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Soil conditioners effects on hydraulic properties, leaching processes and denitrification on a silty-clay soil

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Abstract

Agricultural landscapes are often affected by groundwater quality issues due to fertilizers leaching. To address this worldwide problem several agricultural best practices have been proposed, like limiting the amount of fertilizers and increasing soil organic matter content. To evaluate if these practices may promote groundwater quality enhancement, vadose zone retention time and complex biogeochemical processes must be known in detail. In this study, sequential undisturbed column experiments were performed to determine the amount of nutrients and heavy metals leached after simulated stormwater events. The column was amended with urea then flushed for two pore volumes, then straw residuals were incorporated and flushed for two pore volumes and finally compost was incorporated and flushed for six pore volumes. Dissolved ions, major gasses and heavy metals were determined in leachate samples. Nitrate and nitrite were leached in the urea treatment producing the highest concentrations, followed by compost and straw residuals. The redox conditions were aerobic in all treatments and pH was circumneutral or slightly basic. Denitrification was low but increased with the addition of straw residuals and compost. Heavy metals were all at very low concentrations except for lead and cadmium, which slightly exceeded threshold limits (10 and 1 μg/L, respectively) in all the treatments. The compost treatment, after three pore volumes, was affected by clay swelling due to sodium dispersion, which in turn provoked a reduction of porosity and hydraulic conductivity.

Keywords

Aquifer recharge, fertilizers leaching, denitrification, heavy metals, compost, clay swelling.

1. Introduction

Agricultural activities have affected and keep affecting the environmental quality, since they consist of intensive soil use, which is generally accompanied by the addition of organic and/or inorganic conditioners (Antonopoulos & Wyseure, 1998; Shah et al., 2019). To ensure that environmental quality is not worsen by agricultural activities, it is important to tune the use of amendments on the basis of soils' and plants' requirements and to consider advantages and disadvantages of their use, such as: alteration of the pristine water quality, impoverishment of soil's fertility, nutrients leaching towards groundwater, and variation of soil's physical-chemical properties (Kay et al., 2012; Shah et al., 2019; Zhang & Wang, 2019). The most striking environmental problem of agricultural activities is the groundwater contamination by nitrate (NO_3^-) due to fertilizers leaching (Tilman et al., 2001). NO_3^- is the main groundwater contaminant worldwide (Schlesinger, 2009), since being the most stable nitrogen (N) species it can migrate to great distances from the input zone (Puckett et al., 2011). To solve this problem, recent studies have tried to fully understand the denitrification process in soils (Castaldelli et al., 2019; Putz et al., 2018) and shallow aquifers (Colombani et al., 2019; Hinshaw et al., 2020; Utom et al., 2020). A clear correlation between denitrification and dissolved organic carbon

(DOC) in soils have been found at the global scale (Taylor & Townsend, 2010), since DOC is the principal electron donor for heterotrophic denitrification (Kim et al., 2019). More specifically, it has been found that the labile fraction of DOC drives the in-situ denitrification (Xu et al., 2018) and its reactivity, combined with temperature, determines the denitrification rate (Mastrocicco et al., 2019a; Zarnetske et al., 2011). Nevertheless, to fully determine the redox conditions and the main biogeochemical reactions not only the reactants but also the products must be monitored. These are usually dissolved gasses like O_2, CO_2, CH_4 and N_2 (Mastrocicco et al., 2019b; Rivett et al., 2008).

Beside nutrients, also heavy metals may become important groundwater pollutants in agricultural settings (Busico et al. 2018; Wongsasuluk et al., 2014), since they can influence both the human health and the ecological status of the affected environments (Ke et al., 2017; Kumar et al., 2019; Li et al., 2014). In general, heavy metals are introduced in agricultural landscapes via manure, pesticides and fertilizers' impurities (Belon et al., 2012; Kirschke et al., 2019). Furthermore, heavy metals' solubility and mobility in soils and in groundwater depend also on pH and Eh conditions. In fact, heavy metals' mobility in soils is reduced by increasing pH, soil organic matter (SOM) content and Eh (Sauvé et al., 2000), and is also largely affected by surface complexation reactions on amorphous Fe-hydroxides (Bonten et al., 2008). The latter usually are unstable (dissolve) at low pH and low Eh values, so such conditions may trigger heavy metals release in groundwater (Apul et al., 2005; Colombani et al., 2015). Thus, to fully understand the heavy metals' fate and transport processes it is imperative to assess the Eh and pH conditions and the main redox sensitive species.

In this study two different soil conditioners, straw residuals (SR) and compost (Comp), have been compared versus standard synthetic urea fertilizer (U) to assess nutrients and heavy metals leaching from an undisturbed silty-clay soil column subject to extreme rainfall events. SR are usually incorporated in topsoils to improve soil fertility and to increase crop yields (Liu et al., 2014). Recent studies showed that SR have different beneficial effects on soil properties, like increasing soil water content, while decreasing dry bulk density (ρ_b; Zhao et al., 2019). Comp is a product of biodegradation of organic substrates and it represents a way to recycle organic solids and agri-food wastes, reducing social costs and promoting the circular and green economy (Hargreaves et al., 2008). Recent studies proved that Comp application increases the availability of labile SOM (Liu et al., 2018), while reducing NO_3^- leaching (Basso & Ritchie, 2005) especially in sandy soils (Shrestha et al., 2010). Furthermore, it was argued that Comp incorporation in topsoils is beneficial to some physical soils' proprieties as porosity (Giusquiani et al., 1995) and soil water retention capacity (Ramos, 2017; Sorrenti & Toselli, 2016). Nevertheless, Comp could increase the mobilisation of harmful elements, so caution is required in utilising Comp on soils with elevated concentrations of heavy metals (Beesley & Dickinson, 2010), even though Farrell et al. (2010) demonstrated that Comp application may reduce metals' availability.

In addition to leaching of solute species, also physical changes can be induced by SR or Comp incorporation. Buchmann & Schaumann (2018) stated that the application of Comp reduces clay swelling, improves soil porosity and increases soil structural stability. On the other hand, Hanson et al. (1999) found that fine grained soils may be affected by reduced permeability by sodium (Na^+) induced clay swelling with consequent disruption of soil's aggregates, so attention must be paid to the Comp salinity and Na^+ content. In fact, clay swelling may cause a reduction of soil permeability, because clay minerals once dispersed from soil's aggregates may fill soil pores and reduce water flow (Tao et al., 2019).

From this brief review, it is clear that studies that tackle altogether the complex interactions of nutrient and heavy metals leaching coupled with the soil physical changes induced by soil conditioners are still lacking. The present study aimed to fill this gap monitoring both physical changes and leaching behaviour in well controlled laboratory conditions using SR and Comp as conditioners and U fertilizer as standard practice.

2. Material and Methods

2.1. Soil column experimental set up

The soil used in the experiment was collected from an agricultural field in the Po River Plain, within the central-eastern part of the province of Ferrara, Italy (GPS coordinates 44° 47' 41” N and 11° 42' 20” E). The soil has a clayey silty texture, and the depositional environment is typical of delta plain distal parts. The physical-chemical characteristics of the soil have been described previously in detail in Mastrocicco et al. (2019a) and the undisturbed soil column is the same employed in the previously published experiment.

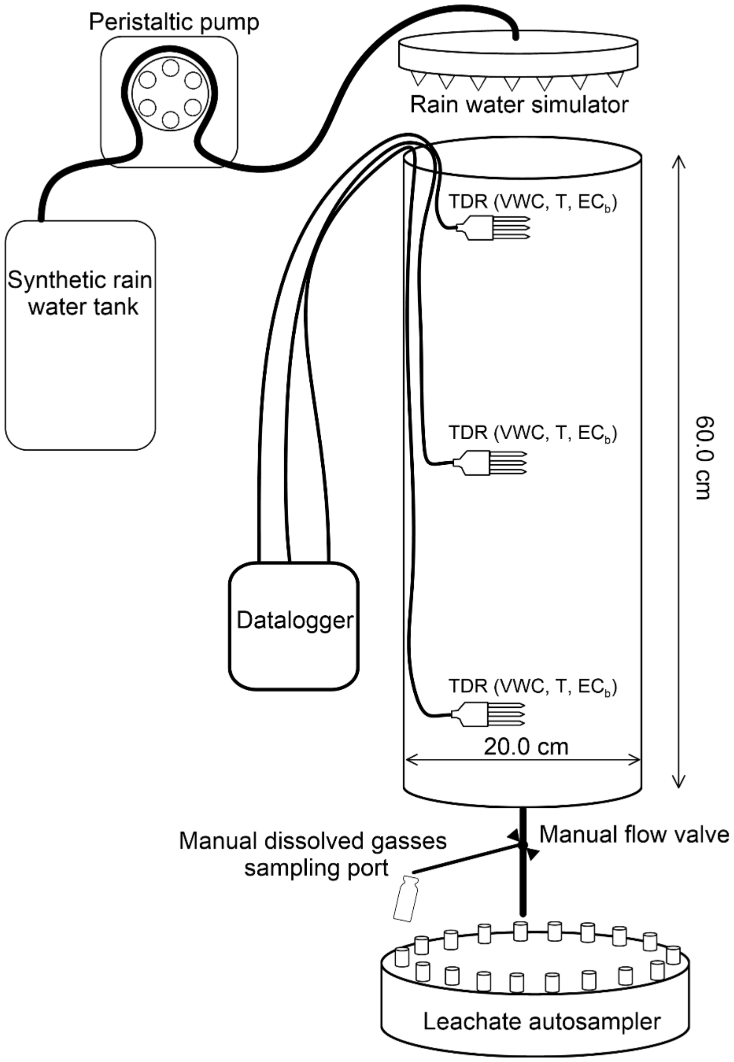

Figure 1: Schematic representation of the laboratory apparatus used in the intact soil column leaching experiment.

Briefly, the leaching experiments were conducted at laboratory conditions at 25 °C to be representative of field conditions during summer time when the majority of storm water events take place in the Po river plain area (Isotta et al., 2014). A large plexiglass column was employed with an internal diameter of 19.6 cm and length of 60.0 cm, provided with polyethylene post-chamber with 2.5 mm porous disc and 2 cm layer of quartz sand, to avoid material loss (Fig.1). The undisturbed soil profile consisted of 55 cm of Hypocalcic Haplic Calcisols that was collected in a lowland agricultural field in the province of Ferrara (Mastrocicco et al., 2019a). An 8 channels peristaltic pump (Minipuls-3 Gilson, UK) was placed on the top of the column as rainfall simulator, at different flow rates (1.46, 2.85 and 4.98 rpm) to reproduce a storm event of 227 mm in 47 hours with synthetic rainwater (mono-distilled water). The choice of selecting the timing and intensity was to be consistent with the previous study (Mastrocicco et al., 2019a) that mimicked a field observed stormwater event. To avoid possible preferential flow due the 8 dripping points, the rainfall simulator was manually rotated approximately every 10 minutes during the simulated rainfall events. Prior to start the experiments, the column was flushed with 2 pore volumes of synthetic rainwater and left drain until stable Volumetric Water Content (VWC) was attained. In the first experiment, 100 kg-N/ha of urea in crushed granules (Table 1) was applied on the top of the soil column and left for 15 days before to start the stormwater event. After all the leachate was collected, the column was flushed with 2 pore volumes of synthetic rainwater and finally was drained with a vacuum pump until the initial VWC was attained. The second experiment was performed on the same undisturbed column by placing 5 cm of undisturbed topsoil collected in the field from a plot where SR of maize were left on ground from the previous year. The topsoil was collected approximately 10 days before the experiment from the field site after a rainy period with a plexiglass column of the same diameter but with sharpened edges and 20 cm long. The plexiglass was gently pushed down to 5 cm from the ground surface; then the nearby soil was removed with a shovel and the topsoil was removed with the aim of a large flat blade brought to the laboratory and gently pushed with a piston on the top of the undisturbed soil column used in the U experiment. The measured amount of N in the topsoil with SR was approximately 30 kg-N/ha. The same stormwater event was repeated and the leachate collected; then the column was flushed using 2 pore volumes of synthetic rainwater and again drained with a vacuum pump until the initial VWC was attained. In the last experiment the topsoil with SR was removed and substituted with 5 cm of topsoil mixed with 0.09 kg of mature Comp from urban organic waste, corresponding approximately to 30 ton/ha of Comp. The measured amount of N in the topsoil amended with Comp was approximately 92 kg-N/ha. Given that Comp effects should last for more cropping seasons, in this last experiment the stormwater event was repeated 6 times to evaluate the Comp long-term effects. Three Decagon probes (5TE) were installed inside the column at 5, 30 and 45 cm to monitor VWC, Temperature (T) and Soil Bulk Electrical Conductivity (ECb). All probes were connected to a Decagon data logger (ECH2O) recording every 10 minutes. The 5TE probes instead of microsensors were chosen since they have a small diameter (0.7 cm) and the probe were inserted horizontally, so the disturbance was relatively low. Besides, the 5TE has a volume of influence of 0.3 L, which can provide a comprehensive averaged information on VWC and ECb around the probe, capturing the variations through the monitored column plane. The leachate samples were collected through an effluent tube fixed at the bottom of the column and discharging into a Redifrac Pharmacia Biotech collector equipped with 15 mL vials. A manual switch was used to sample 6 mL exetainer glass vials for dissolved gasses. pH, Electrical Conductivity (EC) and Temperature (T) were monitored using a portable Hanna instruments meter. Soil’s ECb was converted in EC according to the model of Mortl et al. (2011) and subsequently all EC data were converted into salinity with standard conversion factors (APHA, 1999). It was chosen to not install suction cups within the column to avoid interferences with the unsaturated flow, since negative pressure during sampling could induce changes in the leaching rate.

Table 1: Composition of selected water-soluble fraction of Urea (U), Straw residuals (SR), Compost (Comp) and synthetic rainwater (SR) applied onto the soil column.

i.d.	**pH**	**N_{TOT} (ppm)**	**NO_3^- (ppm)**	**NH_4^+ (ppm)**	**Na^+ (ppm)**	**Cl^- (ppm)**	**SO_4^{2-} (ppm)**	**Cd (ppb)**	**Pb (ppb)**
U	6.8	220	4.4	0.1	55.6	40.5	136	0.6	2.5
SR	7.5	10.3	0	0.1	8.1	5.7	32.3	<0.1	<0.1
Comp	7.6	134	4.1	32.6	450	72.6	7.8	1.6	1.1
SR	6.5	<0.1	0.12	<0.1	0.15	0.26	0.51	<0.1	<0.1

2.2. Sampling and analytical methods

Sediment parameters, especially Total Organic Carbon (TOC) and soil texture, are often utilised to evaluate soil water retention, in fact Rawls et al. (2003) introduced a method based on two different pedotransfer equations to quantify VWC at the field capacity (θ_{33}) and at the wilting point (θ_{1500}). ρ_b and soil moisture were determined using gravimetric methods.

Major anions (F^-, Cl^-, NO_2^-, Br^-, NO_3^-, SO_4^{2-}) were determined on 0.22 µm filtered leachate samples by ion chromatography with an isocratic dual pump (ICS-1000 Dionex) equipped with an AS9-HC high-capacity column and an ASRS-Ultra 4-mm self-suppressor. An AS-40 Dionex auto-sampler was employed to run the analysis, while quality control (QC) samples were run every 30 samples. The detection limit was 0.1 mg/L.

An ICP-OES (PerkinElmer, USA) was used to quantify major cations and trace metals (Ca, Cu, Cd, Fe, Mg, Mn, Ni, Pb, Zn) in leachate water samples after acidification with ultrapure 1 M nitric acid and filtering on 0.22 µm; and for the soil analyses using the aqua regia extraction method (ISO 11466, 1995). The detection limit for leachate samples was 0.1 µg/L and for soil samples was 1.0 mg/kg. A Pharmacia 300 UV/VIS spectrophotometer with appropriate reagent tests (Hach-Lange, UK) was employed to quantify Na^+, K^+, DOC, NH_4^+, NO_3^- and PO_4^{3-}. The detection limit was 0.1 mg/L. Alkalinity was determined using an Alkalinity test (Merk, Germany). Total N (Ntot) was measured in the water soluble fraction was extracted from the solid matrices samples by using Milly-Q (Millipore, USA) water and a sediment to water weight ratio of 1:10; leachates were analysed with LCK 238 LatoN cuvette tests and a CADAS 100 UV/Vis spectrophotometer (Hach-Lange, UK). The detection limit was 0.1 mg/L. Soil exchangeable sodium percentage (ESP) was calculated using the sodium absorption ratio (SAR) of the saturation extract of the soil and Comp following the procedure in Choudhary & Kharche (2018).

Samples for Ar, N_2 and CH_4 determination were collected by overflowing at least 2 times 6-mL gas-tight glass vials (Exetainer®, Labco, High Wycombe, UK) and preserved by adding 100 µL of 7 M $ZnCl_2$ solution to inhibit microbial activity (Babich and Stotzky, 1978). Water samples were analysed by MIMS-Membrane Inlet Mass Spectrometry (Bay Instruments, USA), a PrismaPlus quadrupole mass spectrometer with an inline furnace operating at 600 °C to allow for O_2 removal. The Ar, N_2 and CH_4 concentrations were quantified by the ion current detected at m/z ratios of 40, 28, and 15, respectively. The detection limit was 1.0 µmol/L. CO_2 was calculated using the PHREEQC-3 geochemical code (Parkhurst & Appelo, 2013), knowing major ions, pH and alkalinity.

A modified method from Blicher-Mathiesen et al. (1998) to estimate the N_2 excess (N_{2Exc}) was applied, since it was recently demonstrated to provide reliable N_{2Exc} estimates in field conditions at the same experimental site (Mastrocicco et al., 2019b). Briefly, the method allows to calculate the amount of N_2 degassed (N_{2Deg}) and the N_{2Exc} via the following equations:

$$N_{2Deg} = N_{2Tot}\frac{\left({N_{2Atm}}/{N_{2EQ}}\right)}{\left({Ar_{Atm}}/{Ar_{EQ}}\right)}\ln\left(\frac{Ar_{EQ}}{Ar_{Tot}}\right) \quad (1)$$

$$N_{2Exc} = \left(N_{2Tot} + N_{2Deg}\right) - N_{2EQ} \quad (2)$$

where Ar_{Atm} is the volumetric fraction of Ar in the atmosphere with saturated air and N_{2Atm} is the volumetric fraction of N_2 in the atmosphere with saturated air. Ar_{EQ} is the water dissolved Ar concentration in equilibrium with the atmosphere at the sediment temperature, Ar_{Tot} is the measured water dissolved Ar concentration for a given sample. N_{2EQ} is the water dissolved N_2 concentration in equilibrium with the atmosphere at the sediment temperature, N_{2Tot} is the measured water dissolved N_2 concentration for a given sample. The eluted masses of mineral N (NO_3^-+ NO_2^-+NH_4^+), DOC, Cl^-, SO_4^{2-} and denitrified N (2*N_{2Exc}) were calculated by integrating the measured concentrations respect to the observed leachate volume eluted between each analysed sample and the previous one.

3. Results and discussion

3.1. Volumetric Water Content continuous monitoring

The VWC continuous monitoring (Fig.2) highlights a sudden increase due to the simulated intense rainfall events especially in the top probe (located in the topsoil), and a rapid VWC decrease due to porewater drainage. The rapid increase of VWC in the first rainfall spike in all the three monitoring probes was due to preferential flows in macropores, although from the second spike the VWC increased only in the top and middle probe since the bottom probe exhibited values near to saturation (0.45 m^3/m^3). These results are consistent with the VWC behaviour observed in the same undisturbed column (Mastrocicco et al., 2019a), obtaining the same VWC saturation values in the three probes even if the previous experiment had an initial VWC near to residual values. In the U experiment a perched water table was visible near the half of the column until the end of the third day, due to nearly complete water saturation of the lower soil horizon during the simulated storm event. The perched water table was then rapidly drawdown due to leaching of porewater from the column. The VWC of the SR experiment showed peaks only during the storm events but with faster VWC decrease due to higher infiltrability of the SR topsoil. The larger infiltrability produced a cumulative amount of 6445 mL, while in the U experiment only 5302 mL were leached. The Comp experiment showed different trends respect to the previous ones, in fact during the first elution the VWC was similar to the U and SR experiments, but from the second to the last elution the VWC gradually converged towards similar values over the whole depth of the column. Here the prolonged rainfall caused the nearly full saturation of the soil column, in effect the difference between the VWC of the three probes was minimal at the end of the third elution experiment. Finally, the maximum values recorded in the top probe passed from approximately 0.55 to 0.45 during the Comp experiment, witnessing a porosity reduction in the topsoil. Concomitantly the cumulative leached amount was 6544 mL in the first elution, while in the last one was 4329 mL.

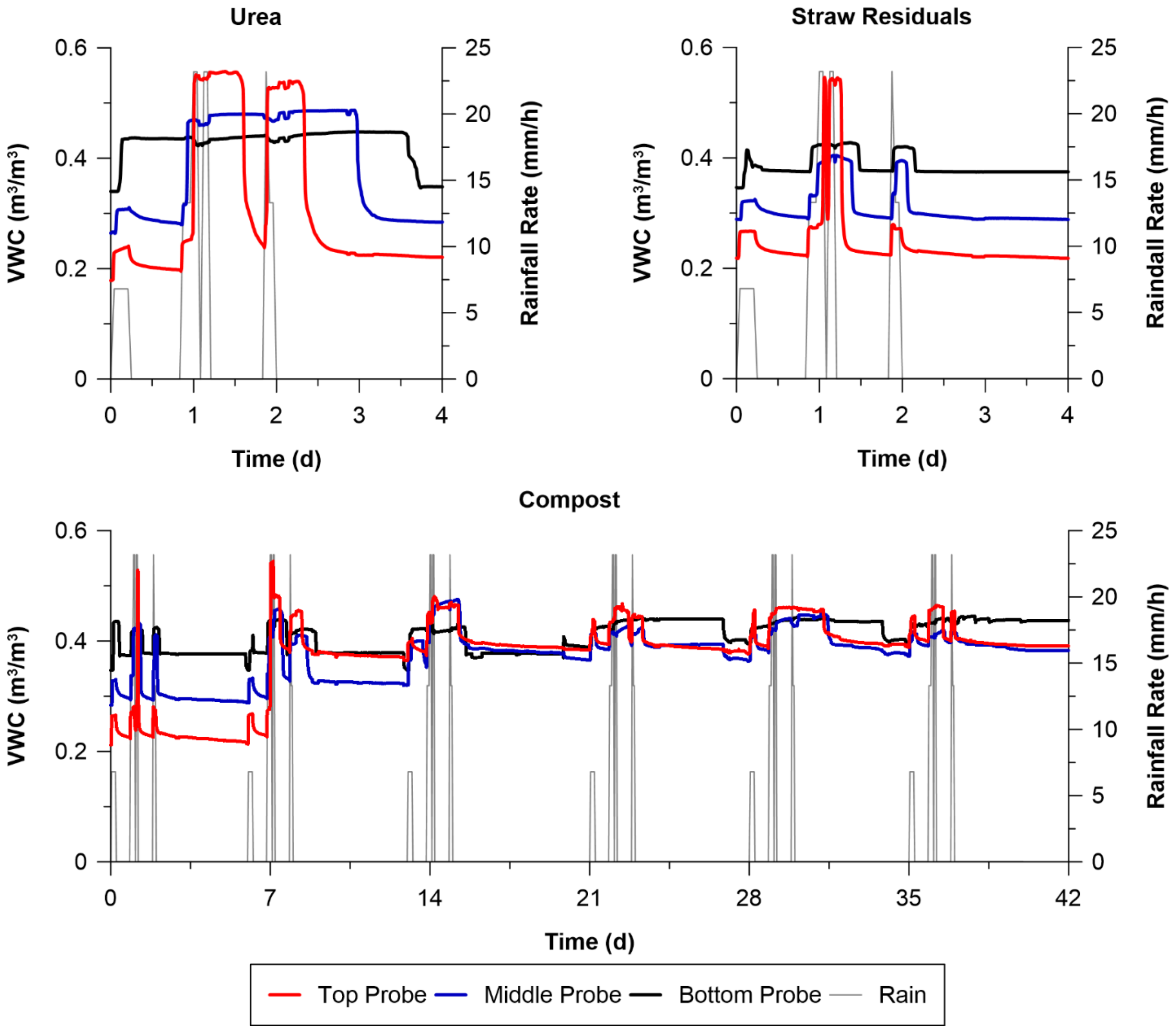

Figure 2: VWC and simulated rainfall during the three laboratory experiments with the addition of Urea (upper left plot), Straw residuals (upper right plot) and Compost (bottom plot).

3.2. TDS continuous monitoring

The results (Fig.3) showed a general TDS reduction in leachate samples during all the experiments.

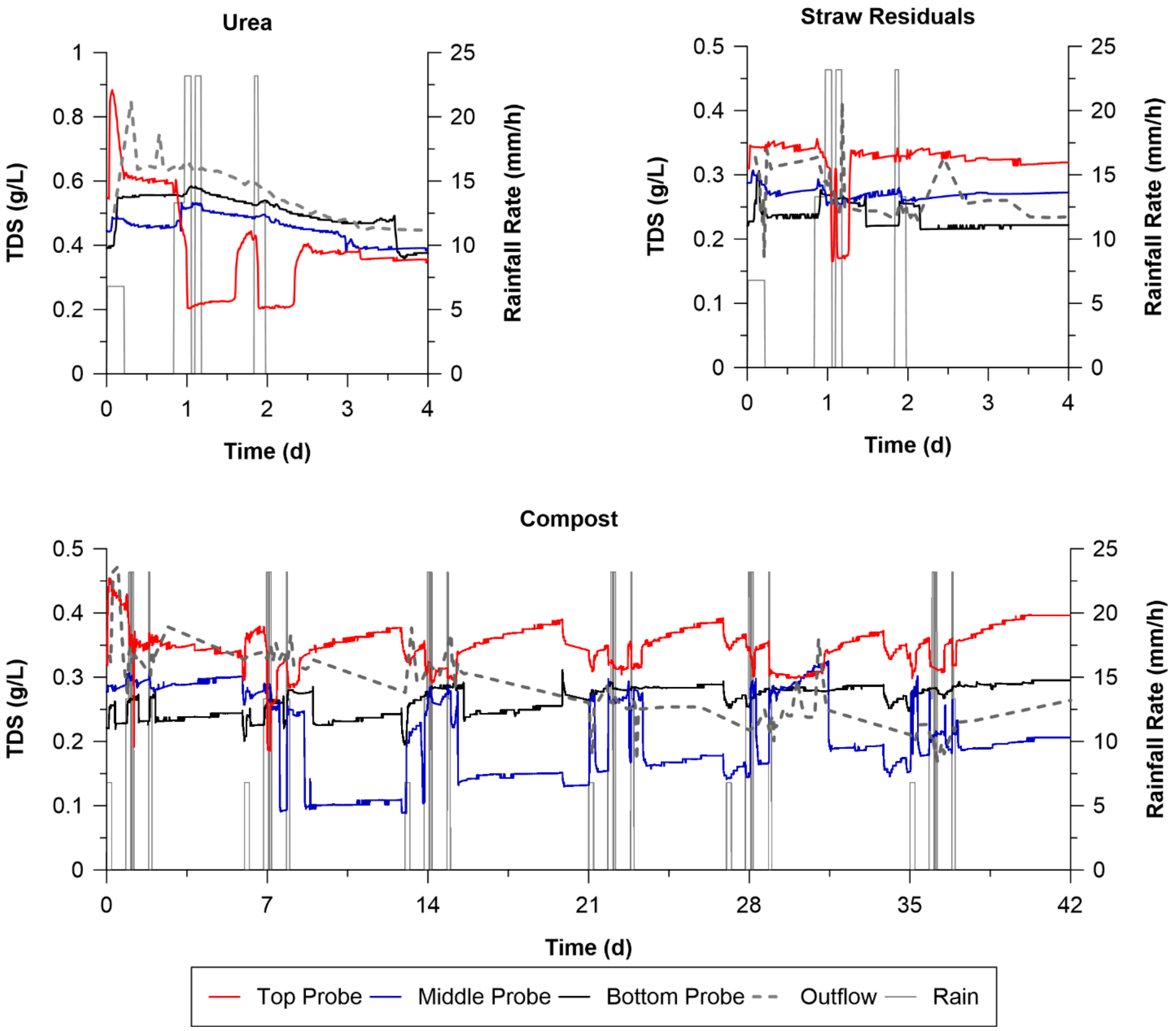

Figure 3: TDS and simulated rainfall during the three laboratory experiments with the addition of Urea (upper left plot), Straw residuals (upper right plot) and Compost (bottom plot). The probes within the column are shown with different colours, while the TDS at the column's outlet is shown with a grey dashed line.

The U experiment presented the highest initial values, with TDS values that reached 0.9 g/L in the top probe due to urea dissolution. TDS rapidly decreased during the storm events, and gradually stabilized around to 0.38 g/L in all probes towards the end of the experiment. TDS concentrations recorded at the column's outflow were similar to the ones recorded in the top probe at the beginning of the experiment and then aligned with those recorded by the middle and bottom probes during the storm events. This is a clear evidence of preferential flow in macropores, as already highlighted in a previous experiment with the same undisturbed column (Mastrocicco et al., 2019a).

In the SR experiment, at the beginning TDS was lower than the one recorded in the U test in all probes, this was due to large TDS gradients that often develops during urea fertilizers dissolution and leaching (Castaldelli et al., 2018; Chao et al., 2017). The top probe showed higher values than the other two except during the intense rainfall events, when TDS decreased rapidly. The middle probe showed a behaviour similar to the top one but with a much more smoothed trend. The bottom probe showed lower TDS values respect to the top and middle ones, with an evident increase during the storm events implying fast solutes transport from the topsoil to the column outflow, with constant values towards the end of the SR experiment. This pattern has been recently recognized also in field experiments (Fishkis et al., 2020). TDS concentrations at the column’s outflow were always close to the ones registered within the column, with spikes after the storm events that confirm the preferential flow in macropores, as denoted before.

The Comp experiment began with same TDS concentrations of the SR experiment. The top probe showed an increase in TDS during the first two rainfall events and a decrease in TDS afterwards. This behaviour was due to the leaching of soluble salts from the Comp after the first rainfall event (Cambier et al., 2014). Conversely, from the third rainfall event onward, the top probe registered a decrement during the elution and an increase in TDS afterwards. This behaviour was due to the desorption of solutes from the Comp at every rainfall event (Sorrenti & Toselli, 2016).

At the beginning of the Comp experiment, the TDS trend at the column’s outflow was similar to the one recorded in the top probe, while after the third elution TDS gradually decreased towards concentrations in between the ones registered at the middle and bottom probes. This behaviour again witnessed preferential flow in macropores that were gradually diminished by changes in the pore structure of the soil column (see paragraph 3.6).

3.3. N speciation, leaching and denitrification

NH_4^+ was very low during the whole duration of the U experiment (Fig.4), consistently with the previous studies where NH_4^+ was completely nitrified in the top 15 cm of soil (Castaldelli et al., 2018). The U experiment recorded much higher NO_3^- concentrations in the leachate samples, than in the SR and Comp experiments. Here, NO_3^- increased after the first rainfall in the first day of the U experiment, reaching a maximum concentration of 520 mg/L; then, NO_3^- gradually decreased due to mixing and dilution with rainwater, reaching a final concentration of 230 mg/L. NO_2^- were low during the initial rainfall events, but started to increase after the second day reaching up to 5 mg/L, suggesting incomplete denitrification for lack of organic substrates. It is interesting to note that NO_2^- were much lower than in a previous experiment (15 mg/L on average) where the same stormwater event was applied at the same column but starting from nearly dry conditions (Mastrocicco et al., 2019a). In fact, it is well known that dry soil conditions hamper bacterial and fungal activity, while the opposite occurs when soil moisture increases (Lund & Goksøyr, 1980).

In the SR experiment, NO_3^- concentrations were much lower than those measured in the U experiment, since the straw residuals were not rich in NO_3^-. The threshold limit of 50 mg/L (Italian Law Decree 152/2006, 2006) was only exceeded at the beginning of the experiment; then, during storm events, NO_3^- decreased towards a final concentration around 13.5 mg/L; NO_2^- and NH_4^+ were very low or below detection limits.

In the Comp experiment the NO_3^- initial concentrations were around 27 mg/L and showed a decreasing trend, apart from some fluctuations during the first three rainfall events. An important aspect which characterised the Comp experiment is that NO_3^- concentrations never exceeded the threshold limit. NO_2^- and NH_4^+ concentrations were very low during the whole duration of the Comp experiment.

From a mass balance calculation, the cumulative mineral N released by the U experiment was 151 kg-N/ha, while for the SR experiment it was 12.6 kg-N/ha and for the first elution of the Comp experiment it was 15.5 kg-N/ha. In the Comp experiment the cumulative mineral N released by the whole elution (6 storm events) was 48.6 kg-N/ha.

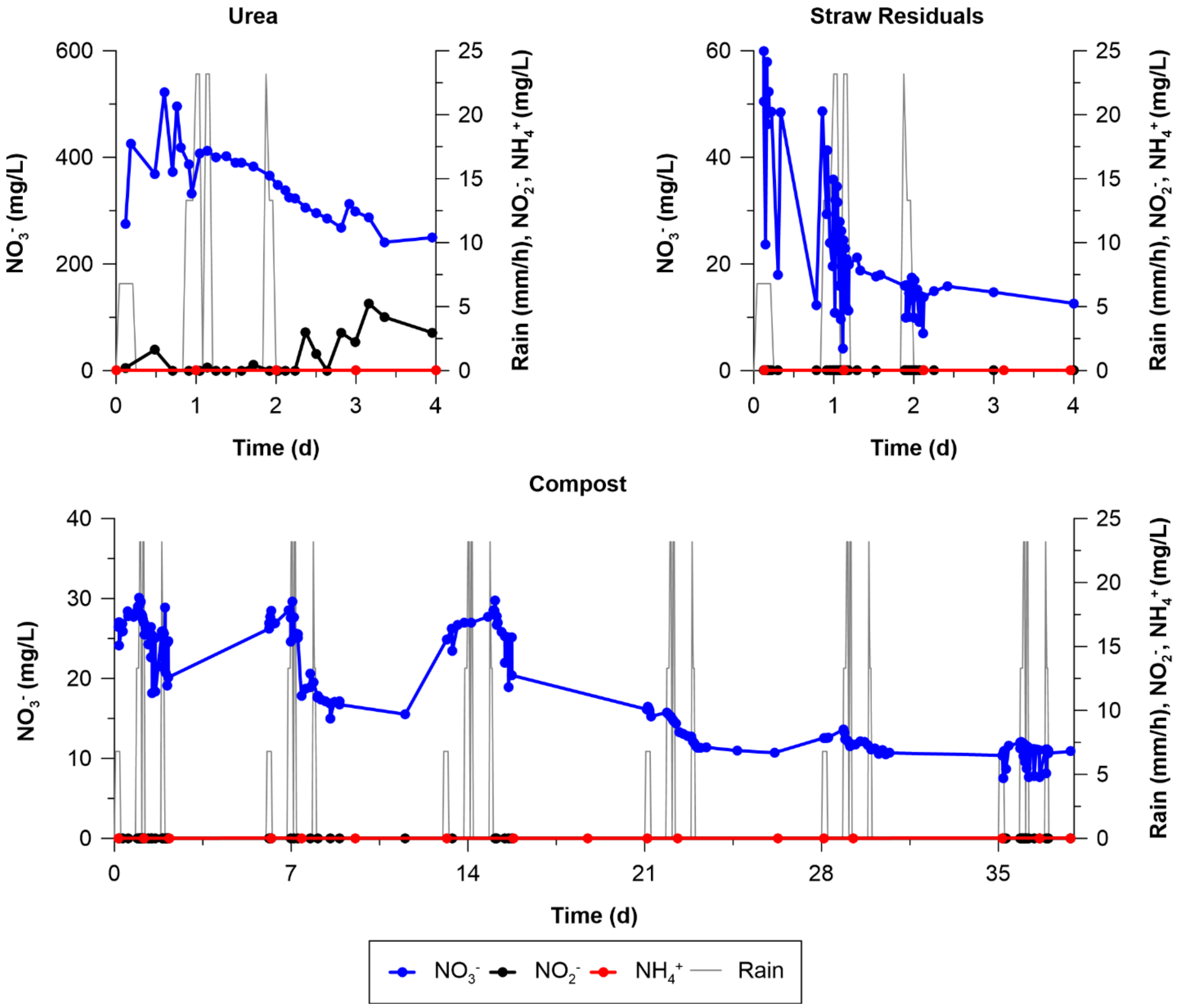

Figure 4: NO_3^-, NO_2^-, NH_4^+ and simulated rainfall during the three laboratory experiments with the addition of Urea (upper left plot), Straw residuals (upper right plot) and Compost (bottom plot).

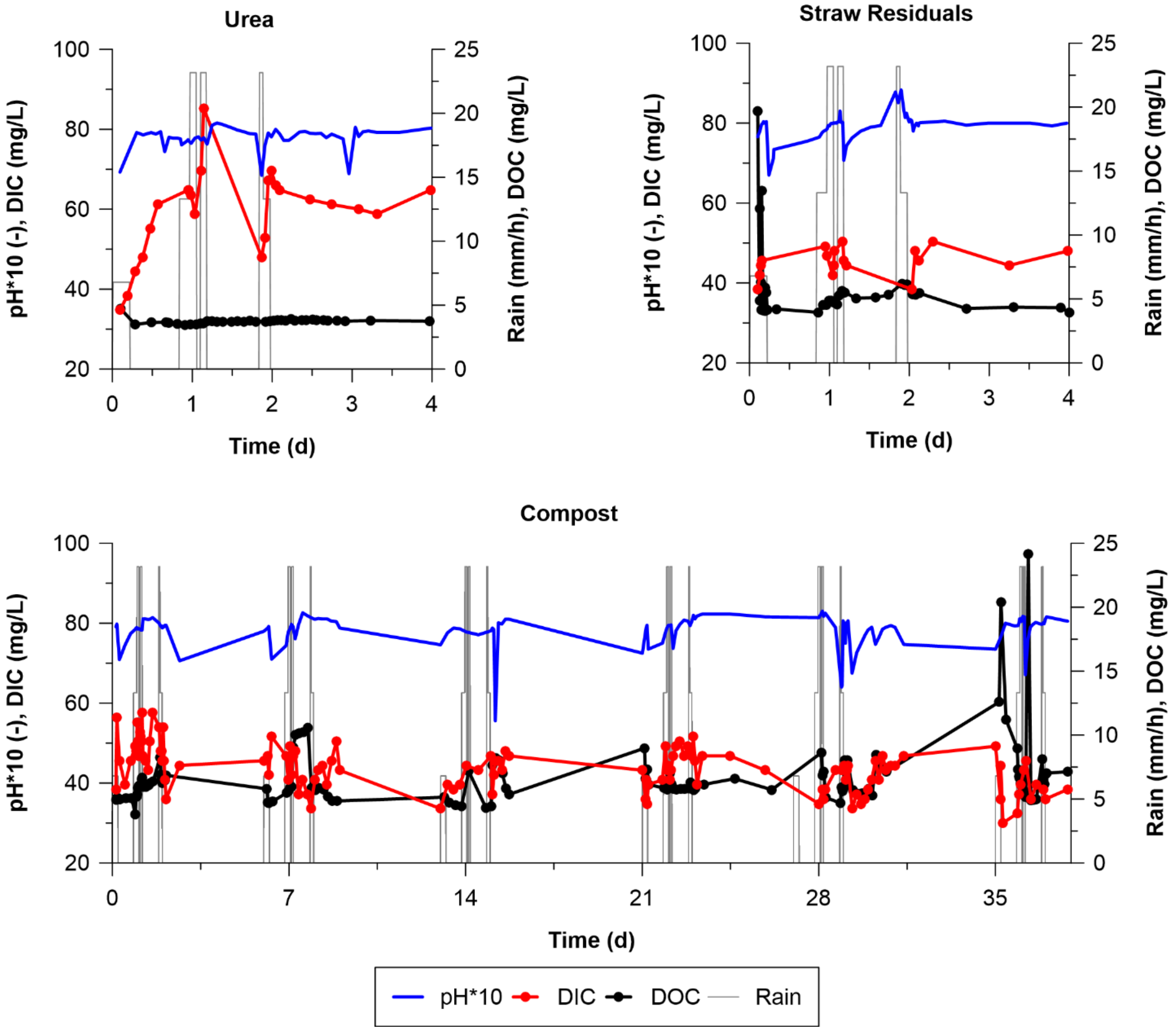

Figure 5: DOC, DIC, pH and simulated rainfall during the three laboratory experiments with the addition of Urea (upper left plot), Straw residuals (upper right plot) and Compost (bottom plot). Note that pH values are multiplied by a factor 10 to make it visible in the plots.

Figure 5 shows DOC, DIC and pH variations in the leachate samples. The U experiment recorded much lower DOC concentrations than the SR and Comp experiments, moreover the DOC in U experiment did not vary significantly during the elution, while in SR and Comp, DOC increased during rainfall events. The constant and low DOC concentrations in U experiment is an indication that in those experiment only residual DOC was flushed away, while a more labile DOC pool was probably flushed in the other two experiments, since both SR and Comp can release organic acids when wetted (Krogmann & Woyczechowski, 2000; Liu et al., 2014).

DIC variations were of the same order of magnitude in all the experiments due to carbonate dissolution, as witnessed by the alkaline pH respect to the slightly acidic pH of the synthetic rainwater (Table 1). The early breakthrough of rainwater due to preferential flow in macropores is also revealed by negative pH shifts recorded immediately after the rainfalls. From a mass balance calculation, the cumulative DOC released by the U experiment was 7.7 kg-C/ha, while for the SR experiment it was 15.1 kg-C/ha and for the first elution of the Comp experiment it was 15.5 kg-C/ha. In the Comp experiment the cumulative DOC released by the whole elution (6 storm events) was 78.6 kg-C/ha, providing a long-term source of leachable DOC.

Figure 6 shows N_{2Exc}, CO_2 and Eh variations in the leachate samples. The U experiment recorded lower N_{2Exc} values than in SR and Comp experiments, except for a spike recorded during the rainfall event at day 1. The same spikes of N_{2Exc} were recorded in SR and Comp during rainfall events with a concomitant decrease of dissolved CO_2, indicating that aerobic respiration diminished when denitrification was boosted, even thou the Eh suggested that oxic spots were prevailing due to mixing with entrapped air, given the unsaturated conditions of the soil. During the last elutions of the Comp experiment the Eh started to slowly decrease, since the near saturated conditions of the column allowed for partial oxygen depletion.

Dissolved CH_4 concentrations in leachate samples were always extremely low, in effect CH_4 was never detected despite the low detection limit of MIMS (data not show), so methanogenesis was considered a negligible process along the soil column profile in all the experiments. From a mass balance calculation, the cumulative NO_3^- denitrified in the topsoil of the U experiment was only 1.9 kg-N/ha, while in the SR experiment it was 8.7 kg-N/ha and in the first elution of the Comp experiment it was 3.2 kg-N/ha. These low denitrification values are not surprising, since the stormwater events here simulated produced fast percolation rates that usually hinder denitrification capacity due to low contact time with the SOM which is immobile, while only DOC can be used by denitrifying bacteria in such fast flow systems (Mastrocicco et al., 2019a). It must be stressed that these storm events have been found to recur much more frequently in the last years in the Mediterranean area and more specifically in the Po river valley (Vezzoli et al., 2015). Coherently with the above statement, in the Comp experiment the cumulative NO_3^- denitrified by the whole elution (6 storm events) was 14.5 kg-N/ha, which was lower than the expected 19.2 kg-N/ha value obtained multiplying the first Comp elution by 6 (storm events). This because the SOM dissolution rate is expected to rapidly decrease with time given that the most mobile fraction is likely to be flushed away with the first storm events.

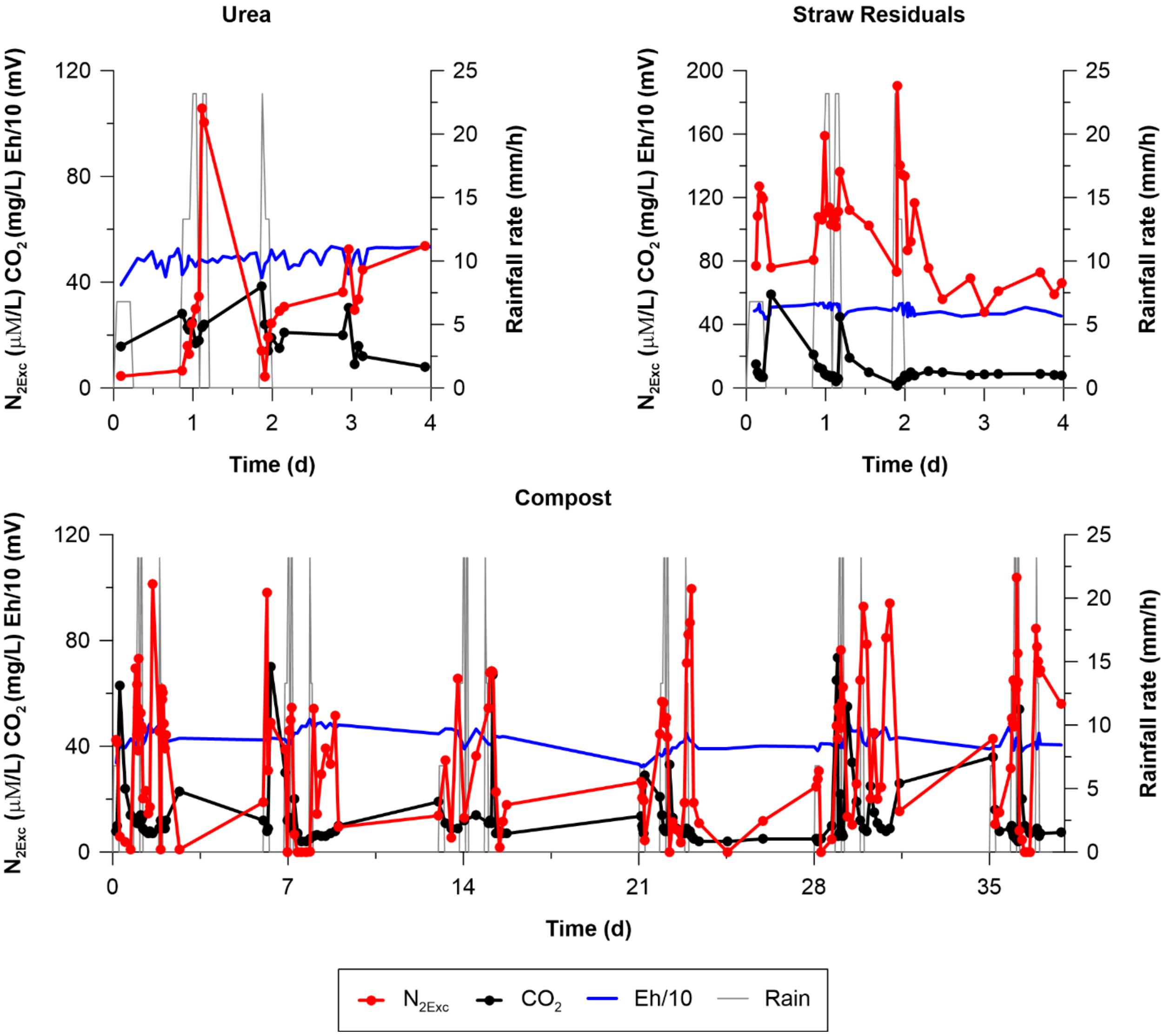

Figure 6: N_{2Exc}, CO_2, Eh and simulated rainfall during the three laboratory experiments with the addition of Urea (upper left plot), Straw residuals (upper right plot) and Compost (bottom plot). Note that Eh values are divided by a factor 10 to make it visible in the plots.

The cumulative masses of DOC, mineral N and denitrified N leached have been summarized in Table 2, where it is apparent that the C/N ratio is shifted towards N in the U experiment and consequently only a small percentage of the leached mineral N has been denitrified.

While in the SR and Comp experiments much greater C/N ratios allow higher percentages of denitrification respect to the leached mineral N after a single stormwater event. The highest denitrified N percentage occurred in the SR experiment, and given that DOC, pH, Eh, and C/N were similar in the SR and Comp experiments, most probably the higher denitrification in SR was due to a higher percentage of labile DOC availability respect to the Comp experiment. This is consistent with results found by Liu et al. (2014) that reviewed 176 published field studies of SR incorporation and calculated an increase in soil active C fraction of 42% on average, although in this study different fractions of DOC were not determined. It must be stressed that in Comp experiment the denitrified N percentage increased from 20.6% to 29.8% after prolonged rainfall events, proofing the long-term action of Comp addition. In fact, according to Xu et al. (2020), the main function of Comp application is the reduction of NO_3^- leaching, and Diez et al. (1997) showed that the Comp application along with intensive irrigation had positive effects on controlling NO_3^- leaching in comparison to other soil conditioners.

Table 2: Leached masses of DOC, mineral N and denitrified N, C/N and ratio of denitrified N over leached N for the Urea (U), Straw residuals (SR), Compost (Comp) stormwater events and for the 6 repeated stormwater events ($Comp_{Tot}$).

	Leached DOC	**Leached N**	**Denitrified N**	**C/N**	**Denitrified N/Leached N**

	(kg-C/ha)	(kg-N/ha)	(kg-N/ha)	(-)	(%)
U	7.7	151	1.9	0.1	1.3
SR	15.1	12.6	8.7	1.2	69.0
Comp	15.5	15.5	3.2	1.0	20.6
Comp$_{\mathbf{Tot}}$	78.6	48.6	14.5	1.6	29.8

3.4. Major dissolved ions

The principal anions present in the leachate samples were Cl^- and SO_4^{2-} (Fig.7). Cl^- is commonly dissolved in natural water, because it isn't adsorbed by the soil (Dev & Bali, 2019) and it is often used as a conservative tracer (Davis et al., 1998).

In the U experiment Cl^- rapidly decreased during the elution due to preferential flow in macropores, reaching a minimum of 10 mg/L, and gradually increased afterwards due to micropores contribution. In the SR experiment, Cl^- was elevated in the first water samples, with a maximum concentration of 16.3 mg/L, and then it decreased with large fluctuations during the rainfall events. In the Comp experiment, Cl^- concentration increased respect to previous experiments, with a maximum concentration of 29 mg/L during the first rainfall event. Then Cl^- gradually decreased until the last storm event (reaching13 mg/L). The Cl^- mass eluted after the six storm events was 74.9 kg-Cl^-/ha while the Cl^- mass in the Comp was only 2.2 kg-Cl^-/ha and considering that the inflow water (Table 1) had very low Cl^- concentrations that contributed with 3.5 kg-Cl^-/ha; this implies that Cl^- was mainly released by dissolution of secondary mineral phases, like halite, which could form during desiccation in soils in micropores (Nachshon et al., 2011) and thus slowly release Cl^- in soil porewater.

The trend for SO_4^{2-} was similar to the one recorded for Cl^- in the all experiments. At the beginning of the U experiment, SO_4^{2-} showed high concentrations (with a maximum of 92 mg/L) and remained always higher than Cl^-, even though it gradually decreased reaching a constant value around 46 mg/L. In the SR experiment, SO_4^{2-} concentrations were high during the rainfall events, especially in the second elution when the maximum concentration (30 mg/L) appeared. After that, SO_4^{2-} decreased reaching a constant value around 3 mg/L, which was even lower than Cl^- concentration. In the Comp experiment SO_4^{2-} concentrations were lower than Cl^- ones and showed a decreasing trend (especially during extreme rainfall events), from 15 mg/L to 4 mg/L. It is worth noting that at the beginning of the Comp experiment, SO_4^{2-} had high initial concentrations and a sudden drop during the first rainfall event, opposite to what has been described for Cl^- at the beginning of the Comp experiment, since the SO_4^{2-} concentration in Comp was very low respect to Cl^-. This again witnesses preferential flow in macropores. The SO_4^{2-} mass eluted after the six storm events was 29.9 kg-SO_4^{2-}/ha, while the SO_4^{2-} mass in the Comp was minimal (0.2 kg-SO_4^{2-}/ha) and the rain water contributed with 6.9 kg-SO_4^{2-}/ha; thus SO_4^{2-} was released by dissolution of secondary mineral phases like gypsum. Finally, PO_4^{3-} in water samples was considered negligible during the whole duration of the U, SR and Comp experiments since it was always below detection limits.

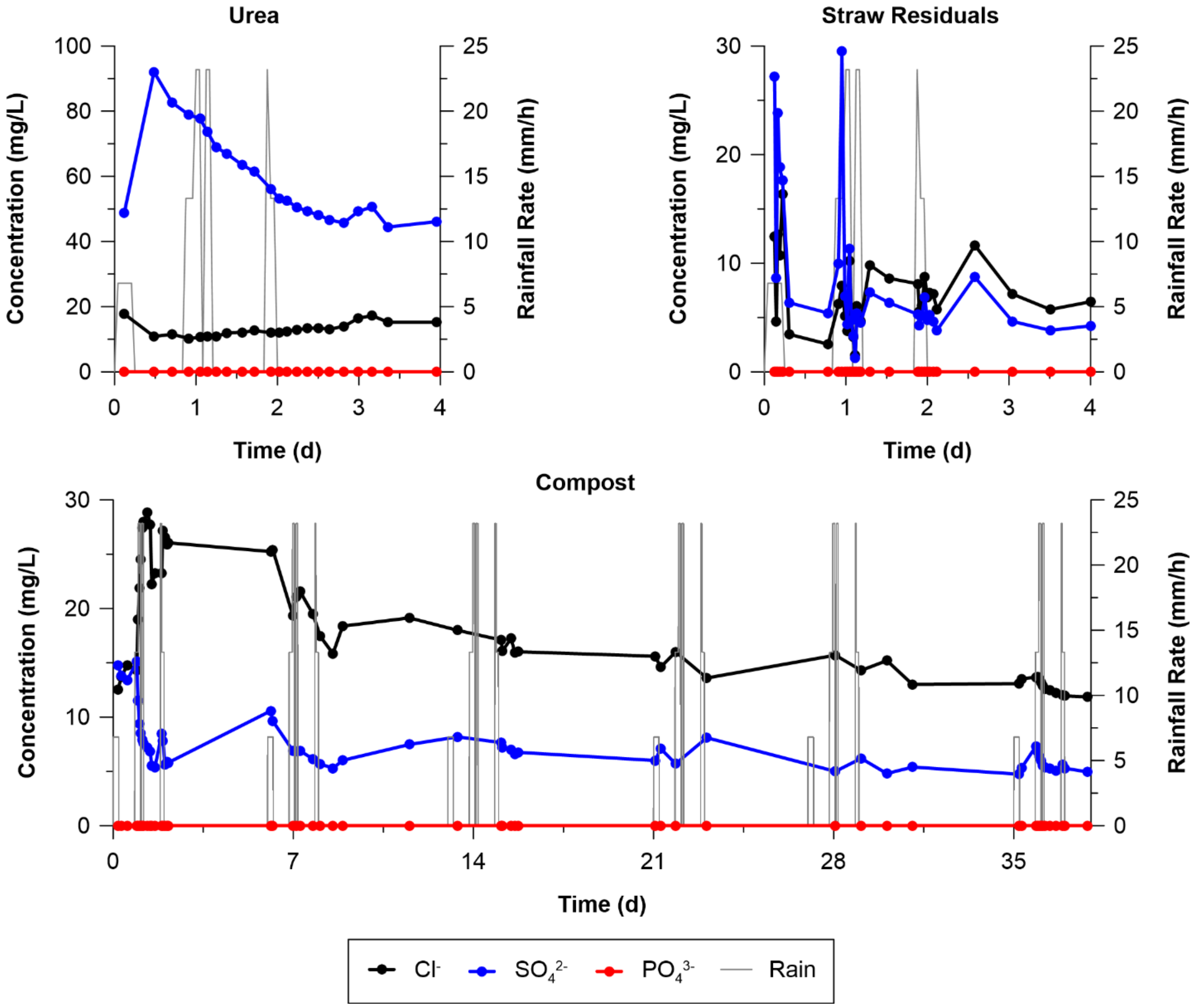

Figure 7: Cl^-, SO_4^{2-}, PO_4^{3-} and simulated rainfall during the three laboratory experiments with the addition of Urea (upper left plot), Straw residuals (upper right plot) and Compost (bottom plot).

The principal cations present in the leachate samples were Ca^{2+} and Mg^{2+} (Fig.8). Both Ca^{2+} and Mg^{2+} trends were similar, especially in the U experiment, with Ca^{2+} showing higher concentrations than Mg^{2+}. This may be due to Ca^{2+} release in the topsoil to buffer the acidity formed by nitrification reactions (Chao et al., 2017). Ca^{2+} content in the U leaching samples decreased during the experiments, while Mg^{2+} had only a gradual decrement. In the U experiment, Na^+ was almost constant over the whole experiment, with an average concentration of 10.6 mg/L. The behaviour of major cations is congruent with the displacement of the initial TDS spike (see Fig.3) induced by urea hydrolysis. In the SR experiment, both Ca^{2+} and Mg^{2+} showed a lower initial concentration than the one recorded for the U experiment, with an initial concentration of 10 mg/L for Ca^{2+} and 1.7 mg/L for Mg^{2+}. Their trends showed an increment until the end of the second rainfall event, a rapid decrease between day 1 and 2, again an increase with the last event and then it became constant. In the SR experiment, Na^{+} showed a smooth increase during the rainfall event, with an average concentration of 7.8 mg/L. In the Comp experiment, Ca^{2+} and Mg^{2+} had the same trend with slightly lower concentrations than the SR experiment. During the Comp experiment, elevated concentrations of Ca^{2+} and Mg^{2+} were recorded in leachate samples in coincidence with the storm events, while Na^{+} remained nearly constant throughout the different elutions except for a slight increase in the last one, from 3.7 mg/L up to 7.2 mg/L. The displacement of divalent cations (Ca^{2+} and Mg^{2+}) followed by monovalent (Na^{+}) was due to the chromatographic effect triggered by the moderate cation exchange capacity of these soils (Castaldelli et al., 2018). This effect was not evident in the U and SR experiments since it may need many pore volumes to produce appreciable variations in leachate samples, as shown by Mastrocicco et al. (2011) with similar soils in water saturated conditions. Finally, K^{+} concentrations could be considered negligible during the whole duration of the U, SR and Comp experiments.

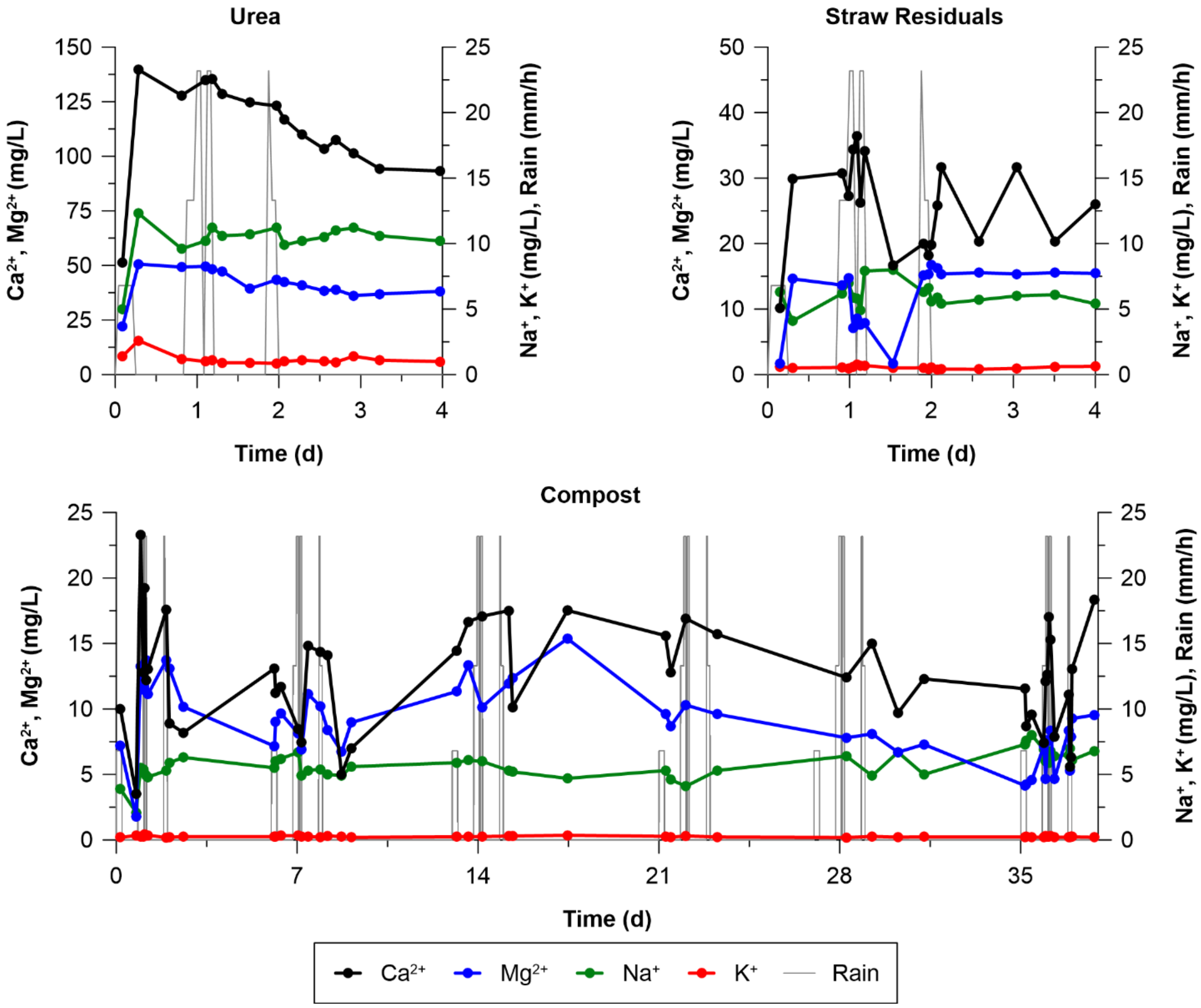

Figure 8: Ca^{2+}, Mg^{2+}, Na^{+}, K^{+} and simulated rainfall during the three laboratory experiments with the addition of Urea (upper left plot), Straw residuals (upper right plot) and Compost (bottom plot).

3.5. Heavy metals leaching

Figure 9 shows that Pb and Cu were the main heavy metals present in leachate water samples. Pb exceeded the WHO threshold limit (10 µg/L) during the whole duration of the U experiment, with an average concentration of 22.1 µg/L, and also during the first three rainfall events in the Comp experiment, with and average concentration of 20.0 µg/L. At the end of the Comp experiment, Pb significantly decreased, with an average concentration of 5.1 µg/L. In the SR experiment, Pb was always below the WHO threshold limit.

Cu followed similar trends to the ones recorded for Pb both in the U and Comp experiments, but always showed concentrations below the WHO threshold limit (20 µg/L). In the SR experiments, Cu showed an anomalous pattern, with low concentrations at the beginning of the experiment which suddenly increase during rainfall events and remained constant, with high values, until the end of the experiment. The SR experiments is the only one having Cu higher than the other analysed compounds. Cd and Zn didn’t exceed WHO threshold limits (5 and 2000 µg/L, respectively) in all experiments; moreover, Cd results were very low, since they have been multiplied by a factor 10 to be shown in Figure 9. Zn appeared in water samples of the U experiment, occasionally in the Comp experiment, and it is not present in the SR experiment. In the U experiment concentrations were higher during the second elution, with a maximum content of 9.0 µg/L; instead, in the Comp experiment Zn was present only during the first and the third storm events, in which concentrations were 3.1 µg/L and 2.0 µg/L, respectively.

Cd trend reflected Cu one in the U experiment, but Cd concentrations continued to decrease until the end of experiment. Conversely, in the SR experiment, Cd pattern was opposite to the Cu one. In the Comp experiment, Cd showed maximum concentrations (2.5 µg/L) at the beginning of the experiment, then decreased from the first to the third rainfall event and then it increased again in the last three elutions. A Zn spike is also present at day 14, possibly released by Comp, although the concentration was low.

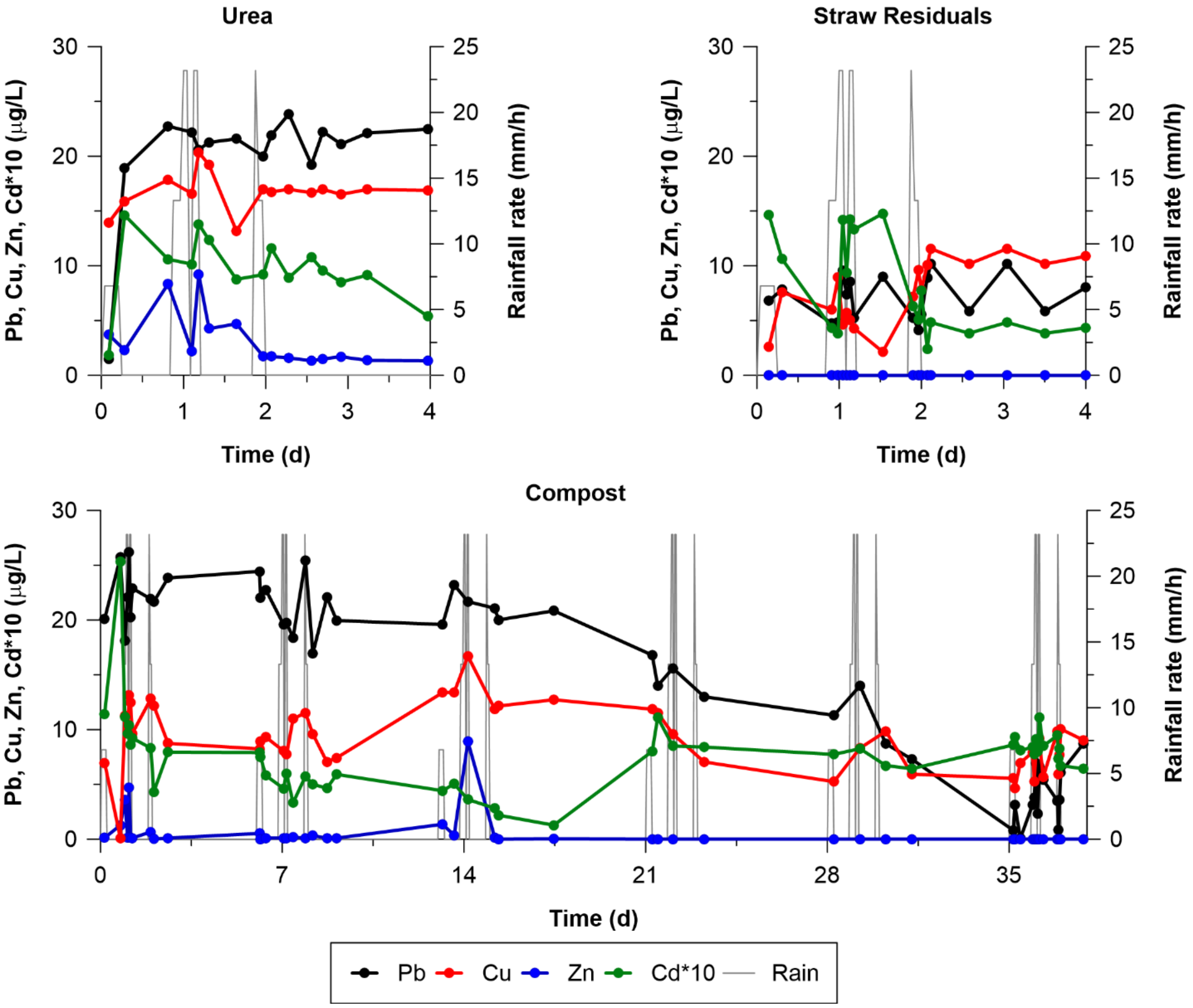

Figure 9: Pb, Cu, Zn, Cd and simulated rainfall during the three laboratory experiments with the addition of Urea (upper left plot), Straw residuals (upper right plot) and Compost (bottom plot). Note that Cd concentrations are multiplied by a factor 10.

Table 3: Summary of the aqua regia extraction tests carried out on soil samples compared with Italian legislative thresholds (Italian Law Decree 152/2006, 2006).

	Cu (mg/kg)	**Cd** (mg/kg)	**Ni** (mg/kg)	**Pb** (mg/kg)	**Zn** (mg/kg)
Italian Legislative Limits	120	2.0	120	100	150
Topsoil	73.4	1.2	114.0	24.9	106.2
Soil at -25 cm	71.4	1.0	108.3	21.0	103.5
Soil at -50 cm	74.9	0.9	114.1	22.9	105.4

Heavy metals in the lower portion of the Po river valley can derive from anthropogenic pollutants or may have a geogenic origin (Di Giuseppe et al., 2014). The sediments of the Po river are rich in Cr and Ni, related to Ophiolite rocks weathering in the hydrological basin, but they are not particularly rich in Pb (Amorosi, 2012; Bianchini et al., 2012) and the heavy metals soil characterization at the beginning of the experiment highlighted concentrations below Italian Legislative Limits (Table 3). So Pb could be derived from anthropogenic activities, like the application of fertilizers onto agricultural fields that could be a direct source of Pb or could have triggered reactions promoting its mobilization (Atafar et al., 2010). Giusquiani et al. (1995) demonstrated that Comp application could cause Pb leaching, and in agreement with their findings elevated Pb concentrations appeared in the leachate at the beginning of the Comp experiment, even though the Pb content in the applied Comp was extremely low (Table 1). Thus, the Pb mobilization was due to reactions triggered by the Comp addition. Likewise, the leachate obtained from the U experiment had an elevated content of Pb while its content in the applied U was extremely low (Table 1). Thus, the Pb mobilization was due to reactions triggered by U addition and not by the U impurities. Finally, it should be stressed that all the heavy metals here monitored were well below the EPA quality water standards for agricultural purposes (EPA, 2017).

3.6. Modification of the soil hydraulic properties due to compost incorporation

The ratio of salinity to sodicity determines the effects of salts and Na^+ on soils: salinity promotes soil flocculation while sodicity promotes soil dispersion (Warrence et al., 2002). The combination of salinity and sodicity of soils is measured by the swelling factor (SF), which predicts whether sodium-induced dispersion or salinity-induced flocculation will affect soil physical properties.

The calculated SF of 0.28, with a combination of ESP equal to 30 and salinity equal to 2 meq/L, indicates that dispersion is likely to occur within the Comp soil column.

Another approach to estimate the effects of salinity and namely Sodium Adsorption Ratio (SAR) on soil physical properties is to assess the potential impacts of various irrigation water qualities on infiltration rates. For example, at SAR equal to 15, a severe reduction in infiltration will occur with an EC equal to 1 dS/m; an EC of 2.5 dS/m or less results in a slight to moderate reduction in infiltration and at EC greater than 2.5 dS/m, there will likely not be a reduction in infiltration.

The variation of the soil hydraulic properties between the initial and final conditions (Table 4) in the Comp experiment highlights the impact of the application of compost as soil conditioner on the soil column after intensive and prolonged rainfall events. θ_{33} and θ_{1500} were calculated according to Rawls et al. (2003), and they were found to be constant from the beginning to the end of experiment. On the other hand, total porosity (Φ_{tot}), that is the ratio between the volume of the soil's pores and the total volume of the column, decreased from 0.55 to 0.47 in the top 15 cm of the column, confirming that empty pores were reduced because of the swelling effect induced by the application of the compost to the topsoil; in the remaining part of the column this effect was not so evident (from 0.46 to 0.45), nevertheless, when considering the weighted average on the whole column the reduction of the total porosity was still evident (from 0.51 to 0.48). At the beginning of the Comp experiment the Available Water Content (AWC), that is the difference between θ_{33} and θ_{1500} expressed as a percentage of Φ_{tot}, was equal to 28% in the topsoil while at the end of the Comp experiment it was equal to 33%, so 5% higher than initial condition thus improving the hydraulic properties of the topsoil. Contrary, the percentage of gravitational water (H_2O_{grav}) within the Φ_{tot} in the topsoil, decreased from 36% to 24% after the compost application. This could also be considered a positive effect if the percolation of harmful species is believed to be an issue in the considered agricultural field. In the remaining part of the column H_2O_{grav} decreased from 24% to 22%, while the weighted average of H_2O_{grav} on the whole column substantially changed from 27% to 23%.

Table 4: Soil hydraulic properties at the beginning of the experiment and after the compost addition in the topsoil of the column.

	INITIAL CONDITION						
Parameters*	**Φ_{tot} (-)**	**Θ_{33} (-)**	**Θ_{1500} (-)**	**AWC (%Φ_{tot})**	**H_2O_{grav} (%Φ_{tot})**	**H_2O_{ret} (%Φ_{tot})**	**ρ_b (gr/cm^3)**
TOPSOIL (15 cm)	0.55	0.35	0.20	28	36	36	1.30
SOIL (40 cm)	0.46	0.35	0.20	33	24	43	1.40
WHOLE COLUMN (55 cm)	0.51	0.35	0.20	32	27	41	1.44
	FINAL CONDITION (after compost application)						
TOPSOIL (15 cm)	0.47	0.35	0.20	33	24	43	1.38
SOIL (40 cm)	0.45	0.35	0.20	34	22	44	1.47
WHOLE COLUMN (55 cm)	0.48	0.35	0.20	33	23	44	1.52

*Total porosity (Φ_{tot}); field capacity (Θ_{33}); permanent wilting point (Θ_{1500}); available water content (AWC) as a % of Φ_{tot}; gravitational water (H_2O_{grav}) as a % of Φ_{tot}; retention water (H_2O_{ret}) as a % of Φ_{tot}; dry bulk density (ρ_b).

Obviously, the retention water (H_2O_{ret}) increased after the compost application on the topsoil, from 36% to 43%. Conversely to what considered for H_2O_{grav} reduction, the increase in H_2O_{ret} could have negative effects on agricultural fields since it may induce waterlogged conditions that are known to be detrimental for most crops. In the remaining part of the column H_2O_{ret} increased from 43% to 44%, while the weighted average of H_2O_{ret} on the whole column changed from 41% to 44%.

Finally, ρ_b which is the ratio between the weight of dry soil and the total soil volume slightly increased after the compost application, both in the topsoil and in the remaining part of the column, because of the swelling effect (see next paragraph for further explanation).

3.7. Clay swelling due to compost incorporation

In this study, it was observed that clay swelling occurred as a consequence of the prolonged simulated rainfall only after the use of compost as amendment on the soil column. In fact, the forces that bind clay particles together are disrupted when too many Na^+ ions come between them. When this separation occurs the clay particles expand, causing swelling and soil dispersion.

Figure 10: Soil column at initial (left picture) and final (right picture) conditions, after the clay's swelling due to the compost addition in the topsoil.

Even though this phenomenon is certainly related to the increment of VWC (it appeared for the first time during the third elution in the Comp experiment), it is most probably driven by the high Na^+ content of the compost applied (approximately 450 mg/kg), because the elevated content of this monovalent cation usually influences soil structure, polarizing clay particles favouring their dispersion (Fig.10).

Moreover, the applied compost was not so rich in Ca^{2+} and Mg^{2+} (44 and 17 mg/kg, respectively), giving a SAR of about 15, which also suggests the possible occurrence of clay swelling, since this phenomenon is highly probable above a SAR of 13 (Choudhary & Kharche, 2018).

The clay swelling observed for the Comp experiment, had a detrimental effect on the infiltration capacity of the soil column as confirmed by the model proposed by Hanson et al. (1999). As already mentioned in a previous paragraph, Comp incorporation influenced soil structure and properties, especially ρ_b and porosity. Different to previous studies (Paradelo et al., 2019), in this study the application of compost caused porosity's decrease and the raise of ρ_b after the experiment (Giusquiani et al., 1995; Zhao et al., 2012). The main cause of porosity's reduction was clay's swelling (qualitative analyses showed in Fig.10), which was due to the raise of VWC and to the elevated Na^+ content in the amendment (Table 1). This side effect explained the elevated content of H_2O_{ret} after the compost application (see Table 4) and the rise of Na^+ content in the leachate, while ions as Ca^{2+} and Mg^{2+} decreased (see Fig.8). The decrease of porosity influenced also AWC (Celik et al., 2004), which increased after the use of compost. However, the increment of AWC could also be justified by the increase of DOC during the Comp experiment (Ramos, 2017).

4. Conclusions

This study describes the effects of straw residuals and compost respect to urea, in reducing nitrate losses from agricultural field situated in vulnerable zones of the province of Ferrara, which may be subject to extreme rainfall events. The results of the laboratory's column experiments show that straw residuals and compost incorporation could decrease nitrate leaching towards groundwater by increasing the denitrification capacity. On the other hand, the treatment with urea showed incomplete denitrification, mostly related to the lack of labile organic substrates, rather than to other inhibitor effects as pH and Eh changes. Furthermore, the results showed that the compost addition modified the physical and hydraulic properties of the soil, because of the elevated sodium content of the employed compost, leading to clay's swelling, which negatively affected water retention and infiltration rate. Thus, an issue to be considered when applying compost to agricultural land is the chance to induce waterlogged conditions if prolonged rainfall events occur. Moreover, further experiments should be conducted with loamy textures soils and different rainfall intensities to widen the obtained results. The main limitations of this study are: (i) three or more undisturbed soil cores should have been used to provide more insights on the statistical representativeness of the obtained results and (ii) the lack of sampling ports within the soil column limited the quantification of the most reactive soil horizons.

Despite the above mentioned limitations, some general conclusions can be drawn: the use of organic conditioners, like straw residuals and compost, have positive impacts on agricultural fields, like the dissolution of labile organic carbon which, by fuelling denitrification, may prevent nitrate migration to shallow groundwater; this without a significant mobilization of potentially toxic elements, such as lead, which was detected at low concentrations only in the initial stage of the compost experiment.

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matter conservation (https://ec.europa.eu/eip/agriculture/en/find-connect/projects/nitrati-ferrara-tecnicheagronomiche-la)

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