Preliminary sources identification of nitric oxide (NO)
emissions in underground mine

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Abstract.
Gas hazards in Polish underground mines are a major problem for the ventilation service. Ensuring appropriate environmental conditions is becoming increasingly difficult, especially with the introduction of new, more stringent restrictions on the concentration limits of harmful gases. According to [1], the most dangerous gases in underground mines are carbon monoxide, hydrogen sulfide, nitrogen oxides, carbon dioxide, sulfur dioxide, and methane. Together with the introduction of new limit values for the above-mentioned gases by the European Union, it is necessary to accurately identify the sources of their emission in mine workings in order to select an appropriate reduction method. This article presents daily measurements of nitric oxide (NO) concentrations in the workings of one of the copper ore mines owned by KGHM Polska Miedź S.A. The measurement results were used for preliminary analysis of sources of gas emissions to underground workings. The analysis is carried out through a graphical interpretation of the measured values. Knowing the details of the technological processes carried out in the mine under consideration (blasting, diesel engine machines, natural oxidation of nitrogen to NO) the graphs were interpreted by assigning individual values of NO concentrations over time to a specific technological process.

1. Introduction
For many years, the mining industry has been cited as one of the world’s biggest air polluters. In spite of this, the ever-increasing demand for raw materials extracted from the earth’s interior does not allow this industry to be closed down completely. What is more, mining plays an important role in the development of civilization, just by providing the necessary raw materials needed in almost every area of life. The great demand for natural resources involves the rapid exploitation of deposits that are easily accessible and the transition to the exploitation of raw materials in parts of the rock mass that are difficult to access, where there are an increase in gas, climatic or seismic risks. The increase in hazards is associated with a decrease in the safety of underground crews, and one of the most problematic is gas hazards [2–5].

The article [6] points out that changing environmental policies are putting a lot of emphasis on reducing the introduction of gases into the atmosphere that contribute to climate change and the increase in the greenhouse effect [7, 8]. Accordingly, from time to time, more and more restrictions are introduced on the maximum concentrations of the above-mentioned gases in the mine. Restrictions are introduced for all sectors of industry, including the mining sector. The purpose of the changes being introduced in underground mining is primarily to improve the safety...
of downstream workers and to reduce emissions of harmful gases into the atmosphere. Reducing the limit values for harmful gases is a major challenge for the mine services. It is connected with introducing technological, technical, and organizational changes. It is not easy to implement such changes in large mining plants.

As described in [6], currently in underground mines, qualitative and quantitative identification of sources of nitrogen oxides is sought. This knowledge is necessary to propose appropriate methods to reduce NOx in the excavations, because of the restrictions contained in [9]. Nitrogen oxides in Polish copper ore mines come from diesel-powered machine engines, process shots, natural oxidation of nitrogen present in the air. However, it is assumed that the largest amount of NOx comes from diesel engines [6, 10, 11].

The paper will analyze the diurnal variations of NOx concentrations in excavations. The result of the research will be a preliminary identification of the sources of nitric oxide emissions. Their preliminary analysis will allow verifying the correctness of the applied measurement method for further research, and this, in turn, will make it possible to select appropriate reduction methods.

2. State of the art

Ventilation in deep underground mines such as those located in Poland (1200+ m below ground level) is a challenging issue. Air quality in an underground mine depends on many factors, such as the mining process (blasting), ventilation, the amount of gases released by the rock mass, and pollution caused by diesel-powered machinery. Therefore it is important to control the relevant gases in the mine atmosphere for the proper functioning of the mine. Methane (CH\textsubscript{4}), carbon monoxide (CO), hydrogen sulfide (H\textsubscript{2}S), sulfur dioxide (SO\textsubscript{2}), and the oxides of nitrogen (NOx) are the main gases polluting the air in mines [4, 10, 12–15]. Air in Polish copper ore mines has been studied in the context of CO and H\textsubscript{2}S in previous research [13, 14]. In this paper, we focused on the gases from the NOx family. Knowledge about the instantaneous level of poisoning gas is the first key issue.

Nitrogen oxides are toxic gases. From the nitrogen oxides group, nitrogen oxide and nitrogen dioxide are analyzed. Both of these compounds are very dangerous and harmful to living organisms and their properties such as colorless-and-odorless-ness make them even more dangerous [16–19]. These chemical compounds enter the body through inhalation, ingestion, or, to a lesser extent, through the skin. [4, 20]. In accordance with polish provisions in force, it is assumed that the permissible value of NO concentration in mine air should not be greater than 2,6 ppm (5 mg/m\textsuperscript{3}), with a minimum oxygen content of 19% [1]. If the nitric oxide (NO) and other nitrogen oxide derivatives contents exceed the limit value, throat irritation and coughing occur. Longer exposure of the underground worker to NO concentration, as confirmed by numerous studies [16–18, 21], may cause chronic respiratory diseases or bronchospasm. If the value of gases is greater than 200 ppm, death occurs in a short time [22, 23].

The constantly changing conditions in underground mine workings, such as an increase in natural hazards, an increase in human awareness of one’s health, and world politics are responsible for the introduction of new, more restrictive regulations related to the emission of specific gases and shortening the employee exposure time. The introduction of new limit values for permissible gas concentrations for mines in Poland and the world often forces organizational, technical, and technological changes. Reorganization of work in underground mining plants is in many cases associated with higher costs.

The impact of nitric oxide and nitrogen dioxide on climate change and the destruction of the ozone hole, confirmed by numerous studies, contributed to the reduction of the permissible values of these chemical compounds [24, 25]. Directive 2017/164/EU, issued in 2017, introduced the following concentration values in the Member States.
Table 1: Valid limit values for nitrogen oxides based on European directives 2017/164/EU [9]

| Name of the chemical compound | 8-hour mg/m³ | 15-minutes ppm | 15-minute mg/m³ | 15-minute ppm |
|-------------------------------|--------------|----------------|-----------------|---------------|
| Nitric oxide                  | 2.5          | 2              | -               | -             |
| Nitrogen dioxide              | 0.96         | 0.5            | 1.91            | 1             |

The legal act [9] additionally introduced a transitional period for the underground mining and tunnel construction sector until August 21, 2023.

During this period concentration limits of such gases as nitric oxide and nitrogen dioxide, before the introduction of strict limits by the new act, are determined by different documents. For nitrogen oxide, the values are those in accordance with the Annex to Directive 91/322 / EEC (25 ppm), for nitrogen dioxide - national concentration values in force on 1 February 2017 (TLV - 3.5 mg/m³, STEL - 7 mg/m³) [9, 26, 27].

Currently, due to the restrictions introduced for the underground mining sector, researches are conducted all over the world to eliminate nitrogen oxide. The development of an appropriate identification and detection method of the NO and NO$_2$ emissions sources is a significant task from assessing the risk and introducing restrictions point of view. Thanks to the knowledge about these sources proper methods can be implemented, allowing reduction or complete elimination of nitric oxide and nitrogen dioxide.

Machines working in excavations to mine the mineral with internal combustion engines are probably the main source of increased nitrogen oxide content in the mine atmosphere. Hence, workings, where machines are operated, should be controlled in the first place in terms of the concentration of harmful gases. Currently, the concentrations of nitrogen oxide and nitrogen dioxide are measured with devices used in mines. First of all, these are personal gas detectors such as Drager PAC 8000 or PAC 8500 and the Dräger X-am 5000 gas meter. In Polish ore mines, ventilation services are mainly responsible for measuring and controlling gas concentrations in workings [28].

3. Mining area for experiment
Measurement of nitrogen oxide concentrations was performed in one of the Polish copper ore mines belonging to KGHM Polska Miedz S.A. O/ZG Polkowice-Sieroszowice is characterized by difficult environmental conditions in underground workings. They are related to the size of the mine and exploitation depth. The mine faces thermal hazards from high primary rock temperatures and gas hazards. The exploitation is lead through the use of explosives defined in regulations, based on room and pillar mining system. Fragmented material is transported by the machines with Diesel engines to the unloading points, from which it is further transported by a system of belt conveyors. The ore by rope transport goes to the surface, from where it is conveyed to enrichment plants. Spaces created due to the ore extraction are excluded from the ventilation network and liquidated by back-filling or roof deflection.

3.1. Location of measurement system
Measurement sensors location in the mine are presented in Figure 1. Fresh air currents are marked with red arrows, while used air currents with blue arrows.
In the experiment, measurements of nitric oxide concentration were conducted in fresh air currents. The first measurement point was located in an excavation near the auxiliary fan, at the very beginning of the mining area. Additional measurement point was situated in the same air current, however, in the middle of the mining area, distant from the auxiliary fans. The remaining two measurement points were located at the end of the mining area. One of them was set up to measure NO concentration in the air current ventilating the whole mining area. The second one, on the other hand, was set up in the air current ventilating blind preparatory excavations contouring the mining area, made as a part of rock-burst prevention prophylaxis. In this region, higher NO concentration should be expected, due to the operation of machines in small, limited areas and difficulties in ventilation of such closed spaces. Measurement points locations were chosen as a result of consultation with mine ventilation crew.

3.2. Measurement system
The measurement was carried out using Drager’s PAC 8000 measuring equipment. The sensors in the mine were suspended from anchor bolts in the middle of the workings below the roof to prevent them from being damaged by machinery travelling through the workings. The sensors used are capable of recording measurement data. The recorded data is transferred to the device, which enables it to be analyzed using a special add-on and the manufacturer’s software. This device was adapted to the measurement in difficult underground conditions - high air humidity, high dustiness, and high temperature. The measurement device is shown in the figure 2, while the basic parameters of the meter are contained in the Table 2.

| Drager PAC 8000 |  |
|---|---|
| **Measuring range** | 0 - 50 ppm |
| **Dimension** | 64 x 84 x 20 mm |
| **Weight** | 106 g |
| **Ambient condition** |  |
| Temperature | -40 to 50°C |
| Humidity | 10 to 90 % r.h. |
| Pressure | 700 to 1300 hPa |

The measurement data analyzed in this article are related to one day and include 4 working shifts. Measurements of NO gas concentration were performed every 1 second. The ore mining
with the use of explosives was carried out at the end of 2nd and 4th shifts. The original record of the results is presented in the graphs below. Graphs from two divisions - the G-51 district and the G-54 district.

4. Measurement data

The measurements in district G-51 was carried out on two days and covered four working shifts. The measurements in district G-54 took place over 4 days. Measurements were taken at four measurement points. All four measurement points were located in the same manner in both mining areas, as described in section 3.1. Recorded data from first measurement point on the G-54 district were presented in terms of 24 hours (as a part of Figure 4 and in terms of 72 hours (Figure 5.) Four characteristic measuring locations were selected: near the auxiliary fan, on the spoil haulage road, next to the excavated face and in the fresh air stream behind the diesel machine route. The measurement locations were selected in consultation with the ventilation service. In addition, an experiment was carried out to measure NO concentrations over three working days at one location.

4.1. G-51 district - daily changes

In the analyzed mining area, in pre-defined measurement points, four sensors measuring NO concentrations were placed. First (ARMC - 0008) in the K - 34 room and P - 24 cross-cut crossing, second (ARMB - 0001) in the K - 26 room and P - 16 cross-cut crossing, third (ARMC - 0001) in K - 3 room and P - 25 cross-cut crossing, while the last one (ARMC - 0007) in the K - 5 room and P - 23 cross-cut crossing (see Figure 1a.)

Charts from below (Figure 3.) are presenting a graphical interpretation of nitric oxide concentration in the chosen points G-51 mining area. Measurement session has been started at 11 am.

Figure 3: Measurement data G - 51 district

By the analysis of the presented chart, it can be stated that the NO concentration in pre-defined points of the G-51 district changes dynamically throughout the day. Speaking of the first measurement device, ARMC-0008, which was located near the auxiliary fan in the fresh
air current, it is visible that NO concentration from the beginning of measurement session till 7 pm varies from 0 ppm till max 5 ppm. After that time a rapid increase is observed to the value of 34 ppm. It should be remembered that one of two blasting activities is performed at the end of the 2nd shift, thus around 7 pm. Therefore, the observed peak is no doubly caused by the presence of nitrogen oxide-containing blasting gases in the fresh air current. Later on, the similarity can be observed concerning the beginning of the measurement. No other peak occurs in this measurement point, and the nitric oxide concentration values vary from 0 to 9 ppm.

In the second measurement point, located on the ore haulage road, where the ARMB-0001 measurement device was placed, recorded values take a similar distribution of values to those measured by the ARMC-0008 device at the beginning of the mining area. Same as in the case of the first point, the increase in NO concentration occurs around 7 pm. The value measured is 11.6 ppm. Although the increase is noticeable, it is not as great as in the first case. Taking into account that this measurement point is located at some distance from the auxiliary fan, the reason for this may be the dilution of post-blasting gases due to its operation. Further nitric oxide concentrations are characterized by a low amplitude. However, there is another increase in the value after 7 am, taking a value of 18.1 ppm. Again, that change is related to the presence of gases in the air current from second blasting performed twice a day.

The remaining two measuring devices (ARMC-0007 and ARMC-0001) located at the end of the G-51 district recorded similar values of NO concentration, which varies from 0 to 1 ppm during the whole measurement session. The exception is visible in both cases around 7 pm, where a peak value of 40 ppm is recorded. This situation is convergent to the previous three, where also the increases in nitric oxide content were related to the presence of post-blasting gases in the fresh air current.

4.2. G-54 district - daily changes

In the analyzed mining area, in pre-defined measurement points, four sensors measuring NO concentrations were placed. First (ARMC-0008) in the K - 23 room and P - 16 cross-cut crossing, second (ARMB-0001) in the K - 12 room and P - 8 cross-cut crossing, third (ARMC-0001) in K - 12d room and P - 21 cross-cut crossing, while the last one (ARMC-0007) in the K - 11d room and P - 21 cross-cut crossing (see Figure 1a.)

Charts from below (Figure 4.) are presenting nitric oxide concentration in the chosen points on the G-54 district during 24h period. The measurement session has been started at 10 am.
Figure 4: Measurement data G - 54 district

ARMC-0008 device placed in free air current directly behind the auxiliary fan recorded the values ranging from 0 to 5 ppm during the whole, 24h measurement session. No concentration values are relatively low, which may be caused by dilution of the gas in interest due to close location to the operating fan and thus quick ventilation of this area. The time in which the permissible values of nitric oxide concentrations were exceeded at this point was less than 2 hours, which is 7.3 % of the examined time. The second measuring device ARMB-0001 placed close to the place in which intensive work of machines is conducted, recorded higher NO concentration values, from 0 to 10 ppm between 10 am till 4 pm. After 4 pm a decrease in NO concentration is observed. Till 7 pm values are not exceeding 3 ppm. Because around 7 pm blasting procedure is performed, nitric oxide concentration raised temporarily in this point to 13 ppm. Afterwords, No concentration in fresh air current is not exceeding 6 ppm until 7 am when the transient increase to the value of 30 ppm is recorded, caused by the second blasting procedure and the presence of post-blasting gases. The time of exceeding the value this day was less than 29%.

The remaining two devices (ARMC-0001 and ARMC-0007) are located in the air currents which have ventilated all the mining area so that this air is treated as used. ARMC-0007 is located at the junction of two used air currents, thus higher than zero values of nitric oxide concentration should be expected. Actual values measured are ranging from 0.5 to 7 ppm. On the other hand, ARMC-0001 is placed in the working with ventilation dam. Daily values measured are not exceeding 7 ppm, however, one divergence is observed around 7 am when the blasting is conducted. The time of exceeding the normalized value (2.6 ppm) in the first area was about 26.4%, while in the second measurement place it was 20.7% of a measurement session.

4.3. G-54 district - three days changes

Additionally, changes in nitric oxide concentration have been analyzed based on data gathered during the three-day measurement session conducted in the G-54 district. The measurement point was located in the K - 23 room and P - 16 cross-cut crossing, and the ARMC-0008 device was used. Graphic interpretation of NO concentration is presented in Figure 5.
Figure 5: Measurement data - G - 54 district in 3 days

The analysis of the charts from above shows that NO concentration values are varying from 0 to 5.5 ppm. Only small changes can be observed during the whole, three-day measurement session. As presented in Figure 5a the values have exceeded or were close to the reference value of 2.6 ppm for most of the first day. However, as shown in Figure 5b and 5c for most of the time recorded values were lower than those accepted by the regulations. The only exception is the last 3 hours of measurements when the NO concentration ranged between 3 and 4 ppm.

5. Conclusions
The article presents the results of measurements aimed at preliminary identification of sources of nitric oxide emissions into excavations. The results and their interpretation allowed the following conclusions to be drawn:

1. The measurements carried out allowed for the preliminary identification of sources of nitrogen oxides in the excavation. A temporary increase in concentrations is observed immediately after technological shots. After ventilation of the excavations from blast gases, the presence of nitrogen oxides in the excavations is mainly related to diesel machinery. Analysing the measurement results, it can be seen that in the G-51 district the highest measurement values occur after 6 am. This is related to the flow of shot gases through the excavations to the exhaust shaft. In addition, a spike in concentration values can be observed after 6 pm, where it is also connected with gunshot gases. A similar situation takes place in the G-54 department, where we can observe a momentary increase in NO at the moment of the flow of gunshot gases. It is concluded that the gunshot gases generate only temporary increases in nitric oxide values. Nevertheless, the NO limit values measured in the excavations were exceeded for a longer period of time, mainly along the ore transport route. These exceedances are therefore mainly related to diesel machinery.

2. A temporary increase in nitric oxide concentrations may be caused by a specific process activity. Continuous mining is connected with conducting specific technological activities which have an impact on increasing concentrations of NO in the excavation. Apart from the standard procedures such as blasting, permanent haulage route - a sudden,
temporary increase in concentrations of harmful gas may have another source. It should be examined whether one of such sources is connected with opening or closing of a dam on the air path to the measurement point. A momentary increase in gas concentrations may also be due to the passage of machinery past the measurement sensor. These conclusions shall be confirmed in subsequent tests.

3 The influence of external factors on the measurement results should be further investigated. Due to the difficult environmental conditions of the Polish copper ore mines, measurement with PAC 8000 under real conditions is not conclusive. As the measurement is not carried out in a laboratory, the result may be influenced by the presence of various factors. As in the case of hydrogen sulphide, described in [28], attention should be paid to the influence of other nitrogen compounds (N₂O, NO₂) on the measured values. Attention should also be paid to the "cleaning" time of the instrument. A sudden large increase in the gas concentration values may cause the device to show exceedance of the limit values in the excavation, even if the actual concentration values are no longer exceeded in the excavation.

4 In further work, longer analyses of changes in nitric oxide concentrations in pits should be carried out to check the repeatability of the results and to accurately identify sources of NO emissions to pits. Attention should be paid to how the increase in nitric oxide concentrations is affected by the number of machines at particular working shifts of the mining district and the number of blasted faces. The qualitative and quantitative identification of NOx sources will make it possible to propose appropriate methods for eliminating the harmful oxide in the atmosphere. is affected by the number of machines at particular working shifts of the mining district and the number of blasted faces.

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