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VARIABILITY OF THE NON-METHANE VOLATILE ORGANIC COMPOUNDS (NMVOC) COMPOSITION IN BIOGAS FROM SORTED AND UNSORTED LANDFILL MATERIAL

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Abstract: The landfill gas (LFG), produced during decomposition of the organic fraction of waste is a major source of air pollutants. It consists mainly of methane and carbon dioxide, but also contains additional gases, such as nitrogen, oxygen, hydrogen, carbon monoxide, hydrogen sulphide, and a large number of trace components. Aliphatic and aromatic hydrocarbons, halogenated hydrocarbons, heterocyclic compounds, alcohols, aldehydes, ketones, terpenes and siloxanes belong to this group. This work presents the results of field studies concerning the concentration of over fifty non-methane organic compounds in municipal solid waste landfill gas. The sites examined were located in the Middle-East macroregion of Poland. The landfills were different in the respect to size, morphology, and age of stored waste. The results reveal that the highest concentrations of the majority of the examined compounds were observed in gas released from the largest landfill at which the waste was not pre-treated prior to deposition. Concentrations often exceeded those found in the literature data. Deposition of waste after separation of biofraction and recyclable materials significantly decreased concentrations of the majority of NMOCs in the LFG.

Keywords: landfill emissions, non-methane organic compounds

INTRODUCTION

Landfill (LFG) gas is potent source of air pollutants. Methane and carbon dioxide are the most evident of them because of their high concentrations. These two gases constitute about 98-99% v/v of typical LFG at the methanogenic phase (Soltani-Ahmadi, 2000). However, LFG poses an additional threat because of the emission of many trace gases which are to harmful to the environment and human health. Additionally they have often malodorous character (Davoli et al, 2003; Dincer et al, 2006). Organic trace compounds present in LFG constitute a group of chemicals called non-methane volatile organic compounds (NMVOCs). The content of the NMOCs ranges from 0.01 to 1.0% of the landfill biogas volume (Lauber et al, 2006). Concentration of NMOCs is mostly dependent on deposited waste morphology and landfill age. Three different mechanisms are responsible for the production of NMOCs and their migration into landfill gas: (1) vaporization (the change of state from liquid or solid to vapour) of organic compounds until the equilibrium vapour concentration is reached, (2) chemical reactions of materials present in the landfill, and (3) biological decomposition of heavier organic compounds into lighter, more volatile constituents (*Guidance for evaluating..., 2006*).

One hundred and sixteen different trace organic compounds were identified in LFG in Great Britain (Herrera et al., 1988). Some of the trace compounds, like benzene, vinyl chloride and tetrachloroethylene are carcinogenic (Lauber et al, 2006). According to the International Agency for Research on Cancer (IARC) ethylbenzene and styrene are possible human carcinogens (carcinogens group 2B). Exposure to harmful air pollutants can also cause respiratory irritation, and damage to the central nervous system (*Guidance for evaluating..., 2006*). Halogenated compounds containing chlorine, bromine, and fluorine are responsible for corrosion of metal elements of pipe systems and engines for LFG combustion. Moreover, chlorofluorocarbons, which are the most common fluorinated species, contribute to the depletion of the stratospheric ozone layer (Rowland and Molina, 1987). Combustion of these compounds in the presence of hydrocarbons can lead to the formation of polychlorinated dibenzodioxins and dibenzofurans (PCDDs and PCDFs). Presence of the majority of halogenated compounds in LFG results from the direct volatilization from solid waste components and it was observed that a fresh waste give a higher emission of these compounds than an older waste (Guidance of gas treatment, 2004). Organic silicon compounds in landfill gas are predominantly present as organosilica compounds, containing Si-O-R bonds with organic substituents (where R= methyl, ethyl) bonded to the silicon atom. Major sources of harmful organic compounds in LFG are household, industrial waste (cosmetics, detergents, textiles, varnishes, building materials) and wastewater treatment sludge (Guidance of gas treatment, 2004).

The concentrations of harmful organic air pollutants in gas produced during anaerobic digestion of organic waste were examined by Eklund et al. (1998), Emerson (1999), Streese et al. (2001), Parker (2002), Shin et al. (2002), Scheutz et al. (2003 and 2007), Zou et al. (2003), Kim et al. (2006), Schafi et al. (2006), Staley et al. (2006), Rasi et al. (2007) and Scheutz et al. (2008). A short survey of these examinations shows that the qualitative and quantitative distributions of NMOCs in landfill gas visibly depend on the landfill size, the waste composition, the age of the deposited waste, and season. Rasi et al. (2007) compared the composition of biogas produced during anaerobic fermentation of municipal solid waste, sewage sludge, and farm waste. They found many aliphatic and aromatic hydrocarbons, halogenated hydrocarbons, organosilica compounds, aliphatic and aromatic sulfides, and the other heterocyclic compounds. The highest concentrations of benzene and halogenated hydrocarbons were observed in the landfill gas (0.6 -2.3 mg, 0.3-1.3, respectively). Otherwise, the highest concentration of toluene was measured in sewage digester gas (2.8-11.8 mg m^{-3}). Farm biogas contained the lowest amount of organic trace compounds. Staley et al. (2006) examined the dependence of NMOCs production on waste type. They concluded that concentration of NMOCs was the highest in the case of digestion of food waste. Paper and yard waste digestion led to the lowest production of these compounds. They also found that production of NMOCs during aerobic decomposition of refuse was higher than in anaerobic conditions.

The aim of the work described here was to compare the qualitative and quantitative composition of landfill gas (mainly NMOCs) from landfills using waste pre-treatment (selection of recyclable fractions and/or biofraction) to those without it (unsorted waste). The landfills used differed in size and age of the stored waste.

MATERIAL AND METHODS

Characteristic of sampling sites

The NMOCs concentrations were analysed in LFG samples taken from degassing wells installed on three municipal solid waste landfills located in the Lubelskie Region. A description of these sites is presented in Table 1.

The samples were taken from old, closed basins in the cases of the *Landfill 2* (waste deposited 10 - 4 years ago) and the *Landfill 3* (waste deposited 13 – 5 years ago), and from a basin still operating after 6 years in the case of the *Landfill 1*. Sewage sludge from the local wastewater treatment plants were deposited on all examined landfills.

Table 1. Description of examined landfill sites.

Property	**Landfill 1**	**Landfill 2**	**Landfill 3**
Year of opening	2001	I. 1997 II. 2003	I. 1994 II. 2002
Total landfill capacity [m^3]	200 000	I. 28 660 II. 54 800	I. 5 200 000 II. 6 500 000
Surface area [ha]	3.17	3.2	I. 6.03 II. 5.59
Annual deposition 2006 [Mg/year]	11 394	5 992	107 730
Cumulative deposition – state on Dec, 2006 [Mg]	56 493	I. 50 600 II. 8 345	I. 896 000 II. 484 765
Waste pre-treatment system	Segregation plant (separation of recycled materials: plastic (PET), metals, glass and biofraction). Prepared biofraction is directed to fermentation together with sewage sludge. The remaining part of thick fraction (ballast) after compressing (to volume density ca. 750 g/m^3) is deposited on the landfill.	Segregation plant (separation of recycled materials: plastic (PET), aluminium, glass. The remaining part of waste (ballast) is deposited on the landfill.	No pre-treatment.
Area covered	The district including the town (>50 000 inhabitants) and 5 neighbouring communes	The district including town (> 20 000 inhabitants) and 3 neighbouring communes	The district including city (> 360 000 inhabitants) and surrounding communes

I – closed, old basin – included in the examination.
II – operated basin.

The *Landfills 1* and 2 were passively vented, while the *Landfill 3* was actively vented and used the biogas for energy production.

The total biogas emission rates were estimated by using the Landfill Gas Emission Model (LandGEM) version 3.02 developed by U.S. Environmental Protection Agency. According to Faour (2007) this model appears to fit the data well.

The examinations were conducted in summer and autumn of 2007. In this period samples were taken four times (except for the analysis of siloxanes which was carried out only once).

The NMOCs being studied were divided into three groups: hydrocarbons, halogenated hydrocarbons and siloxanes. Concentrations of CH_4, CO_2 and O_2 are described separately.

Methods of examination

A portable infrared landfill gas analyzer GA-92 (Geotechnical Instruments, Leamington Spa, UK) was used for the direct determination of methane, carbon dioxide, and oxygen concentrations in LFG.

The sum of NMHC was determined via injection of the landfill gas sample onto the top of an empty chromatographic column of a portable Voyager GC equipped with a photoionisation detector (PID).

Gas chromatograph Voyager (Photovac – Waltham MA, USA) equipped with a 20 µl sample loop, three dedicated capillary columns, oven operated at isothermal conditions (60°C) and photoionization detector (PID) was used for the extensive gas analysis required in this work. The following compounds can be analyzed directly from the gas samples with detection limit lower than 10 ppb: bromomethane, chloromethane, chloroethane, dichloromethane, vinyl chloride, 1-dichloroethylene, acetone, carbon disulfide, vinyl acetate, t-1,2-dichloroethylene, c-1,2-dichloroethylene, methylethylketone (MEK), trichloromethane, 1,1,1-trichloroethane, tetrachloromethane, benzene, 1, 2-dichloroethane, trichloroethylene, tetrachloroethylene, methylisobutyl ketone, c-1,3-dichloropropylene, t-1,3-dichloropropylene, toluene, 2-hexanone, 1,1,2-trichloroethane, dibromochloromethane, chlorobenzene, ethylbenzene, m-xylene, o-xylene, p-xylene, styrene, bromoform, 1,2,2,2-tetrachloroethane, 1,3-dichlorbenzene, 1,4-dichlorbenzene, 1,2-dichlorbenzene.

Nitrogen - 99,999 purity- (BOC Poland) was used as a carrier gas.

For the direct GC-PID analysis the RSD (relative standard deviation) for five independent injections of nitrogen containing analytes at the concentration about 55 μg m^{-3} was better than 7.5%.

A GC-MS system was used to determine of the other gases. Samples collected in 3-liter Tedlar bags were transported to the laboratory and analytes were adsorbed on SPME fiber coated with 85 μm PDMS/Carboxene stationary phase during 15 minutes exposition. Afterwards analytes were desorbed directly in a PTV injector of the GC-MS system. The desorption time was 2 minutes. The GC-MS system (Trace Ultra – PolarisQ, USA) was operated under the conditions shown in Table 2.

Table 2. Conditions of GC-MS system.

The operation conditions of the chromatograph (TRACE ULTRA):			
Injector:	*constant temperature PTV (splitless mode) @ 270°C*		
Capillary column:	RTx 5 (Restek) 60m x 0.25mm d_f=0.25μm		
Oven temperature programming:	45°C (2 min hold) ramp 5°/min to 270°C, 10 min hold		
Carrier gas:	He (99,9996%) @ 40 cm/s		
The MS operating conditions (POLARIS Q):			
The ion source temperature	250°C		
The transfer line temperature	275°C		
Scanning mode I: *Full Scan*	50.0 - 450.0 amu		
Scanning mode II:	SIM: quantitation ions (Q) and qualifiers (QAL)	Q	QAL
	Benzene	78	77
	Toluene	91	92
	Ethylbenzene	106	91
	Xylenes	106	91
	Cumene	120	105
	Mesithylene	120	105
	Trichloroethylene	130	132
	Tetrachloroethylene	166	168, 164
	Dichlorobenzenes	146	148
	Trichlorobenzene	180	182
	Hexamethylocyclotrisiloxane	207	191
	Hexaethylocyclotrisiloxane	277	249
	Hexaphenylocyclotrisiloxane	439	362
	Trimethylotrivinylocyclotrisiloxane	243	215
	Octamethylocyclotetrasiloxane	281	207

Direct determination of volatile organics via isothermal GC-PID is not commonly used in landfill gas examination. SPME-GC-MS technique was previously applied by Davoli et al (2003).

For the five independent analyses, static gas standard mixture contained analytes at the concentration 51 μg m^{-3} with GC-MS system the data given in Table 3 were obtained.

Table 3. Results of measurements of selected analytes in a gas standard mixture.

Compound	Measured concentration [μg m^{-3}]	RSD [% of measured value]
Benzene	54.2	9.1
Toluene	52.1	7.3
Ethylbenzene	51.0	5.3
m-Xylene	56.8	8.1
Cumene	49.2	3.2
Mesitylene	47.0	12.1
Trichloroethylene	56.9	7.1
Tetrachloroethylene	51.4	4.3
1,4-Dichlorobenzene	53.2	7.2
1,3,5-Trichlorobenzene	49.7	4.1
Hexamethylocyclotrisiloxane	46.2	9.2
Hexaethylocyclotrisiloxane	50.7	7.6
Octamethylocyclotetrasiloxane	59.4	12.4

RESULTS AND DISCUSSION

The analysed biogases contained different concentrations of CH_4, CO_2. The concentrations of CH_4 and CO_2 were very low (1.5-2.7 % and 0.01-1.1 % respectively) in contrary in *Landfill 1* where only ballast waste (remaining part of waste) devoid of any biofraction was deposited. Concentrations ranging from 5.7 to 8.9 % of methane and from 0.01 to 2.2 % of carbon dioxide were observed in landfill 2. The highest concentrations of these gases were observed in the biogas used for the energy production (*Landfill 3*). Levels of major components of landfill gas ranged from 56 to 65 % for methane, from 32 to 35% for carbon dioxide. Concentrations of fourteen (from among >50 possible) NMOCs exceeded the detection levels.

Concentrations of non-methane hydrocarbons in landfill gas

The results of measurements of non-methane hydrocarbons (NMHCs) concentrations and the relevant literature data are presented in Table 4.

The highest total concentrations of the non methane hydrocarbons (236-540 mg m^{-3}) were found in LFG from the largest landfill (*Landfill 3*).

From among the analysed hydrocarbons six were detected in the examined biogases.

Benzene, styrene, and acetone were not detected in the LFG from landfills at which the biofraction and recyclable materials were not deposited (*Landfill 1*). But, concentrations of styrene and acetone in the LFG emitted from the *Landfill 3* (unsorted waste deposition) were very high and exceeded the values given in the literature (Table 4). The concentration of styrene in the LFG from the *Landfill 3* ranged from 161 to 380 mg m^{-3}, and from the *Landfill 2* (deposition of waste after removal of recyclable fractions) reached 21 mg m^{-3}, whilst its concentrations in biogas in reported literature (Table 4) were below the detection level. Deposition of products like: packaging, electrical and thermal insulation, fibreglass, pipes, car parts, drinking cups and other food-use items could be a source of styrene. Low levels of styrene occur naturally in a variety of foods, such as fruits, vegetables, nuts, beverages, and meats (NPI, 2007).

Acetone concentrations in biogas from the largest landfill (*Landfill 3*) reached the value of 192 mg m^{-3}. Acetone is a common ingredient in domestic products. It is also found in paints, furniture polish, laundry pre-soaks, varnishes, pharmaceutical preparations, shoe polish. Acetone is also a product of breakdown of body fat (NPI, 2007).

The highest concentrations of benzene (27-40 mg m^{-3}) and toluene (60-94 mg m^{-3}) were found in the LFG from the *Landfill 3*, but these values did not exceed the literature data (0 - 167 mg m^{-3} for benzene, and 0.2 – 202 mg m^{-3} for toluene), as can be seen in Table 4. Toluene concentrations in the LFG from the *Landfills 1* and *2* (deposition of segregated waste) were lower and ranged from 46 to 51, and from 22 to 42 mg m^{-3}, respectively. Benzene can migrate to the landfill gas from deposits of some consumer products like: glues, household cleaning products, paint strippers, some art supplies and petrol (NPI, 2007). Toluene is a common solvent used in the production of paints, glues, printing ink, lacquers. It also can be emitted from mineral wool, plywood, sealing agents, wallpapers, vinyl carpet (EPA, 1994).

From among three analysed xylenes only m-xylene was detected in one of the examined biogases. A concentration of 32 mg m^{-3} was found in the LGF from the *Landfill 3* (deposition of non segregated waste). The total amount of xylenes in the LFG measured by Schuetz et al. (2003) was 85.5 mg m^{-3}. Streese et al., 2001 and Zou et al., 2003 found only o-xylene, the concentration of which ranged from 0.1 to 72 mg m^{-3}. M-xylene and p-xylene occur naturally in petroleum, o-xylene is found in coal tar, petroleum, forest and bush fires, and plant emissions. Xylenes are common in domestic products such as paints, caulks, insecticides and fungicides for yard and garden, hard surface cleaners, lubricating oils, markers, automotive chemicals, varnish and varnish removers, shoe polish, undercoats, adhesives, water proofing compounds, and furniture (NPI, 2007).

Ethylbenzene concentrations in the LFG reported in the relevant literature (Table 4) ranged from 0.1 to 52 mg m^{-3}. The concentration of this compound in the LFGs from the both landfills containing segregated waste (*Landfill 1* and *Landfill 2*) were high (43 and 62 mg m^{-3}, respectively), but at *Landfill 3* (containing non-segregated waste) it was double that of the largest value found in the literature (Zou et al., 2003).

Vinyl chloride which is carcinogenic to living organisms, was not detected in analysed LFGs.

Concentration of chlorinated hydrocarbons in landfill gas

From among 24 analysed chlorinated hydrocarbons four were detected in landfill gases (Table 4). The highest content of trichloroethene (211 mg m^{-3}), exceeding the values reported in the literature (Table 4) several fold, were found in the LFG from *Landfill 3*, where unsorted waste was deposited. Concentrations of dichloromethane and trichloromethane in this gas were also several times over that found in the literature (Table 4). Concentrations of tetrachloroethene did not exceed the values found in the literature and ranged from 3 to 59 mg m^{-3} (Table 4). Unlike the composition of LFG from the *Landfill 3*, trichloromethane, trichloroethene, tetrachloroethene (trichloroethylene) were not detected in the LFG from *Landfill 1,* which collects the waste devoid of recycled materials and biofraction. Only low amounts of dichloromethane was measured in the last gas.

Halogenated hydrocarbons are commonly found in consumer products. Dichloromethane could be a component of paints, polishes and cleaners, deodorants, furniture cleaners, hairsprays, household hard surface cleaners, insecticides, and waterproofing compounds. It does not occur naturally in the environment (NPI, 2007). Trichloroethene is also found in some household products, such as glues, paint removers, spot removers, paints, metal cleaners and typewriter correction fluid. Tetrachloroethene (PERC) is found in spot removers, water repellents, glues, and suede protectors (Guidance for evaluating..., 2006). Trichloromethane can be formed as a result of the chlorination of naturally occurring organic materials. There are no natural sources for this gas (NPI, 2007)

Siloxanes concentration in landfill gas

There is not much information regarding siloxane concentrations in landfill gas. But, in comparison with results obtained by Rasi et al. (2007), it appears that the concentration of siloxanes in the *Landfill 3* biogas was high. The sum of organic silicon compounds measured by these authors was only 0.7 – 4 mg m^{-3}, while the sum of siloxanes measured in this study (in the *Landfill 3*) was over 130 mg m^{-3}. Siloxanes were not detected in LFG from *Landfill 1* (no recyclable fraction and biofraction). Exemplary chromatograms (TIC and mass fragmentograms) are presented in Fig. 1.

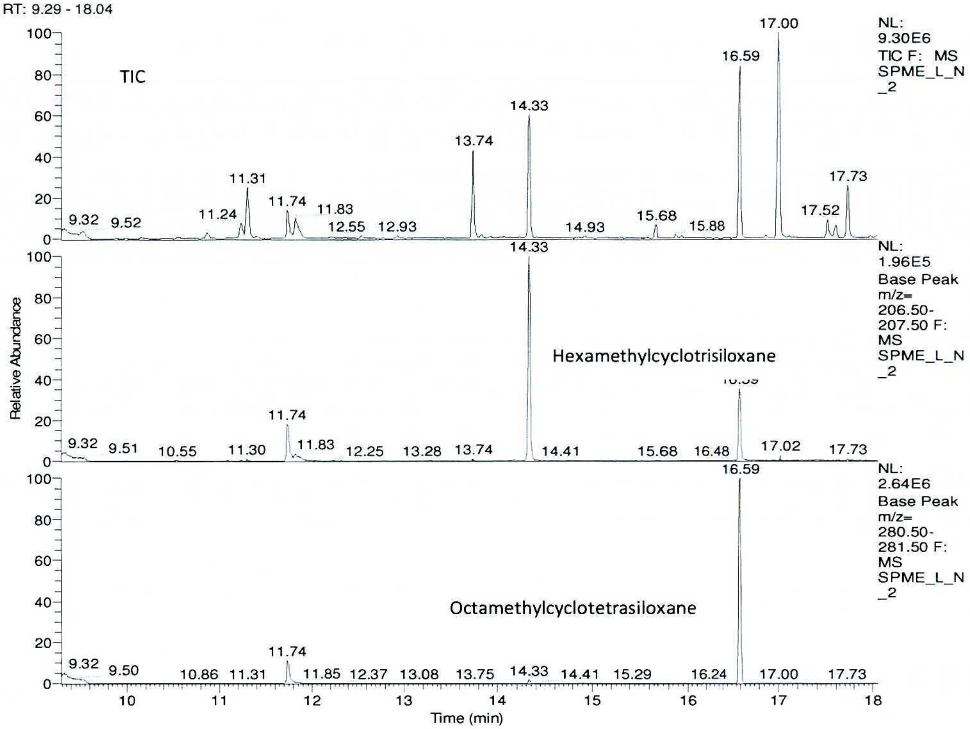

Fig. 1. Chromatograms and mass fragmentograms of siloxanes in the gas from *Landfill 2*.

Quantitative assessment of NMVOCs emission from examined landfills

The annual amounts of NMVOCs emitted from particular landfill site were calculated on the basis of the annual biogas generation. The calculation of the approximate biogas generation in particular years was carried out assuming the first-order decomposition rate equation [Eq. 1] used in U.S. EPA LandGEM model (EPA, 2005):

$$Q_T = \sum_{i=1}^{n} 2kL_oM_ie^{-kt_i} \qquad \text{[Eq. 1]}$$

where:

Q_T - annual biogas generation in a year of calculation (m^3 $year^{-1}$)
k - landfill gas emission constant ($year^{-1}$)
L_o - potential methane generation capacity (m^3 Mg^{-1})
t_i - age of the i^{th} section of waste (year)
M_i - mass of wet waste, placed at time i (Mg)
n - (year of the calculation) – (initial year of waste placement)
i - 1- year time increment

The k value used in a calculation was 0.04 (after EPA's Compilation of Air Pollutant Emission Factors, AP-42).

The potential biogas generation capacities estimated for Polish landfill conditions ranged from 50-250 m^3 $year^{-1}$ (Rosik-Dulewska, 2007). Thus, the L_o values ranged from 25- 125 m^3 $year^{-1}$. The L_o value depends on the composition of waste. The higher the organic fraction in the waste, the

Table 4. Concentrations of non-methane compounds in landfill gases.

Compound [mg m^{-3}]	Zou et al., 2003		Chiriac et al. 2007	Streese et al., 2001	Schuetz et al. 2003	Shafi et al. 2006
	winter	summer				
Hydrocarbons						
NMHC (sum) [1]	-	-	-	-	-	-
Benzene	1.2-15	41-167	-	0.0	1.8	3.10-73
Toluene (methylbenzene)	1.7-23	82-202	8.23	4.16	76.8	-
o-xylene	0.1-4.0	17-72	-	5.7	85.5	-
m-xylene	-	-	3.98	0.0		-
p-xylene	-	-	-	0.0		
Ethylbenzene	0.1-3.5	612-52	-	3.64	24.8	-
Styrene (vinyl benzene)	<DL	<DL	-	-	<DL	-
Cumene (1-methyl-ethylbenzene)	-	-	-	-	-	-
Phenol	-	-	-	-	-	-
Buthylbenzene	-	-	-	-	-	-
Acetone	-	-	-	-	-	-
Chlorinated hydrocarbons						
Dichloromethane	0.2-23	1.5-31	-	-	10.3	-
Trichloromethane	0.5-7.1	4-29	-	-	<DL	-
Tetrachloromethane	0.2-2.1	3-6	-	-	-	-
Dichloroethane	-	-	-	-	-	-
Trichloroethene	0.4-24	6-14	-	-	0.8	0.25-88.0
Tetrachloroethene	3-13	2-59	-	-	47.7	<0.02
Chlorobenzene	0.1-0.8	0.8-3.7	-	-	-	-
1,2-dichlorobenzene	0.1-0.8	0.8-3.7	-	-	-	-
1,3-dichlorobenzene	0.4-7.7	0.3-3.7	-	-	-	-
1,4-dichlorobenzene	0.4-2.1	0.3-4.9	-	-	-	-
1,3,5-trichlorobenzene	-	-	-	-	-	-

[1] Non-Methane Hydrocarbons DL – detection limit - not analysed

higher L_o value. However, we had no detailed knowledge about the morphology of waste deposited in the landfills examined by us. Therefore, the following assumptions were made: the organic fraction content in typical Polish municipal waste (without sorting) is about 40-50% w/w (Rosik-Dulewska, 2007), from that the amount of a biodegradable fraction in the case of the *Landfill 1* (segregation of biofraction and recyclable materials, occasional deposition of sewage sludge after fermentation) will be ca. 25% w/w; in the case of the *Landfill 2* (segregation of recyclable materials, deposition of sewage sludge and biofraction) will be ca. 80% w/w; and in the case of the *Landfill 3* (without waste segregation, occasional deposition of sewage sludge) will be ca. 50% w/w. On this basis the average potential methane generation capacities (L_o) for particular landfills were assumed to be: *Landfill 1* – 60 m^3 Mg^{-1}, *Landfill 2* – 150 m^3 Mg^{-1}, *Landfill 3* – 100 m^3 Mg^{-1}.

Parker, 2002	Emerson, 1999	Rasi et al, 2007	Shin et al., 2002	Eklund et al., 1998	Current study		
					Landfill 1	**Landfill 2**	Landfill 3
Hydrocarbons							
-	-	-	-	-	11-17	<DL	236-540
-	1.2-15.6	0.6-2.3	21.7-35.6	3.0	<DL	21-25	27-40
11.99	-	1.7-5.1	83.3-171.6	55.7	46-51	22-42	60-94
-	-	-	-	-	<DL	<DL	<DL
-	-	-	-	-	<DL	<DL	< DL -32
		-	-	-	<DL	<DL	<DL
6.48	-	-	-	-	<DL -43	<DL - 62	51-117
<DL	-	-	-	-	<DL	<DL -21	161-380
-	-	-	-	-	<DL	<DL	<DL
-	-	-	-	-	<DL	<DL	<DL
-	-	-	-	-	<DL	<DL	<DL
-	-	-	-	-	<DL	< DL -14	19 -192
Chlorinated hydrocarbons							
1.24	6.0-6.1	-	-	-	<DL - 0.3	8-11	44-58
-	0.42-0.43	-	-	-	<DL	<DL-1.2	58-72
-	0.08-0.12	-	-	-	<DL	<DL	<DL
13.26	-	-	-	-	<DL	<DL	<DL
-	1.7	-	-	-	<DL	47-51	196-211
16.64	2.08	-	-		<DL	<DL -2	32-44
11.88	-			-	<DL	<DL	<DL
-	-	-	-	-	<DL	<DL	<DL
-	-	-	-	-	<DL	<DL	<DL
-	-	-	-	-	<DL	<DL	<DL
-	-	-	-	-	<DL	<DL	<DL

The annual long-term biogas generation rate estimated for each landfill is presented in Fig. 2.

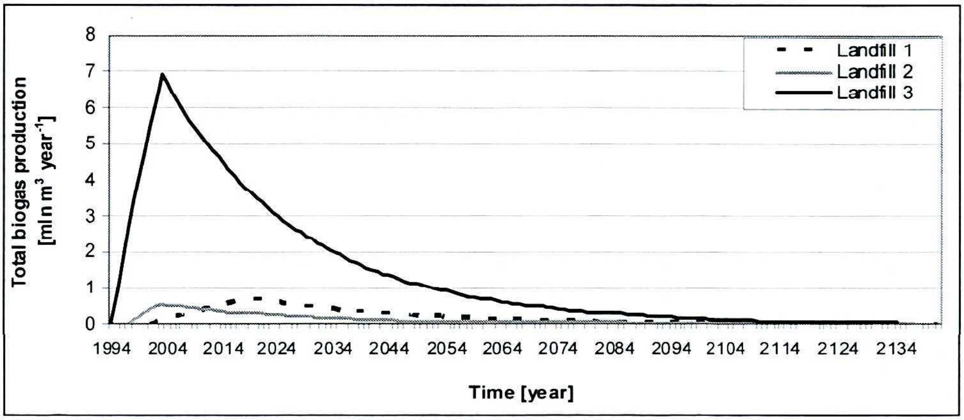

Fig. 2. Long-term biogas generation on three examined landfills (estimated on the basis of LandGEM model (EPA, 2005). The assumed model parameters are described in the text.

The biogas generation in 2007 estimated for the *Landfill 1* was 242 500 m^3 $year^{-1}$, for the *Landfill 2* – 459 600 m^3 $year^{-1}$, and for the *Landfill 3* – 5 904 000 m^3 $year^{-1}$.

The amounts of the particular NMVOCs produced in 2007 by the whole mass of deposited waste, calculated on the basis of data collected in Table 4 and the biogas generation estimated for 2007 are presented in Table 5.

Table 5. Total production of particular NMVOCs in 2007 and their specific production rates (values related to 1 Mg of waste) calculated on the basis of total biogas production and NMVOCs concentrations in the biogas emitted from examined landfills.

NMVOCs	*Landfill 1*		*Landfill 2*		*Landfill 3*	
	Total production [kg year^{-1}]	Spec. prod. rate [mg Mg^{-1} year^{-1}]	Total production [kg year^{-1}]	Spec. prod. rate [mg Mg^{-1} year^{-1}]	Total production [kg year^{-1}]	Spec. prod. rate [mg Mg^{-1} year^{-1}]
Hydrocarbons						
Benzene	-	-	9.7- 11.5	191.6 - 227.2	159.4 - 236	178 -263.3
Toluene (methylbenzene)	9.8- 12.3	173.4 - 217.7	10.1-19.3	199.6-381.4	354.2 - 555	395.3-619.4
m-xylene	-		-	-	<189	<211
Ethylbenzene	<10.4	<184	<28.5	<563.2	301 - 690.7	336-770.8
Styrene (vinyl benzene, ethenylbenzene)	-	-	<9.7	<191.6	950.5-2243.5	1060.8-2503.9
Acetone	-	-	<6.4	<126.4	112-1133.6	125 - 1265.1
Chlorinated hydrocarbons						
Dichloromethane	<0.07	<1.2	3.6-5.1	71.1-100.7	259.8-342.4	290 -382.1
Trichloromethane	-	-	<0.6	<11.8	342.4 -425	382-474.3
Trichloroethene	-	-	21.6 -23.4	426-462.4	1157.2-1245.7	1295.1-1390
Tetrachloroethene	-	-	<0.9	<17.7	189-259.8	210.9-289.9
Cyclic alkilated siloxanes						
Hexamethylocyclotrisiloxane	-	-	<5.2	<102.7	<428	<477.6
Hexaethylocyclotrisiloxane	-	-	<1.9	<37.5	<154	<171.8
Hexaphenylocyclotrisiloxane	-	-	-	-	<18.3	<20.4
Octamethylocyclotetrasiloxane (D4)	-	-	<0.38	<7.5	<184	<205.3

The annual amounts of NMVOCs generated in the Landfill 3 were many times higher than the amounts of the gases produced in the *Landfill 1 and 2*. It results from the 16-18 times higher mass of waste deposited on Landfill 3 in comparison to the other landfills.

The results of quantitative assessment of NMVOCs production in 2007 relative to waste mass unit showed that the unsorted waste (deposited in *Landfill 3*) was the most "productive" with respect to these gases. Only three analysed gases (toluene, ethylbenzene and dichloromethane) were detected in biogas emitted from the landfill where biodegradable and recyclable fraction were not deposited (*Landfill 1*). The largest number of analysed compounds was found in the biogas emitted from *Landfill 3*. Two of them: m-xylene and hexaphenylocyclotrisiloxane were found only in this biogas. The specific production rates of other NMVOCs in *the Landfill 3* were higher than the values calculated for the *Landfill 1* and 2. The significant differences (t-Student test, $\alpha=0.05$) between the specific production rates of NMOCs produced in *Landfill 3* and *Landfill 2* were observed in the cases of toluene, styrene, acetone, dichloromethane, trichloromethane, trichloroethene, tetrachloroethene, octamethylocyclotetrasiloxane. The highest value of specific production rates was calculated for styrene (1060.8-2503.9 mg Mg^{-1} year^{-1}). This was about 13 times higher than the specific production rates in sorted waste deposited in the *Landfill 2*. The specific production rate of trichloromethane in the *Landfill 3* was about 40 times higher than this value in the *Landfill 2*.

Taking into account the age of the landfill it can be assumed that the total biogas production on *Landfill 2* and *3* have decreased over the last few years and the production on *Landfill 1* is still growing (see Fig. 2). However, the total production of NMVOCs in Landfill 1 probably will not increase significantly because of the fact that direct volatilization of these compounds was mainly observed in the initial stage of waste landfilling (Guidance of gas treatment, 2004).

CONCLUSIONS

The results of the examination reveal that:

1. The highest concentration of NMOCs was observed in the LFG from the largest landfill (*Landfill 3*), which collected unsorted waste.
2. The lowest number of NMOCs were detected in the LFG from landfill collecting waste devoid of organic and recyclable fractions (*Landfill 1*). Only three of the analysed compounds: toluene, ethylbenzene, and dichloromethane were detected in the biogas emitted from this landfill. The concentrations of detected compounds were the lowest in comparison to the other LFGs.
3. Siloxanes were not detected in LFG from the basin at which neither recyclable fraction nor biofraction were deposited (*Landfill 1*).
4. Calculation of specific production rate of NMOCs (amount of compound in biogas related to 1Mg of waste and unit of time) suggest that the deposition of waste after the pre-treatment process relaying on separation of recyclable fraction and biofraction leads to significant decrease of NMOCs production. Productivities of NMOCs per unit mass of waste were several times higher for the unsorted waste than for the sorted one. The highest differences in production rates concern such compounds as: trichloromethane, tetrachloroethene, acetone, styrene.
5. Separation of the organic fraction and recycling materials is a good way for minimizing the detrimental influence of landfills on the atmosphere, not only by decreasing the methane and CO_2 emissions, but also to abate the NMOCs emissions, especially compounds such as: m-xylene, toluene, styrene, acetone, dichloromethane, trichloromethane, trichloroethene, tetrachloroethene, hexaphenylocyclotrisiloxane, and octamethylocyclotetrasiloxane.

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