



# **Soil development and organic matter dynamics in the CZO Marchfeld**

*Jasmin Schiefer*

Institute of Soil Research; University of Natural Resources and Life Sciences, Vienna

Institute of Soil Chemistry; University of Delaware



Marshallplan-Jubiläumsstiftung  
Austrian Marshall Plan Foundation

Visiting scholar report

*9<sup>th</sup> March- 31<sup>st</sup> August 2015*

## Introduction

The main purpose of my visit for six months at the University of Delaware was to gain a deep understanding of soil organic carbon (SOC) dynamics as influenced by time, soil depth and different land use. My research site is located at the Danube River near Vienna/Austria. I am analysing soil along a soil chronosequence with a soil age ranging from 10 up to 9000 years under different land use. This study site is a CZO (Critical Zone Observatory) and was part in the international EU-research project “Soil Transformations in European Catchments” (SoilTrEC, 2010-2014). While working for this project I also had the chance to meet Dr Sparks, a well-known scientist in the field for soil chemistry working at the University of Delaware (UD).

During my visit at the UD I was able to learn some new analytical instruments. I also had the chance to learn a lot from the research projects of my colleagues who are mainly specialized on environmental pollution problems due to heavy metals in soil.

The first measurement I performed was a BET analysis. This was done to determine the impact of time on C sorption and C complexation in the clay-sized microaggregates. I also performed a TA/DSC analysis to get more information about the biological stability of OC along the chronosequence.

The main purpose of my visit was to gain knowledge in synchrotron-based techniques, including bulk carbon near edge X-ray absorption fine structure spectroscopy C- XANES. Dr. Sparks group is one of the few soil research groups worldwide working with these techniques. I was able to perform PGM C-XANES on my samples and I also was allowed to use the Toroidal Grating Monochromator (Phosphor edge) to support a colleague.

I also carried out Scanning Electron Microscopy to find differences of carbon location in the clay sized microaggregates along the chronosequence.

Besides my analysis I was able to attend a workshop about synchrotron in geosciences and about soil health at the Cornell University.

I gained great data and knowledge and I also was able to make good connections and gain great knowledge from experts I would not have met in Austria.

## TG/DSC analysis

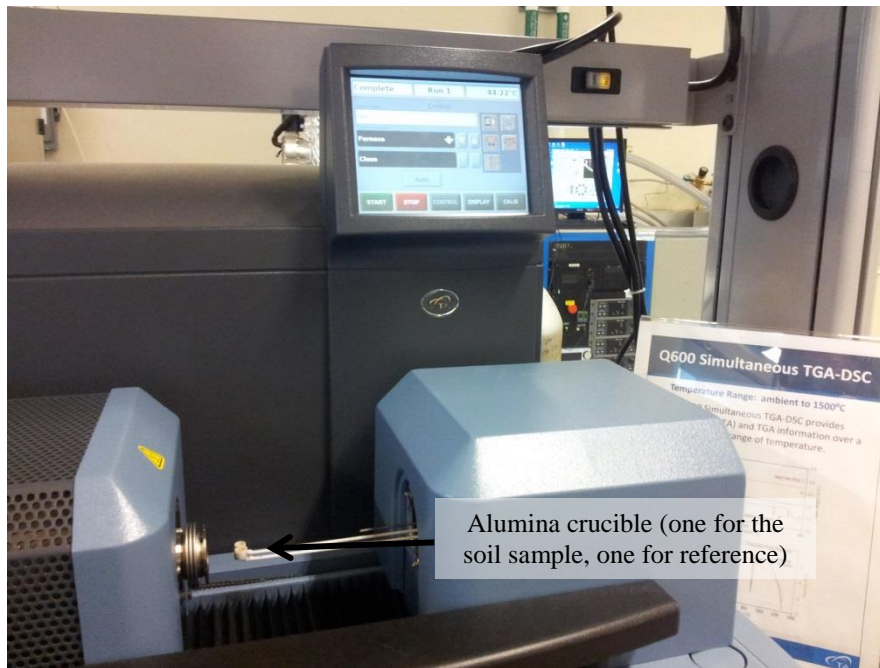
### Introduction

Thermogravimetry provides information about thermal stability and composition of materials (Dell'Abate et al., 2000; Plante et al., 2009). Thermal stability of soil constituents and the relative abundance of more and less labile SOM are determined by the weight loss (TG) whilst the structure and chemical composition of SOM is reflected by the Differential Scanning Calorimetry (DSC) (Lopez-Capel et al., 2005). The energy content derived from DSC in soils also gives information of SOM stabilization through interactions with soil minerals and is directly related to biological stability (Stone and Plante, 2015).

TG analyses have already been performed on our samples. However, no evaluation of the DSC (=energy change) was done. The energy necessary for thermal oxidation/ combustion is determined with the DSC. This needed energy can be directly related to the energy barrier to SOM decomposition, as well as to the energy stored in a soil sample, which can be related to the energy yield (Peltre et al., 2013).

### Material and Methods

The TGA/DSC analyses were performed on a TA Q600 HT TGA/DSC (Figure 1). TA is a local company with the headquarter in New Castle, Delaware. This company is specialized in thermal analysis equipment and cooperates with the University of Delaware. Therefore I was also able to take advantage of their great on-site support and get introduction to some of their products. For the purpose of my study the TA Q600 HT TGA/DSC was most suitable as it provides both- time and frequency domain mechanical analysis of materials in desired temperature range.



**Figure 1:** TA Q600 HT TGA/DSC instrument

Approximately 30 mg of the clay sized fraction was placed in an alumina crucible with an identical but empty crucible used as the reference (see Figure 1). The samples were heated from ambient temperature to 600° C. Heating rate was set at 7° C min<sup>-1</sup> and was kept on isothermal level at 80° C for 15 minutes to completely remove water. The experiments were performed under oxidizing atmosphere of 30 mL min<sup>-1</sup> flow of synthetic air. Analysis of the TG and DSC were performed using the instrumental software.

Weight loss of a soil sample during TGA can be separated into the evaporation of hygroscopic water (up to 200°C), SOM breakdown, and carbonate decomposition (starts at 550°C) (Siewert, 2004). In this study, total weight loss associated with thermal decomposition of organic constituents is presented between 190°C and 550°C (Exo<sub>tot</sub>). This weight loss was further divided after the concept of Lopez- Capel et al. (2005), De la Rosa et al. (2008) into following pools:

- Exo1= labile pool: 190- 390°C
- Exo2= more stable pool: 390- 450°C
- Exo3= stable pool: 450- 600°C.

Clear temperature thresholds haven't been established yet for these three different thermal regions. However, Peltre et al. (2013) states, that these Exo indices were already often been proofed to be usefully to describe sample biological stability.

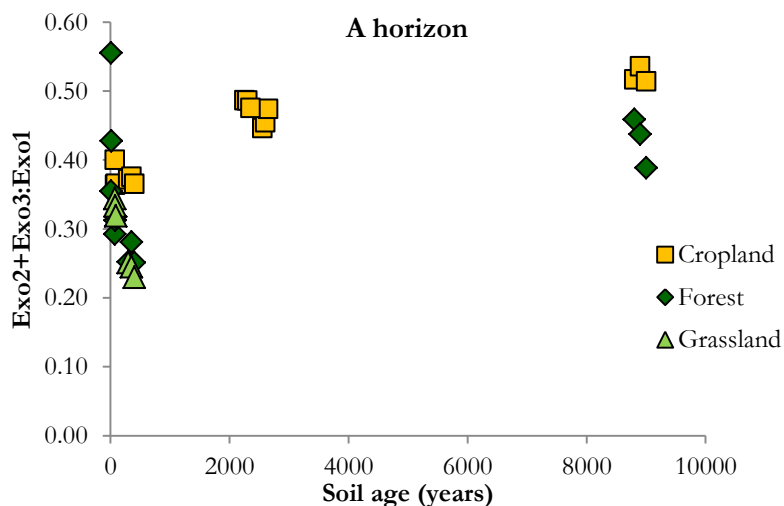
These temperature ranges were also used to integrate the DSC curves. This provides a measure of the total amount of energy consumed or released (exotherm) during the reaction (Plante et al., 2009).

We used following parameters to describe the thermal characteristics of SOM:  $Exo1/(Exo2+Exo3)$ , the amount of energy consumed/released ( $J\ g^{-1}$ ), DSC temperature peak ( $^{\circ}C$ , PT) and the energy density of the clay sized fraction along the chronosequence.

## Results

### TGA mass loss

The mass loss of the labile pool  $Exo1$  represents the oxidation of carbohydrates, proteins, cellulose and carboxyl groups (De la Rosa et al., 2008).  $Exo2$  is attributed to polypehnic and other aromatic structures like lignin (Lopez Capel et al., 2005; Rovira et al., 2008).  $Exo3$  is the most stable fraction containing polycondensed aromatic black carbon (Del la Rosa et al., 2008)



**Figure 2:** Increase of the ratio between the stable SOM pool ( $Exo2+Exo3$ ) compared to the labile SOM pool ( $Exo1$ )

Lopez Capel et al. (2006) introduced the ratio  $Exo1/Exo2+3$ . This relationship gives information of how much labile SOM material, compared to the (more) stable material is in the soil.

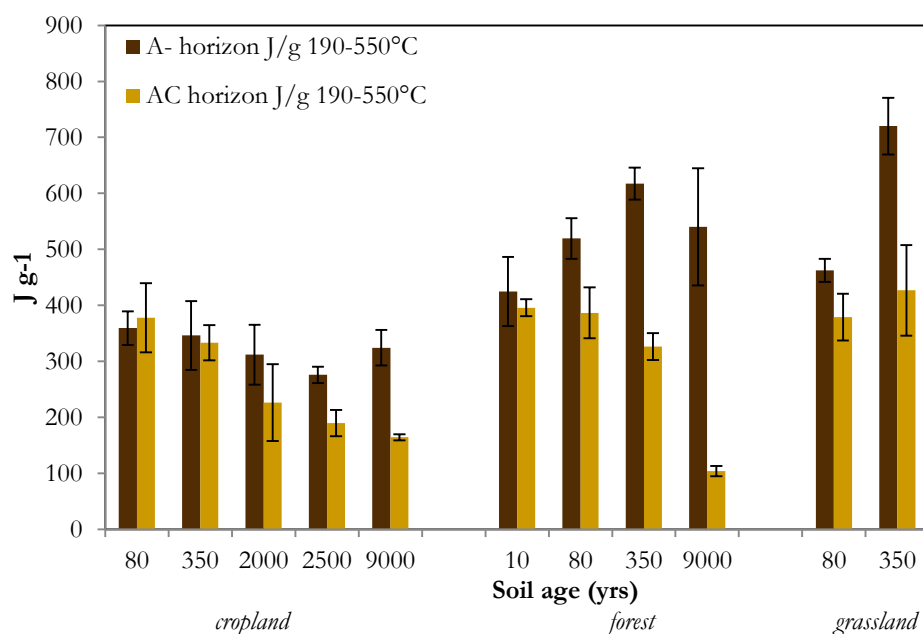
Figure 2 shows the relationship of  $Exo2+Exo3/Exo1$  along the chronosequence in the clay sized fraction (0-10 cm). It can be seen that the relative contribution of chemically stable

(Exo2+Exo3) to labile compounds (Exo1) is increasing. The AC- horizon shows the similar trend but shows a higher ratio. This means, that the composition of the SOM in the AC horizon is more stable but still shows the same proportional change of the biological stability like the A- horizon.

### Differential Scanning Calorimetry (DSC)

#### Energy consumed/ released ( $J g^{-1}$ )

The coordinate axis of DSC data are typically reported in units of microvolts per milligram of sample ( $\mu V mg^{-1}$ ) when reported as raw, uncalibrated signal, or in units of mWatts per milligram ( $mW mg^{-1}$ ) when the instrument has undergone sensitivity or enthalpy calibration (Plante et al., 2009). Energy which was consumed/ released is given in  $J g^{-1}$ . The DSC curve was integrated in the temperature region where SOM oxidation/combustion occurs (190-550°) and in the three different defined Exo regions.



**Figure 3:** Net output of energy  $J g^{-1}$  along the chronosequence in the clay sized fraction

The energy input reflects how much energy is needed for breaking up organomineral associations (Peltre et al., 2013; Schulten and Leinweber, 1999).

The net output of energy is the difference between the input energy needed and the stored energy released which was captured due to autotrophic organisms who capture energy from an abiotic source and store it as chemical bonds between carbon atoms (Rovira et al., 2008).

Energy release (exothermic reaction) differs between the different land uses. Land use systems such as forest and grassland with more fresh material added show a higher energy release than cropland sites (Figure 3).

Along the chronosequence we can see a bigger oxidation of material and release of energy. In the AC- horizon a rather opposite trend occurs. A decreasing exothermic energy content along the soil profile was also found by Stone and Plante (2015).

However, these data are directly related to the amount of organic carbon stored in the clay sized fraction and might rather reflect the OC content. Therefore it is more useful to use energy densities in order to give information of the quality of the organic material.

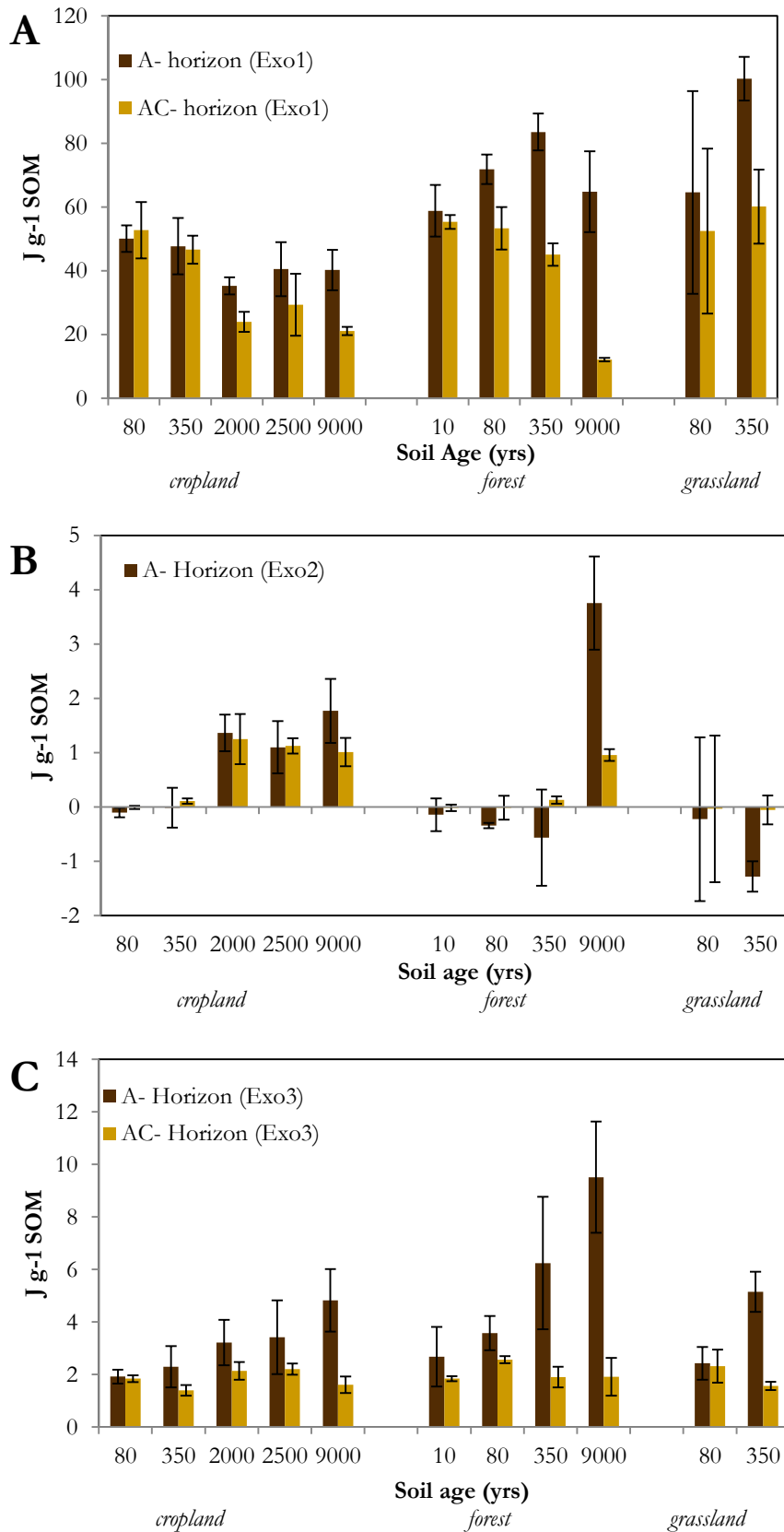
### **Energy density**

TG and DSC can be combined to study the energy density of a matter during decomposition in various temperature ranges (Rovira et al., 2008; Plante et al., 2009; Gao et al., 2013)

Energy density is the total energy released per unit SOM and is therefore calculated by dividing the total energy release with the weight loss of SOM within a temperature range (Rovira et al., 2008; Gao et al., 2013).

Looking at the energy density in the different Exo regions we can see that most energy of SOM oxidation is released in Exo1 (Figur 4, A). Forest and grassland sites release/stores more energy and the AC horizon stores less energy in the thermal area easily accessible for organisms.

Exo2 energy densities are negative in the younger sites (Figure 4, B). This means that more energy was added than released because less energy in form of OM is stored in the thermal stable region. Forest and grassland with young soil age need more energy compared to cropland sites. The oldest forest site (9000 years) shows a clear release of energy. This means that most of these more stable compounds and mineral bound OM can be found in this soil.



**Figure 4:** Energy densities ( $J g^{-1} SOM$ ) along the chronosequence in the clay sized fraction

(A: Exo1 190-390°C; B: Exo2 190- 450°C; C: Exo3 450-550°C)



Energy density in Exo3 (Figure 4, C) shows an increasing trend along the chronosequence. The energy density in the AC- horizon is very similar under different land uses and along the chronosequence. This would indicate, that the same energy to break up biological stable compounds is needed and therefore a similar composition of the most stable bound fraction. SOM that combusts at higher temperatures (Exo2 and Exo3) has a greater energy barrier to decomposition. Another study showed that there is a direct relationship between the stage of decomposition and energy density (Rovira et al., 2008). In young forest and grassland sites the decomposition of labile material (Exo1) is very high but the energy barrier to decompose material at higher temperature (stable material) is very high showing that the SOM is easily available for organisms and therefore not stabilized in the soil.

The measured energy content of SOM can also be used as an index of the energy available for microbial metabolism (Stone and Plante, 2015). This is a next step which should be analysed in Austria to underline the results gained from this analysis.

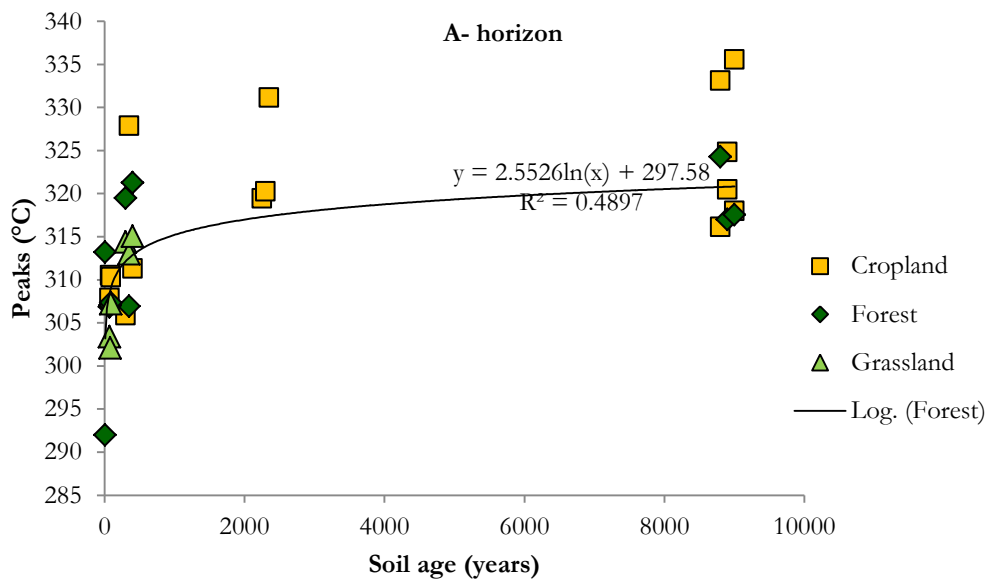
### **DSC Peaks**

An increase of temperature peak can be associated with an increase in C stabilization (Schulten and Leinweber, 1999).

The maximum temperature for exothermic reactions (DSC peak temperature) increases along the chronosequence (Figure 5). The youngest sites show the maximum peak at about 306°C ( $\pm 5.6$ ), sites with 350 years soil age increase its maximum peak at  $\sim 315^\circ\text{C}$  ( $\pm 6.9$ ) and the oldest sites present the highest temperature peak at  $\sim 323^\circ\text{C}$  ( $\pm 6.6$ ). Land use has almost no influence on the maximum peak. The AC horizon also shows the same trend with similar temperatures. Sites older than 2000 years also show a small second peak at  $\sim 450^\circ\text{C}$ .

Plante et al., (2005) related the height of the peak directly to the OC contents. His study showed that a decrease in OC contents decreases the first exothermic peak and the second exothermic peaks reduce to a shoulder to the first peak. This direct relationship cannot be seen in our study. Cropland sites with  $\sim 9000$  years of soil show similar high peaks than forest sites in the same age class. The site with the highest OC content (grassland 350yrs: 75.26 g C kg<sup>-1</sup>) shows no formation of a second peak at 450°C. Cropland sites (and forest) with lower C contents but older soil ages show a formation of a second peak. The formation of the peak therefore seems to be more dependent on soil age than C contents.

Rovira et al., (2008) showed that a decrease of the maximum peak temperature and a flattening of the peak can be connected to decomposition processes. This indicates that the older soils are already more mineralized and are less suspect to decomposition. This is in line with our other analysis and shows that TA/DSC is a useful method for studying SOM dynamics.



**Figure 5:** Maximum temperature for exothermic reactions (DSC peak temperature) in the A- horizon (0-10 cm)

## BET- Specific surface area

### Introduction

Many physical and chemical soil properties are influenced by or closely related to the SSA (Heister, 2016). One of the most important properties influenced by SSA is the organic matter content and strength of binding. A larger SSA provides more surface sites, resulting in a higher reactivity or sorption capacity. Clay sized minerals are known to provide the largest SSA for adsorption mechanisms (Ransom et al., 1998). However, the SSA of clay minerals is further dependent on the clay mineral type (Table 1).

**Table 1:** Specific surface area for clay minerals

*Source: Schachtschabel et al., 1998*

Mineral	Specific surface area [m <sup>2</sup> g <sup>-1</sup> ]
Smectite and Vermiculite	600- 800
Illite	50- 200
Kaolinite	10- 150
Allophane and Imogolite	700- 1100
Goethite and Hematite	50- 150
Ferrihydrite	300- 400

This study is mainly interested in the role of the SSA in SOM build up and storage. Mineral surface areas are of particular importance for the storage of OM (Kahle et al., 2002; Dümig et al., 2012) due to mineralogy, mineral surface properties, multivalent cations, microorganisms and quality of SOM (Mayer, 1994; Sollins et al., 1996)

### Material and Methods

The most common method to analyse the SSA of soils is the BET (Brunauer, Emmet and Teller) measurement (Brunauer et al., 1938). The influence of SOM on mineral surfaces and pores could be demonstrated as only the external area of soil minerals are accessed and only generates low specific surfaces of SOM (<1 m<sup>2</sup> g<sup>-1</sup>) (Wagai et al., 2009).

All measurements of the surface area by means of gas adsorption were performed in triplicates with a Micromeritics ASA 2020 (see Figure 6). Nitrogen gas was used at 77 K at partial pressure regions of 0.01- 0.995 p/p<sub>0</sub>. SSA was calculated from 12-point adsorption

isotherms in the relative pressure range between 0.05 and 0.30 according to the BET equation (Brunauer et al., 1938).



**Figure 6:** BET instrument Micromeritics ASA 2020 in the UD Material Science Lab

Prior to analysis, the samples were freeze dried for at least 24 hours in order to remove adsorbed volatile substances like water vapour.

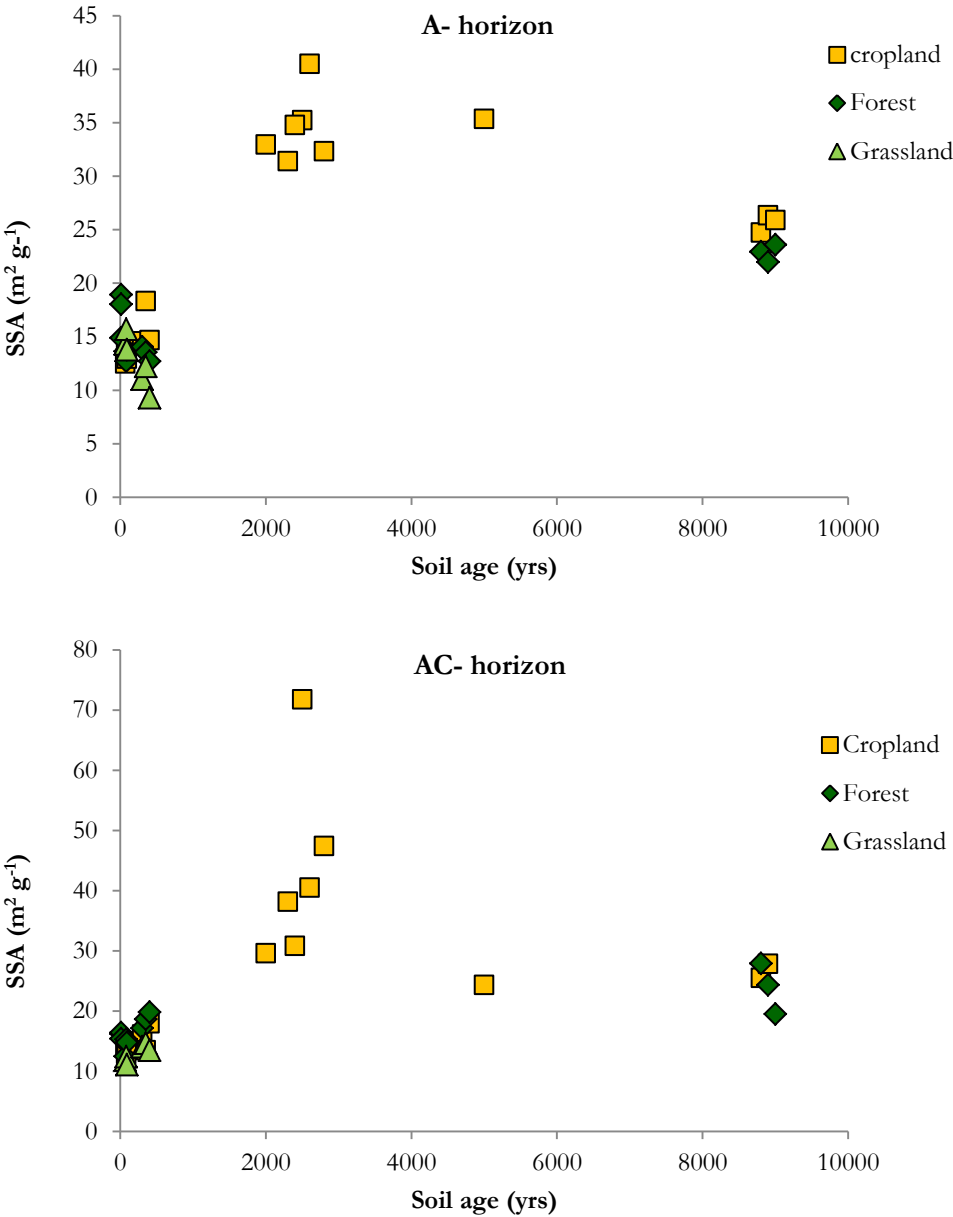
## **Results and discussion**

XRD analyses were performed prior to analysis (at BOKU). These measurements showed that along the chronosequence we do not see a significant difference in the mineralogy of the samples. The presented soils mainly consist of calcite/dolomite, illite and feldspar. Therefore we do not have to consider the different SSA of specific mineral types and can conclude changes to soil formation processes.

Figure 7 presents the SSA in  $\text{m}^2 \text{g}^{-1}$  along the chronosequence in the A horizon. We can see that the land use does not influence the SSA. Cropland sites between  $\sim 2000$  and  $5000$  years have the highest SSA ranging from  $\sim 30$ -  $35 \text{ m}^2 \text{g}^{-1}$ . The large SSA between  $2000$  and  $5000$  years can be explained because weathering processes typically increase SSA of mineral soils

(Kahle et al., 2004) and because of the low OC content in those cropland soils what causes an increase of SSA (Wagai et al., 2009). OC content reduces the SSA due to the inaccessibility of organic matter and of organic matter-filled pores by N<sub>2</sub> and/or or the gluing of small mineral particles to larger aggregates by organic macromolecules (Feller et al., 1992; Kaiser and Guggenberger, 2003).

However, the increasing trend of larger SSAs with increasing soil age does not continue. The oldest sites (~9000 years) have a SSA between 35 and 30 m<sup>2</sup> g<sup>-1</sup>. The AC horizon shows the same trend. Generally, the AC horizon shows slightly larger SSA.



**Figure 7:** Specific surface areas along the chronosequence in the clay sized microaggregates

Other studies showed that increasing OM levels leads to the coverage of the mineral surfaces proportional to the OM content (Mayer, 1994; Wagai et al., 2009). Along our chronosequence the OC content and SSA do not show a strong correlation in the clay sized fraction. Looking at the oldest cropland and forest sites, the OC content strongly varies (cropland 9000yrs:  $\sim 50 \text{ g kg}^{-1}$ ; forest  $\sim 80 \text{ g kg}^{-1}$ ) but the SSA is similar large. The OC content increases from 40 to  $50 \text{ g kg}^{-1}$  ( $\sim 10$  to 80 years) in the forest. Between these two sites, the SSA decreases from 18 to  $13 \text{ m}^2 \text{ g}^{-1}$ . With increasing soil age, the OC content increases to  $60 \text{ g kg}^{-1}$  (350 yrs) but the SSA stays almost the same. The grassland sites show an increase from 44 to  $75 \text{ g kg}^{-1}$  (80 to 350 years). However, the SSA only decreases from 14 to  $12 \text{ m}^2 \text{ g}^{-1}$ . Kaiser and Guggenberger (2003) also showed that at the initial stages of surface loading there is a strong decrease in SSA with increasing OC surface coverage due to preferential sorption at reactive sites such as edges, rough surfaces, or micropores.

A strong significant correlation was found between the SSA  $\text{m}^2 \text{ g}^{-1}$  and the energy density ( $\text{J g}^{-1}$  SOM), derived from the TA/DSC measurements. Decreasing surface sites lead to an increase of labile SOM ( $\text{J g}^{-1}$  SOM; Exo1) which is easily accessible by microorganism. The biological stable material on the other hand shows a strong positive correlation with increasing SSA.

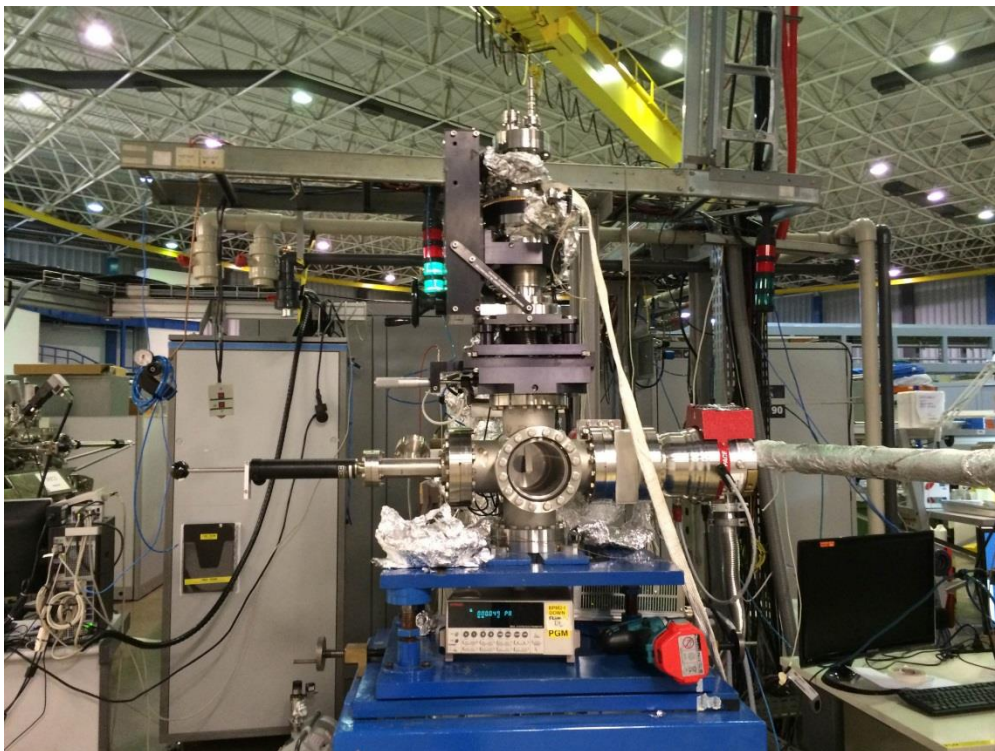
## Synchrotron based PGM C- XANES

### Introduction

Spectroscopic techniques like X- Ray absorption near- edge structure (XANES) is a very useful method to identify the fine structures of organic C in various molecular groups (Lehmann et al., 2008; Solomon et al., 2009). XANES analysis were already successfully used to get insights into transformation and stabilization of SOM (Gillespie et al., 2013).

### Material and Methods

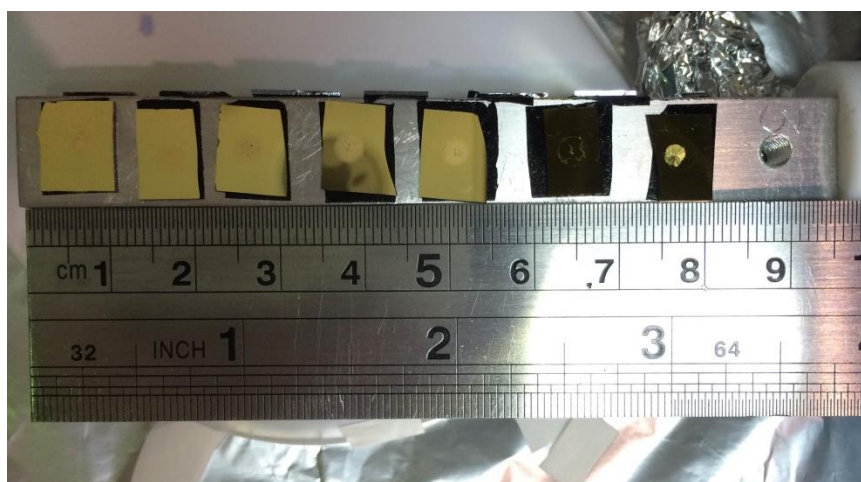
The PGM (Planar Grating Monochromator- Figure 8) covers an energy range from 100 up to 1500 eV providing high energy resolution. The beamline is equipped with an APPLE II type elliptically polarising undulator (EPU). The first optical element in the beam line is a side bounce toroidal mirror that collimates the beam vertically before it gets to the monochromator while the last one consists of a plane mirror coupled to a plane grating in a Petersen like configuration (Cezar et al., 2013).



**Figure 8:** PGM beamline

Samples were prepared by powdering 2 mg of the clay sized fraction as fine as possible. 2 mL of de-ionized water was mixed with the powdered soil in an Eppendorf tube. From this suspension a volume up to 10 micro-litter was deposited onto a gold-coated silicon wafer and air-dried. Up to 7 samples were able to be fixed with CA tape on the metallic sample holder and put into the chamber for analysis (Figure 9).

To gain data the FL and TEY detection methods were used at the same time because the TEY method provides a low signal intensity but high signal- to- noise ratio; the FL provides those ratios the other way round.



**Figure 9:** Metallic sample holder and Au coated Si wafers with soil samples

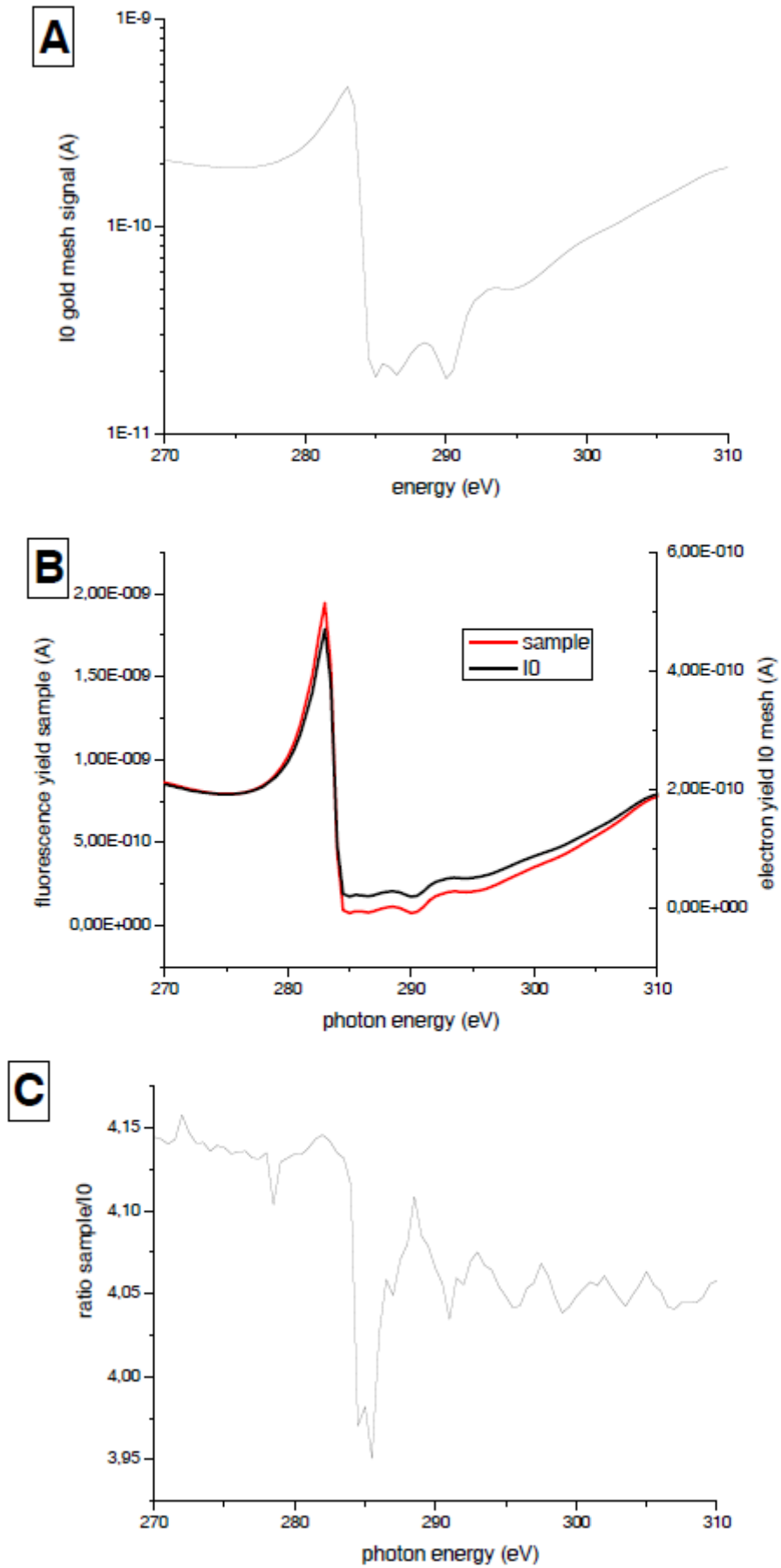
## Results

The results of the PGM C- Xanes are unfortunately not very promising. It seems that there was carbon contamination in the beam line optics. Intensity of the signal was lost around the carbon absorption edge energy.

Figure 10 A shows the I0 signal around the carbon K edge in the beam line where the huge carbon contamination can be seen. Intensity around the carbon edge is lost by a factor of about 20.

Comparing the sample signal to  $\langle c \rangle$  in the beam we cannot see a big difference (Figure 10, B). This is because the real sample signal variation is much smaller than the variations in I0. Therefore, the sample signal is fully dominated by the I0 variations. Dividing the sample signal with the I0 signal (=normalized signal) the data does not resemble to typical absorption edges (Figure 10, C).The presents signals were taken from the oldest forest (A horizon). Other samples looked identically.





**Figure 10:** Signals gained by the PGM- XANES at the C edge

## Scanning Electron Microscopy (SEM)

### Introduction

The UD offers five different electron microscopes and a huge working group which can support. Therefore I was very curious to get more insight into electron microscopes. Scanning Electron Microscopy (SEM) is a common technique used to view the micro-textural features of soil matrix as exposed on its surface, providing information on the size, shape, and the state of orientation and aggregation of soil particles (Eisazadeh and Eisazadeh, 2015).

### Material and Methods

Fine powdered clay sized microaggregates were put on a carbon tape and sputtered with a gold layer. Images were created with a JSM-7400F high resolution scanning electron microscope (Figure 11). The SEM is equipped with an energy- dispersive spectroscopy (EDS) Si-Li X-ray detector (active area = 30 mm<sup>2</sup>) capable of detecting elements. For C detection an accelerating voltage of 30keV and a working distance of 8.5 mm was used.

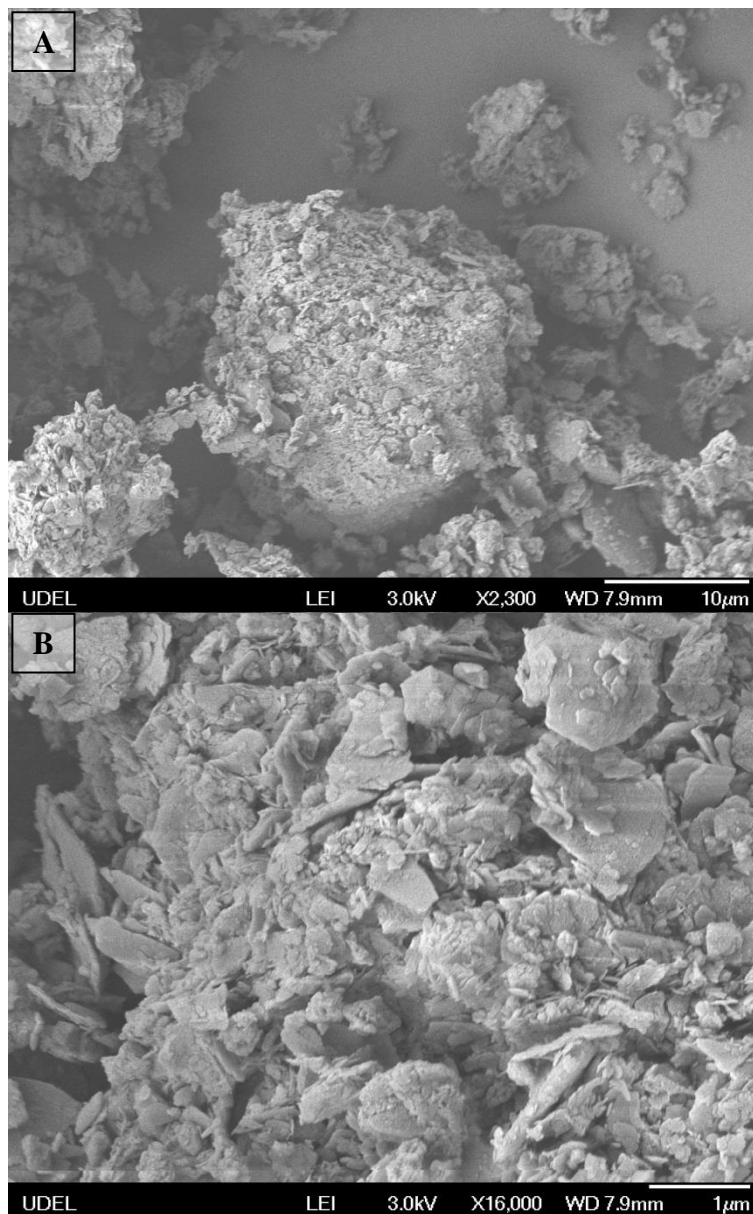


**Figure 11:** Scanning electron microscopy

For taking images accelerating voltage was set to 3kV with changing working distance.

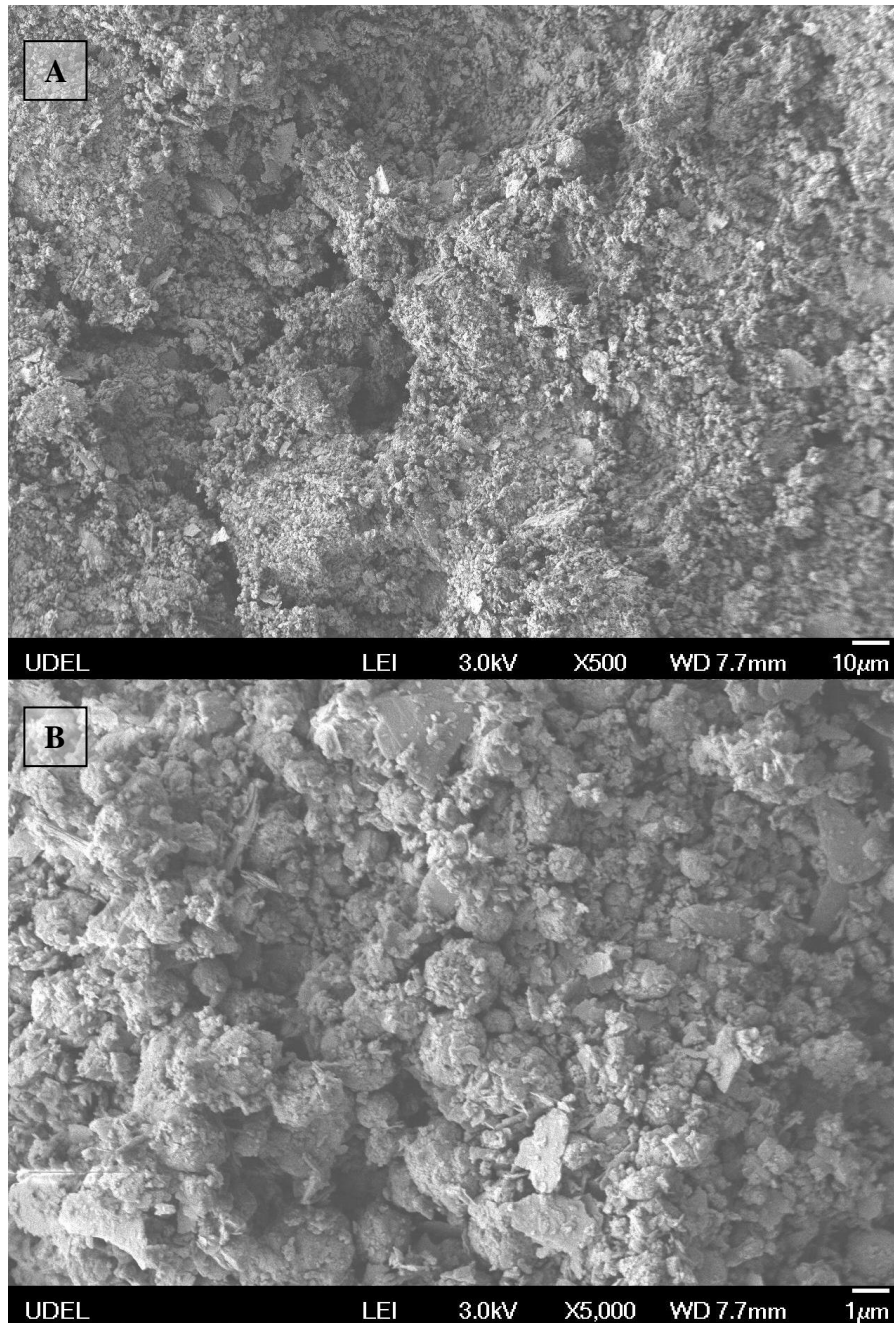
## Results

I used the EDS in order to detect carbon in the architecture of the soil. However, for fixing the soil material on the plate we had to use a carbon tape as there was no other possibility. We did some tests with gold coatings but the EDS was not able to show us reasonable carbon in our soil. SEM is not commonly used for detecting carbon in soils but I wanted to test it and I still was able to take some good pictures.



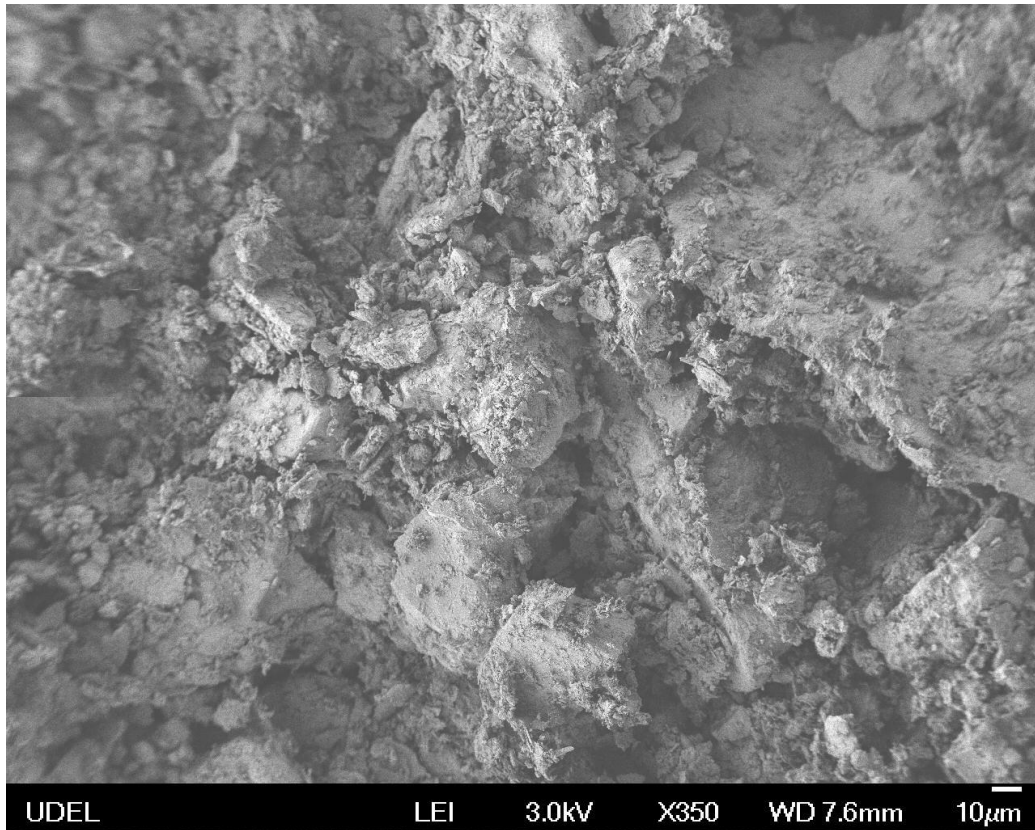
**Figure 12:** SEM image of an aggregate in a forest (9000 years) in the A horizon; A presents the full aggregate (10µm); B is zoomed in to see the structure of the aggregate (1µm)

Figure 12 shows an aggregate in the oldest forest site 9000 years. Zooming in the aggregate we can see the clay minerals and how they stick together. The samples showed a huge heterogeneity of its architecture and therefore a comparison with other samples was difficult.



**Figure 13:** SEM image of the oldest forest in the AC horizon in clay sized microaggregates; A: 10µm; B: zoomed in to 1 µm

The AC horizons in the oldest sites usually always show different soil properties (e.g. very low C content, less clay minerals, very high carbonate content). We can see this difference also with SEM images (Figure 13) as we can see less aggregates and a looser structure and the composition shows more roundly shaped colloids.



**Figure 14:** SEM image of a cropland (900 years) in the Bulk soil (0-10cm)

Figure 14 shows a SEM image of the bulk soil of the oldest cropland site. Between the different land uses and along the chronosequence comparison was also difficult due to the heterogeneous composition and small scale. However, compared to the clay sized fraction we can see a big difference as the particles are much bigger.

## Conclusions

During my visit at the University of Delaware I was able to get a good insight into a US university. I was very privileged to be located in a new building with new laboratories. The institute of soil chemistry works together with many other departments and therefore I had the chance to see and get introduction into a wide variety of analytical instruments besides those which I performed on my samples.

Dr Sparks and his team have a lot of experience and knowledge in synchrotron measurements. Although my analysis did not run very good I was able to learn a lot about synchrotron. Further I was able to support a colleague at the UD with synchrotron analysis (Phosphor edge). I am very thankful that due to my visit I was able to get good connections to synchrotron scientists worldwide.

The results of my performed measurements helped to understand the OM storage in the clay sized fraction. The BET measurements show that weathering processes increases the SSA. A negative correlation with OC was expected but was not found in our soils. The SSA rather influences the energy density gained by the TA/DSC measurements. A high energy release at higher temperature show that these materials are less available for biological decomposition processes. A larger SSA is positively correlated to stable material. As next step microbiological analysis will be done back in Austria to connect the findings gained during my visit at the UD and make clear conclusions. Finally, I got an introduction into different microscopes and was allowed to use a SEM. Looking at my soil in  $\mu\text{m}$  range was very fascinating.

At the moment there are no concrete further collaborations with the UD planned. However, we are still in contact and it is planned to perform the C-XANES again.

## Acknowledgements

*I want to thank the Marshall Plan foundation for giving me the opportunity and financial support to do part of my research for my PhD in the US. My supervisors Prof. Winfried Blum und Georg Lair in Austria strongly supported my stay at the University of Delaware what I do not take for granted. Special thanks to Dr Donald Sparks who invited me to be part of his research group for six months. I am very thankful to his whole team who supported me and added me to their "family". Especially Audrey Gamble, Jason Stuckey, Jason Fishel and Matt Fishel helped me whenever I had a scientific or private question. Thanks.*

## References

- Brunauer, S., Emmett, P. H., Teller E., 1938. Adsorption of gases in multimolecular layers. *J. Am. Chem. Soc.* 60, 309–319
- Cezar, J.C., Fonseca, P.T., Rodrigues, G.L.M.P., Castro, A.R.B. de, Neuenschwander, R.T., Rodrigues, F., Meyer, B.C., Ribeiro, L.F.S., Moreira, A.F.A.G., Piton, J.R., Raulik, M.A., Donadio, M.P., Seraphim, R.M., Barbosa, M.A., Siervo, A. de, R Landers, Brito, A.N. de, 2013. The U11 PGM beam line at the Brazilian National Synchrotron Light Laboratory. *J. Phys. Conf. Ser.* 425, 072015. doi:10.1088/1742-6596/425/7/072015
- De la Rosa, J.M., Knicker, H., López-Capel, E., Manning, D.A.C., González-Perez, J.A., González-Vila, F.J., 2008. Direct Detection of Black Carbon in Soils by Py-GC/MS, Carbon-13 NMR Spectroscopy and Thermogravimetric Techniques. *Soil Sci. Soc. Am. J.* 72, 258. doi:10.2136/sssaj2007.0031
- Dümig, A., Häusler, W., Steffens, M., Kögel-Knabner, I., 2012. Clay fractions from a soil chronosequence after glacier retreat reveal the initial evolution of organo–mineral associations. *Geochim. Cosmochim. Acta* 85, 1–18. doi:10.1016/j.gca.2012.01.046
- Eisazadeh, A., Eisazadeh, H., 2015. N<sub>2</sub>-BET surface area and FESEM studies of lime-stabilized montmorillonitic and kaolinitic soils. *Environ. Earth Sci.* 74, 377–384. doi:10.1007/s12665-015-4044-0
- FELLER, C., SCHOULLER, E., THOMAS, F., ROUILLER, J., HERBILLON, A.J., 1992. N<sub>2</sub>-BET SPECIFIC SURFACE AREAS OF SOME LOW ACTIVITY CLAY SOILS AND THEIR RELATIONSHIPS WITH SECONDARY CONSTITUENTS AND ORGANIC MATTER CONTENTS. *Soil Sci.* 153, 293–299.
- GAO, B., ZHOU, H., JIN, J., SUN, K., 2013. Characterization of the Different Organic Matter from Soils and Sediments. *Spectrosc. Spectr. Anal.* 33, 1194–1197. doi:10.3964/j.issn.1000-0593(2013)05-1194-04
- Gillespie, A.W., Diochon, A., Ma, B.L., Morrison, M.J., Kellman, L., Walley, F.L., Regier, T.Z., Chevrier, D., Dynes, J.J., Gregorich, E.G., 2013. Nitrogen input quality changes the biochemical composition of soil organic matter stabilized in the fine fraction: a long-term study. *Biogeochemistry* 117, 337–350. doi:10.1007/s10533-013-9871-z
- Guggenberger, G., Kaiser, K., 2003. Dissolved organic matter in soil: challenging the paradigm of sorptive preservation. *Geoderma* 113, 293–310. doi:10.1016/S0016-7061(02)00366-X
- Heister, K., 2016. How accessible is the specific surface area of minerals? A comparative study with Al-containing minerals as model substances. *Geoderma* 263, 8–15. doi:10.1016/j.geoderma.2015.09.001
- Kahle, M., Kleber, M., Jahn, R., 2004. Retention of dissolved organic matter by phyllosilicate and soil clay fractions in relation to mineral properties. *Org. Geochem., Selected papers from the Eleventh International Humic Substances Society Conference* 35, 269–276. doi:10.1016/j.orggeochem.2003.11.008
- Kahle, M., Kleber, M., Jahn, R., 2002. Predicting carbon content in illitic clay fractions from surface area, cation exchange capacity and dithionite-extractable iron. *Eur. J. Soil Sci.* 53, 639–644. doi:10.1046/j.1365-2389.2002.00487.x
- Kaiser, K., Guggenberger, G., 2003. Mineral surfaces and soil organic matter. *Eur. J. Soil Sci.* 54, 219–236. doi:10.1046/j.1365-2389.2003.00544.x
- Lehmann, J., Solomon, D., Kinyangi, J., Dathe, L., Wirrick, S., Jacobsen, C., 2008. Spatial complexity of soil organic matter forms at nanometre scales. *Nat. Geosci.* 1, 238–242. doi:10.1038/ngeo155

- Lopez-Capel, E., Bol, R., Manning, D. a. C., 2005. Application of simultaneous thermal analysis mass spectrometry and stable carbon isotope analysis in a carbon sequestration study. *Rapid Commun. Mass Spectrom.* RCM 19, 3192–3198. doi:10.1002/rcm.2145
- Mayer, L.M., 1994. Relationships between mineral surfaces and organic carbon concentrations in soils and sediments. *Chem. Geol.* 114, 347–363. doi:10.1016/0009-2541(94)90063-9
- Peltre, C., Fernández, J.M., Craine, J.M., Plante, A.F., 2013. Relationships between biological and thermal indices of soil organic matter stability differ with soil organic carbon level. *Soil Sci. Soc. Am. J.* 77, 2020–2028. doi:10.2136/sssaj2013.02.0081
- Plante, A.F., Fernández, J.M., Leifeld, J., 2009. Application of thermal analysis techniques in soil science. *Geoderma* 153, 1–10. doi:10.1016/j.geoderma.2009.08.016
- Plante, A.F., Pernes, M., Chenu, C., 2005. Changes in clay-associated organic matter quality in a C depletion sequence as measured by differential thermal analyses. *Geoderma* 129, 186–199. doi:10.1016/j.geoderma.2004.12.043
- Ransom, B., Kim, D., Kastner, M., Wainwright, S., 1998. Organic matter preservation on continental slopes: importance of mineralogy and surface area. *Geochim. Cosmochim. Acta* 62, 1329–1345. doi:10.1016/S0016-7037(98)00050-7
- Rovira, P., Kurz-Besson, C., Coûteaux, M.-M., Ramón Vallejo, V., 2008. Changes in litter properties during decomposition: A study by differential thermogravimetry and scanning calorimetry. *Soil Biol. Biochem.* 40, 172–185. doi:10.1016/j.soilbio.2007.07.021
- Schulten, H.-R., Leinweber, P., 1999. Thermal stability and composition of mineral-bound organic matter in density fractions of soil. *Eur. J. Soil Sci.* 50, 237–248. doi:10.1046/j.1365-2389.1999.00241.x
- Siewert, C., 2004. Rapid Screening of Soil Properties using Thermogravimetry. *Soil Sci. Soc. Am. J.* 68, 1656. doi:10.2136/sssaj2004.1656
- Sollins, P., Homann, P., Caldwell, B.A., 1996. Stabilization and destabilization of soil organic matter: mechanisms and controls. *Geoderma* 74, 65–105. doi:10.1016/S0016-7061(96)00036-5
- Solomon, D., Lehmann, J., Kinyangi, J., Liang, B., Heymann, K., Dathe, L., Hanley, K., Wirick, S., Jacobsen, C., 2009. Carbon (1s) NEXAFS Spectroscopy of Biogeochemically Relevant Reference Organic Compounds. *Soil Sci. Soc. Am. J.* 73, 1817. doi:10.2136/sssaj2008.0228
- Stone, M.M., Plante, A.F., 2015. Relating the biological stability of soil organic matter to energy availability in deep tropical soil profiles. *Soil Biol. Biochem.* 89, 162–171. doi:10.1016/j.soilbio.2015.07.008
- Wagai, R., Mayer, L.M., Kitayama, K., 2009. Extent and nature of organic coverage of soil mineral surfaces assessed by a gas sorption approach. *Geoderma* 149, 152–160. doi:10.1016/j.geoderma.2008.11.032