Thesis of the Ph.D. dissertation

Rheological investigations of soil suspensions

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Introduction and objectives

Soil is a three-phase (gas, liquid and solid) cohesive system, which has a key effect on land ecosystems. It has several functions, but the most important is its role as a water reservoir for plants and microorganisms. Soil has a very complex structure, and under the natural circumstances it has the ability to resist changes and to return to a state of equilibrium after suffering disturbance. However, this equilibrium is fragile, which can be easily disturbed, especially by human intervention.

The structural degradation and desertification of land is increasing all over the world; hence any effort to characterize it effectively is of great practical importance. Several investigations were made to find an early indicator of soil degradation, with more or less success, difficult models were developed which were able to predict some kind of structural changes of soils by using many data determined previously. Unfortunately the only parameter which correlates with the others, and is characteristic to the soil quality has not been found yet. Another problem is that the widely accepted methods need very expensive laboratory instruments, as follows are unattainable by farmers.

Rheology is the study of the deformation and flow of matter under influence of an applied stress. The rheology of suspensions has been in the centre of interest for decades, mainly because of its industrial relevance (ceramics, food industry). It is an appropriate method for structural characterization of different soil samples, and for the comparison of their shear tolerance and resistance against external forces. Rheological measurements can provide advanced quantitative parameters characteristic for soil structure in addition to the shear strength, which is measured by a simple technique based on torsion force measurement in soil mechanics (ASTM Standard, D 2573-94). The strength of physical network developed in soil suspensions depends on the number of particles in unit volume, which are independent in dynamical point of view, and on the number and strength of binding points between them, i.e., on the adhesion forces.

Previous investigations found rheology suitable for characterization of shear strength, the strength of physical network of concentrated suspensions (for example cement and clay suspensions). In publications only the microstructure and its change, for example the effect of machinery used in agriculture, were investigated by oscillatory measurements. Unfortunately no articles are available about the characterization of the strength of physical network forming from soil particles, and not even about the preparing of suspensions and about this measuring method. My investigations were taken within a European specific targeted research project „Indicators and thresholds for desertification, soil quality, and remediation” (acronym: INDEX, GOCE-CT-2003-505450).

The aim was to develop the appropriate way of preparing soil suspension and the exact methodology for rheological characterization (flow curves and shear-time response curves) of soil suspension in corresponding state.

Moreover, I wanted to develop methods to characterize soil quality for non-experts, and to compare the results determined in such a way with the rheological parameters to demonstrate that these simple methods are also adequate to characterize soil quality.

Materials and methods

The rheological properties of aqueous soil suspensions were studied. These were prepared from the sample pool of INDEX (www.soil-index.com) containing selected European soils. The investigated soil samples are of different types of soils originated from different fields under diverse climates and in various stages of either degradation or remediation. The sampling sites such as catenae or experimental plots for soil remediation were situated in Spain, Italy, Germany and Hungary. These sites present a range of different impacts and pressures that not only are likely to promote soil degradation and desertification but also represent different types of plant cover (Santomera catena) and land use (the German Puch samples, the Italian Basilicata and Tuscany samples and the El Aguilucho from Spain). The long term experimental fields in Puch and the biological and conventional agriculture in Italy were compared; while the effect of plant cover was investigated in Santomera catena. In the Spanish El Aguilucho plots, the effect of different remediation processes and the effect of cultivation on terraces (reforestation, adding of mycorrhiza and/or organic matter with or without terraces, and the combination of these processes) were studied. In the Spanish Tres Caminos and Abanilla plots, the effects of different kinds of soil remediation processes were compared (adding of organic matter; mycorrhiza alone/or mixed with soil, adding compost, humoenzimes and sewage sludge). In the Hungarian Gödöllő plots, the effect of soil degradation is studied. During my study, soil samples from the sample pool (9 sampling sites such as catenae, remediation experiments, etc. in Europe) of INDEX Project were tested, sampled in the years 2004 (48 plots) and 2005 (43 plots). Soil suspensions were prepared by adding distilled water. For preparing suspensions the soil fractions < 1 mm were used. Only some examples can be showed, because of the limited extension of the PhD work.

The water content of soil suspensions in corresponding state, which is the water content of equilibrium sediment formed spontaneously from dilute soil suspensions after long standing under gravitational pull, was determined. The mass 4 ± 0.01 g (m_s, g) of soil fraction (<1 mm, soil sample passed through a sieve) was measured into a 10 ml calibrated test tube and 10 ml distilled water was poured into it. Powder and water were mixed with a glass rod thoroughly for ~ 1 min, and then the tube was placed into an ultrasonication bath for 10 s. The mixing and ultrasonication were repeated once again. The plugged tube was turned up and down several (~five) times gently to permit air bubbles to leave the suspension, then the test tube was placed in a rack. The tubes were kept in a vertical position, and particles were allowed to settle down for a week at room temperature (optimally at 25°C). The water content of soil suspensions in corresponding state (WCSSinCS) was determined from glass tube experiments by using the following equation:

$$\mathbf{WCSSinCS = 100\,(V_{sed} - m_s f/\rho_s)/(V_{sed} - m_s f/\rho_s + m_s f)}$$

, where WCSSinCS is given in unit g/100g, V_{sed}, cm^3 is the volume of the formed sediment, the density of water ρ_w is ~1 and that of solid ρ_s is 2.6-2.65 g cm^{-3}, and f = (100 – humidity %)/100).

For supporting the state, that WCSSinCS, which correlates well with the soils water holding capacity, is characteristic for soil quality, the plasticity index according to Arany (K_A, cm^3/100g) was determined using smaller amount of soil than usual. 15 g soil was milled in a mortar, and distilled water was poured into it until a homogeneous plastic paste was formed. After this, the distilled water was added drop-wise till the upper limit of plasticity was realized by the so called thread proof. The determined value was count over 100g amount of the soil sample (MSZ-08 0205:1978), and was compared with the value of WCSSinCS.

The flow and shear-time response curve measurements of soil suspensions were performed with a stress controlled HAAKE RS 150 rheometer using plate-plate (PP20 Ti) and vane (FL20) sensors at temperature 25 ± 0.1 °C regulated by a HAAKE DC 30/K20 thermostat. The measured data were evaluated by means of the RheoWin Data Manager.

In case of flow curve measurements a portion (~5 g) of soil suspension was placed carefully on the sample holding plate and the measuring position was reached with the lowest elevation rate (1.25 mm/min) of apparatus to prevent the breaking of particle network in suspensions. 4 mm thick layer of samples were measured. The flow curve (upward) was determined with a shear rate ramp over a period of 60 s from 0.01 to 10 1/s, and then the ramp was reversed to measure downward flow curve. Evaluation of flow curves resulted in the maximum of the upward curve, the extrapolated yield value and plastic viscosity of the down curve according to the Bingham model ($\tau = \tau_B + \eta_{pl}\ (d\gamma/dt)$ where τ is shear stress (Pa), τ_B is the Bingham yield value (Pa), η_{pl} is the plastic viscosity (Pa s) and $d\gamma/dt$ is the shear rate) for real plastic bodies, as well as in the area between the upward and downward curves as measure for thixotropy, using data analysis option of apparatus.

The shear strength of particle network can be characterized by absolute yield value measured by the vane method. The vane, placed at approximately the centre of the sample volume, was rotated at a constant (very low, 0.1 1/s) velocity and the resulting shear stress was generally recorded over time for 120 s, the gap was 5 mm. After a linear part of torque-time response due to the stretching of the network bonds interconnecting the structural elements (particles or aggregates or both), a maximum was measured. The maximum shear stress can be identified as yield value above which the network bonds start to break. The yield values were calculated with the RheoWin software.

The rheological parameters were compared with the other chemical parameters such as the organic matter (OM), the total organic carbon (TOC) and humic substances carbon (Chum) contents measured in the course of INDEX project, which are well-known quantities in soil science and indicate the quality of soils. The Chum, ppm is the humic substances carbon determined in a filtered and centrifuged 1:20 (solid:liquid) sodium pyrophosphate extract (pH 9.8) with a Shimadzu TOC5050A Total Organic Carbon Analyzer. The TOC, g/100g is the total organic carbon determined by oxidation with K_2CrO_7 in an acidic medium and evaluating the excess of dichromate with $(NH_4)_2Fe(SO_4)_2$, and OM is the organic matter of the soil samples, TOC values were multiplied by the factor 1.72.

The compactness of equilibrium sediments can be characterized by a simple glass tube experiment, by the study of redispersing. Into each glass tube 2 g soil sample was measured and 4 g distilled water was poured into it, to keep the water content in overflow. Powder and water were mixed with a glass rod thoroughly for ~ 1 min, and then the tube was placed into an ultrasonication bath for 10 s. The mixing and ultrasonication were repeated once again. The plugged tube was turned up and down several (~five) times gently to permit air bubbles to leave the suspension, then the test tube was placed in a rack. The tubes were kept in a vertical position, and particles were allowed to settle down for a week at room temperature (optimally at 25°C). In the bottom of the glass tube the equilibrium sediment, and above this the excess of water content appeared. Then the glass tubes were turned up and down as much times, as the equilibrium sediment dispersed. The number of turnings, the number of redispersing was compared with WCSSinCS values.

Field investigations were taken by Pocket Vane Tester (Eijkelkamp, Agrisearch Equipment), which equipment is able to measure the cohesion value, $kgcm^{-2}$, and to characterize the shear tolerance of the upper layer of soil. The cohesion of soil is characteristic for strength soil structure. 50*50 cm large plots were measured after adequate handling (flat surface, saturated with water, after adequate standing time). The axle with vanes connected to it was placed in the soil and was vertically turned around with a certain speed and force. The required force was measured at the breakpoint. By a table containing the adequate cohesion force - scale data, the values of cohesion force (Pa) could be determined, and these parameters were compared with the absolute yield values determined in laboratory.

New scientific results

1. The preparing method of soil suspensions in corresponding state, from soil samples with different mineral content and particle size was developed for reproducible rheological measurements.

1.1. To prepare homogeneous soil suspension the soil fraction with particle size <1 mm can be used. The concentration of suspensions is limited between the lowest and highest amounts of water content, over which solid particles are wetted and homogeneously distributed in space, and this range is different from sample to sample. The water content of soil suspensions (the equilibrium ratio of solid and liquid fraction) has inherent relation to the interfacial and colloid state of soil particle network (i.e., the number of binding points in unit volume), and is characteristic of the structure formation of soils; the suspensions prepared from different soil samples with the water content of their equilibrium sediments are in corresponding state.

1.2. The quality of soils can be characterized by the water content of soil suspensions in corresponding state (WCSSinCS), because it is proportional to the water holding capacity (WHC) of soils. As accepted widely, the better soils have higher WHC.

1.3. Another statement is that the WCSSinCS values in case of my investigations change parallel with the plasticity index according to Arany (K_A). The result of the comparison between WCSSinCS and K_A values verifies the findings, that the soil quality can be qualified by WCSSinCS.

1.4. It was suspected that the redispersing of equilibrium sediments is characteristic of the compactness of soils, as the more compact the soil, the less water it can hold, and the less dispersible the particles are. These measurements revealed however, that this method is neither appropriate to feature soil compaction, nor their strength, since the results could not show any relevant differences between the samples and not even a systematic order.

1.5. It was stated, that only limited number of soil suspensions can be prepared in the same concentration, as the water holding capacity of soils is very different. Consequently only some soil samples' suspensions with equal water content can be compared.

1.6. To make rheological measurement of soil suspensions reproducible, the preparing and measuring methods (the homogenization method of suspensions, the adequate standing time for developing equilibrium sediments, the convenient temperature, and the method of eliminating air bubbles) were standardized. Soil fractions with the particle size under 1 mm were homogenized with distilled water, by glass rod and ultrasonication, at 25 ± 1^{o}C, which was also the temperature of measurement, air bubbles were eliminated by knocking, and the 1-day standing at 25 ± 1^{o}C was enough for soil suspensions to reach equilibrium.

2. The circumstances of the rheological measurement of soil suspensions were standardized. Flow curves of viscoplastic soil suspensions have to be measured at low shear range, as the natural and artificial effects on soils (slipping on a slope, deformation, cultivation) are also in this range. Among the determinable rheological parameters, the initial maximum of flow curves and the thixotropic loop area are characteristic of the deformability of the thixotropic particle network of soils formed slowly in time. The maxima of shear-time response curves,

the absolute yield value (which is the characteristic force for breaking of bonds between particles) correlates with the shear strength of cohesive soils determined according to the ASTM Standard D 2573-94.

3. It was stated from the rheological researches of equilibrium suspensions of soils (from 9 sampling sites such as catenae, remediation experiments in Europe, sampled through 2 years), that the type of flow is viscoplastic, and high initial maximum and significant thixotropy were experienced in almost all cases, which are characteristic of loose aggregates with medium adhesion. The reproducibility of measurements was different from sample to sample, and changed between 1-33 percentages apart from some badly measurable samples. Another statement is, that rheological parameters change parallel with each other, it is enough to measure one of them. The determination of absolute yield value is recommended; because it correlates well with the parameter characteristic of soil strength determined according ASTM Standard Test Method for Field Vane Shear Test.

4. Under identical circumstances for the same suspensions (prepared and stored under the same conditions, the adequate standing time and the convenient temperature for develop of equilibrium sediments) the cohesion force in field and the absolute yield value in laboratory were measured in parallel. It was stated that cohesion force values and absolute yield values correlate well. The pocket vane tester is probably appropriate for monitoring the strength of soils in a given land, and their structural stability in time.

5. By comparing the water content of soil suspensions in corresponding state (WCSSinCS) and the rheological parameters it can be stated that usually the higher the water content the lower the shear tolerance, or in other words the resistance of the soil suspensions against shear is lower, and so their flow ability is higher. But the results of all soil suspensions cannot be compared. Only the results of suspensions with the same mineral content, from plots under similar management or remediation process are comparable.

6. Searching for correlation of a great many parameters measured for several soil samples, it can be inferred that for the samples of catenae and remediation experiments, the WCSSinCS and the absolute yield values are worth to compare with the parameters characteristic of the organic matter content of soils, namely the Chum, TOC, OM values, which are available in the data base of INDEX project.

From these comparisons the following findings can be made:

6.1. The effect of mismanagement (German Puch samples) manifests the decreasing organic matter content and water holding capacity of the soils in parallel. The structural degradation is indicated evidently by gradual decrease in absolute yield values.
6.2. Regarding the bio and conventional agricultural plots (the Italian Basilicata, Tuscany samples), the samples of conventional agriculture – supposedly because of their high salt content – are able to hold relevant higher water content than that of the samples of bio agriculture. The high water holding capacity couples with higher TOC values, but weaker soil structure, and the suspensions with higher water content have also lower shear resistance.
6.3. In case of the Spanish Santomera catena samples, the increase of plant cover made the soil structure definitely stronger, because plants have a long-term effect of increasing organic matter content on soils besides the soil binding effect of plant roots. The increase of plant cover has an increasing effect on shear resistance of soil suspensions, despite of their increasing water holding capacity.

6.4. The Spanish remediation experiments in Tres Caminos proved to be successful, as manifested in the increase of water holding capacity compared to the control sample; the shear resistance also increased, but these two effects did not show the same trend. Two different orders can be shown by grading the samples according to either increasing WCSSinCS or increasing resistance against shear; probably it is the cause of the third decreasing trend of absolute yield value vs. organic matter content curve.
6.5. In case of long-term experiments of adding sewage-sludge on the Spanish Abanilla plots, the amelioration of soil structure manifests itself in increasing absolute yield values (proportional to the other rheological parameters) in parallel with the increasing organic matter content. Humic substances can have aggregating or dispersing effect depending on the amount of available cementing cations. Regarding the soil composition data (www.soil-index.com), these soils have approximately 50 percentage carbonate (15-30 meq Ca^{2+}/100g) content, which is enough to solidify the soil structure for the 1,5 percentage organic matter content, while the higher, 2 percentage of organic matter content has liquefying effect for lack of Ca^{2+} ions.
6.6. It can be stated from terrace experiments of Spanish El Aguilucho catena that the terracing cultivation in its own does not remediate the soil structure, in several cases not even the water holding capacity increases. However the combination of terracing with reforestation and with organic matter addition, or the terracing reforestation combined with adding mycorrhiza mixed with soil can result in a significant amelioration, which manifests not only in the increasing water holding capacity after long time, but also in distinct increase in absolute yield value.

As a conclusion, it can be stated that rheology is an appropriate method to indicate the structural degradation of soils in time. Usually, in case of the same sort of soils, for example samples of a catena (with the same vegetation, but different plant cover), samples under different degree of cultivation, or under remediation experiments, the rheological parameters decrease with the increasing water content of the suspensions; the increase in organic matter content can induce the formation of more shear tolerant aggregate structure when adequate amount of Ca^{2+}-ion is available and the ratio of organic matter content to Ca^{2+}-ion content is also sufficient.

Possible applications

1. The value of WCSSinCS, the water content of suspensions in corresponding state, by which the water holding capacity and its ability to provide water for plants can be characterized, can be determined from simple glass tube experiments; and the degradation of soil can be followed by this simple method.

2. The absolute yield values of soil suspensions (prepared, held and measured under standardized conditions), which are characteristic of the shear tolerance of soil suspensions, and change parallel with the other rheological parameters, can be determined under laboratory conditions.

3. On the basis of field cohesion measurements, it can be stated that the pocket vane tester is able to characterize the strength and shear tolerance of soils under the given humidity conditions. This method can be used for monitoring structural stability of soils.

4. Rheology is able to characterize the optimal remediation of degraded or structure less soils; it is advised to use before expensive field investigations.

Publications

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