Pollution 2022, 8(3): 978-994
DOI: 10.22059/POLL.2022.337344.1328

RESEARCH PAPER

A Comparative Study on Air Quality Measurement and Spatial Distribution of Pollutants in Pars Special Economic Energy Zone (PSEEZ)

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Received: 04.01.2022, Revised: 12.04.2022, Accepted: 01.05.2022

Abstract

Pars special economic energy zone (PSEEZ) in Iran is the second largest energy zone in the world with more than 60,000 operational and non-operational personnel. Considering the nature of the activities being done in PSEEZ, it is rational to expect that a wide range of hazardous materials be present in the air composition of this area. It is shown in this research that Benzene-Toluene-Ethylbenzene-Xylene (BTEX) are the most challenging in PSEEZ and benzene concentration violates the standards in all sampling points. The study area is divided into three subzones of gas refineries, petrochemical complexes and non-operational areas. In the gas refineries, benzene concentration is recorded to be 480 times higher than the standard for exposure limit. The concentration of benzene in petrochemical complexes is also about 160 times higher than the standard limit. Considering the vicinity of the petrochemical complexes the cumulative impacts of BTEX will also worsen the situation regarding BTEX cancer risk. In non-operational areas, benzene concentration reaches 40 times higher than the standard limit which is a serious health challenge. Comparing the data of BTEX distribution with AQI proves that AQI solely is not an appropriate index for assessing the air quality in PSEEZ and defining local indices for air quality assessment with taking hazardous chemicals such as BTEX into account. Moreover, some other pollutants such as heavy metals and H2S are detected in the air quality in significant amounts which raise the need to a reconsideration in location of unprotected non-operational personnel.

Keywords: BTEX; Active sampling; AQI; Heavy metals; PSEEZ.

INTRODUCTION

Air pollution is one of the deadliest environmental challenges of the 21st century which is estimated to kill about seven million people every year (WHO, 2021). About 60% of these deaths are caused by ambient air pollution and due to fatal disorders such as cardiovascular problems, respiratory diseases and a wide range of cancers (Landrigan, 2017; Sima et al., 2021). Industries, vehicles, power generation, agricultural activities, etc. are the main sources of ambient air pollutant (Brauer et al., 2016). Rapid industrialization, global population growth and severe changes in consumption patterns of the societies during last two decades have noticeably intensified the air pollution challenge all over the world, especially in more populated and industrialized areas (Cepeda et al., 2017; Li et al., 2022). Therefore, a great share of the scientific efforts have been dedicated to find an optimum procedure for determination of air quality and reassuring its health. One of the most important achievements in this field was introduction of air quality

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index (AQI) which is a hybrid index for measuring the air quality and its health for human (Li et al., 2018; Tsai & Lin, 2021). AQI considers O_3, particulate matter (PM), CO, SO_2 and NO_2 as the main pollutants in the ambient air that is affecting human health (Heidarinejad et al., 2018). However, AQI seems to be insufficient for evaluation of the air quality of industrialized areas such as industrial parks or energy zones in which a wide range of hazardous chemicals such as volatile organic carbon (VOC) and aromatics are being emitted to the atmosphere (Han et al., 2019; Na et al., 2001). Hence, additional measurement (e.g. VOC, aromatics, heavy metals, etc.) are required in industrial areas and energy zones in order to reassure the safety of inhalation or the personnel of these sites and the inhabitants who live in the vicinity (Wu et al., 2015).

Among different types of industrial areas, the concerns about air pollution are more serious in the energy zones (Ziyarati et al., 2019). Energy zones are vast areas in the vicinity of hydrocarbon natural resources (oil or gas fields) which normally include numerous operational units for extraction, refining and reservation of oil and gas and production of fuels and downstream hydrocarbon-based products (petrochemical products) (Rostami et al., 2019). Due to the nature of the operations and the materials involved in the energy zones, the concentrations of different pollutants such as VOCs, especially benzene-toluene-ethylbenzene-xylene which are known as BTEX and sulfur derivatives such as SO_x and H_2S are significantly high and violates the environmental and public health standards (Ghazizade et al., 2020; Sarkheil et al., 2018). Therefore, conducting a comprehensive measurement and monitoring program which comprises all the hazardous pollutants as well as the AQI is crucial in these zones. Such a comprehensive monitoring not only facilitates better management of the human resource in the operational area but also provides a fundamental database for further studies on developing more inclusive and accurate indices for air quality assessment besides AQI in energy zones and other types of industrial area.

Presenting the most appropriate index and applying a comprehensive method of air pollution measurement for assessment of the air quality in industrial areas has been focused in numerous studies. Rai et al. (2013) focused on air pollution tolerance index (APTI) in the industrial site of Rourkela in India. APTI is mainly focused on the impacts of the air pollution on the plants and is defined by four physiochemical and biochemical responses from the plants leaves which are relative water content, ascorbic acid concentration, total chlorophyll and pH of the extract (Rai et al., 2013). Although this feedback response is an appropriate methodology for assessing the environmental impacts of the air pollution on the plant life of the area, it cannot be a managerial method for large industrial zones with numerous personnel. However, the concept of feedback response analysis can be useful for health risk assessment among the personnel and inhabitants of the industrial areas. Therefore, direct methods of source identification are more preferable than feedback analyses in the large industrial areas such as energy zones, since they provide the possibility of better management on air pollutants from their sources (Huang et al., 2015; Huang et al., 2019). Nandan et al. (2017) studied the impacts of 13 different industries on the air quality in Uttarakhand industrial area in India. They used four air pollutants of respirable particulate matter, suspended particulate matter, SO_2 and NO_2 as the major parameters in their study which are the principal compartments of AQI (Nandan et al., 2017). However, for more polluted areas such as energy zones, it is obvious that AQI is not sufficient solely and hazardous chemicals such as BTEX and VOCs must be considered as well. Mirrezaei and Orkomi (2020) combined the feedback response analysis and source identification approach in order to define the contribution of flare gases to the cumulative BTEX concentration in the atmosphere of Asalouyeh energy area in Iran and its risk for public health (Mirrezaei & Orkomi, 2020). Their study is a good sample of hazardous chemicals analysis in the air of a large energy zone, however, the lack of other parameters such as VOCs and AQI in this research decreases the accuracy of the obtained model for decision making. The study conducted by Kermani et al. (2021) fills the gaps existed in previous study to some extent by including polycyclic aromatic hydrocarbons

(PAHs) and BTEX in their model. They provided a comprehensive spatial and time-based model for assessing the air quality of Tehran, Iran and evaluating the inhalation-based risk of PAHs and BTEX in Tehran (Kermani et al., 2021). Although they are focused on a large urban area, their generic study can be a very good benchmark for further developments in highly-polluted industrial areas, especially energy zones.

In this study, it is tried to provide a comprehensive spatial and time-dependent measurement on air pollution in the Pars special economic energy zone (PSEEZ) in Iran with a special focus on hazardous chemicals as the major pollutants in comparison to AQI. Subsequently, the cumulative impacts of these groups of pollutants on the health risk of the personnel and the inhabitants of the area is analyzed. These results are used for a managerial discussion about the localization of non-operational and official sites in the PSEEZ and the necessity of a reconsideration in human resource health policies in the polluted industrial areas in general.

MATERIAL AND METHODS

PSEEZ in the east of Bushehr in south of Iran, is the second largest energy zone of the world (Ashournejad et al., 2019). South Pars (14,000 ha), is the focal area of PSEEZ with eight active natural gas refinery and 17 active petrochemical complexes. South Pars area is located in the vicinity of Asalouyeh which is an urban area with the population of about 75,000 people including the workers and personnel of PSEEZ (Abbasi et al., 2019). Figure 1 shows the geographical location of South Pars area in PSEEZ.

As it is mentioned, PSEEZ is a vast area including numerous gas refining and petrochemical complexes as well as non-operational sites and areas. Therefore, it is tried to cover as many areas as possible for sampling in order to have a comprehensive assessment of the hazardous chemicals in the air of whole studied area. The sampling points are chosen in a way that a sufficient number of operational and non-operational points be considered in order to have a realistic situation of BTEX distribution all over the PSEEZ and be able to determine the health impacts of these pollutants on all groups of habitats. Since in active sampling, the sampling takes place through the devices attached to the personnel, a combination of outdoor and indoor measurements are carried out, however, due to the nature of the jobs that the workers do during a work day, the samples can be considered as mostly outdoor air. Table 1 shows the information about the sampling points.

In active sampling, the pollutant will be absorbed from the air by appropriate absorbents which are various depending on the nature of the gas which is going to be absorbed. Adsorption is more applicable for non-reacting gases and vapors. Activated carbon, silica gel and porous polymers are the most common adsorbents widely applied for pollutants adsorption from the air (Villacañas et al., 2006).

Adsorbing tubes which are suitable for active sampling in the mixture of organic vapors

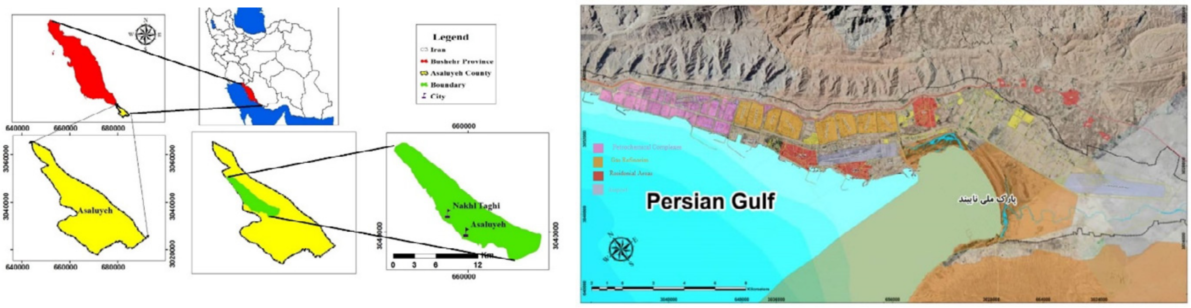

Fig. 1. The geographical location of PSEEZ

Table 1. Detailed information of sampling points

No.	Name	Unit type	Coordinates
1	2nd gas refinery	Operational	N=27.3110 E=52.3524
2	3rd gas refinery	Operational	N=27.3226 E=52.3348
3	4th gas refinery	Operational	N=27.3210 E=52.3402
4	5th gas refinery	Operational	N=27.2948 E=52.3656
5	7th gas refinery	Operational	N=27.2930 E=52.3730
6	Marjan petrochemical	Operational	N=27.3507 E=52.3140
7	Morvarid petrochemical	Operational	N=27.3430 E=52.3345
8	Borzooyeh petrochemical	Operational	N=27.3328 E=52.3341
9	Pardis petrochemical	Operational	N=27.3245 E=52.3356
10	Pars petrochemical	Operational	N=27.3258 E=52.3352
11	Mehr petrochemical	Operational	N=27.3331 E=52.3738
12	Kavian petrochemical	Operational	N=27.3430 E=52.3138
13	Jam petrochemical	Operational	N=27.3303 E=52.3307
14	Bidkhoon	Non-operational	N=27.2838 E=52.4107
15	Asalouyeh	Non-operational	N=27.3003 E=52.3542
16	Airport	Non-operational	N=27.2323 E=52.4403

are normally composed of two connected compartment. The first part is filled with 100 mg of activated carbon separated with polyurethane foam from the second part which is filled with 50 mg of activated carbon. In active sampling, the air is drawn into the adsorbent tubes using a pump in a specific time. The samples adsorbed by each compartment of the adsorption system will be analyzed by gas chromatography (GC) in order to determine the quality and quantity of different pollutants in the sampled air (Heibati et al., 2017). Although activated carbon is a general adsorbent effective for a wide range of hydrocarbons and other pollutants, the adsorbent may need to be changed in cases a specific pollutant is considered to be analyzed (Gouin et al., 2005).

The sampling pumps equipped with the adsorbent tubes are installed to the operational personnel in a backpack and during his work time in the site, the air will be sampled. At the end of the sampling, GC will determines the composition of the inhaled air during his work period (Breuer, 2012). Sampling took place in the period between September 2019 and September

Table 2. Codes and locations of sampling points for AQI measurement

Point code	Location	Coordinates
A	Chaah Mobarak	N=27.3664 E=52.79618
B	Harra	N=27.46672 E=52.67970
C	Nahalestan	N=27.47842 E=52.67970
D	Pars 2	N=27.78463 E=52.11344
E	Phases 6,7,8	N=27.53555 E=52.56575
F	Shirino	N=27.63625 E=52.45909

2020. Sampling duration was 8h which is the working time a worker in the site during the shift. The flowrate of sampling pump is in the range of 0.15 to 0.25 $L.min^{-1}$ from the air that the worker breathes in order to determine the composition of BTEX. For avoiding sorbent saturation, the tube is replaced with a new one after 4 h.

In order to determine AQI in the studied area, six stations of air quality online monitoring are installed in the whole PSEEZ which performed daily sampling and measurement of CO, O_3, NO_2, SO_2 and the particulate matter. The pollutants concentrations in each station are used to calculate the AQI in that station (Zheng et al., 2014). The highest AQI among the six stations are chosen as the total AQI of that day in the whole study area. Then, the results of each day are used for calculating monthly distribution of AQI in the PSEEZ. In localization of the sampling and measurement stations, it is tried to cover all the operational area in the whole PSEEZ. However, it is obvious that increasing the sampling station can significantly increases the accuracy and reliability of the results. Table 2 shows the details about the location of six sampling stations in the PSEEZ for AQI measurement.

The first step in data analysis and spatial distribution is the parameters interpolation which was carried out based on inverse distance weighting (Eq.1) (Varatharajan et al., 2018) and the geostatistical methods of kriging and cokriging (Eq.2) (Gia Pham et al., 2019). These methods are applied using GS^{+}5.1 and Arc GIS10.3 softwares for determination of pollutants spatial distribution in the studied area.

$$\lambda_i = \frac{D_i - a}{\sum_{i=1}^{n}(D_i - a)} \qquad \text{Eq. 1}$$

$$Z^*\left(X_i\right) = \sum_{i=1}^{n}\lambda_i Z\left(X_i\right) \qquad \text{Eq. 2}$$

λ_i, D_i, a and n are the weight of point i, the distance between i and the point being estimated, weighting power of the distance, and number of observations, respectively while $Z^*(X_i)$ and $Z\ (X_i)$ show the estimated amount of the variable in X_i position and the actual amount of the variable I, respectively.

In order to assess the errors and certainty in applying each interpolation method, cross-validation technique is used and the optimum method is chosen based on the results of cross-validation for each variable. Root mean square error (Eq. 3), Nash–Sutcliffe (NS) coefficient (Eq. 4), and R^2 coefficient are the indices based on which the accuracy of the data analysis is evaluated (Asgharnejad, Sarrafzadeh, et al., 2021). As values of R^2 and NS coefficients get closer to 1 and RSME closer to zero, the model performance is more proficient (Asgharnejad & Sarrafzadeh, 2020; Jimeno-Sáez et al., 2018).

$$RSME = \sqrt{\frac{\sum_{i=1}^{n}(O_i - E_i)^2}{n}} \qquad \text{Eq. 3}$$

$$NS = 1 - \left[\frac{\sum_{i=1}^{n}(O_i - E_i)^2}{\sum_{i=1}^{n}(O_i - \bar{O})^2}\right] \qquad \text{Eq. 4}$$

O_i, E_i, $\bar{O}$ and $\bar{E}$ are the observed data, simulated data in the base level, averaged observed data, and averaged simulated data, respectively.

RESULTS AND DISCUSSION

Hazardous chemicals such as hydrocarbons and BTEX are measured by the methodology described in the previous section in the 16 sampling points of table 1. Figure 2 shows the results of chemicals analysis is sampling point 1.

Figure 2 shows that the largest share of the hazardous chemicals in the air composition of sampling point 1 is related to ethylbenzene. However, the permissible exposure limit (PEL) for exposure to ethylbenzene is 100 ppm and the concentration of this chemical in point 1 will not violate the PEL (Knecht et al., 2000). On the other hand, benzene is an extremely hazardous material which may cause fatal diseases and disorders such as a wide range of cancers (Hsieh et al., 2021). According to European Commission, 5 $\mu g.m^{-3}$ (0.001437 ppm) is the permissible exposure limit (PEL) for exposure to benzene and its derivatives in operational sites and for a mid-term exposure (Kumar & Tyagi, 2006). Referring to figure 2 reveals that the benzene detected in the air sample of point 1 are above the minimum standard limit. The concentration

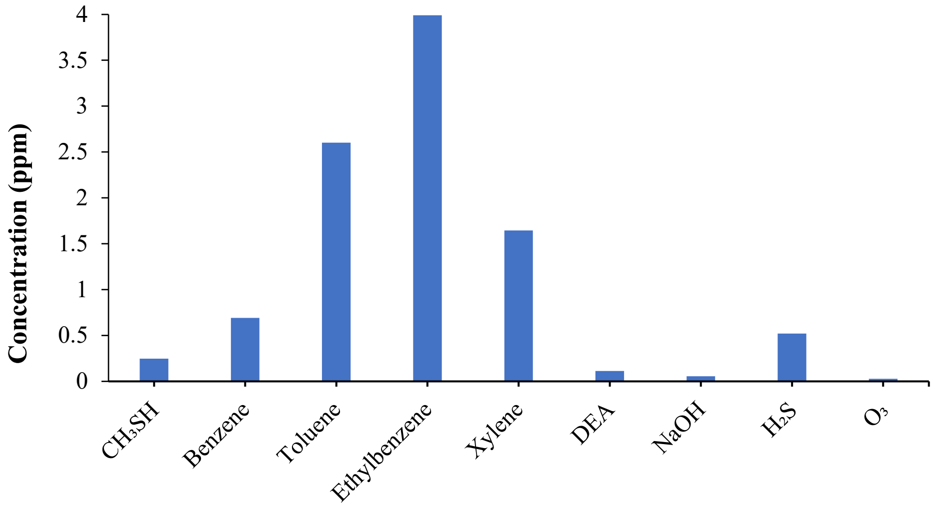

Fig. 2. Concentration of different chemicals in sampling point 1

of benzene (0.69 ppm) is 480 times greater than the PEL which makes sampling point 1 a hazardous area for unprotected personnel such as official and non-operational staff. Apart from benzene, existence of ethylbenzene, toluene and xylene which all are hazardous aromatics will increase the cumulative risk of BTEX in the sampling point 1.

BTEX is mainly emitted during process or tanks filling from gaskets and flanges. The tanks of storing the chemicals have a rubber sealing which may get loose and loose and loose its capability in sealing after a time and it is a huge source of BTEX emission. Moreover, the emissions can also occur during ships, trucks and containers loading. Wastewater treatment plant is also another unit which has a great contribution to BTEX emission due to open and direct vicinity of the polluted effluent with the atmosphere in their ponds (Asgharnejad, Khorshidi Nazloo, et al., 2021; Ziabari et al., 2022). Controlling the BTEX production at the source, regular inspection of the gaskets, flanges and sealing and updating the loading equipment are the solutions that may have great positive impacts on reducing the BTEX emission in industrial complexes such as PSEEZ.

It must be taken into account that points 1 to 5 are related to gas refineries in which the aromatic concentrations is expected to be lower than petrochemical complexes. The main source of aromatics in the gas refineries is those that has been extracted from the hydrocarbon well and delivered to the refinery, while in most of petrochemical complexes, the linear hydrocarbons are fed as the input in order to produce aromatics such as benzene, styrene and xylene. Therefore, PEL violation up to 480 times higher, increases the concern about the air quality of the whole area regarding numerous number of gas refineries and petrochemical complexes. This data intensifies the concerns about the cancer risk of BTEX (esp. benzene) in PSEEZ. Our previous study performed for evaluating the amount of BTEX by passive sampling in PSEEZ showed that the maximum amount of benzene in the area is about 0.0094 ppm which was recorded in petrochemical complexes (Ziabari et al., 2022). However, active sampling showed that the situation is much more severe regarding benzene concentration, since its concentration in gas refineries area is about 480 times higher than the data recorded by passive sampling. This meaningful difference shows the necessity of further studies in the area for BTEX (esp. benzene) concentration with more effective methodologies such as active sampling or high accuracy online sensors.

Surface ozone is another chemical which is more important regarding environmental health problems and its standard for 1h release is 0.08 ppm which is not violated in sampling point 2 (Mulholland et al., 1998).

CH_3SH (methyl mercaptan) is a highly odorant compound which is abundantly found in energy zones and there is a threshold for respiration of this material due to the potential destructive impacts it may cause to lung and other organs of the respiration system (Jiang et al., 2021). However, National Institute for Occupational Safety and Health (NIOSH) has announced 0.5 ppm as the airborne exposure limit of CH_3SH for short-term work period (Mitsubayashi & Hashimoto, 2002). Although figure 2 shows that the concentration of CH_3SH in sampling point 1 rests in the acceptable range suggested by NIOSH, the cumulative effect of this pollutant for long periods may result in long-term impacts on personnel health and safety.

Figure 2 also introduces H_2S as the pollutant with a noticeable concentration in the gas refineries which was also predictable. The main operation carried out in the gas refineries is sulfur recovery unit in which H_2S is separated from the natural gas. H_2S is a toxic gas that may be even fatal and cause asphyxia in high concentration for very short respiration time. However, the PEL of H_2S for a short-term exposure is 15 ppm set by NIOSH (Ni et al., 2012). Figure 2 shows that despite noticeable amount of H_2S in the air composition of point 1, its concentration lays in the acceptable range and does not violate the PEL. However, it cumulative effects in long-term can still be a challenge and must be taken into account similar to CH_3SH.

NaOH is also largely being utilized in gas refineries for gas sweetening and it is rational to

Table 3. The concentration of metals in the fume of welding workshop of sampling point 2

Pollutant	Average concentration ($mg.m^{-3}$)	Control limits		Time weighted average [TWA] ($mg.m^{-3}$)	Modified TWA ($mg.m^{-3}$)
		LCL	UCL		
Fe	4.419	1.677	1.857	5	2.5
Pb	0.033	1.280	1.359	0.05	0.025
Cr	0.014	-0.212	0.324	0.5	0.25
Ni	0.006	-0.522	0.642	0.2	0.1

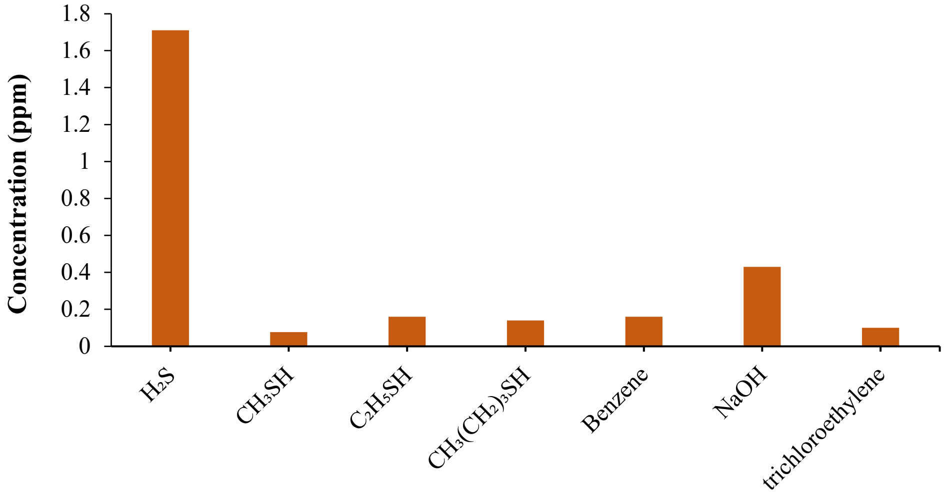

Fig. 3. Concentration of different pollutants in the air composition of sampling point 3

expect high amounts of this material in the air composition due to possible leakage (Kazemi et al., 2014). PEL of NaOH is 1.22 ppm which must not be violated at any time due to its harmful effects (Salocks & Kaley, 2003). Although figure 2 shows its concentration in the safe range, its cumulative effects with H_2S in long terms must be taken into account in risk analyses.

Apart from the pollutants reported in figure 2, existence of specific metals such as Fe and Pb in the air composition of welding workshop is challenging due to hazardous effects of these metals and their carcinogenic impacts (Kim et al., 2015). Table 3 shows the analysis of metals in the fume of the welding workshop of sampling point 2 which are recorded in the gaseous media and from the operational site of welding workshop.

Table 3 shows that the concentration of Fe and Pb are higher than the modified TWA and lay beyond the standard range of these metals. Since metals and hydrocarbons such as BTEX are extremely hazardous chemicals that are not considered in AQI calculation, a reconsideration is necessary in determining the most appropriate index for air quality and health assessment.

Figure 3 illustrates the air quality of sampling point 2 and the concentrations of chemicals in the sample collected from this point. The analysis of sampling point 1 showed that BTEX are the most significant hazardous hydrocarbons in the air composition of the gas refineries. Therefore, it is tried in the continuation of this research to focus on BTEX as an index of the hazardous organics in gas refineries.

Benzene is chosen as the main organics for analysis due to their health issues. The analysis showed that the concentrations of toluene, ethylbenzene and xylene are negligible in point 3,

Table 4. Concentrations of metals in the welding fume of sampling point 3

Pollutant	Average concentration (mg.m^{-3})	TWA (mg.m^{-3})	Modified TWA (mg.m^{-3})
Cu	1.019	0.2	0.1
Cd	0.711	0.01	0.005
Pb	1.738	0.05	0.025
Cr	0.144	0.05	0.025

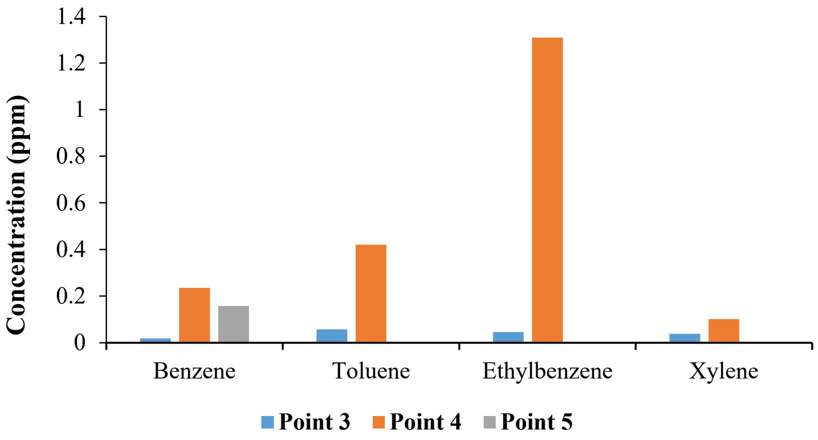

Fig. 4. Concentration of BTEX in sampling points 3, 4 and 5

therefore, they are not presented in figure 3.

Figure 3 shows that similar to point 1, H_2S is still a noticeable pollutant in air composition with a larger amount than point 1. Although concentration of H_2S in point 2 is still below the PEL, its cumulative effects may cause long-term harmful impacts on human health. Similar to point 1, the concentration of CH_3SH is in the acceptable range. Therefore, the concentrations of ethyl mercaptan (C_2H_5SH) and butyl mercaptan ($CH_3(CH_2)_3SH$) are measured for this sampling point in order to assess the cumulative impacts of mercaptans. However, the cumulative amount of mercaptans in this point is about 0.4 ppm which is still below the PEL and acceptable.

Benzene is still a challenge in point 2. The concentration of benzene at this point is 0.16 ppm which is more than 110 times higher than its standard amount and makes it a great health challenge. Table 4 shows the compositions of metals in the welding fume of sampling point 2.

It is shown in table 4 that the concentration of heavy metals in the welding fume of natural gas refineries in PSEEZ is significantly higher than standard values and needs strict regulations for personnel exposure due to their high cancer risk.

Figure 4 shows the analysis of air composition with an emphasis on BTEX in sampling points 3, 4 and 5.

The sources of BTEX in the air are comprehensively introduced in our previous study, however, leakage from gaskets, rings and fittings are the main sources of BTEX emission to the air in gas refineries (Ziabari et al., 2022). Therefore, numerous parameters such as refinery's equipment age, material and design can noticeably affect the amount of leakage and the BTEX concentration in the air composition of a refinery, consequently. That is why the composition of these compounds are different in different sampling points. However, the concerning fact is high amounts of benzene in all sampling points which is remarkably higher than the PEL and needs strict regulations and immediate actions for personnel protection, especially those in

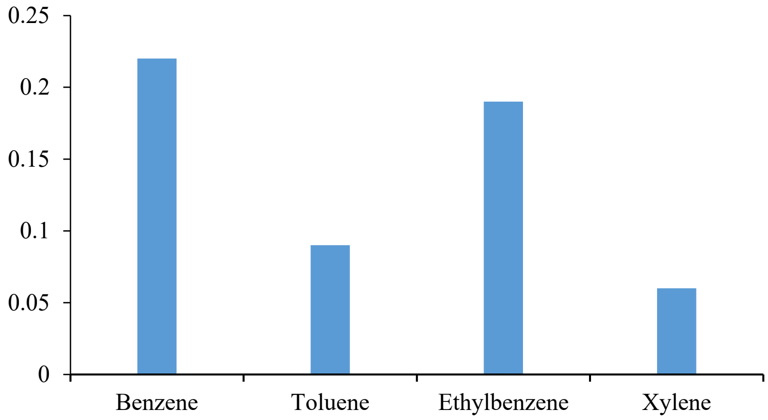

Fig.5. Concentration of different chemicals in sampling point 6

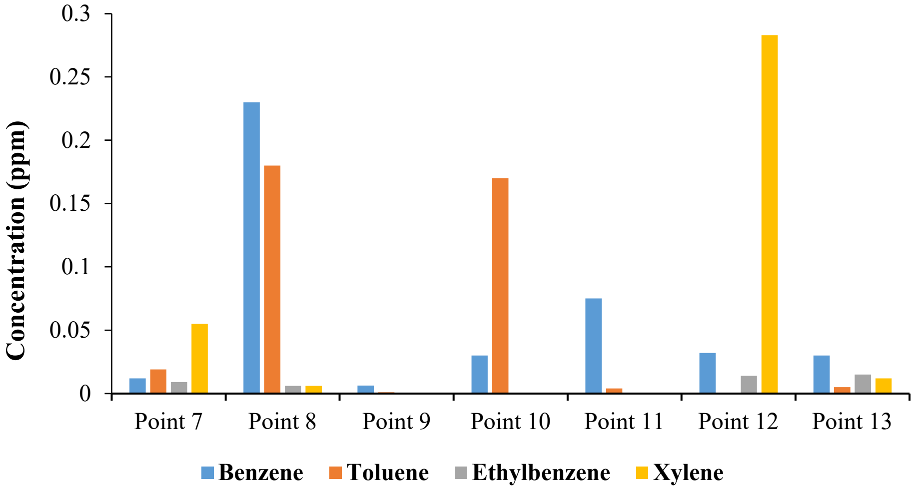

Fig. 6. Concentration of BTEX in sampling points 7-13

non-operational and official positions who are commuting unprotected.

Petrochemical complexes are the other group of operational sites that are focused mainly in west and north-west of PSEEZ and produce a wide range of pollutants in significant amounts. Points 6-13 are related to some of these petrochemical complexes. Figure 5 shows the concentration of BTEX in the air composition of sampling point 6. Due to the nature of the process in petrochemical complexes, different types of hydrocarbons are the most challenging pollutants and the compounds such as H_2S, NaOH and mercaptans are neglected.

It is obvious from figure 5 that benzene is the most challenging pollutant in point 6. The concentration of benzene in this point is 0.22 ppm which is 153 times higher than the PEL of benzene. Furthermore, if the cumulative impacts of BTEX be taken into account, the situation gets even more severe with serious health risk. The data presented in figure 5 emphasizes one more time the necessity of a reconsideration in choosing the appropriate index for air health assessment. Moreover, the level of benzene and its derivatives raises the need to a reevaluation in the localization of official and non-operational units.

Figure 6 shows the analysis of the air composition in points 7-13 regarding BTEX concentration.

As it is shown in figure 6, concentration of BTEX in point 8 is significantly high and violates the PEL. Benzene concentration in point 8 is 160 time higher than the standard amount.

These concentrations for points 7 and 9 are 8 and 4 times higher than PEL, respectively whose cumulative impact with points 6 and 8 creates a drastic health situation. Benzene concentration in points 10 and 11 are 20 and 50 times higher than EPL, respectively while in points 12 and 13 this ratio is about 50 times higher. The cumulative impacts of BTEX in the petrochemical area is dramatically high, since as figure 1 shows they are all located in the vicinity of each other. There must be a reassessment in location of official and non-operational units of petrochemical complexes considering the situation with BTEX concentration. Moreover, modern and high-tech devices of air quality assessment is a critical necessity in this area for online monitoring of the hazardous materials concentrations and continuous risk analysis. Generating a dynamic model for predicting the sources of BTEX, their real-time concentration and spatial distribution regarding geographical conditions such as wind, altitude, precipitation, etc. will noticeably help the decision makers in PSEEZ to increase the human safety parameters and reduce probable losses of human resources due to air pollution.

Apart from benzene, other aromatics may also be challenging in the petrochemical complexes. Although the concentration of toluene is not violating the standard limit (100 ppm) (Andersen et al., 1983), its cumulative impact with benzene and its derivatives will increase the health risk of exposure. As it can be concluded from the analysis of the points 1 to 13, BTEX (especially benzene) are the main compounds that must be considered in air quality assessment plans and programs.

In our previous study, we focused on spatial and temporal analysis of air quality in PSEEZ using passive sampling (Ziabari et al., 2022). It was concluded that although passive sampling is a moderately-accurate method for air quality assessment regarding BTEX distribution and gives a first idea about the situation, it cannot be used as a reference for making managerial decisions due to high response lag and limitation in measurement. Comparing the results achieved in current study with previous one validates the distribution of BTEX all over the PSEEZ regarding the most polluted area. However, active sampling revealed that the critical situation of air pollution (esp. BTEX pollution) is significantly more intensive than what was concluded by passive sampling. The results obtained in this study for BTEX concentration and other pollutants such as metals and H_2S raises the demand for defining multi-parameter and sophisticated indices for air quality assessment in industrial areas based on its local specifications. Moreover, high-tech methods of monitoring and measurement such as active sampling and online monitoring must be employed in order to have a real-time estimation of the air quality and make effective decisions.

This requirement is bolder and more serious when non-operational sites and areas are under consideration. Sampling points 14-16 are focused on some of the most populated non-operational areas in the PSEEZ. Figure 7 shows the concentration of BTEX in these three points.

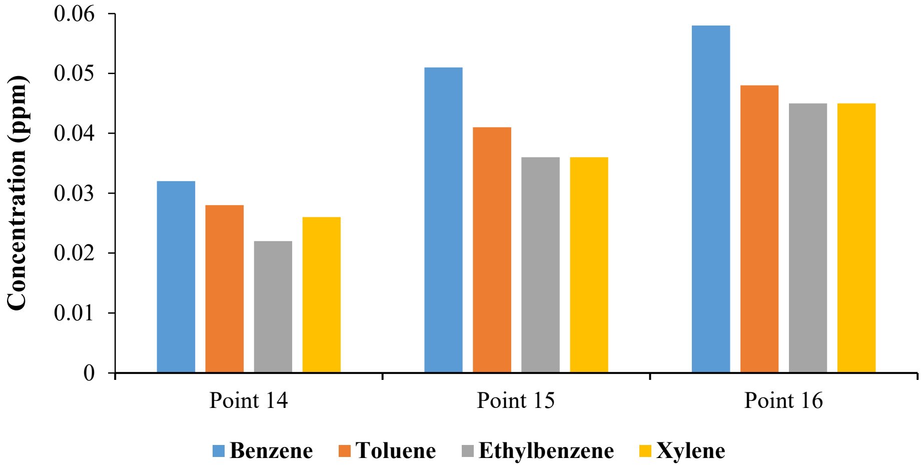

Fig. 7. Concentrations of BTEX in sampling points 14 to 16

Table 5. Grading system based on AQI

AQI range	Condition	Color
0-50	Good	Green
51-100	Moderate	Yellow
101-150	Unhealthy for sensitive groups	Orange
151-200	Unhealthy	Red
201-300	Extremely unhealthy	Violet
> 300	Hazardous	Purple

Table 6. AQI analysis in different months during 2020

Month	No. of green days	No. of yellow days	No. of orange days	No. of red days	No. of violet days	No. of purple days
Jan.	11	18	0	0	0	0
Feb.	7	14	7	1	0	0
Mar.	0	8	15	4	0	1
Apr.	5	15	6	4	0	0
May	5	20	4	0	1	0
Jun.	0	22	7	1	0	0
Jul.	1	21	8	0	0	0
Aug.	0	5	10	8	6	1
Sep.	0	19	3	2	6	0
Oct.	0	18	7	4	0	0
Nov.	6	21	2	0	0	0
Dec.	20	9	0	0	0	0
Total	**55**	**190**	**69**	**24**	**13**	**2**

Figure 7 reveals a horrible fact about the concentrations of BTEX in the non-operational areas. It shows that concentration of benzene in these non-operational sites reaches 40 times higher than the PEL which means a great cancer risk for the inhabitants and unprotected people living in the area. It is mainly due to the geographical conditions of the area and natural phenomena such as wind which moves the pollutants from the operational areas to the non-operational. Moreover, due to lower air movement in non-operational areas comparing operational sites, a temporal accumulation of BTEX may occur which means the BTEX brought from both refineries and petrochemical complexes are gathered together in the non-operational sites every day and generated a hazardous circumstances for the people living in these areas who are naturally unprotected. It is a serious problem that needs urgent action for preventing catastrophic incidents in the area. Continuation of this situation may lead to a human disaster in the forthcoming years and needing to more serious acts such as city evacuation.

Furthermore, making a comparison between benzene and toluene shows that the average concentration of benzene in the studied period is higher than the toluene which means that the ambient air of PSEEZ is more polluted with benzene than toluene. Considering the higher carcinogenic risk of benzene comparing to toluene, it is an unsatisfactory conclusion. However, this finding is in accordance with the results of the previous studies conducted in this study area regarding BTEX concentration (Keramati et al., 2016; Mirrezaei & Orkomi, 2020).

AQI usually varies between 0 and 500. As AQI increases, the air is more polluted and its hazardous impacts on human health is more severe. Table 5 shows the grading system of air quality based on AQI.

Table 6 is the report of AQI analysis in PSEEZ during 2020 segregated based on different months.

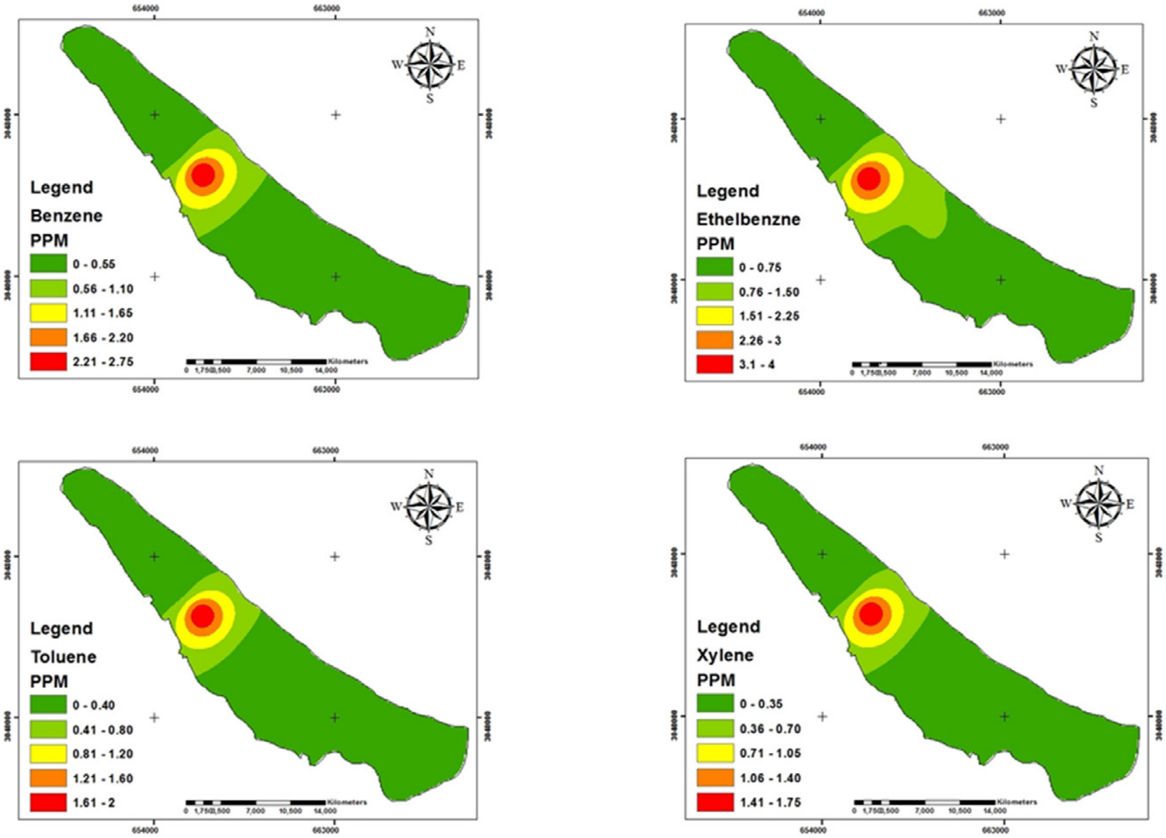

Fig. 8. Spatial distribution of BTEX in the PSEEZ

Table 6 shows that during 2020, more than 67% of the year is good and moderate on the basis of AQI and only 4% of the year are extremely unhealthy and hazardous. However, chemicals analysis, especially BTEX, showed that the air quality of PSEEZ is hazardous at most of the year regarding the concentrations of the pollutants. This comparison proves that AQI is not a suitable index for assessing the air quality in large industrial areas such as PSEEZ and a reconsideration in the management programs and plans is necessary. One of the most important breakthroughs can de defining local indices for air quality assessment that includes hazardous chemicals such as BTEX as well as those employed in AQI definition. Detailed data of AQI analysis for sampling points A-F based of different pollutants are not presented here, since it is not the focus of this study and prolongs the data but they are available upon request. However, these data showed that point C had the highest number of violet and purple days during 2020 regarding AQI. Figure 8 shows the distribution of BTEX in the whole PSEEZ based of the data obtained in active sampling section using GIS.

Point C is in the eastern area of PSEEZ and in the vicinity of phases 15 and 16 of the natural gas refineries. Nevertheless, figure 8 shows that the concentration of BTEX is higher in western side of PSEEZ. This meaningful difference in the distribution of BTEX and AQI raises the need to a reconsideration in air quality assessment indices again. Based on AQI the air quality of western side of PSEEZ is not unhealthy while BTEX analysis shows that its air is extremely hazardous for the personnel and even inhabitants that reside in the non-operational areas. In term of decision making, the results achieved in this research can be significantly helpful for redesigning human resource management programs.

Comparing figure 8 with the results of BTEX distribution in our previous research using passive sampling also reveals important points about the accuracy of passive and active sampling in BTEX measurement (Ziabari et al., 2022). According to our previous study using passive sampling, north-west of PSEEZ had the highest concentration of BTEX which was mainly attributed to petrochemical complexes that are active in the zone (Ziabari et al., 2022). This is also in accordance with the findings of previous studies carried-out in this study area regarding the composition of petrochemical wastes (Ghazizade et al., 2021). However, figure 8 shows that the highest amounts of BTEX are concentrated in the west and central area of PSEEZ which is close to urban area of Asalouyeh and Nakhl-e-Taghi rather than the industrial site. It means that the impact of climatic parameters such as wind and air pressure is huge as well as geographical conditions such as the positions of the mountains and land slope. Therefore and as it can be seen in figure 8, the BTEX generated in the industrial site moves towards the urban area where can cause more fatal effects in comparison to the industrial site. Passive sampling was not able to show this phenomenon well, because there is a meaningful time lag between the sampling and sample analysis in this method. Moreover, there is a high possibility for the adsorbants to get saturated at the very beginning of sampling process due to high concentrations of the pollution in the atmosphere. Hence, it is necessary for the passive sampling to be completed with the more accurate methods such as active sampling or online monitoring. In other words, passive sampling is a very useful method to diagnose the polluted area generally and it provides a large area in which the probability of presence of the pollutant is higher than other parts. With supplementary methods such as active sampling, this wide area can be limited to smaller grids and online monitoring also enables point analysis. Therefore and according to the results of current and previous study, it can be concluded that combination of active and passive sampling can give an acceptable idea about the spatial distribution of BTEX in PSEEZ or any other industrial zone with high amount of atmospheric pollution. As a matter of fact, this conclusion is not limited to BTEX and PSEEZ and can be generalized to any other pollutant and any other industrial or urban area.

CONCLUSION

This study is focused on making a comparative study on effectiveness of AQI as a generally-accepted index for air quality assessment and brings up the idea of a reconsideration in these methods, since, in sophisticated industrial areas such as PSEEZ, AQI cannot define the whole situation of the air composition solely and is not a justifiable index for assessing air health. The results of this study can be an appropriate platform for further development of dynamic models of air quality monitoring and assessment in large industrial areas. Moreover, they can be used as the input of further studies for definition of generic or local indices of air quality instead of AQI for highly-polluted industrial areas such as energy zones. Moreover, it is shown that the hazardous impacts of BTEX in non-operational areas are even more severe than operational sites due to pollution accumulation which needs an urgent managerial action for avoiding human catastrophe. Developing a dynamic system of real-time chemicals measurement and spatial distribution based on the meteorological and operational situation of PSEEZ can be a very big step in environmental management of this large energy area. The data achieved in this research not only highlights the need to this model, but also provide a very good database for development of such a monitoring system and may be a platform for more studies in this field.

GRANT SUPPORT DETAILS

The present research did not receive any financial support.

CONFLICT OF INTEREST

The authors declare that there is not any conflict of interests regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/ or falsification, double publication and/or submission, and redundancy has been completely observed by the authors.

LIFE SCIENCE REPORTING

No life science threat was practiced in this research.

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