RISKS OF SELECTED FIELD OF NANOMATERIALS

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ABSTRACT

Working in stone quarrying and stone processing poses certain risks that must not be underestimated. The safety of workers must be paramount, where work-related injuries can occur, so the use of appropriate personal protective equipment is important, but the less visible risks, such as inhalation of granite stone dust, which can penetrate the respiratory tract, lungs and lung chambers, causing silicosis, chronic obstructive pulmonary disease, kidney disease or lung cancer, must not be underestimated. Chemically, granite dust consists of silica, which is the most abundant, and alumina, potassium, sodium, calcium, iron, ferric and magnesium oxides. For this reason, it is important to take all the nanoparticles of granite stone dust into account and see if they show toxic effects, for example. The aim was to carry out measurements of the concentration of released nanoparticles during granite processing in a selected stone quarry.

Keywords: nanoparticles, dust, stonework, granite, phytotoxicity

INTRODUCTION

Nanoparticles are particles that have one or more external dimensions in the size range of 1 nm - 100 µm. Nanoparticles contain molecules that consist of a surface layer, a shell and a core. Nanoparticles are divided into four basic groups according to their size, namely coarse particles (PM_{10}), fine particles ($PM_{2.5}$), ultrafine particles ($PM_{0.1}$) and aerosol [1]. Nanoparticles pose a risk to human health because they can enter the human body through various routes, such as inhalation (respiratory tract), dermal (mucous membranes and skin), intravenous (injection or damaged tissue) or oral (digestive tract). Nanoparticles are found naturally in nature, but in recent years, due to human activity, they have become increasingly burdensome to the environment because of their toxic, persistent or carcinogenic properties. Nanoparticles can cause certain risks, which can be divided into four categories, where nanoparticles pose a health risk, an environmental risk, a physicochemical hazard and a risk of the unethical use of nanotechnology. The properties of nanoparticles depend on their size [2]. Granite is a hard and tough rock, weather resistant, also resistant to most chemicals and acids. It is mostly composed of quartz, feldspar and mica, these components affect the coloration of the rock. Chemically, granite dust consists of silica, which is the most abundant, followed by alumina, potassium, sodium, calcium, iron and magnesium [3]. Granite dust is hazardous in terms of the inhalation of dust particles Granite dust particles contain respirable crystalline silica, which can most commonly cause silicosis, chronic obstructive pulmonary disease, kidney disease or lung cancer. Exposure to granite dust is assessed by a permissible exposure limit (PEL) of 0.1 mg.m^{-3} for the respirable fraction of silica [4].

MATERIALS AND METHODS

The aim of the experimental part was to measure the concentration of released nanoparticles during the processing of natural stone, specifically granite. For the purpose of the measurements, a full-service natural stone processing company was selected for the application of natural stone in building architecture, and the company's inventory consists of more than 70 types of natural stone with a primary focus on granite, marble and slate. The work activities carried out in the aforementioned indoor hall were selected for the measurement of released nanoparticles during stone processing. Within the hall, the air exchange is controlled only naturally. Also, all the working machines are sprayed with water, which subsequently drains off via waste sumps.

Measurements were carried out with a manual particle size classifier testo DiSCmini. This instrument can detect particles in the range from 10 to 700 nm, with a mean particle size of less than 300 nm. The particle concentration range is from about 1 000 to more than 1,000,000 particles per 1 cm^3. With a time response of 1 s (1 Hz), it can also record the total surface area of particles deposited in the lung chambers (LDSA). The measurement principle is based on the electrical charging of aerosols.

[6].

RESULTS AND DISCUSSION

A total of 4 measurements were taken, targeting different workplaces. The duration of the measurements was set at 15 minutes. During this time, the aforementioned instrument recorded the particle number concentrations and their mean average. Based on these findings, a table was prepared in which these values were compared.

Table 1: Average measurement values

	Ø Particle number concentration [particles/cm^3]	Ø Mean particle diameter[nm]
Measurement 1	67,580	75.5
Measurement 2	52,574	82.3
Measurement 3	48,995	80.7
Measurement 4	39,580	85.9
Average value	**52,182**	**81.1**

Measurement 1

The highest values were measured in the very first measurement at 55,000 – 235,000 particles per cm^3, as the two formatting saws located at the site were in operation and the measurement was carried out through the passage of the entire hall. In the initial part of the experiment, the particle count even jumped to 235,169 particles per cm^3. After that, it stabilised. The average particle number concentration in this measurement was 67,580 particles/cm^3. The mean particle diameter was in the range 60-80 nm and again followed the particle number concentration curve. As the number concentration increased, the mean particle diameter decreased.

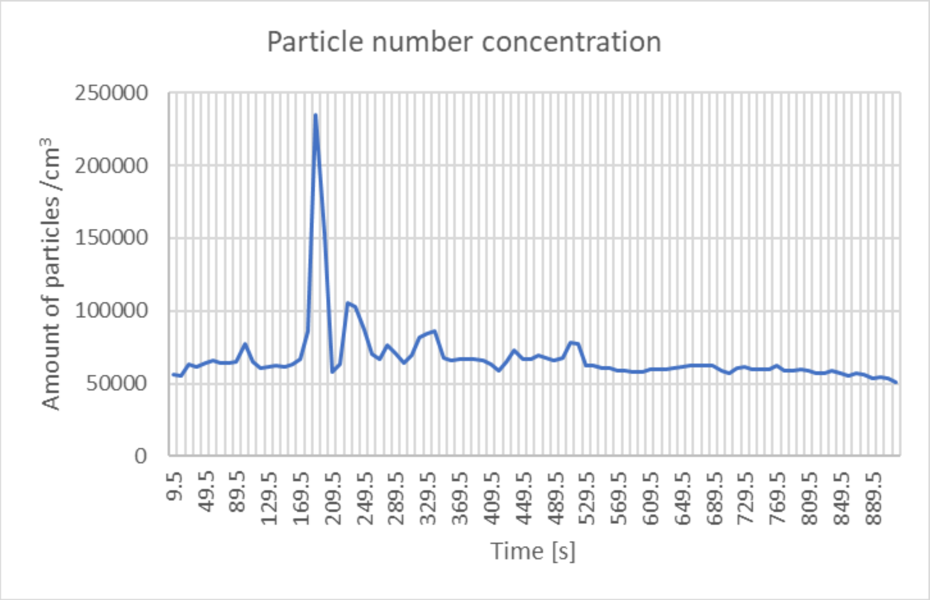

Figure 1: Particle number concentration 1st measurement (passage through the hall)

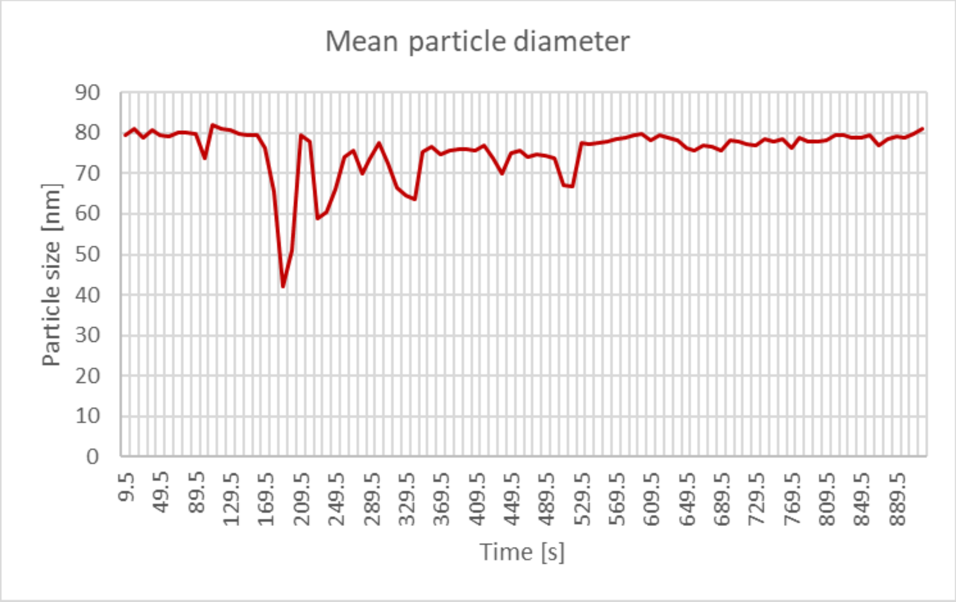

Figure 2: Mean particle diameter 1st measurement

Measurement 2

During further measurements, the number concentration of particles gradually decreased. During the measurements, the highest particle concentration was measured during the machine start-up and the start of cutting and gradually this concentration decreased to a value of 49,389 particles per cm^3. Thus, for this measurement, the average concentration dropped from 67,580 particles/cm^3 measured in the first measurement to 52,574 particles/cm^3. The mean particle diameter reached 79 nm twice and then slowly increased to 84.8 nm.

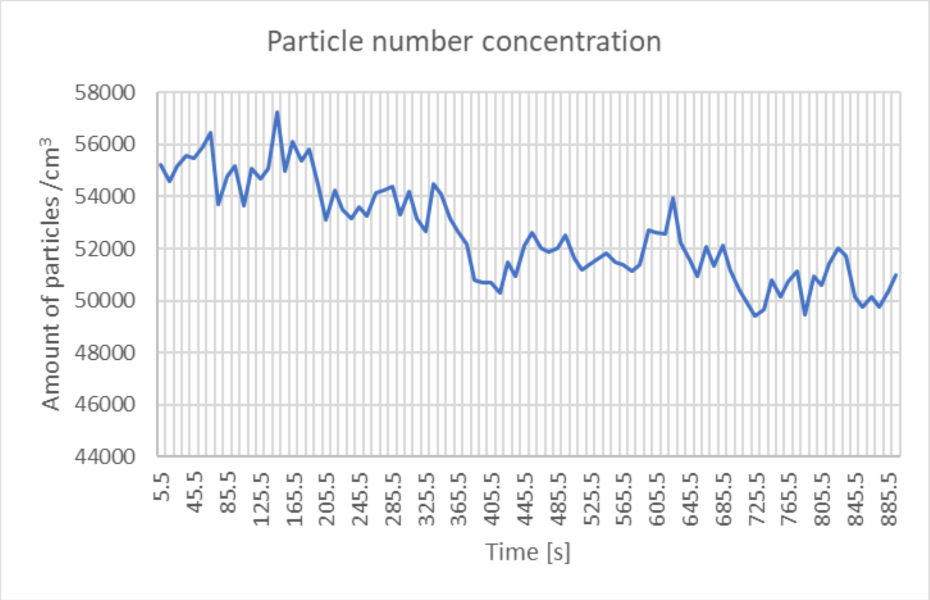

Figure 2 Particle number concentration 2nd measurement (forming saw)

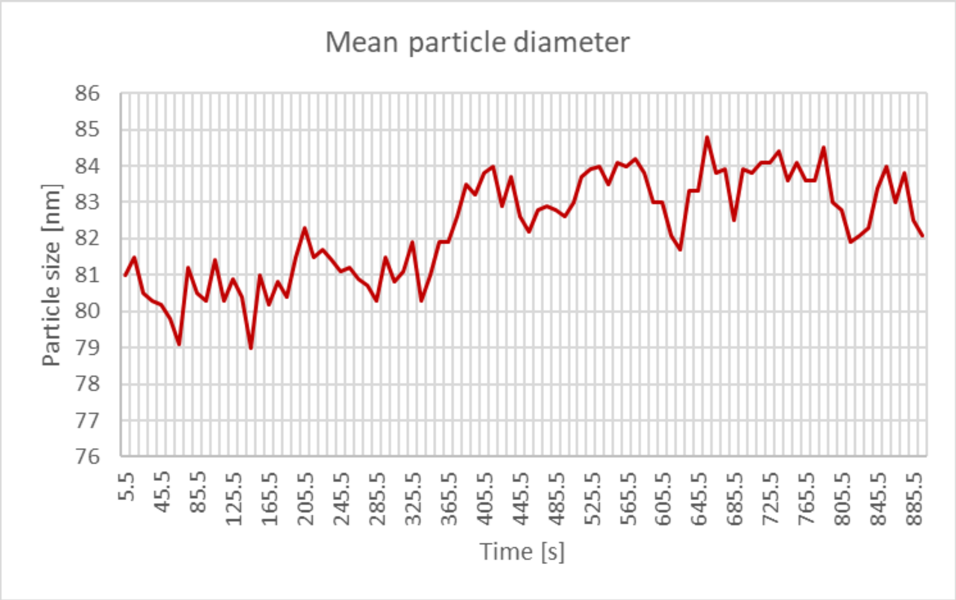

Figure 3 Mean particle diameter of the 2nd measurement

Measurement 3

The third measurement was taken at the grinding arm. During the third measurement, the smallest fluctuations in values were measured and the concentrations remained between 54,000 and 45,000 particles/cm^3 respectively throughout the whole time. Nevertheless, the average number concentration decreased to 48,995 particles/cm^3. This trend was no longer related to the particle size, where the mean diameter of the particles changed continuously and the mean diameter dropped from 82 nm to 76.7 nm in about 4 minutes. This was followed again by an increase in size over time with small fluctuations.

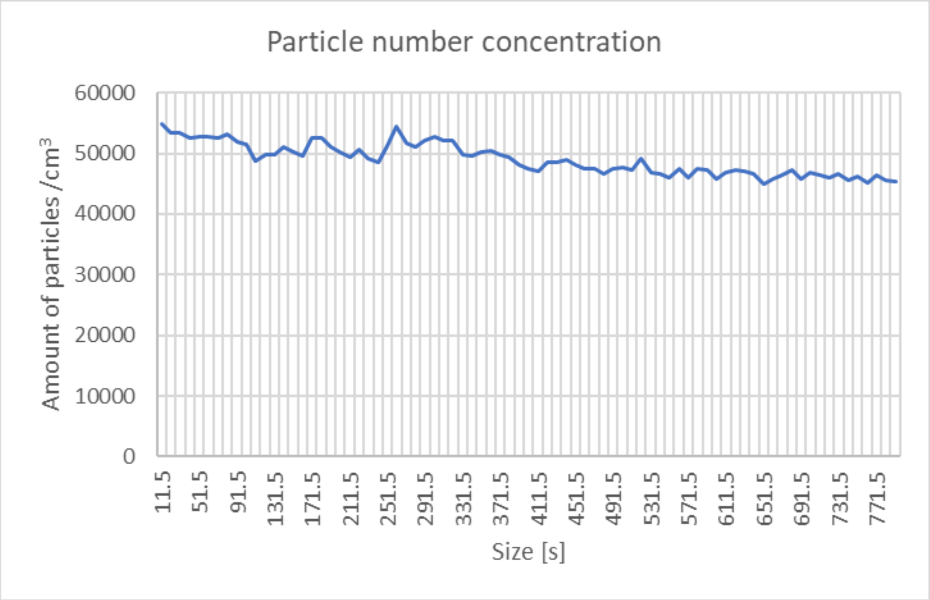

Figure 4 Particle number concentration 3rd measurement (grinding arm)

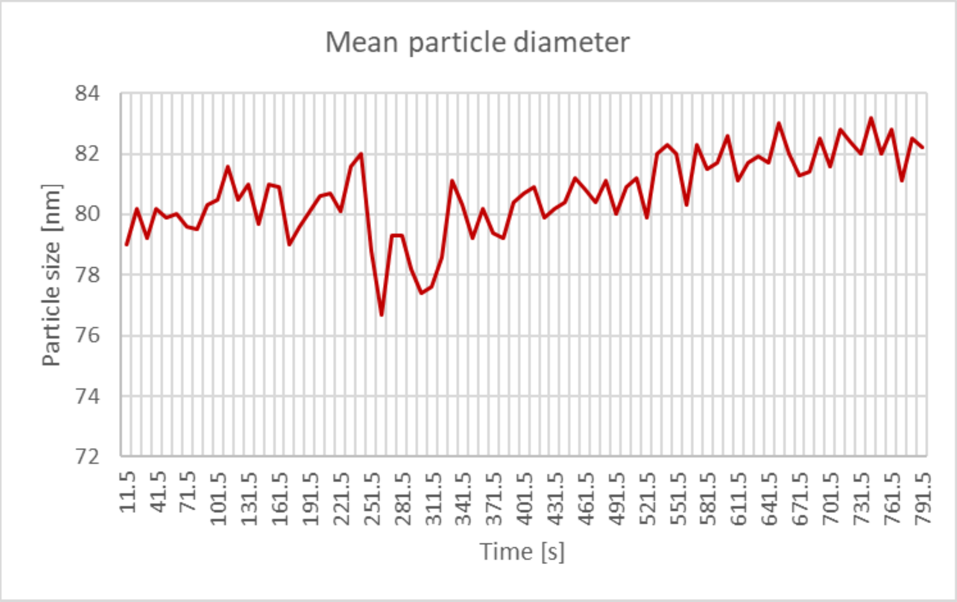

Figure 5 Mean particle diameter of the 3rd measurement

Measurement 4

For the last measurement, it can be seen that no work activities are currently taking place in the hall, as the measured particulate concentration values are at their lowest level. There was no one in the hall except the person taking the measurements, so there was no further swirling of the dust due to the movement of the employees and therefore the smallest fluctuations in the number of particles during the measurements are recorded. The highest measured value of 43,195 particles per cm^3 is also lower than any measured value in previous measurements. The lowest value at all was 36,513 particles per cm^3 measured at the exit of the hall. The average number concentration for this measurement was 39,580 particles/cm^3. In contrast, the mean particle diameter was not out of line with previous measurements, and the values were comparable, with a range of particle diameters from 83.9 - 88.7 nm.

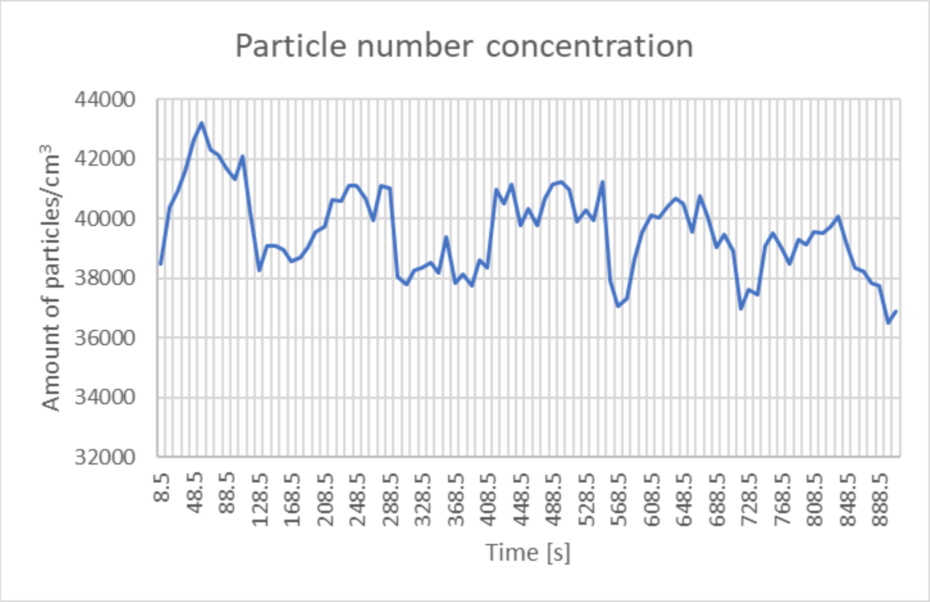

Figure 6 Particle number concentration 4th measurement (lunch break)

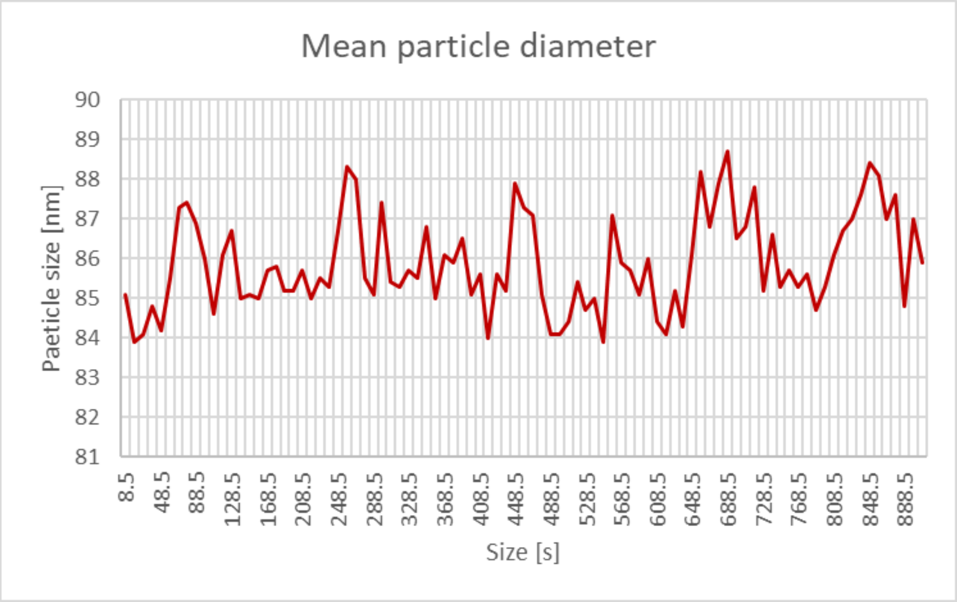

Figure 7 Mean particle diameter of the 4th measurement

Phytotoxicity testing

Toxicity tests of granite dust on white mustard (*Sinapis alba* L.) seeds were carried out according to OECD Test Guideline 208, modified for the purpose of the test [5]. Three vials of waste water from the stone cutting process were collected from the stone quarry and used to determine the toxicity. Three samples (100% concentrate, aqueous leachate and dry matter) were prepared to perform the test. The toxicity test consisted of placing 20 white mustard seeds in a square net on filter paper. Seed seeding for the dry matter sample was done by placing 10 seeds in the centre of the petri dish (direct contact) and 10 seeds in its surroundings (indirect contact). The test was performed in parallel and samples were seeded for control. After 72 h, the root length of each plant was examined, designated the root elongation, and the arithmetic mean of the root length was calculated for all determinations. Two criteria were evaluated, inhibition (numbers greater than 0) and stimulation (numbers less than 0). The results of the toxicity tests on white mustard (*Sinapis alba* L.) seeds showed inhibition in all cases except for the dry weight at indirect contact, which was -2.76%. The highest inhibition was obtained for the direct contact dry matter sample with a value of 32.95%. This was followed by distilled water A with a value of 31.79%, which is interesting since this sample was intended as a control. Further inhibition was achieved for aqueous leachate A with a value of 26.85% and for distilled water B with a value of 25.11%. Inhibition was also achieved for the 100% concentrate with a value of 16.26% for determination A and 9.29% for determination B. Aqueous leachate B achieved an inhibition of 13.06%. From the resulting values, it can be concluded that the samples may have the expected toxic effect, this may be due to the prevalent silica content in the granite.

Table 2 Results of the average root growth inhibition phytotoxicity test on white mustard (*Sinapis Alba* L.) seeds

Sample	Average inhibition [%]	Result
100% concentrate A	16.26	Inhibition
100% concentrate B	9.29	Inhibition
Aqueous leachate A	26.85	Inhibition
Aqueous leachate B	13.06	Inhibition
Dry matter A (direct contact)	32.95	Inhibition
Dry matter B (indirect contact)	-2.76	Stimulation
Distilled water A – control sample	31.79	Inhibition
Distilled water B – control sample	25.11	Inhibition

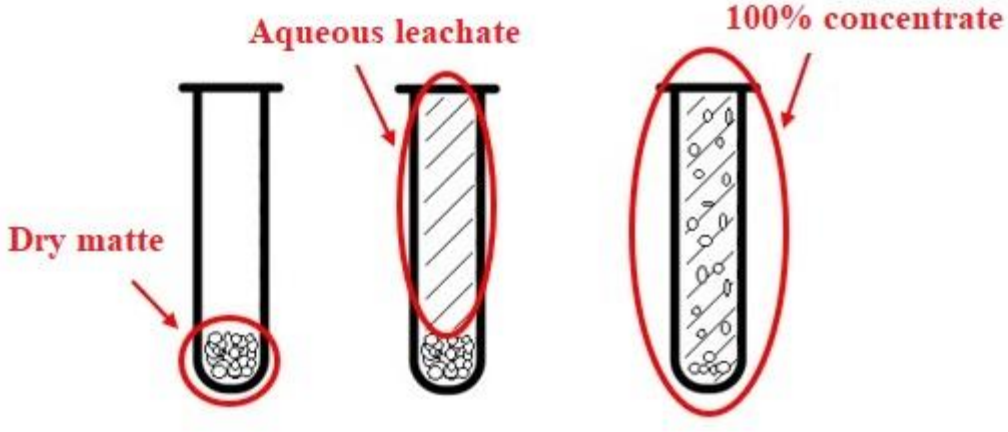

Figure 8 Method of sample preparation

Figure 9 describes the preparation of the samples that were taken while cutting the stone slab from under the rotary table of the saw. Three wastewater samples were collected while the machine was running, and a safe distance was maintained during sampling.

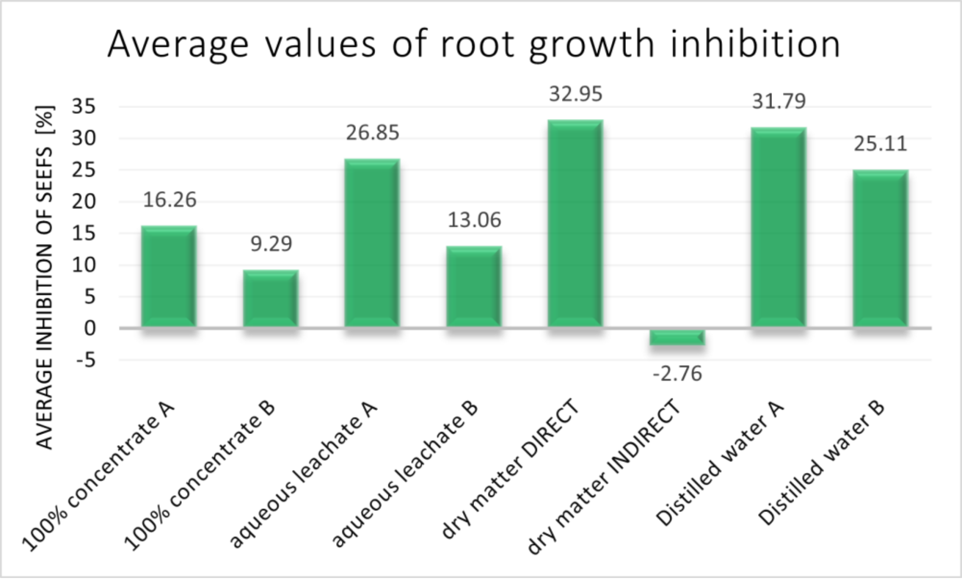

Figure 9 Average values of root growth inhibition of the white mustard

Figure 10 shows the average values of inhibition of growth of the white mustard (*Sinapis Alba* L.) root, where the highest inhibition was achieved by the dry weight sample in direct contact with a value of 32.95%. It was not possible to compare this sample with the other inhibitions, because the test design was different. The indirect contact dry matter sample resulted in stimulation with a value of -2.76 %. For the other samples, comparison is possible because the tests were performed under the same conditions and all of them showed inhibition, which means that the samples may have a toxic effect. This result was expected as granite dust contains SiO_2 and this is considered a carcinogen. This toxicity test on white mustard seeds (*Sinapis Alba* L.) has only confirmed this statement.

CONCLUSION

The aim of each of the above measurements was to assess exposure to particles in the working air and to perform a toxicity test of wastewater on white mustard (*Sinapis alba* L.) seeds. The selected company was a stone masonry company where, as already mentioned, employees are exposed on a monthly basis. Measured work activities are carried out in a covered hall, making year-round operation possible. This provides an ideal environment for sampling. Prior to the measurements, a rapid survey of the workplace was carried out to identify individual locations where elevated concentrations of dust particles may be present. Following the measurements, it was determined that the highest concentrations, including the average concentration, occur throughout the hall and especially when all working machines are in full operation. On the other hand, the lowest concentrations occurred when the working machines were idle (lunch break).

Because of the elevated concentration of these nanoparticles and also because of the assumption of toxicity of this dust based on its composition, three vials of wastewater were collected to confirm this hypothesis. These were subsequently subjected to a toxicity test on white mustard (*Sinapis alba* L.) seeds. The test procedure followed the OECD Test Guideline 208. The result of these tests was confirmation of the toxicity of the granite dust and thus of an increased risk for the employees working in the production hall.

On the basis of the measurements made, individual measures were determined, including new recommendations concerning production workers. The most prominent existing measure to eliminate the increased generation of nanoparticles in the production area is the use of the wet method for cutting and subsequent removal of dust from the floor. Another measure in place is the use of an extraction chamber when using hand tools for finishing stone slabs. New measures that have been recommended are to prevent the formation of higher concentrations of these nanoparticles in the working air, e.g., the introduction of forced ventilation of the hall or the provision of an air purifier in the employees' changing room. Another important measure for employees is the allocation of individual PPE based on a risk assessment of the workplace. Due to the high concentrations of nanoparticles, it is advisable to equip employees not only with e.g., FFP3 respirators but also with protective goggles. The last measure is the regular cleaning of the workplace, which should take place at regular intervals. Violation of this measure could lead to an increase in the concentration of nanoparticles in the area and their deposition in the workplace.

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