Original Research

# Pollution Characteristics and Health Risk Assessment of VOCs in Different Working Environments in Coal Mines

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## **Abstract**

Tailpipe emissions from mining machinery and naturally occurring volatile organic compounds (VOCs) in the coal seam accumulate in a semi-closed environment, threatening the health of underground workers. In order to study the pollution characteristics and potentially harmful effects of volatile organic compounds (VOCs) in different working environments in coal mines, a coal mine in Huainan City, Anhui Province, China, was selected for VOC sampling. VOCs concentration levels, composition, and characteristics of the air in the air intake tunnel, the coal mining face, and the air return tunnel were obtained, and the health risks to workers were evaluated.

The findings of the research study indicate that: (1) The mean concentration of volatile organic compounds (VOCs) in the underground coal mine environment was found to be (2066.67±750) μg/m³, which is significantly higher than the background concentration of the ground environment collected on the same day (55.5±20.3) μg/m³. The mean TVOCs value in the air intake tunnel work environment was (1875±541.67) μg/m³, the mean TVOCs value in the coal mining face work environment was (2362.5±454.17) μg/m³, and the mean TVOCs value in the air return tunnel work environment was (1943±626.33) μg/m³. These findings suggest that VOCs affected the coal mining face most severely. (2) The top components in terms of their volume fraction of volatile organic compounds (VOCs) are isopropanol, carbon disulfide, cyclohexane, methyl bromide, cis-1,3-dichloropropene, chlorobenzene, benzyl chloride, trichloroethylene, n-decane, and chlorofluorocarbon-11. Halogenated hydrocarbons constituted the greatest proportion of VOCs in the three working scenarios, representing 41.9%, 40.9%, and 41.2%, respectively. Alkanes and OVOCs accounted for the next largest proportion, ranging from 24.2% to 26.1% and 17.2% to 21.9%, respectively. The concentrations of aromatic hydrocarbons

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and olefins accounted for 3.1% to 3.7% and 5.3% to 8.11%, respectively, of TVOCs. (3) The results of the health risk assessment indicated that the hazard index (HI) for the non-carcinogenic risk of volatile organic compounds (VOCs) in the underground coal mine environment ranged from 0.077 to 0.279, which did not exceed the threshold value of 1. Consequently, there was no non-carcinogenic health risk. The lifetime carcinogenic risk factor (RISK) ranges from  $4.26 \times 10^{-5}$  to  $2.02 \times 10^{-4}$ , exceeding the threshold  $(1.00 \times 10^{-6})$  by 42.6 to 202 times, indicating a relatively high carcinogenic risk.

**Keywords:** volatile organic compounds (VOCs), the subterranean environment of a coal mine, VOCs concentration level; health risk evaluation

#### Introduction

The quality of underground air in coal mines represents a significant safety and health concern that has been the focus of scientific inquiry for an extended period of time [1, 2]. The enclosed nature of the working environment in coal mines allows for the accumulation of harmful gases, including coal dust, methane, carbon monoxide, and sulfur dioxide. These gases present a direct threat to the health of miners [3-6]. For an extended period, the majority of studies on underground air quality have concentrated on these gases, while there has been a paucity of research on volatile organic compounds (VOCs), including alkanes, alkenes, and aromatic hydrocarbons. The potential health risks to workers from volatile organic compound (VOC) pollution in the subterranean environment of coal mines remain largely unexplored.

Volatile organic compounds (VOCs) are a class of highly reactive organic compounds in the atmosphere. The compounds in question encompass a vast array of substances, ranging from the relatively simple methane to the highly complex aromatic and halogenated hydrocarbons [7]. The role of VOCs in atmospheric chemistry, environmental science, industrial production, and public health is of significant importance. The primary sources of VOCs are industrial emissions, transportation, solvent use, fuel volatilization, and biological emissions [8-20]. The reaction of VOCs in the atmosphere with nitrogen oxides results in the formation of ozone and fine particulate matter (PM<sub>2.5</sub>). These secondary pollutants present a significant risk to human health and environmental quality [4, 5, 8, 9, 20-26]. Consequently, researchers are concentrating their efforts on identifying the sources, emissions, atmospheric transformation processes, and their impact on air quality.

The research on VOCs in open atmospheres is gradually shifting to confined, semi-confined, and restricted spaces, including but not limited to buildings, subways, shopping malls, underground parking lots, tunnels, and other environmental scenarios. Individuals who are engaged in activities within confined, semi-confined, and restricted environments are subjected to prolonged exposure to elevated concentrations of volatile organic compounds (VOCs), which can potentially result in the development of chronic respiratory illnesses,

impairment of the nervous system, and an elevated risk of cancer [10, 12, 18, 20-23, 26-31].

This study aims to examine and assess the concentration fluctuations of volatile organic compounds (VOCs) emanating from both natural and artificial sources within the subterranean environment of coal mines. Additionally, this study aims to elucidate the pollution characteristics and potential health implications for coal mine workers.

In this study, polyvinyl fluoride film VOC gas sampling bags were employed to collect environmental air samples under a variety of working scenarios typical of underground mining operations in a coal mine in Huainan City, Anhui Province, China. The concentration changes and pollution characteristics of VOCs in the coal mine were obtained through laboratory analysis, and a preliminary evaluation of human health risks was conducted using the US Environmental Protection Agency (US EPA) health risk assessment model. This was done to provide basic observational and evaluation data to support improving the air quality in coal mines.

# **Materials and Methods**

## Sampling Location

The present study collected volatile organic compound (VOC) samples from the 2121 (3) coal mining face in the Pansan Coal Mine, situated in Panji District, Huainan City, Anhui Province, China. The initial stage of the sampling process was conducted in the air intake tunnel, situated approximately 1,000 meters from the working face. Subsequently, the samples were retrieved from the working face and transported via the air return tunnel, with the collection process concluding at the 1,000-meter mark.

An open atmospheric background value monitoring point is situated at the entrance to the Pansan Coal Mine, which allows for a more accurate representation of the VOC data in the open atmospheric environment above the mine.

## Sample Collection and Analysis

Reference to the standard number issued by the Ministry of Ecology and Environment: HJ 732-201

"Emissions from Stationary Sources - Sampling of Volatile Organic Compounds – Bag Method", this study employed the sampling bag method for the collection of VOC samples [32]. VOC samples were collected from the ground level of the coal mine for the purpose of obtaining the background values of the ground-level VOC data. A cage elevator was used to walk into the 2121 (3) air intake tunnel of the underground coal mine, and the initial sampling point of the air intake roadway was located at a distance of about 1,000 meters from the coal face. One VOC sample was collected every 100 meters, and a total of 10 VOC samples were collected from the roadway to the coal mining face. Four VOC samples were collected on foot across the 400-meter-long coal face, with sampling points at the down corner, coal shutter, in the middle of the face, and at the upper corner. Then, we moved to the air return tunnel to collect one VOC sample every 100 meters, and a total of 10 VOC samples were collected (Fig. 1).

A total of 24 samples of volatile organic compounds (VOCs) were collected throughout the process. Volatile organic compound (VOC) samples were collected using 2L Tedlar polyvinyl fluoride film sampling bags, and the samples were collected until the gas bag was saturated and sealed. The sampling point is situated at a height of approximately 1.5 meters above ground level, corresponding to the human breathing zone. The samples were protected from light following collection, and component analysis was conducted within 12 hours. During the VOC sample collection

process, real-time meteorological data, including temperature, humidity, and atmospheric pressure, were monitored using a venti-meter, portable anemometer, and manometer (Table 1).

The VOC samples were analyzed using a photon composite source time-of-flight mass spectrometer (Aliben-UVP-TOFMS 1800, Aliben Technology, China, detection range: 100pptv-1ppmv, Accuracy: RSD < 3%). This instrument employs photon ionization and its corresponding composite technology to achieve real-time, full-spectrum ionization of the measured gas sample, whereby the valence electrons of organic molecules or inorganic gas molecules are excited. The sample does not require prior separation, and all volatile organic compounds (VOCs) and inorganic gases present in the sample gas can be ionized simultaneously, with a response time of 1 second or less. Background VOC data from the open atmospheric environment monitoring sites were analyzed concurrently using photon composite source time-of-flight mass spectrometer (Aliben-UVP-TOFMS 1800, Aliben Technology, China). A total of 57 VOCs were analyzed in the samples (Table 2 depicts the detection limits and correlation coefficients of the target compounds).

#### Health Risk Evaluation

In order to investigate the influence of volatile organic compounds (VOCs) on the health of workers in diverse occupational settings within the context of

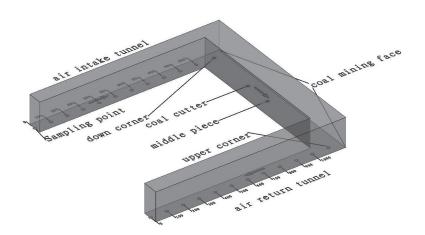


Fig. 1 Schematic diagram of sampling sites

Table 1. Ambient meteorological parameters during testing.

Sports event	Temperature (°C)	Humidity (%)	Air velocity (m/s)	
Accuracy and measurement ranges	±0.3°C -30°C~70°C	±2% 0~80%	±5% 0.1~30m/s	
Air intake tunnel	27±0.33	50.22±1.33	3.37±0.54	
Coal mining face	26±0.44	48.65±2.66	2.65±0.44	
Air return tunnel	29±0.41	52.36±3.55	4.56±1.22	

Table 2. Target compound and correlation coefficients.

Target compound	R <sup>2</sup>	Target compound	$\mathbb{R}^2$
Ethyne C <sub>2</sub> H <sub>2</sub>	0.958	n-heptane, 2_3-dimethylpentane, 2_4-dimethylPentane, 2-methylhexane, 3-methylhexane	
Vinyl	0.948	Methyl methacrylate, 2-hexanone, hexanal	
Formaldehyde, Ethane	-0.389	Styrene	0.908
Propylene	1	o-xylene, m-xylene, p-xylene, ethylbenzene, benzaldehyde	0.965
Methane	0.996	1_2-dichloropropane, cis-1_3-dichloropropene, trans-1_3-dichloropropene_chlorobenzene	
Acetaldehyde	0.974	2-methylheptane, 3-methylheptane, n-octane, isooctane, 2_3_4-trimethylpentane	
Methyl chloride CH <sub>3</sub> Cl	0.957	Trichloromethane	0.964
1,3-Butadiene	0.997	o-Ethyltoluene, m-Ethyltoluene, p-Ethyltoluene, isopropylbenzene, propylbenzene, bis(trimethyl)benzene, 1_2_4-trimethylbenzene, 1_3_5-trimethylbenzene, m-toluylaldehyde	
n-Butene, cis-2-butene, trans-2-butene, acrolein	0.881	Benzyl chloride	0.902
Isobutane, n-Butane	0.935	Naphthalene, n-nonane	0.847
Acetone, propionaldehyde	0.973	Trichloroethylene	0.999
Isopropanol	0.962	1_1_1-Trichloroethane, 1_1_2-Trichloroethane	0.999
Ethyl chloride, vinyl chloride	0.975	m-Diethylbenzene, p-Diethylbenzene	0.903
Isoprene	0.989	Trichlorofluoromethane	0.995
1-Pentene_cis-2-pentene_trans-2-pentene	0.949	n-decane	0.932
Butenal, methacrolein, cyclopentane	0.994	1_2-Dichlorobenzene, 1_3-Dichlorobenzene, 1_4-Dichlorobenzene	
n-Pentane, Isopentane_Tetrahydrofuran	0.959	carbon tatrachloride	
2-Butanone, n-Butyraldehyde	0.922	n-11thane	
Methyl tert-butyl ether	0.954	Monobromodichloromethane	
Carbon disulfide	0.984	Tetrachloroethylene	
Benzene_1_1-dichloroethane_1_2-dichloroethane	1	1_1_2_2-tetrachloroethane	
vinyl acetate	0.999	n-Dodecane, 1_2-dichlorotetrafluoroethane	
Cyclohexane, 1-hexene, methylcyclopentane, dichloromethane	0.999	1_2_4-Trichlorobenzene	
2-methylpentane, 3-methylpentane, 2_2-dimethylbutane, 2_3-dimethylbutane, valeraldehyde	0.947	1_2-Dibromoethane, 1_1_2-Trichlorotrifluoroethane	
1_4-Dioxane, ethyl acetate	0.895	Dibromomethane	0.997
Toluene C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	0.988	Bromoform	
Methyl bromide	0.999	Hexachloro-1_3-butadiene	
1_1-Dichloroethene, trans-1_2-dichloroethene, cis-1_2-dichloroethene	0.997	Hexane	
Methylcyclohexane	0.994		

an underground coal mine, this study employs the United States Environmental Protection Agency (EPA) health risk assessment model to quantify the non-carcinogenic risk hazard index (HI) and the lifetime carcinogenic risk factor value (RISK) [33]. This is achieved through the analysis of VOC components obtained through sampling, with the objective of evaluating the noncarcinogenic and lifetime carcinogenic risks associated with VOCs across a range of occupational scenarios within an underground coal mine [34-36]. The formula for calculating the concentration exposure is as follows:

$$EC = \frac{CA \times ET \times EF \times ED}{AT}$$
 (1)

Where: EC is the pollutant exposure concentration,  $\mu g/m^3$ ; CA is the airborne pollutant concentration,  $\mu g/m^3$ ; ET is the daily exposure time, h/d; EF is the frequency of exposure, d/a; ED is the duration of exposure; AT is the mean survival time.

According to the research on the working hours of the sampled coal miners, the exposure time of ET is taken as 10 h/d; the exposure frequency of EF is taken as 264 d/a; the duration of exposure of ED is taken as 22a; AT (non-carcinogenic) is taken as 365×30×24 h, and AT (carcinogenic) is taken as 365×70×24 h [33].

The formula for calculating the non-carcinogenic risk index is as follows:

$$HQ = \frac{EC}{Rfc \times 1000}$$
 (2)

$$HI = \sum_{i}^{n} HQ_{i}$$
(3)

Where: HQ is the non-carcinogenic risk index; Rfc is the reference concentration, mg/m³. Rfc data mainly comes from the data published by the EPA (Table 3); HI is the non-carcinogenic risk hazard index, i.e., the sum of the non-carcinogenic risk indices of multiple pollutants HQ.

Lifetime Cancer Risk Factor values are calculated using the following formula:

$$Risk = EC \times IUR \tag{4}$$

Where: RISK is the lifetime cancer risk factor value; IUR is the unit inhalation cancer risk.

## Quality Control and Assurance

Prior to sampling, the VOC bag was cleaned on three to four occasions with high-purity nitrogen (99.999%) in order to reduce the interference of the background concentration within the bag. The time-of-flight mass spectrometer with a photon composite source was calibrated on three occasions using a 57-component standard gas produced by Sichuan Zhongce Standard Technology Co., Ltd.

To ensure the accuracy of VOCs data, after diluting 57 types of VOCs mixed standard gas from 500 ppb to 10 ppb, the sample was injected and analyzed repeatedly (7 times). The method detection limit (MDL) was defined as 3.14 times the standard deviation of the calibration quantification results, with a range of  $0.02{\sim}0.08~\mu\text{g/m}^3$ . Seven parallel analysis tests were

conducted using mixed standard gas, and the arithmetic mean X and standard deviation  $SD_5$  of the analysis results were obtained. The instrument precision is expressed as the relative standard deviation (RSD), with a range of 0 45% to 6.46%. The relative error (RE) represents the accuracy, with a range of 0.12% to 6.54%. The specific calculation formula is as follows:

$$MDL = 3.14 \times SD_1 \tag{5}$$

$$RSD = (SD_5/X) \times 100\%$$
 (6)

$$RE = (|X - 5.0|/5.0) \times 100\%$$
(7)

#### **Results and Discussion**

#### **VOCs Concentration Levels**

The analysis of the sampled samples demonstrates the total volatile organic compounds (TVOCs) in the air in three distinct underground work environments: the air intake tunnel, the air return tunnel, and the coal mining face, as illustrated in Fig. 2. The mean concentration of VOCs in the 2121 (3) coal mining face environment is (2066.67±750) μg/m<sup>3</sup>. The mean TVOC value of all samples in the air intake tunnel working environment is (1875±541.67) μg/m<sup>3</sup>. The mean TVOC value of all samples in the underground coal mining face working environment is (2362.5±454.17) μg/m<sup>3</sup>. The mean TVOC value of all samples in the underground air return tunnel working environment is (1943±626.33) μg/m<sup>3</sup>. The lowest concentration of TVOCs was observed in the air intake tunnel, followed by the return air tunnel. The overall concentration of VOCs in the ambient air at the coal mining face is the highest, indicating the presence of the most severe pollution. The relatively low TVOC concentration in the air intake tunnel may be attributed to its primary function of transporting fresh air into the mine to meet the respiratory needs of miners and dilute the harmful gases present therein. The coal mining face is situated at the forefront of the mine, with a confined operational area. A variety of coal mining equipment, including shearers, conveyors, and ancillary devices, operate in conjunction with falling coal and dust. The concentration of volatile organic compounds (VOCs) from the air intake tunnel and those generated by the coal mining face accumulates, resulting in a high value for total volatile organic compound (TVOC) concentration. As the ventilation air flows into the return air tunnel, it is discharged underground, where gas diffusion and exhaust occur. This results in a corresponding decrease in the TVOC concentration.

Furthermore, the study monitored the concentration of volatile organic compounds (VOCs) in the open atmospheric air on the ground in Huainan City. The concentration of VOCs was found to range from

Table 3. Coefficient of health risk assessment, RFC (Reference Concentration for Inhalation Exposure), IUR (Inhalation Unit Risk).

Target compound	RFC mg/m³	IUR μg/m³	Target compound	RFC mg/m³	IUR μg/m³
Ethyne C <sub>2</sub> H <sub>2</sub>	_	_	Heptane	7.00E-01	_
Vinyl	_	_	2-Hexanone	3.00E-02	_
Formaldehyde ethane	_	1.30E-05	Styrene	1.00E+00	_
Propylene	_	_	Xylene	1.00E-01	_
Acetaldehyde	9.00E-03	2.20E-06	cis-1 3-Dichloropropene	2.00E-02	4.00E-06
n-Butene cis-2-butene trans-2- butene acrolein	2.00E-05	_	chlorobenzene C <sub>6</sub> H <sub>5</sub> Cl	_	_
Propanal CH <sub>3</sub> CH <sub>2</sub> CHO	8.00E-03		2-methylheptane 3-methylheptane n-octane isooctane 2 3 4-trimethylpentane	_	_
Isopropanol	_	_	Trichloromethane	_	3.00E-05
Isoprene	_	_	Isopropylbenzene	4.00E-01	_
1-Pentenylbutenal	_	_	1 2 4-Trimethylbenzene	6.00E-02	_
Tetrahydrofuran (THF)	2.00E+00	_	1 3 5-Trimethylbenzene	6.00E-02	_
Carbon disulfide	7.00E-01	_	Benzyl chloride	_	_
Benzene	3.00E-02	7.80E-06	Naphthalene C10H8	3.00E-03	_
Cyclohexane	6.00	_	Trichloroethylene	2.00E-03	4.10E-06
Dichloromethane	6.00E-01	1.00E-08	1 1 1-Trichloroethane	5.00E+00	_
2-methylpentane 3- methylpentane 2 2- dimethylbutane 2 3- dimethylbutane pentanal vinyl acetate	_	_	1 1 2-Trichloroethane	_	1.60E-05
Methyl tert-butyl ether	3.00E+00	_	p-Diethylbenzene m-Diethylbenzene	_	_
Toluene C6H5CH3	5.00E+00	_	1 4-Dichlorobenzene	8.00E-01	_
Methyl bromide	5.00E-03	_	Carbon tatrachloride	1.00E-01	6.00E-06
1 1-Dichloroethylene	2.00E-01	_	n-11thane	_	_
Methylcyclohexane	_	_	Monobromodichloromethane	_	_
Tetrachloroethylene	4.00E-02	2.60E-07	1 1 2 2-tetrachloroethane	_	_
n-dodecane	_	_	1 2 4-Trichlorobenzene	_	_
1 2-Dibromoethane	9.00E-03	3.00E-04	Dibromomethane	_	_
Bromoform	_	1.10E-06	Hexachloro-1 3-butadiene	_	_
Trichlorofluoromethane	_	_			

<sup>&</sup>quot;—" means that the corresponding parameter was not found on the EPA website.

RFC (Reference Concentration for Inhalation Exposure) is the concentration of the target compound queried in the EPA. IUR (Inhalation Unit Risk) is the unit inhalation carcinogenicity risk of the target compound queried in the EPA.

(55.5±20.3) μg/m³, which is considerably lower than the concentration levels observed in underground coal mining environments. The concentration of VOCs in the open atmosphere is typically low [11, 14, 19]. It is possible that special industrial areas may exhibit elevated levels of VOC pollution as a consequence of emissions from local enterprises [6, 27, 34]. It should be noted that certain semi-enclosed spaces, such as tunnels and subways, also exhibit a degree of VOC

pollution. The occupational environment in coal mines is analogous to that of tunnels and subterranean parking facilities, which are equipped with intake, exhaust, and ventilation systems. Consequently, the concentration of VOCs in these environments is higher than that in the open air. (Please refer to Table 3 for a detailed overview of the pollution levels observed in the majority of VOC studies.)

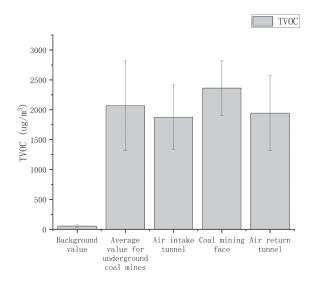


Fig. 2. Concentration levels of TVOCs in different working environments in underground coal mines.

## Composition and Characterization of VOCs

The classification of VOCs is based on their molecular structure and reactivity with OH radicals. This leads to the following categories: alkyne, alkane, alkenes, aromatic hydrocarbons, oxygen-containing VOCs (OVOCs), and halogenated hydrocarbons. Each of these categories possesses a distinct structure and set of chemical properties [7]. The component analysis of the collected samples revealed that the classification of

VOCs in the three different working scenarios of the air intake tunnel, working face, and air return tunnels is as follows: halogenated hydrocarbons > alkanes > OVOCs > alkenes > aromatic hydrocarbons, in descending order of contribution. Halogenated hydrocarbons constitute the predominant contributor to VOCs in all three scenarios, accounting for 41.9%, 40.9%, and 41.2%, respectively. Subsequently, alkanes and OVOCs accounted for 2.4% to 26.1% and 17.2% to 21.9%, respectively. The concentrations of alkenes and olefins accounted for 3.1% to 3.7% and 5.3% to 8.11% of the TVOC concentration, respectively (Fig. 3). Previous studies identified aromatic hydrocarbons in the VOC pollution components in tunnels, subways, and underground garages as the primary contributors to VOCs [14, 16, 20, 23, 28, 35-38]. The primary reason for this is that the predominant mode of transportation within tunnels and underground garages is fuel-powered vehicles, and the aromatic hydrocarbons present in their exhaust emissions contribute the most. However, gasoline vehicles are not typically utilized for underground coal mine operations, and fuel-powered vehicles have no exhaust emissions. This also corroborates the findings of this study, which state that aromatic hydrocarbons contribute the least.

VOC components are classified into alkynes, alkanes, alkenes, olefins, aromatic hydrocarbons, oxygenated VOCs (OVOCs), and halogenated hydrocarbons based on their molecular structure and their reactivity with OH radicals. Each has unique structural and chemical properties.

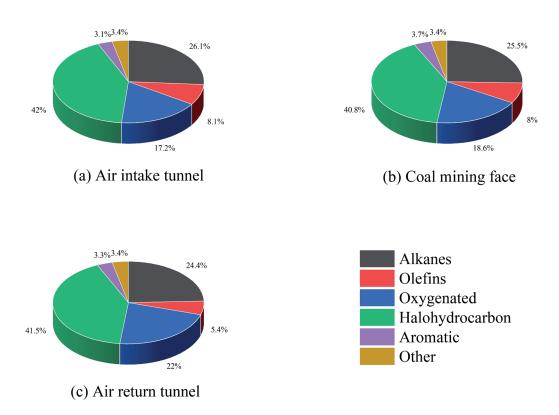


Fig. 3. Classification composition of VOCs in different working environments in underground coal mines

The top 10 VOCs in terms of concentration in the three different working scenarios of the air intake tunnel, working face, and air return tunnel are identical (as illustrated in Fig. 4). The primary contributing components are isopropanol, carbon disulfide, cyclohexane, methyl bromide, cis-1,3-dichloropropene, chlorobenzene, benzyl chloride, trichloroethylene, chlorofluorocarbon-11. n-decane, and Of these. isopropanol (OVOCs) has the highest concentration ratio, possibly due to its use as a preservative and cleaning agent for cable joints in underground wells, effectively preventing corrosion of metal materials. Furthermore, isopropanol can be employed as an explosion-proof agent to prevent fires and explosions in underground mines, as evidenced by its use in the Yangquan coal mine in Shanxi. The results indicate that the concentration of methyl bromide is also considerable. Methyl bromide is employed primarily in agricultural settings to fumigate soil and warehouses in order to eradicate pests and pathogens. The reason for its presence underground is currently unknown. However, it may be due to the geochemical cycle, in which methyl bromide in surface soil is circulated to mining shafts through surface water runoff.

In summary, the volatile organic compounds (VOCs) present in the three working scenarios examined in this study were predominantly halogenated hydrocarbons with the lowest concentration of aromatic hydrocarbons.

Isopropanol, a preservative and explosion-proofing agent frequently utilized in subterranean settings, exhibited the highest concentration of VOCs within the coal mine.

#### Health Risk Evaluation

In studies on the health risk assessment of ambient air VOCs, a non-carcinogenic risk is deemed to exist when the non-carcinogenic risk hazard index exceeds 1, and a carcinogenic risk is considered to exist when the value of the lifetime carcinogenic risk factor is greater than  $1.00\times10^{-6}$  [32, 33]. In this study, the non-carcinogenic risk hazard index and the lifetime carcinogenic risk factor value were calculated using Equations (1), (2), (3), and (4) and Table 3 for the VOC samples collected in the coal mine. The results of the non-carcinogenic and carcinogenic risk assessments of VOCs in the ambient air under three different working scenarios in the coal mine are presented in Fig. 5.

Non-carcinogenic risk assessment of VOC components:

(1) The four samples from the working surface exhibited concentrations in the range of 0.14 to 0.279, which is below the critical threshold of 1, indicating the absence of non-carcinogenic risk. In the  $1.20\times10^{-4}$  to  $2.02\times10^{-4}$  range, the carcinogenic risk is 120 to 202 times the threshold value.

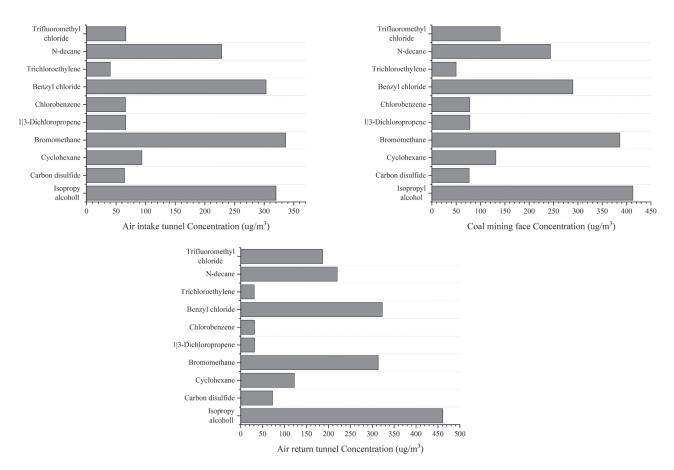


Fig. 4 Top 10 concentrations of VOCs components in different working environments in underground coal mines

- (2) The 10 samples from the air intake tunnel exhibited concentrations in the range of 0.01 to 0.209, which is below the threshold value of 1 and indicates the absence of non-carcinogenic risk. In the range of  $4.28\times10^{-5}$  to  $1.86\times10^{-4}$ , the carcinogenic risk exceeds the threshold by a factor of 42.8 to 186.
- (3) The 10 samples from the air return tunnel are within the range of 0.01 to 0.209, which is below the first threshold and indicates the absence of non-carcinogenic risk. The carcinogenic risk exceeds the threshold by a factor of between 42.8 and 186 at the specified range of  $4.28\times10^{-5}$  to  $1.86\times10^{-4}$ .
- (4) The volatile organic compounds (VOCs) identified in three distinct operational scenario analyses present a considerable carcinogenic risk to human health. The risk values of benzene under the three different scenarios are 2.18×10<sup>-5</sup>, 1.25×10<sup>-5</sup>, and 2.13×10<sup>-5</sup>, respectively. All of these exceed the threshold value of 1.00×10<sup>-6</sup>, indicating a significant carcinogenic risk. Benzene is classified as a Group 1 carcinogen by the International Agency for Research on Cancer (IARC).

In summary, assessing volatile organic compounds (VOCs) in diverse work environments within coal mines has been identified as a significant carcinogenic concern.

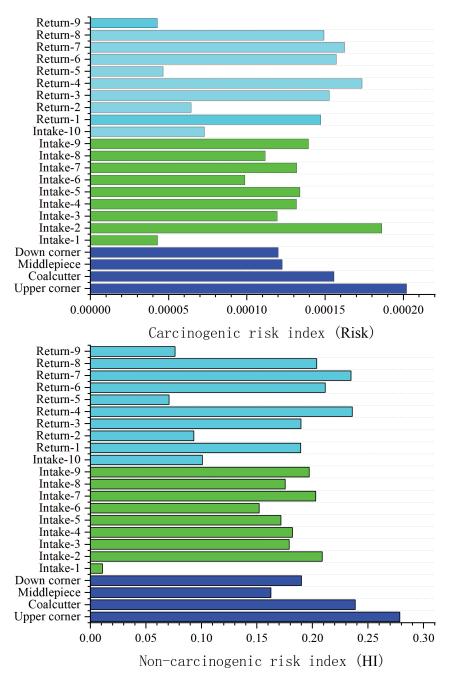


Fig. 5 Classification of VOCs in different working environments in coal mines\_ non-carcinogenic risk hazard index and carcinogenic risk hazard index.

As long-term workplaces for their employees, coal mines must reinforce their ventilation systems, enhance the efficacy of underground air circulation, diminish the accumulation of pollutants underground, and encourage the use of low-emission or emission-free coal mining machinery to curtail tailpipe emissions. Furthermore, regular testing of the underground environment for VOCs is essential to elevate awareness of early warning systems.

#### **Conclusions**

- (1) The mean concentration of volatile organic compounds (VOCs) in the underground coal mine environment was found to be (2066.67±750) μg/m³. This value is considerably higher than the background concentration of VOCs in the ground environment, which was collected on the same day and yielded a mean value of (55.5±20.3) μg/m³. The mean TVOC value in the air intake tunnel was (1875±541.67) μg/m³, the mean TVOC value in the coal mining face was (2362.5±454.17) μg/m³, and the mean TVOC value in the air return tunnel was (1943±626.33) μg/m³. The concentration of VOCs in the air intake tunnel is relatively low, while the concentration in the coal mining face and return air tunnel is higher, indicating that the coal mining face is the most polluted area.
- (2) The components with the highest volume fractions of volatile organic compounds (VOCs) are isopropanol, carbon disulfide, cyclohexane, methyl bromide, cis-1,3-dichloropropene, chlorobenzene, benzyl chloride, trichloroethylene, n-decane, and chlorofluorocarbon-11. The sample composition demonstrates that halogenated hydrocarbons constitute the predominant contributors to VOCs across the three working scenarios, accounting for 41.9%, 40.9%, and 41.2%, respectively. Alkanes and OVOCs account for the next largest proportion, representing 24.2% to 26.1% and 17.2% to 21.9% of the TVOCs concentration, respectively. Aromatic hydrocarbons and olefins account for 3.1% to 3.7% and 5.3% to 8.11% of the TVOCs concentration, respectively.
- (3) The results of the health risk assessment indicated that the hazard index (HI) for non-carcinogenic risk of volatile organic compounds (VOCs) in the underground coal mine environment was 0.077-0.279, which did not exceed the threshold value of 1. Thus, there was no non-carcinogenic health risk. The carcinogenic risk index (RISK) is  $4.26\times10^{-5}$  to  $2.02\times10^{-4}$ , which is 42.6 to 202 times greater than the threshold  $(1.00\times10^{-6})$ , indicating a relatively high carcinogenic risk.

It is imperative that coal mines, as workplaces with long-term employee populations, reinforce their ventilation systems, enhance the efficacy of airflow within the mines, and diminish the accumulation of pollutants underground. It is recommended that the utilization of low-emission or emission-free coal mining machinery be encouraged in order to minimize tailpipe emissions. Regular testing for volatile organic

compounds (VOCs) should also be conducted in underground environments to enhance awareness of potential hazards and facilitate prompt action in the event of an incident.

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#### **Conflict of Interest**

There are no conflicts to declare.

#### References

- LIANG Y. Scientific conception of coal mine dust control and occupational safety. Journal of China Coal Society. 45 (1), 1, 2020.
- LIANG Y., SHENG X., XIAOLIANG Z., BINGYOU J. Current situation and prospects of air quality revolution technology in coal mines. Journal of Mine Automation. 49 (6), 32, 2023.
- 3. HIEU N.T., LEE B.-K. Characteristics of particulate matter and metals in the ambient air from a residential area in the largest industrial city in Korea. Atmospheric Research. 98 (2-4), 526, 2010.
- IJAZ M., AKRAM M., AHMAD S.R., KHAN W.U., THYGERSON S.M., NADEEM F.A. Dust Generation and Respiratory Impact of Underground Coal-Producing Mines in Pakistan. Polish Journal of Environmental Studies. 29 (5), 3611, 2020.
- ZHANG Y., GUI H., HUANG Y., YU H., LI J., WANG M., FANG H., JIANG Y., WANG C., CHEN C. Characteristics of Soil Heavy Metal Contents and its Source Analysis in Affected Areas of Luning Coal Mine in Huaibei Coalfield. Polish Journal of Environmental Studies. 30 (2), 1465, 2021
- ZHONG Z., SHA Q.E., ZHENG J., YUAN Z., GAO Z., OU J., ZHENG Z., LI C., HUANG Z. Sector-based VOCs emission factors and source profiles for the surface coating industry in the Pearl River Delta region of China. Science of the Total Environment. 583, 19, 2017.
- MA C., WANG Z., LIU J., HUANG H., LIU Y., YAN X., LU Y., WANG C., ZHANG X. Preliminary analysis of pollution characteristics of ambient volatile organic compounds and ozone formation potential in Yinchuan metropolitan area. Environmental Chemistry. 41 (3), 801, 2022.
- MANGOTRA A., SINGH S.K. Volatile organic compounds: A threat to the environment and health hazards to living organisms - A review. Journal of Biotechnology. 382, 51, 2024.
- GOODMAN N., NEMATOLLAHI N., WEINBERG J.L., FLATTERY J., KOLEV S.D., TONG M., VARDOULAKIS S., STEINEMANN A. Volatile organic compounds in regular and organic vaping liquids: a public health concern. Air Quality Atmosphere and Health. 18, 307, 2025.

- TONG R., MA X., ZHANG Y., SHAO G., SHI M. Source analysis and health risk-assessment of ambient volatile organic compounds in automobile manufacturing processes. Human and Ecological Risk Assessment. 26 (2), 359, 2020.
- 11. WANG B., LI G., ZHANG X., MA H., WU D., WANG W., WANG X. Pollution characteristics and source analysis of atmospheric VOCs:taking Puyang, one of the "2+26" cities, as an example. Environmental Pollution & Control. 46 (3), 380, 2024.
- 12. MA C., WANG J., ZHANG X., CHEN R., HU Y., GUO Y., ZHANG Z., LI T. Pollution characteristics and health risk assessment of volatile organic compounds (VOCs) in underground garages of urban commercial buildings. Environmental Chemistry. 43 (5), 1465, 2024.
- 13. LI H., ZHANG Y., FU G., HUANG S., LI H., CUI Y., GAO X., HE Q., BAI J., ZHANG G., WEN B. Pollution characteristics and control strategies of volatile organic compounds in coking pollution area in spring. China Environmental Science. 44 (3), 1234, 2024.
- 14. PARK W.M., PARK J.B., ROH J., HWANG S.H. Levels of formaldehyde and TVOCs and influential factors of 100 underground station environments from 2013 to 2015. Human and Ecological Risk Assessment. 24 (4), 1030, 2018.
- 15. REN H., XIA Z., YAO L., QIN G., ZHANG Y., XU H., WANG Z., CHENG J. Investigation on ozone formation mechanism and control strategy of VOCs in petrochemical region: Insights from chemical reactivity and photochemical loss. Science of the Total Environment. 914, 2024.
- 16. YOU G., JIN Z., LU S., REN J., ZHANG Y., HU K., XIE S. Emission factors and source profiles of volatile organic compounds from the automobile manufacturing industry. Science of the Total Environment. 927, 2024.
- 17. YAO L., LUO Z.-W., HUA K., LI Y.-F., GU Y., SONG L.-L., BI S.-Y., YIN S.-H., KOU M.-Q., BI X.-H., ZHANG Y.-F., FENG Y.-C. Characteristics and Source Analysis of VOCs Pollution During Emergency Response in Tianjin. Huanjing kexue. 45 (8), 4448, 2024.
- 18. JING L., CHEN T., YANG Z., DONG W. Association of the blood levels of specific volatile organic compounds with nonfatal cardio-cerebrovascular events in US adults. Bmc Public Health. 24 (1), 2024.
- LIU Y.-T., DU Z.-X., ZHANG X.-M., CHEN S., LIU Y.-Y., ZHANG L.-T. Analysis of Ozone and VOCs Pollution Characteristics, Sources, and Abatement Control Strategies in Hebi. Huanjing kexue. 45 (7), 3839, 2024.
- WANG J., HUANG Y., BO Y., ZHANG Y., ZHANG L. Air pollution characteristics and human health risk assessment of underground parking garages in Xi'an, China. Indoor and Built Environment. 32 (4), 632, 2023.
- ZHANG X., TANG B., YANG X., LI J., CAO X., ZHU H. Risk assessment of volatile organic compounds from aged asphalt: Implications for environment and human health. Journal of Cleaner Production. 440, 2024.
- ZHANG F., WANG M., WANG M., FAN C., TAO L., MA W., SUI S., LIU T., JIA L., GUO X. Revealing the dual impact of VOCs on recycled rubber workers: Health risk and odor perception. Ecotoxicology and Environmental Safety. 283, 2024.
- 23. LIU Y., YANG N., SUN L., WU Y., SONG P., ZHAO Y., LOU K., MAO H. Characteristics and Health Risk Assessment of VOCs in an Underground Parking Garage. Environmental Science. 43 (12), 5453, 2022.
- 24. YANG X., CHENG X., YAN H., SUN Y., ZHANG G. Ground-Level Ozone Production over an Industrial Cluster

- of China: a Box Model Analysis of a Severe Photochemical Pollution Episode. Polish Journal of Environmental Studies. **31** (2), 1885, **2022**.
- 25. XU J., GUI H., FANG H., DAI H., GUO Y., CHEN J., LI C., CHEN C., WANG C. Quantitative Contributions of the Sources, Contamination and Ecological Risk of Heavy Metals in Soils from a Closed Coal Mine of Huaibei Coalfield, Eastern China. Polish Journal of Environmental Studies. 30 (5), 4299, 2021.
- 26. LIANG R., ZHANG R., WEN H., MO J., HUANG M., CHEN H. Effects of Volatile Organic Compounds (VOCs) of *Cinnamomum burmannii* in Its Natural State on Physical and Mental Health. Polish Journal of Environmental Studies. 32 (1), 133, 2023.
- 27. WANG J., YAO Z., WANG M., CHEN S., LONG T., WANG H., LI H., GUO X., HAO J., NIE L. VOCs Pollution Characteristics and Health Risk Assessment in Typical Industrial Parks in Beijing:Environmental Impact of High and New Technology Industries. Environmental Science. 45 (4), 2019, 2024.
- ELIA E.A., STYLIANOU M., AGAPIOU A. Investigation on the source of VOCs emission from indoor construction materials using electronic sensors and TD-GC-MS. Environmental Pollution. 348, 2024.
- LI H., WANG Q.G., SHAO M., WANG J., WANG C., SUN Y., QIAN X., WU H., YANG M., LI F. Fractionation of airborne particulate-bound elements in haze-fog episode and associated health risks in a megacity of southeast China. Environmental Pollution. 208, 655, 2016.
- 30. YU C.-C., ZHAO W.-T., GAO X.-F., CHENG S.-G., HUANG T., YIN Y.-M., ZHAO Z.-L. Distribution Characteristics and Health Risk Assessment of Heavy Metals in Surface Water Around Electroplating Factories. Huanjing kexue. 38 (3), 993, 2017.
- 31. JI W., LIU Z., LIU C., WANG C., LI X. Characteristics of fine particulate matter and volatile organic compounds in subway station offices in China. Building and Environment. 188 (16), 107502, 2021.
- 32. HA S.-H., AHMADI Y., SHIN H.-J., KIM K.-H. Short-term storability of volatile organic compounds in bag sampling systems under ambient conditions. Environmental Research. 256, 2024.
- EPA releases probabilistic risk assessment guidance for superfund. Hazardous Waste Consultant. 20 (7), B17, 2002.
- 34. XIAO H., ZHANG J., HOU Y., WANG Y., QIU Y., CHEN P., YE D. Process-specified emission factors and characteristics of VOCs from the auto-repair painting industry. Journal of Hazardous Materials. 467, 2024.
- 35. SUN L.-N., LIU Y., ZHAO J.-B., SUN S.-D., SONG C.-B., ZHANG J., LI Y.-N., LIN Y.-C., WANG T., MAO H.-J. Pollution Characteristics and Emission Factors of VOCs from Vehicle Emissions in the Tianjin Tunnel. Huanjing kexue. 40 (1), 104, 2019.
- 36. SONG C., LIU Y., SUN L., ZHANG Q., MAO H. Emissions of volatile organic compounds (VOCs) from gasoline- and liquified natural gas (LNG)-fueled vehicles in tunnel studies. Atmospheric Environment. 234, 2020.
- 37. ZHANG X., REN W., YAN L., LIU J., LI Y., HU Y. Distribution and Risk Assessment of VOCs in Road Dust Across Different Urban Areas. Soil & Sediment Contamination. 2024.
- 38. LIU X.-H., ZHU R.-C., JIN B.-Q., MEI H., ZU L., YIN S.-S., ZHANG R.-Q., HU J.-N. Characteristics and Source Apportionment of Vehicular VOCs Emissions in a Tunnel Study. Huanjing kexue. 43 (4), 1777, 2022.