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Anomalies of total column CO and O_3 associated with great earthquakes in recent years

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Abstract. Variations of total column CO and O_3 in the atmosphere over the epicenter areas of 35 great earthquakes that occurred throughout the world in recent years were studied based on the hyper-spectrum data from Atmospheric Infrared Sounder (AIRS). It was found that anomalous increases of CO and/or O_3 concentrations occurred over the epicenter areas of 12 earthquakes among the 35 studied ones. However, increases in both CO and O_3 concentrations were found for 6 earthquakes. The O_3 anomalies appeared in the month when the earthquake occurred and lasted for a few months, whereas CO anomalies occurred irregularly. The duration of CO and O_3 anomalies related to the earthquakes ranged from 1 to 6 months. The anomalies of CO concentration related to the earthquake can be mainly attributed to gas emission from the lithosphere and photochemical reaction, while the anomalous increases in O_3 concentration can be mainly due to the transport of O_3-enriched air and photochemical reaction. However, more work needs to be done in order to understand the mechanism of the CO and O_3 anomalies further.

1 Introduction

Emissions of Rn, He and greenhouse gases (CO, CO_2, CH_4, etc) from the fault zones to the atmosphere, especially from the structurally weak zones such as intersections or bends of faults, can be enhanced by the action of tectonic stress. Numerous field investigations in many cosmically active areas have indicated that the faults act as the conduit for migration of terrestrial gases. For example, increases of gas concentrations in groundwater and soil were correlated to the known crustal vibrations and stress changes (Weinlich et al., 2006; Du et al., 2008; Walia et al., 2009). The correlation between 8 yr measurements of radon flux in gravel and hundreds of earthquakes ($4.6 \geq M_L \geq 0$) indicated that earthquakes preferentially occurred in three pull-apart grabens of the Dead Sea rift valley within the time interval of the first 3 days after the start time of 110 Rn anomalies (Steinitz et al., 2003), indicating gas emission from solid earth to the atmosphere during seismic activity. It was summarized that terrestrial gas anomalies, such as Rn, He, H_2, Hg and CO_2, for the duration of a few hours to dozens of months related to the large earthquakes were found in the areas where the epicentral distances of hundreds of kilometers (larger for larger earthquakes, up to 1000 km or more for magnitude 8), and the amplitude of the anomalies did not show consistent correlation with either earthquake magnitude or epicentral distance (King, 1986; King et al., 2006). Moreover, numbers of pre-earthquake anomalies of the thermal, surface latent heat flux and outgoing long-wave radiation apparently resulted from the earthquake-related gas emission from the lithosphere (Tronin, 2000, 2002; Dey and Singh, 2003; Tronin et al., 2006; Ouzounov et al., 2007).

The investigations of gas-emission-related earthquakes are conventionally conducted on the ground surface. With the development of high-spectrum remote sensing technology, the anomalous variations of some gaseous components in the atmosphere have been retrieved with the hyper-spectral remote data. The anomalous variations are considered as the new indicators for earthquake although the spatial resolution and sensitivity of the sensors are still low. For instance, variations of ozone concentration measured by Total Ozone Mapping

Spectrometer (TOMS) and the Ozone Monitoring Instrument (OMI) were considered to be related with the earthquakes (Tronin, 2002; Ganguly, 2009). The variations of ozone concentration after the earthquakes showed a similar trend. The ozone concentration was low on the day of the earthquake occurrence, increased gradually after the event and reached a maximum value and thereafter decreased to its normal value (Ganguly, 2009; Singh et al., 2007). In addition, increases of CO concentration deduced from Measurements of Pollution in the Troposphere (MOPITT) occurred prior to the 26 January 2001 Gujarat $M_s = 7.6$ earthquake (Singh et al., 2010a), the 15 January 2001 Taiwan $M_s = 7.5$ earthquake (Guo et al., 2006), the 6 June 2000 Jingtai $M_s = 5.9$ earthquake in Gansu Province, northwestern China (Yao et al., 2005) and the $M_s = 6.9$ earthquake of 8 June 2000 in northern Myanmar (Yao et al., 2005). An anomalous variation of the total column water vapor after the Gujarat earthquake was also retrieved using SSM/I microwave radiometer on Tropical Rainfall Measuring Mission (TRMM) satellite (Dey et al., 2004). Therefore, this paper aims at extracting the anomalies of total column CO and O_3 over the epicenters of great earthquakes from AIRS standard products and correlating the anomalies with the earthquakes that occurred in recent years in order to promote the application of hyper-spectrum data in monitoring earthquake.

2 Data and methods

2.1 Data

The monthly data from the Atmospheric Infrared Sounder (AIRS) Version 5 Level 3 standard gridded products were selected as interesting. This data set was represented by the Gaussian grid with spatial resolution of 90 km × 90 km at nadir, approximately 1° (latitude) × 1° (longitude) on the earth's surface and downloaded from the Goddard Earth Sciences (GES) Data and Information Services Center (DISC) (http://disc.sci.gsfc.nasa.gov/AIRS/data-holdings) (Aumann et al., 2003; Won, 2008). We have taken the data of earthquakes from the Center for Earthquake Network of China (http://www.csi.ac.cn/).

2.2 Method

A total of 35 earthquakes with $M_s \geq 7.0$ and focal depth less than 35 km, which occurred throughout the world from January 2010 to August 2012, were selected as interest (Fig. 1). Background values of CO and O_3 were represented by the mean values that were calculated based on the AIRS data of multiple years by extracting total column CO and O_3 data over the epicenter areas of the earthquakes, which is described by Eq. (1).

$$G_{\mathrm{bac}}(x,y,t) = \frac{1}{N}\sum_{i=1}^{N} G_i(x,y,t) \tag{1}$$

$$\sigma(x,y) = \sqrt{\frac{\sum_{i=1}^{N}[G(x,y) - G_{\mathrm{bac}}(x,y)]^2}{N-1}},$$

where $G_{\mathrm{bac}}(x,y,t)$ is the background value, i.e., the multi-year mean value of gas concentrations $G(x,y,t)$ in an area of latitude length x and longitude length y in the month of t during the N years, of which the standard deviation is $\sigma(x,y)$. The mean standard deviation $\bar{\sigma}_{\mathrm{co}}$ is less than 7.9×10^{16} molecules cm^{-2}, and $\bar{\sigma}_{O_3}$ is less than 17 Dobson units (DUs) (Table 1). The N was taken as 9 (from 2003 to 2011), and both x and y as about 3000 km.

The earthquake cases were investigated by analyzing the differences (ΔG) between the monthly mean value of gas concentrations in the i year (G_{mon}) and background value (G_{bac}) of the corresponding month and comparing the images over the epicentral area before and after a seismic event in order to find the CO or O_3 anomalies. The value of ΔG was calculated by Eq. (2). The anomalies were identified by $\Delta G > \bar{\sigma}$.

$$\Delta G(x,y) = G_{\mathrm{mon}}(x,y) - G_{\mathrm{bac}}(x,y) \tag{2}$$

3 Results and discussion

Increases in ΔG of CO (ΔG_{CO}) and ΔG of O_3 (ΔG_{O_3}) before and after 12 earthquakes were found (Fig. 1). The parameters of earthquakes and the general features of gas anomalies are described in Table 2. The anomaly intensities of ΔG_{CO} and ΔG_{O_3} for one pixel related to 12 earthquakes ranged from 1.48×10^{17} to 2.79×10^{17} molecules cm^{-2} and from 28 to 68 DU, respectively. The largest values of ΔG_{CO} and ΔG_{O_3} were found in the month and one month after the 5 April 2010 Baja California earthquake in Mexico occurred, respectively. The durations of the O_3 and CO anomalies ranged from 1 to 6 months and 1 to 4 months, respectively. The areas of the gas anomalies had a wide range of more than 1000 km^2.

3.1 Anomalies of CO concentration

The anomalies of CO concentration observed before and after the great earthquakes can mainly be attributed to gas emission, photochemical oxidation, as well as ^{14}N(np) decay.

The main factor that controlled the CO anomalies related to earthquakes may be the increase of degassing rate from the solid earth into atmosphere. Permeability of rocks and soil can be changed by tectonic stress in the lithosphere during the earthquake generation and occurrence. Increase of permeability in the earth's crust favors upward emission of gases, such as water vapor, CH_4, N_2, H_2 and CO, enhancing the degassing rate of the lithosphere. A worldwide gas-geochemical survey across the active faults revealed anomalies of soil gases located in or near the fault zones, which

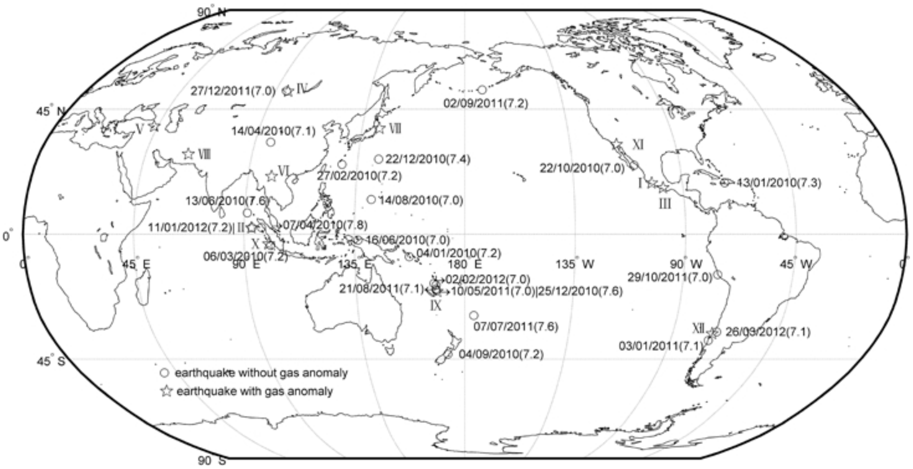

Fig. 1. Epicenter distributions of the 35 studied earthquakes. Arabic numerals are dates in day/month/year and magnitude in brackets. Roman numerals are numbers of earthquake with gas anomaly as shown in Table 2.

Table 1. Mean standard deviation of CO (10^{16} molecules cm^{-2}) and O_3 (DU) in every month.

	Jan	Feb	Mar	Apr	May	Jun	July	Aug	Sep	Oct	Nov	Dec
$\bar{\sigma}_{CO}$	5.8	6.4	6.3	5.8	5.2	5.0	4.9	5.4	6.6	7.9	6.9	5.7
$\bar{\sigma}_{O_3}$	15	17	16	14	13	12	13	13	12	14	16	15

Note: $\bar{\sigma}$ is mean standard deviation of the whole globe.

demonstrated that the active fault zones were the preferential pathways for upward migration of gases in the solid earth (King et al., 2006). Variations both in nitric oxide (Matsuda and Ikeya, 2001) and atmospheric Rn concentration (Yasuka et al., 2006) prior to the January 1995 Kobe earthquake indicated gases emitted from the crust in the epicentral area. In addition, higher values of CO concentrations deduced from MOPITT satellite at the levels of 1000 and 850 hPa one week prior to the 26 January 2001 Gujarat $M_s = 7.6$ earthquake were found (Singh et al., 2010a). In the studied cases, obvious anomalies of CO concentration along the San Andreas Fault in March and April associated with the 5 April 2010 Baja California $M_s = 7.1$ earthquake (Fig. 2a) indicated that the CO anomalies mainly resulted from the emission of CO and CH_4 from the fault zone. Meanwhile O_3 increased, but did not distribute along the fault (Fig. 2b), which indicated that the high values of O_3 concentration could not be directly attributed to O_3 emission.

Additionally, the CO in the atmosphere can be produced by methane oxidation. Oxidation of CH_4 by OH in the atmosphere occurs under the condition of OH radical concentrations of the order of 2.3×10^6 molecule cm^{-3}, resulting in the increase of CO concentration. The photochemical oxidation chain is described by Eq. (3) (Fishman et al., 1979; Fishman and Seiler, 1983). Both anomalies of CO concentration and land surface temperature prior to many earthquakes, e.g., the 26 January 2001 Gujarat $M_s = 7.6$ earthquake (Singh et al., 2010a), the 6 June 2000 Jingtai $M_s = 5.9$ earthquake in Gansu Province, northwestern China (Yao et al., 2005), the $M_s = 6.9$ earthquake of 8 June 2000 in northern Myanmar (Yao et al., 2005) and the 15 January 2001 Taiwan $M_s = 7.5$ earthquake (Guo et al., 2006), were reported. Therefore, the photochemical oxidation of optically active gases (CH_4, CO_2, O_3, etc.) from the solid earth was considered as one of the mechanisms of thermal and chemical anomalies (Tronin, 2006).

$$CH_4 + 4O_2 + 2h\nu_1 + h\nu_2 \rightarrow H_2O + CO + H_2 + 2O_3 \quad (3)$$

Furthermore, radiation reaction of ^{14}N is likely another source of CO. The ionospheric perturbations resulted from a modification of the atmospheric electric field during the earthquake preparation (Trigunait et al., 2004), which may cause air ionization. The air ionization can stimulate the ^{14}N decay to produce ^{14}C. Consequently, ^{14}C is first fixed as CO before being converted into CO_2 (Pandow et al., 1960; Dabas et al., 2007):

$$n + {}^{14}N \rightarrow {}^{14}C + H \quad (4)$$

$$2^{14}C + O_2 \rightarrow 2^{14}CO \quad (5)$$

$$CO + 2O_2 \rightarrow CO_2 + O_3. \quad (6)$$

The reaction products contribute both CO and O_3 to the atmosphere. For instance, anomalous changes in CO and O_3 concentrations above the epicenter of Gujarat earthquake

Table 2. General parameters of the studied earthquakes and features of CO and O_3 anomalies.

No.	Date (d/m/y)	Location			Depth (km)	M_s	Max. of ΔG_{CO}	Max. of ΔG_{O_3}	Duration (month)					
									CO			O_3		
		Place	° N	° E					B	W	A	B	W	A
I	12/04/2012	Michoacán, Mexico	18.4	−102.7	20	7.0	2.27	28		1		2	1	
II	11/04/2012	Off the west coast of northern Sumatra	2.3	93.1	20	8.6	–	26	–	–	–		1	1
III	21/03/2012	Oaxaca, Mexico	16.7	−98.2	20	7.6	2.12	30			2		1	1
IV	26/02/2012	Southwestern Siberia, Russia	51.7	96.0	10	7.0	–	68	–	–	–		1	
V	23/10/2011	Eastern Turkey	38.8	43.5	10	7.3	–	49	–	–	–			1
VI	24/03/2011	Myanmar	20.8	99.8	20	7.2	2.77	30	1		1		1	
VII	11/03/2011	Near the east coast of Honshu, Japan	38.1	142.6	20	9	–	51	–	–	–	2	1	1
VIII	19/01/2011	Southwestern Pakistan	28.8	63.9	20	7.1	1.48	29	1		3		1	2
IX	14/01/2011	Loyalty Islands	−20.6	168.6	10	7.2	–	36	–	–	–			2
X	25/10/2010	Kepulauan Mentawai region, Indonesia	−3.5	100.0	10	7.3	–	31	–	–	–			6
XII	05/04/2010	Baja California, Mexico	32.3	−115.1	33	7.1	2.79	62	2	1	1	3	1	2
XIII	27/02/2010	Offshore Bio-Bio, Chile	−35.8	−72.7	22	8.8	–	44	1	–	–	2	1	

Note: data of earthquakes from center for earthquake network of China; total column CO (10^{17} molecules cm^{-2}) and total column O_3 (DU) from Atmospheric Infrared Sounder. 1 Dobson unit (DU) is about 2.7×10^{16} molecules cm^{-2}. Max. of ΔG_{CO} and Max. of ΔG_{O_3} stand for the anomaly intensities of ΔG_{CO} and ΔG_{O_3} for one pixel, respectively. B, W and A stand for before, when and after the earthquake, respectively.

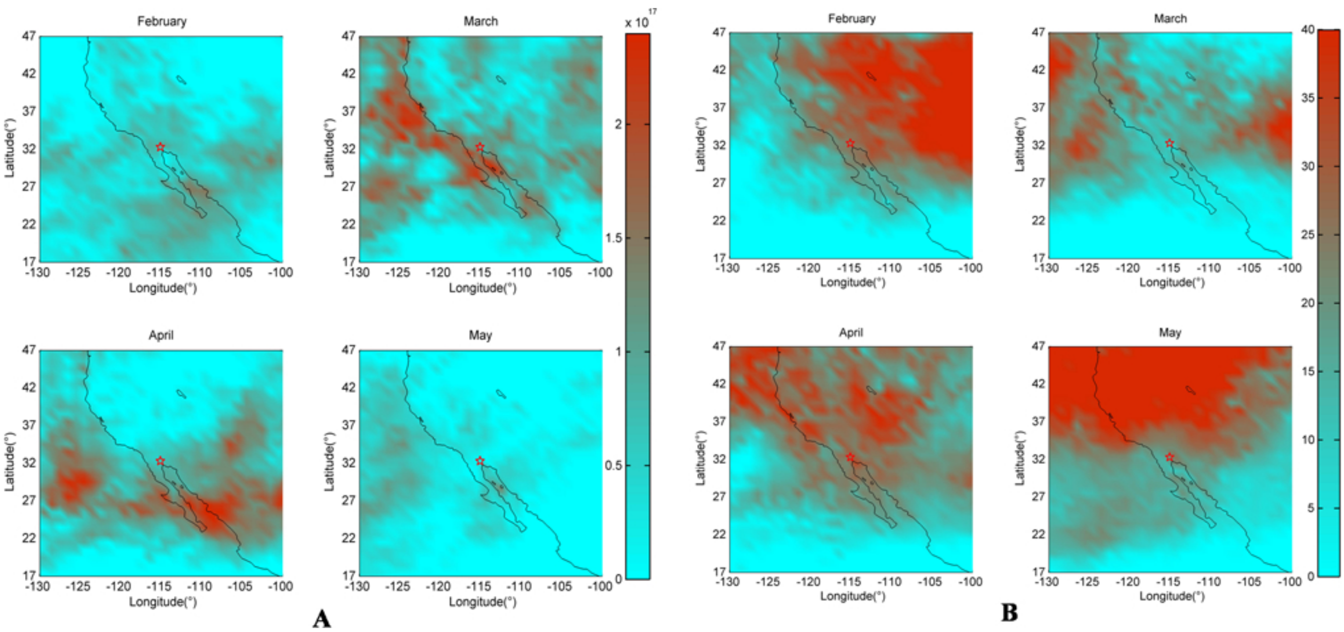

Fig. 2. Distributions of ΔG_{CO} **(A)** and ΔG_{O_3} **(B)** associated with 5 April 2010 Baja California earthquake from February to May 2010, red star stands for the epicenter, CO unit: mole cm^{-2}, O_3 unit: DU.

were measured respectively by MOPITT and TOMS (Singh et al., 2010a; Tronin, 2002). The anomalies of both CO and O_3 concentrations have been found for six earthquakes among the studied cases (Table 2).

3.2 Anomalies of O_3 concentration

Anomalies of O_3 concentration in the atmosphere can be attributed to photochemical reaction, gas emission and convection in the atmosphere.

The anomalies of atmospheric O_3 may be derived from the photochemical production of the gases (vapor, CH_4 and CO) emitted from the lithosphere (Crutzen, 1974). The photochemical oxidation reactions of CH_4 and CO are described by Eqs. (3) and (6) (Fishman et al., 1979).

In addition, O_3 may be formed by exoelectrons emitted by a high electric field, resulting from charge separation during crushing and grinding of crustal rocks according to the experiments (Baragiola et al., 2011). The experiments indicated that different igneous and metamorphic rocks produced

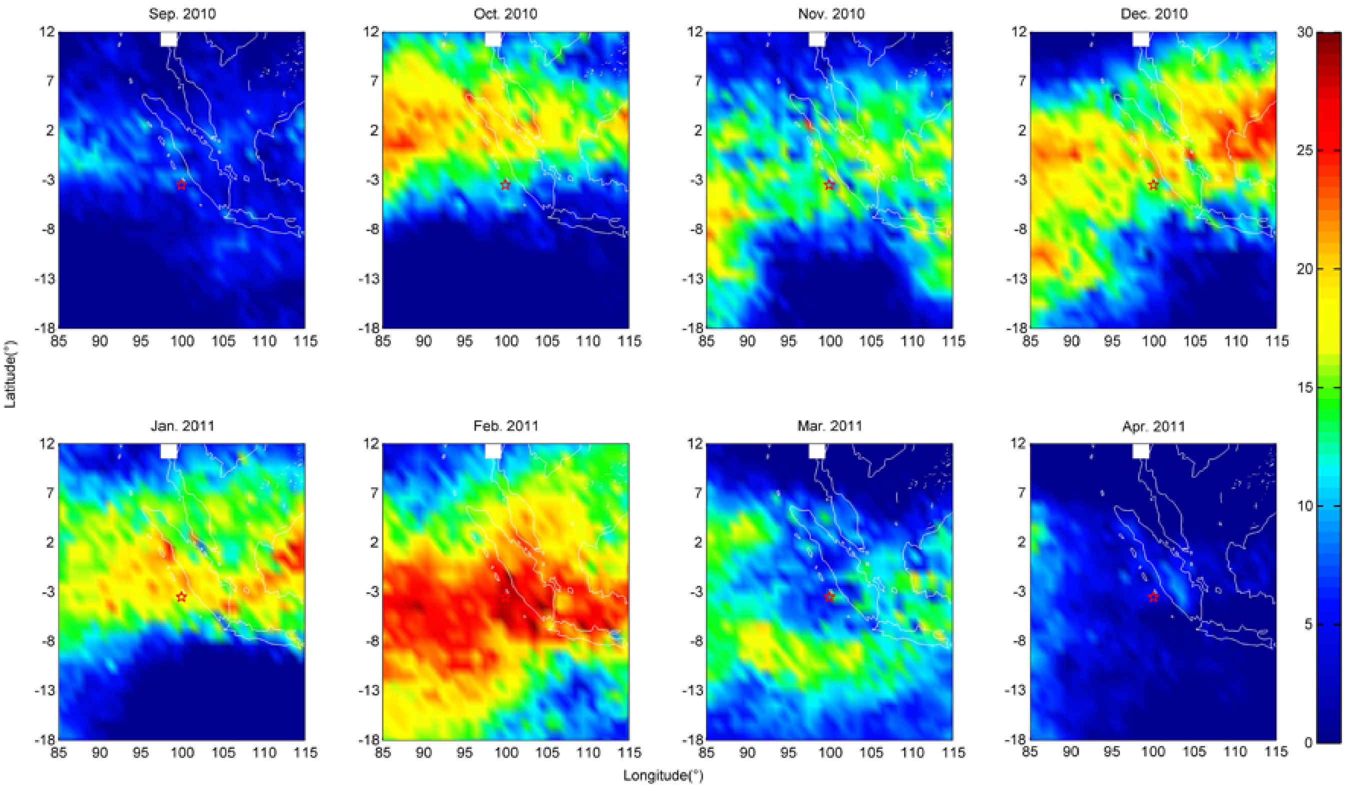

Fig. 3. Distributions of ΔG_{O_3} associated with 25 October 2010 Indonesia earthquake from September 2010 to April 2011, red star stands for the epicenter, unit: DU.

different amounts of O_3, and rhyolite produced the strongest O_3 emission. This suggests that O_3 emission from fracturing rocks can serve as an indicator of impending earthquake.

Moreover, the anomaly of O_3 concentration can be caused by the transport of enriched-O_3 air from higher latitudes. Advection of gaseous compounds of nitrogen oxides (NO_x) from the neighboring high-pressure regions where the earthquake occurred and the atmospheric pressure is intensively low may contribute to the anomalies of O_3 concentration (Ganguly, 2009). Meanwhile, the heat energy can be transmitted from the surface to the upper layers during the process of earthquake activities in the region of low atmospheric pressure that was created by gravity waves (Pal, 2002). Therefore, the convection favors the formations of O_3 concentration and surface air temperature anomalies.

3.3 Case study

3.3.1 Earthquakes without anomalies

No CO or O_3 anomalies were found for 23 earthquakes among the 35 cases (Table 2), which can result from the following factors: the sensitivity of the sensor was not sensitive enough to measure the minor changes of gas concentrations, the data were affected by thick cloud, and/or there were no anomalies at all.

3.3.2 Earthquakes only with O_3 anomalies

Just 6 cases among the studied earthquakes were with O_3 anomalies. High O_3 anomalies mostly appeared in the month when the earthquake occurred and a few months after the event, e.g., the 25 October 2010 Indonesia earthquake (Fig. 3), which could result from dynamical transport (Kondratyev and Varotsos, 2001) and photochemical reaction caused by the earthquake generation. The anomaly of O_3 concentration was found in the week that the Haiti earthquake of 12 January 2010 occurred (Singh et al., 2010b).

3.3.3 Earthquakes with both CO and O_3 anomalies

It was found that just 6 earthquakes among the studied earthquakes were with both CO and O_3 anomalies before and after the main shocks. The O_3 anomalies mostly appeared in the month when the earthquake occurred and a few months after the earthquake. However, high CO anomalies irregularly occurred before and after the earthquakes (Table 2). The beginnings and durations of CO and O_3 anomalies were different from case to case (Table 2) because the photochemical reactions producing CO and O_3 and the dynamical disturbances took place asynchronously. As described by Eqs. (3) to (6), O_3 and CO may be produced by photochemical reaction of CH_4. In turn, an increase of O_3 can enhance rates

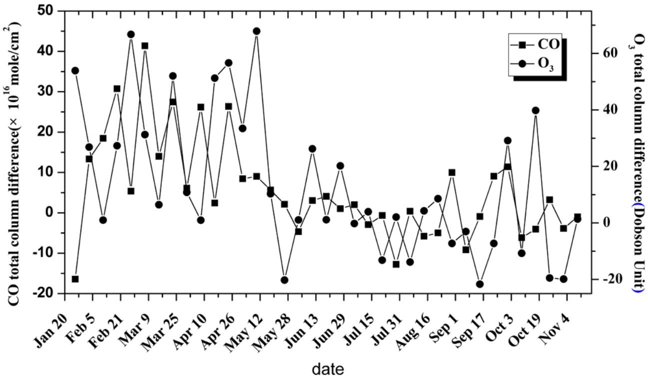

Fig. 4. Variations of differences between 8-day CO and O_3 concentrations in 2010 and the corresponding 8-day mean values in 2008–2009 in the epicenter area of 5 April 2010 Baja California earthquake.

of photolysis and OH radical production in the troposphere, which consequently changes the concentrations of CO, O_3 and other trace gases (Fishman et al., 1979; Fishman and Seiler, 1983; Yurganov et al., 1995; Varotsos et al., 2001; Kato et al., 2004).

In addition, O_3 anomalies are well correlated with CO ones when photochemical oxidations of CH_4 occurred (Yurganov et al., 1995; Kato et al., 2004). For instance, the varied trend of differences of CO and O_3 concentrations between 8-day mean value of CO in 2010 and the corresponding 8-day mean values of 2008–2009 in the epicenter area of the 5 April 2010 Baja California $M_s = 7.1$ earthquake appeared concordant. Higher values of CO and O_3 differences were found 2 months before the earthquake, and then declined sharply to the mean values 1 month after the earthquake (Fig. 4). Such phenomena indicate that photochemical oxidation reaction of CH_4 and CO produces CO and O_3 (Eqs. 3 and 6), which resulted in the increases of CO and O_3 concentrations in the atmosphere.

4 Summary

Among the 35 studied earthquakes, 6 earthquakes were found to be with both CO and O_3 anomalies, and 6 earthquakes just with O_3 anomalies. The beginnings and durations of CO and O_3 anomalies were different from case to case.

The anomaly of CO concentration related to the earthquake can be attributed to the gas emission from the solid earth, photochemical oxidation and ^{14}N(np) decay, while O_3 anomalies to transport of O_3-enriched air, photochemical reaction and O_3 emission from fracturing rocks. Gas emission from the fissures that were produced by tectonic stress in the lithosphere during the earthquake generation and occurrence resulted in the increases of CO and O_3 concentrations in the atmosphere. In addition, atmospheric electric field changes and ionospheric disturbances related to earthquake generation promoted the photochemical reaction and dynamical disturbance, enhancing the CO and O_3 concentrations.

However, the earth is geologically, physically and chemically complex and intensively inhomogeneous, and earthquake generation is a complex process, too. For further investigating the mechanism of the CO and O_3 anomalies, therefore, more work should be done.

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