Methane and carbon dioxide emissions from a loess soil treated with municipal waste water after second step of purification

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A b s t r a c t. The aim of the study was to determine in laboratory conditions CH₄ and CO₂ emissions from a soil with including redox potential (Eh). Experiment was carried out under laboratory conditions on Ap horizon of a loess soil (Orthic Luvisol) flooded with water and municipal waste water after second step of purification. Soil samples were incubated in the darkness at 20°C for 15 days. During incubation, concentrations of CH₄ and CO₂ from the soil were analysed by gas chromatography. Parallely with gas analyses Eh and pH measurement were done. The maximal emission of CH₄ reached values of 0.007 mg C-CH₄ kg⁻¹ on the 7th day in the samples treated with waste water. The incubation of soils in 20°C resulted in 30% higher CO₂ emission with waste water than in the samples treated with water. Redox potential was decreasing to about -110 mV until the 6th day and keep this value to the end of experiment. The maximum emission of CH4 was observed at Eh -119 mV in the soil flooded with waste water.

K e y w o r d s: methane emission, carbon dioxide, municipal waste water, redox potential

INTRODUCTION

Methane is the second most important greenhouse gas after CO_2 and contributes to global warming in about 20% (Bouwman, 1990). The increase of CH_4 is a cause of considerable concern because CH_4 plays an important role in atmospheric chemistry and radiation forcing (Gilbert and Frenzel, 1995). CH_4 in the atmosphere has a lifetime of 12–17 years and its concentration is increasing in the atmosphere at the rate of about 0.8% y⁻¹. It has a global warming potential of about 24.5 times higher in relation to CO_2 and is responsible for approximately 25% of anticipated warming. The main sink for atmospheric CH_4 is oxidation to CO_2 .

Soil production of CH_4 is associated with wetlands, flooded rice production, termite activity, landfills and areas of gas production. About 40% of annual CH_4 emissions are produced in the soil (Mosier *et al.*, 1991). Methanogenesis is affected by many physical and biochemical factors, such as soil pH, redox potential, organic matter content, temperature and soil moisture content (Yu *et al.*, 2001).

In the areas of natural CH_4 production its oxidation by soil-borne microorganisms is very high. Methane in the amount of about 700 Tg is annually consumed in soils. The oxidation of about 5–10% of CH_4 emitted to the atmosphere occurs in the typically aerobic soils. The amount of methane oxidized in aerobic soils globally approximates its annual increase in the atmosphere (about 40 Tg y⁻¹).

The aim of the study was to determine under laboratory conditions the CH_4 emission in a loess soil flooded with water and municipal waste water after the second (II) step of purification.

MATERIALS AND METHODS

Soil material used in the experiment constituted Ap horizon (0–20 cm) of loess soil (Orthic Luvisol). The soil was characterised as follows: sand (2.0–0.05 mm) – 18%, silt (0.05–0.02 mm) – 68%, clay (<0.02 mm) – 14%, pH $_{\rm H2O}$ –6.8, C_{org} – 1.5%.

The air-dry soil was sieved through a 1 mm sieve, and its moisture was set to the level corresponding to soil moisture tension of 159 hPa. Soil portions of 20 g were placed in dark glass incubation vessels (59.8 cm³), and were mixed with 20 ml of waste water. Soil control samples, containing pure water instead of waste water, were prepared in the same way.

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The waste water after the II step of purification (mechanical and biological treatment), could have been applied to the soil as the Polish threshold values for chemical oxygen demand (ChOD), biological oxygen demand (BOD₅), macroelements and heavy metal concentrations for waste water introduced to the soil are shown in Table 1.

 Table 1. Physicochemical parameters of the input waste water (Kotowski et al., 1990)

Parameter	Unit	Range
pН	-	6.47 - 8.41
ChOD	$g O_2 m^{-3}$	30.1 - 56.3
BOD ₅	$g O_2 m^{-3}$	8.3 - 22.6
$NH_{4}^{+}-N$	$g N m^{-3}$	1.1 - 7.1
NO ⁻ 3-N	$g N m^{-3}$	20.2 - 38.4
N-tot	$g N m^{-3}$	22.3 - 43.6
PO ₄ -P	$g P m^{-3}$	3.1 - 6.8
P-tot	$g P m^{-3}$	3.7 - 7.0
Na^+	g Na m ⁻³	24.3 - 69.4
K^+	$g \text{ K m}^{-3}$	11.8 - 27.7
Ca ²⁺	g Ca m ⁻³	59.7 - 95.2
Mg ²⁺ SO ²⁻	$g Mg m^{-3}$	12.6 - 19.7
SO^{2-}	$g SO_4 m^{-3}$	43.6 - 116.3
Cl ⁻	g Cl m ⁻³	67.8 - 121.6
Zn	$mg Zn m^{-3}$	18 - 800
Cu	mg Cu m ⁻³	6 - 198
Pb	mg Pb m ⁻³	7 - 96

All vessels were tightly closed with rubber stoppers and aluminium caps, and incubated in darkness at 20° C for 15 days. Ten times during 15 days of incubation CH₄ and CO₂ concentrations in headspace gas were measured by a gas chromatograph technique with Shimadzu GC-14A and GC-14B chromatograph. After gas analysis, the vessels were opened and measurements of redox potential (Eh) and pH were done.

RESULTS AND DISCUSSION

The dynamic of CH_4 emission during incubation is presented in Fig. 1. The methane content in the headspace was gradually increasing during first 7 days. The highest CH_4 production was on the level of 0.007 mg C- CH_4 kg⁻¹ on the 7th day for soil treated with waste water. Then the concentration of CH_4 for soil samples treated with waste water started to decline, reaching 0.001 mg C- CH_4 kg⁻¹ after 10 days. Maximum production 0.002 mg C- CH_4 kg⁻¹ was observed for the control on the 5th day and kept on the same level.

The concentration of CO_2 increased with time, reaching a value of 87 mg C- CO_2 kg⁻¹ for samples treated with wastewater and 59 mg C- CO_2 kg⁻¹ for control (Fig. 2). During first 6 days of incubation, emission of CO_2 from soil treated with waste water increased faster than in the control, after this time respiration changed in the same way in both treatments until the last day 15 of the experiment. This effect may be explai- ned by easy exhausted decomposition of carbon in the waste water (Schlesinger, 1997).

Methane production was affected by soil redox potential. The maximum emission of CH4 was observed at Eh -119 mV in the soil flooded with waste water (Fig. 3). The critical Eh level for methanogenesis process is about -100 mV. It is important to note that the amount of CH_4 emitted or formed from reduced soil is a measure of the net result of two opposing methanogenesis and methanothrophic proceses: CH₄ production and CH₄ oxidation. Under soil redox conditions ranging from -100 to 500 mV CH₄ oxidation was considerably less than production, and CH₄ oxidation under strongly reducing conditions (Eh \leq -100 mV) was undetectable (Jugsujinda et al., 1995). A decrease of redox potential was triggered by CH₄ emission, however later changes of redox potential were not related to changes in CH₄ emission, e.g., maximum emission at 5th and 7th day, for control and waste water treatment, respectively. Redox potential decreased to about -110 mV until 6th day and keep this value to the end of experiment.

Masscheleyn *et al.* (1993) observed that Eh values of -150 mV was a critical value for soil methane emission; however Stępniewski and Stępniewska (2000) affirmed that beginning of CH₄ production in a soil starts below 50 mV with maximum emission on the level of -150 mV. In our

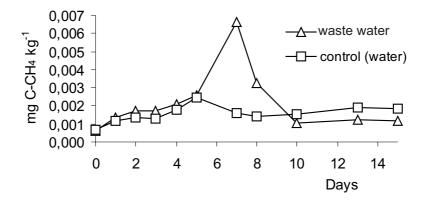


Fig. 1. The emission of CH₄ in the soil treated with water and waste water after the II step of purification.

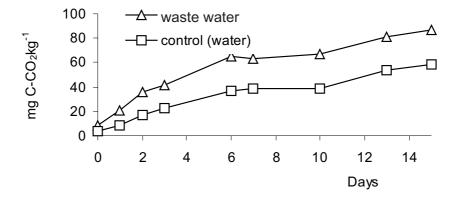


Fig. 2. The dynamic of respiration in the soil treated with water and waste water after the II step of purification.

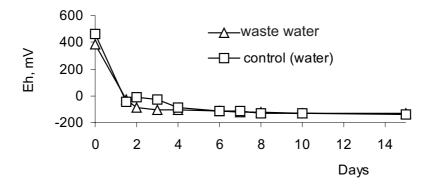


Fig. 3. The dynamic of redox potential in the soil treated with water and waste water after the II step of purification.

experiment maximum CH_4 emission 0.007 mg C- CH_4 kg⁻¹ was observed at Eh below –100 mV, and after that maintained on the level 0.001–0.002 mg C- CH_4 kg⁻¹ up to the end of the experiment.

CONCLUSIONS

The introducing of waste water to the soil (Orthic Luvisol) at 20° C, can be expressed by:

1. The emission of methane reached maximal values of 0.007 and 0.002 mg C-CH₄ kg⁻¹ on the 7th day in the samples treated with waste water and water, respectively.

2. The CO_2 emission reached a value of 87 and 59 mg C-CO₂ kg⁻¹ in the waste water and water treatment.

3. Decreasing of soil redox potential from about +400 mV down to about -100 mV during first two days of incubation and a maintaining of this level till the end of incubation indicated the proper conditions of the metanogenesis process.

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