

## The Chemical Nature of Nitrogen in Native Soil Organic Matter

H. Knicker, R. Fründ and H.-D. Lüdemann

Institut für Biophysik und physikalische Biochemie der Universität,  
W-8400 Regensburg, FRG

Fossil fuels and soil organic matter (SOM) together contain approximately five times more carbon than the biota and the atmosphere. Of this, soil organic matter accounts for about 30% of the carbon present. In addition, SOM has an average carbon/nitrogen ratio of 10/1 and contains a huge fraction of the total nitrogen available for plant growth [1]. Taking into account that the abundance of nitrogen in the earth's crust is much lower than that of carbon, this is a significant fraction of the total nitrogen accessible to the biosphere. Under natural soil conditions, without the addition of mineral fertilizers, SOM provides the majority of the nitrogen necessary for plant growth. It is also thought to be responsible for the interaction between agricultural biocides and the soil [5–7]. The chemical structure of this ubiquitous material, SOM, and especially the chemical nature of the nitrogen are thus of great and general importance. The molecular structure of the nitrogen-containing fraction is, however, still a matter of controversy [2–4].

Structural models based on partial chemical analysis claim that a significant part of the nitrogen is present in the form of heteroaromatic structures, while NMR-spectroscopic studies on  $^{15}\text{N}$ -enriched composts and recent humic material found approximately 85% of the signal intensity in the amide/peptide region of chemical shift and no signals in the range typical for heteroaromatic nitrogen. A major fraction of the native soil organic matter has been in the soil for several

hundred to several thousand years [8, 9]. Compared to these time spans, laboratory-produced material has been fermented for at most 1 year, and it could be argued that heteroaromatic structures are only produced after much longer fermentation periods. This criticism may be overcome by the study of  $^{15}\text{N}$ -CPMAS spectra of soil organic matter with natural  $^{15}\text{N}$  levels. This has not been achieved hitherto, because the low natural abundance (0.4%) and the small gyromagnetic ratio of the  $^{15}\text{N}$  nucleus and therefore its low sensitivity in NMR experiments appeared to make this experiment an impossible one. The most abundant  $^{14}\text{N}$ -isotope (99.6%) cannot be studied by high-resolution NMR because its large nuclear quadrupole moment leads to very broad and unresolved signals, especially in solid-state NMR [10].

In previous systematic studies on  $^{15}\text{N}$ -enriched composts and organic soil extracts [11] our group optimized all spectral parameters for the  $^{15}\text{N}$ -CPMAS

experiment. A crude estimate showed that it should be possible to obtain  $^{15}\text{N}$  spectra with a tolerable signal-to-noise ratio after the accumulation of approximately one million transients. In the present paper we report on the first successful results of such experiments. Six German soils were studied as detailed in Table 1.

In Figs. 1 and 2 some of the spectra obtained are shown. They fully corroborate the conclusions drawn from the studies of short-term composting exper-

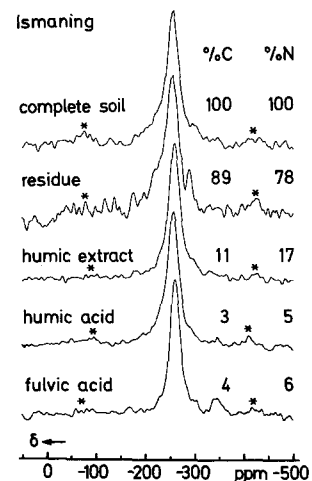


Fig. 1.  $^{15}\text{N}$ -CPMAS spectra obtained at 30.4 MHz of a „black“ calcaric Regosol from Ismaning and the different fractions obtained by the standard aqueous sodium hydroxide extraction procedure (% C and % N at the right side of the spectra give the relative contributions of the various fractions). \* = spinning side bands

Table 1. Origin and some characteristics of the soil samples (top 10 cm)

	Geographical origin	Order	C [%]	N [%]	
Field	Pfaffenhofen	Ba <sup>a</sup>	Cambisol	1.2	0.1
Grassland	Harthausen	Ba	Luvic Cambisol	3.4	0.3
	Oberwarngau	Ba	Rendzina	4.6	0.4
	Ismaning	Ba	„Black“ calcaric Regosol	11.5	0.9
Forest	Solling D1	LS <sup>b</sup>	Spodic distric Cambisol	3.4	0.2
	Göttingen	LS	Chromo-calcaric Cambisol	4.4	0.4

<sup>a</sup> Ba = Bavaria

<sup>b</sup> LS = Lower Saxony

iments [12]. All signals found are in the chemical shift range typical for amide/peptide signals with a small intensity found in the region of free amino groups.

Table 2 gives the most plausible assignments and the relative intensities of the signals. Almost all intensity is found in the chemical shift region of the peptide/

amide nitrogen. However, this is a broad and intense signal, of which more than 80 % of the total intensity could cover some less intense signals at the low-field side (-190 to 230 ppm) of the main peak originating from indoles, purine bases (N-9) and quinone imines. These heteroaromatic structures could thus be hidden within the spectra. However, even in the very improbable case that the total intensity in this chemical shift range results from such structures, they would not contribute more than 10 % to the total signal intensity. In Fig. 1 all fractions derived from the "black" calcareous Regosol with a high carbon content (line 4 in Table 1) by a standard aqueous sodium hydroxide extraction [12] are shown. Also given are the contributions of the individual fractions to the total carbon and nitrogen content of the soil. In all extracts nitrogen is enriched compared to the complete soil. The main and significant differences seen in these spectra are the unexplainable splitting of the amide peak in the extraction residue and the well-developed free amino-group signal in the fulvic acid fraction. This latter feature is typical for all fulvic acid fractions as can be seen from an inspection of Fig. 2. The poor signal-to-noise ratios in the individual spectra lead to large errors in the integrated areas. However, the average values for all six fractions (see Table 2) clearly support the above statement. In addition, the fulvic acids are by definition soluble in dilute aqueous acids and water and the relatively high concentrations of free amino groups are consistent with this high solubility. It should be noted also that all soluble fractions are enriched in nitrogen, having a smaller C/N ratio compared to the total SOM.

The studies on the native material currently suffer from a rather modest signal-to-noise ratio, which can only be improved if significant progress in the instrumental design is achieved. However, within the precision of the existing data it can safely be stated that at most 10 % of the total nitrogen in soil organic matter can be present in heteroaromatic structures or Schiff bases in the samples studied here. This is contrary to the 40 to 50 % claimed from chemical analysis [1, 2].

The great similarity between the spectra of recent and native "fossil" humic material supports the conclusions drawn from the  $^{13}\text{C}$ -CPMAS studies [13], i.e., no sig-

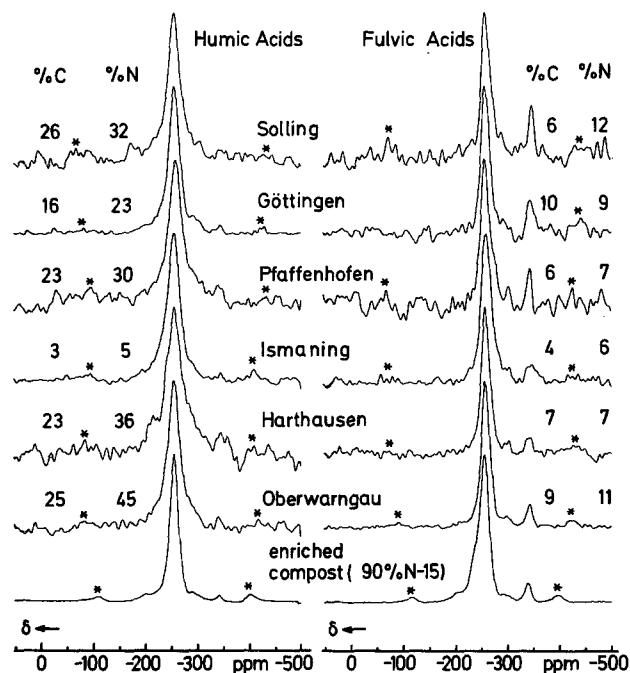


Fig. 2. Comparison of the natural abundance  $^{15}\text{N}$ -CPMAS spectra of humic acids and fulvic acids obtained from the six German soils given in Table 1 with spectra obtained from the  $^{15}\text{N}$ -enriched humic and fulvic acid derived from a *Lolium perenne* compost after 200 days of fermentation ( $^{15}\text{N}$  abundance 90 %). \* = spinning side bands

Table 2. Possible assignment of the  $^{15}\text{N}$  NMR spectra [11] and the average of the relative intensities in spectra of humic matter fraction of soil with  $^{15}\text{N}$  natural abundance. The integration routine sets the total intensity at 100 %. The reproducibility of the integration procedure depends on the signal-to-noise ratio. It is approximately 5 %. Deviations from this stem from rounding off errors

Signal [ppm]	Assignment	Average intensity [%]		
		HE <sup>a</sup>	HA <sup>b</sup>	FA <sup>c</sup>
-190 to -285	Peptide bonds, indole, N-acetyl derivatives of amino sugars, lactame, carbamate, melanoids, Maillard products, N-9 of purine, quinone imine	87 (85-90) <sup>d</sup>	86 (84-90)	83 (81-87)
-285 to -325	NH groups in guanidine, aniline derivates	8 (7-8)	10 (6-12)	6 (4-7)
-325 to -375	Free amino groups of amino acids and -sugar, substituted amines	5 (3-7)	5 (3-6)	11 (7-13)
Missing signals:				
-165 to -185	Pyrroles			
-25 to -65	Schiff bases			
-55	Phenazine derivatives			

<sup>a</sup> HE = NaOH/H<sub>2</sub>O extract

<sup>b</sup> HA = Humic acid

<sup>c</sup> FA = Fulvic acid

<sup>d</sup> Numbers in parentheses: variation among different samples

nificant chemical alterations occur in the humic material after prolonged exposure to the natural environment. Their apparent half-life in nature characterized by their sensitivity to decomposition appears limited rather by their chemical accessibility than by fundamental structural and chemical differences.

Financial support was obtained from the BMFT under research grant 0339137. Profs. K. Haider (Braunschweig) and F. J. Gonzalez-Vila (Sevilla) gave invaluable encouragement and advice.

Received November 30, 1992 and January 28, 1993

1. Schnitzer, M., in: Humic Substances in Soil, Sediment and Water, p. 303 (G. R. Aiken, D. M. McKnight, R. Wershaw, P. McCarthy, eds.). New York: Wiley Interscience 1985
2. Anderson, H. A., Bick, W., Hepburn, A., Stewart, M., in: Humic Substances II, p. 223 (M. B. Hayes, P. MacCarthy, R. L. Malcom, R. S. Swift, eds.). New York: Wiley Interscience 1989
3. Cheshire, M. V., Williams, B. L., Benzing-Purdie, L. M., Ratcliffe, C. I., Ripmeester, J. A.: Soil Use Manag. 8, 90 (1990)
4. Zhuo, S., Wen, Q., Du, L., Wu, S.: Chinese Sci. Bull. 37, 508 (1992)
5. Haider, K. M., Spitteller, M., Reichert, K., Fild, M.: Int. J. Environ. Anal. Chem. 46, 201 (1992)
6. Hassett, J. J., Banwart, W. L.: SSSA Spec. Publ. 22, 31 (1989)
7. Pignatello, J. J.: *ibid.* 22, 45 (1989)
8. Scharpenseel, H. W., Ronzani, C., Putig, F.: Proc. IAEA-Symp. Wien 1968
9. Hsieh, Y.-P.: Soil Sci. Am. J. 56, 460 (1992)
10. Martin, G. J., Martin, M. L., Gouesnard: N-15 NMR-Spectroscopy. Berlin: Springer 1981
11. Almendros, G., Fründ, R., Gonzalez-Vila, F. J., Haider, K. M., Knicker, H., Lüdemann, H.-D.: FEBS Lett. 282, 119 (1991)
12. Knicker, H., Fründ, R., Almendros, G., Gonzalez-Vila, F. J., Martin, F., Lüdemann, H.-D.: Humus-unters.-Finnish Humus News 3, 313 (1991)
13. Fründ, R., Lüdemann, H.-D.: Z. Naturforsch. 46, 982 (1991)

Naturwissenschaften 80, 221–222 (1993) © Springer-Verlag 1993

## $\text{Cs}_2\text{H}_2\text{Si}(\text{P}_2\text{O}_7)_2$ , ein neues Beispiel für Silicium in oktaedrischer Sauerstoffumgebung

K. Königstein und M. Jansen

Institut für Anorganische Chemie der Universität, W-5300 Bonn, FRG

Silicium zeigt gegenüber Sauerstoff eine ausgeprägte Präferenz für die tetraedrische Koordination. Entsprechend klein ist die Zahl der bisher bekannt gewordenen Ausnahmen, z.B. von oxidischen Phasen, in denen Silicium oktaedrisch umgeben ist [1]. Nur drei von ihnen, nämlich  $\text{SiP}_2\text{O}_7$  [2],  $\text{Si}_5(\text{PO}_4)_6\text{O}$  [3] und  $(\text{NH}_4)_2\text{SiP}_4\text{O}_{13}$  [4], entstehen unter Normaldruck. Die übrigen sieben, zu denen  $\text{SiO}_2$  in der Rutilstruktur (Stishovit) [5],  $\text{MgSiO}_3$  im Ilmenit- oder Perowskittyp [6, 7] und  $\text{Sc}_2\text{Si}_2\text{O}_7$  (Pyrochlortyp) [8] gehören, sind Hochdruckformen. Sie lassen sich unter teilweise extremen Druck- und Temperaturbedingungen im Laboratorium herstellen und liegen in den tieferen Bereichen des Erdmantels entsprechend den dort herrschenden Druck- und Temperaturverhältnissen vor. Sie spielen damit geochemisch eine wichtige Rolle.

Wir haben einen überraschend einfachen präparativen Zugang zu weiteren Vertretern mit diesem bemerkenswerten Strukturmerkmal gefunden, der hier am Beispiel der Synthese von  $\text{Cs}_2\text{H}_2\text{Si}(\text{P}_2\text{O}_7)_2$  vorgestellt wird: Röntgenreine, mikrokri-

stalline Pulver entstehen aus amorphem  $\text{SiO}_2 \cdot \text{H}_2\text{O}$  [hergestellt durch Hydrolyse von  $\text{Si}(\text{OEt})_4$  (Janssen) und anschließende Trocknung des Gels während 24 h bei  $100^\circ\text{C}$ ] und  $\text{CsCl}$  (Merck p.a.) in einem Platintiegel durch Übersichten mit 85proz.  $\text{H}_3\text{PO}_4$  (Aldrich) innerhalb von 4–5 Tagen bei  $350^\circ\text{C}$ . Bei einer Gesamteinwaage von 20–40 g war das Cs:Si:P-Verhältnis auf 2:1:6 eingestellt. Sollen Kristalle gezüchtet werden, ersetzt man das amorphe  $\text{SiO}_2$  durch Quarzsplitter, den Platintiegel durch ein senkrecht stehendes, mit einer Schliffkappe verschlossenes Quarzrohr und erhöht die Reaktionsdauer auf mindestens zwei Wochen. In dieser Zeit bilden sich wasserunlösliche, farblose, stäbchenförmige Einkristalle mit den maximalen Abmessungen  $1 \times 0,6 \times 0,5 \text{ mm}^3$ .

Die Kristallstruktur von  $\text{Cs}_2\text{H}_2\text{Si}(\text{P}_2\text{O}_7)_2$  [ $P \bar{1}$ ,  $a = 915,7(1)$ ,  $b = 921,9(2)$ ,  $c = 950,9(1) \text{ pm}$ ,  $\alpha = 94,99(1)$ ,  $\beta = 111,41(1)$ ,  $\gamma = 113,20(1)^\circ$ ,  $Z = 2$ ,  $V_m = 661,5(2) \text{ cm}^3/\text{mol}$ ] wurde an einem Kristall mit den Abmessungen  $0,1 \times 0,06 \times 0,05 \text{ mm}^3$  auf einen  $R$ -Wert von 0,04 verfeinert. Sie

enthält ein eindimensional-polymeres Heteropolyanion aus  $\text{SiO}_6$ -Oktaedern und  $\text{PO}_4$ -Tetraedern. Beide kristallographisch unabhängigen  $\text{SiO}_6$ -Baugruppen haben ein Symmetriezentrum und mit Si-O-Abständen zwischen 175 und 178 pm sowie O-Si-O-Winkeln zwischen  $87,1^\circ$  und  $92,9^\circ$  einen beachtlich regelmäßigen Bau. Die  $\text{PO}_4$ -Tetraeder sind über eine gemeinsame Ecke zu Diphosphatgruppen verknüpft, die die typischen P-O-Abstände für verbrückende und endständige Sauerstoffatome von 155 bzw. 160 pm (Mittelwerte) ausbilden. Die Verknüpfung der beiden Bauelemente zu einem  $\frac{1}{2}$ -Heteropolyanion ist in Fig. 1 in Blickrichtung entlang dem Anion und senkrecht dazu wiedergegeben. Jede Diphosphatgruppe bildet mit zwei terminalen Sauerstoffatomen eine Kante des  $\text{SiO}_6$ -Oktaeders und verknüpft über ein drittes mit dem Nachbaroktaeder. Die Anionenkette sind über Cäsiumkationen miteinander verknüpft. Die Koordination der Cs-Kationen durch Sauerstoff beträgt bei Cs-O-Abständen von 300 bis 380 pm für beide kristallographisch unabhängigen Cäsiumlagen jeweils elf.

Neben dem anscheinend universell anwendbaren Darstellungverfahren – inzwischen haben wir mit allen Alkali- und Erdalkalimetallen neue Verbindungen dieser Stoffklasse hergestellt – bieten die begonnenen Untersuchungen interessante Perspektiven im Hinblick auf hohe Alkaliionenbeweglichkeiten und nach Austausch der Alkalimetall-