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Abstract

ANFO is one of the most commonly used explosives in open-pit mining, usually produced by mixing systems on the blast site. One of the problems usually not considered is the moisture”s influence on the stored ammonium nitrate(V). The influence of moisture on fumes and the detonation process has been investigated by placing ammonium nitrate(V) prills in the climatic chamber. In the investigation, the influence was evaluated for ANFO samples which were produced based on the two types of fuel oils. It was concluded that the 3.0% moisture level resulted in the lowest NOx content in both case studies. Further increased moisture resulted in blending problems (water absorption instead of fuel oils). An additional evaluation was made to stimulate the influence of wetted boreholes. The data showed that the equivalent mass of water present in the borehole would generate more fumes compared with the explosive produced from wetted ammonium nitrate(V) prill. Moreover, it was established that the second type of fuel oil can be applied as a fuel component, especially in the winter season.

Keywords: explosives, ANFO, moisture, fumes, ammonium nitrate(V)

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Influence of the moisture on fumes derived from the ANFO detonation

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Abstract

ANFO is one of the most commonly used explosives in open-pit mining, usually produced by mixing systems on the blast site. One of the problems usually not considered is the moisture"s influence on the stored ammonium nitrate(V). The influence of moisture on fumes and the detonation process has been investigated by placing ammonium nitrate(V) prills in the climatic chamber. In the investigation, the influence was evaluated for ANFO samples which were produced based on the two types of fuel oils. It was concluded that the 3.0% moisture level resulted in the lowest NO_x content in both case studies. Further increased moisture resulted in blending problems (water absorption instead of fuel oils). An additional evaluation was made to stimulate the influence of wetted boreholes. The data showed that the equivalent mass of water present in the borehole would generate more fumes compared with the explosive produced from wetted ammonium nitrate(V) prill. Moreover, it was established that the second type of fuel oil can be applied as a fuel component, especially in the winter season.

Keywords: explosives, ANFO, moisture, fumes, ammonium nitrate(V)

1. Introduction

ANFO (Ammonium Nitrate Fuel Oil) has been widely used in various civil applications since the 1950s due to its low cost and efficiency [1]. It is considered a non-ideal high explosive, in which porous prilled ammonium nitrate (AN-PP), known as an oxidizer, is mixed with fuel oil (FO) in a ratio of approximately 94:6 wt.%.

One of the most important blasting properties is the velocity of detonation (VOD). Based on this the detonation pressure can be determined, which in turn represents the energy of detonation [2–4]. Nikolczuk et al. have shown that besides blasthole diameter [4,5], the phase composition of the mixture is another factor that influences AN-based mining explosives VOD [6]. On the other hand, we should remember about ANFO limitation which may result in misfires. The main limitation of the ANFO application is its lack of water resistance. In a water environment, ANFO dissolves, releasing ammonia and nitrate, and causing infiltration to groundwater [7]. Moreover, Chambers and Wilson stated that it may become desensitized when the water concentration reaches approximately 10% by weight [8]. Water can affect ANFO by reducing the velocity of detonation (VOD), including the transition to a deflagration process. This results in an incomplete reaction of the explosive in the blast hole. Rowland and Mainiero have shown that water contamination of ANFO can cause an increased content of nitrogen dioxide in blasting fumes [9].

To overcome this limitation, several types of research have been conducted into various additives (e.g., grease, resin, asphaltic coating, guar gum, hydrophobic additives), applying a high volume of sensitizers, densifiers, and temperature stabilizers [10], as well as mixing ANFO with emulsion explosives (Heavy ANFO) [11]. The main purpose of this investigation was to develop a method that will

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allow ANFO application in blastholes that are filled with water or, in general, in a wet environment. However, it should be noted that ammonium nitrate is a hygroscopic substance, and its wetness will also depend on how the ANFO-type explosive is stored, transported, and prepared. Araos and Onederra have shown that various water content in ANFO can increase the velocity of detonation (VOD) of tested ANFO samples; however, their research method does not allow the determination of fumes composition [1]. On the other hand, the general research on mining explosives with regard to the content of carbon oxides and nitrogen oxides in their detonation products was discussed by Zawadzka-Małota [12].

This research paper presents an investigation of the effect of the influence of humidity on two ANFO samples (regular ANFO and ANFO obtained based on the alternative FO, fuel oils sample 2). The focus was placed on the practical aspect of the influence of humidity on storing ammonium nitrate porous prills (AN-PP). Factors like fumes composition, blending process, and lack of d detonation were taken under consideration.

2. Materials and methods

2.1. Materials

Yara's International A SA produced UltraAN 70 ammonium nitrate porous prills (AN-PP) in 2023. Ammonium nitrate(V) density was ca. 705 kg m^{-3}. Most of the prill's diameter was in the range of 1–2 mm (larger than 2 mm < 5% wt. and smaller than 1 mm < 3% wt.). AN-PP was characterized by an absorption index above 6.5%.

Fuel oils (FO) sample 1 was a wide-range fuel oil that consisted of linear hydrocarbons. It was delivered by one of the Polish blasting companies in 2022. The sample density was ca. of 873.2 kg m^{-3}.

FO sample 2 was a fuel oil sample purchased from one of the blasting companies that operates in the Polish market. The blasting company tested the sample to evaluate its possible application in ANFO as a fuel component in ANFO. The low-temperature characteristic of FO sample 2 will be discussed in section 3.1.

2.2. Methods

2.2.1. Measurements of fuel oil properties

The fuel oil density was evaluated in a glass pycnometer which was placed in a water bath maintained at 20°C for 30 min. The measurement was done according to [13].

The kinematic density was analysed with an Ubbelholde viscometer at a temperature of 40°C. The detailed methodology was described in [14].

The CP (cloud point) was measured in a Phase Xi apparatus according to standard [15].

The PP (pour point) was established by cooling the sample under the conditions defined in the standard [16].

The flashpoint was measured according to the standard [17]. The results were correlated with the Pensky-Martens test [18]. The flashpoint was determined using the continuously closed cup flash point method using an automatic EraFLASH apparatus (Eralytics).

Obtained low-temperature properties are presented in Table 1.

2.2.2. Climatic chamber

ANFO samples were placed in the WEISS WK 11-600/40 climatic chamber. The climatic conditions were: 25°C and 98% of moisture. Each sample was stored from 1 to 8 h until the desired moisture level in an AN-PP was obtained. Each 15-min stored AN-PP sample was blended in the chamber to obtain an even moisture content level.

2.2.3. Fumes evaluation

Fumes were evaluated according to the standard [19], which is to comply with a directive [20]. Each ANFO charge was of a mass of 600 g. ANFO charge was placed into the steel mortar. The mortar was inside the blasting chamber of a volume of 15 m^3. The 14 g RDX-based charge primed each ANFO sample. The blasting chamber is also equipped with pressure sensors and temperature sensors, which measure the condition of the decomposition process.

After the detonation, the homogenization of the atmosphere took place. Subsequently, fume samples were continuously collected by the ventilation system (for 20 min). The concentrations of CO and CO_2 were evaluated based on the results obtained from the IR (MIR 25e) analyzer. The NO_x was analyzed in a chemiluminescent (TOPAZE 32M) apparatus.

Table 1. Properties of tested fuel oils.

Parameters	Fuel oil sample 1	Fuel oil sample 2
Density at 20°C, (d) kg·m^{-3}	873.2 (±1.2)	875.0 (±1.2)
Viscosity at 40°C, (ν) $mm^2 \cdot s^{-1}$	13.6 (±0.01)	10.32 (±0.01)
Flash point, °C	127.3 (±1.2)	116.7 (±1.0)
Cloud point (CP), °C	8.9 (±1.1)	−25 (±0.78)
Pour point (PP), °C	−32.0 (±2.0)	< −60.0

The detailed measuring method was described in [21].

Calculated concentrations of fumes were presented in Tables 2 and 3.

2.2.4. Sample preparation

Before ANFO samples were produced, AN-PP was subjected to the first drying in a dryer for 24 h at 30°C. Every 6 h the mass of the sample was controlled to evaluate whether the sample was fully dried.

After drying, AN-PP samples were put into the climatic chamber to achieve respectively 1.5, 3.0, 4.5, 6.0, and 7.5% wt. water levels in the prill. Depending on the design moisture content, each sample was weighed after (1–8 h) to evaluate if a desired mass increase was achieved.

After the designed moisture level was reached, the ANFO samples were obtained by blending AN-PP with a FO in a 94-6 ratio. The blending was conducted for 15 min at a rate of 800 r.p.m. ANFO sample 1 was produced by blending AN-PP with FO sample 1. This sample will be treated as indicative material. ANFO sample 2 was obtained by blending AN-PP with FO sample 2 (tested FO).

Each sample was detonated within approx. 45 min after it was removed from the climatic chamber.

3. Results and discussion

3.1. Fuel oil analysis

The fuel oil were presented in Table 1.

According to Table 1, both fuel samples exhibited a lower flash point within the range of 116.7–127.3°C. The low value of the flash point indicates the risk of the fuel explosion process during its storage. However, the temperature of 116.7°C doesn't pose that threat. Both samples show a density of ca. 874.0°C. Obtained fuel oil densities won't negatively influence the end density of ANFO. The viscosity of fuel oil sample 2 is lower (10.32) $mm^2 \cdot s^{-1}$ in comparison with a regular fuel oil sample (13.6 $mm^2\ s^{-1}$). In case of low viscosity, the fuel component could drip from the ammonium nitrate prill. This, in the end, could lead to a misfire. However, the viscosity of ca. 10.0 $mm^2\ s^{-1}$ doesn't show this kind of threat. In comparison to fuel oil sample 2, fuel oil sample 1 exhibits a high cloud point (ca. 8.9°C) which can be explained by the precipitation of mainly saturated simple hydrocarbons from the fuel. The high temperature in the case of fuel oil sample 1 poses a threat due to the possible crystal wax formation and the noticeable appearance of the mist. This indicates that fuel oil sample 1 shouldn't be applied in autumn and winter conditions (at relatively low temperatures).

3.2. ANFO samples and toxic fumes

Based on the preliminary observation during the blending process, it can be concluded that moisture directly influences the AN-PP. It was observed that regardless of the type of fuel oil when the moisture

Table 2. Average fumes volume of ANFO, which was based on FO sample 1.

Explosive	Humidity	The amount of CO_2	The amount of CO	The amount of NO	The amount of NO_2	The amount of NO_x[a]	The sum volume of measured fumes
	%	dm^3/kg	dm^3/kg	dm^3/kg	dm^3/kg	dm^3/kg	dm^3/kg
ANFO sample 1	0	130.3	18.80	6.54	0.58	7.12	156.23
ANFO sample 2	1.5	106.9	17.38	0.41	0.06	0.47	124.75
ANFO sample 3	3.0	111.4	17.51	0.58	0.30	0.88	129.79
ANFO sample 4	4.5	108.3	9.35	2.37	0.14	2.51	120.16
ANFO sample 5	6.0	111.1	7.35	7.5	0.72	8.21	126.66
ANFO sample 6	7.5	105.0	7.35	6.47	0.83	7.30	119.65

[a] NO_x in the table is a total sum of the amount of NO and NO_2.

Table 3. Average fumes volume of ANFO which was based on FO sample 2.

Explosive	Humidity,	The amount of CO_2	The amount of CO	The amount of NO	The amount of NO_2	The amount of NO_x[a]	The total volume of fumes
	%	dm^3/kg	dm^3/kg	dm^3/kg	dm^3/kg	dm^3/kg	dm^3/kg
ANFO sample 1	0	132.3	18.72	8.06	0.81	8.86	159,88
ANFO sample 2	1.5	112.3	15.98	0.64	0.07	0.72	129,0
ANFO sample 3	3.0	113.9	14.86	0.29	0.05	0.34	129,1
ANFO sample 4	4.5	112.3	9.08	3.10	0.16	3.26	124,64
ANFO sample 5	6.0	110.4	6.86	10.02	0.68	10.69	127,95
ANFO sample 6	7.5	104.6	8.91	6.53	0.81	7.35	120,86

[a] NO_x in the table is a total sum of the amount of NO and NO_2.

reached 6.0% or higher, the fuel component wasn't fully absorbed by the AN-PP prill. The fuel oil dribbled from the AN-PP to the bottom of the mixer. This is especially crucial if we consider the AN-PP storage. Usually, AN-PP is stored outdoors in big bags. In the case of the blasting industry, the AN-PP is directly loaded into the tank of the mobile explosive manufacturing unit (MEMU). The only drying process can be performed during the transportation of ANFO components in MEMU to the blast side. However, in Poland, in most cases, blasting companies have their headquarters close to the open-pit mines. By this, it can be assumed that the AN-PP won't be fully dried in the case of high moisture derived from, for example, long-lasting rains. This could lead to the dribbling of the fuel oil in a tanker during blending, resulting in a different oxygen balance and end blasting properties (fumes content).

The concentration of fumes derived from the detonation of ANFO, which was based on fuel oil sample 1 and fuel oil sample 2 is presented in Tables 2 and 3.

Based on the total volume of fumes, and increased temperate and pressure in blasting chamber it can be observed that all samples detonated. Moreover, after each blast test, there were no remains of explosives in the blasting chamber, supporting the statement that each sample decomposed utterly. According to the data gathered in Table 2 and it can be observed that the total amount of CO and CO_2 and NO_x in a fully dried ANFO was 156.2 dm^3/kg (respectively 130.3 of CO_2 and 7.12 dm^3/kg of NO_x). Furthermore, it can be observed that, at a glance, the combined volume of carbon dioxide and carbon monoxide decreased logarithmically. In the case of nitrous oxides, the volume of fumes significantly reduced from 7.12 dm^3/kg to 0.47 dm^3/kg with an increase in moisture up to 4.5%. Over 4.5%, the amount of NO_x increased and reached 7.30 dm^3/kg for a moisture of 7.5%. The total amount of CO and CO_2 and NO_x decreased from 156.2 dm^3/kg and was in the range of ca. 120 to 130 dm^3/kg (depending on the moisture level). The data visualization for the overall NO_x and total CO_2 and CO is presented in Figures 1 and 2, respectively.

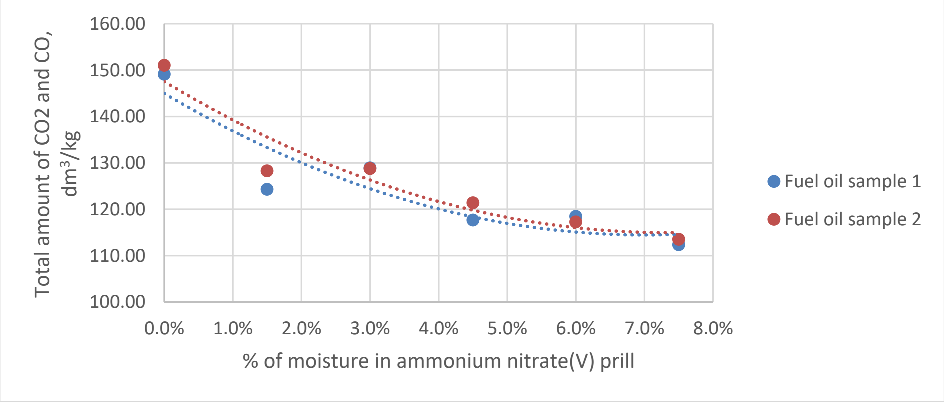

Fig. 1. The influence of humidity on the total amount of CO_2 and CO for both types of ANFO.

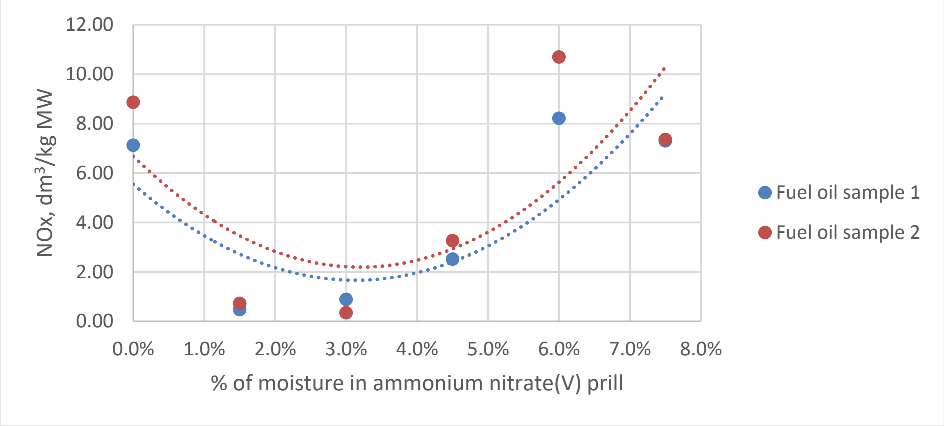

Fig. 2. The influence of humidity on the NO_x for both types of ANFO.

A similar fume analysis for the ANFO obtained based on the FO sample 2 was presented in Table 3.

Similarly to ANFO based on FO sample 1, all ANFO samples were based on FO sample 2 detonated. Moreover, after each detonation, there were no remains of explosives in the blasting chamber. According to Table 2 and it can be observed that the total amount of CO and CO_2 and NO_x in a fully dried ANFO was 151.0 dm^3/kg (respectively 132.3 dm^3/kg of CO_2 and 8.86 dm^3/kg of NO_x). The total volume of fumes was similar to that in ANFO based on FO sample 1. Furthermore, it can be observed that the amount of carbon dioxide and carbon monoxide decreased logarithmically. In the case of nitrous oxide, the amount of fumes significantly decreased from 8.86 dm^3/kg to 3.36 dm^3/kg, with an increase of moisture from 0% to 4.5%. Over 4.5% the amount of NO_x increased and reached 7.35 dm^3/kg for a moisture of 7.5%. The total amount of CO and CO_2 and NO_x decreased from 159.88 dm^3/kg and was in the range of ca. 120 to 130 dm^3/kg (depending on the moisture level). A similar effect was observed with an ANFO based on the FO sample 1. The main difference was the amount of NO_x. The amount of NO_x for a dried sample was lower in the case of ANFO based on FO sample 1 (7.12 dm^3/kg) compared to ANFO based on FO sample 2 (and 8.86 dm^3/kg). The visualization of the data for the overall NO_x and total CO_2 and CO is presented in Figures 1 and 2, respectively.

Based on Figures 1 and 2, it can be observed that the trend line has a polynomial character in both cases. Based on the trend lines, the theoretically zero oxygen balance explosive composition was a slightly negative oxygen balance. Further shift can be explained by the impact of moisture on the general composition of explosives. First of all, the moisture should be treated as an inert component. With the increase of moisture in the ammonium nitrate, the weight of the AN-PP has changed. That means that the weight of the fuel oil wasn't exactly the same as in the case of regular AN-PP, which is characterized by 0.2% moisture content. Moreover, it should be taken under consideration that the proportion of AN-PP:FO (94:6) has only in theory the zero oxygen balance. This means that in our experiment, at first, the oxygen balance shifts towards zero oxygen balance, which is characterized by the lowest concentrations of fumes. In both cases, we have observed that when the moisture level was approximately 3.0%, the amount of NO_x was the lowest. Further increase of the moisture was limiting the absorption capacity. When the moisture content reached 4.5%, the fuel oil was not entirely absorbed by ammonium nitrate(V) prills. This resulted in a lower amount of carbon, which at first oxidized into CO and next to CO_2. This tendency is evident with a moisture of 6.0 and 7.5%. The CO_2 decrease is followed by a stable amount of NO_x. The further increase in moisture will increase NO_x, as well as with a high possibility of misfire. This can be explained by the lack of fuel that provides all species necessary to sustain the detonation (breaking of nitro groups). Considering these results and taking into account the blending problems when the moisture was 6.0% or higher, it was decided to conduct a similar case study, which would allow us to simulate the behavior of ANFO in wetted boreholes. This allowed us to eliminate the dribbling of the fuel oil from the prill. The equivalent of the moisture level was put in the form of water on the bottom of the graduated cylinder (tested moisture levels of 4.5, 9.0, and 10.0%). The exemplary photo of the tested sample is presented in Figure 3. The charge was initiated from the dried side (similar to in the borehole).

The green dying agent shows the height of absorbed water by the ammonium nitrate(V) prill. The measured fumes compositions were presented in Table 4.

Comparing data collected in Tables 2 and 3 with Table 4, one can observe that dependent on the fuel oil used, similar water content resulted in different

Fig. 3. ANFO samples in a graduated cylinder (equivalent to 9.0% humidity).

Table 4. Average fumes volume of ANFO, water in the borehole approach.

Explosive	Water content	The amount of CO_2	The amount of CO	The amount of NO	The amount of NO_2	The amount of NO_x[a]	The total volume of fumes
	%	dm^3/kg	dm^3/kg	dm^3/kg	dm^3/kg	dm^3/kg	dm^3/kg
ANFO based on FO sample 1	4.5	129.3	14.93	4.37	0.36	4.73	148.96
ANFO based on FO sample 1	9.0	230.9	13.01	10.92	1.14	12.06	255.97
ANFO based on FO sample 1	10.0	253.9	12.54	12.01	1.29	13.30	279.74
ANFO based on FO sample 2	4.5	144.4	12.89	8.07	0.70	8.77	166.06
ANFO based on FO sample 2	9.0	142.2	13.21	13.21	0.90	12.31	167.72
ANFO based on FO sample 2	10.0	**Detonation failure**					

[a] NO_x in the table is a total sum of the amount of NO and NO_2.

results. In the case of moisture influence on the prill (Tables 2 and 3), the fumes amount was lower compared to the similar water content that was put on the bottom of the glass pipe. In the second case, it can be observed that when the water content was 10%, ANFO based on FO sample 1 showed a significant increase in CO_2 and NO_x (Table 4). The water absorption process could probably explain this. Water in the glass pipes reached a certain height and was not further absorbed. The excess water accumulated at the bottom of the glass pipe, which influenced fumes. In the case of ANFO based on FO sample 2, it was observed that there was a detonation failure with a water content of 10%. This corresponds with Yasick's research, who concluded that the presence of water above the 10% threshold may result in a detonation failure [22]. However, a detailed analysis that includes VOD tests should be conducted.

4. Conclusions

The paper describes two subjects: first, related to the impact of moisture during the storing of ammonium nitrate, and second, related to the potential application of fuel oils sample 2.

Based on the preliminary results related to the analysis of fuel oil properties it can be preliminary concluded that fuel oil sample two can be used as a fuel component. The cloud point indicates that fuel oil sample 1 (index fuel oils) is probably the summer-type fuel oil, and fuel oil sample 2 is the winter-type fuel oil. This means that fuel oil sample one should be used only in summer conditions. On the other, it was observed a lack of detonation in the case of fuel oil sample 2 (the wet borehole experiment). This was probably caused by the fuel oil aging; however, detailed measurements related to aging and heat of combustion should be made.

The research on the moisture impact on the AN-PP showed that the excess moisture would have a direct impact on the blending of AN-PP with FO. It was observed that with 6% moisture content (AN-PP was characterized by above 6.5% absorption capacity), the non-absorbed part of FO was dribbling from the AN-PP grain. This resulted in a smaller surface contact between AN-PP and FO, which, in the end, may resulted in a higher concentration of CO and CO_2.

Various blasting operators are storing ammonium nitrate (V) outside in big bags. The long-term storage, especially during long-lasting heavy rains, may result not only in the caking of the ammonium nitrate(V) (usually observed at the top layers in the big bags) but also in absorption problems of the fuel oil. It should be considered that the headquarters of blasting operators are close to the mining sides. The drying process may only appear in MEMU systems during transportation. However, the transportation time can be insufficient.

Independently of the fuel oil samples, it was observed that 3% moisture content resulted in the lowest concentration of NO_x, CO and CO_2. This can be explained by the shifting of the oxygen balance towards zero value. It should be remembered that moisture content (as an inert component) influences the AN-PP weight. It means that the proportion between AN-PP and FO won't be 94:6.

Comparing the total fumes volume of samples obtained via an impact of moisture in the climatic chamber (simulating storing) with preliminary research of moisture, it can be stated that detonation of ANFO in partially wetted boreholes result greater volume of fumes. It should be remembered that ANFO is subjected only to dry boreholes; however, a number of observations of blasting works showed that when the water level in the long boreholes was small, ANFO was applied.

Future studies should take into consideration the potential impact on various prill-size ammonium nitrate as well as detailed VOD analysis. In terms of wet boreholes, the continuity of the VOD should be taken into account throughout the entire length of the explosive charge.

Ethical statement

The authors state that the research was conducted according to ethical standards.

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Conflict of interest

The authors wish to confirm that there are no known conflicts of interest associated with this publication, and there has been no significant financial support for this work that could have influenced its outcome.

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