



# Drilling Fluids: Presence of Hazardous BTEXs and Crystalline Silica

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## Abstract

In the oil and gas industry occupational health risks due to drilling fluids is severe. Mixing room, shale shaker room and drill floor are sites where workers are highly exposed to air pollutants, hazardous dust and even substances generated via drilling fluids associated activities. Barite, calcium carbonate and linear paraffin or olefin-based oil are three types of chemical that are greatly used in huge quantities to prepare drilling fluids. These drilling fluids contain hazardous substances and pose health risks. Due to the occupational health risk, Occupational Safety and Health Administration OSHA Europe and USA have issued guidelines for the permissible exposure limit (PEL) to be at 5 mg/m<sup>3</sup> for barium sulphate, 10 mg/m<sup>3</sup> for calcium carbonate, 0.05 mg/m<sup>3</sup> for crystalline silica and 0.05 mg/m<sup>3</sup> for oil mists. Therefore, this study identified the presence of benzene, toluene, ethylbenzene and xylene (BTEX) ionic mists and crystalline silica in the drilling fluids. The grain size distribution of additives used in the drilling fluids was also determined. The results showed the presence of BTEX and crystalline silica based on random sampling. Therefore, the existing control measures are necessary to reduce the occupational health risks. As a control measure, Artificial Intelligence (AI) and Internet of Things (IoT) are necessary to be introduced for the automation of drilling fluids associated activities.

**Keywords:** Drilling fluids; Occupation health risk; Hazardous; BTEX; Barium sulphate

## Introduction

Drilling fluids have a vital role in measuring the success rate of drilling operations. These fluids are important to increase the oil recovery and shorten recovery time (1). Commonly used drilling fluids in the oil and gas industry are water-based, oil-based and synthetic-based muds (2). Drilling operation has three simultaneous systems that work in a boring hole. The first is a rotating system while second is a lifting system. The third system is a circulating system. The rotating system rotates the drill bit while the lifting system is used to lift up and lift down the drill string into the hole. The circulating system will circulate fluids around from the drill stem, out of the drill bit and up again into the hole at the surface.

The drilling fluids are often used to eliminate cuttings from the drilling hole, transport them to the surface and are also used as a stabiliser and supporter to the wellbore (3). Besides, the drilling fluids help to cool and lubricate the drill bit (4). Preparation of drilling fluids starts at the mud mixing hopper. The mixing hopper performs as a chemical mixing station and then the fluids are retained in the mud pits/tanks before being pumped into

the drill hole via a mud pump and a discharge line. These drilling fluids are circulated down the drill string and then out through the bit. The drilling fluids are moved back up to the annulus and straight into the surface. The huge quantities of drill cuttings are composed of rocks and particulate mixtures which are released from geological formations generated during the drilling operation (5). Cuttings that are suspended from the hole by drilling fluids are unwanted and removed when they flow through the shale shaker (4). The above-mentioned drilling fluids flow cycle is illustrated in Figure 1.

The selection of drilling fluids solely depends on their behaviours during the operation despite their drawbacks due to environmental concerns. The drilling fluids cycle will happen at elevated temperature together with agitation. This potentially exposes chemicals as well as oil vapour/mists; subsequently, affecting the health of workers both in short-term and long-term (6). Comprehensive risk assessments of drilling fluid systems need to be conducted by the operator well planners, taking into consideration the aspects of health, environment and safety when deciding on the type of drilling fluids to be used for the system.

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The outcomes of these assessments should be made accessible to all employees who may be exposed to the system.

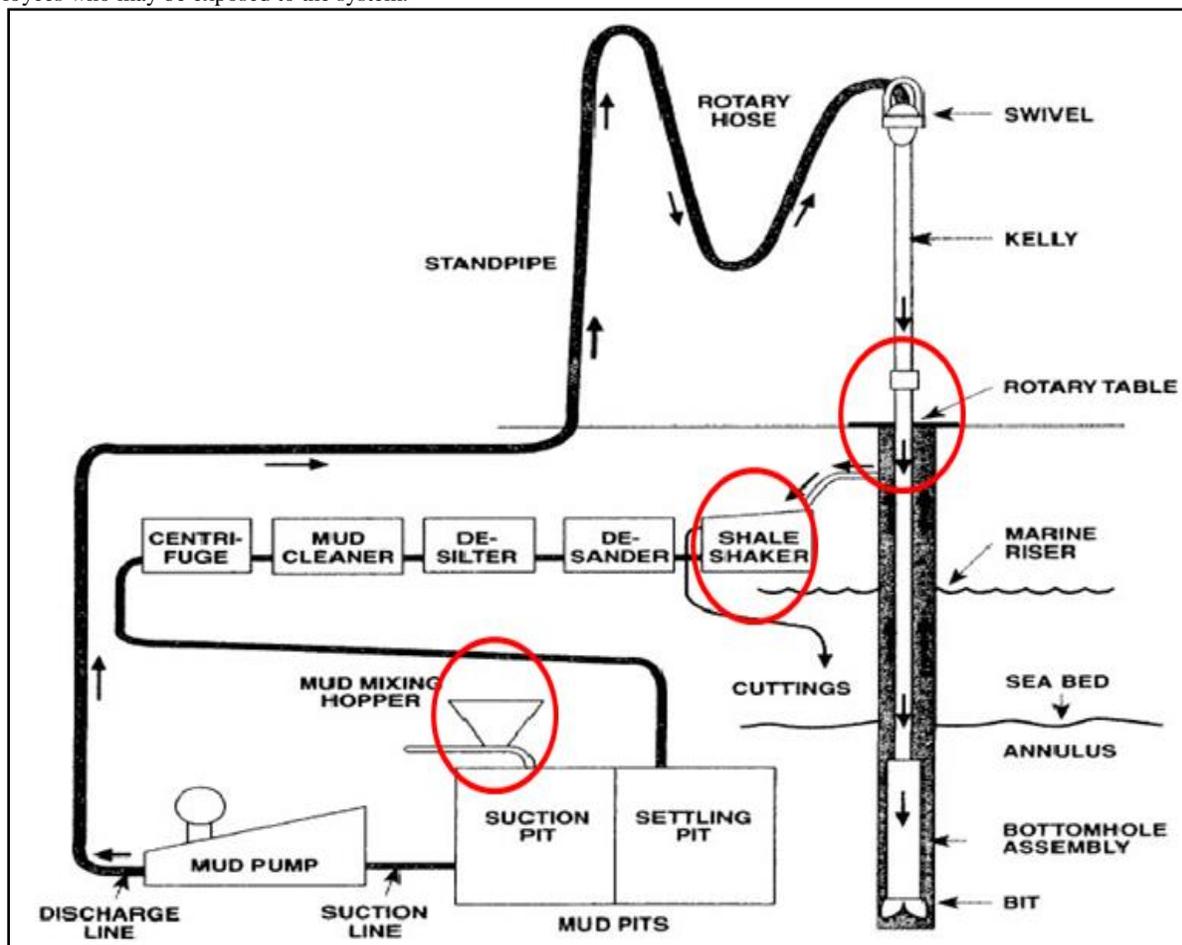


Figure 1: The drilling fluids recirculation and preparation

As highlighted in Figure 1, workers working in these three areas (drilling floor, shale shaker, chemical mixing station and mud pits/tanks) are highly exposed to hydrocarbons and oil mists (7). At the shale shaker, they are possibly exposed by inhaling aerosols and vapour/mists or through dermal contact. Dermal contact predominantly occurs with drilling fluids, lubricants, hydraulic oils and other personnel at the drilling floor. At the chemical mixing station and mud pits/tanks, workers are greatly exposed to burns, or physical injuries due to dermal or eye contact. Potential inhalation risk and explosions or aggressive reactions from improper chemical mixing are also greatly possible in these areas.

Skin irritation and skin diseases are the prevalent short-term health hazards observed when working with drilling fluids (7). Physicochemical properties of the drilling fluids, together with the inherent properties of the drilling fluid additives, are the root cause of these problems and are reliant on the exposure route, either through dermal absorption, inhalation or orally. There are concerns about the break down of organic components or even occurrence of chemical reactions which will produce more toxic components due to the operation of drilling fluids in an open system at elevated temperature and pressure (6). There are facts

that work-related illnesses may only be visible after a few years of exposure to toxic substances (8). Long-term exposure to barite (barium sulphate) in drilling fluids and oil mist/vapour may cause lung diseases (9). Drill cuttings are usually characterised by high content of polycyclic aromatic hydrocarbons (PAHs), which is potentially carcinogenic or mutagenic to mammals and aquatic organisms (10). Chen et al. (11) assessed the inhalator and dermal exposures to PAHs in oil mists and their consequential risks of cancer, specifically lung and skin, with regard to health-risk management. However, very few studies were carried out on oil well drilling workers' exposure hazards (7,12-14).

The basic three components in drilling fluids that are used in large quantities are barite, calcium carbonate and linear paraffin-based oil. The vapour of non-aqueous drilling fluids consists of low-boiling point portion of hydrocarbons, while the mist consists of droplets of the hydrocarbon portion. Although these hydrocarbon fractions may contain insignificant amount of known toxic components like benzene, toluene, ethylbenzene and xylene. They are collectively referred as BTEX, which will evaporate relatively faster, resulting in vapour with higher concentration than the estimated. Exposure to BTEX is correlated with health risks and may cause neurological effects, which is generally to the

central nervous system depression via the oral route, as well as renal and hepatic effects (7,15–17).

Barite is one of the most important components in drilling mud with its principal use as a weighting agent. It is used in substantial tonnages to increase the density of drilling mud due to its high specific gravity, balancing formation pressure and preventing a blowout (18–20). Barite used combinely with other substances like calcium carbonate to produce mud. This mud will be pumped down into the drill hole to control the high pressure formation and avoid explosive discharges of oil and gas from the well. The soft characteristic of barite prevents the drilling equipment from becoming worn. Besides, it is nonmagnetic and does not interfere with the logging drill holes' instrumentation. Basically, the usage of barite in drill hole differs significantly from site to site and depends on factors, such as hole depth and diameter, rocks types and drilling conditions like fractures and hole pressure (21).

Silica consists of silicon and oxygen in the form of silicon dioxide ( $\text{SiO}_2$ ) and is found abundantly on Earth. It exists either in a crystalline or non-crystalline form. Crystalline silica exists in several forms (polymorphs) and the most common polymorph is quartz. The surface of crystalline silica possesses reactive oxygen species when fractured, which is the reason of crystalline silica particles toxicity when inhaled (22). A common component of rock and soils is quartz, and employees may be exposed to dust that contains quartz during the drilling process. When drilling materials contain quartz and are subjected to high temperature, it may cause the quartz to tranform physically and chemically, which are eventually exposed to the workers.

The Agency for Occupational Safety and Health Administration (OSHA) of Europe and the USA have issued the guidelines of permissible exposure limit (PEL) for barite to be at  $5 \text{ mg/m}^3$ ,  $0.05 \text{ mg/m}^3$  for crystalline silica and  $0.05 \text{ mg/m}^3$  for oil mists. The particle size of barite is only controlled by personal protective equipment (PPE) at the cutoff point of  $3.5 \mu\text{m}$ . PPE is not able to filter a size that is finer than this, which means it will possibly enter the respiratory system of workers. Taking into account the occupational risks of drilling fluids, the objective of this research is to identify the existence of hazardous substances, such as BTEX in drilling fluids and mists/vapours that are released into the air, identify the presence of quartz (crystalline silica) followed by particle size analysis of crystalline silica in barite.

## Materials and Methods

### Materials

The barite was sampled under controlled conditions from a barite storehouse. All samplings were done on a random basis. Barite was basically used without further purification. X-ray diffraction (XRD) and particle size analyser (PSA) were the analytical methods used for barite. XRD was used to identify the presence of crystalline silica, while PSA was used to determine the particle size. As for the mists/vapours, the sampling and measuring were conducted during recirculation of drilling fluids. Oil vapour was dispersed into the atmosphere when the high temperature drilling fluids were circulated out from the well. As the drilling floor, shale shaker, chemical mixing station and mud pits/tanks are identified as the highest possible locations where workers are subjected to exposure of mists/vapours, all samplings for BTEX analysis were conducted in these areas. The Gastec sampling method was used to analyse the BTEX level. The details

of analytical methods used in this paper are discussed in subsequent sections.

### Analytical Methods

#### a) Gastec® Gas Sampling System

The Gastec® gas sampling system was used to check the level of BTEX in various locations at the drilling rig. These conventional Gastec tubes used colorimetric technology, whereby the chemical reagent in the gas tube reacted with the gas sample as it was drawn towards the tube via a pump. Detector tubes were specified according to types of gas to be measured, as shown in Table 1. The length of colour stains produced was proportional to the concentration of gas. The concentration may be read immediately by using the calibration scale printed on the tube.

#### b) X-ray Diffraction (XRD)

Barite powder was compacted in the sample holder and placed in the PANalytical XRD Machine for analysis. The XRD patterns were documented with  $\text{Cu K}\alpha$ -radiation ( $\lambda=1.5406 \text{ \AA}$ ). The  $2\theta$  values were scanned from  $10^\circ$  to  $70^\circ$  with 45kV and at a scan speed of  $2^\circ/\text{min}$  at  $25^\circ\text{C}$ .

#### c) Particle Size Analyzer

The particle size distribution (PSD) of barite was measured by using a Malvern Mastersizer 3000 instrument with Hydro EV Flexible volume wet dispersion (23). The particle size was determined as volume percentage of particles classed into 101 logarithmically distributed (log-spaced) size bins that ranged from  $0.01 \mu\text{m}$  to  $3000 \mu\text{m}$ . The signal was transformed into PSD data by using Fraunhofer or Mie scattering theory with the use of a laser device software (24). Fraunhofer approximation is a simplified method. Meanwhile a more accurate data can be obtained by using the Mie theory, but it requires the optical properties (refractive index and absorption coefficient of the sample) and the dispersant. Therefore, the latter provided more precise results (25). The analysis parameters for both barium sulphate is shown in the Table 2.

## Results and Discussions

### a) BTEX Analysis

Benzene, toluene and xylene were detected at various locations in the drilling rig with concentrations of 1ppm, 20ppm and 5ppm, respectively. As there was no benchmark, standards and acts were available to compare the data collected. Therefore, this finding clearly showed and shall be considered as a base case for studying further on the existence of BTEX and its exposure at drilling rigs. Though the hydrocarbon fractions may contain insignificant quantities of toxic components, such as BTEX, these will evaporate at low-boiling point relatively at higher rates, and thus resulting in higher concentrations of BTEX in the vapour phase than expected (7). Furthermore, the high level of BTEX emissions due to ancillary activities associated with drilling operations were also proven by others (26, 27). Despite the challenges in setting the standards for health exposure of drilling fluid to workers, research studies were conducted by the Agency for Toxic Substances and Disease Registry (ATSDR) for BTEXs released during agitation of drilling fluids at high pressure and temperature (7). These results were used as an exposure indicator or lowest observed adverse effect level (LOAEL) for workers' exposure to drilling fluids. This indicator may act as a guideline to help decrease the adverse effects of exposure.

**b) Identification of Crystalline Silica**

The dominant peak as shown in Figure 2a is the XRD analysis result for barite. The samples were analysed at 2θ values from 20 to 35. The peak was close to the selected reference data provided for silicon dioxide, as shown in the Figure 2b. This peak was also

supported and matched with the crystalline silica XRD analysis by others (28,29).

Table 1: Type of gases to be measured

	Benzene Detector	Toluene Detector	Xylene Detector
Measurement Range (ppm)	0.1 to 10	10 to 300	10 to 250
No. Pump Stroke	5	1	1
Correction Factor	1	1	1
Sampling Time (minute/stroke)	1.5	1.5	1.5
Detecting Limit (ppm)	0.05	1	1
Color Change	White to Dark Green	White to Brown	White to Brown
Reaction Principle	$C_6H_6 + I_2O_5 + H_2S_2O_7 \rightarrow I_2$	$C_6H_5CH_3 + I_2O_5 + H_2SO_4 \rightarrow I_2$	$C_6H_4(CH_3) + I_2O_5 + H_2SO_4 \rightarrow I_2$

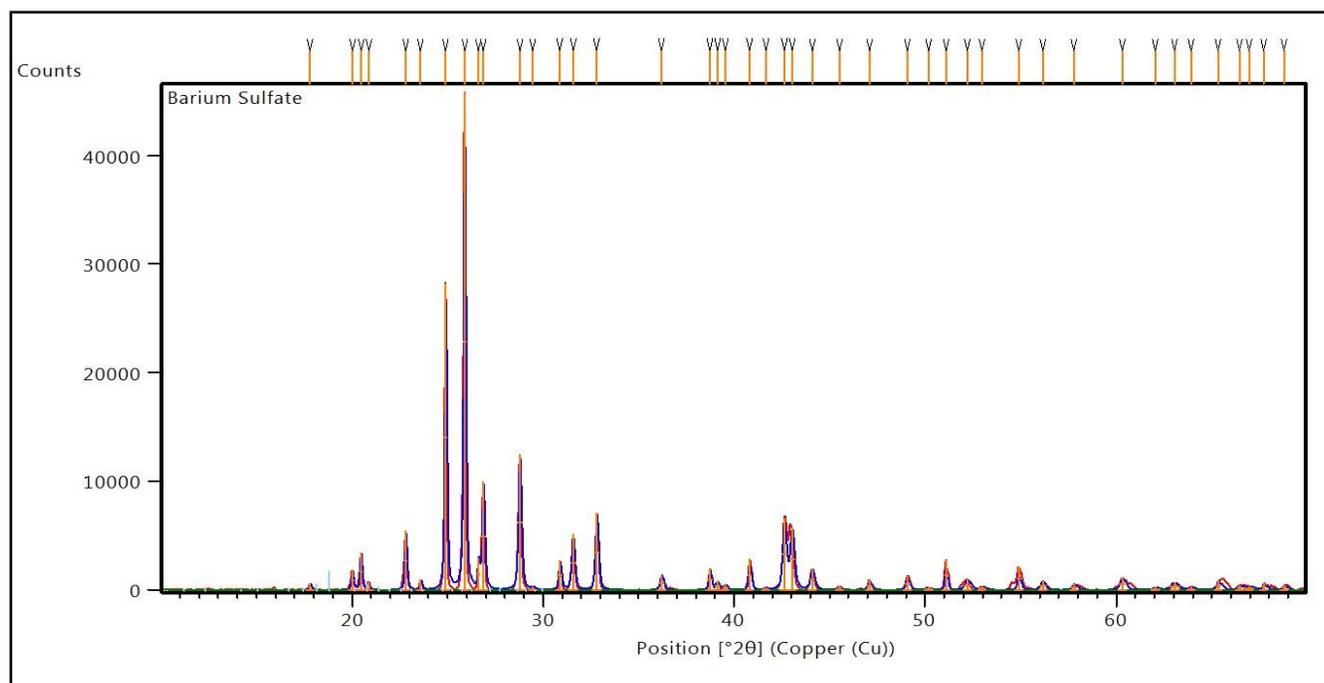


Figure 2a: XRD analysis for barium sulphate

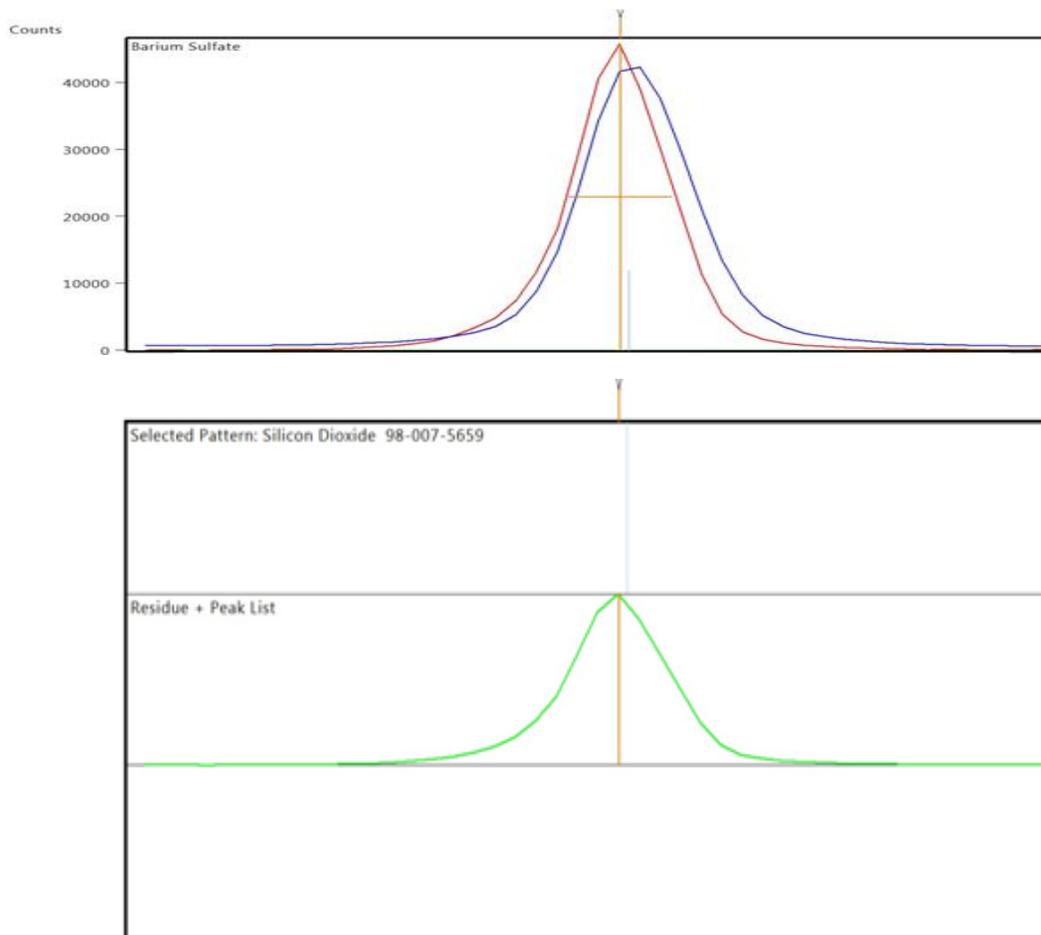


Figure 3b: XRD analysis for barium sulphate with reference data

Table 2: Analysis parameters of barium sulphate

Analysis Parameters	Barium Sulphate
Particle Refractive Index	1.643
Particle Absorption Index	0.010
Dispersant Refractive Index	1.330
Dispersant	Water

The PSD for barite is shown in Table 3, as the cutoff point of 3.5µm filter in breathing apparatus. There were some portions of particle size, which were below 1µm and it will strengthen the threat of these particles. Therefore, it will flow through the filter and possibly be inhaled. Further to the particle size and with confirmation of the crystalline silica presence in barite, the threat was imminent to the workers' health.

**Conclusions**

This paper presents the tangible threats to workers working on drilling operations at drilling rigs, especially activities allied with preparation and recirculation of drilling fluids. The presence of BTEX and crystalline silica in these activities is confirmed by quantitative analysis of samples taken randomly at

the sites. Furthermore, other than the BTEX and crystalline silica, the handling of barite is necessary to adhere to the guidelines where its permissible exposure limit (PEL) is at 5mg/m³.

Table 3: PSD for barite

Measuring	Results
Concentration	0.207%
Span	2.740
Uniformity	1.064
Specific Surface Area	713.1m²/kg
Dv (10)	3.48µm
Dv (50)	17.8µm
Dv (90)	52.2µm

Control measures such as engineering control or PPEs implementation of these activities should also be reviewed and revised to ensure the mitigation of occupational risks. The introduction of new control measures, namely Artificial

Intelligence (AI) and Internet of Things (IoT), which are aligned with the 4<sup>th</sup> Industrial Revolution such as automation in drilling fluids preparation and during circulation, will benefit the workers as well as companies reputation in the long run. Having considered all the risks related to incidental ingestion and inhalation of BTEX, crystalline silica and fine powder chemicals, below are the proposed control measures to minimise the risks:

- i) Substitution – shale shakers to the mud cube system (confined with vacuum)
- ii) Engineering Control – in-situ local exhaust ventilation and isolation
- iii) Personal Protective Equipment – zero-leak breathing apparatus

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## Ethical issue

Authors are aware of, and comply with, best practice in publication ethics, specifically with regard to authorship (avoidance of guest authorship), dual submission, manipulation of figures, competing interests and compliance with policies on research ethics. Authors adhere to publication requirements that submitted work is original and has not been published elsewhere in any language.

## Competing interests

The authors declare that there is no conflict of interest that would prejudice the impartiality of this scientific work.

## Authors' contribution

All authors of this study have a complete contribution for data collection, data analyses and manuscript writing.

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