Chapter 2
Free, Bounded, and Included in Humic Acids Amino Acids: Thermal Properties of Humic Acids from Cropping Systems

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Abstract Almost all nitrogen in surface soil horizons is in organic form (0–90 %). Nevertheless, the chemical composition of nitrogen in organic soil fraction is not completely understood, and little is known of the factors affecting the distribution of organic nitrogen forms in soils.

The continuous cropping and crop rotation influenced the amino acids and properties of humic acids (HA) in soil; these influenced the crop yields. The results indicated that the composition of bound amino acids depends on cropping system and on the availability of nitrogen, phosphorus, and potassium (NPK) from fertilizers. In the soils under continuous cropping, the NPK fertilizer strongly affected the bound amino acid content than manure 38 % vs. 25%, respectively, while the contents in soils under crop rotation were 41 and 27 %, respectively.

Negative effects of continuous cropping on the content of total bound amino acids were decreased by NPK fertilization, but the manure application in continuous cropping of rye was less effective. Thus, NPK was the main driver causing changes in the total amounts of bound amino acids in HA. Crop yields of rye increase with an increase in organic N in bound amino acids and nitrogen in humic acids.

The humic acids extracted from the soils under crop rotation and fertilized with NPK showed highest aliphatic properties, but the humic acids from soils fertilized with manure were most aromatic. Aromaticities of humic acids from soils under continuous cropping of rye fertilized with manure were higher than from crop rotation fertilized with NPK.

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The evidence gathered suggests strong linkages between the soil and fertilizer and manures' quality affects the productivity. Achieving a balance between the agricultural production and conservation of natural resources is necessary to develop sustainable agricultural systems.

Keywords Free and bunded amino acids • Humic acids • Thermal properties

2.1 Introduction

The individual crop is affected by the cropping system in which it is grown. The ecological conditions are determined by many factors (soil, atmospheric environment, and cropping systems). The diversification of cropping systems leads to higher crop yields by influencing plant diseases, weeds, nutrient availability, and root distribution. Diversified crop rotations alter the pattern and degree of nutrient removal from soil. Increasing the amounts of crop residues to soil increases the soil organic carbon pool and the nutrient availability with time. The nutrient availability increases by reduced tillage including the legumes in crop rotations. The crop rotation influences the nutrient uptake by crops, e.g., phosphorus application to preceding crop increases the activity of vesicular–arbuscular mycorrhiza (VAM), which increases the absorption zone of immobile phosphorus (Honermeier 2007).

Multidisciplinary studies of ecological effects on continuous cereal cropping (*decline effect*—decreased crop yields on fields in which the same plant species has been grown continuously) have shown numerous differences in physical, chemical, and biological composition and biochemical properties of soils under rotations and continuous cropping of rye (Cox 1965; Steineck and Ruckenbauer 1976; Wasilewska 1979; Niewiadomski et al. 1980; Truszkowska et al. 1980; Pimentel and Hall 1984; Ryszkowski 1986; Ketcheson 1980; Myśków et al. 1986; Schönhammer and Fischbeck 1987; Wicke and Urban 1988; Łoginow et al. 1990; Kaszubiak et al. 1990; Ryszkowski et al. 1990, 1998; Ryszkowski and Karg 1990, 1992; Crookston et al. 1991; Sieling and Hanus 1992; Johnston et al. 1992; Garz and Stumpe 1992; Copeland et al. 1993; Szajdak et al. 1998; Blecharczyk 1999) (Table 2.1).

2.2 Continuous Cropping

In soils of long-term continuous cropping vs. crop rotation, the lower diversity in metabolites of microbes and products of plant biomass decay have been determined. These substances can create stress conditions for many organisms, including cultivated plants, which may lead to higher susceptibility to pathogens and pests and impair their growth. Under these conditions, pests (weeds, pathogens, insects) develop leading to the outbreaks of crop pests (Jelinowski and Mróz 1979;

Table 2.1 Chemical properties of soils under crop rotation and continuous cropping of rye fertilized with NPK or with manure

Treatments	$pH_{(1\ M.\ KCl)}$	$C_{(organic)}$	$N_{(total)}$	$P_{\cdot(available)}$	$K_{(available)}$	$Mg_{(available)}$
		mg/100 g				
CR control	5.8	680 ± 31.3	72.7 ± 3.3	7.3 ± 0.3	5.9 ± 0.3	2.3 ± 0.1
CR manure	6.2	1180 ± 54.3	110.7 ± 5.1	15.1 ± 0.7	17.4 ± 0.4	5.7 ± 0.2
CR NPK	5.9	648 ± 29.8	69.6 ± 3.2	10.9 ± 0.5	6.8 ± 0.3	1.9 ± 0.1
CC control	5.7	723 ± 33.2	72.7 ± 3.3	6.0 ± 0.3	3.6 ± 0.2	2.7 ± 0.1
CC manure	6.2	1205 ± 55.4	110.7 ± 5.0	13.2 ± 0.6	14.9 ± 0.7	5.5 ± 0.3
CC NPK	5.8	696 ± 32.0	69.6 ± 3.2	9.9 ± 0.4	9.1 ± 0.4	2.5 ± 0.1

Szajdak et al. (2000)

Where *CR-control* crop rotation – control; *CR-manure* crop rotation fertilized with manure; *CR-NPK* crop rotation fertilized with NPK, *CC-control* continuous cropping of rye – control, *CC-manure* continuous cropping of rye fertilized with manure, *CC-NPK* continuous cropping of rye fertilized with NPK. Where $x \pm \Delta x$ — mean values with their confidence limit Δx at $\alpha = 0.05$

Table 2.2 Total primary production ($g{\cdot}dw{\cdot}m^{-2}$) of rye fields from different crop rotation patterns

Production element	Wielichowo			Jelcz-Laskowice	
	Continuous cropping of rye	Rye after potatoes	Rye after field pea	Continuous cropping of rye	Rye after small beans
Yield: grain	314	489	410	196	307
Straw + rye regrowth	759	794	754	968	1182
Weeds	83	41	51	64	27
Dead shoots + shed leaves	374	262	261	635	497
Roots	160	165	169	172	175
Total	1690	1750	1645	2035	2191
$g{\cdot}dw{\cdot}m^{-2}$	742	708	632	871	700
Input of plant Debris into soil (%)	44	40	38	42	32

Łapiński and Ryszkowski (1986) and Ryszkowski and Bernacki (1990)

Wasilewska 1979; Blake et al. 1980; Durska et al. 1986; Witkowski and Zamszyn 1986; Wicke and Urban 1988; Adamiak and Zawiślak 1990; Shcherba 1994; Ryszkowski et al. 1998) (Tables 2.2 and 2.3).

Besides, the soils' incorporation of plant biomass in continuous cropping of rye affects the soils microorganism communities, which leads to the production of secondary metabolites, e.g., phenolic compounds. The soils under continuous cropping of rye accumulate higher quantity of phenolic acids, phenols, and their combinations with amino acids and amino sugars, which inhibit the seed germination, root growth,

Table 2.3 Biomass (B) of the soil invertebrates ($mg \cdot dw \cdot m^{-2}$) in continuous cropping of rye and in energetic cost of maintenance ($kJ \cdot m^{-2}$) (M)

	Wielichowo (1983–1984)				Jelcz-Laskowice (1986–1989)			
	Continuous cropping of rye		Norfolk rotation[a]		Continuous cropping of rye		Norfolk rotation	
Group	B	M	B	M	B	M	B	M
Protozoa	321.4	845.3	373.1	896.1	548.8	1447.4	708.3	1906.9
Nematoda	252.0	163.8	217.4	147.6	179.3	101.2	180.7	102.0
Enchytraeidae	24.4	11.9	15.6	7.6	–	–	–	–
Lumbricidae	85.7	7.4	200.4	15.6	285.0	22.7	3811.0	296.8
Acarina	4.6	0.89	6.9	0.6	11.4	34.6	20.6	55.6
Collembola	26.0	4.7	41.2	7.9	63.5	95.6	45.4	63.5
Winged insect larvae	394.5	8.0	472.6	17.2	1177.6	76.8	1736.0	91.9
Total	1108.6	1041.9	1327.2	1092.6	2265.6	1808.3	6502.0	2516.7

Karg et al. (1986), (1990) and Witkowski and Zamszyn (1986)

[a]Mean values for rye after potatoes and rye after field pea in Norfolk rotation

Table 2.4 Phenolic acids in soils under continuous cropping of rye and crop rotation after harvest in mg kg[1]

Type of cultivation	Phenolic acids: p-Hydroxy benzoic	Vanillic	p-Coumaric	Syringic	Ferulic	Total amount
Continuous cropping of rye	7.48 ± 0.28	14.24 ± 0.54	5.17 ± 0.20	12.49 ± 0.48	11.49 ± 0.44	50.87
Crop rotation	3.67 ± 0.14	3.77 ± 0.14	0.66 ± 0.03	2.98 ± 0.11	1.62 ± 0.06	12.70

Szajdak and Życzyńska-Bałoniak (1994)
Where $x \pm \Delta x$—mean values with their confidence limit Δx at $\alpha = 0.05$

and development of cultivated plants (Guenzi and McCalla 1966; Bu'Lock 1980; Hruszka 1982; Wójcik-Wojtkowiak et al. 1990; Szajdak and Życzyńska-Bałoniak 1994) (Table 2.4).

All negative effects occur in soil under continuous cropping than in crop rotation, and these decreases the crop yields (Gawrońska-Kulesza 1966; Hageman and Schrader 1979; Gonet and Wegner 1993; Gonet et al. 1993; Blecharczyk and Pudełko 1997) (Table 2.5).

2.2.1 Soil Organic Matter

Organic matter in soils consists of a mixture of plant and animal products in various stages of decomposition and substances synthesized during the breakdown of these compounds (Flaig 1971; Stevenson 1986; Paul and Clark 1989). Soil organic matter or humus consists of two major types of compounds: (i) unhumified substances

Table 2.5 The comparison of crop yields (t/ha) growing continuously and in rotation

Authors	Period of research	Crop rotation	Continuous cropping	Rel. (%)
Winter wheat				
Huet and Boyeldiu (1976)	1971–1975	5.52	4.49	73
Kübler (1977)	1966–1975	4.75	3.25	68
Hanley and Ridgman (1978)	1963–1974	4.07	2.78	68
Kürten and Range (1980)	1971–1978	4.26	2.95	69
Heyn and Brüne (1981)	1965–1981	5.74	4.71	82
Ridgman et al. (1985)	1979–1982	4.57	4.33	95
Schönhammer and Fischbeck (1987)	1970–1984	5.04	4.03	80
Claupein and Zoschke (1987)	1971–1985	5.13	4.49	88
Feinstkorn and Kreuz (1988)	1977–1986	6.80	5.68	84
Wicke and Urban (1988)	1976–1985	6.86	5.50	80
Zawiślak et al. (1991)	1963–1989	4.52	3.26	72
Panse et al. (1994)	1980–1992	6.91	6.06	88
Winter barley				
Kürten and Range (1980)	1971–1978	4.84	4.99	103
Buss and Zoschke (1984)	1975–1981	5.84	4.11	70
Wicke and Urban (1988)	1976–1985	6.92	6.19	89
Baltruschat and Dehne (1989)	1971–1982	4.94	5.19	104
Christen and Sieling (1993)	1987–1991	7.60	7.29	96
Panse et al. (1994)	1980–1992	5.43	5.35	99
Winter rye				
Steinbeck and Ruckenbauer (1976)	1960–1975	3.17	2.77	87
Schönhammer and Fischbeck (1987)	1970–1984	4.70	4.21	90
Wicke and Urban (1988)	1976–1985	6.25	5.62	90
Mercik (1989)	1976–1986	4.20	3.73	89
Zawiślak et al. (1991)	1957–1989	4.19	3.45	82
Garz and Stumpe (1992)	1962–1988	4.17	2.94	71
Panse et al. (1994)	1980–1992	6.85	6.75	99
Blecharczyk and Skrzypczak (1994)	1986–1992	6.23	5.76	92
Spring barley				
Johnston and Mattingly (1976)	1970–1975	5.68	5.45	96
Kübler (1977)	1966–1975	4.25	3.55	84
Schönhammer and Fischbeck (1987)	1970–1984	4.09	3.81	93
Krejĉir (1987)	1973–1983	5.93	5.14	87
Feistkorn and Kreuz (1988)	1977–1986	6.40	5.80	91
Wicke and Urban (1988)	1976–1985	4.26	3.62	85
Zawiślak et al. (1991)	1957–1989	4.63	3.63	78
Rous (1992)	1986–1990	6.24	6.22	100
Blecharczyk et al. (1995)	1957–1992	3.86	3.14	81

Blecharczyk and Pudełko (1997)

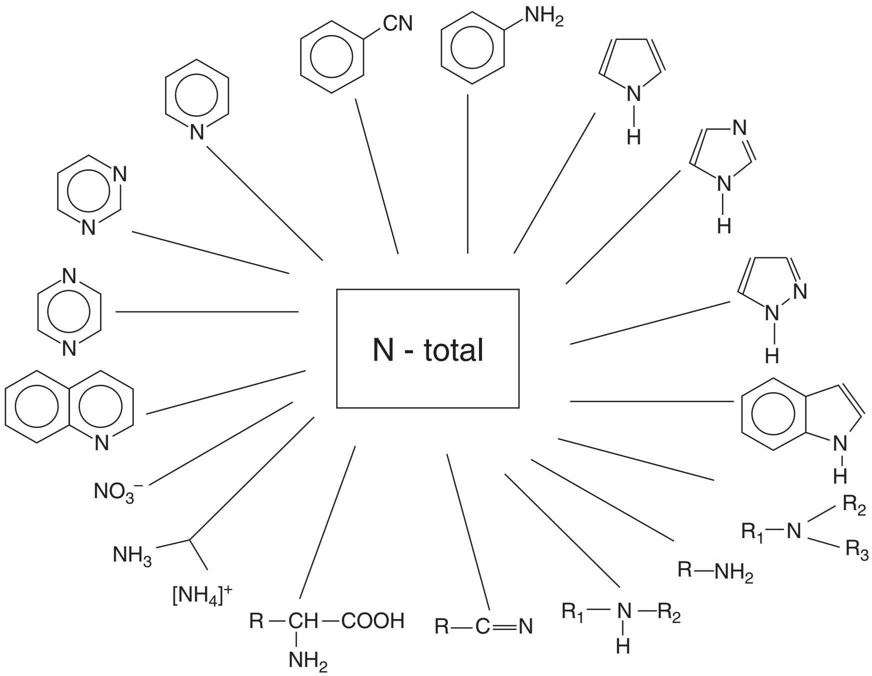

Fig. 2.1 N-derivatives of soil organic matter included in total nitrogen (Schulten and Schnitzer 1998; completed by Szajdak and Życzyńska-Bałoniak 2002)

(ii) and humified remains of plant and animal tissues, which effects on the availability of nutrients for plant growth (Stevenson 1986; Jones et al. 2008).

Almost all nitrogen in surface soil horizons is in organic form (0–90 %) (Fig. 2.1). Nevertheless, the chemical composition of nitrogen in organic soil fraction is not completely understood, and little is known about the factors affecting the distribution of organic nitrogen forms in soils.

Crop rotations, fertilization, and microbiological activity affect the nitrogen levels in soils (Stevenson 1985; Campbell et al. 1991; Szajdak and Österberg 1996; Szajdak and Sokolov 1997; Szajdak et al. 2003).

Humus is composed from 20–60 % of humic acids (HA). The nitrogen (20–40 %) in HA consists of amino acids or peptides, the main unit of protein, which are connected to the central core by hydrogen bonds (Harworth 1971). Amino acids influence the plant growth and thus organic matter increases the soil productivity (Szajdak and Österberg 1996; Szajdak et al. 2003). Amino acids are amphoteric due to the presence of both carboxyl and amino groups in their molecules. Little is known about the variation in amino acid contents in HA in soil under long-time cultivation or with different fertilizer treatments (NPK or manure).

The availability of different forms of nitrogen in soil influences the net primary productivity and vegetation succession gradients in soils (Trojanowski 1973; Vance and Chapin 2001; Jones and Kielland 2002). The cycling of diverse N-containing substances in agriculture soils is still poor. In addition, the relative contribution and function of dissolved organic and inorganic nitrogen compounds in plants and microbial nutrition remains controversial (Owen and Jones 2001; Schimel and Bennett 2004). Some plants are capable of bypassing the mineralization process of nitrogen cycle by directly taking up low molecular weight compounds (up to 1000 Da, viz., amino acids, amino sugars, amines, alkaloids, amides, peptides, etc.). These substances are microbially changed into NH_4^+ and NO_3^- (Chapin et al. 1993; Kielland 1994; Jones et al. 2005a, b; Kielland et al. 2006; Hill et al. 2011).

The size of amino acid pools in soil is small (1–50 μM), but the flux from this pool is very fast (Kielland 1995; Jones and Kielland 2002; Jones et al. 2009). The half-life of amino acid pool in soil is 1–6 h, indicating that free amino acid pool turns over hundreds of times annually in soils (Kielland et al. 2007). Thus, the impact of this quick cycling through the low molecular weight compounds to NH_4^+ and NO_3^- formation remains largely unknown. From the amino acids, there is a very quick formation and excretion of NH_4^+ into the soil with the release of CO_2 (Jones and Kielland 2002). Therefore, they postulated that the soil microbial community might be using free amino acids not as a source of nitrogen but as source of energy. Besides, they (Jones et al. 2005b, 2009) postulated that catabolism and anabolism simultaneously used the 30–40 % of amino acids in respiration and the remaining in cell biomass formation.

The continuous cropping and crop rotation influenced the amino acids and properties of humic acids in soil; these influenced the crop yields. The surface soil condition strongly influenced the qualitative and quantitative forms of amino acids in soil. The adoption of modern, industrialized agricultural production systems has caused degradation of soils (i.e., loss of soil biodiversity, poor soil tilth and imbalanced elemental composition). Environmental consequences of agricultural industrialization were not immediately apparent, but are now being recognized due to (1) fossil-fuel-based mechanization leading to soil erosion in vast areas, (2) animal rearing polluting the nearby water resources with excessive fecal-borne pathogens and nutrient loads, and (3) liberal use of pesticides and fertilizer application having threatened the soil and water quality (Franzluebbers 2008).

2.2.2 Amino Acids

There are three soil quality indicators: (i) chemical, (ii) physical, and (iii) biological. In each of these classes, many soil properties or processes can be selected to indicate soil functional capabilities. Root exudates release considerable amounts of organic substances in soil including the amino acids (Vancura 1967; Claudius and Merhotka 1973; Smyth 1976). In soils, amino acids are formed during the decomposition of plant biomass and from the transamination of keto acids. Despite the high input of amino acids into the soil, their actual concentrations are low because microbes rapidly degrade them. Most of the amino acids in soils occur in bound form in humin–peptide fraction. The binding of amino acids and peptides to humic

Table 2.6 Free amino acids in soil under Norfolk crop rotation in μg·kg^{-1}

Amino acids	Date				
	March 9	May 3	May 30	July 5	August 8
Cysteic acid	255.3 ± 9.7	343.9 ± 13.1	110.5 ± 4.2	125.0 ± 4.8	61.1 ± 2.3
Taurine	67.3 ± 2.6	86.2 ± 3.3	30.3 ± 1.2	55.2 ± 2.1	2.4 ± 0.9
Proline	29.6 ± 1.1	33.0 ± 1.3	–	62.9 ± 2.4	13.8 ± 0.5
Alanine	37.8 ± 1.4	42.4 ± 1.6	14.5 ± 0.6	26.9 ± 1.0	20.8 ± 0.8
Citrulline	202.2 ± 7.6	276.2 ± 10.5	88.9 ± 3.4	171.6 ± 6.5	120.4 ± 4.6
Valine	–	68.9 ± 2.6	13.4 ± 0.5	30.0 ± 1.1	20.0 ± 0.8
Cysteine	59.1 ± 2.3	10.8 ± 0.4	–	–	9.7 ± 0.4
Methionine	15.1 ± 0.6	3.6 ± 0.1	–	3.7 ± 0.1	7.4 ± 0.3
Leucine	7.5 ± 0.3	135.8 ± 5.2	14.7 ± 0.6	53.0 ± 2.0	42.1 ± 1.6
Tyrosine	46.7 ± 1.8	35.3 ± 1.3	24.4 ± 0.9	22.6 ± 0.9	5.9 ± 0.2
Phenylalanine	88.1 ± 3.4	139.1 ± 5.3	39.3 ± 1.5	41.2 ± 1.6	25.0 ± 1.0
β-Alanine	39.3 ± 1.5	45.4 ± 1.7	16.2 ± 0.6	–	–
γ-Aminobutyric acid	9.5 ± 0.4	45.9 ± 1.7	17.2 ± 0.7	70.3 ± 2.7	25.4 ± 1.0
Arginine	–	–	–	–	5.6 ± 0.2
Cystathionine	31.3 ± 1.2	38.8 ± 1.5	7.9 ± 0.3	3.7 ± 0.1	3.4 ± 0.1
Glycine	11.8 ± 0.5	13.2 ± 0.5	6.3 ± 0.2	8.1 ± 0.3	11.2 ± 0.4
Total amount	900.6	1318.5	383.6	674.2	396.7

Życzyńska-Bałoniak and Szajdak (1992)
Where $x \pm \Delta x$—mean values with their confidence limit Δx at $\alpha = 0.05$

acids protects them from rapid degradation (Bremner 1967; Sörensen 1967). In soils under crop rotation, the mean concentration of total free amino acids was 796.0.7 μg kg^{-1} and was 734.7 μg kg^{-1} under continuous cropping of rye (Życzyńska-Bałoniak and Szajdak 1992). There is great variability in free forms of amino acids than bound ones (Tables 2.6, 2.7, 2.8, and 2.9); there are higher turnover rates in crop rotation than in continuous rye cropping.

In 1957, experiments were started on podzolic soil where similar agricultural practices were used, viz. plowing before sowing, sowing, harvesting, and plowing first followed by harrowing. Pesticides were not used in these rotations. The treatments were (i) continuous cropping of rye and (ii) 7-year crop rotation (potato, spring barley, alfalfa, oil seed rape, winter rye, and winter rye). There were three fertilizer treatments: (i) control (soils without any fertilizers), (ii) NPK (N-nitrogen 90 kg/ha, P_2O_5 60 kg/ha, K_2O 120 kg/ha), and (iii) manure (30 t/ha). The experimental field soils were coarse sand (organic carbon: 0.83 %) (Swift 1996). Investigations were made in the 49th year of cultivation. Winter rye had been grown continuously since 1957. The soil pH was 6.02 under continuous cropping of rye and 6.27 under crop rotation. In soil having fertilizer with NPK and fertilizer with manure, the carbon content was 648–796 mg/hg and 1180–1205 mg/hg, and the nitrogen content was 69.7–72.7 mg/hg and 110.7 mg/hg, respectively. The rye culture was fertilized with 270 kg/ha NPK (nitrogen 90 kg/ha, phosphorus 60 kg/ha, and potassium 120 kg/ha).

Table 2.7 Free amino acids in soil under continuous cropping of rye in μg·kg^{-1}

Amino acids	Date				
	March 9	May 3	May 30	July 5	August 8
Cysteic acid	268.1 ± 10.2	395.2 ± 15.0	123.1 ± 4.7	84.2 ± 3.2	106.7 ± 4.1
Taurine	72.8 ± 2.8	108.2 ± 4.1	35.2 ± 1.3	40.4 ± 1.5	45.6 ± 1.7
Proline	212.9 ± 8.1	45.3 ± 1.7	–	71.4 ± 2.8	28.8 ± 1.1
Alanine	30.9 ± 1.2	56.6 ± 2.2	16.2 ± 0.6	18.6 ± 0.7	22.8 ± 0.9
Citrulline	151.0 ± 5.7	374.9 ± 14.3	91.1 ± 3.5	107.5 ± 4.1	143.7 ± 5.5
Valine	–	90.4 ± 3.4	17.1 ± 0.7	28.9 ± 1.1	28.5 ± 1.1
Cysteine	51.0 ± 1.9	5.5 ± 0.2	–	–	3.8 ± 0.1
Methionine	14.1 ± 0.5	4.0 ± 0.2	–	3.0 ± 0.1	5.1 ± 0.1
Leucine	55.6 ± 2.1	164.2 ± 6.2	8.2 ± 0.3	38.0 ± 1.4	49.1 ± 1.9
Tyrosine	44.6 ± 1.7	69.4 ± 2.6	20.2 ± 0.8	21.9 ± 0.8	8.1 ± 0.3
Phenylalanine	65.7 ± 2.5	131.8 ± 5.0	32.7 ± 1.3	39.1 ± 1.5	34.1 ± 1.3
β-Alanine	11.4 ± 0.4	13.2 ± 0.5	–	9.4 ± 0.4	–
γ-Aminobutyric acid	5.9 ± 0.2	40.0 ± 1.5	18.1 ± 0.7	26.5 ± 1.0	2.1 ± 0.1
Cystathionine	26.3 ± 1.0	51.8 ± 2.0	8.2 ± 0.3	–	15.8 ± 0.6
Glycine	24.7 ± 0.9	18.8 ± 0.7	4.9 ± 0.2	7.8 ± 0.3	10.0 ± 0.4
Total amount	1035.0	1569.	347.9	496.7	504.2

Życzyńska-Bałoniak and Szajdak (1992)
Where $x \pm \Delta x$—mean values with their confidence limit at $\alpha = 0.05$

Proline The dominating amino acids in both cropping types were cysteic acid, citrulline, proline, phenylalanine, and taurine. In soils under continuous cropping of rye, the proline concentration was 14–109 % higher than in crop rotation (Tables 2.6 and 2.7). An accumulation of proline under continuous cropping system was reported by Życzyńska-Bałoniak et al. (1986). The accumulation of proline under continuous cropping of rye conditions may be due to its heterocyclic amino acid structure, which could be more resistant to microbial degradation than other amino acids. The accumulation of proline in soils is considered as negative effect. This amino acid is a secondary amine; in the presence of nitrites, proline may form the N-nitrosamines (Fig. 2.2). Proline is a potent toxin, with carcinogenic and mutagenic effects (Pla 1980; Kofoed et al. 1981; Von Hofe et al. 1987; Larsson et al. 1990; Pesci 1992).

Citrulline High concentrations of citrulline were found in soils of both cropping systems. Citrulline is an amino acid, which does not occur in proteins but is an intermediate of the urea cycle. It is a basic, diamine monocarboxylic acid and is readily available source of nitrogen for plants and microorganisms.

β-Alanine The β-alanine content was higher in soils under continuous cropping of rye than in crop rotation. In soil samples taken from fields under crop rotation in March and at the beginning of May, the β-alanine content was threefolds higher than under continuous cropping of rye. Since β-alanine is a constituent of bacterial cell walls, the higher concentration of this amino acid in soils under crop rotation indi-

Table 2.8 Bound amino acids in soil under crop rotation in mg·kg^{-1}

	Date				
Amino acids	Marc 9	May 3	May 30	July 5	August 8
Cysteic acid	9.80 ± 0.40	13.82 ± 0.52	17.92 ± 0.68	1.12 ± 0.04	13.47 ± 0.51
Taurine	1.20 ± 0.05	4.49 ± 0.17	5.52 ± 0.20	2.46 ± 0.09	4.11 ± 0.16
Proline	3.20 ± 0.12	5.09 ± 0.19	2.25 ± 0.09	10.68 ± 0.41	7.03 ± 0.27
Glycine	0.90 ± 0.03	1.79 ± 0.06	3.71 ± 0.14	38.11 ± 1.45	4.98 ± 0.18
Alanine	34.52 ± 1.31	71.03 ± 2.70	77.84 ± 2.95	67.27 ± 2.60	15.88 ± 0.60
Citrulline	34.52 ± 1.31	114.20 ± 4.33	111.55 ± 4.23	94.16 ± 3.58	127.55 ± 4.85
Methionine	0.76 ± 0.03	2.72 ± 0.1	1.66 ± 0.06	1.25 ± 0.05	2.13 ± 0.08
Valine	10.75 ± 0.04	16.86 ± 0.64	19.49 ± 0.74	14.45 ± 0.55	15.34 ± 0.58
Phenylalanine	4.72 ± 0.18	7.54 ± 0.29	4.63 ± 0.17	5.72 ± 0.22	7.06 ± 0.27
Cysteine	24.38 ± 0.93	33.69 ± 1.28	41.42 ± 1.57	28.26 ± 1.07	31.37 ± 1.19
β-Alanine	2.28 ± 0.09	12.24 ± 0.47	21.42 ± 0.81	3.94 ± 1.15	4.18 ± 0.16
Cystathionine	8.69 ± 0.33	13.03 ± 0.49	6.20 ± 0.23	7.06 ± 0.27	3.25 ± 0.12
β-Aminobutyric acid	–	7.88 ± 0.29	7.72 ± 0.29	4.99 ± 0.19	1.23 ± 0.05
Leucine	33.31 ± 1.31	69.05 ± 2.62	67.92 ± 2.60	60.04 ± 2.28	58.04 ± 2.21
γ-Aminobutyric acid	4.15 ± 0.16	5.89 ± 0.22	7.84 ± 0.29	6.30 ± 0.23	5.72 ± 0.22
Ornithine	10.60 ± 0.40	13.69 ± 0.52	19.51 ± 0.74	11.01 ± 0.41	11.80 ± 0.45
Lysine	30.58 ± 1.16	39.84 ± 1.51	49.65 ± 1.88	33.82 ± 1.29	42.58 ± 1.62
Histidine	14.25 ± 0.54	20.41 ± 0.78	21.41 ± 0.81	15.05 ± 0.57	15.17 ± 0.58
1-Methylhistidine	6.25 ± 0.23	5.27 ± 0.20	14.29 ± 0.54	6.18 ± 0.23	8.15 ± 0.31
3-Methylhistidine	–	3.19 ± 0.12	3.87 ± 0.15	8.21 ± 0.31	2.88 ± 0.11
Arginine	15.06 ± 0.57	21.48 ± 0.82	4.12 ± 0.16	18.84 ± 0.72	20.20 ± 0.76
Total amount	249.92	483.2	509.94	438.91	402.11

Życzyńska-Bałoniak and Szajdak (1993)
Where $x \pm \Delta x$—mean values with their confidence limit Δx at $\alpha = 0.05$

cates a higher bacterial biomass in these soils. This result supports the findings of other researchers, showing that in soils under diversified cropping patterns, bacterial biomass increases (Stevenson 1972; Durska and Kaszubiak 1980). Analyzing the amino acid composition in the soils for sulfuric, basic, aromatic, and neutral groups, it was found in sulfur groups, which were most abundant. The concentrations of sulfuric amino acids during plant growth period (except the harvest) were higher in soils under continuous cropping of rye than under crop rotation. Their increased concentrations indicate that soils under continuous cropping of rye were becoming acidic due to biochemical processes originating in this system of cultivation (Życzyńska-Bałoniak and Szajdak 1992).

Bound Amino Acids From the soil samples, the content of bound amino acids was determined after extraction of free amino acids. The mean content of bound amino acids in soils was 416.8 mg kg^{-1}, under crop rotation, and 371.1 mg kg^{-1} in soils under continuous cropping of rye (Tables 2.8 and 2.9).

Table 2.9 Bound amino acids in soil under continuous cropping of rye in mg·kg^{-1}

	Date				
Amino acids	March 9	May 3	May 30	July 5	August 8
Cysteic acid	12.48 ± 0.47	14,06 ± 0.53	11.76 ± 0.45	14.29 ± 0.29	18.27 ± 0.69
Taurine	2.50 ± 0.10	4.89 ± 0.19	6.40 ± 0.24	1.45 ± 0.06	5.36 ± 0.20
Proline	7.50 ± 0.29	9.08 ± 0.35	9.16 ± 0.35	6.57 ± 0.25	20.77 ± 0.79
Glycine	2.95 ± 0.11	4,20 ± 0.16	3.20 ± 0.12	40.19 ± 1.52	2.32 ± 0.09
Alanine	28.15 ± 1.07	69.48 ± 2.64	53.11 ± 2.02	57.48 ± 2.18	10.46 ± 0.40
Citrulline	25.20 ± 0.96	102.19 ± 3.9	76.98 ± 2.92	93.67 ± 3.57	86.50 ± 3.29
Methionine	0.98 ± 0.04	–	1.20 ± 0.05	1.63 ± 0.06	0.53 ± 0.02
Valine	10.04 ± 0.38	16.18 ± 0.61	12.74 ± 0.48	14.57 ± 0.55	16.49 ± 0.63
Phenylalanine	3.80 ± 0.14	5,26 ± 0.20	3.79 ± 0.14	3.62 ± 0.14	3.65 ± 0.13
Cysteine	40.63 ± 1.54	39.78 ± 1.51	24.29 ± 0.92	28.08 ± 1.07	31.25 ± 11.18
β-Alanine	1.74 ± 0.07	2.12 ± 0.08	2.88 ± 0.10	3.85 ± 0.15	3.48 ± 0.13
Cystathionine	5.95 ± 0.23	12.12 ± 0.46	4.64 ± 0.18	8.01 ± 0.30	6.29 ± 0.22
β-Aminobutyric acid	3.88 ± 0.15	6.43 ± 0.24	6.40 ± 0.24	1.72 ± 0.07	2.20 ± 0.08
Leucine	56.33 ± 2.14	67.31 ± 2.56	31.67 ± 1.20	53.98 ± 2.05	42.65 ± 1.62
γ-Aminobutyric acid	6.63 ± 0.25	7.97 ± 0.30	1.57 ± 0.06	6.40 ± 0.24	5.97 ± 0.23
Ornithine	13.96 ± 0.53	10.12 ± 0.38	11.27 ± 0.43	13.70 ± 0.52	12.63 ± 0.48
Lysine	39.28 ± 1.49	28.62 ± 1.09	28.84 ± 1.10	30.44 ± 1.17	36.56 ± 1.39
Histidine	19.13 ± 0.72	18.46 ± 0.70	12.78 ± 0.49	13.10 ± 0.50	17.64 ± 0.67
1-Methylhistidine	10.90 ± 0.40	1.83 ± 0.07	10.21 ± 0.38	9.53 ± 0.36	13.13 ± 0.50
3-Methylhistidine	3.40 ± 0.12	3.50 ± 0.13	8.92 ± 0.34	9.17 ± 0.35	11.54 ± 0.43
Arginine	18.49 ± 0.70	16.20 ± 0.62	15.20 ± 0.58	16.71 ± 0.63	18.64 ± 0.71
Total amount	313.92	439.8	337.01	428.16	366.33

Życzyńska-Bałoniak and Szajdak (1993)
Where $x \pm \Delta x$—mean values with their confidence limit Δx at $\alpha = 0.05$

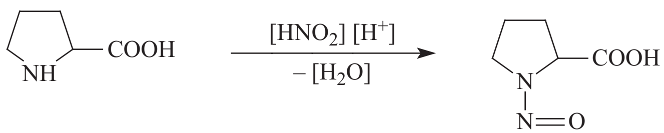

Fig. 2.2 Formation of N-nitrosoproline from proline

The most noticeable differences in the amount of bound amino acid present in the soils occurred during the period of intensive plant growth, i.e., in May. At this time, the concentration of bound amino acids in soils under crop rotation was 51 % higher than in soil samples from continuous cropping of rye. Predominantly bound amino acids in the two systems of cultivation were citrulline, cysteine, alanine lysine, and leucine. The citrulline concentration (20 %) was always higher in soils under crop rotation over the continuous rye cropping soil. Therefore, soils under continuous cropping of rye showed lower nitrogen biological storage capacity,

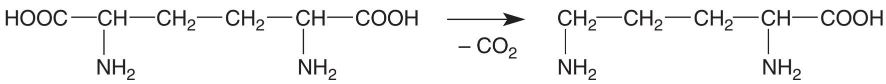

Fig. 2.3 Decarboxylation of α, ε-diaminopimelic acid with the creation of lysine

which is easily available to microbe and plant forms (citrulline). However, analyses of free amino acids did not show differences in citrulline concentrations between soils under continuous and crop rotation. The rates of formation of this amino acid (rates of biochemical processes) are similar in both cropping systems. But lower concentrations of bound forms of citrulline in soils under continuous cropping of rye indicated that catabolic processes (decomposition rates) exceeded the anabolic ones for this amino acid in this cropping system.

Like the free proline, the content of bound proline was considerably higher (200 %) in soils under continuous cropping of rye than in soils under crop rotation (Tables 2.8 and 2.9). The opposite is true for β-alanine. In soils under rotation, the β-alanine concentrations were about 300 % higher than in soils under continuous cropping of rye. The 20 % higher content of bound lysine in soils under crop rotation showed intensive microbiological activity in these soils. Lysine is formed by decarboxylation of α,ε-diaminopimelic acid (Fig. 2.3).

β-Alanine is a constituent of bacterial cell walls (Stevenson 1972; Durska and Kaszubiak 1980). The highest concentrations (49.7 mg kg^{-1}) of bound lysine were found during the intensive growth period of cereals (in May). This concentration was 70 % higher than in soils under continuous cropping of rye (Tables 2.8 and 2.9). The same observation holds true for β-alanine, which is also present in highest concentrations during the intensive growth period of plant. Thus, higher activity of bacteria could be indicated during the intensive growth of plant under crop rotation conditions. Contrarily, the sulfur containing amino acids showed the lowest and neutral amino acids the highest concentrations in bound amino acids in both types of soils (under continuous cropping of rye and under crop rotation). The low concentrations of basic amino acids could be explained due to their high capacity of reacting with reducing sugars and quinones (Holtzlaw et al. 1980).

The quantitative composition of free and bound amino acids in soil depends on the type of cropping. Soils under crop rotation contained higher amount of bound amino acids. The high concentration of some amino acids in crop rotation indicates that these soils are rich in bacterial biomass than soils under monoculture (single plant species cultivated) for years.

Dynamic soil properties are those properties that can change over short time periods (e.g., months, years, and decades) and are used in soil quality assessment because they change quickly with management. They can indicate whether a farm uses agronomically and ecologically sustainable practices. Changes in soil properties with time are a key component of dynamic soil quality assessment. Sustainable cropping systems will improve the soil quality, often through diverse crop rotations, minimal use of tillage for weed control and seedbed preparation, and addition of organic amendments (animal manures, crop residues, and compost). Management systems which decreased the soil quality indicators with time will lead to low soil quality, often induced by cropping systems with low residue production, intensive tillage, and near monoculture cultivation (Franzluebbers 2008).

2.2.3 Amino Acids in Humic Acids

Organic matter in soils consists of a mixture of plant and animal products in various stages of decomposition and substances synthesized during the breakdown of these compounds (Bremner 1967; Flaig 1971; Stevenson 1986; Szajdak and Matuszewska 2000), which may affect the availability of nutrients for plant growth (Stevenson 1986). All nitrogen in surface soil horizons is in organic form. The chemical composition of nitrogen in the organic soil fraction is not understood; little is known about the factors affecting the distribution of organic nitrogen forms in soils. Crop rotations, fertilization, and microbiological activity affect the nitrogen levels in soils (Szajdak and Sokolov 1997; Szajdak and Österberg 1996). Humus is composed of 20–60 % humic acids (HA), and 20–40 % nitrogen in HA consists of amino acids or peptides connected to the central core by hydrogen bonds (Harworth 1971). Little is known about the variability in content of amino acids in HA, in soil under long-time cultivation or applied different fertilization (NPK or manure).

The pH of control soils and under continuous cropping of rye ranged from 5.7 to 5.9 (Table 2.10). The fertilization with NPK or manure decreased the soil acidity to pH 6.2. The organic carbon content in control soils and fertilized with manure ranged from 6.48 to 6.96 and 11.8 to 12.05 g·kg^{-1}, respectively. The nitrogen content in control soil and fertilized with NPK or manure was from 6.97 to 7.27 and 11.07 g·kg^{-1}, respectively (Ryszkowski et al. 1998).

Humic Acids This investigation revealed that total acidity of HA extracted from soils under continuous cropping of rye in control and fertilized with manure was lower than acidity in HA from crop rotation (Table 2.10).

The total acidity of HA from crop rotation was 6.36–10.02 meq·g^{-1} of HA and was from 7.07 to 9.92 meq·g^{-1} of HA for continuous cropping of rye (Table 2.11). The highest total acidity (10.02 meq/g of HA) was observed in HA extracted from crop rotation fertilized with manure, while the lowest total acidity of HA was from crop rotation fertilized with NPK (6.36 meq/g of HA). The HA extracted from soils under crop rotation contained the highest content of phenolic groups (6.46 meq/g of HA).

The total amounts of bound amino acids in all samples of HA from soil under crop rotation were significantly higher than from soils under continuous cropping of rye (Table 2.3). The total amount of bound amino acids was highest (3093.2 mg·kg^{-1}) in crop rotation fertilized with NPK. This was 18 % higher than in HA from soils under continuous cropping of rye fertilized with NPK (2541.4 mg·kg^{-1}) and the lowest of 1888.7 mg·kg^{-1} for the controls under crop rotation (Table 2.12).

Table 2.10 Chemical properties of soils under crop rotation and under continuous cropping of rye, fertilized with NPK, manure or nonfertilized (control) and ash content in HA

Treatment	$pH_{(1\ M\ KCl)}$	$C_{(organic)}$ [g·kg^{-1}]	$N_{(total)}$	HA Ash content [%]
Crop rotation control	5.8 ± 0.2	6.80 ± 0.2	0.727 ± 0.03	8.5
Crop rotation manure	6.2 ± 0.1	11.80 ± 0.4	1.107 ± 0.04	5.6
Crop rotation NPK	5.9 ± 0.2	6.48 ± 0.2	0.696 ± 0.02	7.9
Continuous cropping of rye control	5.7 ± 0.2	7.23 ± 0.3	0.727 ± 0.03	9.0
Continuous cropping of rye manure	6.2 ± 0.3	12.05 ± 0.4	1.107 ± 0.04	5.1
Continuous cropping of rye NPK	5.8 ± 0.2	6.96 ± 0.2	0.696 ± 0.02	7.5

Szajdak et al. (2004)
Control, no NPK or manure, manure 30 t/ha/year; NPK, 90 kg N, 60 kg P_2O_5, 120 kg K_2O/ha/year

Table 2.11 Functional group analysis of HA from soils under crop rotation and under continuous cropping of rye, fertilized with NPK, manure, or nonfertilized (control)

Treatment	Total acidity [meq·g^{-1} of HA]	Phenolic OH groups [meq·g^{-1} of HA]	Carboxylic COOH groups [meq·g^{-1} of HA]
Crop rotation control	7.49 ± 0.3	5.40 ± 0.2	2.09 ± 0.1
Crop rotation manure	10.02 ± 0.4	6.46 ± 0.3	3.56 ± 0.1
Crop rotation NPK	6.36 ± 0.2	4.85 ± 0.2	1.51 ± 0.1
Continuous cropping of rye control	7.42 ± 0.3	4.96 ± 0.2	2.46 ± 0.1
Continuous cropping of rye manure	9.92 ± 0.4	6.06 ± 0.2	3.86 ± 0.2
Continuous cropping of rye NPK	7.07 ± 0.3	4.89 ± 0.2	2.18 ± 0.1

Szajdak et al. (2004)
Control, no NPK or manure, manure 30 t/ha/year; NPK, 90 kg N, 60 kg P_2O_5, 120 kg K_2O/ha/year, meq: milliequivalent

In the soils under continuous cropping, the NPK fertilizer strongly affected the bound amino acid content than manure 38 % vs. 25 %, respectively, while the contents in soils under crop rotation were 41 and 27 %, respectively. Neutral amino acids were in highest proportion (57–69 %) of the total amino acids. The lowest concentrations of basic amino acids (11–19 %) were due to their capacity to react with reducing sugars and quinones. The acidic net charge was smaller (20–27 %) in all samples and was strongest in soils fertilized with manure. The total acidity was higher for HA extracted from soils under crop rotation and continuous cropping of rye and fertilized with manure. The latter was accompanied by correspondingly higher -COOH and phenolic -OH concentration. HA extracted from these soils also contained phenolic groups (19 %) and more carboxylic groups (44 %) than from those soils fertilized with NPK (Table 2.12). This is owing to the concentrations of lignin in manure. During the lignin degradation, components containing benzene rings (factor of aromaticity), carboxyl and hydroxyl, aldehyde, and methoxyl groups are formed (Shu-Yen et al. 1985; Szajdak and Życzyńska-Bałoniak 1994), which

Table 2.12 Mean concentration ($mg \cdot kg^{-1}$ of dry mass of HA ± 95 % confidence interval) of bound amino acids in HA from soils under crop rotation and under continuous cropping of rye, fertilized with NPK, manure, or nonfertilized (control)

Amino acids	Type of cultivation					
	Continuous cropping of rye, control	Crop rotation, control	Continuous cropping of rye, NPK	Crop rotation, NPK	Continuous cropping of rye, manure	Crop rotation, manure
Acidic						
Cysteic acid	34.1 ± 1.3	11.8 ± 0.5	111.5 ± 4.2	98.6 ± 3.7	15.1 ± 0.6	49.5 ± 1.9
Taurine	9.8 ± 0.4	9.1 ± 0.4	23.8 ± 0.9	15.6 ± 0.6	8.9 ± 0.3	20.3 ± 0.8
Phosphoethanolamine	–	9.2 ± 0.3	3.2 ± 0.1	8.7 ± 0.3	8.2 ± 0.4	22.5 ± 0.9
Aspartic acid	–	20.3 ± 0.8	9.9 ± 0.4	12.3 ± 0.5	22.6 ± 0.9	35.6 ± 1.4
Threonine	115.1 ± 4.4	105.9 ± 4.0	102.3 ± 3.9	81.3 ± 3.1	118.1 ± 4.5	135.7 ± 5.1
Serine	116.1 ± 4.4	113.7 ± 4.3	123.6 ± 4.7	211.3 ± 8.0	138.1 ± 5.2	140.5 ± 5.3
Glutamic acid	125.9 ± 4.8	180.6 ± 6.9	137.5 ± 5.2	288.6 ± 11.0	293.3 ± 11.2	257.1 ± 9.8
Neutral						
Proline	171.2 ± 6.5	67.9 ± 2.6	192.4 ± 7.3	154.6 ± 5.9	110.6 ± 4.2	92.4 ± 3.5
Glycine	420.1 ± 16.0	357.6 ± 13.6	314.1 ± 11.9	485.6 ± 18.4	437.8 ± 16.6	492.5 ± 18.7
Alanine	158.5 ± 6.0	165.5 ± 6.3	195.7 ± 7.4	217.2 ± 8.3	190.7 ± 7.3	270.2 ± 10.3
Valine	221.3 ± 8.4	107.3 ± 4.1	171.4 ± 6.5	205.3 ± 7.8	127.2 ± 4.8	162.9 ± 6.2
Cysteine	80.7 ± 3.1	214.1 ± 8.1	218.6 ± 8.3	199.1 ± 7.6	121.5 ± 4.6	144.7 ± 5.5
Cystathionine	66.2 ± 2.5	41.2 ± 1.6	49.6 ± 1.9	80.6 ± 3.1	51.2 ± 2.0	85.9 ± 3.3
Methionine	33.2 ± 1.3	–	98.2 ± 3.7	102.1 ± 3.9	68.4 ± 2.5	53.9 ± 2.0
Isoleucine	49.6 ± 1.9	85.7 ± 3.3	85.7 ± 3.3	160.3 ± 6.1	112.5 ± 4.3	184.2 ± 7.0
Leucine	28.6 ± 1.1	33.1 ± 1.3	93.9 ± 3.6	100.8 ± 3.8	31.5 ± 1.2	64.5 ± 2.5
Tyrosine	107.3 ± 4.1	85.4 ± 3.2	29.5 ± 1.1	52.1 ± 2.0	–	142.7 ± 5.4
β-Alanine	11.3 ± 0.4	8.0 ± 1.6	52.6 ± 2.0	74.1 ± 2.8	16.8 ± 0.6	39.8 ± 1.5
γ-Aminobutyric acid	5.2 ± 0.2	3.6 ± 0.1	41.6 ± 1.6	69.8 ± 2.7	25.7 ± 1.0	34.1 ± 1.3

(continued)

Table 2.12 (continued)

	Type of cultivation					
Amino acids	Continuous cropping of rye, control	Crop rotation, control	Continuous cropping of rye, NPK	Crop rotation, NPK	Continuous cropping of rye, manure	Crop rotation, manure
Basic						
Ornithine	38.1 ± 1.5	57.7 ± 2.2	80.6 ± 3.1	70.6 ± 2.7	66.6 ± 2.5	30.9 ± 1.2
Lysine	120.6 ± 4.6	151.8 ± 5.8	186.7 ± 7.1	195.2 ± 7.4	117.4 ± 4.5	164.3 ± 6.2
Histidine	18.5 ± 0.7	29.1 ± 1.1	131.6 ± 5.0	96.8 ± 3.7	127.3 ± 5.0	98.4 ± 3.7
Arginine	33.2 ± 1.3	30.1 ± 1.1	87.4 ± 3.3	112.6 ± 4.3	60.4 ± 2.3	76.4 ± 2.9
Total amount	*1964.6 ± 74.9*	*1888.7 ± 73.7*	*2541.4 ± 96.5*	*3093.2 ± 117.7*	*2269.9 ± 86.5*	*2799.0 ± 106.4*

Szajdak et al. (2004)
Control, no NPK or manure, manure 30 t/ha/year; NPK, 90 kg N, 60 kg P_2O_5, 120 kg K_2O/ha/year

contributed to acidic properties. Our earlier investigations demonstrated different impacts of NPK and manure on the chemical structure of humic acids extracted from soils under continuous cropping of rye and crop rotation. The application of NPK increased the aliphatic structures in humic acids (HA) than manure application in these treatments. The aromaticity of HA from soils under continuous cropping of rye fertilized with manure was higher than from crop rotation fertilized with manure (Szajdak et al. 2000).

The glutamic acid dominated the acid fraction in all HA, its highest concentrations (293.3 mg·kg^{-1}) were in soils under continuous rye cropping fertilized with manure, and it was 12 % higher than in soils under crop rotation. Among neutral amino acids, glycine, alanine, and valine dominated, with glycine predominant. Their contents in soils under crop rotation fertilized with manure were 492.5 mg·kg^{-1}, i.e., 11 % higher than in soils under continuous rye cropping.

Proline The proline concentrations were 60.3 % lower in soils under crop rotation than under continuous rye cropping. The highest proline concentrations (192.4 mg·kg^{-1}) were in soils under continuous cropping of rye fertilized with NPK, i.e., 20 % higher than under crop rotation. Higher concentrations of proline in soils under continuous cropping of rye than crop rotation may explain its heterocyclic structure. This structure protects it from further degradation. The accumulation of proline in soils is harmful because under acidic conditions, the proline in the presence of nitrite ions may form N-nitrosamine potent toxins, with carcinogenic and mutagenic effects (Kofoed et al. 1981; Larsson et al. 1990).

In soils under crop rotation than under continuous rye cropping, soils fertilized with NPK had higher concentrations of β-alanine (46 %) and lysine (16 %) than with manure. A similar phenomenon was observed in the previous study (Życzyńska-Bałoniak and Szajdak 1993; Szajdak and Österberg 1996; Ryszkowski et al. 1998). This indicated a higher microbial biomass in soils under crop rotation, as the β-alanine and lysine are the typical constituents of bacteria than fungus cell walls (Stevenson 1972; Durska and Kaszubiak 1980). In addition, the positive and linear correlation between the activity of rhodanese and the concentrations of free sulfuric amino acids has been found. Enzyme rhodanese is formed by fungus in soils. Higher activity of rhodanese in soils under continuous cropping of rye indicates higher biomass of fungus, as the activity of rhodanese in soil is the measure of the abundance of fungi (Szajdak 1996).

The nitrogen in the bound amino acids was 22 % higher than in HA from crop rotation fertilized with manure. Lowest nitrogen contents were found in controls for both types of cropping. NPK fertilizers supplied larger amounts of nitrogen, phosphorus, and potassium than manure (Table 2.13).

The crops absorbed more nitrogen, phosphorus, and potassium from NPK than from manure. Probably it was due to disappearance of manure nitrogen, presumably by denitrification (Pratt et al. 1973; Svensson et al. 1991; Klemedtsson et al. 1991; Goulding et al. 1993; Rudaz et al. 1999). Organic and inorganic fertilizers in crop rotation and continuous cropping of rye gave different grain yield of winter rye. The highest yield (5940 kg·ha^{-1}) was observed in crop rotations using NPK as fertilizer,

Table 2.13 Uptake and balance of macronutrients (N, P, K, kg·ha^{-1}·year^{-1}) of winter rye grown continuously and in rotation

Fertilization	Crop sequence[a]	Fertilizers			Uptake			Balance		
		N	P	K	N	P	K	N	P	K
Control	CR	0	0	0	81.5	17.5	44.5	–81.5	–17.5	–44.5
	CC	0	0	0	44.3	9.5	20.6	–44.3	–9.5	–20.6
Manure	CR	150	39.2	174.3	137.3	27.8	85.5	12.7	11.4	88.8
	CC	150	39.2	174.3	97.2	19.7	44.9	52.8	19.5	129.4
NPK	CR	90	26.2	99.6	129.7	26.0	76.0	–39.7	0.2	23.6
	CC	90	26.2	99.6	103.3	21.7	56.5	–13.3	4.5	43.1

Szajdak et al. (2004)
Control, no NPK or manure, manure 30 t/ha/year; NPK, 90 kg N, 60 kg P_2O_5, 120 kg K_2O/ha/year
[a]Average from 1988 to 1996, CR, crop rotation; CC, continuous cropping of rye

Table 2.14 Grain yield of winter rye (kg·ha^{-1})

Years	Crop rotation			Continuous cropping		
	Control	Manure	NPK	Control	Manure	NPK
1993	4430	5930	5350	2480	4730	5310
1994	3580	5220	6060	1960	4420	4610
1995	4380	6050	6420	2980	5620	5980
Average	*4130*	*5730*	*5940*	*2470*	*4920*	*5300*

Szajdak et al. (2004)
Control, no NPK or manure, manure 30 t/ha/year; NPK, 90 kg N, 60 kg P_2O_5, 120 kg K_2O/ha/year

and the lowest yield (2470 kg·ha^{-1}) was in control of continuous cropping of rye. In unfertilized plots in continuous cropping of rye, the yield was above half of the plot with manure. The NPK fertilizer gave 32 % higher aboveground biomass of winter rye and 27 % higher grain yield than manure (Table 2.14).

In summary, the results indicated that the composition of bound amino acids in HA depends on cropping system and on the availability of nitrogen, phosphorus, and potassium from fertilizers. Negative effects of continuous cropping on the content of total bound amino acids were decreased by NPK fertilization, but the manure application in continuous cropping of rye was less effective. Thus, NPK was the main driver causing changes in the total amounts of bound amino acids in HA. Crop yields of rye increase with an increase in organic N in bound amino acids and nitrogen in HA.

2.2.4 Thermal Evaluation of HA Structure

There are three soil quality indicators: (1) chemical, (2) physical, and (3) biological. Within each of these classes, many soil properties or processes can be selected to indicate soil functional capabilities. Soil organic matter is a critical component of soil quality. Accumulation of residues and organic matter at the soil surface is beneficial to soil quality, due to their positive effects on conserving water, preserving nutrients, and creating a suitable habitat for soil biological diversity (Franzluebbers 2008). With the start of degradation of plants and animal residues, HA is produced in soils. During the decomposition, HA is formed with carbon from all major plant components either by direct transformation or by “resynthesis” activity of microorganisms. The polymers of HA are synthesized enzymatically within microbial cell by chemical oxidative condensation following cellular autolysis. Therefore, HA are rarely homogenous; however, they represent accumulation of more resistant end products from many reaction taking place under natural conditions, either directly or indirectly through biological processes.

HA originates randomly from the decay of plant tissues or microbial metabolism–catabolism or both; hence, their chemistry is complex and a function of different ecosystems (vegetation, climate, topography, etc.) in which it is formed (Piccolo et al. 2003). HA provides energy to many biochemical processes in soil (Dziadowiec 1979; Gołębiowska et al. 1996) and also regulates the nutrient dynamics and C/N ratio. The aromatic pathway acts as a major resource quality factor at all levels—both by forming enzymatically recalcitrant molecules and also by the direct toxic effects of phenolic or quinonic monomers.

HA are composed of higher molecular weight (10,000–100,000) compounds containing aromatic rings, peptide chain, and nitrogen in cyclic and aromatic forms. These are created by polymerization, polyaddition, and polycondensation of similar but not identical substrates; therefore, no two humic molecules are identical. Pure humic acids contain 57 % carbon and 4 % nitrogen. Besides, the HA contains primarily COOH groups, phenolic OH groups, alcoholic OH, and some ketonic oxygen. The quantity of HA in soil organic matter depends on the balance between primary productivity and the rate of decomposition (Paul and Clark 1989).

The derivatographic method allows the rapid identification of consecutive stages of organic substances in soils and also estimates the changes in energy levels of these compounds (Leinweber and Schulten 1992; Schnitzer et al. 1974; Shurigina 1971).

In long-term experiments, the continuous rye cropping than crop rotation produces undifferentiated biological metabolites of microbes and plants (Ryszkowski et al. 1990). Therefore, this study aimed (i) to improve the interpretation of derivatographic results of HA from soils under continuous cropping of rye and from soils under crop rotation fertilized with NPK or with manure and (ii) to show that long-term continuous cropping of rye changes the HA structure than in crop rotation.

Table 2.15 shows the weight losses of HA samples in different temperature regions. For all samples, the changes in differential thermal analyses (DTA) and thermogravimetric analyses (DTG) are compatible. Thus, each thermal effect recorded on the DTG corresponded to weight losses of HA. Furthermore, HA are characterized by two exothermic effects: (i) in low temperature (below 350 °C—egzoL) and (ii) in high temperature (above 350 °C—egzoH). All samples of HA characterized also small peak on DTA curve below 100 °C (endothermic effect). The endothermic effect is explained by the disappearance of aliphatic structures

Table 2.15 Parameters of thermal decomposition of humic acids from soils under continuous cropping of rye and from crop rotation fertilized with NPK or manure or without any fertilizer

Samples of HA	Maximum temperature of effects recorded on DTA curves (°C)			Loss of weight corresponding with effects on DTA curves			The rations of area under DTA and DTG curves according to isothermal reactions			$Z = \frac{DTG_N}{DTG_W}$
				DTG	DTG	DTG				
	endo	$egzo_N$	$egzo_W$	endo	$egzo_N$	$egzo_W$	$\frac{DTA_N}{DTG_N}$	$\frac{DTA_W}{DTG_W}$	$\frac{DTA_{N+W}}{DTG_{N+W}}$	
CC control	89	298	429	8.04	6.77	9.99	1.26	4.10	3.14	0.68
CC NPK	100	283	408	10.10	5.92	8.26	1.94	4.51	3.14	0.72
CC manure	98	312	432	12.71	5.27	12.44	2.31	5.33	4.13	0.42
CR control	92	280	415	6.72	6.18	5.42	3.32	3.80	3.55	1.14
CR NPK	98	286	389	8.40	6.69	5.16	3.19	3.44	3.30	1.29
CR manure	90	314	460	7.19	7.14	11.03	3.15	5.36	4.50	0.64

Szajdak et al. (2000)

Where *CC-control* continuous cropping of rye control, *CC-NPK* continuous cropping of rye fertilized with NPK, *CC-manure* continuous cropping of rye fertilized with manure, *CR-control* crop rotation control, *CR-NPK* crop rotation fertilized with NPK, *CR-manure* crop rotation fertilized with manure in HA (Rakovskiy and Filimonov 1967). HA from both kinds of cultivation and fertilized with NPK have lower value of egzoH in comparison with samples fertilized with manure (Table 2.14). For HA from soil under continuous cropping of rye and fertilized with NPK, the value of egzoH was 8.26. For soils under crop rotation, the value of the same parameter was 38 % lower. The fertilization with manure moved the egzoH effects in both soils toward high temperature with simultaneous increase in them (432 and 460 °C). For soil under continuous cropping of rye, and fertilized with manure, the egzoH parameter was equal to 12.44, and for soils under crop rotation, 11 % lower at 11.03. The lower values of egzoH parameters of HA from soils fertilized with NPK than with manure demonstrate that this HA from soils fertilized with NPK contained more aliphatic structures than HA from soils fertilized with manure (Gonet 1989).

Estimation of weight losses (DTG) in samples of HA for endothermic and exothermic effects has affirmed more weight losses in the endothermic range. It might be caused more hygroscopicity of HA samples. The higher weight losses (6.18–7.14) of HA were in the exothermic range (below 350 °C) in soils under crop rotation than from soils under continuous cultivation (5.27–6.77). This phenomenon was reversed above 350 °C, where higher weight losses in HA were observed from continuous cropping of rye than from crop rotation.

The weight loss with applied manure in HA was 12.44 from soils under continuous cropping of rye and was 11.03 from soils under crop rotation. The weight loss in HA with NPK fertilizers was 5.16 from soils under crop rotation, and it was 60% higher from soils under continuous cropping of rye. Manure in both types of cultivation caused the highest weight losses in HA in higher temperature region.

The value of DTAL means the heat of combustion of HA. The higher temperature of decomposition of HA shows higher energy of activation and also explains the differences in the structures of HA. These differences are caused by the type of cultivation and the use of fertilizers. All samples of HA in high temperatures (above 350 °C) have higher values of heat of combustion (DTA:DTG) than HA in full range of temperatures (DTAL + H:DTGL + H). These highest values of this parameter characterized HA extracted from soils under both types of cultivation and fertilized with manure. The lower values of heat of combustion might indicate that the compounds include more aliphatic bonds that are easily degraded (Gonet and Wegner 1990, 1993). As a result of breaking off aliphatic bridges between aromatic structural units, aromatic compounds eliminate with the highest rate (Maryganova et al. 1992). The higher values of heat of combustion of HA from soils fertilized with manure than NPK might show that the linkages of HA contain more aromatic groups than aliphatic.

Parameter Z reflects the ratio between thermolabile and thermostable parts of the humic molecules. The lower results of Z parameter (parameter of aliphaticity) indicate higher aromaticity properties of HA. Thus, the fertilization of NPK irrespective of cultivation leads to the increase of aliphatic structures in HA. Comparison of Z parameter with the type of cultivation shows that HA from crop rotation contains more aliphatic properties than from continuous cropping of rye. This is in line with the findings of others (Hruszka 1982; Szajdak and Życzyńska-Bałoniak 1994), who found higher accumulation of phenolic compounds in soils under continuous cropping of rye than under crop rotation.

These results showed that the crop rotation (i) decreases the temperature of combustion in high temperature range, (ii) causes higher weight losses in low temperature range (DTA egzoL), (iii) decreases the heat of combustion in high temperature range (DTAH:DTG), and (iv) increases the Z parameter. It might indicate higher aliphatic properties of this HA. Furthermore, the manure application irrespective of the type of cultivation increases the temperature of combustion in low and high range of temperatures and also increases the heat of combustion. The HA extracted from the soils under crop rotation and fertilized with NPK showed highest aliphatic properties, but the HA from soils fertilized with manure was most aromatic. Aromaticities of HA from soils under continuous cropping of rye fertilized with manure were higher than from crop rotation fertilized with NPK.

The evidence gathered suggests strong linkages between the soil and fertilizer, and manures' quality affects the productivity. Achieving a balance between the agricultural production and conservation of natural resources is necessary to develop sustainable agricultural systems.

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