Terr. Atmos. Ocean. Sci., Vol. 17, No. 4, 951-959, December 2006

NOTES AND CORRESPONDENCE

Abnormally High CH_4 Concentrations in Seawater at Mid-Depths on the Continental Slopes of the Northern South China Sea

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(Manuscript received 11 October 2005, in final form 20 July 2006)

ABSTRACT

For the first time, CH_4 concentrations in the water column were measured during three cruises in the northern South China Sea. The abnormally high subsurface CH_4 concentrations that were found on the continental slopes may have been released from sediments and/or may have originated in CH_4 gas hydrates.

(Key words: CH_4, South China Sea, Gas hydrates)

1. INTRODUCTION

Methane gas hydrates buried in the upper continental slopes of the northern South China Sea may become an important source of energy in the future, but should the buried CH_4 be released either due to the warming of the seawater or other disturbances, it may merely compound the severity of global warming. As an important long-life greenhouse gas, and one that is regulated by the Kyoto Protocol, CH_4 is now responsible for 20% of global warming (IPCC 2001). Each CH_4 molecule is equivalent to 21 CO_2 molecules in terms of its ability to absorb solar energy (Albritton et al. 1996). As a serious consequence of this, any release of CH_4 from gas hydrates may contribute to further warming of the atmosphere. A cycle of CH_4 gas release may occur where by the seawater is warmed to such a level that it leads to further

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release of CH_4 with subsequent releases leading to increased global warming, higher seawater temperatures, and further CH_4 release (Field and Raupach 2004).

The oceans are a well-known source of CH_4 to the atmosphere in large part because of production in the microenvironments within the biota (de Angelis and Lee 1994; Karl and Tilbrook 1994). Apart from this, CH_4 is generated in hydrothermal vents (e.g., Chen et al. 2005) and is released from sediments mainly through fermentation in an anoxic environment (Martens and Klump 1980; Kipphut and Martens 1982; Ivanov et al. 1991; Tsurushima et al. 1996; Marty et al. 2001; Amouroux et al. 2002; Chang and Yang 2003; Halbach et al. 2004; Kankaala and Bergström 2004). The South China Sea's (SCS) standing as the largest marginal sea in the world (3.5×10^6 km^2) notwithstanding, not until very recently has CH_4 been systematically studied there, and then only for bottom water and sediments (Chuang et al. 2006; Yang et al. 2006). For this reason, here we provide the results of the spatial and vertical distribution of CH_4 in the water column of the northern SCS for the first time based on samples we collected during three cruises, and discuss some abnormally high values.

2. STUDY AREA AND METHODS

Seawater samples were taken during R/V Ocean Researcher III cruise OR-III 896 (25 - 28 August 2003), OR-I 695 (21 - 30 September 2003) and OR-III 983 (7 - 9 July 2004). The station locations are given in Fig. 1. A Seabird SBE 911 plus CTD (Conductivity-Temperature-Depth/Pressure) Rosette system fitted with 2.5-liter Niskin bottles was used to collect discrete water samples. The water samples for CH_4 were collected in 120-ml dark glass bottles with 10 ml of air space left and with saturated $HgC1_2$ added following the method of Johnson et al. (1990). Samples were stored at 4°C but were put in a 25°C constant temperature bath before measurements. A GC-FID (HP 5890 Series II) was used for CH_4 measurements back in the laboratory. The GC had a one-eighth of an inch diameter, 6-foot long stainless steel column filled with 60/80 mesh molecular sieve 5A. The NIST 1 μmol mol^{-1} CH_4 standard was used as the primary standard. CH_4 in N_2 at concentrations of 0, 4.97, 9.77, and 53 ppmv were purchased and used for calibration, for a precision of better than ±5%.

3. RESULTS AND DISCUSSION

The findings from cruise OR-I 695 *vis-à-vis* the vertical distribution of CH_4 in the water column off the Pearl River estuary are illustrated in Fig. 2. The surface values are generally much higher than the saturation value of about 2.07 nM based on the Bunsen solubility coefficient of Wiesenberg and Guinasso (1979). This is typical in the world oceans as CH_4 is produced in the anoxic microenvironment within the cells of phytoplankton (Traganza et al. 1979; de Angelis and Lee 1994; Karl and Tilbrook 1994; SOLAS 2003). Granted that it is very likely the Pearl River transported some high CH_4 water into the study area, but to be realistic, these high values were, for the most part, probably a result of biogenic factors (de Angelis and Lee 1994; Karl and Tilbrook 1994). CH_4 concentrations generally decrease with depth but remain constant below 1000 m in so far as little biogenic CH_4 is generated outside the euphotic zone. Further, the bottom sediments on the lower continental slope and the abyssal plain are low in organic carbon contents (Chen et al. 2006); hence, little fermentation can take place. Some high values do, nevertheless, exist at mid-depths (around 1000 m). These signals may be related to the sediments on the upper continental slope, which are richer in organic carbon (Tsurushima et al. 1996; Zhang et al. 2004). Thus, the unusually high concentrations of CH_4 can most likely be attributed to the anoxic generation of CH_4 and the release of CH_4 from gas hydrates. Stations where high CH_4 values were found at mid-depths are marked as filled symbols in the figure.

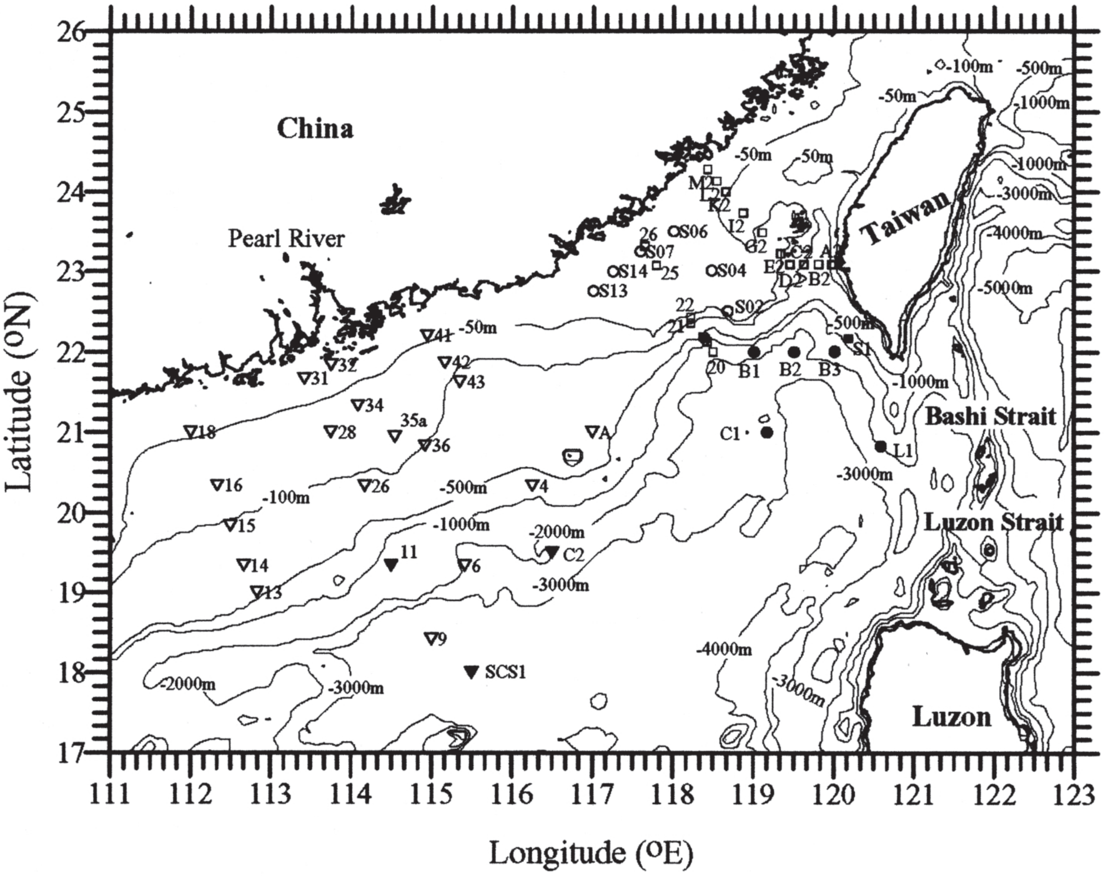

Fig. 1. Study area and station locations (○: OR-III 896; ▽: OR-I 695; and □: OR-III 983). Those marked with filled symbols are where unusually high CH_4 values were found at mid-depths.

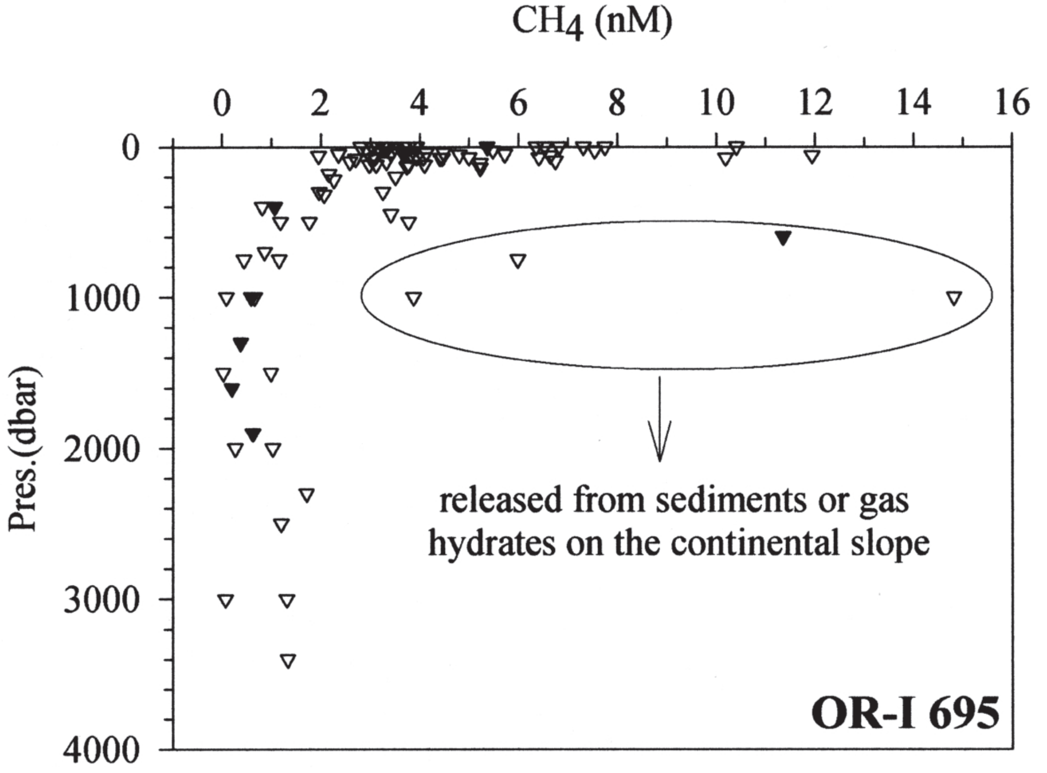

Fig. 2. Vertical distribution of CH_4 in the water column as determined from OR-I 695. The filled symbols are from Stn. C2.

The results from cruise OR-III 896 are plotted against depth in Fig. 3. What is most striking here is the extremely high value of 115 nM detected at a 35-m depth at Stn. B2. Since gas hydrates have been detected in the general area (Chi et al. 1998; Liu et al. 2006; Schnürle et al. 1999, 2006), it is reasonable to link this anomaly with a release of CH_4 from the gas hydrates in the sediments particularly since no other measurements of CH_4 concentrations in the water column in the study area have been reported in the extant literature. Nevertheless, Chuang et al. (2006) have reported values higher than 4473 nM in the pore waters of the sediments and in the bottom seawater not far from our study area. Vertical migration of CH_4 and subsequent advection may have contributed to the relatively high CH_4 values found at several stations during this cruise.

Finally, the results from cruise OR-III 983 showing the vertical distribution of CH_4 is

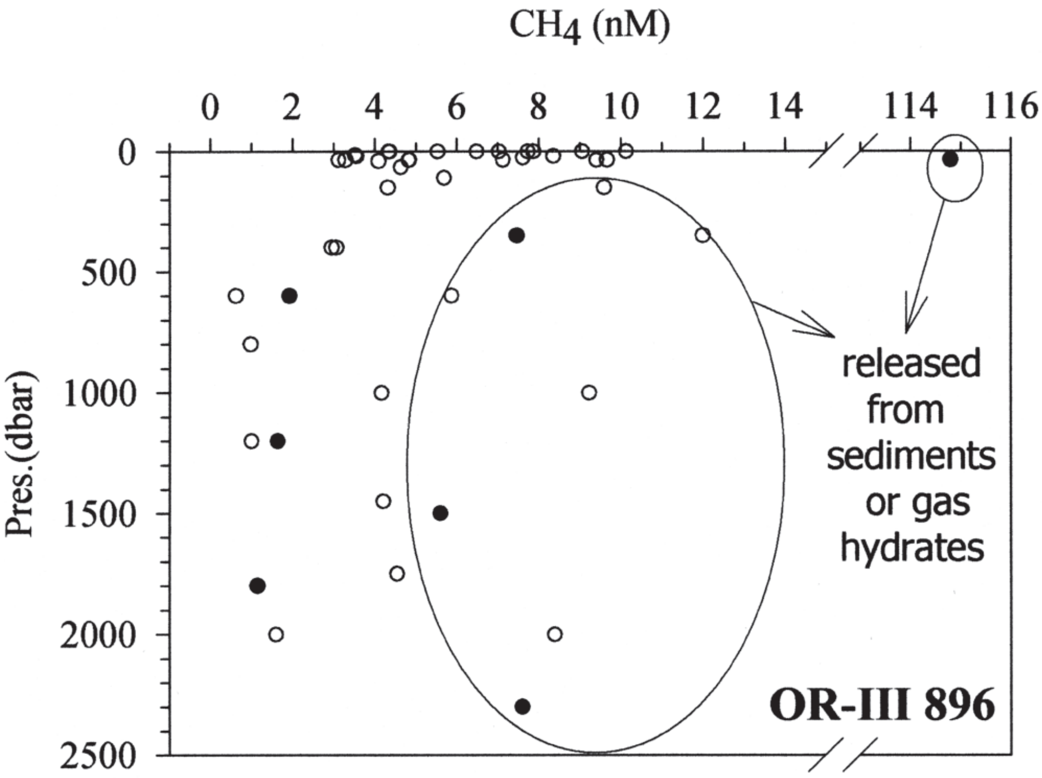

Fig. 3. Vertical distribution of CH_4 in the water column as determined from OR-III 896. The filled symbols are from Stn. B2.

given in Fig. 4. These stations are in the southern Taiwan Strait where the SCS waters and a branch of the Kuroshio meet the Chinese coastal waters (Chen et al. 2004). The fact that higher CH_4 contents are typically found in coastal waters shallower than 200 m than in the open ocean waters explains the large scatter in Fig. 4. However, worth bearing in mind is that because the lower salinity of coastal waters generally confines them to the upper layer, it is very likely that the relatively high CH_4 concentrations in the subsurface waters were released from sediments or contributed to by CH_4 gas hydrates.

Until recently, it was generally accepted that the oceans play only a minor role in the atmospheric CH_4 budget and that they account for a small 2 - 4% of the total CH_4 released into the atmosphere (Cicerone and Oremland 1988; Bates et al. 1996). However, since about the time of the discovery of shelf vents connected to sedimentary gas hydrates, estimates of the

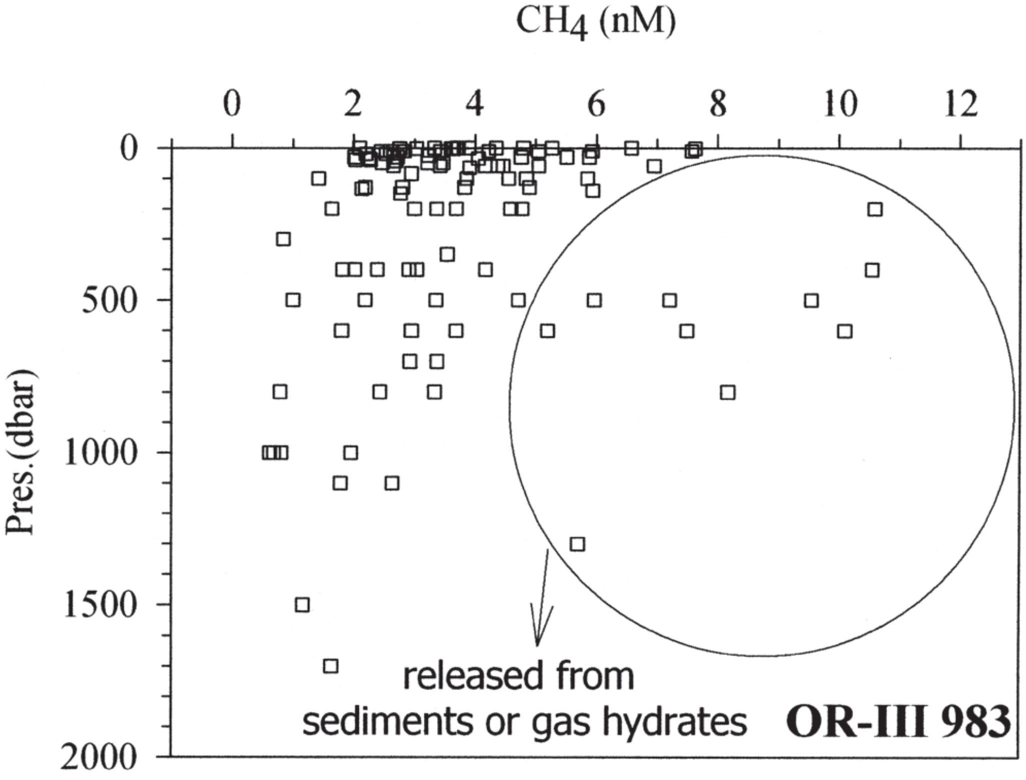

Fig. 4. Vertical distribution of CH_4 in the water column as determined from OR-III 983.

CH_4 emission rate from the seabed to the atmosphere have increased to a somewhat higher 4 - 9% of the global budget (Suess et al. 1999; Hornafius et al. 1999; Judd 2000; Judd et al. 2002; Kvenvolden et al. 2001; Collier and Lilley 2005; Heeschen et al. 2005). Now that it has been determined that there is the potential for the release of CH_4 from new gas hydrate fields, the release rate of CH_4 from the oceans to the atmosphere may have to be thoroughly re-evaluated, and this as expeditiously as possible.

4. CONCLUSIONS

The preliminary study of CH_4 distribution in the water column of the northern South China Sea found substantive evidence of some startlingly high concentrations near stations above the continental slope. There is no question that these high values must have been generated in the bottom sediments which have been found to contain CH_4 gas hydrates.

Acknowledgements The authors wish to thank the constructive comments of T. F. Yang, Y. J. Lee and an anonymous reviewer, which strengthened the manuscript; National Science Council of the ROC for supporting this research (NSC 94-2621-Z-110-001; 94-2611-M-110-001); Aim for the Top University Plan (95C0030211) and the captains and crews of OR-I and III for their assistance.

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