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Methane in the Changjiang (Yangtze River) Estuary and its adjacent marine area: riverine input, sediment release and atmospheric fluxes

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Abstract Dissolved methane (CH_4) was measured in the waters of the Changjiang (Yangtze River) Estuary and its adjacent marine area during five surveys from 2002 to 2006. Dissolved CH_4 concentrations ranged from 2.71 to 89.2 nM and had seasonal variation with the highest values occurring in summer and lowest in autumn. The horizontal distribution of dissolved CH_4 decreased along the freshwater plume from the river mouth to the open sea. Dissolved CH_4 in surface waters of the Changjiang was observed monthly at the most downstream main channel station Xuliujing (121°2′E, 31°46′N), which ranged from 16.2 to 126.2 nM with an average of 71.6 ± 36.3 nM. The average annual input of CH_4 from the Changjiang to the Estuary and its adjacent area was estimated to be 2.24 mol s^{-1} equal to 70.6×10^6 mol $year^{-1}$. Mean CH_4 emission rate from the sediments of the Changjiang Estuary in spring was 1.97 μmol m^{-2} day^{-1}, but it may be higher in summer due to hypoxia in the bottom waters and higher temperatures. The annual sea to air CH_4 fluxes from the Changjiang Estuary and its adjacent marine area were estimated to be 61.4 ± 22.6 and 16.0 ± 6.1 μmol m^{-2} day^{-1}, respectively, using three different gas exchange models. Hence the Changjiang Estuary and its adjacent marine area are net sources of atmospheric CH_4.

Keywords Methane · Changjiang (Yangtze River) Estuary · Sea-to-air fluxes · Riverine input · Sediment release

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Introduction

Methane (CH_4) is a long-lived atmospheric trace gas which is radiatively active. Although its concentration is small compared with major constituents such as carbon dioxide (CO_2), CH_4 has a 20-fold higher potential for global warming than an equal amount of CO_2 and contributes to about 20% of the greenhouse effect (IPCC 2007). CH_4 can influence the Earth's climate indirectly by participating in the photochemical regulation of troposphere O_3 and OH and in the formation of stratospheric H_2O (Crutzen 1991). Atmospheric CH_4 is undergoing increases that range from about 0.5–1% $year^{-1}$ during the past several decades (Rasmussen and Khail 1986; Steele et al. 1992; IPCC 2007), which suggests source-sink imbalance and results in attention to the strength of sources and sinks of atmospheric CH_4. Oceans are a potential source of atmospheric CH_4 (Bange et al.

1994, 1998; Bates et al. 1996) and Bange et al. (1994) estimated that 10.9–17.8 Tg CH_4 are emitted from the global ocean per year. However, CH_4 emission from the oceans is not uniformly distributed geographically. Higher CH_4 concentrations have been observed in some estuaries (Rehder et al. 1998; Sansone et al. 1999; Upstill-Goddard et al. 2000; Marty et al. 2001; Amouroux et al. 2002; Middelburg et al. 2002). Although estuaries represent only about 0.4% of the global ocean area, they account for about 7.4% of the oceanic CH_4 emission (Bange et al. 1994). Middelburg et al. (2002) estimated that estuaries emit 1.8–3.0 Tg CH_4 $year^{-1}$, which are somewhat higher than the estimation by Bange et al. (1994) and represent <9% of the total oceanic emissions. However, these estimations for estuaries have large uncertainties due to high spatial and temporal variability and lack of data, especially for large river estuaries in the world. For example, no data are so far available for the Amazon Estuary, the Mississippi Estuary and large river estuaries in Asia, although sparse data in the waters of the first two rivers had been reported (Lamontagne et al. 1973; Swinnerton and Lamontagne 1974; Bartlett et al. 1990; Devol et al. 1990).

Since rivers usually are found to be supersaturated with CH_4 (de Angelis and Lilliy 1987; de Angelis and Scranton 1993), it is important to understand the degree to which river input and subsequent reactivity in estuaries influence the CH_4 distributions in coastal waters and emissions to the atmosphere. The Changjiang (Yangtze River) is the largest river in Asia, ranking third among the world's rivers. Its drainage basin covers about 1.8 million km^2, which is about one-fifth of the total area of China. A large amount of runoff (903 km^3 $year^{-1}$ averaged from the 1950s to 2005), and sediment (414 million tons $year^{-1}$ averaged from the 1950s to 2005) enter its estuary and the East China Sea (ECS) (Wang et al. 2008). The adjacent coastal environment is eutrophic and influenced by the nutrient load and other pollutants of the Changjiang. Eutrophication may lead to the deposition of high amounts of organic matter which could provide labile organic carbon and generate favorable reducing conditions for the microbial production of CH_4. Therefore, the eutrophication in the Changjiang Estuary may affect the cycling of CH_4 in the water and its subsequent emission to the atmosphere.

We present a study on the distribution of CH_4 in the Changjiang Estuary and its adjacent marine area. The objectives of this study were: (1) to determine the distribution of CH_4 along the Changjiang Estuary, (2) to evaluate the CH_4 emission into the atmosphere, and (3) to evaluate the contribution of the Changjiang to the CH_4 in the ECS.

Methods and materials

Sample collections

Five cruises were conducted on the Changjiang Estuary and its adjacent area during April 25 to May 15 of 2002 by R/V "Haijian 47", November 4–14 of 2002 by R/V "Science No. 1", August 21–29 of 2005 by R/V "Haijian 49", June 2–11 and October 3–13 of 2006 by R/V "Beidou", respectively. The sampling locations are shown in Fig. 1. During the summer cruise in 2005, two surveys were conducted to the estuary during August 21–27 and August 27–29, respectively. Water samples were collected using either 10 l or 20 l Niskin bottles. Subsamples for CH_4 determination were transferred from Niskin bottles into 135 ml or 100 ml glass bottles using the rubber-connecting tube with a glass pipette end. After overflow of approximately 1.5- to 2-fold of bottle volume, 1 ml of 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 the excessive water and stored in a dark box. All the water samples were analyzed after returning to the shore laboratory within 60 days of collection. Data of temperature, salinity and dissolved oxygen were obtained by Sea-Bird 911^{plus} CTD Rosette.

To quantify the flux of CH_4 input to the sea from the Changjiang, CH_4 concentrations were monitored monthly at Xuliujing (121°2′E, 31°46′N, Fig. 1c), the most downstream main channel station, from October 2004 to September 2005. Since it is located at the limit of salt intrusion during dry seasons and at the node where the river estuary begins to become wide, Xuliujing is suitable for observing the freshwater input to the sea from the Changjiang. Water samples were collected using a 10 l bucket. Subsamples for CH_4 determination and the treatment of water samples were the same as above. All the water samples were analyzed within 2 months after collection. Previous experiments showed that the effect of

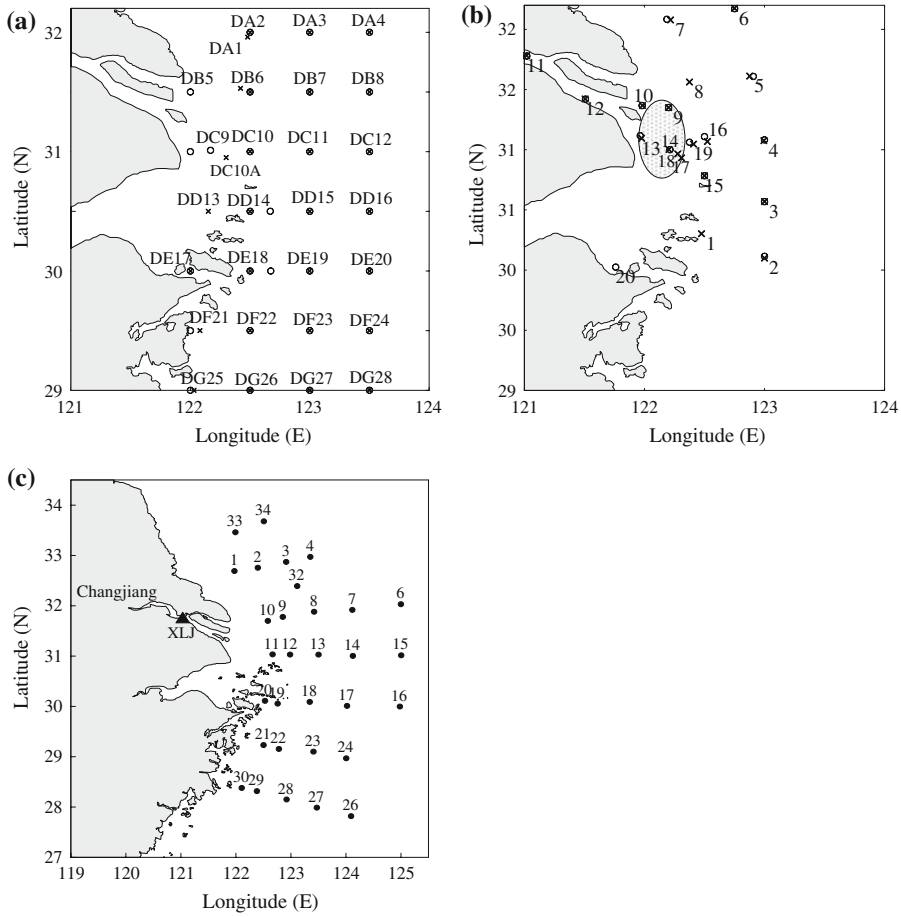

Fig. 1 Sampling locations in the Changjiang (Yangtze River) Estuary **a** April (×) and November (○) of 2002; **b** August 21–26 (×) and August 27–29 (○) of 2005 (*circled area* indicating the turbidity maximum); **c** June, October of 2006 (•) and Xuliujing (XLJ, *solid triangle*)

storage on the sample concentration was small and ignorable (Zhang et al. 2004).

Sediment cores were sampled using a multiple corer (each sediment core 60 cm long and 10 cm i.d.) from station DC 10 and DB6 in the Changjiang Estuary during the spring cruise in 2002. After collection, the cores with 20–30 cm of sediments were selected and left untreated in the plexiglass tubes with the end sealed with air-tight rubber bungs until the beginning of the determination of trace gas release.

CH_4 analysis

In the laboratory, dissolved CH_4 were measured by a GC-14B gas chromatograph using a gas-stripping method (Zhang et al. 2004). CH_4 was separated on a 3 m × 3 mm i. d. stainless steel column packed with 80/100 mesh Porapak Q and detected by a Flame Ionization Detector (FID). Calibration of the FID responses were done by injection of standard gas of 49.6 ppmv CH_4/N_2 (Research Institute of China National Standard Materials) into the stripper filled with blank seawater. CH_4 of the blank seawater had previously been stripped together with other dissolved gases by ultra-pure N_2. After injection, the blank seawater was subsequently analyzed by the same procedure used for unknown samples. Calibration was done every 2 h of operation. The detection limit (DL) for CH_4 analysis in this study was 0.06 nM (DL is defined as CH_4 concentration in 135 mL seawater sample corresponding to two standard deviations of seven replicates of the blank). The precision of repeated analysis of water samples was about 3% for CH_4 in routine sample analysis.

Measurements of CH_4 emissions from the sediments

CH_4 emissions from the sediments at stations DB6 and DC10 in the Changjiang Estuary were determined

using closed chamber technique (Barnes and Owens 1998; Abril and Iversen 2002) during April/May 2002. Measurements were conducted immediately after core collection. After removing the overlying waters carefully, filtered bottom waters were added carefully without gas phase. The top of the tubes was then sealed with air-tight rubber bungs equipped with two stopcocks. An aerated pump was put in half of the water phase to stir the water phase. During 2 days incubation experiments, overlying water samples were carefully taken out at 4 h intervals through one stopcock fitted in the rubber bang for determination of dissolved O_2, and CH_4 changes in the enclosed water phase. The water overlying the core was replenished simultaneously via another stopcock fitted with a syringe containing filtered bottom water. After each sampling, two bottles of filtered bottom water using as replenishment were collected for determination of the CH_4 concentration to correct the CH_4 change of the overlying water. The dissolved CH_4 in the overlying water was analyzed using the gas-stripping method described above. The dissolved O_2 was measured by a DO probe Model 9101Y (Jenco, USA). The emission rates of CH_4 from the sediments were determined from the slope of the CH_4 increase in the overlying water versus incubation time.

Computation of sea-to-air fluxes

Sea to air CH_4 fluxes (F in mol m^{-2} day^{-1}) can be estimated by the following equation:

$$F = k_w\left(C_{obs} - C_{eq}\right) \quad (1)$$

where C_{obs} is the observed concentration of dissolved CH_4; C_{eq} is the air-equilibrated seawater CH_4 concentration, which was calculated for in situ temperatures and salinities using the solubility data of Wiesenburg and Guinasso (1979). We have assumed for these calculations an atmospheric CH_4 mixing ratio of 1.80 ppmv, assuming an annual $\sim$7 ppbv increase, and 1,745 ppbv as the 1998 tropospheric value (IPCC 2007). k_w is gas transfer velocity, which is usually expressed as a function of the wind speed (Raymond and Cole 2001). Various empirical relationships have been derived for estimating k_w. The two most widely used are those of Liss and Merlivat (1986) and Wanninkhof (1992), which are often assumed to define the upper and lower limits for k_w. However, tidal currents may also contribute to turbulence, especially in inner estuaries with shallow waters and high friction on the bottom (Raymond and Cole 2001; Zappa et al. 2003; Abril and Borges 2004). A comparison of published, observationally based predictive models of estuarine transfer velocities showed a general lack of agreement between parameterized transfer models (Raymond and Cole 2001; Abril and Borges 2004). This is largely because there are too few direct measurements of the possible physical controls on gas exchange. Raymond and Cole (2001) derived a relationship ($k_{600} = 1.91\exp\ (0.35u_{10})$ based on a compilation of published k_{600} values in various rivers and estuaries and obtained using different methods [floating chamber, natural tracers (CFC, ^{222}Rn), and purposeful tracer (SF_6)]. This study suggested that k could be significantly higher in estuaries than in open oceanic waters at the same wind speed. Since no direct measurements of gas transfer velocity were made in the Changjiang Estuary, the relationships of Liss and Merlivat (1986) (here after referred to as LM86), Wanninkhof (1992) (hereafter referred to as W92) and Raymond and Cole (2001) (hereafter referred to as RC01) were used to compute k_w. The transfer coefficient was adjusted by multiplying by $(Sc/600)^{-n}$ for LM86 ($n = 1/2$ for wind speed > 3.6 m s^{-1} and $n = 2/3$ for wind speed < 3.6 m s^{-1}), $(Sc/660)^{-1/2}$ for W92, and $(Sc/600)^{-1/2}$ for RC01. Sc was calculated according to the equation by Wanninkhof (1992).

The major uncertainty in the assessment of sea to air gas fluxes is related to the estimation of the gas transfer coefficient, which depends on the wind data used. In this work, we computed the gas transfer coefficients using averaged monthly wind speeds obtained from the monitoring beyond the Changjiang Estuary in 1977–1986, which was 6.7 m s^{-1} for May, 6.8 m s^{-1} for June, 7.6 m s^{-1} for August, 7.2 m s^{-1} for October and 7.6 m s^{-1} for November (cf. Xu 1992). Since during the May 2002 and October 2006 cruises, wind speeds were continuously recorded shipboard using an automated weather station (Campbell Scientifics, UK), the gas transfer coefficients and sea to air fluxes were also estimated using ship based in situ wind speeds.

Results and discussion

Distributions of CH_4 in the Changjiang Estuary and its adjacent area

CH_4 concentrations in the surface and bottom waters of the Changjiang Estuary and its adjacent area during the five cruises from 2002 to 2006 have seasonal variations (Table 1). The highest mean CH_4 concentrations in both the surface and bottom waters occurred in summer, which was about three times higher than the lowest values in autumn. The horizontal distributions of CH_4 in the Changjiang Estuary and its adjacent areas have a conspicuous decrease along the freshwater plume from the river mouth to the open sea (Fig. 2). The relationship between surface CH_4 and salinity in the Changjiang Estuary and its adjacent area (Fig. 3) also support the influence of freshwater. Dissolved CH_4 concentrations initially decrease with increasing salinities at salinities of 0–10 ppt due to a high river end-member concentration and subsequent consumption of methane by oxidation and loss to the atmosphere in the upper part of the estuary (Upstill-Goddard et al. 2000; Abril and Iversen 2002; Middelburg et al. 2002; Abril et al. 2007). At salinities of 10–34 ppt the distribution of CH_4 versus salinity is scattered, and may indicate the influence of other sources such as sediment release, in situ microbial production and input from salt marshes, and water mixing in the outer estuary among different water masses.

CH_4 in other estuaries vary over a wide range from 3 to 1,360 nM at various temporal and spatial scales (Table 2), but are almost always higher than atmospheric equilibrium (2–3 nM). CH_4 in the Changjiang Estuary and its adjacent area falls within but toward the lower end of this range. For example, CH_4 in the Changjiang Estuary is lower than those well documented European river estuaries, i.e., the Humber Estuary (Upstill-Goddard et al. 2000) and the Scheldt, Rhine and Gironde estuaries (Middelburg et al. 2002). CH_4 in the estuarine waters may come from microbial production in water, sediment release, riverine input and inputs of methane-rich water from surrounding anoxic environments (Sansone et al. 1999; Upstill-Goddard et al. 2000; Middelburg et al. 2002). For the European estuaries, riverine input contribute much to the estuarine CH_4 due to high CH_4 in the river waters (Table 3), and wetlands also play important roles. For example, in the Scheldt, Sado and Gironde estuaries, significant CH_4 input from tidal flats caused CH_4 increases at salinities of 20–30 ppt (Middelburg et al. 2002). For the Changjiang Estuary, CH_4 in the river waters is lower than those in the European rivers (Table 3), and CH_4 contribution from the microbial production in water may be low due to very high total suspended matter (TSM) and low particulate organic carbon (POC) in the estuarine water (Zhang et al. 2007). Although CH_4 input from adjacent salt marshes can act as a source of CH_4 to the estuarine water, the low content of organic matter in the salt marshes of the Changjiang Estuary (Zhou et al. 2006) is not favorable for the production of CH_4. Therefore, low CH_4 in the Changjiang Estuary and its adjacent area may be resulted from the low CH_4 in the Changjiang water together with the low net microbial production and low input from adjacent salt marshes.

Table 1 Observed CH_4 concentrations in the surface and bottom waters of the Changjiang Estuary and its adjacent area

Date	Stations	Surface CH_4 nM		Bottom CH_4 nM	
		Range	Average	Range	Average
Apr. 25–May 3, 2002	28	3.54–19.1 (154–782)	7.95 ± 5.24 (326 ± 205)	3.93–29.7	9.74 ± 6.26
Nov. 4–11, 2002	30	2.71–16.1 (123–595)	5.84 ± 3.64 (244 ± 132)	2.86–11.8	5.97 ± 2.55
Aug. 21–29, 2005	40	3.46–88.7 (177–3,841)	18.0 ± 15.8 (810 ± 667)	5.39–89.2	20.6 ± 15.6
June 2–11, 2006	21	3.66–35.07 (149–1,533)	9.46 ± 8.33 (423 ± 368)	4.21–42.30	14.72 ± 9.67
Oct. 3–13, 2006	27	3.71–54.50 (189–2,601)	9.28 ± 10.01 (454 ± 478)	4.33–50.50	11.35 ± 8.89

Numbers in the parentheses are the saturations of methane in %

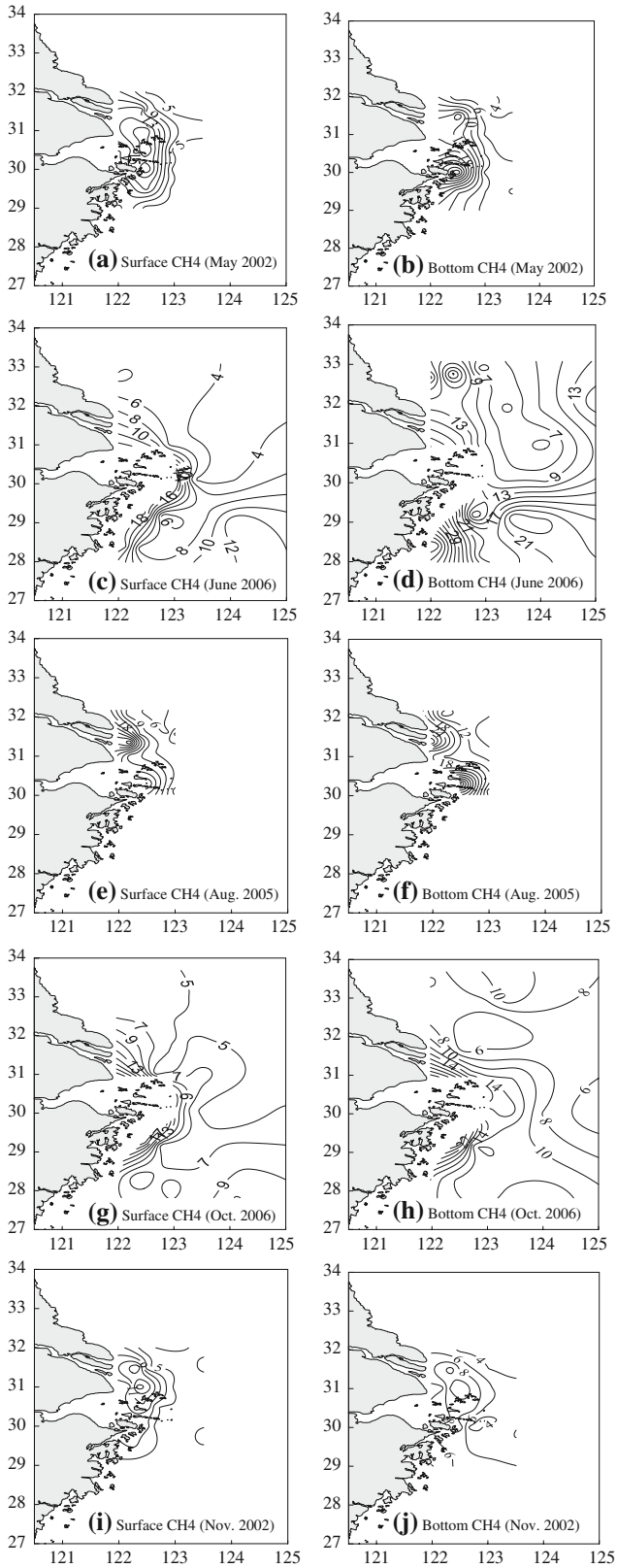

Fig. 2 Horizontal distributions of methane in the surface and bottom waters of Changjiang Estuary

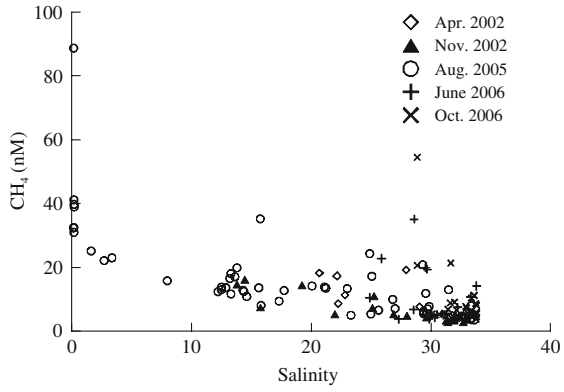

Fig. 3 Relationship between surface methane and salinity in the Changjiang Estuary and its adjacent area

In August 2005, a turbidity maximum (TM) was observed near the mouth of the Changjiang with near bottom TSM concentrations (1,847 ± 1,897 mg l^{-1}) higher than those in the surface water (340 ± 295 mg l^{-1}) by a factor of 5. Sediment accumulation and resuspension of the accumulated sediment are the major mechanism of TM formation in this region (Pan et al. 1999). CH_4 in surface and bottom waters of the TM (16.58 ± 5.47 and 17.51 ± 5.14 nM) were found to be lower than those in the riverine water (48.29 ± 27.18 and 51.24 ± 24.56 nM), but higher than those in the adjacent area (8.37 ± 5.19 and 13.73 ± 8.73 nM). CH_4 concentrations in both surface and bottom waters of the TM were found to be correlated negatively with salinity (not shown, $n = 7$, with $r^2 = 0.88$ and 0.85, respectively), indicating that riverine input play important roles in the distribution of CH_4 in the turbidity maximum zone (TMZ). CH_4 concentrations in bottom water of the TMZ were also found to be correlated positively with TSM ($CH_4 = 0.0023TSM + 13.4$, $r^2 = 0.73$, $n = 15$). Resuspension of sediments can accelerate the release of CH_4 and the high content of suspended particulate matter in the bottom water is favorable for the microbial production of CH_4 (Upstill-Goddard et al. 2000). However, high suspended particles can enhance CH_4 oxidation (Abril et al. 2007), hence CH_4 release from the anoxic bottom sediments during active particle resuspension may account for the correlation between dissolved CH_4 and TSM in this region. Similar phenomenon occurred in May 2002, with resuspension of the sediments observed beyond Zhoushan Island (around stations DD13, DD14, DE17 and DE18), and high CH_4 values were observed in the bottom waters and found to be correlated positively with total suspended matter ($CH_4 = 0.021TSM + 6.5$, $r^2 = 0.83$, $n = 20$). Hence resuspension of the sediments can be an important source of bottom CH_4 in the Changjiang Estuary.

Riverine input of CH_4

The seasonal variation of dissolved CH_4 observed at Xuliujing during the period of 2004–2005 ranged from 16.2 to 126.2 nM with an average of 71.6 ± 36.3 nM (Fig. 4). Since no regular monitor of discharge was made at Station Xuliujing, discharges at Station Datong (about 600 km upstream from Xuliujing) were usually used to represent the water discharge to the sea from the Changjiang (Wang et al. 2008). CH_4 concentrations in the river waters have seasonal variations and correlate positively with the monthly flow rate except January of 2005 ($[CH_4] = 0.002F + 4.91$, $r^2 = 0.61$, $n = 10$) (Figs. 4, 5). This differs from European rivers among which Upstill-Goddard et al. (2000) observed a general decrease in dissolved CH_4 with increasing river discharge. CH_4 concentrations in river waters have large spatial and temporal variations, the lowest CH_4 reported was 2.6 nM in Tyne River (Upstill-Goddard et al. 2000) and the highest was 3,700 nM in the Amazon River (Devol et al. 1990) (Table 3). CH_4 concentrations in the surface waters of the Changjiang in our study fall within but toward the lower end of the reported CH_4 ranges in the worldwide rivers. CH_4 in the river waters may come from in situ production, sediment release, runoff and ground water from organic rich forest and agricultural soils, wetland and floodplains (de Angelis and Lilley 1987; Richey et al. 1988). POC in the river water of Changjiang ranges from 0.5 to 2.5% of total suspended matter in the Changjiang (Wu et al. 2007), which is lower compared with the POC of 2.9–20.1% in European rivers (Abril et al. 2002). Hence, in situ CH_4 production in the river itself may be low and cannot contribute much to the riverine CH_4 in the Changjiang. The high CH_4 content in the river waters may be due to the inputs of methane-rich waters from surrounding anoxic environments rather than in situ CH_4 production in the river system itself. For example, transport of river water over floodplains contributes much to the high CH_4 observed in the Amazon River (Richey et al. 1988). The low CH_4 in

Table 2 Summary of CH_4 measurements in various estuaries in the literatures

Study Area	Stations	Date	Sur. CH_4, (nM)	Sur. *R*, (%)	Salinity	Flux (μmol m^{-2} day^{-1})	References
Tomales Bay	10	Nov. 90–Nov. 91	8–100			6.75–10.1	Sansone et al. (1998)
Columbia River estuary	3	Aug. 1995	12–120		7–23		Sansone et al. (1999)
Parker River estuary		1996/1997	28–930		0–28		
Oregon estuaries						2.5–1,312.5 (181.3)[a]	De Angelis and Lilley (1987)
Alsea estuary		1979–1982	5.7–695	300–29,000	2.0–33.7		
Yaquina estuary		1979–1982	8.1–323	125–42,000	14.3–33.7		
Salmon estuary		1979–1982	123–323	52,000–124,000	20.1–32.1		
Hudson River estuary						350	De Angelis and Scranton (1993)
Tyne Estuary	22	Jan. 1996	13.5–654 (164)	450–20,000 (5,843)			Upstill-Goddard et al. (2000)
Humber estuary	10	March 1996	10.5–237 (94)	304–6,854 (2,670)	0.2–20		
	16	Apr. 1996	3.8–588 (128)	1,357–18,109 (3,998)	0.2–32		
	12	June 1996	14.9–43 1(84.4)	609–16,691 (3,316)	0.2–31		
	11	Oct. 1996	15.5–666 (184)	566–21,048 (6,172)	0.2–31		
	11	Dec. 1996	13.7–520 (166)	372–13,711 (4,430)	0.2–28		
Elbe River estuary	6	May 1994	20–63		6–26		Rehder et al. (1998)
Rhone River plume	9	June 1998	397–1,363				Marty et al. (2001)
European estuaries						(130)[a]	Middelburg et al. (2002)
Elbe	20	Apr. 1997	4.2–111	130–2,980 (580)	0.4–29.3		
Rhine	69	Oct. 96–Nov. 98	4.1–1,026	140–49,700 (8,400)	0–33.8		
Scheldt	63	Jun. 96–Oct. 98	20–485	380–20,400 (3,210)	0.4–33.3		
Gironde	68	Oct. 96–Feb. 98	3.7–559	70–13,400 (580)	0–35.1		
Danube Estuaries	35	July–Aug 1995	(131 ± 42)	(5,340)		(260)[b]; (470)[c]	Amouroux et al. (2002)
Pulicat Lake	52	Dec. 2000	94–501 (242)			(54)[b]; (280)[c]	Shalini et al. (2006)

[a] Averaged value for all of the studied estuaries

[b] K_w was estimated by the LM86 equation

[c] K_w was estimated by the W92 equation

Numbers in the parentheses are the average value

Table 3 Compilation of dissolved methane in various rivers

Rivers	Description	CH_4 (nM)	CH_4 saturation (%)	References
Oregon rivers	1979–1982			De Angelis and Lilley (1987)
McKenzie		5–79	200–2,600	
Willamette		155–298	5,200–11,100	
Alsea		22–729	700–30,300	
Yaguina		276–1,730	9,500–59,800	
Siletz		500–1,100	17,500–38,500	
Mississippi		107–366	3,600–15,200	Swinnerton and Lamontagne (1974)
		11	580	Lamontagne et al. (1973)
Hudson	In summer	98–940	4,400–42,400	De Angelis and Scranton (1993)
	In spring	101–303	2,700–8,100	
Walker creek		140–950	6,000–40,000	Sansone et al. (1998)
Amazon	Open water	460–3,700	16,100–129,500	Devol et al. (1990)
	Main stem	(180 ± 30)	(6,300 ± 1,050)	Bartlett et al. (1990)
	Main stem	(53 ± 91)		Richey et al. (1988)
Orinoco	Main stem, Sep.–March	(170)		Smith et al. (2000)
Ouse	Dec. 1996	(119 ± 47)	(3,861 ± 667)	Upstill-Goddard et al. (2000)
Tyne	Dec. 1996	2.6–146	75–4,129	Upstill-Goddard et al. (2000)
Scheldt		500	17,500	De Wilde and Duyzer (1995)
	Jun. 1996–Oct. 1998	179–485 (282 ± 138)		Middelburg et al. (2002)
Elbe		60–120	1,750–3,500	Wernecke et al. (1994)
	April 1997	111		Middelburg et al. (2002)
Douro	Sep. 1998	63–128		Middelburg et al. (2002)
Rhine	Oct. 1996–April 1998	37–1,437		Middelburg et al. (2002)
Gironde	Oct. 1996–Feb. 1998	10–559		Middelburg et al. (2002)
Thames	April 1997	273		Middelburg et al. (2002)
Yangtze River	Oct. 2004–Sep. 2005	16.2–126.2 (71.6 ± 36.3)		This study

Numbers in the parentheses are the average values

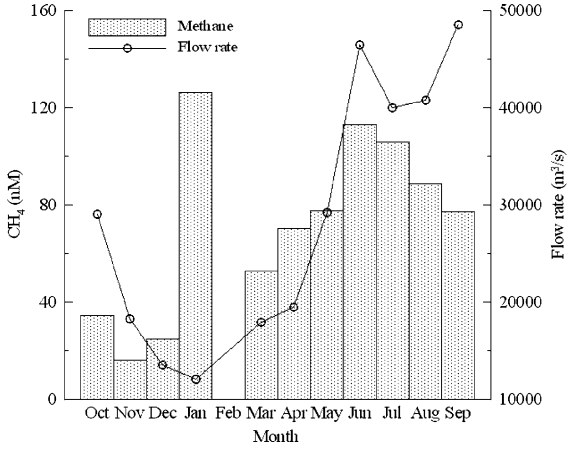

Fig. 4 Monthly variation of methane concentrations at Xuliujing and discharge at Station Datong in the Changjiang (Yangtze River)

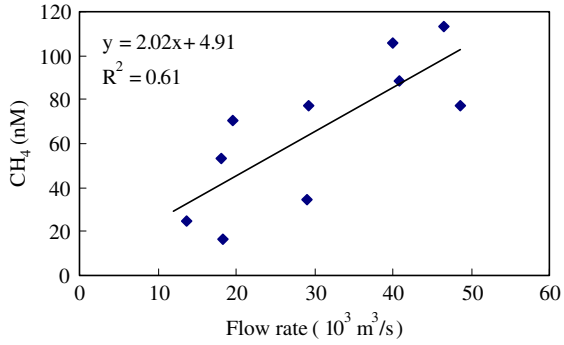

Fig. 5 Relationship between methane concentrations at Xuliujing and discharge of the Changjiang (Yangtze River)

the river water of Changjiang may also be related to the low inputs of methane from surrounding anoxic environments.

We estimated the annual average input of CH_4 from the Changjiang to the Estuary and its adjacent area by multiplying the monthly river water CH_4 concentration by the monthly discharge, which yields a CH_4 flux of 2.24 mol s^{-1} equal to 70.6×10^6 mol $year^{-1}$ for the annual input. Considering the annual water discharge of 898 km^3 $year^{-1}$ for the period of 2004–2005 is similar with the average annual water discharge of 903 km^3 $year^{-1}$ (Wang et al. 2008) at Datong Station during 1950–2005, although CH_4 in the Changjiang water is subject to water discharge variation, it appears that our estimation represents a long term mean value, and indicates that the Changjiang is an important source for CH_4 in the estuary and its adjacent area.

Sediment release of CH_4 in the Changjiang Estuary

CH_4 can be produced through bacterial degradation of organic materials in the coastal sediments, followed by release into the overlying near-bottom waters through exchange at sediment–water interface (Martens and Klump 1980; Sansone et al. 1998; Ivanov et al. 2002). Due to high load of suspended matter and organic carbon, CH_4 in estuarine waters can also be expected to originate from sediment release in the Changjiang Estuary. Accumulation of CH_4 together with the decrease of O_2 in the overlying water was observed during sediment incubation in May 2002. Sediment oxygen consumption rates were calculated to be 32.9 and 66.8 mmol m^{-2} day^{-1} for station DB6 and DC10, respectively. CH_4 emission rate from the sediments were calculated to be 1.73 and 2.21 μmo m^{-2} day^{-1} for station DB6 and DC10, respectively, which supports a net supply of CH_4 from the sediments to the water column in the Changjiang Estuary. The observed CH_4 emission rates are relatively low compared with the CH_4 fluxes from the anoxic coastal marine sediments from Cape Lookout Bight (Martens and Klump 1980) and the Westerschelde Estuary (Middelburg et al. 1996), but are comparable with the results in Danube delta (Ivanov et al. 2002) and Tomales Bay (Sansone et al. 1998). The spatial variation of CH_4 emission rates may be explained by the different conditions such as the O_2 level and content of organic matter. CH_4 emissions from the coastal sediments have seasonal variations with maximum in summer and considerable lower in spring and winter (Bange et al. 1994; Ivanov et al. 2002). In the studied area, strong O_2 depletion occurs in the bottom waters off the Changjiang Estuary in summer (Li et al. 2002; Wei et al. 2006). In combination with the arrival of large amounts of allochthonous and autochthonous organic matter in shallow-water bottom sediments off the Changjiang Estuary, it is reasonable to deduce that methane production in the bottom sediments of the O_2-deficient region should be much higher in summer than in spring. Actually in August 2005, low dissolved oxygen (2–3 mg l^{-1}) was observed in the bottom waters of stations 4–6, correspondingly CH_4 was observed to be enriched in the bottom water and found to correlate negatively with dissolved oxygen ($[CH_4] = -0.74 \times DO + 10.5$, $r^2 = 0.67$, $n = 12$). Therefore, it is necessary to make more measurements on CH_4 emission rates at different seasons in the Changjiang Estuary to assess the source strength of sediment release. Our results suggest that sediment release could be a significant source of CH_4 in the estuarine water of the Changjiang Estuary. Given an area of $\sim3.4 \times 10^4$ km^2 for the Changjiang Estuary (as shown in "Air-sea fluxes of CH_4") and a CH_4 emission rate of 2 μmol m^{-2} day^{-1} from the sediments, the sediment release of CH_4 from the Changjiang Estuary was estimated to be 2.5×10^7 mol $year^{-1}$, which is equal to about 40% of the riverine input of CH_4.

Air-sea fluxes of CH_4

CH_4 saturation in the surface waters of the Changjiang Estuary and its adjacent area ranged from 123 to 3,841% during the five surveys (Table 1), which showed that the surface waters of the region were supersaturated with respect to the atmospheric CH_4 concentrations all year. Hence the Changjiang Estuaries and its adjacent areas represent a source of CH_4 to the atmosphere all year around.

The studied area was divided into two areas (i.e., estuary and marine area) according to the salinity of 30 ppt. For each station we calculated sea to air CH_4 flux based on the actual saturation value and the long term averaged wind speed (Table 4). The greatest uncertainty for the sea-to-air CH_4 flux estimation results from the estimation of gas exchange coefficient. Using different relationships yield significantly different transfer coefficients under the same wind

speed. Generally, using the LM86 relationship yields a lower value, and using W92 and RC01 relationships yield higher values. Another important uncertainty in the assessment of the gas transfer coefficient and sea-air gas fluxes is related to the type of wind data used. Morell et al. (2001) found that fluxes computed using climatological wind speed data often exceed those using ship-based wind speed measurements by over 50%. In this work, we computed the gas transfer coefficients for May 2002 and October 2006 using both ship-based in situ wind speed and long term averaged wind speed. The long term averaged wind speeds were higher than the mean ship-based in situ wind speeds by 30%, hence the obtained methane fluxes estimated using long term wind speed were higher than those using in situ wind speed by 20–80%. Sea to air CH_4 fluxes estimated using long term wind speed will be discussed below, hence our results may be overestimated to some extent.

In general, although the sea to air CH_4 fluxes from the Changjiang Estuary are higher than its adjacent marine area, both had seasonal variations with higher values occurring in summer and lower values in spring and autumn. The annual sea to air CH_4 fluxes from the Changjiang Estuary were estimated to be 35.7 ± 23.9, 69.8 ± 46.8 and 78.6 ± 53.4 μmol m^{-2} day^{-1}, respectively, while those from the adjacent marine area were 9.1 ± 4.6, 17.8 ± 8.9 and 21.0 ± 11.5 μmol m^{-2} day^{-1} using LM86, W92 and RC01 relationship, respectively. Based on the annual sea to air CH_4 fluxes resulted from all models, the annual mean atmospheric CH_4 fluxes for the Changjiang Estuary and its adjacent marine area were 61.4 ± 22.6 and 16.0 ± 6.1 μmol m^{-2} day^{-1}, respectively. These results are lower than those reported for most estuaries (Table 2), e.g., a mean flux of 130 μmol m^{-2} day^{-1} for nine tidal European estuaries (Middelburg et al. 2002), 260–470 μmol m^{-2} day^{-1} for Danube Estuaries (Amouroux et al. 2002) and 181.3 μmol m^{-2} day^{-1} for Oregon estuaries (De Angelis and Lilley 1987). This large spatial variation may partly be due to different studies covering different estuarine sections. For example, CH_4 fluxes from nine tidal European estuaries and Oregon estuaries were obtained mainly in the inner estuaries (Middelburg et al. 2002) and our study mainly covered the outer estuary of Changjiang.

Considering the estimated area ($\sim 3.4 \times 10^4$ km^2 for the Changjiang estuary between 122–123°E and 29–32°N, and $\sim 16.9 \times 10^4$ km^2 for its adjacent area covering the rest between 122–125°E and 28–34°N) and the corresponding annual mean atmospheric CH_4 fluxes, the annual CH_4 emissions from the whole studied region were estimated to be 10.0×10^8 mol $year^{-1}$ by the LM86 equation, 19.6×10^8 mol $year^{-1}$ by the W92 equation and 22.7×10^8 mol $year^{-1}$ by the RC01 equation. The annual CH_4 emissions only from the Changjiang Estuary were estimated to be 4.4×10^8 mol $year^{-1}$ by the LM86 equation, 8.7×10^8 mol $year^{-1}$ by the W92 equation and 9.8×10^8 mol $year^{-1}$ by the RC01 equation. Hence the CH_4 emission from the Changjiang Estuary was one order of magnitude higher than the CH_4 input via Changjiang or sediments.

Riverine input (71×10^6 mol $year^{-1}$) and sediment release (25×10^6 mol $year^{-1}$) together are lower than methane emission (low estimate is 440×10^6 mol $year^{-1}$), implying that biological production in the water column may act as an important source of methane in the Changjiang Estuary.

Conclusions

Dissolved CH_4 concentrations in the Changjiang Estuary and its adjacent area fall within but toward the lower end of the CH_4 range in the worldwide estuaries, and they showed obvious seasonal variation with the highest value occurring in summer and lowest in autumn. The horizontal distribution of dissolved CH_4 in the Changjiang Estuary indicated a decrease of CH_4 concentrations along the freshwater plume from the river mouth to the open sea, suggesting the influence of riverine input. Resuspension of the sediments also play an important role in the distribution of bottom CH_4 in the Changjiang Estuary.

Input via rivers and sediment release are significant sources of CH_4 in the estuarine water of Changjiang Estuary and its adjacent area. The average annual input of CH_4 from the Changjiang to the Estuary and its adjacent area was estimated to be 2.24 mol s^{-1} equal to 70.6×10^6 mol $year^{-1}$. The sediment release of CH_4 from the Changjiang Estuary was estimated to be 25×10^6 mol $year^{-1}$, which is equal to about 40% of the riverine input and may be underestimated due to lack of observation on

Table 4 Methane fluxes from the Changjiang Estuary and its adjacent marine area

Region	Seasons	n	Surface CH_4 (nM)	Surface CH_4 (%)	ΔC (nM)	U_{10} (m/s)	F (LM86) ($\mu mol \cdot m^{-2} \cdot day^{-1}$)	F (W92) ($\mu mol \cdot m^{-2} \cdot day^{-1}$)	F (RC01) ($\mu mol \cdot m^{-2} \cdot day^{-1}$)	Mean Flux ($\mu mol \cdot m^{-2} \cdot day^{-1}$)
Estuary ($s < 30$)	May 2002	10	13.17 ± 4.86	525 ± 196	10.66 ± 4.84	6.7	21.1 ± 9.6	41.1 ± 18.7	44.6 ± 20.3	35.6 ± 12.6
						(5.6 ± 2.3)[a]	11.3 ± 10.1	21.3 ± 14.6	34.1 ± 26.7	
	June 2006	11	12.41 ± 10.37	544 ± 456	10.11 ± 10.39	6.8	22.2 ± 22.9	43.2 ± 44.4	47.2 ± 48.5	37.6 ± 13.4
	Aug. 2005	35	19.59 ± 16.22	876 ± 686	17.41 ± 16.13	7.6	55.4 ± 52.6	108.9 ± 103.4	125.9 ± 119.6	96.7 ± 36.8
	Oct. 2006	3	26.79 ± 25.16	1,284 ± 1,200	24.70 ± 25.17	7.2	67.0 ± 67.9	130.6 ± 132.4	146.3 ± 148.2	114.6 ± 42.0
						(3.1 ± 2.2)[a]	7.9 ± 11.9	14.5 ± 20.5	29.5 ± 23.2	
	Nov. 2002	18	7.39 ± 4.00	300 ± 144	4.96 ± 3.89	7.6	12.7 ± 3.6	25.0 ± 18.9	28.9 ± 21.8	22.2 ± 8.5
	Annual mean		15.87 ± 7.49	706 ± 383	13.57 ± 7.64	7.2 ± 0.4	35.7 ± 23.9	69.8 ± 46.8	78.6 ± 53.4	61.4 ± 22.6
Marine area ($s > 30$)	May 2002	18	5.05 ± 2.49	216 ± 101	2.73 ± 2.45	6.7	5.4 ± 4.7	10.5 ± 9.2	11.5 ± 11.0	9.2 ± 3.2
						(4.9 ± 1.8)[a]	3.3 ± 4.7	5.8 ± 7.3	8.4 ± 10.5	
	June 2006	10	6.22 ± 3.52	289 ± 180	4.01 ± 3.61	6.8	9.3 ± 8.8	18.1 ± 17.1	19.7 ± 18.6	15.7 ± 5.6
	Aug. 2005	5	6.85 ± 3.77	348 ± 187	4.89 ± 3.75	7.6	13.3 ± 11.8	26.2 ± 23.1	35.0 ± 26.4	24.8 ± 10.9
	Oct. 2006	24	7.09 ± 3.62	350 ± 179	5.06 ± 3.63	7.2	13.9 ± 10.0	27.0 ± 19.5	30.3 ± 21.8	23.7 ± 8.7
						(5.9 ± 2.5)[a]	8.4 ± 7.7	14.4 ± 12.0	23.5 ± 21.1	
	Nov. 2002	12	3.53 ± 0.68	161 ± 32	1.33 ± 0.69	7.6	3.7 ± 1.9	7.3 ± 3.8	8.4 ± 4.4	6.4 ± 2.4
	Annual mean		5.75 ± 1.47	273 ± 83	3.60 ± 1.57	7.2 ± 0.4	9.1 ± 4.6	17.8 ± 8.9	21.0 ± 11.5	16.0 ± 6.1

LM86, K_w was calculated using the tri-linear k/u_{10} relationship established by Liss and Merlivat (1986); W92, K_w was calculated using the quadratic k/u_{10} relationship established by Wanninkhof (1992); RC01, K_w was calculated using the k/u_{10} relationship established by Raymond and Cole (2001)

[a] Numbers in the parentheses are the ship-based in situ wind speeds

seasonal variations. Hence, more measurements on the CH_4 emission rates at different seasons in Changjiang Estuary are required to assess the source strength of sediment release.

The Changjiang Estuary and its adjacent area are a significant source of atmospheric CH_4. The annual CH_4 emission from the studied region were estimated to be 10.0×10^8, 19.6×10^8, and 22.7×10^8 mol $year^{-1}$ using LM86, W92 and RC01 relationship, respectively. Due to the large spatial variation of CH_4 fluxes from different estuaries, more studies on typical estuarine systems in the world are required to estimate the estuarine CH_4 emissions accurately on a global scale.

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