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Spatial and temporal variability of BTEX in Paris megacity: Two-wheelers as a major driver

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A R T I C L E   I N F O

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BTEX
Fuel composition
Two-wheelers
Emission ratios

A B S T R A C T

Besides their impacts on health, BTEX play an important role in the formation of secondary organic aerosols and ozone for which limit values are regularly exceeded in Paris megacity and Ile de France region. An enrichment by a factor of 3 in the C7−C9 aromatic fraction in the Paris atmosphere compared to other northern mid-latitude cities was shown in 2013. Here, we combined different approaches to investigate the role of transport-related sources in such enrichment (gasoline composition and vehicle fleet composition): a statistical analysis of a large BTEX dataset including multi-year and multi-site measurements (traffic, background, tunnel) and a coupled experimental and modelling analysis of liquid and headspace composition of representative fuels distributed in Ile de France region (SP95, SP95 E10, and SP98). For the latter the experimental set-up was designed to analyze the composition of 67 VOCs from C2 to C17 in both liquid and headspace phases. The model is able to predict the headspace composition at ± 15% and with an R² > 0.9. First a strong positive spatial gradient in BTEX composition at traffic stations is observed, with higher TEX-to-benzene ratio in Paris center compared to the suburbs and outskirts up to a factor of 2. This gradient reflects differences in fleet composition especially gasoline powered vehicles in Paris with a larger proportion of two-wheelers (15% in 2012). This gradient is also consistent with the inter-annual increase of TEX-to-benzene ratios along with the doubling of two-wheelers use and the decrease in the number of passenger cars. The gasoline evaporation model cannot solely explain the observed spatial variability. Finally, we investigated the potential contribution of two-wheelers to the aromatic enrichment in IDF region by introducing an additional unburned gasoline term to the model. The results support the suggestion that two-wheelers are a potential contributor to this enrichment. Considering the high use of two-wheelers in other European cities such as London or Barcelona if Europe is to decrease transport-related air pollution and inner city traffic, policy makers should consider finding alternatives to the conventionally-powered two-wheelers and supporting electric two-wheelers for example.

1. Introduction

The 20th century was marked by fast growing urbanization phenomena. The higher income concentrated in urban areas is a major cause of urban growth (Baklanov et al., 2016). Nowadays, more than half of the world’s population lives in urban areas (UN, 2012). As a result, the air pollution levels are usually high in these urban areas with a population above 10 million inhabitants called “megacities” (Gurjar and Lelieveld, 2005). The emissions as well as the ambient concentrations of pollutants in megacities can have widespread effects on the population health, urban and regional haze, visibility impairment and ecosystem degradation (Baklanov et al., 2016).

Consequently, air quality monitoring has extended over the last decades beyond the criteria pollutants like carbon monoxide, oxide of nitrogen, ozone, and particulate matter to include measurements of other air pollutants such as volatile organic compounds (VOCs) (Lee et al., 2002). VOCs play an important role in the formation of ozone and photochemical oxidants associated with urban smog (Seinfeld and Pandis, 2006). Studies have focused on the urban levels of VOCs, especially aromatics, due to the known and suspected carcinogenic
nature of these species. Besides their impacts on health, mono-aromatic compounds the so-called BTEX (Benzene, Toluene, Ethylbenzene, and o, m,p-Xylenes) play an important role in the formation of ozone (Carter, 1994) and secondary organic aerosols (Henze et al., 2008). On a global scale, anthropogenic VOCs, typically substituted aromatics (mainly toluene and xylenes), are estimated to contribute to the formation of 1.4–8.6 TgC/yr of SOA (Henze et al., 2008). Moreover, the contribution of individual VOC groups to aerosol concentrations in Los Angeles was estimated to be approximately 62% from aromatics, 13% from biogenic monoterpenes, 18% from alkanes, and 7% from alkenes (Grosjean and Seinfeld, 1989).

Paris and its surrounding region called “Ile de France” is a mid-latitude post-industrial megacity with 10.6 million inhabitants in 2011 (Baklanov et al., 2016). It was found that the ozone production potential over the urban area of Paris is VOC-sensitive over two summers (Deguillaume et al., 2008). Benzene, an important representative of aromatic hydrocarbons, has been a prime target for air quality assessment in the urban atmosphere (Brocco et al., 1997) as it is considered to be a genotoxic carcinogen (WHO, 2000; Bolden et al., 2015).

BTEX are generally compounds associated with traffic emissions (exhaust and fuel evaporation) and TEX can also be released with/by the use of solvents (painting, printing, etc.) (Baudic et al., 2016; Salameh et al., 2014). They constitute an important part of non-methane VOCs in urban areas; in Paris, they account for 24% of the total mass of VOCs but represent 49% of the ozone formation potential (Gros et al., 2011).

While VOC composition is usually consistent between post-industrialized urban cities, a recent study has shown enrichment in the C7–C9 aromatic fraction in Paris atmosphere by a factor of 3 compared to other European cities (Borbon et al., 2013) including French urban areas (Boynard et al., 2014). Based on the potential sources of BTEX from the literature and according to Borbon et al., (2013), the causes of such enrichment would be: (i) differences in gasoline composition, (ii) differences in vehicle fleet composition and role of two-wheelers in particular, and (iii) differences in solvent use related sources. Recent work by Borbon et al. (2018) have shown that traffic emissions were still dominating TEX concentrations in Paris. This paper explores the validity of the remaining hypotheses. Note that in Europe, benzene concentration in fuels is restricted to 1% (volume) since 2000 (Directive 98/70/CE, 1998). The two-wheelers are known as large emitters of gaseous aromatics (Saxer et al., 2006; Costagliola et al., 2014; Platt et al., 2014; Li et al., 2015) compared to other VOCs. In Paris, they would contribute to 47% of road transport VOC emissions in 2010 by the local emission inventory (AIRPARIF, 2013). Indeed the vehicle fleet in Paris includes 15% of two-wheelers in 2012, which is the highest in France, compared to 8% in 2002; in outskirts, the two-wheelers represented 7% in 2012 compared to 4% in 2002 (AIRPARIF, 2013). In opposite, the number of passenger cars has decreased by 4.5% in Paris between 2011 and 2014. Nearly 9% of households in the Ile de France region have one or more two-wheelers they use to go to work. Similar trends of two-wheelers are seen in other parts of Europe: in Barcelona, 34% in 2012 against 24% in 2002; in London 18% in 2011 against 6% in 2000 (Dall'Osto and Querol, 2013).

Here, we combined different dataset and different approaches to analyze the spatial and temporal variability of BTEX in Ile de France region. Such analysis is to provide indication about the origin of BTEX and the potential role of two-wheelers:

- a statistical analysis of a large VOC dataset including multi-season, multi-year and multi-site speciated measurements (traffic, background, tunnel) by the air quality network AIRPARIF.
- a coupled experimental and modelling analysis of liquid and head-space composition of representative fuels distributed in Ile de France region (SP95, SP95 E10, and SP98) is used in order to study the potential impact of the gasoline emissions.

2. Methodology

2.1. Ambient observations and consistency tests

Ambient observations include on-line and off-line techniques at several sites and at different time resolution. In 2001, a long-term monitoring program for VOCs was initiated in France by ADEME (Agence de la Maîtrise de l’Energie et de l’Environnement) and the French Ministry of the Environment. As part of this program, one urban background site in Paris called “Les Halles” was implemented with an online TD-GC-FID (thermo-desorption unit Gas Chromatograph coupled to a Flame Ionization detector) for hourly measurements of 31 NMHCs belonging to the European ozone precursor priority list (Badol et al., 2004; Boynard et al., 2014; Borbon et al., 2018), and operated by the local Air Quality Monitoring Network (AASQA), AIRPARIF. Since 2011, the sampling site was changed to “Siége AIRPARIF” because of public works at “Les Halles” site. The monitoring station of “Les Halles” is located in a small park where the closest busy road is about 100 m distant whereas the “Siége AIRPARIF” site is located at the rooftop of the “AIRPARIF” building surrounded by high density of commercial and residential premises as well as vehicular activities. A traffic site at “Boulevard périphérique - Auteuil” was also implemented for on-line monitoring of BTEX from 1999 to 2011. The site is located along Paris ring-road with 226 000 vehicles per day. Finally, in 2000 AIRPARIF has implemented 15 monitoring sites (7 urban background and 8 traffic sites) for BTEX daily or weekly active sampling with sorbent tubes (Carboxypack X) (Fig. 1 and Table 1 in the supplemental material).

A systematic quality assurance and quality control procedure (Badol et al., 2004; Boynard et al., 2014) was integrated to the measuring systems in order to insure the quality of the data. This procedure consists of regular checks of NMHC response factors by the use of certified calibration standards, control charts based on chromatographic retention times, the identification of missing values, and observations below the method detection limit. The measurement uncertainty of the BTEX was in the range of 7.4–10.8% for off-line measurements and in the range of 3.6–5.2% for hourly online measurements (Badol et al., 2004).

Additionally, consistency tests based on the correlation between isomers like m,p-xylene and o-xylene, with same sources and atmospheric lifetime (for o-xylene and p-xylene), have been applied. A strong correlation is observed between these species with a coefficient of determination $r^2 > 0.9$ for online hourly data, daily, and weekly offline data separately.

Before analyzing the variability, a special attention was paid to the consistency between online and offline techniques which are operated at different time resolutions (online hourly, offline daily and weekly). We evaluated the effect of the time resolution on the concentrations by correlation analysis at the urban background site “Les Halles” for which on-line hourly data from 2003 until 2010, daily offline data from 2003 to 2008, and weekly offline data in 2009 and 2010 are available (Table 1, Fig. 2 in the supplemental material). The comparison of hourly data to daily data is satisfactory with a slope at $\pm 12\%$ on average from unity (ppbv/ppbv) and an average $r^2$ of 0.80. Daily sampling is still able to capture the diurnal variability. However, the comparison of hourly data to weekly data in 2009 and 2010 shows some differences with generally lower $r^2$. For benzene, the comparison is still good and does not change from the hourly versus weekly one. For $> C_6$-aromatics, differences can reach a factor of 50% and the $r^2$ values are lower (0.20-0.70) (Table 1).

The composition of TEX and benzene urban enrichment ratios with different temporal resolutions (hourly and weekly) also shows this difference > 40% in 2009 and 2010. First reason is due to the limited number of points when downscaling hourly data to the weekly especially when we have high hourly values as in 2009. Second reason could be the smoothing of the offline data when integrating observations over one week. Finally, weekly sampling does not capture the day-to-day variability of aromatics. We will therefore pay attention to the time resolution of the dataset when analyzing the spatial variability. While hourly
2.2. Determination of urban enhancement ratios

We applied a commonly used method to determine urban enhancement ratios (ER) (Warneke et al., 2007; Borbon et al., 2013; Salameh et al., 2017) by estimating the slope of a least-square linear regression fit between two compounds, one TEX vs. benzene, depending on the availability of the data at each site and by taking into account the time resolution of the dataset. By using ER, the species are not affected by the background and not sensitive to dilution and air-mass mixing compared with absolute concentrations themselves (Parrish et al., 2007; Salameh et al., 2015). While the effect of photochemical removal cannot be excluded in Paris for the most reactive TEX, Borbon et al. (2013) have shown that there is no evidence of its effect from their diurnal profiles.

The impact of photochemistry on TEX concentrations was pointed out in the Paris plume explored by the ATR-42 aircraft during the MEGAPOLI campaign at a least/minimum distance of 50 km from the urban center which is not the case of the considered sites in this study. Adding to that, Boynard et al. (2014) compared nighttime and daytime datasets in Paris (Les Halles site) for both summer and winter and the comparisons

and daily data sets could be easily combined, the weekly one should be considered independently.

2.2. Determination of urban enhancement ratios

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Table 1

Intercomparison of BTEX hourly (online 2003–2010), daily (offline 2003–2008), and weekly (offline 2009 & 2010) concentrations (ppbv) at « Les Halles » site (b is the y-intercept in ppbv).

<table>
<thead>
<tr>
<th></th>
<th>2003</th>
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<td></td>
<td>daily vs. hourly</td>
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<td><strong>Benzene</strong></td>
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<tr>
<td>Slope</td>
<td>1.15</td>
<td>1.03</td>
<td>1.00</td>
<td>1.13</td>
<td>1.23</td>
<td>0.84</td>
<td>0.90</td>
<td>1.15</td>
</tr>
<tr>
<td>b</td>
<td>0.08</td>
<td>0.02</td>
<td>0.03</td>
<td>0.06</td>
<td>0.12</td>
<td>0.01</td>
<td>0.09</td>
<td>0.04</td>
</tr>
<tr>
<td>r²</td>
<td>0.85</td>
<td>0.77</td>
<td>0.83</td>
<td>0.87</td>
<td>0.78</td>
<td>0.71</td>
<td>0.60</td>
<td>0.69</td>
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<td><strong>Toluene</strong></td>
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</tr>
<tr>
<td>Slope</td>
<td>1.13</td>
<td>0.98</td>
<td>1.04</td>
<td>1.16</td>
<td>0.93</td>
<td>0.89</td>
<td>0.42</td>
<td>0.89</td>
</tr>
<tr>
<td>b</td>
<td>0.13</td>
<td>0.23</td>
<td>0.25</td>
<td>0.09</td>
<td>0.12</td>
<td>0.22</td>
<td>0.73</td>
<td>0.30</td>
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<tr>
<td>r²</td>
<td>0.84</td>
<td>0.64</td>
<td>0.61</td>
<td>0.85</td>
<td>0.87</td>
<td>0.62</td>
<td>0.21</td>
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<td><strong>Ethylbenzene</strong></td>
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<tr>
<td>Slope</td>
<td>1.17</td>
<td>0.83</td>
<td>1.00</td>
<td>1.07</td>
<td>0.91</td>
<td>0.70</td>
<td>0.47</td>
<td>0.96</td>
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<tr>
<td>b</td>
<td>0.02</td>
<td>0.05</td>
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<td>0.01</td>
<td>0.01</td>
<td>0.05</td>
<td>0.09</td>
<td>0.04</td>
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<tr>
<td>r²</td>
<td>0.82</td>
<td>0.73</td>
<td>0.83</td>
<td>0.80</td>
<td>0.86</td>
<td>0.46</td>
<td>0.20</td>
<td>0.69</td>
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<tr>
<td><strong>m,p-xylene</strong></td>
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<tr>
<td>Slope</td>
<td>1.10</td>
<td>0.78</td>
<td>0.90</td>
<td>0.88</td>
<td>0.83</td>
<td>0.76</td>
<td>0.37</td>
<td>0.80</td>
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<tr>
<td>b</td>
<td>–0.11</td>
<td>0.11</td>
<td>0.14</td>
<td>0.01</td>
<td>–0.04</td>
<td>0.15</td>
<td>0.34</td>
<td>0.16</td>
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<tr>
<td>r²</td>
<td>0.82</td>
<td>0.77</td>
<td>0.80</td>
<td>0.79</td>
<td>0.87</td>
<td>0.48</td>
<td>0.18</td>
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<td><strong>o-xylene</strong></td>
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<tr>
<td>Slope</td>
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<td>0.76</td>
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<td>1.01</td>
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<td>0.68</td>
<td>0.27</td>
<td>0.84</td>
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<tr>
<td>b</td>
<td>–0.04</td>
<td>0.03</td>
<td>0.05</td>
<td>0.00</td>
<td>0.00</td>
<td>0.06</td>
<td>0.17</td>
<td>0.07</td>
</tr>
<tr>
<td>r²</td>
<td>0.81</td>
<td>0.75</td>
<td>0.75</td>
<td>0.77</td>
<td>0.84</td>
<td>0.43</td>
<td>0.07</td>
<td>0.63</td>
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</tbody>
</table>
showed that the daytime and nighttime scatterplots agree pretty well for both seasons indicating that ER are not affected by photochemistry.

2.3. Laboratory experiments

In order to analyze the liquid and headspace composition of fuels, we collected three representative types of unleaded gasoline distributed in ‘Ile de France’ region, in spring (April) 2015: gasoline without oxygenates (research octane number = 95; SP95), gasoline with ethanol (SP95 E10), and premium gasoline (research octane number = 98; SP98). According to the French Ministerial Order of 23 December 1999, on the characteristics of the premium unleaded gasoline, the gasoline samples collected in April 2015 correspond to the inter-season class of volatility named “D1+A”.

Each gasoline sample was transferred to a glass vial with a plastic screw cap and a Teflon-lined septum.

For the headspace analysis, the system consists on a supply of zero air at a flow rate of hundred milliliters per minute above the glass capillary inserted in the septum and connected to the fuel sample. A Tee connector allows another dilution of the sample with zero air before injection into the GC-FID analytical system. Once injected, the sample is pre-concentrated on a cold multi-sorbent trap (Tenax and glass beads) at −135 °C. Then the trap is heated at 120 °C and the sample passes along a second additional cold trap of Tenax at −55 °C where it is cooled and then heated at 180 °C. Finally, the sample reaches a third trap where a flow of liquid nitrogen at −200 °C passes, then the sample is heated at 150 °C. The compounds are desorbed and injected into the GC for separation and analysis with the FID detector. The separation is performed using a dual capillary column system of Al2O3/KCl (39 m × 0.32 mm x 5 μm) for C2—C5 and CPSil 5CB (50 m × 0.32 mm x 1.2 μm) for C6—C10 belonging to alkanes, alkenes, alkynes and aromatics. We analyzed the same sample at least 4 times to test the repeatability of the results and the coefficients of variation were below 2% for the main VOCs.

For the liquid phase analysis, we diluted 10 times the fuel samples of 0.5 mL with pure methanol. Then, we used a syringe of 1 μL to inject the fuel into the injector and oven at a temperature of 150 °C for 3 min at a pressure of 8 psi. The liquid injection allows the vaporization of the entire sample in a thermostatic chamber and then it will be introduced directly into the chromatographic column by a carrier gas. We performed the active sampling on Tenax TA tubes allowing the adsorption of C5 to C17 VOCs. The tubes were then analyzed by GC-FID-MS (MS: Mass Spectrometry) equipped with a Restek Rtx-1 column (105 m × 320 μm x 1.5 μm). The VOCs were separated according to the following temperature programming: 35 °C from 0 to 5 min; then at 1 °C/min from 5 to 105 min (135 °C); then at 5 °C/min from 105 to 125 min (250 °C) and the temperature was maintained at 250 °C for 7 min. The total run time was 135 min.

2.4. Prediction of the headspace vapor composition

Headspace compositions of ideal mixtures can be predicted using the fuel’s composition and Raoult’s law, which gives the partial pressure as:

\[ P_i^{\text{mix}} = x_i \times P_i^{\text{pure}} \quad (1) \]

Where \( x_i \) = mole fraction of compound \( i \) in liquid fuel, and \( P_i^{\text{pure}} \) is vapor pressure of compound \( i \) in pure liquid (mmHg) at temperature \( t \) (°C). \( P_i^{\text{pure}} \) is calculated at temperature \( t \) using the Antoine equation (2):

\[ \log(P_i^{\text{pure}}) = a - (b/(c + t)) \quad (2) \]

Where \( a, b \) and \( c \) are Antoine constants. This approach was used for SP95 and SP98.

Ethanol exhibits non-ideal behavior in solution with non-polar hydrocarbons (Bennett et al., 1993; Harley and Coulter-Burke, 2000). Activity coefficients \( \gamma_i \) are used to account for interactions:

\[ P_i^{\text{mix}} = \gamma_i \times x_i \times P_i^{\text{pure}} \quad (3) \]

In the present study, the vapor composition of gasoline SP95 E10 (with 10% ethanol) is predicted using the coefficients calculated by Harley and Coulter-Burke (2000), the measured fuel composition, and equation (3).

By applying this model, based on the mole fraction of VOCs in the liquid phase, we will be able to deduce the mole fraction of each compound in the gas phase in equilibrium with the liquid phase.

3. Results and discussion

3.1. Meteorological conditions

The meteorological parameters were measured at Montsouris Park and Nation station in Paris. The average temperature at both sites in winter varies between 4 °C and 8 °C, around 13 °C in spring and summer, and is higher in summer reaching 20 °C. The wind speed at both sites is around 3 m/s, varying from 2.5 m s\(^{-1}\) to 3.4 m s\(^{-1}\), and the wind rose is uniform in Paris under mainly westerly regime, south-west and north north-east directions. Therefore, the sites are mainly influenced by the urban emissions from Paris megacity (Baudic et al., 2016).

3.2. III-2 spatial variability

It is important to capture local-scale spatial variability, which cannot be accomplished by one site central monitoring station or by one intensive measurement campaign, in order to investigate how the atmospheric composition for BTEX is distributed within Ile de France region. Generally, many factors can influence the spatial distribution like the proximity to roads, industries, etc. (Miller et al., 2011), meteorology, and

Fig. 2. Seasonal variability of toluene/benzene urban enhancement ratio (ppbv/ppbv) at a traffic site at Auteuil and at an urban background site at les Halles.
photochemical depletion. The sites implemented by AIRPARIF are not directly influenced by industrial emissions, they include urban background and traffic sites and the comparison is separated accordingly.

The sum of BTEX average concentrations by taking into account the different temporal resolutions (hourly/daily/weekly), at traffic and urban background sites in Paris intramuros, in the outskirts, and in the suburbs are presented in Fig. 1. Among the traffic sites, Place Victor Basch presents the highest sum of BTEX (15.45 ppbv for 2000–2008 on daily measurements basis, and 8.31 ppbv from 2009 to 2014 on weekly measurements basis) followed by Auteuil and Place de l’Opéra. Most of the traffic sites around the outskirts and the suburbs show lower BTEX sum below 5 ppbv. According to Fig. 1, the BTEX sum at traffic sites exhibits a relatively high spatial variability depending on the site location. This is not true at the urban background sites where all of them have a BTEX sum below 5 ppbv, varying between 1.39 ppbv and 2.67 ppbv. The corresponding speciation of BTEX sum annual concentrations over the available measurement years with different temporal resolution at the traffic and urban background sites is detailed in Table 2.

The annual concentrations over the available measurement years, at traffic sites for benzene range between 0.42 in the suburbs and 1.75 ppbv at Place Victor Basch in Paris, with an average of 0.78 ± 0.39 ppbv (Table 2). At urban background sites, the benzene annual concentrations range between 0.28 in the outskirts and 0.53 ppbv in Paris intramuros with an average of 0.36 ± 0.08 ppbv. Toluene shows for 50% of the sum of BTEX average concentrations at both traffic and urban background sites. TEx show higher levels also at the traffic sites than at the urban background sites by a factor of 2.4–2.6. Toluene shows the highest concentrations with a maximum of 8.01 ppbv at Place Victor Basch whereas at the urban background sites, the maximum reaches 2.40 ppbv in Paris 13ème. The coefficient of variation of all BTEX ranges between 30 and 50% at the traffic sites with weekly measurements only and between 50 and 70% at all the traffic sites; while at the urban background sites it ranges between 20% when considering sites with weekly measurements and 50% when considering all the sites.

3.3. Comparison of concentration ratios/spatial variability

In this section, by taking into account the different temporal resolutions (hourly/daily/weekly), the annual mean concentration ratios at the 15 sites with weekly measurements, have been calculated as the concentration ratios of each TEX over benzene, and not as the urban enhancement ratio. This way of calculation will allow us to compare our results with other studies where they consider a simple ratio between concentrations. The toluene-to-benzene ratio (T/B) over the available measurement years range between 2.64 and 5.08 ppbv/ppbv with an average of 3.78 ± 0.92 ppbv/ppbv at the traffic sites with weekly measurements. At urban background sites with weekly measurements, T/B was in the same range as the traffic sites with an average of 2.95 ± 0.30 ppbv/ppbv. The T/B ratio is of particular interest because it is often used to distinguish the traffic related sources from the other anthropogenic sources (Steinbacher et al., 2005). Additionally, higher T/B ratios may reflect relatively fresh vehicular emission sources. The tunnel experiment results in Île de France region in October 2012, (NMHC measurement performed by online GC-FID), showed a ratio of T/B equal to 3.07 ppbv/ppbv (Baudic et al., 2016, supplement S2), other tunnel study in France, in Marseille (NMHC measurement performed by 2L-stainless steel canister and analyzed by GC-FID and GC-MS techniques), shows a lower ratio of 2.49 (Cros et al., 2004; Boynard et al., 2014). At sites with weekly measurements basis, ethylbenzene/benzene shows close values between the traffic sites (0.48 ± 0.10) and the urban background sites (0.43 ± 0.05); m,p-xylene/benzene varies between 1.07 and 1.92 ppbv/ppbv with an average of 1.54 ± 0.35 ppbv/ppbv at the traffic sites and 0.99–1.47 ppbv/ppbv with an average of 1.26 ± 0.23 ppbv/ppbv at the urban background stations; and the average ratio of o-xylene/benzene at the traffic sites (0.59 ± 0.12) is comparable to the one at the urban background sites (0.53 ± 0.06). While the concentration ratios at traffic sites are in general comparable to the ones at urban background sites, one cannot clearly distinguish the traffic emissions from the local emissions because of the influence of many parameters (site typography and surrounding area, meteorological parameters, etc.), therefore the use of urban enhancement ratios is necessary. The use of urban enhancement ratios ER is ideal to overcome the meteorology impact and the background emissions influence and to distinguish different zones within the study area in different seasons as described in the next sections.

3.4. III-4 seasonal and annual trends of urban enhancement ratios

The annual concentration ratio may change during the different seasons. In some studies, the T/B ratio showed higher values in summer
compared to winter, for instance, at a Swiss urban background site (Legreid et al., 2007) and at a motorway location in an Austrian valley (Schnitzhofer et al., 2008). The seasonal variation of the ratio can result from the seasonal modification of the fuel composition, which is enriched in toluene and other aromatic compounds in summer but not in benzene (Borbon et al., 2003; Schnitzhofer et al., 2008).

We calculated in this section the urban enhancement ratios ER of each TEX over benzene according to the linear regression method described in section II-2. The same tendency was observed for all the ER and the correlations between C7—C9 species were high (r > 0.8), suggesting that the species were originating from common sources. Therefore, we will show the toluene/benzene urban enhancement ratio as representative of the C7—C9 species.

The seasonal variability of the urban enhancement ratio ER is determined at an urban background site Les Halles and a traffic site Auteuil where hourly measurements were undergone (Figs. 2 and 3 in the supplemental material). Generally, the results over all the years show that in winter the ER of toluene vs. benzene at traffic site (3–4 ppbv/ppbv) are comparable to the ones at the urban background site (2–4 ppbv/ppbv). In autumn 2012, when the tunnel experiment in Ile de France region (Baudic et al., 2016) was conducted, the T/B ratio at Les Halles exceeds the one of the tunnel of 3.07 ppbv/ppbv. But higher T/B urban enhancement ratios are observed in summer especially at the urban background site ~6 ppbv/ppbv exceeding the ratios at traffic site Auteuil (~4 ppbv/ppbv). It is the case for all the TEX/B ratios: in winter, ethylbenzene/benzene ratio varies between 0.4 and 0.6 ppbv/ppbv at Auteuil close to the ones at Les Halles 0.3–0.6 ppbv/ppbv but in summer it was close to 0.6 ppbv/ppbv at Auteuil while it reaches 1.0 ppbv/ppbv at Les Halles; m,p-xylene/benzene ratio in winter varies between 1.5 and 2.0 ppbv/ppbv at Auteuil comparable to the ones at Les Halles 1.0–1.7 ppbv/ppbv while in summer it was 1.6–2.2 ppbv/ppbv at Auteuil far lower than at Les Halles where it was between 1.8 and 3.4 ppbv/ppbv; as per o-xylene/benzene, the winter ratio is around 0.6 ppbv/ppbv at Auteuil for two years, when measurements were available, comparable to the ratios at Les Halles 0.2–0.6 ppbv/ppbv, and 0.7 ppbv/ppbv in summer at Auteuil while it reaches 1.2 ppbv/ppbv at Les Halles. The possible main reasons could be additional evaporation sources in summer related or not to traffic sources, or solvent use sources to a less extent especially at the urban background sites. In winter, the domestic heating source especially wood burning leads to higher emissions of benzene (Baudic et al., 2016), therefore, the winter ERs decrease significantly at Les Halles. These sources (especially traffic, domestic wood combustion and gasoline evaporation) have been assessed by Borbon et al. (2018) at the urban background site “Les Halles” in summer (July) and winter (January). The results suggest the presence of fugitive evaporative processes in addition to traffic during both seasons. In winter, the scatterplot lies between the traffic ER in its upper part and the domestic wood combustion ER in its lower part suggesting an additional source of wood combustion for benzene. In summer, the scatterplot is above the traffic ER line and tends to the one of evaporative emissions. This would suggest the presence of fugitive evaporative processes in addition to traffic (Borbon et al., 2018). Furthermore, one cannot exclude the emissions from solvent use but representative ER relative to benzene can hardly be determined due to the diversity of solvents and their speciated emission profiles (Salameh et al., 2014; Borbon et al., 2019). Adding to that, benzene been strongly limited in solvent formulations at 0.1% in cleaning products in Europe.

While the contribution at the traffic site of additional non-traffic sources (especially in winter, like domestic combustion) can be neglected, some seasonal changes in traffic emission composition and vehicle fuel composition can be expected as a result of seasonal changes in fuel composition regulation and temperature-dependent evaporative emissions (Borbon et al., 2018). Moreover, gasoline vehicles under cold-start conditions, when the vehicle was started with a cold engine and cold emission control equipment (especially in winter), emit higher levels of aromatics and TEX-to-benzene ratios compared to stabilized emissions (Singer et al., 1999).

Since we notice a much less pronounced seasonality at Auteuil traffic site compared to Les Halles, the analysis of the spatial variability would rely on annual means at traffic sites while it differentiates summer and winter at urban background where summer ER are two times winter ER.

### 3.5 Spatial variability of the ER

For the other sites where weekly measurements are available, the annual urban enhancement ratios ERs were calculated (Fig. 3). The results show a spatial gradient of ER at traffic sites up to a factor of two: the ERs at traffic sites in Paris intramuros are higher than the ones at the

![Fig. 3. Annual toluene-to-benzene urban enhancement ratio (ppbv/ppbv) at the 5 traffic sites: in Paris intramuros “Victor Basch” and “boulevard Haussmann”; in the outskirts “RN2 Pantin” and “boulevard périphérique-porte d’Auteuil”; and in the suburbs “RN6 Melun”. The error bars correspond to the standard deviation. The ER from highway tunnel experiment in 2012, by Baudic et al., (2016) is also shown.](image-url)
traffic outskirts and higher than the ones at the suburbs. These findings are compared to the ER of toluene/benzene obtained by tunnel experiment conducted inside a highway tunnel in the outskirts, located about 20 km southeast of inner Paris center in autumn 2012 (Baudic et al., 2016). The comparison shows that the ER from the tunnel experiment is lower than the ones found in Paris intramuros and more alike the ones obtained in the outskirts in 2012. The vehicle fleet composition especially the higher proportion of gasoline vehicles with a greater proportion of two-wheelers can be a potential reason of the observed spatial gradient. Indeed, according to Carteret et al., (2014), the dynamic vehicle fleet composition for passenger cars in Ile de France region consists of ~64% on diesel motorization (<71% at the national scale) and 34% on gasoline motorization (>29% at the national scale). Another study conducted by the EGT (Enquête Globale Transport) in 2010, revealed that Paris intramuros has the lowest share of diesel motorization (38%) in the static vehicle fleet composition compared to other departments in the Ile de France region where it reaches 60%. As per the dynamic vehicle fleet, EGT study suggests that Paris intramuros has 50% gasoline motorization, which is higher than the share in Ile de France region (36%) and at the national scale (29%). As per the motorization of two-wheelers, a study conducted by the French ministry of Ecology in 2013 has shown that 99.8% of two-wheelers run on gasoline (www.statistiques developpement-durable.gouv.fr). The results of a statistical study regarding the use of two-wheelers conducted by the French ministry of Environment in 2012 (Source: SOeS, enquête 2RM, 2012) showed that 29% of two-wheelers drivers use their vehicles all over the year in all meteorological circumstances, 48% use their two-wheelers when the meteorological conditions are favorable, and 23% use their vehicles only in summer. According to AIRPARIF (2013), the two-wheelers in Paris intramuros represented 15% in 2012 compared to 8% in 2002. In opposite, statistics for the years 2011–2014 from the French ministry of Environment database report a decrease of the passenger cars by 4% in Paris compared to an increase by 2% in Ile de France region along with a larger dieselization by +12%. Note that the two-wheelers emissions cover the fuel evaporation (run losses), the unburned gasoline emissions, and the exhaust emissions (Lan and Minh, 2013). The delayed implementation of two-wheelers emissions standards in the EU, compared to passenger cars, would result in higher emissions by two wheelers than by passenger cars.

In order to investigate the influence of two-wheelers we refined the previous analysis by using the most recent hourly resolved data at Auteuil traffic site coupled to meteorology. We calculated the monthly urban enhancement ratios for TEX over benzene as reported in Fig. 4 with the daily data of temperature. As already highlighted above, the seasonal cycle in TEX over benzene ratios follows the one of meteorological variables like temperature. For instance the toluene-to-benzene ratio correlates with temperature with an r² of 0.65. However the increasing trend over the years of all the TEX ER, especially C8-aromatics, is not depicted in the temperature time series. This feature implies an additional season-dependent source with increasing emissions over time and supports the potential role of two-wheelers, without excluding the impact of gasoline evaporation. Indeed, milder meteorological conditions in summer favor a greater use of two-wheelers with gaining importance of fuel evaporation, keeping in mind that, according to Borbon et al., (2018), additional non-traffic sources in winter, like domestic combustion, can be neglected at traffic sites. In summer 2011, lower temperature compared to other years can influence the magnitude of the gasoline evaporation emissions for toluene, and to some extent the rainfall, would be the main reason of the ER decrease.

As per the urban background sites, there is no evident spatial gradient according to the ER calculated from daily data. The ERs vary between 3 and 4 in winter and 5–7 in summer at the 3 urban background sites for the same years (Fig. 5) which highlights the impact of additional sources in both season regardless of the site location. The possible sources, as also discussed in Borbon et al., (2018) and the previous section, could be additional evaporation sources or solvent use sources to a less extent, in summer, and the domestic heating source especially wood burning in winter which leads to higher emissions of benzene (Baudic et al., 2016).

Finally, the TEX-to-benzene ER at urban background sites don’t show any spatial gradient while they show a clear seasonality with summer ER twice higher than winter ER. On the opposite, the TEX-to-benzene ER show a strong spatial gradient from suburbs to Paris center at traffic sites while they show a less marked seasonal variability and an increasing multi-year trend. These features point out the role of two-wheeler emissions without excluding the implication of gasoline emissions. Given the greater proportion of gasoline motorizations within Paris intramuros (Carteret et al., 2014), we will now evaluate the impact of gasoline emissions on the ER at the traffic sites.

![Fig. 4. Time series of monthly TEX-to-benzene urban enhancement ratios (ER) and meteorological data (temperature). ER are derived from the slopes of correlation plots for Auteuil (traffic site in the outskirts) from 2008 to 2011.](image-url)
3.6. Gasoline composition analysis

In this section we will discuss the impact of gasoline emissions on the previously calculated ERs. As we mentioned in section 2, the liquid and headspace composition of three representative types of unleaded gasoline (SP95, SP95E10 and SP98) distributed in “Île de France” were evaluated.

3.7. Liquid composition of gasoline

The liquid phase composition at ambient temperature reported in Fig. 6 is characterized by the same species related to aromatics especially toluene and m,p-xylene, as well as by C5—C8 alkanes for the three types of gasoline (Fig. 6 in mass percentage). BTEX account at 44% in SP98, 46% in SP95E10, and 47% in SP95 in the liquid composition with benzene present at 1.3% in weight percentage relatively to the total measured species. Toluene was the major species present in the composition of all gasoline at 21—26% followed by m,p-xylene at 12—14%, and isopentane at ~7—9% in weight percentage. 2,2,4-trimethylpentane, pentane, ethylbenzene, 2-methylpentane, and hexane were present at ~3—4% in weight percentage. VOC higher than C > 10 were below the detection limit in the composition of all the analyzed gasoline. As the major species and the overall fingerprint of the liquid composition are comparable between the three types of gasoline, an average composition profile of gasoline in “Île de France” region is proposed. According to the French Union of Petroleum Industries (UFIP) report in 2015, the gasoline SP95-E10 represented almost 32% of unleaded gasoline sold in France in 2014, the gasoline SP95 is slightly more consumed than SP98.

3.8. Validation of the model

The headspace composition at ambient temperature in weight percentage is characterized by C4—C6 alkanes (76% in SP98, 60% in SP95E10, and 80% in SP95) and C5 alkenes (12% in SP98, 15% in SP95E10, and 8% in SP95) and aromatics mainly BTEX (3% in SP98, 15% in SP95E10, and 5% in SP95) in the three types of gasoline (Fig. 7). Benzene is present at around 1% in SP95E10 and below 1% in SP95 and SP98. As in the liquid phase, VOC higher than C > 10 were below the detection limit in the headspace composition of all the analyzed gasoline. The headspace composition was also tested at two temperatures (10 °C and 40 °C). At 10 °C, the headspace composition of for example, SP95E10 is higher in C4—C6 alkanes (70%), slightly higher in C5 alkenes (17%),
and lower in BTEX (7%, where benzene represents 1%) than at ambient temperature. At 40°C, the headspace composition of SP95E10 includes the same contribution of C4–C6 alkanes (61%) as well as BTEX (17%, where toluene contributes at 12%) as at ambient temperature and slightly lower C5 alkenes (13%) than at ambient temperature. In general, for the same gasoline composition, the BTEX contribution varies slightly at ambient and high temperature but is two times more important than at 10°C.

The correlation between the measured and the modelled headspace (as described in section II-4) compositions of SP95 and SP98 at ambient temperature (Fig. 8, Table 2 in the supplemental material) shows satisfactory agreement at ±15% with a high coefficient of determination ($r^2 > 0.9$). Hence, the model applied is a relevant tool to test the sensitivity of TEX and other VOCs ambient composition to evaporative emissions of fuels with regards to their composition.

3.9. Gasoline emissions: role of two-wheelers

In this section, we will assess the role of two-wheelers (exhaust and gasoline emissions) on the ER at the traffic sites, while evaluating the impact of gasoline emissions, including a gasoline evaporation term and a second term related to the unburned gasoline (equation (4)). We assume that BTEX concentrations at traffic site are a linear combination of traffic emissions, gasoline evaporation, and unburned gasoline, since solvent use at traffic site can be neglected (Borbon et al., 2018). Therefore, the ER from traffic should be a linear combination of traffic tunnel ER, evaporation ER, and unburned gasoline ER (equation (4)).

$$\text{ER}_{\text{traffic site}} = \text{ER}_{\text{Thiais tunnel (Baudic et al., 2016)}} + \text{Gasoline Coefficient} \times (\text{ER}_{\text{evaporation}} + \text{ER}_{\text{unburned gasoline}})$$

(4)

The ER of transport profile used (exhaust fraction mainly but we cannot exclude the fuel evaporation from the running losses) were obtained during Prequalif campaign in a tunnel located in Thiais about 20 km southeast of inner Paris center (Baudic et al., 2016). The composition of the Thiais tunnel emissions is reported in the paper of Baudic et al. (2016), for over 20 VOCs including BTEX as follows: benzene 6 wt%, toluene 22 wt%, and C8-aromatics (ethylbenzene and o,m,p-xylenes) 9 wt%.

The ER related to gasoline evaporation was determined from our model as an average headspace composition profile at ambient temperature. The gasoline evaporation composition, based on the laboratory experiments, covers the diurnal emissions which occur when the vehicle is stationary with the engine off, and the refueling losses which occur while the tank is being filled and the saturated vapors are displaced and vented into the atmosphere (Salameh et al., 2014). The second gasoline
emission term (equation (4)) includes the unburned gasoline largely emitted by 2-stroke motorizations, represented by the mean liquid phase composition obtained by measurements. According to a study conducted by the French Ministry of Ecology (www.statistiques.developpement-durable.gouv.fr), one third of two-wheelers in France were 2-stroke scooters in 2012, known to emit higher hydrocarbons than 4-stroke scooters due to short-circuiting of the fresh charge out the exhaust port. The intake and exhaust ports are open simultaneously, and a large fraction of 15–40% of the fuel-air mixture escapes through the exhaust port along with the old exhaust gases (icct, 2009).

Then, we estimated a gasoline coefficient following equation (4), by using the ER obtained at traffic sites (Auteuil and Victor Basch) in summer over all the years where the high ER are basically related to transport (traffic and fuel emissions).

Fig. 9 shows the ER at two traffic sites in summer, where temperature varies between 18 and 25°C according to Fig. 4, and the estimated gasoline coefficient. If the gasoline emissions (from evaporation and unburned gasoline) explain alone the high ER obtained at different traffic sites, the estimated “gasoline coefficient” must be the same regardless of the species. The latter varies between the compounds with a 2–3 fold and slightly between the sites. Taking into consideration the uncertainties on the ER estimated by measurements (liquid phase composition and ER at traffic sites (section II-1), and tunnel experiment), and by the model (headspace composition), the difference among the gasoline coefficients is reasonable. One should note that when we didn’t consider the unburned gasoline ER occurring during the use of 2-stroke engines, the “evaporation coefficient” variation between the compounds was too high reaching 6 fold (Fig. 9). Therefore, fuel evaporation alone and exhaust emissions cannot explain the urban enhancement ratios obtained in summer at the traffic sites with different typology. These findings support the suggestion that two-wheelers are a potential contributor to this enrichment, based on the vehicle fleet composition in Paris intramuros which includes 15% of two-wheelers in 2012 compared to 8% in 2002; in outskirts, the two-wheelers represented 7% in 2012 compared to 4% in 2002 (AIRPARIF, 2013). According to another report by AIRPARIF in 2016 (AIRPARIF, 2016), the estimated NMVOC emissions from road transport in Paris include 15% from gasoline evaporation, 56% from two-wheelers which are 3 times higher than the emissions from gasoline-powered passenger cars (18%), and 14 times higher than those from diesel-powered passenger cars (4%).

3.10. Implications on health and technology improvement

On one hand, according to the Regional Health Observatory (ORS), 16% of cases of asthma can touch the Parisian population living within 75 m of roadways (>10 000 vehicles/day) which accounts at 2 million including 70 000 young people under 17 years old. Additionally, 58% of the population living in “Ile de France” region had already felt the effects of air pollution on their health, people living near high-traffic lane are more touched. This case is not limited to Paris but also to other big cities.

On the other hand, a study by Hensema et al., (2013), evaluated the emissions and fuel consumption of a standard and a tampered version of a 2-stroke and a 4-stroke moped to estimate whether the measures proposed by the European Commission will have the right output.

![Fig. 9](image_url)

**Fig. 9.** ER of toluene, ethylbenzene, m,p-xylene, and o-xylene over benzene, and evaporation and gasoline coefficients calculated, in summer over several years at two traffic sites (Victor Basch and Auteuil). The ERs from highway tunnel experiment in 2012, by Baudic et al., (2016) are also shown.
results showed that the tested moped did not comply with the limits. The 2-stroke mopeds emit higher particles than the 4-stroke mopeds; it also releases high hydrocarbons emissions. The use of speed limiters increases the fuel consumption of mopeds. It also shows that the Euro 2 mopeds did not comply with the Euro 3 limits. Adding to that, the emission factors of VOCs for the 2-stroke motorcycles are 2–4 times higher than those for the 4-stroke motorcycles under cold-start conditions (Yang et al., 2005). As per France, the results of a study conducted by the Ministry of Ecology (www.statistiques.developpement-durable.gouv.fr), showed that one third of two-wheelers in France are 2-stroke scooters. Based on the findings in this study, it is important to compare European cities with different vehicle fleet composition, different proportion of two-wheelers, etc. in order to suggest new regulations regarding air quality and their feasibility in Europe.

Policy makers should enforce further stringent regulations in the transportation sector regarding emissions as well as promote the usage of alternative means of passenger transport. Such a change would highlight the environmental, economic and social benefits, of these alternative means (such as human powered and electric two-wheelers) as suggested by Weiss et al., (2015).

4. Conclusions

We combined different dataset from 2000 to 2014 and different approaches to investigate the spatial and temporal variability of BTEX in Ile de France region including Paris intramuros, its outskirts and suburbs as well as to give insights on the role of two-wheelers. We conducted a statistical analysis of a large VOC dataset including multi-season, multi-year and multi-site speciated measurements (traffic, background, and tunnel) and we performed a coupled experimental and modelling analysis of liquid and headspace composition of representative fuels distributed in Ile de France region to study the potential impact of the fuel composition on BTEX levels. A special attention was paid to the consistency between online and offline techniques operated at different time resolution (hourly, daily and weekly sampling). For > C6-aromatics, differences reach a factor of 50% between hourly and weekly measurements. The seasonal variability of the urban enhancement ratio ER, at an urban background site at Les Halles and a traffic site Auteuil over all the years shows that in winter the ER of toluene vs. benzene at traffic site are comparable to the ones at the urban background site but in summer the ER are higher at the urban background site where additional evaporative sources can occur. At traffic sites, a specific season can represent the whole year which is not the case of urban background sites where the ER in summer are the highest in general and they are two times the ER of winter.

The spatial gradient of ER at traffic sites is up to a factor of two: the ERs at traffic sites in Paris intramuros are higher than at the traffic outskirts and also than those at the suburbs. The vehicle fleet composition especially the proportion of two-wheelers in Paris, 15% in 2012 compared to 8% in 2002, can be the reason of the observed spatial gradient. No evident spatial gradient was observed at the urban background sites. The applied model to assess the gasoline headspace compositions shows good agreement with the measured composition (±15%) with a high correlation coefficient ($R^2$) > 0.9. By means of the estimation of a gasoline coefficient, we deduced that the gasoline evaporation does not alone explain the summertime ER at two traffic sites (in Paris intramuros and the outskirts) which suggests the potential major effect of two-wheelers (exhaust, gasoline evaporation, and unburned gasoline emissions) especially in Paris intramuros, including 2-stroke as a large emitter of unburned hydrocarbons. Lately, in 2016, the EURO 4 regulation has been imposed on two-wheelers, and we expect to notice a lower TEx emissions enrichment in the coming years at traffic sites. Finally, if Europe is to decrease transport-related air pollution and inner city traffic, policy makers should consider finding alternatives to the conventionally-powered two-wheelers and supporting electric two-wheelers for example. Furthermore, the implementation of the control on emissions at two-wheelers exhaust in the EU, which is delayed compared to passenger car exhaust, can result in a decrease of the emissions. Based on the specific regional variability (e.g. geographic situation, climatic conditions, infrastructure, regulations, etc.), an assessment of the environmental, socio-economic performance of electric two-wheelers should be performed. Especially in the developing world, there are extensive knowledge gaps in dealing effectively with the growing motorcycle population.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jaenoa.2018.100003.

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