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Spatio-Temporal Analyses of Formaldehyde over Pakistan by Using SCIAMACHY and GOME-2 Observations

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ABSTRACT

This study primarily focuses on monitoring of tropospheric formaldehyde (HCHO) column densities over Pakistan during the time period of year 2003 to 2012. Observations from two satellite instruments SCIAMACHY (Scanning imaging absorption spectrometer for atmospheric chartography, on-board ENVISAT-1) and GOME-2 (Global ozone monitoring experiment, on-board Metop-A) were used. Spatial and temporal distributions of HCHO column densities over Pakistan are analysed. Spatial maps were generated in order to see the distribution of HCHO and to identify major hotspots across the country. Seasonal cycle of HCHO over all provinces of Pakistan showed the summer maximum attributed to increase in biogenic emissions and biomass burning activities. Further emphasis was made on source identification of HCHO emissions. It revealed that agriculture fires and extensive use of compressed natural gas (CNG) as fuel also contribute to tropospheric HCHO in Pakistan. World fire atlas data from along track scanning radiometer (ATSR) was used to identify effect of agriculture waste burning on HCHO concentration in Pakistan. Significant correlation was observed between agricultural fires and increased HCHO column densities.

Keywords: Tropospheric HCHO; SCIAMACHY; GOME-2; Biogenic emissions; Agriculture fires; Pakistan.

INTRODUCTION

Formaldehyde (HCHO) is one of the most abundant carbonyl compounds in both distant background sites and polluted urban atmosphere (Ayers *et al.*, 1997; Grosjean *et al*, 2002; Stavrakou *et al.*, 2008). It plays an important role in tropospheric chemistry because it is a secondary product in most of non-methane volatile organic compounds (NMVOC) oxidation chains (Kesselmeier and Staudt, 1999; Stavrakou *et al.*, 2008).

Formaldehyde is emitted in the atmosphere from both natural and anthropogenic sources. Globally, oxidation of methane (CH_4) and NMVOCs accounts for major source of formaldehyde in the atmosphere (Arlander *et al.*, 1995; WHO, 1989; EC, 2001; Seinfeld and Pandis, 2008). During the growing season of vegetation, HCHO is produced from biogenic sources with the largest contribution coming from oxidation of isoprene emitted from terrestrial vegetation (Guenther *et al.*, 1995; 2000; Meller and Moortgat, 2000; Palmer *et al.*, 2003, 2006; Millet *et al.*, 2008).

Anthropogenic sources of formaldehyde include industrial and combustion processes (EC, 2001), biomass burning and agricultural fires which can emit HCHO and other hydrocarbons resulting in secondary formation of formaldehyde (ATSDR, 1999; Seinfeld and Pandis, 2008). Motor vehicles that are not fitted with catalytic convertors and vehicles using compressed natural gas (CNG) as fuel also emit formaldehyde in the atmosphere (WHO, 1989; Kelly *et al.*, 1996; ATSDR, 1999; EC, 2001; Olsen and Willson, 2011; Shah *et al.*, 2012).

HCHO has a very short lifetime, i.e., $\tau \approx 3.4$ hours (Anderson *et al.*, 1996; Sander *et al.*, 2006; Seinfeld and Pandis, 2008). It is removed from the atmosphere mainly by photolysis and its reaction with OH (Arlander *et al.*, 1995; Larsen and Larsen, 1998; Brune *et al.*, 1999; Platt and Stutz, 2008), while nitrate, hydrogen peroxide, chlorine, ozone and hydroperoxyl radicals also react with formaldehyde but they don't play a significant role in determining the fate of HCHO in the atmosphere (EC, 2001; Platt and Stutz, 2008; Seinfeld and Pandis, 2008)

Satellite measurements of HCHO can be used to estimate emissions of NMVOCs (Palmer *et al.*, 2003; Platt and Stutz, 2008; Stavrakou *et al.*, 2009a, b) on spatial and temporal scales, making them very much suitable for air quality studies and for constraining their emissions (Fried *et al*, 2002). Air pollution is the fastest growing environmental

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problem in Pakistan (World bank, 1996; Khattak *et al.*, 2014). Since last few years oil prices are on continuous increase and has compelled public to use alternative fuels such as compressed natural gas (CNG). According to the International Association of Natural Gas Vehicles (IANGV) there are approximately 4 million Natural Gas Vehicles (NGVs) in use worldwide, of which 1.6 million are in Argentina and 1.5 million in Pakistan. Additionally, due to its affordability (CNG is cheaper than gasoline and diesel in Pakistan), a large number of motor vehicles has been shifted from conventional fuel (petroleum and diesel) to CNG. Therefore, increased use of CNG as fuel has resulted in enhanced emissions of HCHO (e.g., Olsen and Wilson, 2011; Shah *et al.*, 2012) especially, in the major cities of Pakistan with high traffic density. Therefore, monitoring of atmospheric trace gases on regular basis is mandatory in order to address air quality issues (Forster *et al.*, 2007).

According to report from economic survey of Pakistan 2012–2013, all of the air quality monitoring stations are non-functional since year 2010 (ESoP, 2013). Thus, satellite instruments play a pivotal role in bridging such gaps, especially, in countries like Pakistan.

This study presents first database of HCHO column densities over Pakistan during the time period of January 2003 to February 2012. Tropospheric columns were retrieved from SCIAMACHY (Scanning Imaging Absorption spectrometer for Atmospheric Chartography - Bovensmann *et al.*, 1999) and GOME-2 (Global ozone monitoring experiment -2; Callies *et al.*, 2000; Munro *et al.*, 2006) using differential optical absorption spectroscopy technique (DOAS - Platt and Stutz, 2008). In the second part of this study, the temporal evolution and seasonal cycles of HCHO over all provinces of Pakistan are investigated. In order to test the statistical significance of observed trends, regression analysis, Mann-Kendal test and bootstrap resampling methods (Gardiner *et al.*, 2008) were adopted. Data from ATSR (along track scanning radiometer) world fire atlas (Arino *et al.*, 2011) was also used to study the effect of agricultural fires, biomass burning and other fire events on the concentration of HCHO in all provinces of Pakistan.

METHODOLOGY AND DATA SETS

Satellite data for HCHO observations was obtained from the TEMIS (Tropospheric Emissions Monitoring Inventory Service) website (http://h2co.aeronomie.be). The version 12 of the GOME-2 (available from 2007–02/2012) and SCIAMACHY (available from 01/2003– 02/2011) HCHO products was used (for details see De Smedt *et al.*, 2012).

Level-2 HCHO monthly data retrieved by DOAS (Chance *et al.*, 2000; Palmer *et al.*, 2001; Wittrock *et al.*, 2006; De Smedt *et al.*, 2008; Platt and Stutz, 2008) technique and averaged on a 0.25° × 0.25° grid and cloud fraction less than 30 percent was downloaded from the TEMIS website for the years 2003–2012 (De Smedt *et al.*, 2008, 2012). Table 1 presents the main features of the two satellite instruments used in this study. De Smedt *et al.* (2008), calculated the total error of HCHO retrieval by taking into account slant column random errors, reference sector

Table 1. Main features of SCIAMACHY and GOME-2 satellite instruments.

S.no	PROPERTIES	SCIAMACHY	GOME-2
1	Instrument	scanning imaging absorption spectrometer for atmospheric chartography	global ozone monitoring experiment -2
2	Data available	2003–Feb. 2012	2007–onward
3	Scanning time	4 s forward + 1 s back scan	4.5 s forward + 1.5 back scan
4	Nadir resolution (km^2)	60 × 30	80 × 40
5	Swath width	960 km	1920 km
6	Global Coverage	6 days	1.5 days
7	Target species	O_3, O_2, O_4, NO, NO_2, N_2O, BrO, OClO, H_2O, SO_2, HCHO, CHOCHO, IO, CO,CO_2, CH_4; clouds and aerosols	H_2CO ,O_3, NO_2, H_2O, BrO, SO_2, HCHO, CHOCHO, IO, clouds and aerosols
8	Wavelength ranges	240–2380nm	240–790 nm
9	Spectral resolution	0.2–1.5 nm	0.2–0.4 nm
10	Equator crossing time (local time)	10:00 am	09:30 am
11	Retrieval methods	DOAS (Platt and Stutz, 2008; De Smedt *et al.*, 2012)	DOAS (Platt and Stutz, 2008; De Smedt *et al.*, 2012)

correction, impact of absorbing aerosols and air mass factor (AMF- Palmer *et al.*, 2001; Martin *et al.*, 2003, 2004) on the monthly and zonally averaged vertical columns from both SCIAMACHY and GOME observations. AMFs used in this study were calculated for both clear (with cloud fraction less than 30%) and cloudy sky conditions. The total error estimated for HCHO monthly columns ranges between 20 and 40% for both GOME-2 and SCIAMACHY data in agreement with the errors 25–30% calculated by Millet *et al.* (2006).

Inter- Satellite Comparison

In order to identify the spatial distribution of formaldehyde across Pakistan a database was prepared from observations of both satellite instruments SCIAMACHY (2003–02/2012) and GOME-2 (2007–02/2012). Fig. 1 shows the comparison of climatological mean of tropospheric HCHO column densities over Pakistan during the years 2007–2011. Additionally, a map of absolute differences between mean HCHO columns from SCIAMACHY and GOME-2 is also presented. Black circles are indicating the location of main cities of Pakistan. Grey and dark brown lines in each map are representing the district and provincial boundaries, respectively. The comparison of both data sets has revealed the similar seasonal cycle (with summer maximum and winter minimum) and the spatial distribution of HCHO sources across the Pakistan is quite similar in both data sets. Especially, HCHO concentrations are higher over the province of Punjab followed by Sindh, Khyber Pakhtunkhwa (KPK) and Baluchistan. However, it can be clearly seen that HCHO concentration exhibited by GOME-2 observations are comparatively lower than exhibited by the SCIAMACHY observations (except green pixels in the difference map). The SCIAMACHY map with finer spatial resolution (60 × 30 km^2) exhibited well confined HCHO plumes and quantitatively larger values as compared to GOME-2 (80 × 40 km^2) maps exhibiting relatively smaller HCHO columns and smeared out over larger areas. These differences could be mainly attributed to different characteristics (see Table 1) of spatial and spectral resolutions and aerosol loading. Especially, cloud treatment in both data set is different as SCIAMACHY has larger spectral coverage (UV, vis, NIR and IR) as compared to GOME-2 (UV and vis). Furthermore, they observe the same scene with a time difference of about 30 minutes. In principal, the observed differences are not as large as compared to the difference in the characteristics of both instruments.

RESULTS AND DISCUSSIONS

Spatial and Temporal Distribution

Hotspots (areas with high concentration of HCHO) were identified from the prepared database. Fig. 1 exhibited main cities (black circles) with relatively large tropospheric HCHO column densities (including Sargodha, Lahore, Faisalabad, Okara, Islamabad, Multan, Bahawalpur, Sukker, Dadu, Umerkot, Karachi and Peshawar).

Table 2 lists the yearly mean of HCHO column densities observed by SCIAMACHY instrument over major cities of Pakistan during the time period of 2003–2011. The HCHO column was taken over the grid box (0.25° × 0.25°) occurring exactly over the respective city. The highest concentrations of HCHO over cities of Lahore, Sialkot, Faisalabad and Bahawalpur were found in 2007, followed by Sargodha and Islamabad in 2004. Overall the city of Lahore (2^{nd} most densely populated city of Pakistan) exhibited the highest HCHO columns during the time period of 2003–2011 followed by Bahawalpur, Sargodha, Multan and Faisalabad. Surprisingly, city of Karachi with relatively larger population and traffic density did not exhibited enhanced HCHO levels. Main reasons could be that Karachi is located on the shores of the Arabian Sea and frequent sea breeze advects relatively clean air to the city in addition to high humidity, and dissipate the HCHO concentrations over larger areas away from the Karachi. Furthermore, it experiences moderate temperature (27°C) throughout the years and probably the biogenic emissions are less as compared to other cities with relatively larger temperature (32°C mean summer temperature). This leads to quantitatively lower mean HCHO VCDs over Karachi. Another probable reason could be that industrial activities might have been decreased in this region because of politically instable situation, security issues, global financial recession and above all the experienced power shortages during the study period. While in case of Islamabad/Rawalpindi and Lahore cities, larger mean HCHO VCDs might be influenced by trans-boundary HCHO pollution from neighbouring regions of India (Khattak *et al.*, 2014). It can be clearly seen from mean wind fields (2004–2011) at 1000 hPa levels over Pakistan and neighbouring countries presented in Fig. 2, prepared by using the NCEP Reanalysis Derived data provided by the NOAA/OAR/ESRL PSD, Boulder, Colorado, USA, from their Web site (http://www.esrl.noaa.gov/psd). No significant behaviour of temporal increase or decrease was observed across all major cities of Pakistan during the selected time period.

Temporal and Spatial Trend Analyses

Temporal evolution of HCHO column densities over Pakistan during the time period of 2003–2012 is shown in Fig. 3, together with the estimated errors on the columns. Formaldehyde columns show a marked seasonal variation dominated by biogenic emissions. To fit the time-series of monthly observations, a model with a linear trend and an intra-annual function and seasonal variations is used (van der A *et al.*, 2006) as given below:

$$m(t) = A + Bt + \sum_{n=1}^{4} C_n \cos(n2\pi t) + \sum_{n=1}^{4} D_n \sin(n2\pi t) + U\delta \tag{1}$$

where $m(t)$ is the observed monthly HCHO *vertical columns* for the month t (expressed in fractional year), A (the annual mean of the reference/first year), B (*annual trend*), C_n, D_n (Fourier terms for seasonality) and U(bias of satellite retrieval) are fitted. A linear least-squares method is used to fit Eq. (1) with the observations and taking their errors into account. In order to assess the statistical significance of the derived annual trends, the uncertainties on the fitted

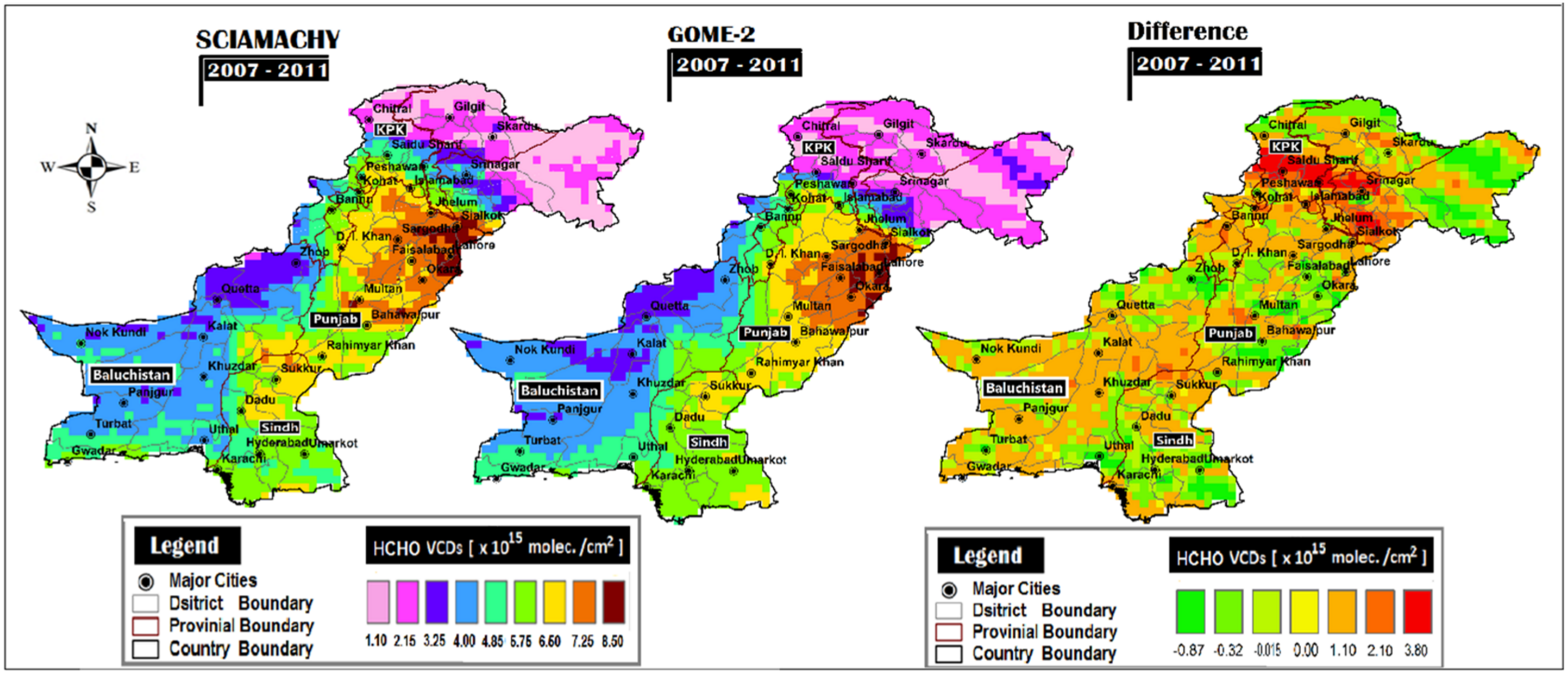


Fig. 1. Spatial maps of mean HCHO column densities retrieved from SCIAMACHY and GOME-2 data during the period of 2007–2011. The scale bar shows the distribution of formaldehyde tropospheric column densities in the range of (× 10^{15} molecules/cm^2) over Pakistan. Black circles are representing the main cities of Pakistan. Also, map of absolute difference between GOME-2 and SCIAMACHY observations is presented.

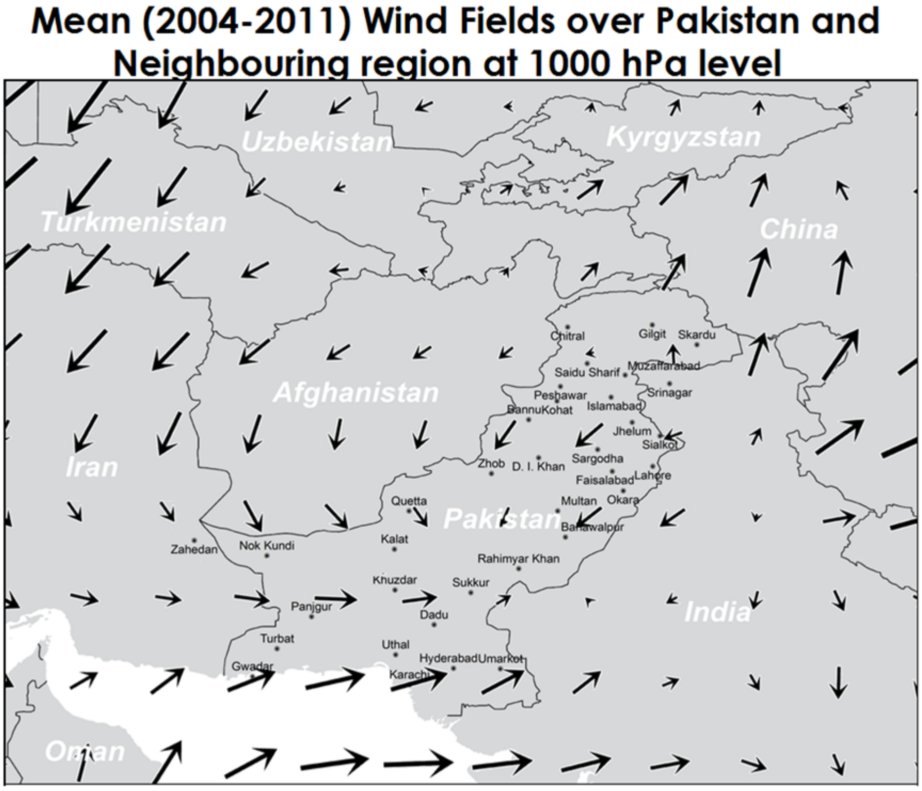


Fig. 2. Wind fields over Pakistan and neighbouring region averaged over 2004–2011. Wind fields are generated from *NCEP* Reanalysis Derived data provided by the NOAA/OAR/ESRL PSD, Boulder, Colorado, USA, from their Web site at http://www.esrl.noaa.gov/psd/. Arrows (wind vectors) are indicating the wind direction and magnitude of each arrow is subject to respective wind speed (larger arrows for higher wind speed and smaller arrows for calm winds). Adopted from Khattak *et al.* (2014).

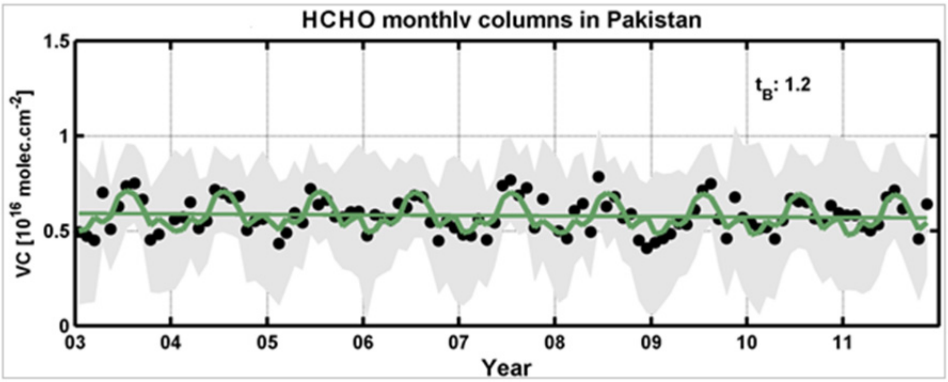


Fig. 3. Time series of HCHO vertical columns densities (VCD) monthly averaged (black dots) over Pakistan from SCIAMACHY observations during the time period of 2003–2012. Green line is representing the fitted time series and linear least square fit.Temporal variation and trend of tropospheric HCHO over Pakistan from 2003–2012 was calculated by applying leaner least square fit (green line) it was found statistically insignificant ($t_B < 2$).

parameters are calculated using the bootstrap resampling method (Gardiner *et al.*, 2008). The statistical significance level of the trend is better than 95% for $t_B = |B/\sigma_B|$ larger than 2 (Weatherhead *et al.*, 1998; van der A *et al.*, 2006). For further details see (De Smedt *et al.*, 2008; 2010)

Fig. 3 presents an example of monthly averaged SCIAMACHY observations of HCHO over the whole Pakistan and the fitted time series using Eq. (1). We find no statistically significant trend over the period 2003–02/2012 in the HCHO columns over Pakistan, which is in opposition to the HCHO observations in India (De Smedt *et al.*, 2010) and other countries from the neighbouring region. A closer look at the data shows that the HCHO columns for season MAM (March–April–May) are slightly decreasing ($-0.6 \pm 0.3 \times 10^{14}$ molec. cm^{-2} yr^{-1}). However, it is not statistically significant as t_B is less than 2 (Fig. 4).

Furthermore, spatial trends that are not easy to interpret in Table 2 were investigated by applying Mann-Kendal test and to check the statistical significance of the data sets used in this study. Fig. 5 exhibits the spatial trends of HCHO columns over Pakistan for both instruments. Only the grid cells with increased or decreased HCHO columns with 95% confidence interval are presented. White colour shows the pixels with statistically insignificant trends. In general, very few pixel have exhibited the statistical significant trends mainly over Baluchistan region. An increasing trend of 1.5–3 × 10^{13} molecules cm^{-2} $year^{-1}$ over the provinces of Baluchistan and Sindh while, KPK and Punjab are showing decreasing trend of –2 × 10^{13} molecules cm^{-2} $year^{-1}$ in SCIAMACHY data (2003–2011). While, GOME-2 data (2007–2011) exhibited the increasing trend over all provinces in the range of 1.5–3 × 10^{13} molecules cm^{-2} $year^{-1}$. The reason for this disagreement is not clear yet. However, the observed trends are so little that the observed difference is expected because both instruments differ in spatial resolution and other aspects (see Table 1).

Source Identification

This study also emphasizes on the source apportionment of HCHO emissions in Pakistan. Contribution from different sources is identified and discussed in further details in the following sections.

Agriculture Fires and Formaldehyde

Agricultural fires emit aerosol particles, greenhouse gases and various trace gases into the atmosphere (Curtzen, 1990). Farmers of Pakistan burn their crops to minimize weeds, pest and to make their field ready for the upcoming growing season. Post-harvest burning of crop residues is a common practice in Pakistan for fertilizing the fields. Peak seasons cover the month of April and May for wheat crop and November for rice paddies. Fire maps over Pakistan for each month from January 2003 to February 2012 were created in order to see the effect of agricultural fires, biomass burning and other fire events on the concentration of HCHO. For this purpose data from ATSR (along track scanning radiometer) world fire atlas of algorithm 2 (temperature above 312°K) was used. Fig. 6(a) shows the spatial distribution of total number of fire events and mean maps of SCIAMACHY observations during the time period of 2003–2012. It can be seen that regions with extensive vegetation fires are exhibiting enhanced HCHO columns. Especially, regions of Baluchistan (dark green triangles), Punjab (brown triangle) and Sindh (red triangle) provinces exhibited enhanced formaldehyde columns consistent to the regions with fire hotspots caused by agriculture fires. It is also worth to mention that the enhanced levels of HCHO over Pakistan during summer months are not only because of agricultural fires. These are contributed mainly by enhanced biogenic emissions (isoprene oxidation) caused by high summer temperature, biomass burning and other anthropogenic activities including road traffic and industrial activities.

Fire events have significant effect on the concentration of HCHO in Pakistan. It can be clearly identified that

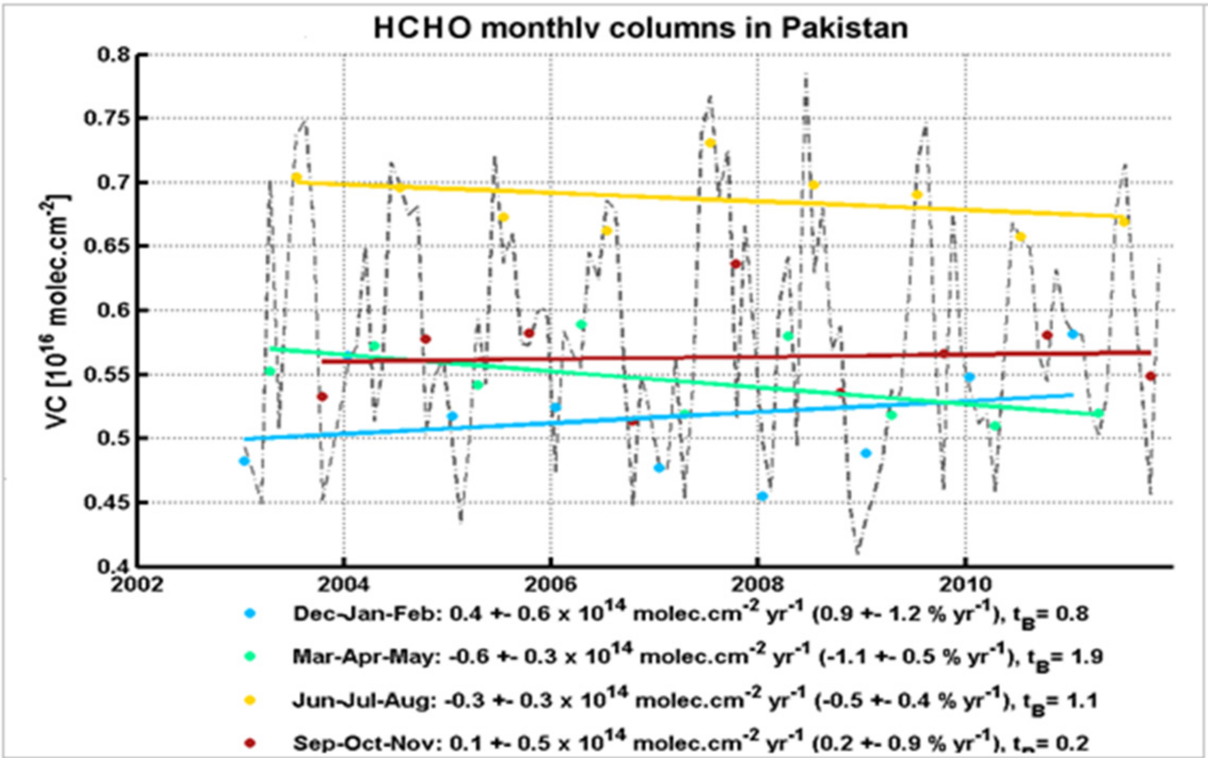


Fig. 4. Temporal trend of tropospheric HCHO VCD for different seasons: December January February (DJF), March April May (MAM), June July August (JJA) and September October November (SON) during the time period of 2003–2011. For $t_B \geq 2$, is considered as of statistical significance of 95% confidence interval.

Table 2. Annual average vertical column densities of HCHO for year 2003–2012 over hotspots areas of Pakistan (unit: 10^{15} molecules cm^{-2}).

S. No.	Cities	2003	2004	2005	2006	2007	2008	2009	2010	2011
1	Islamabad	7.0	6.83	6.16	5.58	6.75	6.66	7.66	5.08	6.83
2	Okara	6.58	7.66	4.91	7.33	8.0	7.75	6.08	7.0	8.25
3	Sargodha	8.83	9.16	7.17	7.25	7.17	8.58	6.75	7.08	7.83
4	Sialkot	7.08	8.33	8.0	7.08	9.16	7.75	6.83	6.0	7.66
5	Lahore	8.83	7.91	7.166	8.41	10.3	8.66	6.66	8.83	6.33
6	Multan	7.66	8.91	9.25	7.42	6.42	7.92	7.17	7.087	6.42
7	Faisalabad	7.58	7.75	8.33	7.75	8.33	7.75	7.83	6.25	7.25
8	Bahawalpur	6.16	7.66	8.25	5.91	9.91	5.66	7.08	7.0	6.08

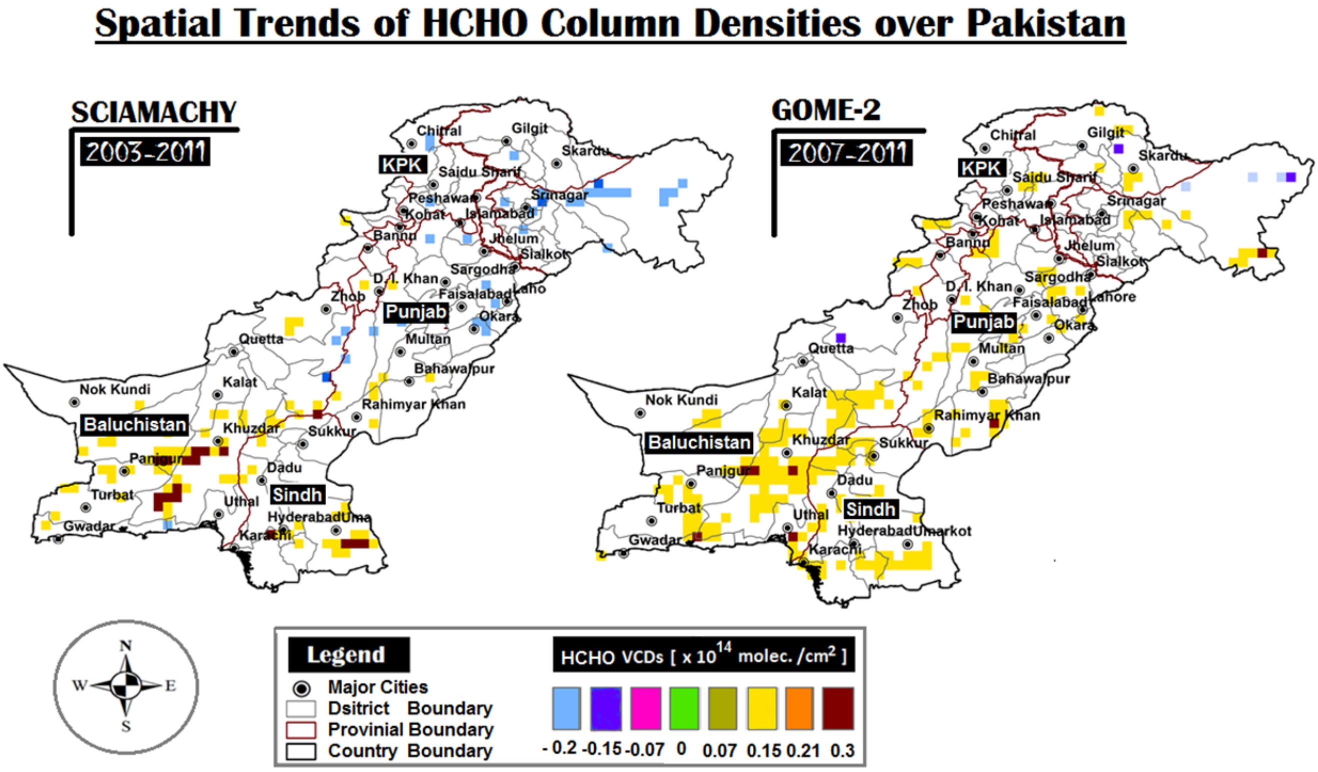


Fig. 5. Absolute annual trends over the period of 2007–2011 for GOME-2 and 2003–2011 for SCIAMACHY datasets. The trends are calculated with 2003 and 2007 as reference year for SCIAMACHY and GOME-2, respectively. Blank areas represent statistically insignificant results.

months with large fire counts (red circle dashed line in Fig. 6(C)) are also exhibiting higher concentrations of HCHO. Fig. 6(C) presents time series of ATSR fire data in red and SCIAMACHY HCHO columns in blue. HCHO columns were considered from only those satellite pixels which exhibited the fire activities. A significant correlation of r = 0.88 (r^2 = 0.77) is observed for total fire events across Pakistan and resulting HCHO columns in Fig. 6(b). A brief summary of total number of fire counts, total and mean HCHO columns and correlations (r) between fire counts and resulting HCHO columns from each province and all Pakistan is presented in Table 3. Both data sets exhibited significant correlation r with maximum from Sindh followed by Punjab, Baluchistan and KPK provinces. It is worth mentioning that in Baluchistan province fire activities are only exhibited in the eastern regions adjacent to Sindh and the similar trend is reflected from enhanced HCHO columns in Baluchistan. While in Punjab Province, although correlation between observed fires and HCHO column is significant, however, the maximum HCHO is not contributed from the fires. As maximum HCHO columns are observed with relatively less fire activities but over densely populated, higher vehicular number and industrial activities. This indicates that the HCHO emissions in Punjab province are mainly contributed from sources other than fire activities, as discussed in following sections.

Vehicles, Fuel Types and Formaldehyde

Emission control legislation standards are hardly adopted and met by most of the vehicles in Pakistan. For instance EURO-II emission standards were introduced in July 2009 for petrol consuming vehicles and in July 2012 for diesel

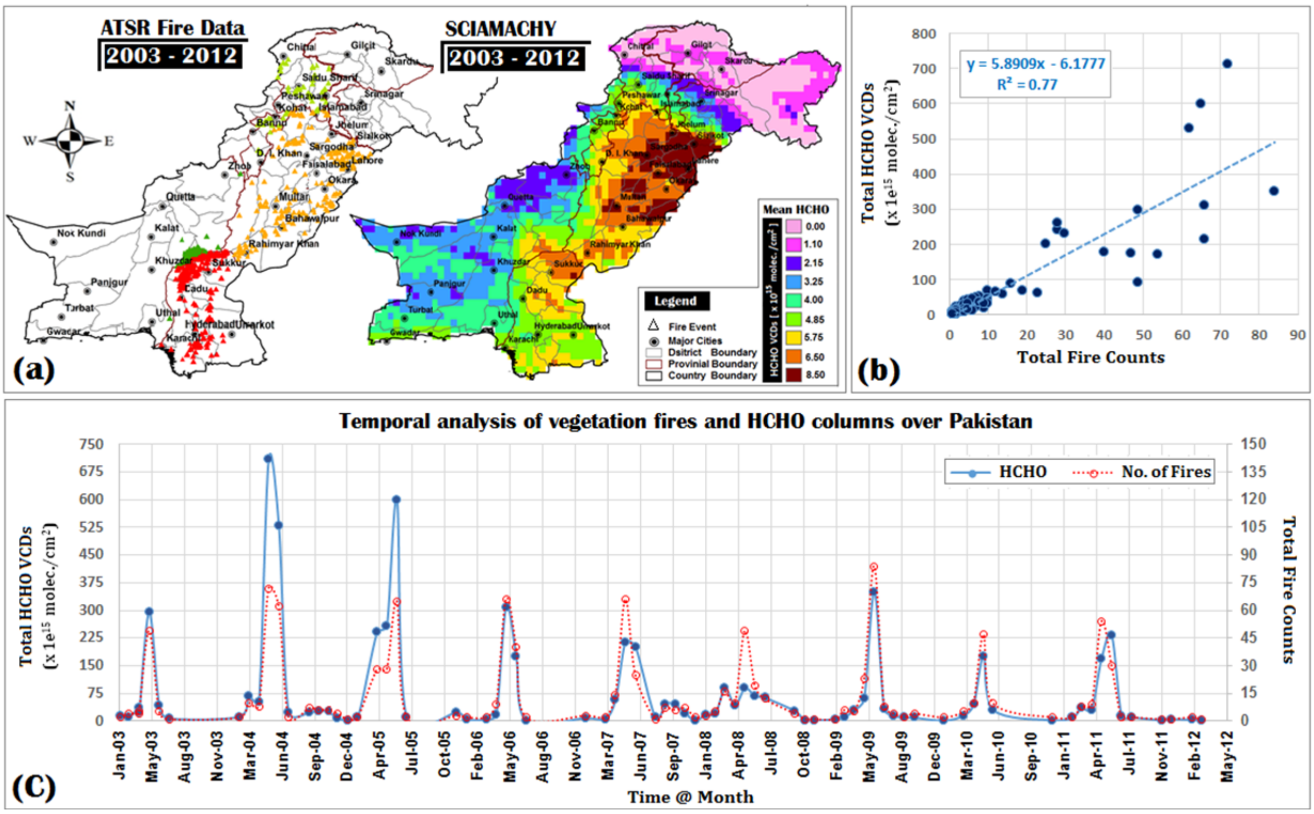
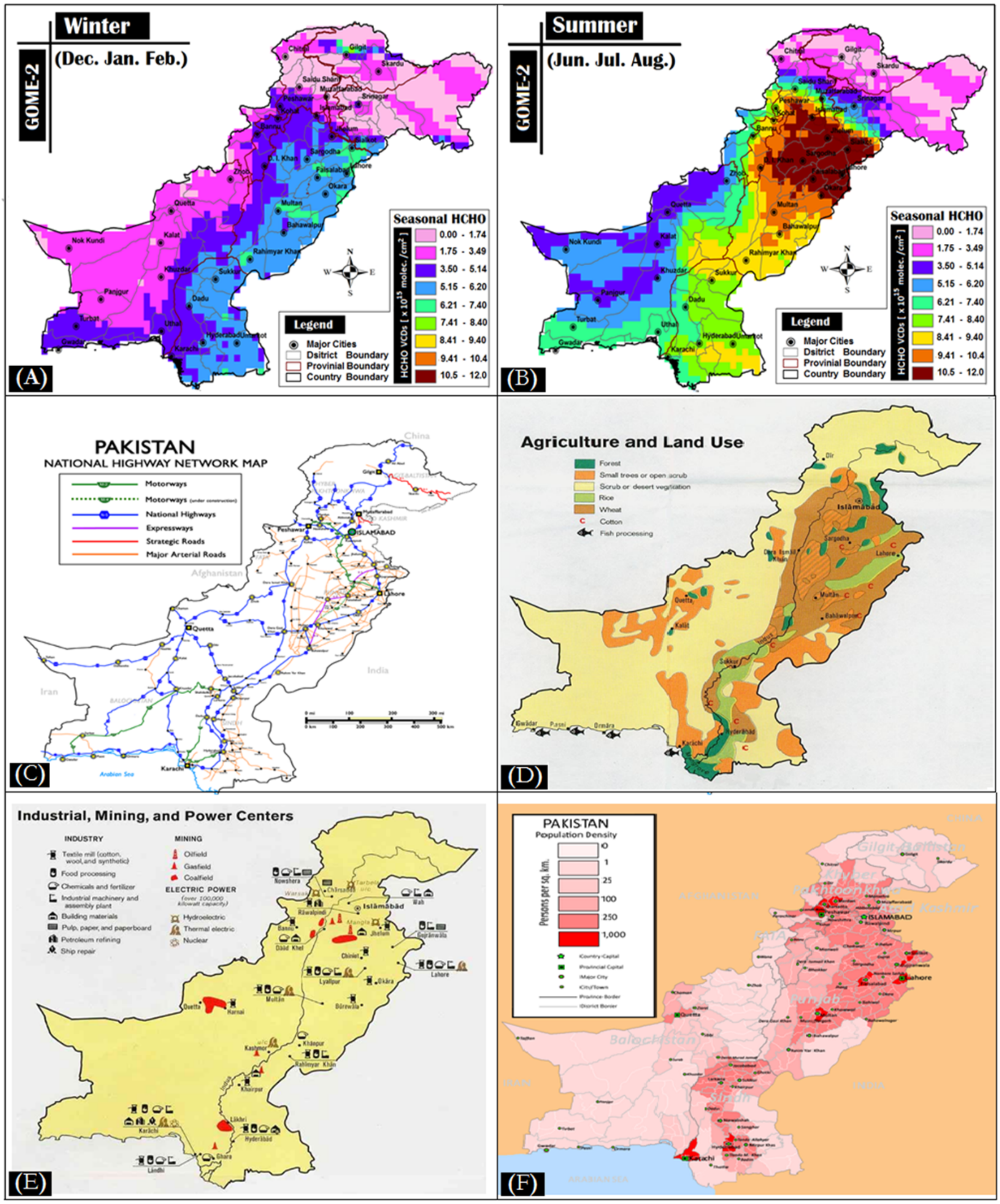


Fig. 6. (a) Long-term mean map of ATSR (along track scanning radiometer) fire data and HCHO VCDss from SCIAMACHY (2003-2012) instrument.(b) correlation between total/sum HCHO VCDs and ATSR fire counts in Pakistan is presented. HCHO VCDs were sum over the pixels having fire events. (c) Effects of fire events on the concentration of HCHO in Pakistan is presented for years 2003 to 2012. Time series of ATSR fire data in red and SCIAMACHY HCHO columns in blue are presented. Similar patterns and coincidence was observed in both fire counts and HCHO columns.

Table 3. Sum and mean vertical column densities of HCHO for year 2003–2012 over pixels exhibiting fire activities across Pakistan.

Region	Total No. of Fire Counts	Total/sum HCHO VCDs (× 10^{15} molec. cm^{-2})	Mean HCHO VCDs (× 10^{15} molec. cm^{-2})	r (r^2)
Punjab	276	1261	4.56 ± 0.6	0.87 (0.77)
Sindh	463	2687	5.80 ± 0.9	0.91 (0.84)
KPK	101	412	4.08 ± 0.7	0.72 (0.52)
Baluchistan	237	1512	6.38 ± 1.4	0.85 (0.73)
Pakistan	1077	5872	5.45 ± 0.8	0.87 (0.77)

vehicles (Pak-EPA). However, recent studies Fatima, (2013) and Khattak *et al.* (2014) indicated vehicular emissions as substantial source of the observed temporal increase in NO_2 and SO_2 columns over Pakistan during the time period of 2003–2012, respectively. Another source of tropospheric formaldehyde in Pakistan is vehicular emissions, especially, the vehicles which are not fitted with catalytic convertors (Gaffney *et al.*, 1997) and the vehicles consuming compressed natural gas (CNG) as fuel. Seasonal mean HCHO column densities over Pakistan for the months of December, January and February retrieved from GOME-2 observation during the time period of 2007–2012 are compared with maps of road networks (for traffic density), population density and, industrial and mining activities in Pakistan. Comparison presented in Fig. 7 shows that provinces with highest anthropogenic activities are also exhibiting enhanced levels of formaldehyde column densities. Especially, the province of Punjab is leading in both HCHO columns and anthropogenic activities followed by Sindh, KPK and Baluchistan during winter months. Seasonal average for the month of December, January and February (Fig. 7(A)) was selected for this comparison because HCHO emissions are mainly due to anthropogenic activities during these months as compared to spring, summer and autumn seasons which are mainly dominated by HCHO emissions from agricultural fires events and biogenic emissions. Similarly, seasonal average for the month of June, July and August (Fig. 7(B)) was compared with HCHO columns with the maps of agriculture and forest cover of Pakistan (Fig. 7(D)) in order to identify the areas affected by HCHO emissions due to



Map sources: C: (national highway and motorways of Pakistan (http://www.nhmp.gov.pk/mapm.) D: (adopted from http://pakmaps.com.pk/agricultural.php) E :(adopted from http://pakmaps.com.pk/agricultural.php) F: (data source of World Trade Press and Population census organisation, Government of Pakistan)

Fig. 7. Compares maps of road networks (C - for vehicular density), industrial, mining and power centres (E), agriculture and forest cover (D) and population density (F) in Pakistan with seasonal averaged map of formaldehyde columns over Pakistan for seasons DJF (A - December, January and February) and JJA (B - June, July and August) retrieved from GOME-2 observations during the time period of 2007–2012.

agricultural fires and biogenic emissions. The comparison clearly indicated that higher HCHO column densities are observed over the areas of KPK, Punjab, Sindh and Baluchistan with larger forest cover and land used for wheat crop cultivation. It supported our hypothesis of summer time maxima in HCHO column densities over Pakistan is due to biogenic emissions and wheat crop residue fires.

According to International Association of Natural Gas Vehicles (IANGV) about 4 million vehicles use Compressed Natural Gas (CNG) and among them 1.5 million exist in Pakistan only. Additionally, as CNG is cheaper as compared to petrol and diesel in Pakistan, its consumption has increased in Pakistan. During last five years about 75% of vehicles are using CNG (ESoP, 2013). Fig. 8(a) presents the comparison of total number of vehicles (in red), CNG vehicles (in green), consumption of petroleum products (in brown) and total CNG consumption (in violet) with HCHO columns (in blue) averaged over three months: December January and February during the time period of 2003 to 2011 from SCIAMACHY data, while Fig. 8(b) presents the respective correlations (r). Although, use of CNG as fuel in Pakistan is increased but seasonal averaged SCIAMACHY observations did not reflect equivalent increase in HCHO columns over Pakistan during the whole time period. However, significant increase is observed during the time period of 2009 to 2011. Especially, the comparison is improved when a decrease is observed in the use of petroleum products. Also, correlation is further improved when seasonal mean HCHO columns are compared with total number of vehicles using CNG as fuel including vehicles shifted from conventional fuel to CNG (green dots in Fig. 8(b)). It indicates that use of CNG as fuel has resulted in the enhanced levels of HCHO columns in Pakistan during the selected time period. However, use of CNG as fuel also results in lowering the emissions of other air pollutants e.g., particulate matter, NO_x, SO_2 (Suthawaree *et al.*, 2012 and references therein).

Seasonal Cycles Observed over Different Provinces of Pakistan

Formaldehyde emissions increases during summer (JJA) and decreases in winter (DJF), because of the increased biogenic emissions of isoprene is driven by temperature (Guenther *et al.*, 1995; Abbot *et al.*, 2003; Palmer *et al.*, 2003, 2006; Millet *et al.*, 2008; De Smedt *et al.*, 2010, 2012). Additionally, it is contributed by the large amount of biomass burning, agriculture and forest fires as discussed in the section 3.3.1. During fall season (SON) biogenic emissions decrease such as the formaldehyde concentrations as well. The lowest HCHO are observed during winter (DJF) season, due to less biomass burning and decreased biogenic emissions. The observed HCHO columns are mainly resulting from industrial and vehicular emissions. It can be clearly identified from the maps of climatologically averaged HCHO data from the GOME-2 observations for the period of 2007–2012 as presented in Fig. 9. Regional analyses were also performed to investigate seasonality in HCHO emissions over four provinces of Pakistan as shown in Fig. 10. As expected, all provinces (with minor exceptions from KPK province) show the same seasonal cycle of maximum HCHO

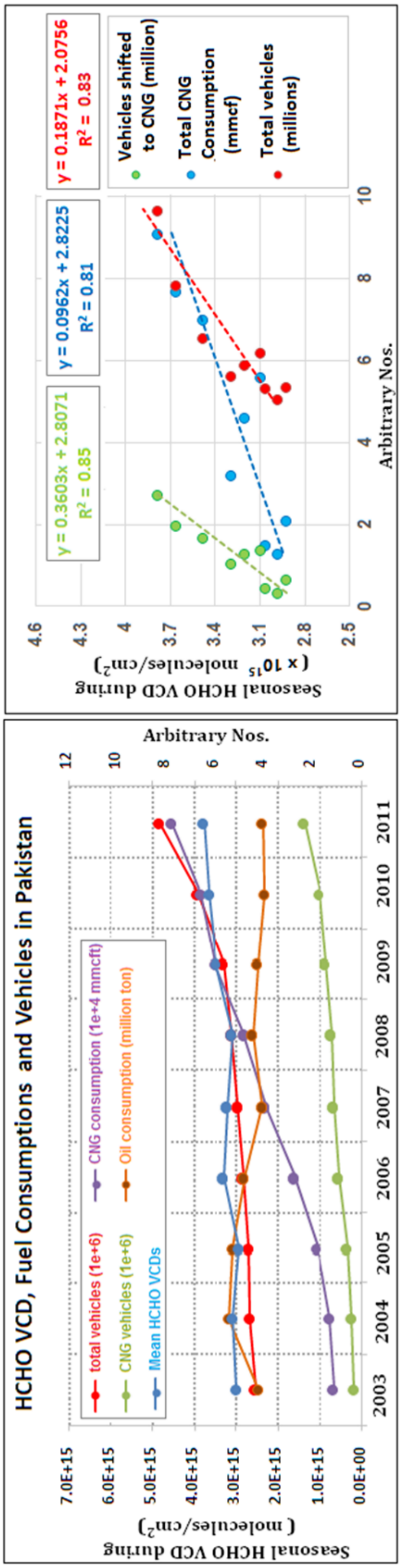


Fig. 8. (a) Seasonally averaged HCHO columns from SCIAMACHY (Brown line with circles) data compared with petroleum products (blue line with circles) and CNG consumption (violet line with circles) by transport sector and total number of vehicles (green line with circles) in Pakistan during the time period of 2003 to 2011. Fig.(b) Presents the correlations between seasonal mean HCHO columns and total number of vehicles (brown dots), total CNG consumptions by transport sector (blue dots) and total number of vehicles shifted from conventional fuel to CNG(green dots). Data source: Ministry of Petroleum Natural Resources and Hydrocarbon Development Institute of Pakistan (HDIP).

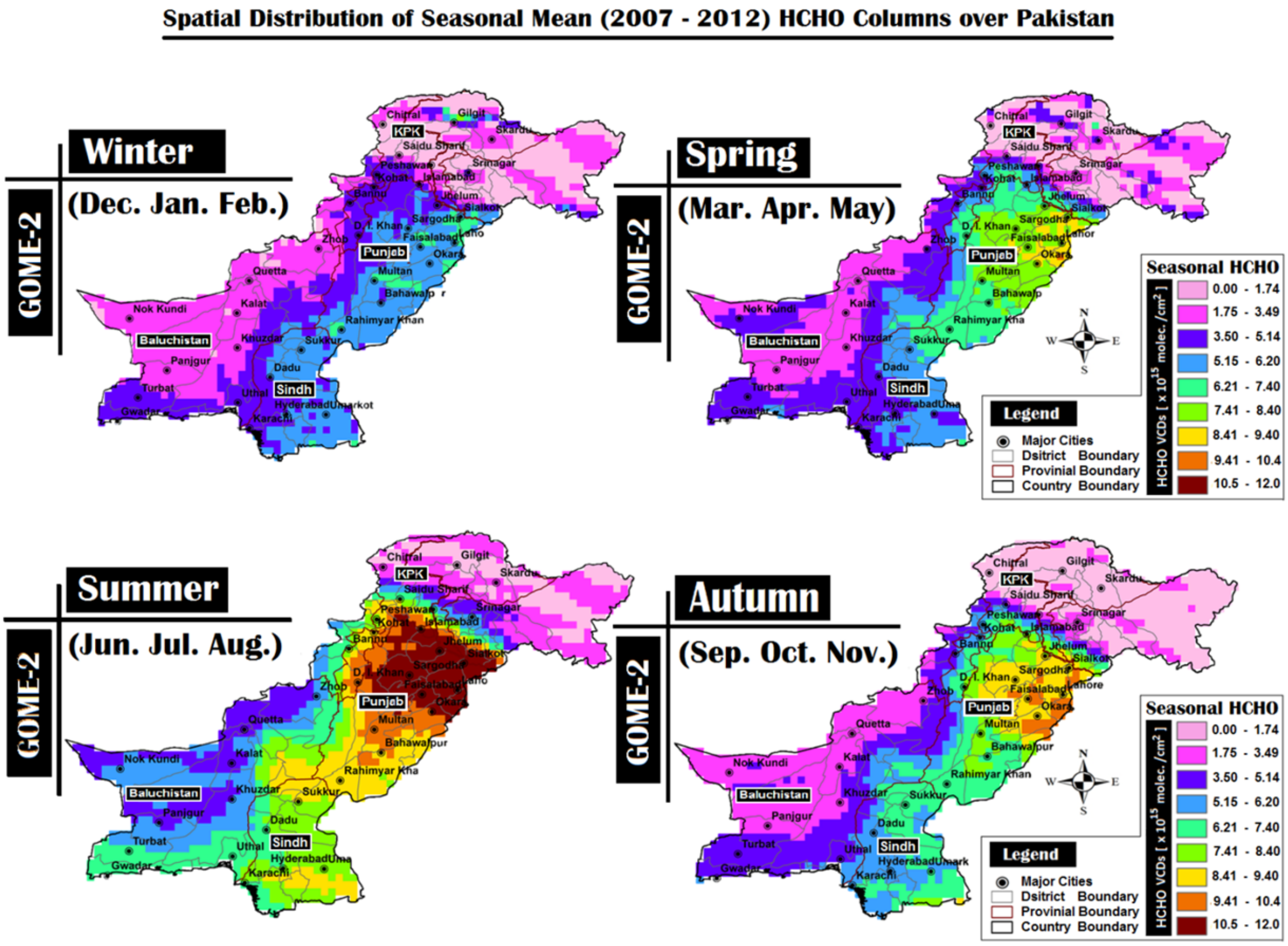


Fig. 9. Seasonal maps of HCHO columns, created with GOME-2 observations between 2007 and 2012 for different seasons: (1) DJF-December January and February, (2) MAM-March, April and May, (3) JJA-June, July and August, (4) SON-September, October and November.

column densities during summer and minimum during winter months. Two smaller seasonal peaks in HCHO columns are observed during April–May and November months. These peaks are attributed to the crop residue burning activities (agriculture fires). During April–May, it is the wheat harvesting season while during November it is rice paddy clearing seasons. The farmers lit their field to clear land for next crop and also to get nutrients for the next growing seasons. It explains the observed smaller peaks in Fig. 10 and is further supported by the ATSR fire data over Pakistan and results presented in Table 3 and Fig. 8. Formaldehyde columns over Punjab are enhanced during the hottest months of summer (June, July and August) and are lowest during winter months (January, February and December) in all provinces of Pakistan except KPK. Seasonal cycle over KPK is less pronounced than in the other provinces. Reasons behind this difference is not clear yet; however, it may be because of KPK consists of 45% of Pakistan's forests (mainly conifer and pine forests - ESoP, 2013), with moderate agricultural practices, and with less vehicle density and industrial activities. Therefore, biogenic emissions are dominant over longer time as compared to the rest of provinces with relatively larger industrial activities, population and vehicular densities, and with less and different forest cover (mainly broad leaves).

CONCLUSIONS

Tropospheric HCHO column measurements from two satellite instruments SCIAMACHY (2003–02/2012) and GOME-2 (2007–2012) over Pakistan were used to prepare first database of HCHO columns densities. Spatial maps were generated for each month to identify areas with high HCHO column densities over Pakistan.

Results indicated that highest yearly mean concentration of HCHO are generally found over city of Lahore (1.03×10^{16} molecules cm^{-2}) followed by Bahawalpur (9.9×10^{15} molecules cm^{-2}), Multan (9.25×10^{15} molecules cm^{-2}) and other cities during the time period of 2003 to 2012. Punjab and Sindh provinces are found to have maximum HCHO column densities due to high population, vehicular density, industrial activities, agricultural practices and fire events as compared to KPK and Baluchistan provinces. While in these provinces observed HCHO columns are mainly contributed from biogenic emissions and agriculture practices. No temporal trend in HCHO columns over Pakistan is observed.

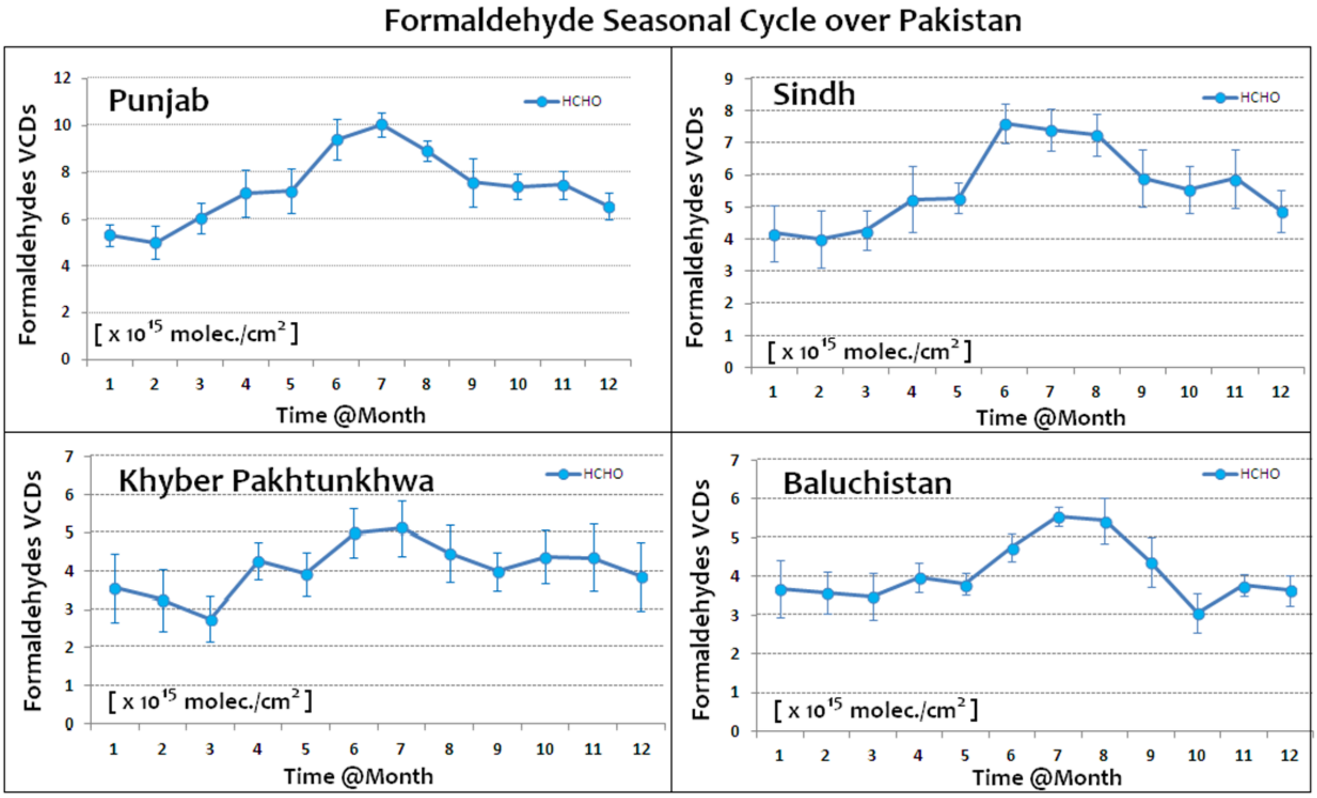


Fig. 10. Seasonal cycle of HCHO in different provinces (Punjab, Sindh, KPK and Bulochistan) of Pakistan derived from SCIAMACHY observations during the time period of 2003–2012. The error bars are representing the standard deviation.

Furthermore, trend analysis for different seasons presented in Figs. 4 and 5 did not show any statistically significant increase or decrease in HCHO data over Pakistan in both data sets.

Seasonal cycle was observed in four provinces of Pakistan. Expected winter minimum and summer maximum is found with slightly different behaviour over KPK province where seasonal cycle is not very well pronounced. Fire maps of Pakistan from 2003–2012 were created in order to see the effect of fire events on HCHO column densities. Results exhibited that crop residue fires significantly influenced the concentrations of tropospheric HCHO in Pakistan. Another anthropogenic source of tropospheric HCHO in Pakistan is vehicular emissions, particularly the vehicles consuming CNG as fuel and also the vehicles using conventional fuels but not equipped with catalytic convertors. While on other hand, extensive usage of CNG as fuel in vehicles might has resulted in significant decrease of other air pollutants such as NO_x, SO_2 and particulate matter over the study region.

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