Original Research

# Effects of Bentonite Addition on Sandy Soil Chemistry in a Long-Term Plot Experiment (I); Effect on Organic Carbon and Total Nitrogen

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#### **Abstract**

In 0.8 m² microplots, a very poor sandy soil that contained only traces of organic matter was enriched with bentonite (BNT) at rates of 0, 3, 6, and 12 kg/m². For 30 years the microplots were planted with different crops and regularly enriched with mineral and organic fertilizers. For the next eight years the microplots were left barren. The soils with BNT added contained significantly higher amounts of organic carbon (OC) and total nitrogen than the control soil (CS). Furthermore, in comparison to CS, organic matter in the soil with 12 kg/m² of BNT contained significantly more humins. Such durable stabilization of OC by BNT can be important for processes of carbon sequestration in soil.

Keywords: sandy soil, bentonite, organic C, total N, humins

# Introduction

The low content of clay in sandy soils usually limits humus accumulation, nutrients, and water availability as well as buffering capacity, which is a reason why many of these soils become acidified [1-5]. Bentonite – a rock containing mainly 2:1 clay mineral montmorillonite, a member of the smectite family – has been recognized in many countries as a very good amendment to improve the properties of such infertile sandy soils [6-16]. However, all of these studies were of short-term character. Therefore, it was difficult to evaluate how permanent would be the improvement of sandy soils by bentonite addition.

Such an evaluation can be performed based on a microplot experiment with a poor acidic sandy soil amended with bentonite (BNT), conducted for 38 years at the Institute of Soil Science and Plant Cultivation in Puławy, in

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eastern Poland (51° 24' N, 21° 57" E). Therefore, the aim of this work was to find out whether BNT addition to the sandy soil affects its properties after such a long period.

The present paper constitutes the first part of the set of two papers on the effects of BNT on soil chemical properties. It concerns the influence of BNT on accumulation of OC and total nitrogen (ToN) in the soils. Studies on soil C and N are important to develop sound strategies for enhancing C and N sequestration in terrestrial ecosystems. Many agricultural practices cause losses of SOM, especially on sandy soils [17]. Soil organic C is an essential element for soil quality, and increased soil organic C is generally associated with improved soil tillage and water-holding capacity, as well as storage and availability of plant nutrients [18]. Presently, considerable attention is given to the potential of soils to act as C sinks [19]. The association of C with mineral phases has been increasingly recognized as a major mechanism stabilizing organic matter against microbially driven degradation in soils [20]. However, the dynamics of 1662 Czaban J., et al.

C accumulation should be considered together with the dynamics of N transformations. Since N is a limiting factor for biological productivity and represents an important SOM constituent, the sequestration of N is closely related to the formation and accumulation of humic material [19], and the rate of C accumulation is controlled by the rate of N accumulation [17].

#### **Experimental Procedures**

## Experimental Design and History of the Plots

The microplot experiment was established in July 1973 on a subsoil (after removing the humus layer to 25 cm depth) of an acidic sandy soil (pH $_{\! {\rm H}_{7}\! {\rm O}}$  5.4) containing approximately 4% of particles < 0.02 mm (PRT < 0.02). In what follows, this exposed subsoil will be called "the basic soil." The basic soil contained only traces of OC and approximately 0.01% of ToN. The basic soil was enriched with BNT (originating from the Milowice coalmine in Sosnowiec, Upper Silesia, Poland), mixed with the upper soil layer to 30 cm depth at rates of: 0, 3, 6, and 12 kg/m<sup>2</sup>, as well as with NPK fertilizers in amounts of 0.03:0.03:0.05 kg/m<sup>2</sup> for nitrogen, phosphorus, and potassium, respectively. BNT added to the soil was in a powdered form with the size of particles < 0.71 mm (PRT < 0.71) after drying at 400°C. BNT contained 1.66% of total K (and 0.39% of K soluble in 10% HCl), Na - 0.73% (0.60%), Ca - 4.95% (4.26%), and Mg - 1.22% (0.60%). Its cation exchange capacity equals 26 cmol(+)/kg. The microplot experiment consists of 16 plots (0.8 m<sup>2</sup>) with concrete walls (1 m diameter, 1 m depth), four replicates for each of four experimental series [21-23].

In the first two years of the experiment the soils were planted with white mustard and lupine in order to enrich them with green manure. Subsequently (for 28 years until 2002), the microplots were planted with potatoes, various cereals (oat, rye, triticale, barley, wheat), alfalfa, and, less regularly, white mustard as the second crop. During these 30 years the soils were enriched with mineral and organic fertilizers (before growing potatoes the soils were fertilized with farmyard manure; after harvest of cereals they were enriched with the residual straw, and after growing of mustard, alfalfa, or lupine with green manure). The pH of the control soil (CS) not amended with BNT had to be regulated several times by CaCO<sub>3</sub> addition. In 1974 the soils were inoculated with Azotobacter chroococcum [23]. Since 2003 the plots were left in bare fallow with no fertilization to find out how stable the organic and mineral soil constituents would be.

# Soil Sampling

Soils were sampled in May 2009 from layers 5-30, 30-55, and 55-80 cm with the use of a soil auger (1 m long). The humus fractions were determined only in the soil layers of 5-30 and 30-55 cm, sampled with a sampling stick

(0.7 m long) in June 2010 from series amended with 0 kg/m² and 12 kg/m² of BNT. The uppermost layer 0-5 cm of the soils was removed before sampling because of intensive and irregular growth of algae on the surface, which would falsify contents of soil C and N. The samples were placed in airtight containers for transport to the laboratory. At the laboratory the samples were stored at 4°C in hermetically sealed containers until processed for chemical analyses. The samples were sieved through 2 mm and homogenized.

## Soil Analyses

Soil texture was determined by the hydrometer method, modified by Casagrande and Prószyński, based on measurements of the density of soil suspensions during progressive sedimentation, supplemented with the sieve method in order to fractionate sand [24]. The contents of particle size classes (sand, 2.0-0.05 mm; silt, 0.05-0.002 mm; and clay, < 0.002 mm) are presented according to the FAO/USDA classification system [25].

The soil organic carbon (SOC) content was determined by the modified Tiurin method in which organic carbon (OC) was oxidized to CO<sub>2</sub> by a mixture of potassium dichromate and sulphuric acid and excess of dichromate was back titrated with a solution of Mohr's Salt [26].

For fractionation of humic substances the Kononova-Bielczikova method was applied using extraction with a mixture 0.1 M  $Na_4P_2O_7$  and 0.1 M NaOH at pH approximately 13 [27]. In the obtained fractions, the OC content was determined by the Tiurin method [26].

Soil total nitrogen (ToN) was determined by a modified Kjeldahl method. Soil was mineralized with H<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>O<sub>2</sub> and then the N-NH<sub>4</sub><sup>+</sup> content was measured by spectrophotometric determination with the use of sodium salicylate, sodium hypochlorite and sodium nitroferricyanide in alkaline environment [28, 29].

All the mentioned soil variables were determined in three replicates.

Additionally, annual means of OC and ToN contents in 0-30 cm soil layers of the soils, determined during a period 1973-85 plus 1990, are presented. In the 1991-2008 period these parameters were not measured.

## Statistical Analysis

For statistical evaluation, the obtained results were subjected to one-way analysis of variance (at P = 0.05) and the means were separated with Tukey's HSD test (with P = 0.05 level of significance). In the figures, the means presented as the full columns or as the numbers presented inside the legends marked with the same letters are not significantly different.

For estimation of the relationships among OC, ToN, and PRT < 0.05, the simple Pearson's correlation analysis was used. Together with correlation coefficients (r), level of probability (P) and number of data pairs (n) are presented in the text.

#### **Results and Discussion**

#### Soil Texture

After 37 years of the experiment, CS contained about 95% of sand, especially 0.5-0.1 mm fraction (83%), approx. 4% of silt, and approx. 1% of clay in the 5-80 cm layer. In comparison with BNTSs, CS was significantly poorer:

- (1) in a fraction with particle diameters smaller than 0.1 mm (PRT < 0.1) in the 5-30 cm and 30-55 cm layers
- (2) in both clay and silt than 12-BNTS in the 5-30 cm layer
- (3) in sand with particle diameters 0.1-0.05 mm (PRT = 0.1-0.05) than all BNTSs in the 5-30 cm and 30-55 cm layers (Fig. 1)

Suzuki et al. [30] also reported that the addition of bentonite into the top 20 cm layer of sandy soil significantly increased the contents of both silt and clay in this layer after 4 years.

The differences between CS and BNTSs in the contents of silt and clay distinctly decreased in the deeper soil layers due to limited transport of these BNT fractions (Fig. 1). In contrast to this, the differences between CS and BNTSs in the content of the fraction of sand PRT = 0.1-0.05 were equal to or even higher in 30-55 cm layers in comparison to the upper one (Fig. 1). This suggests that BNT became partially translocated into deeper soil layers, but the biggest proportion of the finer parts of this rock stayed in the upper soil layer. Lhotský et al. [9] also reported that the migration of bentonite in a sandy soil profile was not considerable. In their study the bentonite, introduced to the 0-45 cm soil layer, increased the content of PRT < 0.002 only to a 60 cm depth after 4 years.

#### Soil Organic C and Total N

The basic soil used to fill the plots contained only traces of OC and approximately 0.1 g/kg of ToN [19]. During the 1974-90 period the content of OC fluctuated widely with

distinct increases after fertilizing with farmyard manure (1974, 1983, and 1990) or alfalfa green manure (1979-81), which were followed by intensive mineralization of the added organic matter during growth of cereals (oat in 1976 and 1984, rye in 1977, oat and barley in 1978) (Fig. 2A). The fluctuations of the ToN content were much smaller, therefore the gradual accumulation of the ToN was observed (Fig. 2B). In contrast to OC, the dynamics of the ToN content can be described by linear functions of time in 66-84% (vs. 6-15% for OC) and differences between experimental series gradually became more significant with time (linear relationship not presented). These results are in agreement with data presented by Hassink [31]. He found that C-to-N ratios of OM decreased in order from partly decomposed plant residues to more processed organomineral-complexed SOM. Data of Knops and Tilman [17] show that agricultural cultivation of prairie soils resulted in lower loss of soil N in comparison to the loss of soil C. Soil recovery to the preagricultural N and C levels is predicted to require 180 yr for N and 230 yr for C. Similar trends were observed in the present study. In comparison with the last determinations in 1990, the OC content in the soils in 2009 dropped (after 12 years of plant cultivation and 7 years of fallowing) by about 20-35%, and the ToN content only by about 5-15%. Also, Dzienia et al. [32] found that the loss of OC was distinctly higher than that of ToN after 7 years of fallowing of sandy soils.

The added BNT could have the influence on the difference in accumulation of C and N. Kobus [33] and Kobus and Pacewiczowa [34] found that losses of C and N from aminoacids, proteins, or lupine straw added to a sandy soil were on a similarly high level. Montmorillonite fraction, separated from bentonite rock, reduced the losses of N in the sandy soil to a distinctly higher degree than those of C. The differences between losses of C and N from proteins or aminoacids were extremely high when these organic compounds were sorbed by montmorillonite before introducing into the soil [33].

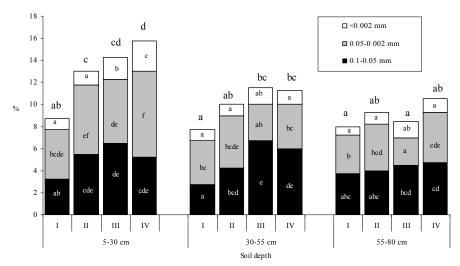


Fig. 1. Effect of the sandy soil amendment with 0 kg/m<sup>2</sup> (I), 3 kg/m<sup>2</sup> (II), 6 kg/m<sup>2</sup> (III), and 12 kg/m<sup>2</sup> (IV) of BNT on the contents of different particle-size fractions in 5-30 cm, 30-55 cm, and 55-80 cm soil layers. Different letters on the bars indicate significant differences between the treatments at P = 0.05.

I - the control soil without BNT added; II, III and IV - soils with addition of 3, 6, and 12 kg/m² of BNT, respectively.

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During the 1974-90 period, both the OC and ToN contents were gradually higher in soils amended with increasing doses of BNT. The average C content in 12-BNTS was significantly greater than those in the CS and 3-BNTS. In the case of the average ToN content, significant differences were found between CS and the soils with the two highest BNT rates (Figs. 3A, 3B). The average contents of both OC and ToN during the 1974-90 period were proportionally linearly related to amounts of BNT doses ( $R^2 = 0.99$  and 0.98, respectively). Also, Yssad and Belthodja [16] observed an increase of OC content in sand enriched with 2.5-10% bentonite after one year.

In 2009 the upper layers of the soil enriched with the highest two BNT rates had significantly higher OC content than those of the two other treatments (Fig. 4A). For the ToN content, only 12-BNTS was significantly different from the other treatments (Fig. 4B). Both the OC and ToN contents in the two deeper soil layers were significantly lower from those in the 5-30 cm layer (Figs. 4A, 4B). The OC and ToN contents were positively correlated (at P <0.01, n = 48) with the content of PRT < 0.05 (r = 0.75 and 0.73, respectively, results from all soil layers) and they were intercorrelated (r = 0.89 at P < 0.01, n = 48), which suggests that the added BNT (especially its highest rate)

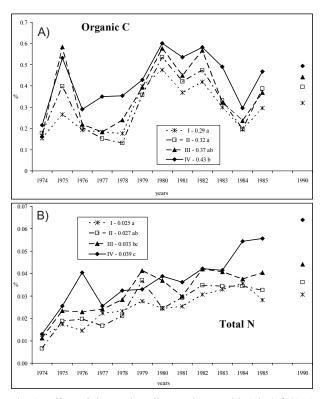
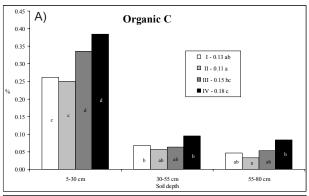


Fig. 2. Effect of the sandy soil amendment with 0 kg/m<sup>2</sup> (I), 3 kg/m2 (II), 6 kg/m2 (III), and 12 kg/m2 (IV) of BNT on annual means of the contents of organic C (A) and total N (B) in the 0-30 cm soil layers during the period 1973-85 plus 1990: Inside the legend the means of org. C and total N contents (in %) for the presented period are shown; different letters in the legends indicate significant differences between the treatments at P = 0.05. I - the control soil without BNT added; II, III and IV - soils with addition of 3, 6, and 12 kg/m<sup>2</sup> of BNT, respectively.



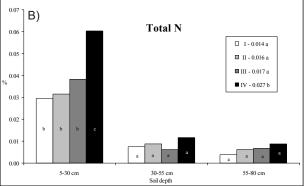


Fig. 3. Effect of the sandy soil amendment with 0 kg/m<sup>2</sup> (I), 3 kg/m<sup>2</sup> (II), 6 kg/m<sup>2</sup> (III), and 12 kg/m<sup>2</sup> (IV) of BNT on the contents of organic C (A) and total N (B) in the soils in 5-30 cm, 30-55, cm and 55-80 cm soil layers and, presented inside the legends (in %) for the whole 5-80 cm soil profile in 2009. Different letters on the bars or placed in the legends indicate significant differences between the treatments at P = 0.05. I - the control soil without BNT added; II, III and IV - soils

with addition of 3, 6, and 12 kg/m<sup>2</sup> of BNT, respectively.

had an essential effect on accumulation of both OC and ToN in the soils, and that in these soils, which were subjected to 7-year fallowing, ToN occurred mainly as a constituent of SOM.

Analyses of the soil samples collected in 2010 confirmed the positive effect of BNT at 12 kg/m<sup>2</sup> on the OC contents in the 5-30 cm and 30-55 cm soil layers. Besides the higher contents of total OC in 12-BNTS than those of CS in both soil layers, SOM of 12-BNTS was, in comparison to that of CS, distinctly richer in non-extractable humins (Fig. 5), which are part of humus permanently bound to mineral parts of soil [27, 35, 36]. The combination of the soil humic acids and montmorillonite clay minerals belongs to the most persistent complexes [27]. Kalisz et al. [36] reported that humins were the SOC fraction, which most strongly correlated with the content of soil clay, ToN and non-labile (non-oxidizable) C. Also, in the opinion of Marland et al. [18], stable C corresponds to organo-mineral soil C or C complexed with soil silt and clay. According to Sparks and Chen [20], the connection of C with mineral phases is a major stabilizing mechanism for protecting OM against microbial degradation in soils, and Kögel-Knabner et al. [37] reported that sorption to minerals generally

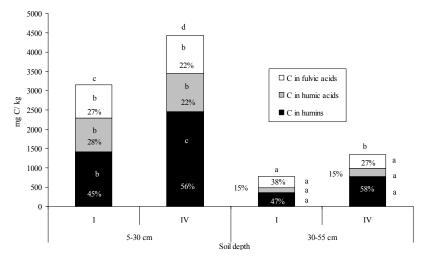


Fig. 4. Effect of the sandy soil amendment with 0 kg/m<sup>2</sup> (I) and 12 kg/m<sup>2</sup> (IV) of BNT on the contents of organic C and its fractions: C in fulvic acids, C in humic acids, and C in humins in 5-30 cm and 30-55 cm soil layers; Different letters on the bars indicate significant differences between the treatments at P = 0.05.

I - the control soil without BNT added and IV - soil with addition of 12 kg/m<sup>2</sup> of BNT, respectively

reduces the bioavailability of OM and its susceptibility toward oxidative transformations. Generally, 2:1-type clays can adsorb greater amounts of organic materials than 1:1 types due to large specific and high-charge densities in 2:1-type clays. The presence of smectite in studies of Indraratne [38] contributed significantly to the retention of C with the organo-mineral complexes, and according to Kögel-Knabner et al. [37], surfaces of 2:1-layer-type phyllosilicates, e.g. smectite might play a more important role in topsoils.

Rühlmann [39] in his study used the OC content of long-term bare fallow soils as an indicator of the size of the most stable SOM pool. Therefore, it is worth emphasizing that observed durable stabilization of OC by BNT in the present experiment is important from the point of view of carbon sequestration in soil. C sequestration by agricultural lands has generated global interest because of its potential beneficial impact on climate change and contribution to sustainability of agriculture. Because of a need to reduce atmospheric CO2 concentrations for the mitigation of climate change, there is much current interest in the possibility of increasing the long-term storage of OC in soils [40, 41]. The addition of bentonite to sandy soils to enhance the sequestration of C and N in the soils, in consequence, to mitigate global warming, has recently been taken under consideration [41, 42]. Churchman et al. [41] reported that the addition of clays (including bentonites) to sandy and degraded soils enhanced plant growth on these soils. Increased plant growth contributes to more intensive C sequestration, through subsequent incorporation of higher amounts of plant residues in soils [41]. Additionally, it should be emphasized that BNT amendment in the presented microplot experiment significantly increased the yield of various crops (potatoes, various cereals, alfalfa, mustard). The effect of BNT on the crop yield was dose-dependent [23].

#### **Conclusions**

During the 30-year period of plant cultivation, when the soils were regularly treated with organic and mineral fertilizers, the initial soil enrichment with bentonite increased the formation of SOM in the upper layer of the soil. The created organo-mineral complexes on the structure of the fine bentonite mineral particles were highly persistent over the subsequent seven-year period of bare fallowing. This phenomenon prevented the fine soil particle fractions from migrating into deeper soil layers. The increased accumulation of organic C and total N in sandy soil resulting from the bentonite addition might be an important measure intensifying C sequestration in soil. The significant differences were found between dynamics of total N and organic C. The total N content was less sensitive to fluctuations related to crop rotation.

#### **Abbreviations**

BNT – the bentonite used in the experiment; CS – the control soil without BNT added; BNTS and BNTSs – a soil or soils containing BNT; 3-BNTS, 6-BNTS and 12-BNTS – soils with addition of 3, 6, and 12 kg/m² of BNT, respectively; PRT < 0.1 or PRT < 0.02 – soil particles with diameters < 0.1 mm or < 0.02 mm, respectively; SOM – soil organic matter; SOC – soil organic carbon; OM – organic matter; OC – organic carbon; ToN – total nitrogen.

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