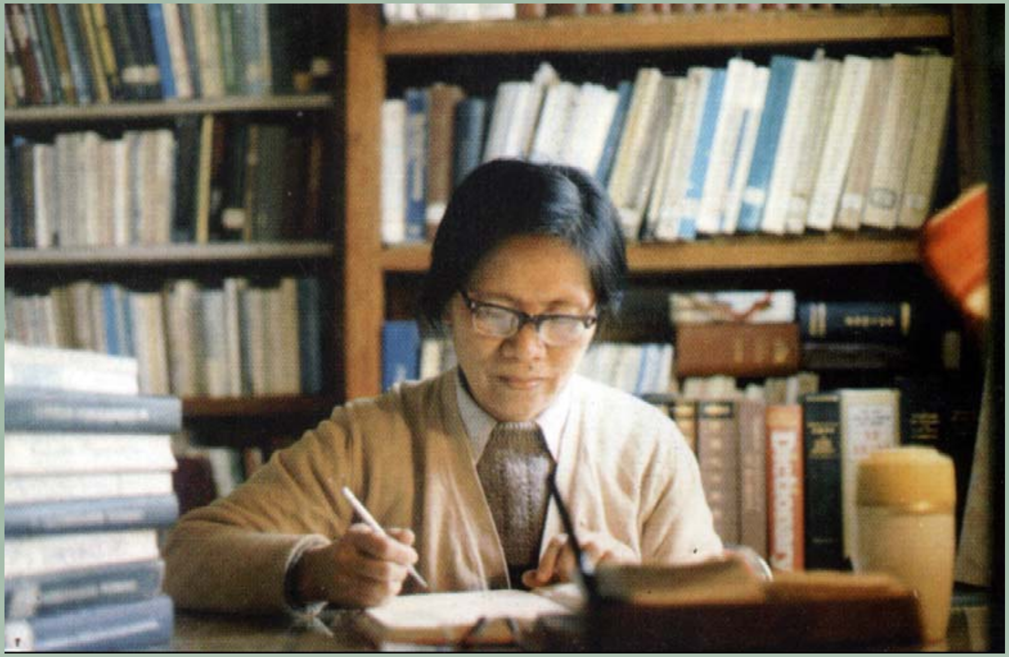
CO_2 Flux and Metabolism in Estuaries

Wei-Jun Cai

Dept. of Marine Sciences
The University of Georgia

10th International Conference on Estuarine Biogeochemistry
May 19-22, 2008
Xiamen University, Xiamen, China

Professor WU Yu-Duan
(1926-1995)



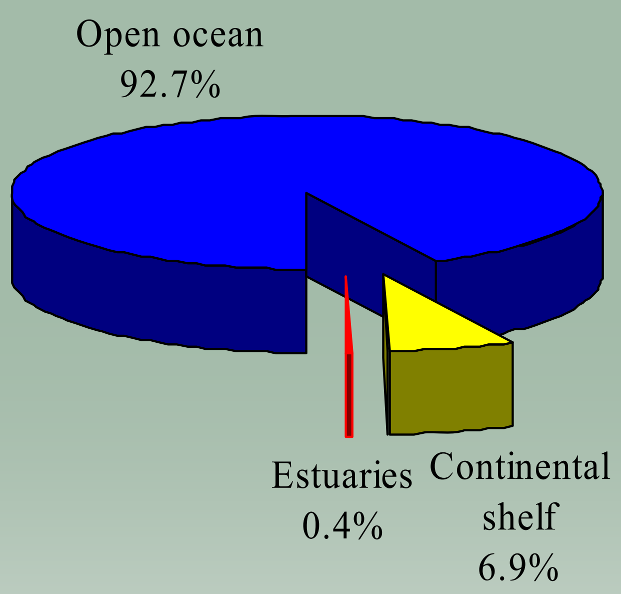
Wu, Y.-D. and W-J. Cai. 1983. Reduction of Cr(VI) by dissolved organics in estuarine water body. *Acta Scientiae Circumstantiae*, **3**:176-182 (in Chinese).

Outline

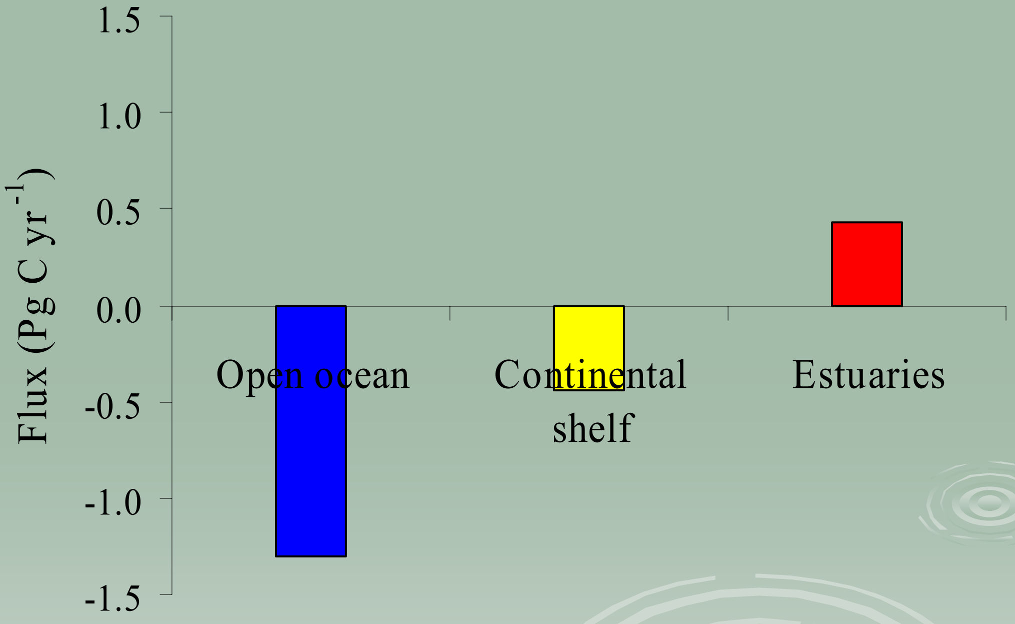
- Introduction
- CO_2 flux in river-dominated vs. marine dominated estuaries
- CO_2 in large river plumes
- Synthesis

Global estuaries are important sources of atmospheric CO_2

Surface area



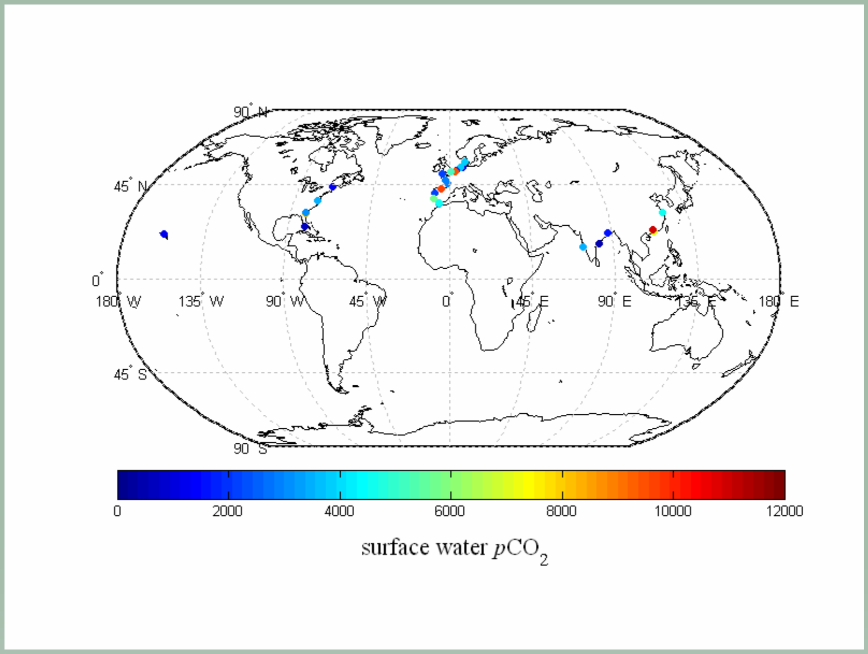
Air-water CO_2 fluxes

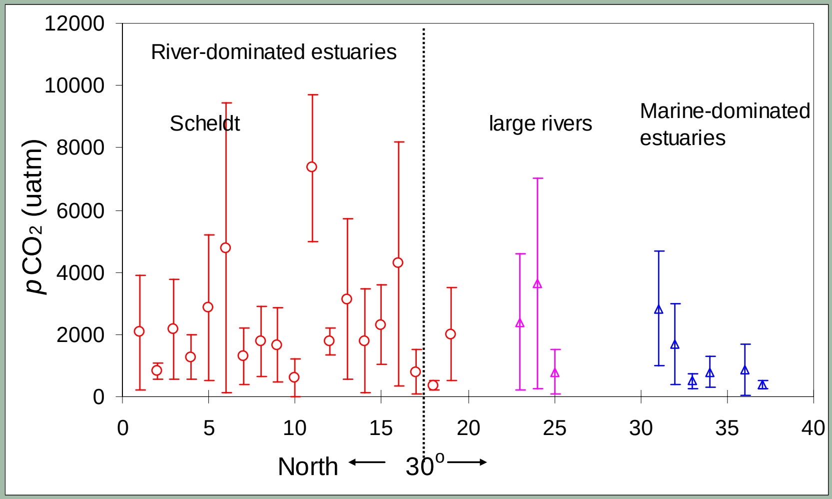


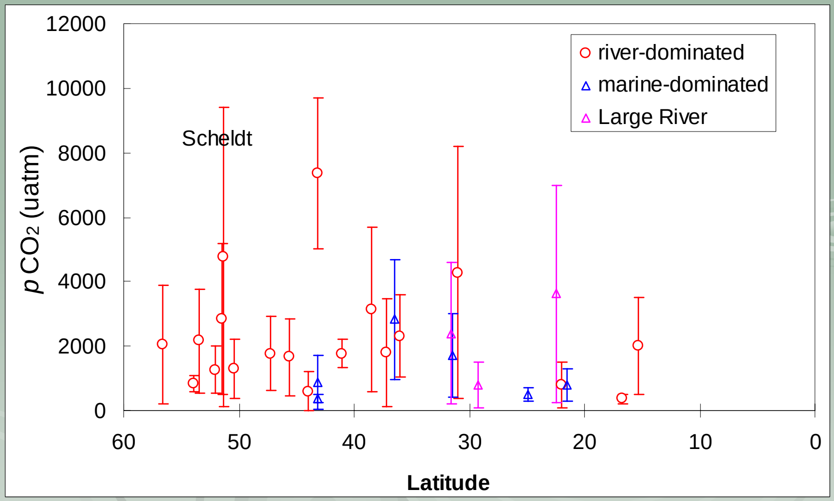
Takahashi et al. 2008

Borges et al. 2005
Cai et al. 2006

Global distribution of estuarine CO_2 research and pattern

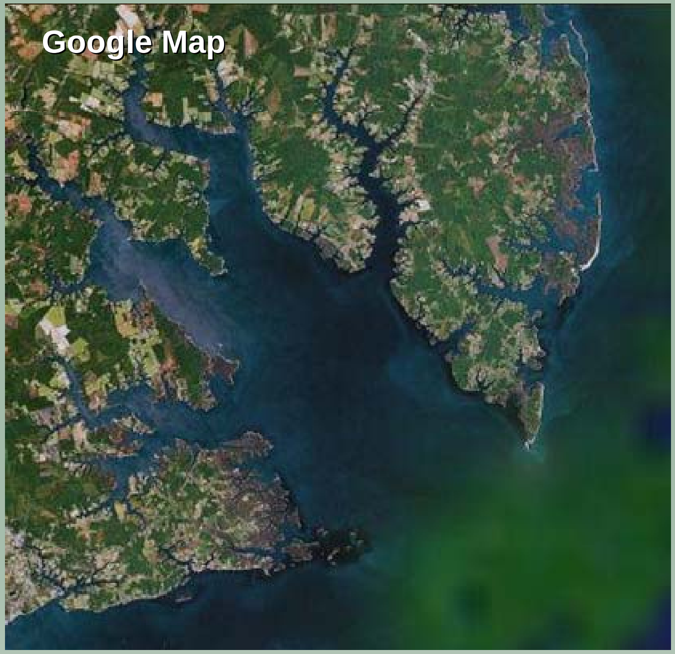


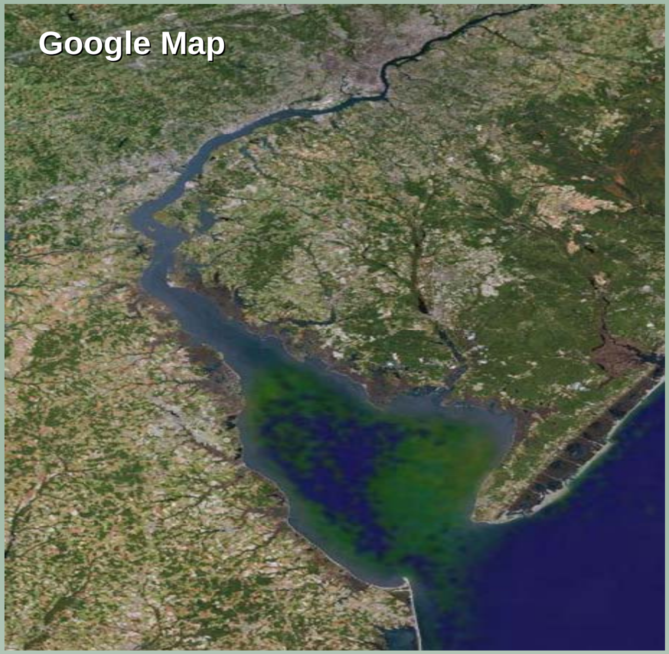




Updated based on data compiled by Borges et al. 2005

Global estuaries show a spectrum of freshwater influence





Marine-dominated estuaries

River-dominated estuaries

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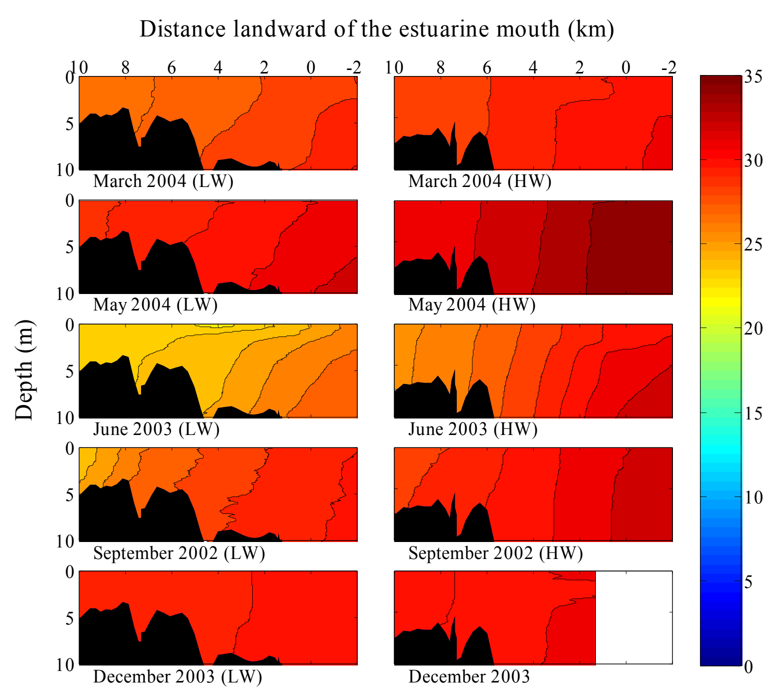
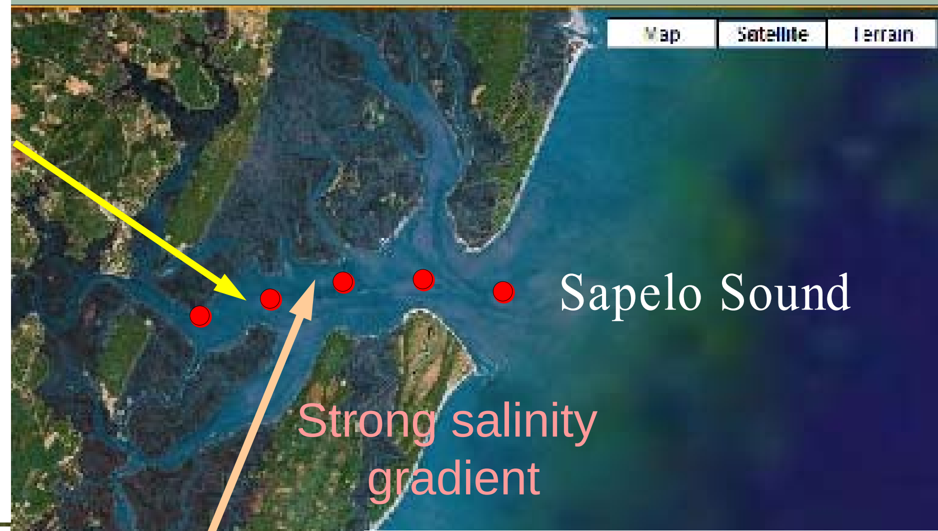
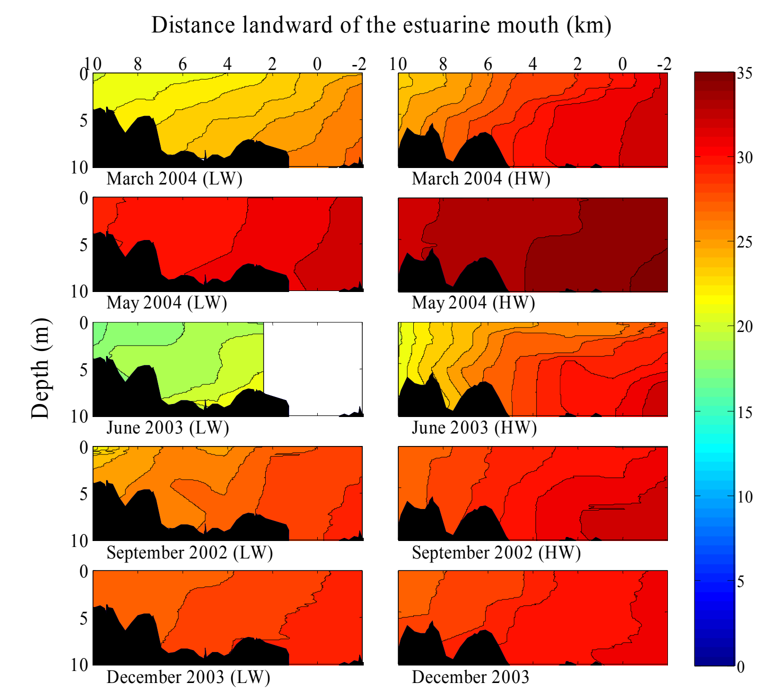


Distance landward of the estuarine mouth (km)
10 8 6 4 2 0 -2
Depth (m)
March 2004 (LW)
March 2004 (HW)
May 2004 (LW)
May 2004 (HW)
June 2003 (LW)
June 2003 (HW)
September 2002 (LW)
September 2002 (HW)
December 2003 (LW)
December 2003
35 30 25 20 15 10 5 0



Map
Satellite
Terrain
Sapelo Sound
Strong salinity gradient



Distance landward of the estuarine mouth (km)
10 8 6 4 2 0 -2
Depth (m)
March 2004 (LW)
March 2004 (HW)
May 2004 (LW)
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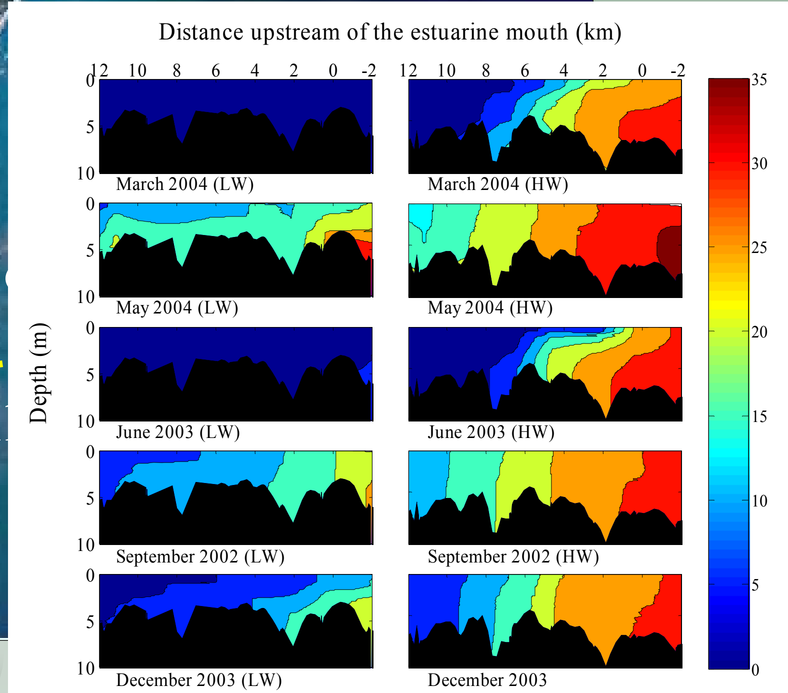
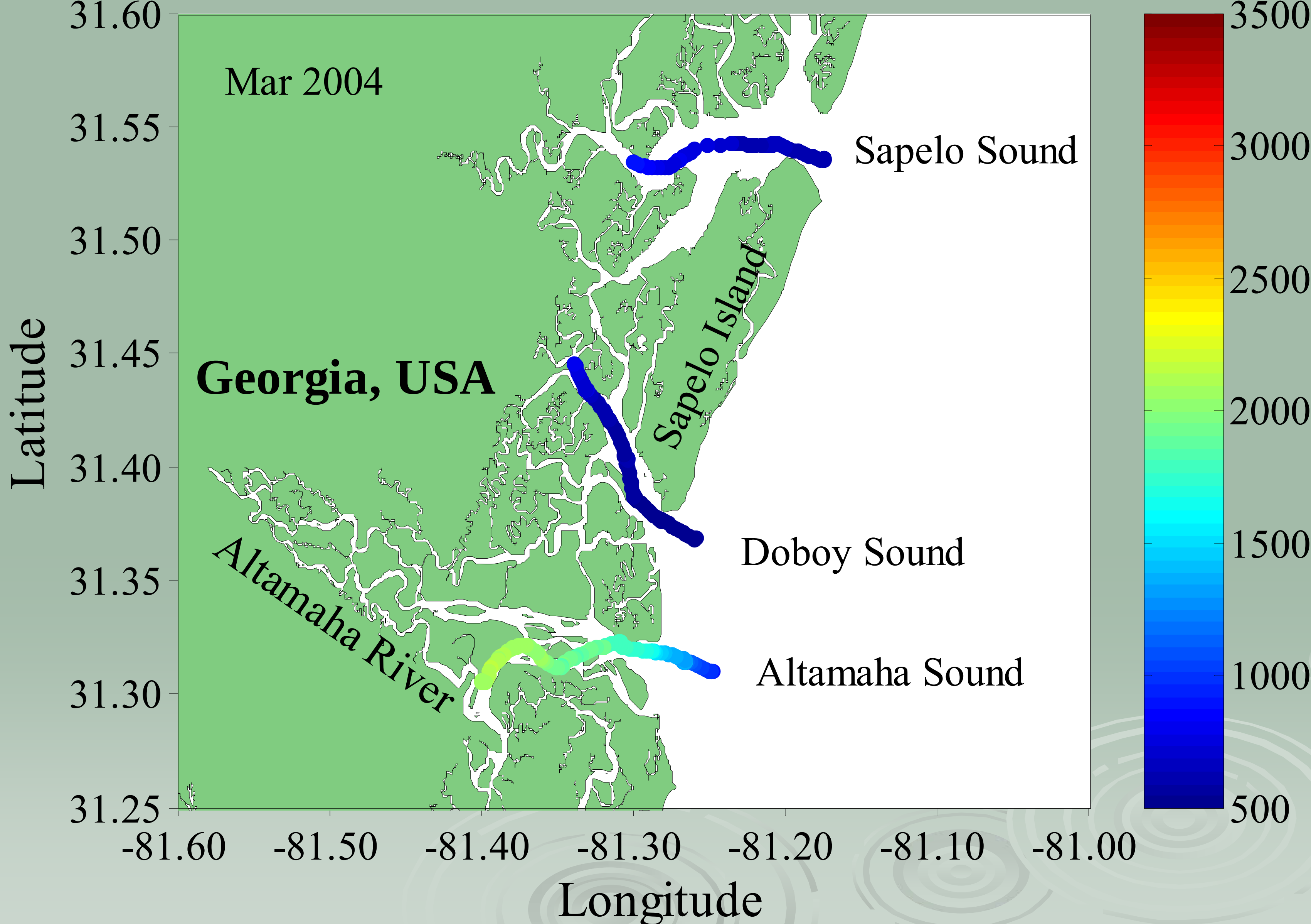
June 2003 (LW)
June 2003 (HW)
September 2002 (LW)
September 2002 (HW)
December 2003 (LW)
December 2003
35 30 25 20 15 10 5 0

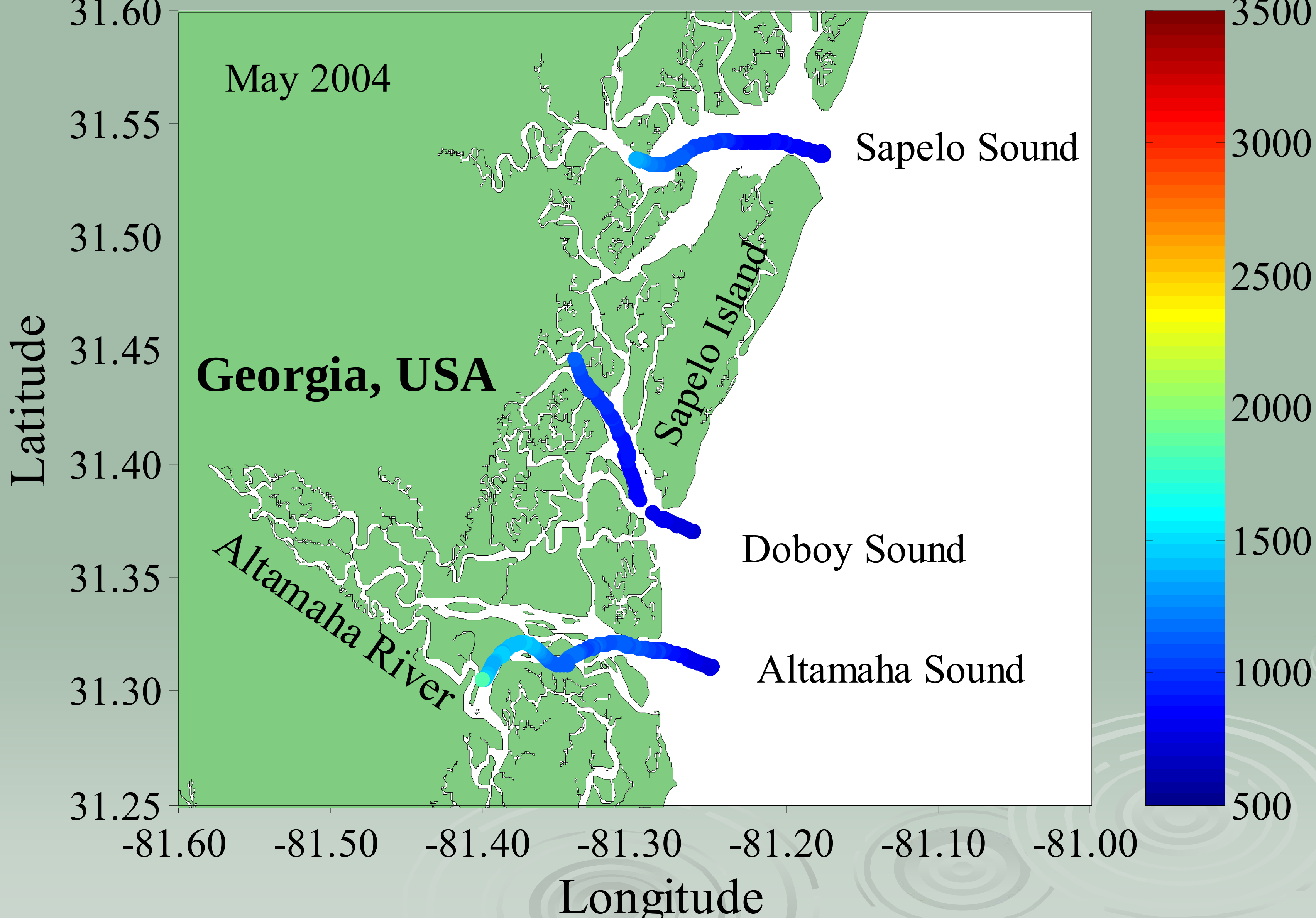


Distance upstream of the estuarine mouth (km)
12 10 8 6 4 2 0 -2
Depth (m)
March 2004 (LW)
March 2004 (HW)
May 2004 (LW)
May 2004 (HW)
June 2003 (LW)
June 2003 (HW)
September 2002 (LW)
September 2002 (HW)
December 2003 (LW)
December 2003
35 30 25 20 15 10 5 0

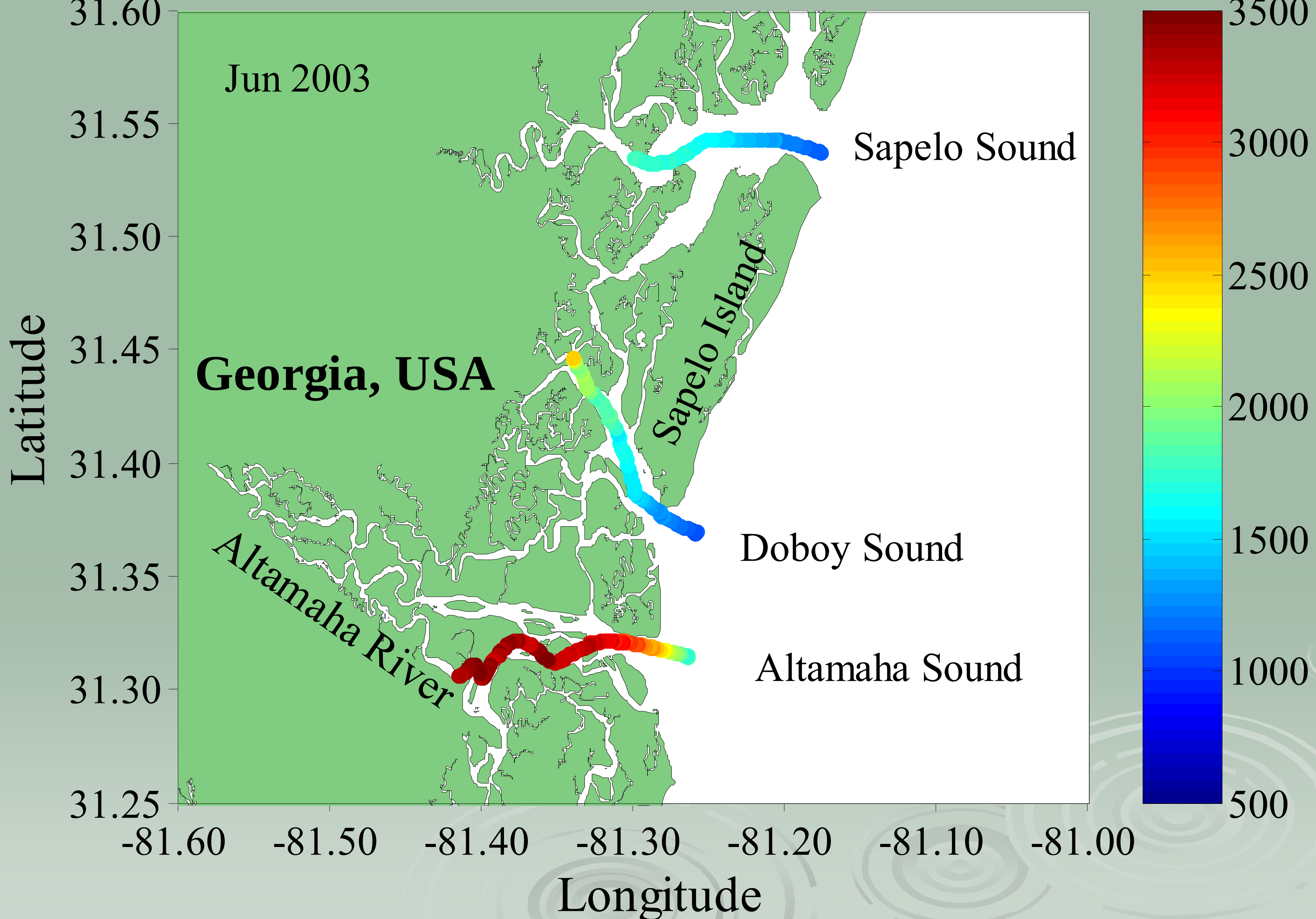
Surface water pCO_2



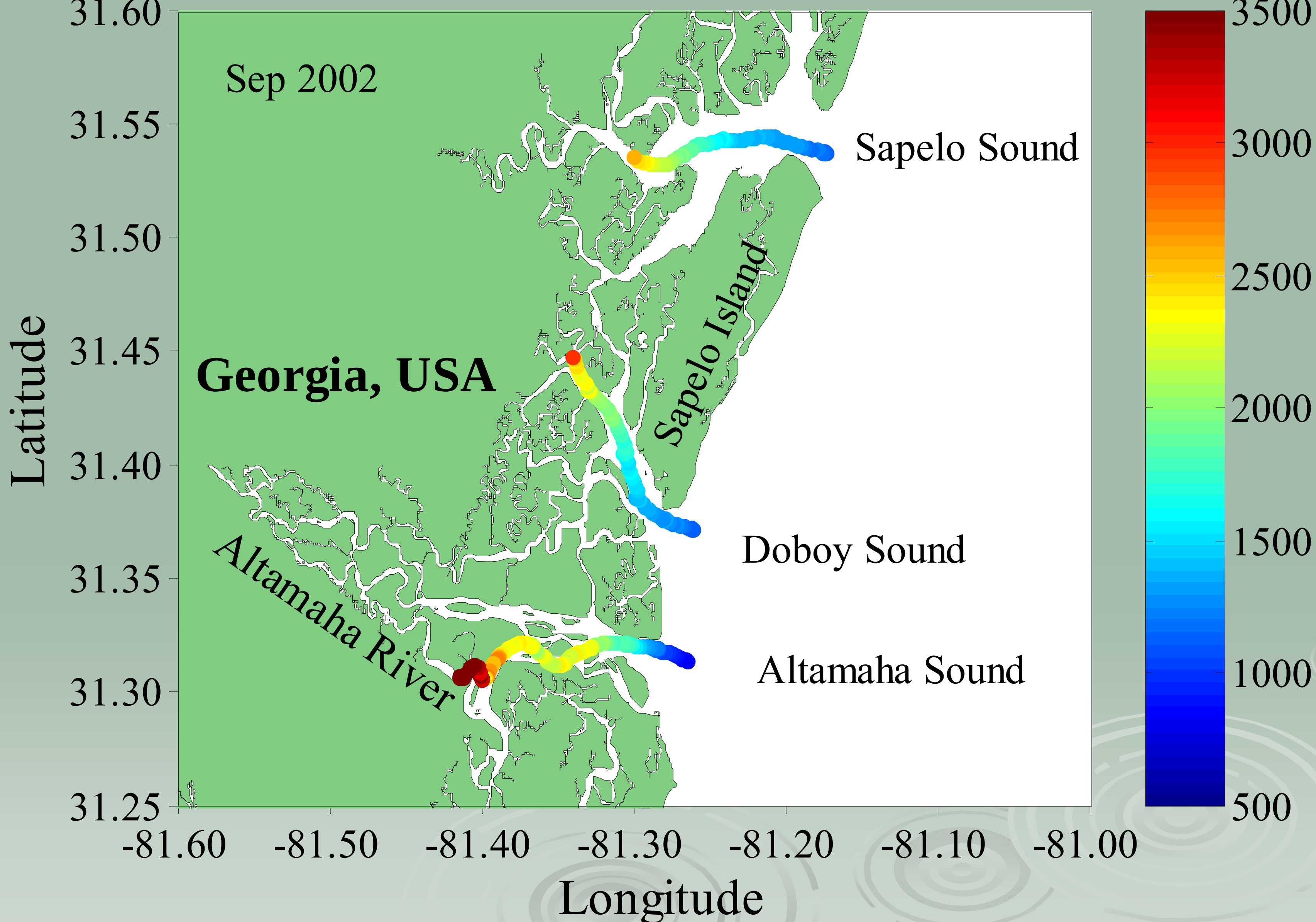
Surface water pCO_2



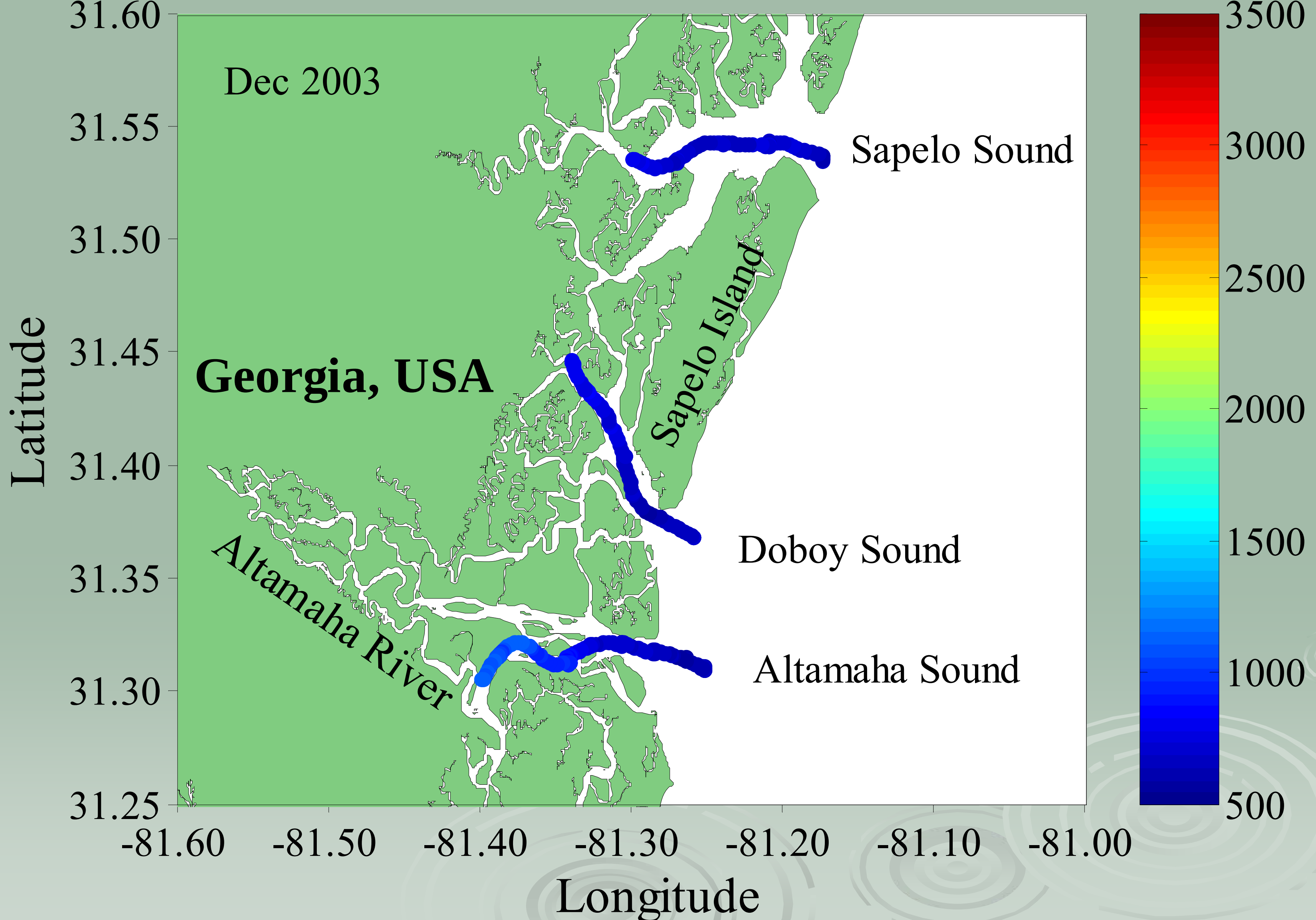
Surface water pCO_2



Surface water $p\text{CO}_2$

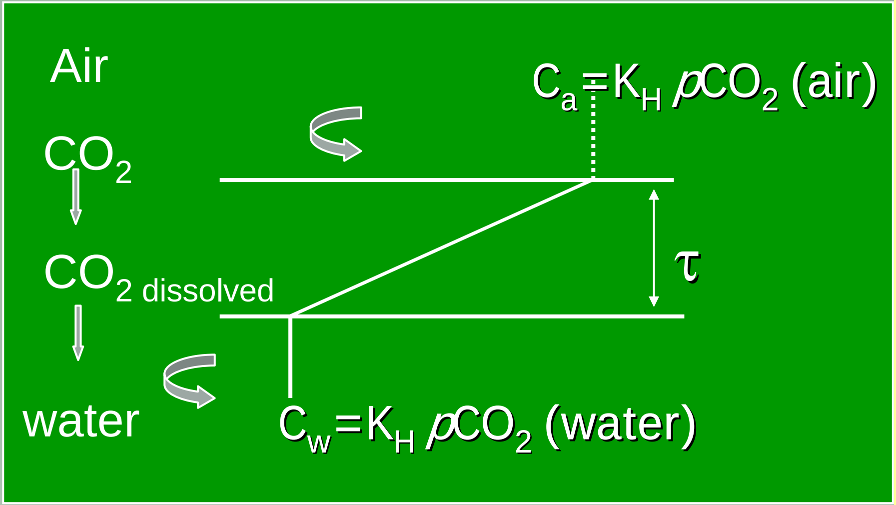


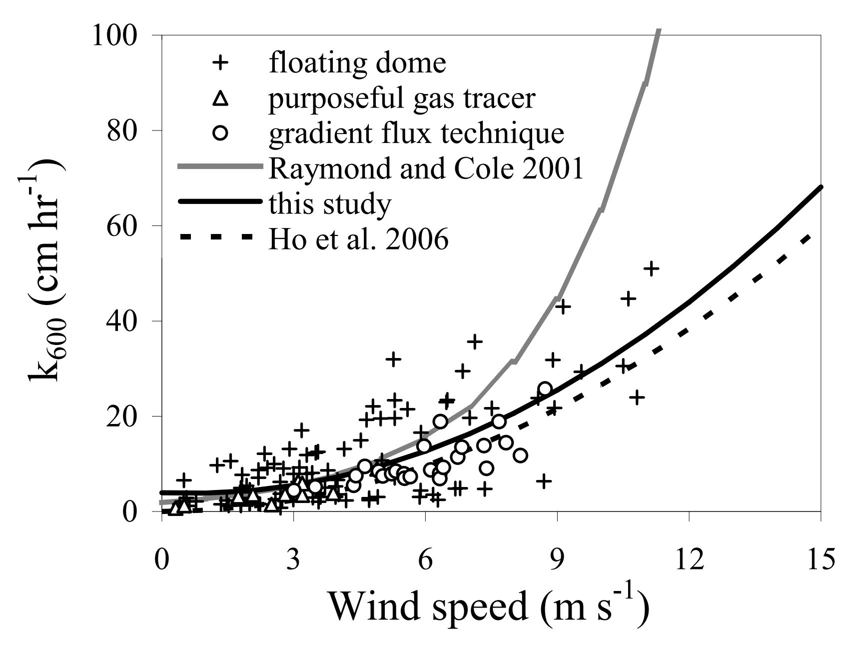
Surface water pCO_2



Gas transfer rate in estuaries

$$Flux = k_T \cdot K_H \cdot (pCO_{2water} - pCO_{2air})$$





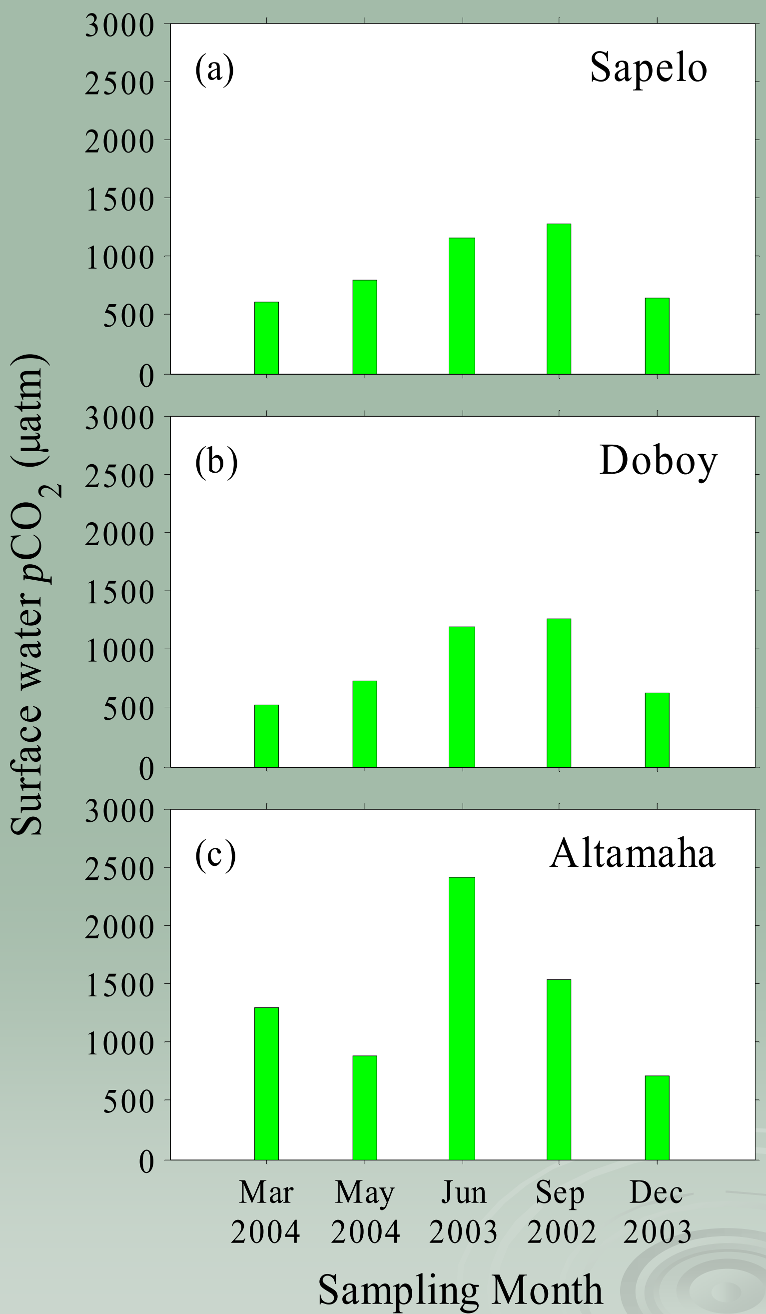
$$k_{600} = 0.314 \cdot U_{10}^2 - 0.436 \cdot U_{10} + 3.990$$

(Jiang et al. 2008, L&O)

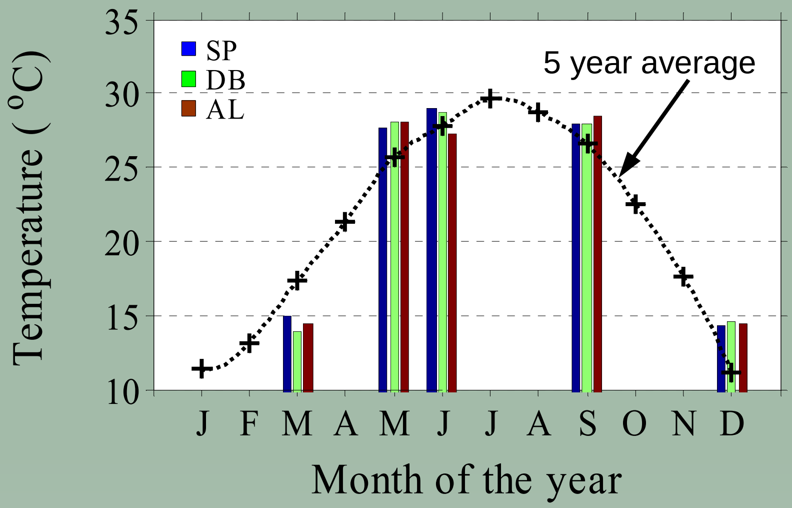
Air-water CO_2 fluxes

(mmol m^{-2} d^{-1})

	Tide	Mar 04	May 04	Jun 03	Sep 02	Dec 03	Annual average
Sapelo Sound	HW	11.76	21.57	36.14	45.38	16.96	26.8
	LW	27.18	48.00	84.26	92.31	29.37	56.1
	Avg.	19.47	34.79	60.20	68.85	23.17	**41.4**
Doboy Sound	HW	5.95	17.47	35.07	42.57	18.10	24.4
	LW	19.76	43.54	104.58	106.51	29.67	61.0
	Avg.	12.86	30.51	69.83	74.54	23.89	**42.7**
Altamaha Sound	HW	52.87	24.05	127.58	75.69	27.17	61.0
	LW	158.51	83.32	248.44	157.91	53.09	137.6
	Avg.	105.69	53.69	188.01	116.80	40.13	**99.3**

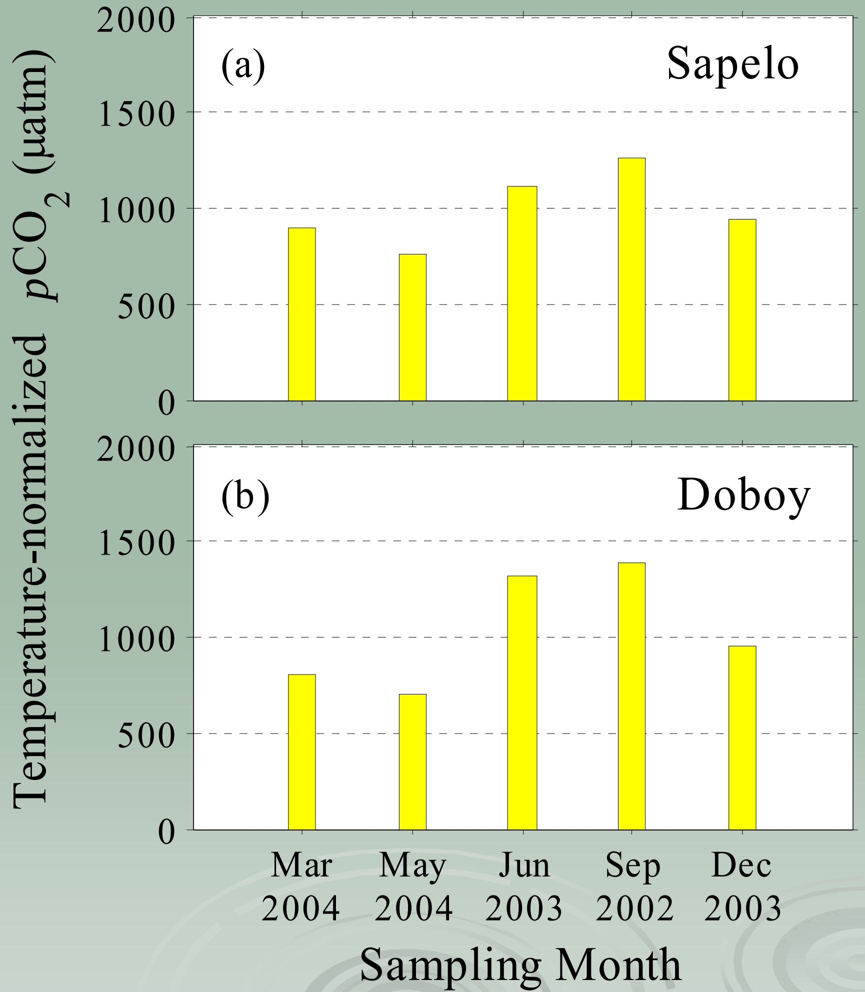


Area-averaged surface water pCO_2

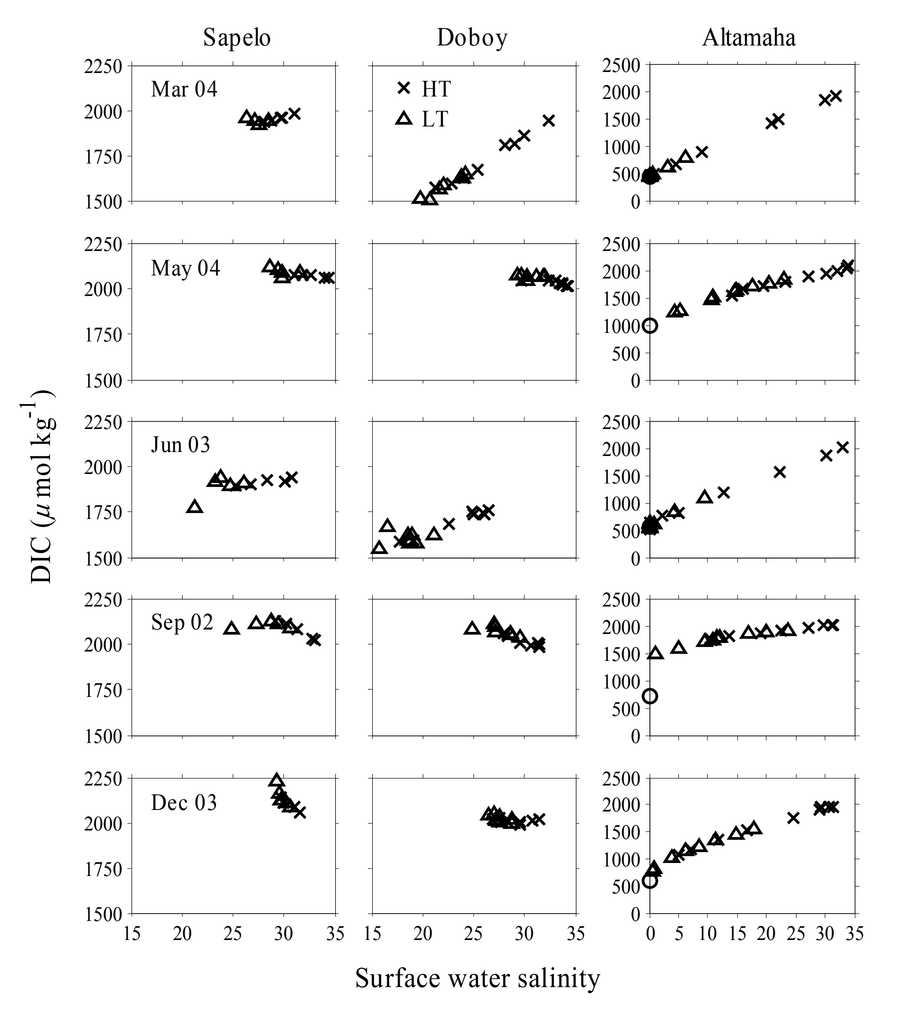


Surface water Temperature

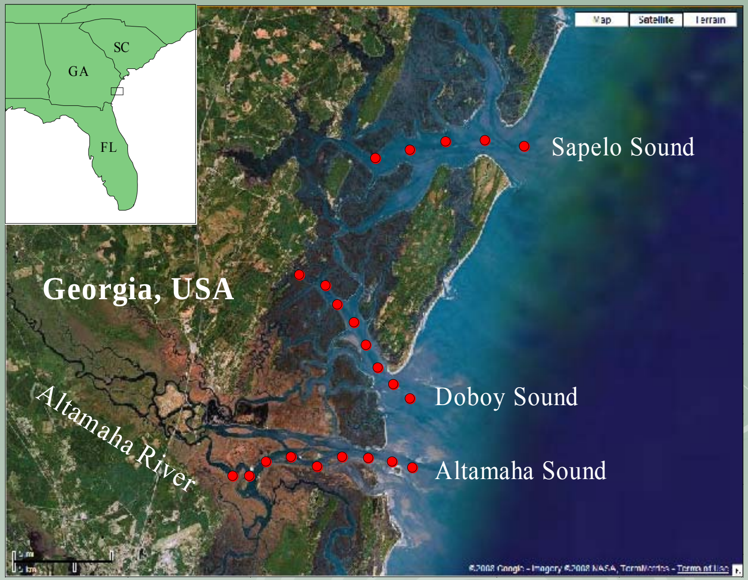
Temperature-normalized surface water pCO_2 in Marine dominated estuaries



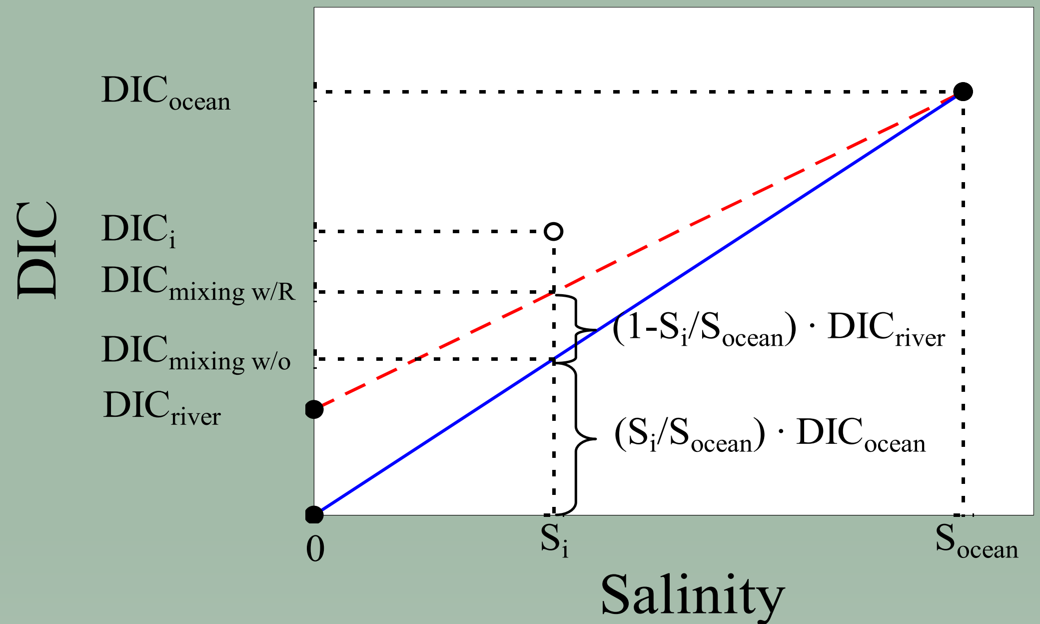
DIC in marsh-surrounded estuaries



DIC~ salinity



Estuarine mixing: riverine vs. non-riverine

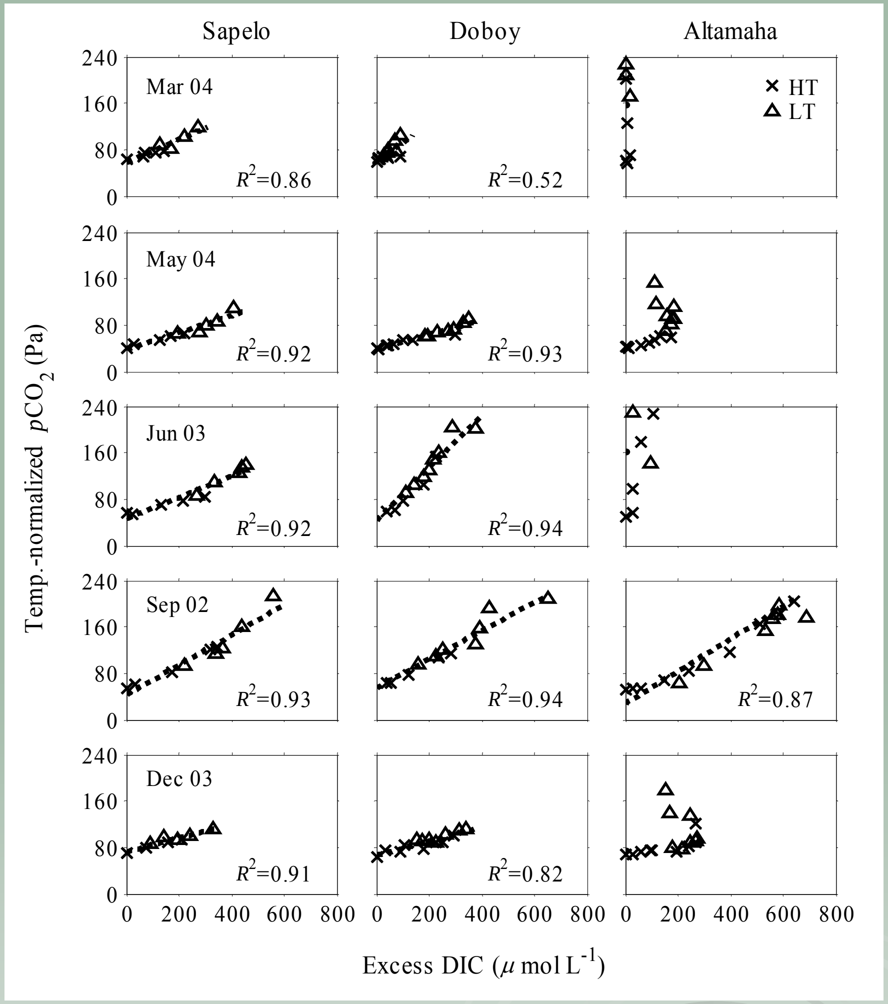


$$DIC_{excess} = DIC_i - DIC_{mixing}$$

$$DIC_{mixing\ \ w/o} = \frac{S_i}{S_{ocean}} \times DIC_{ocean}$$

$$DIC_{mixing\ w/R} = \frac{S_i}{S_{ocean}} \cdot DIC_{ocean} + (1 - \frac{S_i}{S_{ocean}}) \cdot DIC_{river}$$

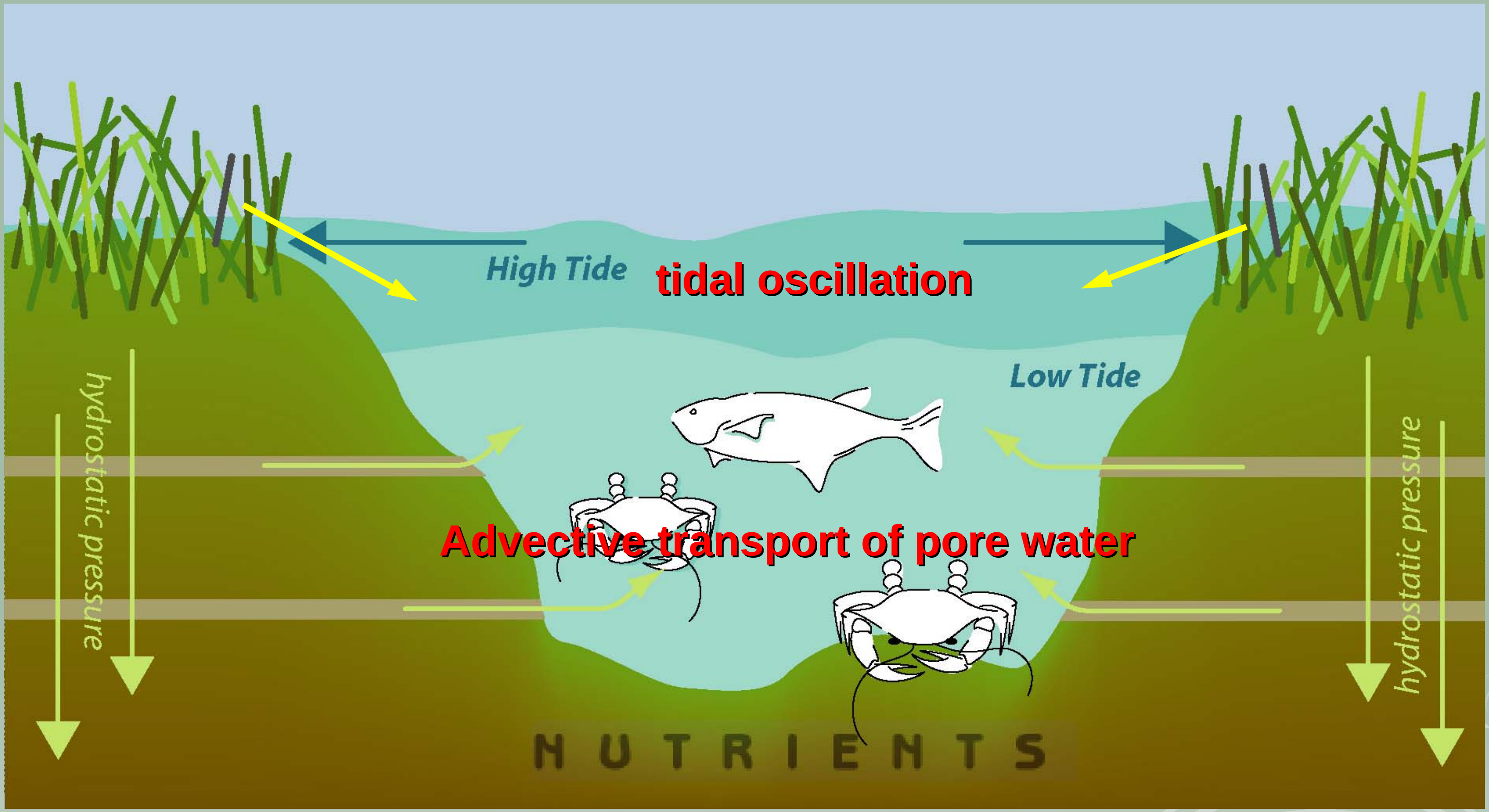
Temp-Norm-pCO_2 ~ excess DIC relationship



1. Temp Norm pCO_2 and exDIC are well correlated in marine-dominated estuaries but not in river-dominated.

2. *Excess* DIC from marsh-estuary controls the seasonal change of pCO_2 in the marine-dominated estuaries

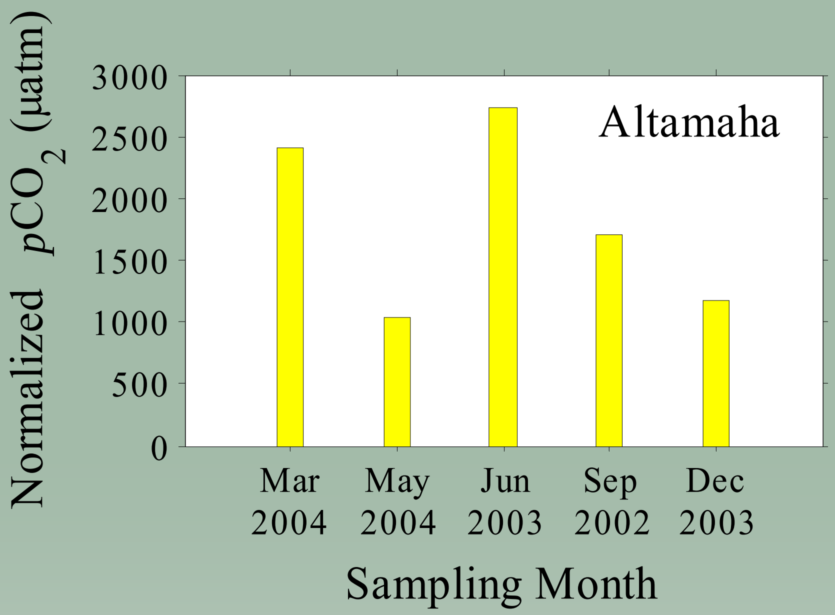
CO_2 sources in marine-dominated estuaries

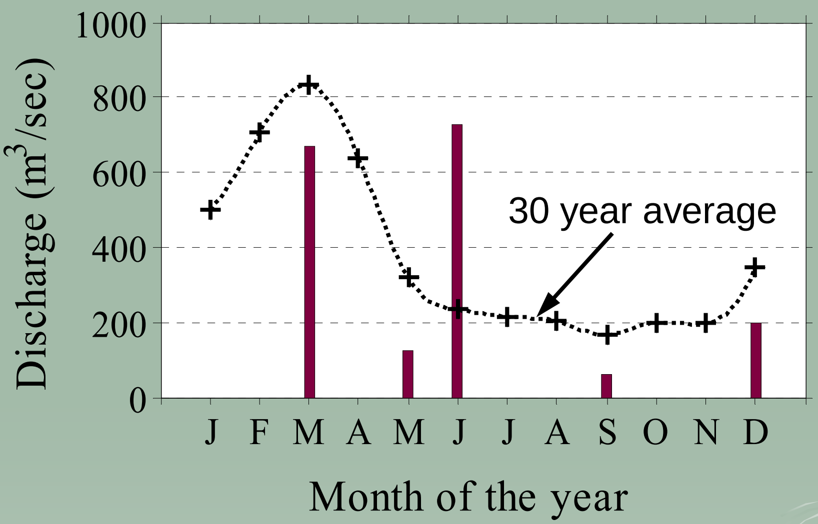


(modified from Jahnke et al. 2003)

Inorganic respiratory products from the intertidal salt marshes play the largest role (Cai and Wang 1998; Cai et al. 1999; Wang and Cai 2004)

Temperature-normalized pCO_2 in river-dominated estuaries

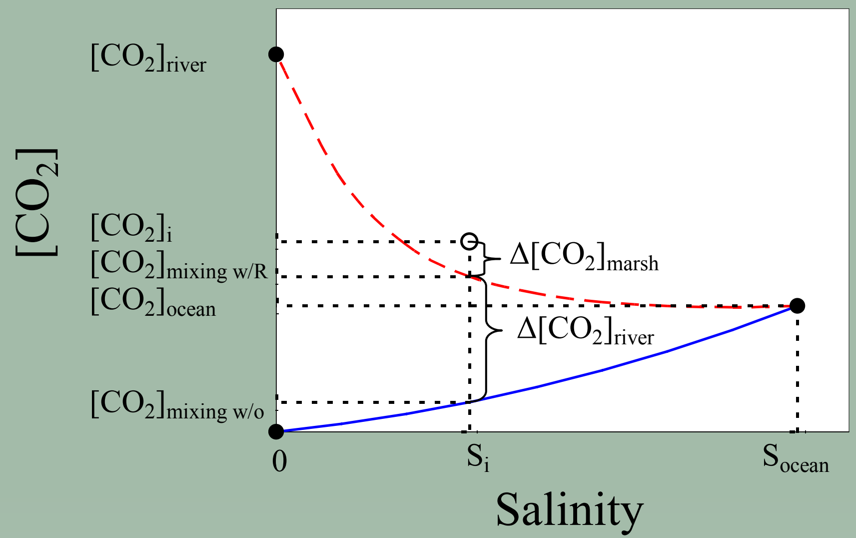


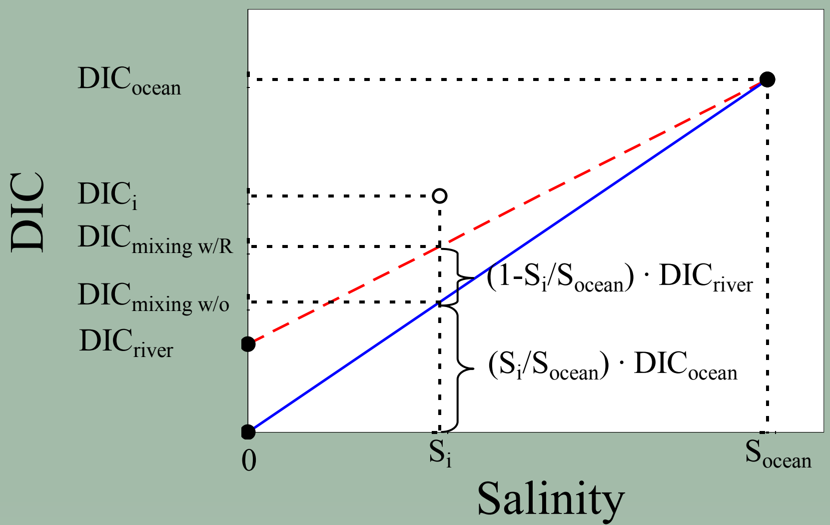


Temp. normalized pCO_2

River discharge rates

CO_2 contributed from river or marsh





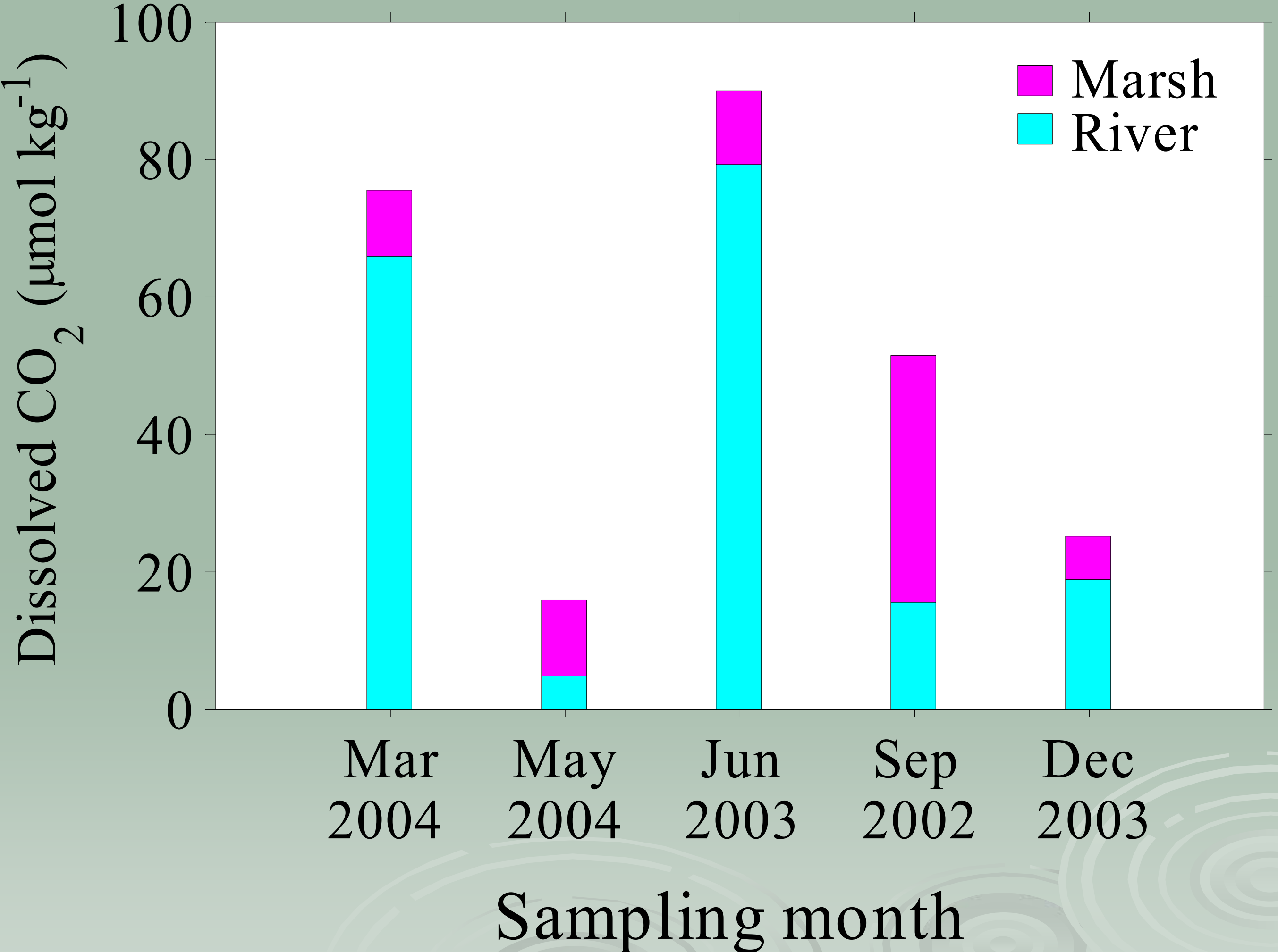
$$\Delta[CO_2]_{marsh} = [CO_2]_i - [CO_2]_{mixing\ w/R}$$

$$DIC_{mixing\ w/o} = \frac{S_i}{S_{ocean}} \cdot DIC_{ocean}$$

$$\Delta[CO_2]_{river} = [CO_2]_{mixing\ w/R} - [CO_2]_{mixing\ w/0}$$

$$DIC_{mixing\ w/R} = \frac{S_i}{S_{ocean}} \cdot DIC_{ocean} + (1 - \frac{S_i}{S_{ocean}}) \cdot DIC_{river}$$

CO_2 contributed from river and marsh



Flux contributed by the river input of DIC

Air-water CO_2 flux:

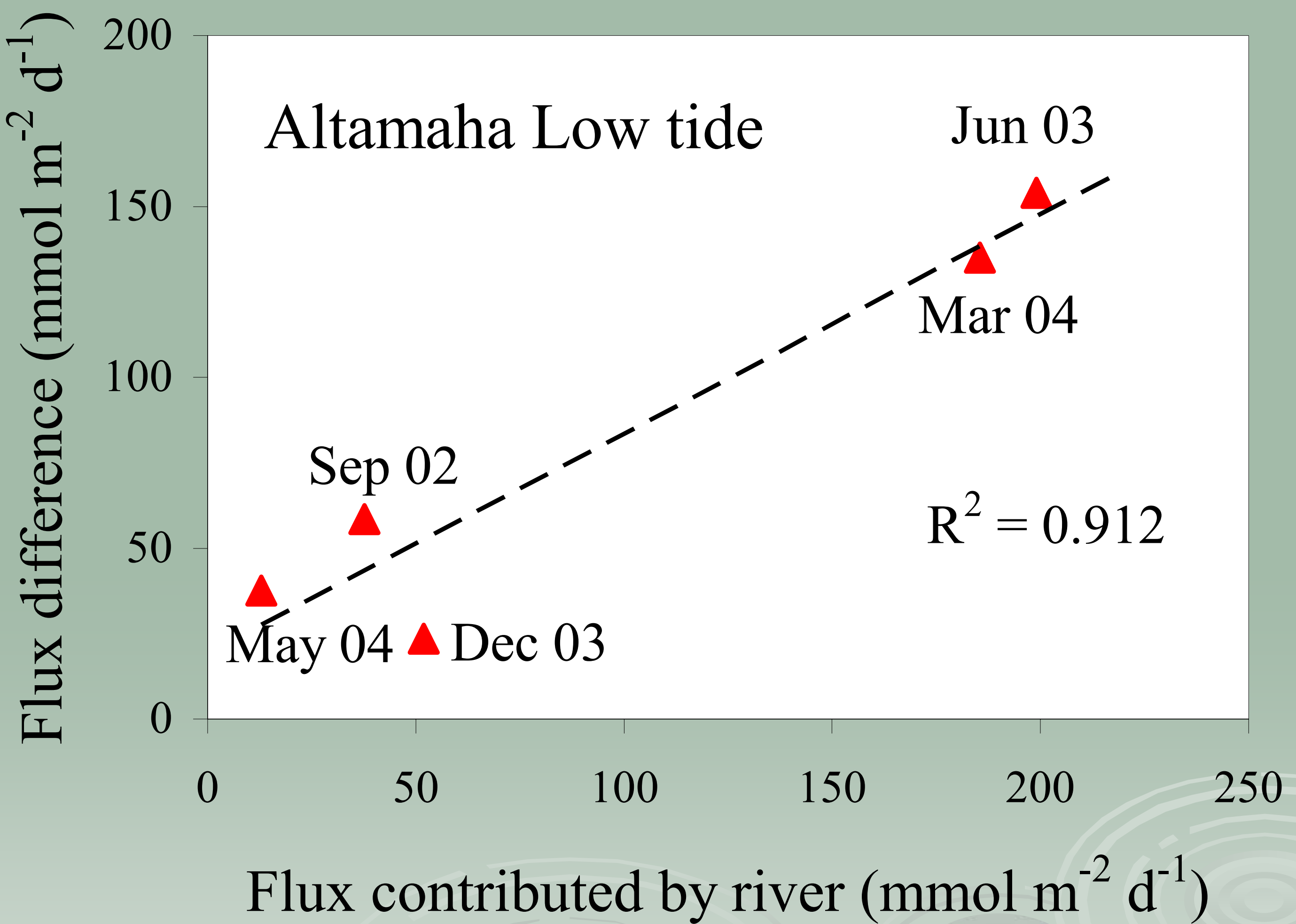
$$F = k \cdot ([CO_{2w}] - [CO_{2a}]) \qquad (1)$$

Differentiate both sides:

$$\Delta F = k \cdot \Delta [CO_{2w}] \qquad (2)$$

Since we already know CO_2 concentration that is contributed by the river; the fluxes contributed by the river can then be calculated according to (2).

River contributed CO_2 vs. flux difference



Conclusions

- The surface water pCO_2 in the **river-dominated estuaries** is much **higher** than that in the **marine-dominated estuaries**.
- The **CO_2 loading from freshwater runoff** is believed to be responsible for the extra higher CO_2 fluxes in the river-dominated estuaries. (explain why river has high CO_2)

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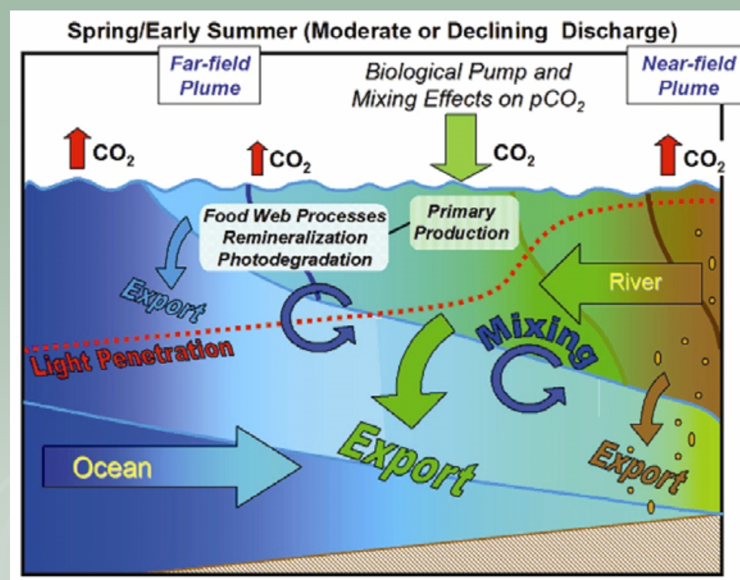
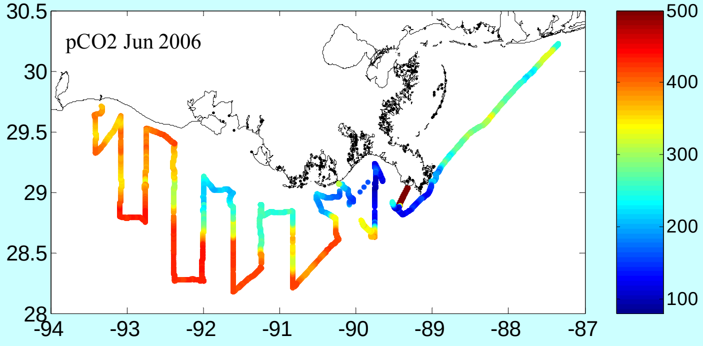
Mississippi River (MR) plume



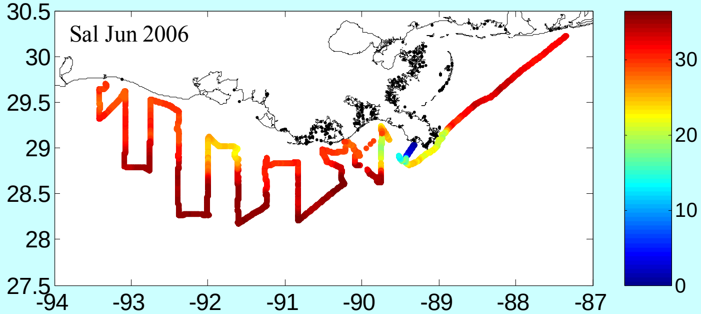
Surface water *p*CO_2 & salinity distribution, MR plume

June 06

pCO_2

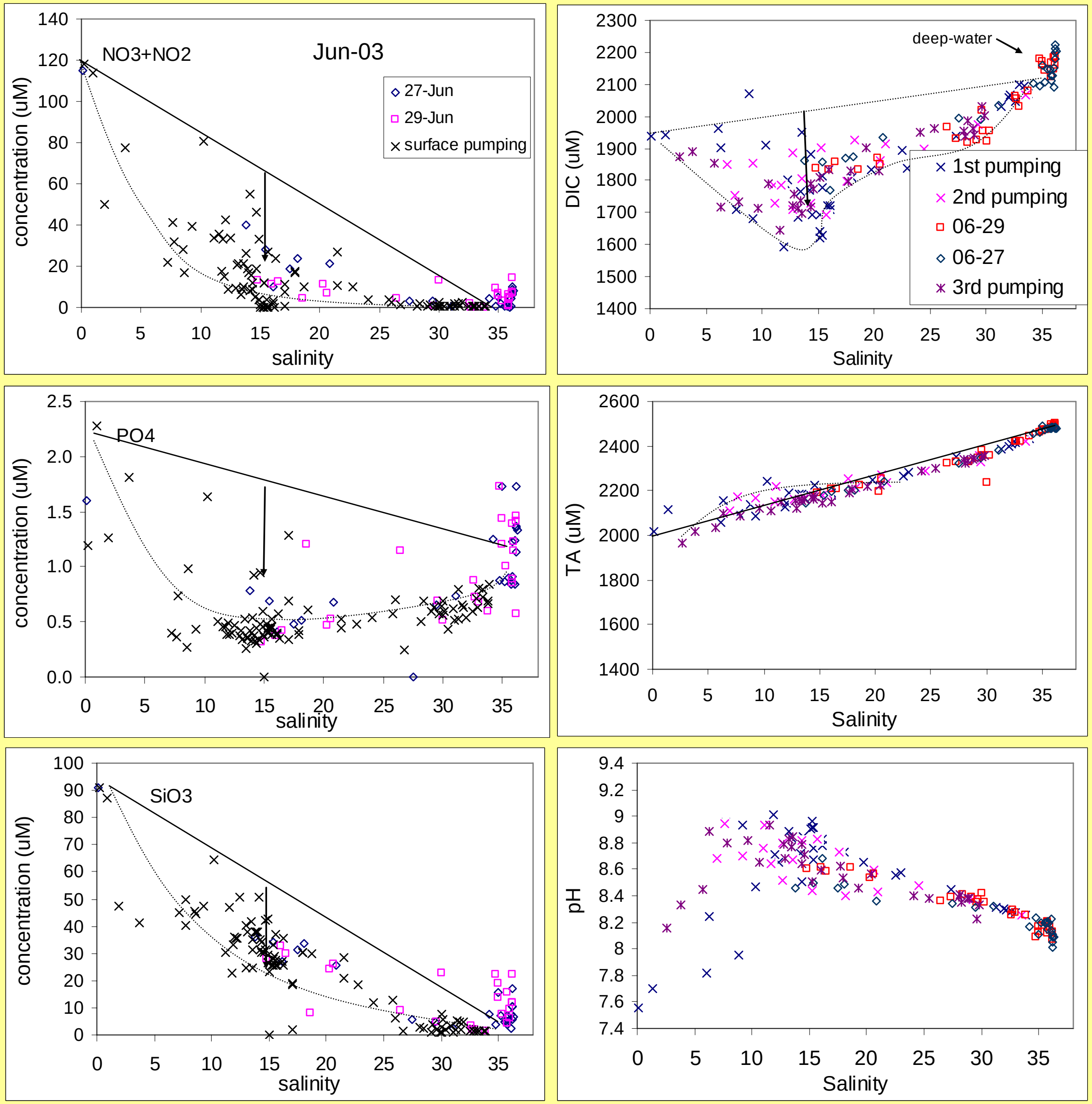


Sal



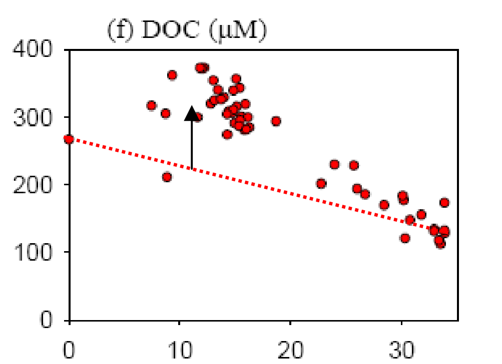
1. High pCO_2 in river end
2. Very low pCO2 in mid sal
3. High in high sal zone

Mississippi River plume, June 2003



(Rodney Powell)

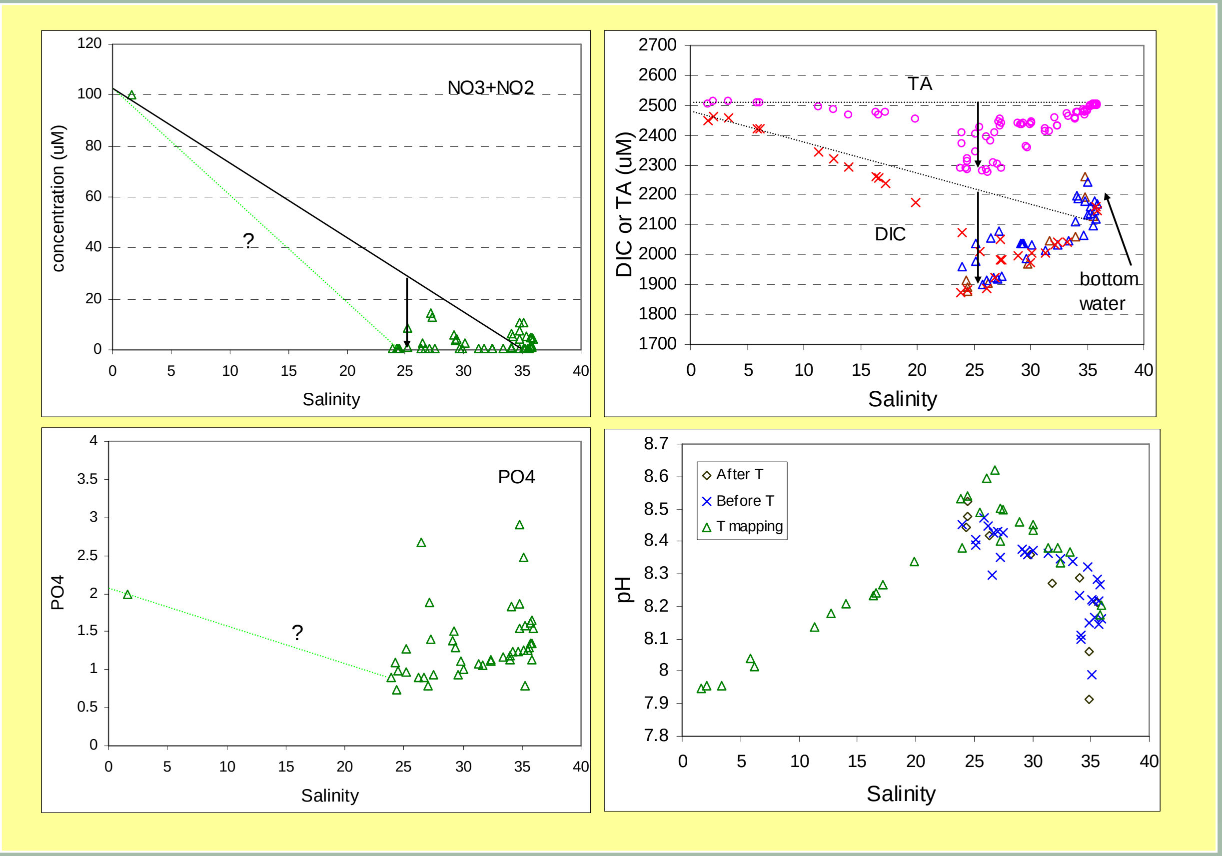
(W.-J Cai)

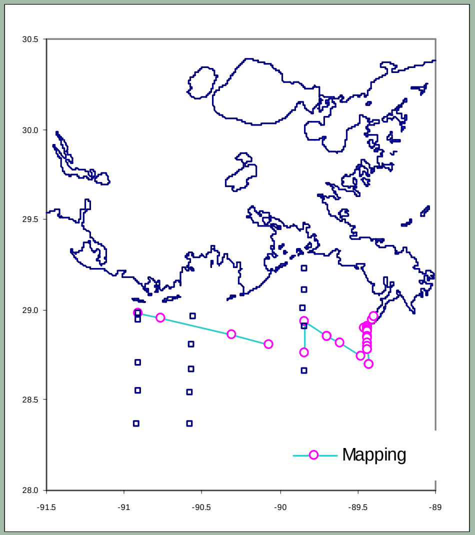


(T. Bianchi)

1. Great DIC removal & nutrient removal at S=15.
2. No TA removal.
3. At S=15, maxΔDIC ~ 430 uM. Appling a Redfield ratio of 6.6, we would predict a max NO_3 removal of 65 uM and maxPO4 removal of 4.1 uM.

August 2004





ΔDIC = 320 uM, ΔTA=210 uM

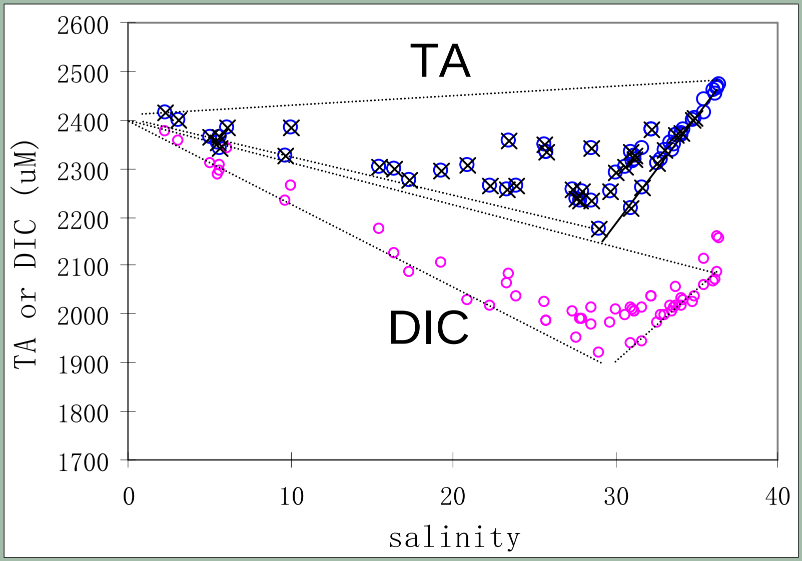
DIC removal due to OC = 320-210/2

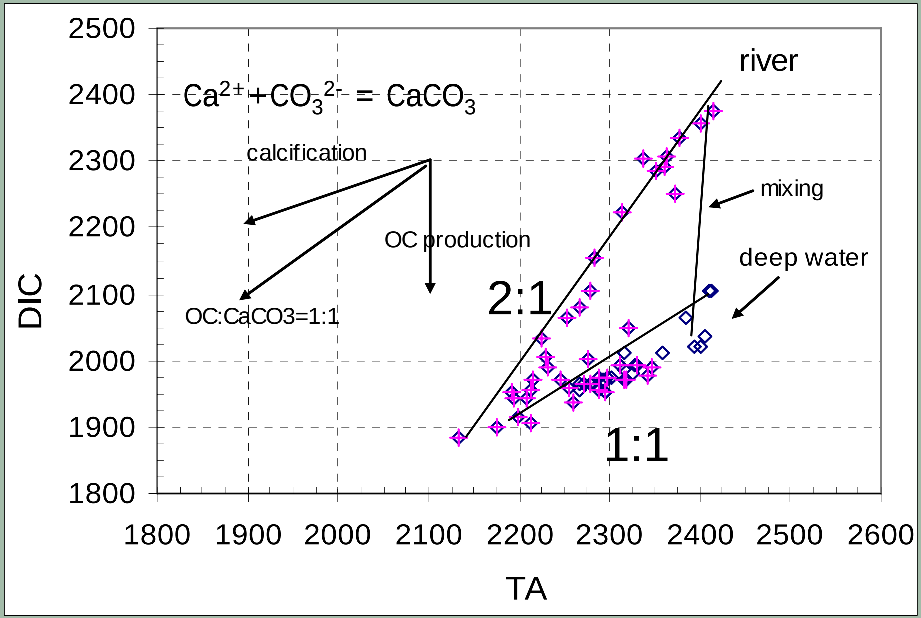
=215 uM

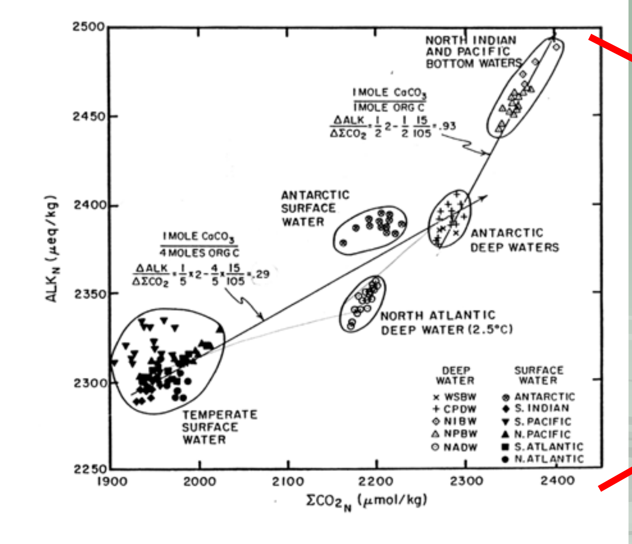
Predicted NO_3 removal = 33 uM

October 2005

mixing



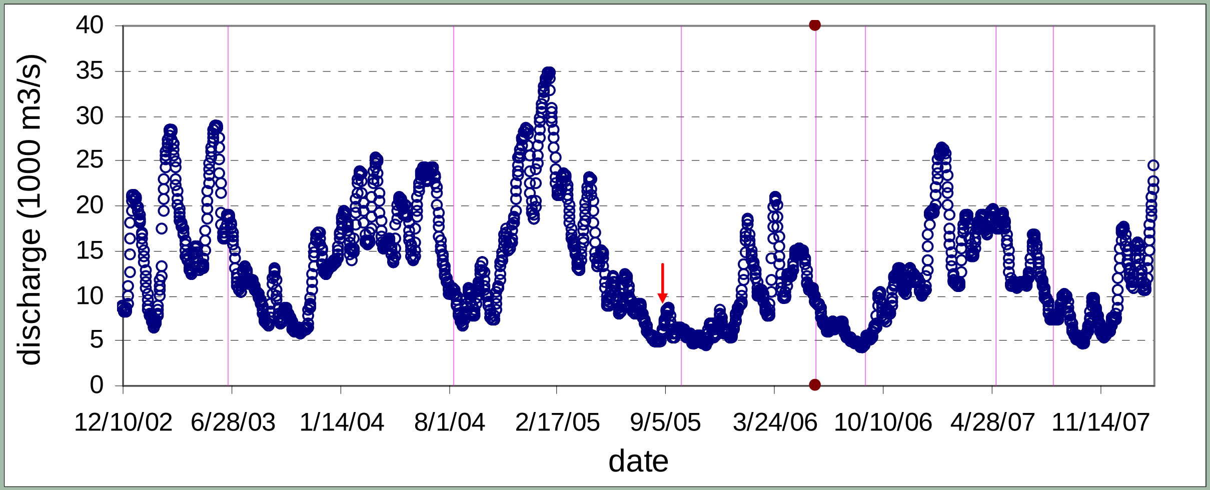




$$\frac{\Delta Alk}{\Delta TCO_2} = \frac{1}{2}x2 - \frac{1}{2}x\frac{15}{105} = 0.93$$

$$\frac{\Delta Alk}{\Delta TCO_2} = \frac{1}{5}x2 - \frac{4}{5}x\frac{15}{105} = 0.28$$

Mississippi River discharge at Tarbert Landing



TA removal (& possibly coccolith bloom) occurs only at low discharge time.

pCO_2 in the Changjiang plume, East China Sea (Tsunogai et al. 1999)

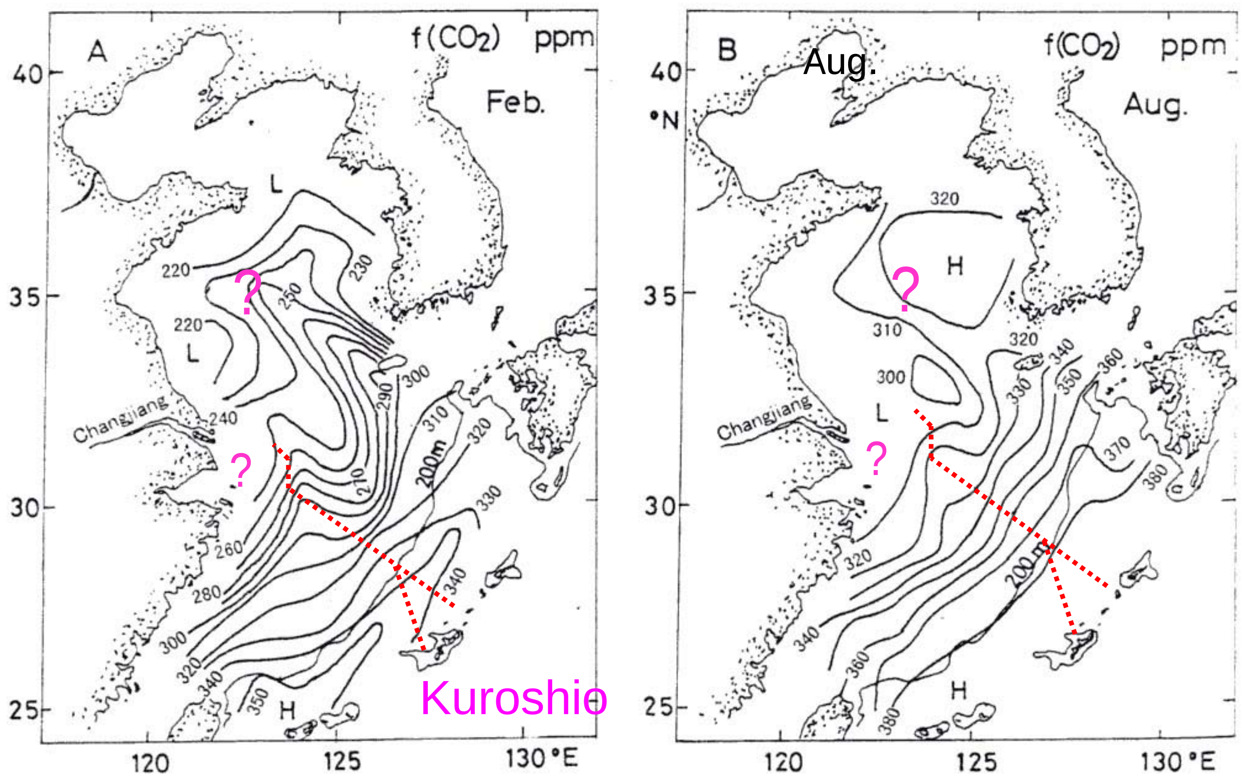
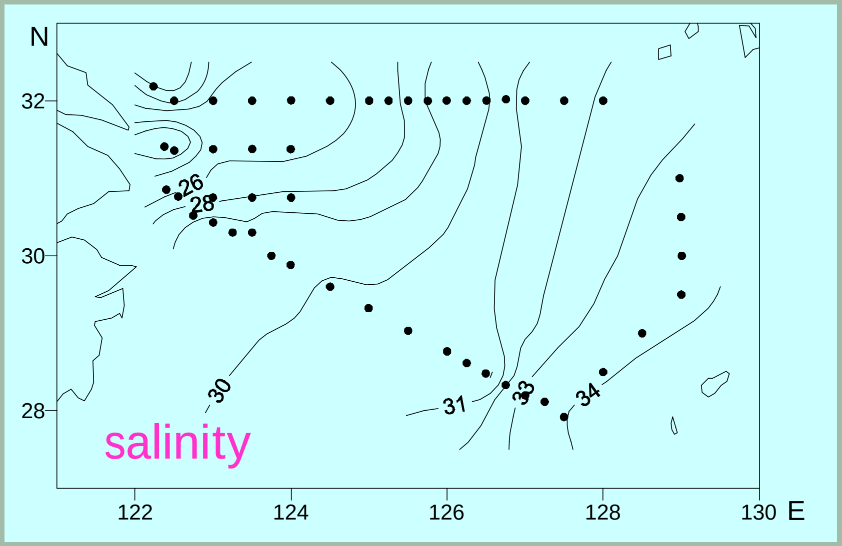
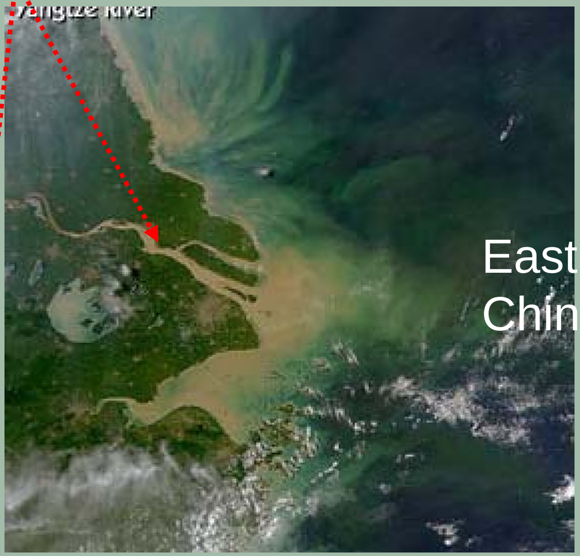
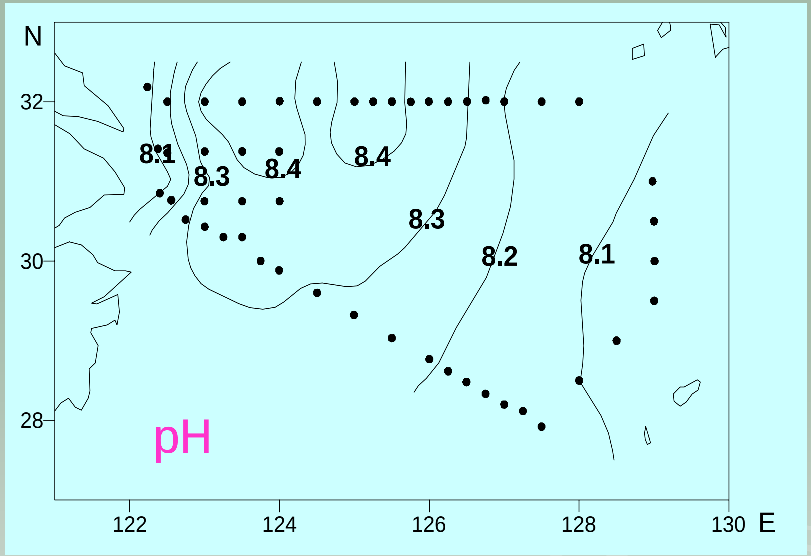


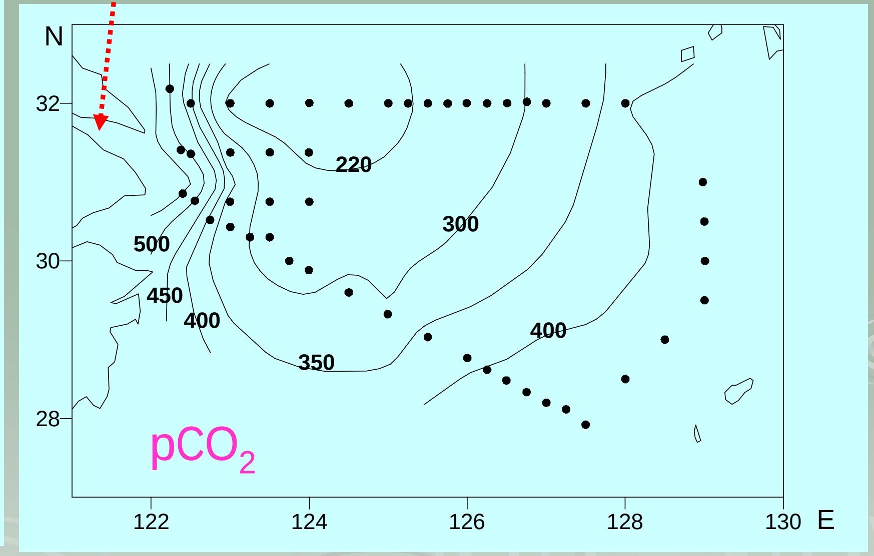
Fig. 4. Distribution of reproduced $f(CO_2)$ values (ppm) in February (A: Feb.) and August (B: Aug.) in the East China Sea including the Yellow Sea.

Changjiang (Yangtze River)



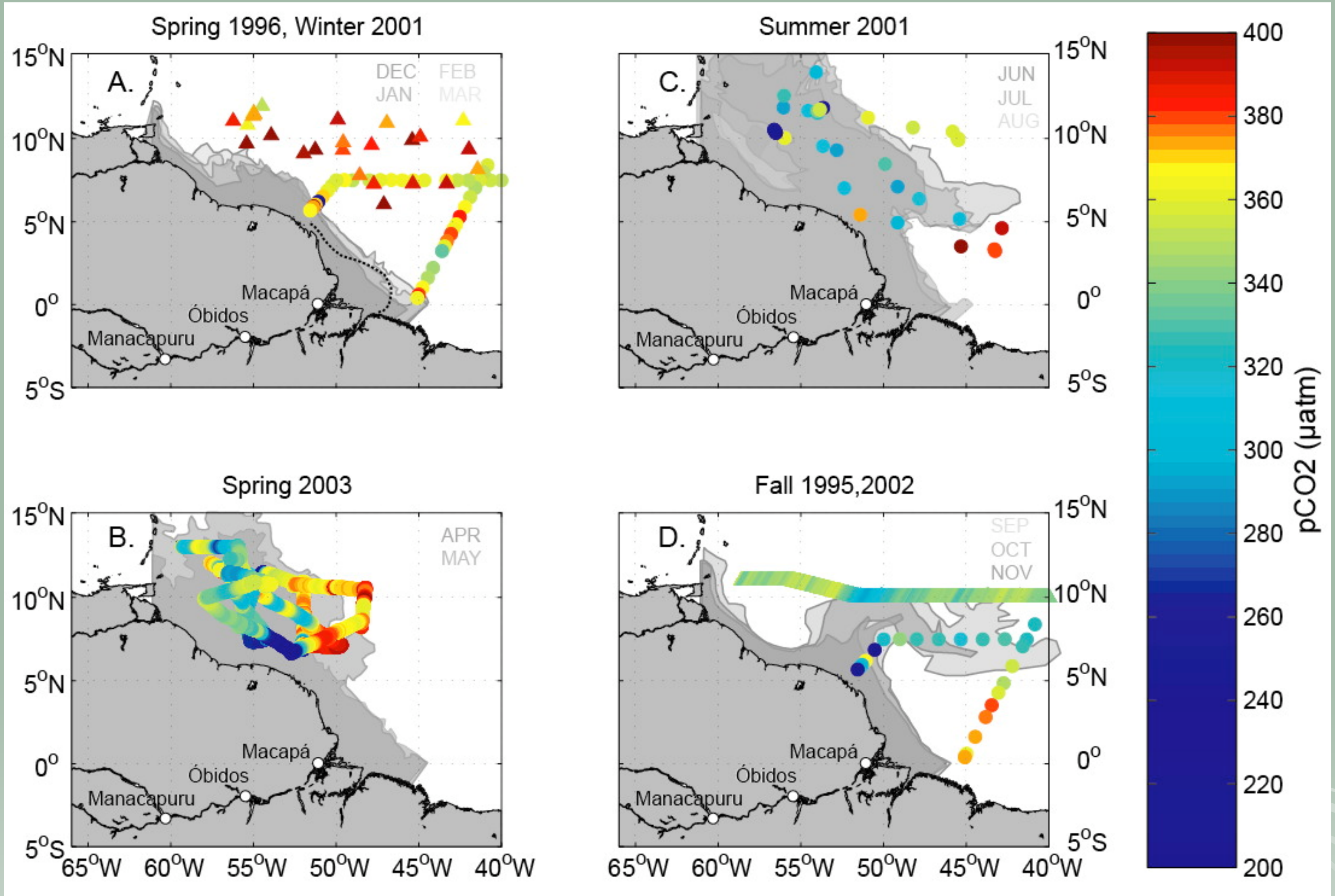






$p CO_2$ in the East China Sea in summer 1998 during the great flood period (Results from the Chinese JGOFS, L. Zhang pers. comm.)

Amazon plume



Cooley et al. GBC : 21, GB3014, doi:10.1029/2006GB002831, 2007

Mixing in the Amazon River plume

vs. in the MR plume

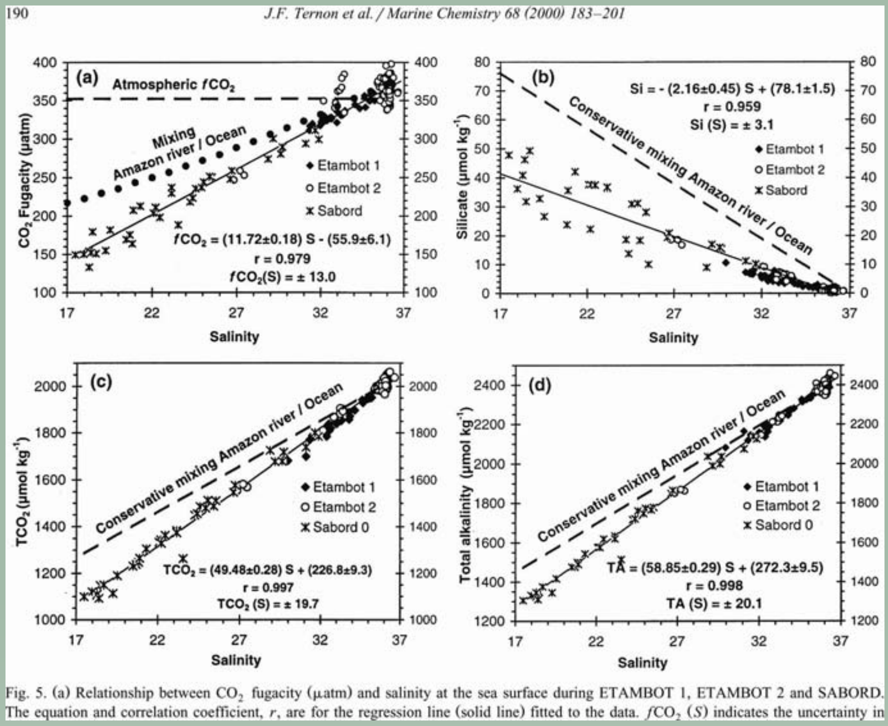
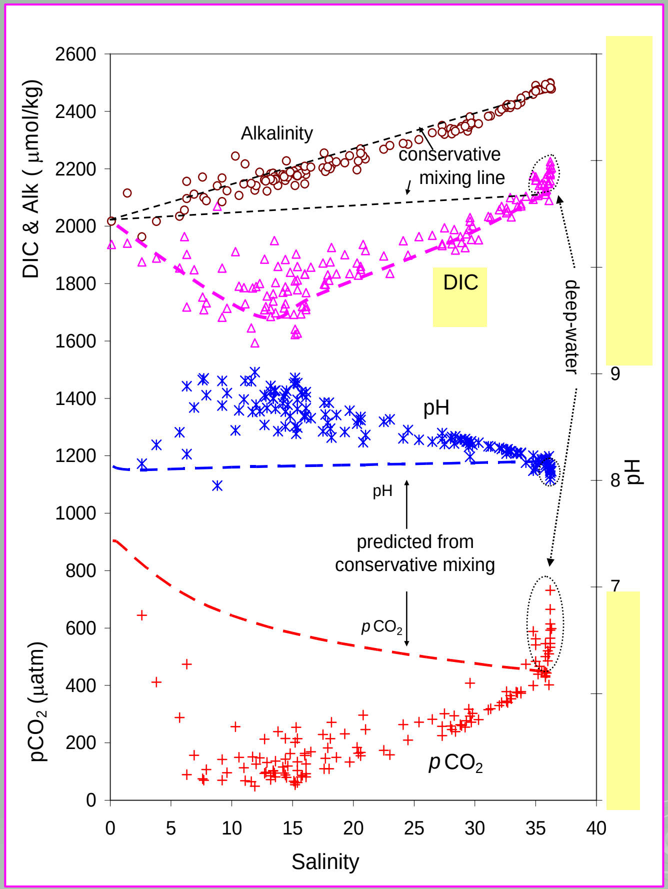


Fig. 5. (a) Relationship between CO_2 fugacity (µatm) and salinity at the sea surface during ETAMBOT 1, ETAMBOT 2 and SABORD. The equation and correlation coefficient, r, are for the regression line (solid line) fitted to the data. fCO_2 (S) indicates the uncertainty in



Amazon River water has low TA & low buffer capacity; in contrast, MR water has high TA and high buffer capacity.

Outline

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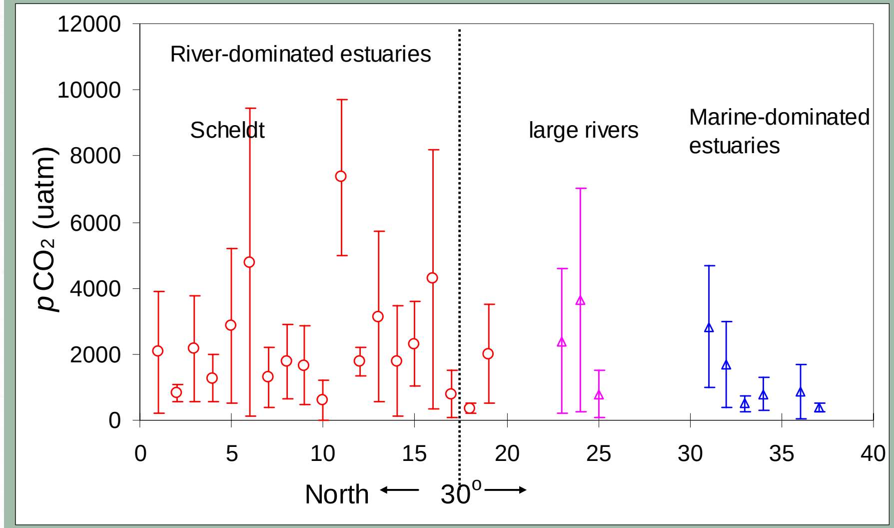
Estuaries on which the global estuarine CO_2 fluxes were based are mainly river-dominated estuaries

TABLE 1. Range of pCO_2, air-water CO_2 fluxes, and gas transfer velocity parameterization (k) in coastal environments. The numbers in parentheses correspond to site identification in Fig. 1. Values in bold are for environments with full annual coverage. k wind parameterization after Carini et al. (1996) = C; Liss and Merlivat (1986) = LM; Nightingale et al. (2000) = N; Raymond et al. (2000) = R; Raymond and Cole (2001) = RC; Wanninkhof (1992) = W; Tans et al. (1990) = T; Wanninkhof and McGillis (1999) = WMcG. D denotes direct measurements with a floating dome.

Site	°E	°N	pCO_2 (ppm)	Air-Water CO_2 Fluxes (mol C m^{-2} yr^{-1})	k	Ref.
Inner estuaries						
Randers Fjord (1)	10.3	56.6	220–3400	4.4	D	Gazeau et al. (2004a)
Elbe (2)	8.8	53.9	580–1100	53.0	D	Frankignoulle et al. (1998)
Ems (3)	6.9	53.4	560–3755	67.3	D	Frankignoulle et al. (1998)
Rhine (4)	4.1	52.0	**545–1990**	**39.7**	D	Frankignoulle et al. (1998)
Thames (5)	0.9	51.5	**505–5200**	**73.6**	D	Frankignoulle et al. (1998)
Scheldt (6)	3.5	51.4	**125–9425**	**63.0**	D	Frankignoulle et al. (1998)
Tamar (7)	−4.2	50.4	**380–2200**	**74.8**	8.0 cm h^{-1}	Frankignoulle et al. (1998)
Loire (8)	−2.2	47.2	630–2910	64.4	13.0 cm h^{-1}/ D	Abril et al. (2003, 2004)
Gironde (9)	−1.1	45.6	**465–2860**	**30.8**	D	Frankignoulle et al. (1998)
Douro (10)	−8.7	41.1	1330–2200	76.0	D	Frankignoulle et al. (1998)
Sado (11)	−8.9	38.5	575–5700	31.3	D	Frankignoulle et al. (1998)
York River (12)	−76.4	37.2	350–1900	6.2	R	Raymond et al. (2000)
Satilla River (13)	−81.5	31.0	360–8200	42.5	12.5 cm h^{-1}	Cai and Wang (1998)
Hooghly (14)	88.0	22.0	**80–1520**	**5.1**	W	Mukhopadhyay et al. (2002)
Godavari (15)	82.3	16.7	220–500	5.5	RC	Bouillon et al. (2003)
Mandovi-Zuari (16)	73.5	15.3	**500–3500**	**14.2**	W	Sarma et al. (2001)



(Table from Borges et al. 2005)

The air-water CO_2 flux of the global estuaries (0.4 Pg C/yr) is quite uncertainty.

Marine-dominated estuaries cover a large portion of the global estuaries

Region	No.	Sound	Flow ratios (average annual)	Type	Fluvial Drainage (mi^2)	Estuarine Drainage (mi^2)	Flow rates (ft^3/s)	Total Area of the non riverine (mi^2)	Total Area of riverine (mi^2)
Northeast	1.01	Passamaquoddy Bay	0.004	N	NA	3200	6.2	157	
	1.02	Englishman Bay	0.003	N	NA	883	1.6	76	
	1.03	Narraguagus Bay	0.002	N	NA	416	0.9	70	
	1.04	Blue Hill Bay	0.002	N	NA	825	1.3	115	
	1.05	Penobscot Bay	0.007	Y	6250	3160	16.1		361
	1.06	Muscongus Bay	0.002	N	NA	346	0.6	72	
	1.07	Sheepscot Bay	0.036	Y	3920	6150	17.6		103
	1.08	Casco Bay	0.002	N	NA	1159	2.1	164	
	1.09	Saco Bay	0.039	N	NA	1771	3.6	17	
	1.10	Great Bay	0.039	N	NA	950	2.0	15	
	1.11	Merrimack River	0.319	Y	2680	2300	8.4		6
	1.12	Boston Bay	0.005	N	NA	670	1.8	69	
	1.13	Cape Cod Bay	0.006	N	NA	771	1.8	548	
	1.14	Buzzards Bay	0.002	N	NA	576	1.2	228	
	1.15	Narragansett Bay	0.008	Y	451	1330	3.2		165
	1.16	Gardiners Bay	0.003	N	NA	400	0.7	197	
	1.18	Great South Bay	0.011	N	NA	845	0.7	151	
	1.19	Hudson River/Raritan Bay	0.046	Y	8037	8467	26.7		298
	1.20	Barnegat Bay	0.033	N	NA	1350	2.3	102	
	1.21	Delaware Bay	0.009	Y	8700	4750	19.8		768
	1.22	Chincoteague Bay	0.012	N	NA	300	0.4	137	
Southeast	2.01	Albemarle Sound	0.216	Y	12434	5804	24.8		922
	2.03	Bogue Sound	0.012	N	NA	680	1.3	102	
	2.04	New River	0.058	N	NA	470	0.8	32	
	2.05	Cape Fear River	0.128	Y	4750	4340	10.1		38
	2.06	Winyah Bay	0.301	Y	8578	9511	20.4		30
	2.07	Charleston Harbor	0.150	Y	14582	1202	16.1		37
	2.08	North and South Santee Rivers	0.138	Y	14582	718	2.7		9
	2.09	St. Helena Sound	0.015	Y	3242	1537	4.6		85
	2.10	Broad River	0.002	N	NA	1000	0.9	100	
	2.11	Savannah River	0.092	Y	9484	916	12.8		33
	2.12	Ossabaw Sound	0.022	Y	3240	1490	3.0		33
	2.13	St. Catherines/Sapelo Sound	0.003	N	NA	965	0.8	75	
	2.14	Altamaha River	0.283	Y	12690	1510	14.9		15
	2.15	St. Andrew/St. Simons Sound	0.008	Y	773	3260	2.5		72
	2.16	St. Johns River	0.185	Y	2860	6500	7.8		258
	2.17	Indian River	0.027	N	NA	1246	1.4	280	
	2.18	Biscayne Bay	0.013	N	NA	1850	3.2	269	
								2976	3233

Conclusion on the current flux estimates

- The air-water CO_2 flux of the global estuaries (0.4 Pg C/yr) is quite uncertainty and is likely **overestimated**.

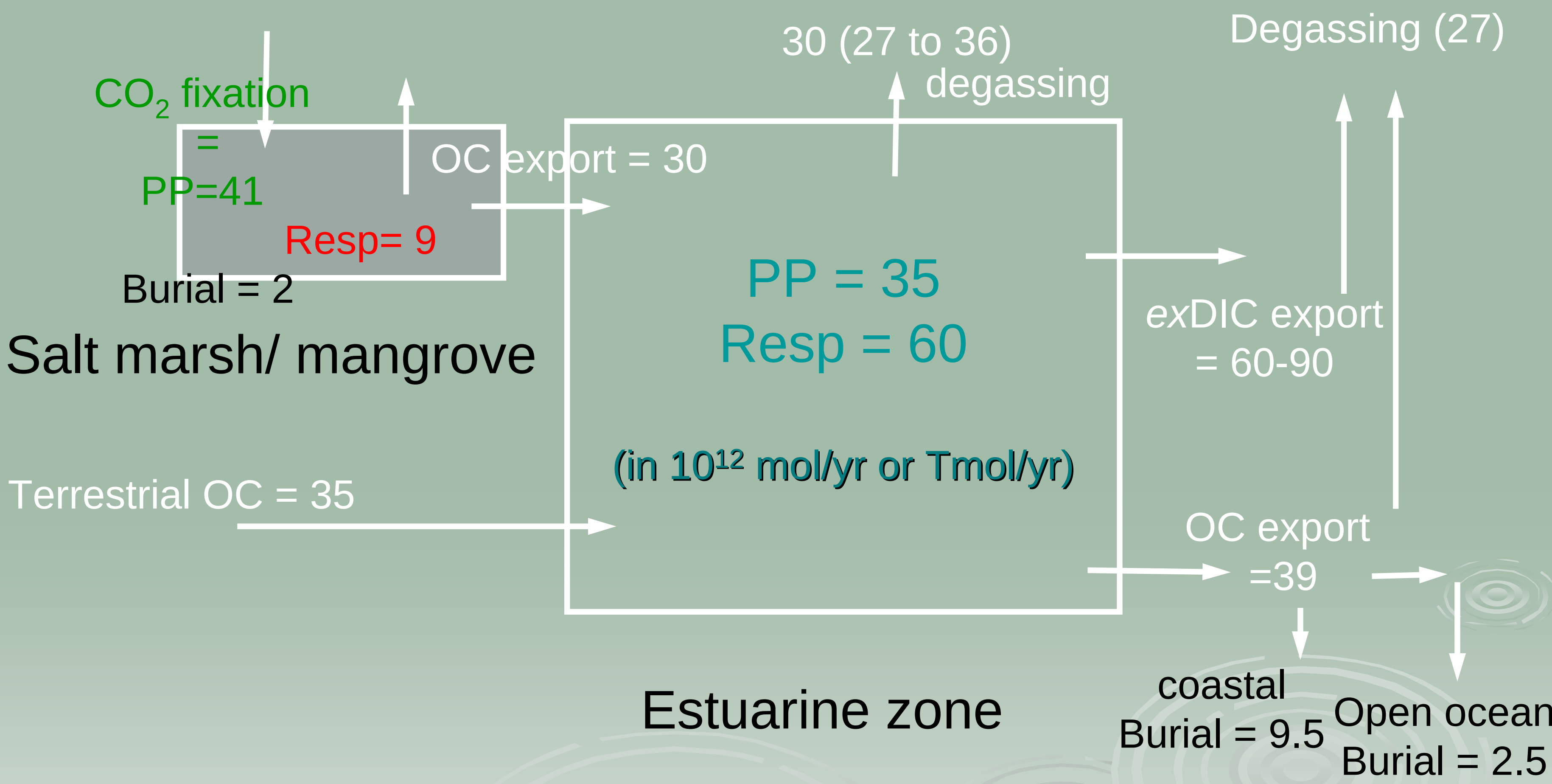
- Marshes and mangroves are highly productive ecosystems that are not yet in the picture.
  - Productivity: 1275 gC/m^2/yr (Woodwell 1973)
  - Area:383,700 km^2
  - Total production or CO_2 fixation: 0.49 Pg C/yr (or 41 Tmol/yr).

- Net sea- (or ground-) air CO_2 flux in estuarine and nearshore systems cannot be constrained with any satisfaction at this stage, but is probably a small CO_2 sink.

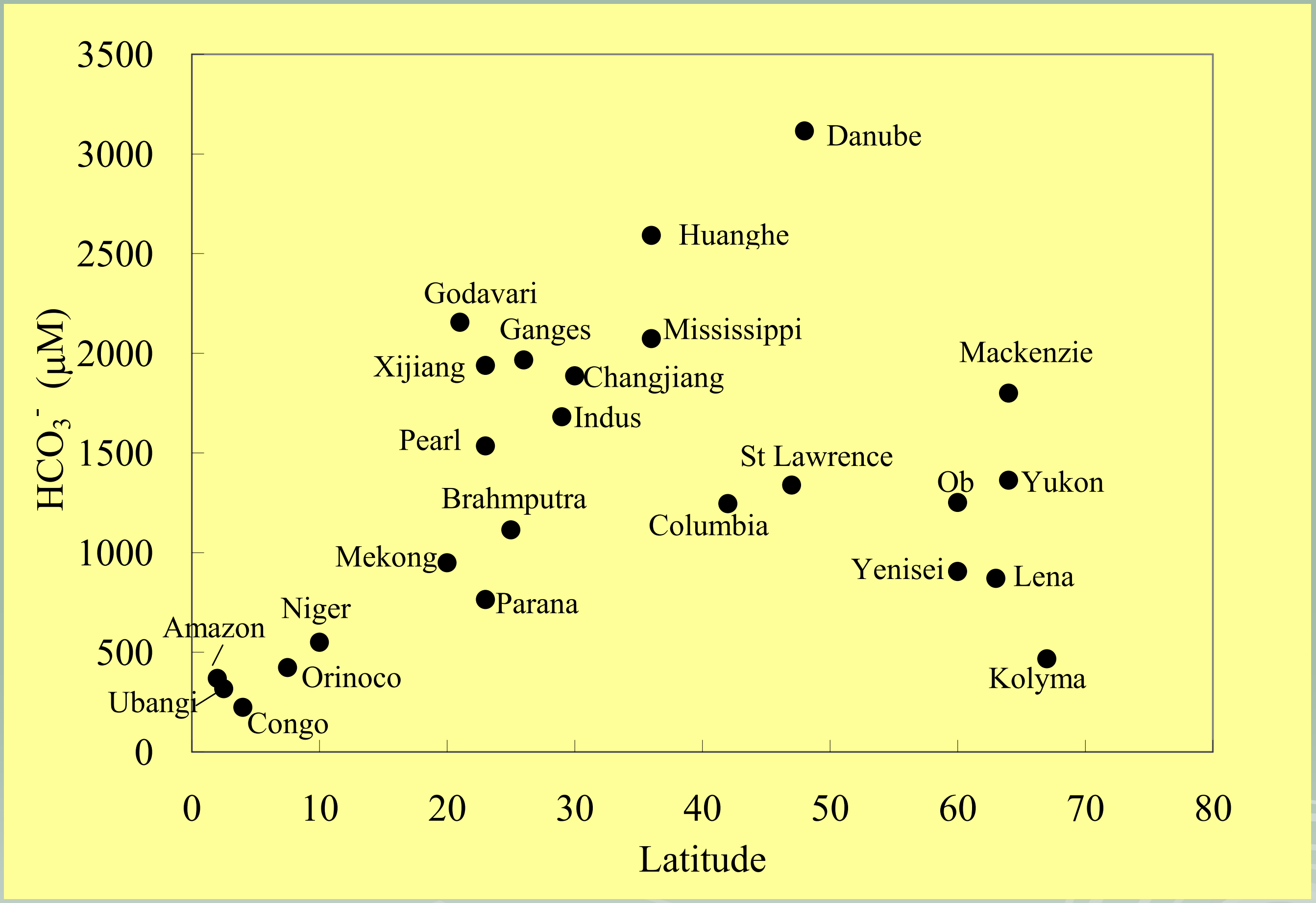
metabolism in estuaries

- PP (total) = 35 Tmol/yr (Smith & Hollibaugh 1993)
- Resp (pelagic) ~ 86 mmol/m^2/d (Hopkinson 2002?)
- Resp (benthic) = 34 mmol/m^2/d (Hopkinson 2002?)
- Resp (total) ~120 mmol/m^2/d = 60 Tmol/yr (Hopkinson 2002?)
- Estuarine is heterotrophic, burning more OC than it produced.

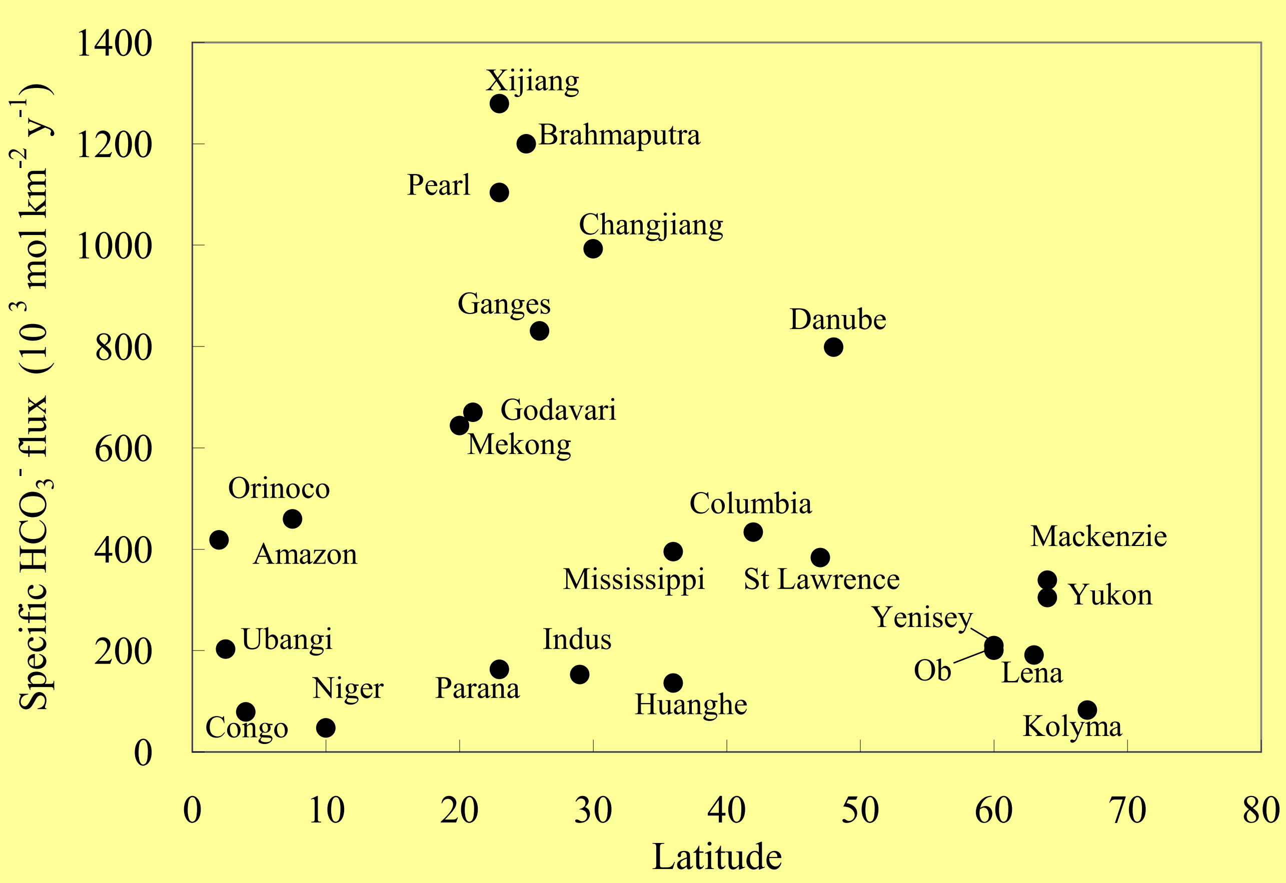
C budget & metabolism in estuaries



Latitudinal distribution of HCO_3 in global rivers



Cai et al. 2008, CSR (in press)



Specific HCO_3^- flux (10^3 mol km^{-2} y^{-1})
Latitude
0
200
400
600
800
1000
1200
1400
0
10
20
30
40
50
60
70
80
Xijiang
Brahmaputra
Pearl
Changjiang
Ganges
Danube
Godavari
Mekong
Orinoco
Amazon
Columbia
Mississippi
St Lawrence
Mackenzie
Yukon
Yenisey
Ob
Lena
Ubangi
Indus
Niger
Parana
Huanghe
Congo
Kolyma

Acknowledgements

- Funding agency:
  - NSF: OCE-9982133; OCE-0425153; OCE-0752110 .
  - NOAA: NA050AR4311161
  - NASA: NNG05GD22G
- Associates: Yongchen Wang, Li-Qing Jiang, Feizhou Chen, Justin Hartmann, Wei-Jen Huang, & Xianghui Guo