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Discussions

Interactive comment on "Methane distribution, flux, and budget in the East China Sea and Yellow Sea" *by* M.-S. Sun et al.

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We are very grateful to the anonymous referee #1 for reviewing and commenting on our manuscript. We considered every comment seriously and gave the responses as follows. We also attached the revised manuscript with this reply for reference.

Q1. Page 7021, Line 16-24: Insufficient details are presented to reproduce the methane concentration measurements in the water column.

Reply: In our laboratory, dissolved methane was measured by gas chromatography using a gas-stripping method, which is a routine sample analysis with precision better than 3% and detection limit of $\sim$0.1 nM. The detailed experimental conditions, including the column packing material, column temperature and the flow rate of stripping gas,

were described in detail in one of our previously published paper (Zhang et al., 2004, JGR). Hence we did not introduce the detailed information in this paper, but cited the above paper (Zhang et al., 2004) instead.

Q2. Page 7022, line 1-20: The authors incubated sediment cores in order to get the flux to the water column. While this incubation process was conducted at near in-situ temperatures, it takes the cores out of their natural environment (e.g. pressure is different) and can lead to errors in their emission estimate. A common method for measuring sediment emission is to measure the sediment methane concentration distribution and compare it with bottom water concentrations in a diffusive flux calculation. Please explain why this incubation technique was used and how it agrees with the concentration gradient technique.

Reply: We agree that core incubation method can lead to errors in estimating CH4 emission rates from the sediments due to change of environment. However, CH4 emission rates from the sediments may be overestimated using the Fick's diffusion law due to the neglect of aerobic methane oxidation at the sediment surface and the occurrence of irrigation and bioturbation (Abril and Iversen, 2002). Actually, we also compared the results obtained by both methods during the survey in May 2011 in this study, and found that CH4 emission rates obtained from Fick's law (2.51±1.67 μmol m-2 d-1, n=4) were generally much higher than those by core incubation method (1.43±0.47 μmol m-2 d-1, n=4). To limit the length of this manuscript, we think it's reasonable to provide only incubation data in this paper.

Q3. Page 7023, line 1-5: The authors did not measure the local atmospheric concentration of methane in their air-sea flux calculations and instead used values from monitoring networks. Local atmospheric concentration gradients of methane have been observed which can influence the sea-air flux calculation substantially. Also, the dissolved surface water concentration of methane was sampled with discrete samples. This causes extremely coarse sampling resolution and can lead to errors when spatial concentration changes and gradients are not sampled. Since automated techniques

exist to get higher spatial measurement resolution (e.g. Gulzow et al., 2011), I'm wondering why this more crude technique was used. This investigation presents data from a continental shelf environment and continental shelves are known to have substantial methane gradients (which is supported by their data in Fig. 3). I'm worried that spatial gradients in surface water CH4 concentrations were missed.

Reply: 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 concentrations were detected in these stations due to terrestrial influence, they make a minor difference in the results of sea-air fluxes. So we thought it was fine to use the annual mean atmospheric CH4 concentration near ECS for the sea-air flux density calculation. We agree that continuous surface methane concentration analysis measurement is a more convenient and efficient way to investigate the large-scale CH4 distribution in surface oceans. However, we did not only measure the surface distribution of CH4, but also were interested in the vertical profiles of CH4 in the East China Sea. Stratification widely occurs in the East China Sea in summer, and we would like to look into its influence on the distribution and sea-air flux of CH4. Now we are developing continuous measurement techniques in our lab. Unfortunately, this technique has not been established yet during the time when we carried out the cruises. So in this paper, we only performed the results from the discrete CH4 samples in water column.

Q4. The authors should indicate how water temperature, salinity, and dissolved oxygen were measured.

Reply: Salinity and temperature data were also measured by the CTD, and wind speeds were measured by the shipboard automatic weather stations at about 10 m above the sea surface. Oxygen data from CTD profiles were calibrated with oxygen measurements from the Winkler titration method (Bryan et al., 1976). Dissolved

oxygen samples for Winkler titration were collected from the Niskin bottles using the same sampling method with CH4 and immediately measured with the Winkler titration method after sampling. We have described the above information in part 2.1.

Q5. I do find steady-state models extremely informative for the calculation of oceanic methane budgets. However, the authors attempt to constrain several different sources and sinks while ignoring others. First, no isotopic measurements of methane were provided in an attempt to fingerprint different sources. Second, the model ignores inputs from methane seepage and groundwater inputs of methane as well as methane losses associated with aerobic methane oxidation in the water column. While all of these can be substantial, the omission of aerobic methane oxidation likely leads to the greatest error. Methane oxidation in the water column is a substantial sink of methane and needs to be considered here. Methane seeps, groundwater inputs, and aerobic methane oxidation in the water column must all be considered before even a preliminary methane budget can be established in this region.

Reply: We agree with the reviewer's opinion that it was really improper that we did not take the groundwater into account, even if lack of reference data for calculation. Actually, we measured some groundwater samples along the coast of the ECS in December 2011 and July 2012. During December 2011, these groundwater CH4 samples were collected at twenty-five sites along the Jiangsu and Zhejiang coastal region (120.857~121.896°E, 30.124~30.956°N), which can also be considered as the fresh groundwater end-member. CH4 concentrations varied significantly at these stations and had a great range of 33~61602 nM, with a median of 271 nM (unpublished data, Zhang et al.). During July 2012, we collected groundwater samples for CH4 measurement along the coast of the ECS (121.371~121.934°E, 30.733~31.976°N; n=8). It indicated that the median CH4 concentration was 758 nM in summer, with a great range of 138~3428 nM, which was much higher than those in winter. We didn't show these data in the previous edition just because we have no data for SGD, hence we can't estimate the CH4 input via groundwater. In the latest version, we tried our best to collect

information about the groundwater discharge to the ECS and gave a rough estimate of CH4 input via groundwater. We contacted Prof. Jinzhou Du at East China Normal University and obtained the updated submarine groundwater discharge (SGD, including submarine fresh water discharge and recirculated saline groundwater discharge) into the ECS to be 0.68×10^8 m3 d-1 and 0.46×10^9 m3 d-1 in dry and wet season, respectively, using Ra isotopes as tracers (Wang and Du et al., unpublished data, personal communication). It is hard to measure CH4 concentrations in the recirculated seawater, so we assume that CH4 concentrations in the fresh groundwater and recirculated saline groundwater are the same. Median CH4 concentration was chosen for calculation since it is less susceptible to abnormally high CH4 concentrations observed in the groundwater. Hence, CH4 fluxes via submarine groundwater discharge were estimated by multiplying the median CH4 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 CH4 concentration in the porewaters ($\sim$0.45 μM, Zhang et al., unpublished data) of the ECS usually is much lower than those in fresh groundwater, the above estimation of CH4 flux via submarine groundwater discharge may be overestimated to some extent. However, our results suggested that groundwater discharge might be an important CH4 source for the ECS, especially in summer. We added the above discussions about the groundwater CH4 to part 4.2 in the revised paper and also updated the abstract and conclusion accordingly. It is well known that the aerobic and anaerobic methane oxidation in the water column and sediment is a huge CH4 sink in the ocean. In this paper, we estimated the result of net CH4 production, which means that the difference between formation and consumption (formation-consumption), so actually we have considered the CH4 oxidation processes during we did this CH4 budget and it was included in the final results. And we also reported that the sea-air gas exchange was the largest external sink of CH4 in ECS, while the largest internal one was undoubtedly the aerobic and anaerobic methane oxidation.

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