

Case Report

Distribution and temporal variation of total volatile organic compounds concentrations associated with health risk in Punjab, India

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ABSTRACT

In December 2019, a novel coronavirus disease (COVID-19) outbreak occurred due to a human respiratory virus that originated in the city of Wuhan, China. During the COVID-19 lockdown, there was a significant improvement in the air quality across the world. We analyzed the data for BTEX over the three years (January to December 2019 to 2021) with pairwise comparison and trend analysis for pre-, during, and post-pandemic periods. This study demonstrates the substantial changes in the concentration of VOCs in the urban area (Punjab) due to the lockdown effects. The results indicate a substantial reduction in the mean TVOCs concentration for all the monitoring stations was found to be 8.89 ± 1.80 , 5.59 ± 1.71 , and $5.57 \pm 1.43 \mu\text{g}/\text{m}^3$ for before, during, and post-pandemic, respectively. The level of TVOCs declined by $\sim 43\%$ for all monitoring stations during the lockdown period compared to the previous years. A higher T/B ratio was found in Patiala ($2.97 \mu\text{g}/\text{m}^3$) before the pandemic, which may indicate vehicle emission sources. The LCR values for benzene were found to be higher in children than in males and females, which indicated the possible risk. The LCR values for benzene exceeded the prescribed value by CPCB for children.

1. Introduction

Coronavirus disease, or COVID-19 was first discovered in Wuhan, China, in December 2019; human transmission was revealed in the year 2020 by World Health Organization [1,2]. COVID-19 was declared a “Global Pandemic” on the 11th of March 2020 by WHO because of its easy spread and high transmission rate almost all over the world within a short period [3–6]. India reported the first case of COVID-19 in Kerala on January 30, 2020; soon after that, an outburst of cases and deaths was reported [6,7,9]. To reduce the transmission rate, many countries,

including India, implemented physical distancing and lockdown measures involving restrictions on tourism transportation, industries, cultural activities, and academic and religious places [7,10]. Due to the lockdown, air pollution levels have been reduced in several countries; restrictions on industrial areas and vehicles, which contribute to air pollution, have also improved air quality [8,10,11].

Air pollution is responsible for causing around 4.2 million deaths every year worldwide, becoming the largest environmental risk factor [12]. Approximately 91% of the world's population lives in hazardous conditions where air quality exceeds the limit set by the World Health

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Organization [12,13]. Environmental contamination by physical, chemical, or biological agents, changing the natural characteristics of the atmosphere, can be termed air pollution causing a negative impact on human health and the surrounding environment due to the increase of dispensable substances in the air [12,14,15]. Unpleasant air quality has always been an issue of global concern as the world is shifting towards fast industrialization and urbanization [16,17]. Every air pollutant has different characteristics and chemical complexity depending upon its sources; it may be a solid, liquid, or gaseous form [14]. Atmospheric pollutants like ozone (O_3), particulate matter (PM), Carbon dioxide (CO_2), Sulphur dioxide (SO_2), Nitrogen dioxides (NO_2), and Volatile Organic Compounds (VOCs) are responsible for causing adverse health effects and are found to be present inside the home as well as outside in the environment [16,18,19]. Industrial emissions, heavy traffic, combustion, traveling, and our living activities are areas where major exposure to air pollutants occurs [20,21]. The reaction between NOx and VOCs forms a variety of oxidizing species, including, ozone (O_3), chlorofluorocarbons (CFC), hydroxyl radicals (OH), and halogenated species [22,23].

Volatile Organic Compounds (VOCs) are a group of organic species that are vital for forming ozone, photochemical smog, and secondary organic aerosol in the troposphere [24–27]. VOCs are emitted from both natural sources like forest fires, agricultural release, and tropical forests acting as the largest VOC source; globally, whereas anthropogenic sources include emissions from industrial processes, tobacco smoke, motor vehicles, gasoline evaporation, and biomass burning, while wood preservatives, disinfectants, moth repellants, stationery supplies, craft materials, and office equipment are the main sources in urban areas [28–31]. VOCs are of great usage and are being used in almost every field, including the industrial sector as preservatives in many household and commercial products like paints, petroleum-based carpets, and refrigerators; certain pharmaceuticals and personal care products like perfumes, deodorants, and skin lotions have large amounts of VOCs. Several concerns are seen related to VOCs, as many of them are genotoxic, neurotoxic, and mutagenic and come in human contact from inhalation [26,32,33].

The class BTEX is gathering more attention among all the VOCs, being a carcinogenic group (group 1) by the International Agency for Research on Cancer (IARC) it is linked with human health [34,35]. It includes benzene, toluene, ethyl-benzene, and xylene (including o, m, and p categories), which have an enormous source of emission inside as well as outside the environment. Fuels, adhesives, paints, aerosol sprays, solvents, cooking, and heating systems, and cleaning products are the foundation of BTEX in the internal zone, where low aeration can also enhance indoor pollutants. Outdoor sources comprise petrol refining, coal, steel, incineration, and petrochemical processes [36,37]. One can be exposed to this class through inhalation or by skin absorption; overall, BTEX exposure is associated with cancer, depression, respiratory illness, and circulatory system damage [38,39]. As per the World Health Organization (WHO), no safe limits are set for the exposure of BTEX species [40,41]. Benzene a gaseous air pollutant and a known carcinogen categorized under Group-1 as per IARC, is widely used in motor fuels, oils, paints, plastics, detergents, and pharmaceuticals responsible for causing several types of cancer, minor and major diseases [42,43].

Although various studies have been reported for early phases of lockdown in countries such as China, Italy, USA [44,45] and a few studies on metropolitan cities of India such as Delhi and Mumbai [46–48]; while some of the studies have been reported in India measuring the impact of covid-19 lockdown on air quality but for a very short-term period [49]. However, a details analysis of BTEX concentration associated with health risks during the lockdown is lacking. None of the previous studies have investigated the analysis of BTEX species for pandemic periods in North India. The major objectives of the current study were (i) to determine real time BTEX concentrations pre-, during, and post pandemic periods in Punjab, (ii) to quantify temporal variation

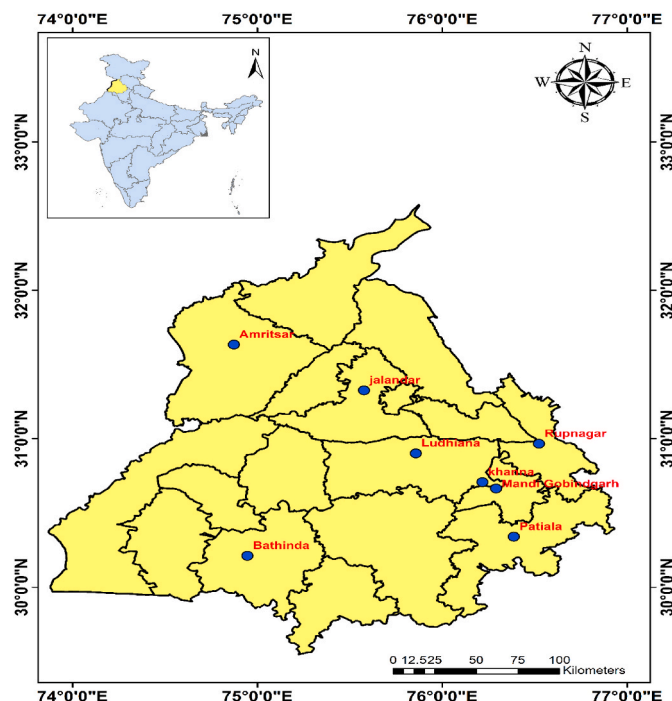


Fig. 1. Study map for different monitoring stations in Punjab.

in TVOC concentrations and (ii) to estimate the health risk assessment of BTEX species in different age groups.

2. Methodology

2.1. Pilot area

Punjab is situated in northern India and extends from latitudes 29.30° N–32.32° N and longitudes 73.55° E to 76.50° E. Bounded by Himachal Pradesh, Arunachal Pradesh, Jammu & Kashmir, Haryana, and some parts of Pakistan. The area of Punjab covers 50,362 square kilometers, which covers 2.29% total area of India. It is composed of 23 districts and 168 statutory cities, and 69 census cities. There are eight cities in the Punjab present on the Central Pollution Control Board (CPCB) site, including Amritsar, Bhatinda, Jalandhar, Khanna, Ludhiana, Mandi Gobindgarh, Patiala, and Rupnagar. Out of these, we have selected 6 following cities with their respective monitoring stations: Amritsar (Golden temple), Jalandhar (Civil lines), Khanna (Kalal majra), Ludhiana (Punjab agricultural university), Mandi Gobindgarh (RIMT University) and Patiala (Model town), due to the availability of data. The study map for different monitoring station has been presented in Fig. 1.

2.2. Data and source

In the present study, secondary data on VOCs (benzene, toluene, ethyl-benzene, and xylene) pollutants were collected from the Central Pollution Control Board (CPCB), Delhi, India on a daily basis. To determine the relative changes (%) in gaseous pollutants for pre-, during, and post-pandemic periods, data from January 1, 2019, to December 31, 2021 was collected from CPCB (<https://app.cpcbcr.com/ccr/#/caaqm-dashboard-all/caaqm-landing>). Data of BTEX were obtained in three phases from January 1, 2019, to December 31, 2019; January 1, 2020, to December 31, 2020; January 1, 2021, to December 31, 2021, to assess their relative and temporal changes in concentrations with respect to the atmospheric quality (<http://app.cpcbcr.com/ccr/#/caaqm-dashboard-all/caaqm-landing>). The data quality assurance and quality control (QA/QC) programs are provided by CPCB through rigorous sampling, analysis and calibration [50]. Due to the

unavailability of BTEX data, Jalandhar is being excluded from the result and discussions for the year 2020. Some of the data were found to be erroneous and incomplete, the partial data were eradicated, and complete data were selected for the results.

2.3. Measures

The time periods were classified into three phases; pre-pandemic, during g pandemic, and post-pandemic period. The time period from January 1, 2019, to December 31, 2019, considered as pre-pandemic phase, the time between January 1, 2020, to December 31, 2020 considered as pandemic phase, and the time between January 1, 2021, to December 31, 2021, consider the ed as the post-pandemic phase.

2.4. Human health assessment

Human health risk assessment (HHRA) is a process to understand the potential impacts of various kinds of pollutants on the health of a person, group of people, or community (<https://www.health.vic.gov.au>). The HHRA is the way to measure the probability of adverse health effects on human beings who are possibly exposed to pollutants in contaminated environmental mediums (<https://www.epa.gov>). The risks to people's health posed by BTEX pollutants were estimated. In the above study, we mainly focused on chronic exposure of VOCs which results in cancer or other health issues [51]. This health risk assessment was carried out referring to the human health assessment manual (part F: supplement to inhalation risk assessment guidelines) issued by USEPA (United States Environmental Protection Agency) [52]. The exposure to the BTEX pollutants via inhalation, dermal contacts, and ingestion was the measured exposure mode to humans. Generally, inhalation is considered the key route of exposure to VOCs for industrial workers. Therefore, the Lifetime cancer risk (LCR) was estimated to assess the carcinogenic risks of VOCs on human health. The main objective of this health risk assessment is to prevent any harmful impacts on human health. According to IARC (international agency for research for cancer), in group 1, Benzene and Ethyl benzene are considered carcinogenic and possibly carcinogenic (group 2B) to humans, while in group 3, toluene and Xylenes are considered non-carcinogenic, which have noxious effects on human health [53]. The regulatory agency uses the HHRA tool to assist in the formulation of policies that protect human health against the adverse effects of air pollution [54]. The four general steps of human health risk assessment are the Identification of hazard by collected data, Dose-response assessment by measuring the level of exposure to pollutants consumed by the human body, Exposure assessment by estimating the duration of exposure to pollutants, and Risk characterization to evaluate the cancer risks in the human population.

2.4.1. Hazard identification

Hazard identification is a method of identifying all kinds of hazards in a particular study area (<https://www.osha.gov>). Generally, this is the first step in the human health assessment, which is used to determine whether exposure to a particular hazard has the potential to cause adverse health effects in humans. It is the way to determine the pollutants in an ambient environment that causes severe health effects in humans, like cancer, birth defects, reproductive effects, death, or other effects (<https://www.epa.gov>). From the collected data, the VOCs were identified, including BTEX, which has a harmful effect on human health.

2.4.2. Dose-response assessment

The term Dose-response assessment is the key factor in the process of hazard characterization. It establishes the relationship between the range of exposure periods and adverse health outcomes in human health. The dose-response assessment aims to describe the amount of toxicity present in the exposures and the adverse health effects on public health [55]. Thus, the dose-response assessment is not calculated in the present study.

2.4.3. Exposure assessment

Exposure assessment (EA) is the process of estimating the duration, frequency, and magnitude of human exposure to a particular hazard in an ambient environment. Generally, it explains sources, routes, and uncertainty in the assessment. (<https://www.epa.gov>). In our study, the major route gets into exposure is that inhalation. We estimated the daily and annual readings for normal and acute exposure periods for different age groups, that is, male (70 years), female (60 years) and children (36 years).

The exposure concentration (EC) ($\mu\text{g}/\text{m}^3$) in the air was calculated using equation [1]:

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

Whereas, EC (mg m^{-3}) = Exposure concentration of the pollutants.

CA (mg m^{-3}) = average concentration of BTEX (benzene, toluene, ethyl benzene, xylene);

ET (h/d^{-1}) = exposure time;

EF (d/y^{-1}) = exposure frequency;

ED (y) = exposure duration;

AT (h) = average exposure time, during the carcinogenic assessment, the average lifetime (per capita life expectancy $\times 365 \text{ d}/\text{y} \times 24 \text{ h}/\text{d}$) was adopted, and during the non-carcinogenic assessment the average period of exposure cycle ($\text{ED} \times 365 \text{ d}/\text{y} \times 24 \text{ h}/\text{d}$) was adopted;

$$CDI = \frac{CA \times IR \times EF \times ED}{BW \times AT} \quad (2)$$

BW $\times$ AT

CDI ($\text{mg kg}^{-1} \text{ day}^{-1}$) = chronic daily intake;

IR ($\text{m}^3 \text{ h}^{-1}$) = inhalation rate;

BW = body weight;

The hazard quotients (HQ) for the inhalation pathway for the non-carcinogenic toluene and xylene compounds were calculated with the following equation:

$$HQ = \frac{EC}{RfC} \quad (3)$$

HQ (mg/m^3) = hazard quotient;

EC (mg/m^3) = exposure concentrations of the pollutants;

RfC = chronic reference concentration of inhalation toxicity;

The risk of potential exposure to cancer for people was calculated by ILCR:

$$ILCR = CDI \times SF \quad (4)$$

ILCR = incremental lifetime cancer risk;

CDI = chronic daily intake;

SF (kg d mg^{-1}) = carcinogenic slope factor.

2.4.4. Risk characterization

Risk characterization is the final phase of human health assessment. According to USEPA risk characterization estimates, when exposure information from the exposure-assessment stage combines with dose-the response assessment, it determines the possibility of having harmful effects of VOCs to nearby individuals and populations (<https://www.ncbi.nlm.nih.gov>).

Non-carcinogenic health risk assessment can be calculated by using an equation (3).

The HQ value should be less than or equal to 1 for the VOCs which have a non-carcinogenic effect on human health. The HQ value is directly proportional to the VOC's toxicity. Higher the value of HQ, i.e.; $HQ > 1$ then there is a potential for the health of humans. The normal range of HQ considered for carcinogens or VOC's risk factor should lie between 10^{-4} to 10^{-3} as to protect human health. The LCR limit considered by WHO under the range between 1×10^{-5} - 1×10^{-6} , whereas the standard limit of LCR set by USEPA is 1×10^{-6} [56]. If the

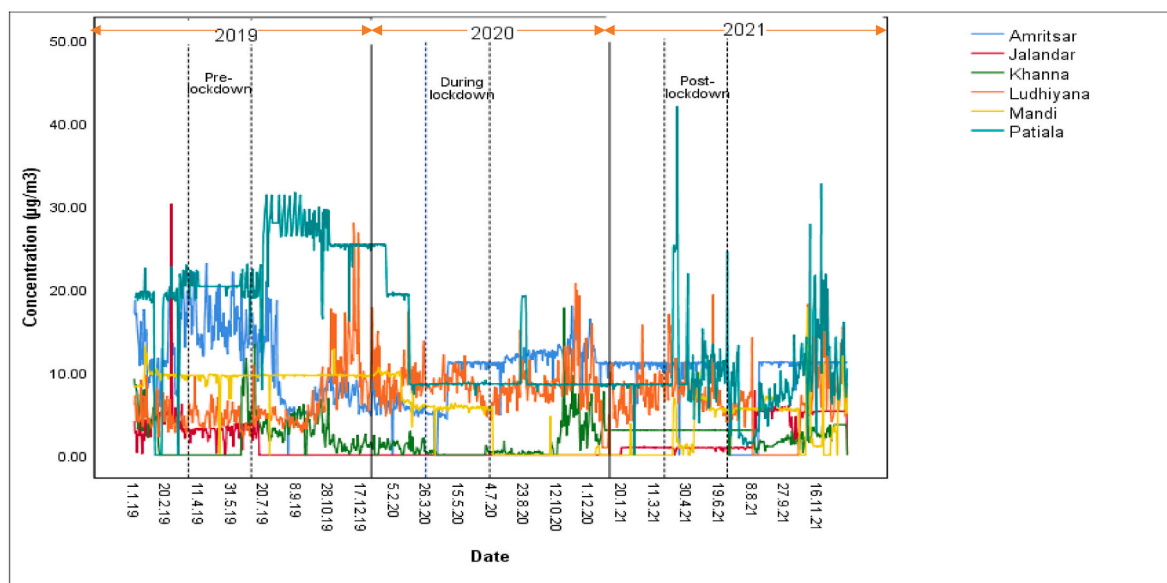


Fig. 2. Time series graph of BTEX for pre-, during, and post-pandemic periods at different stations in Punjab.

calculated value increases, that is 10^{-5} or 10^{-4} , then there are chances of the potential risk of cancer [57].

3. Result & discussions

3.1. Total VOCs levels for before, during and post-pandemic

This study focuses on the determination of considerable changes with respect to air pollutants at selected cities in Punjab, India. The concentrations of total Volatile Organic Compounds (TVOCs) are principally focused on the period before, during, and post-pandemic. The average TVOCs concentration for all the monitoring stations was found to be 8.89 ± 1.80 , 5.59 ± 1.71 , and 5.57 ± 1.43 $\mu\text{g}/\text{m}^3$ for before, during, and post-pandemic, respectively. As a result, a gradual decline is seen in the TVOCs concentration for consecutive periods because of the pandemic and post-pandemic in India. The major factors responsible for the consequential decline in the TVOCs concentration during the pandemic were total and partial restrictions on industrial activities, transportation, and other commercial activities. The mean TVOCs concentrations for all monitoring stations varied between 1.82 ± 2.40 $\mu\text{g}/\text{m}^3$ (JL) to 22.34 ± 5.83 $\mu\text{g}/\text{m}^3$ (PT), 1.21 ± 1.96 $\mu\text{g}/\text{m}^3$ (KH) to 10.85 ± 5.07 $\mu\text{g}/\text{m}^3$ (PT) and 2.46 ± 2.17 $\mu\text{g}/\text{m}^3$ (JL) to 9.50 ± 3.70 $\mu\text{g}/\text{m}^3$ (AM) for before, during and post-pandemic respectively. The trend of average TVOCs concentration was observed as PT (Patiala) > AM (Amritsar) > MG (Mandi Gobindgarh) > LU (Ludhiana) > KH (Khanna) > JL (Jalandhar), PT > AM > LU > MG > KH and AM > PT > LU > MG > KH > JL for before, during and post-pandemic respectively.

The maximum TVOCs concentrations were found to be 31.68 $\mu\text{g}/\text{m}^3$ (PT), 25.44 $\mu\text{g}/\text{m}^3$ (PT), and 42.09 $\mu\text{g}/\text{m}^3$ (PT) before, during, and post-pandemic, respectively. The maximum TVOCs concentrations for all monitoring stations varied from 13.2 $\mu\text{g}/\text{m}^3$ (MG) to 31.68 $\mu\text{g}/\text{m}^3$ (PT), 10.55 $\mu\text{g}/\text{m}^3$ (MG) to 25.44 $\mu\text{g}/\text{m}^3$ (PT), and 3.67 $\mu\text{g}/\text{m}^3$ (KH) to 42.09 $\mu\text{g}/\text{m}^3$ (PT) for the period of before, during and post-pandemic respectively.

An overall decline by -43% with an average of 5.22 ± 1.30 $\mu\text{g}/\text{m}^3$ for all the monitoring stations was observed in the TVOC concentration during the lockdown period, as compared to the previous years. After the lockdown, an increase in the concentration of TVOC by 16% was observed in unlock; this may be due to the re-opening of commercial places, various industries, and transportation as they are responsible for emissions of BTEX [35,39]. The highest TVOC concentration was reported at Amritsar, which may be because of the biomass burning and

pharmaceutical industries, whereas the lowest value was observed at Khanna during the period of lockdown.

3.2. identification of VOC characteristic pollutants before the pandemic

The average VOCs calculated for different monitoring stations were 3.494 , 4.26 , 4.43 , 5.835 , and 5.56 $\mu\text{g}/\text{m}^3$ for Benzene, Toluene, Ethyl-Benzene, MP-Xylene, and Xylene, respectively, before the pandemic. The average value for Benzene varied between 2.42 $\mu\text{g}/\text{m}^3$ (PT) and 5.26 $\mu\text{g}/\text{m}^3$ (MG); for Toluene, the value was between 2.11 $\mu\text{g}/\text{m}^3$ (AM) and 7.18 $\mu\text{g}/\text{m}^3$ (PT) whereas the mean value for Ethyl-Benzene and MP-Xylene was observed from 1.89 $\mu\text{g}/\text{m}^3$ (JL) to 7.15 $\mu\text{g}/\text{m}^3$ (PT) and 1.61 $\mu\text{g}/\text{m}^3$ (JL) to 10.06 $\mu\text{g}/\text{m}^3$ (PT), respectively, while the value for Xylene was observed only in Amritsar i.e., 5.56 $\mu\text{g}/\text{m}^3$. The average trend for Benzene was found to be $\text{MG} > \text{AM} > \text{KH} > \text{LU} > \text{PT}$, and for Toluene, the trend found was $\text{PT} > \text{LU} > \text{AM}$, the mean trend for Ethyl-benzene and MP-Xylene was found to be $\text{PT} > \text{MG} > \text{JL}$ and $\text{PT} > \text{JL}$, respectively; before the pandemic. The maximum values varied from 6.28 $\mu\text{g}/\text{m}^3$ (LU) to 13.42 $\mu\text{g}/\text{m}^3$ (KH) for Benzene, 7.46 $\mu\text{g}/\text{m}^3$ (PT) to 24.58 $\mu\text{g}/\text{m}^3$ (LU) for Toluene, 7.5 $\mu\text{g}/\text{m}^3$ (MG) to 27.38 $\mu\text{g}/\text{m}^3$ (JL) for Ethyl-benzene and 3.46 $\mu\text{g}/\text{m}^3$ (JL) to 10.53 $\mu\text{g}/\text{m}^3$ (PT) for MP-Xylene while for Xylene the value was reported only in Amritsar i.e., 15.45 $\mu\text{g}/\text{m}^3$ (Fig. 1).

During the lockdown, the mean value for BTEX was found to be 4.36 , 1.93 , 22.65 , 5.72 and 9.3 $\mu\text{g}/\text{m}^3$ for Benzene, Toluene, Ethyl-Benzene, MP-Xylene and Xylene, respectively at different monitoring stations. The average trend for Benzene was observed as $\text{KH} > \text{MG} > \text{AM} > \text{LU} > \text{PT}$ and for Toluene, the trend was $\text{AM} > \text{LU}$, whereas a similar trend was reported for both Ethyl-Benzene and Mp-Xylene before the pandemic. The highest BTEX level was observed at Patiala, which is an area defined as the buffer zone between industrial sectors and residential areas. The prime sources responsible for BTEX contribution were vehicle exhaust, industries, and biomass burning [58–61]. According to the study conducted in Algiers city, BTEX contribution was higher along the urban areas or roadside compared with the rural sites, which may be directly linked to the distance of the source emission [62]. Other important sources contributing to the BTEX emissions were paints, adhesives, heating systems, printing processes, furniture, and carpeting [63,64].

3.3. Identification of VOC characteristic pollutants during the pandemic

The average BTEX values calculated during the pandemic were

1.948, 3.73, 3.2, 3.0, and 6.57 $\mu\text{g}/\text{m}^3$ for Benzene, Toluene, Ethyl-Benzene, MP-Xylen, and Xylene, respectively. The average concentration for Benzene varied from 1.24 $\mu\text{g}/\text{m}^3$ (KH) to 3.34 $\mu\text{g}/\text{m}^3$ (MG); for Toluene, the concentration was from 1.75 $\mu\text{g}/\text{m}^3$ (AM) to 6.86 $\mu\text{g}/\text{m}^3$ (LU), Ethyl-Benzene value varied between 3.12 $\mu\text{g}/\text{m}^3$ (PT) and 3.28 $\mu\text{g}/\text{m}^3$ (MG), whereas MP-Xylene's mean concentration was reported in Patiala only i.e., 3.0 $\mu\text{g}/\text{m}^3$ and for Xylene the value was observed only in Amritsar which was 6.57 $\mu\text{g}/\text{m}^3$. The mean trend for Benzene concentrations was observed as $\text{MG} > \text{PT} > \text{AM} > \text{LU} > \text{KH}$, the average trend for Toluene was $\text{LU} > \text{PT} > \text{AM}$, whereas for Ethyl benzene, the trend was found to be $\text{MG} > \text{PT}$ during the pandemic. The maximum concentration for Benzene varied from 2.78 $\mu\text{g}/\text{m}^3$ (LU) to 17.77 $\mu\text{g}/\text{m}^3$ (KH) and for Toluene, the values were from 7.4 $\mu\text{g}/\text{m}^3$ (PT) to 17.93 $\mu\text{g}/\text{m}^3$ (LU), the maximum value for Ethyl Benzene varied between 4.59 $\mu\text{g}/\text{m}^3$ (MG) and 7.62 $\mu\text{g}/\text{m}^3$ (PT), the concentration for MP-Xylene was observed only in Patiala which was 10.38 $\mu\text{g}/\text{m}^3$ and Xylene's value was reported as 8.82 $\mu\text{g}/\text{m}^3$ in Amritsar only, during the period of the pandemic (Fig. 2).

The mean value for BTEX found at the time of lockdown was 1.46, 3.42, 3.06, 1.43, and 6.89 $\mu\text{g}/\text{m}^3$ for Benzene, Toluene, Ethyl-Benzene, MP-Xylene, and Xylene, respectively. The average trend for Toluene during the lockdown was found to be similar to of the pandemic, while others, including Benzene, Ethyl-Benzene, MP-Xylene and Xylene were found to be dissimilar. The maximum values for benzene varied from 1.18 $\mu\text{g}/\text{m}^3$ (KH) to 3.38 $\mu\text{g}/\text{m}^3$ (MG), for Toluene the values were from 1.97 $\mu\text{g}/\text{m}^3$ (AM) to 10.59 $\mu\text{g}/\text{m}^3$ (LU) and for Ethyl-Benzene the values were between 3.28 $\mu\text{g}/\text{m}^3$ (MG) and 3.30 $\mu\text{g}/\text{m}^3$ (PT) during the lockdown. The highest value of BTEX was observed at Amritsar, while the lowest was in Khanna. The high level at Amritsar during the lockdown may be because of the stubble or biomass burning cases, rubber and pharmaceutical industries, and limited transportation activities of essential duty and supply vehicles [65–67].

The BTEX values were observed to be lower during the lockdown than in the corresponding period before the pandemic for all monitoring stations. The key factors responsible for the decline in BTEX emissions during the lockdown were found to be restrictions on vehicular emissions, construction activities, industrial release, and commercial activities, including marketplaces.

3.4. Identification of VOC characteristic pollutants during post-pandemic

The mean BTEX concentration calculated for different monitoring stations were 1.978, 2.88, 2.62, 1.79, and 7.47 $\mu\text{g}/\text{m}^3$ for Benzene, Toluene, Ethyl-Benzene, MP-Xylene and Xylene, respectively, during the post-pandemic period. The mean Benzene values were observed between 0.87 $\mu\text{g}/\text{m}^3$ (LU) and 2.67 $\mu\text{g}/\text{m}^3$ (MG), whereas for Toluene, the values were between 0.94 $\mu\text{g}/\text{m}^3$ (AM) and 5.27 $\mu\text{g}/\text{m}^3$ (LU), the average concentration for Ethyl-Benzene varied from 2.44 $\mu\text{g}/\text{m}^3$ (PT) to 2.88 $\mu\text{g}/\text{m}^3$ (JL), for MP-Xylene the value was 1.79 $\mu\text{g}/\text{m}^3$ in Patiala and Xylene's concentration was reported only in Amritsar which was 7.47 $\mu\text{g}/\text{m}^3$. The average trend for Benzene was found to be $\text{MG} > \text{KH} > \text{PT} > \text{AM} > \text{LU}$, and for Toluene, the trend observed was $\text{LU} > \text{PT} > \text{AM}$, while the Ethyl-Benzene trend was $\text{JL} > \text{MG} > \text{PT}$, for the duration of post-pandemic. The maximum values for Benzene varied from 1.37 $\mu\text{g}/\text{m}^3$ (AM) to 15.07 $\mu\text{g}/\text{m}^3$ (MG). The values for Toluene were between 1.18 $\mu\text{g}/\text{m}^3$ (AM) to 18.26 $\mu\text{g}/\text{m}^3$ (LU), Ethyl-Benzene maximum concentration varied from 7.43 $\mu\text{g}/\text{m}^3$ (MG) to 107.78 $\mu\text{g}/\text{m}^3$ (JL) and for MP-Xylene the maximum value observed in Patiala only, which was 14.97 $\mu\text{g}/\text{m}^3$. In contrast, for Xylene the value was reported only in Amritsar i.e., 8.81 $\mu\text{g}/\text{m}^3$ during the post-pandemic.

The average BTEX value observed during the lockdown were 2.32, 3.15, 2.19, 3.02, and 8.07 $\mu\text{g}/\text{m}^3$ for Benzene, Toluene, Ethyl-Benzene, MP-Xylene, and Xylene, respectively, at different monitoring stations. The average BTEX value varied from 1.2 $\mu\text{g}/\text{m}^3$ (AM) to 3.03 $\mu\text{g}/\text{m}^3$ (PT) for Benzene, 1.02 $\mu\text{g}/\text{m}^3$ (AM) to 6.75 $\mu\text{g}/\text{m}^3$ (LU) for Toluene while for Ethyl-Benzene the values were between 0.83 $\mu\text{g}/\text{m}^3$ (JL) and 3.25 $\mu\text{g}/\text{m}^3$

(PT). The highest BTEX value was reported at Patiala, which may be due to the industrial releases, vehicular emissions and emissions from the airport [68,69].

3.5. Comparative analysis for before, during and post-pandemic

The average levels for BTEX concentrations at all monitoring stations for benzene varied from 2.42 to 5.26 $\mu\text{g}/\text{m}^3$, 1.24–3.34 $\mu\text{g}/\text{m}^3$ and 0.87–2.67 $\mu\text{g}/\text{m}^3$ for the period before, during and post-pandemic, respectively. The VOCs level gradually decreased by –50% for benzene during the lockdown period compared to the corresponding period in 2019, and –8% decreased for benzene during the lockdown period compared to the post-lockdown period, whereas in Toluene VOC level increased in pre lockdown period, and decreased by –15% in lockdown period compared to the post lockdown period. The maximum changes were observed in Patiala during the lockdown period and in Amritsar during post lockdown period for benzene and for Toluene; maximum changes were observed in Ludhiana during the post-lockdown period. The average TVOCs concentration declined by –43% during the lockdown period compared to the corresponding period in 2019 and slightly increased during post lockdown period because of resuming of all manufacturing industries and construction work and also due to vehicular emissions and decreased because of shutting down of industries and manufacturing companies.

The VOCs level gradually decreased by –44% for benzene during the pandemic period compared to the pre-pandemic period and slightly varied in the post-pandemic period, whereas in Toluene, VOCs level decreased by –12% during the pandemic period compared to 2019 and also decreased by –23% during post-pandemic period. The average TVOCs concentration declined by –37% during the pandemic period compared to the corresponding period of 2019.

The high exposure risk in public places may contribute to be increased risk of cancer in the general population [63]. Mainly these VOCs are found in natural form i.e., crude oil, gasoline, diesel and also found in industries, consumer products, and synthetic materials, including plastics, nylon industries, and leather industries [70]. A study conducted in the selected urban area of Malaysia reported a significant reduction in BTEX concentrations (38%–46%) during the lockdown period [71]. Based on a previous study conducted in Maharashtra, India, the VOC levels decreased drastically by 52%, 89%, 80%, and 97% for benzene, toluene, ethylbenzene, and m-xylene, respectively, during the lockdown period compared to the previous year. In the present study, the T/B ratio was found to be lower in the lockdown period as compared to the pre-lockdown period [55]. A similar study conducted in Delhi, India, recorded that the mean TVOC levels at all monitoring stations declined from 9 to 61% during the pandemic period as compared to the pre-pandemic period [9]. Cai et al. (2022) reported higher concentration values for BTEX species during the lockdown period as compared to before the lockdown period. This variation of mean BTEX concentration was suggested to be strongly dependent on meteorological conditions and photochemical activity [72].

3.6. Source identification of BTEX

Toluene and benzene (T/B) ratio are widely used to identify emission sources by vehicle exhaust (traffic), gas stations, industrial facilities, and evaporative emissions of solvents. A T/B ratio from 2 to 8 indicates vehicle exhaust. T/B ratio <2 represent other sources such as: gas station and evaporative emissions of solvent. In the morning T/B ratio was recorded from 2.78 to 5.06 and in the evening, it was between 1.81 and 2.42. Traffic-related sources contributed more to BTEX levels in the morning than in the evening [73].

At the chemical industrial park (CMP) the value of T/B is reported 4.31 ± 6.48 , which is contributed by large-scale industries of plastics, synthetic resins, rubbers, coatings, and chemicals. In petrochemical industries, the T/B ratio obtained was 1.84 ± 3.34 , where the main

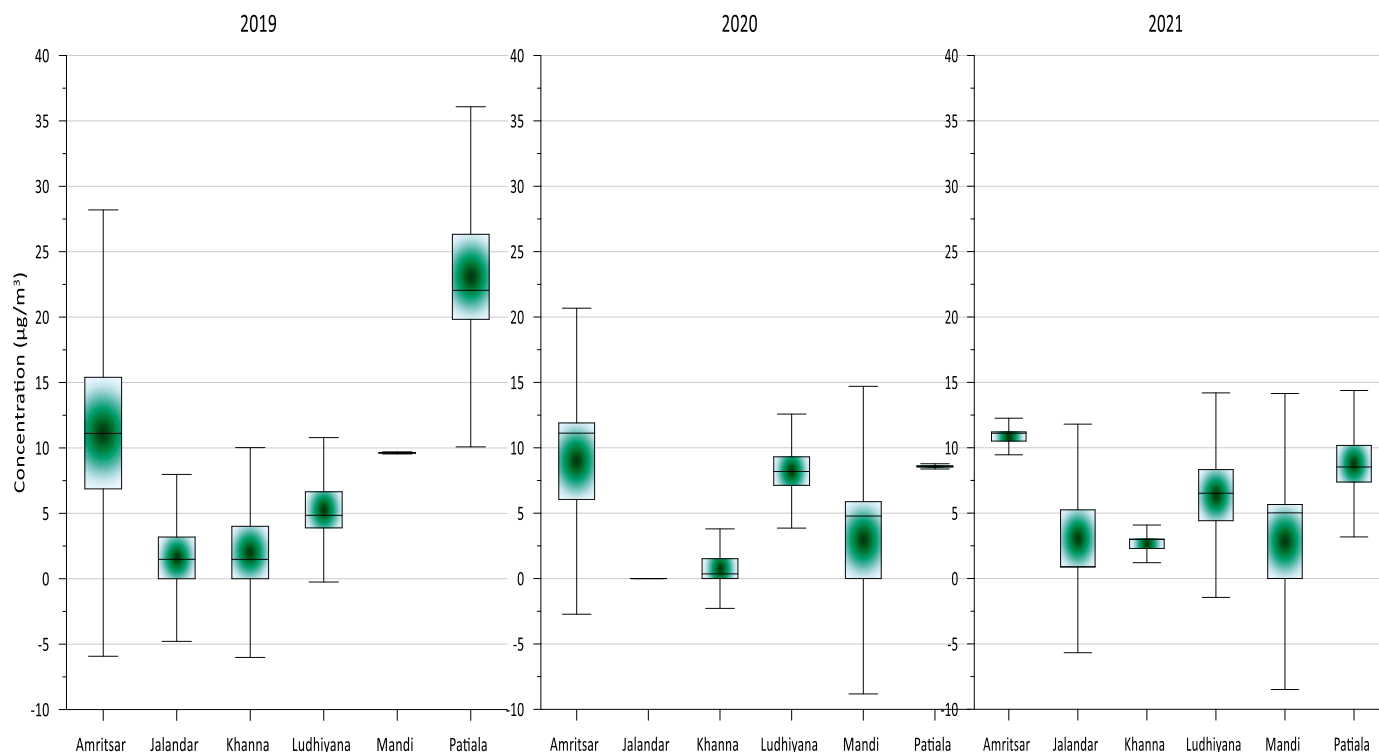


Fig. 3. Box plot of BTEX for pre-, during, and post-pandemic periods at different stations in Punjab.

petrochemical products are benzene, gasoline, and diesel oil [74]. A less than 1 T/B ratio shows non-traffic sources such as coal burning, biomass, and biofuel, while the value of T/B ratio is more than 1, it indicates the major contribution of traffic-related sources. When vehicle emissions act as a major BTEX source which is commonly seen, the T/B ratio was reported low [66]. Before the pandemic, the toluene and benzene (T/B) ratio was calculated for the different monitoring stations and were observed, $0.57 \mu\text{g}/\text{m}^3$ for Amritsar, $1.38 \mu\text{g}/\text{m}^3$ for Ludhiana and $2.97 \mu\text{g}/\text{m}^3$ for Patiala, which indicates non-traffic related sources such as biomass, coal burning and biofuel in Amritsar and Ludhiana.

A higher T/B ratio was found in Patiala ($2.97 \mu\text{g}/\text{m}^3$) before the pandemic, which may indicate vehicle (traffic) emission sources and evaporative emission of solvent [73]. During the pandemic $1.24 \mu\text{g}/\text{m}^3$, T/B ratio observed in Patiala which is found to be low as compared to before the pandemic, which indicates vehicular exhaust or traffic sources, while the T/B ratio was reported high during the pandemic at Ludhiana, which was $4.56 \mu\text{g}/\text{m}^3$ which shows evaporation sources from vehicles, gas station, industrial facilities, and petrochemical industries [66]. During post-pandemic, the T/B ratio is measured $0.8 \mu\text{g}/\text{m}^3$ in Amritsar and $0.93 \mu\text{g}/\text{m}^3$ in Patiala.

Before the lockdown period, the T/B ratio was reported at Amritsar which was $0.46 \mu\text{g}/\text{m}^3$ and $0.64 \mu\text{g}/\text{m}^3$ in Ludhiana, which indicates a non-traffic-related source [66]. The T/B ratio found in Amritsar was $0.92 \mu\text{g}/\text{m}^3$ and $4.18 \mu\text{g}/\text{m}^3$ for Ludhiana during the lockdown period. As compared to 2019, the T/B ratio was reported to be high during the lockdown. When the T/B ratio is found to be < 1 , it denotes non-traffic related sources, while if the value reported > 2 , then it may be attributed to vehicle emission, chemical industries such as synthetic resins, chemical auxiliaries, plastic, rubbers, polyesters, coatings, and polyurethanes [66,75], during the post-lockdown period, T/B ratio was found to be $0.85 \mu\text{g}/\text{m}^3$ at Amritsar and $0.55 \mu\text{g}/\text{m}^3$ at Patiala.

3.7. Health risk assessment

In the present study, we calculated the daily exposure, yearly exposure, lifetime exposure, hazard quotient, chronic daily intake, and

lifetime cancer risk in health risk assessment for pre-, during, and post-pandemic periods. Generally, we made focused on the lifetime cancer risk (LCR) to assess the carcinogenic and non-carcinogenic risks of VOCs [76]. According to Alsobou et al. (2020), Benzene and Eth-benzene cause carcinogenic effects, while Toluene and MP-Xylene cause non-carcinogenic effects on human health [36]. In the epidemiologic investigation, it is found that the ambient emissions of VOCs cause different types of cancer i.e., cancers of the brain, nervous system, endocrine system, and skin, and the possible non-cancer risk of VOCs cause major health effects including allergic, sensory, irritation effect, respiratory effect and chronic damage to liver and kidney [75,77,78]. Among the considered parameters (Benzene, Toluene, Eth-Benzene, MP-Xylene).

Benzene is a strong human carcinogen (Group-A) that causes health risks i.e., headache, nausea, aplastic anemia, leukemia, and blood bone marrow disease. Due to the hazardous health risks posed by ambient emissions of benzene, several agencies USEPA (US Environmental protection agency), WHO (World Health Organization), EEA (European Environmental Agency), Ministry of Environment and Forest (MOEF), India have set air quality standards for benzene (H.Hakim et al., 2019). Various organizations, such as the WHO and the USEPA have established guideline values for BTEX compounds and recommended the limit of LCR (USEPA, 2009). Cancer risks are categorized on the basis of LCR values, if $\text{LCR} > 1.0 \times 10^{-4}$ then it is considered as “definite risks”; $1.0 \times 10^{-4} > \text{LCR} > 1.0 \times 10^{-5}$ as “probable risk,” and $1.0 \times 10^{-5} > \text{LCR} > 1.0 \times 10^{-6}$ as “possible risk” (El-Hashemy et al., 2018).

In the present study, LCR values were calculated at all monitoring stations before, during, and post-pandemic for Benzene, Toluene, Eth Benzene, and MP-Xylene. In Males, The trend of LCR values was observed in benzene as $\text{MG (Mandi Gobindgarh)} > \text{AM} > \text{KH} > \text{LH} > \text{PT}$; $\text{MG} > \text{PT} > \text{AM} > \text{LH} > \text{KH}$; $\text{MG} > \text{KH} > \text{PT} > \text{AM}$ for before, during, and post-pandemic period. In Females, the trend of LCR values was found in benzene as $\text{MG} > \text{AM} > \text{KH} > \text{LH} > \text{PT}$; $\text{MG} > \text{PT} > \text{AM} > \text{LH} > \text{KH}$; $\text{MG} > \text{KH} > \text{PT} > \text{AM}$ for before, during, and post lockdown, whereas in Children, observed as $\text{MG} > \text{AM} > \text{KH} > \text{LH} > \text{PT}$; $\text{MG} > \text{PT} > \text{AM} > \text{LH} > \text{KH}$; $\text{MG} > \text{KH} > \text{PT} > \text{AM}$ for before, during and post-pandemic

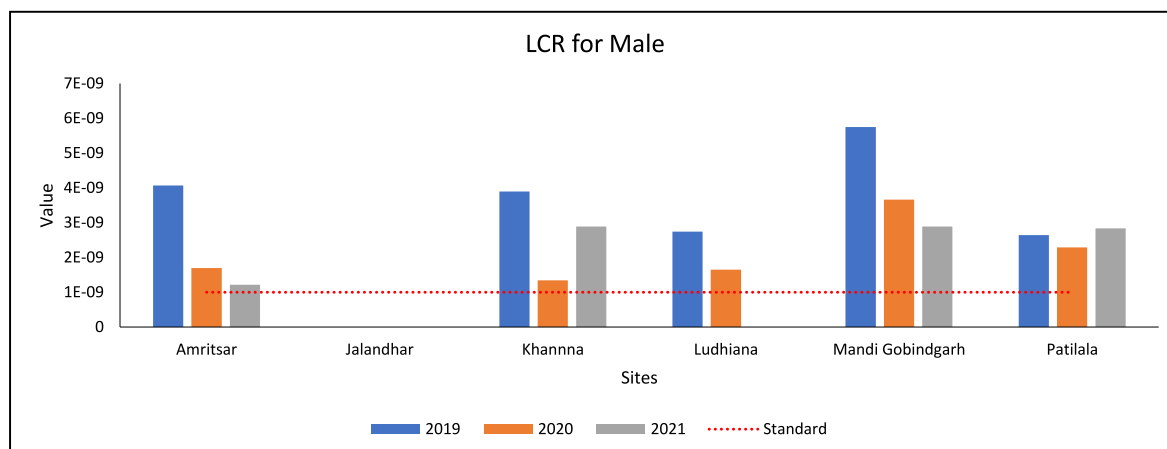


Fig. 4. Male LCR value for different monitoring stations of Punjab for the year 2019–2021.

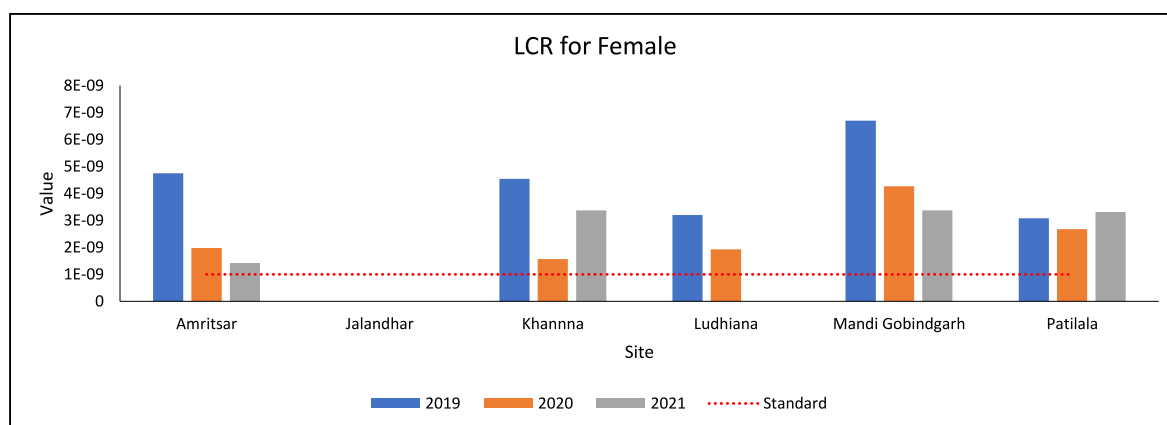


Fig. 5. Female LCR value for different monitoring stations of Punjab for the year 2019–2021.

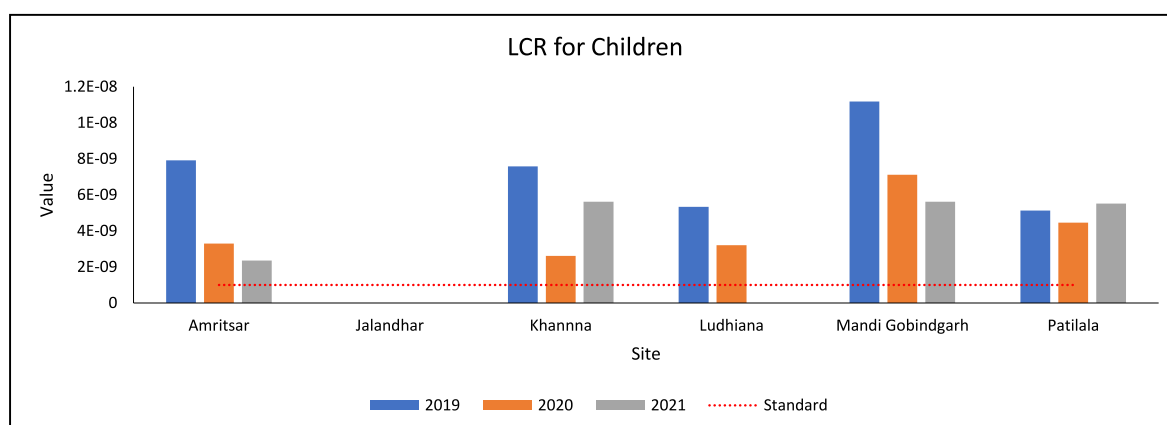


Fig. 6. Children's LCR value for different monitoring stations of Punjab for the year 2019–2021.

period. The LCR value for males, females, and children has been presented in Figs. 3–5, respectively. LCR values observed for toluene for Males were observed as PT > LH > AM; LH > PT > AM; LH > PT > AM before, during, and post-pandemic period. In females trend of LCR values was observed as PT > LH > AM; LH > PT > AM; LH > PT > AM before, during, and post-pandemic period. In Children, the LCR trend observed was PT > LH > AM; LH > PT > AM; LH > AM > PT for before, during, and post-pandemic, respectively (Table 1). The highest LCR values at all monitoring stations in males were calculated at Mandi

Gobindgarh for the before-pandemic period, and the lowest was at Amritsar for the Post Pandemic period, whereas the highest LCR values before the pandemic were recorded at Mandi Gobindgarh, and the lowest values were at Amritsar for post lockdown period among in all monitoring stations (see Fig. 6).

4. Conclusion

In conclusion, an examination of selected VOCs in the Punjab state

Table 1
LCR values for benzene and toluene for pre-, during, and post-pandemic.

	Benzene			Toluene		
	Males					
	pre	during	post	pre	during	post
Amritsar (AM)	4.07E-06	1.7E-06	1.21E-06	2.31E-06	1.92E-06	1.03E-06
Khananna (KH)	3.9E-06	1.34E-06	2.89E-06	0	0	0
Ludhiana (LH)	2.74E-06	1.65E-06	0	3.79E-06	7.52E-06	5.75E-06
Mandi Gobindgarh (MG)	5.75E-06	3.66E-06	2.89E-06	0	0	0
Patilala (PT)	2.64E-06	2.29E-06	2.84E-06	7.83E-06	2.84E-06	2.64E-06
Females						
Amritsar (AM)	4.75E-06	1.98E-06	1.42E-06	2.7E-06	2.24E-06	1.2E-06
Khananna (KH)	4.55E-06	1.57E-06	3.37E-06	0	0	0
Ludhiana (LH)	3.2E-06	1.92E-06	0	4.43E-06	8.78E-06	6.71E-06
Mandi Gobindgarh (MG)	6.7E-06	4.27E-06	3.37E-06	0	0	0
Patilala (PT)	3.08E-06	2.67E-06	3.31E-06	9.14E-06	3.31E-06	3.08E-06
Children						
Amritsar (AM)	7.91E-06	3.3E-06	2.36E-06	4.49E-06	3.73E-06	2E-06
Khananna (KH)	7.58E-06	2.61E-06	5.62E-06	0	0	0
Ludhiana (LH)	5.34E-06	3.21E-06	0	7.38E-06	1.46E-05	1.12E-05
Mandi Gobindgarh (MG)	1.12E-05	7.12E-06	5.62E-06	0	0	0
Patilala (PT)	5.13E-06	4.45E-06	5.51E-06	1.52E-05	5.51E-06	5.14E-06

was carried out for the pre-, during, and post-pandemic periods, along with a comparison with data from lockdown periods. The mean TVOCs concentration for all the monitoring stations was found to be 8.89 ± 1.80 , 5.59 ± 1.71 , and $5.57 \pm 1.43 \mu\text{g}/\text{m}^3$ for before, during, and post-pandemic, respectively. The major factors responsible for the consequential decline in the TVOCs concentration during the pandemic were total and partial restrictions on industrial activities, transportation, and other commercial activities. The level of TVOCs declined by $\sim 43\%$ for all monitoring stations during the lockdown period compared to the previous years. However, after the lockdown, an increase in the concentration of TVOC by 16% was observed in unlock; this may be due to the re-opening of commercial places, various industries, and transportation, as they are responsible for emissions of BTEX. The VOCs level gradually decreased by $\sim 50\%$ for benzene and $\sim 15\%$ for toluene during the lockdown period compared to the corresponding period in 2019, respectively. In the current study, the level of TVOC was observed to be higher for the pre-pandemic period as corresponding to during and post-pandemic periods. A Higher T/B ratio was found in Patiala ($2.97 \mu\text{g}/\text{m}^3$) before the pandemic, which may indicate vehicle (traffic) emission sources and evaporative emission of solvent. The higher level of TVOCs was associated with mobile emission sources and industrial activities. At the chemical industrial park (CMP) the value of T/B is reported 4.31 ± 6.48 , which is contributed by large-scale industries of plastics, synthetic resins, rubbers, coatings, and chemicals. In the present study, LCR values were calculated at all monitoring stations before, during, and post-pandemic for Benzene, Toluene, Eth Benzene, and MP-Xylene. The LCR values for benzene were found to be higher in children than in males and females, which indicated the possible risk. The LCR values for benzene were found to exceed the prescribed value by CPCB for

children. However, the substantial reduction in the VOCs due to the COVID-19 pandemic has been considered experiment for developing better air quality management programs across polluted and industrial areas.

Ethical approval

Not applicable.

Consent to participate

All authors have agreed to authorship, read and approved the manuscript.

Consent for publication

All the authors have permitted publication.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

Data availability

Data will be made available on request.

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