Monitoring of volatile organic compounds in ambient air of Taldykorgan city

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The pollution of ambient air is the main source of risk to human health in the world. There is a direct relationship between level of air pollution and risk of the development of cancer, cardiovascular, respiratory and other diseases. Benzene, toluene, ethylbenzene and *o*-xylene (BTEX) are one of the most toxic volatile organic compounds. The aim of this study was quantification of BTEX in air in Taldykorgan city using solid-phase microextraction followed by gas chromatography with mass-spectrometric detection. In different sampling seasons average concentrations of BTEX varied from 7.50 to 27.1 μg/m^3, from 15.3 to 251 μg/m^3, from 2.40 to 12.8 μg/m^3 and from 2.60 to 21.1 μg/m^3, respectively. The highest concentrations of BTEX were detected in autumn season and were 27.1, 251, 12.8 and 21.1 μg/m^3, respectively, while the highest concentrations of benzene were found in winter. According to the results of the study, average BTEX concentrations do not exceed the daily average maximal permissible levels (MPC) approved by the government of the Republic of Kazakhstan.

Keywords: ambient air; BTEX, SPME; GC-MS; monitoring; Taldykorgan city.

Талдықорған қаласының ауасындағы ұшқыш органикалық қосылыстардың мониторингі

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Бүкіл әлемде атмосфералық ауаның ластануы адамдардың денсаулығы үшін негізгі қауіп көзі болып саналады. Ауаның ластану деңгейі мен онкологиялық, жүрек-қан тамырларының, респираторлық және басқа да аурулардың пайда болу қаупі арасында тікелей тәуелділік бар. Ең улы ұшқыш органикалық қосылыстардың бірі-бензол, толуол, этилбензол және о-ксилол (БТЭК). Бұл жұмыстың мақсаты масс-спектрометриялық детекторы бар газды хроматография және қатты фазалы микроэкстракция әдісімен Талдықорған қаласының ауасындағы БТЭК анықтау және идентификациялау болып табылады. Сынама іріктеудің әртүрлі маусымдарында БТЭК орташа концентрациялары тиісінше 7,50-ден 27,1-ге дейін, 15,3-тен 251-ге дейін, 2,40-тан 12,8-ге дейін және 2,60-тан 21,1 мкг/м^3-ге дейін өзгеріп отырды. БТЭК ең жоғары концентрациясы күзгі кезеңде 27,1, 251, 12,8 және 21,1 мкг/м^3 құрады, дегенмен, бензолдың ең жоғары концентрациясы қыста анықталды. Зерттеу нәтижелері бойынша БТЭК-тің орташа концентрациясы Қазақстан Республикасы Үкіметінің қаулысымен бекітілген орташа тәуліктік ШРК-дан аспайды.

Түйін сөздер: атмосфералық ауа; БТЭК; ҚФМЭ; ГХ-МС; мониторинг; Талдықорған.

Мониторинг летучих органических соединений в воздухе города Талдыкорган

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Во всем мире загрязнение атмосферного воздуха считается основным источником риска для здоровья людей. Существует прямая зависимость между уровнем загрязнения воздуха и риском возникновения онкологических, сердечно-сосудистых, респираторных и других заболеваний. Одними из самых токсичных летчуих органических соединений (ЛОС) являются бензол, толуол, этилбензол и *о*-ксилол (БТЭК). Целью данной работы является идентификация и количественное определение БТЭК в воздухе города Талдыкорган методом твердофазной микроэкстракции с газовой хроматографией и масс-спектрометрическим детектированием. В разные сезоны пробоотбора средние концентрации БТЭК варьировались от 7,50 до 27,1, от 15,3 до 251, от 2,40 до 12,8 и от 2,60 до 21,1 мкг/м^3, соответственно. Максимальные концентрации БТЭК были обнаружены в осенний период и составили 27,1, 251, 12,8 и 21,1 мкг/м^3, соответственно, при этом самые высокие концентрации бензола были обнаружены зимой. По результатам исследования средние концентрации БТЭК не превышают среднесуточные ПДК, утвержденные постановлением Правительства Республики Казахстан.

Ключевые слова: атмосферный воздух; БТЭК; ТФМЭ; ГХ-МС; мониторинг; Талдыкорган.

(2019) Chem Bull Kaz Nat Univ 4:4-13

CHEMICAL BULLETIN

of Kazakh National University

http://bulletin.chemistry.kz/

UDC 543.062 https://doi.org/10.15328/cb1095

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1. Introduction

Fast and uncontrolled population growth, increase of energy consumption and private transportation lead to a serious problem of air pollution in all cities around the world [1]. Air pollution leads to ecosystem failure and creates huge economic and social harm to the society. WHO reported that in 2016 about 4.2 million of premature deaths were caused by ambient air pollution [1]. 91% of deaths were in low- or middle-income countries [1]. Ambient and indoor air pollution causes the highest health risks around the world.

One of the most important stages in the activities aimed at decreasing the ambient air pollution is monitoring [2]. It allows predicting the trends in change of concentrations of contaminants, estimating an efficiency of anti-pollution activities, identification of new dangerous contaminants and key, most dangerous and illegal pollution sources.

One of the most dangerous group of air pollutants is volatile organic compounds (VOCs) which are released into the atmosphere due to biogenic and anthropogenic activity, as well as in the result of the photolysis of gases in the air [2]. The main sources of VOCs in the air are exhaust gases of vehicles, power plants, industrial activities, construction, as well as the emissions from household activities: cigarette smoke, paints, aerosols and cleaning products [3]. Special attention is paid to benzene, toluene, ethylbenzene and xylenes (BTEX) due to their toxicity. Many countries regulate and mandate monitoring BTEX concentrations in ambient air [4].

The problem of air pollution affected not only large cities, but also small ones such as Taldykorgan city. Taldykorgan city is the center of Almaty region and a neighboring city with Almaty. For several decades, this city was considered one of the most environmentally friendly cities in Kazakhstan, as there have never been large industrial plants. Nowadays, the air quality in Taldykorgan has decreased. This can be caused by the intensive expansion of the city, the construction of new residential areas and, accordingly, the increase in the number of vehicles and amount of the heating systems in the cold seasons. Taldykorgan does not have access to the gas pipeline, since gas reserves are located in Western Kazakhstan. As a result, coal is the main fuel for obtaining electricity and heat generation in the city.

Air monitoring in Taldykorgan has never been carried out, so no data on the concentrations of the most common and dangerous pollutants are available. It can be caused by complexity of standard methods for BTEX determination, the need to use modern methods of sample preparation and analysis [5]. Currently, three main approaches are most widely used for determination of BTEX in air [6-11]:

1. Air sampling in containers or canisters with different volume [7–10]. Containers for sampling are made from materials such as Teflon, glass or stainless steel. To concentrate the analytes, the sampled air is passed through sorption tubes, followed by desorption in a thermal desorption unit (TDU) connected to the inlet of gas chromatograph.

2. Passing of air samples through a suitable VOCs-retaining sorbent, followed by transferring the analytes to the inlet of gas chromatograph using TDU [10];

3. Continuous analysis of VOCs concentrations using mobile monitoring stations and portable devices [11,12].

The disadvantages of these methods are:

– The need for cleaning of containers and sorption tubes with high purity helium;

– the need for additional thermal desorption unit for desorption of analytes;

– thermal desorption of analytes from sorption tubes and its transfer to a gas chromatograph is a slow process, which causes wide and poorly separated peaks observed in chromatograms.

These factors result in the absence of information from the official sources about air pollution with BTEX in Kazakhstan although the required equipment is available in responsible laboratories.

Solid-phase microextraction is one of the most perspective methods for VOCs determination in air developed by Arthur and Pawliszyn from Waterloo University (Canada) in 1989 [13-15]. SPME is based on sorption of analytes onto polymeric coating followed by desorption in the GC inlet. SPME is very efficient and popular for screening of VOCs in the air. Several available commercial fibers provide detection of all VOCs or a narrow group of analytes depending on their polarity and volatility. Using SPME in combination with gas chromatography mass-spectrometry (GC-MS), authors of this study identified more than 100 VOCs in the air of Almaty [16].

The objective of this research was to determine the levels of BTEX in ambient air of Taldykorgan in different seasons during 2018-2019 by SPME-GC-MS using method developed by our group [17].

Table 2 – Weather conditions on sampling days

Sampling date	Air tempera-ture, °C	Weather conditions	Wind velocity, m/s	Pressure, mmHg	Humidity, %
10/3/18	13	rainy	1	713	77
12/4/18	15	sunny	6	715	53
14/4/18	24	cloudy	3	705	60
12/07/18	33	sunny	5,8	714	25
14/07/18	32	rainy	5	702	38
16/07/18	34	cloudy	0	701	64
16/10/18	0	snow	0	716	94
18/10/18	5	sunny	2	713	39
20/10/18	12	cloudy	3	719	62
14/01/19	-13	sunny	2	710	72
16/01/19	-3	cloudy	3	715	77
18/01/19	-10	sunny	0	709	91

2. Materials and methods

2.1 Air sampling sites

Sampling was conducted in three sampling sites located in different districts of Taldykorgan city: Karatal, Center and the 2nd Microdistrict. Sampling sites (A1, A2, A3) were chosen in different parts of city for determination of mean and total BTEX concentrations. Sampling sites were located close to the main roadways of the city, but at a distance of more than 15 m from road – Almaty highway, Zhansygurov Street and Kabanbay Batyr Street (Table 1). Meteorological parameters such as temperature, wind speed and humidity (Table 2) were taken from publicly available database (Kazhydromet, 2018-2019).

Sampling was conducted 4 times per year from 5 PM to 6 PM: April 10, 12 and 14; July 12, 14 and 16; October 16, 18 and 20, 2018 and January 14, 16 and 18, 2019. Nine air samples were collected per one sampling day and 27 samples per season.

Table 1 – Sampling sites descriptions

Sampling site	Crossroad (coordinates)	Objects within a radius of 200 m
A1	Rakisheva – Kablisa-Zhyrau (45°00'31.6"N, 78°20'49.1"E)	Almaty highway, new residential microdistricts, university, gas station
A2	Shevchenko – Kabanbay batyr (45°01'13.3"N, 78°22'32.6"E)	Low-rise buildings, shopping complexes Karagash, Shagan, Eurasia, bazaar
A3	Zhansygurova – Naberezhnaya (45°00'36.7"N, 78°24'10.3"E)	Residential buildings, shopping and entertainment complex City Plus, Nazarbaev Intellectual School, school №9, Karatal river, riverside

2.2 Analysis of air using SPME

Ambient air samples were collected into 20-mL crimp-top vials (Agilent, USA) in triplicates by opening vial to air and shaking of ~60 sec to increase air exchange, and sealed with aluminum caps with polytetrafluoroethylene/silicone septa (Agilent, USA). Vials were transported to the laboratory in 1-L glass jars. Prior to sampling all vials and caps were washed by distilled water and conditioned at 160°C during 4 h. Vials with sampled air were placed on Combi-PAL tray (CTC Analytics AG, Switzerland) for further GC-MS analysis. The analytes were passively extracted from vial with air samples using exposed 85 µm Carboxen/Polydimethylsiloxane (CAR/PDMS) SPME fiber at room temperature (T=22°C) for 7 min.

2.3 Air sample analyses with GC-MS

All samples were analyzed using 7890A/5975C GC-MS system equipped with split/splitless inlet (Agilent, Santa Clara, USA) and diffusion pump. Separation of BTEX was conducted using 60 m x 0.25 mm DB-WAXetr (Agilent, USA) column with 0.50 µm film thickness at a constant 1 mL/min helium flow. Temperatures of MS interface, quadrupole and ion source were 250, 150 and 230°C, respectively. Desorption of analytes was conducted in 0.75 mm ID SPME liner (Supelco, USA) in splitless mode at 250°C. Oven temperature was programmed from 40°C (held for 1 min) to 160°C (held for 2 min) with heating rate 10°C/min. Total GC run time was 15 min. MS detector was running in selected ion monitoring (SIM) mode for better sensitivity at *m/z* 78, 91, 106 and 106 amu for BTEX, respectively.

2.4 Calibration and quantification of BTEX

Benzene (99.8%) and toluene (99.8%) were obtained from "EKOS-1" LLP (Moscow, Russia). Ethylbenzene (99.0%) and *o*-xylene (99.0%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). All solutions were prepared in methanol (≥99.9%) purchased from Sigma-Aldrich (St. Louis, MO, USA).

Table 3 – Results of calibration using SPME and GC-MS

Analyte	Retention time (min)	Calibration range (μg/m³)	R^2			
			Spring	Summer	Autumn	Winter
Benzene	7.7	20-200	0.9603	0.9906	0.9780	0.9967
Toluene	9.3	20-200	0.9947	0.9931	0.9988	0.9297
Ethylbenzene	10.6	2-20	0.9905	0.9976	0.9956	0.9729
o-Xylene	11.7	2-20	0.9922	0.9927	0.9711	0.9992

Helium (> 99.995%) was obtained from “Orenburg Tehgas” (Orenburg, Russia).

Calibration was conducted using standard addition method, 1 μL of standard solutions were added into 20-mL vials. Concentrations of benzene, toluene and ethylbenzene, *o*-xylene were different due to their different background concentrations in ambient air. Addition concentrations of BT and EX were 20, 50, 100 and 200 μg/m3, and 2, 5, 10 and 20 μg/m^3, respectively. Obtained calibration curves were linear (R^2>0.99). Calibration results are presented in Table 3. Mean relative standard deviations (RSD) ranged from 1 to 5%.

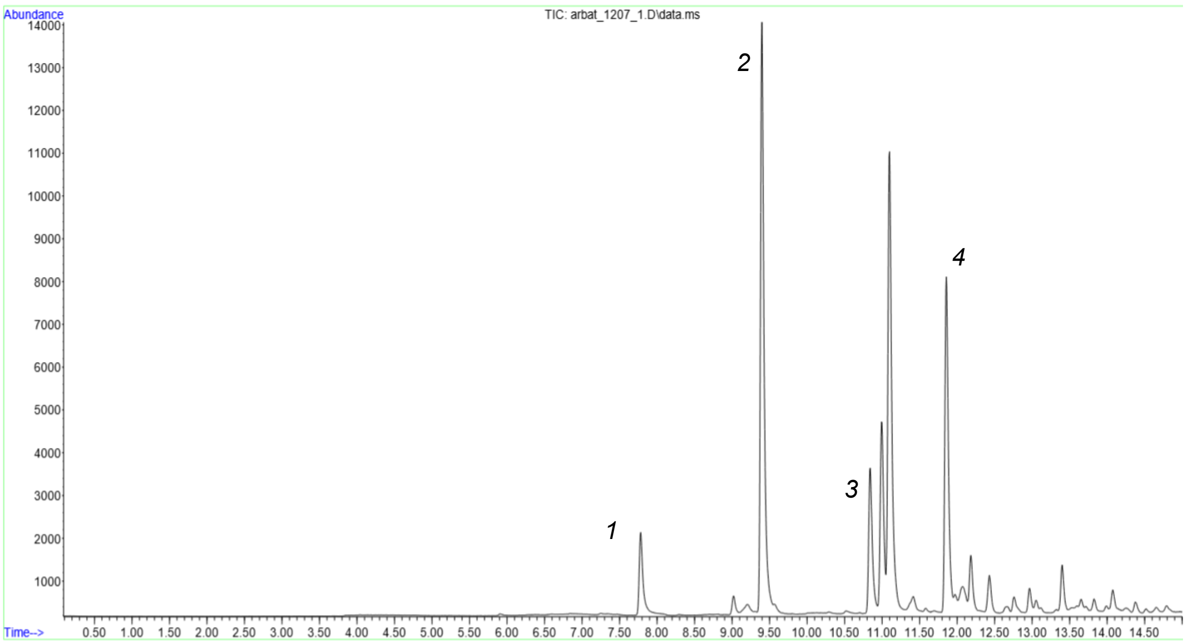
3. Results and discussion

3.1 *Quantification of BTEX in ambient air of Taldykorgan*

Chromatograms obtained for air samples provided high efficiency of peaks separation (Figure 1). Signal to noise ratios were higher than 15:1 for all analytes. Mean concentrations of BTEX were calculated for all 27 air samples in each sampling period (Tables 4 and 5). According to the results, BTEX concentrations in spring and summer were lower than in autumn and winter. Maximum mean TEX concentrations were determined in autumn and were 251, 12.8 and 21.1 μg/m^3, respectively and maximum benzene concentration was observed in winter season and was 27.1 μg/m^3.

In most of the samples concentrations of ethylbenzene and *o*-xylene were 10 times lower than benzene and toluene concentrations (Tables 4 and 5) due to their lower stability in air [18], less content in gasoline [19] and in the exhaust gases of cars [20].

RSDs of the three replicates did not exceed 25%. The greatest deviations are observed in autumn (±43 μg/m^3), which can be explained by random factors such as a car passing close to sampling site or a smoking person nearby. RSDs of most replicates were in the range ±10%. During entire sampling period, only 14 outliers were found (<11% from total samples) caused by damage of vials and subsequent leakage of analytes.



1 – benzene, 2 – toluene, 3 – ethylbenzene, 4 – o-xylene

Figure 1 – Chromatogram of air sample at sampling point A2 at 5 PM on July 12, 2018

Table 4 – Mean concentrations of BTEX in air of Taldykorgan city in spring and summer seasons 2018

		Concentration ± SD (μg/m³)							
Sampling season		Spring 2018			Mean	Summer 2018			Mean
Sampling date		10/04	12/04	14/04		12/07	14/07	16/07	
Benzene	Mean	6.7±3.3	12.6.±4.9	9.6±4.0	9.6±4.1	6.1±1.3	7.3±0.5	9.1±0.5	7.5±0.7
	Max	10.5	18.3	14.1		7.2	21.3	11.5	
	Min	4.4	9.2	6.5		5.4	3.5	7.6	
Toluene	Mean	13.6±5.8	19.8±10.2	17.3±4.1	16.9±6.7	13.1±1.4	15.1±1.4	17.7±3.1	15.3±1.9
	Max	20.0	30.7	22.1		16.3	32.1	22.3	
	Min	8.5	10.4	14.9		11.4	13.2	14.1	
Ethylbenzene	Mean	3.0±0.9	3.5±1.1	2.5±0.4	3.0±0.8	1.9±0.4	2.4±1.5	2.7±0.8	2.4±0.9
	Max	4.0	4.7	2.8		2.3	4.1	3.6	
	Min	2.4	2.9	2.1		1.5	1.4	2.1	
o-Xylene	Mean	1.8±0.3	3.3±0.8	2.7±0.7	2.6±0.6	4.8±1.0	6.9±3.3	5.7±1.5	5.8±2.0
	Max	2.0	4.3	3.1		5.8	10.7	7.5	
	Min	1.4	2.8	1.9		3.8	4.4	4.7	

Table 5 – Mean concentrations of BTEX in air of Taldykorgan city in autumn and winter seasons 2018

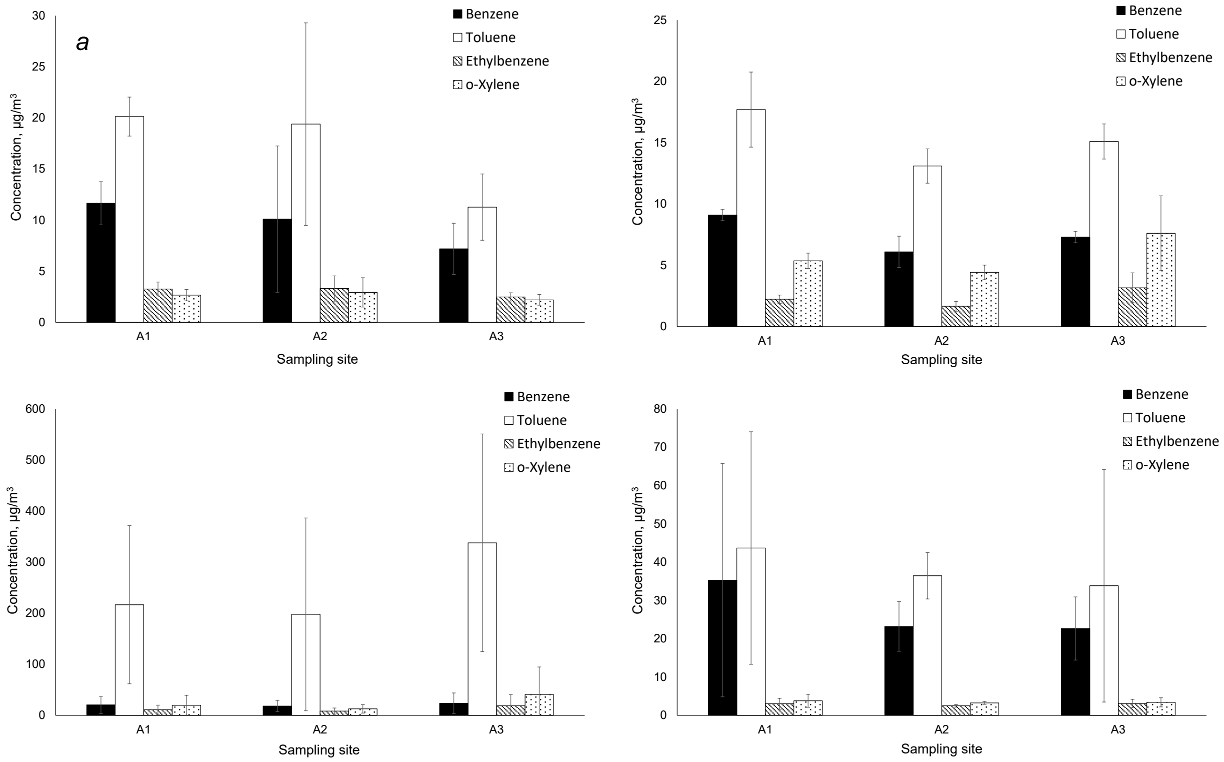
		Concentration ± SD (μg/m³)							
Sampling season		Autumn 2018			Mean	Winter 2019			Mean
Sampling date		16/10	18/10	20/10		14/01	16/01	18/01	
Benzene	Mean	38.9±8.2	15.2±0.4	8.4±1.1	20.8±3.2	44.3±22.7	19.5±2.0	17.4±1.4	27.1±8.6
	Max	46.6	15.7	9.4		70.4	20.9	18.2	
	Min	30.3	14.8	7.2		30.5	17.2	15.9	
Toluene	Mean	531±43	157±25	64.6±8.9	251.±25.7	51.7±22.9	38.7±12.7	23.6±12.9	38±16
	Max	814	227	74.3		77.9	53.2	37.9	
	Min	365	116	56.6		35.6	29.8	12.8	
Ethylbenzene	Mean	26.6±3.8	7.5±1.0	4.1±0.6	12.8±5.6	3.9±0.9	2.6±0.4	2.1±0.3	2.9±0.5
	Max	43.9	8.5	4.8		4.6	2.8	2.5	
	Min	15.1	6.6	3.7		2.9	2.2	1.8	
o-Xylene	Mean	45±24	11.6±1.2	6.3±0.7	21.1±8.9	4.5±1.2	3.3±0.4	2.7±0.8	3.5±0.8
	Max	71.6	12.7	7.1		5.7	3.5	3.6	
	Min	22.2	10.3	5.8		3.4	2.8	2.1	

Concentrations of BTEX were different at three districts of Taldykorgan city (Karatal, Center and the 2nd microdistrict) (Figure 2). The lowest concentrations of BTEX were found in Karatal district while the highest – close to Almaty highway in 2nd Microdistrict. In summer season, on the contrary, the lowest concentrations of BTEX were found in the Center, and the highest – in Karatal district. Karatal district is located in the Eastern part of the city, almost on its suburb close to the Karatal River that provides air circulation (Table 1).

However, the most popular entertainment places are located in Karatal district, which why there is an increased number of people and cars in the summer season. In the 2nd Mictodistrict there is a "ring" of 5 roads, one of which is the Almaty highway with traffic jams and weak air circulation. Results of monitoring in autumn and winter seasons are similar to the ones in the summer. The minimum concentrations of BTEX were determined on Tuesday (April 10) and on Thursday (July 12) due to rain that provides good air circulation.

3.2 The effect of seasons on BTEX concentrations in air of Taldykorgan city

Sampling of air and analyses were conducted during four seasons (Figure 3). Despite the 3 months difference, the



a – spring, b – summer, c – autumn, d – winter

Figure 2 – Mean concentrations of BTEX at different districts of Taldykorgan

seasonal mean concentrations in spring and summer are similar: 9.6 and 7.5 μg/m^3 for benzene, 16.9 and 15.3 μg/m^3 for toluene, 3.0 and 2.4 μg/m^3 for ethylbenzene, 2.6 and 5.8 μg/m^3 for *o*-xylene, respectively.

A significant difference was observed only in the concentration of *o*-xylene that can be caused by an increase in the number of cars in the summer season. Both seasons are characterized by abundant flowering of trees, flowers and other plants, which promotes photosynthesis, purifying the air at the same time. A substantial concentration jump of all compounds was in autumn: 20.8, 251, 12.8 and 21.1 μg/m^3, especially of toluene. These changes can be caused by the beginning of the heating season in October, and also the burning of leaves in open areas. Another factor is the temperature decrease with results in slowing down of air circulation. The maximum concentration of benzene (27.1 μg/m^3) was detected in winter season.

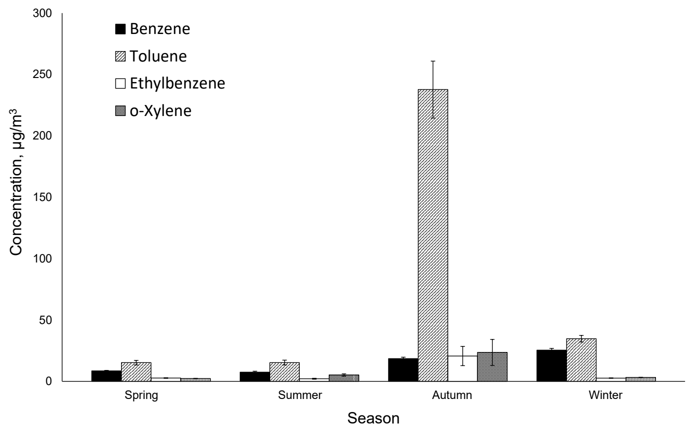


Figure 3 – Concentrations of BTEX in different seasons

On the other hand, the concentration of toluene (38.0 μg/m^3) was about 6 times lower than in autumn. Mean concentrations of ethylbenzene (2.9 μg/m^3) and *o*-xylene (3.5 μg/m^3) were in the same range as in spring and summer. However, average BTEX concentrations do not exceed the daily average maximal permissible levels (MPC) of benzene (100 μg/m^3) approved by the government of the Republic of Kazakhstan.

3.3 Comparison of BTEX concentrations in Taldykorgan and in Almaty cities

Concentrations of BTEX in air of Taldykorgan city in spring were compared with BTEX concentrations in Almaty city (Figure 4) and in other cities around the world (Table 6). Obtained concentrations of benzene and toluene in air of Taldykorgan city were two times lower than in air of Almaty city. Concentrations of ethylbenzene and *o*-xylene in two cities ranged from 2 to 4 μg/m^3.

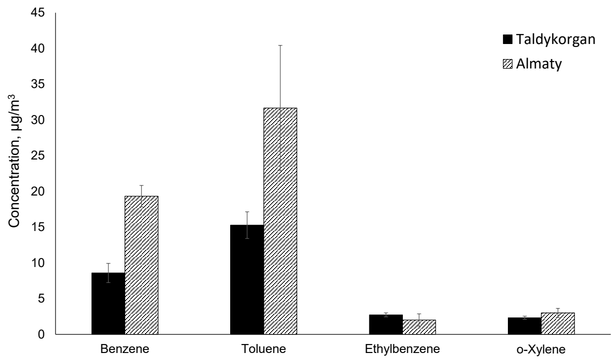


Figure 4 – Concentrations of BTEX in spring 2018 in air of Taldykorgan and Almaty cities

Table 6 – Concentrations of BTEX in ambient air in different cities of the world

Country	City	Concentration, μg/m^3					Reference
		Benzene	Toluene	Ethylbenzene	Xylene		
					m+p	o	
Africa							
Egypt	Cairo[e]	67	16-23	3	9-12	3-4	[18]
America							
Brazil	San-Paulo[e]	10-17	18-28	3-6	10-19	4-6	[19]
Canada	Windsor[e]	0.8	3	0.5	1	0.5	[20]
Chili	Santiago[e]	11-15	14-30	3-7	15-25	6-9	[19]
Asia							
China	Beijing[a]	2	4	2	4	2	[21]
	Hongkong[e]	3-15	5-139	2-25	3-28	1-13	[22]
India	New-Delhi[e]	87	167	17	67	35	[23]
Japan	Tokyo[e]	3-7	-	-	-	-	[24]
	Yokohama[e]	7	20	13	9	3	[25]
Kazakhstan	Almaty[b]	53	57	11	-	14	[17]
	Taldykorgan[d]	7.5	15.3	2.2	3.2	5.2	This study
Philippines	Manila[b]	12	84	-	-	38	[26]
Taiwan	Kaohsiung[e]	7-25	9-57	2-11	10-23	4-9	[27]
Thailand	Bangkok[a]	15-42	-	-	-	-	[28]
Vietnam	Ho Chi Minh[a]	56	121	21	64	23	[29]
Australia							
New Zealand	Christchurch[e]	1-9	2-27	0.6-4	1-23		[30]
Europe							
Belgium	Mortsel[b]	0.6-6	3-16	0.3-3	1-6	0.3-3	[31]
Italy	Bari[b]	0.8-9	0.9-16	0.2-3	0.8-10	0.3-4	[32]
	Rome[e]	40-47	128-138	-	-	-	[33]

Note: a – daily average concentration; b – weekly average concentration; c – monthly average concentration; d – seasonally concentration; e – annually concentration; - – not detected.

Concentrations of BTEX in air of Almaty city are close to those in cities around the world with high levels of air pollution such as New Delhi, Cairo, Rome, Ho Chi Minh city, San-Paulo and Manila (Table 6), while in Taldykorgan concentrations of analytes are significantly lower, which indicates a better level of air quality. However, for all cities it is common that exhaust gases are the main source of BTEX.

4. Conclusions

Thus, the monitoring of VOCs such as BTEX in ambient air of Taldykorgan city was conducted for the first time. Mean concentrations of BTEX in all sampling sites and seasons were 9.6, 16.9, 3.0 and 2.6 μg/m^3 in spring; 7.5, 15.3, 2.4 and 5.8 μg/m^3 in summer; 20.8, 251, 12.8 and 21.1 μg/m^3 in autumn and 27.1, 38.0, 2.9 and 3.5 μg/m^3 in winter, respectively. These concentrations are lower than daily average MPC of benzene (100 μg/m^3) approved by the government of the Republic of Kazakhstan. Daily average concentrations of toluene, ethylbenzene and *o*-xylene are not regulated in Kazakhstan. Minimum concentrations of benzene, toluene and ethylbenzene were found in the summer, for *o*-xylene the minimum concentration was found in the spring. This may indicate good air circulation and high sampling temperature. Maximum concentrations of BTEX were found in autumn season, except for benzene, maximum concentrations for which were detected in winter. Concentrations of BTEX in air of Taldykorgan city were compared with BTEX concentrations in air of Almaty city, Kazakhstan. According to the obtained results, in the spring season the concentrations of benzene and toluene in air of Taldykorgan city were 2 times lower than those in air of Almaty city. The concentrations of ethylbenzene and *o*-xylene were similar in both cities.

Acknowledgments

This work was conducted under the projects "Development of analytical methods, materials and equipment for cost-efficient "green" environmental monitoring" (No. AP05133158), and Ph.D. project of Olga Ibragimova all funded by the Ministry of Education and Science of Kazakhstan.

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