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DETERMINATION OF THE EFFECTS OF HEAT TREATMENT APPLIED TO ANCHOVY ON PUTREFACTION BY ELECTRONIC NOSE

Emre YAVUZER*

Department of Food Engineering, Faculty of Engineering, Niğde Ömer Halisdemir University, Niğde, Türkiye

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ABSTRACT

In this study, the effect of heat treatment on the putrefaction levels of anchovy fish was investigated using an electronic nose system. Sensor data (MQ3, MQ4, MQ5, MQ9, MQ131, MQ135, MQ136, MQ137, MQ138, MQ139, MG811 and TGS813) obtained from raw and cooked anchovy samples during storage periods and the sensitivity of the sensors to odour changes were analysed. Based on the differences of their signals (Δ S) between two states, the effect of heat treatment on the odour dynamics was modelled by linear regression models. For example, modelling results for the MQ136 sensor were determined in the form Δ S(t) = -16.59t + 37.33 (R² = 0.84), showing that cooking significantly decreases sensor responses over time. The findings indicated that cooking was found to delay odorization, likely due to changes in lipid oxidation and volatile compound dynamics, and that low-cost sensors can be developed into an advanced electronic nose system.

Keywords: Anchovy, electronic nose, MQ sensor, heat treatment, putrefaction

HAMSIYE UYGULANAN ISIL İŞLEMIN KOKUŞMA ÜZERINE ETKILERINININ ELEKTRONIK BURUN İLE BELIRLENMESI

ÖZ

Bu çalışmada, hamsi balıklarının bözulma seviyelerine ısıl işlemin etkisi elektronik burun sistemi kullanılarak araştırılmıştır. Depolama süreleri boyunca çiğ ve pişmiş hamsi örneklerinden elde edilen sensör verileri (MQ3, MQ4, MQ5, MQ9, MQ131, MQ135, MQ136, MQ137, MQ138, MQ139, MG811 ve TGS813) ve sensörlerin koku değişikliklerine olan hassasiyetleri analiz edilmiştir. İki durum arasındaki sinyal farklılıklarına (Δ S) dayanarak, ısıl işlemin koku dinamikleri üzerindeki etkisi doğrusal regresyon modelleri ile modellenmiştir. Örneğin, MQ136 sensörü için modelleme sonuçları Δ S(t) = -16.59t + 37.33 (R² = 0.84) biçiminde belirlenmiş ve ısıl işlemin sensör tepkilerini zamanla önemli ölçüde azalttığını göstermiştir. Bulgular, pişirmenin muhtemelen lipit oksidasyonu ve uçucu bileşik dinamiklerindeki değişiklikler nedeniyle koku oluşumunu geciktirdiğini ve düşük maliyetli sensörlerin gelişmiş bir elektronik burun sistemine dönüştürülebileceğini göstermiştir.

Anahtar Kelimeler: Hamsi, elektronik burun, MQ sensörü, ısıl islem, çürüme

⊠: eyavuzer@ohu.edu.tr

: (+90) 388 225 2341

^{*} Corresponding author / Sorumlu yazar

INTRODUCTION

Seafood has an important place in human nutrition with its high protein content, long-chain fatty acids and essential vitamin-mineral profiles. Anchovy (Engraulis encrasicolus) stands out among these products as a species with high economic and nutritional value (Crisinel et al., 2012; Dağtekin et al., 2022). According to worldwide catch data, anchovy is a seafood product intensively especially consumed in the Mediterranean and Black Sea basins (Moon & Kim, 2024; Ye et al., 2024). Omega-3 fatty acids offer various health advantages thanks to their beneficial components such as vitamin B12 and selenium (Öğretmen, 2022; Park et al., 2018). However, the high water activity and protein content of anchovies make it a food that is susceptible to microbial growth and oxidation, hence the risk of rapid spoilage (Özoğul, 2004). Controlling the spoilage process of thermally treated or raw anchovies is critical to safeguard public health and minimize economic losses. In the literature, quality determination methods of fish and fish products are generally based on chemical analyses such as TVB-N, TBARS and PV and microbiological analyses such as TAMB and TAPB (Özoğul et al., 2013; Yavuzer, 2018, 2020). However, these methods have limitations in terms of both cost and time. Especially in rapidly perishable foods, the necessity to carry out the quality determination process with faster and more economical methods encourages the search for new technologies (Wang et al., 2022).

Electronic nose systems are a quality control technology that has become increasingly widespread in the food industry in recent years. These systems are used to determine spoilage levels by detecting volatile components emitted from foodstuffs (Lu et al., 2022). In particular, electronic nose systems integrated with opensource, cost-effective microcontrollers such as Arduino offer low-cost and user-friendly solutions (Yavuzer, 2021). Previous studies have demonstrated the effectiveness of electronic noses in detecting quality changes in fish and other foods (Al Isyrofie et al., 2022; Amorim et al., 2021; Yavuzer et al., 2024).

In this study, the effectiveness of electronic nose technology in determining the spoilage limits of raw and cooked anchovies due to thermal stress was investigated. The low-cost Arduino-based sensor system used in the study offers a feasible model for producers, consumers and the food industry due to its fast solution and easy redesign of the data obtained.

MATERIAL and METHODS

Electronics Components Used in the Device

In the study, the data inputs and outputs of the odour sensors were provided and processed by Arduino Mega 2560 R3, an open source physical programming platform. Arduino Mega 2560 R3 Development Board is an Atmega 2560 based microcontroller board with 54 digital input/output pins. Due to the necessity of using multiple sensors in the study, Arduino Mega Sensor Shield Board was also used. The electronic nose we developed in our previous study (Yavuzer, 2021) was modified and strengthened with additional sensors. Firstly, the device was operated empty for 30 minutes without any sample in order to narrow the ambient odours. Subsequently, sensor readings from the samples placed inside the device were obtained by subtracting the empty readings. The new electronic nose obtained by using MQ3, MQ4, MQ5, MQ9, MQ131, MQ135, MQ136, MQ137, MQ138, MQ139, MG811 and TGS813 sensors is shown in Figure 1 and the specifications of the sensors are given in Table 1.

Fish Material

The anchovies used in the study were caught in the Black Sea/Trabzon/Turkey and delivered to our laboratory under cold chain conditions. The raw anchovy group, whose internal organs were cleaned in an aseptic environment, were immediately subjected to analysis using the electronic nose system. A total of 2 kg of anchovies of homogeneous size (12±3cm) were used in the study. Real-time (1 per minute) sensor readings were taken at room temperature (24°C±3) and the mean and standard deviations of the readings at 0, 2, 4, 6, 8, 10 and 12 hours were processed for the study data. In order to obtain the cooked anchovy group, the anchovy

fish was cooked in oil at 170±15 degrees for about 5 minutes. All sensor readings for the raw

anchovy sample were performed for the cooked anchovy.

Table 1. The sensors used in the study and the gases they measure

Sensor	Measurement					
MQ3	Detects the presence of alcohol gas at an appropriate range of concentrations between					
	0.04mg / L and 4mg					
MQ4	Detects the presence of methane (CNG) natural gas					
MQ5	Isobutane and propane detection					
MQ9	High sensitivity to hydrogen but low sensitivity to alcohol vapor					
MQ131	Detects carbon monoxide (CO) in the environment.					
MQ135	Dedects the amount of ammonia, alcohol vapor, benzene, smoke and carbon dioxide					
	gases					
MQ136	Hydrogen sulphide gas sensor					
MQ137	Ammonia sensor					
MQ138	Acetone, alcohol, toluene,					
MQ139	Freon Gas sensor					
MG811	Air Carbon Dioxide Sensor					
TGS813	Methane, propane and butane sensor					

Mathematical Modeling

Prior to data acquisition, sensors were calibrated using clean air baselines, and all readings were normalized to initial conditions from raw and cooked anchovies. The cooking process changes the VOC levels and this change is detected by different sensors during the storage period. For each sensor, the effect of the cooking process was modelled as follows:

 $\Delta S_i(t) = a_i \cdot t + b_i$

Where;

 $\Delta S_i(t)$: post-cooking odour difference (cooked-raw) for sensor i, at storage time t hours

a: Coefficient representing the rate of change (slope) of the measurement difference with respect to the storage time.

b_i: Constant representing the initial measurement difference.

t: Storage time (hours).

i: Sensor number i(€[MQ3,MQ4,.....,TGS813])

Statistical Analyses

All analyses were conducted in triplicate, and the results are presented as mean values \pm standard deviation (S.D). Data were subjected to analysis of variance (one-way ANOVA).

RESULTS AND DISCUSSION

Although the electronic nose used in the study was calibrated in clean air, the system was operated empty for the first half hour in order to prevent the existing density in the environment from affecting the total odour level. The empty sensor data were recorded and averaged in minutes and then the odour change of the sample added to the environment was processed. Table 2 shows the empty sensor reading averages.

Table 2. Average of the initial (empty) values of the sensors.

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MQ3	MQ4	MQ5	MQ9	MQ131	MQ135	MQ136	MQ137	MQ138	MQ139	MG811	TGS813
265	255	80	235	50	33	349	396	291	351	11	176

The hourly increments of the sensors for raw anchovy are given in Table 3. All sensors with the exception of MG811, detected odour changes in anchovies due to thermal stress. The stability in odour changes increased steadily from hour zero

to hour 12 for sensors MQ3, MQ4, MQ9 and MQ136, whereas a decrease was observed only in the last hour for sensors MQ5, MQ131, MQ135, MQ137, MQ138, MQ139 and TGS813.

Table 3. Hourly increments of sensors for raw anchovy.

Hours	MQ3 x±Sd	MQ4 x±Sd	MQ5 x±Sd	MQ9 x±Sd	MQ131 x±Sd	MQ135 x±Sd
0	4 ± 0.02^{aD}	35±1.41 ^{ьн}	4 ± 0.08^{aD}	16±0.09aF	-12±0.22 ^{bA}	10±0.12 ^{aE}
2	22±0.32 ^{bE}	33±0.14aF	21±0.04 ^{bE}	32±1.05 ^{bF}	-25±0.18 ^{aA}	15±0.91ы
4	46±0.12 ^{cD}	55±1.13cE	32±0.09cC	88±0.21cF	177±1.44cH	169±0.55gG
6	76±0.09 ^{dD}	128±0.44 ^{dE}	58±1.12 ^{dC}	125±1.42 ^{dE}	325±3.52 ^{dD}	152±1.74 ^{fF}
8	107±0.85eC	198±1.85eF	178±1.78eE	255±2.24eG	420±1.32fC	122±2.06eD
10	171±0.14 ^{fD}	355±1.88 ^{fF}	228±2.77gE	418±3.19 ^{fl}	467±3.44gK	95±0.13 ^{dC}
12	188±0.92gD	402±1.98gJ	204±2.55 ^{fE}	498±1.92 ^{gL}	405±2.22eK	44±1.18 ^{cC}
Hours	MQ136 x±Sd	MQ137 x±Sd	MQ138 x±Sd	MQ139 x±Sd	MG811 x±Sd	TGS813 x±Sd
0	-8±0.09aB	52±1.52 ^{aI}	52±0.12 ^{aI}	30±0.25aG	1±0.01 ^{aC}	41±0.04aG
2	6±0.04 ^{bB}	252±3.24 ^{bJ}	118±1.22 ^{ьн}	171±2.24ы	8±0.01 ^{dC}	48±0.01bG
4	28±0.08cB	361±1.45cJ	305±2.44 ^{cI}	242±0.11cE	5±0.05cA	178±2.23сH
6	29±0.54cB	402±0.41 ^{dI}	458±2.68gJ	398±0.55 ^{dH}	4±0.01 ^{bA}	352±1.95 ^{dG}
8	33±2.23 ^{dB}	445±1.65 ^{eJ}	405±1.28 ^{fH}	492±2.95gK	4±0.02 ^{bA}	442±2.48 ^{eI}
10	38±1.32eB	401±0.65 ^{dH}	380±0.49eG	458±1.64 ^{fJ}	5±0.08cA	472±1.62 ^{fL}
12	41±0.22 ^{fB}	362±2.84 ^{cH}	354±1.45 ^{dG}	440±0.42 ^{eA}	4±0.04 ^{bA}	351±2.94 ^{dF}

Different letters (a - g) in the same column and different letters (A - L) in the same row show significant differences (p < 0.05)

The 12 different sensors used in our study measured the time variation of volatile organic compounds from cooked anchovies. The data were analysed to determine the effect of heat treatment on the putrefaction process. Reading data of MQ3, MQ4, MQ5, MQ9, MQ131 and MQ135 sensors on raw and cooked anchovy is given in Figure 1. Previous studies (Yavuzer, 2020, 2021, 2023) have shown that the MQ3 sensor is a successful sensor for detecting odour changes in fish meat. An increase in data was observed during 0-12 hours of storage, with a significant peak at 12 hours, indicating the formation of alcohol during spoilage. The MQ4 and MQ5 sensors are sensitive to combustible gases such as methane and propane, and the negative values of MQ4 in particular are associated with the suppression of methane-type gases in cooked anchovies. This may also be attributed to the reduced emission of combustible gases released as a result of denaturation of proteins by heat. An increase in the data was observed during 0-12 hours of storage with a significant peak at 12 hours, indicating the formation of alcohol during spoilage. The MQ4 and MQ5 sensors are sensitive to combustible gases such as methane and propane, and the negative values of MQ4 in particular are associated with the suppression of methane-type gases in cooked anchovies. This can also be

explained by the low level of combustible gases released as a result of denaturation of proteins by heat. The cooking process almost completely stopped methane production, limiting microbial activity. In other studies on methane detection, it has been reported that the MQ4 sensor can be used to monitor anaerobic processes of food spoilage (Viciano-Tudela et al., 2023; Yavuzer et al., 2024). The sensitivity of the MQ9 sensor to gases such as carbon monoxide and methane showed an increasing trend from the 2nd hour onwards and peaked at the 10th hour. This supports the formation of carbon-based gases during lipid oxidation. The accumulation of gases such as carbon monoxide and methane during spoilage in raw fish indicated increased microbial and enzymatic activities, and cooking significantly reduced the release of these gases. These findings are supported by other studies in which the MQ9 sensor for carbon monoxide detection was associated with food spoilage (Darvishi et al., 2024). The MQ131 sensor for monitoring oxidation processes is an effective tool for air quality analyses (Kumar & Doss, 2023). The MQ131 sensor also showed a stable increase in the cooked anchovy data, indicating that oxidative processes are ongoing. It shows that oxidising gases accumulate in raw anchovies during spoilage, but this process is limited in cooked anchovies.

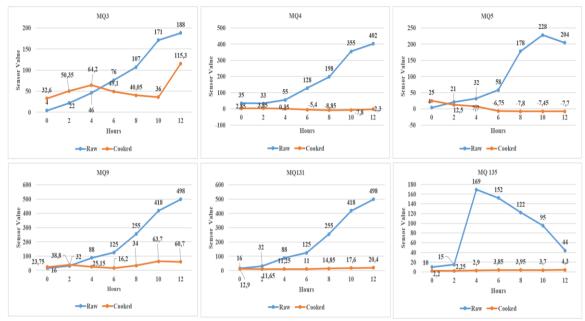


Figure 1. Reading data of MQ3, MQ4, MQ5, MQ9, MQ131 and MQ135 sensors on raw and cooked anchovy

MQ135 is a sensor sensitive to ammonia and similar gases that affect air quality. It has been reported in the literature that the MQ135 sensor is effective in detecting ammonia during food spoilage (Astuti et al., 2021). Reading data of MQ136, MQ137, MQ138, MQ139, MG811 and

TGS813 sensors on raw and cooked anchovy is given in Figure 2. MQ136, MQ137 and MQ138 sensors are sensitive to sulfur compounds, ammonia and aromatic hydrocarbons, and all three are elevated at advanced stages of spoilage.

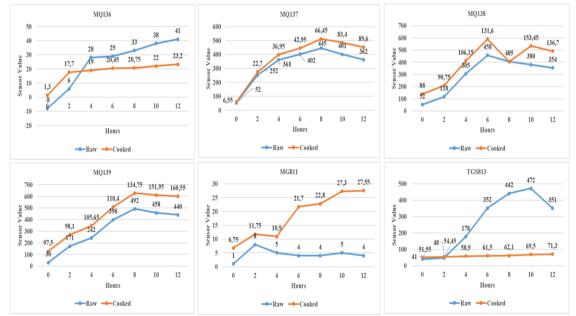


Figure 2. Reading data of MQ136, MQ137, MQ138, MQ139, MG811 and TGS813 sensors on raw and cooked anchovy

MQ139, a sensor sensitive to organic solvents, reflected the amount of aldehyde and ketone type compounds in cooked anchovies and showed a time-dependent increase. The TGS813 sensor showed high sensitivity to carbon-based gases and showed increases in cooked anchovies confirming spoilage.

The data obtained with the combination of these sensors reveals the thermal degradation process of proteins, fats and carbohydrates. The accelerating effect of heat treatment on the putrefaction process has been similarly reported in food spoilage analyses in the literature. (Schneedorferová et al. 2015)

Table 4. Hourly increments of sensors for cooked anchovies.

Hours	MQ3 x±Sd	MQ4 x±Sd	MQ5 x±Sd	MQ9 x±Sd	MQ131 x±Sd	MQ135 x±Sd
0	32.60±2.57aG	2.85±0.12 ^{fB}	25.00±0.93eF	23.75±3.46 ^{bF}	12.90±3.46abE	2.20±0.22aB
2	50.35±3.41 ^{dG}	3.85±0.25gB	12.50±0.09 ^{dD}	38.80±2.63 ^{dF}	11.65±1.48 ^{aC}	2.25±0.16 ^{aA}
4	64.20±3.31eK	0.35±0.03eA	7.70±3.63cC	25.15±3.23bG	11.25±0.53aE	2.90±0.13aB
6	49.10±2.83 ^{dI}	-5.40±0.49cB	-6.75±2.42 ^{bA}	16.20±2.81aE	11.00±2.85 ^{aD}	3.85±0.23 ^{bC}
8	40.05±1.82cG	-8.85±0.77 ^{aA}	-7.80±3.01 ^{aB}	34.00±1.21 ^{cA}	14.85±0.61 ^{cD}	3.95±0.71 ^{bC}
10	36.00 ± 3.82^{bF}	-7.80±0.12 ^{bA}	-7.45±2.76 ^{aA}	63.70±1.41 ^{fG}	17.60±2.25 ^{dC}	3.70±0.33ыв
12	115.30±2.98 ^{fJ}	-2.30±0.40 ^{dB}	-7.70±1.91 ^{aA}	60.70±2.18 ^{eG}	20.40±2.01 ^{eD}	4.30±0.01 ^{cC}
	MQ136 x±Sd	MQ137 x±Sd	MQ138 x±Sd	MQ139 x±Sd	MG811 x±Sd	TGS813 x±Sd
0	1.30±0.09 ^a A	6.55±1.02 ^{aD}	88.00±5.32aI	97.50±3.93 ^a J	6.75±0.08 ^{aC}	51.55±2.33aH
2	17.70±1.29 ^{bE}	22.70±1.52 ^{bF}	90.75±2.14 ^{bJ}	98.10±2.42aK	11.75±0.6 ^{bC}	54.45±0.12 ^{bH}
4	19.00±2.12 ^{cF}	36.95±0.36 ^{cH}	106.15±2.84 ^{cL}	105.65±3.88 ^{bL}	10.90±0.1 ^{bD}	58.90±2.28 ^{cJ}
6	20.45 ± 1.84^{dF}	42.95±1.88 ^{dH}	131.60±3.23 ^{dK}	110.40±3.71 ^{cJ}	21.70±0.12 ^{cG}	61.50±1.88 ^{dD}
8	20.75 ± 1.52^{dE}	66.45±2.51 ^{eI}	149,90±2,42 ^{fK}	134.75±2.55 ^{dJ}	22.80±0.22 ^{dF}	62.10±1.42 ^{dH}
10	$22.00\pm0.20^{\rm eD}$	83.40±0.71 ^{fl}	153.45±3.62gJ	151.95±4.35 ^{eJ}	27.30±0.41 ^{eE}	69.50±2.23eH
12	23.20±0.11 ^{fE}	89.60±3.55gI	136.70±2.44eK	160.55±2.38 ^{fL}	27.55±0.16eF	71.30±2.88efH

Different letters (a - g) in the same column and different letters (A - L) in the same row show significant differences (p < 0.05)

The cooking process alters the levels of volatile organic compounds levels and this change is detected by different sensors during the storage period. For example, according to the regression results for the MQ9 sensor, which we modelled with the highest accuracy:

 $\Delta S_{MO9}(t) = -39.56 \cdot t + 70.28$

This equation shows that the cooking-induced effect of the MQ9 sensor decreases with time, with an initial difference of 70.28 units. As the storage time increased (*t*), the difference was observed to decrease by 39.56 units per hour.

A regression analysis was performed to estimate the measurement differences between raw and cooked anchovies over time and to quantitatively understand the effect of cooking on odour and to model the effect of cooking. The aim is to create a mathematical model to explain the variations in sensor measurements. Time (Hours) and sensor measurement differences (cooked vs. raw) were used as independent variables, while a multiple regression model was created to see which sensors provided the strongest effects. For this, an independent regression model was generated for each sensor (e.g. MQ3, MQ4, etc.). We started with a simple linear regression and then moved to a more complex model. As a first step, the linear relationship between time and measurement differences for each sensor was examined and modelled. The results of the regression analysis are given in Table 5. The relationship between time (Hours) and measurement differences (cooked - raw) was modelled for each sensor:

Among the sensors in the study, the strongest models (R²>0.85) were MQ9, MQ4, MQ5, MG811 and MQ131. Especially MQ9 and MQ4 show significant effects on the change of odour components after cooking.

Weak Models (R²<0.5): MQ135 and MQ137 failed to explain the measurement differences over time. Sensors with high R² values such as

MQ9 and MQ4 would be a more meaningful indicator to understand the effect of the cooking process, while these regression models can be

used to predict the change in odour level during the cooking process.

Table 5. Regression analysis on the effect of heat treatment on putrefaction.

Sensor	Coefficient	Intercept	R ²	Explanation
			Value	
MQ9	-39.56	70.28	0.94	Strong negative relationship; the difference decreases
				over time.
MQ4	-34.57	32.67	0.91	Strong negative relationship; difference decreases rapidly.
MQ5	-23.46	39.38	0.90	Negative trend; decline over time is moderate.
MG811	1.85	2.89	0.88	Slightly positive relationship; difference increases over
				time.
MQ131	-43.57	24.66	0.85	Strong negative trend; difference decreases significantly.
MQ136	-2.50	8.91	0.83	Weak negative trend.
MQ3	-12.78	44.34	0.78	Negative trend; difference decreases over time.
MQ139	-30.86	-10.87	0.75	Moderate negative trend.
TGS813	-34.81	1.06	0.75	Strong negative relationship.
MQ138	-21.69	-43.48	0.52	Moderate negative trend.
MQ137	-16.28	-177.49	0.39	Weak relationship.
MQ135	-3.66	-61.47	0.06	Very weak relationship.

This study evaluated the effects of heat treatment of anchovies on putrefaction processes using an electronic nose system consisting of different gas sensors. MQ3, MQ4, MQ5, MQ9, MQ131, MQ135, MQ136, MQ137, MQ138, MG811 and TGS813 sensors were used to detect and characterise gas emissions from raw and cooked samples at different storage times.

The data obtained revealed that the sensor signals generally increased with increasing storage time in raw samples, indicating the accumulation of gases associated with putrefaction. In contrast, sensor responses in cooked samples remained relatively stable at lower levels, indicating that heat treatment suppresses microbial activity and gas formation. In particular, the sharp increases of sensors sensitive to sulphur compounds such as MQ136 and MQ137 in raw samples indicate that these gases are among the important markers of putrefaction. On the other hand, MQ138 and sensors offered more monitoring of carbon-based organic and compounds, which allowed a wider range of odour profiles to be evaluated.

CONCLUSION

The effect of cooking on the putrefaction process was evaluated by linear regression models on sensor data and it was found that odour changes were more pronounced in raw samples. These results suggest that heat treatment may affect not only microbial spoilage but also gaseous emissions due to lipid oxidation and protein denaturation. These findings demonstrate that electronic nose systems can be effectively employed in food safety and quality control processes. In conclusion, this study has demonstrated quantitatively how heat treatment affects odour formation due to spoilage in sensitive foods such as anchovies and proved the potential of electronic nose systems in such evaluations. In the future, further investigation of the effects of different cooking methods and conditions on odour dynamics will enable the development of more comprehensive modelling for food freshness and safety.

Declaration of Generative AI and AI-assisted technologies in the writing process

During the preparation of this work, the authors used ChatGPT, a language model developed by

Open AI, to improve the readability and clarity of the text. After using this tool, the authors reviewed and edited the content as needed and took full responsibility for the content of the publication.

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