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GREENHOUSE GAS DYNAMICS IN SOILS CONTAMINATED WITH FONOFOS PESTICIDE

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Abstract. The aim of the study was to provide information about the influence of the fonofos pesticide on the process of greenhouse gas formation in two selected soils. In the model experiment soil samples (*Eutric Histosol*, *Mollic Gleysol*) were amended with pesticide as follows: with a dose of 1µg of fonofos/1g of soil and with one ten times higher (10 µg of fonofos/1g of soil) in relation to the control samples, prepared without fonofos addition. The laboratory experiment lasted 42 days. The gas samples (3 cm^3) taken from head space during incubation of soils (6 times after every 7 days of incubation, till the 42^{nd} day) were analysed by gas chromatography (Varian CP-3800 equipped with TCD, FID and ECD detectors) for CH_4, N_2O, CO_2 contents. It was shown that respiration activity was strongly reduced up to 35^{th} day of incubation in each of the soil investigated. The value of *P* was lower than 0.05, which testified to statistically significant differences between average greenhouse gases emission and the fonofos dose at 95% confidence level. Generally, respiration activity returned to the optimum value after 6 weeks from introducing the pesticide into the soil.

Keywords: fonofos, soil, CO_2 , N_2O, CH_4

INTRODUCTION

This paper describes a laboratory soil incubation experiment prepared in order to investigate the effects of a pesticide (fonofos) on the fluxes of CO_2, N_2O and CH_4 in the soil environment. Pesticides are widely used to improve yield and quality of agricultural produce and to control pests and diseases in crop production (Crum *et al.* 1999, McDonald *et al.* 1999). Pesticides (herbicides, insecticides etc.) that are used extensively in agricultural production and rangeland improvement have the potential for leaching into the soil environment, which can potentially result in the contamination of groundwater sources (Zhang *et al.* 2000).

According to Aspelin (1997), the worldwide consumption of pesticides has reached 2,6 million metric tons and 85% of this is used in agriculture (Wilson and Tisdell 2001). The initial use of pesticides was very effective in reducing pest infestations and increasing agricultural production and productivity (Wilson and Tisdell, 2001). However, over time, targeted pests have developed resistance to pesticides, necessitating increasing applications or resulting in rising population of pests or both. After a point, resistance of pests may grow to such an extent that application of pesticides is no longer economical (Wilson and Tisdell, 2001). However, as with fertilizers, the use of pesticides is expected to increase globally during the next 50 years by 2.7 times to $10.1x10^6$ metric tons per year (Tilman *et al.* 2001). The behaviour of pesticides in soil systems depends on their chemical and physical properties and on their interaction with the biotic and abiotic soil components (Cheng 1990, Sanino *et al.* 1999). Several factors including both soil properties (e.g. organic matter, clay content, cation exchange capacity, acidity) and the physical and chemical characteristics of the adsorbed compound may also influence the adsorption and desorption of pesticides on soil components (Pierzyński *et al*. 1994).

In the literature until now rather little attention has been paid to the influence of pesticides on the processes of gas formation in the soil environment. We have taken into consideration changes in emissions of carbon dioxide, nitrous oxide and methane in the soils contaminated with fonofos pesticide.

Carbon dioxide is the most abundant gas, after water, in the volatile phase exsolved from magma (Hernandez *et al.* 2000). It is an important gas which, apart from nitrous oxide and methane, contributes to climate change. The oxidation of organic matter in rocks and soils can produce CO_2 as well as the microbial-aided oxidation of sulphides. Soil CO_2 emission is the sum of root and microbial respiration (Lou *et al.* 2004). Most studies have focused on the effects of temperature and soil moisture content on soil CO_2 flux (Frank *et al.* 2002, Mielnick and Dugas 2000).

Nitrous oxide (N_2O) is a radiatively active atmospheric trace gas implicated in stratospheric ozone destruction. The long atmospheric half-time of N_2O (120 years) contributes to its large radiative forcing potential which is, on a molecule-for-molecule basis, about 280-310 times higher than CO_2 (Mummey and Bluhm, 2000). N_2O production in soil is generated from two dissimiliar energy-yielding microbial processes: nitrification and denitrification. Anthropogenic sources of nitrous oxide from fossil fuel and biomass burning contribute 25% of global emission, whereas emissions from natural soils contribute 43% of the total yearly emissions of N_2O on a global basis (Bouwman 1990, Mummey and Bluhm, 2000).

Methane is an important greenhouse gas which contributes about 15% to global warming (Prieme and Ekelund, 2001, Stępniewska and Szafranek, 2004). The tropospheric half-time of methane is about 7 years and it absorbs radiation in the 3 to 4 μm and 7 to 8.5 μm wavelength ranges (Stępniewska and Szafra-

nek, 2004). Methane concentration in the atmosphere is estimated as 1.8 ppmv (parts per million by volume) and increases by about 0.5% to 1% per year (Prieme and Ekelund, 2001, Stępniewska and Szafranek, 2004). Soil microorganisms which oxidize atmospheric methane are responsible for an estimated 5-10% of the total removal of methane concentrations. However, the mechanisms responsible for the reduction in oxidation rates and the slow recovery are not known (Prieme and Ekelund, 2001). Several causes have been suggested, including nitrogen fertilization, changes in soil gas transport following cultivation (Hansen *et al.* 1993), and slow growth rates of methane-oxidising bacteria (Prieme and Ekelund, 2001).

The objective of this study was to assess the dynamics of gas emissions from soils as affected by the fonofos pesticide. Fonofos is an insecticide applied for corn, fruit trees and decorative plant protection. Fonofos dosage and time of incubation were taken into account during estimating gas concentrations in two types of soils: *Mollic Gleysol* and *Eutric Histosol*.

MATERIAL AND METHODS

The main characteristics of the soil material are reported in Table 1. The soil samples were taken from the Ap level (0-20 cm) the following soils: a *Eutric Histosol* from Hajdów, and a *Mollic gleysol* from Kock, located in the south-east of Poland. The soil samples were not stored in laboratory, but immediately after taking from environment they were used for analyses. In the model experiment, soil samples were amended with the pesticide as follows: with dose equal to 1µg of fonofos/1g of soil and one ten times higher (10 µg of fonofos/1g of soil) in relation to the control samples, prepared without fonofos addition.

Table 1. Main features of the investigated soils

Type of soil	Granulometric composition (%)			%C g $(100\ g)^{-1}$	pH (H_2O)	Water content (g g^{-1})
	1-0.1mm	0.1-0.02 mm	<0.02 mm			
Eutric Histosol	28	36	36	36.5	7.5	27.5
Mollic Gleysol	38	25	37	2.12	7.5	2

The laboratory experiment lasted 42 days and during that time gas samples were taken from the headspace during soil incubation (6 times after every 7 days of incubation) and analysed by gas chromatography (Varian CP-3800, equipped

with TCD, FID and ECD detectors) for CH_4, N_2O and CO_2 contents. Five millilitre sub-samples of the incubation headspace were used for each analysis. Soil, 12 g, was placed in a 60 ml closed glass flask, where 14 ml of distilled water and pesticide doses (0, 1, 10 µg g^{-1}) were added and incubated in a thermostatic chamber at 20ºC. All gas analyses were performed in triplicate (1st and after 7 days of incubation), and all values reported are averages. During the soil incubation experiments the response of soil gas production to varying pesticide concentrations was examined.

RESULTS AND DISCUSSION

The effect of fonofos doses on carbon dioxide (A), nitrous oxide (B) and methane (C) concentration in *Eutric Histosol* and *Mollic Gleysol* is shown in Figures 1 and 2. Till the 14th day of incubation inhibition of carbon dioxide emission in *Eutric Histosol* was observed (Fig. 1A). Carbon dioxide concentration alternated between less than 2% on the 1st day and less than 1% on the 7th day of incubation. Fluxes declined at the beginning of the experiment, followed by a gradual increase to their highest value on the 35th day of the study when they reached the level of 4.6% at single fonofos dosage and 4.2% in the combination with tenfold higher factor, then returned to the value of 4.6% at the end of incubation (42nd day). In contrast to *Eutric Histosol*, in the *Mollic Gleysol* the beginning of CO_2 emission ranged between 1.6-1.8% (Fig. 2A). On the 7th day of the experiment its values increased to 3.3% and 3% for 1 µg g^{-1} and 10 µg g^{-1} of fonofos, respectively. The maximum soil CO_2 fluxes were estimated after 3 weeks of incubation as follows: 10.6% for single fonofos dose and 4.4% for the tenfold higher pesticide dose (Fig. 2A). The control value on the 21st day for *Mollic Gleysol* equaled 11.8%. Consequently, single dosage of fonofos was responsible for 10.2% inhibition of CO_2 flux, whereas the tenfold higher factor resulted in a 62% reduction of carbon dioxide emission, in relation to the control value. After four weeks of incubation, CO_2 flux ranged between 2.2-4.2% for 1µg g^{-1} of fonofos and 1.8-4.2% for 10 µg g^{-1}, on the 28th and 42nd day of the experiment, respectively.

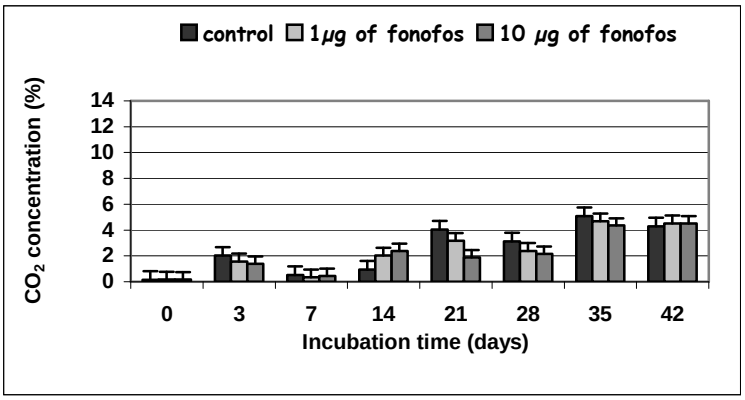
Seasonal fluctuations of soil CO_2 flux, with the maximum value in summer, the minimum in winter and intermediate in spring and autumn, were described by Lou *et al.* (2004). They explained that higher CO_2 fluxes during the summer may be attributed to increased root respiration and activated microbial respiration. In contrast, lower fluxes in winter may be connected with depressed root and microbial respiration caused by low soil temperatures, which is significantly positive correlated with soil CO_2 flux (Lou *et al.* 2004). Maljanen *et al.* (2004) stated that the mineral soil addition did not enhance net carbon dioxide emission from soil under barley in contrast to soil under grass.

Meanwhile, lack of nitrous oxide until the 7th day was found in the *Eutric Histosol* (Fig. 1B). It appeared after one week of the experiment at the level of 0.1% (single dose of pesticide) and 0.08% (10 µg g^{-1} of fonofos). These values were constant up to 21st day of incubation. Four weeks later (28th day) a little increase of N_2O to the value of 0.18% and 0.2% for single and tenfold higher doses were observed, respectively. Till the end of the experiment the level of 0.2% was not exceeded. However, in the *Mollic Gleysol* (Fig. 2B) maximum values obtained for N_2O emission on the 1st day were from 1.23% and 1.19%. Successive days of incubation resulted in a drop of nitrous oxide concentration at the presence of fonofos. An increase to the values of 0.21% and 0.28% towards the end of the experiment (days 35 and 42) were noted. Kinney *et al.* (2005) found that nitrous oxide emission was inhibited by three pesticides (mancozeb, chlorothalonil and prosulfuron). Generally, this inhibition equalled 10-62% and 20-98% at the lowest and the highest dosages, respectively (Kinney *et al.* 2005).

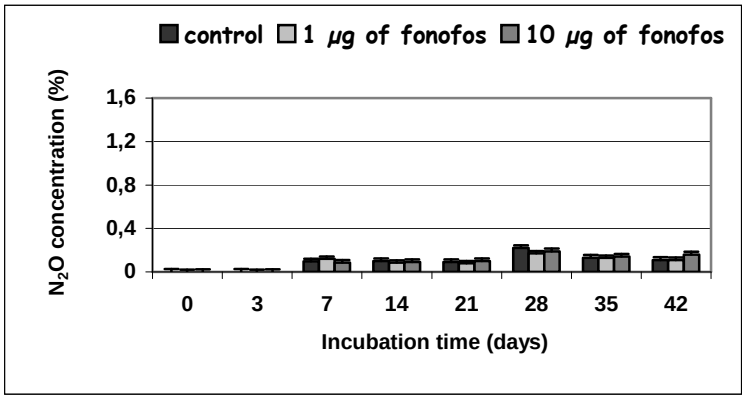
The presence of methane in the *Eutric Histosol* after 3 weeks of incubation (21st day) was detected (Fig. 1C), on the level of 0.47% and 0.23% for the doses of 1µg g^{-1} of fonofos and 10µg g^{-1}, respectively. Strong methane emission at the end of the experiment was noted and reached 3.7% or 3.3%, depending on the dosage of fonofos. Similarly, in the *Mollic Gleysol* (Fig. 2C) till the 21st day of the incubation period methane was not detected, it appeared at a level of 0.2% as a result of 10 µg g^{-1} fonofos supplement, after 3 weeks of incubation. Maximum values equalling 1.5% (single fonofos dose) and 0.77% (tenfold higher factor) were recorded on the 28th day. Later, strong inhibition of methane concentration was observed. However, towards the end of the incubation it appeared again, at a level of 0.2% and 0.17%, respectively to the pesticide doses.

Generally, pesticides decrease methane oxidation rates in the soil (Prieme and Ekelund 2001). Prieme and Ekelund (2001) demonstrated that Dimethoat 40 EC and Tolkan may inhibit the oxidation of atmospheric methane at concentrations likely to be found in the soil following application of the pesticides. Therefore, application of pesticides may be partly responsible for lowered methane oxidation rates in arable soils compared to forest soils (Prieme and Ekelund 2001).

The results obtained on the basis of the laboratory experiment are presented in Table 2. Statistical processing of the data (correlation analysis and ANOVA) was conducted, which allowed determination of the mean values of soil gas emissions and standard deviations. In each case, the value of *P* was lower than 0.05, which showed statistically significant differences between average greenhouse gas emissions and the fonofos dose at 95% confidence level.



A



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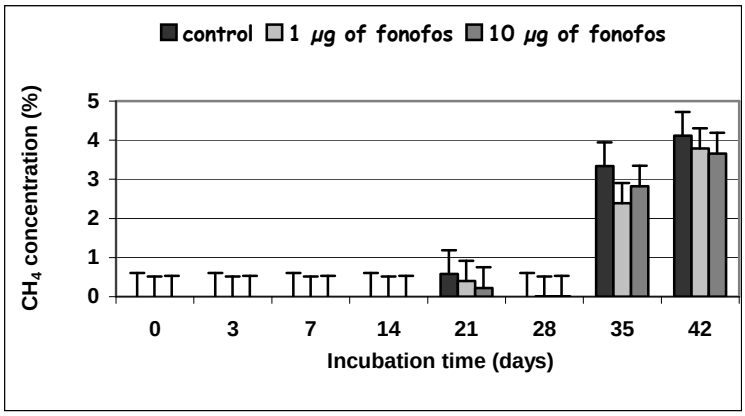
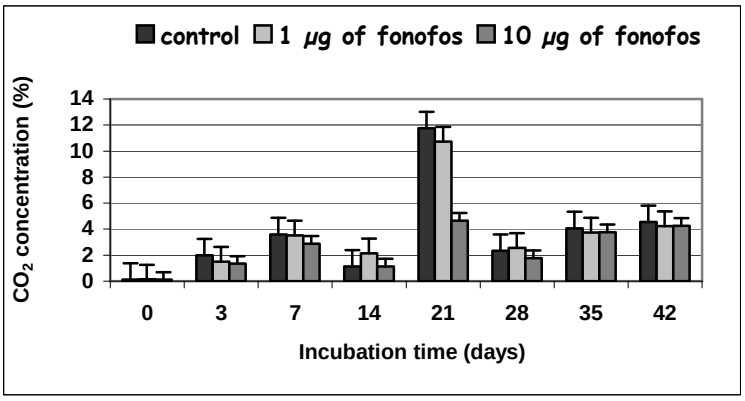
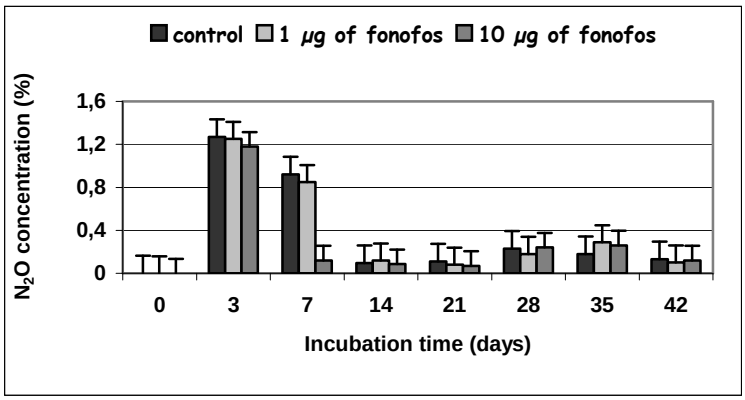


C

Fig. 1. Fonofos doses and carbon dioxide (A), nitrous oxide (B) and methane (C) concentrations in the *Eutric Histosol*



A



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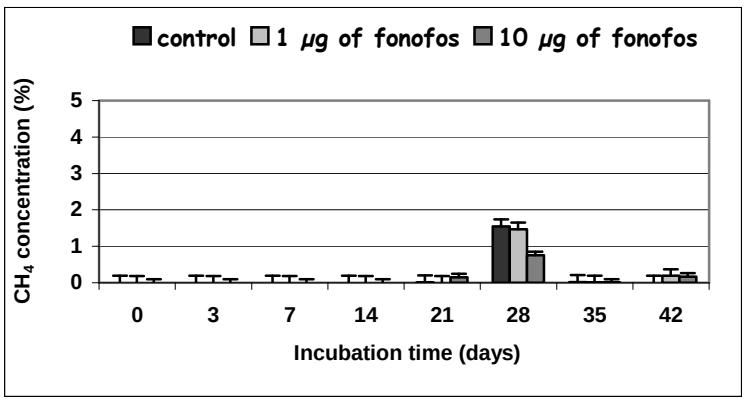

C

Fig. 2. Fonofos doses and carbon dioxide (A), nitrous oxide (B) and methane (C) concentration in the *Mollic Gleysol*

Table 2. The effect of fonofos application on greenhouse gas emissions; mean value, SD (95% half interval of confidence)

	Mollic Gleysol		*Eutric Histosol*	
Pesticide dose	Mean	Standard deviation	Mean	Standard deviation
		CO_2		
0	3.55 (a)	3.65	2.37 (a)	2.13
1	3.31 (a)	3.26	1.77 (b)	1.72
10	2.36 (b)	1.75	1.53 (b)	1.62
		N_2O		
0	0.37 (a)	0.44	0.09 (ab)	0.08
1	0.32 (ab)	0.41	0.08 (a)	0.05
10	0.26 (b)	0.36	0.01 (b)	0.06
		CH4		
0	0.19 (a)	0.53	1.00 (ab)	1.63
1	0.18 (a)	0.50	0.83 (b)	1.40
10	0.11 (b)	0.21	0.84 (b)	1.43

* mean values followed by the same letter are not significantly different at 5% confidence interval

The influence of pesticides on trace gas fluxes has historically received little attention (Kinney *et al.* 2005). Due to general lack of investigation of the effects that pesticides have on soil trace gas fluxes, it may be difficult to ascertain how various individual agricultural practices affect the production and consumption of trace gases in soil (Kinney *et al.* 2005). The laboratory experiment described here was used to demonstrate that a commonly-used pesticide can influence the production and net fluxes of environmentally important and radiative trace gases.

CONCLUSIONS

The laboratory experiment showed that:

1. The *Mollic Gleysol* has the strongest ability to fonofos sorption.
2. The highest pesticide decomposition percentage was observed in the aeration conditions of an *Eutric Histosol*, whereas the lowest one in the *Mollic Gleysol*.
3. Fonofos was completely decomposed or sorbed by the soils during 6 weeks. After that time soil respiration rates returned to the optimum value (mean value before pesticide introduction to the soil).

4. The respiration rate was strongly reduced between the 1st and 35th days of incubation in both types of soils.

5. N_2O appeared after the 1st-7th days of the experiment in the *Eutric Histosol* as well as in the *Mollic Gleysol*.

6. The presence of CH_4 was detected from the 21st day in both of the soils used in this study.

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DYNAMIKI GAZÓW SZKLARNIOWYCH W GLEBACH ZANIECZYSZCZONYCH FONOFOSEM

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S t r e s z c z e n i e . Celem pracy było dostarczenie informacji na temat wpływu pestycydu – fonofosu na proces formowania się gazów szklarniowych w dwóch wybranych glebach. W doświadczeniu modelowym próby glebowe (*Eutric Histosol*, *Mollic Gleysol*) zostały wzbogacone pestycydem w następujący sposób: dawka równa 1 µg fonofosu na 1 g gleby, oraz dawka dziesięciokrotnie wyższa (10 µg fonofosu na 1 g gleby), w odniesieniu do prób kontrolnych, przygotowanych bez dodatku fonofosu. Doświadczenie laboratoryjne trwało 42 dni. Próby gazowe pobierane w ilości 3 cm^3 znad roztworu glebowego (6 razy co 7 dni trwania inkubacji, aż do 42 dnia) poddane zostały analizie z użyciem chromatografu (Varian CP-3800), wyposażonego w detektory TCD, FID i ECD, na określenie zawartości CH_4, N_2O i CO_2. Stwierdzono, iż aktywność respiracyjna ulegała silnej redukcji do 35 dnia inkubacji, w każdej z badanych gleb. Wartość *P* była niższa od wartości 0,05, co świadczy o istnieniu statystycznie istotnych różnic między średnią emisją gazów szklarniowych a dawką fonofosu w 95% przedziale ufności. Generalnie, aktywność respiracyjna powracała do wartości optymalnych po 6 tygodniach od wprowadzenia pestycydu do gleby.

S ł o w a k l u c z o w e : fonofos, gleba, CO_2 , N_2O, CH_4