

# Rheological investigations of Rothamsted soils: Long-term effects of fertilizing systems on soil microstructure

Wibke Markgraf<sup>A</sup>, Chris Watts<sup>B</sup>, Richard Whalley<sup>B</sup> and Rainer Horn<sup>A</sup>

<sup>A</sup>Christian-Albrechts-University zu Kiel, Institute for Plant Nutrition and Soil Science, Hermann-Rodewald-Str. 2, D-24118 Kiel, Germany, Email [w.markgraf@soils.uni-kiel.de](mailto:w.markgraf@soils.uni-kiel.de)

<sup>B</sup>Soil Science Department, Rothamsted Research, Harpenden, Hertfordshire, AL5 2JQ, United Kingdom

## Abstract

A rotational rheometer with a parallel-plate measuring device is used to achieve stress-strain parameters, which define soil as viscoelastic material according to rheological theory. Hence, data deriving from conducted amplitude sweep tests with controlled shear deformation on Rothamsted Soils (Broadbalk long-term experiment) will be presented. The application of farm yard manure over more than 120 years led to an accumulation of organic carbon, resulting into a more rigid microstructural stability – with respect to the three-phase system soil – primarily due to a network of micro roots, and an increased water holding capacity and cation exchange capacity. Water content, texture, organic matter compounds, fungi and hyphae, contents and kinds of clay minerals, carbonates, (hydr)oxides, and cations have an effect on the microstructural stability (rigidity, stiffness), and shear behaviour. Storage modulus  $G'$  (elasticity) and loss modulus  $G''$  (viscosity), the linear viscoelastic range (LVE), pre-yielding and yield point (intersection of  $G'$  and  $G''$ ) characterise the three stages of microstructural degradation of soil on the particle-to-particle scale. A semi-quantitative classification of rigid-nonrigid or elastic-viscous material is applied considering the loss factor  $\tan \delta$  and integral  $z$ , delivering fundamental information about microstructural strength of investigated soil samples and their 'internal network'.

## Key Words

Rheology, Rothamsted, micromechanics, stiffness degradation, long-term fertilization

## Introduction

Rheometry is a useful tool to investigate microstructural changes in soil, which is defined as viscoelastic material. By conducting oscillatory tests, in detail amplitude sweep tests (AST) with controlled shear deformation (CSD), the degree of stiffness or elasticity-viscosity ratio, which is represented by the loss factor  $\tan \delta$ , can be calculated. As the loss factor defines elastic *and* viscous components, this ratio may function as link to microstructural processes, depending on texture, clay mineralogy, water content and organic matter.

## Material and Methods

A silty loam from Rothamsted, UK (long term experiment since 1885) (Powlson 1994; Watts *et al.* 2006), was taken and analysed, considering different properties such as texture, clay mineralogy, soil organic carbon (SOC) content, and manure application. In **Table 1** physicochemical properties are summarised.

**Table 1. Physicochemical characteristics of investigated substrates, Rothamsted (Broadbalk).**

	Sand	Silt	Clay	SOC
		(%)		
FYM*+ N <sub>2</sub>	21	58	21	2.7
FYM				2.8
N <sub>1</sub> PK(Na)Mg				1.0
N <sub>2</sub> PK(Na)Mg	19	58	23	1.0
N <sub>4</sub> PK(Na)Mg <sup>‡</sup>				1.1
N <sub>6</sub> PK(Na)Mg <sup>†</sup>				1.2
Wilderness (grass)	21	57	22	4.0
Bare fallow <sup>§</sup> (Highfield)	7	68	25	1.1

\*FYM farm yard manure (since 1885; N<sub>2</sub> added since 1968) <sup>‡</sup>since 1968

<sup>†</sup>since 1985 <sup>§</sup>Bare fallow – plough/autumn (since 1959) N<sub>1</sub>, N<sub>2</sub>, N<sub>4</sub>, N<sub>6</sub> = 48, 96, 192, 284 kg N as ammonium nitrate

### Amplitude Sweep

According to the method introduced by Markgraf *et al.* (2006), amplitude sweep tests were conducted with a modular compact rheometer MCR 300 to achieve data of stress-strain correlations on the micro scale (particle-particle contact). Recent collected data show significant differences of resulting micromechanical parameters i.e. storage and loss moduli  $G'$  and  $G''$  (Pa), and loss factor  $\tan \delta$  (-) as function of deformation  $\gamma$  (%), which are correlated to the water content, and other factors that may affect the matric potential: texture, single particle properties, pore size distribution, influence of (cat)ions (osmotic potential), and other physicochemical properties. A representative recorded plot of an amplitude sweep test is shown in **Figure 1**. The plots of storage and loss modulus ( $G'$  and  $G''$ ) are generated automatically during a test (Markgraf and Horn 2009).

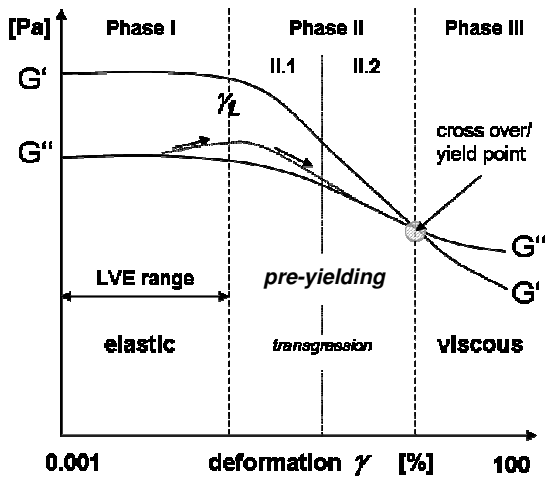


Figure 1. Idealised generated plots of storage modulus  $G'$  (Pa) and loss modulus  $G''$  (Pa) vs. deformation  $\gamma$  (%). In general, three stages of elasticity loss can be defined, showing a gradual transition of an elastic ( $G' > G''$ ) to a viscous ( $G' < G''$ ) character. In phase 1 an elastic behaviour predominates, and a parallel run of  $G'$  and  $G''$  is given. By reaching deformation limit  $\gamma_L$  (%) a yielding character is already given in phase 2 (pre-yielding); an intersection of  $G'$  and  $G''$  marks an absolute yield point. In phase 3 a microstructural collapse occurs and a viscous character is obtained.

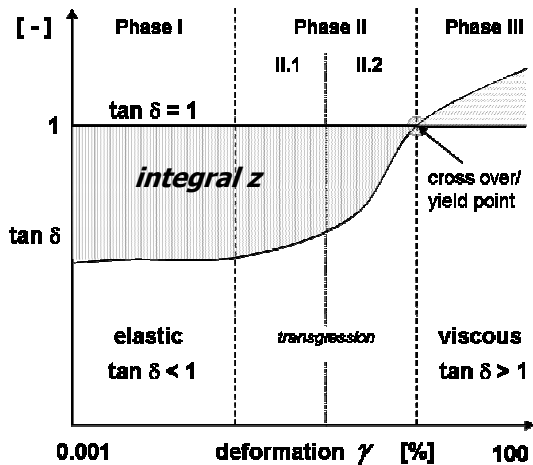


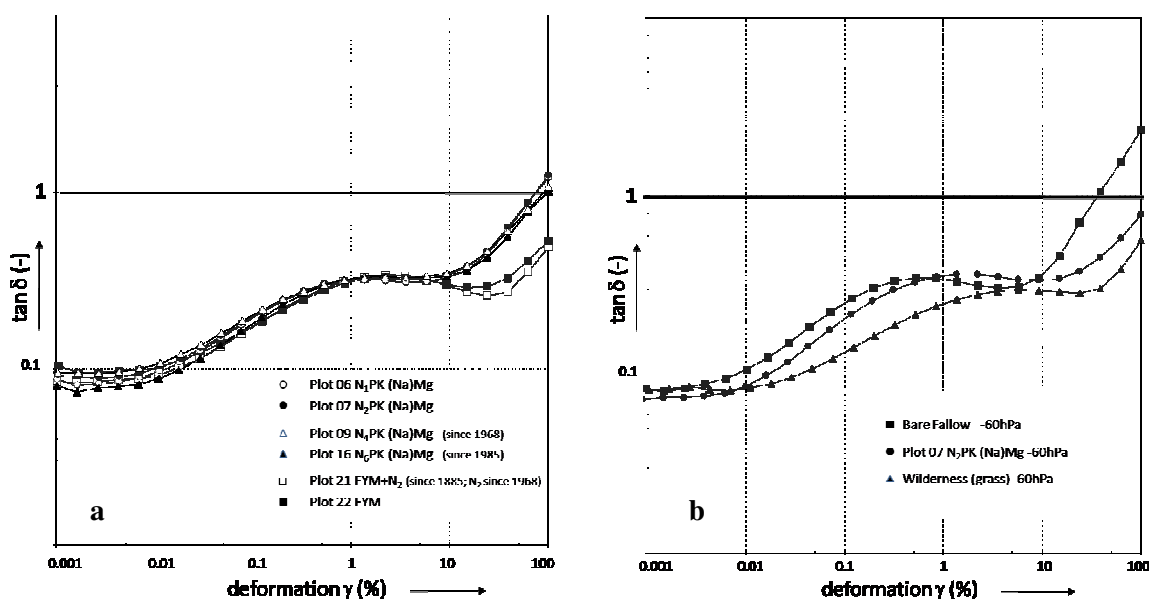
Figure 2. Deriving from one data set, results can be plotted in a loss factor vs. deformation coordinate system. Loss factor  $\tan \delta$  (-) equals the ratio of loss modulus to storage modulus ( $=G''/G'$ ), and may function as analogue expression of elastic ( $\tan \delta < 1$ ), viscoelastic ( $\tan \delta \leq 1$ ) or viscous ( $\tan \delta > 1$ ) behaviour. For further comparison, the integral  $z$  of  $\tan \delta(\gamma)$   $\lim \gamma=0.00\% \rightarrow 1$  to  $\lim \gamma=\text{“cross over point”}$ , with  $\tan \delta=1$  as defined limit on the y-axis can be calculated.

Natural viscoelastic substances react with a temporal delay. This is represented by the phase shift angle  $\delta$ , where  $\tan \delta$  equals the relation of the loss modulus  $G''$  (Pa) to the storage modulus  $G'$  (Pa), defining the relation of imaginary (“lost”) to stored elasticity. If  $\tan \delta < 1$ ,  $G'$  prevails  $G''$ , a gel character is given. Viscous behaviour is defined in case of  $\tan \delta > 1$ ,  $G''$  predominates  $G'$ . Furthermore, a correlation between in **Figure 1**

presented stages (Phases I-III) and phases of stiffness degradation in **Figure 2** become obvious. Due to a decrease of  $G'$ , the ratio of  $G''/G'$  ( $= \tan \delta$ ) increases; if  $\tan \delta=1$  is reached, elastic and viscous parts are equivalent, and an absolute yield point ( $=$ cross-over) is given at a defined deformation (%). If  $\tan \delta>1$ , a viscous character predominates, and a structural collapse occurs; at this stage deformation is irreversible. For further comparison, the integral  $z$  of  $\tan \delta \square(\gamma) \lim \gamma=0.00\%1$  to  $\lim \gamma="cross\ over\ point"$ , with  $\tan \delta=1$  as defined limit on the y-axis can be calculated. This method may allow an even more precise definition of elasticity, rigidity, or stiffness of a soil at the particle-particle scale.

## Results

Collected rheological data from conducted AST was used to achieve information about the influence of different manure applications on microstructural stability, in dependence on soil organic carbon (SOC) as well as inorganic nitrogen applications in combination with farmyard manure (FYM). In **Figures 3a** and **b** results from conducted AST with samples deriving from the Rothamsted Broadbalk long term experiment are shown. In general, curve characteristics are influenced by (i) water content: saturated (**Figure 3a**); unsaturated (**Figure 3b**), (ii) by treatments:  $N_xPK(Na)Mg$ , farm yard manure (FYM), bare fallow or wilderness (grass), (iii) SOC content, and (iv) texture. In comparison, different curve shapes are characteristic: in **Figure 3a**  $\tan(\delta)$  increases slightly within the section of  $\gamma=0.01\dots 1\%$ ; an intersection with the  $\tan(\delta)=1$ -line does occur in few cases only:  $N_2PK(Na)Mg$ ,  $N_4PK(Na)Mg$ , and bare fallow (unsaturated) variations. Furthermore, a slight increase in structural stability can be found as given in **Figure 3a**:  $FYM+N_2 > FYM \gg N_6PK(Na)Mg \geq N_4PK(Na)Mg > N_2PK(Na)Mg \geq N_1PK(Na)Mg$ ; samples which have been treated with farm yard manure since 1885 show a higher degree of stiffness compared to those which have been treated with  $N_xPK(Na)Mg$  within the last 40 years (e.g.  $N_4PK(Na)Mg$ ).



**Figure 3a.** Resulting graphs with  $\tan \delta (\gamma)$  of conducted amplitude sweep tests (AST) with Rothamsted Broadbalk samples:  $N_xPK(Na)Mg$  (saturated), and farm yard manure (FYM; pre-drained) treatments.

**Figure 3b.** Resulting graphs with  $\tan \delta (\gamma)$  of conducted amplitude sweep tests (AST) with Rothamsted Broadbalk samples under unsaturated conditions (pre-drained at  $-60hPa$ ): bare fallow,  $N_2PK(Na)Mg$ , and wilderness (grass).

Secondly, differences in soil organic carbon content may have an effect on the microstructural stability as organic matter leads to a higher water retention, which results into a more stable system. This instant is well defined in **Figure 3b**. Pre-drained samples of wilderness (grass) show a higher microstructural stability than bare fallow, and  $N_2PK(Na)Mg$ . If, in addition, FYM (pre-drained) plots in **Figure 3a** are considered, the influence of SOC becomes even more obvious: wilderness plots have the highest SOC contents (4.0%), followed by FYM (2.7%), bare fallow, and  $N_2PK(Na)Mg$  (**Table 1**). Although bare fallow and  $N_2PK(Na)Mg$  have similar SOC contents (1.1%), textural differences affect shear behaviour, and, deriving from this, stiffness degradation: a more silty texture in case of bare fallow (68% silt) occurs to be less rigid than a loamy clay ( $N_2PK(Na)Mg$ , 56% silt). By calculating integral  $z$ , these structural differences can be expressed

in absolute numbers; according to **Figure 3a**, this results into:

$\zeta_{N_xPK(Na)Mg \text{ saturated}} < \zeta_{FYM; FYM+N2 -150hPa}$ ,

in case of **Figure 3b** into:

$\zeta_{\text{bare fallow -60hPa}} < \zeta_{N_2PK(Na)Mg -60hPa} < \zeta_{\text{wilderness -60 hPa}}$ .

## Conclusions

Investigated Rothamsted samples, which have been treated with farmyard manure since 1885, showed a high degree in microstructural stability, as well as wilderness plots. This is congruent to findings of Tisdall and Oades (1982), Haynes and Naidu (1998), and Watts *et al.* (2006). Furthermore, Haynes and Naidu (1998) pointed out, that 'there is a strong correlation between the amount of fertilizer N applied annually and the quantity of organic C accumulated in the soil'. This instant is also true, if  $N_xPK(Na)Mg$ -treated plots are considered, higher N-contents are correlated to a slight increase in C; due to this, microstructural stability is increased stepwise from  $N_1$ ,  $N_2$ , to  $N_4$ , and  $N_6PK(Na)Mg$  treatments. In general, soil organic carbon improves soil structure and its functionality (Lemmermann and Behrens 1935, Haynes and Naidu 1998). Occurring menisci forces, which are formed due to drainage, maintain pore continuity, and as mentioned above, soil structure. It can be concluded, that rheological techniques and resulting parameters such as  $G'$ ,  $G''$ ,  $\tan(\delta)$  and  $\zeta$  are a useful tool not only to describe and quantify microstructural stability, but also to link structuring processes, which are relevant for up-scaling considerations e.g. improving soil aggregation.

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