Geology, Geophysics & Environment 2023, vol. 49 (2): 101–121

Gases in the near-surface zone of the reclaimed Barycz municipal waste landfill – a case study from southern Poland

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Received: 30 September 2022; accepted: 28 march 2023; first published online: 21 April 2023

Abstract: The formation of biogas at municipal landfills and the significant emission of greenhouse gases from these facilities into the environment were the main reasons for analyzing the molecular composition of soil gas in the near-surface zone at the reclaimed part of the Barycz municipal waste landfill. The relations between the studied components (methane, carbon dioxide, light hydrocarbons and non-hydrocarbon components) and impact of the magnitude of recorded concentrations of methane and carbon dioxide on their emission to the atmosphere were evaluated. Two profiles were determined, along which 41 soil and landfill gas samples were taken at 20-meter intervals. At the same time, emissions were measured at each sampling point using a static chamber with a portable fluxometer. Chromatographic analysis showed that the concentrations of methane and carbon dioxide fluctuated in the ranges: 2.1 ppm – 76 vol% and 0.04 ppm – 11 vol%, respectively. Relatively high concentrations of these gases were determined at many of the measurement points, and this was particularly evident at the A-A' profile, indicating stronger biochemical processes in this part of the landfill, or lateral migration of methane from the neighbouring stage II of the landfill, where biogas extraction is currently taking place. In addition, significant correlations between methane, carbon dioxide, and oxygen were demonstrated, indicating ongoing methane fermentation processes. Based on the study, it can be concluded that the southern part of the A-A' profile is an optimal place to locate a degassing well from which biogas production could be used. However, the research is only preliminary and, it will be necessary to extend the soil gas tests before the final decision on the location of the well is made. Moreover, it has been shown that the concentrations of methane and carbon dioxide measured at points located outside the landfill were low. This means that generated biogas probably does not migrate beyond the boundaries of reclaimed waste landfill, but this will need to be confirmed by performing additional soil gas tests inside and outside the landfill area. The preliminary assessment of the effectiveness of the reclamation carried out was confirmed by the negligible values of the measured methane and carbon dioxide emissions on the surface.

Keywords: landfill, emission, surface distribution, methane, carbon dioxide, biogas, hydrocarbons

INTRODUCTION

In landfills, organic matter decomposition processes and physicochemical transformations occur with the participation of microorganisms. Organic wastes under aerobic and anaerobic conditions undergo biodegradation (Renou et al. 2008, Dudek 2013, Mbachu et al. 2020, Malovanyy et al. 2021, García-Depraect et al. 2022). As a consequence of the transformations that occur, biogas

https://doi.org/10.7494/geol.2023.49.2.101 ISSN 2299-8004 | e-ISSN 2353-0790 | Wydawnictwa AGH

of a specific composition is produced. Its main components are methane (about 55–60 vol%) and carbon dioxide (about 40–45 vol%), as well as other components such as non-methane organic compounds, hydrogen sulphide, nitrous oxide, and mercaptans (Majumdar et al. 2014, Czekała et al. 2016, Pehme et al. 2020, Huang et al. 2022). Carbon dioxide and methane are the main gases that contribute to the worsening of the greenhouse effect and climate change around the world. It should be noted that methane emissions from landfill alone amount to approximately 11% of global emissions (Barlaz et al. 2004, Georgaki et al. 2008, Haro et al. 2019, Delgado et al. 2022).

The phenomenon of biogas formation in deposited waste was first highlighted in the UK in 1934. At that time, methane was identified in landfill gas (Rajchel 2017). In the last decades of the 20th century and the beginning of the 21st century, many papers appeared describing the phenomenon of biogas formation in municipal waste landfills and its industrial use (e.g., Augenstein & Pacey 1991, Manna et al. 1999, Shin et al. 2005, Bove & Lunghi 2006, Themelis & Ulloa 2007, Barros et al. 2014, Ciuła et al. 2020, Alrbai et al. 2022). The increased interest in the capture and disposal of process gases generated in municipal landfills is largely due to legal considerations (including the implementation of the Regulation of the Minister of the Environment of 30 April 2013 on landfills (*Rozporządzenie…* 2013) and the EU landfill directives (EP and CEU 2018). The aforementioned pieces of legislation are intended to guarantee the transition to a closed-loop economy and thus enforce the need to equip landfills with a facility to capture, treat, and use landfill gas for energy purposes or, if this is not possible, to flare it. In the absence of a disposal system for the resulting biogas, numerous toxic substances, often of a carcinogenic nature, are introduced into the environment. At the same time, there is a risk of explosion, the spontaneous combustion of landfills, and the emission of greenhouse gases and odours into the atmosphere (Fatta et al. 1999, Yaqout 2003, Purmessur & Surroop 2019, Vaverková 2019, Campbell 2020, Huang et al. 2022).

In general, landfill gas recovery is no longer carried out in reclaimed municipal landfills that have been operating for several decades for technical and economic reasons. This is due to the fact that methane generation activity is generally low within this type of facility (Porowska 2021). Many revitalized landfills have already undergone a functional change from “lost territories”, primarily to green spaces beneficial to society and the urban environment in terms of ecosystem services and land restoration (Vincevica-Gaile et al. 2023). However, under specific conditions, old, reclaimed landfills can also be productive in terms of the amount of methane generated. Therefore, this study analyses the distribution of concentrations of methane and carbon dioxide, as well as light hydrocarbons and other non-hydrocarbon components (hydrogen, nitrogen, and oxygen) in the near-surface layers in the area of the reclaimed part of the Barycz municipal waste landfill located near Krakow. Although these tests are only preliminary, if high concentrations of methane are found, they will allow the determination of the optimal location of the degassing well and recovery of the biogas in an innovative and economic way. In the future, the methods used may enable the implementation of landfill gas recovery at other reclaimed landfills where it has not been possible so far. Environmental considerations are also important in the studies. They are taken into account by assessing the relations and dependencies between the components and evaluating the impact of the magnitude of recorded concentrations of methane and carbon dioxide on the emission of these gases into the atmosphere. This will allow for an initial assessment of the effectiveness of the landfill surface reclamation method.

CHARACTERISTICS OF THE AREA

The study area is the Barycz municipal refuse tip, located in the southern part of Poland about 12 km south-east of Krakow’s city centre (Fig. 1). The landfill occupies natural depressions and sinkholes created by mining activities. The Barycz rock salt deposit was exploited here between 1924 and 1998. Exploitation of this deposit was carried out from the ground surface using the underground leaching method, without the protection of a roof (Mazurek 2007). As a consequence, this activity led to the creation of many continuous deformations, several local sinkholes, and severe degradation of the ground surface.

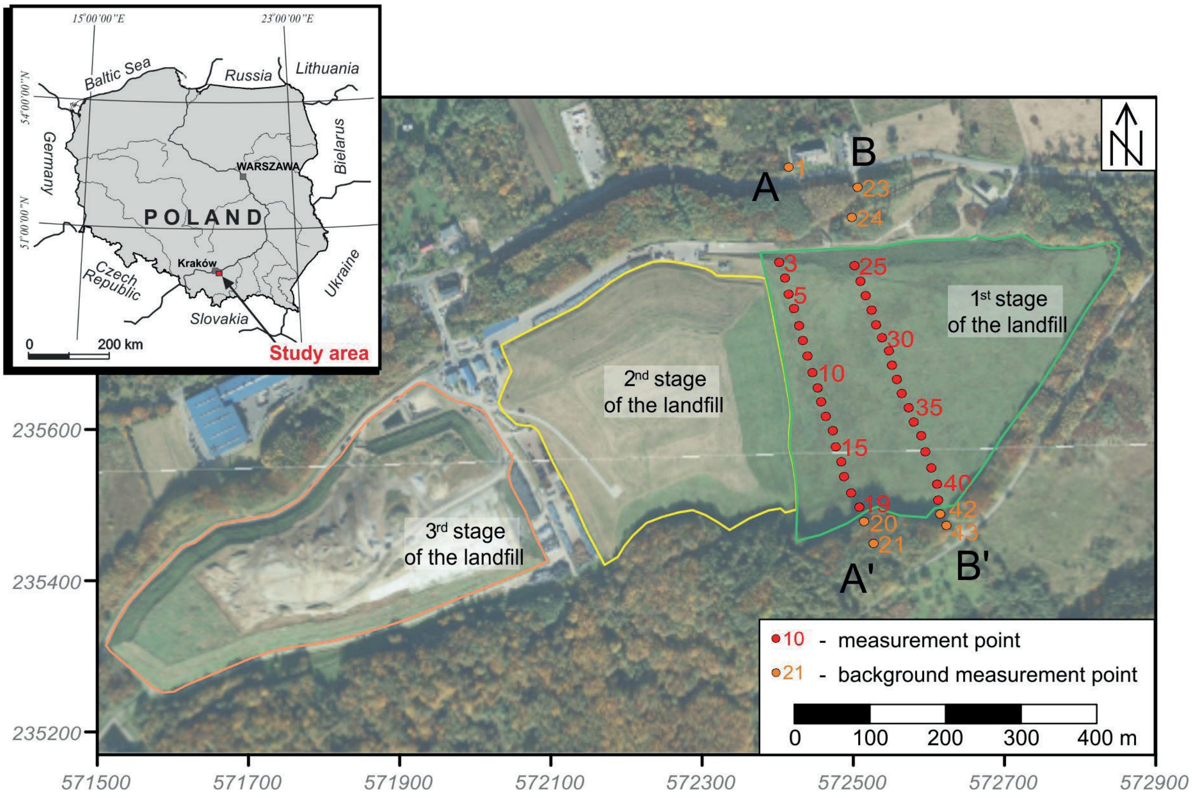

***Fig. 1.** Location of the research area and distribution of measurement points*

Tipping of municipal waste began on the surface of the most degraded areas in 1974 (Mazurek 2007). The site was divided into three parts which differ morphologically and technologically. The waste was initially stored in the eastern part of the complex, commonly referred to as stage I. Waste was stored there in the years 1974–1992. In 1992, storage began in stage II of the landfill, which was completed at the end of 2004. Unfortunately, we do not have data on the type of waste stored in stages I and II of the landfill. The legal provisions of the time did not require keeping records of the type of waste stored. Currently, stage III of the landfill is in operation and the previous two stages have been fully reclaimed (Kuczyńska & Flak 2013). According to d'Obyrn & Wójcik (2015), the reclamation of stages I and II consisted of the application of a levelling layer with a thickness of 0.3–0.5 m, a layer proper with a thickness of 0.5 m and also a 0.25 m layer of fertile soil on the landfill canopy and its slopes, and the entire surface was sown with a grass mixture (Kultys & Flak 2004). In each of the separated plots, the layers were overburdened several times to increase the absorption capacity of the landfill (d'Obyrn et al. 2014).

A landfill degassing facility has been in operation at the Barycz landfill since 1994, the first of its kind in Poland. In 1998, the first power unit, with a capacity of 250 kW, was commissioned there. In the following years, landfill degassing and biogas energy utilisation installations were continuously modernised and expanded (Dudek et al. 2011).

Within the I stage of the landfill where these tests were carried out (Fig. 1), the degassing system of the deposited waste was out of operation.

RESEARCH METHODOLOGY

Reconnaissance geochemical surface surveys were carried out in the oldest part of the site (stage I), where measures to protect the bottom and slopes were limited to the introduction of a protection zone and partial reclamation by backfilling the filled quarters with soil and sowing grasses (Klojzy-Karczmarczyk et al. 2016).

The measurement sites were distributed along two profiles, approximately 100 m apart. The profiles were placed along the slope of the land, which was important for gas migration. The spacing between each geochemical sampling point was approximately 20 m (Fig. 1). Seven measurement points were delineated outside the area of the landfill: points numbered 1, 23, and 24 were situated to the north of the profile lines and points numbered 20, 21, 42, and 43 to the south of them. Measurements were made at these points for reference.

Soil gas sampling

Soil and landfill gas samples were collected in 41 measurement points. To obtain them, a hand sampling kit was used to collect samples from the near-surface layers (Dzieniewicz & Sechman 2002). To collect the analytical material, a stainless-steel probe was driven into the ground with a slide hammer, with a lost spearhead at the end. Gas was collected with a 100 ml gas-tight syringe from a depth that eliminated the significant influence of near-surface factors, i.e., 1.0–1.2 m (Dzieniewicz et al. 1985, Sechman 2006). The sample was then injected into glass bottles filled with a saturated NaCl solution. The excess brine flowed into a second bottle through an injection needle inserted into the cork membrane. This filling, unlike vacuum containers, does not contain atmospheric gas and eliminates the risk of contamination. In addition, the saturated NaCl solution ensured the sealing of the cork during transport (bottles were placed upside down) and as stated by Yan et al. (2011) prevented the dissolution of the ingredients (especially CO_2) in the brine. Furthermore, local atmospheric conditions (temperature and pressure) were recorded at each sampling site, which was used to calculate gas emissions in accordance with the methodology of the device manufacturer and global methodology (West System 2012, Villanueva-Estrada et al. 2019). In addition, the coordinates of the sampling points were recorded using a Garmin 650t. The exact geographic coordinates were used to spatially visualize the analysed components in relation to the topographic situation of the research areas in the form of location maps.

Measurement of emissions

Measurement of the flux of gases (CH_4 and CO_2) released from the soil into the atmosphere was carried out by the static chamber method using a portable diffuse flux meter (West System 2012, Collier et al. 2014, Villanueva-Estrada et al. 2019). This method calculates the emission flux value from the increment of the inflowing and accumulating gas concentrations inside the chamber as a function of time (e.g., Leventhal 1992, Klusman et al. 2000, Korus et al. 2002, 2003). If the increase in gas concentration over time is constant (the increase in concentration versus time is linear), then we use linear regression to calculate the value of the slope of the concentration versus a time curve (Fig. 2). Subsequently, the emission value is determined on the basis of the quotient of the determined slope value and the accumulation chamber parameter, which depends on: i) the volume of the accumulation chamber, ii) the surface area covered by the chamber, and iii) atmospheric pressure and temperature during the measurement.

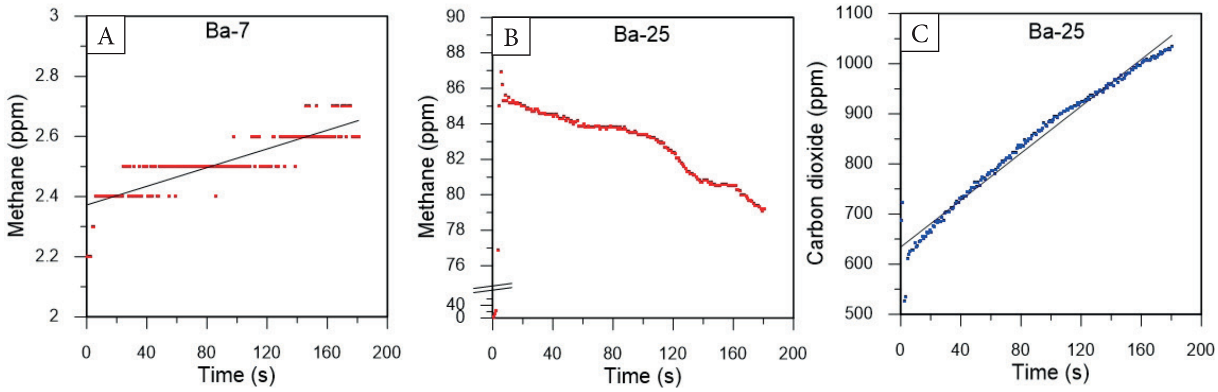

Fig. 2. Graphs of changes in the concentration of methane (A, B) and carbon dioxide (C) over time

A detailed calculation method of flux value is presented in the device manual (West System 2012). The research was carried out using a West System portable soil gas flux meter equipped with a WS-CH4-TLD detector to measure methane, a LI820 detector to measure carbon dioxide – both detectors use the phenomenon of absorption spectroscopy. The operating range and accuracy of the WS-CH4-TLD detector is 0.5–1500 mmol/m^2/day: ±25%, while for the LI820 CO_2 detector is 1.5–1000 mol/m^2/day: ±10%. This study used a standard type A cylindrical accumulation chamber with an internal diameter of 0.2 m and a volume (net volume) of $2.756 \cdot 10^{-3}$ m^3 (West System 2012). Natural emissions were measured at each of the sites selected for study immediately prior to sampling with a geochemical probe. The emission measurement time at each measurement station was 180 seconds, which, as shown in Figure 2, made it possible to record changes in the concentration of both gases in the assumed time period.

Laboratory analysis

Gas samples collected in the field were subjected to chromatographic analysis in the Laboratory of Gas Chromatography and Surface Geochemical Methods, Faculty of Geology, Geophysics and Environmental Protection, AGH University of Krakow for the content of non-hydrocarbon components (hydrogen, oxygen, nitrogen, CO_2), methane and higher alkanes (ethane, propane, i-butane, n-butane, i-pentane, n-pentane) and gaseous alkenes (ethylene, propylene, 1-butene). Flame ionisation detection (FID) and thermal conductivity detection (TCD) were used in the study.

The determinations of the hydrocarbon components were performed on a GC8160 chromatograph from FISONS Instruments. A packed column with an inner diameter of 4 mm and a length of 1.3 m filled with activated alumina (mesh 100/120) was used. The carrier gas (helium) flow was at a rate of 60 mL/min and the thermostat temperature was set by software as follows: 80°C for 2 min, increment from 80 to 200°C (25°C/min), 200°C for 3 min. The FID detector was operated at 270°C and the injection chamber was 100°C. Samples of 2 mL were injected manually using a gas-tight syringe. The analyser was calibrated using 'Scott II' calibrated gases from Supelco and Alltech at two concentration levels. The concentrations of the individual components in the calibration mixtures were approximately 15 ppm and 100 ppm. The detection threshold for the FID detector for light hydrocarbons was 0.01 ppm and the analytical error was estimated to be ±2% of the measured values.

Chromatographic separation of non-hydrocarbon components was performed on a GC6300 chromatograph from Carlo Erba Instruments. Hydrogen, oxygen, and nitrogen were separated on a column packed with 5A molecular sieves. The inner diameter of the metal column was 4 mm and length 2.5 m. The carrier gas (argon) flowed at a rate of 16 mL/min. For the carbon dioxide separation, a column packed with porous polymer type HAYSEP Q was used, and the carrier gas flow rate was 30 mL/min. The thermostat temperature was fixed at 65°C, the TCD detector temperature was set at 60°C, and the filament temperature was set at 260°C. The injection of 2 mL samples was performed automatically, using a VALCO 10-port valve. The analyser was calibrated with a calibration mixture from Air Liquide. The concentrations of the individual components in the calibration mixture were as follows: H_2 – 0.02 vol%, CO_2 – 1.5 vol%, O_2 – 20 vol% and N_2 – 78.48 vol%. The detection threshold of the TCD detector for hydrogen and carbon dioxide was 0.001 vol% in both cases, and for oxygen and nitrogen 0.01 vol%. The error of determination was estimated at ±2% of the measured values.

RESULTS

Statistical description of sets of concentrations measured in soil gas samples

The range of variability in the set of methane concentrations covers 5 orders of magnitude (Table 1). The highest value of methane concentration recorded, of more than 75 vol%, was found in sample no. 17, while the lowest value, i.e., 2.1 ppm, was recorded in sample no. 4. The relatively high standard deviation indicates a strong dispersion of the values analysed in relation to the mean. This is confirmed by the histogram of methane concentrations that were recorded (Fig. 3A), which shows the presence of two clearly separate sets of values. The first is contained in the range up to about 1,000 ppm and the second is the set of values above 9.3 vol%. The probability plot allows the boundaries of the characteristic subsets of methane concentrations to be defined (Fig. 3B).

Of the higher alkane components, only neopentane was found in each of the samples taken (Table 1). For the other alkane components, the percentages of samples in which concentrations exceeded the detection threshold of the FID detector were determined and ranged from 24.4 to 56.1%. The average concentration values of the alkane components show an increasing trend with a growing number of carbon atoms.

Propylene concentrations were generally recorded in the obtained soil gas samples. The maximum concentration values of these components differ by one order of magnitude, and similar relationships are found for the average values (Table 1).

The set of values for carbon dioxide concentration present a relatively wide range of variability covering four orders of magnitude (Table 1). The maximum concentration of carbon dioxide was found in the same sample as the maximum concentration of methane. The minimum value of concentration was found in sample no. 8. The mean value of the carbon dioxide concentration is almost three times higher than the median, suggesting the presence of anomalous values in this set of concentrations. This is confirmed by the histogram of the carbon dioxide concentrations that were recorded. These form three distinct subsets (Fig. 3C), the boundaries of which are marked on the probability plot (Fig. 3D).

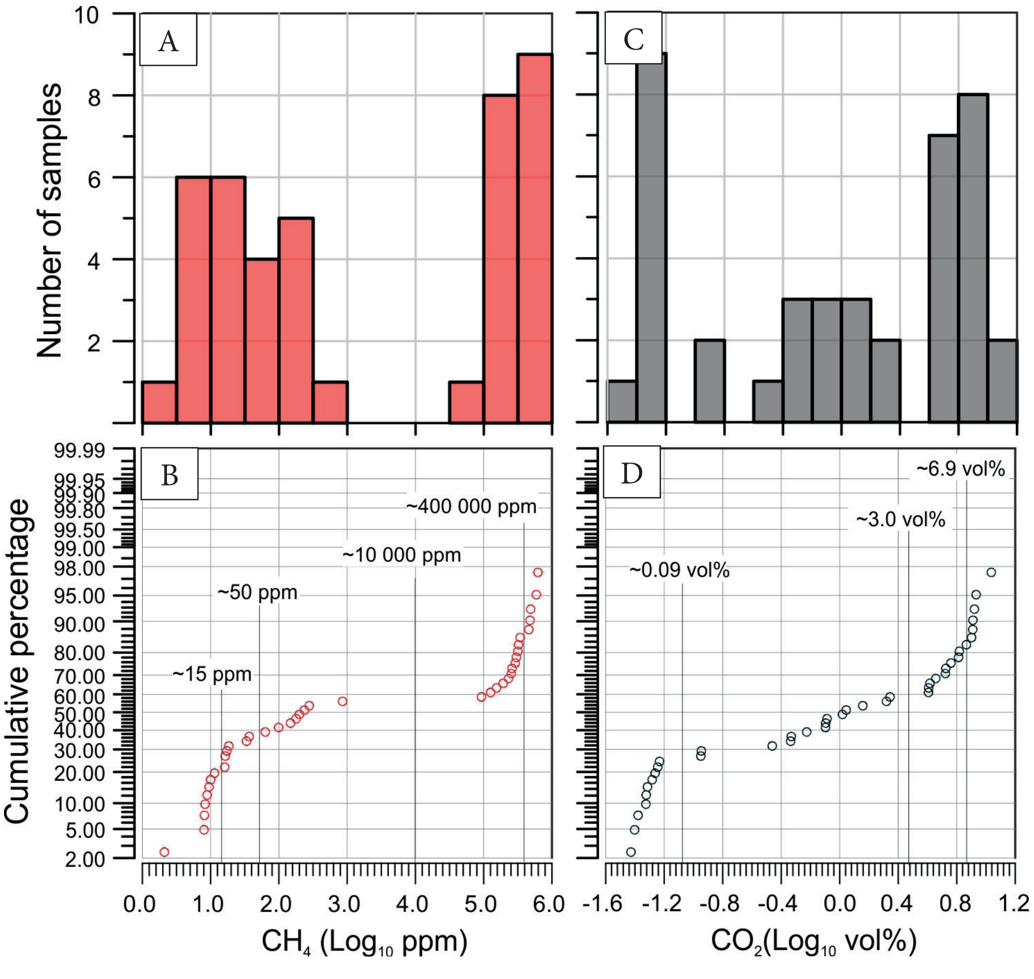

Fig. 3. *Histograms and cumulative frequency diagrams of methane (A and B) and carbon dioxide (C and D) measured in soil gas samples*

Hydrogen concentrations above the detection threshold of the TCD detector were found in almost 88% of the samples taken. The mean and median values for this set of concentrations are identical, so the distribution is close to normal. The relatively low standard deviation indicates a slight dispersion of values around the mean.

The sets of oxygen and nitrogen concentrations exhibit relatively wide ranges of variation (Table 1). For oxygen, the median is slightly lower than the arithmetic mean and vice versa for nitrogen. Negative skewness values for both sets of concentrations indicate that their statistical distributions have left-handed asymmetry.

Table 1

Molecular composition of soil gas samples collected in the reclaimed part of the municipal waste landfill in Barycz and the principal statistical parameters of the concentrations measured

No. of sample	CH_4 [ppm]	C_2H_6 [ppm]	C_3H_8 [ppm]	iC_4H_{10} [ppm]	nC_4H_{10} [ppm]	*neo*-C_5H_{12} [ppm]	iC_5H_{12} [ppm]	nC_5H_{12} [ppm]	C_2H_4 [ppm]	C_3H_6 [ppm]	CO_2 [vol%]	H_2 [vol%]	O_2 [vol%]	N_2 [vol%]
1	33.6	0.01	0.01	<0.01	0.01	0.17	<0.01	<0.01	0.08	<0.01	0.60	0.011	16.1	76.6
3	16.4	<0.01	<0.01	<0.01	<0.01	0.11	<0.01	<0.01	0.04	<0.01	0.06	0.015	18.4	77.1
4	2.1	<0.01	<0.01	<0.01	<0.01	0.05	<0.01	<0.01	0.03	<0.01	0.06	<0.001	18.3	74.7
5	324 000.0	<0.01	<0.01	0.39	0.32	0.07	0.10	<0.01	<0.01	0.08	4.14	0.007	10.6	47.2
6	459 900.0	<0.01	<0.01	0.71	0.5	0.58	0.41	0.15	<0.01	0.22	8.14	0.005	7.5	31.9
7	342 630.0	<0.01	<0.01	0.79	0.68	0.45	0.35	0.13	<0.01	0.15	4.04	0.005	10.5	45.2
8	99.2	0.01	<0.01	<0.01	<0.01	0.04	<0.01	<0.01	0.02	<0.01	0.04	<0.001	18.2	74.8
9	478 100.0	<0.01	<0.01	0.42	0.41	0.19	0.17	0.10	<0.01	0.19	8.56	0.006	7.2	30.6
10	317 000.0	<0.01	<0.01	0.73	0.78	0.5	0.29	0.16	<0.01	0.27	6.49	0.018	8.1	47.5
11	154 500.0	<0.01	<0.01	0.17	0.35	0.45	0.20	0.17	<0.01	0.19	5.32	0.017	7.5	64.2
12	193 200.0	<0.01	<0.01	0.32	0.33	0.74	0.20	0.10	<0.01	0.13	5.28	0.010	7.3	61.1
13	290 500.0	<0.01	<0.01	0.6	0.64	1.12	0.31	0.16	<0.01	0.15	7.97	0.013	3.4	52.4
14	92 930.0	<0.01	0.42	0.2	0.55	0.11	0.31	0.21	<0.01	0.14	4.06	0.053	7.7	71.1
15	199.4	0.02	0.01	<0.01	<0.01	0.08	<0.01	<0.01	0.04	<0.01	0.35	<0.001	17.9	75.3
16	488 000.0	<0.01	<0.01	0.17	0.68	0.48	1.00	0.50	<0.01	0.5	7.34	0.013	6.5	29.2
17	758 600.0	<0.01	<0.01	1.69	0.67	0.91	1.27	<0.01	<0.01	0.99	11.05	0.002	1.6	6.1
18	625 000.0	<0.01	<0.01	0.05	0.22	0.41	3.53	<0.01	<0.01	0.4	8.34	0.003	4.8	19.6
19	591 300.0	<0.01	<0.01	1.37	4.1	0.85	1.01	0.22	<0.01	1.06	10.87	0.011	4.6	18.4
20	17.4	0.01	<0.01	<0.01	<0.01	0.04	<0.01	<0.01	0.02	<0.01	0.46	0.010	17.2	73.6
21	18.5	0.02	<0.01	<0.01	<0.01	0.04	<0.01	<0.01	0.06	<0.01	0.11	0.015	18.4	77.2
23	16.1	0.01	<0.01	<0.01	<0.01	0.03	<0.01	<0.01	0.06	<0.01	0.80	0.014	14.8	79.6
24	8.9	0.03	<0.01	<0.01	<0.01	0.02	<0.01	<0.01	0.04	<0.01	1.44	0.015	15.8	77.5
25	231 300.0	<0.01	<0.01	0.53	0.44	0.20	0.19	0.17	<0.01	0.15	8.12	0.006	7.7	54.8
26	179.2	0.08	0.04	<0.01	0.02	0.04	<0.01	<0.01	0.04	<0.01	0.11	0.017	18.5	77.5
27	126 600.0	<0.01	<0.01	0.11	0.19	0.31	0.21	0.12	<0.01	0.10	5.76	0.013	8.0	66.8
28	301 000.0	<0.01	<0.01	0.79	0.76	0.82	0.49	0.21	<0.01	0.09	6.57	0.007	7.8	49.7
29	148.3	0.20	0.10	0.02	0.02	0.03	<0.01	<0.01	0.13	<0.01	0.47	0.018	14.8	70.0
30	36.7	0.01	<0.01	<0.01	<0.01	0.03	<0.01	<0.01	0.04	<0.01	0.05	0.013	18.2	76.1
31	16.4	<0.01	<0.01	<0.01	<0.01	0.02	<0.01	<0.01	0.02	<0.01	0.05	<0.001	18.3	73.9
32	278.7	0.43	0.18	0.01	0.03	0.01	<0.01	<0.01	0.04	<0.01	1.11	0.010	14.6	78.3
33	10.0	<0.01	<0.01	<0.01	<0.01	0.03	<0.01	<0.01	0.04	<0.01	0.06	<0.001	18.4	76.0
34	11.4	0.02	0.00	<0.01	<0.01	0.01	<0.01	<0.01	0.05	<0.01	2.21	0.012	9.8	81.5
35	236.5	1.93	0.94	0.03	0.14	0.04	<0.01	<0.01	0.04	<0.01	0.82	0.010	11.9	81.7
36	63.2	<0.01	<0.01	<0.01	<0.01	0.08	<0.01	<0.01	0.04	<0.01	0.05	0.004	18.6	77.1
37	8.1	<0.01	<0.01	<0.01	<0.01	0.02	<0.01	<0.01	0.03	<0.01	0.04	0.004	18.7	76.6
38	8.0	<0.01	<0.01	<0.01	<0.01	0.03	<0.01	<0.01	0.03	<0.01	0.04	0.004	18.7	75.9
39	8.3	0.01	<0.01	<0.01	<0.01	0.04	<0.01	<0.01	0.04	<0.01	0.05	0.013	18.4	76.3
40	253 800.0	<0.01	<0.01	0.31	1.36	0.16	0.63	0.64	<0.01	0.41	4.53	0.016	10.8	53.6
41	260 200.0	<0.01	0.86	0.32	0.87	0.14	0.48	0.22	<0.01	<0.01	2.09	0.008	8.7	57.2
42	858.0	0.05	0.03	<0.01	<0.01	0.01	<0.01	<0.01	0.05	<0.01	1.04	0.018	11.8	80.2
43	9.5	0.14	0.06	<0.01	<0.01	0.04	<0.01	<0.01	0.08	<0.01	0.80	0.013	16.0	76.2
Statistical characteristics														
Min.	2.1	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.04	<0.001	1.6	6.1
Max.	758 600.0	1.93	0.94	1.69	4.10	1.12	3.53	0.64	0.13	1.06	11.05	0.053	18.7	81.7
Median	236.5	<0.01	<0.01	0.01	0.02	0.08	<0.01	<0.01	0.02	<0.01	1.11	0.010	11.9	73.9
Mean	153 434.5	0.07	0.06	0.24	0.34	0.23	0.27	0.08	0.03	0.13	3.16	0.010	12.5	62.7
St. dev.	212 017.2	0.31	0.20	0.39	0.69	0.30	0.61	0.14	0.03	0.24	3.48	0.009	5.3	20.1
Skewness	1.2	5.87	3.71	2.15	4.34	1.52	4.24	2.47	1.33	2.79	0.81	2.689	−0.2	−1.3
% samp.	100.0	39.0	24.4	51.2	56.1	100.0	43.9	36.6	56.1	41.5	100.0	87.8	100.0	100.0

Min. – minimum value; Max. – maximum value; St. dev. – standard deviation; % samp. – percentage of samples with concentrations above the detection limit of the detector.

Changes in methane and carbon dioxide emission values

Positive methane emission values (concentration increase over time) were recorded at only six of the 41 study sites. The maximum methane emission value was found at site no. 7 located in profile A-A' (Table 2). The average methane emission value expressed as the median is higher in profile B-B' than in profile A-A' (Table 2). Negative methane emission values (concentration decrease over time) were recorded in 4 test stands, with the highest negative emission value found at site no. 25 (profile B-B'), which is –185.6 mg/m^2/d.

Table 2
Values of methane and carbon dioxide emissions in the reclaimed part of the Barycz municipal waste landfill and principal statistical parameters of the sets of emission values recorded

No. of sample	**Methane emission [mg/m^2/d]**	**Carbon dioxide emission [g/m^2/d]**	**No. of sample**	**Methane emission [mg/m^2/d]**	**Carbon dioxide emission [g/m^2/d]**
Profile A-A'			**Profile B-B'**		
1	–	11.8	22	–	10.6
3	–27.7	45.5	24	–	23.2
4	–	45.5	25	–185.6	33.7
5	–3.3	17.8	26	–21.2	26.0
6	–	17.9	27	–	34.3
7	8.2	17.1	28	5.4	24.9
8	–	13.6	29	–	37.0
9	–	22.2	30	–	22.4
10	–	23.7	31	5.9	12.4
11	–	24.9	32	–	19.4
12	–	23.2	33	–	22.6
13	–	24.9	34	–	28.7
14	–	18.9	35	6.5	24.7
15	–	16.7	36	–	18.3
16	–	19.0	37	–	21.9
17	–	30.3	38	6.0	15.1
18	–	19.0	39	5.6	21.3
19	–	15.4	40	–	26.4
20	–	15.4	41	–	20.0
21	–	18.3	42	–	22.9
			43	–	27.8
Statistical characteristics					
Min.	–27.7	11.8	Min.	–185.6	10.6
Max.	8.2	45.5	Max.	6.5	37.0
Median	–3.3	19.0	Median	5.6	22.9
Mean	–7.6	22.1	Mean	–25.3	23.5
St. dev.	18.3	9.1	St. dev.	71.4	6.7
Skewness	–1.0	1.8	Skewness	–2.5	0.1
% samp.	15.0	100.0	% samp.	33.3	100.0

Min. – minimum value; Max. – maximum value; St. dev. – standard deviation; % samp. – percentage of samples with concentrations above the detection limit of the detector.

In the case of carbon dioxide, a positive emission value was recorded on each test stand. The maximum values of emissions of this gas were found at sites 3 and 4, i.e., in the extreme part of profile A-A'. The average values of carbon dioxide emissions, expressed as mean and median, are higher in profile B-B' than in profile A-A'.

Correlations between sets of measurements of concentrations

Table 3 summarises the values of Pearson's linear correlation coefficients between sets of concentration values for methane, carbon dioxide, hydrogen, oxygen, nitrogen, the sum of C_2-C_5 alkanes, and sum of C_2-C_3 alkenes. Due to the very wide variability ranges of the sets of measurements of concentrations (Table 1), the correlation coefficients were determined after logarithmisation of the concentration values.

The highest positive correlation is seen with the sets of methane concentrations and the sum of C_2-C_5 alkanes. Methane also has a high concordant correlation with carbon dioxide and the sum of C_2-C_3 alkenes. By contrast, there is a negative correlation between methane and oxygen, nitrogen, and hydrogen (Table 3). Carbon dioxide, like methane, is positively correlated with the sum of C_2-C_5 alkanes and the sum of C_2-C_3 alkenes while the opposite is the case with oxygen, nitrogen, and hydrogen. It should be noted that the strongest negative correlation (–0.83) is between carbon dioxide and oxygen.

The highest consistent correlation of hydrogen with nitrogen is expressed by a not very high correlation coefficient of 0.53. In relation to the other components, hydrogen shows weak correlative relationships (Table 3).

Table 3
Correlation coefficient matrix between logarithmic values of the measured components

	CH_4 [ppm]	**CO_2 [vol%]**	**H_2 [vol%]**	**O_2 [vol%]**	**N_2 [vol%]**	**Total C_2-C_5 alkanes [ppm]**
CO_2 [vol%]	0.86	–	–	–	–	–
H_2 [vol%]	−0.17	−0.04	–	–	–	–
O_2 [vol%]	−0.82	−0.83	0.28	–	–	–
N_2 [vol%]	−0.67	−0.60	0.53	0.83	–	–
Total C_2-C_5 alkanes [ppm]	0.91	0.85	−0.11	−0.79	−0.64	–
Total C_2-C_3 alkenes [ppm]	0.83	0.80	−0.15	−0.84	−0.82	0.84

The set of values for oxygen concentration has a high concordance with the set of values for nitrogen concentration and a weak correlation with hydrogen. Negative values of the correlation coefficients were registered in relation to the other sets of concentrations (Table 3). It should be noted that the strongest inverse correlation is between oxygen concentrations and the set of concentrations of the sum of C_2-C_3 alkenes. In this case, the correlation coefficient is −0.84. Similar relationships are found for the set of nitrogen concentrations. A positive correlation was recorded for oxygen, and the correlations are similar in relation to the other sets of concentrations.

DISCUSSION

Molecular composition and relations between sets of concentrations

Attention is drawn to a set of relatively very high methane concentrations in the molecular composition of soil gas samples taken over the reclaimed part of the Barycz municipal waste landfill. These were mainly recorded on profile A-A' (Table 1). This set is clearly exposed as a distinct population of values on the histogram (Fig. 3A). These values range from about 9.3 to almost 76 vol% (Table 1). Taking into account the fact that this part of the landfill has been in operation for almost 50 years, one could assume that the methane generation processes are in their final phase, something which is generally manifested by a marked decrease in methane concentrations. This is because after the active methanogenic phase, air begins to gradually penetrate the waste mass, creating aerobic conditions that inhibit methane production. During this phase, organic compounds that are unavailable to anaerobic microorganisms are biodegraded (Biernat et al. 2011, Cossu et al. 2018). These values are comparable to the results obtained in other similar reclaimed municipal landfills (Mor et al. 2006, Qdais et al. 2010, Aydi 2012, Pazoki et al. 2015).

The range of variation in carbon dioxide concentrations is not as high as that of methane (Table 1). However, the set of high concentration values of this gas (above 3 vol%) is clearly seen on the histogram. The sets of methane and carbon dioxide concentrations show a highly positive linear correlation (Table 3). However, the high linear correlation coefficient (*r*) between these concentration sets (Table 3) may be due to the appearance of two clusters of points in the low and high concentration ranges of both gases in the cross plot (Fig. 4A). The set of high carbon dioxide concentrations correlates very well with the corresponding high methane concentrations (Fig. 4A1). This is most likely the CO_2 formed from acetic acid during acetogenesis which also produces methane (Zacharof & Butler 2004). This implies that intensive gas generation under anaerobic conditions continues in reclaimed landfills (Cossu et al. 2018, Villanueva-Estrada et al. 2019). The increase in methane and carbon dioxide concentrations is accompanied by a decrease in oxygen concentrations. These relationships are expressed by the relatively high negative values of the correlation coefficient (*r*) between oxygen and methane and oxygen and carbon dioxide (Table 3, Fig. 4B, E). These relationships are also very evident in the line graphs (Figs. 5A, B, 6A, B).

The high correlation between carbon dioxide and the sum of C_2-C_5 alkanes and the sum of C_2-C_3 alkenes (Fig. 4C, D, F, G) implies that the generation of alkane components higher than methane and alkene components can occur during complex biochemical processes (e.g., methanogenesis). As reported in the literature (Belay & Daniels 1987, Dave et al. 2020), under favourable conditions the generation of ethane and ethylene in particular can occur at very high methane concentrations, while the generation of higher alkane components is very limited. In samples collected from the reclaimed landfill, ethane and ethylene concentrations above the detection threshold of the FID detector were recorded in only about 40 and 56% of soil gas samples, respectively (Table 1). Characteristically, these components were not found in samples in which the concentrations of methane were very high. This can be explained by the fact that in such cases, the existing analytical capabilities do not allow ethane and ethylene to be recorded. This is because these components recorded on the chromatogram are lost in the noise of the zero line or, in the case of increased sensitivity of the detector, are unnoticeable in the extended, strong methane peak.

Point 17 recorded maximum concentrations of methane and carbon dioxide of almost 76 and over 11 vol% respectively, accompanied by minimum oxygen and nitrogen concentrations of 1.6 and 6.1 vol% (Table 1). In the adjacent samples (samples 16, 18 and 19), methane and carbon dioxide concentrations were also relatively high. The ratio of methane to carbon dioxide concentrations in these samples ranged from 5.4 to 7.5. The values of this ratio are significantly higher in relation to analogous ratios calculated based on the average methane and carbon dioxide concentrations reported in the literature that have been recorded at various municipal landfills worldwide (see e.g., Themelis & Ulloa 2007, Niemczewska 2013, Ciuła et al. 2020, Rodrigo-Ilarri & Rodrigo-Clavero 2020). The significantly higher methane concentrations in relation to the carbon dioxide concentrations measured in the reclaimed landfill in Barycz may be due to two reasons. The first is the manner in which the soil gas sample was taken from a depth of approximately 1.0–1.2 m, i.e., directly from beneath the soil layer acting as a reclamation layer (d'Obyrn & Wójcik 2015). A second reason for the significant predominance of methane concentrations over carbon dioxide may be the complex migration processes of the landfill gas mixture from deeper parts of the waste deposit, where anaerobic biogas generation processes are still taking place. As a result of the migration processes, the lighter methane, which is more mobile than carbon dioxide, reaches the near-surface zone in greater quantities, creating higher concentrations near the surface. It also cannot be ruled out that it is migrating from neighbouring quarters (stage II of the landfill) (Fig. 1).

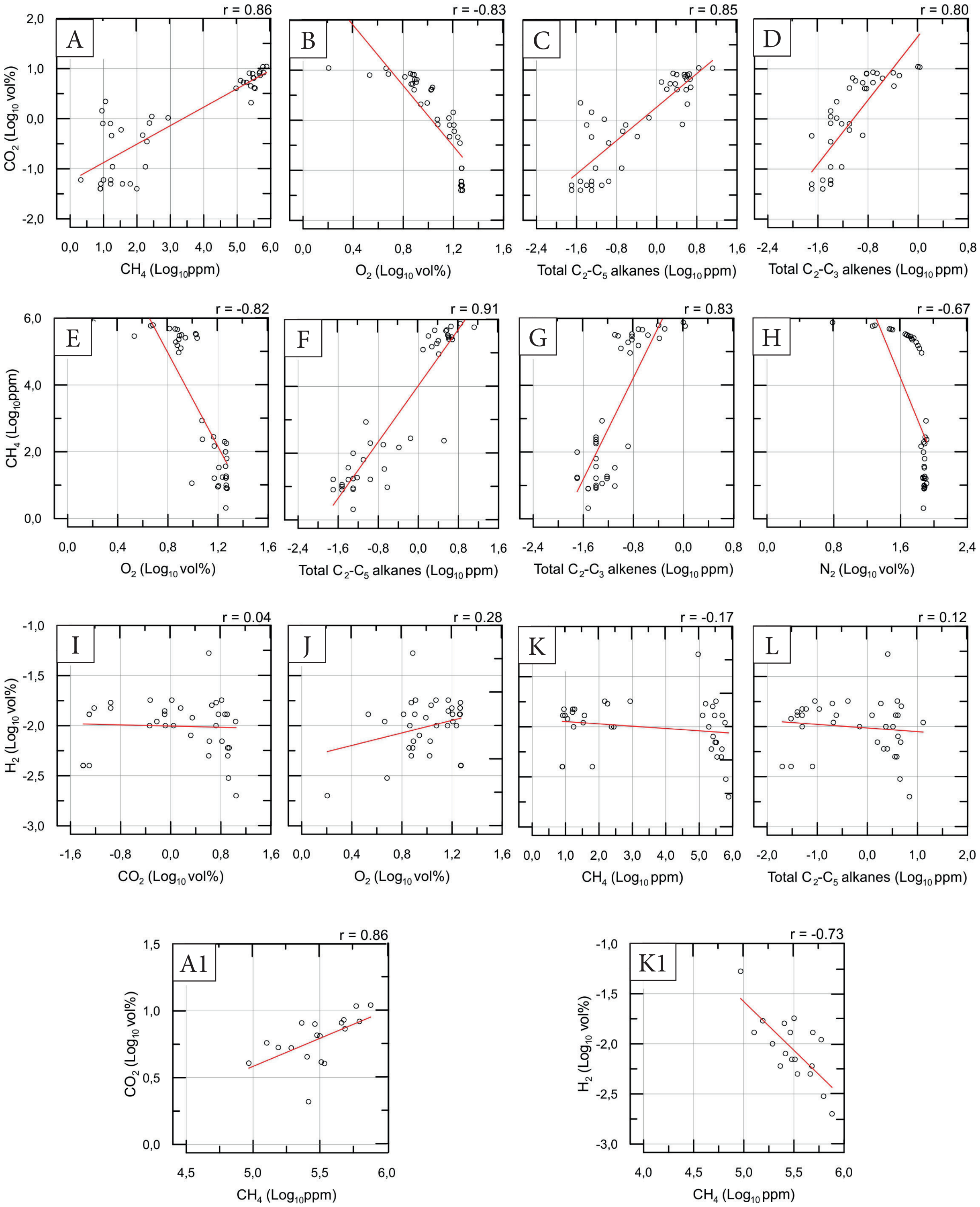

Fig. 4. *Correlation cross plots for sets of concentration measurements from soil gas samples*

Emissions of methane and carbon dioxide into the atmosphere

The negligible atmospheric methane emissions (Table 2) recorded in the reclaimed part of the Barycz municipal waste landfill may initially indicate the effectiveness of the reclamation layer covering the deposited and compacted waste. The trace amounts of methane that escaped from under the seal are oxidized by methanotrophic microorganisms with oxygen diffusing into the near-surface layer (e.g., Czepiel et al. 1996, Scheutz et al. 2009, Huang et al. 2022). Consequently, no or negative methane emissions were recorded on the land surface at most points (Table 2). The presence of very high concentrations of methane and carbon dioxide, found at several points at depths of approximately 1.0–1.2 m (Table 1), does not directly translate into the high atmospheric emissions of these gases. This is confirmed by the lack of a correlation between the concentrations of methane and carbon dioxide and their atmospheric emissions (Fig. 5A, B). Therefore, it can be concluded that the reclamation method for this part of the landfill is probably appropriate. However, these are only preliminary studies that have been carried out for a limited number of measurement points.

Surface distributions of methane and carbon dioxide concentrations

Changes in the concentrations of all components along the profiles were presented as line graphs against the landforms (Figs. 6, 7) and as bubble maps against the terrain map (Figs. 8, 9). Profile A-A’ (Fig. 6), in which the highest concentrations were recorded of carbon dioxide, methane, total butanes, and pentanes, is of particular note. The relatively low concentrations of ethane and ethylene are due to the analytical limitations of the equipment that separates soil gas into its individual components. As mentioned earlier, in the case of very high methane concentrations, they were lost at the tail of the extended methane peak recorded by the chromatograph. This was confirmed by the fact that on the B-B’ profile (Fig. 7), at lower methane concentrations, ethane and ethylene were identifiable. The line graphs, also presented graphically, confirm the high qualitative agreement of the individual components, which was quantitatively shown earlier in the correlation graphs (Fig. 4).

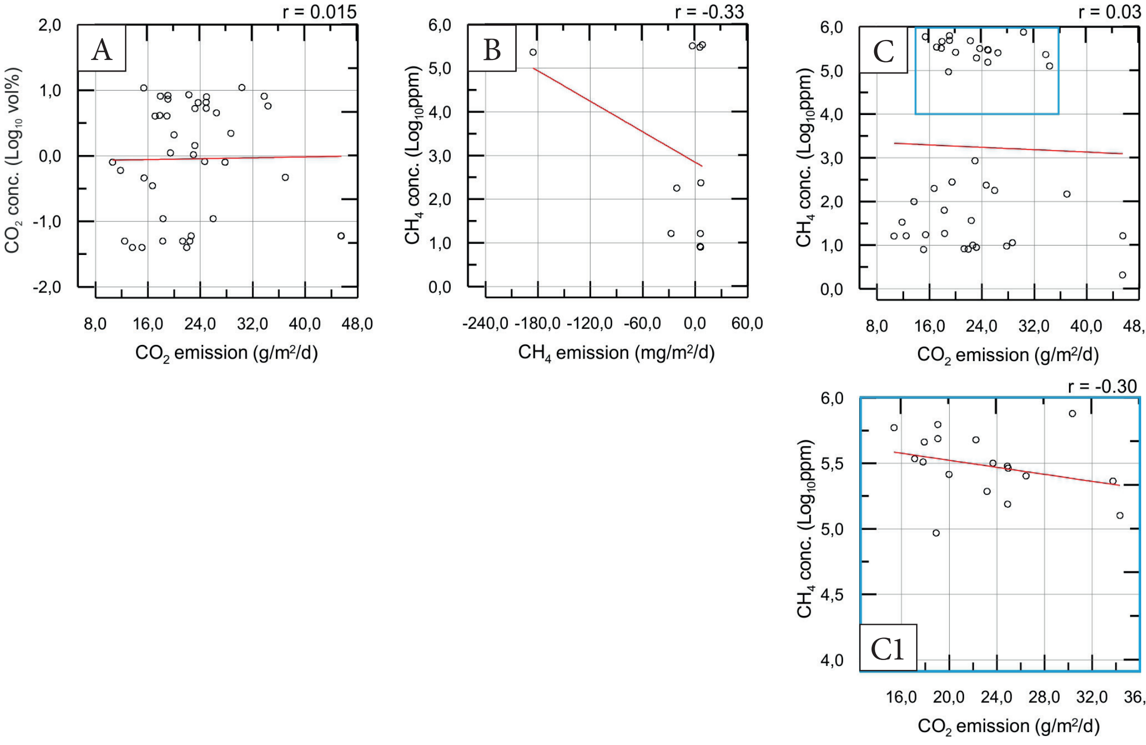

Fig. 5. Correlation cross-plots for sets of concentration measurements and the corresponding emission values

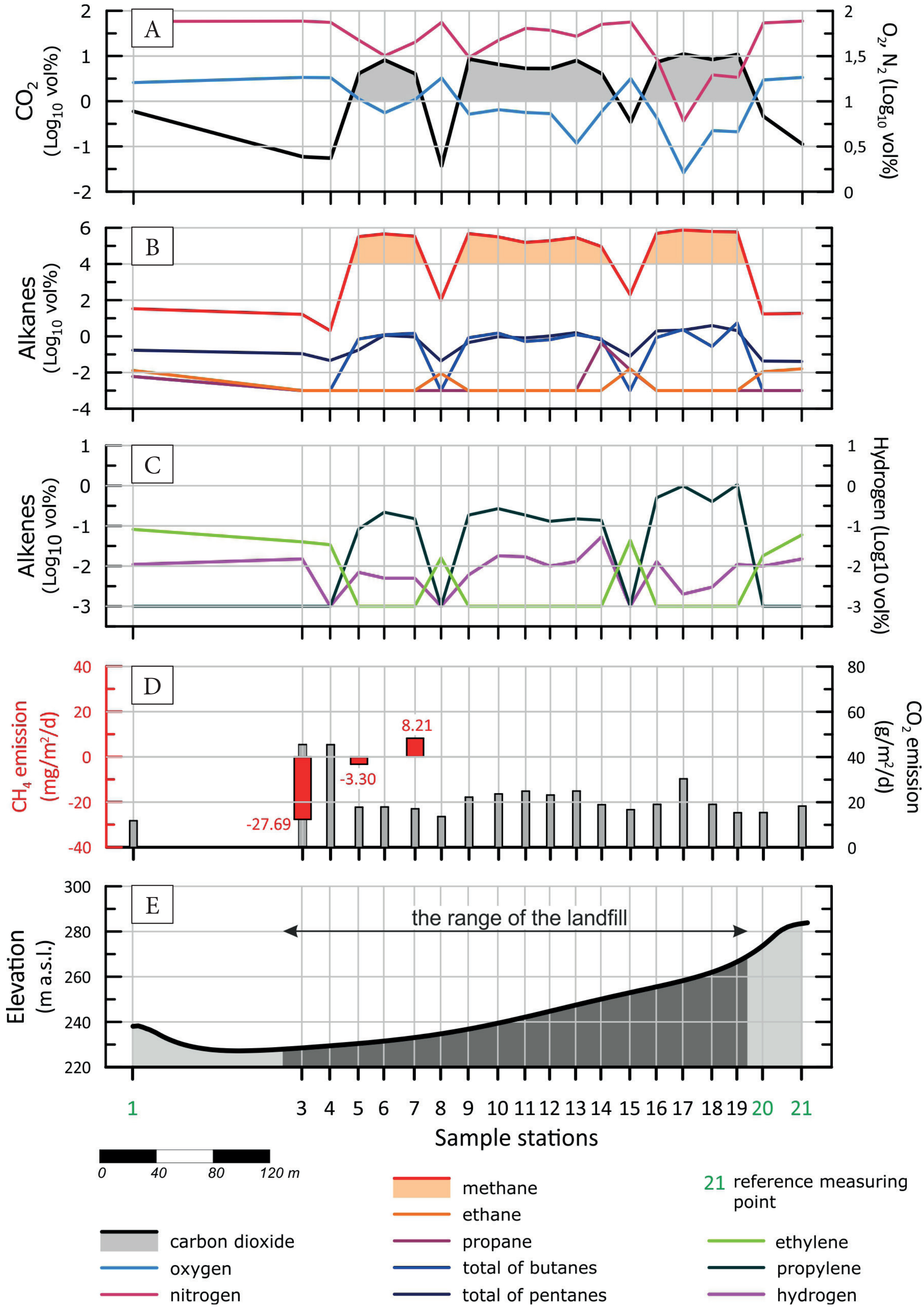

Fig. 6. *Changes in the values of concentration measurements of selected permanent gases (A), alkane components (B), alkene components (C) and the values of methane and carbon dioxide emissions (D) against the background of the terrain (E) along the measurement profile line A-A'*

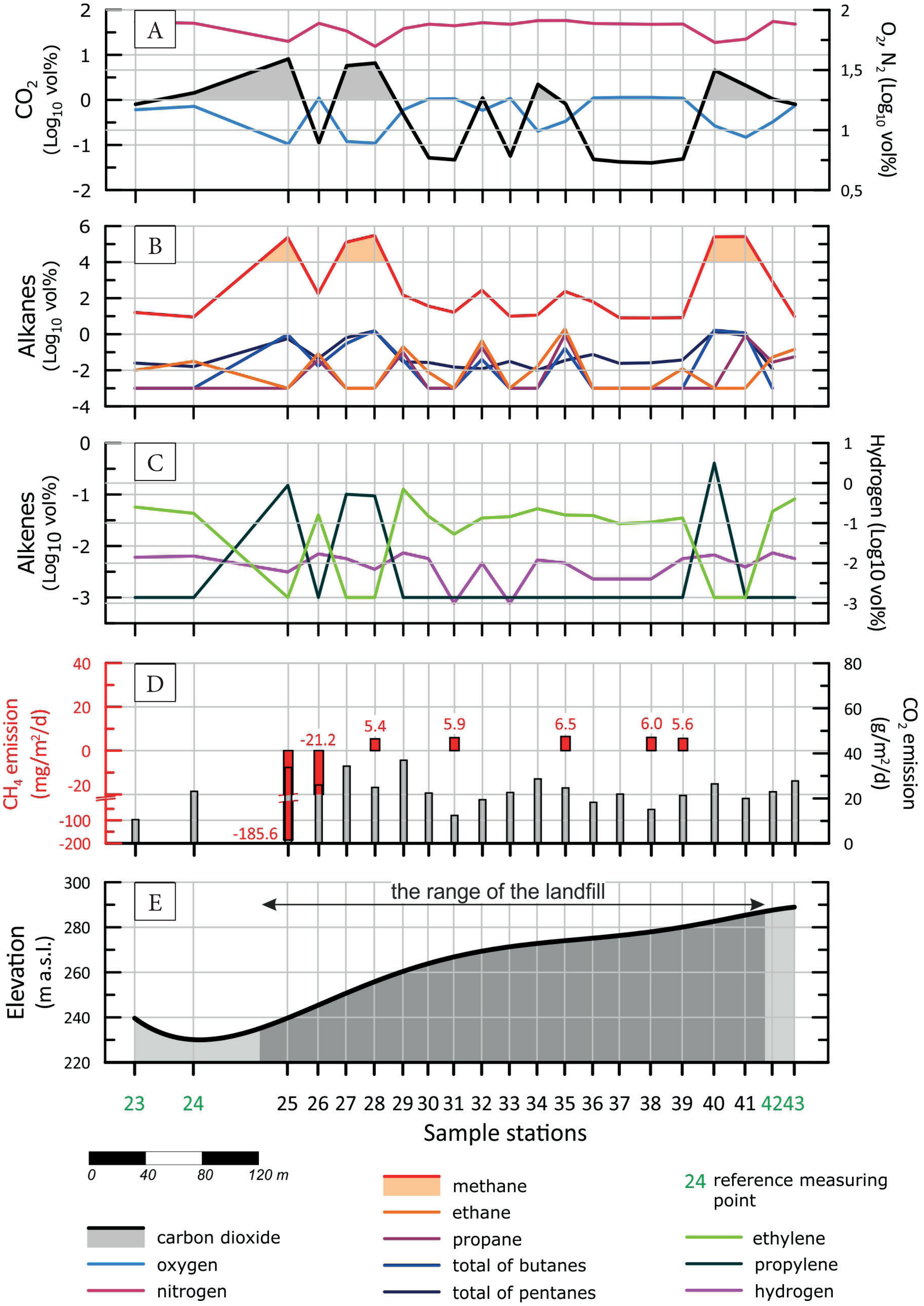

Fig. 7. *Changes in the values of concentration measurements of selected permanent gases (A), alkane components (B), alkene components (C), and the values of methane and carbon dioxide emissions (D) against the background of the terrain (E) along the measurement profile line B-B'*

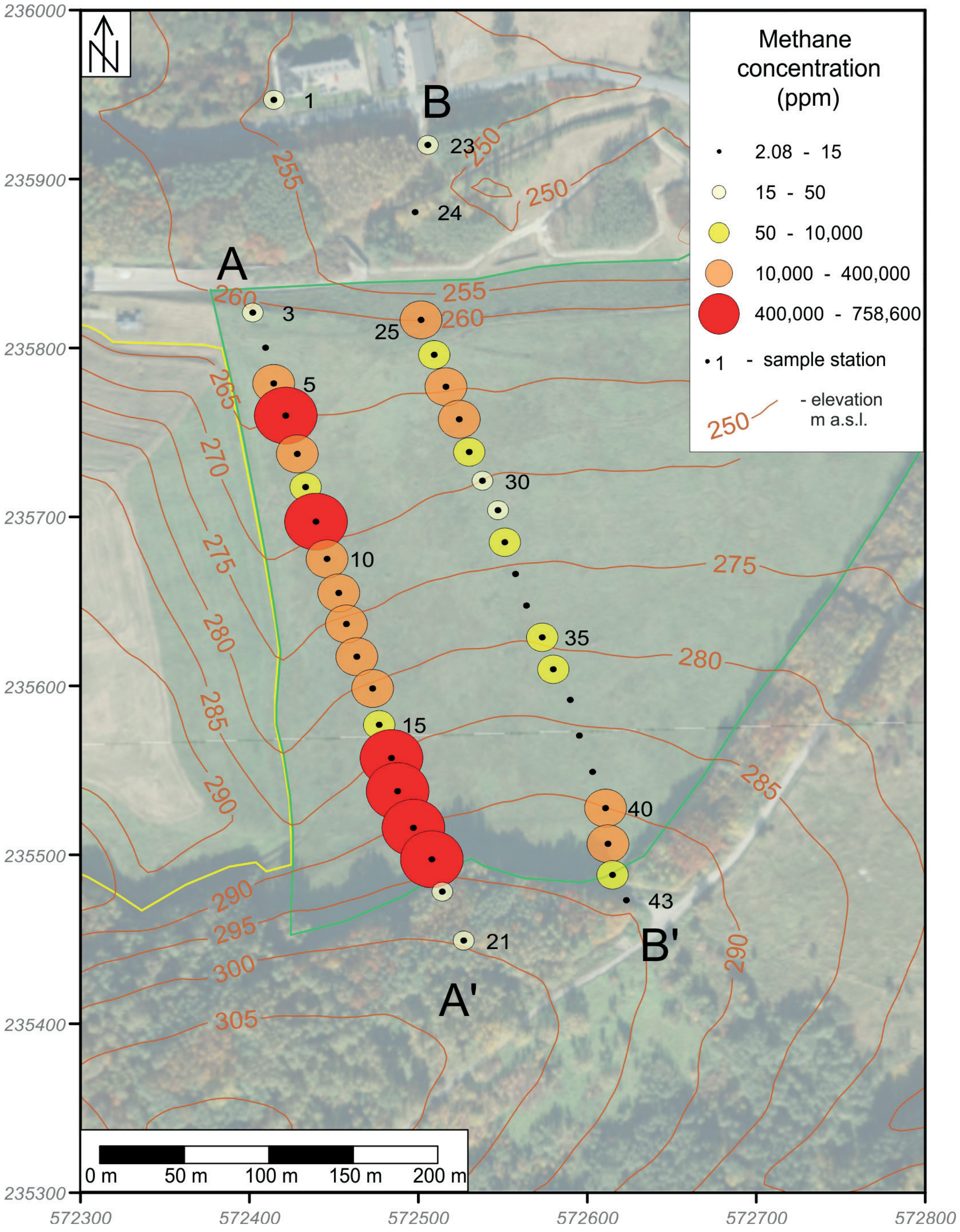

Fig. 8. *Distribution of methane concentrations along measurement profiles in the area of the reclaimed part of the Barycz municipal waste landfill*

On the basis of the diagrams drawn up, it can also be concluded that in the case of profile A-A' the gases (mainly methane and carbon dioxide) accumulate along practically the entire length of the profile, excluding the reference points (1, 20, 21). At the same time, in the B-B' profile there is a concentration of gases which is mainly found behind the ground depression (points: 25–28). At this stage of the study, it is difficult to unequivocally determine the reason for the accumulation of gas at this location, but it can be assumed that it is related to the manner of land reclamation carried out, changes in the arrangement of the isolation layers, or the presence of a drainage ditch.

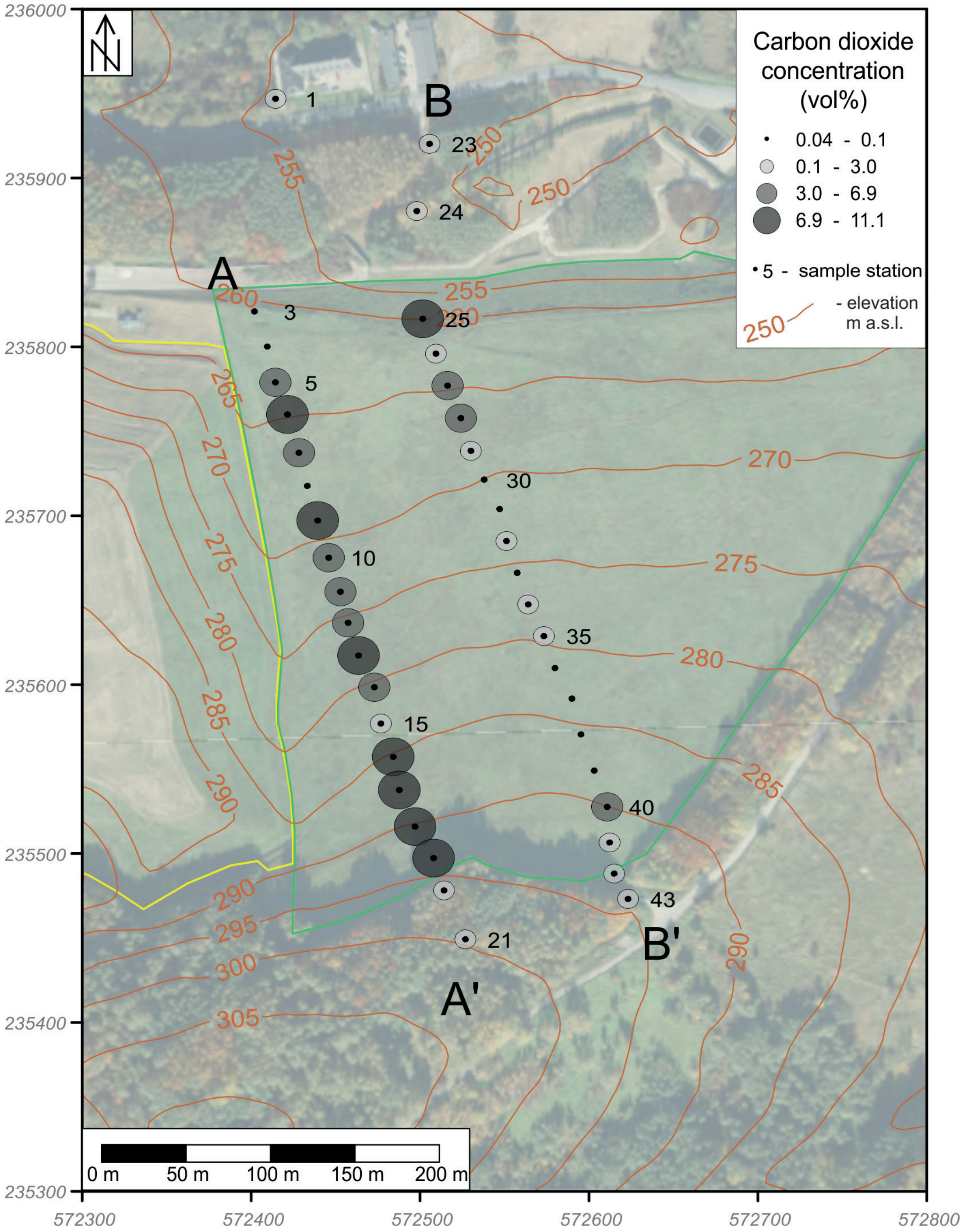

Fig. 9. *Distribution of carbon dioxide concentrations along measurement profiles in the area of the reclaimed part of the Barycz municipal waste landfill*

Similar observations have been reported by other researchers (Ishigaki et al. 2005, Capaccioni et al. 2011, Shen et al. 2018). A second anomalous zone, especially for methane concentrations, can be observed at the end of the B-B' profile (points 40, 41). Morphologically, these points were located at the top of the hill slope, and according to the principle of hydrocarbon movement in a porous medium, methane, the lightest gas, always moves upward in the profile (Bonham 1980). This theory was confirmed by observation during field research. At this sampling points, the syringe plunger was spontaneously forced out by pressure higher than atmospheric, suggesting the accumulation of hydrocarbons under the sealing layer.

The characteristic concentration ranges, determined in the probability diagrams (Figs. 3B, D), made it possible to assume concentration thresholds for methane and carbon dioxide, the changes of which were presented as "bubble" maps along the profiles (Figs. 8, 9). On the basis of these, it can be concluded that on profile A-A' the concentrations of the gases analysed are much higher than on profile B-B', while at the same time clusters of anomalous concentrations occur in similar zones in both cases. The high concentrations along profile A-A' may be the result of migration from the area of stage II of the waste deposit, the boundary of which is adjacent to the aforementioned profile (Fig. 1). Strong biochemical processes are still taking place in this quadrant and biogas is being exploited. Investigations also revealed a four-point zone of methane and carbon dioxide accumulation in the southern part of the A-A' profile (Figs. 8, 9). Hypsometrically, this is the highest-lying zone, which may have favoured the lateral migration of gases upward from the lower parts of the profile. Therefore, biogas probably accumulated here at a depth of about 1 m below the sealing cover. The high concentration of methane (more than 75 vol%) and the location of this zone on an upward slope predispose it to being chosen as a potential location for a degassing well equipped with a gas flaring system. This well would act as a kind of safety valve on an ad hoc basis, and in the event of large amounts of gas being produced at this site, consideration should be given to connecting it to the biogas exploitation system currently operating on the neighbouring landfill site.

Another cluster of relatively high concentrations of methane and carbon dioxide was detected on the slope of a hill located in the northern section of both profiles. This is an area where the terrain slopes steeply, so the reason for the accumulation is probably the presence of some kind of lithological barrier or a more intense migration from the western part of the landfill. Similar gas migrations have been described at Italian landfills by Gandolla et al. (1997).

In light of the results obtained within the landfill, it is important to note that the methane and carbon dioxide measured at reference points located outside the limits of the landfill or at its extremes (1, 20, 21, 23, 24, 42, 43) were relatively low (Table 1). This means that the biogas generated in the reclaimed part of the landfill, despite the presence of local accumulations, does not migrate beyond the boundaries of the landfill and thus does not pose a fire or explosion hazard.

CONCLUSION

Analyses were made of the concentrations of non-hydrocarbon constituents and methane and its higher homologues in 41 gas samples taken from near-surface layers lying at a depth of 1.0–1.2 m in the reclaimed part of the Barycz municipal waste landfill. Prior to geochemical sampling, methane and carbon dioxide emissions were measured using a portable fluxometer from West Systems.

Measurements of the concentrations of soil gas components made it possible to determine concentrations with a wide range of variability, covering 5 orders of magnitude. Concentrations of methane and carbon dioxide are very high at many measurement points, which is particularly marked on profile A-A' where the highest concentrations of these gases were detected. In general, this profile, when compared to profile B-B', has higher concentrations of methane and carbon dioxide, as well as other alkane components, with simultaneously lower values of oxygen and nitrogen. This means that more active biochemical processes are taking place in this part of the deposit than in the eastern part. Furthermore, there are significant correlations between methane, carbon dioxide, oxygen, total alkanes (C_2-C_5), and alkenes in the data sets, indicating that methanogenesis is still ongoing. The negligible emission of methane on the surface may indicate that it migrates laterally and accumulates in a convenient place under the poorly permeable top layer of the reclaimed landfill.

The methane-to-carbon dioxide ratio values for the samples with the highest concentrations detected (16, 17, 18, 19) are much higher than for analogous ratios calculated for similar municipal landfills around the world. This is most likely due to the fact that soil gas is extracted from the zone directly below the reclamation cover, where it is mainly lighter methane that accumulates, or to the ongoing methanogenesis process in the deeper parts of the landfill. Neither can the lateral migration of methane from the neighbouring plot, where biogas extraction is currently taking place, be ruled out.

On the basis of the results of the surveys conducted, it should be concluded that the zone of high methane concentrations measured at several points located in the southern part of the A-A' profile is an optimum place to locate a degassing well equipped with a gas combustion system. However, the research is only preliminary and before the final decision on the location of the well is taken, it will be necessary to extend the soil gas tests in order to accurately identify the variability of the registered methane concentrations over the entire surface of the reclaimed landfill. This well would act as a kind of safety valve on an ad hoc basis, and in the event of large amounts of gas being produced in this location, connecting it to the biogas exploitation system currently operating in the neighbouring section of the landfill should also be considered.

The concentrations of methane and carbon dioxide measured at reference points outside the boundaries of the landfill or in the extreme parts of the landfill (1, 20, 21, 23, 24, 42, 43) were relatively low. This means that the biogas generated on the rehabilitated part of the landfill, despite the presence of local accumulations, probably does not migrate beyond the limits of the landfill and thus does not pose a fire or explosion hazard. The effectiveness of land reclamation carried out is confirmed by the negligible emissions of greenhouse gases into the atmosphere. Moreover, the high concentrations of methane and carbon dioxide detected at various points do not affect their emission into the atmosphere. The effectiveness of the reclamation carried out is also evidenced by the fact that despite the relatively high concentrations of methane and carbon dioxide and the low oxygen values found at a depth of 1.0–1.2 m, no vegetation deficiencies were detected during the field survey. This means that there is sufficient aeration in the topsoil to support plant vegetation, confirming that the reclamation was carried out properly.

The conclusions resulting from these studies should be considered preliminary due to the relatively small number of measurements made. Therefore, this type of research should be extended by placing measurement points in the corners of the grids, e.g., 50 m × 50 m or 25 m × 25 m, and such tests should also be carried out in different weather conditions (seasons).

The authors would like to thank the management board of Miejskie Przedsiębiorstwo Oczyszczania in Krakow and the director, Krystyna Flak, for enabling the research at the landfill in Barycz. The authors thank the reviewers of the paper for their valuable comments. The research was funded by the statutory funds (grant no.16.16.140.315/05) of the Department of Energy Resources, Faculty of Geology, Geophysics, and Environmental Protection, AGH University of Krakow, Poland.

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