

## THE USE OF NATURAL $^{14}\text{C}$ AND $^{13}\text{C}$ IN SOILS FOR STUDIES ON GLOBAL CLIMATE CHANGE

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**ABSTRACT.** Some examples are given to show that the depth distribution curves of natural  $^{14}\text{C}$  and  $^{13}\text{C}$  of thin-layer sampled soil profiles can be used for inferring changes in soil organic matter and climate changes. By using a simple exchange model, we can determine whether decomposition products are fixed by clay or transported downward toward the groundwater table. We can also estimate the amount of the Greenhouse gases,  $\text{CO}_2$  and  $\text{CH}_4$ , produced by the decomposition of the organic matter in terrestrial and paddy soils and emitted from the soil. A change from  $\text{C}_3$  to  $\text{C}_4$  plants, which might occur during a predicted temperature rise in some areas, thereby influencing the carbon balance, can be clearly detected by the  $\delta^{13}\text{C}$  depth profiles. A change in organic matter input can also be calculated under certain circumstances.

### INTRODUCTION

Until now, discussions on the global carbon cycle and the Greenhouse effect have underestimated the importance of the soil compartment. Because the flux rates between the pedosphere/biosphere and the atmosphere are of the same order of magnitude as those between the ocean and the atmosphere on an absolute scale, and even much higher with relation to the pool contents, small variations within the dynamics of the soil compartment can result in or be produced from larger variations of the atmospheric compartment. Thus, the soil compartment has recently become the focus of global change research (Arnold, Szabolcs & Targulian 1990; Bouwman 1990; Scharpenseel, Schomaker & Ayoub 1990).

Existing knowledge of the fluxes of soil organic matter is fragmentary. Little is known about the production and release of methane from rice fields and the behavior of soil carbon under changing climatic conditions. Careful experimental investigations of  $\text{CO}_2$  and  $\text{CH}_4$  flux rates and the influence of climatic changes on biota and soils are difficult, time-consuming and expensive. The natural abundance of carbon isotopes in soil carbon, as a fingerprint of its dynamic history, may help to answer some questions.

### SOILS AND METHODS

Using the thin-layer sampling method (Becker-Heidmann & Scharpenseel 1986) since 1981, we have studied natural abundance of soil carbon isotopes in a variety of soils in Europe and Asia in relation to the main processes of soil organic matter dynamics (Fig. 1, Table 1). Distinctive depth distributions of  $^{14}\text{C}$  activity and  $\delta^{13}\text{C}$  indicate major processes, such as decomposition, percolation, adsorption by clay, plowing, cultivation change from  $\text{C}_3$  to  $\text{C}_4$  or  $\text{C}_4$  to  $\text{C}_3$  crops and climatic change. The data should answer three questions with regard to global climate change: Is the soil a source or a sink of Greenhouse gases? How is the balance affected if the photosynthetically more efficient  $\text{C}_4$  plants displace  $\text{C}_3$  plants? How much methane is produced by wetland soils? Our results do not directly yield the exact values to answer these questions. However, they can test any soil organic matter dynamics model.

The fundamental elements of our model are shown in Figure 2. The steady-state condition is assumed to be approximately valid for most of the soils we studied, because they are either natural soils developed after the last ice age 10 ka ago, or they are soils that have been cultivated continuously over a long period. The model, written in BASIC, calculated the  $^{14}\text{C}$  age of soil organic carbon undergoing a constant rate of exchange with new organic material (Becker-Heidmann 1989).

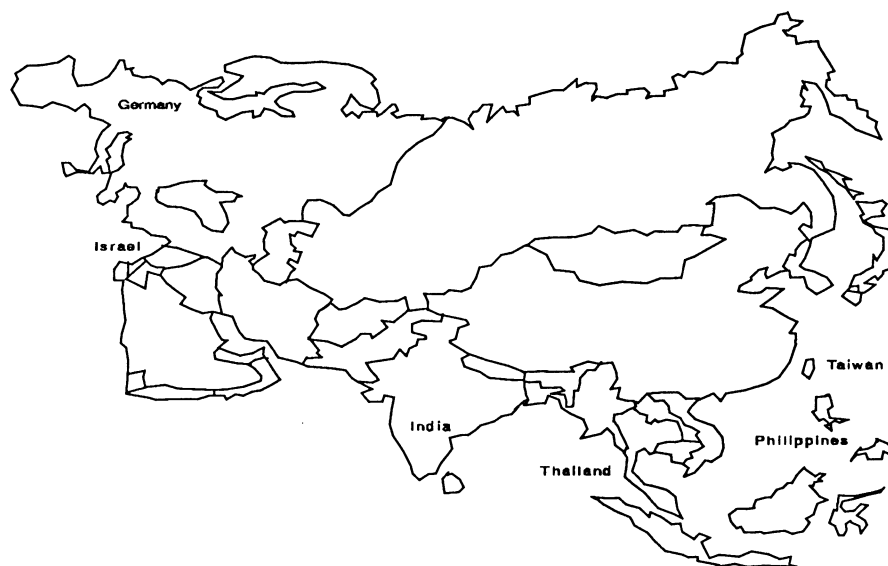


Fig. 1. Map of the locations of soil sampling in Eurasia

TABLE 1. Soil Profiles, Studied for Natural  $^{14}\text{C}$  and  $^{13}\text{C}$ 

Soil order	Location	Climate	Use	References
Spodic Aquic Hapludalf	Wohldorf, Germany	Humid	Forest	Becker-Heidmann & Scharpenseel (1986)
Spodic Aquic Hapludalf (two profiles)	Ohlendorf, Germany	Humid	Forest	Becker-Heidmann & Scharpenseel (1986), Becker-Heidmann (1989)
Aquic Hapludalf	Timmendorf, Germany	Humid	Forest	Becker-Heidmann (1989)
Typic Hapludalf	Klein Altendorf, Germany	Humid	Forest	Becker-Heidmann (1989)
Typic Pelloxerert	Akko, Israel	Mediterranean	Fallow	Becker-Heidmann (1990)
Typic Pelloxerert	Qedma, Israel	Mediterranean	Cotton	Becker-Heidmann (1990)
Udic Rhodustalf	Patancheru, India	Semiarid	Sorghum, pulses	Becker-Heidmann & Scharpenseel (1989)
Typic Pellustert	Patancheru, India	Semiarid	Sorghum, pulses	Becker-Heidmann (1990)
Aeric Tropaquept	Los Baños, Philippines	Humid tropical	Rice	Becker-Heidmann & Scharpenseel (1989)
Aeric Tropaquept	Pangil, Philippines	Humid tropical	Rice	Becker-Heidmann & Scharpenseel (1992)
Aeric Tropaquept	Pao, Philippines	Humid tropical	Rice	Becker-Heidmann (1990)
Haplic Hydraquent	Bugallon, Philippines	Humid tropical	Rice	Becker-Heidmann (1990)
Haplic Hydraquent	Tiaong (L), Philippines	Humid tropical	Rice	Becker-Heidmann (1990)
Typic Haplaquoll	Tiaong (H), Philippines	Humid tropical	Banana, coconut	Becker-Heidmann & Scharpenseel (1989)
Typic Paleudult	San Dionisio, Philippines	Humid tropical	Fallow	Becker-Heidmann & Scharpenseel (1989)
Typic Fluvaquent	Taichung, Taiwan	Humid tropical	Rice	Becker-Heidmann (1990)
Typic Fluvaquent	Pingtung, Taiwan	Humid tropical	Rice	Becker-Heidmann & Scharpenseel (1992)
Sulfic Tropaquept	Klong Luang, Thailand	Humid tropical	Rice	Becker-Heidmann (1990)
Aeric Paleaquult	Khon Kaen, Thailand	Humid tropical	Rice	Becker-Heidmann (1990)

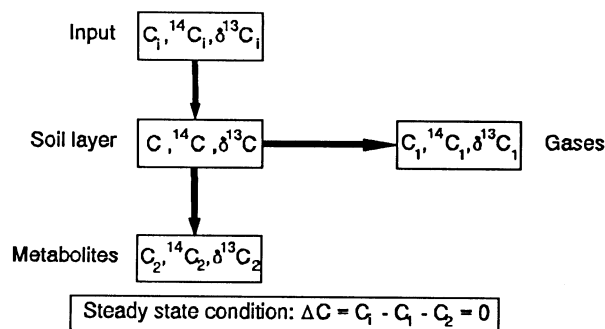


Fig. 2. Simple soil carbon flux model under steady-state conditions

The following calculation estimated the effect of single two-component mixing events on the  $\delta^{13}\text{C}$  value.

$$\delta^{13}\text{C} = \frac{\delta^{13}\text{C}_1 - \delta^{13}\text{C}_2}{1 + \frac{^{12}\text{C}_2}{^{12}\text{C}_1}} + \delta^{13}\text{C}_2 \quad (1)$$

where the subscripts 1 and 2 indicate the mixing components. For  $\delta$  values between  $-90$  and  $+2\text{‰}$ , the following substitution (Becker-Heidmann 1989) introduces relative errors  $<0.001$

$$\frac{c_2}{c_1} = \frac{^{12}\text{C}_2 + ^{13}\text{C}_2}{^{12}\text{C}_1 + ^{13}\text{C}_1} \approx \frac{^{12}\text{C}_2}{^{12}\text{C}_1} \quad \text{with} \quad \frac{\frac{c_2}{c_1} - \frac{^{12}\text{C}_2}{^{12}\text{C}_1}}{\frac{^{12}\text{C}_2}{^{12}\text{C}_1}} < 0.001 \quad (2)$$

where  $c_1$  and  $c_2$  are the molar carbon contents of the two components of the mixture. Thus, Equation (1) becomes

$$\delta^{13}\text{C} \approx \frac{\delta^{13}\text{C}_1 - \delta^{13}\text{C}_2}{1 + \frac{c_2}{c_1}} + \delta^{13}\text{C}_2 \quad (3)$$

Equation (3) is also valid for the partition of a substance into two components. If 4 of the variables, or 3 and the ratio of  $c_2$  to  $c_1$  are known, the unknown 5th can be calculated. Example applications include the decomposition of organic matter into  $\text{CO}_2$  and metabolites (Fig. 2), the mixture of metabolites from  $\text{C}_3$  and  $\text{C}_4$  plants, and the anaerobic decomposition with principally methane, little  $\text{CO}_2$  and metabolites produced.

## APPLICATIONS AND DISCUSSION

For a simple application of our model, we used a single topsoil layer. The  $^{14}\text{C}$  activity of the input ( $C_i$ ) was 100 pMC, and the exchange rate was constant. Figure 3 shows the resulting  $^{14}\text{C}$  age changing with time depending on the value of the exchange rate. The main result is that, for a given soil age, an upper limit exists for the  $^{14}\text{C}$  age, which is specific for the value of the exchange rate. For example, a soil layer cannot reach a  $^{14}\text{C}$  age greater than 10 yr BP, if 10% of its carbon exchanged each year. On the other hand, the exchange rate of soil developed after the last ice age with a  $^{14}\text{C}$  age greater than 6 ka BP cannot be higher than 0.0001. These results are supported by

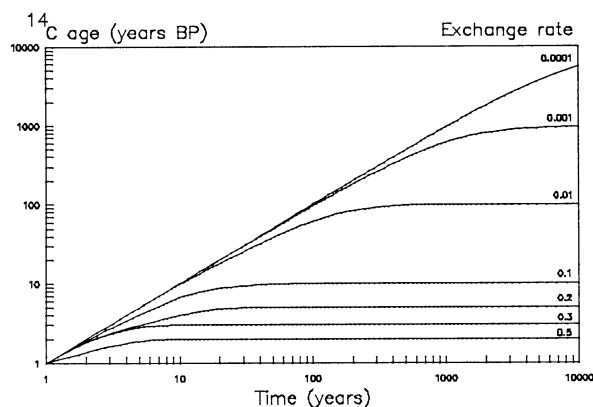


Fig. 3. The development of the  $^{14}\text{C}$  age of a soil layer as a result of a constant yearly exchange of organic carbon (from Becker-Heidmann 1989)

the findings of Cherkinsky and Brovkin (1991), who independently developed a very similar model. The maximum  $^{14}\text{C}$  age of the German soil profiles is between 2 and 5 ka BP, *i.e.*, the exchange rate could have been at most between 0.0001 and 0.001. The reason for such a low exchange rate and, therefore, a large fraction of old organic compounds dominating the soil organic component is probably adsorption of organic matter by clay. This holds true in general, at least for the Alfisols, because the  $^{14}\text{C}$  age is proportional to the clay content, not only within a soil profile, but also for the different profiles (Fig. 4). Similarly, for Mollisols, Tsutsuki *et al.* (1987) found the highest  $^{14}\text{C}$  age in organic compounds associated with fine silt and coarse clay fractions. Recent studies on the  $^{14}\text{C}$  age of interlayer clay-organic complexes support these findings (Theng, Tate & Becker-Heidmann, ms.). In the case of higher carbon input from an increased rate of photosynthesis due to higher atmospheric  $\text{CO}_2$  concentration, soil with such a low exchange rate probably cannot become a sink of carbon. The  $\delta^{13}\text{C}$  depth distribution may also be used to estimate the source or sink factor of soil by applying a model proposed by Bertram (1986).

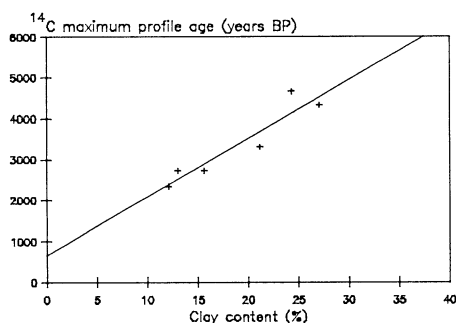


Fig. 4. Relation between the maximum  $^{14}\text{C}$  age of soil profiles and the clay content (from Becker-Heidmann 1989)

Regarding the question of the fate of the yearly input of carbon, either it has left the soil as gas or percolated toward bedrock and groundwater. For at least some soils, the depth distribution of the  $^{14}\text{C}$  age shows that a considerable portion of organic matter has quickly percolated into the profile. We found "bomb carbon" at nearly all horizon boundaries, some places at >1 m depth (Becker-Heidmann 1989; Scharpenseel *et al.* 1989). This carbon continues along a pathway to the rivers and oceans, part of the carbon cycle upon which a large SCOPE/UNEP research program (Degens, Kempe & Weibin 1987) has been focused.

Methane is the second most important soil-borne Greenhouse gas, despite its atmospheric concentration in 1985 of only 1.65 ppm compared to 345 ppm  $\text{CO}_2$ . The radiative adsorption potential of methane is 32 times that of  $\text{CO}_2$  and its annual increase is 1%, whereas the annual rise of  $\text{CO}_2$  is 0.5% (Bouwman 1990: 27). About 20% of methane emissions come from rice-cultivated wetlands and 20% from natural wetlands. Estimates of the annual  $\text{CH}_4$  input from rice wetlands range between 53–114 Tg (Bouwman 1990: 88). Whereas  $\text{CH}_4$  produced in rice soils is modern,  $\text{CH}_4$  from natural wetlands, such as old peat layers, may also contain a certain amount of  $^{14}\text{C}$ -depleted gas (Cicerone & Oremland 1988). From the  $\delta^{13}\text{C}$  depth profiles of our studied soils, we can roughly estimate the amount of methane produced using mixture Equation (3). Methane from bacterial decomposition of organic matter has an extremely low  $\delta^{13}\text{C}$  (Rosenfeld & Silverman 1959; Nakamura, Takai & Wada 1990), leaving the remaining metabolites in the soil with a higher  $\delta^{13}\text{C}$  than known from terrestrial soils, where *ca.* 3‰ enrichment is usual (Bertram 1986). Few of the wetland rice soils that we studied showed a strikingly large difference between the  $\delta^{13}\text{C}$  of the topsoil, containing only slightly decomposed material, and the  $\delta^{13}\text{C}$  of the deeper layers with mostly degraded organic matter. The Aeris Tropaequet from Los Baños, Philippines (*cf.* Table 1) shows the greatest difference, *ca.* 7‰. This soil matches well the criteria for a methane-prone soil (Neue, Becker-Heidmann & Scharpenseel 1990). Martin (1985) found *ca.* 30% of the carbon of added  $^{14}\text{C}$ -labeled rice straw decomposing into  $\text{CH}_4$  in this soil.

The replacement of plants with  $\text{C}_3$ -type photosynthesis by those of  $\text{C}_4$  type could be detected in the  $\delta^{13}\text{C}$  depth distribution in the topsoil of the Udic Rhodustalf at Patancheru, India. A long-lasting crop rotation of chickpea and pigeonpea ( $\text{C}_3$ ,  $\delta^{13}\text{C} = -28\text{‰}$  and  $-27.3\text{‰}$ , respectively) and sorghum and pearl millet ( $\text{C}_4$ ,  $\delta^{13}\text{C} = -14.8\text{‰}$  and  $-13.7\text{‰}$ , respectively) was followed for a short three-year period by grasses ( $\delta^{13}\text{C} = -13.0\text{‰}$  to  $-14.2\text{‰}$ ) (Becker-Heidmann 1989). The expected general trend of increasing  $\delta^{13}\text{C}$  with depth due to decomposition is visible only between 20- and 70-cm depth and is inflected within the topmost 20 cm of the soil, thus revealing the infiltrating isotopically heavier carbon input from the decomposing  $\text{C}_4$  grasses. By using the mixing formula again (Eq. 3), this input can be calculated. Others have used the change in the  $\delta^{13}\text{C}$  depth distribution after a crop rotation at a definite date to calculate the decomposition rate (Cerri *et al.* 1985; Balesdent, Wagner & Mariotti 1988; Martin *et al.* 1990). But these authors probably overestimated the input of the second crop in cases of change from  $\text{C}_4$  to  $\text{C}_3$  and underestimated it in cases of change from  $\text{C}_3$  to  $\text{C}_4$ , because they did not take into account that  $\delta^{13}\text{C}$  generally increases with depth due to decomposition. This kind of calculation is useful, because with rising temperature and/or a changing moisture regime, the vegetation of many regions may change from  $\text{C}_3$  to a more dominant  $\text{C}_4$  type with subsequent alterations in the soil organic matter compartment.

## CONCLUSION

Despite the fact that simple calculations such as those described above can only roughly estimate the impact of climate on soil organic matter, depth distributions of natural  $^{14}\text{C}$  and  $^{13}\text{C}$  abundances prove to be a useful tool for studying soil compartment dynamics attributable to global climate change. We propose to insert natural  $^{14}\text{C}$  and  $\delta^{13}\text{C}$  in state-of-the-art working models of soil organic matter dynamics such as that of Parton *et al.* (1987).

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## REFERENCES

- Arnold, R. W., Szabolcs, I. and Targulian, V. O., eds. 1990 *Global Soil Change. Report of an IIASA-ISSS-UNEP Task Force on the Role of Soil in Global Change*. Laxenburg, Austria, International Institute for Applied Systems Analysis. 110 p.
- Balesdent, J., Wagner, G. H. and Mariotti, A. 1988 Soil organic matter turnover in long-term field experiments as revealed by the  $^{13}\text{C}$  natural abundance. *Soil Science Society of America Journal* 52: 118–130.
- Becker-Heidmann, P. 1989 Die Tiefenfunktionen der natürlichen Kohlenstoff-Isotopengehalte von vollständig dünnsschichtweise beprobten Parabraunerden und ihre Relation zur Dynamik der organischen Substanz in diesen Böden. *Hamburger Bodenkundliche Arbeiten* 13: 1–248.
- Becker-Heidmann, P. (ms.) 1990 Carbon fluxes in important soil classes, with emphasis on Lessivé soils and on soils of the terrestrial, of the hydromorphic, and temporarily submerged environment. Final report to GTZ and DFG: 177 p.
- Becker-Heidmann, P. and Scharpenseel, H. W. 1986 Thin layer  $\delta^{13}\text{C}$  and  $\text{D}^{14}\text{C}$  monitoring of "Lessivé" soil profiles. In Stuiver, M. and Kra, R. S., eds., *Proceedings of the 12th International  $^{14}\text{C}$  Conference. Radiocarbon* 28(2A): 383–390.
- \_\_\_\_\_ 1989 Carbon isotope dynamics in some tropical soils. In Long, A. and Kra, R. S., eds., *Proceedings of the 13th International  $^{14}\text{C}$  Conference. Radiocarbon* 31(3): 672–679.
- \_\_\_\_\_ 1992 Studies of soil organic matter dynamics using natural carbon isotopes. *The Science of the Total Environment*, in press.
- Bertram, H. G. 1986 Zur Rolle des Bodens im globalen Kohlenstoffzyklus. Messung der Temperaturabhängigkeit der Abbauraten des organischen Kohlenstoffs im Boden. *Veröffentlichungen der Naturforschenden Gesellschaft zu Emden von 1814*, 8 (Dissertation). 144 p.
- Bouwman, A. F., ed. 1990 *Soils and the Greenhouse Effect. Proceedings of the International Conference on Soils and the Greenhouse Effect*. Chichester, John Wiley & Sons. 574 p.
- Cerri, C., Feller, C., Balesdent, J., Victoria, R. and Plenecassagne, A. 1985 Application du traçage isotopique naturel en  $^{13}\text{C}$  à l'étude de la dynamique de la matière organique dans les sols. *Comptes Rendus des Sèances de l'Académie des Sciences Paris* T.300(II) 9: 423–428.
- Cherkinsky, A. E. and Brovkin, V. A. 1991 A model of humus formation in soils based on radiocarbon data of natural ecosystems. Abstract. *Radiocarbon* 33(2): 186.
- Cicerone, R. J. and Oremland, R. S. 1988 Biogeochemical aspects of atmospheric methane. *Global Biogeochemical Cycles* 2: 299–327.
- Degens, E. T., Kempe, S. and Weibin, G., eds. 1987 *Transport of carbon and minerals in major world rivers, Part 4. Mitteilungen aus dem Geologisch-Paläontologischen Institut der Universität Hamburg, SCOPE/UNEP Special Issue* 64: 512 p.
- Martin, A., Mariotti, A., Balesdent, J., Lavelle, P. and Vuattoux, R. 1990 Estimate of organic matter turnover rate in a savanna soil by  $^{13}\text{C}$  natural abundance measurements. *Soil Biology and Biochemistry* 22: 517–523.
- Martin, U. 1985 Decomposition of uniformly  $^{14}\text{C}$ -labelled rice straw in a continuously flooded soil in the Philippines. *Hamburger Bodenkundliche Arbeiten* 6: 1–129.
- Nakamura, K., Takai, Y. and Wada, E. 1990 Carbon isotopes of soil gases and related organic matter in an agroecosystem with special reference to paddy field. In Durrance, E. M., Galimov, E. M., Hinkle, M. E., Reimer, G. M., Sugusaki, R. and Augustithis, S. S., eds., *Geochemistry of Gaseous Elements and Compounds*. Athens, Greece, Theophrastus Publications SA: 455–484.
- Neue, H. U., Becker-Heidmann, P. and Scharpenseel, H. W. 1990 Organic matter dynamics, soil properties and cultural practices in rice lands and their relationship to methane production. In Bouwman, A. F., ed., *Soils and the Greenhouse Effect. Proceedings of the International Conference on Soils and the Greenhouse Effect*. Chichester, John Wiley & Sons: 457–466.
- Parton, W. J., Schimel, D. S., Cole, C. V. and Ojima, D. S. 1987 Analysis of factors controlling soil organic matter levels in Great Plains grasslands. *Soil Science Society of America Journal* 51: 1173–1179.
- Rosenfeld, W. D. and Silverman, S. R. 1959 Carbon isotope fractionation in bacterial production of methane. *Science* 130: 1658–1659.
- Scharpenseel, H. W., Becker-Heidmann, P., Neue, H. U. and Tsutsuki, K. 1989 Bomb-carbon,  $^{14}\text{C}$  dating and  $\delta^{13}\text{C}$ -measurements as tracers of organic matter dynamics as well as of morphogenetic and turbation processes. *The Science of the Total Environment* 81/82: 99–110.
- Scharpenseel, H. W., Schomaker, M. and Ayoub, A., eds. 1990 *Soils on a Warmer Earth. Proceedings of the International Workshop on Effects of Expected Climate Change on Soil*. Amsterdam, Elsevier: 274 p.
- Theng, B. K. G., Tate, K. R. and Becker-Heidmann, P. (ms) Towards establishing the age, location, and identity of inert soil organic matter. *Zeitschrift für Pflanzenernährung und Bodenkunde*, VCH-Verlagsgesellschaft, Weinheim, in press.
- Tsutsuki, K., Suzuki, C., Kuwatsuka, S., Becker-Heidmann, P. and Scharpenseel, H. W. 1987 Investigation on the stabilization process of the humus in Molli-sols. *Zeitschrift für Pflanzenernährung und Bodenkunde* 151: 87–90.