Assessment of the mercury emissions from burning mining waste dumps

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One of the sources of atmospheric emission of gases such as carbon monoxide, carbon dioxide, sulfur dioxide, methane, hydrogen sulfide and hydrocarbons are mining waste dumps with the most intensive emission from the burning mining waste dumps.

The performed analyses leave no doubts: the burning dumps are also the source of mercury emissions and, therefore, it is necessary to define the scale of this phenomenon.

For a proper assessment of the environmental risk which can occur and to which the environment and local inhabitants can be exposed, it is important to define the size of the emission of mercury compounds from these objects. Despite the potential threats so far no measurements of mercury concentration which would allow quantifying this phenomenon have been done. The analyses presented in this article fill this gap. Additionally, initial calculation of annual mercury emissions from burning coal mining waste dumps in Poland is presented.

Key words: *coal mining waste dump, mercury emission, recultivation, impact on environment*

Introduction

16 to 30 M Mg (ton) of hard coal mining waste is produced in Poland each year. They are economically utilized, still, a large quantity is deposited in the dumps, of which there are two hundred in Poland. In total, they occupy over 4 thousand ha of the surface. Only in the Silesian Voivodeship, there are around 136 coal mining waste dumps [5], which have lastingly changed the Silesian landscape not only due to their characteristic form, but also due to the burden resulting from the burning of some of them. Currently, it is estimated that around 15 of the Silesian dumps are thermally active; they are located in the central part of the Upper Silesian Coal Basin (Polish acronym: GZW), of Zabrze and in the Rybnik Coal Basin [11].

Currently, at least several dozen hectares are burning, and the resulting thermal states cause burdensome emissions of gases which are the products of oxygenation and gasification of coal to the atmosphere. Decisive for the occurrence of thermal activity in the dumps are the properties of the mining waste.

The mining waste is produced during the first driving, mine roadway's drivage underground as well as in the coal mechanical preparation plants where the mining product is prepared. They differ as to the physical properties. Waste from the driving works contains large particle size fractions (>250 mm), and even bulk waste, the preparation plant waste, on the other hand, is of much smaller granulation. It is estimated that the coal substance content in the mining waste is between 8.5 to 45 % [1, 4, 7].

The thermal processes on the coal mining waste dumps can be exogenic, when there exists an external heat source with an intensity high enough to ignite the coal substance in the waste, or endogenic when the self-heating due to the reactions in the bulk of the deposited material occurs.

In the result of burning of the coal substance at the dump, gases are emitted (carbon monoxide, carbon dioxide, sulfur dioxide, methane, hydrogen sulfide and hydrocarbons) also containing mercury compounds. Generally, it is assumed that the participation of the respective mercury forms in atmospheric emissions is as follows [2]:

- 60 % in the form of metallic mercury vapor Hg^0,
- 30 % in the form of volatile compounds of Hg^{+2} (mainly $HgCl_2$),
- 10 % in solid form in dust,

which allows stating that the largest part of the mercury is emitted in the form of vapor in the gases from the burning dumps.

Mercury compounds present in vapor can transform and react both with other mercury compounds and with other substances emitted from the burning dumps – for example with sulfur dioxide, nitrogen oxides, carbon monoxide as well as hydrogen sulfide [8, 10]. In the result of the transformations, substances with decreased or increased mutagenic activity or toxicity can be formed.

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Therefore, it is important to analyse the emissions of the gases from burning dumps in order to assess properly the environmental risk which can occur and to which the environment and the inhabitants of the nearby areas can be exposed.

Despite the significance of this problem, so far no measurements of mercury concentration which would allow quantifying this phenomenon have been done. The analyses presented in this article bridge this gap.

Besides the measurements of mercury concentration, the article also contains initial calculations of the yearly emissions from the burning mining waste dumps in Poland.

In the hard coal mining and processing waste dumps, a combustion can be observed very often. The fires are a direct outcome of applying inadequate dumping technology and depend on the physicochemical properties of the dumped waste rock.

The fires in the dumps and their increased thermal state occur in all of the European, Asian, African and American coal basins. The data from Russia, Ukraine or China indicate the scale of the problem, which seems much larger there, than in Poland and the EU countries. The methods for managing the burning coal mining waste dumps are very similar in Poland and the world.

The Methodology

The methodology for the assessment of the quantity of fugitive mercury emissions from mining waste dumps which show thermal activity is based on a number of measurement methods and initial tests performed before the measurement. The methodology takes into account most of all the untypical conditions on the objects formed from coal mining waste including their slope and high temperatures.

The temperature measurements at the depth of 1 m in the burning coal mining waste dumps indicated even 1300^{o}C, the temperature measured at the surface of the dump in the thermally active locations generally equal 550-600^{o}C. There are cases when the coal mining waste on the surface of the dump ignites [6].

Summing up, it can be said that the conditions on the coal mining waste dumps are very atypical and impose significant requirements on the measurement equipment.

The methodology of assessment of the fugitive mercury emissions from thermally active surfaces of objects formed from coal mining waste included the following steps: selection of the object for the tests on the fugitive mercury vapor emission, collecting the initial information and preparation of maps, field vision combined with the identification of the surface types of the object, thermo-visual tests of the surface of the object (initial definition of the boundaries of the thermal activity), depth tests of the thermal state, defining the boundaries of the thermal activity, selecting the measurement grid for the emission tests.

The following measurement equipment was employed:

1. Temperature measurement of the dump material on the object's surface - thermal imaging camera Fluke Ti55FT and portable infrared thermometer - Rayngter II - type R2PLT.
2. Temperature measurement of the dump material at the depth of 0.8 – 1.0 metres under the object's surface as well as measurement of the concentration of carbon monoxide CO, carbon dioxide CO_2 and oxygen O_2 - Gas analyser Madur GA-21 and by Madur Electronics Vienna.
3. Measurement of the mercury concentration - The RA-915M analyser.

For the measurement of the emissions of the mercury vapor from the surface of objects formed from coal mining waste a chamber method was applied. This selection was based on the above reasons:

- This method eliminates the impact of external agents which can obstruct or even prevent a proper assessment of the emissions of the mercury vapor from the dump applying other methods. These agents are above all other mercury vapor emitters such as coal-fired power plants, boilers, cocking plants,
- The possibility to measure the emission in points where the gases produced inside are locally emitted,
- The mobility of the measurement set.

Based on the elaborated mercury vapor measurement method, a measurement device has been built (fig. 1). The device comprises a set of the following elements: measurement chamber, mercury vapor concentration meter, internal anemometer in the exit channel of the measurement chamber (at the same time measuring the temperature), the central unit for the acquisition of the measurement data, external anemometer [11]. The measurement device is presented in Fig. 1.

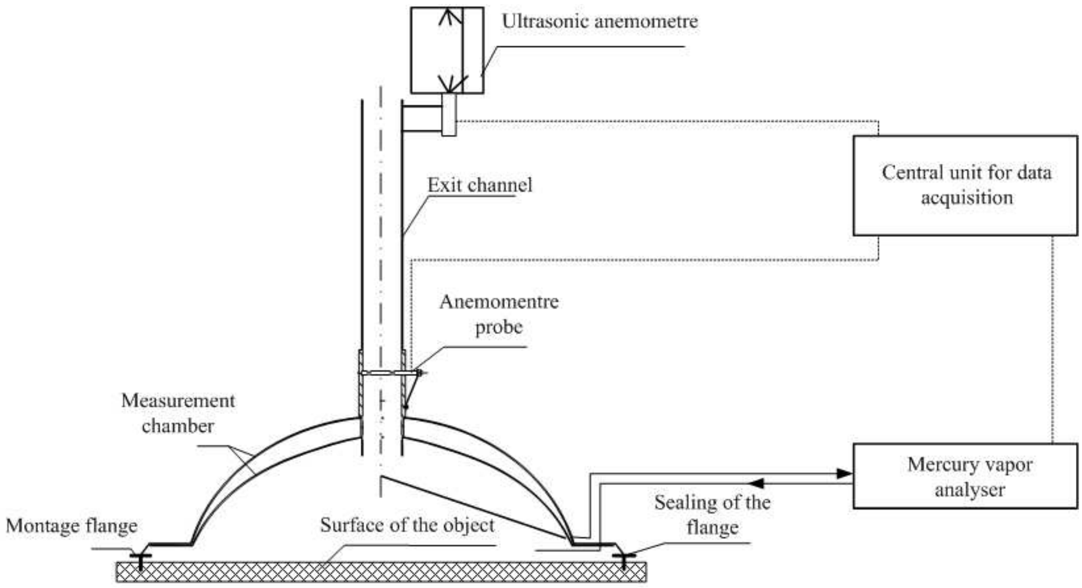

Fig. 1. The measurement device.

The characteristics of the tested object – the coal mining waste dump of the closed KWK „Rymer” mine

The Rybnik Niedobczyce dump was selected for the tests. The dump of the closed KWK Rymer mine was opened at the beginning of the twentieth century and until 1998 comprised of three cones. During the preventive fire suppression works conducted in 1998-2000, two of the cones were “cut” at the height of 50 meters from the elevation of the surrounding area. The dump has been surrounded by an embankment made of coal waste from the ongoing production, in some locations also a screen from a water-ash mixture has also been applied. In the frames of the recultivation works a new dump structure has been formed which remains till the present day. The conducted works resulted in a short-term extinguishing of the seats of fire. Since 2001, however, an ongoing thermal activity in the old and new regions of the dump has been observed. The intensity of the thermal phenomena and their location changes, there are, however, areas in which the thermal activity lasts for more than ten years. The intensity of the thermal phenomena, in particular in the area of the upper scarps of the object from east and west side can be defined as medium to high. The analysis of archival data indicates that the temperatures at the depth of 1 meter quite often oscillate in the limits of several hundred degrees with a clear indication of the presence of carbon monoxide in the gases inside the dumps which confirms the constant progress of the exothermal reactions related to oxygenation of the coal substance in the waste. Hg concentration in the coal waste indicates much higher variability (between 50-400 ppm).

Selection and initial tests on the polygons

Based on the accessible monitoring of the dump of the closed KWK Rymer mine (the owner conducts cyclic measurements of the thermal activity) two areas were selected which were then subjected to detailed tests initially recognizing them as the proper for the location of the test polygons for measuring the mercury vapor emission. These were the following areas:

- scarp in the eastern region of the object previously reinforced by concrete plates (polygon No. 1),
- scarp in the western region of the object at the exit of the technological road to the top (polygon No. 2).

His selection was justified by:

- long-term thermal activity (eastern scarp) and In the development stage (western scarp),
- relatively high intensity of the thermal activities (currently the temperature at the depth of 1 meter reach 200 ^{o}C),
- no preventive, extinguishment attempts in the recent years on these surfaces, which could influence the size of the emission of the fugitive mercury emissions.

The polygons were subjected to initial tests to define the current thermal state.

First the areas were subjected to surface temperature measurements in order to initially define the territorial limits of the polygons.

Figure 2 present thermograms made by the thermovision camera.

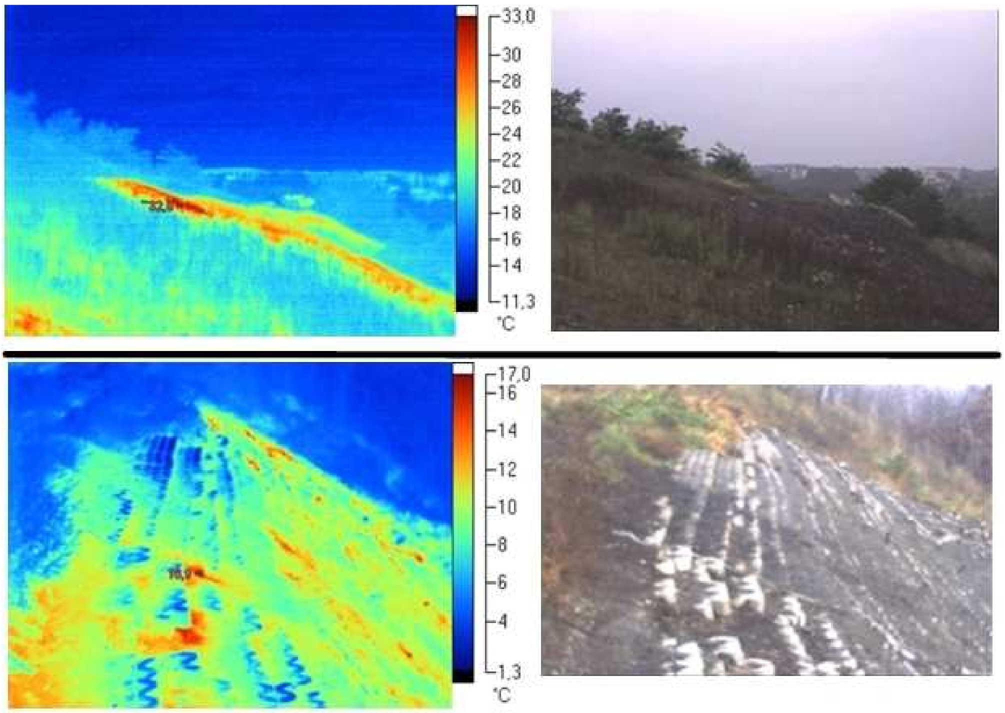

Fig. 2. Thermograms of the eastern and western scarp.

The thermal measurements allowed to define the location of the thermal anomalies on the surface of the dump. Both in the selected area of the eastern and western scarp a clear increase of the dump surface temperature was observed which allowed defining the testing polygons for the analysis of mercury vapor emission with the surface of even several dozens of square meters. Additionally, the area of polygon No. 1 a cavern which is the location of intensive inflow of gases from the inside of the object was observed (chimney emission). The temperatures of the surface were not high (up to several dozens ^{o}C) but together with symptoms such as specific smell or discharge of gases evidently indicated the occurring thermal processes.

Depth tests of the thermal state of the polygons

In the locations of the thermal states identified during the surface tests, depth tests of the thermal state were conducted following a regular measurement grid. The results of the measurements conducted according to the procedure presented in the testing methodology are presented in Table 1. The measurement points No. P1, P2, P3 and P4 from Polygon No. 1 are the same as in Table 1, Table 2 and Table 3.

Tab. 1. The results of the depth tests of the thermal state.

Measurement point No.	**Surface temperature**	**Inside temperature**	**CO**	**CO_2**	**O_2**
-	^{o}C	^{o}C	%	%	%
Polygon No.1					
P1	66	209	0.055	5.07	15.21
P2	58	71	0.434	18.50	0.0
P3	61	70	0.374	8.65	11.16
P4	38	67	0.063	18.50	0.00
P5	27	54	0.017	13.66	6.30
P6	26	55	0.064	18.10	1.10
P7	33	53	0.034	14.30	5.20
P8	35	61	0.110	12.0	48.20
Polygon No.2					
P1	15	29	0.002	19.60	0.00
P2	17	40	0.005	15.40	4.88
P3	16	33	0.006	18.80	1.70
P4	32	58	0.080	18.40	1.80
P5	36	54	0.110	13.40	7.10
P6	18	38	0.060	17.50	3.20
P7	17	34	0.010	19.20	1.05
P8	17	27	0.008	16.10	4.60

The results of the depth tests allowed to identify the degree of the thermal activity in the initially selected area.

Polygon No. 1 was characterised by intensive thermal phenomena which were confirmed by the test results presented in Table 1. The advanced thermal states were confirmed by the temperatures at the depth of 1 m which reached 200 ^{o}C as well as high carbon monoxide levels (carbon monoxide is regarded as the indicative of thermal activity) reaching 0.4 %. In addition to the locations which comprised a homogeneous surface of the tested object characterized by surface emission through the porous structure of the embankments, in the polygon the emission from a cavern directly to the atmosphere – chimney emission occurred. This was the point with the highest temperature measured at the depth of 1 meter.

Polygon No.2 was characterised by moderate values of the parameters which describe the thermal state. The temperature at the depth of 1 meter reached the maximal values of 50 ^{o}C. The occurrence of the thermal state was indicated by the increased carbon monoxide level – up to 0.11 %. On the polygon No. 2 no chimney emissions were located, only the surface emission.

The depth tests of mercury vapor concentration

In the holes used during the depth tests of the thermal state of the polygon No.1, also the measurements of the mercury vapor concentration were taken at the distance of 1 meter above the surface at the location of the depth test. The results of the tests are presented in Table 2.

Tab. 2. The results of the depth tests of the mercury vapor concentration on the example of selected measurement points of polygon No.1.

Measurement point No.	**Surface temperature**	**Inside temperature**	**Hg concentration Background (2m from the hole 1m above the terrain level)**	**Hg concentration (in the hole)**
-	^{o}C	^{o}C	ng/m^3	ng/m^3
P1	66	209	7	870-5100
P2	58	71	6-17	3600-4300
P3	61	70	6-23	4500-5381
P4	38	67	9-14	571-755

The results presented in Table 2 confirm the occurrence of significantly increased mercury vapor concentrations in the porous gases in the locations of thermal activity occurrence in objects formed of coal waste. The concentrations at the depth of 1 meter exceed the concentrations measured above the tested surface by even several hundred times. The increased mercury vapor concentrations in relation to the background as well as the lack of other mercury emitters nearby indicate the emission of mercury vapor to the environment from the thermal activity surface. The measurements of the mercury vapor concentrations in the ground and 1 meter above the surface did not provide information on the fugitive emission of mercury vapor to the atmosphere. Such information was obtained in the result of the conducted tests on the emission applying the elaborated measurement device, dedicated to the measurements of the objects formed from coal waste.

Tests on the fugitive mercury vapor emission

In the result of the initial tests of thermovision analyzes of the dump surface as well as the depth measurements of the thermal state, two testing polygons were identified for the basic tests i.e. the evaluation of the mercury vapor emission to the atmosphere (Fig. 3). Initial test allowed to localize the following measurement points:

- polygon No. 1 – 1 measurement point of the chimney emission (point No. 1) as well as seven measurement points for the surface emission,
- polygon No. 2 – 8 measurement points of the surface emission.

A measurement grid of 2x2 meters was applied on both polygons No. 1 and 2. The grid of the emission measurements was selected so that it did not match the hole for the depth tests which were terminated after the tests were conducted. The measurement of the fugitive mercury vapor emissions is an intermediate measurement and thus, in the field measurements of the values which are necessary for the calculation of the fugitive mercury vapor emissions were taken. During the two-minute long measurement in 10-second intervals, the following values were taken:

- concentration of the mercury vapor inside the measurement chamber,
- the speed of the wind in the surroundings of the measurement device – as the verification measurement (the admissible wind speed for the measurement defined during the laboratory tests was 0.6 m/s).

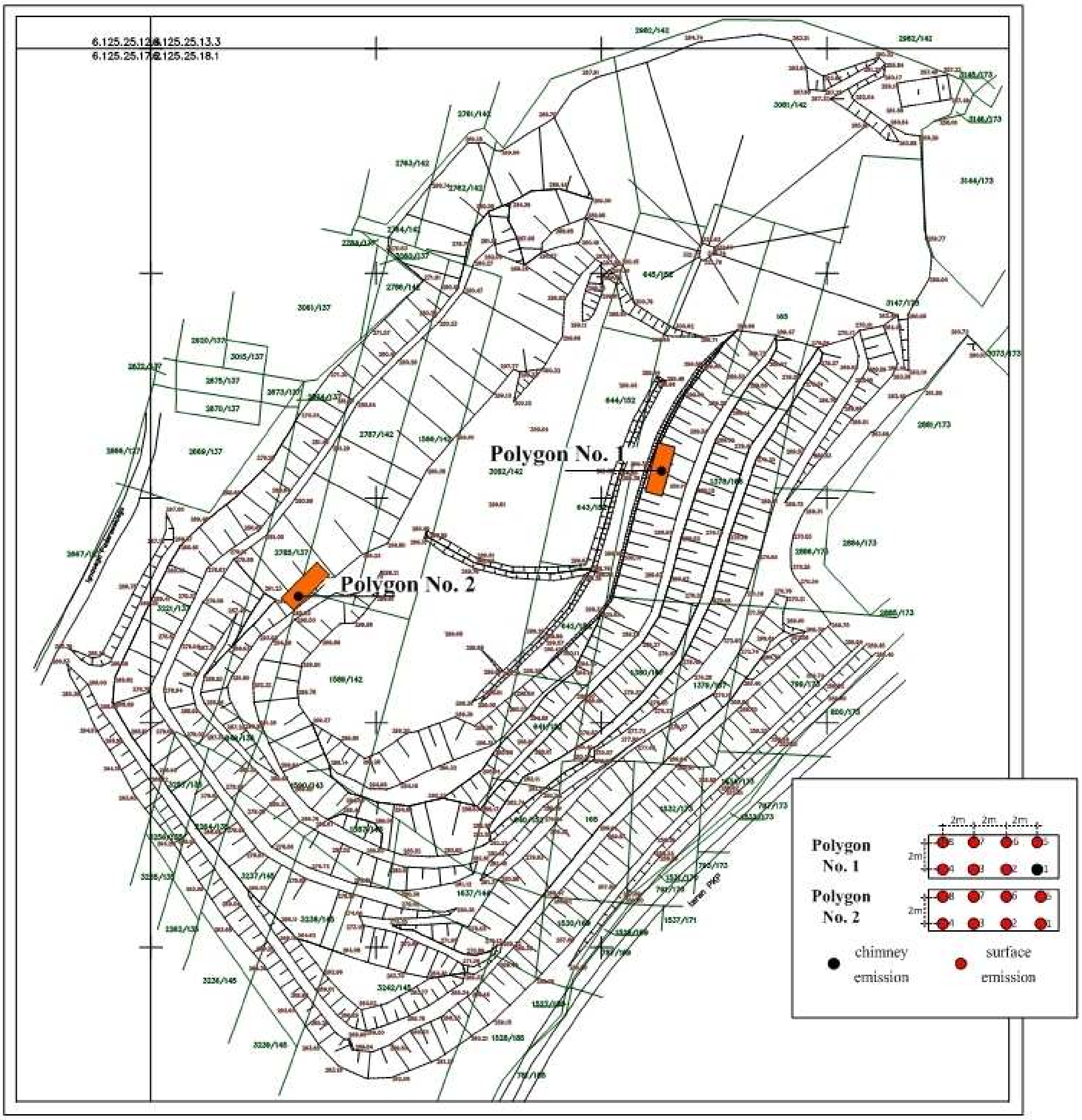

Fig. 3. Location of the testing polygons on the dump of the closed KWK Rymer mine and the location of the measurement points on the polygons.

Calculation of the mercury vapor emission from the object

The calculation of the fugitive mercury emissions consisted in:

- calculation of the chance value of the horizontal speed of the wind during the measurement in order to eliminate the data for the component horizontal speed above 0.6 m/s in the same analysis time of the mercury vapor emission,
- verification of the linearity of the changes in the mercury concentration during the emission analysis,
- calculation of point emission of mercury vapor and assessment of the average emission for the testing polygon.

The average emission for each zone is calculated based on the point emission calculated per 1 m^2 of the surface zone multiplied by the surface of the zone. In the case of polygon 1, in which the chimney emission occurred, the average emission was calculated as the sum of surface emissions from the whole polygon surface and the chimney emission (from the measurement point No. 1).

Table 3 presents the calculated values of the fugitive emission of mercury vapor expressed in g/m^{2}s for the measurement points located on the testing polygons which indicate thermal activity.

Tab. 3. The value of the fugitive emission of mercury vapor on the testing polygons.

Testing polygon	No. of the measurement point	Mercury vapor emissions [ng/m^{2}s]
Polygon No. 1	1	6.15
	2	0.17
	3	0.33
	4	0.25
	5	0.20
	6	0.065
	7	0.057
	8	0.031
Polygon No. 2	1	0.44
	2	1.66
	3	0.032
	4	0.031
	5	0.033
	6	0.03
	7	0.035
	8	0.024

Discussion of the results

The measurement of the emissions of the mercury vapor showed non-zero values at all the measurement points. Thus, it should be recognized that the emission of mercury vapor on the objects formed from coal waste is differentiated most of all due to the type of emission which occurs in the given measurement point. The values of the surface emissions are several times lower than the value of the chimney emission. The surface emission from both test polygons reached the values of 0.024-1.66 ng/m^{2}s. In one of the points of the chimney emission (point 1 on polygon No. 1), the mercury vapor emissions reached the value of 6.15 ng/m^{2}s. The big discrepancy between mercury vapour concentration in Table 2 and mercury vapour emission in Table 3 (for the measurement points No. 1) emerges due to the fact that at this point was the chimney emission which has a larger flow of exhaust gas.

Average surface emissions on the respective polygons equaled:

- polygon No. 1 – 0.907 ng/m^{2}s
- polygon No. 2 – 0.286 ng/m^{2}s

Including the polygon surfaces equaling in both cases, 12 m^2 of the total surface emissions from these areas equaled:

- polygon No. 1 – 8.05 ng/s
- polygon No. 2 – 3.43 ng/s

Each year from 1 m^2 of the tested polygon is emitted around 0.36 g of Hg. If the measured emissions remain the same for a year, then only from these small testing polygons 8.64 g of Hg will enter the atmosphere.

Considering the fact that around 40 ha of mining waste dumps is currently thermally active and extrapolating the obtained results of the emissions in the area, it can be estimated that during a year 14.4 kg of Hg will be emitted to the atmosphere.

The results presented in the article refer to a selected dump where the fire is not very significant, still taking into consideration the Author's tests conducted on other objects the following results can be described:

1. in the analysed case the average Hg concentration in the area of 1 is equal to 2000 ng/m^3 (Table 4)
2. in the case of the dump localised in Zabrze, which was analysed in October 2014, the average concentration in the area of 1 is equal to 20200 ng/m^3 (numerous chimney emissions were observed on this dump) [3].

The above indicates the necessity of further tests since the assessed emission can come in between 14-150 kg over a year. Such considerable range of the prognosis indicates the necessity of monitoring.

Summing up:

- the article presents one of the first assessment attempts at defining in situ the mercury emissions from the burning coal waste dump,

- assuming the current surface of the objects formed from coal waste which are thermally active only at the level of 40 ha, the estimated value of the mercury emissions from this area can equal 14-150 kg per year,
- The presented results characterize single test cycles; it should, however, be stressed that the concentration and composition of the gases can significantly differ between season and also during the day – this suggests the necessity of constant monitoring for better assessment of emissions for the respective burning dumps,
- The article defines only the emission of the mercury to the air according to the literature data [9, 12]; its significant part is dissolved in water or condensates on the surface around the chimney zones,
- The presented results suggest that the impact of the mercury emission from the burning coal waste dumps is significant not only at local or regional scale but also at the national and international level,
- There is no dependence of Hg concentration on inside temperature. This is a typical situation for the dumps formed from coal mining wastes in which no dependence of surface temperature on inside temperature and no dependence of concentration of gases (CO, CO_2, O_2) on inside temperature was confirmed by the results of more than thirty years of monitoring burning coal-mining dumps operated by Central Mining Institute.

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