

# Monitoring of methane and CO<sub>2</sub> from selected sources in the environment in the Czech Republic

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*Abstract:* Some greenhouse emissions – methane and CO<sub>2</sub> – were tracked in three locations in the Czech Republic and one of these is the deactivated coal mine in the region of Ostrava Karvina, the landfill in Nasavrky and the composting plant in the surroundings of Pardubice in Drazkovice. A mobile analyser unit ECOPROBE 5 was used for the measurements. It was realized that in case some technical measures were implemented for the methane recovery and subsequent processing, there is neither danger of contamination in the surroundings, nor risk of explosion. Composting plant is a long-term source of CO<sub>2</sub>. Its emission concentration at the surface level reaches tenths of volume percentage. Methane is produced in minimal concentration.

*Key-Words:* Methane, Carbon dioxide, Landfill gas, Firedamp

## 1 Introduction

Methane is a natural part of the natural environment, found in both the atmosphere and in water, as well as in the ground. It arises from a natural biological process where oxygen is absent, and have a reductive nature.

Natural sources of methane gasses can be found in all kinds of wetlands, wild and free-roaming animals, and in the exchange of gasses between the atmosphere and the oceans.

Anthropogenic sources of methane, however, are a serious problem, in which its volume in the atmosphere has been intensifying markedly. Ranked among them above all is the breeding of domestic livestock, the production and treatment of fossil fuels, landfills, compost boxes, fermentation operations and several chemicals and waste water treatment plant. All of the aforementioned contribute to the production of methane together with other CO<sub>2</sub> greenhouse gasses, which are released into the atmosphere where its ability to absorb infrared radiation consequentially contributes towards warming of atmosphere, as well as methane participates in damaging the Earth's ozone layer. A consequential risk when being in the proximity of sources of methane is the danger of explosion, which can threaten when mixed with oxygen in concentrations in the range of 5 to 15 % (Medis-Alarm – database of hazardous substances, Medistyl, Prague, Czech Republic). The growth in the amount of carbon dioxide in the atmosphere is regarded

as the main cause of global warming, resulting first and foremost from the burning of fossil fuels, but also during composting.

Monitoring concentrations of methane in various emissions – in bio- and mine gasses and suchlike, has a big significance not only from a safety standpoint, but also an economical one. For one thing, when the amount of methane in the gas phase reaches a sufficient concentration, it can be used as a combustible just the same as petrol or diesel, and for another to gas engines during the production of electrical energy [1].

The scope and focus area of this work is firstly on the presence of methane in areas burdened with mining activity, and secondly on greenhouse gas emissions from municipal landfills from waste processing plants including biodegradable waste.

Two approaches can be utilized to determine volatile organic compounds the atmosphere especially in the field. The first is to collect a representative sample of contaminates at the site and then to have the samples evaluated by standard laboratory procedures, such as gas chromatography. This approach, however, does have some shortfalls, in particular the time spent between sampling and evaluating the samples, the difficult pinpointing of the analysis of the individual and specific samples as well as the sometimes difficult handling of the samples under laboratory conditions. Also, when mapping large areas it is necessary to transport large numbers of samples to the laboratory, many of which

when analysed in the laboratory do not contain any of the desired contaminants also, giving rise to unnecessary costs to the project although producing accurate and reliable laboratory results.

The second method, now more commonly in use, is by means of an in-situ mobile analyser. Thanks to their mobility and ease of operation, the operator can easily perform measurements at the site. The amount of the contaminant can be analytically evaluated almost instantly, furthermore, the operator knows exactly where to take samples for future analysis in the lab. The measured values can then be stored in memory or directly displayed on the screen. When the operator finds the presence of a contaminant which is higher than permitted levels, the appropriate corrective action can be implemented or an alarm can be raised.

In this work the ECOPROBE-5 (RS Dynamics, Prague, Czech Republic) mobile analyzer of volatile organic compounds was used.

## **2 Localities in which a significant amounts of methane and carbon dioxide are produced**

During the course of this work three case studies were carried out which monitored the presence of methane and CO<sub>2</sub> to determine the practical uses of a mobile atmospheric analyzer.

### **2.1 An area of dormant mining activity**

Significant sources of methane are present not only in areas that are being intensively mined, but also in areas that have been mined out. Methane, as the main component of mine gas emissions in coal seams, is released even after the deposits in the mine have been extracted [2].

Mining activities in the Ostrava-Karvina district, meaning in the region in which the authors first collected their measurements, slowed down and eventually were halted in 1991 [3].

Old mines even today influence buildings lying inside the safety zones – regarding both the static of the buildings and also the release of methane into the buildings within the proximity of the mines.

This, which in the past wasn't adequately located and secured, was in the Czech Republic and even in the world the cause of many out of the ordinary occurrences connected with sudden gas outbursts and explosions in buildings [4]. Underground engineered networks spread methane under pressure far along the way of least resistance – through tectonic failure, regolith formations being insufficiently gastight, and mainly in the past in the unsystematic and insufficient demolition and

securing of old mineshafts and adits, to which methane circulation occurs even inside the safety zones around mining shafts.

Closed and demolished mines thus present a safety and ecological risk. There have been dozens of cases of methane leakage in Ostrava that resulted in an immediate evacuation of people or explosions causing serious bodily injury, for example the methane explosion which took place on the 20th of April, 1999 in Ostrava, the May 2nd, 1996 Hugo mineshaft explosion also in Ostrava, and gas filling the cables and shafts in Frydlant in the underpass.) Old mine works located in built-up urban areas pose a risk not only for being natural collectors for the conduction and accumulation of methane, but are also the cause of surface cave-ins [7–10] – for example, the collapse of the entrance to a mine-shaft on November 17th, 1973 in Silesian Ostrava, created a crater of about 3500 m<sup>3</sup>.

There are no written records for many mining shafts from the 19th or 20th centuries, and those which have been marked and designated as old mines and former mining shafts only significantly lower the real estate value of the property and surrounding real estate. Releases of methane into the atmosphere, therefore, present a serious safety risk for the population, and are coupled with high costs regarding the prevention of and dealing with emergency situations. It is therefore necessary to regularly follow the content of methane in the atmosphere and also that of selected sites which fall outside the monitoring network.

#### **2.1.1 Description of the Orlova reference sites**

A significant European coal deposit is located in the Hornoslezska basin. It covers a land area of over 7 000 km<sup>2</sup> and has a tectonically predetermined triangular shape. It is situated on both the territories of Poland and the Czech Republic, lying roughly between the towns of Ostrava, Cracow and Gory Tarnowskie, the southwestern parts of which are located in the Czech Republic part of Upper Silesia and represent an amount of 1550 km<sup>2</sup> of carbon coal [5].

One area significantly damaged by mining activities was the ancient town of Orlova, located in the south-western part of the Czech Hornoslezska basin. For example, the company OKD, DPB Paskov, the Czech Republic (Dulni pruzkum a bezpecnost – Exploration and Mining Safety) measured very high concentrations of methane emissions at a playground in December, 2004 – with measurements of well over 67 % of methane concentration. This emergency situation is now at present solving the way how tapped methane can be used in the production of electricity.

## 2.2 Municipal Waste Landfill site

Landfilling municipal solid waste is relatively the least demanding way of waste disposal, however it creates a wide range of complications, the most important of which is the development of landfill gas in the sites. The gradual biological course through which organic waste degrades develops landfill gas spontaneously in four phases.

In the first phase, atmospheric aerobic microorganisms degrade organic materials in the presence of oxygen, producing CO<sub>2</sub> gas. Afterwards acidic fermentation occurs, when with the help of anaerobic organisms aliphatic acids are produced. The gaseous products, in addition to the CO<sub>2</sub>, even contain measurable quantities of hydrogen. During the third phase of biological decomposition, the initial phases of methanogenic microorganismic development starts, leading to an anaerobically stabilized methanogenic phase with widespread methanogenic microorganismic culture. A stable formation of methane takes place in the final stage, accompanied with a simultaneous production of CO<sub>2</sub>. Moisture levels in the garbage have a decisive influence on the whole process and on the creation of the gasses.

Gases produced in the landfill sites create pressure and escape into the environment [6]. Here, there is the risk of an explosion, caused by the innate thinness of naturally occurring aerobic soil layers. If the concentration of methane gas in the dump reaches significantly high levels, there may be the possibility of it becoming an important local source of energy. The Nasavrky municipal waste landfill, which has measured such high levels, has been in operation since 1994. It has a total capacity for approximately 400 000 m<sup>3</sup> of waste, and the landfill gas produced here is used to produce electricity.

## 2.3 Composting centre

Composting uses the process of aerobic biological decomposition, the aim of which is to quickly disintegrate the organic components of the waste and convert it to stable mature compost or humus substances for agricultural uses. During this process, operates aerobic organisms for oxygen, which serves as a nutrient and energy source. Part of carbon cell tissue microorganisms is a part shall be released as CO<sub>2</sub>. Composting takes advantage of the process of aerobic biological decomposition, the objective of which is the fastest decomposition of organic waste components and to transform them into a stable mature compost or humus substance which is applicable for plant growth. During this time, aerobic microorganisms are affected by oxygen, which serves as protein and a source of energy. One part of the carbon cellular tissue of the microorganism binds itself, the other part is released as

CO<sub>2</sub>. It occurs in hydrolyzed protein, saccharide and fat. A raise in temperature is also produced, when the products of hydrolysis are partly changed into organic acids and CO<sub>2</sub>.

Composted waste disposes of itself; furthermore it allows original materials to return to their inherent state in the food chain.

The compost centre in Drazkovice has been in operation since 2004, processing biological waste from the town of Pardubice and its surroundings. It handles grass, branches, leaves, sediment and sludge from water sewage plants, and green waste from recycling centres. It has the capacity to process 9 000 tonnes a year.

## 3 Experimental

### 3.1 Instrumentation

The portable analyzer ECOPROBE 5 (RS DYNAMICS Ltd., Prague, Czech Republic) equipped with a PID and IR detector (which enables automatic recording of measured places position using GPS) was used to measure greenhouse gas emissions from selected sources. Methane and carbon dioxide content was monitored using a standard infrared detector measuring procedure, which consisted of three phases – from cleaning the measuring cell, to rinsing the sample, and to its own measurements. The detector measures methane and CO<sub>2</sub> according to firm documentation in the range of 0–500 000 ppm with a detection limit of 20 ppm; allowing measurement in units of ppm and in mg/ m<sup>3</sup>.

A controll analysis of sources of methane in prepared model gas mixtures was carried out with the GC 2010 Shimadzu gas chromatograph. Separation took place in a ZB-1 (30 m × 0.25 mm; internal diameter of 0.5 μm) capillary column with a stationary phase of 100% polydimethylsiloxane and using FID detector.

Certified standard gas mixtures (Linde, Technoplyn, Czech Republic) were used to calibrate in concentrations of 2.25 % vol. and 30 % vol. of methane respectively, mixed with synthetic air and supplied in 10-litre pressurized containers.

Before any actual measurements on the accuracy of the analyzer took place, the gas mixtures were placed by the analyzer into gas-tight, plastic bags lined with aluminum foil.

### 3.2 Controlled tests on the analyzer.

The device was first tested in the laboratory using a calibration gas mixture with a 2.25 % concentration of methane in synthetic air before any practical use in the field (Linde, Technoplyn certified laboratory). An infrared detector was used to monitor the content of

methane. The cell was cleaned using clean air before each measurement.

The program QC Expert 3.0 was used to statistically analyze the results of ten repeated measurements. The calculated statistical characteristics are as follows:

- Median: 2.36 % vol.
- Arithmetic mean: 2.36 % vol.
- Standard deviation: 0,021 % vol.
- Confidence interval (95 %): lower limit of 2,34 % vol., vol. upper limit of 2.37 % vol.

The results mentioned above show that the accuracy in measurement was adequate—documenting a low value of standard deviation; the median and arithmetic mean differ from the correct declared values with a positive error in the value of 4.9 %, which is considered acceptable regarding accuracy when analysing such gasses.

Table 1 illustrates how accuracy of measurements were obtained, even in the case of further concentrations of methane. Measured gas mixtures of methane with air were prepared in bags by mixing natural gas with air. Their concentrations were probed using the independent gas chromatography method, and then lastly measured using the ECOPROBE 5. From the values shown in Table 1, it is clear that the percentage of error in measuring does not exceed 6 % rel. and in all cases show positive results.

## 4 Results and interpretation of field measurements

Three series of measurements were carried out in three different locations in the Czech Republic where it was deemed important to monitor levels of methane and CO<sub>2</sub> with a standpoint on protecting the environment and to safeguard the local population – the abandoned Orlova and Ostrava mining areas, the Nasavrky municipal landfill site in the Pardubice region, and the Pardubice-Drazkovice bio-waste compost center.

### 4.1 The playground location in Orlova

Initially monitored in 2004, air samples in the city of Orlova were found to be heavily contaminated with methane, by up to 67 % vol. Intervention implemented by the Ministry of the Environment, the Czech Mining Institute, and other companies and organizations involved in and who deal with air quality analyses have made a marked improvement on the site - measurements taken in 2007 during the course of this work showed (Table 2) that the release of methane in the area had been almost completely eliminated (the registered value lay below the detection limit), thereby significantly increasing the quality of life and especially the safety of

the population in the area. Gas samples were taken 50 cm below the ground surface.

### 4.2 The Nasavrky site

It is clear from the results found at the municipal landfill site (Table 3 and Fig. 1) that surface methane emissions are minimal. Concentrations around 10 cm below the surface range from  $1 \cdot 10^3$  to  $8 \cdot 10^3$  ppm (0.1 to 0.8 % vol.) CH<sub>4</sub>; in the immediate vicinity of a vertical gas pipeline covered with coarse gravel readings were more in the  $1,8 \cdot 10^4$  ppm (1.8 % vol.) CH<sub>4</sub> range. This condition can be influenced by the fact that gas emerging at this landfill is tapped and used to produce electricity. The vertical gas pipeline, which is normally sealed closed with a gas-tight head, measured high concentrations of methane, to the extent of some  $1,5 \cdot 10^5$  to  $6,2 \cdot 10^5$  ppm (15 to 62 % by volume) CH<sub>4</sub>; during the process of taking measurements at this site, readings at a new phase of the landfill were significantly lower at  $1,51 \cdot 10^5$  to  $3,74 \cdot 10^5$  ppm (15.1 and 37.4 % vol.). Vertical gas wells are interconnected with plastic pipelines and conduits placed in the cavity of the landfill site, which allows the forming methane to be tapped and drawn to the cogeneration unit. The electricity produced is supplied to the power grid.

To summarize, methane gas emissions at this landfill pose only a minimal risk to the environment and pose no danger of exploding when the plant is run according to standard operating procedures.

In the different measuring points of the landfill was found concentrations CO<sub>2</sub> between  $10^3$  ppm and  $10^5$  ppm (Fig. 2); average content of CO<sub>2</sub> in the atmosphere is about 380 ppm.

### 4.3 The Pardubice – Drazkovice site

Biologically decomposing waste is usually processed into compost at compost centres. Given that the humus being produced uses the aerobic process, it is possible to assume that from well-aired dump sites, first and foremost will be the escape of CO<sub>2</sub> gas. Methane will form only in exceptional cases when there is a lack of oxygen.

The measured values (Table 4) confirmed this assumption. Miniscule amounts of methane were found at only eight points from a total of 19 measuring points (Fig. 3), and no more than in tens of ppm (in thousands volume). At all measuring stations an increased amount of CO<sub>2</sub> was found to be no more than from tens to units in decimal places. Given that compost is a long-term continuous source of CO<sub>2</sub>, it can be concluded that it significantly contributes to the increase of greenhouse gas concentrations in the atmosphere (Fig. 4).

## 5 Conclusion

Three case studies were conducted during the course of this work which tracked the occurrence of methane and CO<sub>2</sub> in various locations around the Czech Republic in order to verify the possibilities of the practical usages of a mobile air analyzer and also to quantify the production of methane and carbon dioxide in densely populated areas where mining activities have taken place, and at municipal waste and compost sites. Measurements showed that when technical interventions were implemented, the situation improved significantly – the release of methane into the surrounding areas where mining had taken place were almost completely eliminated, and the quality of life of the people living here increased. Landfill and compost sites hardly contribute, in terms of methane emissions, any pollution to the environment, nor pose a significant risk of explosion.

Increased CO<sub>2</sub> content was found at all measuring points at both municipal landfill and even at the compost site. Given that this is a long-term, continuous source of CO<sub>2</sub>, it can be concluded that it contributes increasing concentrations of greenhouse gases to the atmosphere.

The ECOPROBE-5 (RS-Dynamics, Prague, Czech Republic) analyzer of volatile organic compounds is very effective in detecting and localizing concentrations of air contaminants. The device provides a relatively cheap way of conducting any work involving exploration and decontamination.

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Table 1. Determination of both the methane gas chromatographs and mobile analyzer.

Meas. number	GC determination [% of vol.]	Analyzer determination [% of vol.]	Relative error [%]
1	32,90	33,48	1,80
2	27,40	28,10	2,55
3	15,32	15,48	1,04
4	6,45	6,80	5,43
5	4,06	4,18	2,96
6	2,89	2,93	1,38
7	2,00	2,06	3,00
8	1,45	1,48	2,07

Table 2. The concentration of methane measured in the monitored location after corrective interventions were implemented; basic experimental conditions

Meas. number	Methane average [ppm]	Ambient pressure [torr]	IR temperature [°C]
1	9.999984E-05	766.56	17.81
2	9.999984E-05	766.58	17.73
3	9.999984E-05	766.68	17.65
4	9.999984E-05	766.75	17.59
5	9.999984E-05	766.80	17.55
6	9.999984E-05	766.76	17.52
7	9.999984E-05	766.71	17.46
8	9.999984E-05	766.69	17.35
9	9.999984E-05	766.68	17.24
10	9.999984E-05	766.70	17.14
11	9.999984E-05	766.77	17.09
12	9.999984E-05	766.74	17.00
13	9.999984E-05	766.78	16.88
14	9.999984E-05	766.70	16.73
15	9.999984E-05	766.83	16.60
16	9.999984E-05	766.81	16.48

Note: The experimental data contained in the table are in the form of original output from the Ecoprobe 5 device.

Table 3. Methane and CO<sub>2</sub> concentrations measured at the municipal waste landfill site; basic experimental conditions

Meas. number	Methane average [ppm]	CO <sub>2</sub> average [ppm]	Ambient pressure [torr]	IRT [°C]
1	6.266271E+05	5.161475E+05	719.30	20.69
2	3.073388E+03	1.842326E+03	719.36	20.85
3	8.030229E+03	3.895802E+03	719.33	20.99
4	9.999984E-05	1.592605E+03	719.23	21.08
5	3.737618E+05	4.621990E+05	719.24	21.11
6	1.412444E+03	2.363105E+03	719.25	21.21
7	1.516165E+05	2.030845E+05	719.30	21.30
8	9.999984E-05	1.545730E+03	719.26	21.40
9	9.999984E-05	1.534731E+03	719.20	21.46
10	9.999984E-05	1.393770E+03	719.15	21.58
11	5.993883E+05	5.452466E+05	719.12	21.53
12	5.333709E+03	1.762335E+03	719.24	21.61
13	6.169921E+05	5.423540E+05	719.24	21.54
14	1.838813E+03	1.672984E+03	719.30	21.61
15	9.999984E-05	1.597914E+03	719.27	21.66
16	9.999984E-05	1.455341E+03	719.25	21.73
17	5.839904E+05	5.460939E+05	719.26	21.66
18	6.200769E+05	5.237869E+05	719.25	21.68
19	5.963750E+03	1.889026E+03	719.26	21.76
20	6.151864E+05	5.449049E+05	719.42	21.70
21	5.912987E+03	1.888353E+03	719.29	21.84
22	6.124066E+05	5.555843E+05	719.35	21.73
23	6.117172E+05	5.581136E+05	719.31	21.80
24	1.788256E+04	1.269984E+04	719.42	21.84

25	9.999984E-05	1.676375E+03	719.38	21.87
26	9.999984E-05	1.371741E+03	719.49	21.92
27	9.999984E-05	1.322339E+03	719.28	21.98
28	9.999984E-05	1.277386E+03	719.16	21.98
29	2.477059E+02	1.358409E+03	719.06	21.98
30	9.999984E-05	1.257399E+03	719.31	22.06

IRT – temperature of IR cell

**Note:**

The experimental data contained in the table are in the form of original output from the ECOPROBE 5 device.

Measurements no. 2, 3, 4, 6, 8, 9, 10, 12, 14, 15, 16, 19, 20, 21, 24x, 25, 26, 27, 28, 29\*, 30 - were taken from the surface of the landfill.

Measurements no. 1, 5\*\*, 7\*\*, 11, 13, 18, 22, 23 were taken at the pipeline.

\* – in close proximity to the pipeline

\*\* – at the new phase of the landfill.

Table 4. The concentration of methane and CO<sub>2</sub> measured at the compost centre; basic experimental conditions.

Meas. number	Methane average [ppm]	CO <sub>2</sub> average [ppm]	Ambient pressure [torr]	IR temperature [°C]
1	9.999984E-05	1.396841E+03	746.30	22.85
2	9.999984E-05	1.579699E+03	743.84	20.79
3	9.999984E-05	1.602400E+03	743.85	20.64
4	9.999984E-05	1.521845E+03	743.87	20.50
5	9.999984E-05	3.262560E+03	743.32	20.04
6	9.999984E-05	1.707692E+03	743.26	19.83
7	2.967034E+01	6.872938E+03	743.22	19.64
8	9.999984E-05	2.971713E+03	743.24	19.40
9	2.744669E+00	7.175774E+03	743.28	19.17
10	9.999984E-05	4.285667E+03	743.32	18.28
11	9.999984E-05	2.065585E+03	743.37	18.05
12	1.350054E+01	7.017792E+03	743.29	17.82
13	9.999984E-05	4.315320E+03	743.36	17.62
14	9.999984E-05	1.482023E+03	743.70	17.34
15	4.743554E+01	3.978467E+03	743.71	16.91
16	9.019339E+02	1.045557E+04	743.77	16.67
17	9.999984E-05	1.758225E+03	743.89	16.43
18	2.673212E+01	3.271621E+03	743.96	16.16
19	1.922722E+01	3.955014E+03	743.97	15.97

IRT – temperature of IR cell

Note: The experimental data contained in the table are in the form of original output from the ECOPROBE 5 device.

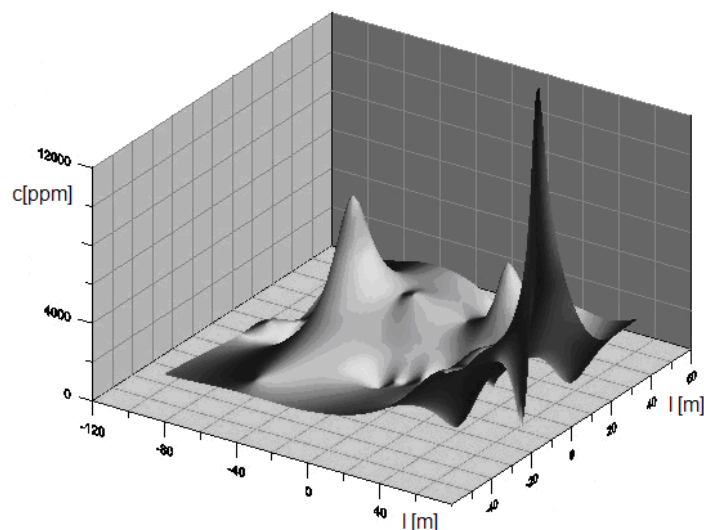


Fig. 1 A 3D-visualization of measured values of the surface concentration of methane at the municipal waste landfill site.

$c$  – concentration of methane [ppm]  
 $l$  – distance of measurement points

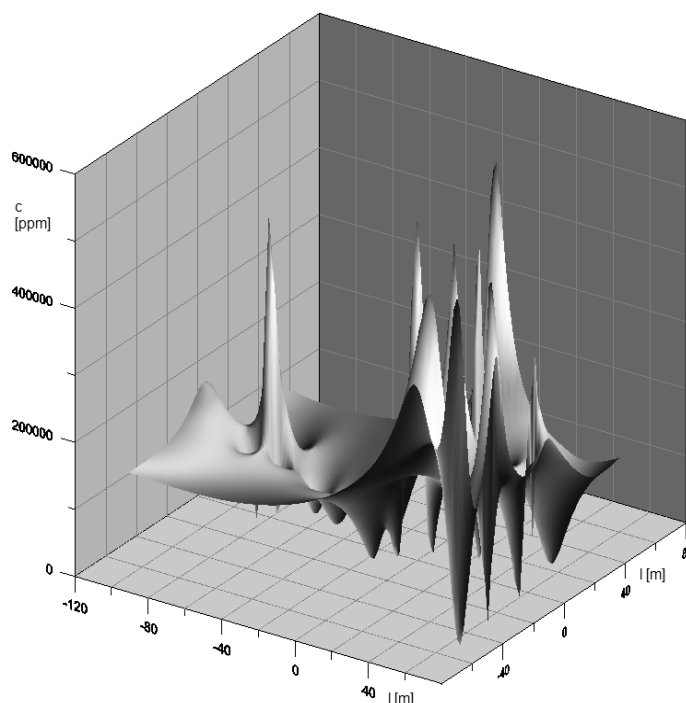


Fig. 2 A 3D-visualization of measured values of the concentration of CO<sub>2</sub> at the municipal waste landfill site.

$c$  – concentration of CO<sub>2</sub> [ppm]  
 $l$  – distance of measurement points [m]

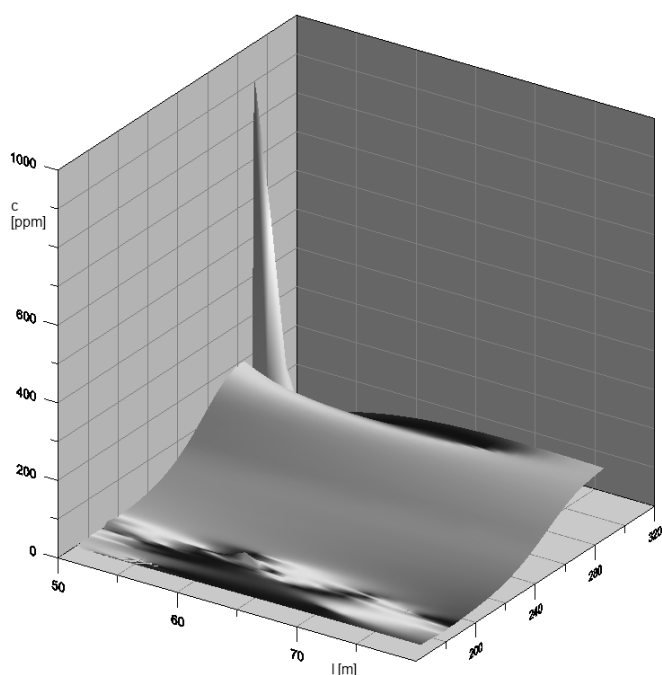


Fig. 3 A 3D-visualization of measured values of the concentration of methane at the compost site.

$c$  – concentration of methane [ppm]  
 $l$  - distance of measurement points [m]

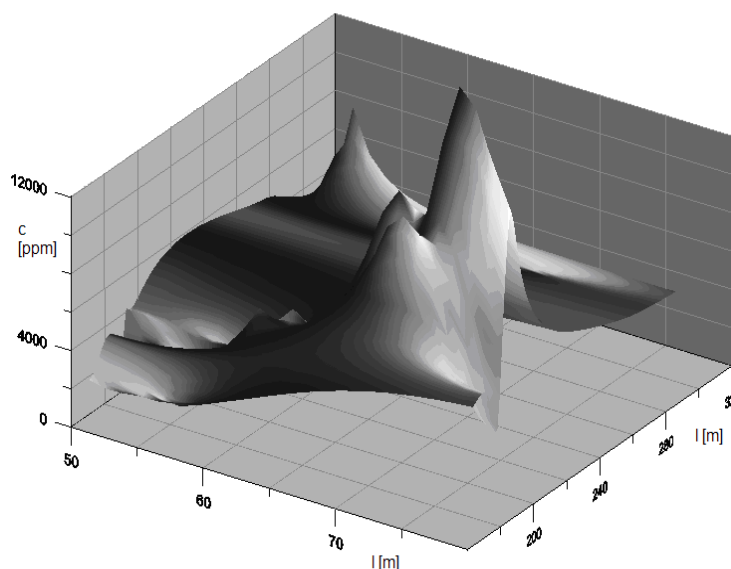


Fig. 4 A 3D-visualization of measured values of the concentration of CO<sub>2</sub> at the compost site.

$c$  – concentration of CO<sub>2</sub> [ppm]  
 $l$  - distance of measurement points [m]

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