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FORMATION AND DISSOLUTION OF SALT CRUSTS AS A RAPID WAY OF NITRATE MOBILIZATION IN A TILE DRAINED AGRICULTURAL FIELD UNDER A TEMPERATE CLIMATE

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Abstract

Agriculture is widely recognized as one of the human activities that have a major impact on pollution of water resources. In agricultural fields, the formation of salt crusts during dry periods and their fast dissolution due to irrigation or rainfall events can induce the leaching of water with an elevated content of dissolved species towards surface and ground waters. This process is rather common in arid environments but it also occurs in coastal plains in temperate environments. The formation of salt crusts was studied in a 6.3 ha experimental site located in the Po River Delta (Northern Italy). The soil, consisting of interfluvial silty-clay deposits recently reclaimed and equipped with tile-drains to avoid water-logging conditions, was investigated for vertical spatial heterogeneity via depth profiles and for horizontal spatial heterogeneity collecting numerous surface soil samples. Extreme drought conditions were recorded over the monitoring period (summer-autumn 2012), leading to soil fracturing and then to fast water percolation during the first rainfall events in autumn. Major ions concentration, measured in pore-water, showed nitrate peaks of several grams per liter, suggesting the dissolution of nitrate salts. Results from this study highlighted: (i) that the fertilizers applied to the field site were evapoconcentrated in the top soil; (ii) a marked spatial heterogeneity in the salt crusts formation, which was unevenly distributed over the field with a preferential appearance in the hollows; (iii) a rapid mobilization of nitrate towards tile-drains after the first rainfall events, due to preferential flow through soil cracks developed during the summer season.

Keywords: nitrate, evapoconcentration, percolation, tile-drains, temperate climate.

1. INTRODUCTION

The growing demand of land for agricultural needs has led to the intensification of reclamation works in wetland areas. This practice may induce several problems such as soil salinization (Mastrocicco et al. 2013a), decalcification (Van den Berg and Loch 2000), and heavy metals exports (Bai et al. 2011; Molinari et al. 2013). Additionally, in order to guarantee a good crop yield, these soils require a large use of fertilizers. Reactive nitrogen (N) losses from agricultural practices have been acknowledged as one of the major issues both in developed and emerging countries, being responsible for surface waters eutrophication (Lassaletta et al. 2009; Romero et al. 2012) and groundwater nitrate (NO_3^-) contamination (Galloway et al. 2008; Howarth et al. 2012). In fact, when the amount of N applied via manure and chemical fertilizers exceeds crop requirements, N may be transferred vertically or horizontally to ground and/or surface water bodies (Billen and Garnier 2000; Dinnes et al. 2002). Furthermore, in reclaimed areas, surface water bodies are rarely buffered by landscape elements, which have been removed due to intensification of agriculture (Balestrini et al. 2011; Hefting et al. 2005). These problems are rather common in Italy (Mastrocicco et al. 2013a). During the nineteenth century, the rapid urbanization of Italian coastlines required the widening of residential and agricultural areas, thus mechanical draining of coastal swamps has been a common practice. Today, most of the reclaimed areas are intensively cultivated with highly nutrient-demanding crops, which require a large use of fertilization and chemical treatment. These areas also require a large amount of water for irrigation in order to avoid salinity stress to the crops due to the presence of soluble salts accumulated in the sediments during the reclamation works.

Another issue to guarantee an adequate crop yield in waterlogged salt affected soils is to provide soil aeration and an appropriate root growth (Sharma and Gupta 2006). Tile-drains are a well-established drainage technology able to remove surplus water and excess salts. Singh et al. (2006) demonstrated that poorly drained soils reclaimed by tile-drains, recorded an increase in crop yield but also in NO_3^- leaching to the surface water system. Niazi et al. (2008) showed that in Pakistan even if tile-drains increased crop yield, surface water was negatively affected by their installation since the drained water was found to have a very high salinity. Christen et al. (2001) found that the installation of tile-drains in several field sites in Australia, was often responsible for the discharge of excessive water volumes and salt loads to the receiving surface water bodies.

Holding what said so far, it follows that in reclaimed lowland the combination of a wide application of N fertilizers and the extensive installation of tile-trains is a major concern, since these latter can act as a shortcut in the export of dissolved species from agricultural land to surface waters. Concentrated discharge through tile-drains is of difficult analysis (Dinnes

et al. 2002) since the activation of tile-drains, and the relative N export, is not a homogeneously distributed phenomenon neither in space nor in time.

In coastal environments, the mitigative effect of the sea often induces the existence of microclimatic zones with reduced precipitation and higher temperature. In these conditions, especially over dry summer periods, dry deposition and evapoconcentration of N-containing salts are favoured, as well as the development of soil cracks. At the beginning of the wet season, pulses of N-rich water derived from the dissolution of the salt crusts accumulated over the dry season, might be transported downwards through the soil cracks, increasing nutrient leaching towards groundwater and the tile-drains, which may then transfer the N-rich water to surface waters (Dayyani et al. 2010; Rozemeijer et al. 2010). N species distribution in the percolating soil water is governed by steep redox gradients depending on the presence of oxic/anoxic conditions, soil organic matter (SOM) and microbial communities (Ramesh Kumar and Riyazuddin 2012; Washington et al. 2006), and also by the residence time, which in turn depends on soil hydraulic conductivity (Burt and Pinay 2005). The aim of this study are: (i) to identify the processes responsible for the accumulation of salt crusts over the field surface during dry periods, (ii) to understand the fate of the N-rich water derived from the dissolution of the salt crusts immediately after the first rainfall events, and to (iii) identify similarities and differences with analogous processes occurring in arid climate, in order to understand if the mitigative measures proposed for those environments may be successfully applied even in temperate climate.

2. STUDY SITE

The study site is located in the Po River Delta (Northern Italy) approximately 13 km from the Adriatic Sea and is characterized by a microclimate influenced by the sea. The annual cumulative rainfall during the study period ranged between 500 and 700 mm, with peaks in autumn and spring. Sprinkle irrigation was also applied to the field site when necessary, typically during July and August, with an amount ranging from 40 to 80 mm per year. The minimum temperature is always above 0 °C due to marine thermoregulation, with an average of 3 °C in January and 25 °C in July. The actual evapotranspiration during the study period ranged between 420 and 540 mm, with peaks in summer and early autumn (http://www.arpa.emr.it/sim/?agrometeo/bollettino_mensile).

The sedimentary facies reflect climate change and human impact that deeply modified the local hydrological system (Amorosi et al. 2002). The area is characterized by an interplay of deltaic and littoral deposits with a diachronous splay of Po distributary channels, associated with inland delta deposits reclaimed from 1860 to the present day (Di Giuseppe et al. 2014). The area consists of topographically depressed zones (interdistributary bays now kept dry by the reclamation works) enclosed by topographic highs (paleochannels and paleodunes). The experimental site (Fig. 1) occupies a total

area of 6.35 ha and is located in a depressed zone at -3 ± 0.3 m above sea level (a.s.l.). Five units were recognized at the experimental site, with variable thickness and not always simultaneously present in the soil profiles. From the ground surface downward they are: (i) a well aerated clayey-silt unit affected by tillage and root growth, ubiquously present from the ground surface down to 0.65 m below ground level (b.g.l.); (ii) a layer particularly rich in SOM from 0.65 to 1.00-1.50 m b.g.l., depending on the sampling location; (iii) fluvial sands and sandy-loam lenses poor in SOM, mainly present in the south-western corner of the field site, from 1.00 to 2.00 m b.g.l.; (iv) an anoxic clayey-silt rich in SOM, with carbonate inclusions and iron hydroxides (always above 5%), from 1.50 to 4.00 m b.g.l.; and (v) a decalcified-anoxic peat layer, mainly present in the south-eastern corner of the field site, from 2.00 to 4.00 m b.g.l..

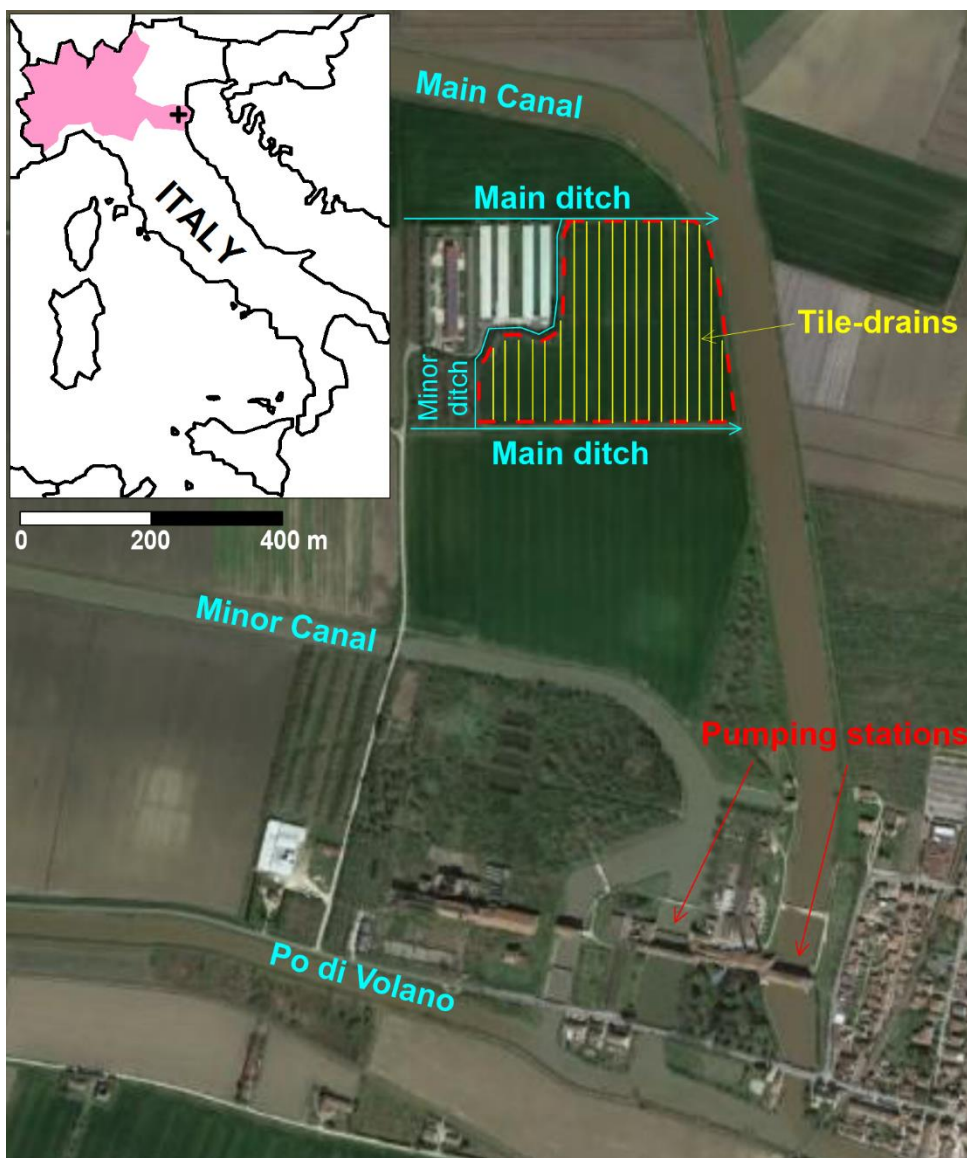


Figure 1. Field site location (red polygon) with the main hydraulic features highlighted: tile-drains (yellow lines), pumping stations (red arrows), ditches, canals and the Po di Volano River (cyan lines).

Since 1960, the experimental site has been intensively cultivated with maize and winter cereals using synthetic urea during the growing season and pig slurry in autumn as soil fertilizers. In 1992, tile-drains were installed at approximately 1.35 m b.g.l. and with a spacing of 10 m (Fig. 1) to prevent water-logging conditions during winter time and to feed the field with the canals' water during summer time. To drain the field, the tile-drains provide gravity drainage of groundwater towards the ditches when their stage is lower than the tile-drains elevation; the water collected in the ditches is then discharged by gravity in the main canal (Fig. 1). For irrigation purposes, the water is derived by gravity from the minor canal and input in the ditches; when the stage in the ditches is higher than the tile-drains elevation, surface water may flow into the field (Fig. 1). A detailed topographic survey performed with a total station Nikon DTM-450 showed that the northern main ditch collects most of the run-off, since the field has a slope of 1‰ from South to North, while the tile-drains tend to discharge the majority of the drained water towards the southern main ditch.

As in many other temperate regions, conventional tillage is widely applied throughout the Po River plain and especially in the low-lying portion of the Po watershed where poorly drained, clayey soils are present, making it difficult to apply more conservative techniques like ploughless tillage. Even in the study site mouldboard ploughing to a depth of 20-40 cm b.g.l. is performed in autumn to control weeds and bury plant residues, followed by seedbed preparation and sowing in spring. Deep ploughing, down to 60 cm b.g.l., is also applied to the field site every 3-4 years, to facilitate water percolation towards tile-drains.

3. MATERIALS AND METHODS

Core samples were collected in six sampling campaigns (three during the dry season and three during the wet season) from October 2011 to September 2014 by mean of an Eijelkamp Agrisearch auger equipment. 24 sampling locations, homogeneously distributed over the field site, were investigated in each sampling campaign. At each location, samples were taken at different depths, typically every 30-50 cm or when a change in stratigraphy was recognized. All the 432 soil samples, collected over the whole study period, were stored in polyethylene (PE) bags under vacuum in the field and maintained refrigerated while transported to the Sedimentology Laboratory of the University of Ferrara. In the laboratory, the soil samples were homogenized at room temperature and a physical characterization was performed for the resulting mixture, in triplicates (Tab. 1). Samples were not washed, as this would preferentially remove components of the system that are associated with finer minerals.

Samples were grouped into two different horizons: (i) an upper horizon from 0 to 0.65 m b.g.l. classified as "silty clay loam" according to the USDA-SCS (1984) textural classification, with an extremely homogeneous soil texture because

of the ploughing practices; and (ii) a lower unstructured and calcic horizon from 0.65 to 1.20 m b.g.l., with higher content of sand and reduced content of silt.

Particle size curves were obtained using a sedimentation balance for the coarse fraction and an X-ray diffraction sedigraph 5100 Micromeritics for the finer fraction; the two regions of the particle size curve were connected using the computer code SEDIMCOL (Brambati et al. 1973). The SOM was measured by dry combustion (Tiessen and Moir 1993). The carbonate content was determined with a Chittick gasometrical apparatus (Dreimanis 1962). Soil and porewater pH were measured using a Hanna meter, incorporating a temperature probe for compensation.

Saturated (θ_s) and residual (θ_r) water content were measured according to the gravimetric method proposed by Gardner (1986); porosity (ϕ) was measured gravimetrically using water saturated soil sub-samples then oven dried (Danielson and Sutherland 1986). The dry bulk density (ρ_d) was derived from the formula:

$$\rho_d = (1 - \phi)\rho_s \quad (1)$$

where ρ_s is the grain specific gravity, defined as the ratio between the mass of the mineral grains and that of an equal volume of fresh water.

To estimate the hydraulic conductivity (k_s) distribution along the vadose zone profile both pedotransfer functions and field measurements via a 2800K1 Guelph Permeameter were performed. The range of k_s values obtained via pedotransfer function were derived using Rosetta 1.1 neural network code (Schaap et al. 2001). The percentage by weight of sand, silt, clay, the soil textural classes and the ρ_d were used to compute vertical profiles of k_s . The k_s measured via the Guelph Permeameter were obtained applying a steady-state constant head to the unsaturated deposits, using a Mariotte bottle system constituted by plastic tubes (Elrick and Reynolds 1992).

Table 1. Sediment characteristics and their standard deviation.

Parameter	Upper Horizon (0-0.65 m b.g.l.)	Lower Horizon (0.65-1.20 m b.g.l.)
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Grain size (%)		
Coarse sand (630-2000 μm)	0.00 \pm 0.0	0.00 \pm 0.0
Medium Sand (200-630 μm)	0.6 \pm 0.1	0.0 \pm 0.0
Fine Sand (63-200 μm)	7.4 \pm 0.3	1.5 \pm 1.4
Silt (2-63 μm)	49.2 \pm 3.1	62.4 \pm 4.2
Clay (< 2 μm)	42.8 \pm 3.4	36.1 \pm 2.9
Organic matter (%)	8.1 \pm 1.5	8.9 \pm 2.4
Hydraulic conductivity (m/day)	1.7 \pm 2.4	1.1 \pm 0.3
Bulk density (Kg/m ³)	1.15 \pm 0.05	1.45 \pm 0.1
Grain specific gravity (g/cm ³)	2.68 \pm 0.02*	2.62 \pm 0.02*
Saturated water content (%)	58.5 \pm 0.6	39.3 \pm 0.4
Residual water content (%)	13.0 \pm 0.2	14.8 \pm 0.3

*data from Di Giuseppe et al. (2016)

To monitor the soil water movement, TDR probes (Decagon Devices, Inc. Pullman, WA) were employed to measure volumetric water content (VWC), temperature and bulk electrical conductivity (EC_b) at three different locations within the field site. The probes, located at -5, -30 and -50 cm b.g.l., were connected to data loggers recording every 30 minutes. Two of the TDR profiles showed reliable data throughout the whole duration of the monitoring period, while the third TDR profile, located in the central-eastern part of the field where clayey soils are abundant (Fig. 1), showed extremely low VWC and EC_b values in summer, probably because of a lack of contact between the probes and the soil due to the presence of fractures (Vogel et al. 2005). For this reason, the measurements of the third TDR profile will not be considered in the following discussion.

The raw TDR data were calibrated using the marsh soil of the experimental site, since TDR probes are pre-calibrated for a different medium-fine mineral soil (Mortl et al. 2011). The calibration procedure was performed with a third order polynomial function; the fit was good with an R^2 of 0.991. The EC_b was converted to pore-water electrical conductivity (EC) according to Vogeler et al. (1996); EC was converted to total dissolved solids (TDS) using a linear relationship tested in the laboratory, with a slope of 0.6501 and an R^2 of 0.968.

Major ions were determined in pore-water using Milly-Q water to extract water-soluble ions from the soil samples, with a soil to water weight ratio of 1:5. The resulting mixture was sealed in jars, shaken for 1 h, and centrifuged for 1 h at 25

°C to separate the sediment from the solution. Pore-water samples were filtered through 0.22 µm Dionex polypropylene filters, prior to be analysed. Major ions were analysed using an isocratic dual pump ion chromatography ICS-1000 Dionex. A Spectrum meteorological station 500 m far from the experimental field was used to record precipitation, solar radiation, wind speed, humidity, minimum and maximum temperatures.

4. RESULTS AND DISCUSSION

Figure 2 (upper plot) shows the continuous monitoring of the VWC during the period 03/2012-09/2012 at three different depths. During spring, the precipitation events provoked an increase in the VWC with peaks in the sensor closer to the ground surface with respect to the lower ones. On the contrary, in summer the intense precipitation event occurred on the 7th of July (24 mm) provoked a sudden VWC increase in the lower probes. This unusual behaviour was due to cracks developments induced by evaporation caused by the high temperatures (Figure 2 lower plot) that reached values up to 45 °C at the beginning of July. Accordingly, the soil temperature during the storm event of the 7th of July drastically dropped down in the lower sensors, witnessing a very fast water percolation.

The 60 mm of sprinkler irrigation provided to the field site from the 28th of June to the 5th of September do not induce remarkable improvement in the VWC of the sensor closer to the ground surface, probably because they were largely intercepted by crop's canopy and leaves. On the other hand, the activation of the tile-drains (located at a depth of approximately 1.35 m b.g.l.) in irrigation mode on the 10th of July may have contribute to keep high the VWC in the lower sensors, since in this field the capillary rise is typically in the order of 80 cm (Fig. 2 upper plot).

In early September, with the decrease of the soil temperature and after few days of intense precipitation events, the soil cracks gradually started to shrink and the VWC peaks returned to be higher in the upper sensor with respect to the lower ones. At the same time, a gradual decrease in soil temperature was recorded from the lower sensors, indicating slow water percolation through the porous matrix.

Along with VWC and temperature, even soil chemistry may play a role in the formation of soil cracks. The mean sodium alkali ratio (SAR) of the 432 soil samples is as low as 0.9, although it is characterized by a wide standard deviation (0.8). The SAR is often associated with soil crusting due to swelling of clay particles, which usually impair infiltration and increase runoff and erosion (Mace and Amrhein 2001). On the contrary, soil cracking is directly associated with soil salinity (Lima and Grismer 1994). The lowest SAR values (0.3-0.4) found at the field site are associated with top soil samples, while the highest values (3-4) are associated with deep saline soils at least 1 m b.g.l.. This finding is in agreement with the elevated soil cracking experienced by these agricultural soils.

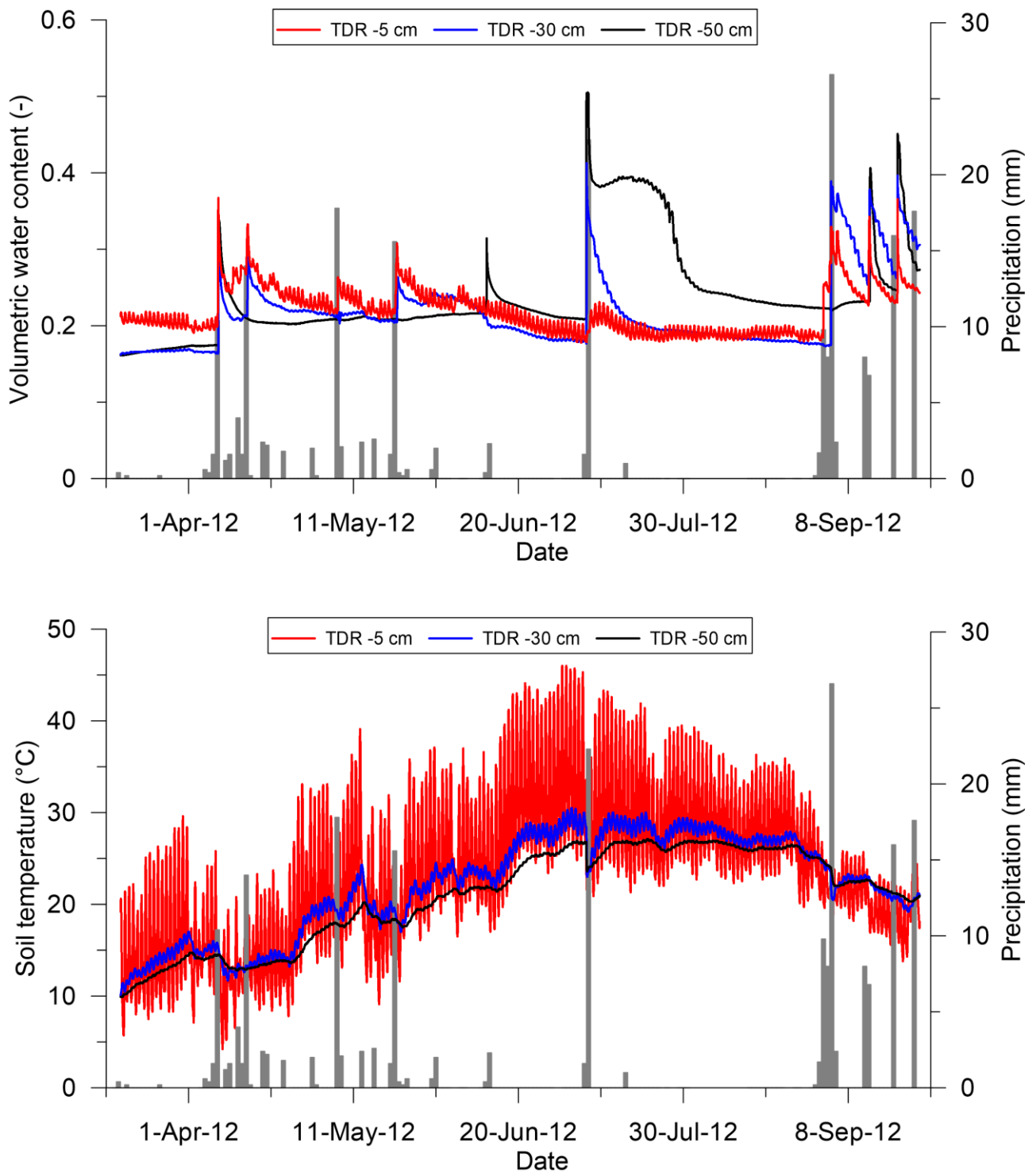


Figure 2. Volumetric water content from TDR (upper panel) at different depths compared with the daily precipitation (grey bars) and soil temperature (lower panel) at different depths compared with the daily precipitation (grey bars).

Even the tillage technique could have a remarkable influence on crack development and thus on water and dissolved species infiltration. Ploughless tillage was demonstrated to contrast cracks development by increasing plant residues near the soil surface, which reduce soil temperature and evapotranspiration, augment soil water content, and increase nutrients

and organic matter accumulation near the soil surface. However, it was also found responsible to favour cracks development by increasing the soil bulk density of the top soil, reducing air-filled porosity, and facilitating the development of vertically-oriented fissures, due to increased earthworm activity and to the presence of stable root channels (Rasmussen 1999). Since ploughless tillage is most suited to drier and more stable soils, its eventual beneficial effect has never been tested on the study site, which is characterized by a poorly drained clayey soil. Consequently to properly assess the role of the tillage technique on crack development and dissolved species percolation on this study site a detailed soil physical analysis of the long-term application of various tillage should be performed to understand the impacts on crop productivity, soil properties and economic costs and benefits.

Figure 3 reports the variation of the EC_b (upper plot) and of the porewater TDS (lower plot) during the period 03/2012-09/2012. During the summer period, the same inversion pattern described for the VWC was evident even for the EC_b values recorded by the upper and lower sensors. EC_b went down to values near zero in summer due to soil desiccation in the sensor closer to the ground surface, while the lower probes show some spikes during intense precipitation events. These peaks once normalized for the VWC and converted into TDS concentrations became breakthrough curves of the applied fertilizers.

The highest peak recorded of 3.5 g/L, is consistent with the results obtained in a laboratory experiment using the soil from the same experimental field amended with synthetic urea (Colombani et al. 2014). It is important to note that the highest TDS concentrations were not detected by the upper probe, but in the lowest one. The TDS of the upper soil was maintained quite high for all the spring until June, given the low amount of precipitations and the fertilizer input: 60 kg-N/ha/y of pig slurry on the 15th of October 2011 and 180 kg-N/ha/y of synthetic urea on the 15th of May 2012. The fast TDS decrease in the upper probe coincides with the growth stage of maize plants that transpired the available water content and the dissolved fertilizer. The storm event of the 7th of July 2012 dissolved and mobilized the salts accumulated at the beginning of the summer season inducing a sudden TDS increase in the lower soil horizon due to the fast percolation through soil cracks and macropores. Conversely, the prolonged rainfall events at the beginning of September 2012 produced an increase in TDS in the upper soil horizon because of the slow leaching of the evapoconcentrated salts through the porous matrix once the summer cracks disappeared.

From the continuous monitoring is clear that the fast migration of dissolved species derived from the salt crusts dissolution, happened mainly during summer, but to understand which chemical species were transported towards the lower horizon and thus possibly to the tile-drains and to the surface water bodies, a further analysis was needed.

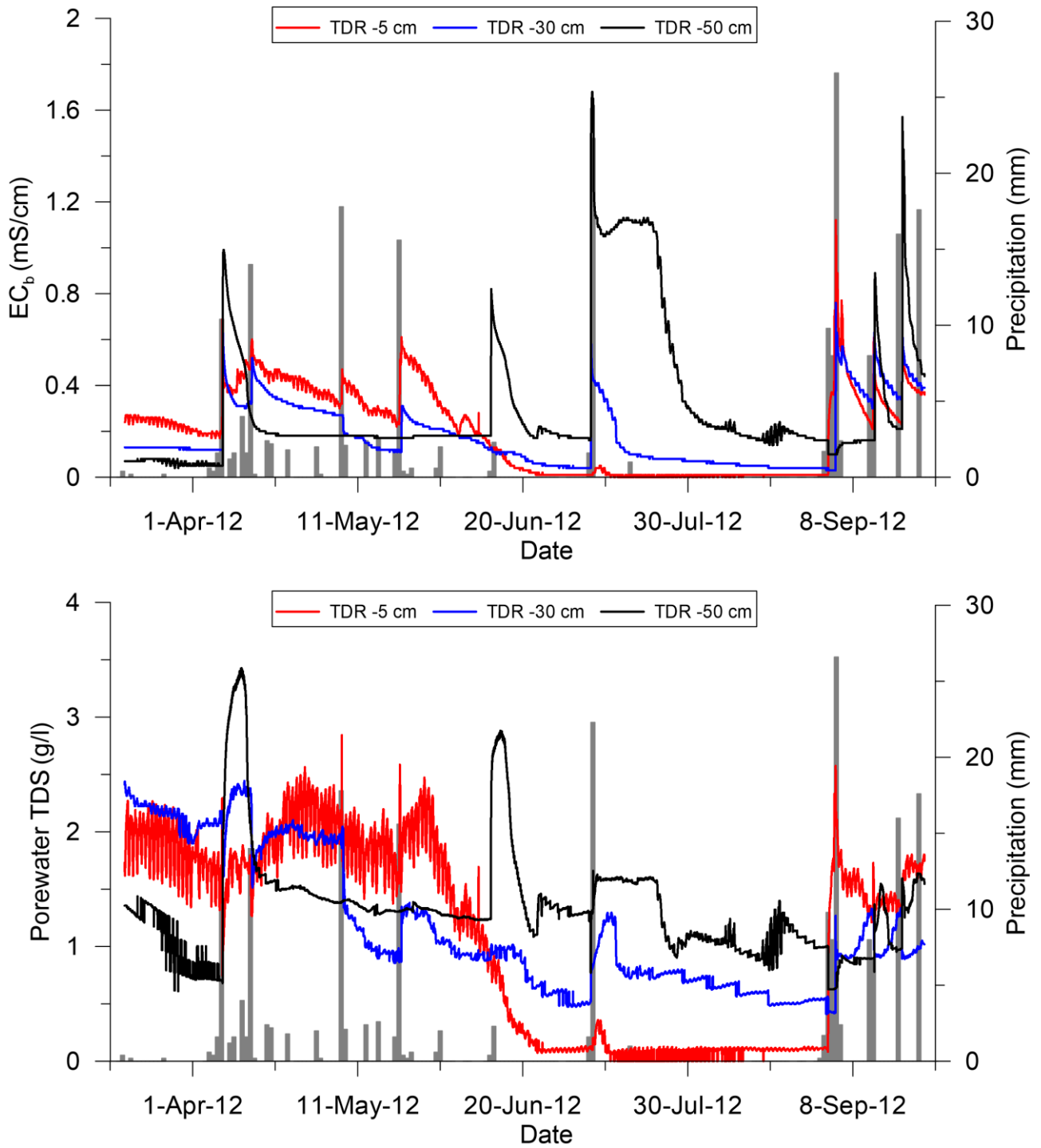


Figure 3. EC_b derived from TDR probes monitoring at different depths (upper panel) compared with the daily precipitation (grey bars), and TDS in porewater at different depths (lower panel) compared with the daily precipitations (grey bars).

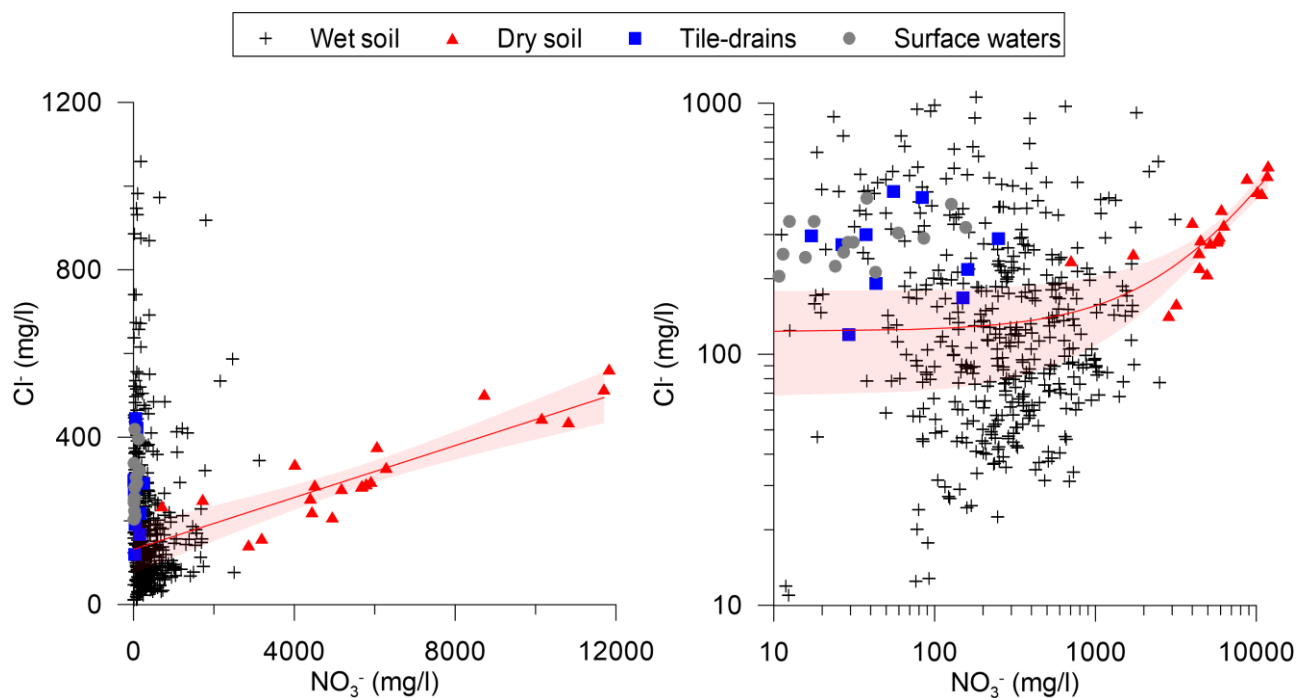


Figure 4. Scatter diagram of Cl^- versus NO_3^- in soils, subsurface tile-drains and surface waters using linear (left plot) and logarithmic (right plot) axis to enhance the visualization of the lower concentrations. The red solid line represents the linear correlation between Cl^- versus NO_3^- in dry soils during July 2012 and its 95% confidence intervals (shaded area).

Figure 4 shows the chloride (Cl^-) versus NO_3^- concentrations in soils, subsurface tile-drains and surface waters (namely the main ditches to the North and to the South of the experimental field, and the main canal to the East of the experimental field). To compare soil samples with water samples, the concentrations were expressed in mg/L dividing the soil concentration (mg/kg) by their VWC (gravimetric water content * bulk density). Soil samples were subdivided in two groups: the wet soil samples with a VWC of at least 20% and the dry soil samples collected in July 2012 with a VWC closer to the residual water content (see Tab. 1). For dry soil samples, usually collected in the top 10 cm of the soil profile, the linear correlation between Cl^- and NO_3^- (red solid line in Fig. 4) has a regression coefficient of 0.73, showing a clear evapoconcentration trend with exceptionally elevated NO_3^- concentrations. These samples were collected near the sites where the salt crusts were observed. A marked spatial heterogeneity in the formation of salt crusts was detected; salt crusts were unevenly distributed over the field with a preferential appearance in the hollows, where top soil samples show very high Cl^- , NO_3^- and K^+ content (Tab. 2). The wet soil samples never exhibit such elevated NO_3^- concentrations, while Cl^- was occasionally found at high concentrations because of the capillary rise of local groundwater, which was demonstrated to have a high salinity (Mastrocicco et al. 2015). NO_3^- were found occasionally at high concentration in both tile-drains and surface water bodies surrounding the experimental field site, with 50% of the tile-drains samples and 30% of surface water samples exceeding the maximum admissible limit of NO_3^- in surface water (50 mg/L according to

the Council Directive 98/83/EC). These excesses are all occurring in the spring period. Although this trend may seem directly related to the dissolution of NO_3^- rich salt accumulated on the ground surface over the summer season, it is not straightforward to identify and quantify the sources of NO_3^- in this zone. In fact, even the elevated geogenic reactive N pool (up to 70 mg-N/kg) present in the peaty sediment found in the lower horizon at the experimental site, may supply ammonium which is readily nitrified to NO_3^- in oxic condition (Mastrocicco et al. 2013b). Besides, it is not possible to exclude that the application of pig slurry (60 kg-N/ha/y) in autumn could have contribute to the high NO_3^- concentrations in surface water via the slow mineralization of the organic N, as recently shown by Balestrini et al. (2016). Moreover, the fact that the main canal samples show the same Cl^- and NO_3^- concentrations of the ditch samples suggests that the processes occurring at the experimental site are probably acting even in nearby agricultural land, since the small amount of water discharged from the ditches in the main canal (which has a high discharge and thus a high dilution capacity), cannot alone explain the elevated Cl^- and NO_3^- concentrations found in the main canal.

Table 2: Major ions distribution in top soil samples (0-10 cm) collected in flat zones (S) and in hollows (S_h) during July 2012.

Sample	Cl^-	NO_3^-	SO_4^{2-}	Na^+	Mg^{2+}	K^+	Ca^{2+}
i.d.	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
S01	62	2401	130	51	23	124	31
S02	40	1665	70	28	18	78	114
S03	30	1720	79	22	14	87	135
S04	79	2513	123	68	22	117	74
S05	87	2996	140	71	30	125	101
S06	121	3070	279	94	35	130	186
S_h01	240	5052	362	150	76	297	465
S_h02	107	3398	288	91	49	189	202
S_h03	102	3491	299	113	37	155	351
S_h04	130	3467	246	121	57	203	286
S_h05	239	6637	549	208	102	340	443
S_h06	126	3163	170	80	51	145	175

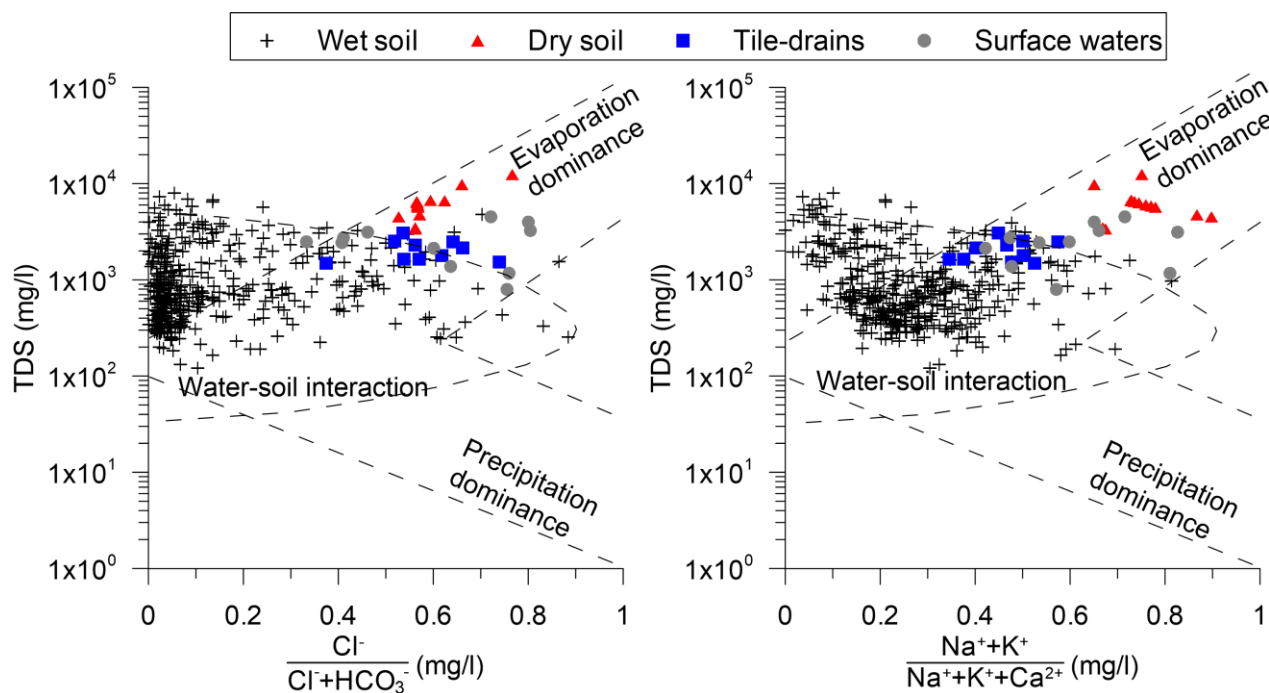


Figure 5. Gibbs diagrams for anions (left panel) and cations (right panel).

The Gibbs diagrams (Gibbs 1970) used to infer the processes dominance in the studied field site (Fig. 5) show that water-soil interaction is the prevailing process for all the wet soil samples, while for the dry soil samples evaporation is by far the most important process. The tile-drains and surface water samples fall on the border between the preceding two fields, indicating a non-negligible contribution of evapoconcentration processes in the tile-drain leachates that flow into the main ditches and finally into the main canal. The minor ditch at the left border of the field site (see figure 1 for location) is even more affected by evaporation processes; here direct evaporation from the water body plays an important role as shown by the surface water samples of the Gibbs diagrams plotting in the evaporation dominance area (Fig. 5).

The evaporation dominance area, where the dry soil samples plot, is by far the most representative for the processes occurring in arid environments. Salt crusts, attributed to evaporation, wetting and drying cycles, and soil capillarity, have been documented in the upper unsaturated zone in many arid areas. Hamdi-Aissa et al. (2004) showed that the rising of shallow groundwater induces intense soil salinization resulting in the formation of salt crusts, namely calcite, gypsum and halite; accordingly, Ibrahimi et al. (2013) demonstrated that salts accumulation seems to be a function of the water table fluctuation frequency and they also showed that the dominant cations present in the soil solution are $\text{Ca}^{2+} > \text{Na}^+ > \text{Mg}^{2+} > \text{K}^+$, and the dominant anions are $\text{SO}_4^{2-} > \text{Cl}^- > \text{HCO}_3^-$. Accordingly, a study from Smith and Compton (2003) showed that the dominant minerals are halite, calcite, Mg-calcite, dolomite and gypsum and they demonstrated that the seasonal concentration of these salts is followed by flushing by through-flow during the wet season. Also Weisbrod et al. (2000) found that in arid areas, fractures might form preferential flow-paths across the unsaturated zone so when recharge events

activate water flow through the fractures, the dissolution of the precipitated salts occur and the dissolved ions are readily transported toward the water table, bypassing the slow matrix percolation. This mechanism, by reducing the residence time within the top soil matrix, prevents the eventual degradation of dissolved species and results in a peak of the TDS value that eventually decreases as the reservoir of soluble salts is depleted.

These issues are widespread especially in arid and semiarid areas, but the present study reports that salts accumulation and fast percolation of high TDS water through fractures can occur even in temperate climate. Nevertheless, results from this study has shown not only similarities with respect to the literature concerning salts accumulation in arid environments but even some remarkable differences. In particular, the rising of shallow groundwater and its subsequent evaporation, evoked for the formation of salt crusts in arid environments, seems to play an important role even in the present field study, as well as the role of fractures in facilitating the deep percolation of high TDS water after the first rainfalls event. On the other hand, if in arid climates the most common minerals derive from the precipitation of Ca^{2+} , Mg^{2+} , Na^+ , K^+ , SO_4^{2-} , Cl^- and HCO_3^- ions, in the studied field site the high content of NO_3^- in the top soil suggests the precipitation even of NO_3^- salts, like potassium nitrate and/or sodium nitrate. The high content of NO_3^- in the top soil may be due both to the capillary rise and to the remnants of fertilization practices. In the first case, the high content of mineral N present in groundwater and transported towards the top soil by the capillary rise, may be due to the mineralization of the abundant organic matter, that produces ammonium in the reducing condition present in this aquifer, which is then nitrified to NO_3^- during the dry periods, which are characterized by the lowering of the water table and by the establishment of oxic conditions even at deeper depth below the ground surface. This process is not likely to occur in arid environment where soils naturally have less organic matter than the ones present in more humid environments (West et al. 2014). In the second and most probable case, remnants of synthetic urea and manure applied to the field site may have been transformed into NO_3^- in the oxic conditions present at the soil surface and not fully used up by plant suffering due to the extreme dry and hot conditions of summer 2012; this leads to the creation of NO_3^- pools which may not be present in arid environment where agricultural practice are usually less intensive.

These findings suggest that processes that are acknowledge to be rather common in arid environments may also play an important role in coastal plains in temperate environments, especially during the summer season when prolonged drought conditions are becoming more and more frequent. For instance, large anomalies concerning the average monthly rainfall, the average minimum and maximum monthly temperatures with respect to the reference climate values of the period 1961-1990, were registered in the Po plain in the summers of 2003, 2006, 2012 and 2015 (<http://www.agenziainterregionalepo.it/dati-idrologici.html>). Concurrently, in the above mentioned years the Po River, from whom surface water is derived by a diffuse canal network and largely used for irrigation (Fabian 2012), experienced severe low-flow during the season of greater water demand. This caused a severe decline in the availability of surface

water resources for irrigation, which induces prolonged stress to the crops and the formation of salt crusts over the agricultural fields ultimately leading to a scares crop yield. These conditions are thought not only to pose threat to the productivity of agricultural fields more and more often in the near future but also to endanger water resources and soil fertility in the long term.

5. CONCLUSIONS

This paper highlights the role of evapoconcentration processes in the formation of salt crusts rich in nitrate over an agricultural field located in the Po Plain. The accumulation of salts on the ground surface is usually neglected in temperate climates but the present study clearly showed that the recurrent drought conditions experienced in the Po Plain in the last decade, might lead to the establishment of an evaporation dominance environment at least during the summer season. The specific results from this study showed that during the dry and hot summer months, salt crusts rich in nitrates accumulate in the top soil with a marked spatial heterogeneity, and with a preferential appearance in the hollows. In the same period cracks appear in the top soil because of the elevated percentage of clay present in these agricultural fields, of the high soil salinity and of use of conventional tillage. With the first rainfall events, pulses of N-rich water derived from the dissolution of the salt crusts, were transported downwards through soil cracks, increasing nutrient leaching towards groundwater and the tile-drains, which may then transfer the N-rich water to surface waters, ultimately leading to surface waters eutrophication. Together with the evapoconcentration of N pools derived by the application of fertilizer (synthetic urea and pig slurry), also the elevated geogenic reactive N pool present in the peaty sediment found in the lower horizon at the experimental site, may have contribute to the high nitrate concentrations registered both in the tile-drains and in the surface water bodies. A quantitative analysis of nitrate concentration found in the main water bodies, also suggested that the processes evocated for the experimental site are widespread even in nearby agricultural land.

Unlike dry areas, where salt accumulation recurrently take place over long periods and over large areas and is thus acknowledged and sometime properly managed, in temperate areas this phenomenon is rather intermittent and its impact has only recently rose interest on evapoconcentration processes and fast percolation in agricultural fields, simply because of the increase in drought events. For these reasons further investigation on the processes governing the formation of salt crusts and the eventual transport of dissolved species towards surface and ground waters, once these salts crusts have been dissolved, is still needed. To face issues deriving from prolonged drought conditions, which will even be intensified by the forecasted climate change, more sustainable agricultural practices have to be taken in consideration, such as: (i) a more accurate time schedule of fertilizer application, with particular reference to the climatic conditions (rainfall and temperature); (ii) the application of frequent irrigations with small quantities immediately after the application of

fertilizers to avoid the widespread formation of salt crusts; and (iii) the development of buffer zones enabling the abatement of excess nitrogen loads.

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