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Ji-Hyung Park
Guest-Editor Biogeosciences

Dear Dr. Park,

Please find enclosed the revised version of ms bg-2017-444.

We thank yours and the 3 referee's comments and suggestions for improvement.

We have reduced the sentence in the abstract you requested. As we replied to the reviewers, there is no size limit for the abstract in Biogeosciences and the length of our abstract reflects the descriptive nature of the paper of a rather large data-set.

We have defined partial pressure of CO2 and ppm. Text now reads: "The dissolved concentration of CO2 is expressed as pCO2 in parts per million (ppm), following Henry's law"

Please find hereafter, the replies to the 3 referees' comments.

We sincerely hope that the present version of the manuscript is acceptable for publication in Biogeosciences

Best regards
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Referee#1

Reviewer comment: I read this manuscript with interest as it contains an excellent set of data in a large estuary. It is, however, a bit long especially the abstract. I have sampled in the Mekong Delta several times myself but the branch and place names are not familiar even to me. They should be omitted from the abstract.

Reply: We thank the reviewer for her/his positive evaluation of the paper. We kept the location names in the abstract; The Mekong delta is composed of different branches/rivers so it is necessary to name them in the abstract to clearly specify where we sampled; further south of our sampling area the Hau river (refer to figure 1) is an important component of the delta that was not sampled; in the paper we report two distinct data-sets, one of which is a mangrove site located in Ca Mau peninsula; this is a relatively extensive mangrove area that is frequently referenced by name in literature. In Biogeosciences, there is no size limit for the abstract. We acknowledge that our abstract is a bit long, but this reflects the descriptive nature of the paper of a rather large data-set.

Reviewer comment: 1. The deltaTA/deltaDIC ratio of 0.55-0.87 is attributed only to aerobic degradation of organic matter and sulfate reduction. I don't understand why dissolution of calcite/aragonite and dolomite is not at play.

Reply: We have added a discussion on the possibility of CaCO3 dissolution, and text now reads: "The slope of the linear regression of ΔTA versus ΔDIC ranged between 0.55 and 0.87. Such values might result from a combination of aerobic organic matter degradation (-0.2) and dissolution of $CaCO_3$ (or $CaMg(CO_3)_2$) (2.0). Accordingly, these values of relative changes of ΔTA *versus* ΔDIC would require that $CaCO_3$ dissolution corresponded to 34 and 48% of aerobic organic matter degradation, respectively. Such a large $CaCO_3$ dissolution is very unlikely in the Mekong delta because Ca^{2+} and Mg^{2+} showed conservative mixing as a function of salinity (Fig S3), and because particulate inorganic carbon (PIC) is relatively low in the Mekong delta compared to POC. The %PIC of TSM reported by Huang et al. (2017) is one order of magnitude lower (~0.1%) than the %POC of TSM we report (1-8%, Fig. 5)."

Reviewer comment: 2. Many figures show good correlations but with only a few points. The high correlation coefficients, however, may not be statistically significant due to the small sample size. The p values should also be shown.

Reply: We have added p values to the regressions

Reviewer comment: 3. The authors stated, correctly, that CH4 has received much less attention on shelves compared to CO2. But, surely the authors know that Tseng et al., CSR, 2017,135,23-34 published CH4 data on shelves off the Mekong River delta.

Reply: We now refer to the Tseng et al. (2017) CH4 data, text reads: "The CH_4 concentration in the most off-shore sampled station was indeed close to atmospheric equilibrium in April 2004 (2 nmol L^{-1}) for a salinity of 31.9, but was higher in October 2004 (17 nmol L^{-1}) reflecting the lower salinity of 17.0. These values encompassed the CH_4 concentrations of 4-6 nmol L^{-1} reported by Tseng et al. (2017) 150 km away from the Mekong delta river mouth."

Reviewer comment: 4. A recent paper in JGR Biogeosciences(Huang et al., 2017, 122,1239) reported carbon export from many rivers around the SCS. A comparison would be of interest.

Reply: We have included the Huang et al. (2017) reference in the discussion of PIC (refer to above reply) and river TA and DOC concentrations, text now reads:

"Our TA values converge with the median (1082 µmol kg^{-1}) of a large data-set during 1972-1996 period from 42 stations in the lower Mekong delta compiled by the Mekong River Commission and reported by Li et al. (2014), and the average of TA data (1026 µmol kg^{-1}) acquired by Huang et al. (2017)."

and

"Within the freshwater zone (salinity <1), DOC values (2.4±0.2 mg L^{-1}, n=19) were within the range (0.9-5.1 mg L^{-1}) reported by Huang et al. (2017), and δ^{13}C-DOC values (-27.8 ± 0.6 ‰, n=19) were again consistent with a dominance of terrestrial C3 vegetation inputs, and close to values reported by Martin et al. (2013) slightly upstream in the lower Mekong"

Referee#2

Reviewer comment: The Ms by Borges et al sampled waters from the three branches in the Mekong delta and examined dissolved and particulate carbon and their C isotopes for carbon geochemical processes. The Ms provides important data for C characterization and controls in the important world River Mekong. Overall, the Ms is well organized with good writing style. I have some changes for improvement of the MS.

Reply: We thank the reviewer for her/his positive evaluation of the paper.

Reviewer comment: Abstract: This part seems to be longer than the journal guideline.

Reply: In Biogeosciences, there is no size limit for the abstract. We acknowledge that our abstract is a bit long, but this reflects the descriptive nature of the paper of a rather large data-set.

Reviewer comment: P2 L13: just say "tropical" is better due to that the study sites are located in the tropical climate biome.

Reply: We have kept "temperate" and "tropical", since the majority of CO2 and CH4 data have been primarily reported in temperate estuaries. Also, the convergence of data in the Mekong with data in temperate estuaries is informative.

Reviewer comment: P4 L 9: updated references should be added

Reply: We have added Testa et al. (2012) (doi: 10.1002/9781118412787.ch15)

Reviewer comment: P6 L16-17 two Ganges?

Reply: Typo was corrected.

Reviewer comment: In the section of "2.1": The annual transports of sediment and solute by Mekong are revised by Li and Bush (2015). I have noted the paper is cited by authors. Li, S.Y. y, Bush, R.T., 2015. Changing fluxes of carbon and other solutes from the Mekong River. Scientific Reports 5, 16005 DOI: 10.1038/srep16005

Reply: We have added the revised estimates of solute and solid transport given by Li and Bush (2015). Text now reads: "The annual sediment load was ~130-160 million tons in the 1960's and 110 million tons in the 1990's according to Milliman and Farnsworth (2011). Li and Bush (2015) report a less dramatic decrease of annual sediment load from 171 million tons for the pre-regulated period (1923-1991) to 168 million tons for the regulated period (1992-2007). Estimates of the annual solute transport ranges between 40 and 123 million tons (Meybeck and Carbonnel, 1975; Gaillardet et al., 1999; Li and Bush, 2015)"

Reviewer comment: P9 What's the pore size?

Reply: The porosity of GF/F filters is 0.7 µm. This information was added to text.

Reviewer comment: P12 L3 Atmospheric CO2 of 362 ppm may be not a good data

Reply: Atmospheric pCO2 (mixing ratio in dry air) was around 376 ppm in 2003-2004. Once the atmospheric CO2 mixing ratio is converted from dry air to humidity saturated air (as required for CO2 flux computations), the values are around 362 ppm. We have added this information to text, that now reads: "The atmospheric pCO_2 values were converted from dry air to humidity saturated air using the water vapour formulation as function of salinity and temperature given by Weiss and Price (1980). For the three sampling periods, the dry air CO_2 mixing ratio averaged 376±4 ppm and the humidity saturated air CO_2 mixing ratio averaged 362±3 ppm."

Reviewer comment: P17 L15-18, how is the figure of 0.2 and 0.9 from?

Reply: We added this information, and text now reads : "The theoretical relative change of ΔTA *versus* ΔDIC was derived from the stoichiometry of biogeochemical reactions, based on Brewer and Goldman (1976) for aerobic respiration, on Smith and Key (1975) for $CaCO_3$ dissolution, and on Froelich et al. (1979) for anaerobic reactions"

Reviewer comment: P18 L12-13 Does the positive relation between __13C-DIC and %O2 can indicate organic matter degradation?

Reply: Yes, this relation is indeed consistent with expectations when organic matter degradation is the driving force behind the variations in both these parameters: organic matter degradation leads to O2 consumption and a preferential release of 12CO2 (since organic matter is isotopically light compared to the background DIC pool), leading to more negative delta 13C-DIC values

Reviewer comment: Table 1: Areal fluxes are presented as mean/median_S.D. will be better.

Reply: We have added to Table 1 the SD of the mean.

Referee#3

Reviewer comment: The manuscript Carbon dynamics in the Mekong Delta by Borges et al. present a valuable dataset of importance to understand the carbon dynamics not only of the Mekong River delta but also the understanding of this dynamics in large river estuaries. However, there are a few points that should be considered that would help to make the manuscript more suitable for publication.

Reply: We thank the reviewer for her/his positive evaluation of the paper.

Reviewer comment: The authors present data and discussion aiming to understand the carbon dynamics but information regarding, for example, the transport and degradation of carbon or factors controlling primary productivity is completely missing in the introduction. The manuscript introduction basically refers to CO2 and CH4 fluxes to the atmosphere, which is only a small part of the story presented. In section 2.1, despite the interesting and detailed information about geology and demography in upper basing, it is too long and most of this information is not essential for the manuscript. Instead more attention should be given to describe the carbon inputs from upstream the area, the vegetation, geomorphology, and hydrology of the delta and explaining where the delta starts. How the main channels differ from the side channels and mangrove creeks. Such information would be more useful to help interpret the results than social and economic information, which could be shortly mentioned in the introduction. Also, would be interesting to know how the tidal works in the area. How long time is each tidal cycle? What is the water level change in the mouth and in the most upstream site? Does the tide can significantly increase the residence time of the water?

Reply: The results and discussion of the paper are strongly focussed on CO_2 and CH_4 dynamics and their exchange with the atmosphere, and this is reflected in the introduction. The title of the ms was modified to put emphasis on CO_2 and CH_4. As part of the special issue on the "human impacts on carbon fluxes in Asian river systems", one of the aims of paper is to provide a baseline evaluation of C cycling in the Mekong delta that is faced with numerous threats. As such, we need to describe these threats and their consequences to the local population. Fundamental research on biogeochemical cycling in estuaries should be also made in a societal context, particularly in Asia. Finally, most of the information in the site description does relate to C cycling in the delta. For instance, in order to correctly interpret C cycling in the Mekong delta we need to take into account that nearly all of the original mangroves have been converted into shrimp farming ponds. We also included information on the riverine part of the Mekong River, and discuss in detail the carbon variations in the freshwater end-member of the delta.
Definition of the spatial extent of the delta and information on the tide has been added as requested by the reviewer, text now reads: "The upper limit of the delta (limit of the tidal influence) is the city of Phnom Penh in Cambodia, and at the coast it extends in the North from the mouth of the Saigon River to Cape Ca Mau in the South. The delta is meso-tidal with a mean tidal amplitude of 2.5 m at the estuarine mouth and a maximum tidal amplitude of 3.8 m" Information on nutrient inputs from the delta to the coastal zone has also been included, text now reads: "The nutrients inputs to the continental shelf from the Mekong delta sustain high phytoplankton growth in the Mekong river plume (Grosse et al., 2010) that is one the most productive areas of the South China Sea (Liu et al., 2002; Qiu et al., 2011; Gao et al., 2013; Loisel et al., 2017)"

Reviewer comment: In section 2.4 would be helpful for the reader if you explain the purpose of the mixing model informing what kind of information you can get from it and why this is important.

Reply: Text now reads: “Mixing models were used to investigate sources and sinks of TA, DIC, O_2 and $\delta^{13}C_{DIC}$ along the salinity gradient.”

Reviewer comment: Despite the large list of papers regarding CO2 and CH4 fluxes from estuaries and large rivers none of them are mentioned in the discussion of section 3.4. Including this would improve the quality of the discussion.

Reply: We limited on purpose the comparison with large Asian estuaries (Pearl and Yangtze) that also border the China Sea in addition to the Mekong. Indeed, a general comparison with all World large estuarine systems would be a (very large) synthesis paper on itself, and such discussion is outside the scope of the present paper. We could have listed in a Table previous reported CO2 fluxes in all World large estuarine systems, although this is not very original on itself, nor very informative. If the reviewer has an interest in such comparisons, we invite her/him to consult the Cai et al. chapter (Carbon dioxide dynamics and fluxes in coastal waters influenced by river plumes, Chapter 7, pp. 155-173, Biogeochemical Dynamics at Large River-Coastal Interfaces: Linkages with Global Climate Change (Editors: T.S. Bianchi, M.A. Allison, and W.-J. Cai), 704 pp., Cambridge University Press).

Reviewer comment: Most of the discussion is about the controls of pCO2, which was already covered before and perhaps some information presented here would be more relevant to the earlier discussion. In this section, the authors should focus the parameters that would be more directly related to fluxes such as pCO2, wind and water velocity. pCO2 and wind speed are the two inputs for the fluxes calculation and despite pCO2 was nicely detailed, the wind speed data was not even mentioned and information regarding water velocity other than discharge would be interesting to be included. Sawakuchi et al 2017 (Front. Mar. Sci. 4:76), Alin et al 2011 and Borges et al 2004, shown that in large rivers and estuaries k is dependent on a mixture of pCO2, wind, and water flow and therefore is site specific. In tidal areas, water velocity could change significantly depending not only the season but the daily with the influence of the tides. This should also be covered here.

Reply: We thank the reviewer for reminding us of the importance of tidal currents in controlling the gas transfer velocity (k) in estuarine environments. As mentioned in the M&M we used the Raymond and Cole (2001) parameterisation as a function of wind speed. As also mentioned in the M&M, this parameterisation provides minimal (i.e conservative) estimates of k. We did not compute fluxes with other parameterisations because we did not have measurements of currents. Also it has been shown numerous times in literature that the use of the different parameterisations leads (unsurprisingly) to different values of fluxes, and we found superfluous to re-iterate this discussion in the present paper. Although we do not discuss in detail the variability of wind speed measurements, we have added the average wind speeds in Table 1.

Reviewer comment: To better show the spatial difference between main channels, side channels, mangrove creeks and the outer estuary. Statistical tests would be required to make the discussion more robust.

Reply: We have added p values of the regressions in figures as also required by Reviewer 1. We have added statistical tests where necessary.

Reviewer comment: Page 4, L21: April and Borges, 2004 is not in the References list.

Reply: Date was corrected from 2005 to 2004 in the reference list.

Reviewer comment: Page 5, L30-32: The same information is presented in the description of the river and should be removed from the introduction.

Reply: In the introduction are given the ranks compared to other World rivers. This information is important to situate the Mekong as a major World river. Text was not modified.

Reviewer comment: Page 6, L1-6: This is also in the methods section. Perhaps it would be better presenting it just there and remove it from the introduction.

Reply: Refer to above answer. Text was not modified.

Reviewer comment: Page 7, L27-29: This could be replaced by densely populated

Reply: Indeed, but we prefer to keep the quantitative information rather than replacing by a qualitative interpretation.

Reviewer comment: Page 9, L5-7: How much water was used and how it was collected and transferred to the serum bottles? Were there replicates? Consider the same for 13C-DIC.

Reply: Additional information was included and text now reads: “Water for the determination of CH_4 was sampled in duplicate with a silicone tube from the 1.7L Niskin bottle into 50 ml borosilicate serum bottles, allowing the flushing of 2-3 times the final volume, then poisoned with 100 µl of a saturated solution of $HgCl_2$ sealed with a butyl stopper and crimped with an aluminium cap”

Reviewer comment: Page 10, L22-24: Recent papers have shown that estimated k values for CO2 are different from CH4. Thus, a single model would not be the best way to tackle the flux estimates. If not possible to use different models for each gas, at least this limitation should be mentioned.

Reply: We are familiar with the recent papers dealing with differences in k for CO2 and CH4. However, this has solely shown with floating chamber measurements, an approach prone to several methodological caveats. Further, there is little understanding of the actual mechanisms that could explain such differences of k among gases. Anyway, we believe this level of refinement in the computations of CO_2 and CH_4 values is superfluous given the enormous spatial and seasonal variations of the fluxes driven by those of the concentrations.
Our data we will not help resolving this problem; using a single but broadly used k600-wind relationship for our flux calculations has the advantage to allow simple corrections if a new parameterization is published for the Mekong delta in the future

Reviewer comment: Page 10, L24-28: Please add here the atmospheric CO2 retrieved from NOAA and the distance from the station to the mouth of the Mekong River.

Reply: Text now reads: "During the three sampling periods, the dry air CO_2 mixing ratio averaged 376±4 ppm and the humidity saturated air CO_2 mixing ratio averaged 362±3 ppm."

Reviewer comment: Page 12, L11-13: Please show the correlation between pCO2 and O2.

Reply: We have added a figure showing the highly significant correlation between pCO2 versus %O2 and δ^{13}C-DIC. Text now reads: "The pCO_2 values in freshwaters were significantly correlated to $\%O_2$ (Fig. 4) indicating biological control of both these variables. Similarly, the correlation between pCO_2 and δ^{13}C-DIC (Fig. 4) results from the degradation of organic matter that leads to a preferential release of $^{12}CO_2$ (since organic matter is isotopically light compared to the background DIC pool), leading to more negative delta δ^{13}C-DIC values."

Reviewer comment: Page 12, L21-23. Please present the 13C-DIC values here.

Reply: Text now reads: "The impact of biological activity on CO_2 dynamics in the uppermost freshwater part of the estuary, was confirmed by δ^{13}C-DIC values that were higher in April 2004 (-8.7±0.4 ‰, n=5) compared to December 2003 (-10.6±0.6, n=6 ‰) and October 2004 (-10.9±0.3 ‰, n=15)"

Reviewer comment: Page 12, L23-25: What happens with other variables like POC, DOC, and TSM? The same discharge can be observed during the rising and falling water period, however, there will be different inputs of these materials depending if it is rising or falling waters. Furthermore, please consider adding in Fig 4 the channels and the outer estuary, similarly as you did in Figure 10.

Reply: As mentioned above, the primary focus of the paper is CO2 and CH4 dynamics, so we plotted these data plus those that are immediately explicative such as O2 and δ^{13}C-DIC. Plotting other variables POC, etc… would bring little added value given the limited number of data (only 3 three cruises, when change of POC, TSM as a function of discharge are notoriously variable). We did not add the data in channels and outer estuary as a function of discharge, as they are also affected by local mixing processes and production/removal processes (inputs from shrimp farms) that are independent of discharge.

Reviewer comment: Page 13, L4-5: Are these other tropical estuaries large systems, and where they are located?

Reply: We added in text that the cited estuaries are located in Kenya. These are smaller systems than the Mekong, although we did not find relevant to mention this in text.

Reviewer comment: Page 13, L5-7: Neither the O2 decrease or the pCO2 increasing patterns are not very clear in Fig 3. In April 2004 pCO2 increased from km 40 to 60, but then it decreased toward the mouth.

Reply: Indeed, that is mentioned P12 L30.

Reviewer comment: Page 13, L11: Please inform if the Phnom Penh is similar in terms of size/discharge to the Mekong

Reply: Phnom Penh is a city located on the Mekong river.

Reviewer comment: Page 13, L16-17: Considering this finding you could exclude the long-term change explanation given above.

Reply: The sequence of sentences provides a reasoning with hypothesis and test of hypothesis. We did not change text.

Reviewer comment: Page 13, L22-30: You need to make a link to how all this information regarding these cations affects DIC and consequently pCO2. The way it is presented it seems out of context and does not contribute to the understanding of the C dynamics.

Reply: We assume that readers will be aware that total alkalinity in freshwaters mainly corresponds to HCO_3^-, and that DIC is predominately constituted by HCO_3^-. Rather than adding a substantial amount of text to explain this, we opted not to change the text.

Reviewer comment: Page 14, L6: The Oct 2004 cruise you have samples collected farther out the mouth in the plume. This could be pure or almost pure ocean water and may be related to this very low pCO2 values observed. In addition later in Page 15, L5 you have mentioned that there was a phytoplankton bloom in the outer estuary.

Reply: Yes, we went more offshore due to very good weather conditions during this cruise, but the highest salinity in Oct 2004 was 27 lower than the highest salinity in April 2004 of 31. Ocean ("pure marine") salinity is typically 35, so well above the observed max salinities in the river plumes. Additionally, the phytoplankton growth is observed in the salinity gradient from 10 to 27 and not only in the high salinity range. Finally, a higher primary production in October than during the other two cruises is consistent with remote sensed seasonal cycles of phytoplankton biomass. Text now reads "Reported seasonal cycles of remote sensed Chlorophyll-*a* concentration also indicate higher phytoplankton biomass and primary production in October compared to April and December (Gao et al. 2013; Loisel et al. 2017)."

Reviewer comment: Page 14, L14: Could the depleted 13 C signature in the DIC be related with a large input of C4 plant material?

Reply: The DOC and POC stable isotope composition indicates a large predominance of terrestrial C3 material in the freshwaters of the Mekong. While there are some sugar cane (i.e. C4 vegetation) plantations in the area, their contribution is likely modest and cannot result in massive inputs that could impose the signature of delta 13C-DIC, without altering the isotopic signal and concentrations of aquatic DOC and POC. Hence, the explanation we give (mix of degradation organic matter of C3 origin and rock dissolution) is most likely.

Reviewer comment: Page 14, L17-18: What would be the expected 13C signature in the DIC from the weathering carbonate and silicate?

Reply: The delta 13C-DIC from dissolution of CaCO3 comes ½ from CaCO3 (delta 13C =

0) and ½ from CO2 used in dissolution (typically from organic matter degradation). delta 13C-DIC from dissolution of silicate rocks comes exclusively from CO2 used in dissolution (typically from organic matter degradation). This is relatively trivial information, we did not change text.

Reviewer comment: Page 15, L7: On page 14 L6 you say that the lowest pCO2 was 314. Which is the right value?

Reply: One value is the absolute minimum, the other is the value in the most marine station (highest salinity). We did not change text.

Reviewer comment: Page 15, L15-24: Seidel et al 2015 (Marine Chemistry 177,p 218–231) and Medeiros et al 2015. (Global Biogeochem. Cycles, 29, p677–690) may give you valuable information regarding this discussion.

Reply: We thank the reviewer for the suggested references, but we considered a comparison with the Amazon to be outside the scope of this already very long paper.

Reviewer comment: Page 15, L28-30: Despite the trends observed in Fig 5 for the variables, these different patterns does not seem to be statistically significant. Please add the proper statistical tests results to make your point more convincing.

Reply: We added p values.

Reviewer comment: Page 16, L26-29: You have mentioned above that %POC, TSM and 13C POC in the side channels indicate large primary production. I am not sure if I got it right, but the model seems to not see the same trend, is that right?

Reply: Both are occurring. Phytoplankton growth affects δ^{13}C-POC, and heterotrophy leads to high CO_2, CH_4, and low O_2. We have added a sentence to clarify this, and text now reads: “Although there is indication of phytoplankton development based on δ^{13}C-POC (see above), the overall system was net heterotrophic leading to accumulation of CO_2, CH_4 and light DIC, and decrease of O_2.”

Reviewer comment: Page 17, L10-13: If the side channels have lower water velocity than the main channels, higher sediment deposition is expected in this areas differently from the main channels were the water flow would wash out the fine organic sediment. If you have such condition then these shallow side channels could accumulate C fueling anaerobic degradation and CH4 production.

Reply: We fully agree, and that’s indeed what is probably going on, but we do not have data on currents to demonstrate that, so we did not include this in text.

Reviewer comment: Figure 1. Add spatial scale bar and a North arrow.

Reply: We added the scale bar. We did not add a “North arrow”, the plots are oriented to the North, as by convention.

Reviewer comment: Figure 3. Please consider changing the colored circles into different shapes. This would make easier to distinguish between rivers.

Reply: We kept the original symbols that guide the reader in interpreting the plots by discriminating the side channels (triangles) from the main estuarine branches (all with circles).

Reviewer comment: Figure 4. Would be interesting to see the channels and the outer estuary here as well, similarly to Fig 10.

Reply: Please refer to above reply on similar comment.

Reviewer comment: Figures 5, 6, 7 and 9. Same as figure 3.

Reply: Please refer to above reply on similar comment.

Carbon dynamics and CO_2 and CH_4 outgassing in the Mekong Delta

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Abstract

We report a data-set obtained in the three branches (My Tho, Ham Luong, Co Chien) of the Mekong delta (Bến Tre province, Vietnam) in December 2003, April 2004, and October 2004, of biogeochemical variables related to carbon cycling ~~(pH, total alkalinity (TA), O_2 saturation level ($\%O_2$), calculated partial pressure of CO_2 (pCO_2), dissolved CH_4 concentration, particulate (POC) and dissolved (DOC) organic carbon concentration and stable isotope composition (δ^{13}C-POC, δ^{13}C-DOC), particulate nitrogen (PN), dissolved inorganic carbon (DIC) stable isotope composition (δ^{13}C-DIC), total suspended matter (TSM))~~. Both the inner estuary (upstream of the mouth) and the outer estuary (river plume) were sampled, as well as side channels. The values of the partial pressure of CO_2 (pCO_2) ranged between 232 and 4,085 ppm, O_2 saturation level ($\%O_2$)~~$\%O_2$~~ between 63 and 114 %, and CH_4 between 2 and 2,217 nmol L^{-1}, within the ranges of values previously reported in temperate and tropical meso- and macro-tidal estuaries. Strong seasonal variations were observed. In the upper oligohaline estuary, low pCO_2 (479-753 ppm) and high $\%O_2$ (98-106%) values were observed in April 2004 most probably related to freshwater phytoplankton growth owing to low freshwater discharge (1,400 m^3 s^{-1}) and increase of water residence time; during the two other sampling periods with a higher freshwater discharge (9,300-17,900 m^3 s^{-1}), higher pCO_2 (1,895-2,664 ppm) and lower $\%O_2$ (69-84%) values were observed in the oligohaline part of the estuary~~. During the~~In October 2004~~ sampling~~, important phytoplankton growth occurred in the off-shore part of the river plume as attested by changes in the contribution of particulate organic carbon (POC) to total suspended matter (TSM) (%POC)~~,~~ and the stable isotope composition of POC (δ^{13}C-POC), ~~POC:PN ratios,~~ possibly related to low TSM values (improvement of light conditions for phytoplankton development), leading to low pCO_2 (232 ppm) and high $\%O_2$ (114%) values. Water in the side channels in the Mekong delta was strongly impacted by inputs from the extensive shrimp farming ponds. The values of pCO_2, CH_4, $\%O_2$, stable isotope composition of dissolved inorganic carbon (δ^{13}C-DIC) indicated intense organic matter degradation that was partly mediated by sulfate reduction ~~(presumably~~ in sediments~~)~~, as ~~indicated~~ revealed by the slope of total alkalinity (TA) and DIC co-variations. The δ^{13}C-POC variations also indicated intense phytoplankton growth in the side channels, presumably due to nutrient enrichment related to the shrimp farming ponds. A

dataset in the mangrove creeks of the Ca Mau province (part of the Mekong delta) was also acquired in April 2004 and October 2004. These data extended the range of variability of pCO_2 and $\%O_2$ with more extreme values than in the Mekong delta (Bến Tre), with maxima and minima of 6,912 ppm and 37%, respectively. Similarly, the maximum CH_4 concentration (686 nmol L^{-1}) was higher in the Ca Mau province mangrove creeks than in the Mekong delta (Bến Tre, maximum 222 nmol L^{-1}), during the October 2004 cruise (rainy season and high freshwater discharge period). In April 2004 (dry season and low freshwater discharge period), the CH_4 values were much lower than in October 2004 (average 19±13 and 210±158 nmol L^{-1}, respectively) in the Ca Mau province mangrove creeks, owing to the higher salinity (average 33.2±0.6 and 14.1±1.2, respectively) that probably led to higher sediment sulfate reduction, leading to inhibition of sediment methanogenesis and higher anaerobic CH_4 oxidation. In the inner estuarine region (three branches of the Mekong delta), CO_2 emissions to the atmosphere averaged 121 mmol m^{-2} d^{-1}, and the CH_4 emissions averaged 118 μmol m^{-2} d^{-1}. The CO_2 emission to the atmosphere from the Mekong inner estuary was higher than reported in the Yangtze and Pearl River inner estuaries. This was probably due to the lower salinity in the Mekong delta branches, possibly due to different morphology; relatively linear channels in the Mekong delta versus funnel-shaped estuaries for the Yangtze and Pearl River inner estuaries.

1. Introduction

Estuaries are the main pathways for the transfer of particulate and dissolved matter ~~between~~ from land to the ocean (through rivers). Particulate and dissolved matter undergo strong transformations, as estuaries are sites of intense biogeochemical processing (for example, Bianchi, 2006) that in most cases leads to substantial emissions of greenhouse gases such as carbon dioxide (CO_2) and methane (CH_4) (for example, Borges and Abril, 2011). Most estuarine environments are net heterotrophic ecosystems (~~for example,~~ Gattuso et al., 1998; Testa et al., 2012), leading to the production and emission to the atmosphere of CO_2 and CH_4. The production of CO_2 and CH_4 is modulated by various physical features resulting from estuarine geomorphology such as water residence time (Borges et al., 2006; Joesoef et al., 2017), tidal amplitude and vertical stratification (Borges, 2005; Koné et al., 2009; Crosswell et al., 2012; Joesoef et al., 2015), and connectivity with tidal flats and saltmarshes (Middelburg et al., 2002; Cai, 2011). Highly eutrophic (Cotovicz Jr et al., 2015) or strongly stratified estuarine systems (Koné et al., 2009) can exceptionally act as sinks of CO_2 due to high carbon sequestration, although high organic matter sedimentation can concomitantly lead to high CH_4 production and emission to the atmosphere (Koné et al., 2010; Borges and Abril, 2011).

The global CO_2 emissions from estuaries have been estimated by several studies (Abril and Borges, 2004; Borges 2005; Borges et al., 2005; Chen and Borges, 2009; Laruelle et al., 2010; 2013; Cai, 2011; Chen et al., 2012; 2013) and range from 0.1 to 0.6 PgC yr^{-1}, equivalent in magnitude to 5-30% of the oceanic CO_2 sink of ~2 PgC yr^{-1} (Le Quéré et al., 2016). These values were derived from the scaling of air-water CO_2 flux intensities (per surface area) compiled from published data that were extrapolated to estimates of the global surface of estuaries. The most recent estimates are lower than the older ones, reflecting the increase by an order of magnitude of the availability of data on air-water CO_2 fluxes, and more precise estimates of surface areas of estuaries structured by ~~typology~~ types (for example, Dürr et al., 2011). The global estimates of CH_4 emissions from estuaries are also relatively variable ranging between 1 and 7 $TgCH_4$ yr^{-1} (Bange et al., 1994; Upstill-Goddard et al., 2000; Middelburg et al., 2002; Borges and Abril, 2011), and are modest compared to other natural (220-350 $TgCH_4$ yr^{-1}) and anthropogenic (330-335

$TgCH_4\ yr^{-1}$) CH_4 emissions (Kirschke et al., 2013). Unlike CO_2, the most recent global estimate of estuarine CH_4 emissions is the highest because it accounts for the direct emissions of CH_4 from sediment to atmosphere (when inter-tidal areas are exposed) (Borges and Abril, 2011). Yet, published estuarine CH_4 emissions are most probably under-estimated because they do not account for CH_4 ebullition and gas flaring, although emissions to the atmosphere of CH_4 originating from gas ~~-richsy~~ sediments in coastal environments have been shown to be intense (Borges et al., 2016; 2017). Reported CO_2 and CH_4 emissions from rivers are also highly uncertain and the ~~reported~~ proposed values also span a considerable range. Global riverine CO_2 emission estimates range between 0.1 $PgC\ yr^{-1}$ (Liu et al., 2010) and 1.8 $PgC\ yr^{-1}$ (Raymond et al., 2013), while riverine CH_4 emission estimates range between 2 $TgCH_4\ yr^{-1}$ (Bastviken et al., 2011) and 27 $TgCH_4\ yr^{-1}$ (Stanley et al., 2016). Both CO_2 and CH_4 riverine emissions mainly occur in tropical areas (Borges et al., 2015a,b).

The first studies of CO_2 and CH_4 dynamics and emissions from estuaries were carried out during the late 1990's in Europe (Frankignoulle et al., 1996; 1998; Middelburg et al., 2002) and the USA (Cai and Wang, 1998). Since then, CO_2 data coverage has tremendously increased with additional studies at sub-tropical and tropical latitudes (for example Sarma et al., 2012; Chen et al., 2012; Rao and Sarma, 2016) and in the large river-estuarine systems such as the Amazon (Lefèvre et al., 2017), the Mississippi (Huang et al., 2015), the ~~Changjiang (~~Yangtze (Changjiang) (Zhai et al., 2007; Zhang et al., 2008), and the Pearl (Guo et al., 2009; Zhou et al., 2009). The number of studies on CH_4 in estuarine and coastal environments has not increased in recent years as spectacularly as those concerning CO_2, attracting less research efforts because the marine source of CH_4 to the atmosphere (0.4-1.8 $TgCH_4\ yr^{-1}$, Bates et al., 1996; Rhee et al., 2009) is very modest compared to other natural and anthropogenic CH_4 emissions (Kirschke et al., 2013); although,~~.~~ ~~Continental~~ continental shelves and estuaries are more intense sources of CH_4 to the atmosphere ~~of CH_4~~ than the open ocean, in particular shallow and permanently well-mixed coastal zones (Borges et al., 2016; 2017). Yet, numerous large river-estuarine systems remain totally uncharted with respect to CO_2 and CH_4 data, such as the Mekong although it is the World's 10^{th} largest river in water discharge (470 $km^3\ yr^{-1}$), 12^{th} largest in length (4,800 km), and 21^{st} largest in drainage area (795,000 km^2) (Li and Bush, 2015).

As a contribution to the special issue in *Biogeosciences* on "Human impacts on carbon fluxes in Asian river systems", we report a data-set obtained in the three branches (My Tho, Ham Luong, Co Chien) of the Mekong delta (Fig. 1) in December 2003, April 2004, and October 2004 of biogeochemical variables related to carbon cycling (pH, total alkalinity (TA), O_2, calculated partial pressure of CO_2 (pCO_2), dissolved CH_4 concentration, particulate (POC) and dissolved (DOC) organic carbon concentration and stable isotopic ~~(SI)~~ composition, particulate nitrogen (PN), dissolved inorganic carbon (DIC) stable isotopic~~SI~~ composition, total suspended matter (TSM)). The aim of the paper is to give a general description of carbon cycling with an emphasis on CO_2 and CH_4 dynamics in the Mekong delta estuarine system, that can be used as a reference state to evaluate future changes in response to ~~changes~~ modifications in hydrology related the construction of planned large dams (leading to water abstraction and sediment retention), eutrophication, shoreline erosion, and sea-level rise.

2. Material and methods

2.1. Description of the Mekong River and Delta

Himalayan rivers (Yangtze, Mekong, Salween, Ayeyarwady, Ganges, Brahmaputra, ~~Ganges,~~ Indus) are among the World's largest. The Mekong River is one of the longest rivers among the Himalayan watersheds, ranking it 12th longest river in the World. It flows 4,800 km from the eastern part of the Tibetan Plateau through six different countries (China, Myanmar, Lao People's Democratic Republic (PDR), Thailand, Cambodia, Vietnam), into the South China Sea, draining an area of 795,000km^2. The basin is divided into the Upper Mekong (parts of China and Myanmar, surface of 195,000 km^2, first 2,000 km in length), and the Lower Mekong (parts of Lao PDR, Thailand, Cambodia and Vietnam, surface of 600,000 km^2). The Upper Mekong is mountainous (altitude 400-5,000 m) with no significant large tributaries and a low population density (<10 inhabitants km^{-2}). The Lower Mekong is lowland, drains very large tributary river systems, and is densely populated (80-460 inhabitants km^{-2}). Climate ranges from cold temperate in the Upper Mekong to tropical monsoonal in the Lower Mekong. The annual flow of the Mekong River is ~470km^3, ranking 10th among the World largest rivers (Dai and Trenberth, 2002).

Water source is snowmelt in the Upper Mekong, and surface runoff in the Lower Mekong. Seasonal variations in freshwater flow are controlled by the East Asian monsoons, resulting in an annual unimodal flood pulse. About 75% of the annual flow occurs in four months (July-October). The delta is divided into two main rivers, the Hau and the Tien, that share equally the total freshwater discharge. The Tien river further divides into the My Tho, Ham Luong and Co Chien River branches (Fig. 1) that deliver 8, 14 and 23%, respectively, of total freshwater from the Mekong network (based on the average of five different estimates reported by Nguyen et al. (2008)). The annual sediment load was ~130-160 million tons in the 1960's and 110 million tons in the 1990's according to ~~(~~Milliman and Farnsworth~~,~~ (2011). Li and Bush (2015) report a less dramatic decrease of annual sediment load from 171 million tons for the pre-regulated period (1923-1991) to 168 million tons for the regulated period (1992-2007). Estimates of ~~The~~ the ~~solute~~ annual solute transport ranges between 40 and ~~is~~ 123 million tons (Meybeck and Carbonnel, 1975; Gaillardet et al., 1999; Li and Bush, 2015). Exposed lithological strata are dominated by shales (43.2%), followed by carbonates (21.4%), shield rocks (18.2%), sands and sandstone (8.4%), basalts (5.8%) and acid volcanic rocks (2.9%) (Amiotte Suchet et al., 2003). The Mekong River basin is populated by 70 million people and this population is expected to increase to 100 million by 2050 (Varis et al., 2012). Recent and fast economic development has substantially increased the use of water resources (Piman et al., 2013), in particular for agriculture, energy (hydropower), and fishery (Västilä et al., 2010). Until recently, the Mekong River was considered one of the last unregulated great rivers with a flow regime close to its natural state (Adamson et al., 2009). Economic development in the region has led to the construction of several dams mainly for the production of hydropower, potentially affecting water and sediment flows (Fu et al., 2008; Wang et al., 2011; Lu et al., 2014; Piman et al., 2013; 2016). The construction of major infrastructures is planned on the transboundary Srepok, Sesan and Srekong Rivers, which contribute up to 20% of the total annual water flow of the Mekong (Piman et al., 2016).

The Mekong River delta covers an area of 50,000 km^2 and is the third largest tide-dominated delta in the World after the Amazon and Ganges-Brahmaputra deltas. The upper limit of the delta (limit of the tidal influence) is the city of Phnom Penh in Cambodia, and at the coast it extends in the North from the mouth of the Saigon River to Cape Ca Mau in the South. The delta is meso-tidal with an average tidal

amplitude of 2.5 m at the estuarine mouths and a maximum tidal amplitude of 3.8 m, and tides have mixed diurnal and semi-diurnal components, with a dominance of the semidiurnal (period ~12 h) component (Takagi et al., 2016). It is tremendously important in the food supply and economic activity of Vietnam, as it sustains 90% of rice (>20 million tons annually) and 60% of seafood national production. The development of shrimp farming in the delta has led to the reduction of mangrove forests (de Graaf and Xuan, 1998; Nguyen et al., 2011) that nowadays only remain significantly in the Ca Mau Province. Shrimp farming started in the late 1970's, accelerated during the mid-1980's until present (de Graaf and Xuan, 1998; Tong et al. 2010). The delta is populated by more than 17 million people (>80% in rural areas), representing nearly a quarter of Vietnam's total population, with an annual population growth of more than 2%. The delta is a low-lying area with an average elevation of < 2 m above sea level, making it one of the most vulnerable deltas in the World to sea level rise (IPCC, 2014). The decrease in freshwater and sediment delivery combined to the rising sea-level and subsidence, as well as coastal (shoreline) erosion are potential threats for economic activities in the Mekong delta, for instance due to the impact of salinity intrusion on agriculture, compromising economy and livelihood of local populations (Smajgl et al., 2015). Several studies predict that a large fraction (70-95%) of the sediment load could be trapped by hydropower reservoirs if all of the planned infrastructures are effectively build (Kummu et al., 2010; Kondolf et al., 2014). In addition, sediment river delivery could also ~~change~~ vary in response to changes in climate (Västilä et al. 2010; Lauri et al., 2012; Darby et al., 2016). This would have important consequences on the sediment deposition in the delta that seems to have already shifted from a net depositional (accretion) regime into a net erosion regime (Anthony et al., 2015; Liu et al., 2017). The nutrients inputs to the continental shelf from the Mekong delta sustain high phytoplankton growth in the Mekong river plume (Grosse et al., 2010) that is one the most productive areas of the South China Sea (Liu et al., 2002; Qiu et al., 2011; Gao et al., 2013; Loisel et al., 2017).

2.2. Sampling

Sampling in ~~the~~ three branches of the Mekong delta (My Tho, Ham Luong, Co Chien, Fig. 1) was carried during three field campaigns (29/11/2003-05/12/2003;

02/04/2004-07/04/2004; 14/10/2004-19/10/2004) on the inspection boat of the Bến Tre Fishery Department, in collaboration with the Research Institute for Aquaculture N°2 (Ho Chi Minh City). Sampling in the mangrove creeks of the Ca Mau province was carried during two field campaigns (10/04/2004-14/04/2004; 23/10/2004-25/10/2004) with a speed boat. The map of the sampling stations in the mangrove creeks of the Ca Mau province is given by Koné and Borges (2008) who reported pCO_2, $\%O_2$ and TSM data.

Samples for pH, TA, O_2, TSM, POC and δ^{13}C-POC, PN, δ^{13}C-DIC were collected and analysed at all stations of all three field campaigns. Samples for ~~Dissolved~~ dissolved CH_4 concentration were~~as~~ collected during the two last field campaigns, for DOC during the last field campaign, and for dissolved silica (DSi) during the second field campaign.

2.3. Sample collection and analysis

Salinity and water temperature were measured in-situ using a portable thermosalinometer (WTW Cond-340) with a precision of ±0.1 and ±0.1°C, respectively. Subsurface waters (top ~~30 ~~1 ~~c~~m) were sampled with a 1.7 L Niskin bottle (General Oceanics) for the determination of pH and dissolved gases sampled with a silicone tube. Water for the determination of O_2 was sampled in a Winkler type borosilicate bottle and the oxygen saturation level ($\%O_2$) was measured immediately after collection with a polarographic electrode (WTW Oxi-340) calibrated on saturated air, with an accuracy of ±0.1%. pH was also sampled in a Winkler type of bottle and measured immediately after collection with a combination electrode (Metrohm 6.0232.100) calibrated on the U.S. National Bureau of Standards scale as described by Frankignoulle and Borges (2001), with a precision and estimated accuracy of respectively ±0.001 and ±0.005 pH units. Water for the determination of CH_4 was sampled in duplicate with a silicone tube from the 1.7L Niskin bottle into~~in~~ 50 ml borosilicate serum bottles, allowing the flushing of 2-3 times the final volume, then poisoned with 100 µl of a saturated solution of $HgCl_2$ sealed with a butyl stopper and crimped with an aluminium cap. The CH_4 concentration was measured by the headspace technique (Weiss 1981) using a gas chromatograph ~~(GC) ~~with flame ionization detection (~~GC-FID, ~~Hewlett Packard ~~HP ~~5890A), calibrated with certified

CH_4:N_2 mixtures of 10 and 200 ppm~~v~~ CH_4 (Air Liquide, France), with a precision of ±5%. Water for the analysis of δ^{13}C-DIC was sampled in 12 mL Exetainer vials and poisoned with 20 µL of a saturated $HgCl_2$ solution. A He headspace was created, and ~300 µL of H_3PO_4 was added to convert all DIC species to CO_2, and after overnight equilibration, part of the headspace was injected into the He stream of an Elemental Analyzer – Isotope Ratio Mass Spectrometer (EA-IRMS; ThermoFinnigan Flash1112 and ThermoFinnigan Delta+XL) for δ^{13}C measurements, with a precision of better than ± 0.2 ‰.

Samples for TSM were filtered on pre-weighed and pre-combusted (5 h at 450°C) 47 mm Whatman GF/F filters (0.7 µm porosity), rinsed with bottled ~~mineral~~ drinking water to avoid salt contributions, and subsequently dried. Samples for POC, PN, and δ^{13}C-POC were filtered on pre-combusted 25 mm Whatman GF/F filters (0.7 µm porosity) and dried. These filters were later decarbonated with HCl fumes under partial vacuum for 4 h, re-dried and packed in Ag cups. POC and PN were determined on a ThermoFinnigan Flash EA1112 using acetanilide as a standard, and the resulting CO_2 was measured on a ThermoFinnigan delta+XL interfaced via a ConfloIII to the EA. Reproducibility of δ^{13}C-POC measurements was better than ± 0.2 ‰. Samples for DOC and δ^{13}C-DOC, TA, DSi, major cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}) were obtained by pre-filtering water on cellulose acetate filters for DSi, and pre-combusted Whatman GF/F filters for the other variables, followed by filtration on 0.2 µm cellulose acetate syringe filters (Sartorius). DOC and δ^{13}C-DOC were stored in 40 ml borosilicate bottles and preserved by addition of 50 µL of H_3PO_4, DSi and major cations were stored in 20 ml high density polyethylene scintillation vials and preserved with HNO_3 (50 µl from DSi, 10 µl for major cations), and TA was stored un-poisoned in 100 ml polyethylene vials. DOC concentrations and δ^{13}C signatures were measured with a modified Thermo HiperTOC TOC-analyzer, interfaced with a Thermo delta +XL IRMS as described by Bouillon et al. (2006). DSi was measured with the colorimetric method of Koroleff (1983), with a precision of ±0.1 µmol L^{-1}. TA was measured on 50 ml samples by automated Gran titration with 0.1 M HCl as titrant, with a reproducibility of ±1 µmol kg^{-1}. Samples for major cations were measured by inductively coupled plasma ~~–~~ atomic emission spectrometry (ICP-AES) and with a reproducibility better than ±3 %.

The dissolved concentration of CO_2 is expressed as pCO_2 in parts per million (ppm), following Henry's law (Henry, 1803). Measurements of TA and pH were used

to compute pCO_2 and DIC using the carbonic acid thermodynamic dissociation constants of Cai and Wang (1998), with an estimated accuracy of ±5 % and ±5 µmol kg^{-1}, respectively (Frankignoulle and Borges, 2001). Measured TA and pH values were well within the range of applicability of the pCO_2 calculation according to Abril et al. (2015), with pH>7 and TA > 1,000 µmol kg^{-1}, even in freshwaters.

Air-water fluxes of CO_2 (FCO_2) and CH_4 (FCH_4) were calculated according to:

$$F=k.\Delta G \quad (1)$$

where F is the flux of the gas, ΔG is air-water gradient of the gas and k is the gas transfer velocity.

Values of k were computed using wind speed field measurements with a handheld anemometer, and the parameterization as a function of wind speed given by Raymond and Cole (2001) (the "non-dome" parameterisation). The k values in estuarine environments are highly variable and parameterizations as a function of wind speed are site-specific due to variable contribution of fetch limitation and tidal currents (Borges et al., 2004). The parameterization of Raymond and Cole (2001) probably provides minimal k values, so the FCO_2 and FCH_4 values given hereafter are considered to be conservative estimates. Atmospheric pCO_2 values were retrieved from the National Oceanic and Atmospheric Administration Earth System Research Laboratory atmospheric measurement network data-base at station Guam (Mariana Islands, 13.386°N 144.656°E), located in the Pacific Ocean, approximately at the same latitude as Mekong delta. The atmospheric pCO_2 values were converted from dry air to humidity saturated air using the water vapour formulation as function of salinity and temperature given by Weiss and Price (1980). For the three sampling periods, the dry air CO_2 mixing ratio averaged 376±4 ppm and the humidity saturated air CO_2 mixing ratio averaged 362±3 ppm. For CH_4, a constant atmospheric value of 1.8 ppm was used. The Henry constant of CO_2 and CH_4 was computed from salinity and temperature according to Weiss (1974) and Yamamoto et al. (1976), respectively, and the Schmidt number for CO_2 and CH_4 was computed from temperature according to Wanninkhof (1992). The air-water CO_2 and CH_4 values were area-averaged and scaled to the surface of the three estuarine branches using surface areas derived from satellite images with Google Earth.

2.4. Mixing models

Mixing models were used to investigate sources and sinks of TA, DIC, O_2 and $\delta^{13}C$-DIC along the salinity gradient. We used a mixing model for TA, DIC and O_2 that assumes conservative mixing and no gaseous exchange with the atmosphere for a solute (E), according to:

$$E_S = \left(\frac{E_M - E_F}{Sal_M - Sal_F}\right) Sal + E_f \quad (2)$$

where E_S is the concentration of E at a given salinity (=Sal), E_F is the concentration of E at the freshwater end-member (with a salinity of Sal_F), E_M is the concentration of E at the marine end-member (with a salinity of S_M).

The conservative mixing of $\delta^{13}C$-DIC was computed according to Mook and Tan (1991):

$$\delta^{13}C \cdot DIC = \frac{Sal(DIC_F \delta^{13}C \cdot DIC_F - DIC_M \delta^{13}C \cdot DIC_M) + Sal_F DIC_M \delta^{13}C \cdot DIC_M - Sal_M DIC_F \delta^{13}C \cdot DIC_F}{Sal(DIC_F - DIC_M) + Sal_F DIC_M - Sal_M DIC_F} \quad (3)$$

where Sal is the salinity of the sample, DIC_F and $\delta^{13}C_F$·DIC are, respectively, the DIC concentration and stable isotope composition at the freshwater end-member, DIC_M, and $\delta^{13C}C_M$--DIC are, respectively, the DIC concentration and stable isotope composition at the marine end-member.

2.5. Data-set

The geo-referenced and timestamped data-set is available as a supplemental information of the paper.

3. Results and discussion

3.1. Spatial and seasonal variations in the main branches of the Mekong delta (My Tho, Ham Luong, Co Chien)

The three sampling cruises covered three distinct phases of the hydrological cycle (Fig. 2): low water (April 2004), close to high water (October 2004), and falling water

(December 2003). This strongly affected the salinity intrusion into the three inner estuarine channels (My Tho, Ham Luong, Co Chien): in December 2003 and October 2004, freshwater was observed throughout the inner estuarine channels down to the mouths, while in April 2004, the salinity intrusion occurred up to 60 km upstream of the estuarine mouths (Fig. 3). The pCO_2 values showed a general inverse pattern compared to salinity and strongly decreased offshore from the mouth of the three delta arms in December 2003 and October 2004, while the decreasing pattern of pCO_2 ~~occurs~~ occured within the three estuarine channels in April 2004. In December 2003 and October 2004, the pCO_2 values upstream (freshwater) ranged between 1,895 and 2,664 ppm, well above atmospheric equilibrium (362 ppm), and above the range of values (703-1,597 ppm) reported by Alin et al. (2011) in the upstream reaches of the Mekong the river network during the high water period (September-October 2004-2005). This difference might be due to a stronger human influence on the densely populated Mekong delta, or to geomorphology (lowland rivers versus higher altitude rivers). The pCO_2 values from the extensive dataset in the Mekong River at Tan Chau (~100 km upstream of the ~~delta~~area we sampled) ranged between 390 and 4,861 ppm and averaged 1,325 ppm (Li et al., 2013), encompassing the pCO_2 values we obtained in the freshwater part of the delta. The pCO_2 values in five streams of the Red River network in Northern Vietnam ranged between 750 and 2,400 ppm and averaged 1,597 ppm (Le et al., 2017), comparable to the pCO_2 values we obtained in the freshwater part of the Mekong delta. The pCO_2 values in freshwaters were significantly correlated to $\%O_2$ (Fig. 4) indicating biological control of both these variables. Similarly, the correlation between pCO_2 and δ^{13}C-DIC (Fig. 4) resulted from the degradation of organic matter that leads to a preferential release of $^{12}CO_2$ (since organic matter is isotopically light compared to the background DIC pool), leading to more negative δ^{13}C-DIC values. The high pCO_2 values in freshwaters in December 2003 and October 2004 corresponded to low $\%O_2$ values (69-84%) indicative of degradation of organic matter. In April 2004, the most upstream sampled stations of the delta (freshwater) were characterised by pCO_2 values (479-753 ppm) closer to atmospheric equilibrium and high $\%O_2$ values (98-106%) indicative of freshwater phytoplankton development during low water, probably related to an increase of water residence time related to low freshwater discharge (Reynolds and Descy, 1996), as also observed in other tropical rivers (for example Descy et al., 2017). Phytoplankton development during low water was also

reported in the Upper Mekong River (confluence with the Tonle Sap River) by Ellis et al. (2012), based on elemental and lignin analyses. The impact of biological activity on CO_2 dynamics in the uppermost freshwater part of the estuary, was confirmed by δ^{13}C-DIC values that were higher in April 2004 (-8.7±0.4 ‰, n=5) compared to December 2003 (-10.6±0.6, n=6 ‰) and October 2004 (-10.9±0.3 ‰, n=15). Indeed, pCO_2 was positively related to freshwater discharge, while $\%O_2$ and δ^{13}C-DIC were negatively related to freshwater discharge (Fig. 45), as also shown in other tropical rivers such as the Oubangui (Bouillon et al., 2012; 2014). The dataset in the Mekong River at Tan Chau reported by Li et al. (2013), shows a similar seasonal pattern, with lower pCO_2 values during low water (March-May) and higher pCO_2 values during high water (October-December). In April 2004, there was a marked increase of pCO_2 from the most up-stream stations (salinity 0) to the stations located at 60 km from Vĩnh Long (corresponding roughly to a salinity of 2). This increase of pCO_2 was mirrored by a general decrease of $\%O_2$, suggesting enhanced organic matter degradation in the oligohaline estuarine region, typical of estuarine environments (for example, Morris et al., 1978; Bianchi, 2006). In parallel, there was a general increase of DSi from salinity 0 to 2 suggesting that part of the enhanced organic matter degradation in the upper estuary in April 2004 was fuelled by the decay of freshwater diatoms due to haline (osmotic) stress (for example, Muylaert and Sabbe, 1999; Ragueneau et al., 2002), as also observed in other tropical estuaries such as the Tana and the Kidogoweni in Kenya (Bouillon et al., 2007a,b). In December 2003 and April 2004, a general gradual increase of pCO_2 was also observed along the estuarine channels towards the mouth, although the $\%O_2$ decrease was less marked than in April 2004. The TA values at zero salinity ranged from ~960 to ~980 µmol kg^{-1} in October 2004 and December 2003, respectively, significantly lower than in April 2004 (~1,400 µmol kg^{-1}) (Mann Whitney (MW) test at 0.05 level, $p<0.0001$). These values are higher than the HCO_3^- concentration of 949 µmol kg^{-1} reported by Meybeck and Carbonnel (1975) at Phnom Penh from January 1961 to 1962. The data of Meybeck and Carbonnel (1975) were obtained about 230 km upstream of our sampling sites in the Mekong delta, so the difference could be due to the general downstream increase in dissolved ions typically observed in rivers (for example, Whitton 1975), but we cannot exclude methodological differences, or long-term changes. Li and Bush (2015) did not identify clear long-term trends in HCO_3^- at two stations in the Lower Mekong ~~river~~ River from 1960 to 2011. Our TA values converge

with the median (1082 μmol kg^{-1}) of a large data-set during the 1972-1996 period from 42 stations in the lower Mekong delta compiled by the Mekong River Commission and reported by Li et al. (2014), and the average of TA (1026 μmol kg^{-1}) reported by Huang et al. (2017). The seasonal variations of TA follow those of freshwater discharge (Fig. 45), as also shown in other major rivers such as the Mississippi (Cai et al., 2008) and the Oubangui (Bouillon et al., 2012; 2014). TA in freshwater was correlated to Ca^{2+} with a slope of 2.0 (Fig. S1) consistent with the weathering of calcite ($CaCO_3$, HCO_3^-:Ca^{2+} = 2:1) and to Mg^{2+} with a slope of 2.2 consistent with the weathering of dolomite ($(Ca,Mg)CO_3$, HCO_3^-:(Ca^{2+},Mg^{2+}) = 2:1). Such stoichiometric ratios between HCO_3^- and Ca^{2+} and Mg^{2+} might also result from weathering of silicate rocks such as anorthite (Ca-plagioclase feldspar, $CaAl_2Si_2O_8$, HCO_3^-:Ca^{2+} = 2:1), chlorite ($Mg_5Al_2Si_3O_{10}$, HCO_3^-:Mg^{2+} = 2:1) or olivine ($MgSiO_4$, HCO_3^-:Mg^{2+} = 2:1). However, Li et al. (2014) have shown based on an extensive water chemistry dataset that carbonate rock weathering largely dominates silicate weathering in the Lower Mekong River, and this seems to be also the case in the Upper Mekong River (Manaka et al., 2015). TA in freshwater was also correlated to Na^+ but with a slope of 0.5, lower than expected from the weathering of Albite ($NaAlSi_3O_8$; HCO_3^-:Na^+ = 1:1), and to K^+ but with a slope of 14, higher than expected from the weathering of microcline (K-Feldspar, $KAlSi_3O_8$, HCO_3^-:K^+ = 1:1). Weathering of calcite alone would not account for all of the TA, but this would be the case for a mixture of weathering of calcite and dolomite (Fig. S2), also in agreement with the analysis of Li et al. (2014).

As a function of salinity, pCO_2 and $\%O_2$ showed in the three delta channels, regular decreasing and increasing patterns, respectively (Fig. 56). The lowest off-shore pCO_2 value was observed in October 2004 (314 ppm at 27.0 salinity), lower than in December 2003 (509 ppm at 17.9 salinity) and April 2004 (423 ppm at 31.9 salinity). TA showed a linear evolution against salinity, indicative of near conservative mixing behaviour. This was consistent with a near conservative mixing behaviour of major cations (Ca^{2+}, Mg^{2+}, K^+, Na^+) (Fig. S3). DIC generally followed the seasonal and spatial patterns of those of TA. δ^{13}C-DIC showed a typical increasing pattern with salinity (Mook and Tan 1991; Bouillon et al., 2012), resulting from the mixing of freshwater with more negative δ^{13}C signatures (-14 to -8 ‰) and marine water with a δ^{13}C signature close to 0‰. The ^{13}C-depleted signature in freshwater DIC results mainly from the degradation of organic matter, which contributes CO_2 with a

signature close to that of the source organic carbon which in the Mekong delta for POC ranged between -28 and -26 ‰, and from the weathering of carbonate and silicate minerals (which are typically driven by reaction with CO_2 derived from organic matter). CH_4 showed very strong seasonal variations in freshwaters of the Mekong delta with values < 20 nmol L^{-1} in April 2004 and values ranging between 25 and 220 nmol L^{-1} in October 2004 (significantly different, MW test p<0.0001). The seasonal CH_4 variation could result from the flooding of riparian and floodplain areas and/or CH_4 inputs from surface run-off during the rainy season and high water period leading to high CH_4 values in October 2004. The downstream decrease of CH_4 in the estuarine salinity mixing zone is typical (Borges and Abril 2012; Upstill-Goddard and Barnes, 2016), resulting from CH_4 riverine loss in the estuary due to emission to the atmosphere, microbial CH_4 oxidation and mixing with marine waters that have CH_4 concentrations close to atmospheric equilibrium (Rhee et al., 2009). The CH_4 concentration in the most off-shore sampled station was indeed close to atmospheric equilibrium in April 2004 (2 nmol L^{-1}) for a salinity of 31.9, but was higher in October 2004 (17 nmol L^{-1}) reflecting the lower salinity of 17.0. These values encompassed the CH_4 concentrations of 4-6 nmol L^{-1} reported by Tseng et al. (2017) 150 km offshore from the Mekong delta river mouth.

TSM values showed marked spatial gradients in October 2004 with high values up to 447 mg L^{-1} in freshwaters and ~~very~~ low values (2 mg L^{-1}) in marine waters. In April 2004 and December 2003, TSM values in freshwaters were significantly lower (MW test, p<0.0001) and the spatial variations along the salinity gradient were less obvious. POC concentration ranged between 0.2 and 4.0 mg L^{-1}, and the seasonal and spatial variations of POC were very similar to those of TSM. %POC values ranged between 2 and 4% typical for the corresponding range of TSM values in World rivers (Meybeck, 1982; Ludwig et al., 1996) and in estuaries (Abril et al., 2002), and within the range measured in the lower Mekong just upstream of the confluence with the Tonle Sap river during an annual cycle by Ellis et al. (2012). However, %POC values were distinctly higher (up to ~13%) in marine waters in October 2004 probably resulting from a phytoplankton bloom, as also testified by low POC:PN ratios (as low as 4.9), high $\%O_2$ (up to 114%) and δ^{13}C-DIC (up to 0‰) values, and low pCO_2 (as low as 232 ppm at salinity 12.9) values. The phytoplankton bloom probably resulted from higher light availability in marine waters owing to lower TSM values (down to 2 mg L^{-1}). Reported seasonal cycles of remote sensed

Chlorophyll-*a* concentration also indicate higher phytoplankton biomass and primary production in October compared to April and December (Gao et al. 2013; Loisel et al. 2017). The $\delta^{13}C$ ~~values of~~ POC values in the freshwater part of the delta (salinity <1) from the 3 sampling campaigns averaged -26.7 ± 0.7 ‰ (n=34), distinctly higher than the data from Ellis et al. (2012) which averaged -29.8 ± 0.9 ‰, but similar to data collected by Martin et al. (2013; average -26.4 ‰) at the same site as the Ellis et al. (2012) study. These $\delta^{13}C$-POC values are consistent with the expected dominance of terrestrial C3 vegetation in the riverine organic carbon load.

In October 2004, DOC showed a decreasing pattern while $\delta^{13}C$-DOC values ~~decreased~~increased, as typically observed in estuaries (Bouillon et al., 2012). Within the freshwater zone (salinity <1), DOC values (2.4±0.2 mg L^{-1}, n=19) were within the range (0.9-5.1 mg L^{-1}) reported by Huang et al. (2017), and $\delta^{13}C$-DOC values (-27.8 ± 0.6 ‰, n=19) ~~are~~ were again consistent with a dominance of terrestrial C3 vegetation inputs, and close to values reported by Martin et al. (2013) slightly upstream in the lower Mekong. The $\delta^{13}C$ values were significantly lower in DOC than POC for the same samples in October 2004 (Fig. ~~6~~7) (Wilcoxon matched-pairs test at 0.05 level $p<0.0001$), probably reflecting the more refractory nature of riverine DOC compared to POC, the latter being removed faster during estuarine mixing, being gradually replaced by POC of phytoplankton origin with a higher $\delta^{13}C$ value.

3.2. Distinct patterns in side channels compared to the main branches of the Mekong delta

The sampled biogeochemical variables showed distinct patterns in the side channels of the Mekong delta compared to the main channels (My Tho, Ham Luong and Co Chien), irrespective of the sampling period. The observed patterns are consistent with the influence from the very extensive ponds devoted to shrimp farming that border the side channels of the Mekong delta (Tong et al. 2010). TSM, POC and %POC values were generally higher in the side channels than in the three main estuarine channels. In December 2003, TSM and POC were statistically higher in the side channels than in the three main channels (MW test $p=0.0273$ and $p<0.0001$, respectively), but not for the other two cruises, although the statistical comparisons were probably obscured by the mixing induced changes along the salinity gradient. The DOC concentrations from the October 2004 cruise were also

higher in the side channels (MW test p=0.0267). Higher %POC values could indicate a higher contribution of phytoplankton biomass to TSM, and this is consistent the δ^{13}C-POC values that ~~are~~ were about 5-6 ‰ lower than the values in the three main estuarine channels at the same salinity values. There is an isotopic fractionation by phytoplanktonic primary production of about 20‰ during DIC uptake (Hellings et al., 1999), corresponding roughly to the difference in δ^{13}C values between POC (overall average: -27.4±1.8‰) and DIC (overall average: -8.2±2.4‰) in the side channels. The phytoplankton primary production was probably sustained by high inorganic nutrients inputs from shrimp farming ponds typically observed in adjacent channels (for example Cardozo and Odebrecht, 2014) or within the ponds themselves (Alongi et al., 1999a). Yet, the more negative δ^{13}C-DIC values in the side channels indicate sustained CO_2 production from organic matter degradation related to the shrimp ponds (Alongi et al., 2000~~),~~) (MW test p=0.0253 in December 2003 and p=0.0040 in April 2004). This is consistent with generally higher pCO_2 values and lower $\%O_2$ in the side channels compared to the adjacent estuarine channels. As for TSM and POC, pCO_2 and $\%O_2$ were only statistically different between side and main channels in December 2013 (MW test p<0.0001 for both), as the statistical comparisons were probably obscured by the mixing induced changes along the salinity gradient. Although there was indication of phytoplankton development based on δ^{13}C-POC (see above), the overall system was net heterotrophic leading to accumulation of CO_2, ~~and~~ CH_4 and light DIC and decrease of O_2. The distinctly higher CH_4 values in side channels compared to main estuarine channels would indicate that part of the organic matter degradation in the side channels occurs in sediments (MW test p=0.0369 in April 2004 and p<0.0001 in October 2004). Alongi et al. (1999b) showed that methanogenesis in the sediments of shrimp farming ponds themselves is low in the Ca Mau Province. This allows to suggest that the high CH_4 in the side channels were presumably coming from the side channels sediments and not from the shrimp farming ponds. The generally higher TA values in the side channels than in estuarine channels could also indicate the effect of diagenetic anaerobic processes (for example, Borges et al., 2003) (MW test p<0.0001 in December 2003 and October 2004). ~~The concentrations of Ca^{2+} and Mg^{2+} did not show marked deviations as a function of salinity in the side channels compared to estuarine channels (Fig. S3), indicating TA generation was unrelated to dissolution of $CaCO_3$ or $CaMg(CO_3)_2$.~~

We further explored data using the difference (or anomaly) between observed data and data predicted from conservative mixing models, noted Δ (Fig. ~~7~~8). Negative $\Delta\delta^{13}$C-DIC values were correlated to those of ΔO_2 and ΔDIC, in particular in the side channels, as expected from production of CO_2 and consumption of O_2 due to degradation of organic matter. In October 2004, distinct positive $\Delta\delta^{13}$C-DIC were associated to positive ΔO_2 and negative ΔDIC in the Ham Luong and Co Chien resulting from high phytoplankton production in the most off-shore waters, as mentioned in the previous section. The relation between positive ΔDIC and negative ΔO_2 in the side channels also indicates that degradation organic matter, while negative ΔDIC and positive ΔO_2 indicate in October 2004 in the Ham Luong and Co Chien confirm the occurrence of high phytoplankton production in the most off-shore waters. The slope of the linear regression of ΔDIC as a function of ΔO_2 in the side channels ranged from 3.4 to 4.4. These values are distinctly higher than those expected from the degradation of organic matter following the Redfield stoichiometry ($\Delta DIC:\Delta O_2$ = 106:138 = 0.8). The slope of the relation between ΔDIC and ΔO_2 in October 2004 in the Ham Luong and Co Chien (1.4) was lower than in the side channels but still higher than the one predicted from Redfield stoichiometry. One possible explanation is that the change of concentration due to the exchange of gases with atmosphere (equilibration) is faster for O_2 than CO_2 due to the effect on the latter of buffer capacity of seawater. Another explanation that could explain the distinctly higher $\Delta DIC:\Delta O_2$ ratio in the side channels relates to anaerobic organic matter degradation in sediments that seems higher compared to estuarine channels as also suggested by higher CH_4 concentrations. The relative change of TA and DIC can be used to identify the processes involved in the generation of these quantities (for example Borges et al., 2003). The theoretical relative change of ΔTA *versus* ΔDIC was derived from the stoichiometry of biogeochemical reactions, based on Brewer and Goldman (1976) for aerobic respiration, on Smith and Key (1975) for $CaCO_3$ dissolution, and on Froelich et al. (1979) for anaerobic reactions. The slope of the linear regression of ΔTA *versus* ΔDIC ranged between 0.55 and 0.87. Such values might have resulted from a combination of aerobic organic matter degradation ($\Delta TA:\Delta DIC$ = -0.2) and dissolution of $CaCO_3$ (or $CaMg(CO_3)_2$) ($\Delta TA:\Delta DIC$ = 2.0). Accordingly, the calculated values of relative changes of ΔTA *versus* ΔDIC would require that $CaCO_3$ dissolution corresponded to 34 and 48% of aerobic organic matter degradation, respectively. Such a large $CaCO_3$ dissolution is very unlikely in

the Mekong delta because Ca^{2+} and Mg^{2+} showed conservative mixing as a function of salinity (Fig. S3), and because particulate inorganic carbon (PIC) is relatively low in the Mekong delta compared to POC. The %PIC of TSM (~0.1%) reported by Huang et al. (2017) is one order of magnitude lower than the %POC of TSM (1-8%) we report (Fig. 6). The values of the slope of the linear regression of ΔTA *versus* ΔDIC (range 0.55-0.87) were intermediary between the theoretical slopes for aerobic organic matter degradation (ΔTA:ΔDIC = -0.2) and sulfate-reduction (ΔTA:ΔDIC = 0.9), suggesting that TA and DIC were produced from the combination of these two processes. Such scenario is very likely, sulfate-reduction dominating in the sediments, and aerobic respiration dominating in the water column. Our data does not allow to determine~~,~~ whether these processes mainly occurred in the side channels or in the shrimp farming ponds themselves, although Alongi et al. (1999b) showed a strong dominance of aerobic respiration over other diagenetic degradation processes in sediments of shrimp ponds in Cau Mau Province. This would then allow to suggest that sulfate-reduction was mostly occurring within the side channels. The ΔTA:ΔDIC slope from the side channels correlated negatively to average salinity (Fig. ~~8~~9) which is counter-intuitive since a higher contribution of sulfate-reduction (ΔTA:ΔDIC ratio closer to 0.9) would have been expected at higher salinity (e.g. Borges and Abril 2011). This pattern might result from a higher aerobic respiration in the water column of the side channels during the periods of low water (higher salinity), and/or a lower signal from sulfate-reduction occurring within the shrimp farming ponds. ~~This~~ The former scenario is consistent with the negative correlation between ΔO_2 and salinity (Fig. ~~8~~9). ~~This could be due to higher exchange of water between the shrimp ponds and the adjacent channels during the low water (dry season) period.~~

3.3. Comparison with the Ca Mau mangrove creeks

The Ca Mau peninsula accounts for the largest proportion of remaining mangrove forests in the Mekong Delta system. Data were gathered in two mangrove creek networks (Tam Giang and Kiên Vàng) allowing the comparison with data in the three estuarine channels of the Mekong delta (My Tho, Ham Luong and Co Chien) and associated side channels (hereafter referred to as Bến Tre Mekong delta, based on the name of the Province), where the bordering mangroves forests have been

cleared for the implementation of shrimp farming ponds. Data comparison is limited to the April and October 2004 cruises (Fig. ~~9~~10). pCO_2 was negatively related to $\%O_2$ in Ca Mau creeks and the Bến Tre Mekong delta owing to organic matter degradation as confirmed by the positive relation between $\Delta\delta^{13}$C-DIC and $\%O_2$. ~~However, d~~Data in the Ca Mau mangrove creeks allowed to expand the range of variations of pCO_2, $\%O_2$ and δ^{13}C-DIC; the maximum pCO_2 value in the Ca Mau mangrove creeks was 6,912 ppm compared to 2,926 ppm in the Bến Tre Mekong delta; the minimum $\%O_2$ and δ^{13}C-DIC were, respectively, 37% and -14.6‰ in the Ca Mau mangrove creeks compared to 66% and -11.4‰ Bến Tre Mekong delta. As previously noted by Borges and Abril (2011), the spatial variations of pCO_2 and $\%O_2$ in the Ca Mau mangrove creeks were related to the size of the creeks, the narrower and presumably shallower creeks being characterized by higher pCO_2 and lower $\%O_2$ and δ^{13}C-DIC values. ~~As previous noted by Koné and Borges (2008), there were no significant seasonal variations of $\%O_2$ and pCO_2 in the Ca Mau mangroves creeks, despite the fact that s~~Salinity was highly variable among the two sampling cruises (Fig. 11), on average 33.2 in April 2004 and 14.1 in October 2004 (MW test $p<0.0001$), following the hydrological cycle (Fig. 2). The seasonal variations of CH_4 ~~on the other hand~~ were also very marked (MW test $p<0.0001$), with much lower values in April 2004 (range 4-46 nmol L^{-1}, average 19 nmol L^{-1}) than in October 2004 (range 19-686 nmol L^{-1}, average 210 nmol L^{-1}). This is probably related to the salinity seasonal changes, the lowest CH_4 values corresponding to the highest salinities. We hypothesize that the increase of salinity leads to an increase of benthic sulfate-reduction due to the increase of SO_4^{2-} availability, and a decrease of the transfer of CH_4 from sediments to the water column due to a partial inhibition of methanogenesis and/or an enhancement of anaerobic CH_4 oxidation. Such a hypothesis is consistent with the negative relationship in mangroves between sediment-air CH_4 fluxes and salinity (Borges and Abril 2011). The pCO_2 was higher and $\%O_2$ was lower in October than April 2004, although the differences are not as dramatic as for CH_4, albeit statistically significant (Fig. 11). This could indicate the occurrence during the rainy season (October) of the input of high CO_2 and low O_2 waters or additional organic matter (that fuelled remineralisation) from freshwater (surface runoff).- In October 2004, the CH_4 concentrations in the Ca Mau mangroves were generally higher than in the Bến Tre Mekong delta three main channels, yet, the highest CH_4 concentrations were recorded in the side channels of the Bến Tre Mekong delta, most probably resulting

from intense methanogenesis fuelled by high organic matter loads from the shrimp farming ponds.

3.4. CO_2 and CH_4 emissions to the atmosphere

As expected from the distribution of pCO_2, the FCO_2 values were higher in the inner estuarine branches (My Tho, Ham Luong, Co Chien) than in the outer estuary (river plume) and the side channels (Table 1). In addition, wind speed was lower in the side channels and mangrove creeks than in the more open waters of the inner and outer estuary. Although the pCO_2 in the side channels was higher than in the adjacent inner estuarine branches at similar salinities (Fig. ~~5~~6), the overall pCO_2 within the inner estuarine branches was higher, owing to high values in the upper estuary. Despite some variations in wind speed among the cruises, ~~The~~ the seasonal variations of FCO_2 in the inner estuarine branches followed the hydrological seasonal cycle, with the highest FCO_2 values in October 2004 during high water and the lowest FCO_2 values in April 2004 during low water (Table 1). The FCO_2 in the inner estuarine branches were well correlated to freshwater discharge (Fig. ~~10~~12). This indicates that the FCO_2 seasonal variations are related to the riverine inputs either directly as CO_2 or as organic matter that can be degraded within the estuary. During our cruises seasonal variations in water temperature were weak (range 26.7-31.5°C, on average 29.2°C), owing to the sub-tropical climate, consequently marked seasonality of pCO_2 and FCO_2 due to modulation of biological activity by water temperature does not occur unlike in temperate estuaries (for example Frankignoulle et al., 1998). The potential contribution of riverine organic carbon and CO_2 inputs in sustaining estuarine FCO_2 was computed from freshwater discharge multiplied by POC and excess DIC (EDIC), respectively (EDIC is computed as the difference between observed DIC and DIC computed from TA and the atmospheric pCO_2 value, Abril et al., 2000). The average for the three cruises of riverine input of POC (60×10^6 mol d^{-1}) and EDIC (53×10^6 mol d^{-1}) exceeded FCO_2 in the three estuarine branches (53×10^6 mol d^{-1}), showing that these inputs were sufficient to sustain the CO_2 emissions from the estuary, and that part of the riverine POC and EDIC is transported to the outer estuary (river plume). FCO_2 in the side channels and outer estuary (or river plume) showed a less significant correlation with water discharge (Fig. ~~10~~12), because other processes than riverine inputs control CO_2 dynamics in

these systems such as the inputs of carbon from the shrimp farming ponds for side channels, and primary production for the outer estuary. A phytoplankton bloom in the river plume in October 2004 explains why FCO_2 values were equivalent to those in December 2003, although freshwater discharge was about two times lower.

Differences of FCH_4 among the two 2004 cruises were very marked, with values in inner estuarine branches more than four times higher in October than April 2004 (MW test $p<0.0001$). In April 2004, the FCH_4 values in the side channels of the Bến Tre Mekong delta were equivalent to those in the Ca Mau mangrove creeks, but were more than two times higher in October 2004.

The average FCO_2 in the inner estuarine branches of the Mekong delta (118 mmol m^{-2} d^{-1}) is higher than in the Pearl River inner estuary (46 mmol m^{-2} d^{-1}, Guo et al., 2009) and the Yangtze River inner estuary (41 mmol m^{-2} d^{-1}, Zhai et al., 2007), the two other major river systems bordering the East China Sea that have been documented for CO_2 dynamics. The higher value in the Mekong is probably related to the dominance of freshwater in the inner estuary and low salinity intrusion within the estuary, related to the geomorphology (relatively narrow and linear estuarine channels, compared to the typical “funnel” shape estuarine morphology in the Yangtze and Pearl River estuaries). Indeed, the average salinity in the Pearl River inner estuary was 17 (Guo et al., 2009), higher than the average salinity of 4 in the Mekong inner estuarine branches during our cruises. The average FCO_2 in the Ca Mau mangrove creeks (89 ~~μmol~~ mmol m^{-2} d^{-1}) was well within the range (-8-862 ~~μmol~~ mmol m^{-2} d^{-1}) and close to the average (63 ~~μmol~~ mmol m^{-2} d^{-1}) of CO_2 fluxes in mangrove estuarine creeks compiled globally by ~~Call et al. (2015)~~Rosentreter et al. (2018).

The FCH_4 seasonal variations within a given estuary and the FCH_4 variations from one estuary to another are notoriously large, so comparison of the FCH_4 in the Mekong delta with previously published studies is uneasy. The average FCH_4 value in the inner estuarine branches of the Mekong delta (118 μmol m^{-2} d^{-1}) is within the range of values in European estuaries (17-1,352 μmol m^{-2} d^{-1}) compiled by Upstill-Goddard and Barnes (2016), but distinctly higher than the range of values for Indian estuaries (7-15 μmol m^{-2} d^{-1}) reported by Rao and Sarma (2016). The FCH_4 in the Yangtze ~~River~~ and Pearl River ~~estuary~~ estuaries reported by Zhang et al. (2008) and Zhou et al. (2009) of 61 and 64 μmol m^{-2} d^{-1}~~,~~, respectively, ~~is~~ are also higher than the range of FCH_4 in Indian estuaries. The FCH_4 in the Mekong delta inner estuarine

branches was higher than the value in the Yangtze River and Pearl River ~~estuary~~ estuaries probably because of the lower salinity intrusion into the Mekong delta (see above). The average FCH_4 in the Ca Mau mangrove creeks (160 µmol m^{-2} d^{-1}) was well within the range (9-409 µmol m^{-2} d^{-1}) and close to the average (283 µmol m^{-2} d^{-1}) of CH_4 fluxes in mangrove estuarine creeks compiled globally by Call et al. (2015).

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Author contribution. AVB designed the experiment and carried out sample collection in the field. AVB, SB and GA analysed the samples, interpreted the data, and drafted the manuscript.

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Table 1: Average ± standard deviation of air-water fluxes of CO_2 (FCO_2 in mmol m^{-2} d^{-1}) and CH_4 (FCH_4 in µmol m^{-2} d^{-1}), and wind speed (m s^{-1}) in December 2003, April 2004 and October 2004, in the three inner estuarine branches of the Mekong delta (My Tho, Ham Luong and Co Chien), respective river plume and side channels, and in Cau Mau province mangrove creeks.

	FCO_2 (mmol m^{-2} d^{-1})	FCH_4 (µmol m^{-2} d^{-1})	Wind speed (m s^{-1})
December 2003			
Inner estuarine branches (IEB)	122±33		
River plume (RB)	56±25		
IEB+RB	90±33		5.3±3.2
Side channels	85±45		4.6±3.6
April 2004			
Inner estuarine branches	105±64	43±14	
River plume	18±6	7±4	
IEB+RB	69±35	29±12	8.1±2.9
Side channels	37±31	19±17	5.1±1.3
Ca Mau mangrove creeks	61±68	22±17	3.5±3.5
October 2004			
Inner estuarine branches	135±73	193±162	
River plume	44±129	46±9	
IEB+RB	70±159	87±32	6.1±5.7
Side channels	88±19	701±890	3.8±3.0
Ca Mau mangrove creeks	116±78	298±224	3.9±2.6
Average of cruises			
Inner estuarine branches	121±57	118±68	
River plume	39±49	26±10	
IEB+RB	76±80	58±23	
Side channels	70±37	360±387	
Ca Mau mangrove creeks	89±79	160±121	

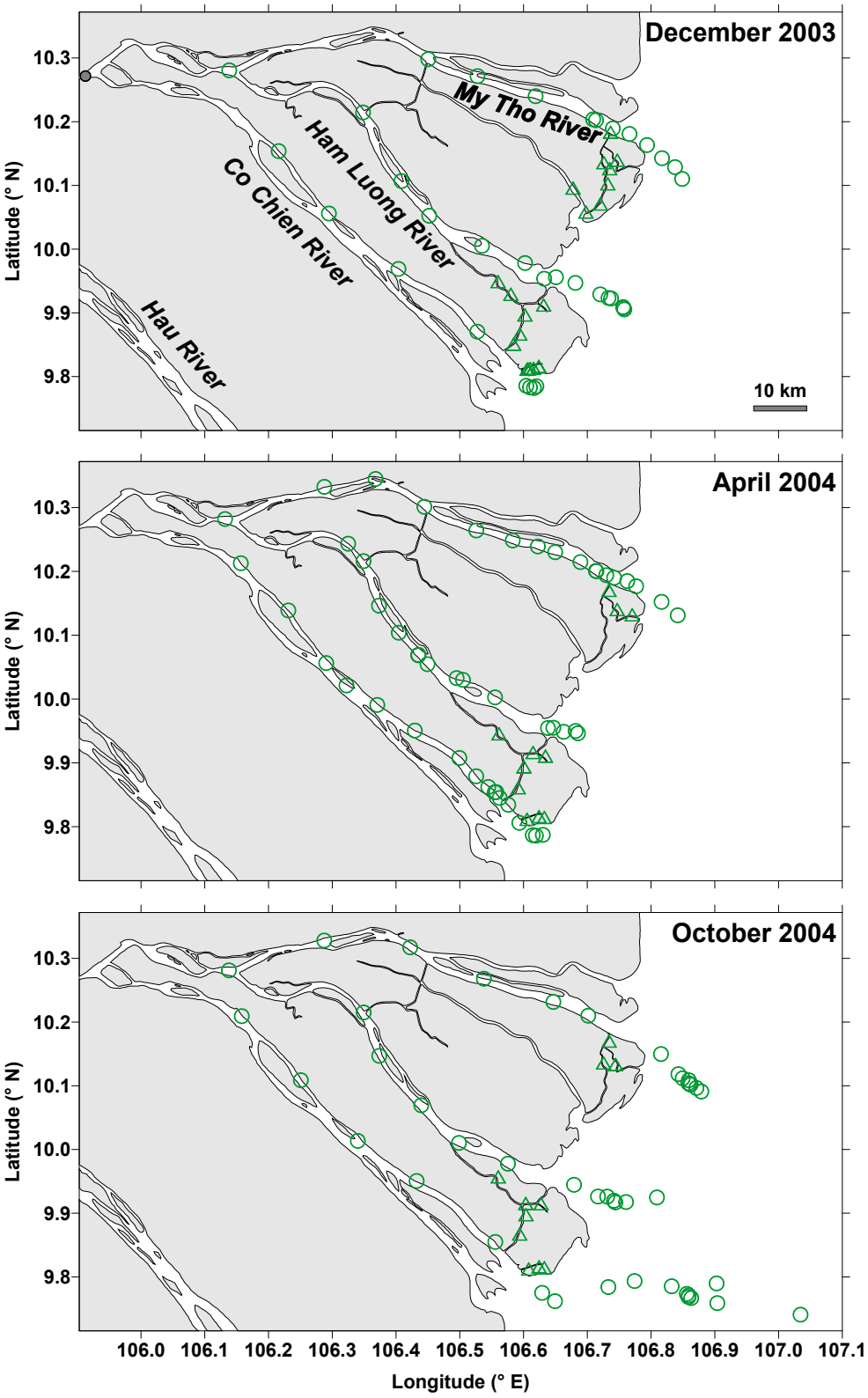

Fig.1 – Map of sampling stations in December 2003, April 2004 and October 2004, in the three inner estuarine branches of the Mekong delta (circles) (My Tho, Ham Luong and Co Chien) and side channels (triangles). Small grey dot indicates the location of the bridge across the river at the city of Vĩnh Long from which the distance downstream is calculated in Figure 3.

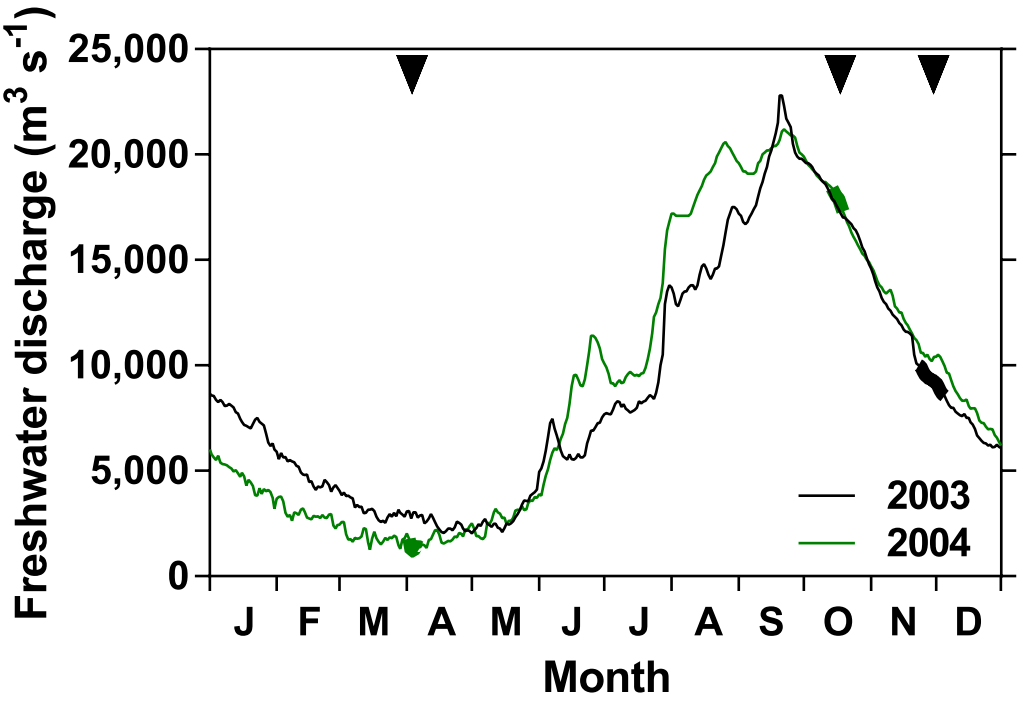

Fig. 2 – Seasonal evolution of daily freshwater discharge in the Mekong River at Tan Chau in 2003 and 2004. Thick lines and black triangles indicate the three sampling periods

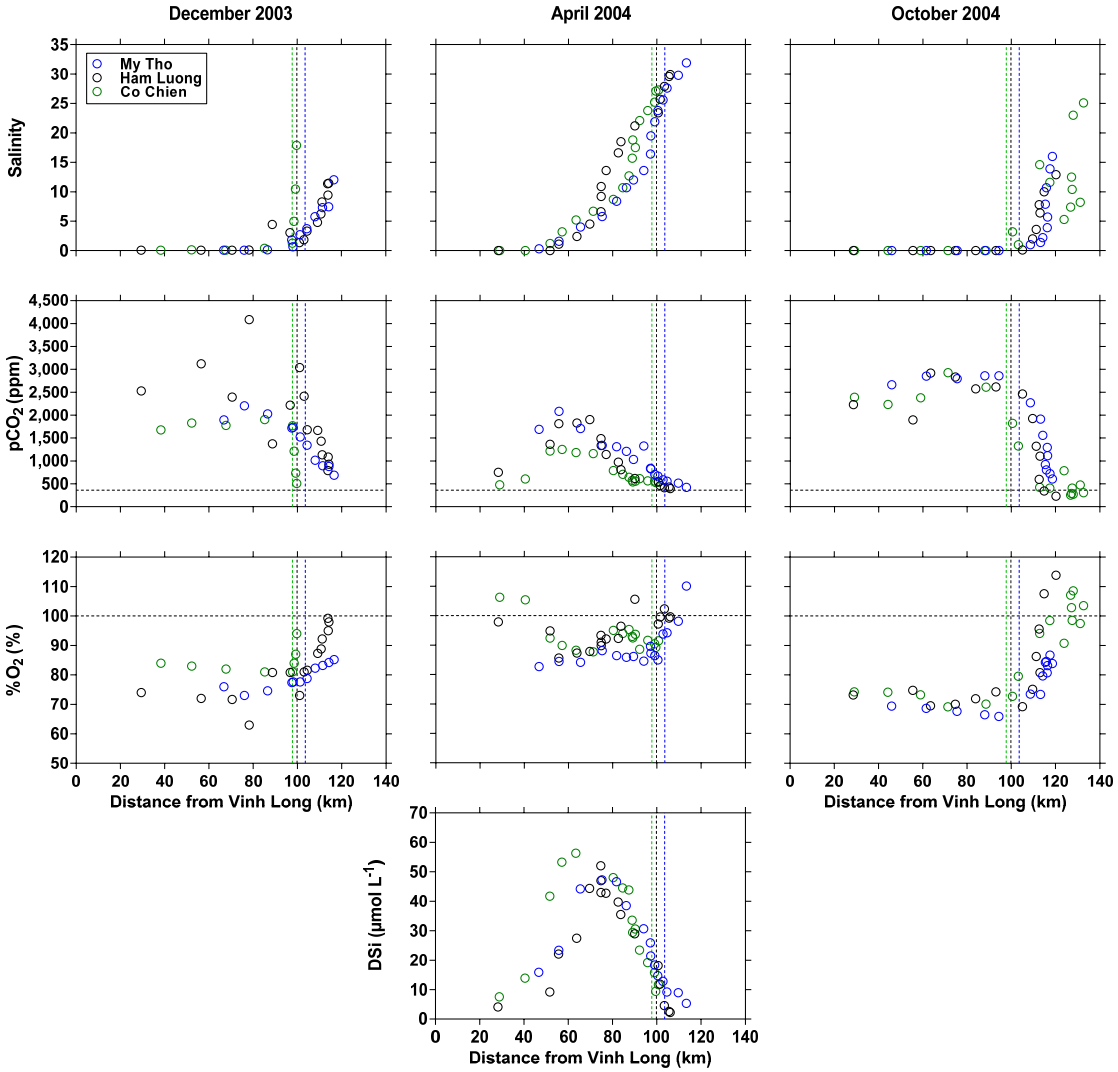

Fig. 3 – Distribution as a function of distance downstream of the city of Vĩnh Long of salinity, partial pressure of CO_2 (pCO_2 in ppm), oxygen saturation level ($\%O_2$ in %), and dissolved silica (DSi in µmol L^{-1}) in the three branches of the Mekong delta (My Tho, Ham Luong and Co Chien), in December 2003, April 2004 and October 2004. The vertical dotted lines indicate the location of the river mouths.

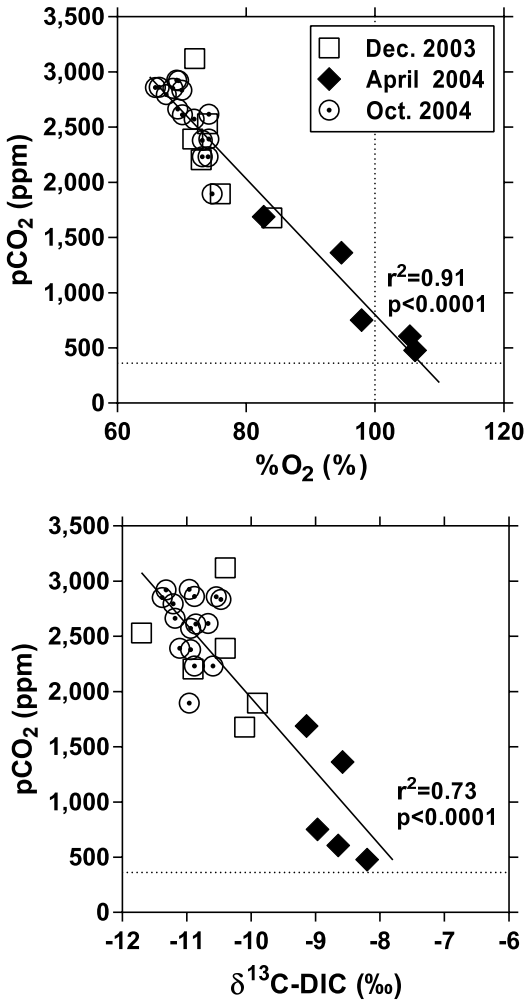

Fig. 4 - Variation of the partial pressure of CO_2 (pCO_2 in ppm) as a function of oxygen saturation level ($\%O_2$ in %) and stable isotope composition of dissolved inorganic carbon (δ^{13}C-DIC in ‰) in the freshwaters (salinity 0) of the three branches of the Mekong delta (My Tho, Ham Luong and Co Chien), in December (Dec.) 2003, April 2004 and October (Oct.) 2004. The vertical dotted line indicates O_2 saturation (100%), the horizontal line indicates the average atmospheric pCO_2 value

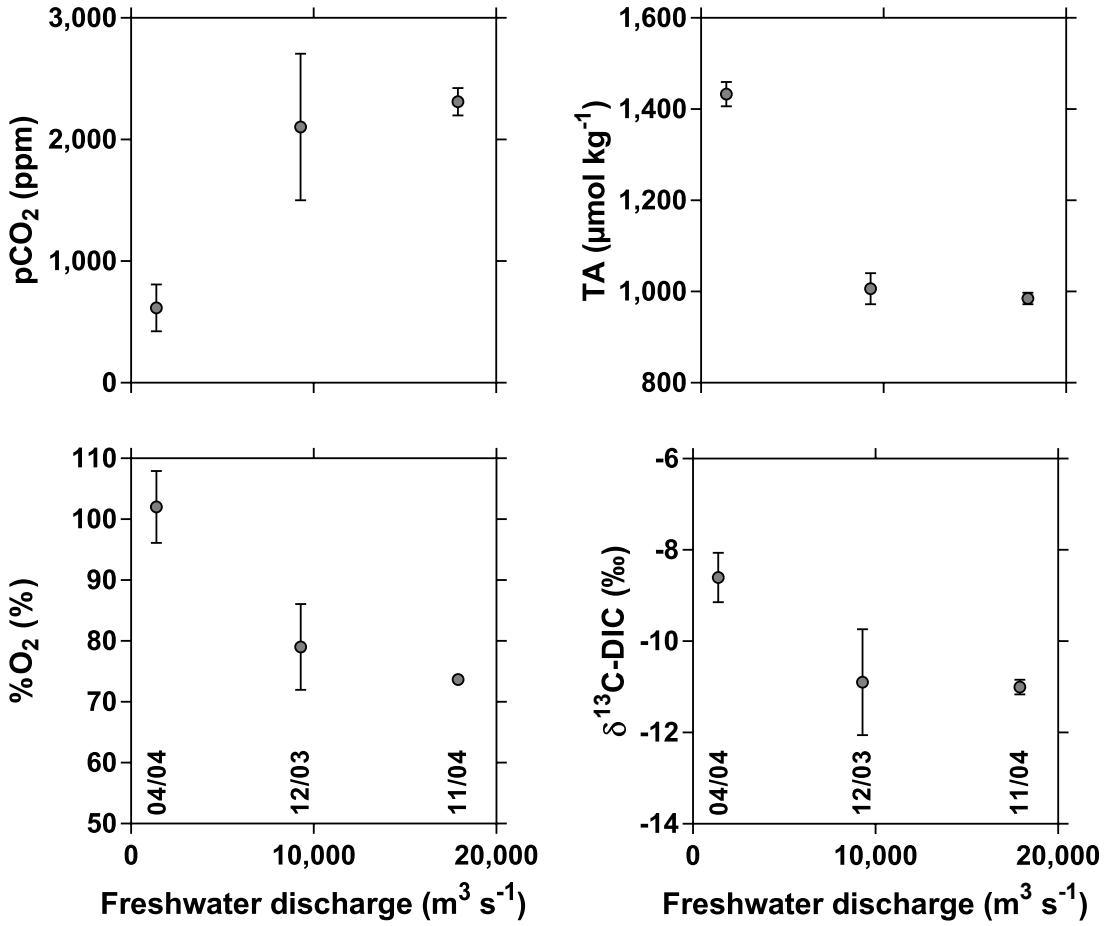

Fig. 54 – Variation as a function of freshwater discharge (m^3 s^{-1}) of the partial pressure of CO_2 (pCO_2 in ppm), oxygen saturation level ($\%O_2$ in %), total alkalinity (TA in µmol kg^{-1}) and stable isotope composition of dissolved inorganic carbon (δ^{13}C-DIC in ‰) in the freshwaters (salinity 0) of the three branches of the Mekong delta (My Tho, Ham Luong and Co Chien), in December 2003, April 2004 and October 2004. Sampling dates (MM/YY) are indicated in the bottom panels.

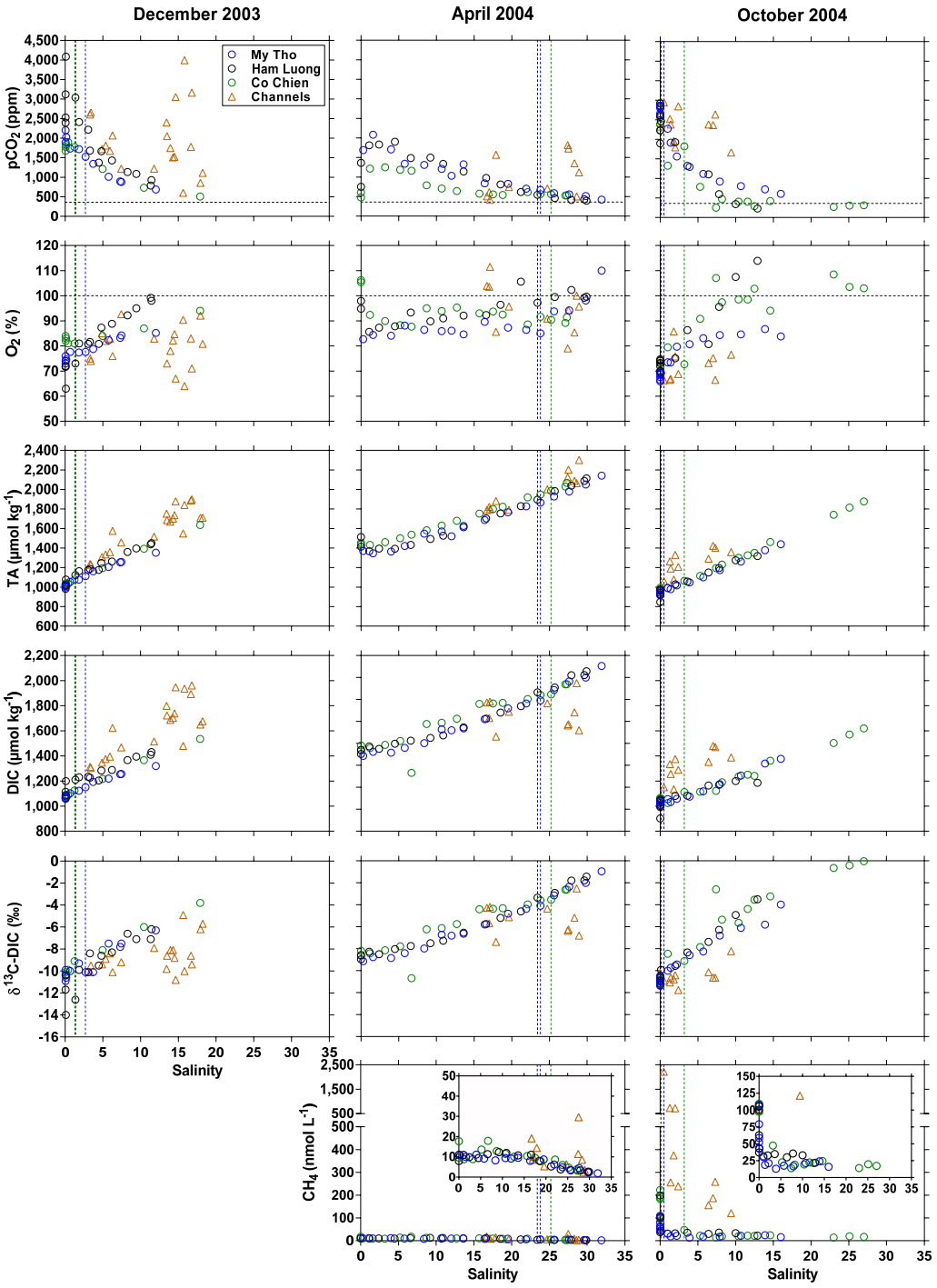

Fig. ~~65~~ - Distribution as a function of salinity of the partial pressure of CO_2 (pCO_2 in ppm), oxygen saturation level ($\%O_2$ in %), total alkalinity (TA in µmol kg^{-1}), dissolved inorganic carbon (DIC in µmol kg^{-1}), stable isotope composition of DIC (δ^{13}C-DIC in ‰), dissolved CH_4 concentration (nmol L^{-1}), total suspended matter (TSM in mg L^{-1}), particulate organic carbon (POC in mg L^{-1}), percent of POC in TSM (%POC in %), POC to particulate nitrogen ratio (POC:PN in mg:mg), stable isotope composition of POC (δ^{13}C-POC in ‰), dissolved organic carbon (DOC in mg L^{-1}), and stable isotope composition of DOC (δ^{13}C-DOC in ‰) in the three branches of the Mekong delta (My Tho, Ham Luong and Co Chien) and side channels, in December 2003, April 2004 and October 2004. The vertical dotted lines indicate the location of the river mouths. Horizontal dotted lines indicate the CO_2 and O_2 atmospheric equilibrium

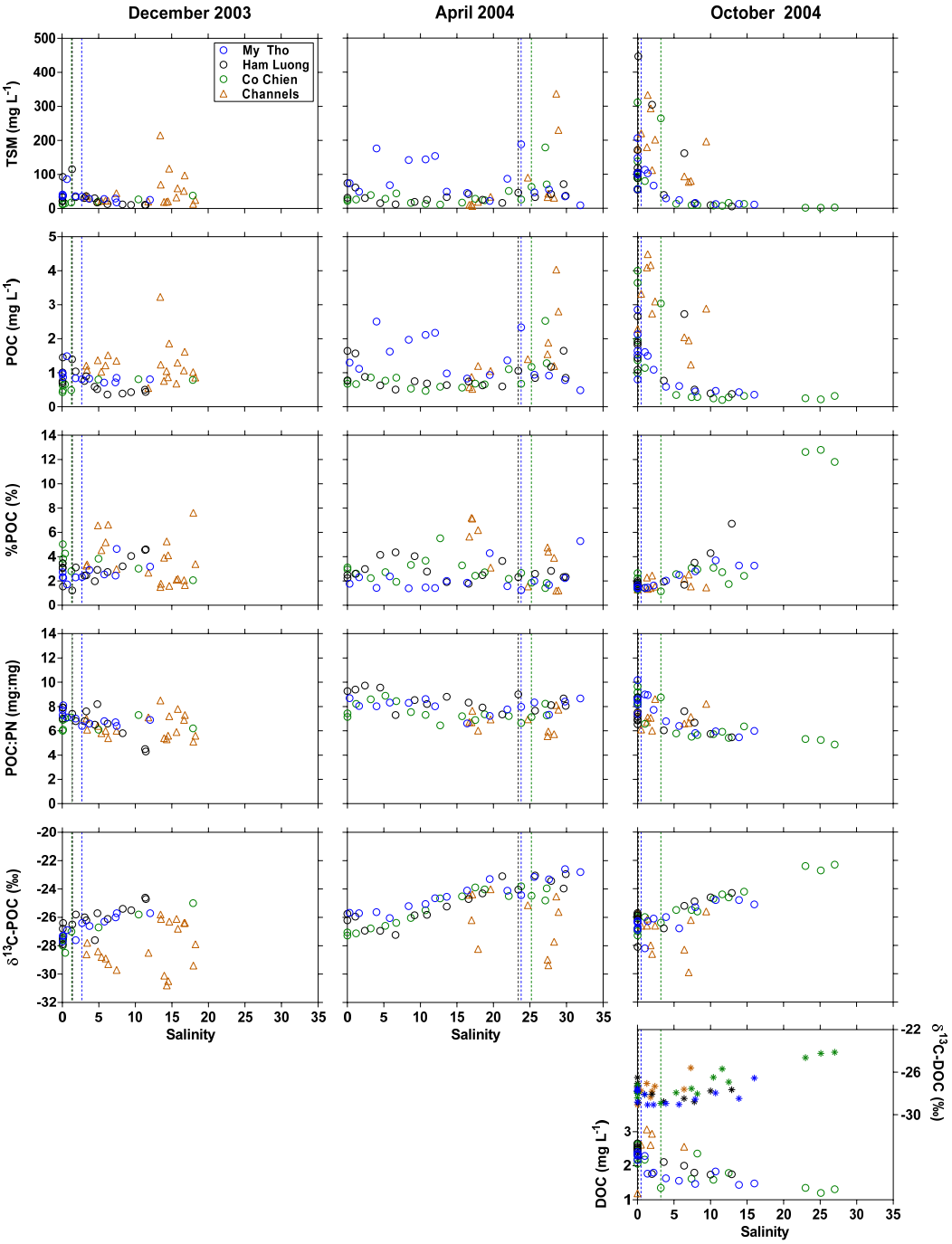

Fig. ~~65~~ (continued)

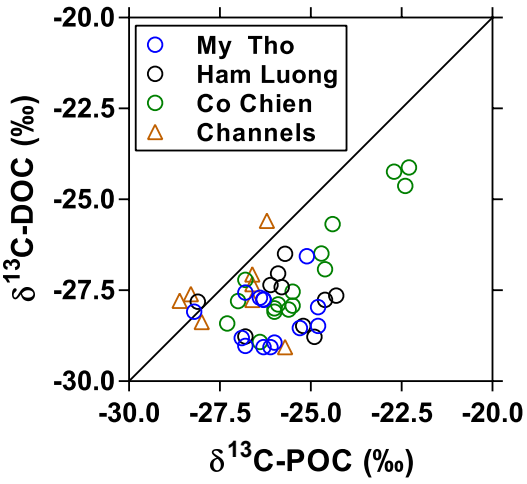

Fig. 76 .: Stable isotope composition of dissolved organic carbon (δ^{13}C-DOC in ‰) as a function of the stable isotope composition of particulate organic carbon (δ^{13}C-POC in ‰) in the three branches of the Mekong delta (My Tho, Ham Luong and Co Chien) and side channels, in October 2004. The solid line indicates the 1:1 line.

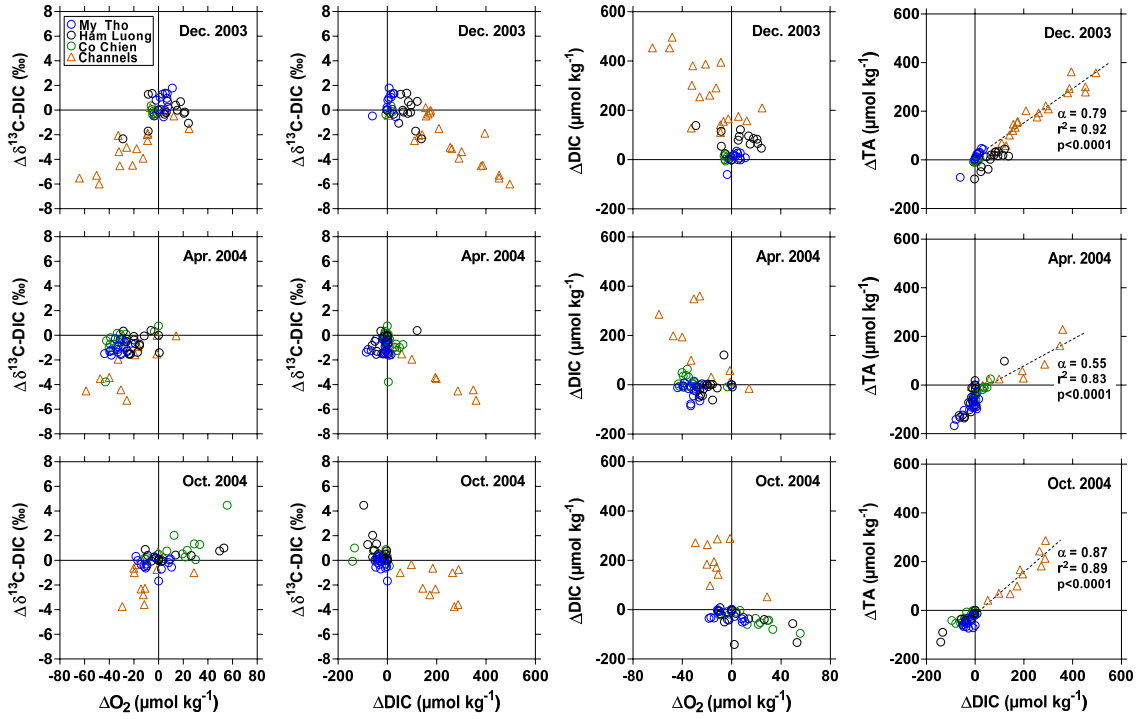

Fig. 8~~7~~ – Deviations from conservative mixing lines of stable isotope composition of dissolved inorganic carbon (DIC) ($\Delta\delta^{13}$C-DIC in ‰) as a function of O_2 (ΔO_2 in µmol kg^{-1}) and of DIC (ΔDIC in µmol kg^{-1}), of ΔDIC as a function of ΔO_2, and of total alkalinity (ΔTA in µmol kg^{-1}) as function of ΔDIC, in the three branches of the Mekong delta (My Tho, Ham Luong and Co Chien) and side channels, in December (Dec.) 2003, April (Apr.) 2004 and October (Oct.) 2004. α indicates the slope of the linear regression line (dotted line).

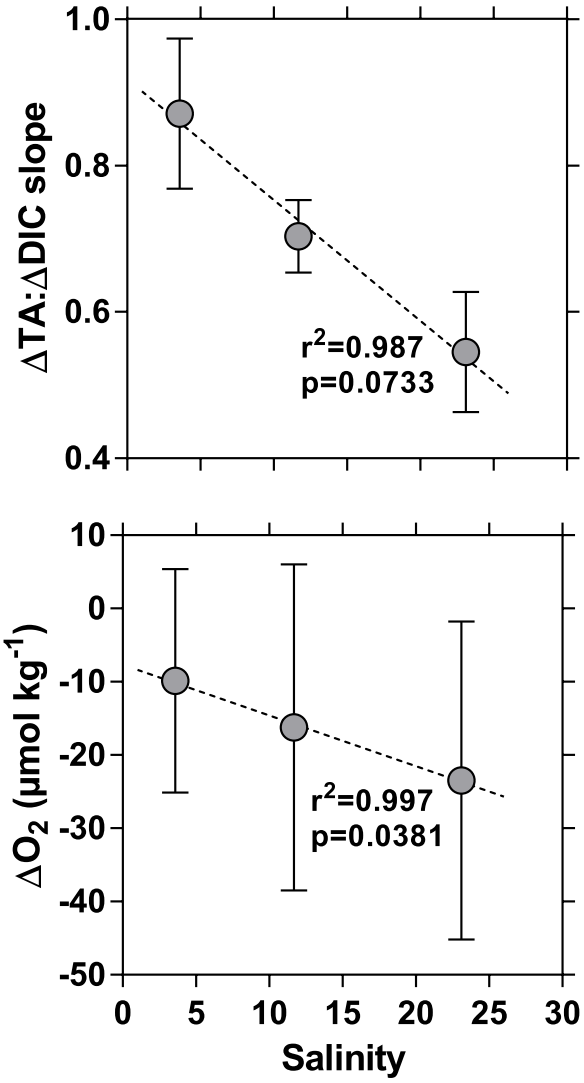

Fig. ~~98~~ – Variation as a function of salinity of the slope of regression line of the deviation from conservative mixing lines of total alkalinity (ΔTA in μmol kg^{-1}) and of dissolved inorganic carbon (ΔDIC in μmol kg^{-1}), of O_2 (ΔO_2 in μmol kg^{-1}) in the side channels of the Mekong delta in December 2003, April 2004 and October 2004. Dotted line indicates the linear regression. Error bars indicate standard deviation.

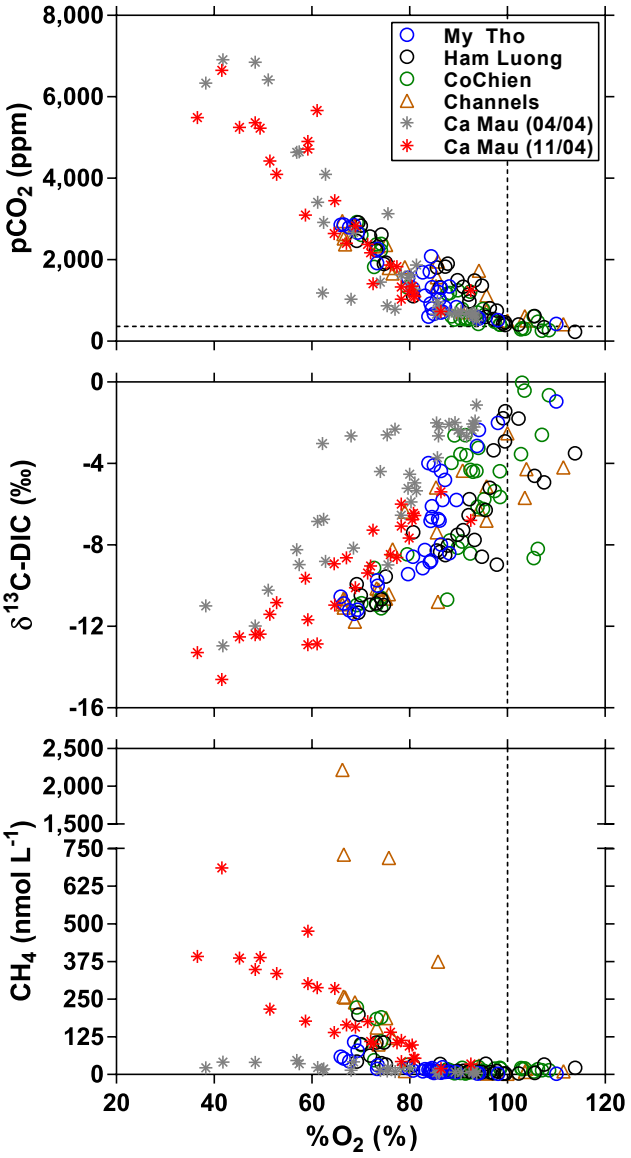

Fig. 10~~9~~ - Distribution as a function oxygen saturation level (%O_2 in %) of the partial pressure of CO_2 (pCO_2 in ppm), stable isotope composition of dissolved inorganic carbon (δ^{13}C-DIC in ‰), dissolved CH_4 concentration (nmol L^{-1}), in the three branches of the Mekong delta (My Tho, Ham Luong and Co Chien) and side channels, and in the mangrove creeks of the Ca Mau Province in April 2004 and October 2004. The vertical dotted line indicates O_2 saturation (100%), the horizontal line indicates the average atmospheric pCO_2 value.

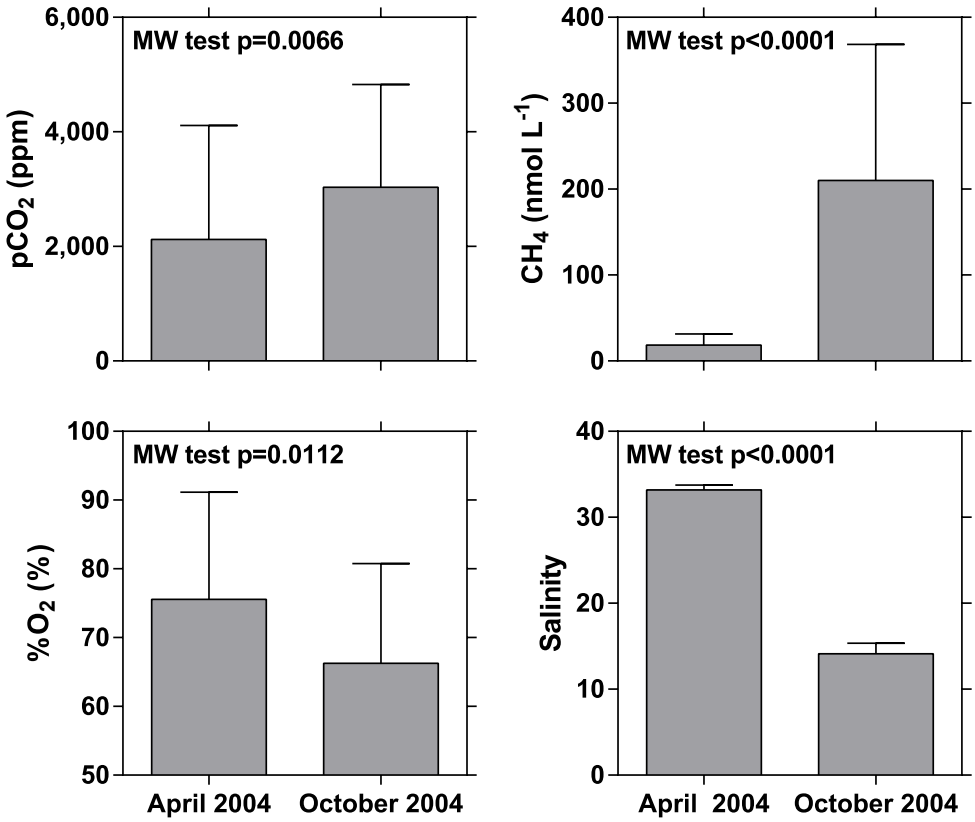

Fig. 11 – Average ± standard deviation of the partial pressure of CO_2 (pCO_2 in ppm), oxygen saturation level ($\%O_2$ in %), dissolved CH_4 concentration (nmol L^{-1}) and salinity in the mangrove creeks of the Ca Mau Province in April 2004 and October 2004. MW = Mann Whitney (at 0.05 level).

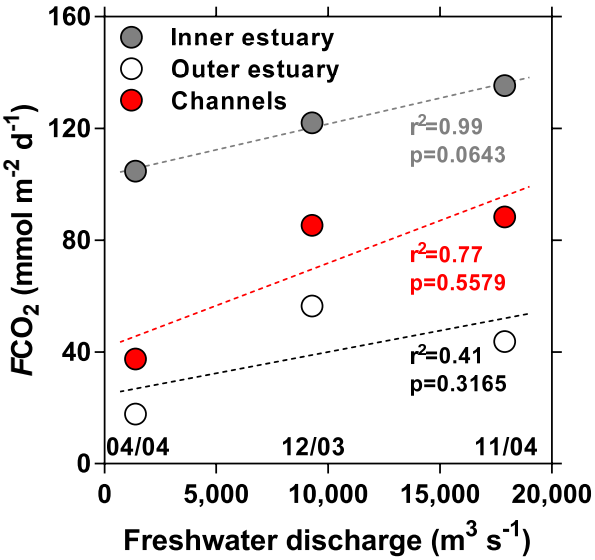

Fig. 120 – Average air-water CO_2 fluxes (FCO_2 in mmol m^{-2} d^{-1}) in the inner and outer estuary and side channels of the Mekong delta as function of freshwater discharge (m^3 s^{-1}), in December 2003, April 2004 and October 2004. Sampling dates (MM/YY) are indicated in the bottom of the panel. Dotted lines indicate the linear regression lines.

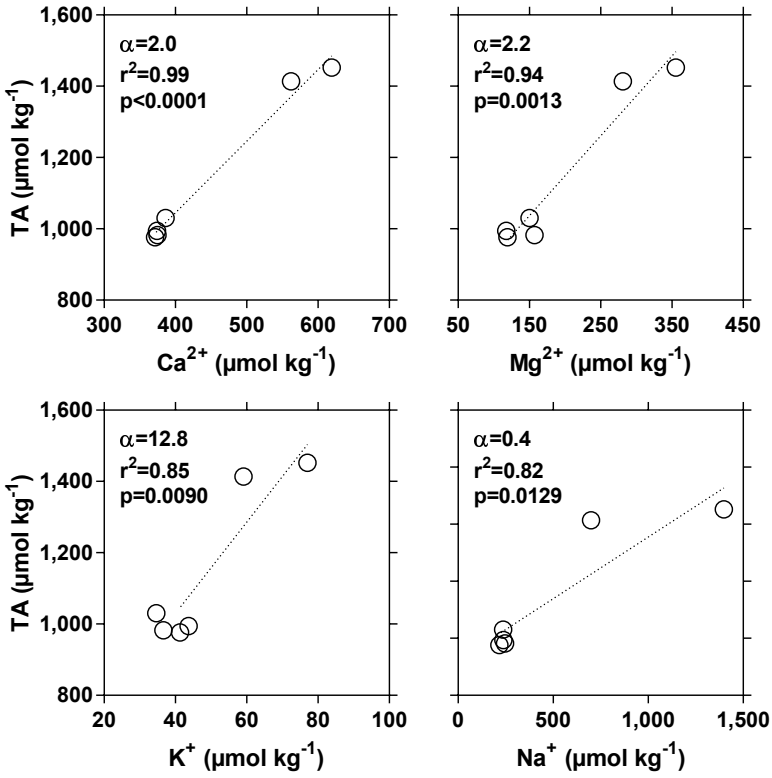

Figure S1 – Variations of total alkalinity (TA in µmol kg^{-1}) as a function of Ca^{2+}, Mg^{2+}, K^{+} and Na^{+} (all in µmol kg^{-1}) in the freshwaters (salinity 0) of the three branches of the Mekong delta (My Tho, Ham Luong and Co Chien), in December 2003, April 2004 and October 2004. α indicates the slope of the linear regression line (dotted line).

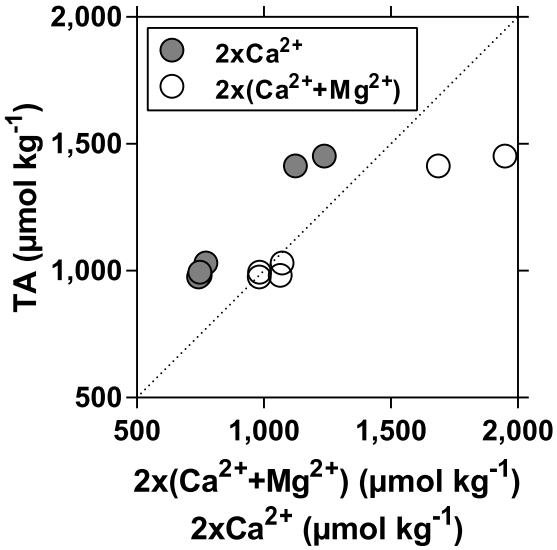

Fig. S2 - Variations of total alkalinity (TA in µmol kg^{-1}) as a function of 2 x Ca^{2+} and 2 x (Ca^{2+} + Mg^{2+}) (both in µmol kg^{-1}) in the freshwaters (salinity 0) of the three branches of the Mekong delta (My Tho, Ham Luong and Co Chien), in December 2003, April 2004 and October 2004. Dotted line indicates the 1:1 line. If TA was due exclusively to weathering of calcite $CaCO_3$ the data points would fall on the 1:1 line. Deviation from the 1:1 line indicate a contribution of weathering of dolomite ($MgCa(CO_3)_2$) to TA.

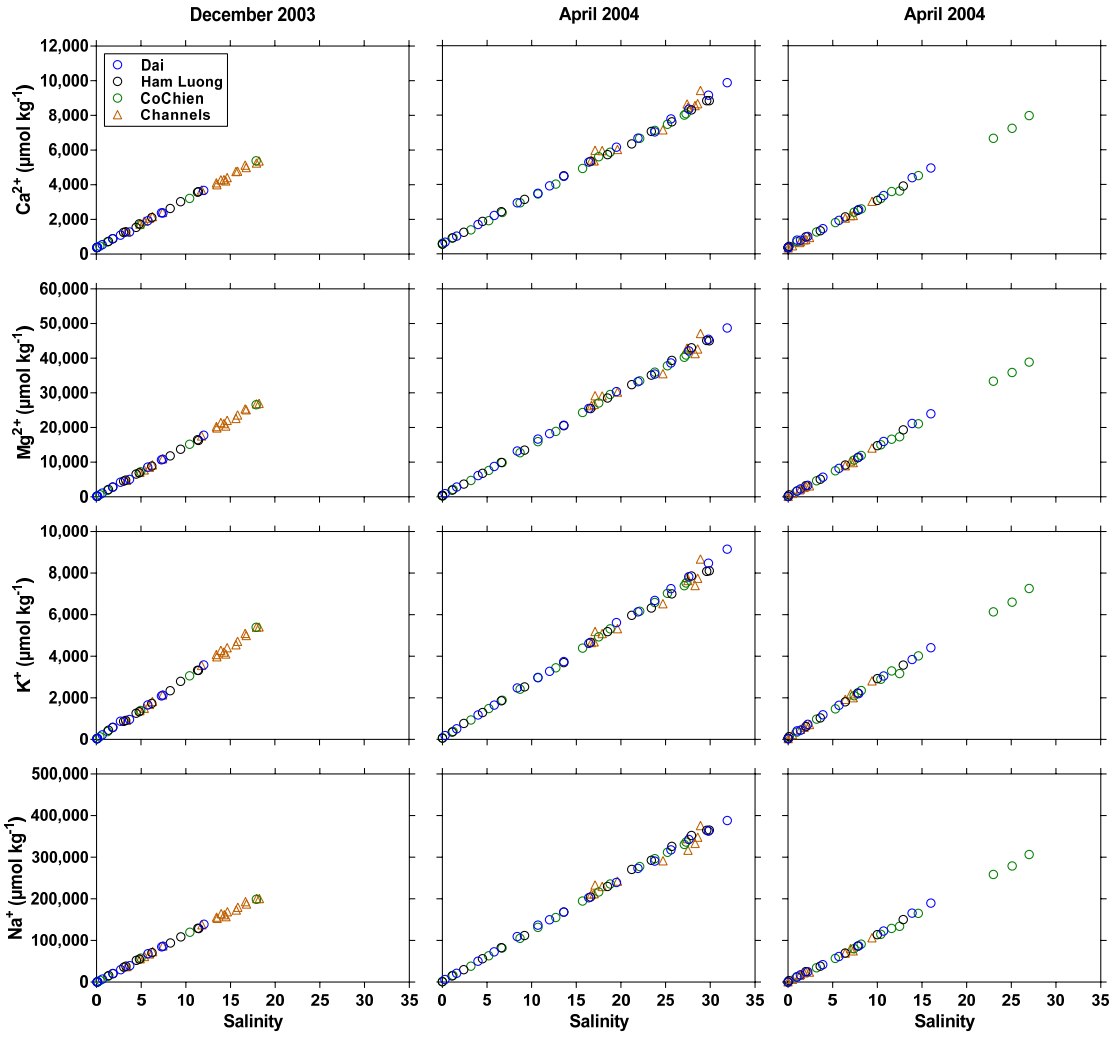

Fig. S3 - Distribution as a function of salinity of Ca^{2+}, Mg^{2+}, K^{+} and Na^{+} in the three branches of the Mekong delta (My Tho, Ham Luong and Co Chien) and side channels, in December 2003, April 2004 and October 2004.