Monitoring of Pollutants in an Active Mining Dump Ema, Czech Republic

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Abstract

The mining activities carried out within the area of Ostrava City are responsible for at least six mine dumps of loose materials arising as wastes from mining of mineral resources. In the past there were difficulties with efficient separating of waste rock and tailings from coal and thus high amounts of coal substance remained in the waste, thus being prone to self-ignition. The thermal activity in dumps is responsible for many hazardous substances that pollute the environment and harm human health in the surroundings. Analysing the occurring pollutants in Ema Dump (Czech Republic) using the GC chromatography method, concentrations of CO_2 *and* CH_4 *were determined in three sampling points during three measurements executed from January to March 2016. The highest measured concentration of* CO_2 *in Ema Dump was 20 722 ppm. The top concentration of* CH_4 *in Ema Dump was 707 ppm. The monitoring of* SO_2 *in Ema Dump was carried out between April 2015 and January 2016. The final concentrations were identified using two measuring methods, namely the thorin method and the method with methylsulfonazo III as an indicator in dependence on different gas flow rates (1.5–3.0 l* min^{-1}*) during sampling. The measured concentrations of* SO_2 *ranged from 7.21 to 31.50 mg* m^{-3}*, while the top concentration was taken in January 2016.*

Keywords: monitoring, Ema Dump, pollutants

Introduction

Unfavourable air conditions in the Ostrava Region are predominantly caused by the high concentration of heavy industry plants in the region and the geomorphological conditions of the Upper Silesian Coal Basin. During bad dispersion conditions the pollution concentrates, particularly in winter months. Due to the mining activities within the City of Ostrava at least six mine waste dumps were heaped, which contain loose waste materials from mineral mining. Dumps have been shaped near all mines in the region as mine wastes had to be disposed of since the very start of mining. Mine dumps may be regarded as typical features of the mining landscape. In dumps that are classified as flammable, the potential of coal self-ignition is a serious problem. In the reducing medium of dumps and the sections with no access of air endothermal reactions take place. High-temperature carbonisation of coal takes place at the temperatures < 1000°C. The risks arising in connection with the dumped Carboniferous waste rock are permanent. This way, harmful substances may release in water or combustion products into the air. There are also threats of heating and endogenous fire. Emissions of volatile and partially volatile organic substances are released into the atmosphere during carbonisation. Subsequently, PAHs appear via the condensation of such substances.

In case of an insufficient supply of oxygen into the combustion zone, the burning dumps are the producers of CO_2, CO, NO_x, SO_x, HCl, HF, hazardous metals and other substances [1–3].

Material And Methods

The study deals with monitoring of the occurrence of selected gas pollutants, which were detected using the chromatographic method in a thermally active mine dump Ema. Another gaseous pollutant of interest was SO_2. Different flow rates during sampling were used to identify the most efficient determination method of SO_2.

The characteristics of Ema Dump

Ema Dump is the only conical dump in the Ostrava Region. It is found in the city quarter Slezská Ostrava. It covers an area of 21.3 ha and its volume is over $2.6 \cdot 10^6$ m^3. Apart from the Carboniferous waste rock, building, municipal and household wastes were dumped there during the Second World War. Later on, it was topped with sand and topsoil. In 1952 the materials in the dump ignited and the burning process inside the dump body, where the temperature reaches up to 1 500°C, has lasted to date. Due to such high temperatures, its southern burning bank is not grassed. The current owner of the dump, company RPG RE Land, s.r.o., Ostrava, administers the mine waste dump as a forest land having the forest function [4–6].

For the initial detection of gas substances (CO_2, CH_4) occurring in Ema Dump, we chose three sampling points (EMA1, EMA2, EMA3). The sampling point EMA1 is a smouldering point on the top of the dump (approximately 315 m a.s.l.). It is a bulge with surrounding vegetation cover protected by a forest from the north. The sampling point EMA2 is situated on the southern bank that is burning. It is an outlet placed below a mound and it is surrounded by crystalline aggregates of elementary sulphur.

The sampling point EMA3 is an interspace in the mound, which was shaped to protect against hazardous gas. It is fenced and the sampling probe was placed in the gap in the fence. To study the occurrence of SO_2 we selected the sampling point EMA2.

Sampling of gaseous substances

The sampling of CO_2 and CH_4 gas samples in Ema Dump detecting the gases by means of a GC analysis was implemented 3 times from January to February 2015 in the sampling points EMA1, EMA2, and EMA3. The sampling of gas samples to determine SO_2 using the volumetric analysis lasted from April 2015 to January 2016 in the sampling point EMA2 in regular monthly intervals.

Methodology of gas substance analyses using GC method

The gas samples in Ema Dump were detected using a gas chromatograph YL 6100GC (Young Lin Instrument CO., Ltd., Korea) with a thermal conductivity detector (TCD) and flame ionization detector (FID) operated in series. The analysis was carried out using capillary columns HP-PLOT Q (Agilent Technologies, USA) with the following dimensions: 30 m × 0.53 mm. The sorbent thickness was 40 µm. The dimensions of GsBP-PLOT MLSVE 5A (GS-Tek, USA) were 30 m × 0.53 mm and the sorbent thickness was 50 µm operated in series via a six-way diverter valve. After the initial detection of gas substance samples, the representatives of greenhouse gases (CO_2 and CH_4) were selected to calculate the concentrations. To calibrate and calculate the concentrations of CO_2 we used the mixture of calibration gases SIAD with an injection of 0.5 ml directly into the septum. To gain the concentration of CH_4 we used a separate calibration procedure (injection of 0.2 ml of CH_4 into a gas-collecting tube, followed by an injection of 0.5 ml of such diluted gas into the gas chromatograph septum).

Methodology of volumetric analysis

The method of SO_2 analysis was grounded in two standardised methods: ČSN EN 14791 Stationary source emissions - Determination of mass concentration of sulphur dioxide – Reference method [7], and ČSN 83 4711 – 5 Measurement of emissions of sulphur dioxide, sulphur trioxide, sulphuric acid, and the total content of sulphur oxides from air polluting sources. The determination of total content of sulphur trioxide and sulphuric acid and the content of sulphur dioxide [8]. The titration to determine SO_2 was carried out using a digital burette Solarus (Hirschmann, Germany) and it was repeated 3 times for each sample. The aim was to prepare a methodology that could be applied for such type of samples and following research in thermally active dumps. To compare the results of the different titrations, we used four different flow rates in each sampling, ranging from 1.5 – 3.0 l min^{-1}, namely: 1.5 l min^{-1} (Q_1), 2.0 l min^{-1} (Q_2), 2.5 l min^{-1} (Q_3) and 3.0 l min^{-1} (Q_4). Therefore, we sampled four different volumes of gas, i.e. V_1 at gas flow rate Q_1, V_2 at gas flow rate Q_2, V_3 at gas flow rate Q_3 and V_4 at gas flow rate Q_4.

Results

The aim of the study was to obtain reference information on gases occurring on the thermally active dump Ema. Considering the used standard for the GC analysis, only CO_2 and CH_4 could have been quantified by means of gas chromatography. The results imply that the content of the different substances changed in dependence on the character of the sampling points as well as on the varying intensity of burning of the dump materials in the different sections of the dump Ema.

The concentrations of CO_2 ranged from 3795–20 722 ppm during the different verification measurements. The top concentration of CO_2 was identified in the sampling point EMA1, situated at the foot of the dump. Thanks to the thermal activity the surroundings of the bulge are covered with vegetation even in winter and the sampling point is protected by a forest from the north. The measured values of CO_2 differed there and ranged from 20 722 ppm (February 2015) to 4 774 ppm (March 2015). It may be said that the sampling point EMA1 is well protected from the weather conditions and the concentration of CO_2 is higher also due to insufficient circulation of air. In the sampling point EMA2, except for the first measurement (January 2015), CO_2 was also detected. However, its measured values did not show high fluctuations as in case of the sampling point EMA1. They ranged from 6 448 ppm (March 2015) to 9 930 ppm (February 2015). We may suppose that the sampling point EMA2 was not influenced by the climatic conditions only; there is an outlet in the dump and the concentration of CO_2 also depends on the intensity of burning and the character of the burning material. The sampling point EMA3, which is found in the interspace of the mound, manifested almost identical values of CO_2 (3 941 ppm in January and 3 795 ppm in March). At the same time, these were the lowest concentrations of CO_2 taken in all the sampling points and all measurements. As the mound is supposed to disperse the pollutants into the atmosphere, the lowest concentrations of CO_2 out of all sampling points could have been expected there. Because CO_2 is heavier than the air [6], it may accumulate in the area of the mound and disperse into the atmosphere at higher atmospheric exposure. Thus, higher content of CO_2 may have been

Tab. 1 Final concentrations of SO_2 drawn at the flow rates Q_1–Q_4 using two types of volumetric methods in April 2015 – January 2016 in the sampling point EMA2 [Legend: MSIII – methylsulfonazo III]

Tab. 1. Koncowa koncentracja SO2 stwierdzona dla przepływów Q_1–Q_4 z wykorzystaniem dwu metod wolumetrycznych w okresie kwiecien 2015 – styczeń 2016 w punkcie poboru próbek EMA2 [Legenda: MSIII – methylsulfonazo III]

Month	Q_1 l min^{-1}		Q_2 l min^{-1}		Q_3 l min^{-1}		Q_4 l min^{-1}	
	Thorin	**MSIII**	**Thorin**	**MSIII**	**Thorin**	**MSIII**	**Thorin**	**MSIII**
IV	9.80	8.51	9.80	7.23	9.79	10.21	9.80	7.36
V	10.20	10.50	10.20	7.85	10.21	11.36	10.20	10.90
VI	12.33	11.42	12.34	9.57	12.33	10.30	12.33	10.28
VII	10.41	10.96	10.57	9.56	10.53	8.95	10.54	10.96
VIII	7.33	6.17	7.32	6.33	7.32	6.78	7.32	5.98
IX	9.20	7.38	9.20	7.66	9.20	6.11	9.20	8.89
X	30.18	28.18	30.17	28.34	30.15	25.89	30.18	26.39
XI	7.21	6.04	7.05	5.82	7.05	4.24	7.05	4.02
XII	21.00	21.55	20.92	18.99	20.92	17.26	20.92	20.36
I	31.50	29.00	31.50	25.36	31.53	26.78	31.50	27.96

measured in the sampling point (13 130 ppm, February 2015).

The concentrations of CH_4 ranged from 37–707 ppm during the verification measurements. The content of CH_4 was not identical during the different months. In the sampling point EMA1, similarly to CO_2, the top concentration was measured in February 2015 (707 ppm), when there were the most severe meteorological conditions (wind velocity of 27 km hod^{-1}). On the other hand, the lowest concentration of CH4 was taken in the third point in March 2015 (38 ppm), as in the case of CO2. In the sampling point EMA2 (outlet in the dump body) its concentration values were from 60 ppm (January 2015) to 495 ppm (February 2015). In the sampling point EMA3 the concentration of CH_4 ranged from 209 ppm (January 2015) to 285 ppm (March 2015).

Within the monitoring of SO_2 in the Ema sampling point EMA2, surrounded by crystalline aggregates of sulphur, we compared two volumetric methods. Table 1 states the final concentrations of SO_2 obtained using two methods, four flow rates and two types of indicators.

The final mean concentrations of SO_2 taken during different flow rates imply that using two types of titration analysis, slightly different results were obtained. Based on the obtained results, a direct dependence on the season cannot be proven. Nevertheless, save for one exception (November 2015) when the concentration of SO_2 decreased, it may be stated that during cooler months (October 2015, November – December 2015, January 2016) an increase in the concentration of SO_2 was observed. The gas cloud released from the sampling point EMA2 was determined for SO_2 using the Thorin method and it ranged from 7.05–31.53 mg m^{-3}. The concentration of SO_2 determined using the titration method and the indicator of methylsulfonazo III ranged from 4.02 to 29.00 mg m^{-3}. However, these are very low concentrations that do not endanger human life. Still, considering the different character of the disposed material in Ema and its high thermal activity, it would be suitable to establish long-term monitoring of SO_2 in hot-spots zones of Ema.

Discussion

The composition of gas substances that liberated into the atmosphere from the thermally active dumps differ based on the dumped materials as well as due to the absence/presence of the soil cover. In thermally active dumps, burning may cause subsidence due to the burning of the overlying beds, forest fire or may endanger the health due to the flue dust emissions, gas pollutants, hazardous elements and organic compounds. An important aspect informing on the advances of thermal activity is the composition of the dump material. The evidence of high amounts of sulphates indicates previous weathering processes [9].

Within the first study we focused on the detection of gas substances in the thermally active dump Ema. Abundance of CO_2 and CH_4 was confirmed in all the sampling points and during all three samplings. There was one exception with CO_2 as it was not confirmed during the measurement in January 2015 in the sampling point EMA2. Based on the data informing us on the rapid changes in the concentrations of SO_2, CO_2 and CH_4 during several seconds or minutes in thermally active dumps, CO_2 need not have been detected. The content of CH_4 in thermally active dumps does not only depend on the coal quantity and degree of its coalification, but on the properties of the cover too. In places where the coal beds outcrop onto the surface, or where they are covered by gas-permeable rocks, the coal-bearing formations are free of or poor in gas. With regard to the fact that both the gases are not generated at low temperatures (50–79°C) [10] near the dump body surface, they may be considered as indicators of a high thermal activity inside the dump. Methane is released at temperatures exceeding 120°C. Because thermal activity inside the dump reaches 1500°C, we expected detecting CH_4 in all the sampling points in Ema. Rather low concentrations of CH_4 and CO_2 were identified in the sampling point EMA3, which is located in the upper interspace of the mound. As the stones had been heaped in order to dilute and disperse the gases, the lower concentrations did not come as a surprise.

Fluctuations in the values of CH_4 may thus inform on the abundance of other gases too, which could not have been detected using the given standard. Certain gases may have a synergetic effect. Some gases need not be dangerous to human health by themselves, but may take over the toxic effect from another gas. The harmful effect of CO_2 on human health was determined as the concentration of 5000 ppm. This limit concentration was exceeded, namely in January and February 2015 in the sampling point EMA1 (9598 ppm and 20 722 ppm respectively), in February and March 2015 in the sampling point EMA2 (9930 ppm and 6448 ppm respectively) and February 2015 in the sampling point EMA3 (13 130 ppm). With regard to the position of the monitored thermally active dumps located in the vicinity of built-up areas, these are still negligible values directly affecting the hot-spots zones only.

We used the method of GC chromatography to qualitatively detect other gas substances occurring in Ema, namely the occurrence of ethane. Its abundance is typical for thermally active dumps as it forms predominantly during mine fires and fires due to higher hydrocarbon decay. Among mine gas it is also detected as the product of coalification. As a rule, it occurs in low quantities, usually as an admixture of methane [9], which was established in the majority of the sampling points in EMA. It is much more dangerous than methane as its explosive mixture ignition temperature is lower than in CH_4. Explosions of such mixtures are also more abrupt. In the gas samples we qualitatively established hydrogen which arises also in mine fire and fire due to the decay of hydrocarbons from coal. Along with CH4 and nitrogen it is rare in the exhaled gas. We also established the presence of oxygen that is usually used up during the processes of burning under the formation of combustion products.

Considering the permanent thermal activity in Ema we may suppose that the occurrence of pollutants will vary along with further burning and other gas compounds may also occur. Therefore, it would be advisable to carry out a long-term monitoring to study the occurrence of gas substances and pollutants in Ema in detail and to evaluate the risks of their further negative impacts on human health and environment. We may realistically assume that if the thermal activity continues in an uncontrolled manner in the monitored dumps, the content of CO_2 and CH_4 may increase by about 20% in CO_2 and 2.5% in CH_4 [10].

Another monitored gas pollutant was SO_2 that occurs in a thermally active dump only if the dumped waste rock or tailings contain sulphur. During self-ignition reaching 1060°C sulphur liberates from the dump body in the form of SO_2 [6, 9]. For the initial detection of SO_2 we chose the sampling point EMA2 situated on the southern burning bank of the dump.

To determine SO_2 in the gas sample we used two manual titration methods based on the used indicator. The thorin indicator issues from ČSN EN 14791, grounded in the method 6 US EPA GOV [11] and the methylsulfonazo III indicator is described in ČSN 83 4711-5. To prepare the optimal determination methodology we compared the efficiency of flow rates during sampling in dependence on the final concentration of SO_2. One of the aims of the study was to propose the most suitable sampling method and titration analyses suitable to determine SO_2. During the titration analysis for methylsulfonazo III indicator, worse subjective reading of the equivalence point occurred due to an increase in the flow rate and lower visibility of the colour transition. This determination could have been burdened with an error in reading the consumption of volumetric agent in the equivalence point. To identify the concentration of SO_2 by thorin, sampling at gas flow rate 2.5–3.0 l min-1 appeared as most effective. The visual accuracy of indicating the equivalence point was also excellent as it manifested by a clear visibility of the colour transition.

With regard to the fact that a different concentration range of SO_2 (7.05–31.53 mg m^{-3}) was identified using thorin indicator than using methylsulfonazo III (4.02–29.00 mg m^{-3}), we also carried out a verification of the titration analyses. The results imply that the titration methods for thorin also showed lower values of RSD (Relative Standard Deviation) (0.00–0.28%) than in the titration method for methylsulfonazo III (0.00–2.24%). In addition, we found that using the selected titration method to determine SO_2 for methylsulfonazo III, the method recovery Re ranged from 57.03 to 111.31%, while the ideal recovery is Re = 95–105%. Only 15% of the obtained data could have been taken as satisfactory. With regard to the reference thorin method, the interval of the determination error in the sample drawn at flow rate Q_1 (1.5 l min^{-1}) was from 2.62 to 19.78%, at flow rate Q_2 (2.0 l min^{-1}) from 2.36 to 22.81%, at flow rate Q_3 (2.5 l min^{-1}) from 2.21 to 26.74%, and at flow rate Q_4 (3.0 l min^{-1}) from 2.67 to 42.90%.

We may thus state that at higher gas flow rates during sampling, random errors increased using the titration method for methylsulfonazo III indicator, which may have been caused by external influences as well as by the used method. Based on the results of recovery verification, where the majority of the satisfactory data fell in the flow rate Q_1 (1.5 l min^{-1}), lower flow rates than our minimal flow rate Q_1 should be tested for the application of methylsulfonazo III as an indicator during sampling. Reducing the amount of concentrated gas in the absorption solution H_2O_2 we may arrive at better visibility of the colour transition indicating the equivalence point and potential errors in reading the volumetric agent consumption. The optimal flow rate could range from 0.5 to 1.0 l min^{-1}. On the grounds of the SO_2 concentrations obtained using the Thorin method, we may say that the method shows stable results even at increasing the flow rates and appears as ideal for further determinations of SO_2. As for the effect of SO_2 on human health we detected the concentrations from 2.85 to 14.29 mg m^{-3} in Ema, which already causes an aftertaste in the mouth, and 14.29–57.17 mg m^{-3}, which irritates eyes. Similarly to CO_2, such concentrations impact human health only near the hot-spots zones.

As the identified risks arising in relation to the dumped Carboniferous waste rock are permanent, gaseous combustion products may be released. For further monitoring of SO_2 concentrations in Ema it would be suitable to continue in the monitoring at least 3 × in a month. This way, sufficient data could be obtained as for the quality of the atmosphere, monitoring of the thermal activity processes and the fact that the concentrations of SO_2 in the gas pollutants vary greatly. It is also advisable to monitor all the hot-spots zones in the dump. Considering the persisting thermal activity in Ema, temperature monitoring in the sampling point may also be recommended.

Conclusion

Thermally active dumps are sources of a range of pollutants. Before own remediation and reclamation works, in situ analytical assessment of abundant substances must be carried out. Among the phenomena of interest there are gases liberated on the dump surface as they may be responsible for a number of pollutants.

Considering the diverse character of the dump materials in Ema, which also influences the final concentrations of pollutants during burning, long-term monitoring of the observed indicators would be advisable in all hot-spot zones, while the gas emissions would be assessed for health risks. To monitor the concentrations of SO_2 it would be advisable to use a continuous method to check the obtained data and thus compare the analytical accuracy of the obtained results.

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Monitoring zanieczyszczeń na składowisku odpadów górniczych Ema (Czechy)

Działalność górnicza związana z wydobyciem węgla, prowadzona na rejonie miasta Ostrawa obejmuje poza działalnością górnicza sześć składowisk odpadów górniczych W przeszłości występowały trudności utrzymywaniem w odpadach niskich zawartości węgla zatem w odpadach pozostały znaczne ilości substancji węglowej, podatnej na samozapłon. Aktywność termiczna w wysypisk jest odpowiedzialna za emisję wielu substancji niebezpiecznych, które zanieczyszczają środowisko i szkodzą zdrowiu ludzi w okolicy. Analizując zanieczyszczenia występujące na składowisku Ema (Czechy), stosując metodę chromatografii GC, określono stężenia CO_2 *i* CH_4 *w trzech punktach poboru prób, podczas trzech pomiarów wykonanych w okresie od stycznia do marca 2016 r. Najwyższe zmierzone stężenie* CO_2 *na składowisku Ema wynosiło 20 722 ppm. górne stężenie* CH_4 *wyniosło 707 ppm. Monitorowanie zawartości* SO_2 *na składowisku Ema przeprowadzono w okresie od kwietnia 2015 r. do stycznia 2016 r. Końcowe stężenie* SO_2 *określono z wykorzystaniem dwu metod wykorzystując jako wskaźnik thorin i methylsulfonazo III dla natężenia przepływu gazu (1,5–3,0 l* min^{-1}*) podczas pobierania próbek. Zmierzone stężenia* SO_2 *wahały się od 7,21 do 31,50 mg /*m^3*, najwyższe stężenie zostało stwierdzone w styczniu 2016 roku.*

Słowa kluczowe: monitoring, składowisko Ema, zanieczyszczenia