Study on selected odorous compounds at the “Barycz” municipal landfill site in Krakow, Poland

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Untersuchung ausgewählter Geruchsstoffe auf der Deponie „Barycz“ in Krakau, Polen

Abstract

The aim of the present investigation was to determine time variation of selected odorous compounds emitted at the different parts of the „Barycz” municipal landfill site in Krakow, Poland. Air samples were collected at four sampling points using charcoal adsorption tubes followed by solvent (CS_2) desorption and analysed by GC-FID and GC-MS. For quantitative analysis 13 compounds were selected: ethanol, pentanol, heptane, methylcyclohexane, benzene, toluene, ethylbenzene, p-xylene, o-xylene, α-pinene, β-pinene, p-cymene and limonene. The results indicated that the concentrations of odorants in the air varied and strongly depended on the sampling point. The most influential factors were: leak of biogas from the surface of the dump, failures of the landfill gas collection system, heavy truck traffic and machinery operations, filling containers with compost and meteorological parameters, especially precipitation and wind speed.

Keywords

Landfill odours, volatile organic compounds (VOC), GC-FID, GC-MS, “Barycz” municipal landfill site, Krakow, Poland

1 Introduction

Offensive odour associated with the decomposition of waste is of major concern to landfill operators since it leads to public opposition to landfill sites. Gaseous landfill emissions are a nuisance as well as a potential health hazard and therefore the accurate prediction and control of these emissions is an integral part of landfill design and operation (STRETCH ET AL., 2001). Products of the waste decomposition not only appear in the biogas, but also in leachates. Landfill odours are also released from fresh waste during their transport and landfill operations (e.g. crushing by compactors) (ALLEN, 1997; JAMES, 1997; MCKENDRY, 2002).

All compounds emitted from landfills can be classified in the groups: aliphatic and aromatics hydrocarbons, alcohols, aldehydes, ketones, acids, esters, sulphur/nitrogen containing organic compounds and chlorinated hydrocarbons. Landfill odorants generally have very low olfactory thresholds and in a consequence are detected by a human nose at very low concentrations (sometimes below the detection limit of measuring equipment). The type of odour is also affected by the composition and age of waste, local weather conditions, technology of landfilling, biogas utilisation, protection and reclaiming of landfill (SENANTE ET AL., 2003, ZOU ET AL., 2003).

A number of techniques have been developed for the analysis of odorous gases from landfills. The most common method for measuring odour concentrations was olfactometry, based on sensory analysis with human nose as a detector. Odour measurement techniques use also sensors (the electronic nose). Gas chromatography (GC) coupled with various detectors (FID, PID), especially mass spectrometry (MS) is the most popular method applied for the characterization of the chemical composition of odorous gas samples (DINCER, 2006).

The development of analytical techniques such as solid phase microextraction (SPME)-GC-MS and the use of techniques such as thermal desorption (TD)-GC-MS for the chemical characterisation of odorous mixtures are examples of efforts to identify the different compounds responsible for the odour. The implementation of techniques combining the separation and analysis of volatile compounds with their simultaneous sensory recognition of their odour characteristics and their intensity at an olfactory detection port (ODP) like SPME-GC-FID/ODP or TD-GC-FID/ODP allows for the acquisition of valuable information on the single components of the odorous mixture (LORNAGE ET AL., 2005).

The simple analytical techniques GC-FID and GC-MS were used to investigate the concentrations of selected odorous compounds at the landfill site “Barycz”, Krakow (Poland). Samples were collected at four sampling points. The dependence of the compounds concentrations upon the sampling sites were discussed. The correlations between obtained odorous gases concentrations and meteorological conditions: wind speed, precipitation, atmospheric pressure, and humidity were also investigated.

2 Characterisation of the “Barycz” municipal landfill site

The “Barycz” landfill site for the cities of Krakow (about 740 000 inhabitants) and Wieliczka (about 18 000 inhabitants) is located in the southern part of Cracow, close to the border of Wieliczka municipality. It was established in 1974. The area of the landfill (36 ha) has been divided into three parts: part I (12 ha) operated until 1992, part II (13 ha) operated until 2004 (both reclaimed), and part III (11 ha) which is currently exploited in accordance with the European Union Standards. The “Barycz” municipal site receives 170 000 tons of waste per year, from household, production plants, shopping premises and services. The deposited waste are crushed with compactors, disinfected with chlorinated lime and covered with a 20-cm layer of soil. At the landfill site a gas collection system has been installed. Landfill biogas collected by gas collection system is used for generation of electricity and heat. The landfill site has also its own sorting plant and composting plant for green waste. Nowadays the “Barycz” landfill site is one of the best managed and modern facilities in Poland (MPO, 2006).

3 Experimental

3.1 Sampling

Air samples were collected at four sampling points from September 2005 to October 2006. Sampling points represented the different stages and ages of solid waste management (Figure 1): on the surface of reclaimed dump (A), in the vicinity of the composting plant (B), near the area where the fresh waste were disposed (C), and near the leachate pond (D). The sampling was performed using the charcoal tubes packed with 100 mg charcoal. The air flow was forced through sampling tubes by aspirators and it was set at 60-90 dm^3/h for about 2 h. The tubes were installed about 40 cm over the landfill surface. When taking air samples readouts meteorological parameters were carried out. After sampling tubes were sealed with fitting and transported to the laboratory.

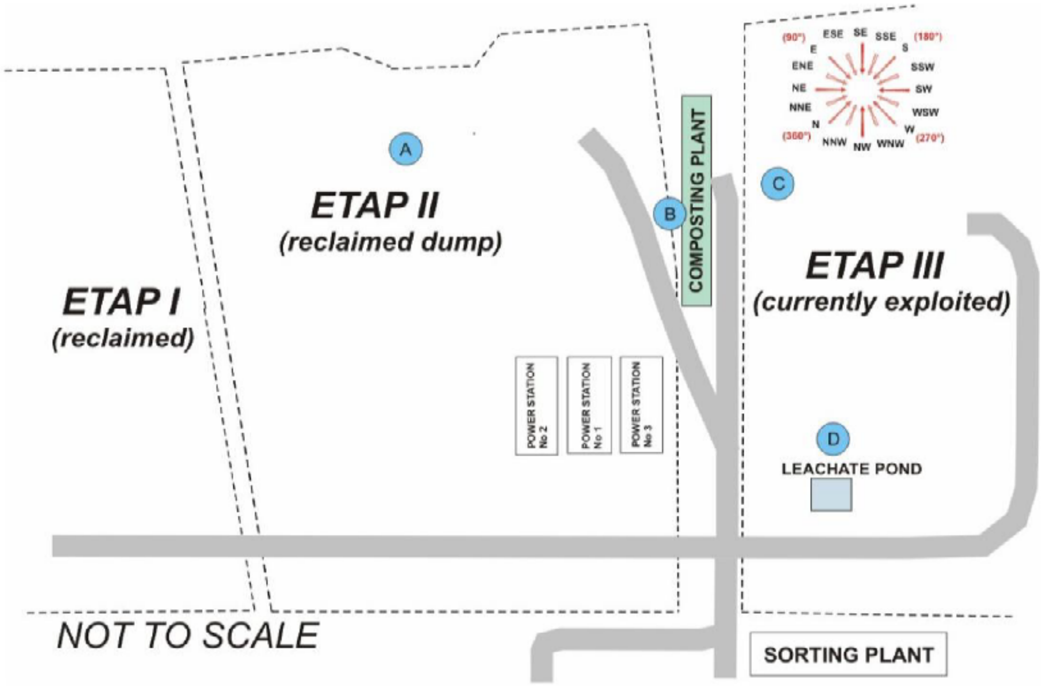

Figure 1 Schema of the municipal solid waste landfill site “Barycz” (not to scale): A-D – air sampling points: A – on the surface of reclaimed dump, B – in the vicinity of the composting plant, C – near the fresh waste, D – near the leachate pond

3.2 GC analysis

The adsorbed samples were recovered by desorption with carbon disulphide (Fluka 84714) and analysed by GC-FID. GC instrument (Varian CP-3800) was equipped with capillary column CP PoraPLOT Q (25 m x 0.25 mm x 8 μm) with helium as the carrier gas. Temperature programming was 100°C for 1 min with an increase to 200°C at 10°C/min hold for 10 min in 200°C, ramp of 10°C/min up to 250°C and hold for 10 min. The temperature of injector and FID detector was 120°C and 250°C, respectively. A split ratio was set to 1:30. The sample volume introduced into the injector was 3 μl. The compounds identification was possible by comparing their retention times with those of standards.

Mass spectrometry coupled with gas chromatography (GC-MS) was also used for identification of volatile organic compounds (VOC) in the air over the landfill. The GC-MS analysis was performed using a HP 6890 gas chromatograph. The GC column was HP-5 MS (60 m x 0.25 mm x 0.25 mm) with the programmed temperature from 35°C (2 min) to 200°C at an increasing rate of 5°C/min. The flow rate of carrier helium was $1 cm^3$/min. The detector was MSD 5973 HP, the ionisation voltage was set at 70 eV and detection of positive ions from 10 to 200 m/z. Fragmentation pattern identification was carried out by comparing with the Wiley IV database of mass spectra. Solvent-extracted (volume: 3 μl) sample was taken and injected into the chromatograph.

Quantification was proceeded only for thirteen substances: ethanol, benzene, pentanol, heptane, methylcyclohexane, ethylbenzene, toluene, p-xylene, o-xylene, α-pinene, β-pinene, p-cymene, limonene. The calibration was performed using series of standard mixtures containing known amounts of all thirteen compounds in carbon disulphide. Calibration lines were constructed by plotting integrated peak areas against concentrations of compounds.

4 Results and discussion

Aliphatic and aromatic hydrocarbons, terpenes, alcohols and esters were the majority of VOCs identified in the air over the landfill site (Figure 2). Toluene and p-xylene were found to appear most frequently in the examined samples in all points of measurements (over 60% of air samples). The frequency of occurrence of other odorous compounds varied and depended on the sampling sites.

In the point A (on the surface of reclaimed dump) the presence of almost all examined compounds was observed

The major compounds found in the point B (in the vicinity of the composting plant) were ethanol, aromatics hydrocarbons and terpenes.

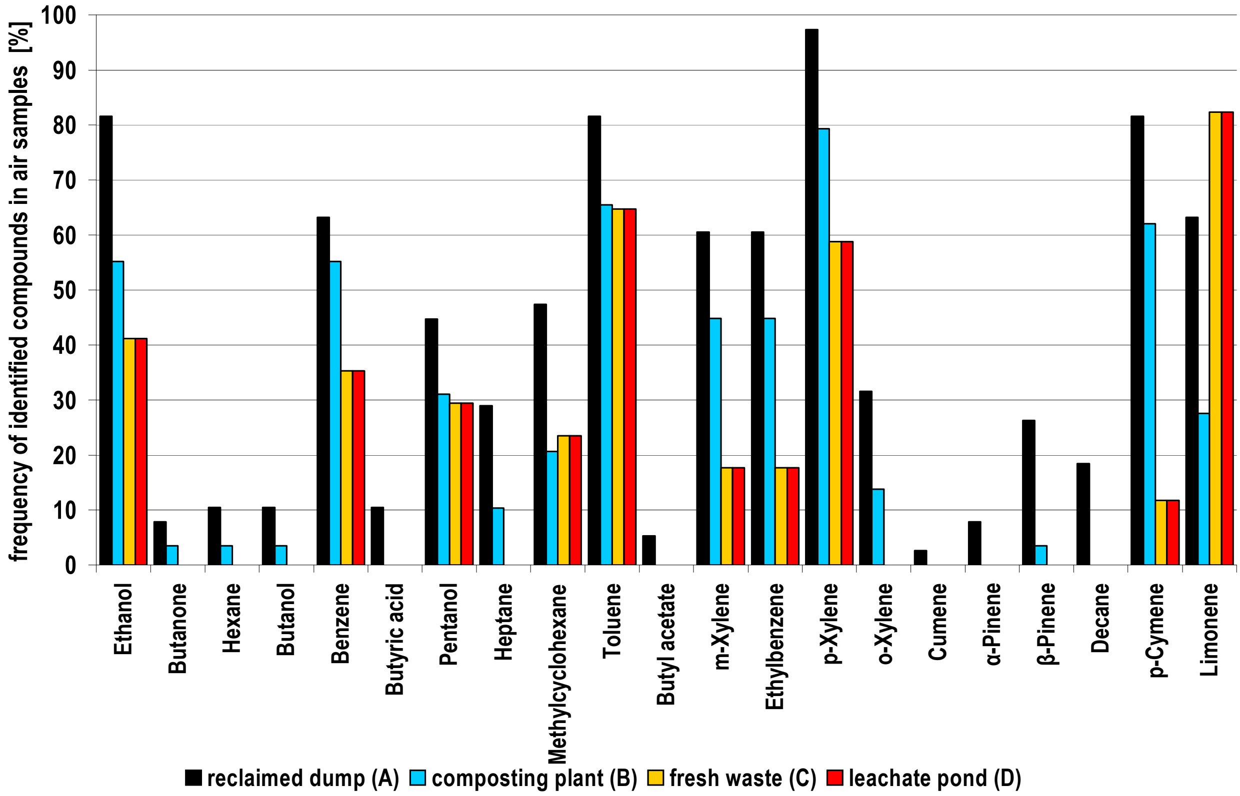

Figure 2 Frequency of identified compounds in air samples taken in air sampling points

Limonene was identified in 80% of air samples coming from the points C (near the fresh waste). In the point D, near the leachate pond, the presence of aromatics hydrocarbons and limonene were observed.

Appearance of aromatics hydrocarbons in the point A (on the reclaimed dump) might be explained by the presence of biogas escaping through the surface. In other places aromatics hydrocarbons could derive from the motor exhaust of machines working nearby (compactors, trucks transporting fresh waste to the landfill). Limonene is regarded as the product characteristic to the emission from the fresh waste. Other source of limonene is the biodegradation of green waste. Ethanol might be generated by the decomposition of fruits, vegetables and green waste present in recently disposed waste.

The concentrations of compounds (minimal, maximal and mean) measured in all sampling points are presented in Table 1.

Table 1. The VOC concentration ranges and (mean) concentration at “Barycz” landfill site

Compounds	Concentration [µg/m^3]			
	Reclaimed dump (A) n = 33	**Composting plant (B)** n = 29	**Fresh waste (C)** n = 17	**Leachate pond (D)** n = 17
Ethanol	7.1* - 338.9 (28.6)	3.5* - 516.2 (26.1)	8.0* - 330.0 (37.2)	8.1* - 346.6 (35.7)
Benzene	1.4* - 270.2 (9.3)	1.3* - 46.5 (5.1)	2.0 *- 81.8 (4.8)	1.1* - 179.8 (15.5)
Pentanol	2.1* - 73.5 (5.5)	2.9*	11.0*	4.6*
Heptane	0.9* - 48.2 (3.2)	1.1*	ND	4.7*
Methylcyclohexane	1.3* - 32.1 (32.1)	0.9*	5.9*	4.6*
Toluene	1.5* - 311.0 (37.0)	1.1* - 48.6 (6.9)	2.3*- 51.2 (7.9)	21.6
Ethylbenzene	1.3* - 116.3 (13.1)	2.8* - 18.9 (12.1)	6.5*	4.0*
p-Xylene	1.6* - 235.1 (83.4)	2.0* - 38.1 (5.0)	ND	1.4* - 23.1 (2.6)
o-Xylene	2.0*- 39.1 (33.8)	1.0*	ND	ND
α-Pinene	172.9 - 323.3 (228.6)	ND	ND	ND
β-Pinene	9.0* - 171.9 (22.7)	56.4	ND	ND
p-Cymene	3.5* - 965.3 (28.6)	3.1* - 53.2 (10.1)	7.9*	5.3*
Limonene	5.0* - 415.5 (9.3)	6.5*- 308.1 (31.7)	5.6* - 260.1 (75.6)	6.1* - 520.0 (179.7)

*** limit of detection, ND – not detected**

Figures 3-6 present variations of concentrations of volatile organic compounds in the points A, B, C and D during the period of measurements.

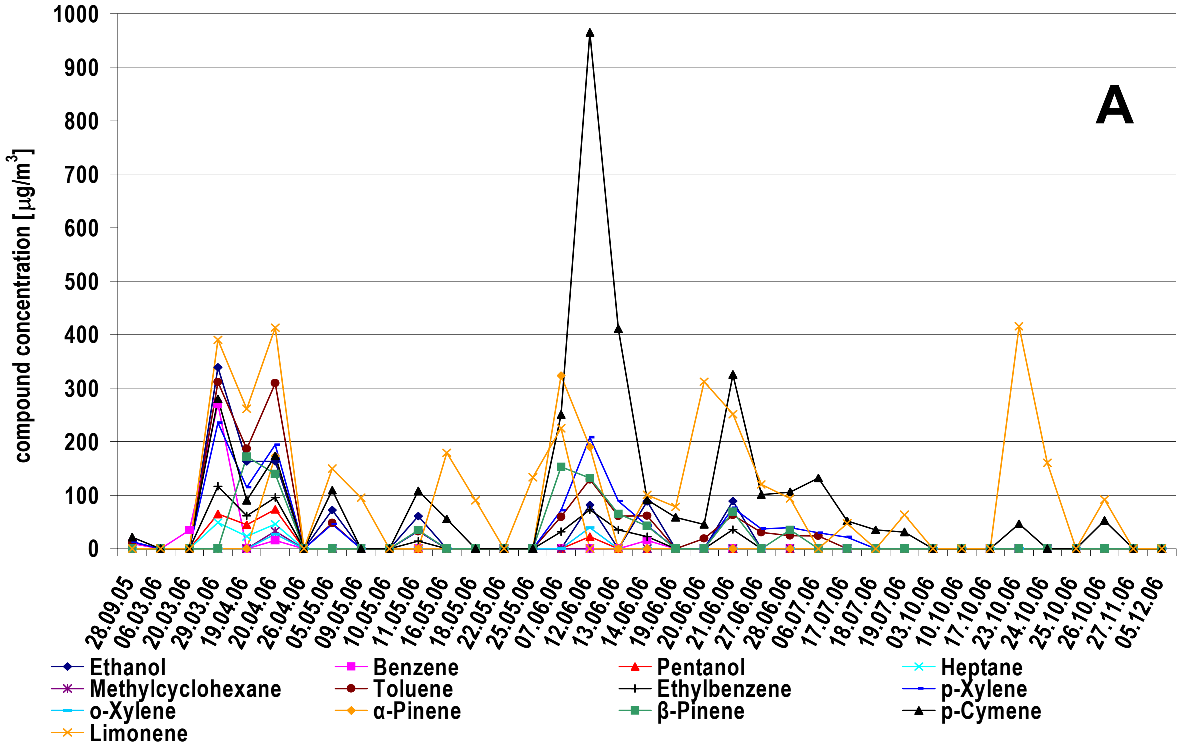

Figure 3 Variations of concentrations of volatile organic compounds in the point A (on the surface of the reclaimed dump)

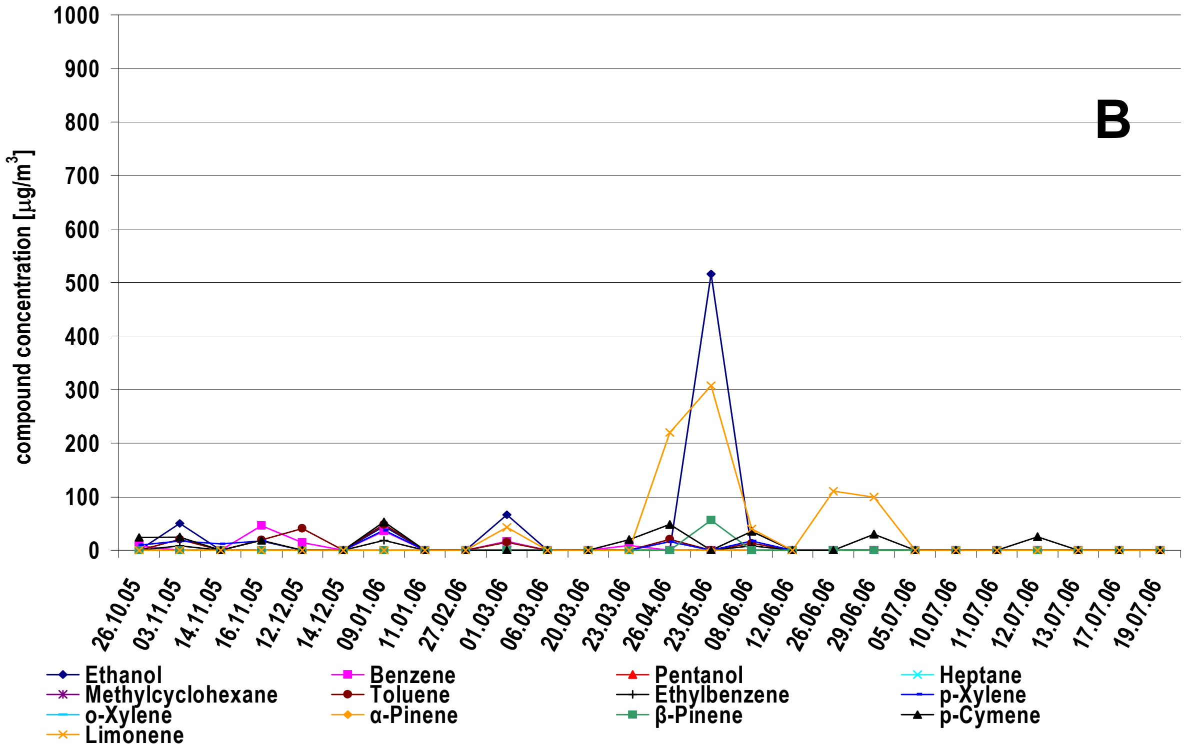

Figure 4 Variations of concentrations of volatile organic compounds in the point B (vicinity of the composting plant)

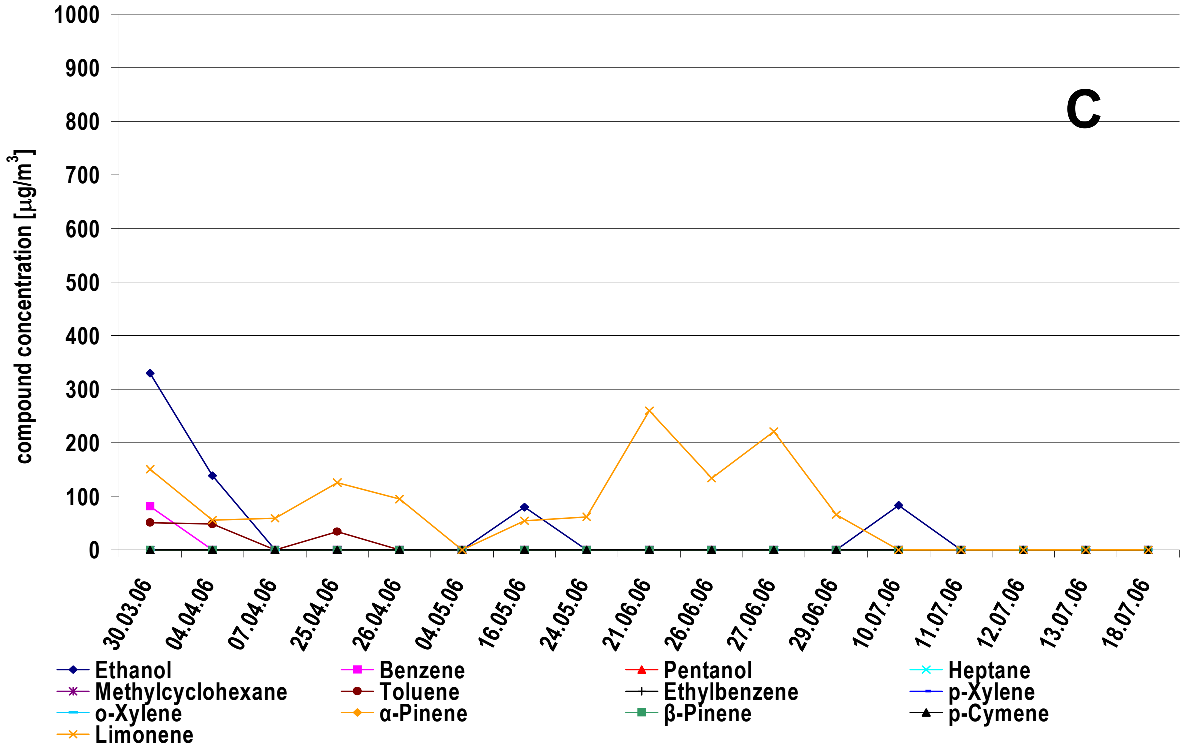

Figure 5 Variations of concentrations of volatile organic compounds in the point C (near the fresh waste)

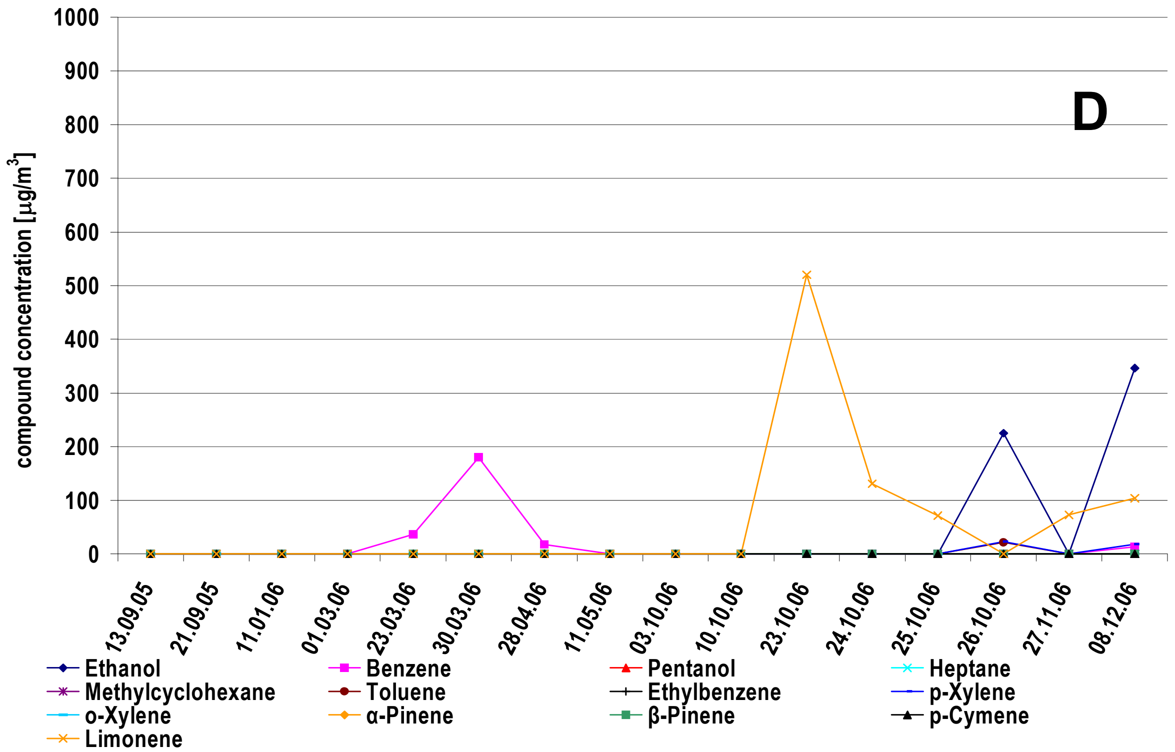

Figure 6 Variations of concentrations of volatile organic compounds in the point D (near the leachate pond)

The results indicate that the odorant concentrations in the air on the landfill site vary and strongly depend on the sampling point. The highest concentrations of all odorants were found in the point A (on the surface of reclaimed dump) while lowest were observed for the points D (leachate pond). Limonene and ethanol were considered to be the compounds with the highest concentration in the point B, C and D. In the point A (reclaimed dump) the highest concentrations were observed for p-cymene.

The results received at the point A (surface of the reclaimed dump) show the correlation between the leak of biogas from the dump surface and compound concentrations (Figure 7). During the days when the surface of the dump was untreated (29.03.2006, 19.04.2006 and 20.04.2006) the leak of biogas and its characteristic odour of biogas were observed. After covering the surface of the dump with new soil layer the odorant concentrations decreased and the odour was not detected. Uncontrolled emission from the landfill was also due to the technical problems with the biogas collection system.

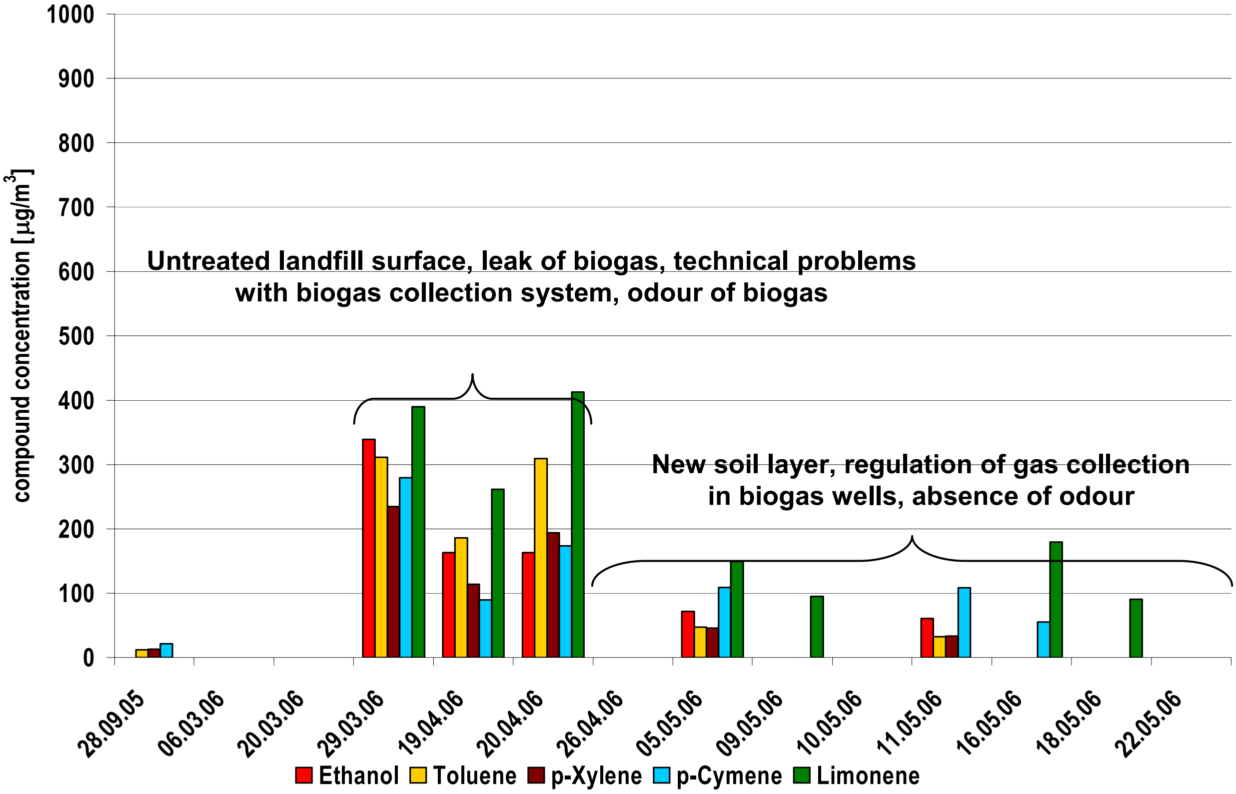

Figure 7 Concentration of selected compounds identified in the point situated on the surface of the reclaimed dump (A)

It was found that concentrations of examined odorants were affected by some meteorological parameters, especially wind speed (Figure 8) and precipitation. During rainfall or snowfall significant decrease of VOC concentrations in the air was observed. High relative air humidity led to a drop in VOC concentrations. When the atmospheric pressure dropped, increase of odorous compounds was observed.

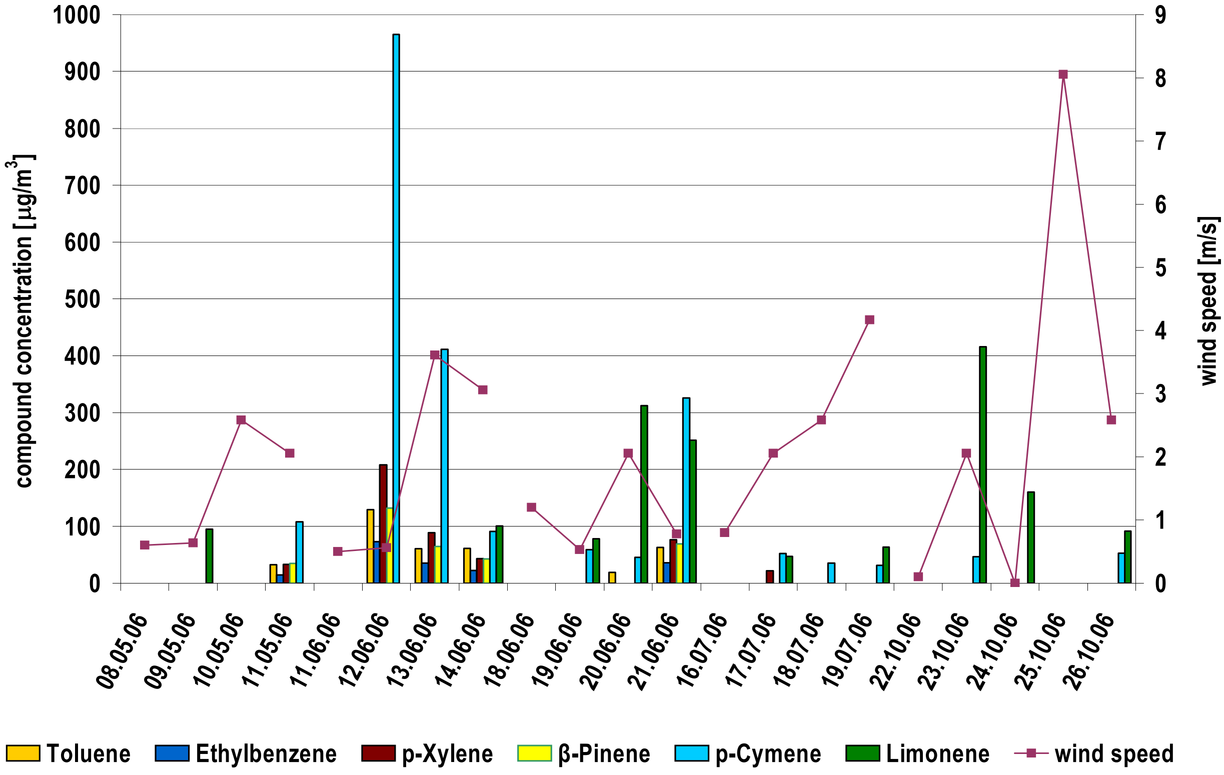

Figure 8 Short term effect of wind speed on the compound concentrations in the point A

5 Summary

In this study, 21 chemical compounds were identified in the air at the different points of the landfill site “Barycz” in Krakow, Poland. 13 compounds were selected for further quantification. The results indicated that the concentrations of odorants in the air varied and strongly depended on the sampling point. The highest concentrations of VOC were observed in the point situated on the surface of the reclaimed dump, the lowest – near the leachate pond. The concentrations of compounds were influenced landfill activities: the leak of biogas from the surface of the dump, the failures of the landfill gas collection system, the heavy truck traffic and machinery operations, shovelling the compost and filling of the compost containers.

The observed variation of compounds concentration might be also attributed to the different values of meteorological conditions during the period of measure. It was found that concentrations of examined odorants were significantly affected by meteorological parameters, especially wind speed and precipitation. During the days with high atmospheric pressure, the concentration of detected compounds tended to be lower.

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6 Literature

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