels and degradation, control (without amendment) and blank (without NH_4^+) samples were prepared in triplicate and analysed along with the others. After 24 h, samples were collected from each vessel and centrifuged at 4,000 rpm for 20 min to separate the liquid phase from the amendment. The supernatants were then stored at 4ºC during 24-48h until analysis (see the *Chemical analysis* section).

<u>2.3.2. Desorption experimental design</u>

The desorption isotherms were determined following OECD guideline 106 (OECD, 2000), placing amendment (50 g) with previously sorbed NH_4^+ (at all concentrations) in contact with 0.01 M $CaCl_2$ (50 mL) solution for 24 h in 100 ml plastic vessels. Analysis of the liquid phase was then performed as described in the *Chemical analysis* section.

<u>2.3.3. Sorption and desorption isotherms</u>

The sorption and desorption results for NH_4^+ were matched against the linear, Freundlich, and Langmuir isotherm models. The Freundlich model is described as follows:

$$C_s = K_F \cdot C_w^{\,n} \qquad (1)$$

where C_s (mg kg^{-1}) and C_w (mg L^{-1}) are the sorbed and solution concentrations at equilibrium respectively, K_F (mg^{1-n} L^n kg^{-1}) is the Freundlich distribution coefficient, and n (dimensionless) is the Freundlich exponent. The linear model is manifested when the Freundlich exponent is equal to 1.

Unlike the Freundlich model, the Langmuir contemplates a limited number of sorption sites that become saturated in a monolayer sorbent. It is described as follows:

$$C_s = \frac{C_{max} \cdot K_L \cdot C_w}{1 + K_L \cdot C_w} \qquad (2)$$

where K_L (L mg^{-1}) is the Langmuir constant, and C_{max} (mg kg^{-1}) is the maximum sorbed concentration.

2.4. Statistical analysis

Statistical analyses were applied to experimental data through the open source software PSPP (Free Software Foundation, Inc.). Significance of differences of the means (n=9) of the COD, TP and TN removal among the infiltration experiments was investigated by means of one-way ANOVA using a post hoc test (Tukey). The homogeneity of variances was verified by Levene test. Only the first 9 irrigation events were considered for the statistical analysis due to their steady state pattern.

2.5. Chemical analysis

Liquid phase (SWW and $CaCl_2$) samples from the column inlets and outlets and from the batch sorption and desorption experiments were analysed for their pH (Crison MM-41) (UNE-EN-ISO-10523:2012). Also, COD was determined by the dichromate method (UNE-77004:2002), TN by using oxidative digestion with peroxidisulfate (UNE-EN-ISO-11905-1:1998) and TP by the ammonium molybdate spectrometric method (UNE-EN-ISO-6878:2005) (Merck Spectroquant TR420 and Spectroquant Pharo 100 Spectrophotometer). TOC analysis was performed by combustion and infrared spectrophotometry (Shimadzu TOC-VCSH analyzer with an autosampler ASI-V) (UNE-EN-ISO 5814). The dissolved ions (NO_2^-, NO_3^-, PO_4^{3-}, Cl^-, SO_4^{2-}, NH_4^+, Na^+, K^+, Ca^{2+}, Mg^{2+}) were analysed using a 930 Compact Ion Chromatography Flex (autosampler 858 Professional Sample Processor) coupled to a Titrando 809 (autosampler 814 USB Sample Processor) for HCO_3^- ions (Metrohm).
Soil and amended soil (before and after the column experiment) samples were analysed at different depths for OM by the loss-on-ignition method at 360ºC for 24h, for total Kjeldahl nitrogen (TKN) by the Kjeldahl method (Bloc Digest 6 for mineralization and automatic Pro-Nitro A distillation unit, Selecta) (UNE 77318:2001), for NO_3-N after extraction following the method described by Griffin et al. (2011) by a two-channel advanced compact ion chromatograph apparatus and for total phosphorous (TP) after microwave acid digestion by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) quantification.

3. Results and discussion

3.1. Hydraulic and redox conditions of the infiltration experiments

Suction pressures monitored by tensiometers during two irrigation events (once a week) are shown in Fig. 2. Coherent wetting and drying cycles were obtained only for column S and column S+W. The response of the tensiometers to the irrigation indicates hydraulic properties of the columns that are largely difference. The shape of the curves and arrival time of the wetting front already reveal that column S+W has higher hydraulic conductivity if compared to that of column S. Differences between hydraulic conductivities are mainly related to differences in the value of the bulk densities (Table 2).

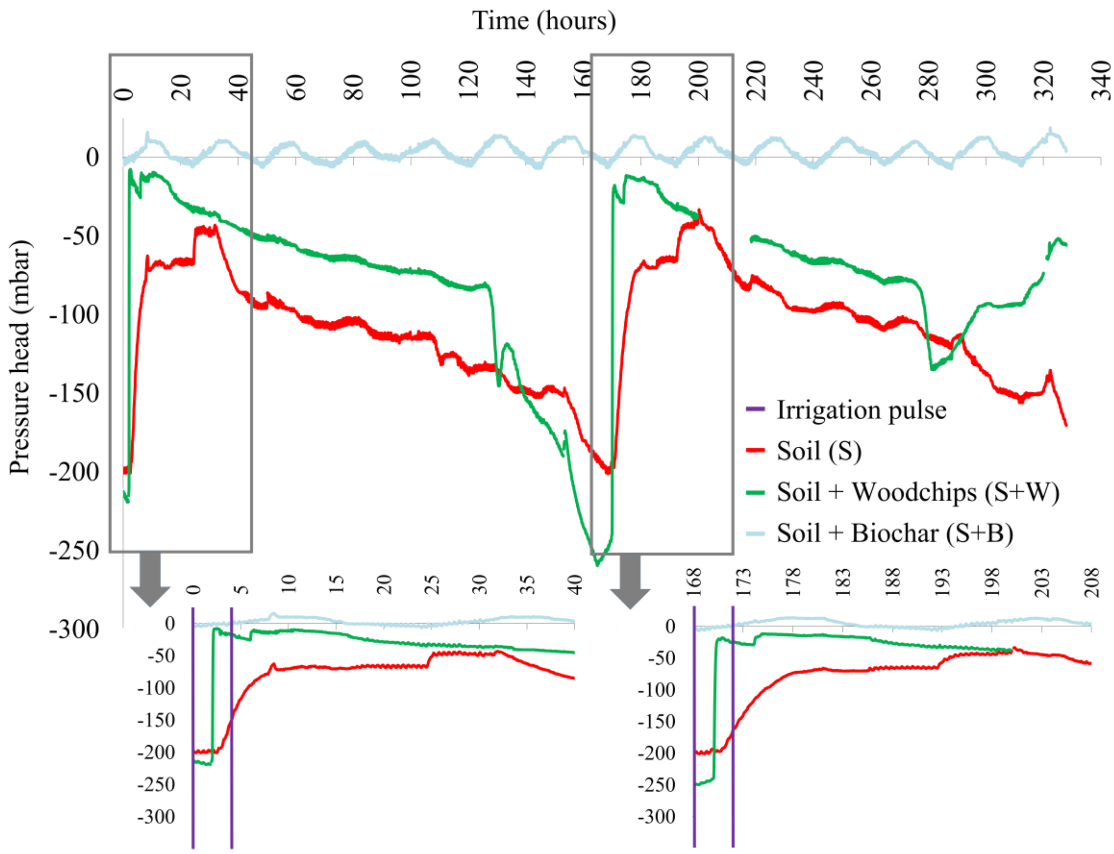

Fig. 2. Tensiometer water cycles at two irrigation events with two irrigation pulses each event. The irrigation was performed at time 0, 4, 168 and 172 hours.

It can be recognized that pressure head in the column amended with woodchip (S+W) increases rapidly 2 h after the first irrigation. The effect of the second irrigation pulse is observed again after 2 h. As indicated by the sharp slope of the descending curve, most of the water have already drained after approximately 16 h, a behaviour that agrees with the observations performed during experimental control.

The increase in pressure head in the column S due to the first irrigation pulse occurs slower and the maximum value is reached only after 8 h. Once the second pulse of irrigation is applied, increasing pressures are registered after 20 h. The descending part of the curve reveals that drainage in the column S takes place during approximately 40 h. Unfortunately, it was not possible to register reliable data of pressure heads in the column S+B. Indeed, the tensiometer installed in this column provided always values that were oscillating around 0 mbar independently of the irrigation schedule. The strong sorption capacity of biochar may impact the tensiometer measurements by over suctioning water from its ceramic cup. Indeed when a strong tension is applied, the tensiometer empties and periodic water refill should be performed to avoid erratic measurements. The refill consists in the immersion of the tensiometer in water after extraction of the device from the column. Such a procedure results in a column disturbance that is inevitable and for this reason it was decided not to proceed to the refilling assuming the risk of losing tension data to safeguard the stability of the hydraulic dynamics.

The lack of tensiometer data from column S+B can be offset by the data about oxygen concentration (Fig. 3). The variation in oxygen concentration reflects the infiltration of the wetting front. Data from the oxygen probes support the conclusion about hydraulic conductivity of column S and S+W drawn by using tensiometer data. Indeed, hydraulic conductivity of these two systems represent the two extremes with lowest and highest value whereas column S+B presents an intermediate behaviour between columns S and column S+W. As expected from the column set-up parameters (Table 2), the drainage of the column amended with biochar presents a lower residence time than to the column S as also observed during the monitoring of the experiment.

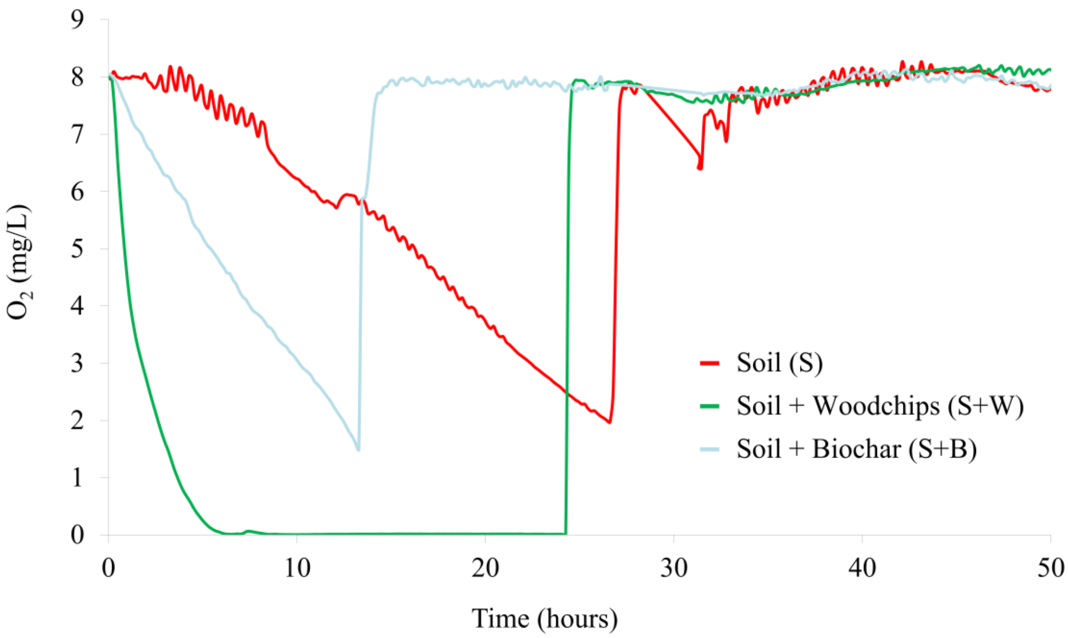

Fig. 3. Oxygen concentrations from the upper oxygen probe of each column during one irrigation event.

Regarding redox conditions in the infiltration experiments, oxygen concentrations in S+W decrease and after approximately 5 h the system reaches anoxic conditions that lasts up to 24 h after the irrigation. This is the proof that the additional OM supplied by woodchips amendment enhances microbial activity that consumes the available dissolved oxygen to degrade this OM and wastewater-originated nutrients. On the other hand, the lowest oxygen concentrations in the S and in the S+B columns are punctual (1.97 and 1.49 mg L^{-1}, respectively) and never reach the 0 mg L^{-1} implying that oxic conditions are predominant. Anoxic conditions were also measured in different systems when a microbial community is using woodchips as a carbon source when added to the soil (Meffe et al., 2016) or in woodchips bioreactors (Schipper et al., 2010).

3.2. Chemical Oxygen Demand (COD)

OM removal is shown in terms of COD for the three infiltration experiments in Fig. 4.

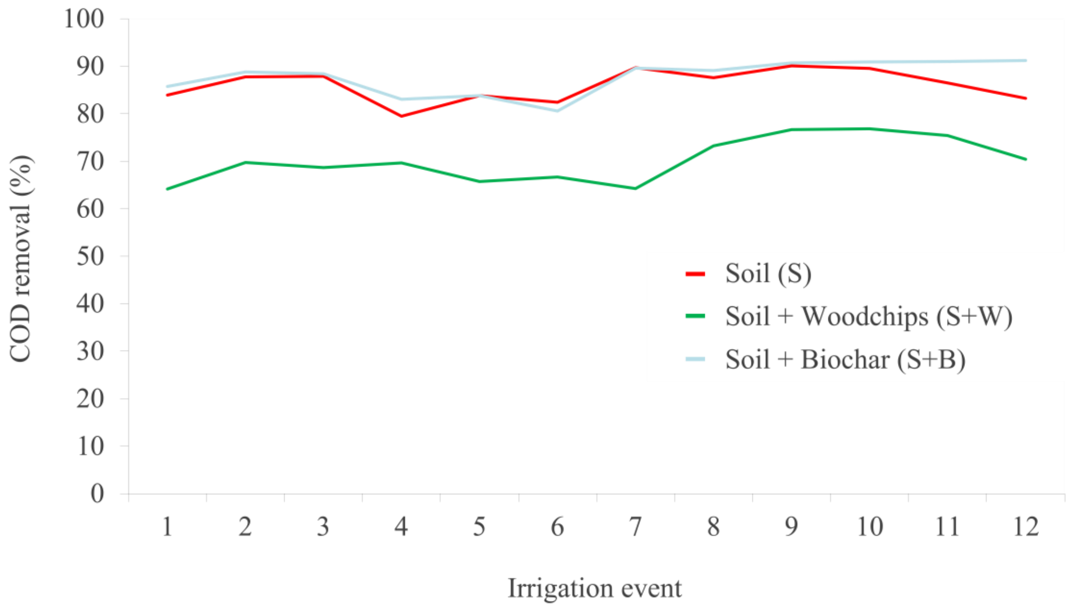

Fig. 4. COD removal percentages in each column effluent.

Columns S and S+B exhibit the best performance in terms of COD removal (in average 86.0% and 87.7%, respectively). Whereas, column S+W is less efficient in the attenuation of COD (70.1%). Indeed, COD removal is significantly lower in the S+W than in the other two experiments ($p<0.001$). Although the microbial activity seems to be more developed in the S+W column (see following section of nutrients), only the biodegradable OM is actually treated. Indeed, the obtained results suggest that the addition of woodchips as a source of OM is responsible also for the leachate of non-degradable OM. Besides that, it has to be considered that the amendments of the soil increase hydraulic conductivity reducing retention times in the columns. This holds true especially for column S+W, that shows the shortest residence times among the systems and therefore the less attenuation of COD may be related to its hydrodynamic.
The performance of S and S+B columns are very similar indicating that the addition of biochar as an amendment has not any effect in the COD removal efficiency. Despite this, we found differences in the OM retained in the columns S and S+B (Table 3). The content of OM before and after the experiment in the soil is almost halved likely due to microbial consumption. Whereas, the microbial consumption of OM in the mixture S+B does not seem to occur despite columns S and S+B shows a similar nitrification rate and COD attenuation. The addition of biochar alters the microbial activity involved in nitrification and denitrification processes (DeLuca et al., 2006; Lai et al., 2013). An alteration of nitrifying bacteria community, which mechanism is not clear, might explain the same nitrification potential observed for soil while less OM is degraded. This behaviour was also found in forest soils when evaluating the effect of wildfire-produced charcoal in their nitrogen cycling (DeLuca et al., 2006).

3.3. Nutrients

TP and TN removal percentages at the column effluents are shown in Fig. 5 for the three infiltration experiments.

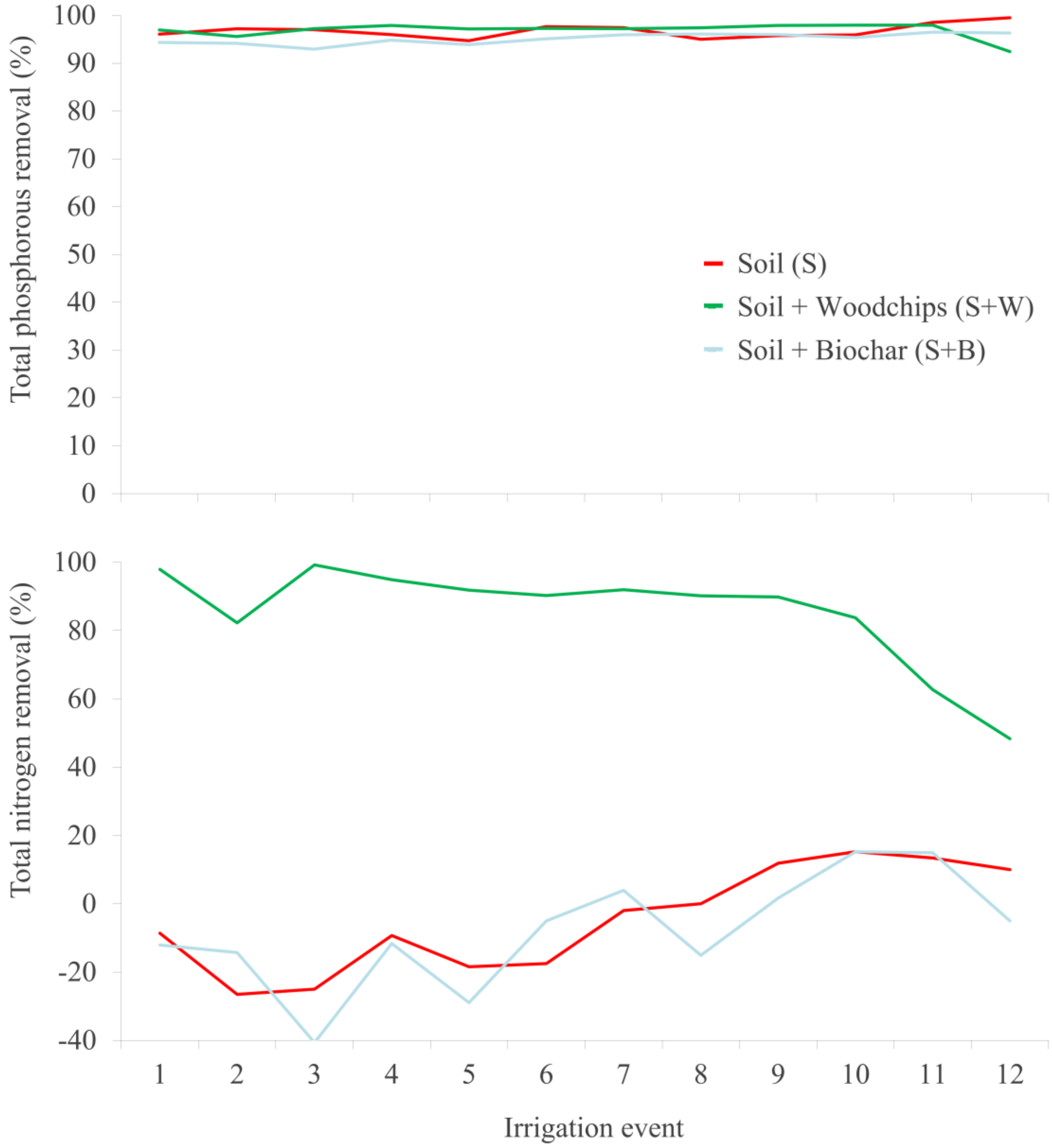

Fig. 5. Nutrient (TP and TN) removal percentages in each column effluent.

From the very beginning of the assay, the three systems show a similar behaviour with respect to TP attenuation. However, in the column S+B (94.8%) this attenuation was significantly lower ($p<0.01$) than in the columns S (96.3%) and S+W (97.2%). The concentrations of this species at the column effluents were very stable with only a minor deviation from the average. Indeed, average TP concentrations at the effluent are 0.16±0.07 mg L^{-1} for column S, 0.15±0.08 mg L^{-1} for column S+W and 0.24±0.05 mg L^{-1} for column S+B. The obtained removal in all cases reaches values higher than 95% indicating that this nutrient does not imply a concern in a treatment technology where calcareous soils are present. In fact, the precipitation of orthophosphate PO_4-P in the presence of calcium, which is abundant in the tested soil (~35 g kg^{-1}), could explain its removal from the infiltrating water (Duchafour, 1984). As indicated by the data of Table 3, the retention of TP can be fully explained by sorption and/or precipitation processes. The accumulation of this nutrient is limited to the first 5 cm of the soil whereas in the amended columns TP content continues to increase up to the sample depth (11 cm). The reason for the accumulation of TP at deeper levels in the amended columns can be related to their faster hydrodynamic (higher hydraulic conductivity).

Following our results, it appears that selected amendments do not have any impact in TP attenuation as also confirmed by a previous study using soil mixed with a thinner type of woodchips (Meffe et al., 2016). However, published data about the capacity of these materials to retain TP are controversial. On one hand, woodchips have been described as able to sorb PO_4-P from dairy soiled water (Ruane et al., 2011). On the other hand, Bock et al. (2015) refer the use of biochar amendments necessary to deal with the scarce removal of TP by woodchips. Although our addition of biochar do not improve TP attenuation in soil, significant increase in TP removal by sorption onto biochar has been observed by Kizito et al. (2017) when investigating treatment through constructed wetlands.

Table 3. Nutrients and OM concentrations before irrigation, along the soil and amended soils profile and average concentrations after irrigation.

	Depth (cm)	Organic matter ($mg\ g^{-1}$)	N-NO_3 ($mg\ kg^{-1}$)	Total Kjeldahl nitrogen ($mg\ kg^{-1}$)	P ($mg\ kg^{-1}$)
S	B.I.	19.80	11.48	710.00	322.44
	A.I.	11.82±2.01	11.65±14.59	684.00±34.35	371.02±83.22
	0-1	14.80	37.64	740.00	513.45
	2-3	11.10	7.30	670.00	375.34
	4-5	10.30	4.83	670.00	332.24
	6-7	12.90	3.59	650.00	311.32
	9-10	10.00	4.88	690.00	322.74
S+W	B.I.	44.40	11.23	850.00	343.47
	A.I.	23.40±1.93	40.87±20.36	978.00±75.63	419.39±40.76
	0-1	22.10	74.19	1100.00	476.78
	2-3	22.10	41.93	980.00	434.85
	4-5	26.30	36.73	910.00	421.16
	6-7	22.00	31.72	920.00	369.33
	10-11	24.50	19.77	980.00	394.82
S+B	B.I.	38.90	11.48	840.00	341.15
	A.I.	38.54±5.18	79.41±88.39	808.00±100.85	411.15±35.26
	0-1	31.20	233.79	920.00	434.40
	2-3	37.20	67.77	890.00	436.98
	4-5	44.10	48.55	800.00	439.23
	6-7	42.90	29.48	760.00	373.48
	10-11	37.30	17.49	670.00	371.67

B.I.: Before irrigation; A.I.: After irrigation

S: Soil; S+W: Soil + Woodchips; S+B: Soil + Biochar

Concerning TN, results were different among the columns (Fig. 5). Indeed, TN removal is significantly higher in the S+W than in the other two experiments ($p<0.001$). Negative values of removal percentages reported for column S and S+B indicate that instead of attenuation, lixiviation of nitrogen from the inlet and from the soil is occurring. NH_4^+ was not detected at both columns´ outlets meaning that this species is transformed to NO_3^- by nitrification processes occurring during its infiltration (Fig. 6). The nitrification is effectively supported by the oxic conditions established in both columns (Fig. 3). Average concentration of TN, mainly in the form of NH_4^+, in the SWW is 50.75±10.60 mg L^{-1} and average N-NO_3 effluent concentration in column S and S+B of 50.19±5.23 and 52.10±6.00 mg L^{-1}, respectively confirm the total oxidation of NH_4^+ (Fig. 6). In column S+B, the removal of TN is also due, to a lower extent, to sorption processes fostered by the presence of biochar (Table 3). Indeed as reported by Gronwald et al. (2015), the incorporation of biochar in soil increases the retention of NO_3^- especially when using pyrochar from woodchips. In the general balance, the amount of produced N-NO_3 is higher in the S+B column pointing out a promotion of nitrification due to the alteration of the soil microbial community when biochar is added to soil as reported by DeLuca et al. (2006).

Different behaviour was observed for the soil amended with woodchips presenting a higher TN removal. Regardless of the predominant nitrogen species at the effluent during the first 9 irrigation events was NO_3^-, its average concentration (N-NO_3: 3.49±2.33 mg L^{-1}) reflects that NO_3^- is further transformed. The removal of NO_3^- can occur by denitrification, dissimilatory nitrate reduction to ammonia (DNRA), anaerobic ammonium oxidation (ANAMMOX) and/or biomass incorporation. DNRA is excluded since there is no increase in NH_4^+ concentrations in the column effluent. ANAMMOX is unlikely to occur since it is a process inhibited when the concentration of OM is high (González-Cabaleiro et al., 2015; Nordström and Herbert, 2018) and the S+W column has a high input of OM due to the addition of a labile carbon source. Biomass incorporation may happen as there is a slight increase in N-NO_3 in the amended soil with woodchips (S+W) after irrigation in the upper part of the column (Table 3). This accumulation also occurs in S and, to a higher extent in the S+B column (Table 3) due to its higher sorption capacity. However, it has not an important impact in the removal of N-NO_3. According to approximated balance calculations, the nitrogen accumulated as TKN+N-NO_3 accounts for only 2.61%, 12.13% and 14.35% for columns S, S+W and S+B, respectively.

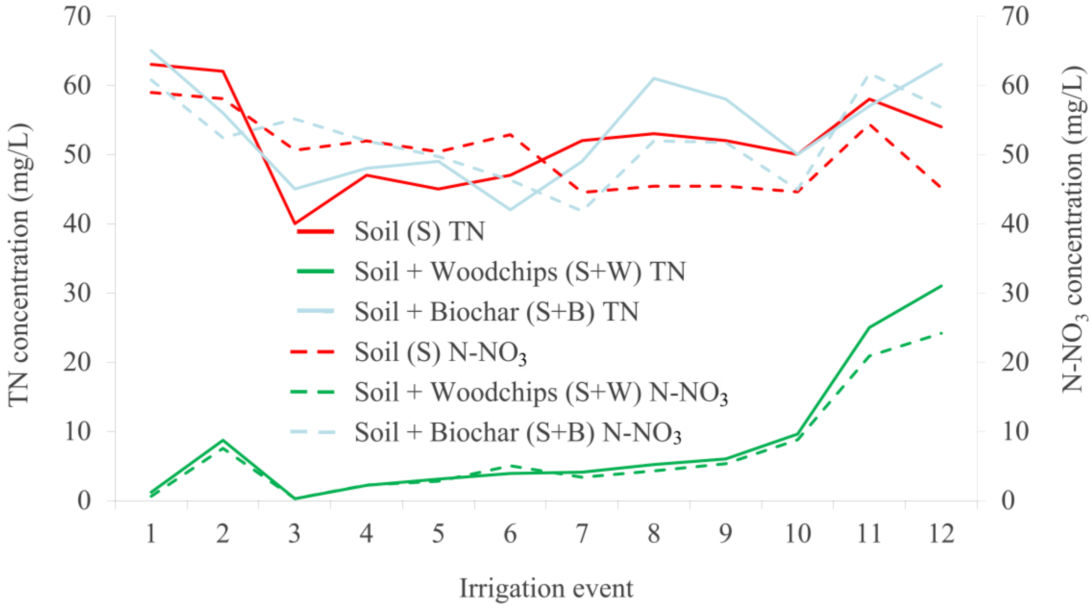

Fig. 6. Total nitrogen (TN) and N-NO3 concentration in all infiltration experiments.

Therefore, the obtained results indicate that in the column amended with woodchips, NO_3^- is removed by denitrification. It is a respiratory process in which nitrogen oxides are used as terminal electron acceptors in place of oxygen and produces gas as the terminal reduction product (Hillel and Hatfield, 2004). Anoxic conditions are the overwhelming environmental factor controlling denitrification since oxygen is thermodynamically more favourable as electron acceptor than NO_3^-. During 19 hours, corresponding approximately to the drainage time, redox conditions turn anoxic and denitrification can take place (Fig. 3). The denitrification as the main nitrogen removal process occurring in the S+W column is corroborated by data measured during the last 3 irrigation events. In the S+W column, there is a decrease of TN removal (Fig. 5) due the appearance at the column effluent of higher N-NO_3 concentrations (Fig. 6). When plotting the evolution of the alkalinity (mainly in form of HCO_3^- at the experimental pH), a specular trend with N-NO_3 can be observed (Fig. 7). The occurrence of denitrification is coupled to an increase in alkalinity based on its stoichiometric definition (Nordström and Herbert, 2018) and vice versa. Data observed during the last 3 irrigation events show a decrease of alkalinity as a consequence of the inhibition of denitrification.

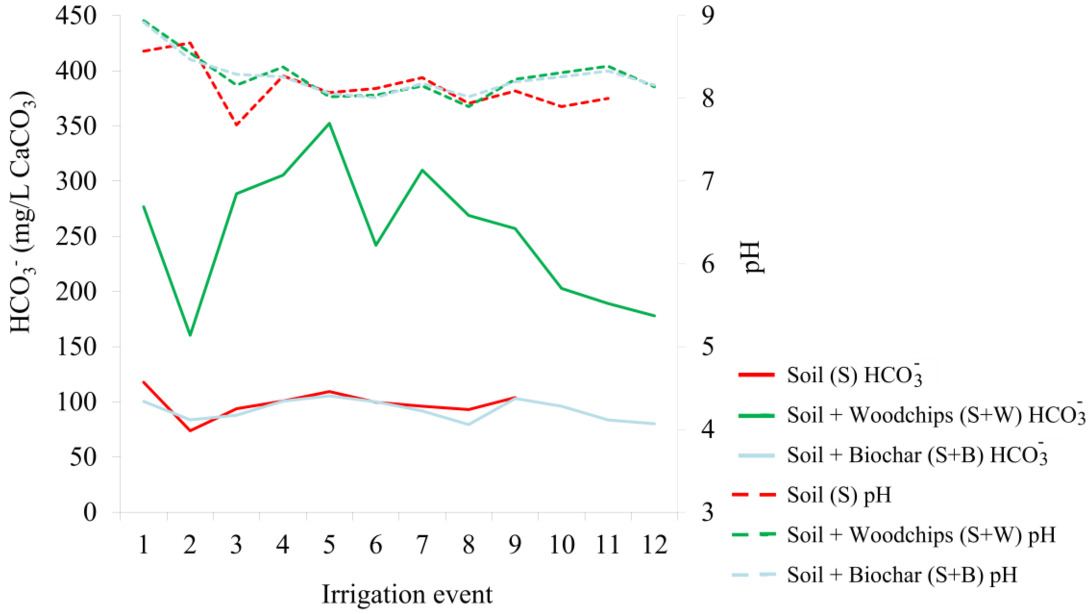

Fig. 7. pH and HCO_3^- evolution in the three infiltration experiments

This inhibition can be derived from an OM limitation. The C/N ratio and the type of OM are important factors controlling the activity of denitrifier bacteria (Fang et al., 2018; Kłodowska et al., 2018). At the end of the experiment almost half of the initial OM in the S+W has been consumed, besides the organic carbon that the SWW is supplying. Only biodegradable organic carbon can be used as a carbon source by denitrifiers (Narkis et al., 1979). It seems that once all the biodegradable OM is degraded, the denitrification is inhibited and NO_3^- starts leaching. On one hand, the addition of woodchips increases the content of biodegradable OM fostering denitrification on the other it provides also non-biodegradable OM. The non-biodegradable OM is progressively dissolved and transported through the outlet reducing the removal performance of the S+W column in terms of COD (Fig. 4). It is remarkable that although the reduced retention time of SWW in the column amended with woodchips, the removal efficiencies of nitrogen are very high (> 90%) when the system has enough biodegradable OM.

3.4. NH_4^+ sorption

The results of the batch experiments are summarized in Table 4. First, it can be noticed that both sorption and desorption of NH_4^+ onto woodchips follow a linear sorption isotherm model (R^2=0.991 and R^2=0.998, respectively). On the other hand, the Freundlich isotherm model describes better the non-linear sorption and desorption of NH_4^+ onto biochar (R^2=0.98 and R^2=0.97, respectively). Non-linear sorption of NH_4^+ onto different chars was also found in the literature (Gronwald et al., 2015) indicating a limited number of sorption sites (Hale et al., 2013). K_f values reflect the sorption and desorption affinity of NH_4^+ onto biochar however K_f units are n-dependent and not comparable if n values are different. Therefore, a range of K_d values calculated for each initial concentration were used to compare sorption affinity among the studied amendments. Calculated sorption K_d values range 5.76-10.81 L kg^{-1} and 21.35-193.18 L kg^{-1}, for woodchips and biochar, respectively. Results indicate that sorption of NH_4^+ onto biochar is one order of magnitude higher than onto woodchips being the average percentage of NH_4^+ sorbed 2.58

times higher. This difference increases after desorption up to 5.85 times, indicating that biochar is a better sorbent to retain NH_4^+.

Table 4. Sorption and desorption model variables and model fitting adjustments.

			Sorption	Desorption	C_0 (mg L^{-1})	Sorption removal(1) (%)	Final removal(2) (%)
Woodchips	Langmuir	K_L	0.01	-			
		C_{max}	2131.21	-	Average	27.25	10.64
		R^2	0.92	-			
	Freundlich	K_f	8.45	7.04			
		n	0.97	1.21	30	34.00	13.15
		R^2	0.97	0.996			
	Linear	K_d	7.91	17.40	600	28.98	13.43
		R^2	0.99	0.998			
Biochar	Langmuir	K_L	0.05	0.07			
		C_{max}	3212.05	4058.75	Average	70.37	62.23
		R^2	0.91	0.95			
	Freundlich	K_f	224.90	310.15			
		n	0.59	0.69	30	89.50	85.31
		R^2	0.98	0.97			
	Linear	K_d	23.18	99.32	600	51.23	42.20
		R^2	0.84	0.96			

Units: K_L (L mg^{-1}); C_{max} (mg kg^{-1}); K_f ($mg^{(1-n)}\cdot L^n$) kg^{-1}; K_d (L kg^{-1})

(1) Average value considering only sorption
(2) Average value considering sorption and desoprtion

However, the sorption capacity of the materials is less pronounced when added to soil in a 3% (w/w). The selected amount of amendment is insufficient to render sorption processes as important as the biological attenuation. Other authors have found that although NH_4^+ was sorbed onto chars, its retention is limited in time meaning that it is not efficient in removing nutrients (Gronwald et al., 2015).
It is evident from our research, that the amendments with woodchips are more effective for nitrogen removal than amendments with biochar. Woodchips act primarily as a labile source of carbon promoting biodegradation, being more effective for nutrient attenuation than the sorption capacity of biochar. Also, these results confirm that denitrification is the main process for nitrogen attenuation rather than sorption onto woodchips as was also hypothesized in previous experiments (Meffe et al., 2016).

4. Conclusions

- The incorporation of amendments in the soil has an effect on the hydrodynamics, decreasing the retention time through it.
- COD is well-attenuated by biodegradation in soil, while biochar only incorporates sorption as an additional sink process.
- Results suggest that the addition of woodchips increases both biodegradable and non-biodegradable OM reducing its removal efficiency in terms of COD.

- Amendments have no effect on TP attenuation since sorption and precipitation that are taking place already in the soil almost completely remove phosphorous species.
- The woodchip amendment reduces TN leachate by denitrification processes. However, higher content of amendments should be added in order to increase both sorption and degradation processes and to assure a higher durability of the treatment.
- The biochar amendment affects the soil microbial community promoting nitrification and also increases sorption capacity of NO_3^-.
- Sorption of NH_4^+ onto woodchip amendment is a minor process in the TN attenuation if compared to the microbial degradation.
- Sorption of NH_4^+ onto biochar after desorption is 5.85 higher than onto woodchips demonstrating that biochar is a better sorbent to retain NH_4^+.
- Obtained results indicates that woodchips used as amendments are more effective than biochar. This labile carbon source has also the advantage that it is easily provided by the vegetation filter without further post-processing.

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