



Field and laboratory study of nitrogen mineralization dynamics in four Tunisian soils

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ABSTRACT

Prediction of nitrogen mineralization from soil organic matter is important when we try to optimize nitrogen fertilization and assess adverse nitrogen impacts on the environment. Thus, four non-fertilized soils were selected in Northern Tunisia to investigate, throughout a field and laboratory approach, the influence of soil properties on nitrogen mineralization and to classify them according to their potentially mineralizable nitrogen and kinetics. Our field results showed an enrichment in inorganic nitrogen contents mainly in surface horizons. These contents decreased with depth following different patterns depending on the soil type. The highest content of inorganic nitrogen was recorded in the Calcisol ($232.09 \text{ mg kg}^{-1}$) due to high organic carbon and nitrogen amounts and low C:N ratio throughout the profile. The lowest content was recorded in the Luvisol ($< 30 \text{ mg kg}^{-1}$) because of its large clay-silt fraction and low pH level (4.8 ± 0.1) especially in depth. The vertical distribution of ammonium and nitrate contents showed marked monthly variations. During January and February, the decrease in inorganic nitrogen contents was attributed to lower soil temperature and higher moisture causing the nitrate to be more leached. In March, inorganic nitrogen contents reached their maximum in surface horizons. These contents started to decrease in April and regressed in May and June except for the Vertisol, which still recorded high-inorganic nitrogen content. The laboratory results presented the following decreasing order of potentially mineralizable nitrogen and kinetics: Calcisol > Vertisol > Cambisol > Luvisol, and revealed two fractions constituting organic nitrogen supplies. An active fraction with a rapid mineralization and a passive fraction slowed down by clays and resistant to biodegradation.

1. Introduction

Nitrogen (N) is an important element for plant growth. A deficiency in this element most often results in reducing crop production especially in arid and semi-arid regions (St Luce et al., 2011). These areas are already poor in N because of their soils' low Organic Matter (OM) content. The depletion of soil N and thus insufficient N availability can reduce soil fertility and land productivity in such zones (García-Gil et al., 2000; Batlle-Bayer et al., 2010). In order to solve this deficit, inorganic N fertilizers should be supplemented particularly in cultivated crops (Schröder, 2014).

Currently, N deficiency has been widely reported in arid and semi-arid regions and considerable efforts have been made to develop alternative or complementary cost-effective practices for N fertilization (e.g., N fixed by legumes, N in irrigation water and mineralization of crop residue, manure, compost) (Goulding et al., 2008). Indeed, the costs of commercial inorganic N fertilizers are prohibitory and beyond

the reach of many limited resource farmers. Moreover, N is one of the most difficult nutrients to manage in agriculture. This difficulty results from challenges in assessing its amount required by the plant and in synchronizing its availability to meet a specific crop demand (Kpombekou-A and Genus, 2012).

Recently, several adverse environmental effects related to N have been traced back to poor manure management practices and inappropriate inorganic fertilizer applications (St Luce et al., 2011). Agronomists, for instance, use greater amounts of inorganic N fertilizer than required. They have a great difficulty in predicting and quantifying N fertilizer needs. They usually apply manure at uniform rates during growing and fallow up periods. Moreover, the underestimation of inorganic N released from soil OM mineralization results in the application of excess N fertilizer, leading to the potential for environmental contamination due to leaching as well as surface runoff losses. This results in high levels of nitrate in ground and surface waters (Mulvaney et al., 2001). Furthermore, N gases might also be generated

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due to an excess of N fertilizer would be emitted into the atmosphere contributing to global warming. These occurrences may eventually have detrimental effects on terrestrial and aquatic life (Schröder, 2014).

In arid and semi-arid regions, very little knowledge has been acquired about N mineralization dynamic as well as its availability. In Tunisia, for instance, few laboratory studies were carried out on soils sampled from surface horizon of alluvial plain and amended with different organic residues (manure, composts ...) (Jedidi et al., 1994, 2004; Saidi et al., 2015). These studies investigated the effects of different amendments on mineralization of N in the soil and on its chemical and microbial biomass properties. Other works from other regions reported differences in N transformations when the same manure was incorporated into samples selected from topsoil of some south-eastern states of USA (Sistani et al., 2008; Kpomblekou-A and Genus, 2012). Some of the observed differences might be attributed to the soil ability to adsorb ON, increased aeration in sandier soil and different C:N ratios. Indeed, in the case of soil with low C:N ratio and high N content, the decomposition results in inorganic N release depending on soil type and various environmental factors (quantity and quality of soil OM, soil temperature and water content, drying and rewetting events ...). Nevertheless, in a soil with a high C:N ratio and low N content, microorganisms can use soil inorganic N forms to satisfy their N need. This type of N transformation is called microbial immobilization decreasing the soil inorganic N pool, as well as plant N availability (Hofman and Van Cleemput, 2004). Moreover, high salinity level in soils has been proven to have adverse effects on the microbial activities (toxic ion effects) and therefore N mineralization (Lodhi et al., 2009). Although these research investigations were important to gain full understanding of the N mineralization dynamics, they were conducted under laboratory conditions, which generally leads to an over-estimation of the N mineralization processes in real field conditions. In addition, the majority of these laboratory studies considered the mineralization of N in only the soil surface horizons. To our knowledge, soil ON mineralization was rarely approached through a full field methodology particularly focusing on inorganic N distribution according to depth. Such a resource is still unattainable and the way to extrapolate soil N availability from field data is urgently needed especially in arid and semi-arid regions. Information on the relative N rate being released, adsorbed, and potentially leached is an absolute necessity as it may be of great help in making the best choice of management practices increasing the N use efficiency and restricting N losses in the environment.

In this context, the present study aims to better investigate, throughout a fieldwork in a semi-arid zone, the influence of pedo-climate conditions (soil temperature, soil moisture) and some soil properties on N mineralization dynamics in four non-fertilized Tunisian soils. The other goal is to propose through a laboratory incubation approach, a classification according to the potentially mineralizable N and kinetics of the different studied soils.

2. Materials and methods

2.1. Soil sampling and physicochemical analysis

For this study, we selected four non-fertilized soils developed under contrasted pedogenetic conditions in North Tunisia (Fig. 1). The chosen soils are the most representative of the soil order and the climate zone they come from. Moreover, they are undisturbed soils, which show a pedological interest, mainly on the morphological and analytical level of organic matter. Indeed, we collected a Luvisol (0–230 cm depth, 36°49'30" N and 8°41'58" E, 731 m elevation) in the Ain Draham forest area characterized by A₀A₁ (0–20 cm) dark surface horizon overlying a light-coloured E-leached layer (20–60 cm). The B_t clay-rich horizon is in a varying depth of 60–130 cm and a consolidated C-horizon from 130 to 230 cm. In addition, we collected a Vertisol and a Cambisol (Oued Zarga region) both from Béja Governorate. It is a narrow agricultural

zone with a significant bioclimatic variability. The Vertisol (0–122 cm depth, 36°51'17" N and 9°12'40" E, 314 m elevation) and the Cambisol (0–326 cm depth, 36°41'27" N and 9°22'31" E, 139 m elevation) were both cultivated (cereal crops) and selected in field plots that had not received any previous N fertilization. The Vertisol of Béja region is a heavy clay soil characterized by large and deep cracks. It has a sub-angular blocky A_p-surface horizon (0–30 cm) covering the (B)-horizon (30–54 cm) with a prismatic structure and the consolidated C_{ca} calcareous horizon (54–122 cm). The Cambisol has an A_p-surface horizon (0–26 cm) overlying a B_t clayey horizon (26–102 cm) with higher oxide contents and B_{ca} and C_{ca} deep calcareous horizon (accumulation of secondary carbonates). Finally, we sampled a Calcisol (0–115 cm depth, 36°10'47" N and 8°42'56" E, 700 m elevation) in the Kef forest area situated in the North West of Tunisia. This soil is characterized by a dark-coloured A₀A₁ (0–20 cm) and (B) (20–45 cm) surface layers with a high OM content and a well-developed granular structure above a light calcareous C_{ca}-horizon (45–115 cm). The main bioclimatic characteristics of the studied sites are detailed in Dridi and Arfaoui (2017).

For all sites, we dug three pits for each soil type (field replicates) taken relatively near each other. Thus, three samples (one sample from each horizon of the three digged soil profile) were gathered from each horizon of the four studied soils in January 2015 (14 horizons of the four studied soils were considered; see Table 1 below). Moreover, to give a precise idea about the characteristics of the studied soils, we collected the samples in Mars and June 2015. The values of the physicochemical soil properties were nearly the same for the three sampling dates. Then, 42 samples (3 samples from each horizon of the studied soil × 14 horizons) were air dried and sieved through a 2 mm stainless sieve and stored in sealed containers at 4 °C. Later, the soil samples were analyzed for the main physicochemical soil properties according to international standards. We measured the soil pH level (ISO 10390) and the electrical conductivity (EC) (ISO 11265) in the soil aqueous extract (1:5 soil: water ratio). We determined the soil texture using the Robinson pipette method after oxidation of the OM with H₂O₂ and clay dispersion by hexametaphosphate solution (NF X31-107). We also characterized the soils samples for Total Calcium Carbonate (TCaCO₃) content using the volumetric method (NF ISO 10693). We determined the Organic Nitrogen (ON) by the modified Kjeldahl method (NF ISO 11261) and we measured the Total Organic Carbon (TOC) by the sulfochromic oxidation method (ISO 14235). The extraction of inorganic N forms as ammonium (NH₄-N) and nitrate (NO₃-N) was achieved with KCl (1 M) according to ISO standards (ISO/TS 14256-1). The assay was performed by distillation with MgO for ammonium N and Dewarda reagent for nitrate N. N released during distillation was trapped in 2% boric acid and estimated by titration with a solution of H₂SO₄ (0.01 N). We performed three analytical replications for each analysis.

2.2. The experimental protocol

The follow-up of the monthly variation of NH₄-N and NO₃-N contents, the soil temperature and moisture in the studied soils was the object of an experimental study achieved during January–June 2015 period. A specific soil thermometer was used to measure, once a month, the soil different horizons temperature in situ. As for soil moisture (NF ISO 11465) and inorganic N forms (NH₄-N and NO₃-N), they were measured from 42 samples taken monthly from each horizon of the same (12) digged soil-pits (3 soil-pits for each soil type).

In the laboratory, we followed under controlled conditions, the evolution of NH₄-N and NO₃-N contents according to the incubation time. The laboratory experiment focused just on the upper soil layer of the four studied soils. The samples were air dried for a one-week period and sieved through a 2 mm sieve removing all impurities like roots and large pieces of crop residues. 50 g of each sample were placed in 200 ml flasks. Then, 72 containers (triplicate soil samples of each studied soil (4 soils) × 6 weeks) were pre-incubated for 1 week at 1/2 of field

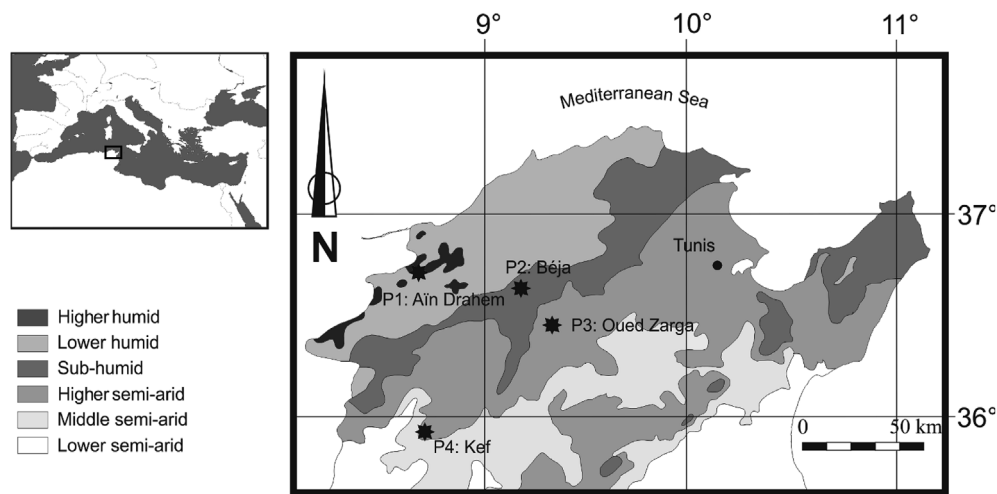


Fig. 1. Localization of the studied soils according to bioclimatic zones (P1: Luvisol (Aïn Drahem), P2: Vertisol (Béja), P3: Cambisol (Oued Zarga), P4: Calcisol (Kef)).

capacity (with distilled water) and at the ambient laboratory temperature (22 °C) to reactivate the microbes. Finally, the containers were restored to an equivalent soil moisture at 2/3 of field capacity and kept in an incubator at 28 °C for six weeks. We measured $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ contents every incubation week. We destroyed three samples for each studied soil per week. After each extraction, humidity was adjusted once again.

2.3. N mineralization kinetics

Reaction kinetics for mineralization of soil organic N was determined by statistical analysis using the formula given in equation (1), which allows approaching the size of labile and resistant soil OM compartments (Saidi et al., 2015).

$$N_t = N_0 (1 - e^{-kt}) \quad (1)$$

Where:

N_t is the content of cumulative N mineralized in time t expressed in mg kg^{-1} ;

N_0 is the potentially mineralizable N expressed in mg kg^{-1} ;

k is the mineralization constant expressed per week $^{-1}$;

t is time of incubation expressed in week.

2.4. Statistical analysis

Data from field and laboratory experiments were subjected to analysis of variance by the SPSS statistical program (version 20). Pearson's correlation analysis was used to test relationships between N mineralization parameters (N_0 , k , $N_0 \times k$) and properties of the studied soils (pH, EC, sand, silt, clay, TCaCO_3 , TOC, ON and C:N). Soil samples were gathered in 2015 for physicochemical analyses and laboratory experiments. The average of three values (sampling replicates) of each parameters were used for the correlation matrix.

3. Results

3.1. Physicochemical properties of the studied soils

The main physicochemical properties of the studied soils are reported in Table 1. All results are the average of three determinations of field sampling replicates. An important variability among soils and horizons is shown by the data. For example, large differences in soil OM content were recorded as illustrated by TOC and ON contents that ranged, respectively, between 0.17% in the Cambisol (Oued Zarga) and 3.71% in the Calcisol (Kef) and between 0.24‰ in the Vertisol (Béja) and 3.4‰ in the Calcisol (Kef). The various studied soils exhibited

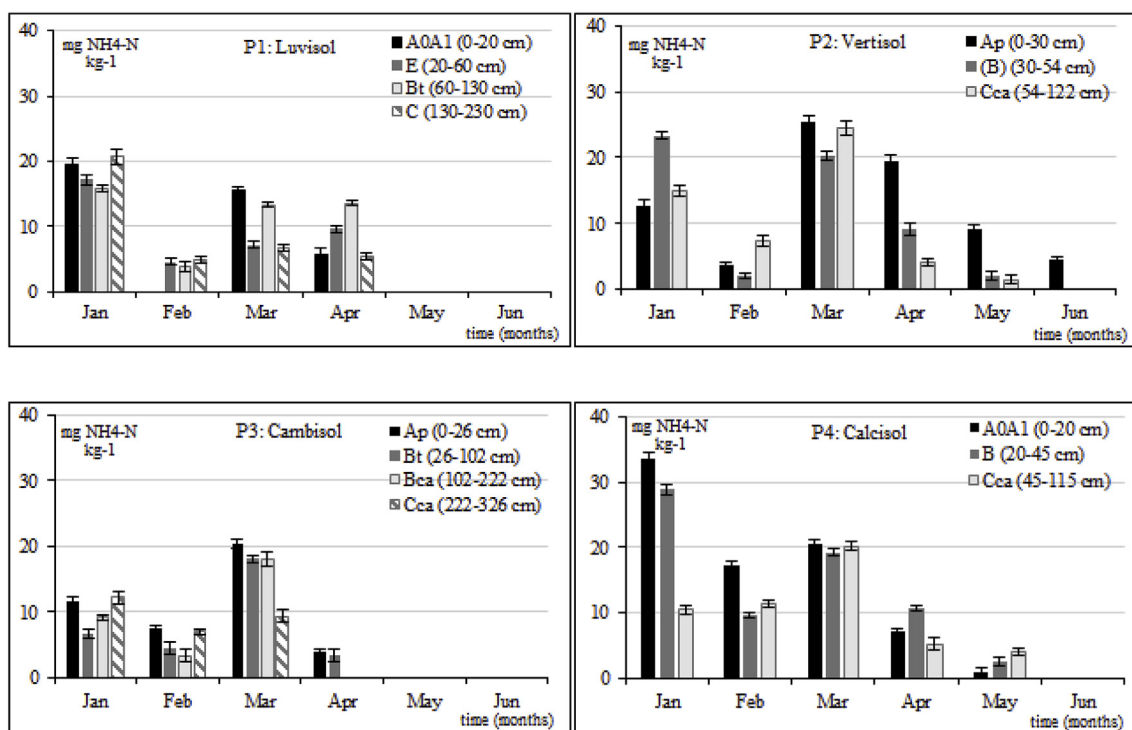
Table 1

Selected physicochemical properties of the four studied soils (values shown are means \pm standard deviation, $n = 3$ sampling replicates).

Soil	Depth (cm)	Horizons	pH	EC (dS.m^{-1})	Sand %	Silt %	Clay %	TCaCO_3 %	ON ‰	TOC %	C:N
P1: Luvisol (Aïn Drahem)	0–20	A_0A_1	6.1 ± 0.1	0.2 ± 0.1	62.00 ± 1.4	17.03 ± 0.2	21.02 ± 1.2	1.0 ± 0.0	1.68 ± 0.0	2.43 ± 0.0	14.46 ± 0.1
	20–60	E	6.7 ± 0.2	0.1 ± 0.0	61.00 ± 1.5	21.01 ± 0.4	18.00 ± 0.1	6.5 ± 0.3	0.95 ± 0.1	1.00 ± 0.0	10.61 ± 1.2
	60–130	B_t	4.8 ± 0.1	0.1 ± 0.0	21.00 ± 1.0	11.03 ± 0.1	68.00 ± 2.4	1.0 ± 0.1	1.14 ± 0.0	0.69 ± 0.0	6.06 ± 0.2
	130–230	C	5.1 ± 0.4	0.1 ± 0.0	63.67 ± 1.3	2.77 ± 0.0	33.58 ± 1.4	3.2 ± 0.1	0.68 ± 0.1	0.41 ± 0.0	6.09 ± 0.7
P2: Vertisol (Béja)	0–30	A_p	8.3 ± 0.3	0.3 ± 0.1	26.95 ± 1.2	42.97 ± 0.1	30.09 ± 0.6	30.5 ± 0.8	2.14 ± 0.1	2.58 ± 0.0	12.07 ± 0.5
	30–54	(B)	8.2 ± 0.1	0.3 ± 0.1	28.01 ± 1.1	49.00 ± 0.7	23.00 ± 0.3	28.2 ± 0.0	1.84 ± 0.1	1.52 ± 0.0	8.27 ± 0.2
	54–122	C_{ca}	8.1 ± 0.2	0.9 ± 0.2	27.00 ± 1.0	53.00 ± 0.2	20.00 ± 0.5	77.6 ± 1.5	0.36 ± 0.0	0.24 ± 0.0	6.65 ± 0.3
P3: Cambisol (Oued Zarga)	0–26	A_p	7.9 ± 0.1	0.2 ± 0.1	46.01 ± 1.3	37.06 ± 0.2	17.00 ± 0.2	2.3 ± 0.1	1.49 ± 0.1	1.43 ± 0.0	9.62 ± 0.4
	26–102	B_t	7.8 ± 0.1	0.1 ± 0.1	18.00 ± 1.3	22.00 ± 0.0	60.03 ± 3.1	0.0 ± 0.0	1.18 ± 0.0	0.50 ± 0.0	4.24 ± 0.1
	102–222	B_{ca}	8.2 ± 0.0	0.2 ± 0.0	42.00 ± 1.0	34.00 ± 0.4	24.03 ± 0.8	36.4 ± 0.4	0.54 ± 0.0	0.17 ± 0.0	3.15 ± 0.1
	222–326	C_{ca}	7.9 ± 0.2	1.3 ± 0.2	41.81 ± 1.1	33.57 ± 0.5	24.62 ± 1.1	51.7 ± 0.7	0.39 ± 0.0	0.19 ± 0.0	4.88 ± 0.4
P4: Calcisol (Kef)	0–20	A_0A_1	7.9 ± 0.1	0.3 ± 0.0	18.17 ± 1.0	45.27 ± 0.1	36.60 ± 0.1	7.0 ± 0.1	3.40 ± 0.4	3.71 ± 0.1	11.03 ± 1.5
	20–45	(B)	8.2 ± 0.2	0.2 ± 0.1	20.30 ± 1.4	35.59 ± 0.1	44.13 ± 1.5	8.1 ± 0.1	2.80 ± 0.2	3.30 ± 0.3	11.77 ± 0.2
	45–115	C_{ca}	8.4 ± 0.0	0.3 ± 0.0	25.82 ± 1.2	34.80 ± 0.1	39.40 ± 0.8	22.0 ± 0.5	2.40 ± 0.1	2.50 ± 0.1	10.42 ± 0.0

EC: Electrical Conductivity, TCaCO_3 : Total calcium carbonate content, ON: Organic Nitrogen content, TOC: Total Organic Carbon content.

(a)



(b)

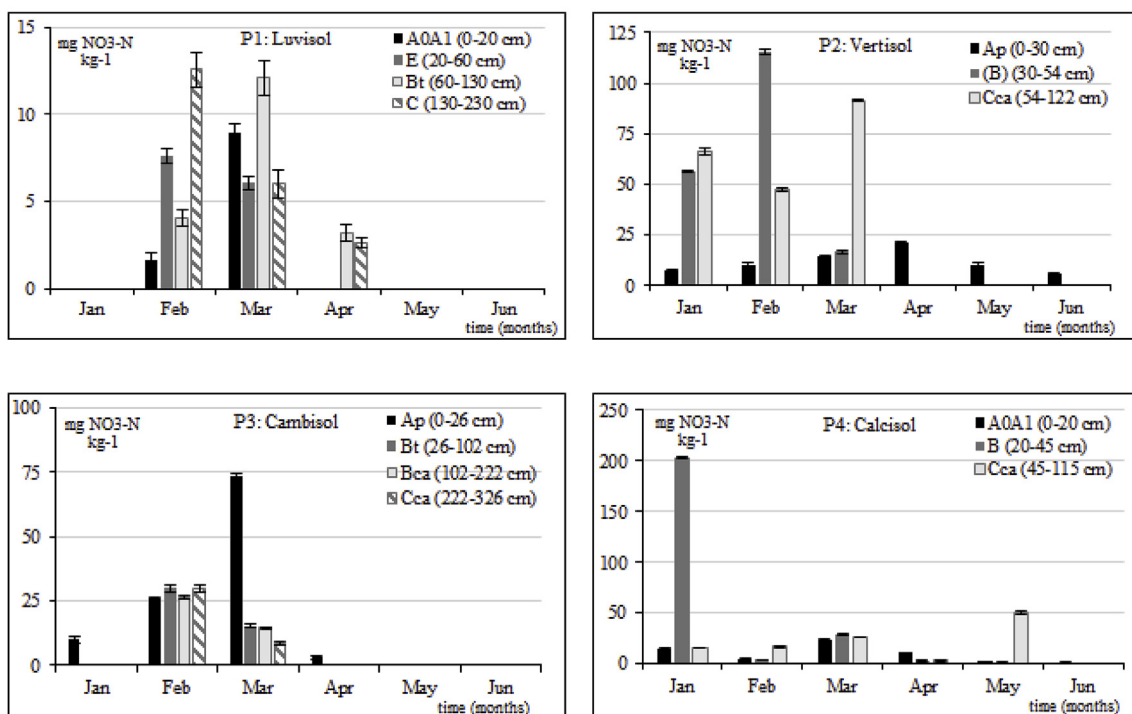


Fig. 2. Monthly variation of (a) ammonium ($\text{NH}_4\text{-N}$) and (b) nitrate ($\text{NO}_3\text{-N}$) N contents in the different soil horizons of the studied soils: P1: Luvisol (Ain Draham), P2: Vertisol (Béja), P3: Cambisol (Oued Zarga), P4: Calcisol (Kef). Bars indicate \pm standard deviation, $n = 3$ sampling replicates.

comparable discontinuities between surface and deep horizons. This is obvious in the OM vertical profile characterized by a TOC and ON contents decrease with the increase of soil depth. Similar to OM distribution, the highest C:N ratio values were recorded in surface horizons

and decreased with depth in the majority of the studied cases. The pH values were around eight in most of the studied soils except for Luvisol, which recorded an acid pH level. The soil texture was dominated by silt and clay content ($> 60\%$) throughout the profile. These size fractions

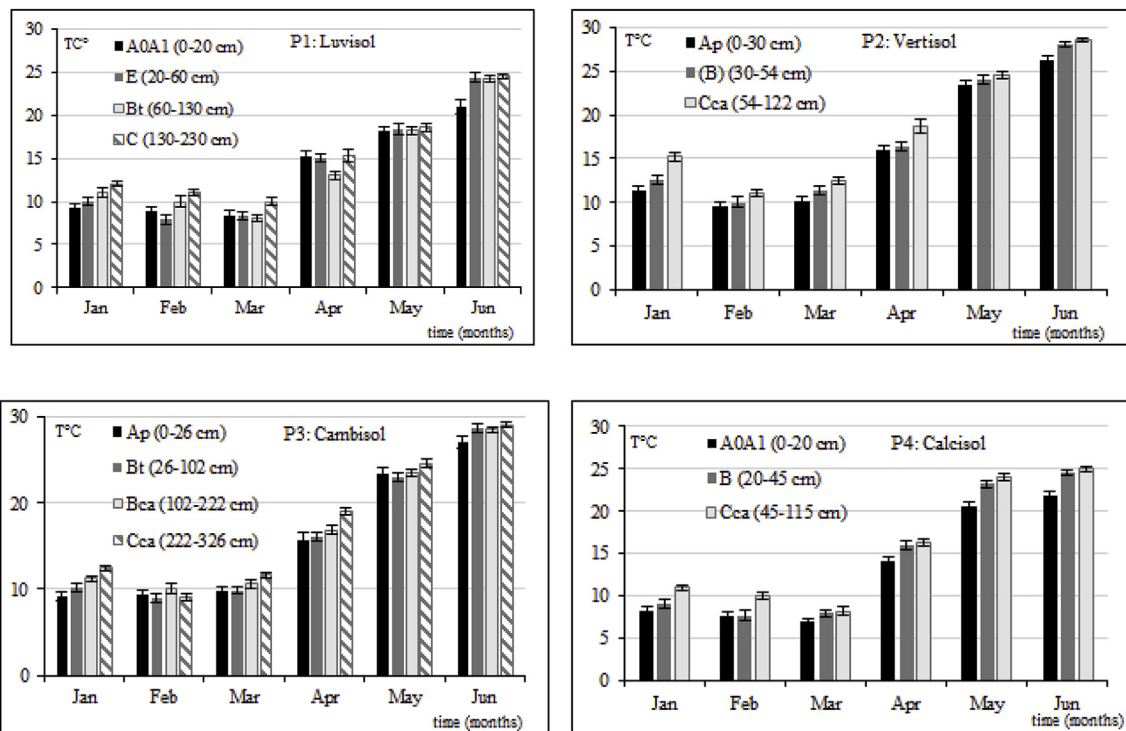


Fig. 3. Monthly variation of temperature ($T^{\circ}\text{C}$) in the different soil horizons of the studied soils: P1: Luvisol (Aïn Draham), P2: Vertisol (Béja), P3: Cambisol (Oued Zarga), P4: Calcisol (Kef). Bars indicate \pm standard deviation, $n = 3$ sampling replicates.

showed the highest quantities in almost all the studied soils except for the Luvisol, which recorded a large amount of sand fraction (62%) especially in surface horizons. The electrical conductivity (EC) values were very low and increased as we moved from the surface horizons to the deep horizons for most of the studied soils.

3.2. Field study of N mineralization

Details of $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ monthly production, soil temperature and soil moisture according to depth are presented respectively in Figs. 2–4. Inorganic N distribution differs from one horizon to another in the four studied soils. In general, the highest $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ contents were recorded in surface horizons and decreased with depth following different patterns depending on the soil type (Fig. 2). Indeed, the highest inorganic N contents were recorded in (B)-horizon of the Calcisol (Kef region) with values that reached $203.25 \text{ mg kg}^{-1}$ for $\text{NO}_3\text{-N}$ and 28.84 mg kg^{-1} for $\text{NH}_4\text{-N}$. The lowest inorganic N contents were recorded in the Luvisol (Aïn Draham region). These values remained $< 20 \text{ mg kg}^{-1}$ throughout the profile for $\text{NH}_4\text{-N}$. However, the $\text{NO}_3\text{-N}$ values were negligible during the whole experimental period (Fig. 2). Similarly, the low inorganic N contents are noted in the Cambisol (Oued Zarga region). The $\text{NH}_4\text{-N}$ had nearly the same behavior observed in the case of the Luvisol but the $\text{NO}_3\text{-N}$ showed low contents mainly in deep horizons (Fig. 2). The curves of Fig. 2 show noticeable monthly variations in N mineralization. In January, $\text{NH}_4\text{-N}$ contents were low and did not exceed 34 mg kg^{-1} with no tendency to accumulate in surface horizons. Their distribution was relatively homogeneous in the four studied soils. These low $\text{NH}_4\text{-N}$ contents remained higher than $\text{NO}_3\text{-N}$ contents. During this month, soil temperature profiles also showed low values (Fig. 3). Nevertheless, soil moisture profiles reached high values for all the studied soils except for the E-horizon of the Luvisol, which recorded only 5% (Fig. 4). Indeed, this eluvial horizon showed more than 60% of sand fraction. In the case of the Calcisol and the Vertisol situated separately in the Kef and Béja regions, $\text{NO}_3\text{-N}$ tends to migrate in depth. They recorded $203.25 \text{ mg kg}^{-1}$ and 66.19 mg kg^{-1} , respectively, especially in deep

layers. The (B)-deep horizon of the Vertisol also recorded high $\text{NO}_3\text{-N}$ contents (115 mg kg^{-1}) in February. It was a period of N leaching caused by rainfall events ($81.4\text{--}139 \text{ mm}$ of rain in the Béja area and $64.8\text{--}74.2 \text{ mm}$ in the Kef area during January and February months) and probably by the macro-pore flow, characteristic for cracks in the case of the Vertisol. Higher $\text{NO}_3\text{-N}$ availability in these soils was most likely lacking, unless it was synchronized with plant uptake as it can easily be leached. In February, $\text{NO}_3\text{-N}$ contents increased in almost all horizons of the studied soils (Fig. 2). Later in March, when soil temperatures rose and humidity decreased (Figs. 3 and 4), the $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ values reached their maximum (Fig. 2). The contents of $\text{NO}_3\text{-N}$ mainly increased in the upper layers to ensure plant growth. In April, the $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ contents started to decrease gradually in most of the studied soils. These contents remained relevant especially in the surface horizons of the Vertisol, which recorded 40.28 mg kg^{-1} . In May and June, we noted a regression of $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ contents in the Luvisol, the Cambisol and the Calcisol (Fig. 2). These soils maintained low values during the dry season. However, the Vertisol recorded relatively high-inorganic N contents ($\approx 20 \text{ mg kg}^{-1}$) during this warm period.

3.3. Laboratory study of N mineralization

Fig. 5 shows laboratory results of $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ contents released over the incubation time of each studied soil (only surface horizons were considered). Similar to the field study results, the highest inorganic N contents were recorded in the Calcisol. These contents slightly decreased over time, but remained important mainly for $\text{NO}_3\text{-N}$ even at the end of incubation. Indeed, the Calcisol showed a maximum of $255.27 \text{ mg kg}^{-1}$ of $\text{NO}_3\text{-N}$ content in the first week compared to $218.66 \text{ mg kg}^{-1}$ at the end of incubation. However, the $\text{NH}_4\text{-N}$ content was low and varied from 13.76 mg kg^{-1} to 2.14 mg kg^{-1} . Expressed as the initially present Organic Nitrogen (ON), the total inorganic N contents ($\text{NH}_4\text{-N} + \text{NO}_3\text{-N}$) released during the incubation period, represented 43.76%. Likewise, the lowest inorganic N contents were recorded in the Luvisol. These small contents did not exceed 17 mg kg^{-1}

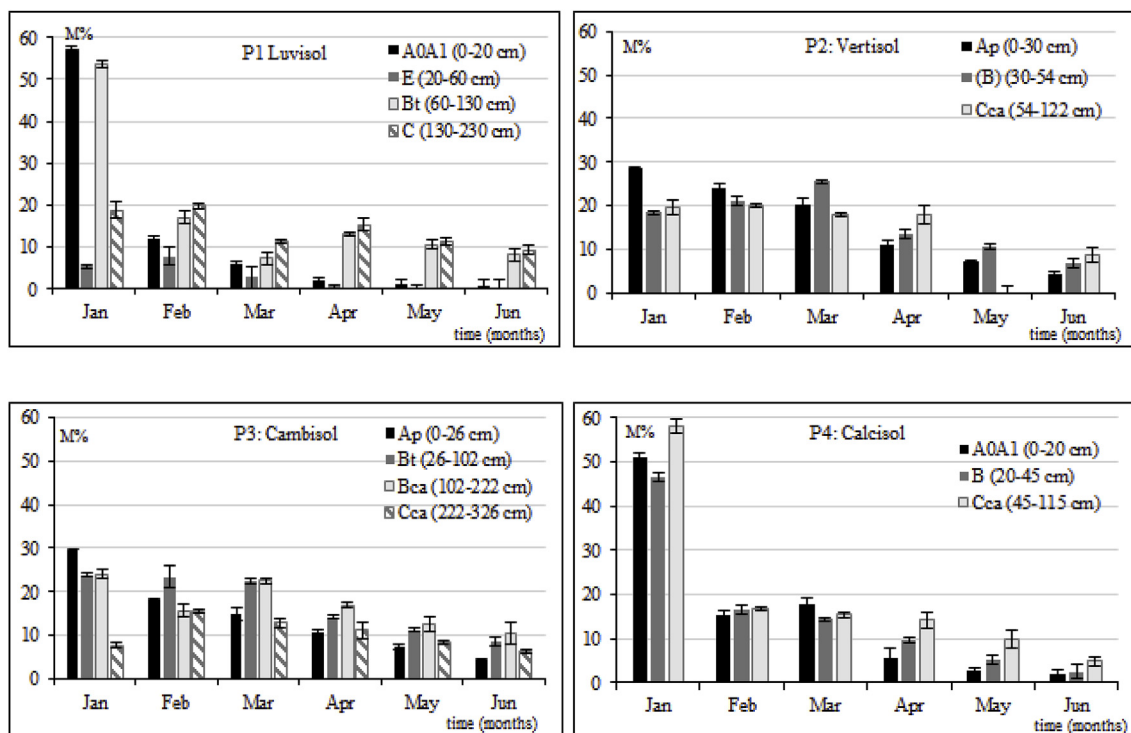


Fig. 4. Monthly variation of moisture (M %) in the different soil horizons of the studied soils: P1: Luvisol (Ain Draham), P2: Vertisol (Béja), P3: Cambisol (Oued Zarga), P4: Calsisol (Kef). Bars indicate \pm standard deviation, $n = 3$ sampling replicates.

for $\text{NH}_4\text{-N}$ and 9 mg kg^{-1} for $\text{NO}_3\text{-N}$. In this soil, the total inorganic N contents produced during the incubation period, represented only 5.47% of ON. The Vertisol and the Cambisol revealed relatively low inorganic N contents during the incubation period. These contents rarely exceeded 17 mg kg^{-1} for $\text{NH}_4\text{-N}$ and 22 mg kg^{-1} for $\text{NO}_3\text{-N}$.

They represented 7.30% and 9.60% of ON, respectively. In the case of these two soils, the N mineralization gradually decreased from the fourth week of incubation. Indeed, the Vertisol recorded 6.49 mg kg^{-1} of $\text{NH}_4\text{-N}$ and 22.45 mg kg^{-1} of $\text{NO}_3\text{-N}$ and the Cambisol displayed 9.89 mg kg^{-1} of $\text{NH}_4\text{-N}$ and 9.50 mg kg^{-1} of $\text{NO}_3\text{-N}$. These contents

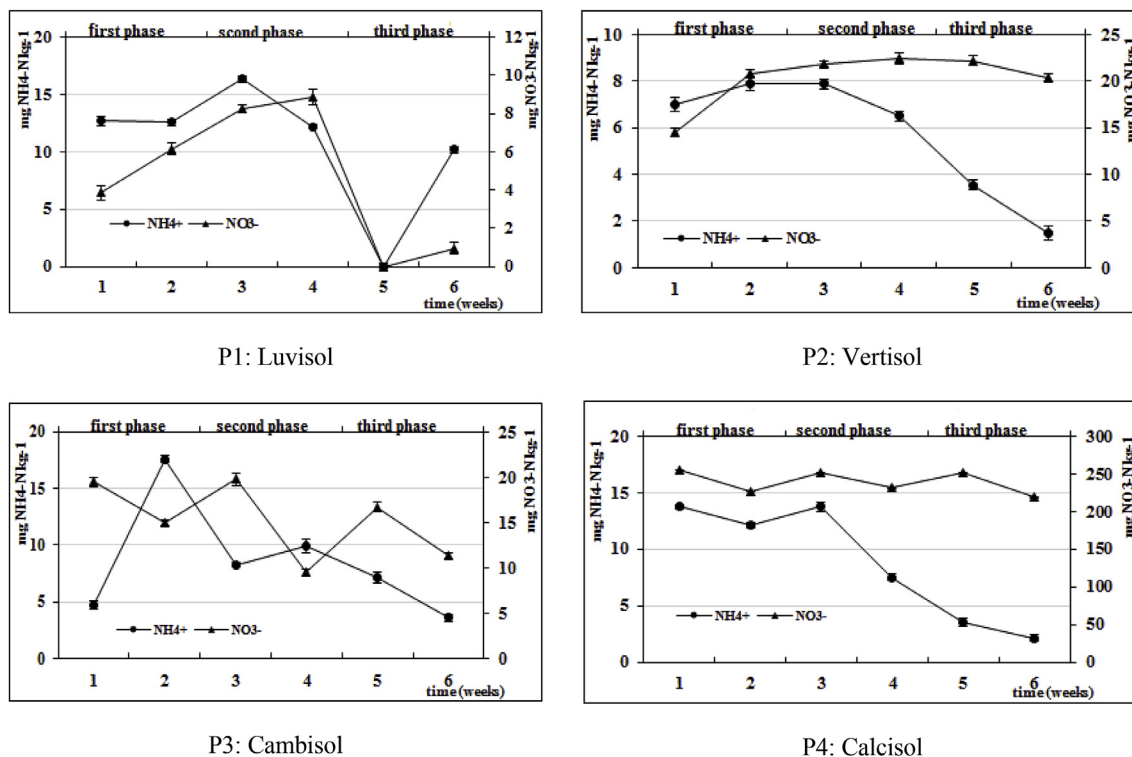


Fig. 5. Variation of ammonium ($\text{NH}_4\text{-N}$) and nitrate ($\text{NO}_3\text{-N}$) N contents as function of incubation time (weeks) of each studied soil: P1: Luvisol (Ain Draham), P2: Vertisol (Béja), P3: Cambisol (Oued Zarga), P4: Calsisol (Kef). Bars indicate \pm standard deviation, $n = 3$ sampling replicates.

Table 2

Parameters of N mineralization kinetics ($No \times k$), potentially mineralizable N (No) and constant rate (k).

	No	k	No \times k
P1: Luvisol	128.6 \pm 1.2	0.34	44.2
P2: Vertisol	286.3 \pm 2.9	0.19	55.5
P3: Cambisol	214.3 \pm 3.4	0.32	69.0
P4: Calcisol	468.5 \pm 2.8	0.21	99.3

No: Potentially mineralizable N in mg kg^{-1} .

k: mineralization constant rate expressed per week^{-1} .

No \times k: N mineralization kinetic expressed in $\text{mg kg}^{-1} \text{ week}^{-1}$.

slightly decreased at the end of the incubation (fifth and sixth week). However, the N mineralization was canceled during the fifth week in the case of the Luvisol. It was rather a period of N immobilization. The N mineralization was then restarted with 10.18 mg kg^{-1} and 0.96 mg kg^{-1} of $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ contents, respectively. In general, the inorganic N content was dominated by nitrate form during almost any incubation time in most of the studied soils.

The curves of Fig. 5 show three phases for each studied soil. A first phase of intense activity (a rapid or fast mineralization) was observed mainly during the first ten days of incubation. The second phase (a slowdown) was characterized by a decrease in inorganic N contents. This is due to the reduction in the easily metabolized substances present in the soil (Jedidi et al., 1994). It was also a phase of the inorganic N organization during the first four weeks of incubation. The third phase (a stabilization phase) was characterized by relatively slow degradation kinetics and corresponded to the mineralization of non-labile soil OM.

The estimated parameters (potentially mineralizable N and kinetics) of the exponential negative equation of the first order and the coefficients of determination of the four studied soils were summarized in Table 2. The results show a wide dispersion of values concerning the potentially mineralizable N (No) expressed as mg kg^{-1} dry soil after 6 weeks of incubation. No varied from 468.5 mg kg^{-1} to 128.6 mg kg^{-1} . They present the following decreasing order: Calcisol > Vertisol > Cambisol > Luvisol. However, the mineralization constant (k), expressed in week^{-1} , did not present the same order. It had the following descending order: Luvisol > Cambisol > Calcisol > Vertisol. Moreover, the calculation of the product $No \times k$ expressed in $\text{mg kg}^{-1} \text{ week}^{-1}$ allowed us to predict N mineralization kinetics, which had the following descending order: Calcisol > Cambisol > Vertisol > Luvisol. The Calcisol had the highest No (468.5 mg kg^{-1}) and N mineralization kinetic ($99.3 \text{ mg kg}^{-1} \text{ week}^{-1}$) whereas the Luvisol had the lowest No (128.6 mg kg^{-1}) and N mineralization kinetic ($44.2 \text{ mg kg}^{-1} \text{ week}^{-1}$) with N mineralization constant $k = 0.34 \text{ week}^{-1}$.

Pearson's correlation analysis was used to find out possible relationships between N mineralization parameters (No, k, $No \times k$) and properties (pH, EC, sand, silt, clay, TCaCO_3 , TOC, ON and C:N) of surface horizons of the four studied soils. Correlation ($r^2 = 0.94$, $p < 0.05$) and regression ($R^2 = 0.88$, $p < 0.05$) results revealed a positive relationship between the potentially mineralizable N (No) and ON contents. However, we obtained a negative correlation between N mineralization constant (k) and (1) clay ($r^2 = -0.87$, $p < 0.05$), ($R^2 = 0.76$, $p < 0.05$), (2) TCaCO_3 contents ($r^2 = -0.78$, $p < 0.05$) ($R^2 = 0.61$, $p < 0.05$) (See Fig. 6 of regression lines).

4. Discussion

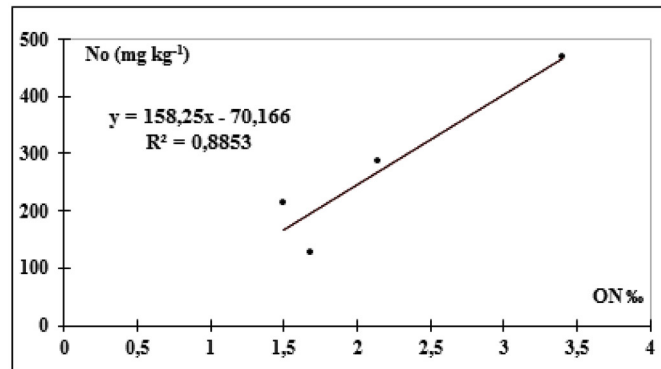
Field and laboratory results showed that the highest values of total inorganic N contents ($\text{NH}_4\text{-N} + \text{NO}_3\text{-N}$) was recorded in the Calcisol (Kef region). This soil exhibited the greatest amount of TOC (3.71%) and ON (3.40‰) mainly in surface horizons. The C:N ratio recorded low values (≈ 10) throughout the profile. The lowest inorganic N contents were noted in the Luvisol. The C:N ratio was high (14.46) in surface horizons and slightly decreased according to the depth (6.02).

The main cause of these low inorganic N contents is certainly the depletion of OM content especially in the deep layers (0.41% of TOC and 0.68‰ of ON). Our results are consistent with those obtained by Duguet et al. (2006) who noted an increase in N mineralization with TOC and ON enrichment of the soil. Furthermore, correlation ($r^2 = 0.94$, $p < 0.05$) and regression (Fig. 6 a) ($R^2 = 0.88$, $p < 0.05$) analysis showed that the potentially mineralizable N (No) has positive relationship with ON contents. This result clearly indicate that ON is an important soil component affecting N mineralization in soil. Nevertheless, the A_0A_1 -surface horizon of the Luvisol had a sandy soil texture ($= 62\%$), which normally provides favorable conditions for microbial activities and mineralization processes (greater aeration, large pore spaces facilitating the microbial attack) (Honeycutt et al., 2005a; Sistani et al., 2008). Moreover, this horizon recorded relatively great TOC (2.43%) and ON (1.68‰) contents but high C:N (14.46). Indeed, in addition to TOC and ON contents, the C:N ratio is extensively used to better predict N mineralization in soil (Hofman and Van Cleemput, 2004). In fact, in the case of the Luvisol (Aïn Draham region), which has high C:N ratio (14.46) and low N contents, micro-organisms were most likely using the soil inorganic N to satisfy their N need resulting in the N immobilization. This may decrease the soil inorganic N pool, as well as the plant N availability. However, in the case of the Calcisol (Kef region) with a low C:N ratio and an OM content rich in N, the decomposition results in a great inorganic N release. In addition, the input of N in the Luvisol is provided by fresh plant debris, which recorded a high C:N ratio suggesting the presence of less decomposed OM mainly in surface layers. The Luvisol is, in fact, characterized by the presence of a litter horizon since it was developed under forest vegetation (*Quercus ilex* and *Quercus suber*) of the Aïn Draham area. Moreover, the excessive soil acidity checked especially in depth ($\text{pH} = 4.8$) (Table 1) contributes to the prevention of the OM degradation. Indeed, the soil acidity is among the main factors that negatively affect the OM mineralization (Amlinger et al., 2003).

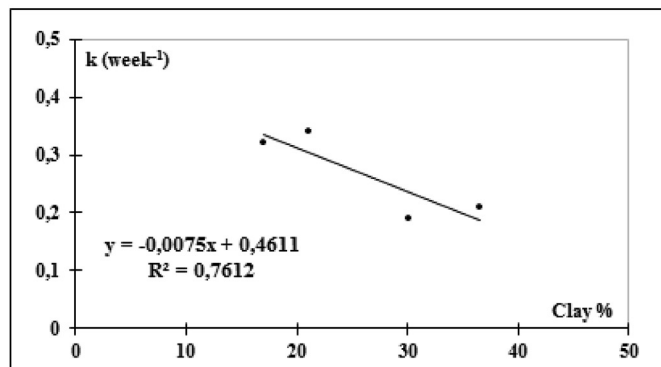
The optimum pH for soil biomass growth is usually between 7 and 8. The N mineralization is limited and nitrification is inhibited at low pH levels (Amlinger et al., 2003).

The fine soil texture affected the low inorganic N contents noted in field and laboratory experiments in most of the studied soils. Indeed, the clay-silt fraction was about 40% throughout the profile of the Luvisol and > 70% in B_t deep horizon (Table 1). It remained higher than 55% throughout the profile of the Cambisol and 70% of the Vertisol (Table 1). Moreover, correlation ($r^2 = -0.87$, $p < 0.05$) and regression (Fig. 6 b) ($R^2 = 0.76$, $p < 0.05$) analysis revealed a negative relationship between N mineralization constant (k) and clay contents in the four studied soils. These results were in line with those achieved by Sistani et al. (2008) who have shown an N mineralization decrease in a soil characterized by an increase in clay and silt contents. In effect, the ammonium was bound by the clay minerals thus preventing its oxidation to nitrate. The authors have also revealed that the organic material was bound by clay-silt particles, thereby protected from microbial degradation. Nevertheless, the high percentage of clay-silt fractions ($\approx 80\%$) recorded in the Calcisol did not prevent the N mineralization. It was probably the great OM content, the low C:N and the optimal pH level, which are the main factors that increased the N mineralization in soil. Many other researchers have underlined the OM bound to clay-silt size fractions was more humified and highly recalcitrant to biodegradation (e.g., Schmidt and Kögel-Knabner, 2002). A previous study on ON distribution in fine fractions was conducted on the same studied soils (Dradi and Arfaoui, 2017). Results proved an important contribution of the fine fraction ($< 50 \mu\text{m}$) (65% (Calcisol) to 98% (Luvisol) of the soil ON) to the ON immobilization in soils. Moreover, the extraction of the different humic substances (fulvic acids, humic acids and humine) from the fine fraction and the analysis of the ON in all separate fractions showed the presence of large proportions of ON incorporated within the humin. In fact, the ratio of ON of the humin to ON of the fine fraction ($\text{ON}_H/\text{ON}_{<50\mu\text{m}}$) ranged between 52% and 90% in almost all

(a)



(b)



(c)

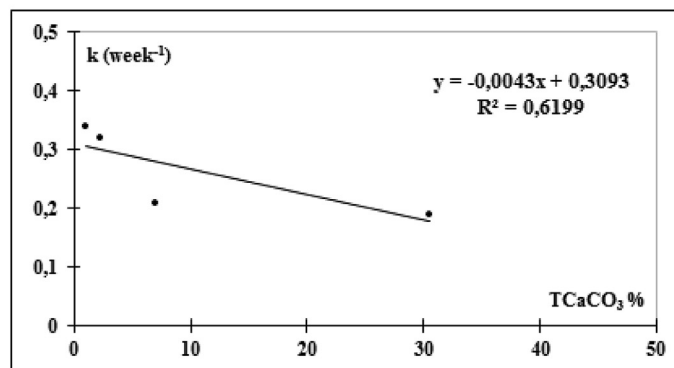


Fig. 6. The regression of (a) No and ON contents, (b) k and clay contents, (c) k and $TCaCO_3$ contents.

the studied horizons (14 horizons).

The carbonate calcium ($CaCO_3$) content in soil also seems to have adverse effect on N mineralization in both field and laboratory studies. Besides, correlation ($r^2 = -0.78$, $p < 0.05$) and regression (Fig. 6 c) ($R^2 = 0.61$, $p < 0.05$) analysis showed a negative relationship between N mineralization constant (k) and $TCaCO_3$ contents. Indeed, we noted a $TCaCO_3$ content higher than 30% in Ap-surface horizon of the Vertisol and in the B_{ca} and C_{ca} -horizons of the Cambisol. For these horizons, the N mineralization was depressed by Ca^{2+} cations, which saturate the OM free sites and through a crystalline coating of calcium carbonate limiting microorganisms attack (Bouagila and Gallali, 2008).

Apart from the soil properties, which directly affect the N mineralization dynamic, some environmental factors (soil temperature and moisture) also seem to have a great influence. The Fig. 2 shows the balance between N mineralization, N immobilization, leaching and atmospheric losses. In general, N mineralization was restricted to the winter months (January and February) mainly in surface horizons of all the studied soils. The decrease in inorganic N contents mostly for NO_3-N

was attributed to the low soil temperature (constraint on microbial activity) and high water volumes causing a further leaching of the nitrate (Abera et al., 2012) and its accumulation in the depth ($203.25\ mg\ kg^{-1}$ of NO_3-N in the Calcisol and $66.19\ mg\ kg^{-1}$ in the Cambisol). Moreover, the excessive moisture saturates the pores and reduces the soil aeration, thereby slowing the decomposition process (Knoepp and Swank, 2002; Cardenas et al., 2017). N mineralization reached one or two peaks when the soil temperature and humidity conditions became favorable for the different microbial processes (March). Indeed, the NH_4-N and NO_3-N values reached their maximum. The contents of NO_3-N increased especially in surface horizons of all the studied soils. It is the active growth period. The ammonium ions were rapidly oxidized into nitrate form indicating a greater nitrification (i.e., a conversion of ammonium into nitrate). Accordingly, the N mineralization was accelerated with the increasing soil temperature (De Neve et al., 2003). It was also important when the soil moisture was close to field water holding capacity, which is about 10–35% (depending on soil type, see Fig. 4) of gravimetric moisture content and declined with soil

drying (Wang et al., 2006; Watts et al., 2007). Therefore, both of the soil temperature and moisture are among the main pedo-climate conditions, which directly affect the mineralization of ON in soil (Nunan et al., 2000; De Neve et al., 2003). The inorganic N contents ($\text{NH}_4\text{-N} + \text{NO}_3\text{-N}$) started to decrease in April and regressed in May and June except for the Vertisol, which recorded high-inorganic N contents ($\approx 20 \text{ mg kg}^{-1}$). It is noteworthy to state that as soils dry, ammonia oxidation decline due to constraints on ammonium diffusive transport, ultimately reducing the activity due to physiological limitations imposed by water stress (Wang et al., 2006). Besides, the decrease of inorganic N contents that occurred in the stated soils might be due to the denitrification and immobilization process. The mineralization of ON in the Vertisol was under the influence of the wetting and drying cycles since it was developed under contrasted bio-climate conditions (wet winter versus dry summer). These fluctuations have a great impact on the microbial activity (stimulating effect) thus increasing the N mineralization (Kruse et al., 2004). Indeed, the swelling of clays during remoistening of dried soil by rain would increase the surface contact between live biomass and organic compounds and favor their biodegradation (Wang et al., 2006; Watts et al., 2007). In general, our results showed the dominance of $\text{NH}_4\text{-N}$ form under normal field conditions at surface as well as in deep horizons (Fig. 2). However, $\text{NO}_3\text{-N}$ form prevailed under optimal laboratory conditions (Fig. 5). Therefore, nitrification is further inhibited at extreme soil temperatures and moisture than ammonification (Wang et al., 2006; Cardenas et al., 2017).

Our laboratory results presented the following decreasing order of the potentially mineralizable N (No) and Kinetics: Calcisol > Vertisol > Cambisol > Luvisol. Moreover, the used model distinguished two fractions constituting ON supplies for all studied soils: An active fraction that is quickly mineralized (first phase) and a passive or slowly mineralized fraction (second and third phases). The first fraction (No) of highly labile nature (Jedidi et al., 1994; Saidi et al., 2015), and therefore characterized by a rapid mineralization, would escape the stabilizing action of clays. This first fraction certainly plays a source role for soil N mineralization as shown by some previous studies (e.g., Wang et al., 2006). Several authors have suggested that the active fraction of the soil OM (No) might serve as an indicator of the more mineralizable N (Delphin, 2000). However, the second passive fraction (ON-No) was chemically and/or physically stabilized and resistant to microbial biodegradation. In fact, the formation of chemical bonds between humic N-rich compounds and clays with iron oxides may cause a slower N mineralization (Uzoho and Igbojionu, 2014). Thus, significant contents of ON supplies in the four studied soils could not be readily mineralized and available for plants. Tunisian farmers and managers have to consider this important matter when planning N fertilization.

Based on our field and laboratory results, we can therefore suggest a reduction of N fertilizer doses mainly during the non-growing and rainy period (possibly with another larger application in March). During the growing period (maximum of inorganic N contents), farmers should assess the content of the available N in each soil type and synchronize its release with each crop demand. Indeed, they can rely on mineral N input originating from the mineralization of soil OM. This can reduce the N fertilizer cost and restrict undesirable N losses into the environment. The N applied at this stage is by far the most effective (just before the crops start growing rapidly). Earlier applications can increase loss opportunities mainly during rainy periods. In the case of Béja region (Vertisol), farmers have to take into account the inorganic N contents released during the earlier dry season (40.28 mg kg^{-1} in April and $\approx 20 \text{ mg kg}^{-1}$ in May and June), mainly if another N fertilization dose needs to be applied.

5. Conclusions

Estimates of inorganic N contents throughout a field and laboratory

approach in four non-fertilized soils of a semi-arid region (North Tunisia) clearly demonstrated that soil properties and pedoclimatic conditions directly affect N mineralization as well as its kinetics.

Our field results showed that the highest inorganic N contents were recorded in the Calcisol due to the high OM amount and low C:N ratio. The lowest contents were recorded in the case of the Luvisol because of a large clay-silt fraction and low pH level. Over the winter months, the inorganic N contents (mostly for $\text{NO}_3\text{-N}$) decreased in all the studied soils. Low soil temperature appeared to be the main limiting factor. High moisture values mainly affected $\text{NO}_3\text{-N}$ contents in the soil by being further leached and accumulated in depth above the root zone. N mineralization occurred along the growing season (March) because of higher temperature combined with greater soil moisture. In April, N mineralization started to decrease gradually and regressed in May and June except for the Vertisol, which still recorded relatively high-inorganic N contents during this warm period of 2015. The mineralization of N in the Vertisol was most likely caused by the wetting and drying cycles, which greatly impact the microbial activity.

Our Laboratory results were suitable for comparative estimates of the potentially mineralizable N and kinetics of different studied soils. Both presented the following decreasing order after six weeks of incubation: Calcisol > Vertisol > Cambisol > Luvisol. Moreover, two fractions constituting ON supplies were distinguished by our laboratory results. An active fraction with a rapid mineralization and a passive fraction slowed down by clays and resistant to biodegradation. Hence, the estimates of fertilizer doses depend on crop N requirements and the soil's ability to supply N from different soil ON fractions, which is difficult to quantify since it depends on several environmental factors. It is also governed by many pedogenetic characteristics and physicochemical properties specific to the soil.

Based on our field and laboratory results, N fertilization can be carefully managed in order to reduce harmful environmental impacts such as nitrate leaching mainly by avoiding excessive or unnecessary N fertilization rates. Indeed, Tunisian farmers should get their soil samples analyzed. They also need to consider inorganic N contents in order to adjust the optimum N fertilizer doses to crops. Moreover, the calculation of adequate organic or chemical N fertilizer doses should consider the contents of mineral N supplied by the mineralization of different soil ON fractions when developing fertilization strategies.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jafrearsci.2019.03.021>.

References

- Abera, G., Wolde-meskel, E., Beyene, S., Bakken, L.R., 2012. Nitrogen mineralization dynamics under different moisture regimes in tsoils. *Int. J. Soil Sci.* 7, 132–145.
- Amlinger, F., Götz, B., Dreher, P., Geszt, J., Weisteiner, C., 2003. Nitrogen in biowaste and yard waste compost: dynamics of mobilisation and availability - a review. *Eur. J. Soil Biol.* 39, 107–116.
- Battle-Bayer, L., Batjes, N.H., Bindraban, P.S., 2010. Changes in organic carbon stocks upon land use conversion in the Brazilian Cerrado: a review. *Agric. Ecosyst. Environ.* 137, 47–58.
- Bouagila, H., Gallali, T., 2008. Soil organic carbon fractions and aggregate stability in carbonates and no carbonated soils in Tunisia. *J. Agron.* 2, 127–137.
- Cardenas, L.M., Bol, R., Lewicka-Szczepak, D., Gregory, A.S., Matthews, G.P., Whalley, W.R., Misselbrook, T.H., Scholefield, D., Well, R., 2017. Effect of soil saturation on denitrification in a grassland soil. *Biogeosciences* 14, 4691–4710.
- Delphin, J.E., 2000. Estimation of nitrogen mineralization in the field from an incubation test and from soil analysis. *Agronomie* 20, 349–361.
- De Neve, S., Sleutel, S., Hofman, G., 2003. Carbon mineralization from composts and food industry wastes added to soil. *Nutrient Cycl. Agroecosyst.* 67, 13–20.
- Dridi, I., Arfaoui, A., 2017. Organic nitrogen distribution in seven Tunisian soil types under contrasting pedogenetic conditions. *Environ. Earth Sci.* 76, 205.
- Duguet, F., Parent, L.E., N'dayegamiye, A., 2006. Compositional indices of net nitrification in cultivated organics soils. *Soil Sci.* 171, 886–901.
- García-Gil, J.C., Plaza, C., Soler-Rovira, P., Polo, A., 2000. Long-term effects of municipal solid waste compost application on soil enzyme activities and microbial biomass. *Soil Biol. Biochem.* 32, 1907–1913.

- Goulding, K., Jarvis, S., Whitmore, A., 2008. Optimizing nutrient management for farm systems. *Phil. Trans. Roy. Soc. B* 363, 667–680.
- Hofman, G., Van Cleemput, O., 2004. Soil and Plant Nitrogen. International Fertilizer Industry Association, Paris.
- Honeycutt, C.W., Griffin, T.S., He, Z., 2005a. Manure nitrogen availability: dairy manure in Northeast and Central U.S. soils. *Biol. Agric. Hortic.* 23, 199–214.
- Jedidi, N., Van Cleemput, O., M'Hiri, A., 1994. Quantification des processus de minéralisation et d'organisation de l'azote dans un sol en présence d'amendements organiques. *Can. J. Soil Sci.* 75, 85–91.
- Jedidi, N., Hassen, A., Van Cleemput, O., M'Hiri, A., 2004. Microbial biomass in a soil amended with different types of organic wastes. *Waste Manag. Res.* 22, 93–99.
- Knoepp, J.D., Swank, W.T., 2002. Using soil temperature and moisture to predict forest soil N mineralization. *Biol. Fertil. Soils* 36, 177–182.
- Kpomblekou-A, K., Genus, A., 2012. Nitrogen transformations in broiler litter-amended soils. *Int. J. Agron.* 1–12 2012.
- Kruse, J., Kissel, D.E., Cabrera, M.L., 2004. Effects of drying and rewetting on Carbon and Nitrogen mineralization in soils and incorporated residues. *Nutrient Cycl. Agroecosyst.* 69, 247–256.
- Lodhi, A., Arshad, M., Azam, F., Sajjad, M.H., 2009. Changes in mineral and mineralizable N of soil incubated at varying salinity, moisture and temperature regimes. *Pakistan J. Bot.* 41, 967–980.
- Mulvaney, R.L., Khan, S.A., Hoef, R.G., Brown, M.H., 2001. A soil organic nitrogen fraction that reduces the need for nitrogen fertilization. *Soil Sci. Soc. Am. J.* 65, 1164–1172.
- Nunan, N., Morgan, M.A., Scott, J., Herlihy, M., 2000. Temporal changes in Nitrogen mineralization, microbial biomass, respiration and protease activity in a clay loam soil under ambient temperature. *Proc. Roy. Ir. Acad.* 100, 107–114.
- Saidi, N., Akef, S., Bouzaiane, O., Kallali, H., Ben Aissa, N., M'Hiri, F., Jedidi, N., Downer, J., 2015. Carbon and nitrogen mineralization in clay loam soil amended with different composts. *Adv. Appl. Agric. Sci.* 3, 20–34.
- Schmidt, M., Kögel-Knabner, I., 2002. Organic matter in particle-size fractions from A and B horizons of Haplic Alisol. *Eur. J. Soil Sci.* 53, 383–391.
- Schröder, J.J., 2014. The position of mineral nitrogen fertilizer in efficient use of nitrogen land: a Review. *Nat. Resour.* 5, 936–948.
- Sistani, K.R., Adeli, A., McGowen, S.L., Tewolde, H., Brink, G.E., 2008. Laboratory and field evaluation of broiler litter nitrogen mineralization. *Bioresour. Technol.* 99, 2603–2611.
- St Luce, M., Whalen, J.K., Ziadi, N., Zebbarth, B.J., 2011. Nitrogen dynamic and indices to predict soil nitrogen supply in humid temperate soils. *Adv. Agron.* 112, 55–102.
- Uzoho, B.U., Igbojionu, G.U., 2014. Carbohydrate distribution of particle size fractions of soils in relation to land-use types in Mbaise, Southeastern Nigeria. *J. Biol. Agric. Healthc.* 4, 27–36.
- Wang, C., Wan, S., Xing, X., Zhang, L., Han, X., 2006. Temperature and soil moisture interactively affected soil net N mineralization in temperate grassland in Northern China. *Soil Biol. Biochem.* 38, 1101–1110.
- Watts, B.D., Torbert, H.A., Prior, S.A., 2007. Mineralization of N in soils amended with dairy manure as affected by wetting/drying cycles. *Commun. Soil Sci. Plant Anal.* 38, 2013–2116.