STUDY ON THE AIR QUALITY DURING THE OPERATION OF THE *MIZIA* QUARRY

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ABSTRACT. The operation of quarries is normally associated with air pollution. As a result of mining and transportation activities, particulate matter (dust), carbon monoxide (CO), carbon dioxide (CO_2), nitrogen oxides (NO_x), sulfur dioxide (SO_2), and (volatile) hydrocarbons can generally be emitted. This paper presents studies on those pollutants in the *Mizia* quarry for limestone blocks. The measured concentrations of all gaseous pollutants in the quarry air are below (or equal to) the threshold values for protecting the human health. Particulate matter concentrations determined on the territory of the quarry exceed the maximum permissible values, i.e. the hourly average norm for the protection of human health. The higher values were measured in dry weather. Since the excess of the limit values is not extremely high, wearing proper dust masks by the workers is suffices to preserve their health for the whole range of work activities except direct drilling, where additional measures are needed to decrease dust release, such as dust collection and water spraying. Concentrations of gaseous air pollutants determined at the exit of the exhaust pipe of a working Fadroma haul-dump machine, a representative of the heaviest equipment used in the quarry, are at the low edge of the ranges that are presented in the literature for the heavy duty diesel engines. Concentrations of air pollutants released by the operating quarry practically do not pose hazards to the surrounding environment.

Keywords: quarry for limestone blocks, air pollution

ИЗСЛЕДВАНЕ НА КАЧЕСТВОТО НА ВЪЗДУХА ПО ВРЕМЕ НА РАБОТАТА НА КАРИЕРА "МИЗИЯ"

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РЕЗЮМЕ. Експлоатацията на кариерите обикновено се свързва със замърсяване на въздуха. В резултат на минни и транспортни дейности могат да се отделят прахови частици, въглероден оксид (CO), въглероден диоксид (CO_2), азотни оксиди (NO_x), серен диоксид (SO_2) и (летливи) въглеводороди. Докладът представя проучвания за тези замърсители в кариера „Мизия" за варовикови блокове. Измерените концентрации на всички газообразни замърсители във въздуха в кариерата са под (или равни на) праговите стойности за защита на човешкото здраве. Концентрациите на прахови частици, определени на територията на кариерата, надхвърлят максимално допустимите стойности, т.е. средната почасова норма за защита на човешкото здраве. По-високите стойности са измерени при сухо време. Тъй като превишаването на пределно допустимите стойности не е изключително високо, носенето на подходящи маски за прах от работниците е достатъчно, за да се запази здравето им за целия спектър от дейности, с изключение на пряката пробивна дейност, където са необходими допълнителни мерки за намаляване на отделянето на прах, като събиране на праха и оросяване. Концентрациите на газообразни замърсители на въздуха, определени на изхода на ауспуха на работеща фадрома - представител на най-тежкото оборудване, използвано в кариерата, са в ниския край на диапазоните, представени в литературата за тежкотоварните дизелови двигатели. Концентрациите на замърсителите на въздуха, емитирани от работещата кариера, практически не представляват опасност за околната среда.

Ключови думи: кариера за варовикови блокове, замърсяване на въздуха

Introduction

Quarrying and stone cutting industries have a significant role in our economy. However, these activities are associated with health and environmental impacts. Usually, particulate matter, or PM (dust with a diameter of 1-75 μm) is the main air pollutant released by such industries. Particles with aerodynamic diameters of less than 50 μm (termed Total Suspended Particulate matter, or TSP) can be suspended in the atmosphere, and those with aerodynamic diameters of less than 10 μm, i.e. PM_{10} (inhalable particles) can be transported over long distances and enter the human respiratory system (Sayara, 2016).

Generally, particulates from diesel engines, including those used in the quarries, contain primary carbon particles and secondary sulfate and nitrate aerosols formed from SO_2 and NO_x. The EPA found that while coarse and fine particles can increase respiratory symptoms and impair breathing, fine particles are more likely to contribute to serious health effects. Most of the particulate emissions from diesel engines are significantly smaller than 2.5 microns (Chevron Corporation, 2007).

In addition, carbon monoxide (CO), carbon dioxide (CO_2), nitrogen oxides (NO and NO_2 expressed as NO_x), sulfur dioxide (SO_2), and (volatile) hydrocarbons (VOCs) can be emitted as a result of blasting, mining and transportation activities.

Emissions of pollutants from these industries can lead to chronic health effects, such as decreased lung capacity and lung cancer resulting from long-term exposure to toxic air pollutants, as well as to a high degree of respiratory morbidity. Carbon monoxide is primarily generated by combustion processes. The toxicity of CO stems from its ability to reduce the oxygen-carrying capacity of blood by preferentially bonding to hemoglobin. While NO is non-toxic by itself, it contributes to the ozone formation and NO_2 can irritate the lungs and lower resistance to respiratory infection. SO_2 is primarily produced by the combustion of fuels containing sulfur. It is a moderate lung irritant. Along with NO_x, it is a major precursor to acidic deposition (acid rain). VOCs are not criteria air pollutants, though some specific compounds are classified as toxic. Their importance stems from their role in forming ozone. All hydrocarbons in the atmosphere are considered VOCs, as are many other types of organic compounds. The reactivity and toxicity of hydrocarbons depends on their chemical structure. Under most conditions, alkenes and aromatics are more reactive than alkanes. The harmful effect of organic compounds depends on their structure. Most hydrocarbons are non-toxic at low concentrations; some low molecular weight aldehydes are carcinogenic, and some monocyclic and polycyclic aromatic hydrocarbons (PAH) are suspected or known carcinogens (Chevron Corporation, 2007).

Table 1 lists typical output ranges of the basic toxic material in diesel fumes, as reported by different authors (Grenier, 2005; Tschanz et al., 2010; Resitoglu et al., 2015; Nett Technologies Inc., 2018). The lower values can be found in new, tuned, and clean diesel engines using low sulfur fuels, while the higher values are characteristic for older equipment.

Table 1.
Range of emissions from diesel engines

Pollutant	Unit	Range
CO	mg/m^3	6 - 1700
CO_2	vol. %	0.5 - 12
VOCs*	mg/m^3	90 - 1860
NO_x	mg/m^3	90 - 1880
SO_2	mg/m^3	5 - 390
DPM	mg/m^3	1 - 300

DPM - Diesel particulate matter; * - as n-octane

Table 2 presents legal requirements for some air pollutants that can enter the air through the diesel exhaust.

Table 2.
Limit values for some air pollutants

Pollutant / Norm	1	2	3	4
SO_2 (Ordinance12, 2010)	350	125	-	20
NO_x (Ordinance12, 2010)	200	-	40	30
PM_{10} (Ordinance12, 2010)	-	50	40	-
$PM_{2,5}$ (Ordinance12, 2010)	-	-	25	-
CO (Ordinance12, 2010)	10*	-	-	-
CO_2 (NIOSH, 2007)	-	0.58**	-	-
n-octane (NIOSH, 2007)	-	350***	-	-
TSP****(Ordinance14, 1997)	0.50	0.25	0.15	-

1 - Hourly average norm for the protection of human health, $\mu g/m^3$; 2 - Daily average norm for the protection of human health, $\mu g/m^3$; 3 - Average annual norm for the protection of human health, $\mu g/m^3$; 4 - Norm for protecting natural ecosystem, $\mu g/m^3$; * - maximum average for 8 hours in one 24 hours period, mg/m^3; ** vol % - REL - TWA - recommended exposure limits - a time-weighted average concentration for up to a 10-hour workday during a 40-hour workweek; *** TWA, mg/m^3; **** - in mg/m^3 .

The degree of air pollution with the above-mentioned pollutants by the quarrying activity depends on: the type and composition of the extracted material, the mining technology, the mode of transportation, the level of mechanisation, as well as on the local microclimate conditions. That is why for obtaining a “real picture” of the situation "in situ", measurements are needed.

The work presented in this paper is aimed at determining the concentrations of the eventual pollutants emitted under real working conditions of the *Mizia* quarry, as well as to assess their possible harmful effect to the workers and to the environment. The results obtained can serve as a basis for proposing mitigation measures.

Methods and materials

The studied quarry is near the village of Varbesnitsa, the municipality of Mezdra, in Northwest Bulgaria. Climatically, the area falls within the moderate continental subregion of the European continental climatic zone. The average monthly air humidity is 72%, with a maximum in winter (December - 85%) and a minimum in summer (August - 59%). With regard to the wind, quiet weather prevails. Northwest winds with an average annual speed of 1.6 m/s are predominant.

Large premium limestone blocks are extracted in the quarry. Once the size of the block is determined, the edges of the block are determined by drilling holes. High technology diamond wire saws slice the massive beds in the quarry into blocks. Cooling water prevents the diamonds from overheating and suppresses the dust produced by the cutting equipment. The wire saws are also used to slice bigger blocks in the sealable sizes. The quarry workers pick up the stone blocks using loaders equipped with handling forks. Waste limestone, which is an unavoidable by-product of the quarrying and processing, is taken out from the production place with Fadroma haul-dump machines.

Eventual pollution can arise mainly from the drilling activities and from the work of loading and transportation machines. In addition, in windy conditions, dust from the quarry bottom can be raised. People can be exposed to limestone dust and other eventual pollutants in the workplace by inhalation and skin and eye contact.

Analyses for dust and gaseous pollutants were made at three points: first, immediately at the drilling point while the drilling was carried out; second, at the opposite end of the quarry while slicing with the wire saws and cargo operations were carried out; and third, outside the quarry in the nearby forest. In addition, exhaust gases were measured at the tailpipe end of one of the Fadroma haul-dump machines while it was working. The measurement is representative, since all haul-dump machines used in the quarry are the same age and produced by the same company.

A manual "Dräger" pump with a volume of 100 mL and two indicating tubes for each measured gas at each sampling point were used. Where necessary, tubes applicable for different concentration ranges of pollutants were used. Measurements with tubes for CO and n-octane are generally based on oxidation-reduction processes, while measurements with tubes for CO_2, SO_2 and NO_x are generally based on changes in the pH of the substance in the tubes. Both types of reactions lead to colour change of the substances and/or added reagents-indicators in the tubes. More precisely, the following reactions were used (Dräger, 2011):

For CO:

$$5CO + I_2O_5 \xrightarrow{H_2S_2O_7} 5CO_2 + I_2$$

Color change: white → brownish green

For n-octane:

$$C_8H_{18} + I_2O_5 \rightarrow I_2$$

Color change: white → green

For CO_2:

$$CO_2 + N_2H_4 \rightarrow NH_2–NH–COOH$$

Color change: white → pale violet/blue violet

For NO_x:

a) $NO + Cr^{VI} \rightarrow NO_2$

b) NO_2 + o-diphenyl benzidine → blue grey reaction product

Color change: yellow → blue grey

For SO_2, depending on the concentration range, where the second reaction is for the lowest concentrations of SO_2:

$$SO_2 + I_2 + 2H_2O \rightarrow H_2SO_4 + 2HI$$

Color change: grey blue →white

$$SO_2 + Na_2[HgCl_4] + \text{methyl red} \rightarrow Na_2[Hg(SO_3)_2] + 4HCl$$

Color change: yellow → orange .

Personal aspirators for dust, type PAP-4S, with flow rate of 2.0 L/min and FPP-15 filters were used at sampling points 1 and 2 for 60 min and two parallel samples were taken for each point. The sampling time was 8 hours for sampling point 3. Before and after the sampling, filters were weighed on an analytical balance (±0.00001 g). Dust sampling was done in two days – on one it was sunny and slightly windy, and on the other it was cloudy, wet and quiet.

Results and discussion

Results from the in-situ measurements (averaged values from 2 parallel determinations) are presented in Table 3.

By comparing the results, presented in Table 3, with the data from Table 1 and the values from Table 2, the following can be stated:

- Concentrations of gaseous air pollutants (NO_x, CO, CO_2, SO_2, and VOCs presented as n-octane) in the working atmosphere of the quarry are below or equal to the norms for the protection of human health.

Table 3.
In-situ determined concentrations of some air pollutants

Pollutant / Point	S1	S2	S3	Pipe
SO_2, mg/m^3, dry	0.3	0.3	<0.3	6
SO_2, mg/m^3, wet	0.3	0.3	<0.3	6
NO_x, mg/m^3, dry	0.2	0.2	<0.1	0.5
NO_x, mg/m^3, wet	0.2	0.2	<0.1	0.5
CO, mg/m^3, dry	8	10	5	20
CO, mg/m^3, wet	8	10	4	20
CO_2, vol %, dry	0.4	0.4	0.2	0.8
CO_2, vol %, wet	0.4	0.4	0.2	0.75
n-octane, mg/m^3, dry	160	210	<100	525
n-octane, mg/m^3, wet	210	350	<100	630
TSP, mg/m^3, dry	31	7	0.045	-
TSP, mg/m^3, wet	25	5	-	-

S1 – site immediately at the drilling point; S2 – site at the opposite end of thequarry; S3 – site in the nearby forest; pipe - at the tailpipe end of one of the Fadroma haul-dump machines

- Concentrations of gaseous air pollutants determined at the exhaust exit of the Fadroma haul-dump machine are at the low edge of the ranges presented in the literature for the heavy duty diesel engines.

- Practically, the work in the quarry does not pollute the surroundings with NO_x, CO, CO_2, SO_2, and VOCs.

- TSP concentrations determined on the territory of the quarry exceed the maximum permissible values, i.e. the hourly average norm for the protection of human health. Significantly higher excess concentration is observed at the measuring site situated immediately at the drilling point and under dry conditions. Values are of the same order of magnitude as those measured for a similar quarry by another author at 500-700 m outside their quarry (Sayara, 2016). Higher TSP concentrations were determined in dry conditions than in wet. Summer was found as the season with the highest TSP concentration by (Sayara, 2016), too. The precipitation helps in sinking these pollutants (wet deposition) and most of the produced dust is wetted and mixed with soil and can not be easily re-suspended.

- In terms of air pollution with dust, TSP concentrations determined in the nearby forest show that the quarry activity does not pose a negative effect on the environment.

Carbon monoxide in the diesel exhaust results from the incomplete combustion of the fuel. Although CO is produced in rich mixtures during operation, a small portion of CO is also emitted under lean conditions (Resitoglu et al., 2015). Diesel engines are lean combustion engines. So, the formation of CO is minimum in the properly tuned diesel engines. Hydrocarbon emissions are composed of unburned fuels as a result of insufficient temperature which occurs near the cylinder wall. Since unburned hydrocarbons continue to react in the exhaust stream, if the temperature is above 600°C and oxygen is present, diesel engines normally emit low levels of hydrocarbons. That is why the hydrocarbon emissions from the tailpipe may be significantly lower than the hydrocarbons leaving the cylinder (Resitoglu et al., 2015). Particulate matter emissions in the exhaust gas result from the combustion process. They may originate from the agglomeration of very small particles of partly burned fuel, from partly burned lube oil, from ash content of fuel oil, and from cylinder lube oil. Diesel engines use highly compressed hot air to ignite the fuel. At high temperatures (above 1600°C) in the cylinders, the nitrogen from the air reacts with oxygen and NO_x emissions are generated (Resitoglu et al., 2015).

When hydrocarbon fuel is burned with the correct amount of air in a diesel engine, the benign gases that are left are predominately water vapor, carbon dioxide, and nitrogen (Chevron Corporation, 2007).The total amount of air polluting gases and soot in the diesel exhaust is less than 1% (Resitoglu et al., 2015).

Exhaust gas recirculation (EGR) systems are usually used to reduce NO_x emissions. The exhaust gas is recirculated back into the combustion chamber and mixed with fresh air at intake stroke. A richer mix is achieved by displacing some of the intake air, but it is still lean compared to petrol engines. The lower peak temperature is achieved by a heat exchanger that removes heat before re-entering the engine, and works due to the higher specific heat capacity of exhaust gases than air. At this, the efficiency of combustion is worsened, the combustion temperature is decreased which means reducing the formation of NO_x. However, the negatively impacted efficiency leads to the production of soot particles. With the greater soot production, EGR is combined with a particulate matter filter in the exhaust gases system. EGR (with a PM filter) is widely used in high-duty diesel vehicles, including in those working in the *Mizia* quarry. The vehicles are also equipped with a diesel oxidation catalyst (DOC) which oxidizes HC and CO emissions. Most probably, the Fadroma haul-dump machines are equipped with a selective catalytic reduction (SCR) system, since the producer is amongst the world leaders implementing SCR in its high-duty vehicles. The SCR system is used to minimise NO_x emissions. Water and N_2 are released as a result of the catalytic conversion of NO_x in the exhaust gas.

The presence of the described technologies explains the low concentrations of pollutants measured in the exhaust of a working Fadroma haul-dump machine. Low concentrationsof polluting gases (below standard thresholds) have also been measured in other studies on the air quality in and around quarries and stone cutting industries (Sayara, 2016).

The presence of a visible dust cloud is a good sign that respirable dust is present, even though such clouds are mostly larger-sized particles (Organiscak et al., 2003).

Different studies obtained different values for the ratio PM_{10} / TSP but generally the reported values are in the range of 0.44-0.74 and most often - around 0.5 (Brook et al. 1997; Marcazzan et al., 2001; Kermani et al., 2003). In addition, the study of the Canadian National Air Pollution Surveillance Network showed that on average $PM_{2.5}$ accounted for 49% of the PM_{10} (Brook et al. 1997).

Considering the ratio of 0.5, it can be stated that the air outside the quarry meets the air quality standards with respect to PM_{10} and $PM_{2.5}$. However, this is not the case inside the working quarry. The limestone powder does not contain free silica and there is no danger of developing silicosis or other types of pneumoconiosis. However, powder exposure from limestone has an irritant effect on the upper respiratory tract. Some measures must be taken. Wearing proper dust masks by the workers is enough (Health and Safety Authority, 2010) for the whole range of works except for direct drilling, where additional measures are needed to decrease dust release, as described below.

Both wet and dry methods are available to reduce the drill dust (Organiscak et al., 2003). Wet drilling systems pump water into the bailing air from a water tank mounted on the drill. The water droplets in the bailing air trap dust particles as they travel up the annular space of the drilled hole, thus controlling dust as the air bails the cuttings from the hole. The drill operator controls the flow using a control valve. Dry collection systems require an enclosure around the area where the drill stem enters the ground. This enclosure is constructed by hanging a rubber or cloth shroud from the underside of the drill deck. The enclosure is then ducted to a dust collector, the clean side of which has a fan. The fan creates a negative pressure inside the enclosure, thus capturing dust as it exits the hole during drilling. The dust is removed in the collector, and clean air is exhausted through the fan. Wet systems can be more efficient, but may freeze in winter. Dry systems require careful maintenance of the drill deck shroud.

The waste limestone, an inevitable by-product of the quarrying and processing, is crushed to provide aggregate for making roads inside and around the quarry. The dust from these roads inside the quarry can be controlled by spraying plain water or water with some surfactants added by using spraying systems with suitable nozzle types (Spraying Systems Co., 2008).

Conclusions

As a result of our study the following conclusions can be drawn:

- Concentrations of gaseous air pollutants (NO_x, CO, CO_2, SO_2, and VOCs presented as n-octane) in the working atmosphere of the *Mizia* quarry for stone blocks practically do not pose hazards to the workers since they are below or equal to the norms for the protection of human health.

- TSP concentrations determined on the territory of the quarry exceed the maximum permissible values, i.e. the hourly average norm for the protection of human health. Higher amounts of dust were found in dry weather and on the measuring site situated immediately at the drilling activity.

- Wearing proper dust masks by the workers is sufficient to preserve their health. Additional measures, such as dust collection and water spraying, are needed to decrease dust release at direct drilling.

- Equipment used in the quarry is properly fitted with the air protection systems.

- Concentrations of air pollutants (NO_x, CO, CO_2, SO_2, and VOCs presented as n-octane and TSP) released by the working quarry do not pose hazards to the surrounding environment.

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