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# Simple and accurate quantification of BTEX in ambient air by SPME and GC–MS

Nassiba Baimatova

*Al-Farabi Kazakh National University*

Bulat Kenessov

*Al-Farabi Kazakh National University*

Jacek A. Koziel

*Iowa State University, koziel@iastate.edu*

Lars Carlsen

*Awareness Center*

Marat Bektassov

*Al-Farabi Kazakh National University*

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# Simple and accurate quantification of BTEX in ambient air by SPME and GC–MS

## Abstract

Benzene, toluene, ethylbenzene and xylenes (BTEX) comprise one of the most ubiquitous and hazardous groups of ambient air pollutants of concern. Application of standard analytical methods for quantification of BTEX is limited by the complexity of sampling and sample preparation equipment, and budget requirements. Methods based on SPME represent simpler alternative, but still require complex calibration procedures. The objective of this research was to develop a simpler, low-budget, and accurate method for quantification of BTEX in ambient air based on SPME and GC–MS. Standard 20-mL headspace vials were used for field air sampling and calibration. To avoid challenges with obtaining and working with ‘zero’ air, slope factors of external standard calibration were determined using standard addition and inherently polluted lab air. For polydimethylsiloxane (PDMS) fiber, differences between the slope factors of calibration plots obtained using lab and outdoor air were below 14%. PDMS fiber provided higher precision during calibration while the use of Carboxen/PDMS fiber resulted in lower detection limits for benzene and toluene. To provide sufficient accuracy, the use of 20 mL vials requires triplicate sampling and analysis. The method was successfully applied for analysis of 108 ambient air samples from Almaty, Kazakhstan. Average concentrations of benzene, toluene, ethylbenzene and o-xylene were 53, 57, 11 and 14  $\mu\text{g m}^{-3}$ , respectively. The developed method can be modified for further quantification of a wider range of volatile organic compounds in air. In addition, the new method is amenable to automation.

## Keywords

Solid-phase microextraction, GC–MS, Standard addition, BTEX Ambient air pollution, Air analysis

## Disciplines

Agriculture | Bioresource and Agricultural Engineering | Environmental Sciences

## Comments

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## Authors

Nassiba Baimatova, Bulat Kenessov, Jacek A. Koziel, Lars Carlsen, Marat Bektassov, and Olga P. Demyanenko

1       **Measurement of benzene, toluene, ethylbenzene and *o*-xylene concentrations in ambient**  
2 **air of Almaty, Kazakhstan, by solid-phase microextraction and gas chromatography - mass**  
3 **spectrometry**

4  
5 Nassiba Baimatova<sup>1</sup>, Bulat Kenessov<sup>1\*</sup>, Jacek A. Koziel<sup>2</sup>, Lars Carlsen<sup>3</sup>, Marat Bektassov<sup>1</sup>, Olga  
6 Demyanenko<sup>1</sup>

7  
8 <sup>1</sup> Center of Physical Chemical Methods of Research and Analysis, al-Farabi Kazakh National  
9 University, Almaty, Kazakhstan

10 <sup>2</sup> Department of Agricultural and Biosystems Engineering, Iowa State University, Ames, IA,  
11 USA

12 <sup>3</sup> Awareness Center, Linkøpingvej 35, Trekroner, DK-4000 Roskilde, Denmark

13 **\*Corresponding author:** e-mail: bkenesov@cfhma.kz, tel.: +7 727 2921374, postal address:  
14 Center for Physico-Chemical Methods of Research and Analysis, Department of Chemistry, Al-  
15 Farabi Kazakh National University, 96A Tole bi street, Almaty, 050012, Kazakhstan

16  
17       **Abstract**

18       Kazakhstan is experiencing unprecedented growth in large urban areas with unintentional,  
19 negative impact on air quality. Benzene, toluene, ethylbenzene and xylenes (BTEX) are one of the  
20 most ubiquitous and hazardous ambient air pollutants of concern. There is no published  
21 information on BTEX concentrations in ambient air of Almaty, the largest city of Kazakhstan,  
22 mainly due to a complexity and budget limitations of standard air sampling and analytical  
23 procedures. The objective of this research was to develop a simple, vial-based method for whole  
24 air sample collection, and then measure BTEX concentrations in ambient air of Almaty. Gas  
25 samples were prepared using solid-phase microextraction (SPME) and analyzed with gas  
26 chromatography–mass spectrometry. Air sampling method was optimized for simplicity,  
27 improved stability, and recovery of BTEX concentrations in samples. Air samples were collected  
28 at six locations in different areas of Almaty on March 31, April 2 and 4, 2015 at 8 A.M. and 8  
29 P.M. Mean concentrations of BTEX analytes at different sampling times ranged from 24 to 89,  
30 from 32 to 96, from 6 to 23 and from 7 to 32  $\mu\text{g}/\text{m}^3$ , respectively. Mean (of all analyzed 108  
31 samples) BTEX concentrations were 53, 57, 11 and 14  $\mu\text{g}/\text{m}^3$ , respectively. BTEX concentrations  
32 decreased with the increased elevation. Highest concentrations were measured on the coldest day  
33 when most BTEX originated from residential heating. Obtained results suggest that ambient air in  
34 Almaty should be of much greater concern. Measured BTEX concentrations were comparable with  
35 those in the most polluted large cities around the world.

36

37 **Keywords**

38 BTEX; air pollution; monitoring; Almaty; solid-phase microextraction; GC-MS.

39

40 **1. Introduction**

41 Rapid population growth, urban sprawl, increased energy usage and transportation cause  
42 serious air pollution in many cities around the world (Lan and Minh, 2013). Air pollution causes  
43 disruption of ecosystems and creates economic and social cost. It can lead to significant risks to  
44 human health at both local and regional scales all over the world. According to the World Health  
45 Organization (WHO), outdoor air pollution was responsible for the death of 3.7 million people  
46 under the age of 60 in 2012, 90% of whom lived in developing countries (WHO, 2014). The WHO  
47 air quality database continuously increases and covers today 1,600 cities in 91 countries (WHO,  
48 2014) demonstrating significant problems with urban air quality.

49 One of the most hazardous groups of air pollutants are volatile organic compounds (VOCs)  
50 (Caselli et al., 2010; EPA, 2010; Wark and Warner, 1977). Within VOCs, special attention is paid  
51 to benzene, toluene, ethylbenzene and *o*-, *p*- and *m*-xylenes (BTEX). BTEX are emitted to the  
52 atmosphere from both anthropogenic and biogenic sources (Alghamdi and Khoder, 2014), and can  
53 further be formed photochemically (Atkinson and Arey, 2003). In larger cities, the main sources  
54 of BTEX are the transportation, power plants, industrial enterprises, and construction works  
55 (Gelencsér et al., 1994; Helmig and Thompson, 2014; Lerner and Kohajda, 2014).

56 Major BTEX exposure routes for humans are either through the respiratory system or  
57 through skin contact or through (Li and Li, 2014). These compounds can also pose a serious threat  
58 to human health through interaction with chemical compounds present in the body (Table A1 in  
59 SM). Benzene is known as a Group 1 carcinogen to human's health (Caselli et al., 2010; Kerbachia  
60 et al., 2006). Benzene's cancer risk evaluation guide (CREG), defined as target risk  
61 level/inhalation unit risk ratio at 0.03 ppb ( $0.1 \mu\text{g}/\text{m}^3$ ) (Letter Health Consultation, 2015) the  
62 regional screening level (RSL) being 0.1 ppb (Atlantic Risk Assessment, 2012). An oral cancer  
63 slope factor for benzene (CSF) derived from an extrapolation from inhalation dose-response data  
64 ranges from  $1.5 \times 10^{-2}$  to  $5.5 \times 10^{-2} (\text{mg}/\text{kg}/\text{d})^{-1}$  (EPA, 2009).

65 Many countries regulate and mandate monitoring BTEX concentrations in ambient air.  
66 Thus, the U.S. EPA has established a reference concentration (RfC) of  $30 \mu\text{g}/\text{m}^3$  for benzene in air  
67 based on hematological effects in humans (EPA, 2009). In the European Union, average annual  
68 concentration of benzene is limited to  $5 \mu\text{g}/\text{m}^3$  (European Commission, 2010). In Kazakhstan,  
69 maximum allowable concentrations (MAC) of benzene for a single and 24-h average

70 measurements are 300 and 100  $\mu\text{g}/\text{m}^3$ , respectively (Russian Ministry of Health, 2003) – 20-60  
 71 times the limit within the European Union.

72 According to previously reported studies, BTEX are found in highest concentrations in a  
 73 typical ambient large city air among all other VOCs. Reported concentrations of BTEX in ambient  
 74 city air varied from 0.8 to 87, 3 to 268, 0.9 to 167 and 0.3 to 38  $\mu\text{g}/\text{m}^3$ , respectively for the four  
 75 BTEX compounds (Table 1).

76

77 Table 1 – Ambient air BTEX concentrations in selected cities in the world

| Country        | City                      | Concentration, $\mu\text{g}/\text{m}^3$ |         |              |                      |          | Reference                        |
|----------------|---------------------------|---|---------|--------------|----------------------|----------|----------------------------------|
|                |                           | Benzene                                 | Toluene | Ethylbenzene | Xylene<br><i>m+p</i> | <i>o</i> |                                  |
| Africa         |                           |   |         |              |                      |          |                                  |
| Egypt          | Cairo <sup>e</sup>        | 67                                      | 16-23   | 3            | 9-12                 | 3-4      | (Khoder, 2007)                   |
| America        |                           |   |         |              |                      |          |                                  |
| Brazil         | Porto Alegre <sup>e</sup> | 22                                      | 37      | 20           | 36                   | -        | (Grosjean, 1998)                 |
|                | Sao Paulo <sup>e</sup>    | 10-17                                   | 18-28   | 3-6          | 10-19                | 4-6      | (Gee and Sollars, 1998)          |
| Canada         | Windsor <sup>e</sup>      | 0.8                                     | 3       | 0.5          | 1                    | 0.5      | (Miller and Xu, 2012)            |
| Chile          | Santiago <sup>e</sup>     | 11-15                                   | 14-30   | 3-7          | 15-25                | 6-9      | (Gee and Sollars, 1998)          |
| Asia           |                           |   |         |              |                      |          |                                  |
|                | Beijing <sup>d</sup>      | 2-3                                     | 6-9     | 2-3          | 3-5                  | 2        | (Zhang and Mu, 2012)             |
| China          | Beijing <sup>a</sup>      | 2                                       | 4       | 2            | 4                    | 2        | (Liu and Mu, 2009)               |
|                | Hong Kong <sup>e</sup>    | 3-15                                    | 5-139   | 2-25         | 3-28                 | 1-13     | (Lee and Chiu, 2002)             |
| India          | New Delhi <sup>e</sup>    | 87                                      | 167     | 17           | 67                   | 35       | (Hoque and Khillare, 2008)       |
| Japan          | Tokyo <sup>e</sup>        | 3-7                                     | -       | -            | -                    | -        | (Laowagul and Yoshizumi, 2009)   |
|                | Yokohama <sup>e</sup>     | 7                                       | 20      | 13           | 9                    | 3        | (Tiwari et al., 2010)            |
| Kazakhstan     | Almaty <sup>b</sup>       | 53                                      | 57      | 11           | -                    | 14       | This study                       |
| Nepal          | Kathmandu <sup>e</sup>    | 2-13                                    | -       | -            | -                    | -        | (Gautam, 2004)                   |
| Philippines    | Manila <sup>b</sup>       | 12                                      | 84      | -            | -                    | 38       | (Balanay and Lungu, 2009)        |
| Taiwan         | Kaohsiung <sup>e</sup>    | 7-25                                    | 9-57    | 2-11         | 10-23                | 4-9      | (Hsieh and Yang, 2006)           |
| Thailand       | Bangkok <sup>a</sup>      | 15-42                                   | -       | -            | -                    | -        | (Leong et al., 2002)             |
| Turkey         | Eskişehir <sup>a</sup>    | 1                                       | 6       | 0.3          | 0.5                  | 0.4      | (Demirel and Ozden, 2014)        |
|                | Kocaeli <sup>c</sup>      | 2                                       | 36      | 10           | 37                   | 13       | (Pekey and Yilmaz, 2011)         |
| Vietnam        | Ho Chi Minh <sup>a</sup>  | 56                                      | 121     | 21           | 64                   | 23       | (Huong and Nguyen, 2014)         |
| Australia      |                           |   |         |              |                      |          |                                  |
| New Zealand    | Christchurch <sup>e</sup> | 1-9                                     | 2-27    | 0.6-4        | 1-23                 |          | (Mccauley, 2005)                 |
| Europe         |                           |   |         |              |                      |          |                                  |
| United Kingdom |                           | Up to 6.3                               | -       | -            | -                    | -        | (DEFRA UK, 2012)                 |
| Belgium        | Mortsel <sup>b</sup>      | 0.6-6                                   | 3-16    | 0.3-3        | 1-6                  | 0.3-3    | (Buczynska and Krata, 2009)      |
| Italy          | Bari <sup>b</sup>         | 0.8-9                                   | 0.9-16  | 0.2-3        | 0.8-10               | 0.3-4    | (Caselli et al., 2010)           |
|                | Rome <sup>e</sup>         | 40-47                                   | 128-138 | -            | -                    | -        | (Brocco and Fratarcangeli, 1997) |

Note: <sup>a</sup> – 24-h average concentration  
<sup>b</sup> – 1-week average concentration  
<sup>c</sup> – Monthly average concentration  
<sup>d</sup> – Seasonally averaged concentration  
<sup>e</sup> – Annual average concentration  
 -- Not reported

79 Almaty is the largest city in Kazakhstan with the increasing population of approx. 1.5  
80 million. Almaty is considered as one of the most attractive places in Kazakhstan to live. However,  
81 the unintended consequence of the economic growth is that the air pollution in Almaty over the  
82 past 15 y has reached levels comparable with the most polluted cities in the world (Kazakhstan  
83 Today, 2008). The reasons are complex, but the main factors are geography, increasing number of  
84 vehicles, infrastructure not adequate to fully accommodate growth, and fuel quality. Today more  
85 than 500 thousand registered cars in Almaty of which 60% are at least than 10 y old, some of  
86 which have outdated emissions control technology (Kadyrbaev, 2015; Seidakhmetova, 2014). The  
87 geographical location of the city exacerbates air pollution. Almaty is surrounded by the Trans-Ili  
88 Mountains and located in valleys of the Big and Small Almatinka Rivers. Mountains and hills limit  
89 the horizontal movement and exchange of air. Cold air from mountains often causes temperature  
90 inversions and poor vertical air movement. In addition, Almaty ranks as #1 (out of 17  
91 cities/provinces) in Kazakhstan on respiratory, endocrine and blood diseases, cancer and bronchial  
92 asthma per capita (Konurkulzhaeva, 2014).

93 According to a recent screening of the air quality with solid phase microextraction (SPME)  
94 and gas chromatography – mass spectrometry (GC-MS) (Carlsen et al., 2013), more than 100  
95 VOCs were identified in Almaty ambient air, with BTEX being the most abundant. However, to  
96 date, there is no actual data on concentrations of BTEX in the ambient air of Almaty, mainly due  
97 to budget limitations and complexity of standard analytical methods. The objective of the present  
98 study is to remedy this.

99 Current standard approaches for quantification of BTEX (EPA, 1999; Feng and Mitra,  
100 2000; Quality Assurance Team, 2004) are mainly based on trapping analytes into evacuated  
101 canisters or onto sorbent tubes followed by thermal desorption, cryogenic focusing and GC-MS.  
102 Despite of good reliability, these techniques are quite complex, labor-, time-consuming, and  
103 require additional sampling and sample preparation equipment. Additional problems may include  
104 carryover of analytes and clogging of the cryogenic focusing system, which considerably limit the  
105 application of standard methods, not least in developed countries.

106 To remedy these problems solid-phase microextraction (SPME) (Elke and Jermann, 1998;  
107 Khaled and Pawliszyn, 2000; Martos and Pawliszyn, 1999, Augusto et al., 2001) constitutes an  
108 attractive alternative method for screening and quantification of VOCs in air. The SPME  
109 technology combines sampling and sample preparation. SPME is based on passive extraction of  
110 VOCs by a thin polymer coating followed by desorption of analytes in GC injection port. The use  
111 of SPME does not require thermal desorption unit. Desorption of VOCs from SPME is rapid, and  
112 it does not require cryogenic focusing. SPME fiber cleanup is done in GC injection port and is not  
113 required after the analysis of a previous sample, i.e., SPME fibers can be reused for gas sampling.

114 SPME is widely used for determination range of VOCs in ambient air (Chai and Tang,  
115 1998; Elke and Jermann, 1998; Haberhauer-Troyer et al., 1999; Italiana and Tumbiolo, 2005;  
116 Koziel and Jia, 1999; Koziel and Pawliszyn, 2001; Prikryl and Sevcik, 2008; Tuduri et al., 2002;  
117 Tumbiolo and Gal, 2004; Yassaa et al., 1999). Researchers (Xiong et al., 2004) reported on BTEX  
118 sampling with SPME in the presence of ozone. (Table A2 in Supplementary Material, SM).  
119 Review of SPME applications for indoor air is presented elsewhere (Koziel and Novak, 2002).  
120 Most recently, SPME has also been used to quantify BTEX concentrations in vehicle exhausts  
121 (Baimatova et al., 2015) and hot industrial gas streams (Woolcock and Koziel, 2013, 2015).  
122 Despite the high efficiency of SPME for determination of VOCs in air (Table A2 in SM), there are  
123 still challenges limiting its application and its standardization. The most crucial problem is the  
124 insufficient accuracy of the method for determination of VOCs in air. Specifically:

- 125 • competition between analytes due to a low sorbent capacity of the fiber;
- 126 • uncontrolled adsorption of analytes on metal parts of fiber holder;
- 127 • effects of turbulence and diffusion boundary layer (around the SPME) on the rate of  
128 sampling with exposed SPME fibers;
- 129 • effects of air temperature on SPME extraction efficiency.

130 Some authors report problems with labor-intensive calibration, i.e., requirement to  
131 construction of a system for generation of air with known concentration of the analyte  
132 (Haberhauer-Troyer et al., 1999; Tumbiolo and Gal, 2004). However, many of these challenges  
133 can be addressed with (e.g.) retracted SPME fiber approach (Woolcock et al., 2015; Baimatova et  
134 al., 2015).

135 The objective of this research was to develop a simple method for sample collection and  
136 analysis and then measure BTEX concentrations in ambient air of Almaty applying SPME-GC-  
137 MS. Air sampling was optimized for higher simplicity, recovery, and stability of BTEX  
138 concentrations.

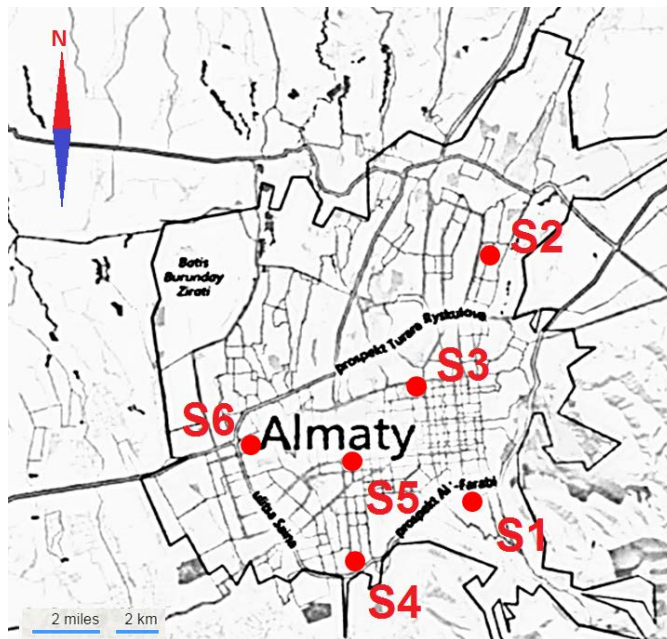
139

## 140 **2. Experimental**

### 141 *2.1 Air sampling sites*

142 Samples were collected at six sites located in five different districts (Bostandyk, Auezov,  
143 Medeu, Almaly and Turksib) of Almaty city, Kazakhstan (Fig. 1). Sites S1-S6 were chosen in  
144 different parts of the city for assessment of average and representative pattern of BTEX in the  
145 whole city. Sites S1-S6 are located near the main streets of the city – al-Farabi Ave., Abay Ave.,  
146 Sain Str., Suyunbay Ave. Samples were taken at the height 1.5-1.8 m above the ground, which  
147 where the major inhalation by pedestrians takes place. Sampling was taken at the distance >15 m

148 from the road. Meteorological parameters such as temperature, wind speed and humidity of the air  
 149 were obtained from publically-available data base (Kazhydromet, 2015).  
 150



151

152 Figure 1 – Location of sampling sites S1-S6

153

154 Air sampling was done on March 31, April 2 and 4, 2015. Sampling at each location was  
 155 carried out at 8 A.M. and 8 P.M using ‘crowd-sourcing’, i.e., trained students from our research  
 156 group. Air samples were collected into 20 mL vials in triplicates. Thirty six samples were taken  
 157 each day; the total number of analyzed samples was 108. Vials were packed into 1 L clean glass  
 158 jars, sealed and transported to the laboratory (Fig. A1 in SM). Sample vials were removed from  
 159 jars immediately before the analysis to minimize interferences to BTEX concentrations. All air  
 160 samples were analyzed within 4 h after collection. Measured BTEX concentrations were not  
 161 adjusted for temperature and pressure changes between sampling sites (Table 2) and analysis,  
 162 which contribute uncertainties to concentration measurement.

163

164 Table 2 – Weather conditions on sampling days

| Date      | Air temperature, °C |        | Condition | Wind speed, m/s | Pressure, mm | Humidity, % |
|-----------|---------------------|--------|-----------|-----------------|--------------|-------------|
|           | 8 A.M.              | 8 P.M. |           |                 |              |             |
| 3/31/2015 | -10                 | -4     | sunny     | 1               | 691          | 60          |
| 4/2/2015  | -4                  | 0      | snowing   | 3               | 689          | 77          |
| 4/4/2015  | +4                  | +11    | sunny     | 0               | 690          | 60          |

165

166 *2.2 Air sampling by SPME*

167 Ambient air samples were collected into 20 mL crimp-top vials (i.e., by opening vial to air  
 168 and shaking of ~60 sec to increase air exchange) and then sealed with aluminum caps equipped



169 with PTFE-Silicone septa (Agilent, USA). Crimp-top vials were chosen over screw top vials to  
170 minimize analyte losses based on preliminary experiments. Prior to sampling, all vials and septa  
171 were washed by a distilled water and pre-conditioned at 160 °C for 4 h. Vials with air samples  
172 were placed into the Combi-PAL (CTC Analytics AG, Switzerland) agitator for further analysis  
173 by GC-MS. Air samples were passively extracted from vial using exposed 100 µm  
174 polydimethylsiloxane (100 µm PDMS) SPME fiber (Supelco, Bellefonte, PA, USA). 100 µm  
175 PDMS fiber is not the most selective fiber for BTEX (Elke and Jermann, 1998; Paschke and Vrana,  
176 2006; Popp and Paschke, 1997). However, the use of PDMS was associated with improved data  
177 reproducibility in this research. This was likely due to a higher volume of PDMS fiber coating and  
178 less pronounced competition between analytes (Pawliszyn, 2012). Extraction was done at a  
179 constant temperature of 30 °C for 3 min, pre-incubation time was set to 3 min. The optimal  
180 extraction time was chosen experimentally as equilibration time between SPME coating and vial  
181 headspace (Figure A2 in SM).

182

### 183 *2.3 Air sample analyses with GC-MS*

184 All gas samples were analyzed on 7890A/5975C Triple-Axis Detector diffusion pump  
185 based (Agilent, Santa Clara, USA) GC-MS equipped with split/splitless inlet. For separation of  
186 BTEX, a 30 m × 0.25 mm HP-INNOWax (Agilent, USA) column with film thickness 0.25 µm  
187 was used. The constant flow of He in column was 1 mL/min. Temperatures of ion source,  
188 quadrupole and MS interface were 230, 150 and 250 °C, respectively. Thermal desorption of  
189 analytes from SPME fiber in GC injector was done in splitless mode at 250 °C using 0.75 mm i.d.  
190 liner (Supelco, USA). Oven temperature was programmed from initial 40 °C (held for 3 min) to  
191 150 °C (held for 1.5 min) at the heating rate of 20 °C/min. GC column retention times for BTEX  
192 were 3.5, 4.9, 5.8 and 6.4 min, respectively. Detection was carried out in selected ion monitoring  
193 (SIM) mode at m/z 78, 91, 106 and 106 for selective detection and quantification of the four BTEX  
194 constituents, respectively. Total GC run time of the analysis was 10 min.

195

### 196 *2.4 Calibration and quantitative determination of BTEX*

197 Benzene (99.8%) and toluene (99.8%) were obtained from EKOS-1 LLP (Moscow,  
198 Russia). Ethylbenzene (99.0%), and *o*-xylene (99.0% purity) were purchased from Sigma-Aldrich,  
199 St. Louis, MO, USA. Methanol (HPLC grade) was obtained from AppliChem (Darmstadt,  
200 Germany). Helium (>99.995%) was purchased from “Orenburg-Tehgas” (Orenburg, Russia).

201 Presence of BTEX in the air is a common challenge for many air quality laboratories where  
202 special air handling and conditioning is not feasible. Due to the presence of BTEX in the indoor  
203 air of the lab, calibration plots were obtained by a standard addition method. To prepare calibration

204 samples, open 20-mL vials were left on a laboratory table for 15 min followed by an injection of  
 205 1  $\mu\text{L}$  aliquots of liquid BTEX standard solutions and sealing with crimped tops. The advantage of  
 206 such methodology is that it does not necessarily require knowing real concentrations of analytes  
 207 in calibration samples because the obtained calibration slope should be equal to the slope for  
 208 external standard calibration. The proposed approach substantially simplified the calibration  
 209 process because “zero” air was not required for the calibration. Filling vials with “zero” air would  
 210 also be complicated. Calibration for benzene and toluene was done separately from ethylbenzene  
 211 and *o*-xylene because of different target concentration ranges (Table 3). Detailed description of a  
 212 strategy for preparation of calibration samples is provided in SM.

213 Obtained SIM mode chromatograms were integrated for peak area counts. BTEX  
 214 compounds were identified using retention times of single analytes and spectral matches. Obtained  
 215 calibration plots for BTEX were linear in the whole studied standard addition concentrations range  
 216 20-200  $\mu\text{g}/\text{m}^3$  for benzene and toluene and 2-20  $\mu\text{g}/\text{m}^3$  for ethylbenzene and *o*-xylene (Fig. A3 in  
 217 SM) with the squared correlation coefficients  $R^2 > 0.99$  (Table 3). Mean relative standard deviations  
 218 ranged from 1 to 5%. According to the calibration, BTEX concentrations in lab air are 63, 44, 2  
 219 and 3  $\mu\text{g}/\text{m}^3$ , respectively.

220

221 Table 3 – Results of GC-MS calibration by SPME fiber

| Analyte          | GC Column Retention time, min | Concentration range, $\mu\text{g}/\text{m}^3$ | $R^2$  | Intercept, kAU | Slope, (kAU $\text{m}^3$ )/ $\mu\text{g}$ | C in lab air, $\mu\text{g}/\text{m}^3$ |
|------------------|-------------------------------|---|--------|----------------|---|--|
| Benzene          | 3.5                           | 20-200  | 0.9937 | 35 $\pm$ 4     | 0.55 $\pm$ 0.03                           | 63                                     |
| Toluene          | 4.9                           | 20-200  | 0.9946 | 60 $\pm$ 1     | 1.40 $\pm$ 0.08                           | 44                                     |
| Ethylbenzene     | 5.8                           | 2-20  | 0.9927 | 5.0 $\pm$ 2.0  | 2.9 $\pm$ 0.2                             | 2                                      |
| <i>o</i> -Xylene | 6.4                           | 2-20  | 0.9934 | 23 $\pm$ 5     | 8.1 $\pm$ 0.5                             | 3                                      |

Note: kAU - Kilo Arbitrary Units

222

## 223 2.5 Optimization of air sampling procedure

224 Optimization of air sampling consisted of:

### 225 2.5.1 Comparison of the mass extracted by SPME from 250 mL bulbs and from 20 mL vials.

226 Prior to sampling, vials and bulbs (Sigma-Aldrich, St. Louis, MO, USA) were washed by  
 227 distilled water and pre-conditioned at 160  $^{\circ}\text{C}$  during 4 h. Ambient air samples were collected in  
 228 bulb by pumping at flow rate 1 L/min during 5 min and into 20 mL crimp-top vials (i.e., by opening  
 229 vial to air and shaking of  $\sim$ 60 sec to increase air exchange) and then sealed with aluminum caps  
 230 with PTFE-Silicone septa (Agilent, USA). All samples were analyzed in triplicates by SPME-GC-  
 231 MS using the method as for analyses of gas samples in vials.

232 The objective of this experiment was to compare BTEX mass extracted by SPME from the  
 233 same air located in 250 mL calibrated bulb and from 20 mL vial. Masses extracted from the bulb

234 were 3%, 17%, 18% and 9% higher than those from vial for BTEX, respectively (Table 4). The  
235 difference is in the range of standard deviation (Table 4) meaning that BTEX can be extracted  
236 from 20 mL vial without a significant loss of recovery.

237

238 Table 4 – Comparison of BTEX mass extracted from air samples collected with glass bulbs and  
239 vials

240

| Compound         | Mass extracted by SPME, pg |            |
|------------------|----------------------------|------------|
|                  | 250 mL bulb                | 20 mL vial |
| Benzene          | 2.7±0.2                    | 2.7±0.6    |
| Toluene          | 2.3±0.6                    | 1.9±0.1    |
| Ethylbenzene     | 0.88±0.08                  | 0.7±0.1    |
| <i>o</i> -Xylene | 1.30±0.03                  | 1.2±0.1    |

241

### 242 *2.5.1 Study of a stability of BTEX concentrations inside vials*

243 BTEX concentration in air inside vials may change due to a difference of their concentrations  
244 in a sampled and outside (e.g., lab) air. Stability of BTEX concentrations inside vials during their  
245 transportation and storage was checked by analysis of BTEX concentrations in vials filled with  
246 ‘clean’ air at different time periods - 1, 5 and 12 day after sampling. ‘Clean’ air was collected in  
247 mountains at a distance of 15 km from Almaty and a height of 2700 m in relatively non-polluted  
248 area (N43<sup>0</sup>3.303’; E76<sup>0</sup>58.563’).

249 BTEX concentrations in ‘clean’ air samples were less than 12% of those in the ambient air  
250 for up to 12 d of a sample storage in vials using the proposed sampling approach. Such results  
251 indicate the effectiveness of the proposed approach and very good stability of BTEX  
252 concentrations inside vials (Fig. A4 in SM). This result is important because it shows that small  
253 leaks via septa and a concentration gradient between sampled and ambient air are negligible.  
254 Problems with sample stability associated with air sampling can be sometimes detrimental as  
255 analyte concentrations inside sample bags and containers may vary during storage and  
256 transportation and cause problems with accuracy of the results.

257

## 258 **3. RESULTS AND DISCUSSIONS**

259

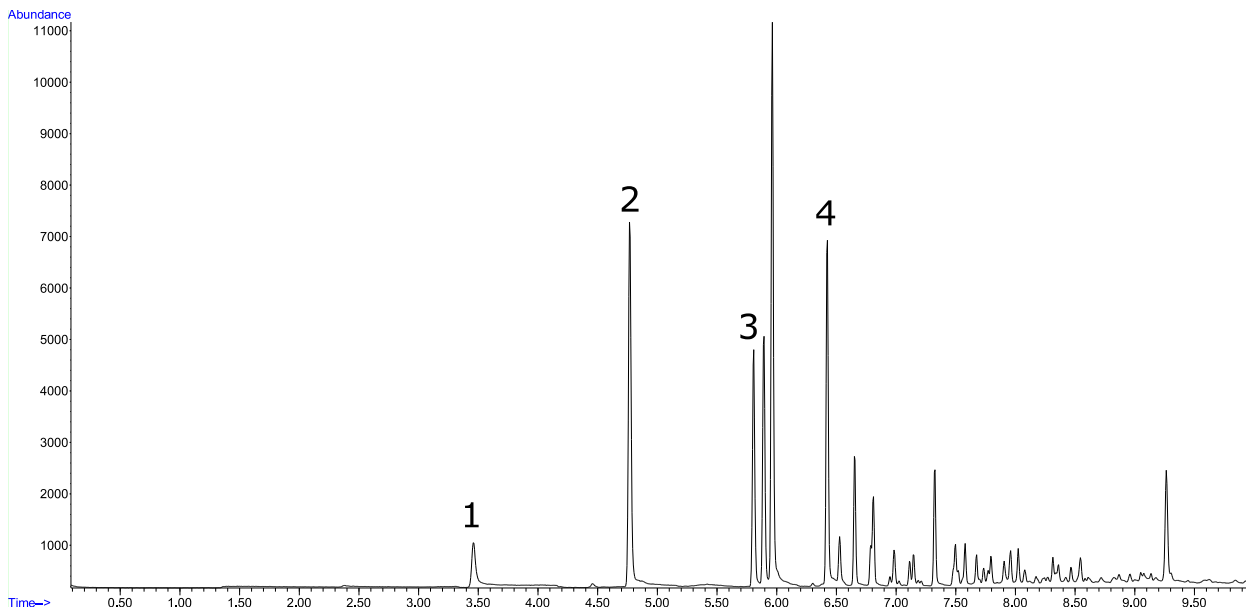
### 260 *3.1 Quantification of BTEX concentrations in ambient air of Almaty*

261 Developed method was applied to air samples in Almaty city. Examples of the analyzed  
262 air are presented in Fig. 2. Chromatograms of air samples had a high resolution of the relevant  
263 peaks (Fig. 2), signal to noise ratio being greater than 15:1 for all analytes in the studied samples.  
264 Mean concentrations (for all 18 air samples per all six locations) of benzene, toluene, ethylbenzene  
265 and *o*-xylene at different sampling periods ranged from 24 to 89, 32 to 96, 6 to 23 and 7 to 32

266  $\mu\text{g}/\text{m}^3$ , respectively. Average concentrations of BTEX compounds calculated as a mean of all 108  
 267 measurements were 53, 57, 11 and 14  $\mu\text{g}/\text{m}^3$ , respectively.

268

269



270

271

272 Figure 2 – Chromatogram of air sample collected at site S3 at 8 P.M. on April 2, 2015.

273

273 Note: 1 – benzene ( $36 \mu\text{g}/\text{m}^3$ ), 2 – toluene ( $67 \mu\text{g}/\text{m}^3$ ), 3 – ethylbenzene ( $12 \mu\text{g}/\text{m}^3$ ), 4 – o-xylene  
 274 ( $18 \mu\text{g}/\text{m}^3$ )

274

275

276

276 Table 5 – Mean concentrations of BTEX in air at different time periods and locations of Almaty  
 277 city

278

| Time of sampling > | Concentration $\pm$ Standard Deviation, $\mu\text{g}/\text{m}^3$ |             |              |             |             |             |             |             |              |             |             |
|--------------------|--|-------------|--------------|-------------|-------------|-------------|-------------|-------------|--------------|-------------|-------------|
|                    | 8:00 A.M.  |             |              | 8:00 P.M.   |             |             | Daily       |             |              | All         |             |
| Date of sampling > | March 31   | April 2     | April 4      | March 31    | April 2     | April 4     | March 31    | April 2     | April 4      |             |             |
| Benzene            | Mean   | 85 $\pm$ 23 | 89 $\pm$ 73  | 26 $\pm$ 10 | 63 $\pm$ 17 | 33 $\pm$ 10 | 24 $\pm$ 3  | 74 $\pm$ 23 | 61 $\pm$ 58  | 25 $\pm$ 7  | 53 $\pm$ 41 |
|                    | Max  | 122         | 237          | 37          | 88          | 51          | 27          | 122         | 237          | 43          | 237         |
|                    | Min  | 58          | 46           | 17          | 43          | 21          | 20          | 43          | 23           | 17          | 17          |
| Toluene            | Mean   | 43 $\pm$ 22 | 96 $\pm$ 195 | 46 $\pm$ 30 | 59 $\pm$ 41 | 62 $\pm$ 32 | 32 $\pm$ 13 | 51 $\pm$ 33 | 79 $\pm$ 134 | 39 $\pm$ 23 | 56 $\pm$ 80 |
|                    | Max  | 82          | 494          | 98          | 133         | 100         | 55          | 133         | 494          | 98          | 494         |
|                    | Min  | 26          | 10           | 24          | 18          | 22          | 19          | 18          | 10           | 19          | 10          |
| Ethylbenzene       | Mean   | 8 $\pm$ 3   | 23 $\pm$ 42  | 10 $\pm$ 8  | 13 $\pm$ 8  | 10 $\pm$ 4  | 6 $\pm$ 1   | 10 $\pm$ 7  | 16 $\pm$ 30  | 7 $\pm$ 4   | 11 $\pm$ 17 |
|                    | Max  | 13          | 108          | 20          | 27          | 17          | 7           | 27          | 107          | 20          | 107         |
|                    | Min  | 6           | 4            | 5           | 4           | 4           | 5           | 4           | 4            | 5           | 4           |
| o-Xylene           | Mean   | 9 $\pm$ 4   | 32 $\pm$ 66  | 10 $\pm$ 8  | 15 $\pm$ 10 | 13 $\pm$ 7  | 7 $\pm$ 2   | 12 $\pm$ 8  | 22 $\pm$ 46  | 8 $\pm$ 6   | 14 $\pm$ 27 |
|                    | Max  | 15          | 166          | 24          | 31          | 22          | 9           | 31          | 166          | 24          | 166         |
|                    | Min  | 6           | 3            | 5           | 3           | 4           | 4           | 3           | 3            | 4           | 3           |

279

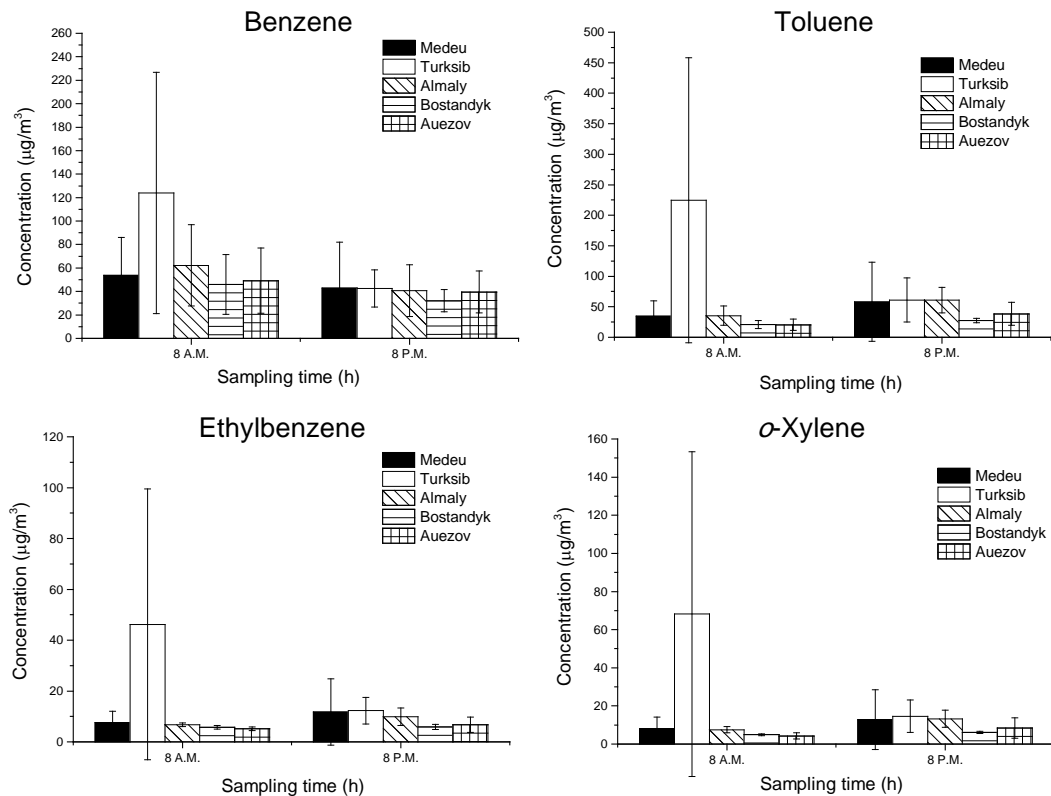
280

281 Concentrations of ethylbenzene and *o*-xylene were approx. one order of magnitude less  
 282 than those of benzene and toluene (Table 5), which may be explained by their lower stability in air  
 283 (Prinn et al., 1987), concentrations in a gasoline (Carlsen et al., 2013) and exhaust gases of cars  
 284 (Baimatova et al., 2015). Similar relationship between BTEX concentrations was also reported in  
 285 earlier studies (Baimatova et al., 2015).

286 Relative standard deviations of triplicate ambient air measurements did not exceed 25%  
 287 with most replicates being in the range of 10%, which is excellent and sufficient considering the  
 288 simplicity of the approach for sampling of ambient air. Over the whole study, only twelve misses  
 289 were found (<11% of total samples), likely caused by a damage of vial crimps and subsequent  
 290 leakage.

291 BTEX concentrations in air in five studied districts of Almaty (Medeu, Turksib, Almaly,  
 292 Auezov, Bostandyk) were different from each other (Fig. 3). The lowest concentrations of BTEX  
 293 were found in Bostandyk district, the largest - in Turksib district. Bostandyk district is situated in  
 294 upper (south) part of city, closer to mountains, where circulation of mountain-valley air is likely.  
 295 Turksib district is situated at the lower altitude, close to the city center, which is typically  
 296 overloaded with traffic jams and has a poor air circulation.

297



298

299

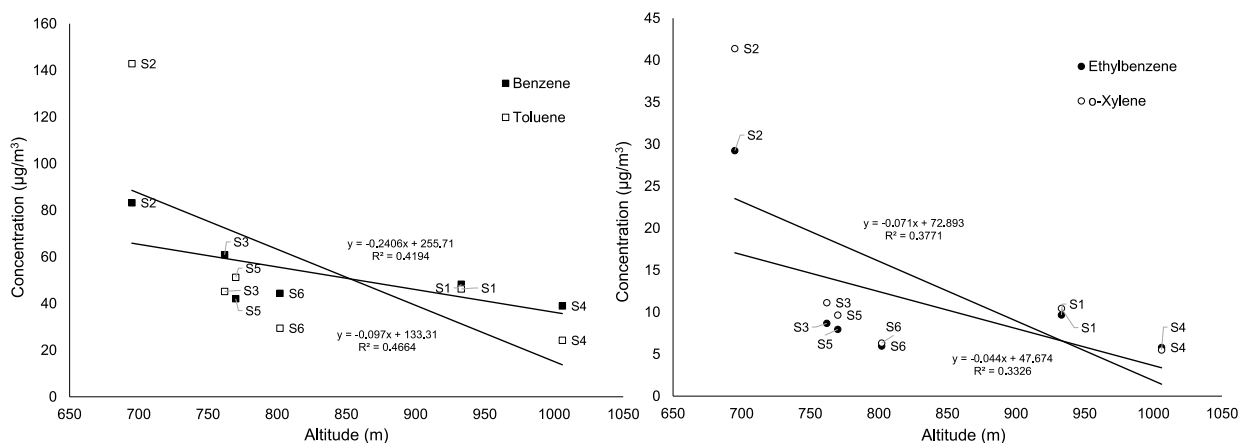
Figure 3 – BTEX concentrations in air of different districts of Almaty city

300

301 Daily mean BTEX concentrations (mean concentration for morning and evening sampling  
 302 periods and six locations at a single day) ranged from 25 to 74  $\mu\text{g}/\text{m}^3$ , 39 to 79  $\mu\text{g}/\text{m}^3$ , 7 to 16  
 303  $\mu\text{g}/\text{m}^3$ , and 8 to 22  $\mu\text{g}/\text{m}^3$ , respectively (Fig. A5 in SM). The lowest BTEX concentrations were  
 304 measured on Saturday (April, 4) likely due to higher temperature, improved air circulation in the  
 305 Almaty airshed and lower traffic. In addition, higher day-night air temperature differentials  
 306 encourage air exchange and speed up chemical reactions in the air.

307 BTEX concentrations are regulated all over the world (Table 1). Concentrations of BTEX in  
 308 Almaty, Kazakhstan are close to reported concentrations of BTEX in cities with major air quality  
 309 problems such as New Delhi, Cairo, Rome, Ho Chi Minh City, Sao Paulo, or Manila (Table 1)  
 310 where vehicle exhausts are the main sources of BTEX, such as in Almaty (Balanay and Lungu,  
 311 2009; Carlsen et al., 2013). The main difference of Almaty from these cities is a climate requiring  
 312 efficient heating system in October-April. In Almaty, substantial part of pollution (about 20%)  
 313 originate from emission of power plants and private residential heating systems (Carlsen et al.,  
 314 2013).

315 BTEX concentrations were inversely proportional to the altitude of the sampling sites (Fig.  
 316 4). In the upper, southern part of Almaty (closer to the mountains), concentrations of BTEX were  
 317 slightly lower than those at the lower parts (Table A3 in SM, due to the absence of major industrial  
 318 factories and wind direction from the mountains downward towards the city. The average elevation  
 319 of the upper part of the city is 1,000 meters. At that altitude, there are more deciduous and  
 320 coniferous trees and herbs, which may absorb hydrophobic BTEX (Kolmakov, 2015).



321

322

323

Figure 4 – Effect of altitude on measured BTEX concentrations

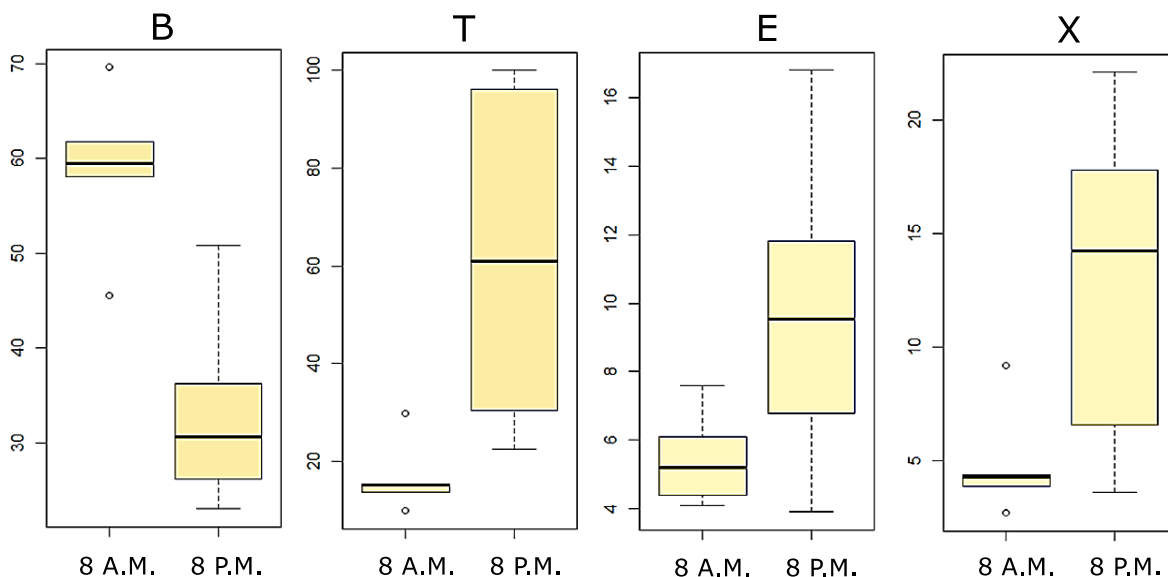
324

325 *3.2 Statistical analyses of BTEX concentrations – effects of time of day, sampling day, and*  
 326 *location*

327 ANOVA studies were performed applying the R statistical software (R Core Team, 2015).  
328 There was no statistically significant difference between the single sampling sites. Thus, we  
329 focused on (1) daily variation between morning and evening samplings and (2) day-to-day  
330 variation mornings and evenings. Considering weather conditions for each sampling day, it is  
331 apparent that the three days are not identical. As shown in Table 2, sampling days were  
332 significantly different (Kazhydromet, 2015).

333 Hence, in the case of benzene we found statistical significance for concentration decreases  
334 from 8 A.M. to 8 P.M. for day 1 and day 2, whereas for day 3 virtually no change in the benzene  
335 concentration during the day was observed. For toluene, ethylbenzene and *o*-xylene, the median  
336 values were higher in the evening than in the morning. However, only for day 2 statistical  
337 significance was observed between morning and evening concentrations. For day 2, there was a  
338 snowfall in the morning and the occurrence of traffics jams was observed throughout the city.  
339 Thus, benzene concentrations were significantly lower at 8 P.M. than those at 8 A.M. (95% level,  
340  $p=0.0013$ ) (Fig. 5A), whereas concentrations of toluene (Fig. 5B), ethyl benzene (Fig. 5C) and *o*-  
341 xylene (Fig. 5D) were all higher in the evening (95%,  $p=0.015$ , 90%,  $p=0.070$ , and 95%,  $p=0.037$ ,  
342 respectively). For day 3, benzene concentrations were lower in the evening (weak statistical  
343 significance at the 90% level,  $p=0.098$ ). On day 1, it was sunny and later snowing overnight. Next  
344 sampling day, the weather became warmer, temperature of air from day 1 to day 3 varied from -  
345  $10/-4$  °C to  $+4/+11$  °C (Table 2).

346



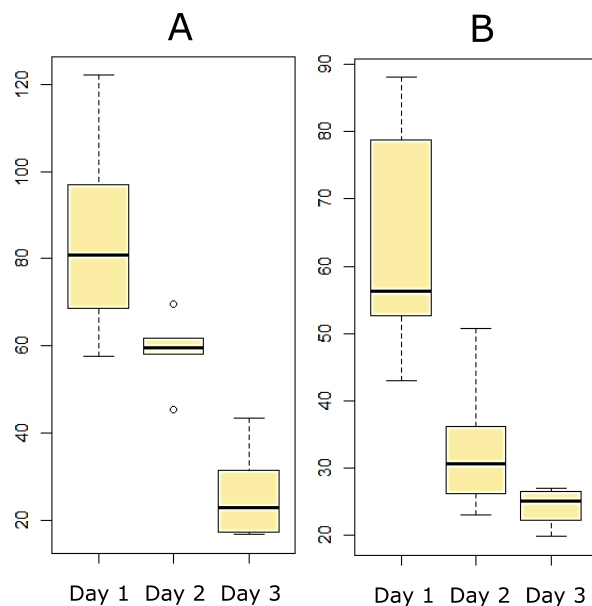
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348

349 Figure 5 – Variation in concentrations of B: benzene, T: toluene, E: ethyl benzene and X: *o*-  
350 xylene between morning (8 A.M.) and evening (8 P.M.)

351

352 Day-to-day variations were significant. Thus, both for the 8 A.M. (Fig. 6A) and the 8 P.M.  
 353 (Fig. 6B) samplings benzene concentrations were significantly decreasing from day 1 to day 2 (8  
 354 A.M.: 95% level,  $p_{\text{day 1, day 2}} = 0.046$ , 8 A.M.: 95% level  $p_{\text{day 2, day 3}} = 3.2e-4$ ) and further to day 3 (8  
 355 P.M.: 95% level,  $p_{\text{day 1, day 2}} = 0.0046$ , 8 P.M.: 90% level  $p_{\text{day 2, day 3}} = 0.067$ ). In the cases of toluene,  
 356 ethyl benzene and *o*-xylene the 8 A.M. concentrations were found to drop from day 1 to day 2 and  
 357 the increase again to days 3, whereas for the 8 P.M. samplings non-statistically significant  
 358 decreases were observed from day 1 to day 2 and further to day 3. Further data will be necessary  
 359 for more in-depth analyses, e.g., including variations from location to location, which based on the  
 360 available data is not possible.



361

362

Figure 6 – Day-to-day variation of benzene. A: 8 A.M., B: 8 P.M.

363

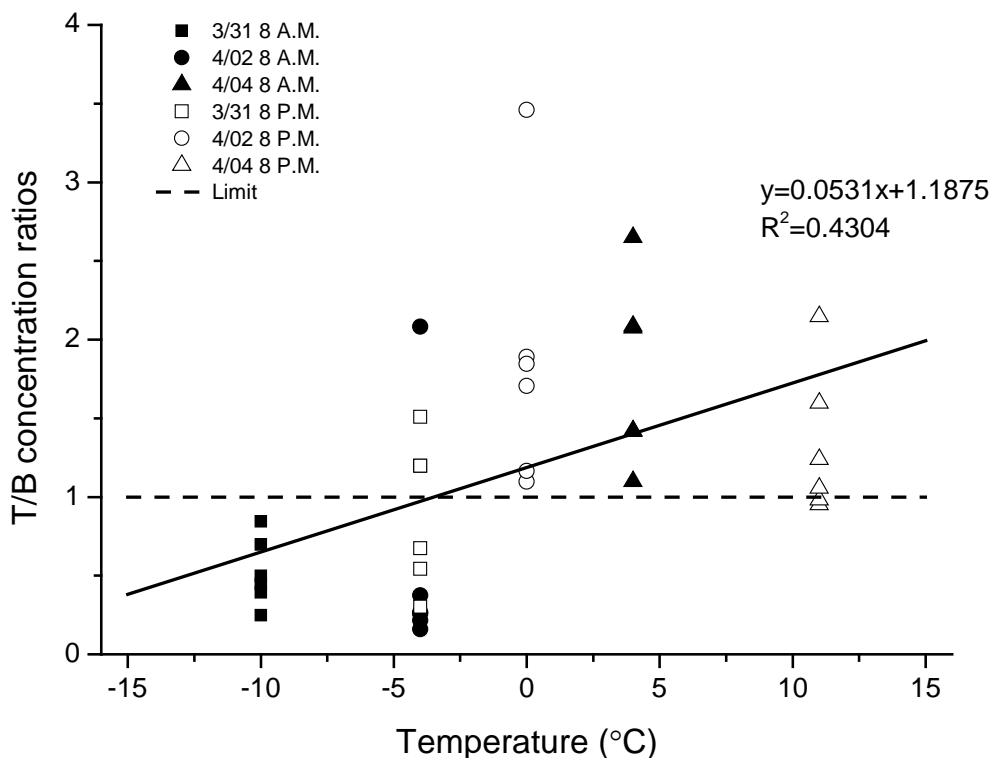
### 364 3.3 Identification of BTEX emission sources

365 Toluene to benzene concentrations (T/B) ratio depends on the main source of air pollution,  
 366 distance from the source and environmental conditions (Guo et al., 2007; Kerbachia et al., 2006;  
 367 Khoder, 2007). The T/B ratio in the studied air samples increased with the increase of the air  
 368 temperature (Figure 7). Five measurements provided T/B ratios higher than 2. The highest T/B  
 369 ratio (3.4) was observed in Turksib district. At sub - 0 °C sampling temperatures, the T/B ratio  
 370 was below 1 in 15 out of 18 samples. Such ratios may indicate that significant fraction of BTEX  
 371 originate from non-traffic related sources (Liu et al., 2015; Moreira dos Santos et al., 2004). At  
 372 lower temperatures, residential heating is likely the main source of BTEX. In Almaty, most power  
 373 plants and private houses use natural gas and coal as fuel. On Saturday evening, in half of all  
 374 sampling locations, the T/B ratio was close to 1. This may be due to the proximity of these locations  
 375 to districts with private houses, where on Saturdays local people traditionally prepare their own



376 saunas for steaming and washing. In addition, the amount of traffic on the weekend is much lower  
377 compared to weekdays.

378 Thus, the bulk of BTEX emissions in Almaty originate both from traffic and residential  
379 heating. The obtained results indicate that at lower temperatures, more BTEX likely originate from  
380 heating while at higher temperatures – from traffic. These results are in agreement with our  
381 previous data indicating that end of heating season in Almaty correlated with decreased BTEX  
382 concentrations in ambient air by the factor of 3 to 5 (Bektasov et al., 2015). However, more  
383 research is required to confirm this finding.



384

385 Figure 7 – Toluene/Benzene concentration ratios at different sampling sites and sampling days  
386 and times

387

### 388 Conclusion

389 The main results of this research are as follows:

- 390 – Simple whole air sampling method for BTEX was developed utilizing crimped vials,  
391 SPME and GC-MS. For quantification of BTEX, external standard methods was used; however  
392 slope factors of calibration plots were determined by a standard addition method, which did not  
393 require a “zero” air. Measurement errors were low considering the simplicity of collection method.  
394 New method can be a good alternative for low-budget air quality monitoring for BTEX. Adding  
395 new target VOCs of concern to urban air quality is possible with this method. The optimized

396 approach based on SPME-GC-MS appears as an attractive alternative for air pollutants monitoring  
397 in developing countries. Further improvement could require reducing the detection limit, which is  
398 possible by using a shorter GC column or more selective & sensitive detector, such as a triple  
399 quadrupole MS. It is also possible to increase the effectiveness of SPME fiber by using 20 mm  
400 fiber length.

401 – At different sampling times, mean concentrations of benzene, toluene, ethylbenzene  
402 and *o*-xylene in ambient air samples from Almaty, Kazakhstan ranged from 24 to 89, from 32 to  
403 96, from 6 to 23 and from 7 to 32  $\mu\text{g}/\text{m}^3$ , respectively. Lowest BTEX concentrations were  
404 determined on Saturday due to higher temperature and lower traffic. Mean BTEX analyte  
405 concentrations over all locations and sampling periods were 53, 57, 11 and 14  $\mu\text{g}/\text{m}^3$ , respectively,  
406 being comparable with those in the most polluted cities around the world. Further research of  
407 greater scope and duration is warranted. Several aspects deserve more work, e.g., diurnal and  
408 seasonal variations, and addition of other primary air pollutants (e.g., PM-10, PM-2.5, SO<sub>x</sub>, NO<sub>x</sub>,  
409 CO, and ozone. Our earlier work (Carlsen et al., 2013) showed the presence of PAHs. Caution  
410 should be exercised when interpreting results that stem from this relatively short in duration air  
411 quality survey. More research that focuses on long-term (e.g., all seasons), weekday vs. weekend,  
412 and diurnal variations is warranted. Specific focus on the effects of elevation (and therefore  
413 location within the city), atmospheric inversions, wind direction, and levels of other important air  
414 pollutants such as PM, CO, SO<sub>x</sub>, NO<sub>x</sub>, ozone, and PAHs should be studied.

415 – Single BTEX concentrations in ambient air of Almaty were always below local  
416 regulatory thresholds. However, these thresholds are not very useful because: 1) they were  
417 established >15 y ago and have not been updated since then; 2) they are much higher than those  
418 for many other countries. The review and update of air quality standards is recommended  
419 considering ancillary public health reports from the region.

420 – ANOVA studies showed that measured benzene concentrations dropped significantly  
421 from the 8 A.M. sampling to the 8 P.M. sampling, whereas the reverse was observed for  
422 concentrations of toluene, ethylbenzene and xylene possibly due to lower vapor pressures and a  
423 high tendency to bind to a particular matter.

424 – A significant day-to-day variation was found. For both the 8 A.M. and the 8 P.M.  
425 samplings, benzene concentrations significantly dropped from day 1 to day 2 and further to day 3,  
426 whereas for toluene, ethyl benzene and *o*-xylene a concentrations were observed to decrease from  
427 day 1 to day 2 and then increase again on day 3. These variations are not immediately  
428 understandable but are assumed to be due to changing weather conditions in combination with  
429 BTEX vapor pressure differences and their affinity to bind to a particulate matter.

430 – The T/B ratios varied depending on a sampling temperature. At lower (below 0 °C)  
431 temperatures, T/B ratios were mostly below 1 meaning that significant fraction of BTEX originate  
432 from residential heating. At higher temperatures, the T/B ratios were mostly higher than 1  
433 indicating that BTEX originate from traffic. More research over longer time periods is needed to  
434 confirm these findings.

435 It is recommended that coordinated research, regulations, and education work towards the  
436 decrease of BTEX concentrations and improving overall air quality in Almaty begins. There are  
437 many good examples of how elevated levels of air pollutants were lowered using civic involvement  
438 and multi-agency approach. More stringent car exhausts emission and fuel quality control, public  
439 awareness, education, and incentivizing technological and behavioral changes can work.

440

#### 441 **Supporting information**

442 Additional information as noted in the text. This information is available free of charge.

443

#### 444 **Conflict of interest**

445 The authors declare no competing financial interests.

446

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449 4185/GF4 “Development of semi-automatic station for monitoring concentrations of volatile  
450 organic contaminants in ambient air of cities using chromatographic methods”.

451

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