Purpose of the visit

The project “Does light fraction of Chernozem soil contain stable to mineralization pool as a charred material? Organic matter hydrophobicity as a factor of organic carbon stabilization” was carried out in the Department of Geography at University of Zurich with the financial support of ESF Molter Grant during October-November 2009. The purpose of this project was to investigate chemical nature of organic matter (OM) in Chernozem soil from central part of Russia with respect to content and quality of charred material in it. As pyrogenic carbon/black carbon (BC) is supposed to contribute significantly to the highly stable OM pool in Chernozemic soils (Schmidt et al., 2002) our particular aim was to test localization of charred material in separate stable OM fractions of Chernozem. For this project we used Kursk long-term (60 year) bare fallow experiment in native steppe. Total organic carbon (OC) content in fallow decreased rapidly from about 50 to 26 mg/g soil and as stabilized on this plato level for two decades is assumed to represent stable OC pool. We analyzed it for BC content and made a comparison with native steppe.

In previous study OM was found to be stabilized in fallow mostly by sorption and occlusion with minerals (in density fractions of $\rho>2cm^3/g$) that accounts for ~20 from total 26 mg/g of OC. But surprisingly it also partially preserves as free OM in light fraction (LF) (isolated at $\rho<2cm^3/g$), comprising the rest ~5 mg/g of total OC which we will hereafter call “stable LF”, meaning that part of native steppe LF which survived after 60 years of fallow. We paid attention to this fact as LF is normally considered to be the most easily degradable part of soil OM. At that in previous studies we registered for stable LF in comparison to initial LF:

- stronger hydrophobicity (water-repellency in contrast to its initial wetability)
- higher H/C ratio (0.68 as for char on Hammes scheme, 2006)
- enrichement in organic carbon (up to 30%)

First question which initiated present study raised during discussion on “SOM composition and turnover” Summer School in Freising, 2009. **Does “stable LF” represent a BC pool?** Positive answer would explain its above underlined properties. Moreover LF stability would be explained then by chemical recalcitrance of aromatic BC structures. Another mechanism of stable LF preservation in soil except chemical recalcitrance can be negative feedback from rapid mineralization of hydrophilic OM moieties which must slow down water-soluble enzyme delivery to its surfaces. Therefore another consequent question followed - **can stable LF become water-repellent due to concentration of BC aromatic structures upon mineralization that in turn becomes a factor of OM stabilization in it?**

Description of the work carried out during the visit

To quantify BC content and quality we used an improved Benzene Polycarboxylic Acids (BPCA) method of Glaser et al, 1998 (Brodowski et al., 2005, Schneider et al., 2009).

In total 26 samples have been successfully analyzed, comprising:

– 16 bulk soil samples from steppe and fallow profiles down to 80 cm depth

– 10 samples of isolated LF (<2 g/cm^3) in topsoil, 40-50 and 80-90 cm.

Handling and analyzing obtained data on BC evolved integration with total OC and soil bulk densities data determined in previous studies. Therefore estimation of BC stocks and correlation between total OC and BC mineralization was followed up.

As well we carried out balance calculations for BC in both profiles at abovementioned three depths. We did not take into account contributions of mineral fractions as their impacts are estimated to be negligible. Therefore among heavy density fractions (>2 g/cm^3) only clay is considered to have a considerable contribution into total BC content. Its value is calculated on difference between bulk content and sum of LF contributions (LFs from fine and coarse silts). Unfortunately, direct measurement of BC content in clay could not be possible because of time-consuming analysis at a time limit of the Project.

Description of the main results obtained

BC is supposed to contribute significantly to the high stable OM pool in Chernozemic soils (Schmidt et al., 2002). Its contribution is estimated by present study as 6-9% and 3-7% of total OC increasing with depth (values for down to 80 cm) in steppe and fallow accordingly. Detected quite high content of natural pyrogenic organic structures in Kursk Chernozem support the hypothesis of fire being an important factor of its pedogenesis reported in *Schmidt et al., 1999, Eckmeier et al., 2007*.

<u>Answering to particular questions posed in the title of the present project:</u>

Does “stable LF” represent a BC pool? – no, we found that LF is not the major compartment for BC storage. It contains only about 20% of total BC content, whereas the rest part is mostly localized in clay fraction. Nevertheless we can state that stable LF is enriched in BC (by factor of 15 in comparison to bulk content and by factor of 3 to initial LF in native steppe).

Can stable LF become water-repellent due to concentration of BC aromatic structures upon mineralization that in turn becomes a factor of OM stabilization in it? – probably yes, change of LF property from wettability to water-repellency can be ascribed by its high enrichment in BC mentioned above. Concentrated hydrophobic BC structures may act in favor of OM stabilization for example by shielding it from water-soluble enzymes.

Interestingly, we got even more results than expected in respect to BC stabilization.

Results of present study show that BC is generally stable in Chernozem soil. Its stock in fallow decreased only by ~8% (12.3 and 11.3 t/ha in 80 cm profile). Whereas total OC stock is depleted by 22% in the same 80 cm profile. This losses occurred rapidly in the first years of the long-term experiment and it has been in a steady-state equilibrium for almost five decades now. Therefore one can extrapolate actually no further significant loss of BC from soil. Therefore we conclude that BC can represent a stable carbon pool during centuries even under degradation soil use. Another argument for stability of BC structures in soil is that its chemical quality remains almost unchanged. Only 5% decrease of less condensed structures and consequently the same increase in the most condensed structures was reliably detected.

BC is present in a significant amount deep (values down to 80 cm) in Chernozem profiles. 1.9-1.2 g/kg soil in steppe profile decreasing with depth and 1.6-1.1 g/kg soil in fallow profile. All heavy density fractions (> 2g/cm^3, among them clay is responsible on more than 80%) preserve 1.3-1.0 g/kg soil of BC (for topsoil and 80-90 cm). Therefore we see that LF contribution to total BC content is not major and even diminishes with depth. Furthermore all detected total losses of BC are fully described by losses in LF, whereas no losses are calculated for heavy fractions (i.e. clay). Clay in Chernozem soil probably absolutely preserves the most part of BC (~70%). Where BC stabilization can be ascribed to occlusion in clay. Chemically recalcitrant BC structures can also provide co-stabilization of OM that survives long-term fallow conditions for example by strong interaction with hydrophobic moieties of OM making it less available for enzymatic break down or just shielding it from water-soluble enzymes delivery and/or etc.

Future collaboration with host institution

Together with Prof.Schmidt research group we plan to work on the results obtained for bulk soil samples as well as for density fractions. As mentioned above balance calculations revealed major role of clay fraction in storage and preservation of the most part of BC. Further interesting step will be to analyze according clay fractions to full-fill the BC balance and therefore to confirm major role of clay in BC preservation by its direct measurements.

Projected publications/articles resulting or to result from the grant.

The results obtained are considered to be reliable, plausible and already self-contained for being published in the Short Communications of Soil Biology and Biochemistry Journal (to be submitted by the end of 2009). This preliminary investigation shows high necessity and interest of further analyses of the object (long-term fallow experiment in Kursk Chernozem, Russia) for purpose of modeling OC dynamics. ESF Molter program granting will be accordingly acknowledged in the out coming publication.

Other comments

Thanks to ESF Molter Grant I experienced a new progressive method of quantification and qualification pyrogenic OM pools in soils. My personal research experience benefited greatly from the laboratory work and intensive interesting discussions in the research team of Prof.Schmidt. It significantly contributed to my present knowledge and skills, and made me more prepared for a further post doctoral research. I was inspired by scientific discussions with well-known professors like Prof.Torn and Prof.Dittmar whose lectures I had a chance to attend during my stay in the University of Zurich. I am happy to have made good friends and to stay in touch further with active European researches as well as PhD students in my research field.