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# **Styrene Gas Leak Incident Analysis in Vishakapatnam: Event Tree Analysis, Root Cause Analysis and Threat Zone Determination Using ALOHA Software''**

# **M.Vijay a++\***

*<sup>a</sup> Faculty of Engineering and Technology, Annamalai University, Annamalainagar – 608002, Tamil Nadu, India.*

*Author's contribution*

*The sole author designed, analyzed, interpreted and prepared the manuscript.*

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# **ABSTRACT**

The Visakhapatnam gas leak incident happened on May 7, 2020, at LG Polymers chemical plant in RR Venkatapuram, Visakhapatnam district, Andhra Pradesh, India, resulted in fatalities and several injuries. This study is about a comprehensive analysis of the incident and also focuses on the causes of the gas leak, the nature of the chemical industry, the subsequent response and its impact on Environment and Human Health. A detailed study about styrene gas leaks, the chemicals involved, and also about styrene-related accidents, safety data, and relevant laws and acts governing chemical storage. The work identifies various factors contributing to the gas leakage, including tank design, temperature control, recirculation systems, inhibitor addition protocols, and the risk of polymerization and runaway reactions. Methodologies like ALOHA for threat zone

*++Director, Centre for Disaster Management;*

*\*Corresponding author: E-mail: drmvijaydirectoraucdmtn@gmail.com;*

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determination, Event Tree Analysis (ETA) for consequence determination, and Root Cause Analysis (RCA) were employed to identify the causes and consequences of the incident. The main factors contributing to the accident were identified as the company's failure to adhere to proper styrene storage standards and severe defects in the construction of the storage tank. This catastrophe serves as a stark reminder of the critical importance of adhering to safety regulations in the chemical sector, as well as highlighting the importance on the reliability of process industries. The results from these analyses aimed to enhance safety measures within the chemical industry to prevent similar calamities in the future.

*Keywords: Polymerization; ALOHA; event tree analysis; root cause analysis.*

#### **1. INTRODUCTION**

Styrene, a common product of the petrochemical industry worldwide, isan aromatic organic chemical produced through the catalytic reaction ofbenzene and ethylene, forming Ethylbenzene, followed by dehydrogenation. It isa clear, colorless to yellow, oily liquid with a sweet odor at low concentrations.Styrene is used in the production of plastics, paints, synthetic rubbers, protectivecoatings, and resins. While it is liquid at ambient temperatures and consideredreasonably safe to handle and transport, it is inherently flammable and toxic,classified as a Group 2A carcinogen[1-5].

An incident of uncontrolled release of Styrene vapor occurred On May 7, 2020, at LG Polymers formerly known as Hindustan Polymers, was established in 1961 in Visakhapatnam, India. Originally focused on manufacturing Polystyrene and its Co-polymers, the company merged with Mc Dowell & Co. Ltd. of the UB Group in 1978. Subsequently, LG Chem (South Korea) acquired Hindustan Polymers, renaming it LG Polymers India Private Limited (LGPI) in July 1997. The company imports styrene monomer from Dubai, Singapore, and South Korea. The incident, commonly known as the "Vizag Gas Leak," resulted in the tragic loss of 12 lives and required hospital treatment for 585 individuals. This release of Styrene vapor is considered one of the major incidents of its kind from a bulk storage tank globally. In response, a team from the CBRN (Chemical, Biological, Radiological, and Nuclear) unit of the National Disaster Response Force (NDRF) in Pune, along with an expert team from the National Environmental Engineering Research Institute (NEERI) in Nagpur, was swiftly dispatched to Vishakhapatnam to assist the state government in managing the crisis. Polystyrene production involves heating styrene to initiate a rapid, exothermic reaction. Styrene has a tendency to self-polymerize, even at ambient temperatures,

which can cause issues like heat generation and blockages [6]. In Tables 1 & 2, physical properties and exposure limits of styrene gas were clearly mentioned. The rate of selfpolymerization doubles with every 10°C increase in temperature, potentially leading to a dangerous runaway reaction [7,8]. To prevent this, styrene is mixed with a polymerization inhibitor, typically TBC, at controlled concentrations.

"Styrene, poly butadiene (if an impact-grade product is desired), mineral oil (lubricant and plasticizer), and small amounts of recycled polystyrene, antioxidants, and other additives are charged from storage (1) into the feed dissolver mixer (2) in proportions that vary according to the grade of resin to be produced. Blended feed is pumped continuously to the reactor system (3) where it is thermally polymerized to polystyrene" (Fig. 1 & 2) [9].

#### **2. FACTORS LEADING TO STYRENE GAS LEAK ACCIDENT**

This Styrene vapour release, shown in Fig. 3 widely referred to as "Vizag Gas Leak", is a unique major Styrene vapourrelease incident from a bulk storage tank anywhere in the world.Nearly 20,000 people from 17,000 houses/residences of RRV Puram, Nandamuri Nagar, Kamparapalem, Padmanabha Nagar, SC/ BCColony, Meghadripeta Colony were evacuated, and arrangements weremade at 23 rehabilitation centres maintained by GVMC as well Simhachalam Devasthanam authorities [9]. Major factors leading to Styrene gas leak accident were as follows:

# **2.1 Tank Design and Specification**

A lined carbon steel tank is commonly preferred for the bulk storage of styrene monomers. But the M6 tank used in the process was constructed with mild steel without internal lining and is externally insulated, which is a non-conformance to the laid-down standards and guidelines. It operates at atmospheric pressure and is equipped with a flame arrestor/ventilator (N6) and a vent/dip hatch (N1). Additionally, it has a manhole/foam pourer (N2). To prevent dead packets filled with styrene, the number of nozzles must be kept to a to a minimum, but there are 17 nozzles in the M6 tank. The life extension program of the storage tank should be performed every 50 years as per PESO (Petroleum and Explosives Safety Organization), but the tank was 53 years old at the time of the accident. The

literature on storage styrene monomer says that the tank should be cleaned once every 2 years, but the company informed us that their standard protocol is to clean tanks once every 5 years. The formation of rust took place, which inhibits the role of TBC mainly due to improper maintenance of the tank. The tank design does not have a flare system to burn styrene into carbon dioxide or a cryogenic system to condense styrene vapors. From all the abovementioned factors, it clearly indicates that the tank is inferior to storing styrene in bulk amount [10].



**Fig. 1. Process description of expandable polystyrene**



**Fig. 2. Schematic diagram of styrene handling plant**

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#### **Table 1. Physical properties of styrene gas**

#### **Table 2. Exposure limits of styrene gas**





**Fig. 3. A file photo of styrene gas leaking out of a tank in LG Polymers unit, in Visakhapatnam**

#### **2.2 Tank Temperature Measurement and Control**

To accurately assess temperature variations, there must be 4 or 5 temperature probes in different zones of the 12-meter-tall M6 tank storing liquid styrene, but the multiple

measurement points that were distributed across its height were not adequate. Due to thermal layering, warmer Styrene rises to the top of colder Styrene, creating self-induced thermal stratification in Styrene storage. The M6 tank temperature was estimated at 41.7 °C based on DCS level percentage data recorded from April 28th to the early hours of May 7th, 2020. The company's protocol of maintaining a maximum temperature of 35 °C for styrene storage is unsupported by literature. Considering the flash point of Styrene Monomer (31°C) and autopolymerization initiation simulations (33.9°C), guidelines recommend not exceeding 25°C. Despite consistently recording a bottom temperature of approximately 17 °C, the M6 tank operators neglected to measure the much higher temperature at the top level. The absence of a vapor temperature probe in the tank's upper section contributed to management complacency [11].

#### **2.3 Recirculation and Refrigeration System**

Proper refrigeration-recirculation systems need to be provided, as the tank's insulation prevents the dissipation of exothermic polymerization heat. The refrigeration system, manually operated from 8:00 a.m. to 5:00 p.m. daily, was switched off early on May 6th, 2020, as reported in the logbook. Continuous operation of the refrigeration system is essential, especially in Visakhapatnam, where temperatures typically range from 20°C to 36°C, to ensure temperatures throughout the tank remain below 20°C. The refrigeration system should have been equipped with an automated instrumentation system with a temperature sensor to prevent human error and reactive hazards. The replacement of the float swing pipe arrangement with a dipleg arrangement disrupted the natural chemical circulation system, resulting in cooled Styrene Monomer being pumped back into the refrigeration system. As a consequence, the temperatures at the bottom of the M6 tank were recorded at low temperatures around 17 °C.

# **2.4 Ineffective Inhibitors**

"Preventing the polymerization of styrene vapor in the storage tank is challenging because inhibitors are ineffective against vapors. This leads to the accumulation of polymer on the inside of the tank's roof, forming stalactites over time. These stalactites can contaminate the styrene and potentially create hotspots where polymerization reactions can escalate uncontrollably. When accumulated polymer falls into the styrene below, it can act as a catalyst, initiating further polymerization. During the accident, with the styrene level at about 7 meters in the M6 tank, the falling polymer lumps would have dropped through a depth of approximately 5

meters, causing an impact and friction with the styrene liquid. This impact could have generated more free radicals of styrene, initiating or exacerbating polymerization at the top layers of<br>the tank. The lack of a temperature the tank. The lack of a temperature measurement system at the top level of the tank prevented the management from detecting and controlling the runaway polymerization. Moreover, the M6 tank, being an old tank, is prone to rust and other contamination. These contaminants could have also acted as catalysts, further accelerating polymerization and leading to runaway reactions" [12].

# **2.5 Polymerization & Runaway Reaction**

Polymerization occurred due to free radical reactions initiated thermally or catalytically. As the temperature in the upper zone of the M6 Tank exceeded 35 °C (estimated at 41.7 °C), the effectiveness of the TBC inhibitor was lost, leading to thermal radical polymerization. Being an adiabatic tank, the heat generated could not be dissipated, resulting in a further increase in temperature, further polymerization, and ultimately, a runaway reaction. Runaway polymerization occurs at temperatures above 65 °C, which can lead to violent vapor eruptions or excessive pressure buildup. The combination of thermal radical polymerization and polymerization due to the presence of a catalyst caused the polymerization in the M6 tank. The exothermic Styrene monomer polymerization reaction, evolving at 16700 kcal/kg mole or 160.36 kcal/kg, contributed to the temperature increase. With no effective inhibitor available, temperatures in the hotspot areas at the top layers of the tank rose above 65 °C, triggering a runaway polymerization reaction. If excess heat is not adequately dissipated, the product temperature will continue to rise, further accelerating the rate of polymerization.

#### **3. THREAT ZONE DETERMINATION USING ALOHA**

"ALOHA (Areal Locations of Hazardous Atmospheres) is the hazard modeling software program for the CAMEO software suite, which is widely used to plan for and respond to chemical and hazardous materials emergencies. The details about the Styrene gas vapor release can be entered into ALOHA, and it will generate threat zone estimates for various types of hazards. ALOHA can model toxic gas clouds, flammable gas clouds, BLEVEs (Boiling Liquid Expanding Vapor Explosions), jet fires, pool fires, and vapor cloud explosions. The threat zone estimates are shown on a grid in ALOHA and they can also be plotted on maps in MARPLOT, Esri's Arc Map, Google Earth, and Google Maps. The red threat zone represents the worst hazard level; the orange and yellow threat zones represent areas of decreasing hazards" [13–15].

# **3.1 ALOHA: Key Program Features**

- A. Generates a variety of scenario-specific output, including threat zone pictures, threats at specific locations, and source strength graphs.
- B. Calculates how quickly chemicals are escaping from tanks, puddles, and gas pipelines and predicts how those release rates change over time.
- C. Models many release scenarios: toxic gas clouds, BLEVEs (Boiling Liquid Expanding Vapor Explosions), jet fires, vapor cloud explosions, and pool
- D. Evaluates different types of hazards (depending on the release scenario): toxicity, flammability, thermal radiation, and overpressure.
- E. Models the atmospheric dispersion of chemical spills on

# **3.2 ALOHA: Procedures - Threat Zone Determination**

- a. Start ALOHA
- b. Click the site data and select the location by adding longitude, latitude and elevation of the LG Polymers Pvt Ltd, Visakhapatnam.Longitude-83<sup>0</sup>12'42.38‖E& Latitude - 17<sup>0</sup>45'28.73‖ N Elevation – 16 meters
- c. Select the date & time from the site data minute. The release occurred at 02:47Am on May 7, 2020.Set the constant time value and enter the date and time of the incident
- d. Choose the chemical that is being released –styrene monomer–select Chemical from the setup menu. A Chemical Information dialog box appears with a list of the chemicals in ALOHA's chemical library.
- e. In the Set Up menu, point to Atmospheric, and then select User Input. The first Atmosphericoptions dialog box appears, then input the values of wind velocity, wind direction, ambient temperature & humidity
- f. In the setup menu, point to the source and input the values of tank dimensions, mass of styrene in the tank, type of tank failure,

diameter of the opening, height of the opening, temperature of the styrene.

- g. In the display menu, select text summary to find the total amount of vapor released and the threat zone
- h. Usage of MARPLOT
- i. In ALOHA, go to the Sharing menu, point to MARPLOT, then select go to map to start MARPLOT. If this is the first time you've used MARPLOT, a dialog box may appear directing you to browse to the location of your MARPLOT (Mapping Application for Response, Planning and Local Operational Tasks) is a general purpose mapping application program with the following features:
- Easy-to-use GIS interface
- Ability to add objects (such as schools or chemical facilities) to the map and mark them using MARPLOT's set of symbols or an inserted picture;
- Allows you to customize the maps by specifying which layers appear and whether objects in those layers (such as roads) are labeled;
- Simple, all-inclusive search mechanism formapobjects;
- Easily displays ALOHA® threat zones. MARPLOT was developed jointly by the National Oceanic and Atmospheric Administration (NOAA) and the Environmental Protection Agency (EPA).

#### **4. CONSEQUENCES DETERMINATION USING EVENT TREE ANALYSIS (ETA)**

Event Tree Analysis (ETA) is a systematic method used to assess the possible outcomes resulting from an initial event. The analysis begins by identifying the initiating event and then systematically exploring all potential subsequent events, taking into account the effectiveness of safety barriers and other relevant factors. The process involves developing a graphical representation, or tree structure, that illustrates the various event sequences and their associated probabilities. Each branch of the tree represents a potential sequence of events, and conditional probabilities are assigned based on the state of safety barriers. Consequences are then analyzed for each event sequence, considering factors such as human health, environmental impact, and economic loss. The analysis culminates in a comprehensive risk assessment, which enables organizations to identify potential

hazards, evaluate risks, and implement<br>appropriate risk mitigation measures. ETA appropriate risk mitigation provides a structured approach to understanding

the potential consequences of accidental events, allowing organizations to identify and mitigate risks effectively [16].







**Fig. 5. Threat zone estimation in map using ALOHA software**











#### **4.1 Steps Involved in Construction of ETA**

- 1. Identify (and define) accidental (initial) event that may give rise to unwanted consequences
- 2. Identify the barriers that are designed to deal with the accidental event
- 3. Construct the event tree
- 4. Describe the (potential) resulting accident sequences
- 5. Determine the frequency of the accidental event and the (conditional) probabilities of the branches in the event tree
- 6. Calculatetheprobabilities/frequenciesforthei dentifiedconsequences(Outcomes)
- 7. Compile and present the results from the analysis

#### **4.2 Event Tree Analysis in Styrene Gas Vapour Leak Accident**

Event tree analysis was employed to investigate the Visakhapatnam gas leak incident. The initiating event of the Vizag gas leak was identified as the early shut-down of the refrigeration system of the styrene storage unit.

Various safety barriers and monitoring systems were in place within the plant, including the temperature monitoring system, temperature alarm, VOC (Volatile Organic Compounds) alarm, and the use of inhibitors such as Tertiary Butyl Catechol (TBC). However, the accident investigation revealed significant flaws in the temperature monitoring system, as the temperature alarm did not activate during the incident. Fortunately, the VOC alarm functioned correctly, detecting the leak promptly. However, the last barrier, the inhibitor (TBC), was out of stock at the time of the disaster due to the lockdown, significantly exacerbating the incident's consequences. (Fig. 7) This highlights the crucial role of the lockdown situation in contributing to the severity of the incident [17].

# **5. ROOT CAUSE ANALYSIS**

Root Cause Analysis (RCA) is a systematic process for identifying the underlying causes of problems or incidents. It involves a thorough investigation aimed at determining the primary factors that led to an issue. The process typically involves several steps, including identifying the problem, gathering data, analyzing the data to determine the root cause, and implementing corrective actions to prevent recurrence. RCA helps organizations not only address the immediate symptoms of a problem but also identify and eliminate the underlying causes, thereby reducing the likelihood of similar issues in the future [18]. It is a crucial tool for continuous improvement and risk management in various fields, including manufacturing, healthcare, information technology, and quality management. (Fig. 8) The major parameters that influenced the increase in temperature of styrene in the tank (M6) are mainly.

# **5.1 Tank Design**

- 1) 53-year-old atmospheric mild steel without any inside lining, insulated outside
- 2) 17 nozzles were used.
- 3) Conical roof on an inside structure
- 4) Provided with a re-circulatory cooling system
- 5) Change of design in the suction and discharge. No HAZOP and risk assessment for the modified design that falls under the management of change under the OSHA PSM standard
- 6) The last cleaning and maintenance of the tank was in 2015. Recommended cleaning every 2 years.

#### **5.2 Tank Temperature Measurement and Control**

- 1) Single temperature measuring probe at the bottom of the tank, M6
- 2) Temperature measurement is restricted to the bottom zone; the top and middle zones might have different temperatures.
- 3) Thermal stratification in the tank
- 4) Temperature protocol of LG Polymers: 350  $^{\circ}$ C
- 5) Tank top temperature is 41.7 °C, estimated from DCS level percentage data recorded on April 28, 2020.
- 6) Incorrect assumption of the bottom temperature as the bulk temperature of the tank
- 7) Inadequate time for cooling

#### **5.3 TBC Monitoring (Inhibition Depletion Characteristics)**

- 1) No addition of TBC in the on-site storage tanks since the last 10 year
- 2) Unavailability of TBC Stock
- 3) TBC stratification in the tank due to inefficient mixing in the tank design
- 4) Decrease in TBC concentration in styrene. Unaware of inhibitor depletion characteristics

# **5.4 Operating Procedures**

- 1) Maximum polymer content-1000/500ppm
- 2) Standard Operating Procedures (SOP) are not updated to suit lock down period
- 3) No daily sampling
- 4) Log sheets and log books do not have detail activities carried out
- 5) Maximum Temperature limit for styrene in the tank 35<sup>0</sup>C

# **5.5 Availability of Documents**

- 1. Documentation was inaccessible
- 2. Procedures and manuals were not available during the time of the investigation
- 3. Tank drawings do not show internal arrangements
- 4. Validation of the refrigeration system was unavailable
- 5. Apaucity of basic Process Safety Information was observed
- 6. Process safety information is the foundation for a Process Safety Management program

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**Fig. 8 Ishikawa Fish bone diagram for Vizag Gas Leak**

#### **5.6 Knowledge/Talent Deficit**

- 1. Operators could not identify the nozzles of the tank
- 2. Personnel on-duty/in-charge: lack basic emergency operations
- 3. Personnel were unaware of detailed knowledge on Styrene storage best practices
- 4. Safety officer, Shift in-charges, engineers are not qualified in engineering and not competent also
- 5. Process Safety Competency/Training is key driver to keep the work force abreast in the latest in Process Safety Management

#### **5.7 Styrene Quality Testing**

- 1. Collection of representative sample was not ensured
- 2. Only one sample from the bottom of the tank was tested

#### **5.8 Process Safety Management Framework**

1. A disciplined framework for managing the integrity of hazardous operating systems and processes by applying good design principles of engineering and operating practices, CCPS definition

- 2. No HAZOP and Risk Assessment Studies before Installation of Storage tanks
- 3. Little to no understanding of Risk Based Process Safety
- 4. Absence of monitoring of dissolved oxygen inside the tank.

#### **6. RESULTS**

#### **6.1 Threat Zone Determinations Using ALOHA**

The total amount of styrene released from the M6 tank is 92,412 kilograms for a wind velocity of 3.22 mph from a south direction at a height of 20 m, an air temperature of 280 °C, and a relative humidity of 76%. The Red Zone of Acute Exposure Guidelines Levels 3 (AEGL 3 = 1100 ppm) is around 864 meters, which is the airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience lifethreatening health effects or death. The Orange Zone of Acute Exposure Guidelines Levels 2 (AEGL  $2 = 130$  ppm) is around 2.5 km, which is

the airborne concentration of a substance above which it is predicted that the general population,<br>including susceptible individuals, could susceptible individuals, could experience irreversible or other serious, longlasting adverse health effects or impaired ability to escape. The Yellow Zone of Acute Exposure Guidelines Levels 1 (AEGL  $1 = 130$  ppm) is around 7.1 km, which is the airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience notable discomfort, irritation, or certain asymptomatic non-sensory effects. However, the effects are not disabling and are transient and reversible upon cessation of exposure. (Fig. 4 and This threat zone determination is used to determine the evacuating region and usage of personal protective equipment. For concentrations of 20 ppm, use a National Institute for Occupational Safety and Health (NOISH)-approved respirator with an organic vapor cartridge and a full face piece. For concentrations of 200 ppm, use a National Institute for Occupational Safety and Health (NOISH)-approved air respirator with a full face piece. For concentrations of 700 ppm, which are immediately dangerous to life and health (IDLH), use a National Institute for Occupational Safety and Health (NOISH)-approved selfcontained breathing apparatus (SCBA) with a full face piece operated in pressure demand or other positive pressure mode equipped with an emergency escape air cylinder.

# **6.2 Event Tree Analysis (ETA)**

ETA is used to predict the consequences of the initiating event (ie) early shutdown of refrigeration system which leads to the major accident if.

- Failure of both temperature and VOC alarms
- Failure of Inhibitor addition

# **6.3 Root Cause Analysis (RCA)**

- Incorporate suctions wing pipe and educator system for efficient mixing.
- Ensure effective cooling systems with backup cooling to maintain a maximum temperature of 25°C.
- Keep the number of nozzles in the tank to a minimum required.
- Construct the tank with carbon steel and coat the inside with rust- resisting inorganic zinc silicate material.
- Support the tank roof without side structures.
- Paint the outside of storage tanks white or aluminum and consider insulating them.
- Define tank life and carry out tank cleaning and coating every two years.
- Review Standard Operating Conditions with upper and lower parameter limits.
- Implement High Critical Standard Operating Procedures if there is high polymer content.
- Maintain understandable, clear, and concise log book entries.
- Increase sampling frequency during dormant periods (pandemic, turnaround, business cycles).
- Review and update procedures after any Management of Change.
- Thermal radical polymerization occurs
- Avoid over looking increases in polymer level
- Prevent the formation of condensed styrene without TBC in the top layer of the tank.
- Monitorandcontroltemperaturestoensureth eystaybelow35°C (Estimated 41.7°C on 28.04.2020).
- Be vigilant as the runaway polymerization reaction can start at about 34°C (Harold Fisher).
- Note that Huiand Hamielec Kinetic models are valid between100°C to 200°C under adiabatic conditions (Kaypear).
- Be aware of non-adiabatic conditions where volumetric vapor generation due to the heat of reaction balances vent rate through relief devices.

# **7. CONCLUSION**

The increasing number of industrial accidents, exacerbated by the lockout of major chemical factories, underscores the urgent need to address workplace safety. This study primarily focuses on the Vizag gas leak, delving into its causes and consequences. Investigative tools like event tree analysis, root cause analysis, and Aloha software were utilized to examine the disaster. Various sources provided data on the accident's causes and the prevailing weather conditions. By simulating climatic and source data in Aloha software, the study produced contour plots of the accident area, categorizing it into different zones based on styrene concentration. These plots, based on acute exposure guideline levels (AEGL), helped classify the affected area. These findings were then compared with the actual circumstances at the time of the disaster, detailing which areas were affected and to what extent. ETA was conducted to uncover the causes of the incident and the events that transpired during the accident. The main factors contributing to the accident were identified as the company's failure to adhere to proper styrene storage standards and severe defects in the construction of the storage tank. This catastrophe serves as a stark reminder of the critical importance of adhering to safety regulations in the chemical sector, as well as highlighting the impact of the lockdown on the reliability of process industries.

#### **DISCLAIMER (ARTIFICIAL INTELLIGENCE)**

Author(s) hereby declare that NO generative AI technologies such as Large Language Models (ChatGPT, COPILOT, etc) and text-to-image generators have been used during writing or editing of manuscripts.

#### **COMPETING INTERESTS**

Author has declared that no competing interests exist.

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