

Estimation of soil fluxes of the greenhouse gases ( $\text{CO}_2$ ,  $\text{N}_2\text{O}$ ,  $\text{CH}_4$ ) for the Hungarian agriculture lands and forested area.

Ph.D. Theses

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## **Introduction and aims**

Atmospheric environmental research in Europe is increasingly focusing on global aspects during the last decades. The reason is, the emission and concentration of the short lifetime pollutants have decreased in the local, regional and continental scale. The reduction of the emission of short lifetime gases from anthropogenic sources turned the attention to the long lifetime, global pollutants like greenhouse gases (GHG). Estimation of greenhouse gas emission from industrial and energy use sources is relatively simple, but our knowledge concerning soil GHG flux of the agriculture fields is still uncertain. Some of EU-V and EU-VI framework programs are also working on these problems.

The most important greenhouse gases of agriculture origin are the following: nitrous oxide (background concentration: 320 ppb, greenhouse effect in CO<sub>2</sub> equivalent: 298), methane (background concentration: 1.9 ppm, greenhouse effect in CO<sub>2</sub> equivalent: 25) and the carbon dioxide (background concentration: 370 ppm).

The result of the denitrification process in the soil is the emission of nitrous oxide which is a long lifetime gas. If the water content of the soil is high, anaerobic decomposition of organics will be the beneficiary process resulting in methane emission. The animals and the manure management are also serious methane sources. However, dry soils may absorb the methane. The dry and well ventilated soil oxidizes the methane in the mineral layer by chemolithotrophic microorganisms. The decomposition of the organic matters in soil (heterotrophic respiration), beside of autorotrophic respiration results in considerable carbon dioxide emission, as well.

Comparing the effect of the N<sub>2</sub>O and the CH<sub>4</sub> to the carbon dioxide from the agriculture soils we can state that the influence is of the same magnitude and the major source of the N<sub>2</sub>O is the agriculture. The subject of my Ph.D. thesis is give an estimation on the soil fluxes of the greenhouse gases (methane, nitrous oxide) from the agriculture and forested soil on the basis of measurements and modeling.

## **Applied methods**

1. Static chamber method was used for sampling, to detect concentration changes in the chamber during exposure. Two types of chambers were applied depending on the place and the project: small chambers: (A=80 cm<sup>2</sup>, V=400 cm<sup>3</sup>, h=5 cm) and large chambers (at Bugac-puszta) (A=2,500 cm<sup>2</sup>, V=12,500 cm<sup>3</sup>, h=5 cm), respectively. 10

ml samples were taken in an evacuated, glass vial closed by a septum. The sample intervals:  $t=0$ ,  $t=10$ ,  $t=20$  and  $t=0$ ,  $t=15$ ,  $t=30$ . Selection of sample intervals depended on preliminary tests.

2. An HP 5890 Serial II. gas chromatograph was used to measure the concentration in the soil gas samples. The detector was an HP 5972 MSD for the  $N_2O$  measurement. Later an HP 5890 Serial II gas chromatograph was used combined with a FID and an ECD detector for the simultaneous measurement of  $N_2O$  and  $CH_4$ .
3. The DNDC (Denitrification-Decomposition) biogeochemical model was used for the evaluation of soil gas fluxes like  $CH_4$ ,  $CO_2$  and  $N_2O$ . The model consists of two parts. The first part includes the crop growth, meteorological and soil parameters and evaluates the soil pH, redox potential, vegetation characteristics and farming practices. The second one is modeling the soil properties and estimates the gas fluxes including GHGs.

## Theses

1. I developed a method to detect the soil flux of greenhouse gases. Static chambers were used for sampling. Permanent rims were covered and closed by the upper part of the chambers only for the duration of samplings. After closure, samples (minimum three samples) were taken at  $t=0$ , 10, 20 and 30 minutes by a gas-proof syringe. The exact duration of sampling (20 or 30 minutes) depends on the structure of soil, was preliminary determined. A total of 10 ml of samples were injected into evacuated vials of 10 ml volume, respectively. The soil gas fluxes were calculated by the differences of the concentrations.
2. I developed a method to measure the mixing ratio of nitrous oxide in the vials of static chamber samplings down to the atmospheric background (320 ppb). Concentration changes of nitrous oxide were measured by a gas chromatograph combined with a mass-spectrometer (HP 5890 II.-HP 5972, equipped by HP-PlotQ column [30m x 0.53mm x 40 $\mu$ m]). The method was applied in the  $C \geq 320$  ppb mixing ratio range.
3. I developed a method for simultaneous detection of nitrous oxide and methane by a gas chromatograph with Carbonplot column (30m x 0.25mm x 0.25 $\mu$ m), detected by electron capture detector (GC-ECD) and flame ionization detector (GC-FID), respectively. Because methane is not stable in vials for long time, I measured all samples in the first 48 hours. The method was applied in the  $C \geq 320$  ppb and  $C \geq 2$  ppm

mixing ratio ranges for N<sub>2</sub>O and CH<sub>4</sub>, respectively.

4. According to the sampling and measurement methods above I determined the N<sub>2</sub>O soil fluxes at different sites in Hungary. The sites were the followings: Bugac-puszta (semiarid grassland on sandy soil), Isaszeg-Nagytarcsa (sandy loess soil, cambisol), Gödöllő (loess soil monoliths transplanted from Isaszeg), Szurdokpüspöki (dry grassland on mountain heavy clay soil), Tetves-rét, Nyírjes (Mátra region), Bodrogek (Bodrog region). The calculated soil flux varied between -1.5 and 6.9 kg N ha<sup>-1</sup> year<sup>-1</sup> with the median of 0.8 kg N ha<sup>-1</sup> year<sup>-1</sup>. The standard deviation is 1.2 kg N ha<sup>-1</sup> year<sup>-1</sup>. The N<sub>2</sub>O flux depends on the soil temperature and soil moisture. Wetness of soil is one of the main drivers in N<sub>2</sub>O production, dry soil does not favor the denitrification processes.
5. According to the sampling and measurement methods above I determined the CH<sub>4</sub> soil fluxes at different sites in Hungary. The sites were the followings: Bugac-puszta (semiarid grassland on sandy soil), Gödöllő (loess soil monoliths transplanted from Isaszeg), Szurdokpüspöki (dry grassland on mountain heavy clay soil), Bodrogek (Bodrog region). The calculated soil flux varied between -6.4 and 7.8 kg CH<sub>4</sub> ha<sup>-1</sup> year<sup>-1</sup>, with the median of -0.2 kg CH<sub>4</sub> ha<sup>-1</sup> year<sup>-1</sup>. The standard deviation is 1.6 kg CH<sub>4</sub> ha<sup>-1</sup> year<sup>-1</sup>. The magnitude and direction of the methane flux is mainly controlled by soil temperature and moisture.
6. I carried out a computer simulation for the country range estimation of GHG fluxes. I applied the DNDC (Denitrification-Decomposition) biogeochemical model for the evaluation of soil gas fluxes like CH<sub>4</sub>, CO<sub>2</sub> and N<sub>2</sub>O. I used the measured data for the model validation. The simulated N<sub>2</sub>O, CH<sub>4</sub> and CO<sub>2</sub> average flux values in Hungary between 2002-2006 years were the following: 28.0±4.2 kt N year<sup>-1</sup>, -11.8±(-1.8) kt C year<sup>-1</sup>, 27.3±4.1 Mt C year<sup>-1</sup>, respectively. Because the limited number of measured soil CO<sub>2</sub> flux data for the validation, the uncertainty of the modeled CO<sub>2</sub> soil gas fluxes is higher than that of N<sub>2</sub>O or CH<sub>4</sub>. The modeled CO<sub>2</sub> soil emission is in the same magnitude than the amount of CO<sub>2</sub> from the industrial, energy use and municipal emissions. We have note that the CO<sub>2</sub> uptake of plants is in balance with the CO<sub>2</sub> soil emission in longer term.
7. To establish the total methane balance for Hungary I used statistical data of methane fluxes for the wetland areas, rice fields and animal husbandry combined with soil flux simulation by DNDC model. The net methane emission of wetland areas, rice fields, animal husbandry and soil flux was 3.1±0.458 Mt CO<sub>2</sub> equivalent in the years 2002-

2006. The emission of animal husbandry and the wetlands were dominating in that period. We have to note that role of wetlands in methane balance is uncertain, further research is needed in this field.

8. I made preliminary estimation for the effects of change of the climate and management activity on N<sub>2</sub>O and CO<sub>2</sub> soil fluxes. The simulation showed that the effect of the predicted changes in climate parameters decreases the N<sub>2</sub>O soil emission (-31%) but increases the CO<sub>2</sub> soil emission (+27%). The change in land-use is accompanied with changes in the soil gas emissions. The grass-arable change increases the N<sub>2</sub>O, decreases the CO<sub>2</sub> emission, but the two effects approximately balanced. The afforestations - compared to the grass or the arable lands - causes considerable N<sub>2</sub>O (one order) and CO<sub>2</sub> (two-three orders) emission decrease.
9. I determined the emissions of soil greenhouse gases for the whole Hungarian agriculture/forested lands. It concluded that the total GHG emission of agriculture/forested lands expressed in carbon dioxide equivalent is 116 Mt CO<sub>2</sub> year<sup>-1</sup>, comparable with the industrial, energetic and municipal emissions (71.6 Mt CO<sub>2</sub> year<sup>-1</sup>). We have to note that plant uptake of CO<sub>2</sub> may balance the soil (autotrophic and heterotrophic) respiration of carbon dioxide on long time scale. In this case, the N<sub>2</sub>O and the CH<sub>4</sub> emissions from the agriculture/forested lands share the 23% of the industrial, energetic and municipal emissions (71.6 Mt CO<sub>2</sub> year<sup>-1</sup>). We have also to note that the rate of simulated CO<sub>2</sub> emission have higher uncertainty in comparison to CH<sub>4</sub> and N<sub>2</sub>O.

## PUBLICATIONS

### Peer reviewed journal articles

1. Grosz, B. Horváth, L. and Machon, A., 2008: Modelling soil fluxes of nitrogen and carbon gases above a semi arid grassland in Hungary. *Cereal Research Communications* 36 Suppl., 1523-1526. IF: 1,19
2. Flechard, C.R., Ambus, P., Skiba, U., Rees, R.M., Hensen, A., van Amstel, A., van den Pol-van Dasselaar, A., Soussana, J.-F., Jones, M., Clifton-Brown, J., Raschi, A., Horvath, L., Neftel, A., Jocher, M., Ammann, C., Leidfield, J., Fuhrer, J., Calanca, P.L., Thalman, E., Pilegaard, K., Di Marco, C., Campbell, C., Nemitz, E., Hargreaves, K.J., Levy, P., Ball, B.C., Jones, S., van de Bulk, W.C.M., Groot, T., Blom, M., Domingues, R., Kasper, G., Allard, V., Ceshia, E., Cellier, P., Laville, P., Henault, C., Bizouard, F., Abdalla, M., Williams, M., Baronti, S., Berretti, F. and

- Grosz, B., 2007: Effects of climate and management intensity on nitrous oxide emissions in grassland systems across Europe. *Agriculture, Ecosystems and Environment*, **121**, 135-152. [doi:10.1016/j.agee.2006.12.024](https://doi.org/10.1016/j.agee.2006.12.024) IF: 1,832
3. Nagy, Z., Pintér, K., Czóbel, Sz., Balogh, J., Horváth, L., Fóti, Sz., Barcza, Z., Weidinger, T., Csintalan, Zs., Dinh. N.Q., Grosz, B. and Tuba, Z., 2007: The carbon budget of semi-arid grassland in a wet and a dry year in Hungary. *Agriculture, Ecosystems and Environment*, **121**, 21-29. [doi:10.1016/j.agee.2006.12.003](https://doi.org/10.1016/j.agee.2006.12.003) IF: 1,832
  4. Machon, A., Grosz, B., Horváth, L., Pintér, K. and Tuba, Z., 2008: Non-CO<sub>2</sub> greenhouse gas flux measurement above a nature reserve grassland in Kiskunság in an unusual year. *Cereal Research Communications* 36 Suppl., 203-206. IF: 1,19
  5. Horváth, L., Grosz, B., Machon, A., Balogh, J., Pintér, K. and Czóbel, Sz., 2008: Influence of soil type on N<sub>2</sub>O and CH<sub>4</sub> soil fluxes in Hungarian grasslands. *Community Ecology* 9 (Suppl.) 75-80. DOI: 10.1556/Com.Ec.9.2008.S11. IF: 0,604
  6. Machon, A., Horváth, L., Weidinger, T., Grosz, B., Pintér, K. and Tuba, Z., 2010: Estimation of net nitrogen flux between the atmosphere and a semi-natural grassland ecosystem in Hungary. Sent for the *Agriculture, Ecosystems and Environment* (in press).
  7. Horváth, L., Grosz, B., Tuba, Z., Nagy, Z., Czóbel, Sz., Balogh, J., Péli, E., Fóti, Sz., Weidinger, T. and Pintér, K., 2010: Estimation of nitrous oxide emission from Hungarian semi-arid sandy and loess grassland; effect of grazing, irrigation and application of fertiliser. Submitted to *Agriculture, Ecosystems and Environment*.
  8. Horváth, L., Grosz, B., Czóbel, Sz., Nagy, Z., Péli, E., Szerdahelyi, T. and Szirmai, O. and Tuba, Z., 2008: Measurement of methane and nitrous oxide fluxes in Bodrogek, Hungary; preliminary results. *Acta Biologica Szegediensis* 52(1), 119-122.
  9. Czóbel, Sz., Horváth, L., Gál B., Szerdahelyi, T., Szirmai, O., Nagy, J., Cserhalmi, D., Fogarasi, G., Péli, E., Rabnecz, G., Grosz, B. and Tuba, Z., 2009: Ecophysiological studies in the Bodrogek: Measurement of yearly C and N<sub>2</sub>O balance in typical wetland habitats of the Bodrogek. *Thaiszia J. Bot. Košice* 19, Suppl. 1, 331-343. ISSN 1210-0420.

## Posters, books, conference abstracts

1. Horváth, L. and Grosz, B., 2005: Nitrous oxide emission from soil of Hungarian semi-natural grasslands. Fourth International Symposium on Non-CO<sub>2</sub> Greenhouse Gases (NCGG-4), Science, Control, Policy and Implementation, Utrecht, The Netherlands, 4-6 July 2005. Book of abstracts p. 28.
2. Horváth, L., Grosz, B., Weidinger, T., 2006: Estimation of nitrous oxide emission from Hungarian semi-arid sandy and loess grasslands; effect of grazing, irrigation and application of fertiliser. Open Science Conference on “The GHG Cycle in the Northern Hemisphere”, Sissi-Lassithi, Crete 2006 november 14-18. Előadások összefoglalói, p 163.
3. Grosz, B., Machon, A., Horváth, L. and Weidinger, T., 2007: Measurement and modelling of N<sub>2</sub>O and CH<sub>4</sub> fluxes at a grassland ecosystem in Hungary. *Marie Curie ILEAPS workshop Helsingborg*, Sweden, October 2007. (Poster).
4. Machon, A., Grosz, B., Horváth, L. and Weidinger, T., 2007: Measurement and modelling of fluxes of nitrogen compounds above a semi-natural grassland ecosystem in Hungary. *Marie Curie ILEAPS workshop Helsingborg*, Sweden, October, 2007. (Poster).
5. Pintér, K., Nagy, Z., Balogh, J., Barcza, Z., Kristóf, D., Weidinger, T., Grosz, B., Machon, A., Horváth, L. and Tuba, Z., 2007: Components and micrometeorological measurement of carbon and nitrogen budget on landscape scale. *32th Scientific Days of Meteorology, 2006. Cloud physics and micrometeorology*. (Editors: Weidinger, T. and Geresdi, I.), *Hungarian Meteorological Service*, Budapest, 161–168. (In Hungarian).
6. Horvath, L., Grosz, B., Tuba, Z., Nagy, Z., Czóbel, Sz., Balogh, J. and Pintér, K., 2007: Estimation of nitrous oxide emission from Hungarian semi-arid sandy and loess grasslands; grazing exclusion and effect of irrigation and application of fertiliser. Nitrogen 4<sup>th</sup> Conference, 1-5 October, 2007, Costa do Saúpe, Brazil. Abstracts.
7. Machon, A., Horváth, L., Grosz, B., Weidinger, T., Pintér K., and Tuba, Z.: Measurement and modelling of fluxes of nitrogen compounds above a semi-natural grassland ecosystem in Hungary. NitroEurope General Assembly and Open Science Conference, Gent/Belgium, 2008 február 17-22., Konferencia kiadvány, p. 65.
8. Grosz, B., Horváth, L., and Machon, A.: Modelling soil fluxes of greenhouse gases

(CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O) for Hungary. NitroEurope General Assembly and Open Science Conference, Gent/Belgium, 2008 február 17-22., Konferencia kiadvány, p. 75.

9. Horváth L., Grosz B., Czóbel Sz., Nagy Z., Péli E.R., Szerdahelyi T., Szirmai O. és Tuba Z., 2008: Metán és dinitrogén-oxid fluxusmérések Bodroghözben; kezdeti eredmények A Magyar Növénybiológiai Társaság IX. Kongresszusa 2008. július 7-9. Szeged, S6-32. előadás
10. Grosz B., Horváth L., Machon A., Hidy D. és Tuba Z. (2008): Légköri üvegházhatású gázok mérlegének meghatározása mezőgazdasági területek és erdők fölött Magyarországon DNDC modellel. In: (ed.: Sáhó Á.) A levegőkörnyezet állapota: ökológiai kölcsönhatások és egészségügyi kockázatok. A 33. Meteorológiai Tudományos Napok 2007 kiadványa, 45-49.  
[www.met.hu/pages/seminars/metnapok/33\\_MTN\\_2007.pdf](http://www.met.hu/pages/seminars/metnapok/33_MTN_2007.pdf)
11. Machon A., Horváth L., Grosz B., Weidinger T., Pintér K., Nagy Z. és Tuba Z. (2008): Tájéleptékű nitrogénmérleg meghatározása mérések és a DNDC modell alapján. In: (ed.: Sáhó Á.) A levegőkörnyezet állapota: ökológiai kölcsönhatások és egészségügyi kockázatok. A 33. Meteorológiai Tudományos Napok 2007 kiadványa, 58-62. [www.met.hu/pages/seminars/metnapok/33\\_MTN\\_2007.pdf](http://www.met.hu/pages/seminars/metnapok/33_MTN_2007.pdf)
12. Horváth, L., Alberti, G., Balogh, J., Barcza, Z., Birkás, M., Czóbel, Sz., Davis, K., Farkas, Cs., Führer, E., Grosz, B., Koós, S., Machon, A., Marjanovic, H., Nagy, Z., Peressotti, A., Pintér, K., Tóth, E., 2010: Methodologies, (Haszpra L., ed.) Atmospheric Greenhouse Gases: The Hungarian Perspective, Springer (in preparation).
13. Grosz, B., Barcza, Z., Churkina, G., Gelybó, Gy., Haszpra, L., Hidy, D., Horváth, L., Kern, A., Kljun, N., Machon, A., Somogyi, Z., 2010: Models and their adaptation, (Haszpra L., ed.) Atmospheric Greenhouse Gases: The Hungarian Perspective, Springer (in preparation).
14. Grosz, B., Barcza, Z., Churkina, G., Gelybó, Gy., Haszpra, L., Hidy, D., Horváth, L., Kern, A., Kljun, N., Machon, A., Pásztor, L. 2010: Arable lands, (Haszpra L., ed.) Atmospheric Greenhouse Gases: The Hungarian Perspective, Springer (in preparation).