Methane Distribution, Fluxes, and Budget in the East China Sea and Yellow Sea

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Abstract

We measured dissolved methane (CH4) concentrations, saturations, and air-sea fluxes and sediment-water fluxes during five cruises in March, May, August, October, and December of 2011 in the East China Sea (ECS) and the Yellow Sea (YS). CH4 concentrations had obvious spatial and seasonal variability due to the complex mixing of different water masses and other variables. Maximum CH4 concentration, sea-air and sediment-water fluxes all occurred during summer. CH4 concentration decreased gradually from the coastal area to the open sea, and high levels of CH4 generally appeared near the Changjiang Estuary and outside the Hangzhou Bay. In early spring
and winter, CH4 in the shelf region had a uniform distribution from the surface to the bottom, while it increased gradually with depth in other seasons. Subsurface CH4 maximum occurred at a depth of about 200 m in the slope region during May, October, and December. The CH4 levels at the bottom were generally higher than at the surface, and this was enhanced during summer due to the occurrence of hypoxia in the bottom waters. Changjiang Diluted Water, Kuroshio, and Taiwan Warm Current Water affected the geographic distribution of CH4 in the ECS, and these water bodies contributed about 3.45, 2.97, 14.60 mol·s⁻¹ of CH4 to the ECS during summer and 2.11, 5.28, 5.20 mol·s⁻¹ CH4 during winter, respectively. Sediment was also a significant source of dissolved CH4 in the ECS, and we estimated the average sediment-water CH4 flux of the ECS and YS as about 1.06 and 0.73 μmol·m⁻²·d⁻¹, respectively. We used a box model to calculate preliminarily the CH4 budget in the ECS, which suggests that the main CH4 sources in the ECS were in situ CH4 formation in water column and sediment emissions. Air-sea exchange was the major external sink of CH4 in the ECS. We estimated total annual CH4 emission from the ECS and YS to be about 4.09×10⁹ mol/yr, hence the ECS and YS are active areas for CH4 production and emission.

1 Introduction

Methane (CH4) is an active atmospheric trace gas that is responsible for about 23% of the global greenhouse effect, and also participates in atmospheric chemistry and the biogeochemical cycle of global carbon (Crutzen and Zimmermann, 1991; Quay et al., 1999; IPCC, 2013). The global atmospheric CH4 has increased significantly since the industrial revolution, and was reported as 1803±2 ppb in 2011, which is about 2.5-fold higher than that (722±25 ppb) in 1750 (IPCC, 2013). The continuing rise of atmospheric CH4 indicates an imbalance of sources and sinks. Natural sources are responsible for about 40% of global CH4 emission (Shakhova et al., 2010), among which the ocean accounts for only about 0.4-5.0% of the total emission (Crutzen, 1991; Bange et al., 1994; Reeburgh, 2007). Although most of oceanic CH4 are
oxidized by $O_2$ and sulfate in both aerobic and anaerobic environment before emission, ocean still releases about 11-18 Tg CH$_4$ yr$^{-1}$ (Bange et al., 1994) into the air. In marine ecosystems, CH$_4$ distributions and emissions have large spatial and temporal variations (Bange et al., 1994, 2004; Kock et al., 2008; Forster et al., 2009; Zhang et al., 2004, 2008a). Shelf areas and estuaries were estimated to contribute about 75% to the global oceanic CH$_4$ emissions, although they just cover a small part of the world’s oceans (Bange et al., 1994). However, this estimate still has great uncertainties due to large spatial and seasonal variations and limited area coverage.

The East China Sea (ECS) and the Yellow Sea (YS) together forms an important marginal sea of the northwestern Pacific Ocean. This is one of the largest continental shelves in the world, with a total surface area of $1.2\times10^6$ km$^2$. The ECS opens its north to the YS with the straight line from the northern tip of the mouth of the Changjiang (Yangtze River) toward the Jeju Island as the boundary (the blue dashed line in Fig. 1). The ECS stretches south to the Taiwan Strait, and is adjacent to the western Pacific along its east edge. Its total area is about $7.7\times10^5$ km$^2$, and the average water depth is about 72 m. This wide and river-dominated shelf receives large amounts of fresh water ($9.03\times10^{11}$ m$^3$·year$^{-1}$), sediment ($4.14\times10^8$ t·year$^{-1}$) (Wang et al., 2008), and nutrients (Zhang et al., 1996; Gao et al., 2012) from the Changjiang. The hydrographic characters of this region are also influenced greatly by a circulation system including the Kuroshio, Tsushima Warm Current, Yellow Sea Warm Current on the eastern boundary of the shelf, the Coastal Currents along the western side and the Taiwan Warm Current dispersing out in the middle shelf (Su, 1998; Zhang et al., 2007; Yuan et al., 2008).

So far oceanic CH$_4$ emission is poorly quantified, owing to lack of the temporal continuity and areas coverage (Bange et al., 2009). In particular, data on CH$_4$ in coastal areas of China are scattered and fragmentary. In early 1990s, Tsurushima et al. (1996) observed the horizontal and vertical distribution of CH$_4$ along the section “PN line” in the ECS. Rehder and Suess (2001) surveyed the distribution of CH$_4$ in surface waters along the main path of Kuroshio, which only covered a small part of areas in
the East China and South China Sea. Zhang et al. (2004) reported distributions and fluxes of CH$_4$ in the ECS and the YS in spring 2001, and they also estimated CH$_4$ input from the Changjiang and CH$_4$ export from the shelf to Kuroshio water. Yang et al. (2010) reported the seasonal variation of CH$_4$ concentrations and air-sea fluxes in the north YS during 2006 and 2007. Ye et al. (2015) and Zhang et al. (2008a) reported CH$_4$ distributions and fluxes in the ECS in summer, but the former emphasized the influence of hypoxia on CH$_4$ distribution in the bottom water, while the later mainly introduced the high spatial variability of CH$_4$ depth profiles along four sections. Although these results give us a glimpse of CH$_4$ in coastal waters of China, they are still far from understanding the seasonal variations of CH$_4$ distribution and emission, and quantifying CH$_4$ sources and sinks in these areas. Thus more data on CH$_4$ in coastal and shelf waters of China are still needed to further enrich the global oceanic CH$_4$ database, and to understand the biogeochemical cycle of CH$_4$ in the shelf areas and their regional contribution to global oceanic CH$_4$ emission.

In this paper, we characterized the spatial distribution and seasonal variation of dissolved CH$_4$ in the ECS and YS based on data collected during five cruises in 2011, and identified factors that affected these patterns. We also estimated fluxes at the sea-air and sediment-water interfaces to determine the amount of CH$_4$ released by the ECS into the atmosphere and the amount that escaping from sediments into the water column. We used a box model to calculate the preliminary CH$_4$ budget in the ECS, identify the main sources and sinks of dissolved CH$_4$ in this area, and estimate the contribution of different sources to CH$_4$ in ECS quantitatively. The ultimate aims of this research are to provide a deep understanding of dissolved CH$_4$ in the ECS, and to improve our knowledge of CH$_4$ cycle in the shelf region.

2 Materials and methods

2.1 Seawater sampling and analysis

Five cruises were conducted in the ECS and YS during 2011 to collect data at
different locations (Fig. 1, Table 1). Seawater samples were collected at different
depths using 5-L or 8-L Niskin bottles mounted to a Sea-Bird CTD rosette. Surface
waters were collected at a depth of ~2 m, and bottom waters were typically collected
at ~3 m above the seafloor. Two subsamples for CH$_4$ determinations were transferred
from the Niskin bottles into glass vials (~117 mL) using a silicone tube. After
overflow of approximately 1.5- to 2-fold of bottle volume, 1 mL of a saturated
solution of HgCl$_2$ was added to inhibit microbial activity. Then, the sample bottle was
immediately sealed with a butyl rubber stopper and an aluminum cap (to exclude
excess water) and stored upside down in a dark box (Zhang et al., 2008a). All water
samples were analyzed after return to the laboratory, within 60 days after collection
(Zhang et al., 2004). Salinity and temperature data were measured by the CTD, and
oxygen data from CTD profiles were calibrated with oxygen measurements from the
Winkler titration method (Bryan et al., 1976). Wind speeds were measured by the
shipboard automatic weather stations at about 10 m above the sea surface.

Dissolved CH$_4$ from seawater samples was measured using a gas-stripping method
and a GC-14B gas chromatograph (Shimadzu, Japan) with a flame ionization detector
(FID) (Zhang et al., 2004). FID responses were calibrated using known volumes of
CH$_4$ standards (2.02, 4.18, and 50.0 ppmv, Research Institute of China National
Standard Materials). There was a linear relationship between FID response and CH$_4$
concentration, so a multi-point calibration method was used to determine CH$_4$
concentration based on chromatographic peak area. The precision of this method was
better than 3% during the routine analysis of the seawater samples (Zhang et al.,
2004).

2.2 Sediment sampling and incubation experiments

The emission of CH$_4$ from sediments was measured by the closed chamber
incubation method (Barnes and Owens, 1999). Sediment samples were collected by a
box corer at different sampling stations (Fig. 1, red triangles). Only samples with
undisturbed sediment surfaces were used. At each station, 15 sediment cores were
collected using plexiglass tubes that had openings on both ends (i.d.= 5 cm, height =
30 cm), with the bottoms sealed using air-tight rubber bungs. Just prior to the
beginning of flux measurements, ambient bottom water was added carefully (with no
gas headspace), and then the core was capped with a plexiglass top that had gas-tight
O-ring seals and two sampling ports. All cores were arranged around a central shaft
which was supported by magnets that rotated at 60 rpm, and were placed in a
water-filled tank that was held at ambient room temperature using a recirculating
water temperature-controlled bath. Ten glass bottles filled with ambient bottom water
were placed in the same tank and used as blank. Cores were incubated in the dark for
24–48 h. Three overlying water samples were collected at 4-h to 8-h intervals,
transferred into 56.5 mL glass bottles, and treated with 0.5 mL HgCl₂ to inhibit
microbial activity. At the same time, two bottled water samples were also treated with
0.5 mL HgCl₂ as a blank. The CH₄ concentrations of all samples were measured by
the gas-stripping method described above. Sediment-water CH₄ flux was estimated
from the slope of the CH₄ increase in the overlying water as a function of time. The
effect of temperature discrepancy (usually 0.8-10.5°C) on the CH₄ emission rate from
sediments was corrected by the Arrhenius empirical equation (Aller et al., 1985; Song
et al., 2015). When temperature increases by 10 °C, the chemical reaction rate (here
referring to CH₄ production and consumption rate) will increase by 2~4 times. We
took 3 times for calibrating the calculation of sediment-water CH₄ fluxes accordingly.
Use of the Arrhenius equation for temperature correction is usually reasonable and
acceptable when an incubation experiment is not conducted at the in situ temperature
(e.g. Aller et al., 1985; Song et al., 2015).

2.3 Saturation and sea-to-air flux calculations

The saturation (R, %) and sea-to-air flux (F, μmol·m⁻²·d⁻¹) of CH₄ were calculated
by the following formulas:

\[ R(\%) = \frac{C_{obs}}{C_{eq}} \times 100 \]  \hspace{1cm} (1)

\[ F = k \times (C_{obs} - C_{eq}) \]  \hspace{1cm} (2)

where \( C_{obs} \) is the observed concentration of dissolved CH₄ and \( C_{eq} \) is the
air-equilibrated seawater CH₄ concentration, calculated from the \textit{in situ} temperature and salinity and the solubility data of Wiesenburg and Guinasso (1979). Atmospheric CH₄ was not measured in this study. Instead, an annual mean atmospheric CH₄ mixing ratio of 1902 ppb at three observation stations near the East China Sea (LLN, TAP and SDZ) in 2011, from the NOAA/ESRL Global Monitoring Division in situ program (http://www.esrl.noaa.gov/gmd), was used for all calculations. Although seasonal variations in atmospheric CH₄ mixing ratios were detected in these stations due to terrestrial influence, they make a minor difference in the results of sea-air fluxes. In formula 2, \( k \) stands for the gas transfer coefficient, which is a function of wind speed and Schmidt number (Sc), generally estimated by the empirical equations. Various empirical equations were published to estimate \( k \). Nightingale et al. (2000) reported an evaluation of sea-air gas exchange in coastal ocean, and the corresponding value lies near the median of extensive methods and models (Cockenpot et al., 2015). Wanninkhof (2014) improved the methodology and updated the relationship between gas exchange and wind speed based on his previous research over the last two decades (Wanninkhof, 1992). The new relationship between \( k \) and Sc was constructed using the modified global ocean \(^{14}\text{C} \) inventories and improved wind speed products, and it can be well applied to the gas exchange study at the intermediate winds of 4-15 m/s. Both methods (hereafter N2000 and W2014) were chosen to calculate sea-air fluxes in this paper.

\section*{3 Results}

\subsection*{3.1 Hydrography of the ECS}

The hydrography of the ECS is highly variable due to the influence of three main water masses including the Changjiang Diluted Water, Taiwan Warm Current Water, and Kuroshio (Su, 1998; Li and Su, 2000; Zhang et al., 2007; Qi et al., 2014). These influences are evident in the temperature-salinity (T-S) curves along all sections during May, October, and December (Figs. 2 and 3). The salinities at stations near the Changjiang Estuary (\textit{i.e.} C0, B1 in May; P01, F03 in October; F02, P01 in December) were less than 32, due to the influence of Changjiang Diluted Water (CDW). In
contrast, the Kuroshio affected the T-S relationships at stations on the continental slope (i.e. CJ, D1, D9, ED and G8 in May; P12, E10 in October; E10 in December). Moreover, water columns of these stations could be divided into four layers according to their T-S relationships: (i) Kuroshio surface water (KSW) was present at a depth of 0~50 m, and this water had high temperature and salinity; (ii) Kuroshio subsurface water (KSSW) was at a depth of 50~300 m, and this water had a lower temperature than the surface water; (iii) Kuroshio intermediate water (KIW) was present at a depth of 300~800 m, and had lower salinity and temperature than the upper water; and (iv) Kuroshio deep water (KDW) was at 800 m and lower, and this high-density water had a temperature of about 5°C.

The Taiwan Warm Current Water (TWCW) also affected the mid-shelf of the ECS, as indicated by the high temperature and a moderate salinity 33.0~34.5 psu in the southwestern region of the ECS (stations T01, T03 in May; Z01, Z03 in October; Z02, Z03 in December). The shelf water mixed with water from the CDW, TWCW, KSW, and KSSW, and its salinity was 32~34 psu. High CH4 levels were usually present in areas impacted by the CDW, and low CH4 levels were present in the water from the Kuroshio Current.

### 3.2 Seasonal variations of CH4 in the ECS and YS

Table 2 shows the range and average of temperature, salinity, and CH4 concentrations in surface and bottom waters of the ECS and YS during the five cruises of 2011. Considering the large spatial difference among different cruises, we divided the sampling region into four subareas based on the boundary of the ECS and YS (blue dashed line in Fig. 1), the line of salinity 30 (green curve in Fig. 1) and the 200m depth line (red curve in Fig. 1). They were the YS, the Changjiang Estuary (S≤30), the ECS shelf (S>30, depth≤200 m) and the ECS slope (S>30, depth>200 m).

The ECS shelf was surveyed during all cruises and was chosen to compare the average surface and bottom CH4 concentrations during different seasons (Fig. 4). It can be seen that both surface and bottom CH4 concentrations had obvious seasonal variations, with the highest level occurring in summer and the lowest level in early...
spring (March). The salinity during August was the lowest due to the surge of Changjiang runoff in summer. CH$_4$ concentration in the Changjiang (135.3±36.9 nmol·L$^{-1}$) was usually about 10-30 times higher than that in the ECS, and this enhanced CH$_4$ concentration in the ECS together with high CH$_4$ production with increasing temperature. During the five cruises, bottom CH$_4$ concentrations were usually higher than those at the surface, especially during summer.

3.3 Geographic Distribution of CH$_4$ in the YS and ECS

Figure 3 shows the geographic distributions of temperature, salinity, and CH$_4$ in surface and bottom waters of the YS and ECS in 2011. Two cruises were in spring (March, Fig. 3a; May, Fig. 3b). During May, surface and bottom water temperature increased gradually from north to south, and temperature was relatively low (2~3°C) in the bottom water on the edge of the ECS continental shelf. Surface and bottom salinity increased gradually from the Changjiang Estuary to the southeast. Dissolved CH$_4$ concentrations in surface and bottom waters gradually declined from the Changjiang Estuary towards the open sea during spring. High CH$_4$ concentrations in the surface water appeared near Changjiang Estuary (T05: 29.67 nmol·L$^{-1}$ in March; C0: 21.38 nmol·L$^{-1}$ in May) due to the influence of the Changjiang Diluted Water. CH$_4$ concentrations in the bottom were slightly higher than in the surface, and highest levels were observed at F03 (30.63 nmol·L$^{-1}$) and F04 (19.58 nmol·L$^{-1}$) during March and at B1 (17.81 nmol·L$^{-1}$) and D1 (20.01 nmol·L$^{-1}$) during May. In the southeastern continental shelf of the ECS, CH$_4$ concentrations were relatively low (about 2~3 nmol·L$^{-1}$), mainly due to the influence of the CH$_4$-depleted Kuroshio surface water. This is consistent with the results reported by Rehder and Suess (2001) and Tsurushima et al. (1996).

Temperature in the surface and bottom waters increased from north to south during August (Fig. 3c). Salinity had a similar trend with spring, but CDW had an obvious extension in the ECS during summer, and surface salinity was below 32 at most
regions of the continental shelf. Dissolved CH$_4$ increased with increasing temperature and freshwater discharge during summer (about 33,484 m$^3$·s$^{-1}$, more than 2-times than during spring; *Changjiang Sediment Bulletin*, 2011). The mean surface and bottom CH$_4$ concentrations were 8.21 nmol·L$^{-1}$ and 11.88 nmol·L$^{-1}$, respectively. Just as in spring, high CH$_4$ concentrations in the surface and bottom waters were present near the Changjiang Estuary and outside Hangzhou Bay. Particularly, high bottom CH$_4$ concentrations (10.51~12.48 nmol·L$^{-1}$) were observed in the high turbidity zone of the Changjiang Estuary (~122°00′-122°20′E, 30°50′-31°15′N; Shen, 2012), together with low oxygen concentrations (2.10~2.82 mg·L$^{-1}$). Besides, high temperature during summer may lead to water stratification, which prevents dissolved CH$_4$ in bottom waters from diffusing into upper waters, and thereby further enhance the CH$_4$ accumulation in the bottom water.

During October, surface seawater temperature and salinity increased gradually from northwest to southeast (Fig. 3d). Bottom temperatures in the ECS were almost all in the range of 19~22°C, but there was a cold bottom center (below 10°C) on the southeastern region of the YS. Water with high temperature and salinity at the southeastern corner of the studied area might have been affected by the northward branch of the Kuroshio. CH$_4$ concentrations during autumn were significantly lower than during summer. Bottom CH$_4$ concentrations of the entire ECS shelf were relatively high (above 8.0 nmol·L$^{-1}$), especially at coastal areas, *i.e.* the Changjiang Estuary (P01, P03), the mouth of Hangzhou Bay (T05), and the surrounding waters of Jeju Island (A10, D07). On the contrary, CH$_4$ concentrations were quite low (about 3 nmol·L$^{-1}$) in the southeastern part of the ECS continental shelf due to the influence of CH$_4$-depleted Kuroshio surface water.

The geographic distributions of surface and bottom temperature and salinity during December (Fig. 3e) were similar to that recorded during October, but CDW only had a slight influence. The CH$_4$ level of the whole ECS and YS during December was far below the levels during August and October, and the average CH$_4$ concentration in the surface waters (4.07 nmol·L$^{-1}$) was slightly lower than that in the bottom waters (4.53
nmol·L⁻¹). Surface CH₄ concentrations in the YS were slightly higher than those in the ECS, and high CH₄ concentrations occurred in the southern YS near Cheju Island, while sporadically high levels of CH₄ in the bottom waters mainly occurred near the continental slope in the ECS. To sum up, CH₄ concentrations in the surface and bottom waters of the YS and ECS during winter were uniform and stable, and were 3~5 nmol·L⁻¹ in most regions.

3.4 Depth Distribution of CH₄ in the ECS

Section PN (red solid line in Fig. 1) extends from the Changjiang Estuary southeast towards the Okinawa Trough and across the CDW and the mainstream of the Kuroshio. Section E (purple solid line in Fig. 1) lies across the entire shelf of the ECS, and extends from the coastal area of Zhejiang and Fujian provinces east towards the Okinawa Trough. We used these representative sections to study the hydrological and chemical characteristics of the ECS. Here we choose the top buoyant water (depth less than 200 m) to analyze the depth distribution of dissolved CH₄ on the ECS shelf.

Figure 5 shows the depth distributions of temperature, salinity, and CH₄ along section PN during March, May and October, and section E during December. Seawater temperature and salinity gradually increased with distance from the shore, but the depth profiles had seasonal variations. During early spring (March, Fig. 5a) and winter (December, Fig. 5d), the water column in the middle of ECS shelf was almost well-mixed in the top 100 m, and temperature and salinity along section PN were nearly uniform from the surface to the bottom; however, the depth profiles of temperature and salinity were stratified during late spring (May, Fig. 5b) and autumn (October, Fig. 5c). Perennial stratification in the water column occurred in the Changjiang Estuary, while water column stratification in the middle shelf began to occur during late spring, faded during the fall and disappeared completely during December.

Correspondingly, dissolved CH₄ concentrations along section PN and section E gradually decreased with distance from the shore, and the maximum CH₄
concentration of surface water was near the shore. During March and December, CH₄ concentrations were relatively uniform from surface to bottom, but they increased gradually with depth during May and October. Particularly, high bottom CH₄ values were usually observed at stations close to the continental shelf, especially in the shelf break area. The bottom CH₄ concentration at P09 during October reached 12.16 nmol·L⁻¹, almost 2-fold higher than the surface level.

Figure 6 shows depth profiles of seawater temperature, salinity, and CH₄ concentrations at stations CJ, P12, and E10 (red circles in Fig. 1) located at the continental slope where the mainstream of the Kuroshio flows northeastward along the 200 m isoline. The mixed layers at the sloping region ranged between 30 and 120 m in depth and became deeper from spring to winter, below the mixed layer water temperature decreased gradually. Salinity showed maximum at around 100-200 m, then declined sharply and reached minimum at about 500 m, below which a slight increase occurred with depth. All CH₄ concentrations increased initially with depth, and reached maximum at around 200 m, then decreased to yield a minimum at 500 m. The first CH₄ peak (3-6 nM) may be explained by advective supply from the adjacent continental slope, where bottom waters usually contain high levels of CH₄ (Ye et al., 2015). The second CH₄ peak occurred at a depth of 600 m during May and at 800 m during October. CH₄ concentrations further increased below 800 m during May and December, suggesting the existence of CH₄ sources in sediments.

3.5 Sediment-water CH₄ fluxes in the YS and ECS

Sediment-water fluxes of CH₄ from the ECS and YS had an obvious seasonal variation, with the maximum occurring in summer (Fig. 7) during which the flux was about 2-times higher than the other seasons. CH₄ was emitted from the sediments at most stations and acted as a net source of CH₄ in the water column. CH₄ release from sediments also had obvious spatial and temporal variation. The sediment incubation experiments (“sample” in supplementary Figure 1) at P01 indicated that the CH₄ concentration in the overlying waters increased linearly with incubation time (t) (March: [CH₄] = 0.59×t + 6.33, r² = 0.73; October: [CH₄] = 0.19×t + 2.64, r² = 0.85;
December: $[\text{CH}_4] = 0.23 \times t + 4.37$, $r^2 = 0.95$), and the sediment-water CH$_4$ flux at P01 was 1.93 $\mu$mol·m$^{-2}$·d$^{-1}$ during March, 0.72 $\mu$mol·m$^{-2}$·d$^{-1}$ during October and 1.60 $\mu$mol·m$^{-2}$·d$^{-1}$ during December, respectively. Station C1 (near the Changjiang river mouth) had a sediment-water CH$_4$ flux of 2.94 $\mu$mol·m$^{-2}$·d$^{-1}$ during August, much higher than any other sites; this might be ascribed to the low oxygen concentration in the overlying water (3.25 mg·L$^{-1}$ based on Winkler titration) and the rich organic carbon in the sediment (Lin et al., 2002; Kao et al., 2003).

Due to the limit of weather and lab resources, our sediment collection in August 2011 mainly covered the coastal areas. To avoid spatial bias induced by our sampling area, we added the sediment-water CH$_4$ fluxes obtained from a cruise in August 2013 (Figure 1, stations labelled by the black star) to provide data for the shelf and slope regions. As estimated, average sediment-water CH$_4$ flux from the ECS and YS was about 1.06 and 0.73 $\mu$mol·m$^{-2}$·d$^{-1}$ in 2011, respectively. Based on their surface areas (about $7.7 \times 10^5$ and $3.8 \times 10^5$ km$^2$), the annual CH$_4$ emission from sediments of the ECS and YS in 2011 was about $2.98 \times 10^8$ and $1.01 \times 10^8$ mol, respectively. This indicated that sediments were an important source of CH$_4$ in the bottom waters. However, the estimate of CH$_4$ released from the sediment had great uncertainties because of the scant sampling stations in each survey and the high spatial variation of sediment-water CH$_4$ flux.

### 3.6 Sea-air CH$_4$ fluxes in the YS and ECS

To eliminate the influence of large spatial difference, we divided the sampling region into four subareas, estimated the area using grid method and calculated the sea-air fluxes with N2000 and W2014 for each subarea. The CH$_4$ saturation and average area-weighed sea-air flux density were shown in Table 3. CH$_4$ saturation in the YS had an obvious seasonal variation, with that in autumn much higher than in spring. However, Yang et al. (2010) reported that average surface CH$_4$ saturation in the YS was highest (515.2% ± 231.5%) during August. Surface CH$_4$ saturations in the ECS also showed seasonal variation, with the maximum CH$_4$ saturation occurring in summer, followed by late spring, autumn, winter and early spring. These results were
consistent with the results reported by Ye et al. (2015). Highest CH$_4$ saturation was observed at the Changjiang Estuary. We recorded the highest CH$_4$ saturation at station T05 (1007%) in March, station C0 (858%) in May, and station E01 (1558%) in August. In general, the surface waters of the YS and ECS were all oversaturated with atmospheric CH$_4$, except for some sporadic stations during spring. Thus, the YS and the ECS were net sources of atmospheric CH$_4$.

Sea-air CH$_4$ fluxes calculated using the N2000 equation were quite similar to those estimated from the W2014 equation, and they also showed seasonal and spatial variations in the wide ECS shelf, with the highest CH$_4$ flux occurring in the late spring and the lowest in early spring. In August, although the estuary only covered 25% of total observation area, it was responsible for about 46% of total CH$_4$ emission from ECS. It indicated that sea-air exchange of CH$_4$ in coastal areas was extremely intense, much greater than on the shelf area. Sea-air CH$_4$ flux density in the shelf water of the ECS was about 11.61 μmol·m$^{-2}$·d$^{-1}$ during summer, which was much higher than the previous research (merely 2.81–6.89 μmol·m$^{-2}$·d$^{-1}$) by Zhang et al. (2008a). According to N2000 and W2014 equation, the annual average area-weighed sea-air CH$_4$ flux density of the ECS and YS was about 9.75 μmol·m$^{-2}$·d$^{-1}$ during 2011. Based on the areas of the YS (~380000 km$^2$) and ECS (~770000 km$^2$), we estimated the total CH$_4$ emission from them as 4.09×10$^9$ mol (about 0.065 Tg) during 2011. Bange (1994) estimated the global oceanic CH$_4$ emission was 11–18 Tg CH$_4$·year$^{-1}$, so the YS and ECS accounted for about 0.45% of the global oceanic emission. This value was much higher than its corresponding area proportion of 0.32%, indicating that the YS and ECS are active areas for CH$_4$ production and emission.

4 Discussion

4.1 Factors influencing CH$_4$ distribution in the ECS and YS

The concentration, saturation, and sea-air and sediment-water fluxes of CH$_4$ in the ECS and YS all had obvious seasonal variations. Mean CH$_4$ saturation ($R_{CH4}$) had a linear correlation with mean water temperature (T) in the surface water ($R_{CH4} =$
13.91×T – 30.10, r² = 0.77; Supplementary Figure 2) and bottom water (R_{CH4} =
33.50×T – 225.03, r² = 0.76; Supplementary Figure 2) during different seasons.
Average sediment-water fluxes of CH4 showed a weak correlation with average T
(F_{CH4}=0.06T+0.03, R²=0.3), suggesting that CH4 emission from the sediments
increases with temperature. It was reported that CH4 production rate increases with
temperature in the range of 0-30°C (Liikanen et al., 2002; Glissmann et al., 2004).
Besides, the high temperature may enhance the relative abundance and diversity of
methanogenic communities (Høj et al., 2008; Metje and Frenzel, 2005).
Yvon-Durocher et al. (2014) reported seasonal variations of CH4 emissions from
diverse ecosystems using meta-analysis, and showed that CH4 emissions increased
significantly with seasonal increases of temperature due to increase of CH4 production
from methanogens and anaerobic microbial communities. Our results were consistent
with these previous studies, and supported the view that water temperature played an
important role in regulating the seasonal variation and distribution of CH4 in the ECS
and YS.

The sediment incubation experiments and the depth profile of CH4 in the ECS all
indicated that sediment release was a significant source of CH4 in bottom waters,
especially at the shelf break area. Lin et al. (1992) found that organic carbon
concentrations in bottom sediments increased across the shelf break, and were greatest
in sediments at depths of 1000-1500 m in the ECS, suggesting that high CH4 in
bottom waters may come from high CH4 production and subsequent release from the
organic-rich sediments. Previous studies also showed that many submarine mud
volcanoes and hydrothermal vents occur along the continental slope of the ECS (Zhao
et al., 2006; Kawagucci et al., 2011). Methane-containing fluid was episodically
vented, then transported to the water column. CH4 in the hydrothermal fluid has been
considered as a thermogenic origin and the CH4 level may be 10^4-10^7 times higher
than those in the ambient seawater (Kawagucci et al., 2011). When released from the
vent, it forms buoyant plumes rapidly (Tsunogai et al., 2000). During the dilution,
CH4 can be oxidized quickly in the plume due to the microbial oxidation (De Angelis
et al., 1993). The residual CH$_4$ spreads into the upper seawater. Hence, CH$_4$ release from sediments, mud volcanoes and hydrothermal fluids may also influence the CH$_4$ distribution in the bottom waters, especially at the continental slope.

CH$_4$ formation and consumption in the water column are also important factors that influence the distribution of CH$_4$ in the ECS and YS. Subsurface methane maxima were observed in this study, which have been considered to be a common phenomenon in the open sea (Reeburgh, 2007). Early studies demonstrated that advective transport of CH$_4$ or in situ CH$_4$ production by microbes in anoxic microenvironments led to excess CH$_4$ in the mixed layer (Scranton and Brewer, 1977; De Angelis and Lee, 1994; Karl and Tilbrook, 1994). More recent results suggest that under conditions with rich oxygen and specific nutrient limitation, a variety of methyl-rich organic phosphorus or sulfur compounds were all likely to be utilized by microorganisms and served as precursors of CH$_4$ production (Karl et al., 2008; Damm et al., 2008; Zindler et al., 2013; Florez-Leiva et al., 2013). The bottom water incubation experiments (“blank” in section 2.2 and in Supplementary Figure 1) at some stations (L1 in May, J1 in August, A10 and A02 in October and R07 in December) in this study indicated that CH$_4$ concentration increased linearly with incubation time. This suggested that in situ CH$_4$ production might be another source of the excess CH$_4$ in the bottom waters. Moreover, CH$_4$ production in the water column can be enhanced by hypoxia (Ye et al., 2015). Extremely high bottom CH$_4$ values (20-26 nM) were found near the Changjiang Estuary and outside Hangzhou Bay during August 2011, together with low oxygen level (2.00-4.00 mg/L) and high particulate organic carbon flux (3900-7300 mg C·m$^{-2}$·d$^{-1}$; Hung et al., 2013). Both high bottom water production and sediment release may contribute to this.

Riverine input plays an important role in regulating the distribution of CH$_4$ in the YS and ECS. CH$_4$ concentration in the river water of Changjiang was about 10-40 times higher than that of the ECS (Zhang et al., 2004; 2008), and the freshwater discharge from the Changjiang during summer was much greater than during winter (Table 4), therefore the widespread dispersal of Changjiang plume had a great impact
on CH$_4$ distribution, especially in summer. Similar to the CDW, the Kuroshio and TWCW had different effects on the ECS during summer and winter. During summer, water input from the TWCW ($2.39 \times 10^6$ m$^3$·s$^{-1}$) was much greater than that from the Kuroshio ($0.89 \times 10^6$ m$^3$·s$^{-1}$) (Zhang et al., 2007), and the CH$_4$ level of the TWCW (6.11 mol·L$^{-1}$, Ye et al., 2015) was almost two-fold of that in the Kuroshio (2.91 mol·L$^{-1}$). Thus, the TWCW had a greater influence on CH$_4$ distribution in the ECS than the Kuroshio during summer, while they had comparable influence during winter due to similar water discharges and CH$_4$ concentrations. Thus, the mixing of different water masses and their seasonal variations directly impact CH$_4$ distribution in the ECS.

Submarine groundwater discharge (SGD) has been recognized as an important pathway for material transport to the marine environments (Burnett et al., 2006). It usually contains high levels of CH$_4$, and can serve as an important CH$_4$ source for the coastal ocean (Bugna et al., 1996; Corbett et al., 2000; Santos et al., 2009; Lecher et al., 2015). SGD is a mixture of fresh groundwater and recirculated seawater, and there is no CH$_4$ data available for either of them for the ECS. We collected some groundwater samples as fresh groundwater end-member along the coast of the ECS in December 2011 and July 2012. During December 2011, groundwater samples were collected at twenty-five sites along the Jiangsu and Zhejiang coastal region (120.857°~121.896°E, 30.124°~30.956°N). CH$_4$ concentrations varied significantly at these stations with a great range of 33~61602 nM and a median of 271 nM (Zhang et al., unpublished data). During July 2012, eight groundwater samples for CH$_4$ measurement were collected along the coast of the ECS (121.371°~121.934°E, 30.733°~31.976°N). CH$_4$ concentrations ranged between 138 and 3428 nM with a median of 758 nM. CH$_4$ concentrations in fresh groundwater end-member along the coast of the ECS were much higher than those in the seawater. Hence submarine ground water discharge might be an important CH$_4$ source for the East China Sea and could influence its CH$_4$ distribution.

4.2 Preliminary estimate of CH$_4$ budget in the ECS
In order to quantify the contributions of different sources and sinks to dissolved CH$_4$ in the ECS, CH$_4$ budget was estimated preliminary based on data presented here and collected from previous research. Zhang et al. (2007) re-estimated the nutrient budget of the ECS using a box model during summer and winter. According to mass conservation, the water and salinity balance of the ECS can be expressed as:

$$\sum_{i=1}^{n} WFi + \Delta Q = 0$$  \hspace{1cm} (3)

$$\sum_{i=1}^{n} WFi \times Ci + \Delta Mi = 0$$  \hspace{1cm} (4)

where $WFi$ represents the water flux of inputs (+) and outflows (-) over the shelf; $\Delta Q$ is the water mass distinction caused by sea level change in the ECS; $Ci$ is the salinity or value of a certain element for a known water mass; and $\Delta Mi$ is the increase or decrease of the given element during exchange at the sediment-water and sea-air interface. The inflow to the ECS Shelf includes water from the Taiwan Strait (TWCW), riverine input from the land-mass (of which the Changjiang accounts for about 90–95% or more), and incursion of the Kuroshio from north of Taiwan and over the broad shelf mainly composed of KSW (~25%) and KSSW (~75%) (Zhang et al., 2007). The exchange between the ECS and the YS is taken into account as well. The outflow refers to currents through the Tsushima/Korea Strait (Zhang et al., 2007).

As with the shelf water budget in the ECS (Zhang et al., 2007), we estimated the budget of dissolved CH$_4$ for summer and winter. The Kuroshio and TWCW were hardly observed during our summer cruise because of the limited investigation region, so the corresponding data were from the literature (Ye et al., 2015) and unpublished data for the ECS that was collected in July 2013. Data for riverine CH$_4$ were from our on-going monitoring project at station Xuliujing (121°2´ E, 31°46´ N), which is the most downstream main channel station at the Changjiang. Considering that the sea-air fluxes values from W2014 and N2000 relationships were quite similar, we took those estimated by W2014 for budget calculation. Submarine groundwater discharge (SGD) data for the ECS is rather limited. Gu et al. (2012) estimated the SGD in the Changjiang effluent plume to be about (0.2-1.0) $\times$ 10$^9$ m$^3$ d$^{-1}$ during summer and no
SGD data is available for the whole ECS in literature yet. Hence it is difficult to
estimate the CH$_4$ input to ECS via SGD quantitatively. Fortunately, Prof. Jinzhou Du
from East China Normal University provided us their update and unpublished SGD
data obtained using Ra isotopes as tracers for the ECS (including submarine fresh
water discharge and recirculated saline groundwater discharge), which is $0.68 \times 10^8$ m$^3$
d$^{-1}$ and $0.46 \times 10^9$ m$^3$ d$^{-1}$ in dry and wet season, respectively (Du et al., unpublished
data, personal communication). It is hard to determine CH$_4$ concentrations in the
recirculated seawater, so we assume that CH$_4$ concentrations in the fresh groundwater
and recirculated saline groundwater are the same. Median CH$_4$ concentration was
chosen for calculation since it is less susceptible to abnormally high CH$_4$
concentrations observed in the groundwater. Hence, CH$_4$ fluxes via submarine
groundwater discharge were estimated by multiplying the median CH$_4$ concentration
by the SGD, which yielded a flux of 0.21 mol/s and 4.01 mol/s for winter and summer,
respectively. SGD is a mixture of fresh groundwater and recirculated seawater, among
which the latter could account for 90% of the discharge or more (Burnett et al., 2006),
but considering CH$_4$ concentration in the porewaters (~0.45 μM, Zhang et al.,
unpublished data) of the ECS usually is much lower than those in fresh groundwater,
the above estimation of CH$_4$ flux via submarine groundwater discharge may be
overestimated to some extent.

Table 4 lists the discharges of various water masses and their CH$_4$ concentrations,
and Figure 8 shows a preliminary estimate of the CH$_4$ budget in the ECS. We ignored
the effects of evaporation and precipitation because of unavailable data and the low
water fluxes of these processes. During summer, the TWCW transported 14.60 mol·s$^{-1}$
of CH$_4$ to the ECS via Taiwan Strait, the Kuroshio transported 2.97 mol·s$^{-1}$ of CH$_4$,
the CH$_4$ input from CDW is 3.45 mol·s$^{-1}$, and sediment released 14.70 mol·s$^{-1}$ of CH$_4$.
Groundwater might contribute 4.01 mol·s$^{-1}$ CH$_4$ to the ECS, which is comparable to
the input via river runoff. However, CH$_4$ emission at the sea-air interface reached
138.40 mol·s$^{-1}$ and CH$_4$ export from the ECS was 18.12 mol·s$^{-1}$. Consequently, to
maintain a balance of the CH$_4$ in the ECS, the rate of in situ net CH$_4$ formation (i.e.
CH₄ production-CH₄ oxidation) should be 116.73 mol·s⁻¹, which contributed more than 70% of the CH₄ sources in summer.

During winter, the Kuroshio imported 5.28 mol·s⁻¹ of CH₄ into the ECS (1.8-fold more than in summer), and the TWCW imported 5.20 mol·s⁻¹ of CH₄ (1/3 of that in summer). Although the winter discharge of the Changjiang was almost equal with the water inflow YS, CH₄ input by Changjiang (2.11 mol·s⁻¹) was significantly higher than that from the YS (0.06 mol·s⁻¹). CH₄ emission from sediments was 8.38 mol·s⁻¹ and CH₄ input from groundwater was about 0.21 mol/s during winter (only 5% of that in summer). CH₄ release from the ECS into the atmosphere was about 81.28 mol·s⁻¹ and the CH₄ export out of the ECS was 13.14 mol·s⁻¹. Thus, the net CH₄ production rate of seawater during winter was inferred to be 73.18 mol·s⁻¹ to balance the CH₄ loss by sea-air exchange and outflow.

However, the above results were merely a rough estimate with large uncertainties. Firstly, there were potential errors involved in the measurements and calculations of sea-air fluxes. Secondly, the estimation of CH₄ input via SGD was quite crude due to the limited available data about SGD and groundwater CH₄. Thirdly, we performed sediment incubations only at several stations during each survey, and the results were far from representative of sediment emission from the whole ECS due to large spatial and seasonal variations. Finally, some CH₄ sources and sinks were neglected in this estimation. For example, aerobic CH₄ oxidation has been shown to be a substantial sink of CH₄, however, no estimates of methane oxidation extents and rates were made in the water column here. Seepage of thermogenic methane from the sediments was also ignored due to lack of data. Hence the role of net in situ microbial production might be exaggerated by estimating it as the difference between sources and sinks. Although our method of estimation was not perfect, we demonstrated a variety of CH₄ sources and sinks for the ECS and roughly estimated their relative contribution. It suggests that in situ production in the water column and sediment emissions are major CH₄ sources in the marginal shelf seas, while sea-to-air release was the major external sink of CH₄ in the ECS. Groundwater might be an important source of CH₄ in the
ECS, especially in wet seasons. Hence more research work on CH$_4$ production and consumption as well as CH$_4$ in groundwater discharge is needed to further understand the CH$_4$ budget in the ECS.

5 Conclusions

CH$_4$ distribution and emission in the ECS and YS had obvious spatial and seasonal variations, and were also influenced by various factors, including mixing of different water masses, water temperature, freshwater input, sediment release, hydrothermal seepage and oxygen levels in the water column. We estimated the CH$_4$ budget of the ECS using a box model, and the results indicated that in situ seawater production and sediment release might be the major CH$_4$ source, while sea-air exchange was the major external sink of CH$_4$ in the ECS. Groundwater might be an important source of CH$_4$ in the ECS, especially in wet seasons. The ECS and the YS together was estimated to release about $4.09 \times 10^9$ mol of CH$_4$ per year into the atmosphere, which accounts for about 0.45% of the global oceanic emission and was much higher than its corresponding area proportion of 0.32%. Hence the YS and ECS were active areas for CH$_4$ production and emission.

Author contributions

M.-S. Sun collected and analyzed water samples in October and December 2011. G.-L. Zhang designed the sampling strategy. M.-S. Sun and G.-L. Zhang prepared the manuscript. X.-P. Cao collected and analyzed water samples in March, May, and August 2011. X.-Y. Mao provided hydrological data for March, October and December of 2011. J. Li provided hydrological data for May and August of 2011. W.-W. Ye provided some data for calculation of the methane budget of the East China Sea.

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along a north-south transit in the western Pacific Ocean, Biogeosciences, 10(5),
Table 1. Characteristics of the five cruises in the East China Sea and the Yellow Sea.

<table>
<thead>
<tr>
<th>Survey period</th>
<th>Research vessel</th>
<th>CTD</th>
<th>Station no.</th>
</tr>
</thead>
<tbody>
<tr>
<td>13 Mar. - 10 Apr., 2011</td>
<td>Dong Fang Hong 2</td>
<td>Sea-Bird 911 plus</td>
<td>42</td>
</tr>
<tr>
<td>11 May - 7 June, 2011</td>
<td>Experiment 3</td>
<td>Sea-Bird 911 plus</td>
<td>54</td>
</tr>
<tr>
<td>10-30 August, 2011</td>
<td>Bei Dou</td>
<td>Sea-Bird 917</td>
<td>38</td>
</tr>
<tr>
<td>16 Oct. - 8 Nov., 2011</td>
<td>Dong Fang Hong 2</td>
<td>Sea-Bird 911 plus</td>
<td>55</td>
</tr>
<tr>
<td>20 Dec. 2011-7 Jan., 2012</td>
<td>Dong Fang Hong 2</td>
<td>Sea-Bird 911 plus</td>
<td>46</td>
</tr>
</tbody>
</table>
Table 2. Temperature, salinity, and CH₄ concentrations in surface and bottom waters of the Yellow Sea and East China Sea during five cruises in 2011. Numbers indicate ranges and average ± SD (SD gives the average difference between the average value and the individual values).

<table>
<thead>
<tr>
<th>Season</th>
<th>Depth</th>
<th>Temperature (°C)</th>
<th>Salinity (psu)</th>
<th>CH₄ (nmol·L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>March</td>
<td>surface</td>
<td>4.32~19.03</td>
<td>29.79~34.60</td>
<td>2.39~29.67</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(10.68 ± 3.06)</td>
<td>(33.16 ± 1.08)</td>
<td>(4.47 ± 4.09)</td>
</tr>
<tr>
<td></td>
<td>bottom</td>
<td>5.48~16.13</td>
<td>32.00~34.49</td>
<td>2.63~30.63</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(10.06 ± 2.40)</td>
<td>(33.26 ± 0.75)</td>
<td>(5.10 ± 4.97)</td>
</tr>
<tr>
<td>May</td>
<td>surface</td>
<td>16.40~26.17</td>
<td>30.45~34.59</td>
<td>1.88~26.39</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(21.57 ± 3.00)</td>
<td>(33.14 ± 1.40)</td>
<td>(6.04 ± 5.58)</td>
</tr>
<tr>
<td></td>
<td>bottom</td>
<td>4.00~23.92</td>
<td>24.21~34.90</td>
<td>1.31~30.36</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(15.78 ± 4.62)</td>
<td>(33.07 ± 1.99)</td>
<td>(6.41 ± 5.11)</td>
</tr>
<tr>
<td>August</td>
<td>surface</td>
<td>21.93~28.25</td>
<td>22.57~33.99</td>
<td>3.71~33.62</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(25.91 ± 1.45)</td>
<td>(30.22 ± 2.72)</td>
<td>(8.21 ± 6.02)</td>
</tr>
<tr>
<td></td>
<td>bottom</td>
<td>9.01~24.99</td>
<td>28.69~34.47</td>
<td>6.20~26.22</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(20.75 ± 2.98)</td>
<td>(33.02 ± 1.62)</td>
<td>(11.88 ± 4.59)</td>
</tr>
<tr>
<td>October</td>
<td>surface</td>
<td>17.89~26.18</td>
<td>28.06~34.46</td>
<td>2.44~13.52</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(21.91 ± 2.26)</td>
<td>(32.84 ± 1.47)</td>
<td>(5.03 ± 1.68)</td>
</tr>
<tr>
<td></td>
<td>bottom</td>
<td>4.12~24.19</td>
<td>30.87~34.67</td>
<td>2.50~15.24</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(17.38 ± 5.43)</td>
<td>(33.41 ± 1.23)</td>
<td>(7.51 ± 2.93)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.94~23.46</td>
<td>29.87~34.70</td>
<td>3.01~6.03</td>
</tr>
<tr>
<td>December</td>
<td>surface</td>
<td>15.23 ± 4.28</td>
<td>33.33 ± 1.22</td>
<td>(4.07 ± 0.63)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.84~23.45</td>
<td>30.91~34.73</td>
<td>3.03~10.20</td>
</tr>
<tr>
<td></td>
<td>bottom</td>
<td>(14.83 ± 4.08)</td>
<td>(33.48 ± 1.07)</td>
<td>(4.53 ± 1.33)</td>
</tr>
</tbody>
</table>
Table 3. Surface CH$_4$ saturation, sea-air CH$_4$ fluxes and the average area-weighed flux density in the Yellow Sea and East China Sea.

<table>
<thead>
<tr>
<th>Region</th>
<th>Months</th>
<th>Area ratio</th>
<th>R(CH$_4$)</th>
<th>U$_{10}$</th>
<th>F(W2014)</th>
<th>F(N2000)</th>
<th>average area-weighed flux density</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>(μmol·m$^{-2}$·d$^{-1}$)</td>
<td></td>
<td>(μmol·m$^{-2}$·d$^{-1}$)</td>
<td></td>
<td>(μmol·m$^{-2}$·d$^{-1}$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>R(CH$_4$)</td>
<td>U$_{10}$/m s$^{-1}$</td>
<td>F(W2014)</td>
<td>F(N2000)</td>
<td>average area-weighed flux density</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(μmol·m$^{-2}$·d$^{-1}$)</td>
</tr>
<tr>
<td>YS</td>
<td>Mar.</td>
<td>25%</td>
<td>94-148 (117)</td>
<td>2.2-12.1 (8.3)</td>
<td>-0.56-9.59 (2.31)</td>
<td>-0.55-9.09 (2.23)</td>
<td>0.57</td>
</tr>
<tr>
<td></td>
<td>May</td>
<td>12.7%</td>
<td>94-161 (123)</td>
<td>6.4-10.3 (8.3)</td>
<td>-0.37-3.49 (2.05)</td>
<td>-3.8-3.64 (2.05)</td>
<td>0.26</td>
</tr>
<tr>
<td></td>
<td>Aug.</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>Oct.</td>
<td>41.2%</td>
<td>101-376 (218)</td>
<td>1.6-9.9 (5.1)</td>
<td>0.04-30.47 (6.42)</td>
<td>0.04-29.59 (6.59)</td>
<td>2.68</td>
</tr>
<tr>
<td></td>
<td>Dec.</td>
<td>42.9%</td>
<td>105-238 (146)</td>
<td>2.9-13.6 (7.2)</td>
<td>0.31-16.58 (3.87)</td>
<td>0.39-15.52 (3.86)</td>
<td>1.62</td>
</tr>
<tr>
<td></td>
<td>Estuary</td>
<td>Mar.</td>
<td>0.1%</td>
<td>(1007)</td>
<td>(0.2)</td>
<td>(0.05)</td>
<td>(0.33)</td>
</tr>
<tr>
<td></td>
<td>May</td>
<td>3.1%</td>
<td>161-858 (490)</td>
<td>1.3-11.3 (5.8)</td>
<td>0.15-50.49 (26.54)</td>
<td>0.27-48.23 (27.00)</td>
<td>0.83</td>
</tr>
<tr>
<td></td>
<td>Aug.</td>
<td>26.1%</td>
<td>172-1558 (578)</td>
<td>1.9-8.9 (5.7)</td>
<td>2.25-118.23 (27.22)</td>
<td>3.06-120.19 (28.34)</td>
<td>7.25</td>
</tr>
<tr>
<td></td>
<td>Oct.</td>
<td>2.2%</td>
<td>(558)</td>
<td>(8.7)</td>
<td>(51.27)</td>
<td>(50.69)</td>
<td>0.11</td>
</tr>
<tr>
<td></td>
<td>Dec.</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>ECS shelf</td>
<td>Mar.</td>
<td>75%</td>
<td>91-340 (139)</td>
<td>0.3-13.5 (7.9)</td>
<td>-1.85-52.57 (4.67)</td>
<td>-1.75-49.61 (4.52)</td>
<td>3.45</td>
</tr>
<tr>
<td></td>
<td>May</td>
<td>76.3%</td>
<td>87-1049 (252)</td>
<td>1.2-23.6 (9.0)</td>
<td>-4.30-138.96 (16.36)</td>
<td>-3.99-129.83 (15.79)</td>
<td>12.27</td>
</tr>
<tr>
<td></td>
<td>Aug.</td>
<td>73.9%</td>
<td>195-528 (287)</td>
<td>3.3-8.4 (6.2)</td>
<td>1.66-24.99 (11.40)</td>
<td>2.00-26.09 (11.82)</td>
<td>8.58</td>
</tr>
<tr>
<td></td>
<td>Oct.</td>
<td>52.9%</td>
<td>128-317 (215)</td>
<td>0.8-11.9 (7.3)</td>
<td>0.72-27.51 (10.50)</td>
<td>0.85-26.26 (10.42)</td>
<td>5.53</td>
</tr>
<tr>
<td></td>
<td>Dec.</td>
<td>54.8%</td>
<td>128-213 (163)</td>
<td>3.7-14.1 (8.9)</td>
<td>1.26-23.49 (8.42)</td>
<td>1.47-22.15 (8.15)</td>
<td>4.54</td>
</tr>
<tr>
<td>ECS slope</td>
<td>Mar.</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>May</td>
<td>7.9%</td>
<td>93-157 (128)</td>
<td>4.5-15.2 (9.7)</td>
<td>-0.97-17.47 (4.81)</td>
<td>-0.94-16.19 (4.55)</td>
<td>0.37</td>
</tr>
<tr>
<td></td>
<td>Aug.</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>Oct.</td>
<td>3.7%</td>
<td>186-211 (199)</td>
<td>8.4-10.1 (9.2)</td>
<td>11.44-12.84 (12.14)</td>
<td>11.37-12.44 (11.90)</td>
<td>0.44</td>
</tr>
<tr>
<td></td>
<td>Dec.</td>
<td>2.3%</td>
<td>(232)</td>
<td>(11.7)</td>
<td>(25.84)</td>
<td>(24.59)</td>
<td>0.58</td>
</tr>
</tbody>
</table>
Table 4. Data used for calculation of the CH$_4$ budget in the East China Sea.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Summer</th>
<th>Winter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water exchange between ECS and YS (Sv)</td>
<td>-0.009$^a$</td>
<td>0.013$^a$</td>
</tr>
<tr>
<td>Evaporation (Sv)</td>
<td>-0.0068$^a$</td>
<td>-0.010$^a$</td>
</tr>
<tr>
<td>Rainfall (Sv)</td>
<td>0.031$^a$</td>
<td>0.0062$^a$</td>
</tr>
<tr>
<td>Terrestrial input (Sv)</td>
<td>0.0393$^a$</td>
<td>0.0122$^a$</td>
</tr>
<tr>
<td>Taiwan Strait water (Sv)</td>
<td>2.39$^a$</td>
<td>1.22$^a$</td>
</tr>
<tr>
<td>Kuroshio water (Sv)</td>
<td>0.89$^a$</td>
<td>1.81$^a$</td>
</tr>
<tr>
<td>Outflow of ECS (Sv)</td>
<td>-3.33$^a$</td>
<td>-3.05$^a$</td>
</tr>
<tr>
<td>Groundwater discharge (m$^3$·s$^{-1}$)</td>
<td>5300</td>
<td>790</td>
</tr>
<tr>
<td>Avg. CH$_4$ concentration in Changjiang (nM)</td>
<td>87.90$^b$</td>
<td>173.26$^b$</td>
</tr>
<tr>
<td>Avg. CH$_4$ concentration in TWCW (nM)</td>
<td>6.11$^c$</td>
<td>4.26</td>
</tr>
<tr>
<td>Avg. CH$_4$ concentration in Kuroshio (nM)</td>
<td>3.34$^c$</td>
<td>2.91</td>
</tr>
<tr>
<td>Avg. CH$_4$ concentration in YS (nM)</td>
<td>6.56$^d$</td>
<td>4.33</td>
</tr>
<tr>
<td>Avg. CH$_4$ concentration in shelf of ECS (nM)</td>
<td>5.44$^c$</td>
<td>4.31</td>
</tr>
<tr>
<td>Avg. sea-air CH$_4$ flux ($\mu$mol·m$^{-2}$·d$^{-1}$)</td>
<td>15.53</td>
<td>9.12</td>
</tr>
<tr>
<td>Avg. sediment-water CH$_4$ flux ($\mu$mol·m$^{-2}$·d$^{-1}$)</td>
<td>1.65</td>
<td>0.94</td>
</tr>
<tr>
<td>Median groundwater CH$_4$ concentration (nM)</td>
<td>758</td>
<td>271</td>
</tr>
</tbody>
</table>

Note: Positive values represent water import from an external source and negative values represent water export from the ECS. 1 Sv =10$^6$ m$^3$·s$^{-1}$; a. data from Zhang et al. (2007); b. unpublished data from an on-going monitoring project at Xuliujing station in the lower Changjiang; c. data from Ye et al. (2015); d. unpublished data from observations in July 2013.
Fig. 1. Sampling locations in the East China Sea and the Yellow Sea during the five cruises in 2011. Black solid dots: seawater sampling locations; red solid triangles: sediment sampling locations; red solid line: PN line; blue dashed line: boundary between the East China Sea and the Yellow Sea; purple solid line: section E; red solid circle: the station depth more than 1000 m; red curve: the depth of 200 m line; the red curve: the salinity of 30 line; black star in August: sediment incubation stations (1, 2, 3) in August 2013.
Fig. 2. Temperature-salinity diagrams and CH₄ concentrations in the East China Sea during May, October, and December of 2011. The dominant water masses are classified as previously described (Li and Su, 2000; Qi et al., 2014) and indicated by rectangular outlines. CDW: Changjiang Diluted Water; SMW: Shelf Mixed Water; KSW: Kuroshio Surface Water; KSSW: Kuroshio Subsurface Water; KIW: Kuroshio Intermediate Water; KDW: Kuroshio Deep Water; TWCW: Taiwan Warm Current Water. Black dots: non-CH₄ sampling point; Color dots: CH₄ sampling points, with concentrations indicated by color scale.
Fig. 3. Geographical distribution of temperature (°C), salinity (psu), and CH₄ (nmol·L⁻¹) in surface and bottom waters of the study area during March (a), May (b), August (c), October (d), and December (e) of 2011.
Fig. 4 Comparison of the average surface and bottom CH$_4$ concentrations in the ECS shelf during different seasons
Fig. 5. Depth distributions of salinity (psu), temperature (°C), and CH$_4$ (nmol·L$^{-1}$) along section PN during March (a), May (b) and October (c) and section E during December (d).
Fig. 6. Depth profiles for CH$_4$ (nmol·L$^{-1}$), salinity (psu), and temperature (°C) at station CJ in May, station P12 in October, and station E10 in December.
Fig. 7. Seasonal variation of sediment-water CH$_4$ fluxes from the East China Sea and Yellow Sea.
Fig. 8. CH₄ budget of the East China Sea during summer and winter.