

ҐРУНТОЗНАВСТВО ТА ГЕОГРАФІЯ ҐРУНТІВ

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CHANGES IN SOIL CARBON AND NITROGEN DYNAMICS DURING A THREE YEAR CROP ROTATION ON A CHERNOZEM SOIL IN THE SOUTHERN UKRAINE

Soils in the southern Ukraine have been reported to have lost 32% to 40%, or 51 to 71 t ha⁻¹ of their original soil organic matter (SOM) pool between 1881-1981, mainly due to inappropriate soil management by collective farms during 1930-1981. In this period agricultural management was directed towards irresponsible expansion of arable fields and short-term yield increases. Modern, sustainable agricultural management is slowly being introduced. There is a need to assess to what extent such methods stabilize and build new SOM to support and increase fertility both in the short and long-term. This study investigates the influence of a modern crop rotation (onion-tomato-barley) on one field, which was tilled, fertilized, irrigated and harvested in response to the crops needs, on the dynamics of total organic carbon (TOC) and total nitrogen (TN) storage in the fertile topsoil of a Chernozem typical for southern Ukraine. Crop residue remained on the field. The results of three years (2007-2009) of quarterly monitoring of the key topsoil parameters TOC, TN, extractable mineral N (NH₄⁺, NO₃⁻, NO₂⁻), pH, potential net N mineralisation (MIN) and nitrification (NITR) rates and physical characteristics (bulk density, soil texture) are discussed. Moderate (114 kg N ha⁻¹ yr⁻¹) and low (28 kg N ha⁻¹ yr⁻¹) N fertilizer applications together with adequate drip irrigation for onion and tomato and incorporation of plant residue did significantly change the C and N pools. Total organic carbon and TN contents of the topsoil horizon (0-74 cm) were found to increase by 20% (26.8 t C ha⁻¹) and 38% (5.9 t N ha⁻¹), respectively. Largest

increases were measured in the surface layer (0-27 cm) with a 45% increase in TOC and a 36% increase in TN content. The largest average soil NH_4^+ content of the topsoil horizon (0-74 cm) was observed in 2009 under barley ($154.9 \pm 41.3 \text{ kg N ha}^{-1}$) and the maximum average NO_3^- content was $166.9 \pm 44.5 \text{ kg N ha}^{-1}$ under tomato in 2008. Mineralisation and nitrification rates significantly varied between years and with season and were largest in the first year of the crop rotation (onion), $41.0 \pm 57.3 \text{ kg N ha}^{-1}$ and $36.6 \pm 74.4 \text{ kg N ha}^{-1}$ for MIN and NITR, respectively. The incorporation of plant residues and efficient N fertilizer applications within a crop rotation appeared to be effective in stabilizing the existing SOM and promoting SOM build-up.

Keywords: nitrogen, carbon, nitrate, ammonium, mineralization, nitrification, soil organic matter

Introduction

The presence of organic matter contributes to good soil fertility. Soil organic matter (SOM) conservation and accumulation needs to be a priority in arable land management. This however was not the case in the Ukraine during the Soviet Union leadership. During 1930-1981 many fields were managed by collective farms («kolkhoz»). Financial incentives directed their agricultural management towards annual maximum yield only without taking measures to prevent water and soil erosion or organic matter depletion. Land, not normally considered suitable for cultivation was also farmed. Even since independence lack of government support has prevented many farms to become profitable and change from short-term yield driven management to one promoting long-term sustainability. Consequences of this agricultural mismanagement are a serious loss in SOM, as was demonstrated for an important farming region in the southern part of the Ukraine, the steppe zone of Odessa Oblast. Here, the southern chernozem black soils are considered a natural resource and have been farmed for more than 200 years and in many years between 85-90 % of these soils are ploughed [1, 33]. Southern sub-type of chernozem of a steppe has less SOM (3-6% in the upper 30 cm) compared to typical chernozems of a steppe (6-8%) or a forest-steppe (7-12%) [28, 50]. Farming between 1881-1981 decreased the SOM by $51\text{-}71 \text{ t ha}^{-1}$ from $126\text{-}221 \text{ t ha}^{-1}$ in 1881 to $75\text{-}150 \text{ t ha}^{-1}$ in 1981 [28, 32, 45]. It is therefore important to develop strategies that will increase SOM and use mineral fertilizers combined with drip irrigation to improve environmental and economic outcomes. Sustainable management of arable land provides an opportunity to improve soil conditions and increase fertility, decrease soil erosion, and reduce N_2O emissions by denitrification [38]. One efficient way to increase SOM is incorporation of plant residues and straw [15]. In many regions animal manure applications are limited, because they can be as much as three times more expensive than mineral fertilizers. The mineralisable N content of plant residues may exceed the amount of N entering soil as mineral fertilizers. But according to previous studies [20, 39] the simultaneous input of plant residues and N fertilizer are important and promote an increase in aggregate formation. It is known that soil aggregates physically protect

SOM [46] and they play an important role in SOM stabilization [15]. In crop rotations the use of plant residues for SOM enrichment is possible and cost-effective. Plant residues incorporated into the soil will be slowly decomposed and mineralized by the microbial community and provide plant nutrients for the following growing season [31, 34]. The above processes are influenced by the physical and chemical properties of soil, microbial composition and climatic conditions and therefore may be very different in different soils. The article theme is topical and have been significant for agricultures.

An important consideration in studies of changes in SOM content is the depth of the soil profile. In their review of literature, Baker et al. [3] pointed out that many researchers had studied soil carbon (*C*) not below a depth of 30 cm and thereby may have over-estimated soil *C* sequestration rates for reduced tillage systems compared to tilled systems. It is also important to consider the influence of plant roots on the soil *C* balance at the depth exceeding 30 cm and changes in bulk density which is often associated with reduced tillage systems. According to Halvorson et al. [17, 18], soil bulk density increases with reduced tillage and less crop residue inputs. This means that if soil is receiving no *C* input an apparent increase in the mass of *C* will be observed if samples are taken at the same depth. On the other hand Snyder et al. [42] reported that increased crop residue return linked to *N* application rates can reduce the soil bulk density. In order to reliably monitor changes in soil organic *C* content that results from different rates of *N* application, we would need deep soil sampling [42].

The *object* of study is the fertility topsoil horizon (0-74 cm) of southern chernozem. The *subject* of study is changes in soil *C* and *N* contents in this particular layer of southern chernozem soil. The *aim of this article* was to investigate the influence of agricultural management (crop rotation design, plant residue and mineral *N* fertilizer input, and tillage treatments) on the dynamics of total organic *C* (TOC) and total *N* (*TN*) storage in southern black soil in the area of the «Petrodolinskoye» research monitoring station National Mechnikov's University of Odessa (ONU) in 2006-2009. To increase assessment of the precision of *C* and *N* dynamics studies were carried out of the entire topsoil profile (0-74 cm), which was divided into 4 layers according to genetic and morphological features (0-27 cm, 27-44 cm, 44-60 cm and 60-74 cm).

The *theoretical aspect* of this study meaning is to demonstrate why for arable lands in general and for chernozem in particular a whole profile of fertility layer (at least until the floor of ploughing) is needed to be investigated to estimate precise *C* and *N* contents. From *practical point of view* we explain what issues can be met during element content estimations in appropriate layer per appropriate area. We believe that our work both elucidates interesting results and highlights critical issues for computation of those informative parameters, which are widely used in biogeomodelling.

Materials and Methods of the researches

Study site

This study was carried out at the Petrodolinskoye Atmospheric Research Monitoring Station of Regional Centre for Integrated Environmental Monitoring and Ecological Studies (RCIEM) of National Mechnikov's University of Odessa (ONU). The station is located near «Mirnoye» settle (46°27'22.12"N; 30°20'9.94"E), 27 km southeast of Odessa and was established in 2006 within the framework of the NitroEurope IP of the FP6 programme. The 8 ha field had a relatively homogeneous topography with an elevation of 66 m above a sea level ordinary. The soil was a black soil typical for the south of the Ukraine (Chernozems Vermi-Calcic (CH vec), [13]) (Table 2). The climate is temperate continental, with an annual average air temperature of 10.1°C with a minimum mean of 7.1°C and maximum mean of 13.5°C; air relative humidity of 76.0%; wind velocity 3.9 m s⁻¹; prevailing direction from North, Northwest and total precipitation of 464 mm. Detailed meteorological data (rainfall, air temperature and relative humidity were measured 8 times per day) for the study years and were obtained from the state meteorological station «Odessa», 30 km away from our field site (Fig. 1). A meteorological station was set up at the Petrodolinskoye field site in November 2007 and provided rainfall, air temperature and relative humidity, atmospheric pressure, soil temperature and moisture, soil heat flux, wind speed and direction, photosynthetic active radiation, global and net radiation measurements at a frequency of 10 sec for 2008 and 2009 (Fig. 1). For 2008 and 2009 datasets from the Odessa and the Petrodolinskoye sites were in good agreement, with no more than 10% variation.

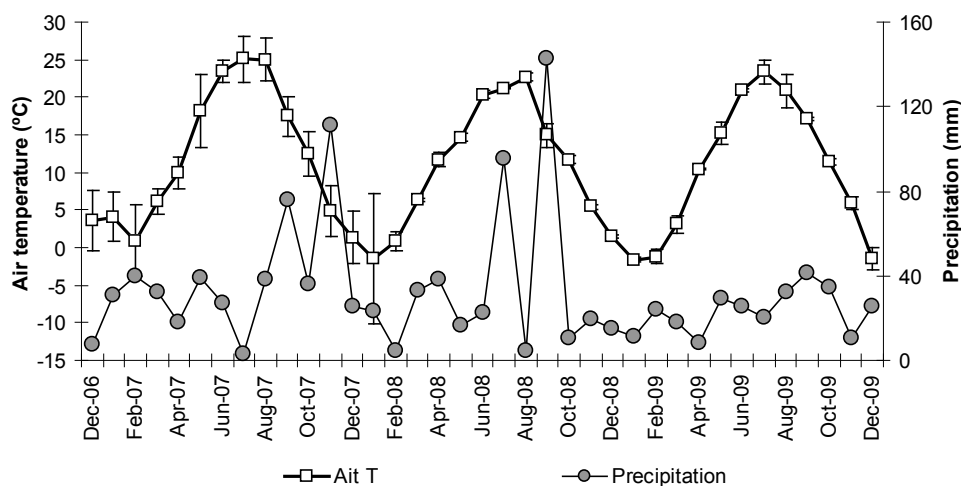


Fig. 1. Average monthly air temperature and total precipitation for the study area in Dec 2006 – Dec 2009 (2006, 2007 data were kindly obtained from the Meteorological Station «Odessa» and 2008, 2009 data were measured on the study field)

Crop rotation and management

The study site had been under active agricultural management for more than 200 years. However, the detailed history of the agricultural management is unknown. Before autumn 2006 the area was managed by a collective farm («kolkhoz»). They declined to provide us with any information about the agricultural history of this field. We therefore assume a management that would have been normal for collective farms. The main way to improve the soil fertility would have been by included legumes (pea, bean or alfalfa) in crop rotation every 2nd-4th year. Mineral N fertilizer input would have been low (approximately 0-5 kg N per ha⁻¹). All arable fields were deep ploughed (40-60 cm) annually at a time prescribed by the regional administration rather than in response to weather, crop and soil characteristics. Plant residues would have been burned, harvested or ploughed deeply into the soil. Surface irrigation using either short-jet/long-jet fixed/mobile devices would have taken place.

The study field 8 ha in size was leased in autumn 2006 from the Association of Agricultural Enterprises «Granit». In 2006 the crop was wheat. The crop rotation used during the study period was onions in 2007, tomatoes in 2008 followed by barley and winter wheat in 2009. The crops were grown with an application of mineral fertilizers and drip irrigation (Table 1). Fertilizer was applied as $CO(NH_2)_2$ -N, NH_4NO_3 -N; $NH_4H_2PO_4$ -P and -N; KNO_3 -K and -N; KH_2PO_4 -K and -P. Rates and split applications are detailed in Table 1.

To prevent plant diseases and to suppress weeds, pesticides and herbicides were applied to all crops, except to the winter wheat in autumn 2009. The onion and tomato crops were drip irrigated during May until the middle of August 2007 (totally ca. 140 m³/ha⁻¹) and July-June 2008 (totally ca. 147 m³/ha⁻¹) respectively. Due to the difficult economic situation on the farm, in 2008 the field was not tilled after harvest and in 2009 barley grown for fodder was not irrigated. The following tillage methods were used: deep ploughing (25 and 40 cm depths), disking (10 cm depth), dragging (10 cm depth), subsurface cultivation (10 cm depth), inter-row cultivation (5 cm depth), tiller cultivation (5 cm depth) (Table 1).

Soil sampling and analyses

Soil sampling was conducted on three plots within the study field four times per year (once per season) from December 2006 to October 2009. These plots were located triangular equidistantly, approximately 50 m away from the atmospheric monitoring station situated in the centre of the field. Plots were triangular, with each side measuring about 10 meters. On each plot three soil profiles were collected using a 7 cm diameter and 30 cm long soil corer [21]. Each of soil sampling profile had 4 distinct morphological layers (0-27 cm, 27-44 cm, 44-60 cm and 60-74 cm). The weight of the intact samples varied between 0,7 and 1,5 kg depending on sampling horizon. All intact soil samples were used to determine the bulk density and soil moisture content according to ISO 11272 [23] and ISO 11465 [24] respectively. For further analyses samples from the same layers in each plot were integrated to

Table 1.
**Details of the agricultural management for the three year
 crop rotation practiced on the study field**

Year	Crop	Date of Sowing	Date of Harvesting	Type of Residue	Tillage [date]	Fertilizer input rates				
						Date of split application	N, kg ha-1	P, kg ha-1	K, kg ha-1	Split application
2007	Onion	01 Apr	31 Jul – 17 Aug	Left-over onions lying in/on soil (approx. 20% of crop)*	Ploughing 40 cm [Dec '06] Ploughing 25cm [02 Sep] Disking 10 cm [05 Oct] Ploughing 25 cm [05 Nov] Ploughing 40 cm [20 Nov] Cultivation 10 cm [04 Dec] Cultivation 10 cm [06 Dec]	May	76,2	9,7	39,6	With drip irrigation
						Jun	15,2	2,2	13	
2008	Tomato	18 Apr	07 -31 Aug	Whole plants with left-over tomato-fruits (15% of crop)*	Dragging 10 cm [15 Apr] Inter-row cultivation 5 cm [20 May] Inter-row cultivation 5 cm [25 May] Weeding and replanting [29 May]** Tiller cultivation 5 cm [30 May]	Jun	14,1	1,3	6,3	With drip irrigation
						July	14,1	1,3	6,3	
2009	Barley	01 Apr	08 Jul	Barley stubbles (10 cm)	Disking 10 cm [30 Mar] Disking 10 cm [10 Oct]	Apr	57,2	17,5	33,2	Surface
	Winter wheat	15 Oct	-	-	-	-	0	0	0	-

*The % residue remaining on field was estimated for onion, but measured for tomato, **manual weeding and replanting where crop did not establish

one composite sample. Total numbers of such composite samples for each sampling event (each season) for the study area were 12. These samples were analyzed for soil texture [26], for chemical characteristics, potential net *N* mineralization (MIN) and potential net nitrification (NITR) by the Soil Laboratory of the ONU. Methods, described in detail by Kaurichev [27] and Vadyunina and Korchagina [49], were used for determination of TOC (chromic acid oxidation) and TON (modified Kjeldahl method). KCl extractable (2% KCL) NH_4^+-N , and water extractable $NO_2^- -N$ and $NO_3^- -N$, were determined by colorimetric analysis. The *pH* of a soil suspension in water (ratio soil:water = 1:5) was determined using a *pH*-meter (Fisher Brand Hydrus 400) according to ISO 10390 [22]. SOM content was calculated by multiplying the TOC content with the conversion factor of 1.724 [6, 35, 43, 55]. We used the traditional 1.724 conversion factor instead of the updated value of 2.0 [7] to allow comparison of our results with earlier literature SOM data.

Some parameters were analysed less frequently (4 samples in December 2006 and 4 samples in October 2009): samples were extracted with water and analysed for CO_3^- , HCO_3^- , Cl^- , SO_4^{2-} , Ca^{2+} , Mg^{2+} , Na^+ , K^+ -ions and total salts, the cation exchange capacity and exchangeable Ca^{2+} , Mg^{2+} , Na^+ and K^+ , P_2O_5 and K_2O [27, 49].

All chemical analyses were undertaken on three replicates; if differences between results and the mean values exceeded by 10% the analyses were repeated.

We carried out analyses to determine MIN and NITR in each layer of the topsoil. To estimate MIN and NITR rates in vitro soil samples (100 g), covering the seasonal pattern over the study period, were incubated in a temperature-regulated chamber at 20°C and at a water content of 27% of field capacity for 28 days [25]. Fresh soil samples and incubated samples were analyzed for NH_4^+-N , $NO_2^- -N$ and $NO_3^- -N$ [27, 49]. MIN rates were calculated as:

$$MIN = (NH_4^+_{inc} + NO_3^-_{inc} + NO_2^-_{inc}) - (NH_4^+_{frs} + NO_3^-_{frs} + NO_2^-_{frs}) \quad (1)$$

where the indexes 'inc' represents 'incubated soil' and 'frs' represents 'fresh soil'.

NITR rates were calculated as:

$$NITR = (NO_3^-_{inc} + NO_2^-_{inc}) - (NO_3^-_{frs} + NO_2^-_{frs}) \quad (2)$$

For correlation analysis we also calculated potential net ammonification (AMMON) rates as:

$$AMMON = NH_4^+_{inc} - NH_4^+_{frs} \quad (3)$$

The plant samples of tomato crop were collected for determination of total *C* and *N* by mass spectrometry. Samples of all above-ground plant material in 4x0.25 m² representative subplots distributed across the site were collected and dried in paper bags at 80°C until constant weight. Analyses were conducted on ANCA-SL elemen-

tal analyzer coupled to a 20-20 tracer mass spectrometer by Plant and Soil Science Laboratory, Faculty of Life Sciences, University of Copenhagen.

Statistical analysis

We used correlation analysis to investigate relationships between studied soil parameters, fertilizers input and meteorological data. We also calculated significance tests for comparison of the average values using Student t-test (normal distribution). All the analyses were carried out with SPSS Statistics (version 20.0 for Windows, IBM, 2011) and STATISTICA (version 8.0 for Windows, StatSoft, Inc., 1984-2007). Diagrams and trends were built by using MS Excel 2010.

Results and Discussion

Analysis of meteorological observations during 2007 – 2009 (Fig.1) showed rainfall was much lower in 2009 (281 mm) than in the previous two years (477 mm in 2007 and 426 mm in 2008). Year of 2007 was the warmest: the annual average temperature was $12,4 \pm 9,2^\circ\text{C}$ compared to $10,8 \pm 8,3^\circ\text{C}$ and $10,3 \pm 9,3^\circ\text{C}$ in 2008 and 2009, respectively and the average January and July temperatures were $4,0^\circ\text{C}$ and $25,1^\circ\text{C}$ compared to $-1,5$ and $21,2^\circ\text{C}$ in 2008 and then $1,7$ and $23,4^\circ\text{C}$ in 2009, respectively (Fig. 1).

The southern chernozem black soil texture for the study site was a heavy loam, which was reasonably homogenous along the profile (Table 2).

Table 2.

The physical and chemical characteristics of the field site. Data are averages of 4 measurements per year during the period Dec 2006 – Oct 2009

Parameter	1 st layer (0-27 cm)		2 nd layer (27-44 cm)		3 rd layer (44-60 cm)		4 th layer (60-74 cm)		Number of observations N
	Mean	Std	Mean	Std	Mean	Std	Mean	Std	
pH	6,96	0,49	7,09	0,41	7,79	0,57	8,48	0,24	33
Bulk density (g cm ⁻³)	1,29	0,15	1,43	0,05	1,48	0,09	1,53	0,10	33
Clay (%)	59,43	0,04	60,64	0,73	60,90	0,15	55,15	0,24	4
Sand (%)	11,59	0,21	9,10	0,98	11,93	0,23	9,76	0,43	4
Silt (%)	28,98	0,17	30,26	0,39	27,17	0,21	35,09	0,23	4
Moisture (% by volume)	31,13	3,11	33,49	2,64	31,60	3,42	31,21	2,25	33
SOM (%)	3,12	0,23	2,65	0,46	2,04	0,59	1,20	0,46	33
TOC (%)	1,81	0,13	1,53	0,27	1,19	0,34	0,65	0,23	33
Inorganic C (%)	0,01	0,04	0,01	0,04	0,13	0,25	0,90	0,66	27
TN (%)	0,18	0,05	0,17	0,06	0,18	0,10	0,13	0,04	33

The average depth of the topsoil horizon was 74 ± 3 cm. The average bulk density over the three year observations increased from $1,29 \pm 0,15$ g/cm³ in the top layer (0-27 cm) to $1,53 \pm 0,10$ g/cm³ at the lowest sampling depth (60-74 cm), this difference was significant at $P < 0.00001$ (Table 2). Bulk densities of the topsoil (0-74 cm) for the three individual years were slightly, but not significantly different. The average bulk densities and soil moisture contents of the topsoil horizon (0-74 cm) had no statistically significant differences between onion (2007), tomato (2008) and barley (2009) seasons and were $1,43 \pm 0,03$ g/m³ and $27,6 \pm 8.15\%$ in 2007, $1,46 \pm 0,09$ g/m³, and $32,7 \pm 1,1\%$ in 2008, $1,40 \pm 0,10$ g/m³ and $31,0 \pm 2,8\%$ in 2009.

The average *pH* significantly ($P < 0,00001$) changed from neutral ($6,96 \pm 0,49$) in upper layer (0-27 cm) to alkaline ($8,48 \pm 0,24$) in the lowest layer (60-74 cm) in 2007-2009 (Table 2). The average *pH* value of the topsoil (0-74 cm) was significantly largest under tomato (2008; *pH* $7,85 \pm 0,12$ at $P < 0,007$) compared to onion (2007; *pH* $7,37 \pm 0,16$) and barley (2009; *pH* $7,51 \pm 0,38$). For the surface layer (0-27 cm) the same tendencies were observed, but the highest *pH* for 2008 was $7,26 \pm 0,56$ ($P < 0,05$). The *pH* was significantly negatively correlated with TOC (Table 3) storage in the profile ($r = -0,72$, $P < 0,0001$).

Table 3.

Correlation coefficients between variables in profile of topsoil horizon
(* $P < 0,0001$, ** $P < 0,001$, *** $P < 0,05$ at $n = 132$)

Variable	pH	Bulk Density (g cm ⁻³)	Avail. water (%)	TOC (%)	TN (%)	DIN (%)	NH ₄ ⁺ (µg N g ⁻¹)	NO ₃ ⁻ (µg N g ⁻¹)	MIN (µg N g ⁻¹)	NITR (µg N g ⁻¹)
Bulk density (g cm ⁻³)	0,49*									
Available water (%)	-0,05	0,14								
TOC (%)	-0,72*	-0,66*	0,03							
TN (%)	-0,12	-0,32**	0,08	0,51*						
DIN (%)	0,13	-0,12	0,08	0,02	0,24***					
NH ₄ ⁺ (µg N g ⁻¹)	-0,15	-0,20***	0,09	0,25***	0,43*	0,23***				
NO ₃ ⁻ (µg N g ⁻¹)	0,20***	0,01	0,02	-0,13	-0,05	0,78*	-0,41*			
MIN (µg N g ⁻¹)	-0,14	0,04	-0,31**	-0,01	-0,22***	-0,55*	-0,47*	-0,22***		
NITR (µg N g ⁻¹)	-0,22***	-0,04	-0,24	0,12	-0,11***	-0,44*	-0,04	-0,39*	0,85*	
AMMON (µg N g ⁻¹)	0,09	0,14	-0,19***	-0,21***	-0,24***	-0,32**	-0,81*	0,21***	0,52*	-0,02
Air T (°C)	-0,07	0,20***	0,30**	-0,07	-0,33**	0,03***	-0,07	0,07	-0,42*	-0,46*

The calculated *SOM* content [6] in the surface layer (0-27 cm) was $3,12 \pm 0,23\%$ or $110 \pm 8 \text{ t/ha}^{-1}$ and decreased with depth to $1,20 \pm 0,46\%$ ($P < 0,00001$ at 60-74 cm), which is equivalent to $25 \pm 9 \text{ t/ha}^{-1}$ (Table 2). The *TOC* content also significantly declined ($P < 0,00001$) from $1,81 \pm 0,13\%$ in the top layer to $0,65 \pm 0,23\%$ in the lowest layer (Table 2). The inorganic *C* fraction in the two upper layers (0-44 cm) was very small, but in the lowest horizon the percentage of carbonates (present as white soft granules of CaCO_3) was 90 times larger ($P < 0,00001$) (Table 2). The average *TN* content ranged from $0,13 \pm 0,04\%$ (60-74 cm depth) to $0,18 \pm 0,05\%$ (depth of 0-27 cm) of the dry soil weight ($2,8 \pm 0,9 - 3,9 \pm 1,1 \text{ t ha}^{-1}$) and was statistically-valid at $P < 0,00001$ (Table 2). *TOC* and *TN* were positively correlated ($r = 0,51$; $P < 0,0001$) in the entire topsoil horizon (Table 3) and in the top three layers ($r = 0,39$ at $P < 0,025$ in layer 1st; $0,68$ and $0,78$ at $P < 0,0001$ in 2nd and 3rd, respectively). Both, *TOC* and *TN* were negatively correlated with the average bulk density ($r = -0,66$; $P < 0,0001$ for *TOC* and $r = -0,32$; $P < 0,001$ for *TN*) (Table 3).

To provide the full picture of *TOC* and *TN* storage we investigated their content in the whole profile of the topsoil horizon and contribution of each morphological layer during 2006-2009 crop rotation. Over the 3 years *TOC* and *TN* content of topsoil horizon (0-74 cm) increased by 20% and 38%, respectively (Fig.2).

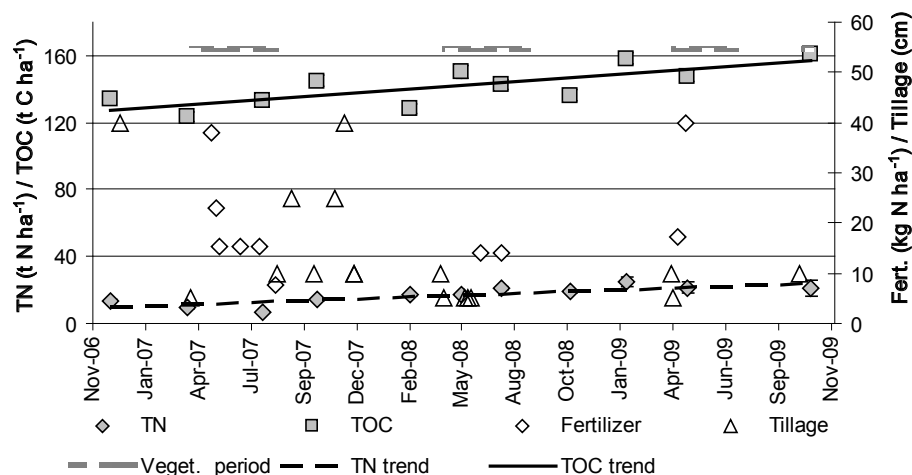


Fig. 2. The changes in *TN* ($r^2 = 0,646$; $y = 0,0133x - 509,7$) and *TOC* ($r^2 = 0,597$; $y = 0,0284x - 980,05$) content of the topsoil (0-74 cm) during the crop rotation

TOC increased from $134,4 \pm 2,6 \text{ t C ha}^{-1}$ in Dec 2006 to $161,1 \pm 2,0 \text{ t C ha}^{-1}$ in Oct 2009 ($P < 0,001$) and the *TN* content from $15,4 \pm 0,6 \text{ t N ha}^{-1}$ to $21,3 \pm 4,5 \text{ t N ha}^{-1}$ over the same period ($P < 0,05$). All four layers contributed to the overall increase, however, the largest increase was found in the surface layer (0-27 cm) with a 45% increase ($P < 0,00001$) in *TOC* and a 36% increase ($P < 0,05$) in *TN* content (Fig. 3). Accumulation of *C* and *N* differed between years and for individual soil layers. During 2007

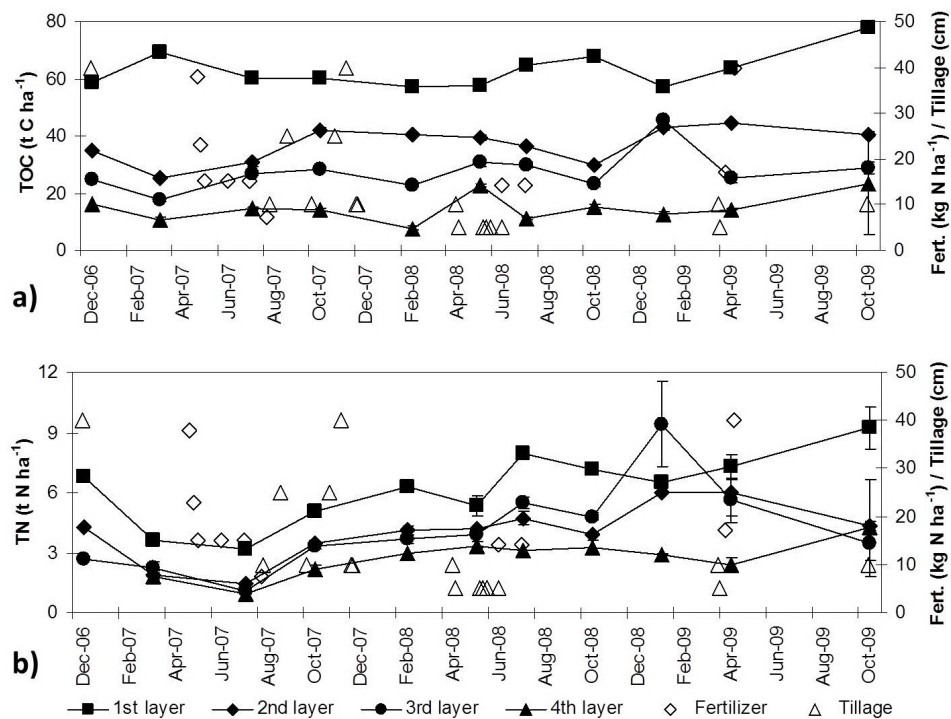


Fig. 3. Variations in TOC (a) and TN contents (b) in the 4 layers of the topsoil horizon (0-27, 27-44, 44-60, 60-74 cm) over a three year crop rotation (2007 onion, 2008 tomato, 2009 barley) in southern Ukraine

(onion crop) we observed an increase in TOC of 7,8% ($P < 0,05$) in the whole topsoil horizon over the period December 2006 to October 2007. TOC contents in the individual layers differed and significant increased by 21,5% ($P < 0,001$) and 13,8% ($P < 0,001$) in 2nd and 3rd layer respectively, but decreased by 11,2% ($P < 0,05$) in 4th layer (Fig. 3a). In 2008 (tomato crop) TOC increased ($P < 0,05$) by 6% in the entire 74 cm horizon (Fig. 3a). The significant increases ($P < 0,001$) of 19% and 97,2% were observed in the 1st and 4th layers, but in 2nd layer TOC decreased by -26,3% ($P < 0,00001$) (Fig. 3a). In 2009 (barley crop) TOC difference was not statistically significant for 0-74 cm horizon. TOC increased in the 1st layer by 36,5% ($P < 0,01$), but declined by 53,1% ($P < 0,00001$) in the 3rd layer (Fig. 3a).

During 2007 (from December 2006 to October 2007) the TN content of the 74 cm horizon decreased by 9,0% ($P < 0,05$); we measured losses in the 1st and 2nd layers by 25,6% ($P < 0,01$) and 18,7% ($P < 0,01$) respectively, but gains by 24% ($P < 0,05$) and 30% ($P < 0,05$) in the 3rd and 4th layers, respectively (Fig. 3b). For the tomato growing season (2008) the TN content increased by 12,3% ($P < 0,05$); it increased by 13,9% ($P < 0,01$) and 31,5% ($P < 0,001$) in the 1st and 3rd layers respectively (Fig. 3b). In 2009, there were no significant differences in TN content for the 74 cm horizon.

Nevertheless *TN* significantly increased by 42,2% ($P < 0,01$) in the 1st layer, and decreased by 63,1% ($P < 0,00001$) in 3rd one (Fig. 3b). The soil *C/N* ratio in the 74 cm topsoil horizon decreased throughout the study period due to the dynamic of rising *TN* content exceeded slight increasing of *TOC* content (Fig. 4).

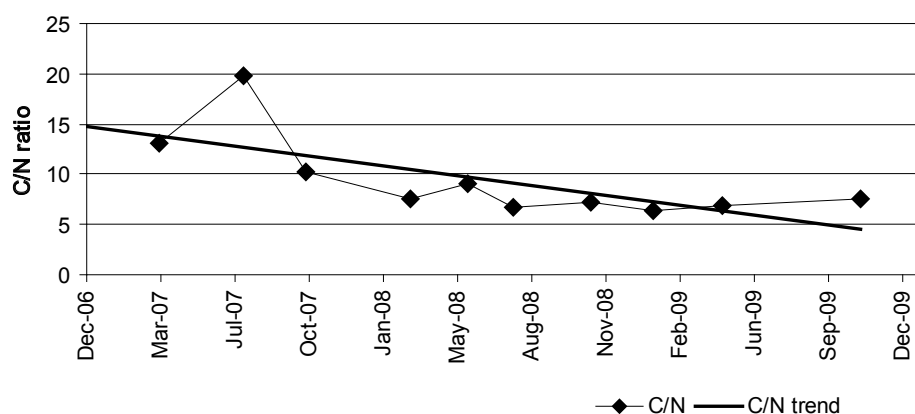


Fig. 4. Changes in *C/N* ratio in the 74 cm top horizon during the crop rotation onion-tomato-barley-winter wheat ($r^2 = 0,492$)

The onion crop residue had a *C/N* ratio of approximately 15 (the exact ratio is unknown) and was ploughed into the soil in autumn 2007 (Table 1) and is likely to mediate the *TN* increasing together with *N* fertilizer application ($P < 0,00001$), compared to summer 2007 (Fig. 3b). Tomato plants and fruits ($C/N=12$, 2076 ± 178 kg *C* ha⁻¹ and 173 ± 15 kg *N* ha⁻¹, *C/N* ratios of under-ground parts of plants were not estimated) remained on the field from August 2008 until the end of March 2009 when they were incorporated into the soil by disking (Table 1). The barley stubble probably had *C/N* ratio of 10. The exact amount of *N* in the residue was unknown, we therefore assumed that the average return of straw and root biomass of wheat/barley under fertilization on black chernozem was approximately the same as in the literature [10] and equal to 2903 ± 369 kg *C* ha⁻¹ and 290 ± 37 kg *N* ha⁻¹. Disking in October 2009 (Table 1) with further decomposition of plant residues appears to affect to significant increasing *TOC* ($P < 0,01$), compared to April 2009 (Fig. 3a).

In the onion season the *TOC* content increased 1,3 times more than during the tomato season and 4 times more than during the barley season ($P < 0,001$). Maximum significant accumulation ($P < 0,05$) of *TN* by 12,3% occurred during the tomato year. Onion growing caused a decline ($P < 0,05$) in *TN* by 9% (Fig. 2, Fig. 3b). However, the trend for *TN* storage was 1,8 times higher than for *TOC*. A steady decline of the *C/N* ratio over this crop rotation took place (Fig. 4), as apparently a result of the different *C/N* ratios of the plant residues as well as different *N* application scheme and soil management practice. Onion growing caused *C* sequestration and *N* loss from soil and increased the *C/N* ratio to 19 in July 2007 (Fig. 3, 4). However the tomato

crop season contributed to the C/N ratio reduction by almost 50%. During barley growing in 2009 the ratio was stabilized at 8.

Soil extractable NH_4^+ and NO_3^- content in the 4 soil layers varied and depended on factors such as fertilizer input, tillage periodicity and air temperature. Correlations between extractable mineral N concentrations and these variables were strongest for the top soil layer (0-27 cm). Ammonium and nitrates were negatively correlated ($r = -0,41$; $P < 0,0001$). The largest average NH_4^+ content was observed in 2009 during barley growth ($154,9 \pm 41,3$ kg N ha $^{-1}$) but for 2007 and 2008 was approximately 3,5 times lower (Table 4, Fig. 5a). A significant increase ($P < 0,00001$) in NH_4^+ content started after the tomato harvest in autumn 2008 and continued during the barley growing season (2009). Differences in NH_4^+ concentrations between the top layer and the three lower layers were largest ($P < 0,00001$) in 2009, when barley was grown. The correlation between NH_4^+ concentration in the top layer (0 – 27 cm) and TOC content was significant ($r = 0,74$; $P < 0,0001$).

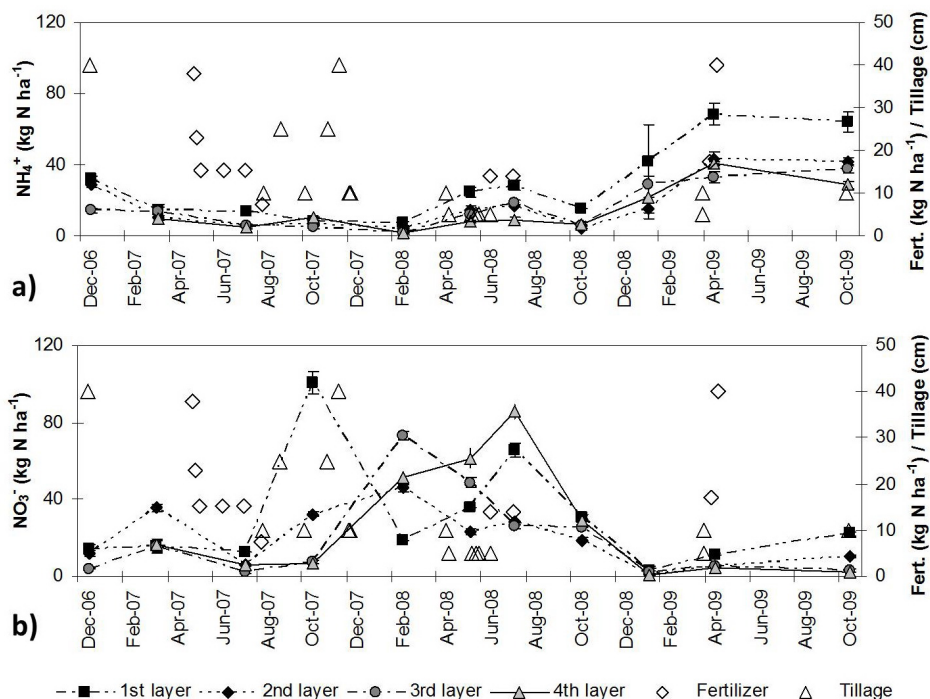


Fig. 5. Variations in extractable NH_4^+ (a) and NO_3^- (b) contents in the 4 layers of the topsoil horizon (0-27, 27-44, 44-60, 60-74 cm) over a three year crop rotation (2007 onion, 2008 tomato, 2009 barley) in southern Ukraine.

The variations of NO_3^- content was characterized by large fluctuations between and within the layers from September 2007 to September 2008 (Fig. 5b). The maximum average NO_3^- content was $166,9 \pm 44,5$ kg N ha $^{-1}$ during 2008 (tomato) and was

2,3 and 7,2 times ($P < 0,00001$) than in 2007 (onion) and 2009 (barley), respectively (Table 4). In July 2007 (onion) we registered a significant decrease in concentration of extractable mineral N ($P < 0,01$) and TN (0,05) after an input of *ca.* 100 kg N ha⁻¹. A combination of ploughing (40 cm) (20th of November 2007) and high rainfall in November 2007 (110 mm) could cause the leaching of NO_3^- down to the lower soil depths. In the first half of 2008 NO_3^- redistribution took place is likely due to soil tillage and fertilizer application as well as possible NO_3^- leaching during heavy rainfall (95 mm) in July 2008. We showed that in the top layer (0-27 cm) NO_3^- concentrations were strongly positively correlated ($P < 0,0001$) with air and soil temperature (to 10 cm depth) ($r = 0,84$ and $0,86$), fertilizer input ($r = 0,80$), amount of precipitation ($r = 0,79$) and soil moisture content to 10 cm depth ($r = 0,64$) but negatively correlation with TOC ($r = -0,76$; $P < 0,0001$).

Table 4.

Soil extractable NH_4^+ , NO_2^- and NO_3^- content, MIN and NITR rates during the crop rotation in the top soil horizon (0 – 74 cm). Data shown are averages (\pm std) of seasonal measurements ($n = 4$), each from 3 composite samples

Variable	2007 onion	2008 tomato	2009 barley
NH_4^+ (kg N ha ⁻¹)	45,5 \pm 21,5	44,3 \pm 26,0	154,9 \pm 41,3
NO_2^- (kg N ha ⁻¹)	0,37 \pm 0,46	0,48 \pm 0,57	0,47 \pm 0,18
NO_3^- (kg N ha ⁻¹)	71,7 \pm 56,8	166,9 \pm 44,5	23,2 \pm 15,6
MIN (kg N ha ⁻¹)	41,0 \pm 57,3	-11,9 \pm 100,2	-57,9 \pm 39,0
NITR (kg N ha ⁻¹)	36,6 \pm 74,4	-19,0 \pm 89,6	14,7 \pm 44,9

MIN and NITR rates varied between years in total and during every season (Table 4, Fig. 6). The highest average MIN was 41,0 \pm 57,3 kg N ha⁻¹ ($P < 0,001$) during onion growth (2007) compared to 2009, when we observed a net consumption of available mineral N forms (Table 4). There were no statistically significant differences regarding NITR during studied period (Table 4). During barley growth, when a large NH_4^+ content was detected in soil samples, the average annual nitrification rate was 14,7 \pm 44,9 kg N ha⁻¹. Seasonal fluctuations were larger ($P < 0,01$) during onion and tomato growth compared to barley growth (Fig. 6). For the years in which onion and tomato were grown, significant largest MIN ($P < 0,05$) and NITR ($P < 0,01$) rates were measured in spring. Deep ploughing (40 cm) in November 2007 appears to stimulate both processes in the three upper soil layers. Differences between layers changed with season and crop, but overall MIN and NITR rates were the largest in the 1st layer (3,6 \pm 34,8 kg N ha⁻¹ and 13,1 \pm 32,9 kg N ha⁻¹ respectively at $P < 0,05$), and the smallest in the 4th layer (-11,6 \pm 31,0 kg N ha⁻¹ and -9,1 \pm 29,8 kg N ha⁻¹ respectively at $P < 0,01$). Significant linear correlations in the top horizon (0-74 cm) were found between MIN and NITR rates ($r = 0,85$; $P < 0,0001$, Fig. 7), MIN and NH_4^+ content ($r = -0,47$; $P < 0,0001$), ammonification and NH_4^+ content ($r = -0,81$; $P < 0,001$), NITR and NO_3^- ($r = -0,39$; $P < 0,0001$).

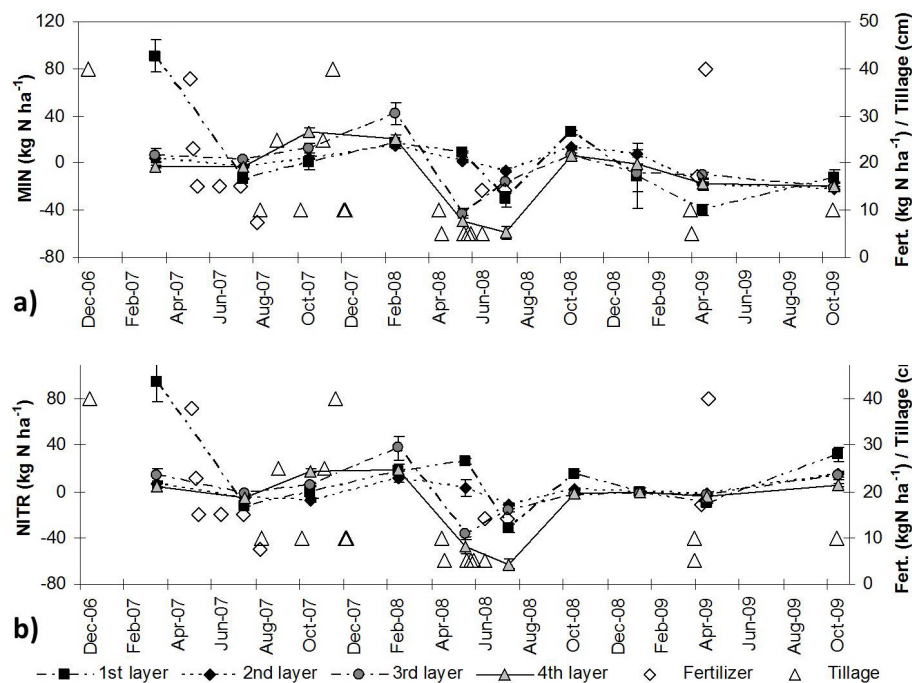


Fig. 6. MIN (a) and NITR rates (b) in the 4 layers of the topsoil horizon (0-27, 27-44, 44-60, 60-74 cm) over a three year crop rotation (2007 onion, 2008 tomato, 2009 barley) in southern part of Ukraine.

The low humus content observed at the study site (3-6% in the surface layer of 30 cm) is typical for southern black soils in the Ukraine and has been decreasing during the last 100 years at an average rate of 0.6% per year [28]. There are various means by which the fertility of such impoverished soils can be improved, *e.g.* reducing tillage intensity, decreasing black fallow periods (soil is ploughed but not planted) [47], stimulating primary productivity by fertilisation and irrigation or changing from monocultures to crop rotations [53]. This study has introduced a 3 year crop rotation with residue incorporation, which successfully increased the total C (by 20%) and N (by 38%) content of the topsoil (0-74 cm) (Fig. 2). For comparison, Duiker and Lai [11] reported a linear relationship between residue application rates and volumetric soil organic C content both for zero till and ploughing for a luvisol in Ohio, and Campbell et al. [10] observed a strong correlation between soil organic C storage and residue C input ($y = 0,44x - 3,2$; where x is the residue C input in $t\ ha^{-1}$; $r^2 = 0,81$ at $P < 0,05$) in black chernozem during 1987-1997 under a wheat monoculture.

Campbell et al. [10], who calculated TOC and TN changes based on element mass per equivalent soil mass method [9, 12] (for 0-15 cm depth they equalized to the sample with the lightest mass of sample ($1478\ t/ha^{-1}$) since they had not sampled beyond 15 cm depth), found that a crop rotation of fallow-wheat, fallow-wheat-wheat,

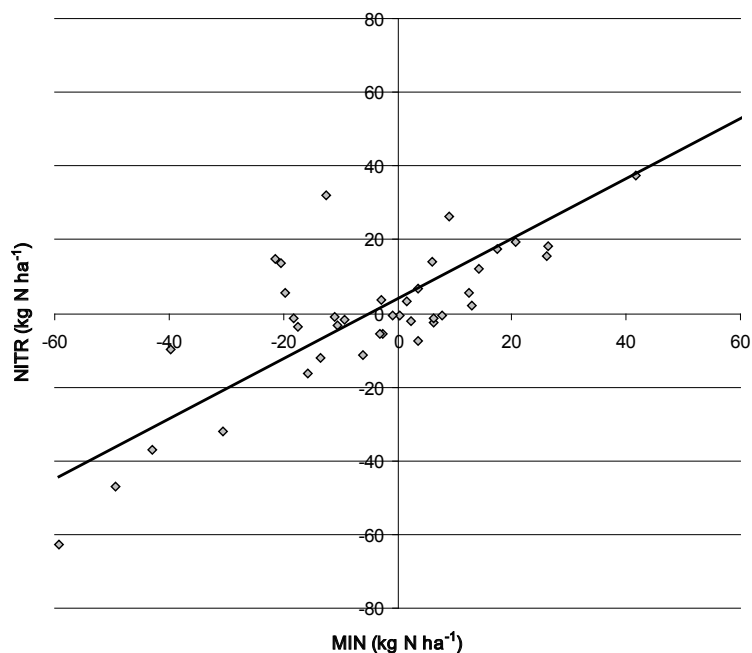


Fig. 7. Correlation between MIN and NITR rates ($r = 0,85$; $P < 0,0001$).

continuous wheat with fertilizer ($N+P$) input increased organic C by 3930, 5210, 1950 kg C ha⁻¹ and total N by 490, 250, 390 kg N ha⁻¹, respectively in the top 0-15 cm soil layer over a 10 year period. For the comparison with our data we assumed that this increase was approximately linear with time and recalculated it for the 3 year period. Also we recalculated our results of the 1st layer by decreasing the depth to 15 cm instead of 27 cm and using the same equalized bulk density (0.99 g/cm⁻³) as Campbell et al. [10] did, to avoid overestimation due to seasonal and inter-annual changes in bulk densities (from 1.1 to 1.6 g/cm⁻³). Such a simple reduction of depth underestimates the real increases of elements in the surface layer, but allows us to make a preliminary comparison of our dataset with the 10 year investigation of black chernozem by Campbell et al. [10]. The recalculated data for our onion-tomato-barley-winter wheat (Dec 2006 – Oct 2009) rotation demonstrated that the absolute increase of TOC ($P < 0,05$) and TN (statistically non-significant; $P < 0,56$) was 594 kg C ha⁻¹ (or 2,0%) and 147 kg N ha⁻¹ (or 4,4%) which was in good agreement with 585-1563 kg C ha⁻¹ (or 1,7-5,2%) and 75-147 kg N ha⁻¹ (or 2,4-5,3%) of the literature data [10], respectively. However, our data showed that for an assessment of soil fertility in arable lands, being regularly deep ploughing, it is necessary to study the entire top horizon to reflect short-term as well as long-term changes. We found that over the three years significant changes ($P < 0,01$) took place even the lowest layer (60-74 cm) although this differed from observations in the upper layer: decreasing

C storage (Fig. 6). The main uncertainty in these estimates appears to be associated with the methodology used to calculate *C* and *N* contents. Including the field measured bulk density in the calculation can overestimate the rate of increase, as agricultural practices can influence the bulk density in surface horizons. For example using heavy machinery and drip irrigation may compact the soil and thereby increases the bulk density, whereas ploughing would have the opposite effect [30]. This study provided evidence of this; during the onion (2007) and tomato (2008) seasons active agricultural machine activity (for chemical treatments), cultivation and drip irrigation increased ($P < 0,001$) the bulk density up to $1,52 \pm 0,02 \text{ g/cm}^3$ in the surface layer and by $1,60 \pm 0,02 \text{ g/cm}^3$ in the bottom layer of the topsoil horizon. Using the standard bulk density estimate would ignore important information of the physical soil condition at the appropriate time of sampling and can be used only for comparison in shallow depth. We consider the most accurate way to present information of the element content (*e. g.* *C* and *N*) is to present the content in whole topsoil profile and can be achieved for deep soils only by accurate bulk density measurements for each genetic/or equal (*e.g.* each 10 cm depth) soil layer. However for comparison with the literature it is necessary to use the conventional approach for shallow soil depth and calculate the *C* and *N* content from its mass per equal depth of soil [9, 12].

In our study the bulk density had a negative correlation with *TOC* ($r = -0,66$; $P < 0,0001$) in the whole topsoil horizon, obviously because the soil organic matter increase leads to an increase in porosity and consequently a decline in bulk density. This has been reported in the literature [4, 54]. The highest bulk density, and also pH, was observed for the tomato crop (2008), which was caused by crop type, active machine activity (inter-row cultivation and frequent pesticide application) and soil moisture (regular drip irrigation and heavy precipitation) during the growing season compared to the other two years considered in this study.

High quality residues and *N* fertilizer were assumed to increase aggregate turnover [20, 39] and interactions between residue and fertilizer inputs can influence physical *SOM* stabilization [14]. Our study showed that the rate of increase in *TOC* and *TN* was not consistent during the study period (December 2006 — October 2009) and depended on crop type and associated with differences in *N* application rate and scheme, agricultural management practice, climatic factors (*e.g.* precipitation and temperature).

The seasonal variations in *TOC* and *TN* contents could be large, for example the *TOC* increased by $39,5 \text{ t C ha}^{-1}$ in the whole topsoil horizon in 2008/2009 autumn/winter period and the *TN* increase over this period was $5,8 \text{ t N ha}^{-1}$ (Fig. 2, Fig. 3) with the bulk density estimates. Campbell et al. [10] proposed following reasons for these variations are 1) site variability or place of sampling (inter-row or row area sample) could contribute to this discrepancy, 2) crop residue (fresh plants and roots) taken in the samples in the autumn were tough and remained on the sieve and thus were discarded, but during the autumn and winter this material could be weathered and/or partially decomposed and thus passed through sieve and be included in the soil sample thereby increasing the measured *TOC* and *TN* content in winter samples.

Application of *N* fertiliser and residue incorporation, ploughing and irrigation influence the rate of microbial decomposition of organic matter to mineral *N* compounds (mineralisation) and the rate of NH_4^+ oxidation to NO_3^- (nitrification). The interdependence of these processes and NH_4^+ and NO_3^- contents were reflected by significant linear correlations in the top horizon (0-74 cm) between *MIN* and *NITR* rates (Fig. 7), ammonification and NH_4^+ content, *NITR* and NO_3^- content.

In arable soils large NH_4^+ and NO_3^- contents are transient. Their fate is incorporation into the plant and microbial biomass, absorption of NH_4^+ into the «humic» and clay structures within the soil [5, 36], gaseous losses as nitric oxide, nitrous oxide and di-nitrogen [8, 37, 40, 41] and for NO_3^- leaching into ground water and/or lower soil horizons [16]. Large concentrations are usually only visible within the first 1 to 2 weeks after fertiliser application or ploughing. In this study soil samples were not always taken immediately after fertilizer application, tillage treatments and residue incorporation; consequently only few examples of transient increases in mineral *N* concentrations were recorded. For example, tillage in April 2008 and tillage and fertilization in April 2009 increased soil available NH_4^+ and NO_3^- concentrations. The steady increase in NH_4^+ content and of *MIN* and *NITR* rates after tomato harvest can be explained by the incorporation of the tomato residue by disking (the *N* content of the above ground biomass was $173 \pm 15 \text{ kg N ha}^{-1}$). Consequently after spring fertilization of the barley crop (57 kg N ha^{-1}), in April 2009, the NH_4^+ content of the 74 cm top horizon was $184,9 \pm 15,4 \text{ kg N ha}^{-1}$ equivalent to a concentration of $19,1 \pm 2,7 \text{ mg N kg}^{-1}$ (Fig. 4a). This was a significant increase ($P < 0,05$) from the average NH_4^+ content calculated for the study period ($81,5 \pm 29,6 \text{ kg N ha}^{-1}$). Our results did not confirm the usual observation that NH_4^+ is nitrified immediately after fertilizer application. For example, Maly et al. [29] showed increased *NITR* rates and increased NO_3^- concentrations during an incubation experiment using arable soils (chernozem, cambisol, fluvisol and luvisol). We did not observe *NITR* increased in April 2009 samples after fertilization event (Fig. 5), but we registered significant increase ($P < 0,001$) of *NITR* ($66,0 \pm 12,2 \text{ kg N ha}^{-1}$ for whole topsoil horizon) later in the October 2009 samples. At the same time total *MIN* was negative ($-74,3 \pm 14,9 \text{ kg N ha}^{-1}$), due to active consumption of NH_4^+ , available in soil ($172,0 \pm 11,2 \text{ kg N ha}^{-1}$) and new produced, by nitrifiers and other soil microorganisms.

In 2007 the onion crop accumulated most of the mineral *N* applied in its bulbs (predominantly in the NO_3^- form). In late summer and autumn sufficient onion bulbs and residue were ploughed into the top 25 cm that is likely to cause a significant increase ($P < 0,00001$) of the NO_3^- content up to $100,6 \pm 6,1 \text{ kg N ha}^{-1}$ in the surface layer (0-27 cm). It was demonstrated that in autumn 2007 deep ploughing (40 cm) followed by heavy precipitation contributed to NO_3^- migration down and accumulation in the lower layers in soil profile; but no significant leaching took place (Fig. 4b). The lack of NO_3^- leaching in this soil was already demonstrated by Umarov's research [48].

In the surface (0-30 cm) layer there was no significant difference between average mineral *N* concentrations of 2007 and 2008. They were approximately $15.8 \pm 6.5 \text{ mg}$

$N\text{ kg}^{-1}$, the same ranges was reported by Wang et al. [52] for a chernozem in a natural steppe. We can conclude that in this period soil condition was sustainable, almost all incorporated and new produced mineralized compounds of mineral N were entirely consumed by plants and soil communities. For 2009 the annual average concentration of inorganic N significantly increased ($P < 0,05$) up to $20,5 \pm 6,0\text{ mgNkg}^{-1}$ mainly due to high ammonium concentration ($17,1 \pm 3,7\text{ mgN kg}^{-1}$). We measured the seasonal interrelationship between MIN and $NITR$ processes in vitro. MIN and $NITR$ rates were significantly higher ($P < 0,05$) in October – March samples (Fig. 6). The microbial community in samples from those periods appears to be under thermal suppression [48] in the soil reach in organic residues, that is why suitable incubation condition gave a push to grow – which was reflected on MIN and $NITR$. That was an evidence of significant role of ammonification in soil enriched with plant residues under conditions of optimal temperature and moisture. Biological N_2 -fixation was not investigated, because rates in an N rich agricultural soil are usually insignificant and less than $0,7\text{-}1,0\text{ kg N ha}^{-1}\text{ month}^{-1}$ in total [20].

We assume that ammonifying and nitrifying activities in summer samples could be lower possibly due to:

1) soil exhaustion during active consumption period of available vital nutrients by onion and tomato, that could cause decreasing microorganisms activity;

2) harmful effect of active use of pesticides (insecticides, fungicides and herbicides) on microbiota [2, 44] especially in summer 2008;

3) contamination of complex fertilizers with fluorine compounds, as the results of insufficient decontamination after superphosphate synthesis by the fertilizers producers. This can affect microbial community [51].

All these suggestions need further detailed investigation.

Conclusions

We stated that moderate ($114\text{ kg N ha}^{-1}\text{ yr}^{-1}$) and low ($28\text{ kg N ha}^{-1}\text{ yr}^{-1}$) N fertilizer applications together with adequate drip irrigation for onion and tomato, respectively, is likely to be well-balanced system for crop production in investigated soil type in southern Ukraine.

We concluded that the strategy of restoration of productivity of southern chernozem black soils by using of plant residues and efficient N fertilizers application within a crop rotation system which was carried out by farmer – holder of investigated field from Association of Agricultural Enterprises “Granit” for three year appeared to be an effective way of both restoration and augmentation of the key features (TOC and TN content) determinative of soil stratum fertility under intensive crop management in the southern part of the Ukraine.

It is evident that right crop rotation management, right plant residue practice, right fertilization and right tillage can significantly increase TOC and TN storage, as a consequence promoting new SOM build-up. Further investigations are needed to better understand the whole picture and find critical gaps.

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ДИНАМІКА ЗМІН ҐРУНТОВОГО ВУГЛЕЦЮ ТА АЗОТУ ВПРОДОВЖ ТРЬОХЛІТНЬОЇ СІВОЗМІНИ В ЧОРНОЗЕМАХ НА ПІВДНІ УКРАЇНИ

Резюме

У данній роботі розглядається вплив сучасного менеджменту, на прикладі сівозміни (цибуля-томат-ячмінь), на динаміку зміни кількості загального органічного вуглецю

та загального азоту в родючому шарі чорноземів південних в 2006-2009 рр. Нами було показано, що внесення поживних залишків та ефективне використання азотних добрив при відповідному сівозміні виявилось ефективним способом стабілізації існуючої органічної речовини ґрунту (ОРГ) та сприяння утворенню нової ОРГ в чорноземах південних.

Ключові слова: азот, вуглець, нітрати, амоній, мінералізація, нітрифікація, органічна речовина ґрунту

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ДИНАМИКА ИЗМЕНЕНИЙ ПОЧВЕННОГО УГЛЕРОДА И АЗОТА НА ПРОТЯЖЕНИЕ ТРЕХЛЕТНЕГО СЕВООБОРОТА В ЧЕРНОЗЕМАХ НА ЮГЕ УКРАИНЫ

Резюме

В данной работе рассматривается влияние современного менеджмента, на примере севооборота (лук-томат-ячмень), на динамику изменения количества общего органического углерода и общего азота в плодородном слое черноземов южных в 2006-2009 гг. Нами показано, что внесение поживных остатков и эффективное использование азотных удобрений при соответствующем севообороте похоже выявилось эффективным способом стабилизации существующего органического вещества почвы (ОВП) и содействия образованию нового ОВП в черноземах южных.

Ключевые слова: азот, углерод, нитраты, аммоний, минерализация, нитрификация, органическое вещество почвы.