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# An observation of ambient levels and reactivity of VOCs in the atmosphere of Agra, India

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***Abstract:*** ***The present study comprises the seasonal variability of volatile organic compounds (VOCs) namely; benzene, toluene and xylene in the ambient air of Agra during summer and winter, 2015-2016. The mean levels of VOCs in ambient air during weekdays and weekends were also calculated. Furthermore, Propylene Equivalent Concentration (PEC) has been calculated to find out the VOCs reactivity toward ozone formation. Further, the relationships of VOCs with meteorological parameters (relative humidity and wind speed) have been estimated. The concentrations of all VOCs were found to be higher during winter as compared to summer could be due to high stability and low planetary boundary layer in the winter. After comparing the mean levels of VOCs during weekdays-weekends, it is observed that the studied VOCs were higher during weekdays and weekends during summer and winter, respectively. The values of PEC were observed to be higher during winter in contrast to summer. It is reported that xylene and toluene contributed the most among studied VOCs in ozone formation during summer and winter, respectively. After identifying the association between VOCs and relative humidity, weak to moderate negative correlation were observed during studied season.***

***Keywords: VOCs, Seasonal, Meteorological parameters, Propylene Equivalent Concentrations, Correlation***

## I. INTRODUCTION

VOCs, one of the important ambient air pollutants which are mainly characterized by high vapour pressure and low boiling points [1,2]. It is group of diverse organic species which have crucial role in various atmospheric processes such as ozone, secondary organic aerosol and photochemical smog formation in the troposphere [3]. VOCs are produced by both biogenic and anthropogenic sources which are also influenced by meteorological conditions and emission sources strength [4,5]. Besides atmospheric processes in the ambient environment, VOCs may have adverse impacts on public health and vegetation, even at very small levels. Hazardousness of VOCs can be assessed in terms of short-term and long-term exposures to human beings which is mainly characterized by non-carcinogenic (sensory, respiratory problems, liver-kidney impairment) and carcinogenic (lung, blood, kidney and biliary tract cancer) effects [6,7].

Ubiquitous characteristics of VOCs and their transformation and emission nature, it is an urgent necessary to understand atmospheric of chemistry VOCs in the ambient environment. A number of studies regarding qualitative and quantitative terms of VOCs have been carried out in the urban, rural, mountainous and remote region across the world. In the Indian context, limited studies have been performed which pertains to examination of ambient VOCs and their ozone forming potential in the urban environment. Therefore, the present work has been attempted in order to evaluate the VOCs levels in the urban site of Agra city, India. It has mainly focused on the following objectives: (a) seasonal variation of VOCs; (b) weekdays-weekend variation; (c) estimation of propylene equivalent concentrations (PEC) and (d) evaluation of association between VOCs and meteorological conditions.

## II. MATERIALS AND METHODOLOGY

### STUDY AREA

Agra city is bounded by four districts namely; Mathura in the north, Firozabad in the east and Dhaulpur and Bharatpur districts of Rajasthan in the south and west, respectively. It covers an area of 4027 $km^2$ which is situated 27˚11´ N latitude and 78˚02´ E longitude on the bank of river Yamuna. The city is located at the height of 169 meters from mean sea level. It comes under the semi-arid type region having more variability of temperature. The city experience 46-50 ˚C during daytime and goes down to 30 ˚C during summers. On the other hand, the range of temperature is found to be approximately 6-8 ˚C during daytime and as low as 4 ˚C in the night-time during winters. Humidity is in enormous condition in the ambient air. The rainy season is from July to September, receiving a rainfall of about 67 cm per year.

The population of Agra is 4380793 as per the 2011 census, ranking $41^{st}$ in India (out of a total of 640).The district has a population density of 1084 inhabitants per square km and a growth rate of 21% over the decade 2001-2011. Of the total population, males are in majority accounting for 53% and women are 47%. Various types of industry, manufacturing plants and automobile industry are prevalent in the Agra city. Figure 1 depicts the sampling location in Agra.

### DATA ACQUIREMENT

Data has been taken from Central Pollution Control Board (CPCB) which is statuary governmental organization under the Ministry of Environment and Forests (MoEF) [8]. It was established on 22 September, 1974 under section 3 of the Water (Prevention and Control of Pollution) Act, 1974. CPCB is also entrusted with the powers and functions under the Air (Prevention and Control of Pollution) Act,1981. CPCB acts as a technical wing and provides technical services to MoEF. It co-ordinates the activities of the State Pollution Control Boards by providing technical assistance and guidance and also resolves disputes among them.

Air pollutant data for VOCs such as benzene, toluene and xylenes have been collected for summer (2015) and winter (2015-16). It is noted that the analysis has been carried out for two months during summer (May-June, 2015) and winter (Dec-Jan, 2015-16). In addition to this, two meteorological parameters viz. relative humidity (RH) and wind speed (WS) have been collected.

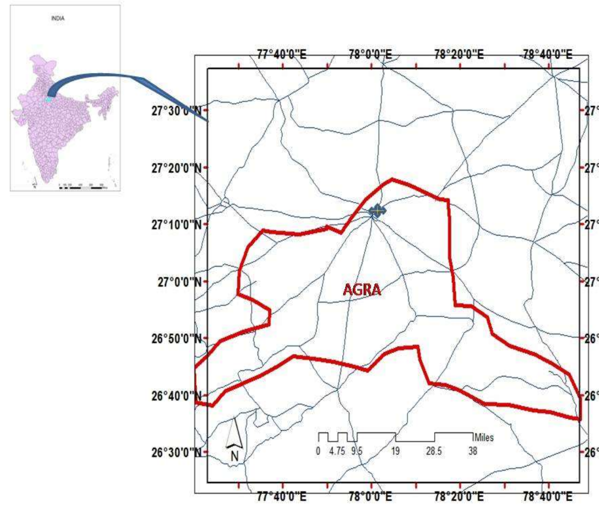


Figure 1 Map showing the sampling location in Agra

### Estimation of propylene-equivalent concentration (Prop-Equiv)

To estimate the reactivity and the contribution of individual VOCs to photochemical O3 formation, the propylene-equivalent concentration (PEC) (Chameides et al., 1992) and the maximum incremental reactivity (MIR) (Carter, 1994) are calculated [9,10]. The Prop-Equiv (i) of hydrocarbons i is defined as:

$$\text{Prop-Equiv}(i) = \text{Conc.}(i) \times k\text{OH}(i) / k\text{OH (propylene)}$$

Where Conc.($i$) is the concentration of VOC$i$ (µg/m³), $k$OH($i$) as rate constants for the reaction with VOC$i$ and OH and $k$OH (propylene) as rate constants for the reaction with propylene and OH. Prop-Equiv ($i$) is a measurement of the concentration of VOC$i$ on an OH-reactivity based scale normalized to the reactivity of propylene. Table 1 lists the photochemical properties of targeted VOCs.

Table 1 Photochemical properties of measured VOCs

| Sr No | Species | $k_{OH}\times10^{12}$ ($cm^3$ $molecule^{-1}s^{-1}$) at 298 K |
|---|---|---|
| 1 | Benzene | 1.23 |
| 2 | Toluene | 5.96 |
| 3 | m/p-xylene | 18.95 |
| 4 | o-xylene | 13.7 |

Carter 1994

## III. RESULTS AND DISCUSSION

### (a) Descriptive statistics of VOCs during summer and winter

In the present section, the observed ambient VOCs levels of Agra during the two seasons have been discussed. Table 2 explains the mean levels of VOCs along with other statistical parameters during the summer and winter. In summer, the average concentrations ranged from 0.73 to 2.38 µg/m³ (with a mean value of 1.15±0.28 µg/m³) for benzene, 1.11 to 11.66 µg/m³ (with a mean value of 3.17±1.92 µg/m³) for toluene and 0.64 to 5.36 µg/m³ (with a mean value of 1.20±0.71 µg/m³) for xylene. On the other hand, mean levels of toluene (55.59 µg/m³) was found to be highest followed by xylene (14.35 µg/m³) and benzene (14.11 µg/m³). The toluene and xylene showed the higher variability of 62.09 and 63.38 %, respectively.

Table 2 Summary of statistical parameters of Benzene, Toluene and Xylene (µg/m³) in Agra during two seasons

| | Range | Average | Median | SD | CoV |
|---|---|---|---|---|---|
| | **Summer** | | | | |
| Benzene | 0.73-2.38 | 1.15 | 1.09 | 0.28 | 24.66 |
| Toluene | 1.11-11.66 | 3.17 | 2.64 | 1.92 | 60.70 |
| Xylene | 0.64-5.36 | 1.20 | 1.01 | 0.71 | 59.13 |
| | **Winter** | | | | |
| Benzene | 7.80-24.02 | 14.11 | 14.29 | 3.67 | 26.01 |
| Toluene | 19.27-225.88 | 55.59 | 48.38 | 34.51 | 62.09 |
| Xylene | 3.63-49.82 | 14.35 | 11.14 | 9.10 | 63.38 |

Prevailing meteorological conditions and distribution of emission sources near or around the sampling site could be attributed as the variability of VOCs in the ambient environment [11]. In addition to this, vehicular exhaust, evaporative emissions and fuel combustion also contributed in the ambient VOCs levels [12]**.** The lower levels of VOCs during summer could be due to increased photochemical degradation (higher temperature and solar radiation) [13]. In contrast, lesser dilution of pollutants due to atmospheric stability increases the VOCs levels during winter [14].

There is a great variation observed in the concentration of benzene, toluene and xylene between summer and winter (Figure 2). The concentrations of benzene, toluene and xylene were noticed to be much higher in winters than summer. These are more reactive and hence their concentration decreases quickly in the ambient air when photochemical reaction takes place. The rate of photochemical reaction is higher in summer than winter. Also the mixing height increases with temperature during summer and hence the concentration of these compounds decreases during summer because of mixing.

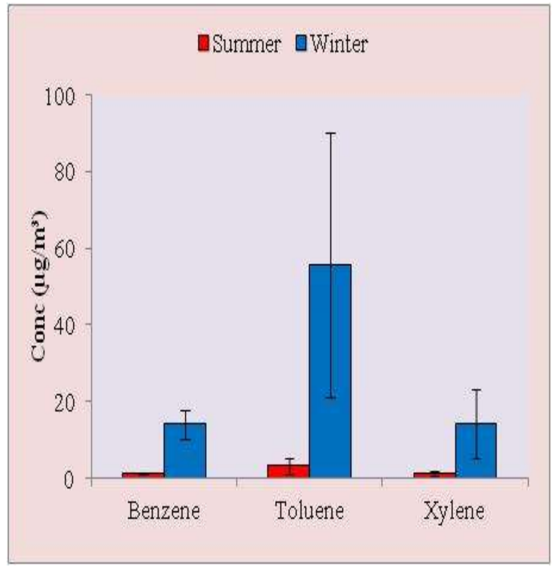


Figure 2 Concentrations of benzene, toluene and xylene during the two seasons

The observed dataset of VOCs in the present study is compared with the previous studies carried out across the world and presented in Table 3. It is noted that the VOCs levels are found to be in the significant concentrations during winter in the present study.

Table 3 Comparative analysis of observed VOCs (µg/m³) in Agra with the previous studies

| City | Benzene | Toluene | Xylene | Reference |
|---|---|---|---|---|
| Summer (Agra) | 1.15 | 3.17 | 1.20 | Present study |
| Winter (Agra) | 14.11 | 55.59 | 14.35 | Present study |
| Chennai, India | 38.23 | 156.14 | 24.87 | Mohan and Ethirajan (2012) [15] |
| Delhi, India | 48 | 85 | 22.5 | Hoque et al.(2008) [16] |
| Northern Italy | 23.6 | 98.8 | 27.75 | Geiss et al.(2009) [17] |
| Beijing, China | 2.37 | 3.97 | 4.46 | Liu et al.(2009) [18] |
| Greater Cairo, Egypt | 87.20 | 213.80 | 140.80 | Khoder (2007) [19] |

### (b) Variability of VOCs during Weekdays and Weekends

The estimates of VOC levels during weekdays (WD) and weekends (WE) have been also examined in order to see differences between WD and WE. The results of difference between weekdays and weekends can provide some insight into the effect of vehicular emissions on the measured VOCs. Figure 3 illustrates the variability of VOCs for weekdays and weekends during summer. During weekdays, the average concentration of toluene showed mean value of 3.27±2.11 µg/m³ followed by xylene (1.23±0.80 µg/m³) and benzene (1.15±0.30 µg/m³). However, variability of VOCs for weekend during summer showed 1.13±0.23, 2.92±1.39 and 1.12±0.43 µg/m³ for benzene, toluene and xylene, respectively.

In contrast, higher VOCs levels have been observed for winter during weekends as compared to weekdays (Figure 4). It could be due to less depletion of VOCs via photochemical degradation in the weekdays and afterwards emissions of fresh VOCs in the weekend may accumulate the higher levels of VOCs in the weekends. It is clearly noticed that the levels of VOCs were found be higher during weekdays as compared to weekends which indicates human activities have significant effect on the emissions of VOCs. Apart from this, another reason for higher levels in weekdays could be vehicular emissions [15].

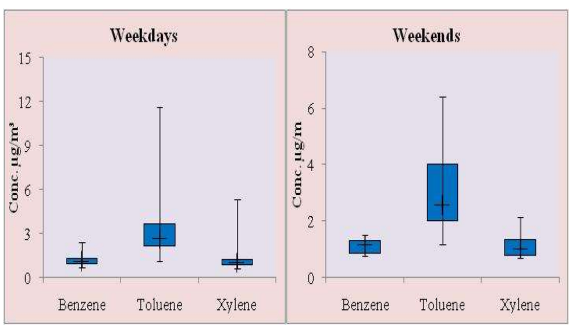


Figure 3: Box plot of concentrations of benzene, toluene and xylene in weekdays-weekends during summer.

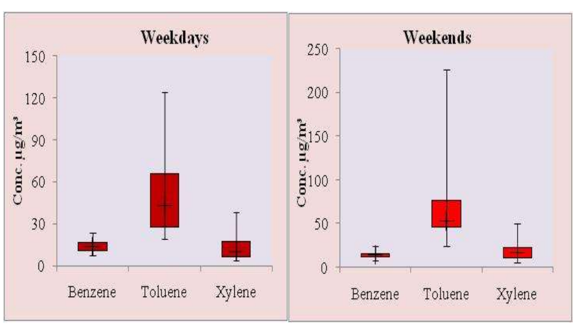


Figure 4: Box plot of concentrations of benzene, toluene and xylene in weekdays-weekends during winter.

**(c) VOCs reactivity in terms of Propylene Equivalent Concentration (PEC)**

The variability of PEC of benzene, toluene and xylene during the two seasons is shown in Figure 5. The average PEC ranged from 0.03 to 0.11 µg/m³ (0.05±0.01 µg/m³) for benzene, 0.25 to 2.64 µg/m³ (0.72±0.44 µg/m³) for toluene and 0.40 to 3.33 µg/m³ (0.74±0.44 µg/m³) for xylene. It means that xylene had highest contribution in ozone production followed by toluene and benzene during summer. In case of winter, average PEC of benzene, toluene and xylene exhibited the values as 0.66±0.17, 12.60±7.82 and 8.91±5.65 µg/m³, respectively. Toluene was found to be highest contributor followed by xylene during winter. PEC method is useful as it ranks the reaction rate of a species as well as its atmospheric concentration. The observed results of the PEC for Agra during both seasons are comparable with the studies carried out by various studies [20,21,22].

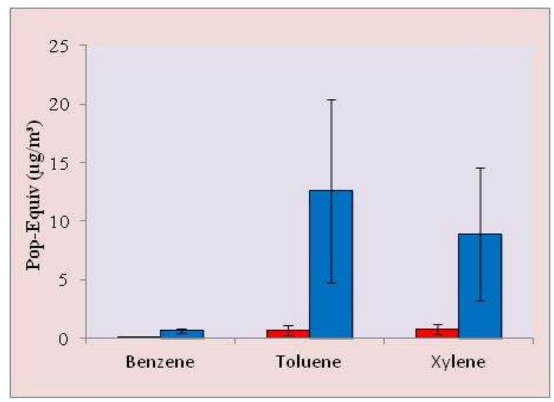


Figure 5 Propylene Equivalent Concentrations (PEC) of benzene, toluene and xylene during summer and winter

**(d) Relationship of studied VOCs with meteorological variables**

The levels of VOCs are also dependant on meteorological conditions besides emission sources. Therefore, associations between studied VOCs and meteorological parameters have also been examined. Figure 6 and **7** depict the scatter plots between VOCs and relative humidity for summer and winter, respectively. Summer seasons showed negative moderate significant correlation of relative humidity with all VOCs. While, toluene and xylene showed weak negative correlation whereas benzene showed no significant correlation during winter.

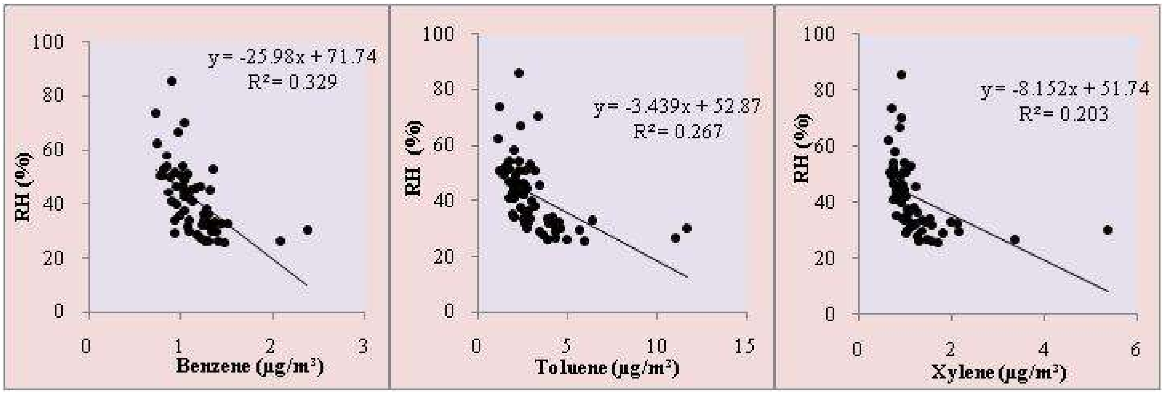


Figure 6: Scatter plot of benzene, toluene and xylene with relative humidity during summer

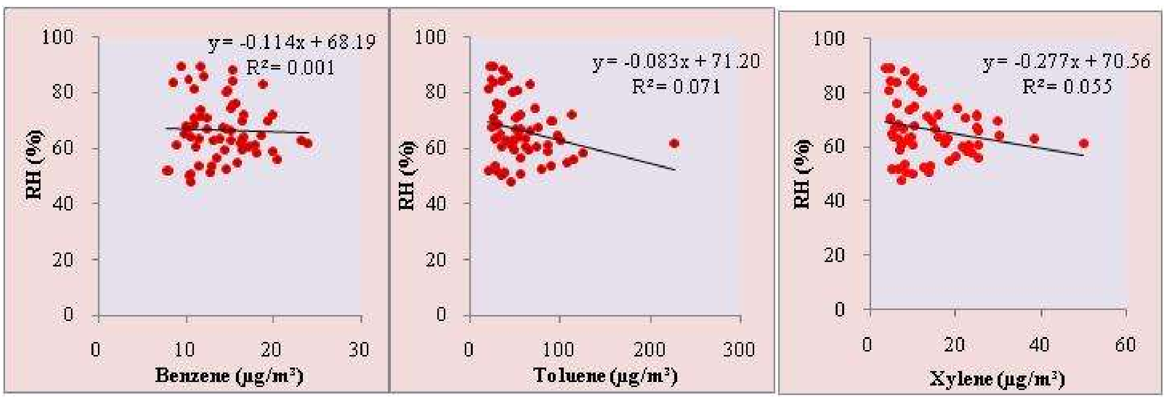


Figure 7: Scatter plot of benzene, toluene and xylene with relative humidity during winter

Similarly, the relationships between VOCs and wind speed have been also evaluated. Benzene and xylene showed weak negative correlation with wind speed whereas toluene showed no correlation during summer (Figure 8). In contrast, benzene showed negative highly significant correlation whereas toluene and xylene showed negative moderately significant correlation with wind speed during winter (Figure 9).

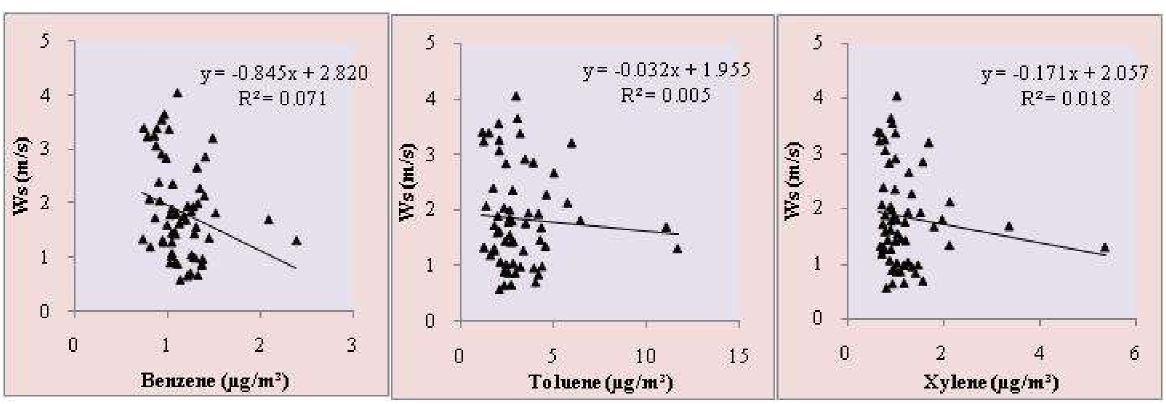


Figure 8: Scatter plot of benzene, toluene and xylene with wind speed during summer.

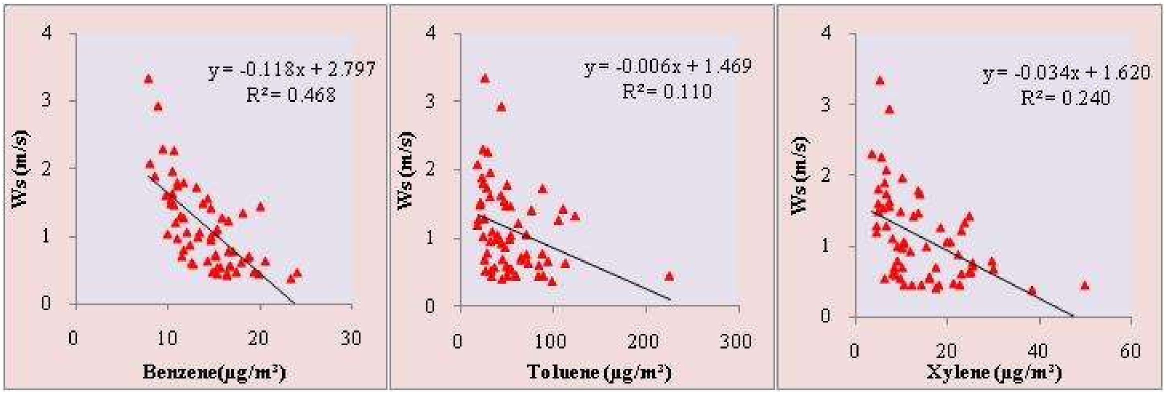


Figure 9: Scatter plot of benzene, toluene and xylene with wind speed during winter.

## IV. CONCLUSIONS

The present work pertains to evaluation of the seasonal variability of VOCs, weekdays-weekend difference, reactivity of VOCs and relationships of VOCs with meteorological parameters during two seasons of 2015-16 in Agra, India. The concentrations of all VOCs are found to be higher during winter as compared to summer could be due to calm conditions and high atmospheric stability in the winter. It is observed that the studied VOCs were observed to be higher during weekdays and weekends during summer and winter, respectively. The values of Propylene Equivalent Concentration were observed to be higher during winter in contrast to summer. It is reported that xylene and toluene contributed the most among studied VOCs in ozone formation during summer and winter, respectively. After identifying the association between VOCs and relative humidity, weak to moderate negative correlation are observed during studied season. On the other hand, wind speed showed weak to high negative correlation with the targeted VOCs.

The present study is a first attempt in terms of VOCs and their role in ozone production in the urban atmosphere of Agra, India. It may be useful to understand the regional environmental chemistry of the urban atmosphere. It can also be used to effective abatement strategies for pollution reduction in terms of VOCs and ozone. Further, more experimental and modelling studies are required in order to identify the effective and efficient technological measures for the pollution mitigation strategies.

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