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Fluctuations in methane and carbon dioxide concentrations in the near-surface zone and their genetic characterization in abandoned and active coal mines in the SW part of the Upper Silesian Coal Basin, Poland

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ABSTRACT

The objective of this paper is to determine the origin and variability of methane and carbon dioxide concentrations in the near-surface zone and of coalbed methane in the SW part of the Chwałowice Trough and adjacent areas of the Main Syncline of the Upper Silesian Coal Basin (USCB). For this purpose soil-gas samples were taken at 202 measuring points, arranged along 5 profiles located in the mining area of the abandoned 1 Maja mine and directly adjacent areas as well as in the vicinity of four abandoned and remediated mining shafts. The maximum methane and carbon dioxide concentrations in the gas samples measured exceeds 22 and 9 vol%, respectively. The carbon isotope composition of methane and carbon dioxide was determined in samples in which elevated concentrations of these gases were found. Moreover, seven coalbed gas samples and bituminous coals were collected from coal seams exclusively from virgin parts of the Anna, Marcel, Jastrzębie, and Zofiówka mines. These data were supplemented with results of archival research for genetic interpretation of coalbed gases.

Research reveals that typical humic low- and medium-volatile bituminous coals occur in Mississippian and Pennsylvanian coal-bearing strata in the study area. Fluctuations in methane and carbon dioxide concentration in the near-surface zone are related to the lithostratigraphy and tectonics of the area as well as to complicated methane depth distribution. Faults may play an important role in the microseepage of gases from deep to the near-surface zone. The connection of near-surface gases with subsurface gases was confirmed by similar stable carbon isotope composition in the methane recorded in the soil-gas samples and in the gas samples from the coal seams and sandstones of the Carboniferous formations. Distribution of anomalous methane concentrations recorded in soil-gas samples taken from profiles may indicate natural gas accumulations in the top zone of the Pennsylvanian coal-bearing formations. One example of this kind of accumulation is the Marklowice natural gas field, located within the mining area of the Marcel coal mine. Relatively high methane concentrations measured in soil gas in the vicinity of shafts I and III indicate that the degassing systems of closed and remediated mining shafts are not fully effective. Increases in carbon dioxide concentrations in the surface zone and frequent associated decreases in methane concentration were most often the result of microbial methane oxidation.

1. Introduction

The Upper Silesian Coal Basin (USCB) is the largest coal basin in Poland; coal mining has been conducted here for over 250 years (Jureczka and Galos, 2007). Significant amounts of unconventional natural gas may be accumulated in the Upper Carboniferous coal-bearing strata. The following types of gas can be found in coal deposits: (i) coalbed methane (CBM), (ii) coal-mine methane (CMM), and (iii) abandoned-mine methane (AMM) (Hadro and Wójcik, 2013). The origin of gas accumulated in the Carboniferous formations of the USCB, its spatial distribution, and the amount of resources have been studied by many scientists (e.g., Kotarba, 2001; Kotarba and Lewan, 2004; Kwarciński and Hadro, 2008; Hadro and Wójcik, 2013; Kędzior, 2009, 2019; Kędzior et al., 2013). According to data of the Polish Geological Institute – National Research Institute, recoverable resources of methane from coal seams in the area of the USCB may amount greater than 102 billion m^3. Methane extraction from the USCB coal-bearing series in 2018 amounted to 320 million m^3 (PGI-NRI, 2020), representing

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quantities of gas obtained from demethanation of bituminous coal mines and exploited independently by means of wells drilled from the surface (lPGI-NRI, 2020). Pre-mining gas drainage from coal seams is also carried out in the USCB, thus reducing the gas hazard during subsequent exploitation of hard coal (Szlązak et al., 2013; Kędzior and Dreger, 2019). These types of activities are carried out in many other coal basins around the world (e.g., Noack, 1998; Sang et al., 2010; Karacan, 2009a, 2009b; Karacan et al., 2011; Hummel et al., 2018).

In the area of the USCB, a significant amount of methane is released into the atmosphere (Duda and Krzemień, 2018; Dreger, 2019; Kędzior and Dreger, 2019; Swolkień, 2020). It has been estimated that 541 million m^3 of methane was released in 2018 by the ventilation systems of active hard coal mines in the USCB (PGI-NRI, 2020). In addition to the direct efflux of methane from mining shafts, methane is also capable of vertical migration and microseepage through rock overburden. In this case, this gas uses a system of faults, cracks, and micro-fractures in overburden (Thielemann et al., 2001; Karacan and Olea, 2014). Uncontrolled gas migration through overburden may become more intense in the event of the cessation of coal mining and mine closure. This type of migration is the result of the appearance of the "piston effect", a phenomenon based on the displacement of gases accumulated in free spaces of the rock mass by a rising water table (Kotarba, 2002; Krause and Pokryszka, 2013; Sechman et al., 2017). The surface effects of gas migration through rock overburden can be studied using the soil-gas method (e.g., Jones and Drozd, 1983; Klusman, 1993; Tedesco, 1995; Matthews, 1996; Harbert et al., 2006; Sechman et al., 2013, 2017, 2019, 2020), which involves testing the molecular and isotopic compositions of soil-gas samples taken at a shallow depth (1–2 m). Changes in the concentration of methane and its gaseous homologues tested in soil-gas samples, as well as non-hydrocarbon components (e.g., CO_2), create anomalous zones, which may indicate the generation of microbial gas at shallow depths (Le Mer and Roger, 2001) or active processes of gas migration and/or microseepage from deep accumulations to the Earth's surface (e.g., Klusman, 1993; Tedesco, 1995; Saunders et al., 1999; Sechman et al., 2011; Sechman, 2012; Tang et al., 2019). The results of soil-gas studies obtained in active and abandoned hard-coal mines may be useful for determining the optimal location of wells to be drilled for the purpose of searching for gas accumulations, and also enable assessment of gas hazards in the areas of abandoned hard-coal mines. Studies of this kind have been carried out in Poland in the areas of closed hard-coal mines in the Lower Silesian Coal Basin (Sechman et al., 2013, 2017) as well as in the USCB in abandoned and active hard-coal mines (Sechman et al., 2019, 2020).

The research results presented in the present publication represent a continuation of previously published research results from the USCB (Sechman et al., 2019, 2020). The purpose of this research is to assess the variability of methane and carbon dioxide concentrations in the near-surface zone in relation to the deep spatial distribution of the methane content in coal seams, along with genetic evaluation of deep and near-surface gases. The present soil-gas research and geochemical investigation cover the main study area of the SW part of the Chwałowice Trough as well as adjacent areas of the SW part of the Jejkowice Trough and W part of the Main Syncline of the USCB (Fig. 1A).

2. Outline of the geological structure and occurrence of coalbed gases

2.1. Outline of geological structure

The study area, located in the western part of the USCB within the zone of fold tectonics (Kotas, 1990), covers the southern part of the Chwałowice Trough, which extends from the Orlova-Boguszowice (O—B) overthrust in the east to the Michałkowice-Rybnik (M-R) overthrust and Jejkowice Trough in the west (Fig. 1A). The zone of fold tectonics is situated in the western part of the USCB and extends from its western boundary to the O—B overthrust in the east. This zone includes folded structures of the Alpine type in the form of brachysynclines (Jejkowice and Chwałowice Troughs) and the M-R and O—B overthrusts (Fig. 1A).

The lithological profile of the study area includes Carboniferous (upper Mississippian and Pennsylvanian) coal-bearing strata as well as Miocene strata and Quaternary sediments in overburden. The basement of the upper Carboniferous strata consists of Devonian clastic and carbonate strata and lower Carboniferous (lower and middle Mississippian) clastic strata. The upper Carboniferous formations are divided into three lithostratigraphic series (Kotas, 1990, 1995), namely, the Paralic, Upper Silesian Sandstone, and Mudstone Series (Fig. 2).

The Upper Mississippian-Serpuchovian and lower Pennsylvanian-Bashkirian Paralic Series consist of the deepest Petřkovice Beds (the group of coal seams numbered in the 900 s), followed by the Hrušov (numbered in the 800 s), Jaklovec (numbered in the 700 s), and Poruba (numbered in the 600 s) Beds (Fig. 2). This series, with a total thickness of over 2000 m, is a predominant element in the area under discussion, built of a complex of claystones and sandstones with marine fauna levels. In the Hrušov Beds, between the marine levels, a rotten-stone horizon occurs. There are numerous coal seams (several dozens), characterized by modest thicknesses (up to 1.4 m in the Poruba Beds). The coal seams belonging to the Poruba Beds constituted the element with the richest coal reserves in the former 1 Maja mine.

The lower Pennsylvanian-Bashkirian Upper Silesian Sandstone Series is a complex of sandstones with thick beds, mainly of a middle- and coarse-grained character, sometimes including the conglomerate type. Shalestone inserts present in the sandstones accompany the coal seams. This series is divided into the Saddle (coal seams 501–510) and Ruda (seams 407–420) Beds (Fig. 2). Coal seams within this series are thick but not very numerous. The whole series, especially the Saddle Beds, is characterized by substantial coal resources (particularly seams 505 and 507 in the study area). The thickness of the series increases as one moves northward, from zero to several hundreds of meters (Buła and Kotas, 1994). In the vicinity of Rybnik, the Jejkowice Beds, additionally distinguished at the bottom of the Upper Silesian Sandstone Series, are built of coarse-grained sediments without coal seams (Kotas, 1995).

The uppermost lower Pennsylvanian-Bashkirian Mudstone Series, which occurs only partially in the northern part of the study area (the Marcel coal mine), is erosionally reduced to the lower Załęże Beds (Fig. 2), forming a clay- and mudstone complex with thin coal seams. The pre-Miocene surface of the top of Carboniferous strata displays an erosive denuded character with numerous paleo washouts and ridges running WNW–ESE. The greatest differences in absolute height between individual sites reaches 200 m.

Miocene strata, which cover all of the coal-bearing series within the study area, were formed as a thick complex of clays interbedded by sands. Within the depressions in the Carboniferous top surface are sands and gravels, the equivalents of beach sands found in the Czech part of the basin. The thickness of Miocene strata in the study area ranges from approximately 12 to several hundred meters. Quaternary sediments, representing a type of water-glacial and river accumulation, cover the whole area and comprise clays, sands, and gravels.

The main tectonic element in the study area is the Chwałowice Trough, a brachysyncline elongated parallel to the O—B and M-R overthrusts (Fig. 1A). The beds decline at various angles from the west and east towards the throw axis, as well as from the south to the north. The dip angle of the beds is changeable and fluctuates between 6 and 12 degrees in the central part up to about 40 degrees within the east flank of the Chwałowice Trough, whereas within the west flank the synclinal orientation of beds is disrupted by other smaller folds with small and narrow synclines and anticlines running parallel to the M-R overthrust. The dip of the beds is substantial in that part of the area, around 70 degrees, but the strike of the beds is adjusted to the structure of folds (generally dominated by a NS strike). The Chwałowice Trough is cut by faults running perpendicular to the throw axis (WNW–ESE). The largest

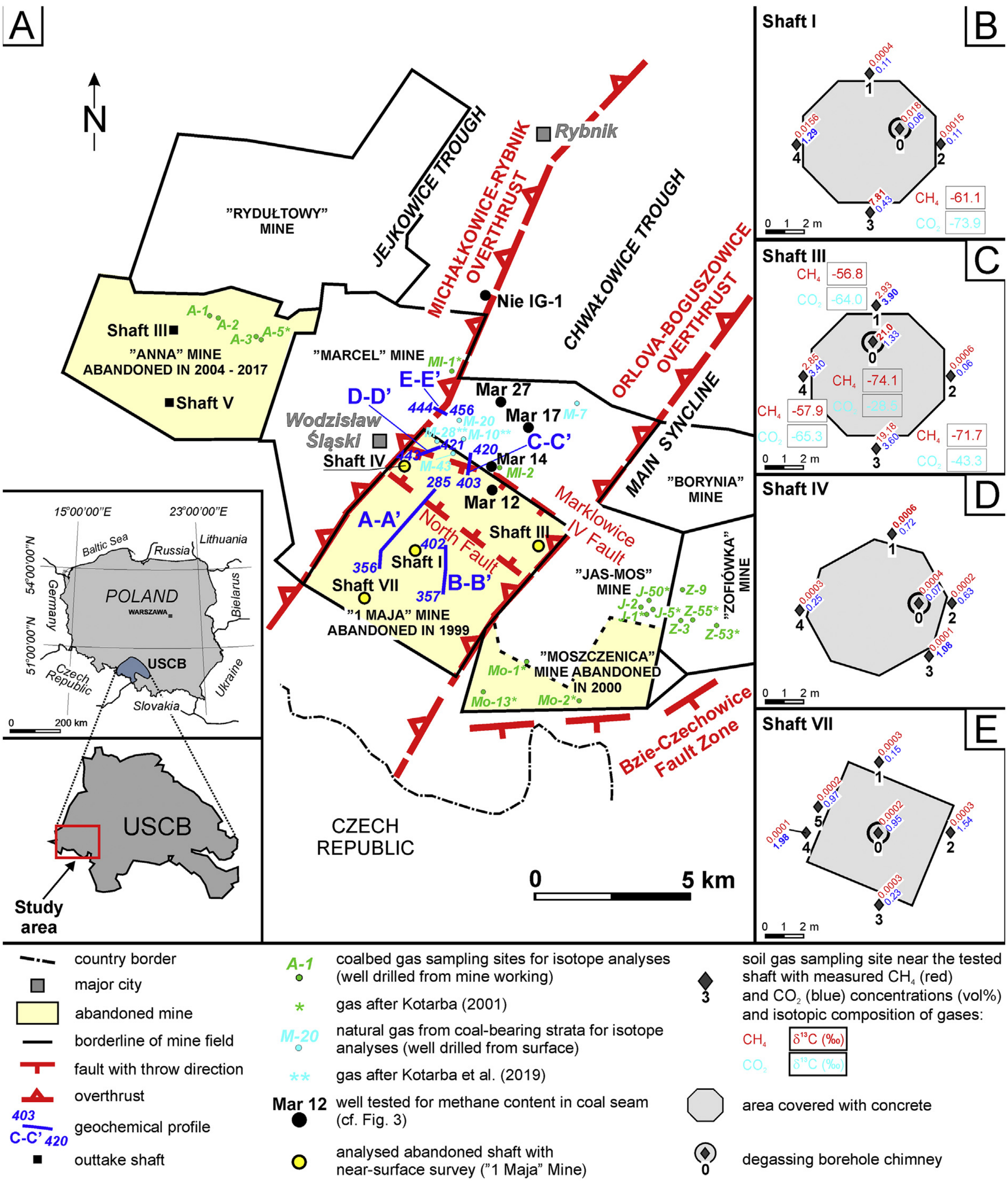

Fig. 1. (A) Geological map showing the location of geochemical study with geological cross-sections, and distribution of methane and carbon dioxide concentrations in the vicinity of abandoned shafts of "1 Maja" Coal Mine. Shafts: (B) I, (C) III, (D) IV and (E) VII.

faults are the North Fault, with a throw of 320 m to the north, and the Marklowice IV Fault, with a throw of about 100 m to the south (Fig. 1A).

The essential tectonic elements in the study area are the overthrusts. The M-R overthrust is a plane inclined at an angle of 30–40 degrees, with a shift amplitude of 750 m. This overthrust constitutes the western boundary of the Chwałowice Trough, separating it from the Jejkowice Trough, another synclinal structure of the USCB fold zone located in the westernmost part of the basin (Fig. 1). The western boundary of the Jejkowice Trough is equivalent to the range line of Carboniferous coal-bearing formations. The O—B overthrust, a plane inclined at an angle of 35–40 degrees, with a shift amplitude of about 1000 m, constitutes the boundary between the USCB fold and disjunctive zones. The latter is the dominant tectonic zone of the entire USCB, including, inter alia, the Main Syncline, an extensive brachysyncline structure with an NW–SE extent and gently dipping beds, with the dips rarely exceeding 15° (Kotas, 1990), cut with a system of large latitudinal faults (Sechman et al., 2019, 2020). This structure covers a significant part of the basin.

2.2. Spatial distribution of the methane content

The study area is characterized by the varied and complex

STRATIGRAPHY					LITHOSTRATIGRAPHY Local division after Kotas (1995)		MAXIMUM THICKNESS (m)	IDENTIFICATION NUMBERS OF COAL SEAMS (local division)
Division after Cohen et al. (2013)		Division after Harland et al. (1982)						
PENNSYLVANIAN	MOSCOVIAN	CARBONIFEROUS	WESTPHALIAN	C	Krakow Sandstone Series	Łaziska Beds	1100	201 - 216
				B	Mudstone Series	Orzesze Beds s.s.	500	301 - 327
	BASHKIRIAN			A		Załęże Beds	1500	328 - 364 401 - 406
			NAMURIAN	C	Upper Silesian Sandstone Series	Ruda Beds	810	407 - 420
				B		Saddle (Zabrze) Beds	200	501 - 510
MISSISSIPPIAN	SERPUKHOVIAN			A	Paralic Series	Poruba Beds	1100	601 - 630
						Jaklovec Beds	380	701 - 723

Fig. 2. Stratigraphy and lithostratigraphic classification of the USCB.

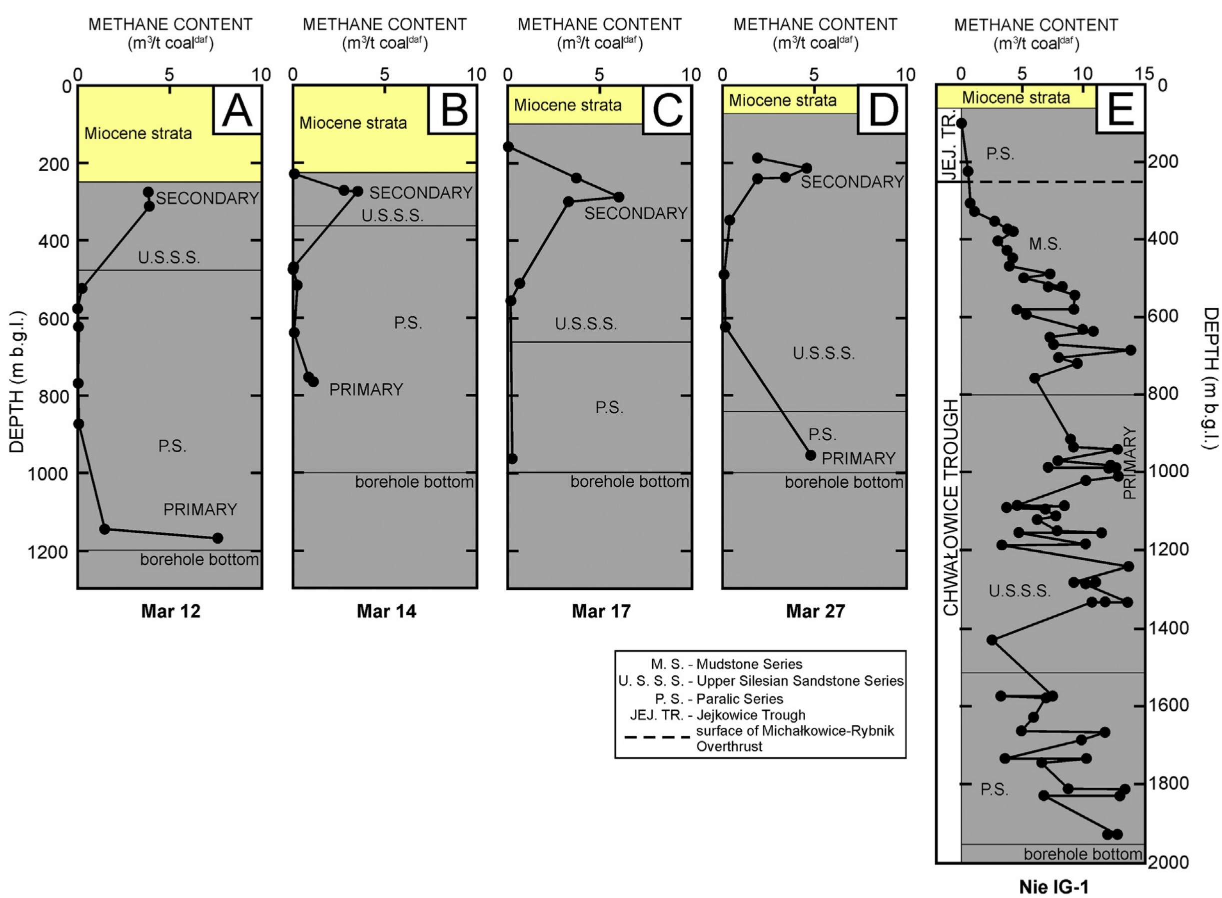

Fig. 3. Depth distribution of the methane contents in coal seams in the wells (modified after Kędzior, 2004, 2009; Kędzior and Dreger, 2019): (A) Marklowice 12, (B) Marklowice 14, (C) Marklowice 17, (D) Marklowice 27 and (E) Niedobczyce IG-1. SECONDARY – the secondary methane accumulation zone, PRIMARY – the primary methane accumulation zone, U.S.S.S. – the Upper Silesian Sandstone Series, P.S. – the Paralic Series; JEJ. TR. – JEJKOWICE TROUGH.

occurrence of methane. Two forms of methane occurrence in coal-bearing strata are typical: adsorbed methane in coal seams (micropores) and free methane included both in coal seams (breaks and macropores) and adjacent rocks (sandstones). The methane depth distribution is complicated and represents the “southern” methane pattern of the USCB (after Kotas, 1994), with several methane zones in the profile (Fig. 3A–E), especially the secondary methane zone, with high methane content (> 4.5 m^3/t $coal^{daf}$), located in the topmost part of the Carboniferous strata (Fig. 3A–D). This zone is the result of the secondary accumulation of microbial methane (e.g., Kotarba and Pluta, 2009) and/or the migration of thermogenic gas from deeper coal beds towards the surface (Kotarba, 2001). There are also accumulations of free methane, located in porous and permeable sandstones lying within the area adjacent to Miocene cover and constituting commercial accumulations (the Marklowice deposit of free methane in the Marcel coal mine). The thickness of the secondary methane zone is variable, not exceeding 100–200 m. This zone becomes thinner and gradually vanishes to the north and west. A subsequent zone of rapid reduction of methane content occurs below the secondary methane zone, with a thickness of approximately 500 m; the methane content in coal seams does not exceed 0.5 m^3/Mg $coal^{daf}$. In the area of the absence of the secondary methane zone (northern part of the study area and Jejkowice Trough), the zone of reduced methane content reaches the Carboniferous top (Fig. 3E) and includes coal seams degassed in the geological past due to erosion (Kotas, 1994; Kotarba, 2001; Kędzior, 2004, 2009), whereas the thin Miocene overburden is not a barrier for migrating gases here. The deepest zone is the so-called primary methane zone, where the methane content in coal seams increases again to > 4.5 m^3/t $coal^{daf}$ (Fig. 3A–D). This zone contains mainly indigenous thermogenic gases, produced as a result of the coalification process in the late Carboniferous period (Kotarba, 2001). The depth range of this zone has not been determined in detail (Fig. 3E). The presented methane depth distribution is typical of the southern part of the basin (e.g., Kotas, 1994; Kędzior, 2004, 2009) and also occurs in nearby regions (Sechman et al., 2019, 2020) and in the Czech part of the USCB (e.g., Weniger et al., 2012a, 2012b).

Within the Chwałowice Trough, a general increase in methane content is observed from the O—B overthrust towards the central part of the trough (Kędzior, 2002, 2009). In the vicinity of the overthrust, methane content in coal seams does not exceed 1 m^3/Mg $coal^{daf}$, whereas in the middle part of the Chwałowice Trough the methane content is well over 4.5 m^3/Mg $coal^{daf}$. It seems likely that the reason for this methane distribution is the presence of developed systems of fissures accompanying the overthrust through which the methane can migrate outside of the coal-bearing series. The zone of the O—B overthrust is assumed to be a gas pathway between the trough and surrounding areas (Tarnowski, 1971). Moreover, higher methane content was found in the coal seams lying on the eastern side of the O—B overthrust, within the USCB disjunctive tectonics zone (area of the Jas-Mos mine), than on the western side (e.g., Kędzior and Dreger, 2019). Similarly, on the eastern side of the M-R overthrust, high methane content, significantly exceeding 4.5 m^3/ t $coal^{daf}$, was found (Niedobczyce IG-1 borehole; Fig. 3E), most likely due to the sealing of the coal seams by the overthrust surface. In this case, the overthrusts are capable of sealing the coal seams lying in their foreground. On the other hand, lack of a secondary accumulation zone in the profile of this borehole was caused by the insignificant thickness of the Miocene strata (Fig. 3E). Previous studies on the horizontal methane distribution in the area of the USCB fold zone (Kędzior, 2002, 2009) have pointed to the occurrence of isolated methane-bearing zones running parallel to the M-R overthrust. The zones are characterized by increased methane content (4–6 m^3/t $coal^{daf}$ or more) related to neighboring areas (Kędzior, 2009).

The current distribution of the methane content in the study area is also governed by fault tectonics. It has been observed that faults often divide a coal deposit into blocks with various level of gas saturation, and displace gas-bearing zones according to throw direction. One example is the large regional Bzie-Czechowice Fault, located outside the study area, which displaces methane-bearing coal seams 600 m to the south (e.g., Kędzior, 2009; Sechman et al., 2019). The Marklowice IV Fault has a similar effect in the study area. Permeable fault zones and accompanying breaks can serve as pathways for gas migration and thus migrating gas can saturate coal seams in the vicinity of the faults (e.g., Kędzior, 2009).

Within the mine field of the Marcel coal mine, a free methane accumulation, known as Marklowice gas field, was found in porous and permeable sandstones of the Poruba, Saddle, and Ruda beds (Fig. 2), which are interbedded by coal seams (e.g., Kędzior, 2009; Kędzior and Dreger, 2019). The primary gas resources have been estimated at more than 800 million m^3, making this accumulation the largest in the Polish part of the USCB. The gas accumulated in the elevated part of the Carboniferous top surface, covered by a low-permeable Miocene seal cover (stratigraphic gas trap) (Kędzior, 2009). The source of methane inflow was the methane-bearing coal seams of both the Marcel and 1 Maja mines. The free methane was collected in 1950–1974 by means of 44 surface boreholes with depths of 130–300 m, drilled for the purpose of degassing the rock mass and thereby reducing the methane hazard in the proposed coal mine to ensure the safety of miners at work (Kędzior, 2012). During operation, it turned out that the daily yield of methane increased as the reservoir pressure decreased, which meant that the amount of gas in the reservoir was successively supplemented with methane desorbing from coal seams (Kędzior, 2012). During that period, about 330 million m^3 of methane was collected. Demethanation efficiency amounted to 40–50%, that is, the methane content in coal seams located among the sandstones was reduced by approximately one-half (Kędzior and Dreger, 2019). Later, the collection of free methane continued, albeit in smaller quantities (approximately 0.5 million m^3 yearly), along with coal-mine methane, via the underground drainage system of the Marcel mine; the methane was used for the purposes of the local power industry or sold to external consumers (Kędzior, 2012; Kędzior and Dreger, 2019).

The average total annual methane emissions for the Marcel mine amount to approximately 23 million m^3, of which approximately 4 million m^3 are captured by underground methane drainage systems and used, while the rest is emitted into the atmosphere (Annual Report, 2020).

3. Scope of the research and methodology

3.1. Soil-gas sampling

A patented measuring kit was used to collect soil-gas samples from a depth of approximately 1.2–1.5 m. Samples were taken with a steel probe, a gas-tight syringe, and gas-tight vessels. The volume of each sample was 100 mL. More details on the method of sampling are described in previous publications (e.g., Sechman et al., 2011, 2017, 2018, 2019; Twaróg et al., 2018). Soil-gas samples were collected along 5 measuring lines at points approximately 50 m apart. However, the distance between points varied due to built-up areas and topography. The tests were carried out along the following profiles in 2005: A–A′, Mszana West; B–B′, Mszana Central; C–C′, Marklowice; D–D′, Wodzisław; and E–E′, Marcel (Table 1). Four profiles were located within or adjacent to the liquidated 1 Maja mine; one (E–E′) was located in the area of the active Marcel coal mine (Fig. 1A). In total, 172 soil-gas samples were taken along these profiles in 2005. Additionally, in selected sections of the A–A′ and B–B′ profiles, soil-gas sampling was again carried out in 2006, with 30 samples of soil gas being taken. In this case, fragments of profiles in which elevated methane and/or carbon dioxide concentrations had been noted a year earlier were selected for the study. In total, 202 soil-gas samples were collected along the measurement lines (Table 1).

Soil-gas samples were also collected in the zones of four abandoned

Table 1
Number of measuring points on the profiles and in the vicinity of shafts, as well as the number of samples selected for isotopic analyses.

Profile/or abandoned shaft	Name of profile/name of coal mine	Range of measurement points	Number of measuring points		Number of isotopic analyses
			May 2005	April 2006 *(range of points)*	
A–A'	Mszana West	285–356	72	21 *(300 – 320)*	2
B–B′	Mszana Central	357–402	46	9 *(371–379)*	4
C–C′	Marklowice	403–420	18	–	0
D–D'	Wodzisław	421–443	23	–	0
E–E'	Marcel	444–456	13	–	0
Shaft I	1 Maja mine	0–4	5	–	1
Shaft III	1 Maja mine	0–4	5	–	4
Shaft IV	1 Maja mine	0–4	5	–	0
Shaft VII	1 Maja mine	0–5	6	–	0

and remediated shafts of the 1 Maja mine (Fig. 1B-E). In this case, the measuring points were located within a radius of several meters from the shaft, in the vicinity of the concrete slabs closing the rock-filled shaft space. In addition, gas samples were taken from the shaft's degassing pipes or chimneys. These samples, measuring 100 mL in volume, were collected with gas-tight syringes. Gas was recovered after rinsing the syringe several times with gas leaking from the well. In total, 17 soil-gas samples were taken in the zones of 4 mine shafts (I, III, IV, and VII) and 4 gas samples from the ventilation holes of each shaft (Table 1, Fig. 1B–E).

3.2. Coal and coalbed gas sampling

Seven samples of coalbed gas and bituminous coal were collected from coal seams exclusively from virgin parts of the Anna (A-1, A-2, and A-3), Marcel (Ml-2), Jastrzębie (J-2), and Zofiówka (Z-3 and Z-9) mines (Table 2, Fig. 1A). A special sampling procedure was applied for the collection of "free" gases from the coal seams (Kotarba, 2001). In the fresh faces of drifts, holes, 4–6 m deep and 4.2 cm in diameter, were drilled into the coal seams. Following the installation of a gas probe, samples were collected from the deepest 0.5 m interval of each borehole and transferred into glass vessels (500 cm^3 in volume) filled with a saturated NaCl solution. Three natural gas samples (M-7, M-20, and M-43) from producing wells drilled from the surface were collected from sandstones and coals of the Lower Bashkirian coal-bearing strata in the Marklowice field of the Marcel mine (Table 2, Fig. 1). All gas samples were taken directly at wellheads in metal containers (1000 cm^3 in volume).

The results of the previous published geochemical studies of ten coalbed gases from the Anna (A-5* sample), Marcel (Ml-1*), Jastrzębie (J-1*, J-5*, and J-50*), Moszczenica (Mo-1*, Mo-2*, and Mo-13*) and Zofiówka (Z-53* and Z-55*) mines (Kotarba, 2001), and two natural gases (M-10** and M-28**) from the Marklowice field of the Marcel mine (Kotarba et al., 2019) in the study area were also used for genetic interpretation. The locations of these samples are shown in Fig. 1.

3.3. Field and laboratory analyses of soil-gas samples

All gas samples were analysed in a field laboratory. Methane and carbon dioxide concentrations were determined using a SRI 810C gas chromatograph equipped with flame ionization (FID) and thermal conductivity (TCD) detectors. Details of the research methodology have been presented in previous publications (Sechman et al., 2013, 2017, 2019, 2020). From the set of all gas samples analysed in the field, 11 samples with elevated methane and/or carbon dioxide concentrations were selected. These samples were sent for tests of ethane and propane content as well as of isotopic composition.

A Fisons Instruments GC 8160 gas chromatograph equipped with an FID detector was used for ethane and propane identification. The details of the analytical methodology have been presented in previous publications (Sechman et al., 2011, 2013; Sechman, 2012). The analyzer was calibrated at two concentration levels, using Air Liquide calibration standards. Ethane concentrations in calibration standards were 1.92 and 14.1 ppm; propane concentrations were 1.99 and 14.6 ppm. The detection limit of the FID detector was 0.01 ppm for light hydrocarbon components. Analytical error was estimated at ± 5% of measured values (Sechman et al., 2020).

3.4. Molecular composition of coalbed gases

The molecular compositions of coalbed and natural gases (CH_4, C_2H_6, C_3H_8, *i*-C_4H_{10}, *n*-C_4H_{10}, N_2, CO_2, O_2, H_2, He, and Ar) were analysed in a set of columns on Hewlett Packard 5890 Series II, Hewlett Packard 6890 Series, and Chrom 5 gas chromatographs equipped with flame ionization (FID) and thermal conductivity (TCD) detectors.

3.5. Vitrinite reflectance

Aliquots of bituminous coals were embedded in epoxy resin mounts. After hardened, the mounts were polished at room temperature with 1-μm diamond powder. The reflectance of collotelinite was measured according to standard procedures (ISO 7404-2, 7404–3, 7404–5, and

Table 2
Information on coalbed gas and coal sampling sites in Upper Carboniferous coal seams and coal-bearing strata in the area of Chwałowice and Jejkowice Troughs as well as vitrinite reflectance (Rr) and stable carbon isotope composition of gas accumulated coals.

Sample code	Mine/Well/Trough	Seam No.	Stratigraphy	Depth below surface (m)	Depth below U. Carb. top (m)	R_r (%)	$\delta^{13}C$ (Coal) (‰)
Mine sample (coalbed gas)							
A-1	Anna/J.T.	722	Ser. (N-A)	795	713	1.05	−23.8
A-2	Anna/J.T.	722	Ser. (N-A)	806	751	0.96	−24.0
A-3	Anna/J.T.	718	Ser. (N-A)	613	470	1.10	−24.8
Ml-2	Marcel/Ch.T.	507	L.B. (N—B)	252	28	n.a.	−24.1
J-2	Jastrzębie/M.S.	510/1	L.B. (N—B)	635	271	1.24	−24.3
Z-3	Zofiówka/M.S.	404/3	U.B. (W-A)	615	58	1.06	n.a.
Z-9	Zofiówka/M.S.	418/1–2	M.B. (N—C)	640	15	1.10	−24.2
Well sample (natural gas)							
M-7	Marklowice-7/Ch.T	–	L.B. (N—B)	232	156	–	–
M-20	Marklowice-20/Ch.T	–	L.B. (N—B)	264	94	–	–
M-43	Marklowice-43/Ch.T	–	L.B. (N—B)	192	0	–	–

Ch. - Chwałowice Trough; J. - Jejkowice Trough; M.S. - Main Syncline;
Ser. - Serpukhovian; U. - Upper; M. - Middle; L. - Lower; B. - Bashkirian; N-A - Namurian A; N—B - Namurian B; N—C - Namurian C; U. Carb. - Upper Carboniferous
n.a. - not analysed;

recommendations on the basis of the standardization of the International Committee for Coal and Organic Petrology). Surface-reflected monochromatic light at a wavelength of 546 nm was used with an Opton-Zeiss photometer microscope equipped with a 45× oil-immersion objective coupled with a 10× ocular. Standard magnification was optimal for measuring reflectance. A non-drying immersion oil with a refraction index of $n = 1.518$ at 21 to 23 °C and light with a wavelength of 546 nm was used for the reflectance measurements. The microscope photometer was calibrated according to the standard procedures described by Stach et al. (1982) and Taylor et al. (1998). Each calibration performed in this study employed one of these standards: beryllium (0.490%Ro), yttrium garnet (0.904%Ro), or gadolinium-gallium-garnet (1.719%Ro). For bituminous coals, the measured reflectance comprised the mean maximum (Rmax°), intermediate (Rint°), and minimum (Rmin°), determined under polarized light. This differentiation between VR measurement methods was made according to the procedure described in Kilby (1988, 1991). The mean random reflectance was calculated as the sum of Rmin°, Rint°, and Rmax°, divided by three.

3.6. Analyses of stable carbon and hydrogen isotopes

Stable carbon isotope analyses were performed using a Finnigan™ Delta Plus mass spectrometer (MS). Methane, ethane, and carbon dioxide were separated chromatographically and individually combusted in a ceramic reactor filled with copper oxide, chromium oxide, and platinum catalyst at 980 °C. Carbon dioxide produced by the on-line system was transmitted to the MS. Following the removal of carbonates and bitumen, coal samples selected for stable carbon isotope analyses were combusted in sealed glass tubes (Sofer, 1980). The stable carbon isotope data are expressed in δ-notation (δ^{13}C, ‰) relative to VPDB (Coplen, 2011). For isotopic normalization, three internal standards were used, calibrated via the dual-inlet system method using the international standards RM8563, NBS 22, and NBS 19. Analytical precision, established as standard deviation from 10 measurements, was estimated at ± 0.2‰.

Stable hydrogen isotope analysis of methane was performed in a Thermo Scientific™ Delta V Plus MS coupled with a GC IsoLink™ interface connected with a Trace GC Ultra chromatograph. The methane was separated chromatographically and reduced to gaseous hydrogen in a high-temperature ceramic reactor at 1420 °C. The stable hydrogen isotope data were reported in δ-notation (δ^{2}H, ‰) relative to VSMOW (Coplen, 2011). For isotopic normalization, three internal standards were used, calibrated via the dual-inlet system method using the international standards VSMOW2, SLAP-2, and GISP. Analytical precision, established as standard deviation from 10 measurements, was estimated at ± 3‰ for methane.

4. Results

4.1. Results of vitrinite reflectance and stable carbon isotopic analyses of coals accumulated coalbed gases

Vitrinite reflectance and stable carbon isotope composition of coals accumulated coalbed gases ranged from 0.82 to 1.24% and from −24.8 to −23.4‰, respectively (Table 2; Kotarba, 2001; Kotarba et al., 2019).

4.2. Statistical evaluation of methane and carbon dioxide concentrations detected in soil-gas samples along profiles and in the vicinity of abandoned shafts

Methane and carbon dioxide concentrations measured in soil-gas samples collected along 5 profiles varied from 0.5 ppm to over 22 vol% and from 0.04 to greater than 9 vol%, respectively (Table 3). The average value of methane concentration was 3 orders of magnitude higher than the median, indicating the presence of anomalous values in the tested set of concentrations. For the set of carbon dioxide concentrations, the difference between the average and the median was not as high, only approximately 0.5 vol% (Table 3).

The histogram constructed for the set of logarithmic methane concentration values (Fig. 4A) was characterized by clear right-sided asymmetry. The modal class was defined by the range − 3.8 to −3.6, corresponding to a concentration of 1.6–2.5 ppm. Based on the probability plot (Fig. 4B), five characteristic methane concentration ranges were selected: < 1 ppm, 1–2.5 ppm, 2.5–8 ppm, 8–30 ppm, and > 30 ppm. Above 8 ppm, clearly elevated methane concentrations were visible; above 30 ppm a separate set of anomalous values could be distinguished (Fig. 4A, B).

The statistical distribution for the set of logarithmic carbon dioxide concentrations was bimodal (Fig. 4C). The set representing carbon dioxide concentration up to approximately 0.16 vol% was less numerous; the modal class was in the range − 1.25 to −1.1, corresponding to a concentration range of 0.056 to 0.08 vol%. The set of higher values, with a significantly larger number, was characterized by modal values ranging from −0.2 to −0.05, corresponding to a concentration range of 0.63 to 0.89 vol% (Fig. 4C). Based on the probability plot (Fig. 4D), the following characteristic ranges of carbon dioxide concentration were selected: < 0.16, 0.16–0.53, 0.53–3.0, and > 3 vol%. It should be noted that significant anomalous concentrations of carbon dioxide were found above 3 vol%.

The A–A′ and B–B′ profiles stand out in terms of maximum and average concentration values (Table 3, Fig. 5A). Along the remaining profiles (C–C′, D–D′, and E–E′), significantly lower values of methane concentration, which did not exceed 8 ppm, were recorded. These profiles were characterized by similar mean and median values for the methane concentration sets (Table 3), indicating a small proportion of anomalous methane concentrations recorded along these profiles.

The maximum values of carbon dioxide concentration recorded on the studied profiles ranged from 4.14 to 9.14 vol%. The highest carbon dioxide concentration was recorded on the A–A′ profile (Table 3, Fig. 5B). The variation in average carbon dioxide concentration for the studied profiles was relatively small.

In the vicinity of the abandoned shafts of the 1 Maja coal mine, methane and carbon dioxide concentrations varied within the ranges 0.0001–21 vol% and 0.06–3.9 vol%, respectively (Table 3). The average values of methane concentration in the vicinity of mining shafts I and III were 4 orders of magnitude higher than the average values of this gas in the vicinity of shafts IV and VII. As many as 4 samples taken in the vicinity of shaft III contained anomalous concentrations of methane (Fig. 1C). A significantly higher average value of carbon dioxide concentration was recorded in the vicinity of mining shaft III in relation to other shafts.

4.3. Correlation between methane and carbon dioxide concentrations

Cross plots between sets of values representing logarithmic methane and carbon dioxide concentrations were constructed separately for sets obtained along the profiles (Fig. 6A, B) and for sets obtained in the mine shaft zones (Fig. 6C, D). The coefficient of determination (R^2) was calculated for two ranges of methane concentration: above and below 30 ppm. This value was adopted based on statistical distributions constructed for the methane concentration set (Fig. 4A, B).

The correlation cross plots showed that the sets of methane and carbon dioxide concentration values obtained along the profiles were not correlated (Fig. 6A, B), due to very low R^2 values. This applied to correlation plots constructed for methane concentrations both above (Fig. 6A) and below (Fig. 6B) 30 ppm. Values of methane concentration above 30 ppm showed a consistent trend of changes with carbon dioxide; values below 30 ppm showed the opposite trend. The diagram showing the result of directional correlation showed no clear predominance of either congruent or non-congruent changes between methane and carbon dioxide (Fig. 6E).

Table 3
Selected statistical parameters of methane and carbon dioxide concentrations in gas samples measured in the area of Chwałowice Trough and in the vicinity of abandoned shafts of 1 Maja mine.

Name of profile/shaft	Number of samples	Maximum value		Mean value		Median		Percentage of samples with concentration over	
		CH_4 (vol%)	CO_2 (vol %)	CH_4 (vol%)	CO_2 (vol %)	CH_4 (vol%)	CO_2 (vol %)	8 ppm of CH_4 (%)	3.0 vol% of CO_2 (%)
Chwałowice Trough (all measurement points along profiles)	202	22.20	9.14	0.17	1.33	0.0002	0.88	7.9	11.4
A–A' Mszana - West	72	0.061	9.14	0.0013	1.31	0.0002	0.75	6.9	9.7
A–A' Mszana - West *	21	7.82	1.97	0.37	0.87	0.0003	0.88	2.8	0.0
B–B′ Mszana - Central	46	3.90	5.44	0.086	1.53	0.0002	1.17	10.9	17.4
B–B′ Mszana - Central[a]	9	22.20	5.69	2.48	1.48	0.0006	0.46	44.4	22.2
C–C′ Marklowice	18	0.0008	4.61	0.0002	0.96	0.0003	0.53	0.0	5.6
D–D' Wodzisław	23	0.0003	4.14	0.0002	1.62	0.0002	1.65	0.0	17.4
E–E' Marcel	13	0.0004	6.61	0.0002	1.40	0.0002	0.88	0.0	7.7
Measurement points in the vicinity of abandoned shafts	21	21.00	3.9	2.56	1.09	0.0004	0.72	38.1	14.3
Shaft I	5	7.81	1.29	1.57	0.40	0.016	0.11	80.0	0.0
Shaft III	5	21.00	3.90	9.19	2.46	2.93	3.40	80.0	60.0
Shaft IV	5	0.0006	1.08	0.0003	0.55	0.0003	0.63	0	0
Shaft VII	6	0.0003	1.98	0.0002	0.97	0.0002	0.96	0	0

[a] Measurements repeated in April 2006 at selected sites of A–A' and B–B′ profiles.

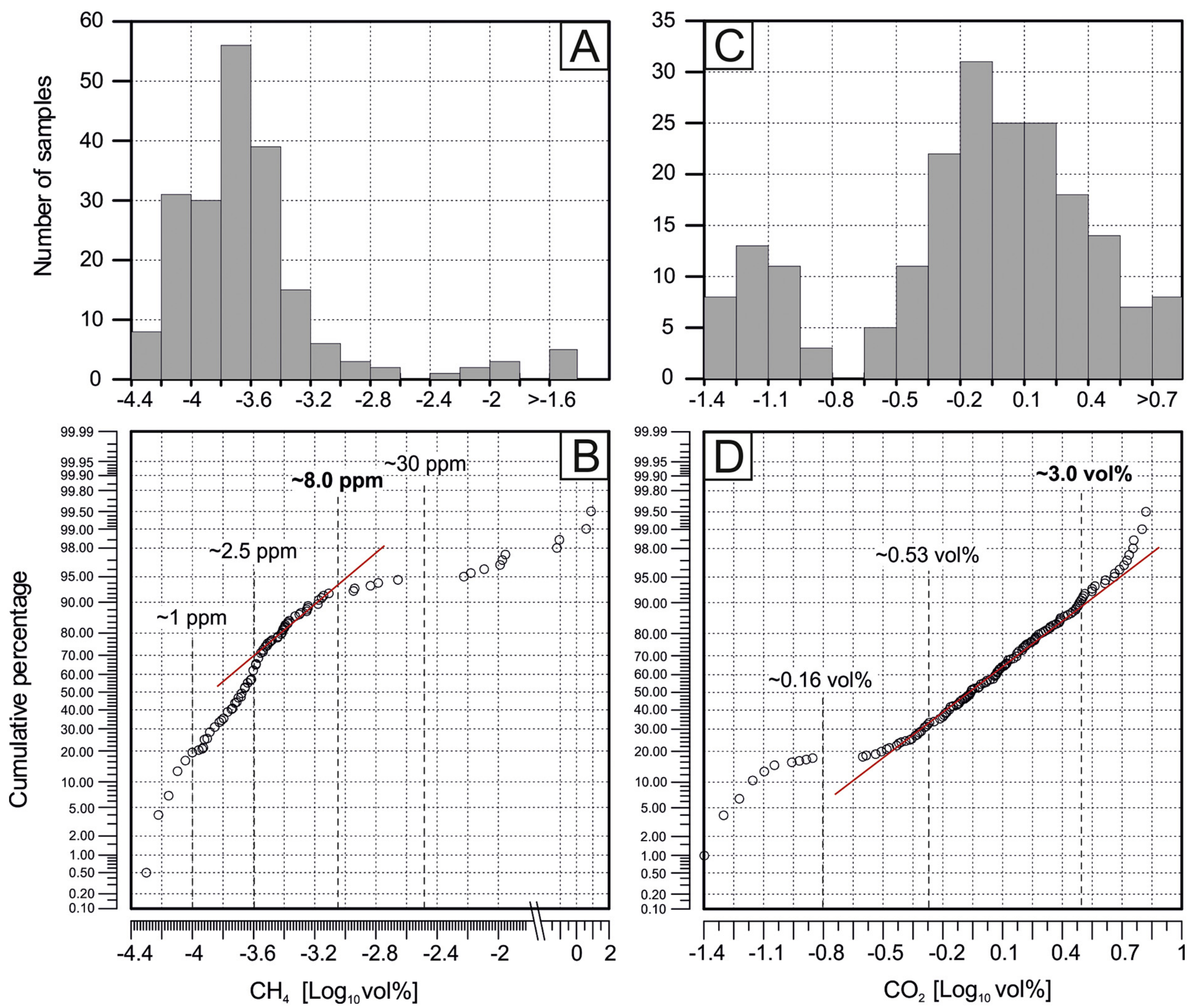

Fig. 4. Histograms and cumulative frequency diagrams of (A and B) methane and (C and D) carbon dioxide concentration measured in soil gas samples along five measurement lines.

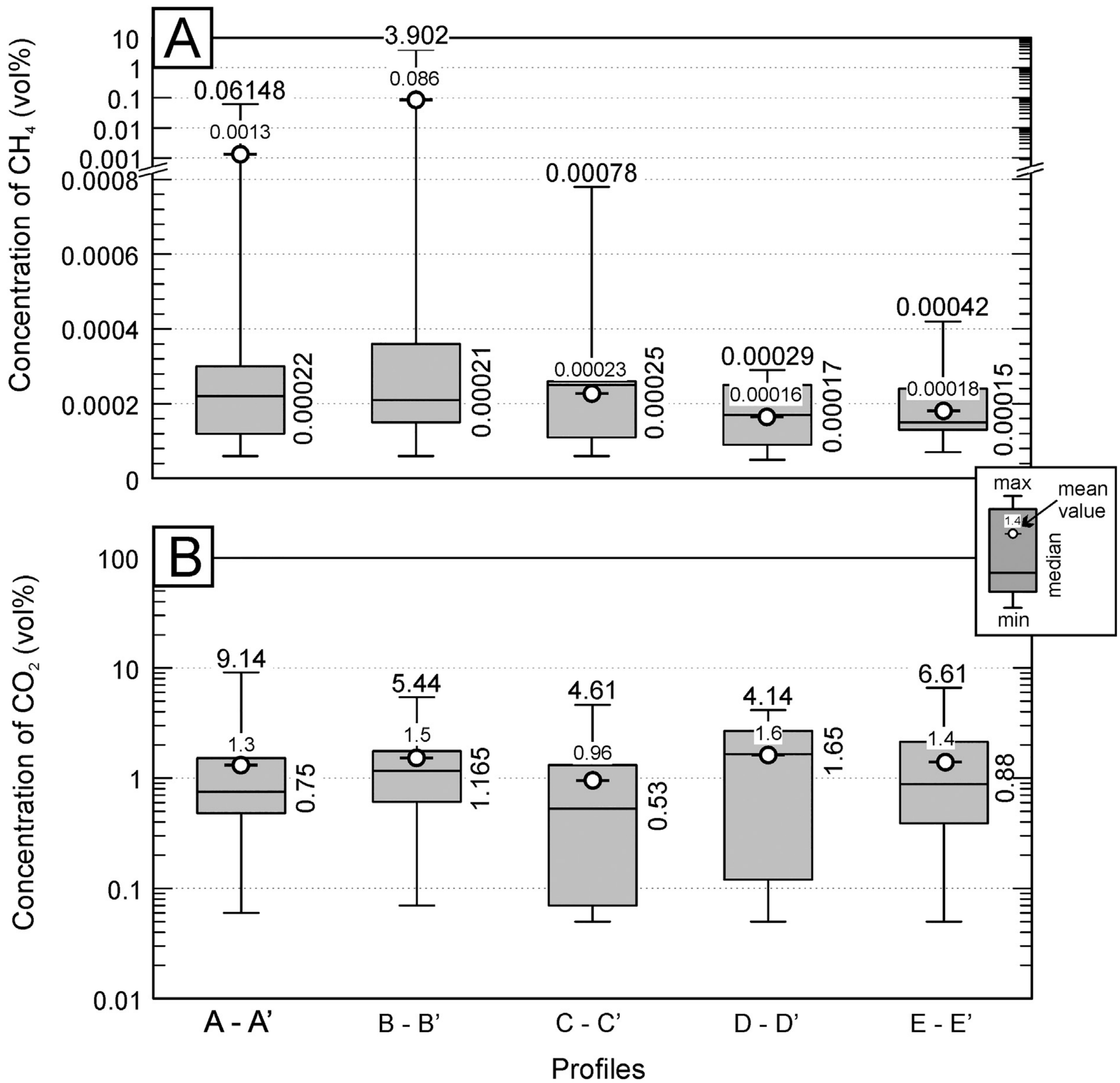

Fig. 5. Box-plots of (A) methane and (B) carbon dioxide concentration measured in soil gas sampling stations along measurement lines (profiles).

Methane and carbon dioxide concentration sets obtained in the vicinity of shafts also showed a low level of correlation. The trend line on the correlation charts for methane concentrations above and below 30 ppm was analogous to the sets of concentration values obtained along the profiles. A distinctly elevated R^2 value was determined for the graph showing the correlation between the set of methane concentrations below 30 ppm and the corresponding carbon dioxide concentrations (Fig. 6D). It can therefore be concluded that in the vicinity of abandoned mine shafts the set of methane concentrations below 30 ppm exhibited a negative trend of changes in relation to the corresponding concentrations of carbon dioxide. However, the low strength of correlation between these data sets was due to a coefficient of determination (R^2) of only 0.5 (Fig. 6D).

4.4. Background values

The iterative method was applied to determine the background value (BV) for methane and carbon dioxide (Sechman and Dzieniewicz, 2011). The threshold level value for anomalies was determined using the formula TLV = BV + 3σ.

The background (BV) and threshold level (TLV) values for methane and carbon dioxide anomalies were determined separately for the data sets obtained in May 2005 and in April 2006. These parameters (BV and TLV) differed significantly for the methane concentration set (Table 4). The background value for the methane concentrations measured in April 2006 was more than 6 times that calculated for the set obtained in May 2005. In the case of the TLV parameter, the difference was more than 21 times. In the case of carbon dioxide, the difference in background values was relatively small (Table 4). The TLV parameter calculated for the results obtained in April 2006 was about 30% higher than that obtained in May 2005.

4.5. Results of molecular composition and indices and of stable carbon and hydrogen isotope analyses of coalbed and soil gases

The analysed coalbed gases from the Mississippian and Pennsylvanian coal-bearing strata in the study area (Table 2, Fig. 1) varied in terms of both their molecular and stable isotopic ratios (Tables 5 and 6; Kotarba, 2001). The molecular compositions were dominated by methane ranging from 59.6 (J-2 sample, Table 5) to 99.0 vol% (Z-55 sample, Kotarba, 2001).

Concentrations of higher hydrocarbons in the coalbed gas samples

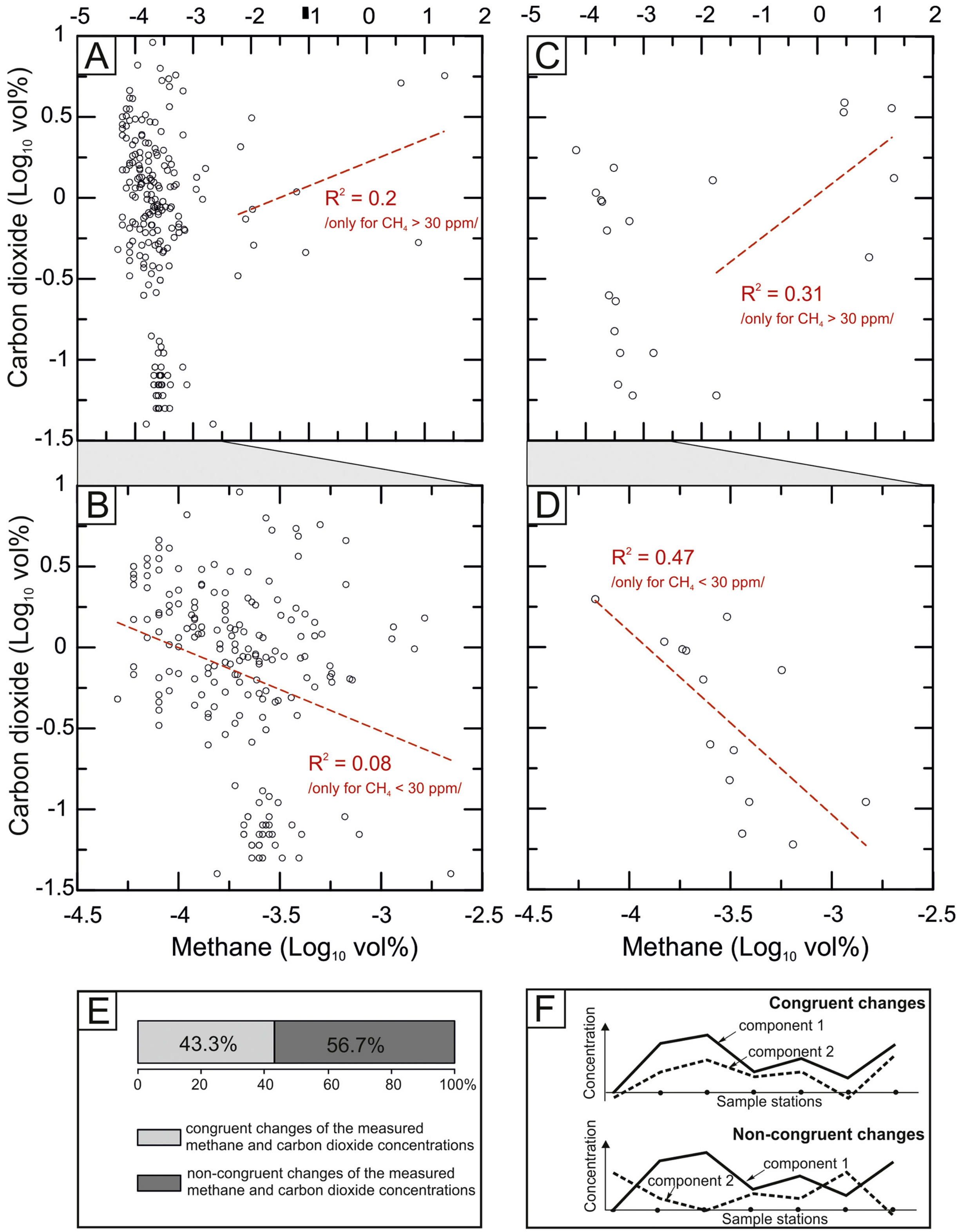

Fig. 6. Correlation diagrams between CH_4 and CO_2 for (A and B) data sets obtained along profiles, (C and D) data sets obtained in the vicinity of abandoned shafts, (E) results of directional correlation between CH_4 and CO_2 concentrations, and (F) examples of congruent and opposite changes of values.

varied within the following ranges: C_2H_6, from 0.00 to 5.31 vol% (A-1, Table 5); C_3H_8, from 0.00 to 0.97 vol% (A-1, Table 5). Among the non-hydrocarbon gases, the most common was N_2, with concentrations varying from 1.00 (Z-55 and Z-4; Kotarba, 2001) to 33.4 vol% (J-2, Table 5). The concentration of CO_2 ranged from 0.00 to 6.5 vol% (J-2, Table 5). The concentration of helium was low, from 0.00 to 0.46 vol% (J-2, Table 5). Molecular hydrogen occurred only in the A-1, A-2, and A-3 samples (Anna mine), varying from 0.005 to 0.09 vol%, and in the Ml-2 sample, 2.12 vol% (Table 5). Hydrocarbon (C_{HC}) and carbon dioxide-methane (CDMI) indices varied from 14 to > 100,000 (Table 6) and from 0.00 to 9.83 (Table 6; Kotarba, 2001), respectively. Stable isotope values of hydrocarbon gases ranged as follows (Table 6;

Table 4
Background values and threshold level values for methane and carbon dioxide concentrations.

Statistical parameter	Methane		Carbon dioxide	
	May 2005	April 2006	May 2005	April 2006
BV (vol%)	0.00016	0.00099	0.48	0.59
TLV (vol%)	0.00037	0.00796	1.46	1.89

BV - background value; TLV - threshold level value.

Table 5
Molecular composition of coalbed gases, natural gases from coal-bearing strata and near-surface gases analysed for isotope composition (cf. Table 6).

Sample code	Molecular composition (vol%)							
	CH_4	C_2H_6	C_3H_8	N_2	CO_2	He	Ar	H_2
Mine sample								
Ml-2	89.1	0.02	0.00	10.2	0.51	0.01	0.12	2.12
A-1	86.9	5.31	0.97	5.8	0.72	0.03	0.05	0.09
A-2	93.8	1.36	0.12	4.0	0.72	0.03	0.007	0.005
A-3	90.3	0.08	0.0009	9.1	0.30	0.00	0.04	0.09
J-2	59,6	0,003	0,00	33,4	6,5	0,46	0,007	0,00
Z-3	72,9	0,006	0,00	26,6	0,49	0,03	0,014	0,00
Z-9	88,3	0,00	0,00	11,3	0,25	0,07	0,014	0,00
M-7	90.1	0.00	0.00	9.8	0.00	0.02	0.07	0.000
M-20	88.9	0.00	0.00	9.9	0.10	0.04	0.03	0.000
M-43	56.5	0.01	0.00	41.6	1.44	0.02	0.49	0.000
Near-surface gases (Profile A–A')								
303	0.00067				4.58			
304	0.00027				6.32			
306	0.0002				9.14			
329	0.0005				5.74			
Near-surface gases (Profile B–B′)								
375	0.00038				5.44			
374	3.90				5.13			
Near-surface gases (near old shafts of 1Maja mine)								
Shaft I/3	7.81	0	0		0.44			
Shaft III/0	21.00	0.0060	0		1.33			
Shaft III/1	2.93	0	0		3.91			
Shaft III/3	19.18	0.0065	0		3.64			
Shaft III/4	2.85	0	tr.		3.43			

Kotarba, 2001): $\delta^{13}C(CH_4)$ from −79.9 (Z-55, Kotarba, 2001) to −48.8‰ (A-2, Table 6); $\delta^2H(CH_4)$, from −220 (Ml-2, Table 6) to −161‰ (Mo-1, Kotarba, 2001); $\delta^{13}C(C_2H_6)$ = −48.4‰ (one Ml-2 sample, Table 6). Stable carbon isotopic composition of carbon dioxide varied from −18.5 (Z-9, Table 6) to 2.8‰ (A-5, Kotarba, 2001).

The analysed natural gases of wells drilled from the surface of the Pennsylvanian coal-bearing strata in the study area (Fig. 1, Table 5) varied in terms of both their molecular and stable isotopic ratios (Tables 5 and 6; Kotarba et al., 2019). Concentrations of gaseous hydrocarbons in the natural gas samples varied within the following ranges: CH_4 from 56.5 (M-43, Table 5) to 90.1 vol% (M-7, Table 5); C_2H_6 from 0.00 to 0.01 vol% (M-43, Table 5); C_3H_8 from 0.00 to 0.0001 vol% (M-10 and M-28, Kotarba et al., 2019). Among the non-hydrocarbon gases, N_2 varied from 9.38 (M-10, Kotarba et al., 2019) to 41.6 vol% (M-43, Table 5). The concentration of CO_2 ranged from 0.00 to 4.04 vol% (M-28, Kotarba et al., 2019). The concentration of He was low, ranging from 0.01 (M-10, Kotarba et al., 2019) to 0.04 vol% (M-43, Table 5). Molecular hydrogen does not occur in natural gases (Table 5; Kotarba et al., 2019). Hydrocarbon (C_{HC}) and carbon dioxide-methane (CDMI) indices varied within the following ranges: from 5762 to > 100,000 (Table 6) and from 0.00 to 4.50 (Table 5; Kotarba, 2019), respectively. Stable isotope values of hydrocarbon gases ranged as follows (Table 6; Kotarba, 2001): $\delta^{13}C(CH_4)$ from −78.5 (M-20) to −72.5‰ (M-43, Table 6); $\delta^2H(CH_4)$ from -–213 (M-43, Table 6) to −209‰ (M-28, Kotarba et al., 2019); $\delta^{13}C(C_2H_6)$ from −48.0 (M-28, Kotarba et al., 2019) to −46.1‰ (M-43, Table 6). The stable carbon isotopic composition of carbon dioxide varied between −18.6 (M-10, Kotarba et al., 2019) and 14.2‰ (M-43, Table 6).

The analysed near-surface gases in a selected samples collected to isotopic analysis, from the A–A′ and B–B′ profiles and near the abandoned shafts of the 1 Maja mine in the study area (Fig. 1, Table 1) varied in terms of both their molecular and stable isotopic ratios (Table 5 and 6). Concentrations of gaseous hydrocarbons varied within the following ranges: CH_4 from 0.0002 (Sample 306, A–A′ profile, Table 5) to 21.0 vol% (abandoned shaft III/0, 1 Maja mine, Table 5); C_2H_6 0.000 to 0.0065 vol% (abandoned shaft III/3, 1 Maja mine, Table 5). Among the non-hydrocarbon gases, CO_2 ranged in concentration from 1.33 (abandoned shaft III/0, 1 Maja mine, Table 5) to 9.14 vol% (Sample 306, A–A′ profile, Table 5). Hydrocarbon (C_{HC}) and carbon dioxide-methane (CDMI) indices varied within the following ranges: from 2930 (abandoned shaft III/3, 1 Maja mine, Table 6) to > 100,000 (Table 6), and from 0.00 to 100 (%) (Table 6). Stable carbon isotope values ranged as follows (Table 6): $\delta^{13}C(CH_4)$ from −74.1 (abandoned shaft III/0, 1 Maja mine) to −56.8‰ (abandoned shaft III/1, 1 Maja mine); $\delta^{13}C(CO_2)$, from −73.9 (abandoned shaft I/3, 1 Maja mine) to −18.6‰ (Sample 303, A–A′ profile).

4.6. Changes in methane and carbon dioxide concentrations along the profiles

Changes in methane and carbon dioxide concentrations along the profiles are presented in the form of line graphs combined with schematic geological cross sections. These plots highlight the zones of anomalous values of each of the tested gases.

In May 2005, 72 soil-gas samples were taken along the A–A′ profile. Additionally, a selected fragment of the profile was tested again in 2006; 21 samples were taken (Fig. 11). The methane and carbon dioxide concentrations measured in May 2005 along the A–A′ profile fluctuated within the following ranges: 0.00006–0.06 and 0.06–9.14 vol%, respectively. The methane concentrations measured in April 2006 along the selected section of the profile fell within a range of 0.0001–7.8 vol%, which was significantly wider than the previous year. The range of carbon dioxide concentration was narrower in 2006 than in 2005, ranging from 0.04 to about 2 vol%. Along the A–A′ profile, between points 313 and 305, one zone of anomalous methane concentrations was found. It should be noted that the methane anomalies recorded in 2005 and 2006 within this zone do not overlap. In addition to the anomalous zone mentioned above, two one-point increases in concentration values were recorded on this profile at points 289 and 341 (Fig. 11B).

In May 2005, 46 soil-gas samples were taken along the B–B′ profile. Additionally, the selected fragment of the profile was tested again in 2006; 9 samples were taken (Fig. 12). Methane and carbon dioxide concentrations measured in May 2005 along the B–B′ profile fluctuated within the following ranges: 0.00006–3.9 vol% and 0.07–5.44 vol% (Table 3, Fig. 12A, B). The methane concentrations measured in April 2006 along the selected section of the profile fell within a range of 0.0003–22.2 vol%, which was wider than the previous year (Table 3, Fig. 12B). Carbon dioxide concentrations measured in 2006 were at a level similar to that of the previous year, ranging from 0.07 to 5.69 vol % (Table 3, Fig. 12A). In 2006, the maximum values of methane and carbon dioxide concentration in 2006 were recorded at the same measuring point (372). Along the B–B′ profile, two distinct zones of anomalous methane concentrations were identified within the following ranges of points: 372–375 and 390–394. In addition, single increases were noted in methane concentration at points 361 and 366 (Fig. 12B). Anomalous concentrations of carbon dioxide occurred within the point zones 361–464, 372–379, and 388–392, as well as at point 398.

The concentrations of methane and carbon dioxide measured in 18

Table 6
Isotopic composition and molecular indices of coalbed gases and natural gases from coal-bearing strata, and near-surface gases.

Sample code	Molecular indices		Stable isotopes (‰)			
	C_{HC}	CDMI	$\delta^{13}C(CH_4)$	$\delta^{2}H(CH_4)$	$\delta^{13}C(C_2H_6)$	$\delta^{13}C(CO_2)$
Mine sample						
Ml-2	4089	0.60	−77.2	−220	−48.4	−16.3
A-1	14	0.82	−50.8	n.a.	n.a.	n.a.
A-2	63	0.76	−48.8	−190	n.a.	n.a.
A-3	1159	0.33	−49.8	−194	n.a.	n.a.
J-2	19,867	9.83	−70.5	n.a.	n.a.	n.a.
Z-3	13,018	0.67	−70.0	−184	n.a.	n.a.
Z-9	–	0.30	−74.4	−180	n.a.	−18.5
Well sample						
M-7	> 100,000	–	−77.6	n.a.	n.a.	n.a.
M-20	> 100,000	0.11	−78.5	n.a.	n.a.	n.a.
M-43	5762	2.50	−72.5	−213	−46.1	−14.2
Near-surface gases (Profile A–A')						
303	n.a.	100	n.a.	n.a.	n.a.	−18.6
304	n.a.	100	n.a.	n.a.	n.a.	−20.2
306	n.a.	100	n.a.	n.a.	n.a.	−19.7
329	n.a.	100	n.a.	n.a.	n.a.	−20.6
Near-surface gases (Profile B–B′)						
375	n.a.	100	n.a.	n.a.	n.a.	−20.2
374	> 100,000	n.a.	−71.4	n.a.	n.a.	n.a.
Near-surface gases (near old shafts of 1Maja mine)						
Shaft I/3	100,000	5.3	−61.1	n.a.	n.a.	−73.9
Shaft III/0	3500	5.9	−74.1	n.a.	n.a.	−28.5
Shaft III/1	100,000	57.1	−56.8	n.a.	n.a.	−64.0
Shaft III/3	2930	15.9	−71.7	n.a.	n.a.	−43.3
Shaft III/4	100,000	54.6	−57.9	n.a.	n.a.	−65.3

$C_{HC} = CH_4/(C_2H_6 + C_3H_8)$; CDMI = $[CO_2/(CH_4 + CO_2)]$ 100 (%); n.a. - not analysed.

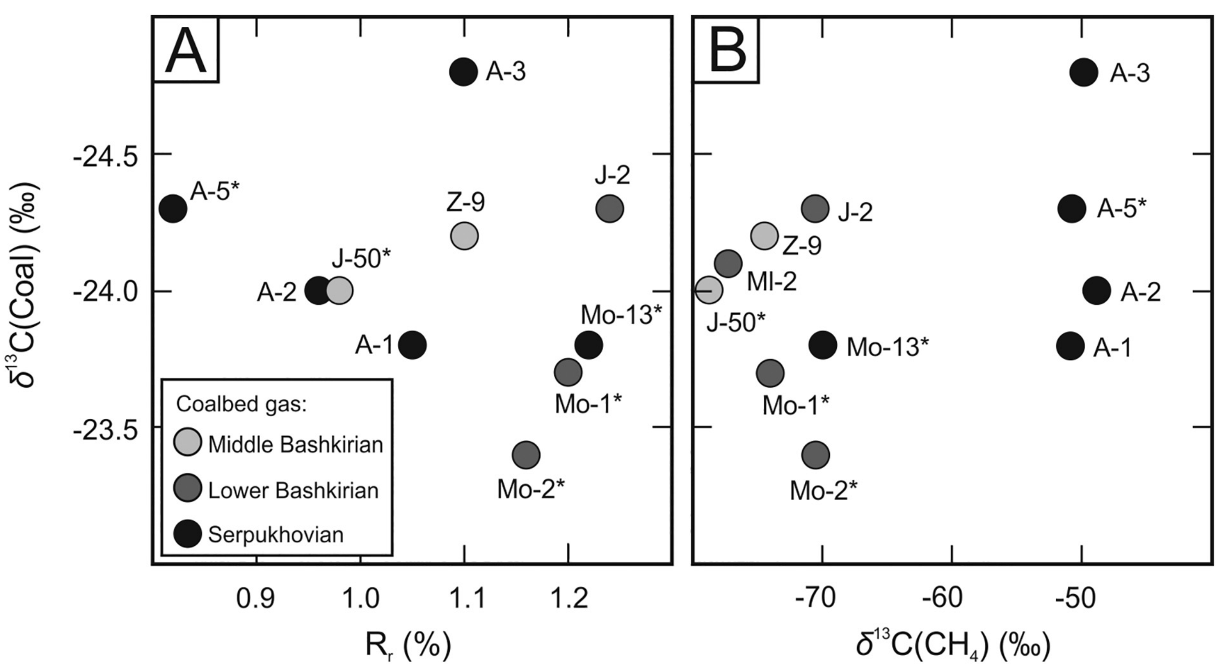

Fig. 7. $\delta^{13}C$(Coal) values versus (A) vitrinite reflectance of analysed coals accumulated coalbed gases and (B) $\delta^{13}C(CH_4)$ values of analysed coalbed gases.

soil-gas samples along the C–C′ profile varied within the following ranges: 0.6–7.8 ppm and 0.05–6.1 vol%, respectively (Table 3, Fig. 13A). Methane concentration exceeded the TLV value only at point 411. Anomalous values of carbon dioxide concentration occurred within two small zones: 407–410 and 419–420 (Fig. 13A).

In 23 soil-gas samples taken along the D–D′ profile, methane was found at a trace level, not exceeding 3 ppm; carbon dioxide concentration ranged from 0.05–4.14 vol%. Carbon dioxide concentrations formed a fairly extensive anomalous zone located in the central part of the profile between points 427 and 437 (Fig. 13C).

The E–E′ profile was the shortest, as only 13 soil-gas samples were taken (Fig. 14). The concentrations of methane and carbon dioxide varied within the following ranges: 0.7–4.2 ppm and 0.05–6.61 vol%, respectively (Table 3, Fig. 14A). Methane concentration exceeded the TLV limit only at measuring point 453. Zones of anomalous concentrations of carbon dioxide were found at three locations of the

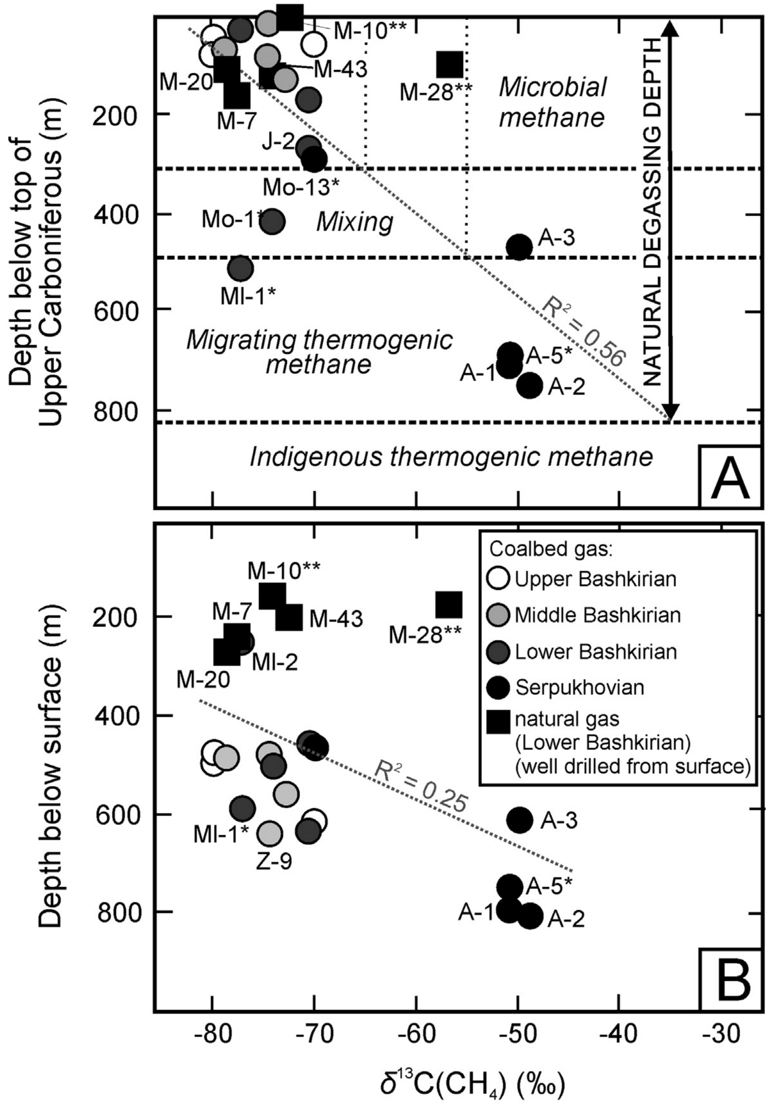

Fig. 8. $\delta^{13}C(CH_4)$ values of coalbed gases from analysed area versus depth **(A)** below top of Upper Carboniferous strata and base of Miocene caprock and **(B)** below surface. $\delta^{13}C(CH_4)$ values after Table 3, Kotarba (2001) and Kotarba et al. (2019).

profile: zones 445–447 and 451–452 and point 455 (Fig. 14A).

4.7. Changes in methane and carbon dioxide concentrations in the vicinity of abandoned shafts

Among the 4 mining shafts tested, the maximum concentrations of methane and carbon dioxide were found in the vicinity of shaft III (Table 3, Fig. 1C). In the vicinity of this shaft, 5 samples were taken; relatively high values of methane and carbon dioxide concentration were recorded in as many as 4. These concentrations varied within ranges of 2.85–21 and 1.33–3.9 vol%, respectively. It should be noted that the maximum value of methane concentration was found at the outflow from the degassing hole; of carbon dioxide, in soil-gas sample 1 (Fig. 1C).

The results of the measurements completed in the vicinity of shaft I showed an increased value of methane concentration only at point 3, and of carbon dioxide only at point 4 (Fig. 1B). In the vicinity of shafts IV and VII, methane concentrations were at a trace level, ranging from 1 to 6 ppm. The maximum values of the concentration of carbon dioxide around each shaft were 1.08 and approximately 2 vol%, respectively (Fig. 1D, E).

5. Discussion

5.1. Interpretation of the relationship of the geological structure and deep methane content of coal seams with the distribution of methane and carbon dioxide concentrations detected in soil-gas samples along the profiles

The reason for the elevated average methane and carbon dioxide concentrations recorded along the A–A′ and B–B′ profiles in relation to the others (Table 3, Fig. 5) may be their location in the central part of the mining area of the abandoned 1 Maja mine (Fig. 1A), which was closed down in 2004 (Czaja, 2009). Therefore, the shutdown of drainage and ventilation systems may very well have been the cause of gas accumulation in the mining excavations and rock mass. As a consequence, this could have intensified the migration of reservoir gases to the surface through fault and fracture systems. In Poland, phenomena of this type have taken place in areas of decommissioned LSCB mines (Sechman et al., 2013, 2017). Secondary gas-bearing zones, interpreted in geological cross sections, may also have significance for the level of recorded methane concentrations in the near-surface zone. These types of gas-bearing zones were clearly visible along profiles A–A′ and B–B′ (Figs. 11C, 12C). In this respect, the B–B′ profile deserves special attention. Profiles C–C′, D–D′, and E–E′ are located in the vicinity of the

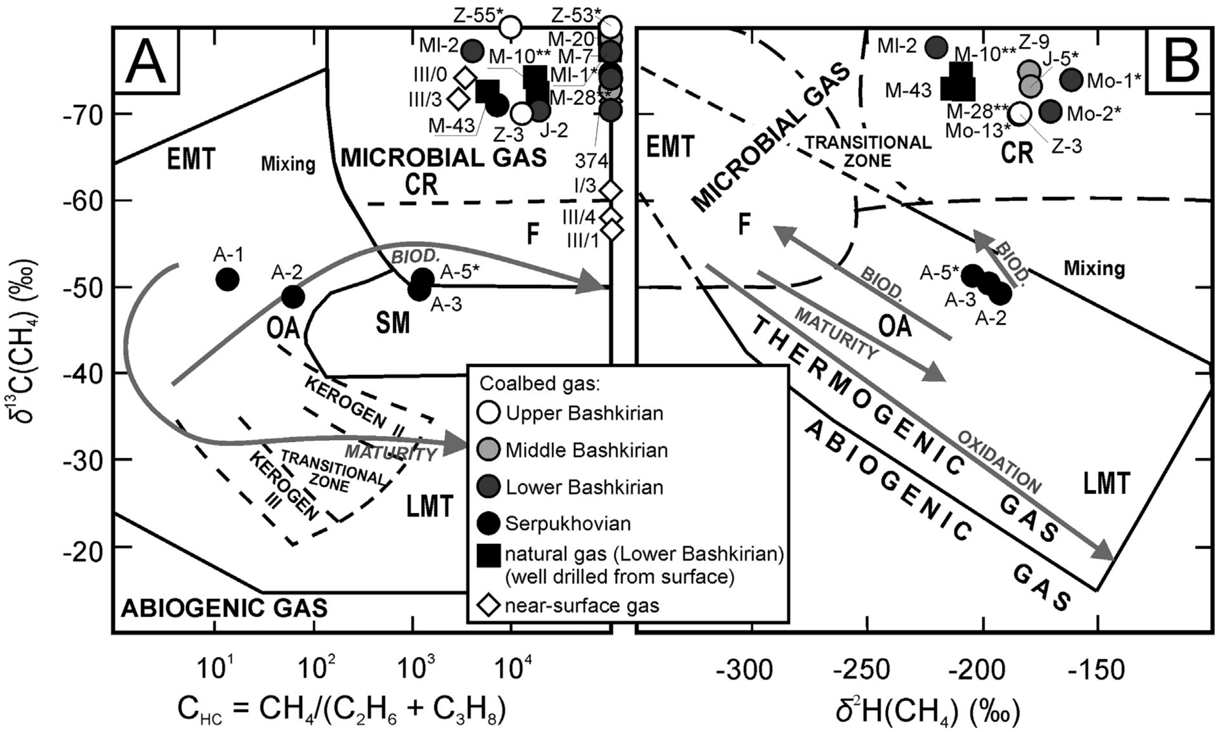

Fig. 9. Genetic characterization of analysed coalbed, natural and soil gases using $\delta^{13}C(CH_4)$ versus (A) hydrocarbon index (C_{HC}) and (B) $\delta^{2}H(CH_4)$. Compositional fields and arrow directions of maturity and oxidation after Milkov and Etiope (2018). Stable carbon isotope composition of methane of coalbed gases after Kotarba (2001). Key for analysed gas samples in Table 1, and previously analysed A-5*, J-1*, J-5*, J-50*, Mo-1*, Mo-2*, Mo-13*, Ml-1*, Z-53* and Z-55* coalbed gas samples after Kotarba (2001) and M-10** and M-28** natural gas samples from coal-bearing strata after Kotarba et al. (2019).
CR – CO_2 reduction, F – methyl-type fermentation, SM – secondary microbial, EMT – early mature thermogenic gas, OA – oil-associated thermogenic gas, LMT - late mature thermogenic gas.

active Marcel mine (Fig. 1), whose ventilation system was active during the surface geochemical survey. In addition, within the mining area of this mine, the Marklowice natural gas field was exploited for several decades. The deposit is currently in the final stage of gas exploitation. Degassing of the rock mass, carried out both in the past and at present, negatively affected the vertical migration activity of coalbed gases through the overburden. As a result, relatively low methane concentrations were measured here in the near-surface zone (Fig. 5A).

The negative correlation trend between methane and carbon dioxide for a set of methane concentrations < 30 ppm (Fig. 6B, D) may suggest the presence of microbial processes occurring in the surface zone (e.g., Potter et al., 1996; Whiticar, 1999; Le Mer and Roger, 2001; Mills et al., 2013; Vigneron et al., 2017). This trend is particularly visible in a graph constructed based on concentrations measured in the vicinity of mining shafts (Fig. 6D).

A significantly higher level of BV and TLV parameters determined for methane (Table 4) for the results obtained in 2006 as compared to 2005 may be due to technical reasons, as a consequence of the method of selecting fragments of profiles for resampling. Fragments of profiles A–A′ and B–B′ were reselected for the 2006 survey based on the results obtained in 2005. It should be noted that we selected only those profile fragments where anomalous methane concentrations had been recorded in 2005. Thus the background calculated for the results of 2006 clearly had to be higher, since it was determined only for the anomalous zones of the studied profiles.

Along the A–A′ profile, the anomalous methane concentrations were recorded at points 305–313 (Fig. 11B), in the vicinity of the secondary methane accumulation zone in the topmost part of the Carboniferous strata (Fig. 11C). The zone of anomalous carbon dioxide concentrations measured in the soil gas had shifted slightly relative to the methane anomaly towards the north fault (Fig. 11A). This may indicate that this fault played an important role in the migration of coalbed gases from Carboniferous formations to the near-surface zone. Along the A–A′ profile, anomalous decreases in methane concentration to below 1 ppm were also found (e.g., points 297–305 and 320–324) (Fig. 11B). Decreases in methane concentration at these points were accompanied by increases in carbon dioxide concentration (Fig. 11A). These relationships may indicate that microbial oxidation of methane to carbon dioxide occurred in the surface zone, as confirmed by the results of isotope studies: in near-surface gases at points 303, 304, 306, and 329, carbon dioxide predominated (CDMI values = 100%) (Table 6). The results of stable carbon isotope analyses of carbon dioxide (Fig. 11A) indicate that this gas component originated during the oxidation of methane.

The B–B′ geochemical profile cuts through two faults with small drop heights of approximately 30–50 m. These faults cut the Mississippian coal-bearing strata (Fig. 12C) and are probably pathways for gas migrating from the deep subsurface, as confirmed by anomalous concentrations of methane and carbon dioxide recorded in zones 361–365 and 390–394 (Fig. 12A, B). However, the most extensive zone of anomalous concentrations of gases appeared in the central part of the profile between points 371–378 (Fig. 12A, B). This anomaly, along with the northern anomaly, created a form of “halo anomaly” located above the elevated part of the Carboniferous coal-bearing strata. These types of near-surface anomalies are known from the geochemical literature (e.g., Jones and Drozd, 1983; Xuejing, 1992; Klusman, 1993; Tedesco, 1995; Jones et al., 2000) and indicate the presence of hydrocarbon accumulation at depth. The presence of the interpreted secondary gas-bearing zone and the direction of the increase in methane content may indicate that gas, trapped under low permeable or impermeable Miocene strata, had accumulated in the elevated part of the Carboniferous coal-bearing formations (Fig. 12C). This possibility was also indicated by the results of isotope studies. Carbon dioxide in near-surface gases of point 375 ($\delta^{13}C$ value = −20.2‰; CDMI = 100%; Table 6, Fig. 12A)

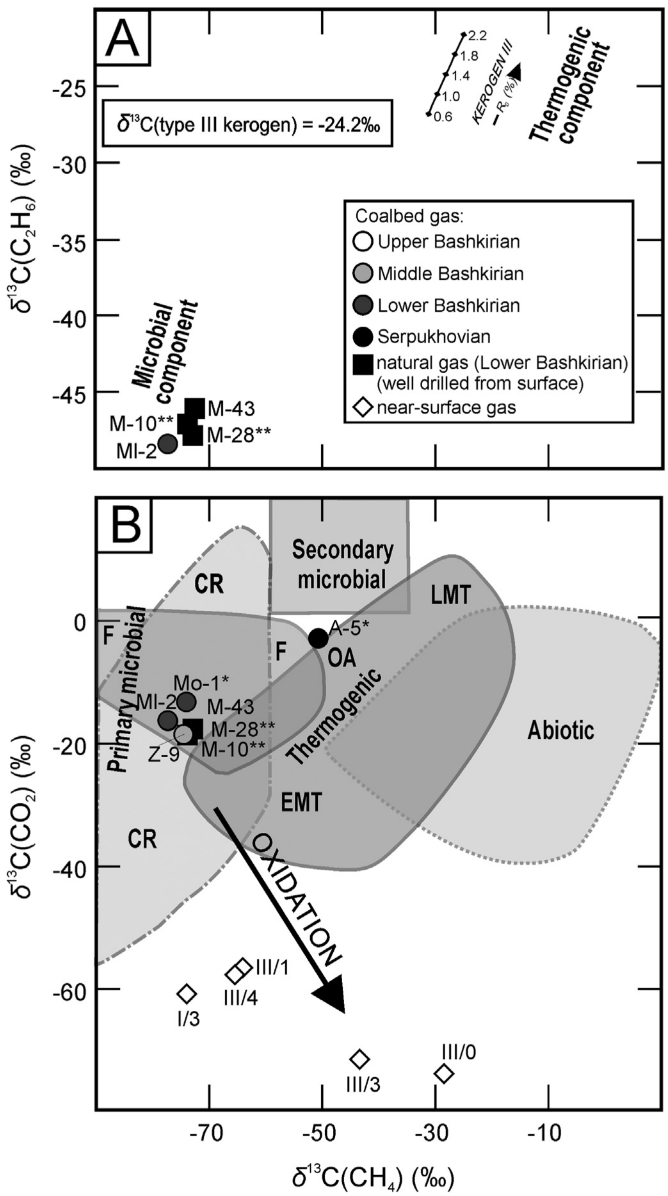

Fig. 10. Genetic characterization of analysed coalbed, natural and soil gases using (A) $\delta^{13}C(C_2H_6)$ and (B) $\delta^{13}C(CO_2)$ versus $\delta^{13}C(CH_4)$. (A) Vitrinite reflectance curves (R_o) for type III kerogen after Berner and Faber (1996). Average $\delta^{13}C$ values −24.2‰ for Type-III kerogen (six coal samples, Table 3), and (B) Compositional fields after Milkov and Etiope (2018) modified by authors. Stable carbon isotope composition of coalbed methane after Kotarba (2001). Key for analysed gas samples in Table 1, and previously analysed A-5*, J-1*, J-5*, J-50*, Mo-1*, Mo-2*, Mo-13*, Ml-1*, Z-53* and Z-55* coalbed gas samples after Kotarba (2001), and M-10** and M-28** natural gas samples from coal-bearing strata after Kotarba et al. (2019).

originated during the oxidation of methane, whereas methane at point 374 ($\delta^{13}C$ value = −71.4‰; Table 6, Fig. 12B) was generated during microbial processes, which may have occurred under favorable conditions in the surface zone (e.g., Klusman, 1993; Whiticar, 1994; Le Mer and Roger, 2001); however, a similar isotope composition was determined in sample M-43 ($\delta^{13}C$ value = −72.5‰; Table 6, Fig. 12C) taken from a depth of 192 m from the Marklowice-43 well (Table 2), which is the drilling depth of sandstones in the top part of the Mississippian coal-bearing strata. Therefore, the microbial methane found in the near-surface zone may be the result of migration from the above-mentioned gas accumulation.

The C–C′ and D–D′ profiles intersect the Marklowice IV Fault (Figs. 1A, 13). The primary gas-bearing zone is located at a depth of approximately 800 m; the secondary deep-gas zone may appear locally directly under the Miocene overburden (Fig. 13B). In this case, the Marklowice IV Fault may have been important for the retention and accumulation of methane under the impermeable Miocene overburden. Unfortunately, changes in methane concentrations recorded in the near-surface zone along the C–C′ and D–D′ profiles did not confirm the presence of free methane accumulated in fault traps, given that trace concentrations of methane were measured here (Figs. 13A, C). Nevertheless, zones of anomalous carbon dioxide concentrations appear along both the C–C′ and D–D′ profiles (points 408–410 and 426–434) precisely at the intersection of the Marklowice IV Fault with the topmost surface of the Carboniferous strata (Fig. 13A, C). At points where anomalous concentrations of carbon dioxide were found, methane concentrations clearly dropped, even below 1 ppm. Therefore, carbon dioxide may be a product of bacterial methane oxidation in the near-surface zone (e.g., Potter et al., 1996; Whiticar, 1999; Mills et al., 2013; Vigneron et al., 2017). Initially, microseepage of methane through the Miocene overburden may have occurred, followed by microbial assimilation to carbon dioxide in the surface zone, as confirmed by correlation plots for methane concentrations < 30 ppm (Fig. 6A, B). This is all the more likely because similar relationships between methane and carbon dioxide have been recorded in other parts of the USCB (Sechman et al., 2019, 2020).

The absence of anomalous methane concentrations along the E–E′ profile may be related to its location within the Marcel mine area (Fig. 1A). Natural gas exploitation carried out in the Marklowice field located within the Marcel mine and the pre-mining degassing of coal seams conducted here may have led to the degassing of the rock mass. In addition, the ventilation system of the mining excavations in the Marcel mine was not conducive to the natural vertical migration of methane through the rock overburden. Nevertheless, a gradual increase in methane concentration from trace values to 4.5 ppm at point 453 along the profile from NW to SE was characteristic (Fig. 14A). At points where carbon dioxide increased, a relative decrease in methane concentration was noted. These relationships once again confirm that microbial processes can affect the final level of methane concentrations recorded in the near-surface zone.

5.2. Genetic characteristics of coalbed gases, natural gases of wells drilled from the surface to the Pennsylvanian coal-bearing strata, and near-surface gases in the vicinity of abandoned shafts of the 1 Maja mine

5.2.1. Coalbed gases and natural gases of wells drilled from the surface to the Pennsylvanian coal-bearing strata

Within the southern part of Chwałowice Trough, coal is diverse in rank (Kotas et al., 1983). Medium-volatile bituminous coal (coking coal) lies in the southern part of the trough. The rank changes to high-volatile bituminous coal towards the north (power coal, which occurs in the vicinity of Rybnik). The volatile matter content in the coals in the study area varies between 23 and 35% (Kotas et al., 1983). This diversity in coal rank is caused by both the varying depths of coal seams and the regional trend of increasing coalification of the seams towards the south, where the coking coal occurs.

The stable carbon isotope composition of coals where the analysed coalbed gases are accumulated within the Mississippian and Pennsylvanian coal-bearing strata in the Jejkowice and Chwałowice troughs and the western part of the Main Syncline of the USCB varies from −24.8 to −23.4‰ (Table 2, Fig. 7A), which is typical of humic organic matter (e.g., Whiticar, 1996; Galimov, 2006), with vitrinite reflectance values from 0.82 to 1.24% (Fig. 7A, Table 2; Kotarba, 2001), which are characteristic of bituminous coals. Assessments of the depositional conditions and hydrocarbon potential of bituminous coals in the USCB are presented in Kotarba and Clayton (2003) and Kotarba et al. (2002).

The variability of the stable carbon and hydrogen isotope

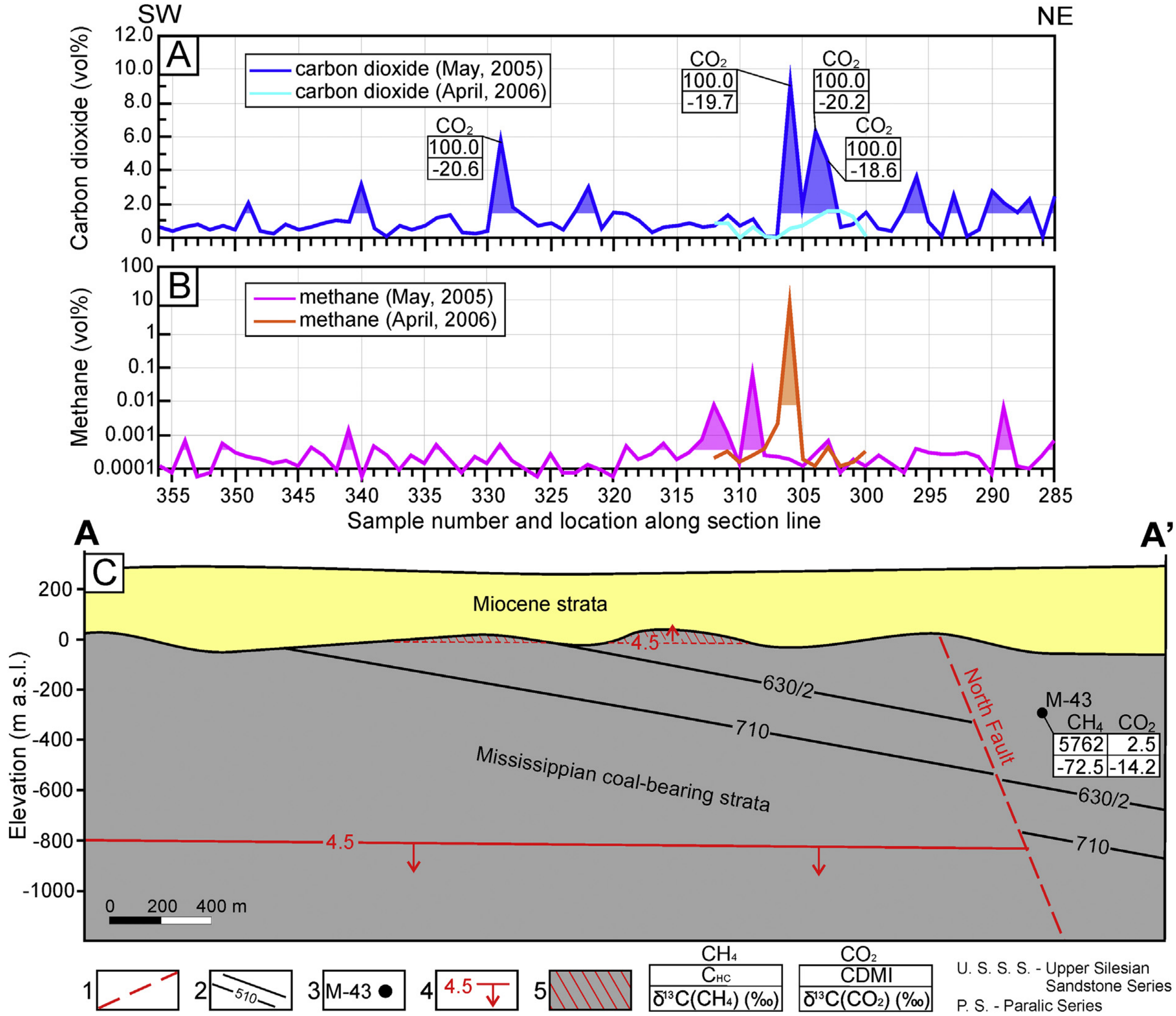

Fig. 11. Changes of (A) CO_2 and (B) CH_4 concentrations referred to (C) A – A' ("Mszana West") geological cross-section. 1 - main faults, 2 - coal seam, 3 - coalbed gas sampling site, 4 - line of methane content of 4.5 m^3/t $coal^{daf}$ with arrow indicating the direction of increasing values, 5 - shallow (secondary) coalbed methane zone.

composition of methane (Figs. 7B, 8) and stable carbon composition of ethane (Fig. 10A) and carbon dioxide (Fig. 10B) of the coalbed gases and natural gases accumulated in the top zone of the Pennsylvanian coal-bearing strata beneath the impermeable Miocene claystone and mudstone cover of the Marklowice field of the Marcel mine (Fig. 1) reveal that methane and ethane were mainly generated during microbial processes. Moreover, isotope fractionation and partitioning may have also been caused by multistage physicochemical processes of sorption/desorption and diffusion during the migration of thermogenic gases (Pernaton et al., 1996; Prinzhofer and Pernaton, 1997; Wingerning and Jüntgen, 1977) through the Mississippian and Pennsylvanian coal-bearing strata (Kotarba, 2001).

The generation of thermogenic gases (methane and an insignificant volume of higher C_2–C_4 gaseous hydrocarbons and carbon dioxide) proceeded for several Myr during the bituminous stage of coalification and finished at the end of the Variscan orogeny at the turn of the Pennsylvanian and Permian. Later, through a period of approximately 270 Ma, up to the sedimentation of the low-permeable Miocene cover, the uplifted Upper Carboniferous coal-bearing strata were subjected to erosion, denudation, and intensive degassing. In the study area, the natural degassing zone reaches a depth of approximately 800 m beneath the top of the Upper Carboniferous strata (Fig. 8A). An indigenous (autochthonous) thermogenic methane zone occurs below this level (Fig. 8A). In the coalbed methane of the Anna mine (Jejkowice Trough, Fig. 1) (A-1, A-2, A-3, and A-5 samples), a thermogenic component (Fig. 9) from the migrating thermogenic zone was observed (Fig. 8A).

Secondary microbial processes within coal basins, recognized by Kotarba (1988, 1990, 2001), Rice (1993), Scott et al. (1994), and Smith and Pallasser (1996), involved ^{12}C-enriched methane (less than −55‰) (e.g., Schoell, 1988; Whiticar, 1994) and ^{13}C-depleted ethane (−61 to −52‰) (Lillis, 2007) as characteristic microbial gases. In the southern part of the USCB, Upper Carboniferous coal-bearing strata were sealed by a Miocene cover along with infiltrative Paleocene meteoric waters containing methane-producing archaebacteria and their nutrients (Kotarba and Pluta, 2009). In the study area, the microbial ethane component dominated in coalbed and natural gases (Fig. 10A). Microbial methane and a smaller amount of ethane migrated and saturated coal seams. Both primary microbial (e.g., Z-9, Ml-2, and M-43, Table 5, Fig. 10B) and thermogenic carbon dioxide (A-5, Kotarba, 2001) occur in the analysed coalbed and natural gases.

5.2.2. Near-surface gases in the vicinity of abandoned shafts of the 1 Maja mine

The relatively high values of methane and carbon dioxide concentration recorded in the vicinity of shafts of the abandoned 1 Maja mine (Figs. 1A–E) indicate that the closed shafts I and III and the related near-shaft zones are paths for the migration of gases from the depths. In

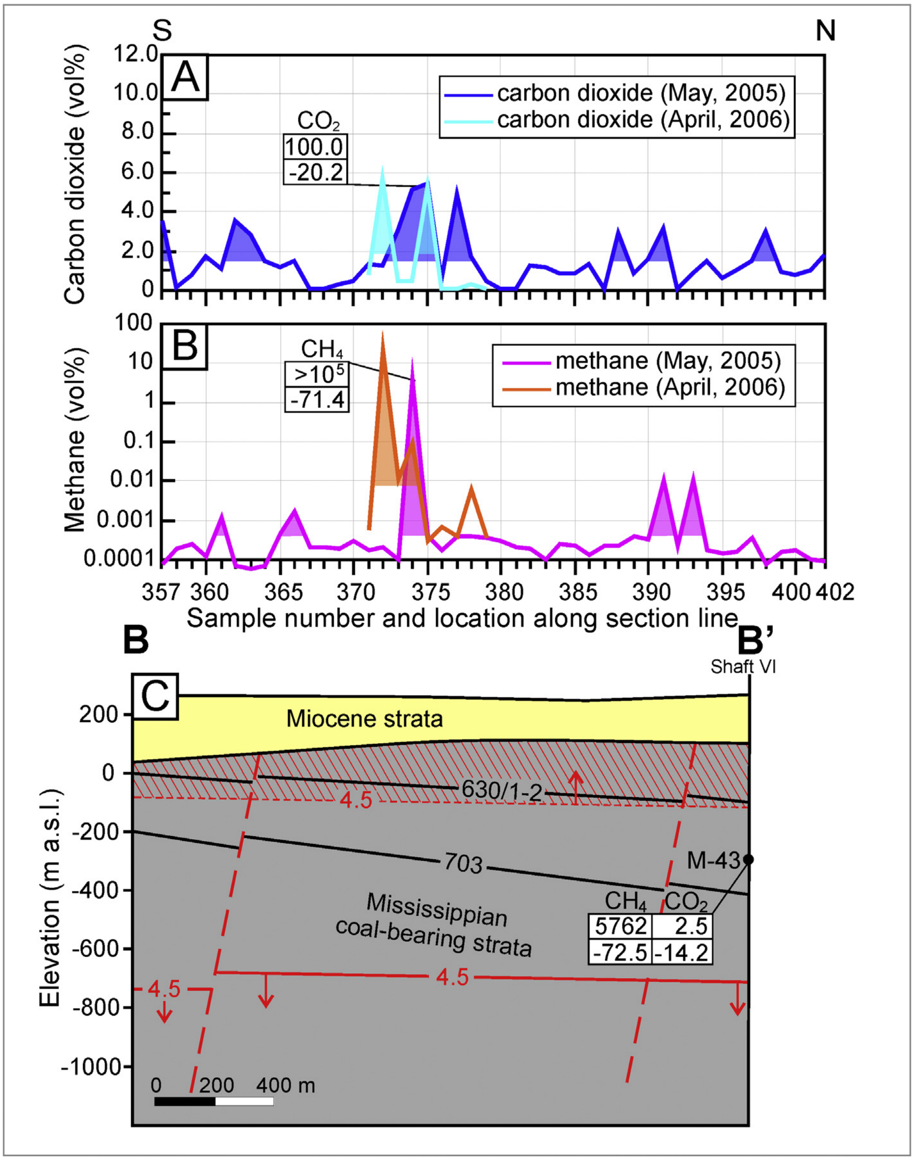

Fig. 12. Changes of (A) CO_2 and (B) CH_4 concentrations referred to (C) B – B′ ("Mszana Central") geological cross-section. Symbols as in Fig. 11.

this respect, it is possible to distinguish shaft III (Fig. 1C), in which very high methane concentrations were found, both in the sample taken from the degassing pipe (21 vol%) and in the three soil-gas samples taken in the vicinity of this shaft. High concentrations of carbon dioxide accompanying high concentrations of methane may indicate partial microbial oxidation of methane in the surface zone. This is confirmed by the cross plot of the correlation between methane and carbon dioxide (Fig. 6D). The relatively high concentration of methane recorded in the sample taken from the degassing pipe of shaft III may be the effect of gas outflow from the rock mass to the inner space of the shaft. Outflow of methane via this shaft drainage system cannot be excluded (Czaja, 2009). The main element of the degasification system of abandoned shafts is a degassing pipeline approximately 25 m long and approximately 0.2 m in diameter, embedded inside the shaft, which extends below the clay insulation plug (Czaja, 2009). This pipeline sticks out about 3 m above the concrete slab closing the shaft. Thus, rather than accumulating in the inner space of the shaft, methane is blown out into the atmosphere. According to Czaja (2009), a degassing system of this kind is effective, as confirmed by the results of methane concentration measurements of the gas flowing out of the degassing pipeline of the shaft III of the 1 Maja mine in 2004, when the methane concentration ranged from 34 to 60 vol% (Czaja, 2009). Undoubtedly, the outflow of methane into the atmosphere through a degassing pipeline significantly reduced the potential for methane migration through the fractures of rock mass in the vicinity of the shaft. Nevertheless, methane migration along these paths has not been completely stopped, since a relatively high concentration of methane was found in soil-gas samples taken in the zones of two closed mining shafts (Fig. 1A–C). The results of isotope studies indicate the deep origin of these gases; the results of stable carbon isotope analyses of the methane of near-surface gases in the vicinity of shafts I and III of the 1 Maja mine (Fig. 1A–C) reveal that this gas component, like coalbed gases from the Marcel, Moszczenica, Jastrzębie, and Zofiówka mines and natural gases from the Marklowice field of the Marcel mine (Fig. 9A, B), was generated during microbial processes (Fig. 9A). Enrichment of carbon dioxide with ^{12}C-isotopes (from −65.3 to −28.5‰) and methane in ^{13}C-isotopes (from −74.1 to −56.8‰), along with an increase in carbon dioxide concentration (from 1.33 to 3.91) and CDMI values (from 5.9 to 57.1) of gases in the vicinity of shaft III of the 1 Maja mine (samples 1, 3, and 4) compared to gas from the degassing borehole chimney (sample 0) (Tables 5, 6, Figs. 1C, 10B), was caused by the oxidation of microbial methane in the near-surface zone.

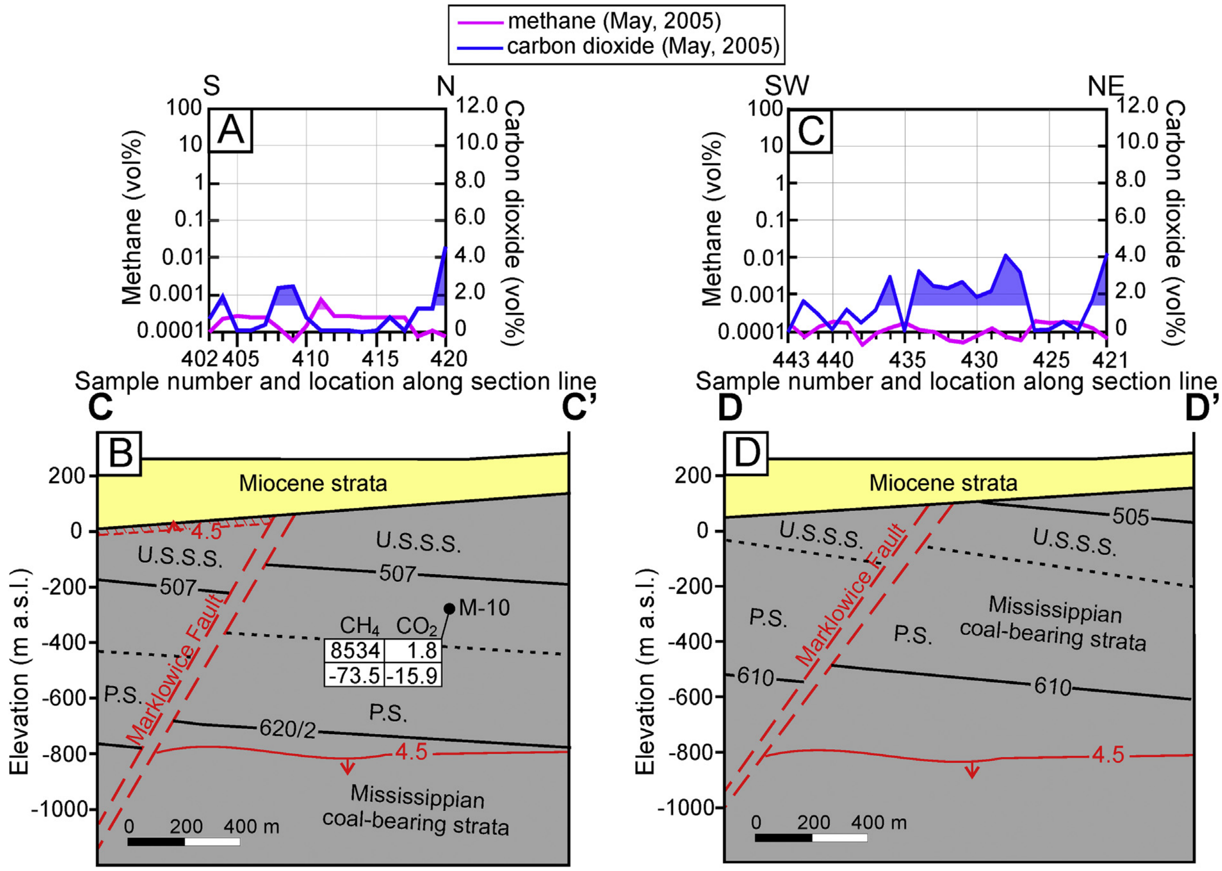

Fig. 13. Changes of (A and C) CH_4 and CO_2 concentrations referred to (B) C - C′ (”Marklowice”) and (D) D - D' (”Wodzisław”) geological cross-section. Symbols as in Fig. 11 (U.S.S.S. - Upper Silesian Sandstone Series, P.S. - Paralic Series).

6. Summary and conclusions

In 2005 and 2006, a surface geochemical survey was carried out in Chwałowice Trough in the western part of the USCB. Soil-gas samples were taken from a depth of about 1.2 m along the lines of five geochemical profiles (A–A′, B–B′, C–C′, D–D′, and E–E′) located in the area of the abandoned 1 Maja mine and in directly adjacent areas (Fig. 1). A geochemical survey was also carried out in the vicinity of 4 abandoned and remediated mining shafts. In 223 soil-gas samples, the chromatographically determined concentrations of methane and carbon dioxide ranged from 0.5 ppm to more than 22 vol% and from 0.04 to more than 9 vol%, respectively. In 11 selected soil-gas samples with elevated methane concentrations, ethane and propane concentrations as well as stable carbon isotope composition in methane and carbon dioxide were analysed. The results of these tests were compared with molecular and isotopic compositions determined for gas samples taken from coal seams and for samples taken from boreholes drilled from the surface (Marklowice field of the Marcel mine).

Statistical analysis and changes in methane and carbon dioxide concentrations measured in soil-gas samples, supplemented with the stable carbon isotope composition of methane and carbon dioxide for selected surface and deep subsurface samples, integrated with the model of geological structure, genetic type, and maturity of coals and of distribution of methane contents in coal seams, enabled us to draw the following conclusions:

a) Typical humic low- and medium-volatile bituminous coals occur in the Mississippian and Pennsylvanian coal-bearing strata in the main study area (SW part of the Chwałowice Trough) and adjacent areas (SW part of the Jejkowice Trough and W part of the Main Syncline of the USCB).
b) Generation of thermogenic gases (methane and an insignificant volume of higher C_2-C_4 gaseous hydrocarbons and carbon dioxide) within the Mississippian and Pennsylvanian coal-bearing strata proceeded for several Myr during the bituminous stage of coalification and finished at the end of the Variscan orogeny. Later, through a period of approximately 270 Myr, up to the sedimentation of the impermeable Miocene overburden, the uplifted Upper Carboniferous coal-bearing strata were subjected to erosion, denudation, and intensive degassing. In the study area, the natural degassing zone extends to a depth of approximately 800 m beneath the top of the Upper Carboniferous strata. An indigenous (autochthonous) thermogenic methane zone occurs below this depth.
c) The coalbed and natural gases (mainly methane) occurring in the secondary zone of accumulation in the top zone of the Pennsylvanian coal-bearing strata beneath the Miocene cover were mainly generated during microbial processes. However, at least some of them may have originated during thermogenic processes and migrated from deep coal-bearing strata.
d) The reason for the relatively increased concentrations of methane and carbon dioxide recorded in the soil-gas samples taken along the A–A′ and B–B′ profiles, compared to samples taken from the other profiles, may be their location in the central part of the abandoned mining area of the 1 Maja mine. Stoppage of drainage and ventilation systems may have caused gas accumulation in mine excavations and in porous sedimentary rocks, and then intensified their migration to the surface through a fault and fracture system.
e) Anomalous methane concentrations recorded along the A–A′ profile may be associated with the presence of a secondary methane accumulation zone located at a depth of approximately 300 m in the top part of the Carboniferous coal-bearing formations; the northern fault may play an important role in the microseepage of gases to the

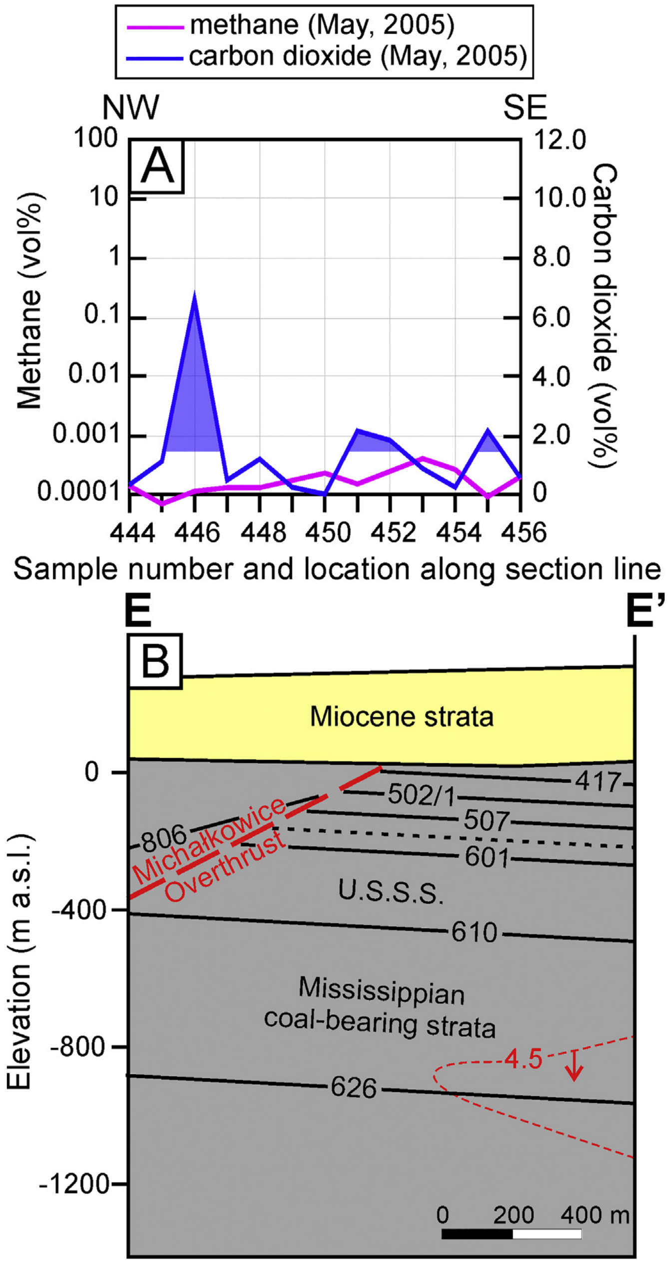

Fig. 14. Changes of (A) CH_4 and CO_2 concentrations referred to (B) E - E' ("Marcel") geological cross-section. Symbols as in Fig. 11 (U.S.S.S. - Upper Silesian Sandstone Series, P.S. - Paralic Series).

near-surface zone.

f) Zones of anomalous concentrations of methane and carbon dioxide appearing in the central part of the B–B′ profile form a "halo" anomaly above the elevated part of the Carboniferous strata. This type of anomalous zone indicates the presence of free methane accumulation in the elevated top part of the Carboniferous formations under the low-permeable, autochthonous Miocene strata. The connection of near-surface gas with subsurface gas was confirmed by similar stable carbon isotope composition in the methane recorded in the soil-gas sample (sample 374, $\delta^{13}C$ value −71.4‰) and in the gas sample from the borehole reaching Carboniferous formations (sample M-43, $\delta^{13}C$ value −72.5‰).

g) Increases in carbon dioxide concentrations measured in soil-gas samples and the accompanying decreases in methane concentration were most often the result of microbial methane oxidation, as confirmed by the results of stable carbon isotope composition.

h) Abandoned mining shafts I and III and their adjacent zones are convenient paths for gas migrating from deep subsurface coal-bearing strata. The degassing system of closed and remediated mining shafts is insufficiently effective, as indicated by the relatively high concentration of methane recorded in the soil-gas samples taken in the vicinity of abandoned mining shafts I and III located in the area of the former 1 Maja mine.
1 Maja mine.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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