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Effect of land-sea air masses transport on spatiotemporal distributions of atmospheric CO_2 and CH_4 mixing ratios over the south Yellow Sea

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Abstract: To reveal the spatiotemporal distributions of atmospheric CO_2 and CH_4 mixing ratios and regulation mechanisms over the China shelf sea, two field surveys were conducted in the south Yellow Sea in China in November 2012 and June 2013, respectively. Observed results showed that mean atmospheric CO_2 and CH_4 mixing ratios were 403.50 ± 13.70 ppm and 1934.1 ± 33.6 ppb in November 2012, and 396.40 ± 12.30 ppm and 1919.2 ± 30.2 ppb in June 2013, respectively. An improved data filtering method were established to flag diverse sources of atmospheric CO_2 and CH_4 in survey area. Fe found that, compared to the influences of air-sea exchange, the spatiotemporal distributions of atmospheric CO_2 and CH_4 mixing ratios over the south Yellow Sea were dominated by land-sea air masses transport, which was driven by seasonal monsoon. In addition, atmospheric CO_2 and CH_4 mixing ratios over the south Yellow Sea could be elevated remarkably in a distance of approximate 20 km offshore by land-to-sea air masses transportation from the Asia Continent during early winter monsoon.

Keywords: carbon dioxide, methane, monsoon, marine boundary air, shipborne underway measurement.

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1 Introduction

Carbon dioxide (CO_2) and methane (CH_4) are the two most important greenhouse gases, playing critical roles in Earth's radiation balance (AGGI, 2014). Since the industrial revolution era (~1750), atmospheric CO_2 and CH_4 mixing ratios have increased and reached their highest values of 415.7 ± 0.1 ppm and 1908 ± 2 ppb in 2021, which were about 149% and 262% of the preindustrial levels (WMO greenhouse gas bulletin, 2022). Increasing of atmospheric CO_2 and CH_4 was unequivocally attributed to anthropogenic emissions, e.g., industrial production, deforestation, fossil fuel consumption (Houghton, 2003; Peters et al., 2012), and natural source-sink processes (Zang et al., 2017).

For decades, increasing CO_2 and CH_4 mixing ratios have attracted more and more attention from science community. According to the observation platforms or methods, shipborne observation was considered as one of six common and important methods for studying the greenhouse gases (Matsueda et al., 1996; Daube et al., 2002; Dlugokencky et al., 2005; Crosson, 2008; Fang et al., 2015). Based on shipborne discrete sampling and measurement, latitudinal distribution of CH_4 mixing ratio with a shape drop in the area of 20 °N in marine boundary air of the North Pacific Ocean were reported, which was mainly influenced by air masses transportation driven by both winter monsoon and trade wind (Matsueda et al., 1996; Dlugokencky et al., 2005). In coastal area of the Bohai Sea, seasonal variations of atmospheric CO_2, CH_4 and N_2O mixing ratios were mainly influenced by land-sea air masses transportation based on discrete sampling observation (Kong et al., 2010). Moreover, periodic observed CO_2 and CH_4 mixing ratios in marine boundary air were also used to improve the accuracy of calculated air-sea CO_2 flux in the northern South China Sea and the Luzon Strait (Zhai et al., 2015), and assess impacts of several episodic oil and gas spill events on abnormal air-sea CH_4 flux in the Bohai Sea (Zhang et al., 2014).

In recent years, high-accuracy shipborne continuous observation method has been developed and applied to observe greenhouse gases in marine boundary air (Nara et al., 2014; Zang et al., 2017; Reddick et al., 2019), which could reveal more detailed information associated with their source-sink processes. Latitudinal distributions of both CO_2 and CH_4 mixing ratios in the China shelf sea boundary air in early spring were observed, which were similar to that in the north Pacific Ocean (Matsueda et al., 1996; Zang et al., 2017), and mainly impacted by atmospheric chemical processes,

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air-sea interaction in Yangtze River estuary area and land-sea air masses transportation (Zang et al., 2017; Liu et al., 2018). Meanwhile, as important anthropogenic hot spot sources of atmospheric CO_2 and CH_4, oil and gas platforms in global oceans were paid more attention currently. Peak values of CO_2 and CH_4 mixing ratios in downwind area of oil and gas platforms were observed by shipborne continuously measurement systems in the North Sea, the South China Sea and Bohai Sea. Combined with the Gaussian plume model, CH_4 emissions could be quantified via "top-down" approach (Nara et al., 2014; Riddick et al., 2019; Zang et al., 2020; Jia et al., 2022).

Monsoon is a kind of climatic phenomenon in which the dominant wind system changes with seasons (Lyu et al., 2021). The East Asian monsoon (EAM), comprising the East Asian summer monsoon (EASM) and East Asian winter monsoon (EAWM), is an important component of the Earth's climate system and has a significant influence on the socioeconomic, agricultural and cultural development of East Asia (Huang, 1985; Zou et al., 2018; Lyu, et al., 2021). Previous studies have shown that the Asian monsoons played an important role in the global and regional climate variability (Huang, 1985; Chang et al., 2000; Ding et al., 2007; Zhan and Li, 2008). On the one hand, spatiotemporal distributions of CO_2 and CH_4 in marine boundary air were influenced by multiple processes, such as land-sea air masses transport (Bartlett et al., 2003; Zang et al., 2017), ship emission (Warnekeet et al., 2005; Law et al., 2013; Bouman et al., 2017; Ding et al., 2018) and oil and gas platforms (Nara et al., 2014; Reddick et al., 2019; Zang et al., 2020). On the other hand, greenhouse gases have been observed and studied in East Asia and Pacific Ocean based on land (island)-based stations (Fang et al., 2015; 2017; Luan et al., 2016), ship and plane observation platforms (Matsueda et al., 1996; Bartlett et al., 2003; Dlugokencky et al., 2005). However, as an important pathway of atmospheric components transportation between the Asia Continent and Pacific Ocean, spatiotemporal distributions and regulate mechanisms of CO_2 and CH_4 in the China shelf seas boundary air were still rare (Zhang et al., 2007; Zang et al., 2017; Liu et al., 2018).

In this study, atmospheric CO_2 and CH_4 mixing ratios in boundary air of the South Yellow Sea (SYS) were simultaneously observed by a self-assembled shipborne CRDS (Cavity Ring-down Spectroscopy, Picarro G2301, USA) system in November 2012 and June 2013, when typical periods of the EASM and the EAWM. The major objects of this work were (1) to optimize an improved data filter approach for shipborne underway continuous observed atmospheric CO_2 and CH_4 mixing

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ratios, (2) to investigate the influence of air-sea exchange on the spatiotemporal distributions of CO_2 and CH_4 mixing ratios in boundary air of the SYS, and (3) to reveal the regulating mechanism of seasonal monsoon on spatiotemporal distributions of CO_2 and CH_4 in boundary air of the SYS during the field surveys.

2 Method and materials

2.1 Observation area

The Yellow Sea is a semi-enclosed marginal sea, located on the western part of the Pacific Ocean, adjacent by China to the north and west, and Korean Peninsula to the east (Zhang and Chu, 2018; Wang et al., 2021). It is a main pathway of air mass transport between the Asia continent and Pacific Ocean, and can be divided into two basins: the North Yellow Sea (NYS) and the SYS (Lyu et al., 2021). The SYS covers an area of about 10.8×10^4 km^2, with an average depth of 44 m, and is strongly influenced by the EAM system (Zou et al., 2018). As showed in Fig. 1, to study the distributions of atmospheric CO_2 and CH_4 mixing ratios and their regulation mechanisms, two campaigns were conducted from 2nd to 8th November, 2012 and from 22nd to 29th June, 2013, respectively, both of which were typical periods of the EAM (including summer monsoon and winter monsoon). In order to ensure the comparability of observations, parallel observed CO_2 and CH_4 data from the three ground stations (LAN, JGS, TAP) in vicinity of the study area, were presented and studied in this study.

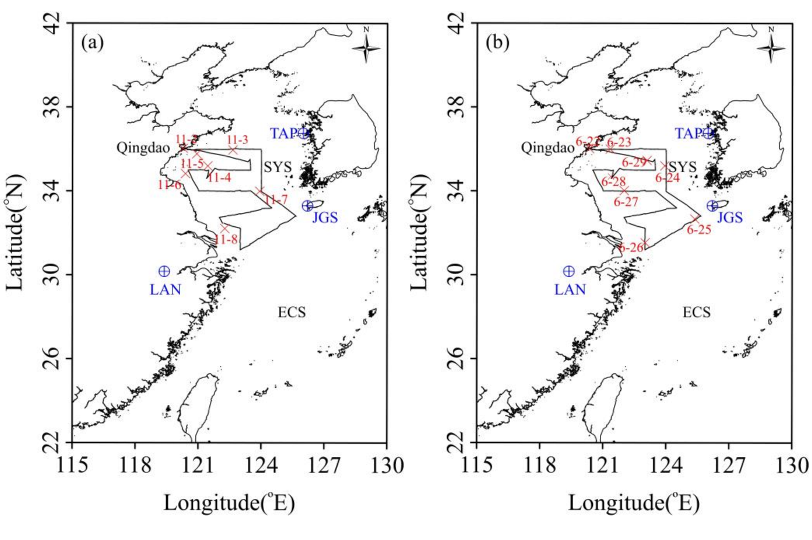

Fig. 1. Observation area in the SYS. The thick solid black lines represent cruise tracks in November

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2012 (a) and June 2013 (b). Symbols represent the Tae-ahn Peninsula station (TAP, 36.73 °N 126.13 °E, 20 m above sea surface), Jeju Gosan station (JGS, 33.30 °N 126.20 °E, 25 m above sea surface) and Lin'an station (LAN, 30.18 °N 119.44 °E, 138 m above sea surface), respectively. ECS represents the East China Sea. The Red Crosses represent the beginning locations of each natural day.

2.2 Measurement of atmospheric CO_2 and CH_4 mixing ratios

During the field surveys, the air inlet was fixed at the highest point of the bow, about 15 meters from the sea, and near the meteorological sensors to avoid anthropogenic contamination, (Zang et al., 2017). Atmospheric CO_2 and CH_4 mixing ratios were measured using a Picarro system (G2301, Picarro Inc., USA). The Picarro analyzer, which can acquire one measurement every 5 seconds, and correct the measurements influenced by water vapor (Rella et al., 2013), has been proven to be excellent for measuring CO_2 and CH_4 with high precise and accuracy (Crosson, 2008; Fang et al., 2013).

Fig. 2 showed the schematic diagram of the CO_2 and CH_4 observation system, ambient air was pumped via the dedicated tube by an external vacuum pump, and passed through a membrane filter (1.0 μm, whatman Inc., USA), a self-assembled drying-tube filled with magnesium perchlorate [$Mg(ClO_4)_2$] and another filter, respectively, to remove particles and water vapor. Then, regulated by valve sequence setting, dry and clean air sample as well as the standard gases flowed into the CRDS analyzer through 8 port multi-position valve (Valco Instruments Co. Inc. USA) with a flow rate of 200 mL·min^{-1} controlled by a mass flow controller (Beijing Seven-star electronics Co. LTD. China). Before each campaign, three standard gases were used to calibrate the CRDS analyzer. Linear functions were yielded based on measurement results and the standard values of standard gases, i.e., 254.53 ppm, 365.14 ppm and 569.99 ppm for CO_2, and 1601.0 ppb, 1925.5 ppb and 2317.7 ppb for CH_4, respectively. The used standard gases were propagated from the WMO primary standards (WMO/GAW 2004 scale for CH_4, 2007 scale for CO_2), to guarantee the consistency, trace ability and international comparability of observed data (Dlugokencky et al., 2005).

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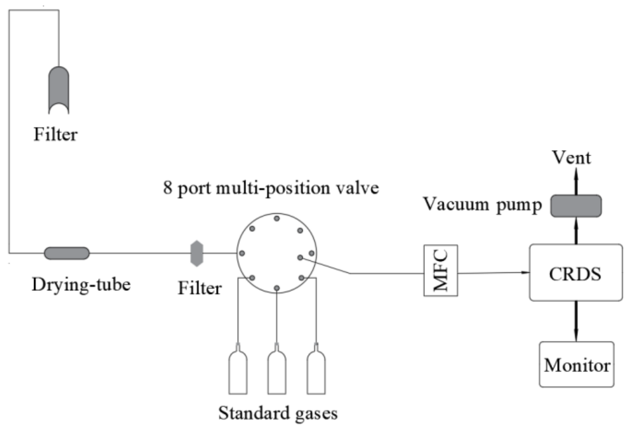

Fig. 2. Schematic diagram of the shipborne Picarro system for observing atmospheric CO_2 and CH_4.

2.3 Meteorological data

Both of the two campaigns were conducted by a special designed marine survey ship named "*Dongfanghong II*", which was designed and built for multiple disciplines research in marine environment, including a ship-based atmospheric science lab. Meteorological data, including time, latitude, longitude, cruising speed and direction, wind speed, wind direction, relative humidity, air pressure and temperature were observed by the special meteorological sensors with resolution of 10 seconds, and were used to filter and flag the observed CO_2 and CH_4 mixing ratios and verify simulated wind fields.

2.4 Air mass transport model

HYSPLIT (Hybrid Single Particle Lagrangian Integrated Trajectory Model, HYSPLIT) is a model developed by the National Oceanic and Atmospheric Administration's Air Resources Laboratory (NOAA-ARL) and the Bureau of Meteorology of Australia, which can calculate the air mass transportation combined with the National Centers for Environmental Prediction (NCEP) reanalysis data. The principle of simulating the air mass transportation path as follows: assuming that particles in the air are floating in the wind, their moving trajectory is the integral of their position vectors in time and space (Zhang et al., 2011; Xia et al., 2018). Backward trajectory analysis uses the mixed single-particle Lagrangian integral transport and diffusion model to calculate the air particles forward, analyzes the influence of air mass transportation on the spatial and temporal distribution of atmospheric components in the observation area by tracking the transport path, and

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infer their potential sources. The main parameters required to calculate the backward trajectory are the altitude, latitude and longitude of the starting point. Generally, the calculation is carried for 3 days (72 h) (Zhan et al., 2009；Zhang et al., 2017; Zhang et al., 2019).

3 Results

3.1 Atmospheric CO_2 mixing ratios

During the field surveys, atmospheric CO_2 mixing ratios ranged from 392.75 ppm to 688.10 ppm with an average value of 403.50 ± 13.70 ppm in November 2012 (Fig. 3a and Fig. 3b), and ranged from 389.28 ppm to 967.60 ppm with an average value of 396.40 ± 12.30 ppm in June 2013 (Fig. 3c and Fig. 3d), which was consistent with the changing characteristics of the EAM. Seasonal variations were comparable with the typical observation results of the north hemisphere. Abnormal high observation values might be attributed to exhaust gases of ship or anthropogenic interference of analyzer.

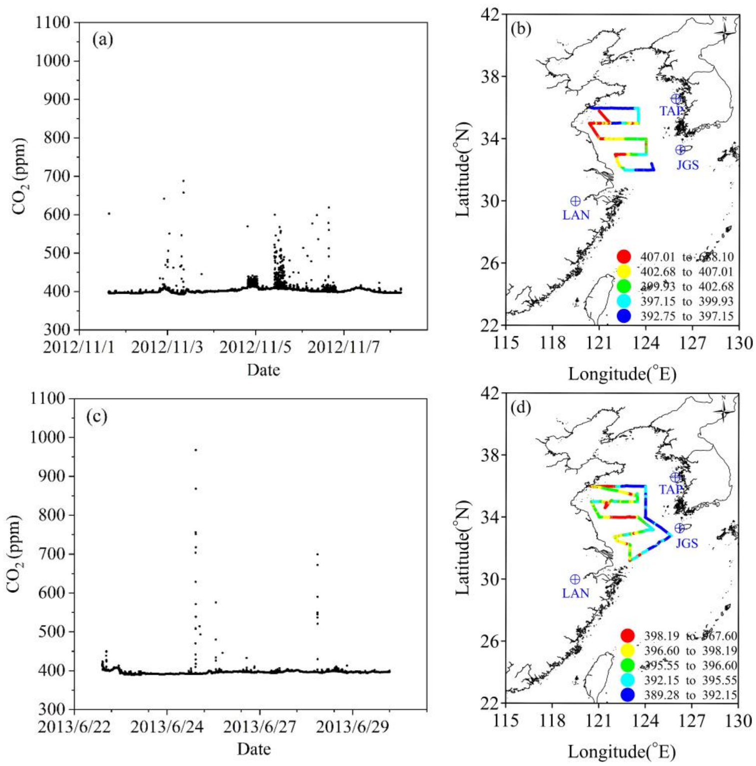

Fig. 3. Temporal（a and c）and spatial （b and d）distribution of CO_2 mixing ratios in November 2012 and June 2013 in the SYS.

Our observed mean CO_2 mixing ratios were lower than previous studies' mean values of 405.00 ppm and 410.70 ppm in the YS and ECS in March 2013 and March 2017, respectively (Zang et al., 2017；Liu et al., 2018). Moreover, observed mean atmospheric CO_2 mixing ratio was almost equal to results observed at the TAP (401.37 ppm) and JGS (403.77 ppm) stations, but approximate 9 ppm higher than MBL-CO_2 reference (394.41 to 394.78 ppm in latitude zone of 30 °N to 37 °N) (www.esrl.noaa.gov/gmd/ccgg/GHGreference, download data: 2022-10-10) in November 201, and almost equal to results observed at the LAN (396.43 ppm) and JGS (398.10 ppm) stations and MBL-CO_2 reference (397.38 to 397.92 ppm in latitude zone of 30 °N to 37 °N) in June 2013.

3.2 Atmospheric CH_4 mixing ratios

Atmospheric CH_4 mixing ratios ranged from 1870.6 ppb to 1986.0 ppb with an average value of 1934.1 ± 33.6 ppb in November 2012 (Fig. 4a and Fig. 4b), and ranged from 1820.8 ppb to 2179.0 ppb with an average value of 1919.2 ± 30.2 ppb in June 2013 (Fig. 4c and Fig. 4d). Our observed results comparable with observed results at TAP stations, and historical data of 1915.5 ppb in the SYS in March 2013 (Zang et al., 2017), while higher than the MBL-CH_4 references in November 2012 (1869.5 to 1880.3 ppb) and June 2013 (1835.3 to 1846.6 ppb).

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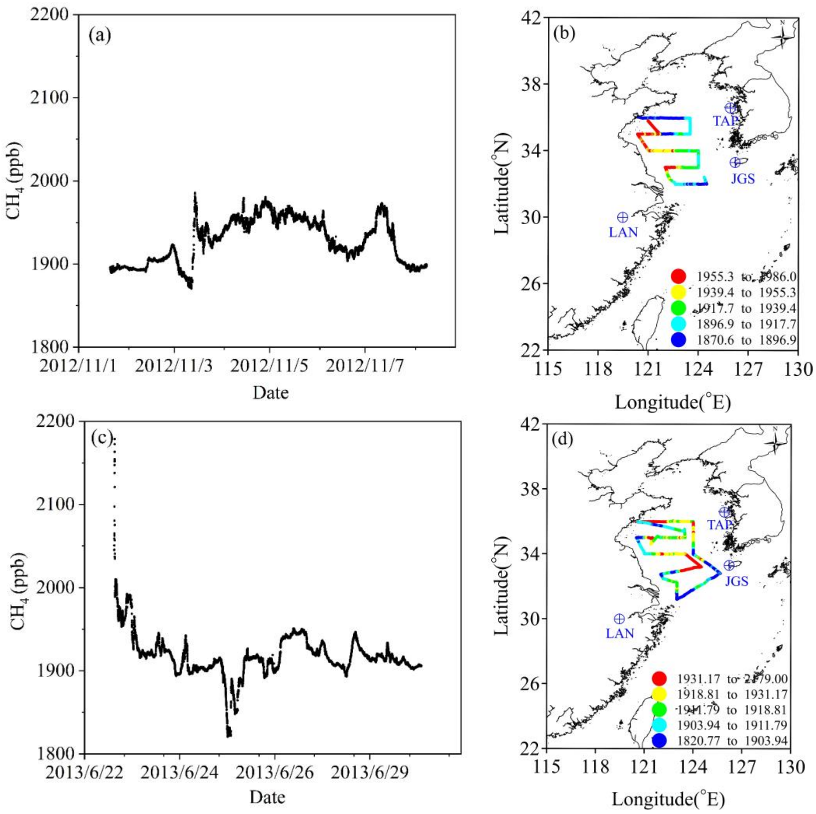

Fig. 4. Temporal (a and c) and spatial (b and d) distribution of CH_4 mixing ratios in November and June of the SYS.

3.3 Wind data

Observed wind records were averaged to hourly data for subsequently analysis. As shown in Fig. 5a, during the survey of November 2012, wind speed ranged from 0.05 to 20.46 m/s with an average value of 8.09 ± 4.17 m/s. Dominate wind direction was from north and northeast, indicated the air masses flowed from the Asia continent to the Pacific Ocean. As shown in Fig. 5c, during the survey of June 2013, wind speed ranged from 0.08 m/s to 9.42 m/s with an average value of 4.72 ± 1.79 m/s. Conversely, the predominant wind direction turned into south or southeast, which promoted air masses flowing from the Pacific Ocean to the Asia continent. In addition, the observed dominant wind directions (Fig. 5a and Fig. 5c) were consisting well with the simulated wind fields (Fig. 5b and Fig. 5d), suggested the typical features of winter and summer monsoon, which were ideal cases to study effects of land-sea air masses transportation on the spatiotemporal variations of

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CO_2 and CH_4 mixing ratios in the MBL of the SYS.

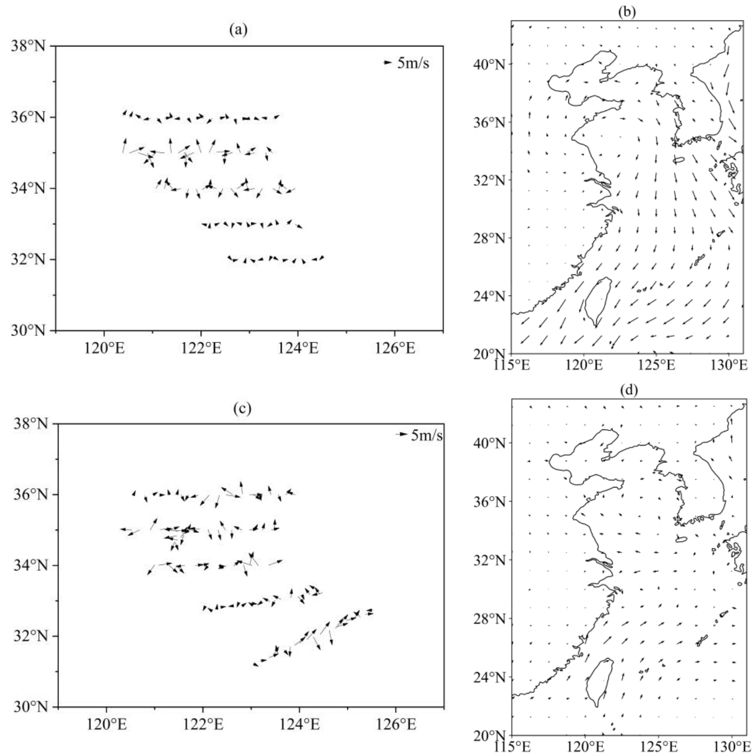

Fig. 5. Observed wind direction and speed (a and c) and simulation of wind fields (b and d) over the SYS. The simulated wind fields were plotted based on the ERA5 hourly data on pressure levels provided by the European Centre for Medium-Range Weather Forecasts (ECMWF), (https://cds.climate.copernicus.eu/cdsapp#!/dataset/reanalysis-era5-pressure-levels?tab=form, download date: 2022-11-04) and drawn by python 3.7.0.

4. Discussion

4.1 Optimization of data filter approach

Generally, CO_2 and CH_4 mixing ratios decreasing with increasing altitude and distance away from continent, and decreasing latitude (Matsueda et al., 1996; Bartlett et al., 2003; Zang et al., 2017). Spatiotemporal distributions of atmospheric CO_2 and CH_4 mixing ratios in shelf seas read not only natural characteristics, but also multiple anthropogenic processes, such as marine oil and gas exploration (Nara et al., 2014; Zang et al., 2020), land-sea air mass transportation (Kong et al., 2010; Liu et al., 2018) and malfunction of observation instrument (Zang et al., 2017). Although some preliminary data processes have been reported (Zang et al., 2017; Liu et al., 2018), a specific data filtering approach for shipborne continuous observation should be optimized to distinguish impacts of diverse source-sink processes on observed CO_2 and CH_4 mixing ratios along the cruise tracks, especially in the shelf seas.

Firstly, observed atmospheric CO_2 and CH_4 mixing ratios along the cruise tracks in November 2012 and June 2013 were corrected by a linear function, which was established by measurement and propagated values of three CO_2 and CH_4 standard gases. The corrected data were averaged every one minute and named as Raw Data for the subsequently process.

Secondly, according to voyage record, the abnormal values that caused by mal-function of instrument or impacted by manual refilling the drying-tube were flagged (Zang et al., 2017).

Thirdly, when the ship stopping for sampling at discrete stations or cruising downwind with speed lower than wind speed, observed CO_2 and CH_4 mixing ratios could be impacted by ship's exhaust gas and human activities (Zang et al., 2017; Liu et al., 2018), despite the air inlet was fixed between the chimney and the bow. According to voyage record, previous studies considered 3 knots as the criterion to flag data influenced by ship's exhaust gas and human activities, without statistical analysis (Zang et al., 2017; Liu et al., 2018). For instances, as showed in Fig. 6a and Fig. 6b, when ship speed dropped from normal speed of 11 knots to less than 3 knots, the observed CO_2 mixing ratio varied from a smooth pattern with SD (standard deviation) value less than 0.10 ppm to intensive fluctuation pattern with SD value greater than 1.20 ppm, due to influences of ship emissions and human activities. According to the quality control criteria of CO_2 (SD less than ± 0.10 ppm), which recommended by the World Meteorological Organization Global Atmospheric Watch (WMO/GAW), 3 knots was guaranteed as the threshold ship speed. Results showed that, 15.5% and 21.9% of total observed data in November 2012 and June 2013 were flagged as influenced by human activities.

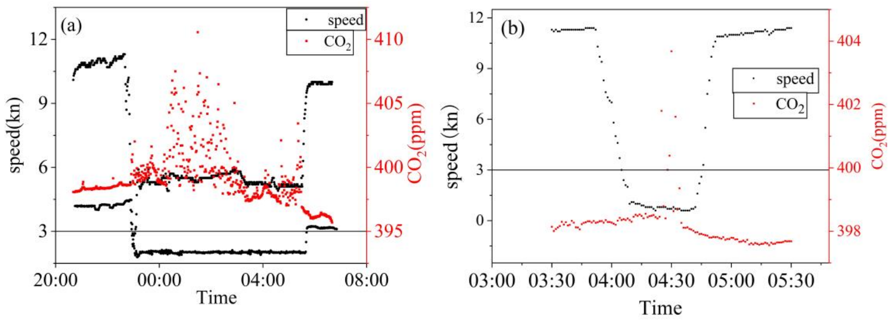

Fig. 6. Variations of observed CO_2 mixing ratios and ship speed from 20:40 on 28th to 6:40 on 29th June 2013 (a) and 3:30 to 5:30 on 3th November 2012(b).

Finally, the Pauta criterion ("3σ" method), a widely used data quality control approach in atmospheric greenhouse gas observation (Zhang et al., 2013; Fang et al., 2015; Zang et al., 2017), was introduced to filter and flag the non-background observation results. To optimize this process, observation data that covered period of 0.5, 1, 2 and 4 hour was calculated, respectively. Any deviations between observed results and average value lying outside ± 3 SD were considered as non-background data and should be flagged. This procedure was repeated until no outliners were identified (Zhang et al., 2007). Result showed that data calculated hourly by the Pauta criterion was optimal, because it could not only flag dispersed values, but keep the smooth data well.

Based on the optimized approach, observed data could be filtered and flagged as shown in Fig. 7, the remained data accounted for 79.5% and 75.7% of original data in November 2012 and June 2013, respectively, which were considered as background data, and used for further analysis.

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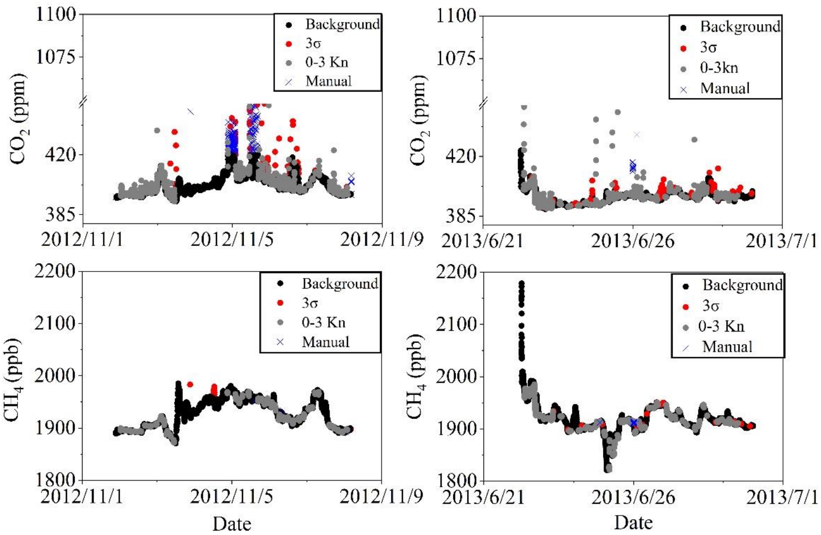

Fig. 7. Filtered results of CO_2 (a, b) and CH_4 (c, d) mixing ratios in November 2012 and June 2013, the ordinates of a and b are truncated in the range of 450 to 1050 ppm. Black points represent the background data (Background), the red points represent the data filtered out by the Pauta criterion (3σ), the green points mean the data influenced by ship emissions at low speed (0-3 Kn), and the blue crosses indicate unreasonable data that were manually screened (Manual).

4.2 Influence of air-sea exchange on distribution of atmospheric CO_2 and CH_4 mixing ratios

Air-sea exchange is a dynamic process when CO_2 and CH_4 molecules diffusing between the interface of surface seawater and overlying atmosphere. Source and sink of atmospheric CO_2 and CH_4 mean they were emitted from or absorbed by seawater. In fact, the magnitude of air - sea CO_2 and CH_4 exchange varied dramatically in spatial and temporal scale in coastal seas (Yang et al., 2016; Gao et al., 2019). Generally, CO_2 and CH_4 emitted from the seawater into the air were difficult to trace by atmospheric measurements because they could dilute sharply (Schmale et al., 2005; Kourtidis et al., 2006; Zhai et al., 2013), only shallow seeps areas and coastal regions, could influence the mixing ratios of local atmospheric CO_2 and CH_4 directly and be measured (Leifer et al., 2006; Luo et al., 2015). Despite the dissolved CO_2 and CH_4 were not observed in our field surveys, the published data showed that sea-to-air CO_2 fluxes were 6.0 ± 8.8 mmol/m^2/day in November 2012 and 2.6 ± 4.3 mmol/m^2/day in June 2011 (Wang and Zhai, 2021), and sea-to-air CH_4 fluxes were 6.4 µmol/m^2/day in November 2002 and 15.7 µmol/m^2/day in June 2006 (Zhang

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et al., 2008), respectively, in the SYS.

To estimate the effects of air-sea exchange on mixing ratios of atmospheric CO_2 and CH_4, we used a simple method described by Kourtidis et al. (2006) and optimized by Zang et al. (2020): assumed that a box located above the survey area, with a ceiling of 10 meters which corresponding to the height of air inlet in our field surveys. The contents of atmospheric CO_2 and CH_4 were only impacted by air-sea exchange. When CO_2 and CH_4 were vented into or absorbed from the box, their mixing ratios would increase or decrease homogeneously, caused by the mean calculated results of sea-to-air CO_2 and CH_4 fluxes.

For CH_4, generally, coastal shallow seas are source of atmospheric CH_4, accounting for approximate 75% of global ocean emissions (Bange et al., 1994; Bates et al., 1996). However, according to the calculation formula that given by Zang et al. (2020), sea-to-air CH_4 flux of 50.8 μmol/m^2/day would result in an increasing of 2 ppb of atmospheric CH_4 mixing ratio in the MBL. Thus, the impacts of the reported mean sea-to-air CH_4 fluxes (6.4 μmol/m^2/day and 15.7 μmol/m^2/day in November 2002 and June 2006) on the atmospheric CH_4 would not exceed 1 ppb (Zhang et al., 2008). In addition, based on the same method, we calculated the impacts of the reported mean sea-to-air CO_2 fluxes (Wang and Zhai, 2021) on the atmospheric CO_2 mixing ratios was no more than 14.1 ppb. Thus, it was reasonable to conclude that influences of air-sea exchange on distribution of atmospheric CO_2 and CH_4 mixing ratios were negligible, compared to the observed variability of atmospheric CH_4 (Fig.3 and Fig. 4).

4.3 Influences of land–sea air mass transportation on spatiotemporal distribution of atmospheric CO_2 and CH_4 mixing ratios

The EAWM is closely related to atmospheric compounds transportation from the Asia continent to the Western Pacific (Yu et al., 2014). Since two surveys were conducted in November 2012 and June 2013, when the typical winter and summer monsoon season in their early phases, respectively (Lyu et al., 2021; Lin'an et al., 2022), the observation data could give us an ideal opportunity to study the impacts of land-to-sea air mass transportation on spatiotemporal distribution of atmospheric CO_2 and CH_4 mixing ratios over the SYS. The observed atmospheric CO_2 and CH_4 mixing ratios were higher in November 2012 (Fig. 8) than that in July 2013 (Fig. 9). Except for the Section 1 (S1) and the right end of Section 2 (S2), the spatial distributions were

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gradient with offshore distance (Fig. 8).

In situ observed data demonstrated that the dominant wind direction was W-NW-NNW for section 2, 3, 4 and 5 in November 2012, suggested the air masses were transported from the Asian Continent to the Pacific Ocean (Fig. 5 and Supplementary data). Generally, CO_2 and CH_4 mixing ratios were higher in continent than that of the MBL, land-to-sea air mass transportation driven by the EAWM could result in the horizontal transmission of greenhouse gases (Zhang et al., 2007; Zang et al., 2017; Liu et al., 2018). Due to the subsequently mixing, CO_2 and CH_4 mixing ratios would decline along the windward (Bartlett et al., 2003; Kourtidis et al., 2006; Liu et al., 2018). Meanwhile, the mixing ratios of atmosphere CO_2 and CH_4 were low and homogeneous in Section 1 and right end of Section 2, because the dominant wind direction was ENE-SE-S, indicated air masses were transported from the open Pacific Ocean with low content of CO_2 and CH_4, because of weak human activities (Matsuda, 1996; Bartlett et al., 2003; Zang et al., 2017).

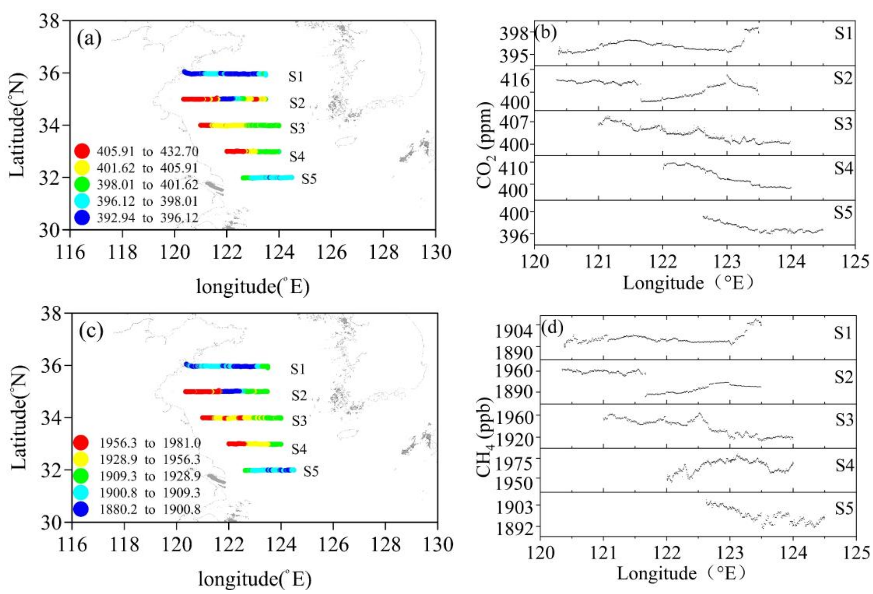

Fig. 8. Spatial distributions of CO_2 and CH_4 mixing ratios in the survey area in November 2012.

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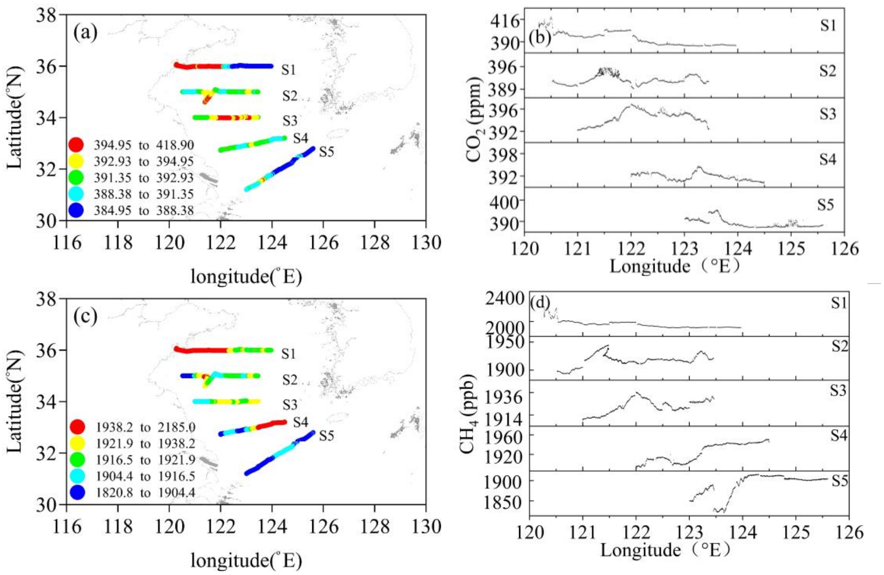

Fig. 9. Spatial distributions of CO_2 and CH_4 mixing ratios in the survey area in July 2013.

Furthermore, back trajectory analysis showed that almost all the transport track were originated from the Asian Continent in November 2012, and the South China Sea and West Pacific Ocean in July 2013 (typical characteristics of the early summer monsoon) (Fig. 10), which resulted in higher atmospheric CO_2 and CH_4 mixing ratios in November 2012 (Fig. 8) than that in July 2013 (Fig. 9). Seasonal variations of atmospheric CO_2 and CH_4 mixing ratios were consistent with the variations of atmospheric CO_2 mixing ratios in West Pacific Ocean, where atmospheric components distributions were dominated by maritime air masses from the Pacific Ocean and polluted air masses from the Asian Continent (Matsuda, 1996; Zhang et al., 2007).

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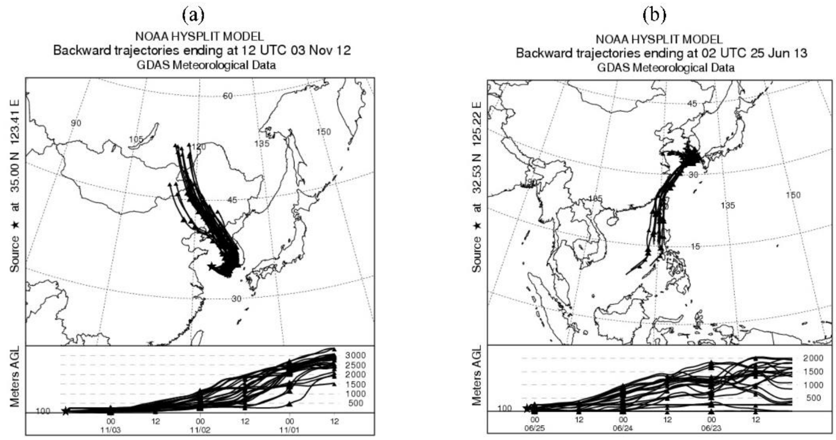

Fig. 10. Three-day air back-trajectories of two typical locations, a (35.00 °N, 123.41 °E) and b (32.53 °N, 125.22 °E).

4.4 Estimated distance of air mass transportation

As shown in Fig. 11, atmospheric CO_2 and CH_4 mixing ratios fluctuated in the same phase along with wind direction, indicated their variations were dominated by the same emission and air masses transportation, which was in agreement with previous studies (Zang et al., 2017; 2020).

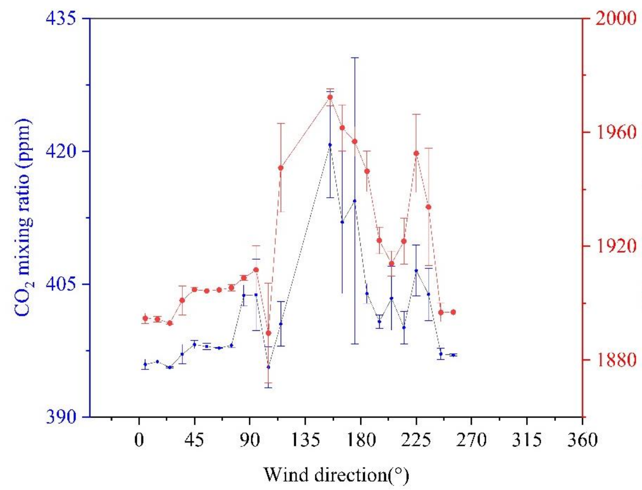

Fig. 11. Atmospheric mixing ratios of CO_2 and CH_4 as a function of wind direction. Error bars indicate two standard errors within each wind direction bin.

Simulation studies of gas seeps in the Black Sea and the Nord Stream pipeline gas leaks in the

Baltic Sea showed that atmospheric CH_4 mixing ratio could be enhanced by the upwind emission source in distance of 5 to 30 km (Kourtidis et al., 2006; Jia et al., 2022). NOAA's MBL-CO_2 and MBL-CH_4 values were 394.56 ppm and 1875.4 ppb, respectively, at the same latitude zone with the survey area in November 2012. ΔCO_2 and ΔCH_4 represented deviations between observed atmospheric CO_2 and CH_4 mixing ratios and MBL-CO_2 and MBL-CH_4 references. As shown in Fig. 12, we assumed that the effects of mixing and dilution during the transportation was linear (Kourtidis et al., 2006), the further the observation site away from continent, the lower the ΔCO_2 and ΔCH_4 values in each survey section. According to the calculated slope values, the inflection points of gradient could be set at 123.30 °E, 123.50 °E and 123.40 °E for section 3, 4 and 5, respectively. Moreover, the offshore distances away from continent could be calculated as approximate 27.0, 26.3 and 11.7 km, respectively, with a mean value of 21.7 km. Thus, spatial distributions of atmospheric CO_2 and CH_4 mixing ratios in the China shelf sea could be impacted remarkably by land-to-sea air mass transportation during early phase of the EAWM.

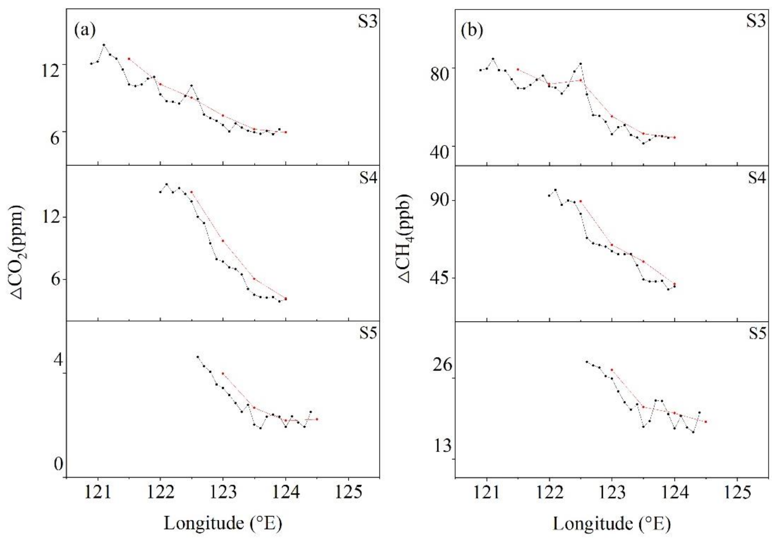

Fig. 12. The average value of ΔCO_2 (a) and ΔCH_4 (b) per 0.1 (black) or 0.5 longitude (red).

5. Conclusions

Based on the continuous observed CO_2 and CH_4 mixing ratios and meteorological parameters over the south Yellow Sea in November 2012 and June 2013, a data filter method was optimized and established, which could be used to flag CO_2 and CH_4 mixing ratios influenced by diverse

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natural and human activities. Spatial and seasonal variations of atmospheric CO_2 and CH_4 mixing ratios over the SYS were mainly regulated by the EAM, while the influence of air-sea exchange was slight or negligible. Summer monsoon resulted in relatively low atmospheric CO_2 and CH_4 mixing ratios with a gradient increasing from southeast to northwest. Conversely, winter monsoon enhanced land-to-sea air masses transportation with high CO_2 and CH_4 mixing ratios, which induced decreasing patterns with increasing distance offshore. Effect of land-to-sea air mass transportation on enhanced CO_2 and CH_4 mixing ratios was assessed as a distance of approximate 20 km offshore in the early period of the EAWM.

Code availability. The code that is used for figure plotting (python) can be provided upon request.

Data availability. The ERA5 hourly data on pressure levels provided by the European Centre for Medium-Range Weather Forecasts (ECMWF), https://cds.climate.copernicus.eu/cdsapp#!/dataset/reanalysis-era5-pressure-levels?tab=form, download date: 2022-11-04). The simulated MBL values produced by NOAA, www.esrl.noaa.gov/gmd/ccgg/GHGreference, download data: 2022-10-10.

Author contributions

Li jiaxin prepared the main part of the paper and performed the corresponding analyses. Zang Kunpeng provided the original data that are used within this study and helped with the data analyses and the preparation of the paper. Lin Yi, Chen Yuanyuan and Liu Shuo provided valuable comments on data processing and, as well as help in the drawing of Fig. 5. Fang Shuangxi, Qiu Shanshan and Jiang kai suggestions for revising the paper and further standardized the paper. Xiong Haoyu, Qing Xuemei and Hong Haixiang helped download the MBL data required for the article.

Competing interest

This manuscript is approved by all authors for publication, and we have no competing interests to declare that are relevant to the content of this article.

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