Surface ozone variability in the urban and nearby rural locations of tropical India

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Surface ozone variability at Pune (an urban location) and nearby rural locations has been studied using KI solution chemical method. The measurement showed well-marked diurnal cycle of ozone concentration with minimum at sunrise and maximum at noon hours. Simultaneous measurements of humidity and temperature along with ozone suggest that the ozone concentration is directly proportional to temperature and inversely proportional to humidity. The averaged diurnal variation of ozone during different months and two seasons, viz. winter and spring show high ozone concentration over the rural locations than the urban location. Higher ozone concentration at the rural locations may be due to slower titration of ozone by nitric oxide in the evening hours.

Keywords: Diurnal variations, meteorological parameters, nitric oxide titration, surface ozone, traffic emissions.

OZONE (O_3) plays an important role in a chemistry of the earth's atmosphere, even though it is a minor constituent in terms of abundance. Ozone plays an important role in the atmospheric environment through radiative and chemical processes. Ozone absorbs IR radiation and thus is one of the greenhouse gases in the troposphere[1–3]. Ozone does not have direct natural sources, but is produced in the atmosphere. Tropospheric ozone plays a central role in the oxidative chemistry of the troposphere; it has an important impact on the radiative balance of the atmosphere, and is known to have detrimental effects on human health and agricultural crop production. For these reasons, understanding the processes which control the origin, trends, distribution and effects of tropospheric ozone are important to atmospheric chemistry research over the last few decades. Ozone is produced in the troposphere through oxidation of a precursor, i.e. carbon monoxide or hydrocarbons in the presence of high concentrations of NO_x. The tropical troposphere rich with water vapour and intense radiation flux is the most favourable region for the production as well as transport of many atmospheric gases. Many studies around the globe have reported that the surface O_3 in rural locations near the industrial areas has increased significantly. Ozone comes in contact with life forms on the earth's surface and shows its destructive nature. It damages the leaves and affects plant growth, thus reducing crop yields[4]. Human health is also affected by high concentrations of ozone. Surface O_3 is mainly produced photochemically with anthropogenic/natural emissions of precursor gases. Many studies have pointed out the increase in surface ozone over most of the rural areas in the northern hemisphere[5–8].

The problem of tropospheric ozone changed dimensions about fifteen years ago, when it was realized that increased surface ozone is not only a local urban problem as a global increase of surface rural ozone concentration, especially in the northern hemisphere, was observed during the 20th century, which has been attributed to photochemical production[9–12]. Measurements made during the second half of the last century at many sites show that the present levels of ozone have more than doubled[9,13]. There are inadequate studies related to tropospheric chemistry in the tropical region. This is the region of large biogenic and pyrogenic emissions of trace gases, including NMHCs, which result in high OH radical concentration, thus making it the most active photochemical region of the atmosphere. Estimations made using the chemical transport model showed that on increasing the anthropogenic emissions, ozone production efficiency was maximum over the Indian region, followed by Japan and China. This can be explained on the basis of increase in OH peroxy radicals[14]. Brasseur *et al.*[15] also suggested that the sensitivity of climate to ozone changes was the largest in the tropics.

Over the Indian region, a few scattered surface measurements of ozone are being carried out based on UV ozone sensor and chemical methods[16–18]. These measurements are restricted to a few rural and urban locations. However, no simultaneous measurements using the same techniques were carried out at the rural and urban locations, for a comparative study. Hence a project on simultaneous measurements at both urban and the surrounding rural areas was initiated with the help of the Department of Science and Technology, New Delhi. The results of the study are presented in this communication.

Surface ozone observations at a time interval of 1 min have been made continuously with KI solution chemical method at three locations, Pune (18.32°N, 73.55°E, 559°m asl), Belser and Mutha, Maharashtra, India. Pune is an urban location, while Belser and Mutha are rural locations. Belser is located 45 km southeast of Pune, while Mutha is located 30 km west-southwest of Pune. All three locations are at the same height above the sea level. The experimental site in Pune is located in the campus of the Agriculture College, which is near (<100 m) the heavy traffic city road and surrounded by college buildings, staff quarters and the Meteorology Office building (Figure 1). Simultaneous observations of temperature, humidity and wind at the same time interval have also been carried out since December 2006 in the three locations. Data were converted to hourly means and utilized to study the diurnal variation during different months and seasons. The working principle and details of the electrochemical

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ozone sensor are given by Sreedharan and Tiwari[19]. The ozone sensor (KI solution ozone bubbler) has been compared with a UV ozone sensor (O_3 42 M, Environment S. A.) by operating both the sensors simultaneously at the Indian Institute of Tropical Meteorology (IITM), Pune. The correlation coefficient for ozone above 1 ppb measured using both the sensors was 0.84, which is highly significant. The difference observed between the two ozone sensors was of the order of 5–7 ppb during noon hours only, for the remaining period of the day both sensors showed good agreement. The KI solution ozone sensor shows low ozone values in the noon hours compared to the other sensor. Meteorology parameter sensors were calibrated at India Meteorological Department, Pune.

The average diurnal variation of surface ozone over three locations has been studied for different months during winter and spring seasons. Figure 2 depicts the diurnal variation of ozone during January 2007 for the three locations. It can be seen from Figure 2 that the ozone is minimum during early morning hours and maximum during noon hours[20]. This feature has been observed at all three locations; however, ozone concentrations were observed to be higher at the rural locations than the urban location. The rate of increase of ozone from morning to noon time was more or less the same in all the three locations, but the rate of decrease of ozone during evening hours was less in the rural locations than at the urban location for the winter season (Table 1). The less ozone destruction at rural locations during the evening and night hours causes higher ozone concentration than that of the urban location. The minimum ozone concentration observed in the morning hours at the rural locations was more than 15 ppb, while at the urban location it was less than 10 ppb during winter months.

Ozone destruction takes place through dry deposition and NO_x scavenging during evening and night hours. A more convenient way to characterize a site as rural in terms of ozone would be based on the magnitude of the titration effect due to nitric oxide (NO). Freshly emitted

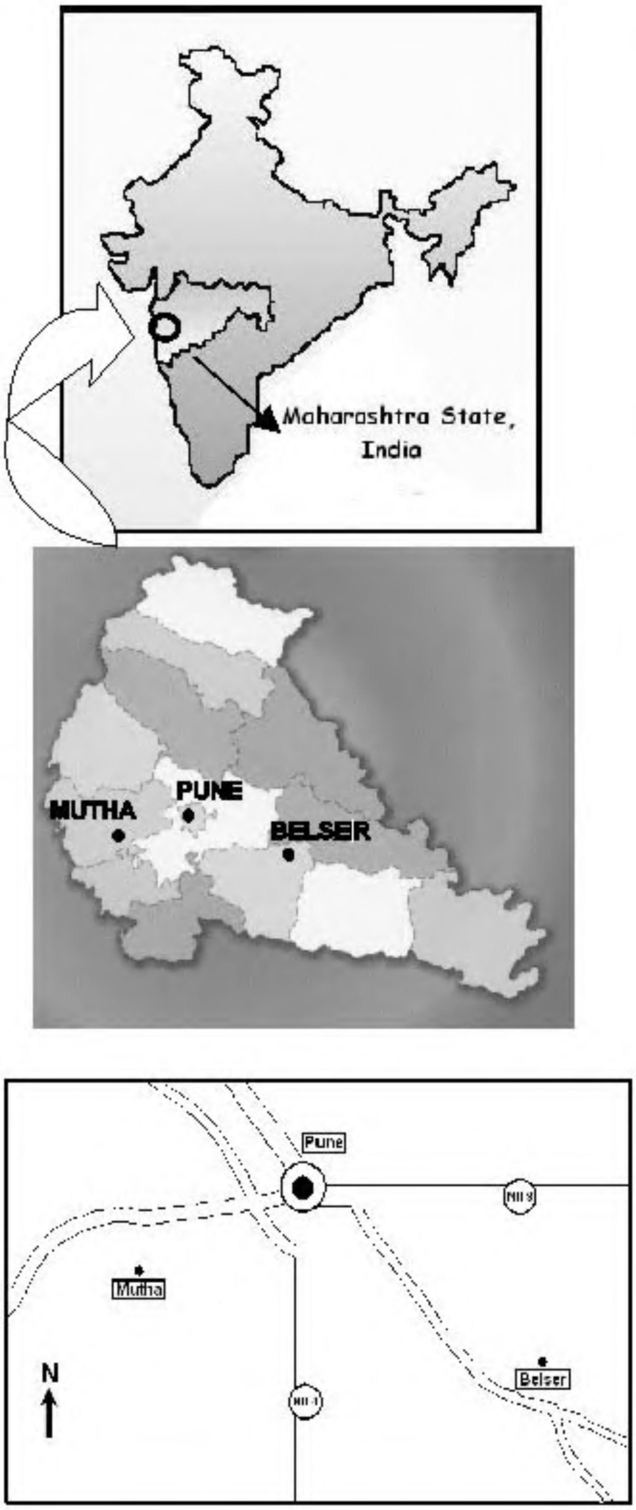

Figure 1. Map showing location of experimental sites.

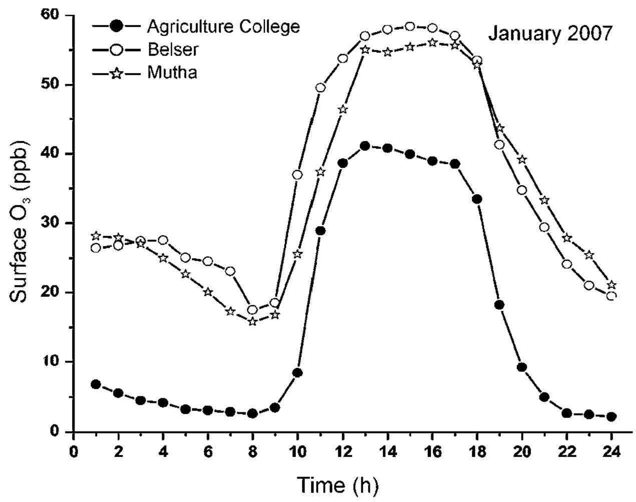

Figure 2. Diurnal variation of surface ozone at the urban and rural locations.

Table 1. Rate of change of ozone during morning and evening hours at the three locations

	Winter		Spring	
Location	8–11 h (ppbv/h)	17–19 h (ppbv/h)	8–11 h (ppbv/h)	18 to 20 h (ppbv/h)
Agriculture College, Pune	8.4	–6.8	7.2	–3.5
Belser	7.2	–5.4	5.6	–6.0
Mutha	7.3	–4.3	7.3	–6.7

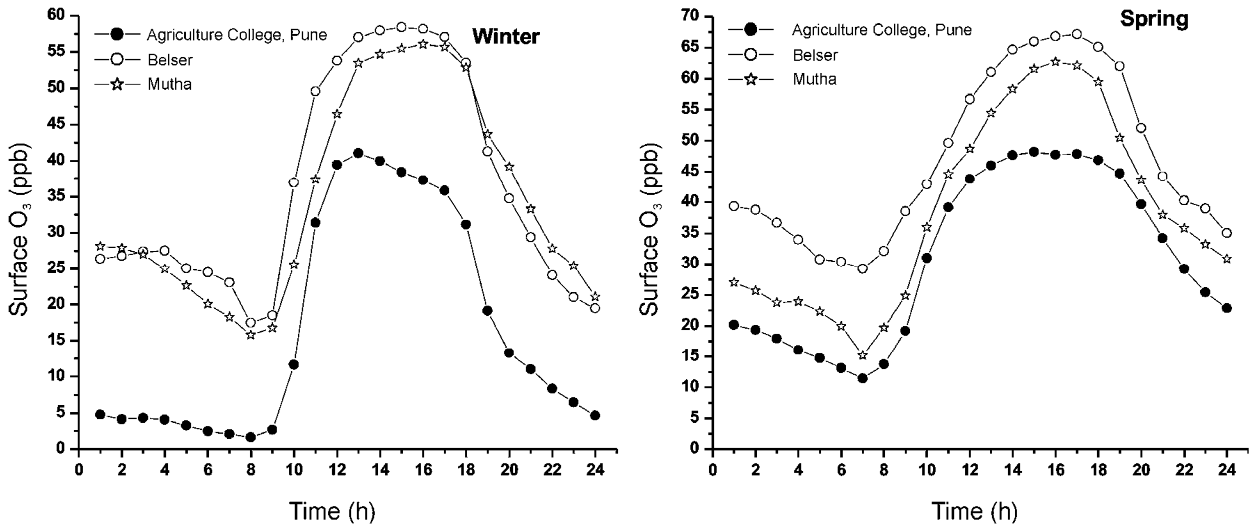

Figure 3. Diurnal variation of surface ozone during winter and spring seasons.

NO reacts with O_3 to form NO_2 on a timescale of about 2 min by the following reaction:

$$NO + O_3 \rightarrow NO_2 + O_2.$$

Since more than 90% of the emissions of oxides of nitrogen occurs as NO, an amount of ozone equivalent to the flux of the emitted NO will be converted[21] to NO_2. In other words, on a timescale of minutes, practically all of the local NO_2 in the troposphere is produced at the expense of O_3. NO concentration may be the cause for the lesser ozone destruction at the rural locations and more at the urban location, because in the latter location NO concentration is higher due to peak vehicular activity in the evening hours[17,18]. Hence higher ozone in the rural locations may be the combined effect of slower titration by NO in the evening hours and the greater ozone formation due to pollutants transported from the nearby polluted locations. Similar findings have been reported in earlier studies at rural sites, Anantapur and Gadanki, Andhra Pradesh, India[18,22]. The average diurnal variation during winter (December–February) and spring (March–May) seasons was also studied (Figure 3). It can be noticed from Figure 3 that even averaged diurnal variation during both the seasons shows higher ozone concentration at the rural locations than the urban location.

Significant difference in ozone concentration between the rural and urban locations was noticed during the winter season. However, during spring season this difference was comparatively less. Ozone concentration at the two rural locations was more or less the same during the winter season, but differed during the spring season. The difference in ozone concentration between the rural (both sites) and urban sites was significant at 5% level in the winter season. However during spring, this difference was significant at 5% level for one rural location (Belser) only. The ozone difference between the other rural location (Mutha) and the urban location (Pune) was not statistically significant in spring season. The higher concentration of ozone at both the rural locations suggests that ozone pollution is not restricted to the urban region, but has spread to the surrounding rural region also.

Ozone concentration during the monsoon season was less at all three locations due to cloudy sky conditions and rainfall activity, resulting in the washout of pollutant precursor gases. Diurnal variation was also not as systematic as observed in the other seasons. Ozone formation was most conducive during warm, dry and cloudless days with low wind speeds; these conditions most often occur with high-pressure systems. Further rainfall at the three locations is not uniform; Belser is categorized as a drought-affected area, while Mutha receives more rainfall than Pune. Therefore, diurnal variation during the monsoon season (June–September) is not presented in the study.

Comparison between ozone and meteorological parameters like temperature and humidity at all three locations has been made. Figure 4 elucidates the relation between ozone, temperature and humidity for three locations. It can be seen from Figure 4 that ozone is directly proportional to temperature and inversely proportional to humidity. Correlation coefficient between ozone and temperature was 0.94, 0.95, 0.94, while between ozone and humidity it was –0.93, –0.94, –0.94 for Pune, Belser and Mutha respectively. The correlation coefficients were highly significant at 1% level of significance. Though there is no direct impact of temperature on ozone, a significant positive correlation has been observed between the two. Temperature can be assumed as proxy of terrestrial radiation because radiation controls the atmospheric temperature. Rather, radiation controls both temperature and ozone. Moreover, temperature and humidity are anti-correlated; that is enhancement in temperature reduces the humidity favouring the ozone production process. Negative correlation between ozone and humidity can be justified as when humidity increases, the major photochemical paths for removal of ozone are photolysis followed by the reaction of O (^{1}D) with water vapour and reaction of HO_2 with ozone[10]. Also, higher humidity levels are associated with greater cloud abundance and atmospheric instability, the photochemical process is slowed down and the ground level ozone is depleted by deposition on water droplets.

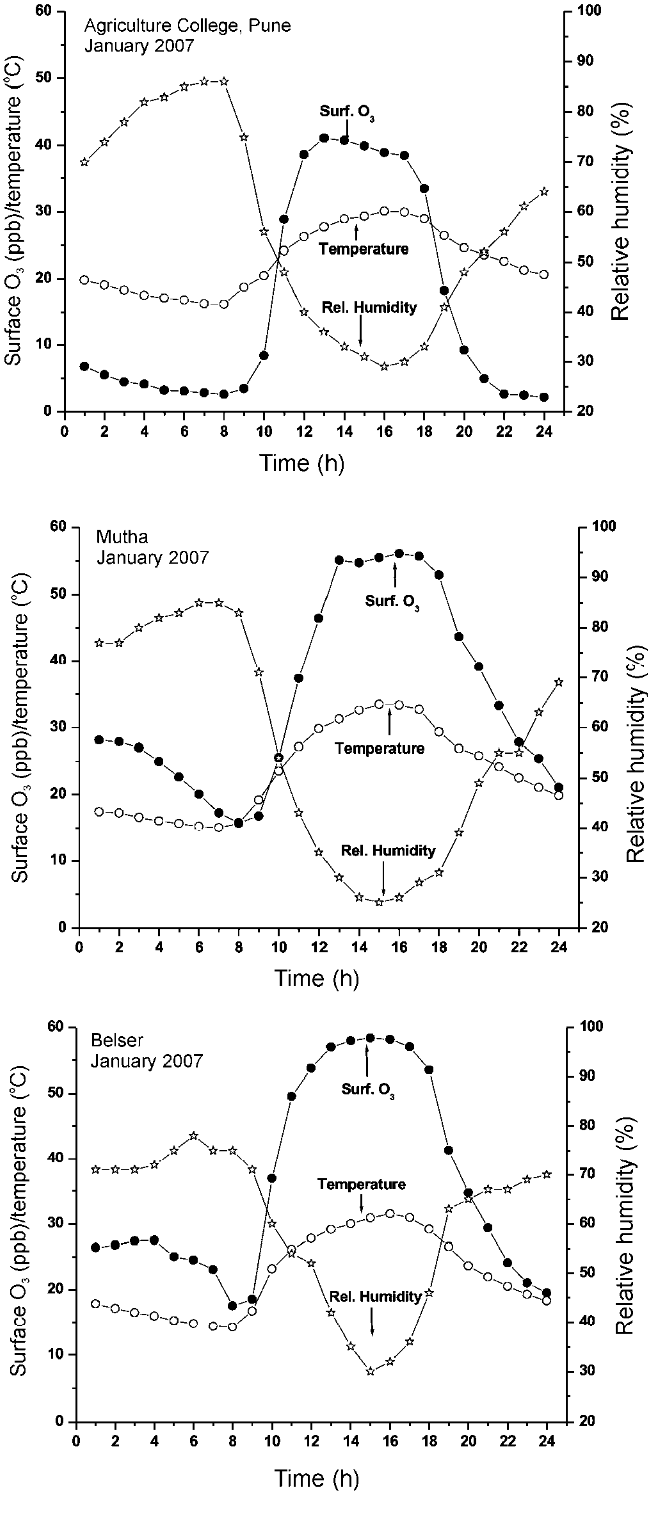

Figure 4. Relation between temperature, humidity and ozone.

The percentage contribution of various directions to averaged diurnal ozone concentration during winter and spring seasons is depicted in Figure 5. The figure represents a pie diagram of ozone concentrations from various directions plotted with observed data of wind direction and ozone during 24 h of the day at three locations. The averaged diurnal variation during winter and spring seasons has been computed using daily data of ozone and wind direction. The percentage contribution of ozone from each direction during winter and spring seasons has been computed and depicted in the form of a pie diagram.

In general during the winter season, the winds are easterly or southeasterly and change to westerly or southwesterly from April. Similar features are observed in Figure 5, at all three locations. The southeast sector contributes maximum during the winter season and the southwest sector contributes maximum during the spring season. Pune which is close to both the rural locations, is located towards the northwest of Belser and towards the east-northeast of Mutha. However, it has been noticed from the wind-direction data observed at the two rural locations that winds never blew from Pune to any of the rural locations during both seasons. Hence the possibility of transport of ozone from Pune to the rural locations is rejected. Therefore, at first, it can be expected that ozone production is controlled by precursor transport at both the rural locations. The precursor transport may be from the nearby road traffic emissions, because highways/major roads run near both the locations. A national highway (NH 9) runs west-east, 25 km away towards the north and one major road runs northwest–southeast, 5 km away towards the southeast side of Belser (Figure 1). It can be seen from Figure 5 that wind directions from the southeast and northeast sectors contribute maximum to ozone concentration during the winter season. Contribution of the southeast sector is also good during the spring season. Winds from the highways/roads bring more pollutants to the observation site, which may result in more ozone production. Similarly, another national highway (NH 4) runs north-south, 20 km away towards the east and one major road runs east-west, 10 km away towards the north of Mutha. It can be clearly seen from Figure 5 that for this location also winds from the highways/roads contribute maximum to ozone concentration.

Analysis of the hourly ozone data showed that (i) surface ozone at the rural locations was higher than that at the urban location during winter and spring seasons; (ii) the rate of ozone increase from morning to afternoon was more or less the same, but the rate of decrease in the evening hours differed for the rural and urban locations in the winter season, (iii) surface ozone was directly proportional to temperature and inversely proportional to humidity and (iv) though earlier studies suggested higher ozone concentration at rural areas due to slower titration of ozone by NO and transport of ozone from the nearby urban location, the present study points out the major contribution from the road traffic emissions, rather than ozone transport from the nearby urban location, Pune. Increase in transport vehicles with provision of good roads to meet the needs of a growing population may be contributing considerably to ozone pollution. Thus ozone pollution is not restricted to the urban region only, but has become severe in rural areas also. The results of this study are preliminary and need confirmation with more data for a sufficient period.

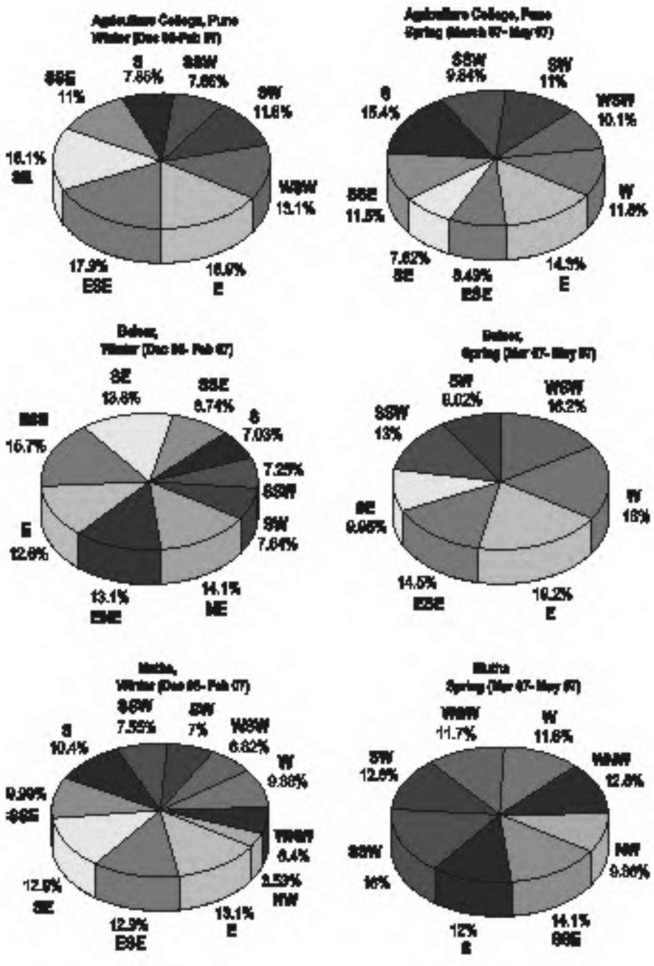

Figure 5. Percentage contribution from various directions to surface ozone.

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ACKNOWLEDGEMENTS. We thank the Director, IITM, Pune, for encouragement. This work was supported by the Department of Science and Technology, New Delhi.

Received 6 June 2008; revised accepted 21 October 2008

Molecular characterization of *Bt* cauliflower with multiplex PCR and validation of endogenous reference gene in Brassicaceae family

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Bt **cauliflower is one of the important genetically modified (GM) crops approved for Biosafety Research Level 1 field trials in India. Towards developing reliable qualitative and quantitative PCR methods for detecting and monitoring GM crops, in the present study, molecular detection of *cry1Ac* gene CaMV 35S promoter and an endogenous gene in *Bt* cauliflower was carried out by simplex and multiplex PCR. Furthermore, validation of S-locus receptor kinase (*SRK*) as the endogenous reference gene for the Brassicaceae family using simplex PCR has also been undertaken.**

Keywords: *Brassica oleracea* var. *botrytis*, endogenous reference gene, multiplex PCR, S-locus receptor kinase gene.

THE global area under cultivation of genetically modified (GM) crops has increased dramatically from 1.7 m ha in 1996 to 114.3 m ha in 2007, with 23 countries growing GM crops, including 12 developing countries and 11 industrial countries[1]. Since more than two dozen GM crops are being developed and are under different stages of field-testing in India[2], concerns have been expressed about the potential risks associated with their impact to the environment, biological diversity and human health. To address these concerns, effective and reliable GM detection methods need to be put in place on priority to meet the national regulatory/legal and labelling requirements.

Multiplex PCR (MPCR) is a variant of conventional PCR, including two or more pairs of primers in a single reaction to simultaneously amplify corresponding genes. The MPCR-based detection method is most reliable, efficient and cost-effective and has also been successfully employed in various GM crops. A reliable MPCR protocol has been established for efficient detection of transgene neomycin phosphotransferase and endogenous gene 1-aminocyclopropane-1-carboxylate synthase in GM tobacco and tomato[3]. Molecular screening based on MPCR involving amplification of endogenous reference genes for soya and maize, *35S* promoter and *nos* terminator for the detection of GM soya and maize has also been developed[4]. Recently, the simultaneous detection of *vip3A*-type insecticidal gene, *npt*II, *35S* promoter and *nos* terminator in transgenic maize and cotton lines (Cot102) has been reported by MPCR assay[5]. The simplex and MPCR systems were standardized and employed to identify events Mon 1445 and Mon 531 from other GM cottons and GM crops[6]. Multiplex PCR assay to detect GM Roundup Ready soybean in foods has also been developed[7]. Two separate MPCR assays were developed[8] for the detection of transgenic papaya line 55-1 and transgenic squash line CZW-3. In GM detection, for reliable MPCR, endogenous reference gene is an important component; and immense efforts have been made to validate the reference genes for different crops. Some of the validated endogenous reference genes are *zein* or *invertase1* genes for maize, *lectin* or *hsp* (heat shock protein) genes for soybean, *BnACCg8*, *cruciferin* or *HMGI/Y* genes for rapeseed, *LAT52* gene for tomato, *SPS* gene for rice and *Sad1* gene for cotton[9]. So far, validation of an endogenous reference gene for cauliflower has not been reported.

Brassica oleracea var. *botrytis* (cauliflower) is an important vegetable crop grown for its edible inflorescence. It is highly vulnerable to insect-pests that cause about 20–30% yield loss[10]. *Bt* cauliflower with *cry1Ac* gene, developed by Sungro Seeds Research Ltd, India, has been approved for Biosafety Research Level 1 field trials.

In the present study, S-locus receptor kinase (*SRK*) gene, which is a female determinant of the genetic mechanism named as self-incompatibility (SI) in angiosperms, has been validated as an endogenous reference gene for the family Brassicaceae. The qualitative assay for detection of transgenes, viz. *cry1Ac* and *CaMV 35S*

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